Users' Reports

The activities in 1991 were presented and discussed in the 9th PF symposium.
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Backreflection X-ray standing-wave (BRXSW) data collected at the BL-IA workstation [1] were analyzed to determine the atomic structure at the CaSrF$_2$/GaAs(111)B heteroepitaxial interface [2].

The photon-energy resolution of the current BL-IA beamline optics is ca. 0.95 eV (FWHM) at 3.1 keV, which is dominated by the Darwin width of the InSb monochromator used. The assumed Gaussian energy profile and the estimated resolution are supported in the middle panel of Fig. 1 in [1], where the added GaL + AsL emission data from GaAs substrate is consistent with a theoretical profile calculated for Ga and As atoms lying on the (220) planes. The origin of the GaAs unit cell is here chosen at the center of the Ga-As bond. It is worth noting that the data is very close to the theoretical curve taking no account of the extinction effect [3]. This is because of the shallow penetration of soft X-rays and the grazing detection angle used. The top panel in Fig. 1 of [1] shows a SrL emission profile observed from the 100Å-thick Ca$_{0.39}$Sr$_{0.61}$F$_2$ epilayers near the GaAs 220 Bragg peak. The exciting standing-wave field intensity modulated along a direction 35.3° off the surface normal. The solid line in the top panel shows a theoretical fit assuming a slight tetragonal distortion in the epitaxial Ca$_{0.39}$Sr$_{0.61}$F$_2$ crystal. An equally good fit was obtained for the Sr emission data collected from the same sample using the (113) Bragg planes at ca. 3.6 keV.

Table 1 lists the Sr layer positions $z_i$ at the heteroepitaxial interface and coherent fractions $f_c$ of the Sr atoms, determined from least-squares fits to the BRXSW emission data collected using the substrate GaAs $hkl$ reflection. $N$ is the nominal number of F-(Ca, Sr)-F layers parallel to the interface, determined from Fresnel reflectivity measurements [4]. The backreflection geometry was not useful here because 1.9 keV photons for the normal-incidence GaAs 111 reflection excite no useful fluorescence in the epilayers. The $f_c$ values indicate a slightly expanded (0.7%) epilayer spacing relative to the bulk GaAs(111) spacing.

Figure 1 draws three lines, $z = z_i (111)$, $z_i (220)$ and $z_i (113)$, in the unrelaxed GaAs lattice. The three lines nicely meet at a common point which defines the interface position of Sr atoms projected onto the (110) plane. The projected position is almost atop the center of the As-Ga bond at vertical distance of 2.38Å. This is not a high-symmetry position on the GaAs(111) surface, halfway between the possible adsorption sites T4 and T. The short vertical distance suggests one or both of the F and As layers missing from the heteroepitaxial interface.

The non-crystallographic adsorption site and the significantly lower coherent fractions for the 220 and 113 reflections apparently suggest multiple adsorption sites for Sr atoms and the formation of a domain structure in the epitaxial crystal.
The surface electronic properties of GaAs can be effectively improved by the sulfur or selenium treatment. We have been studying this surface structure by means of various surface analysis techniques. As a result, we found that gallium, arsenic and sulfur bonds on the (NH₄)₂Sₓ-treated GaAs (100) surface were changed with annealing in vacuum. The surface structure is classified into the following five stages:

1) On the initial surface, there remains a thin (~10 nm) and yellowish film of amorphous sulfur, containing probably water.

2) In vacuum at room temperature (RT), the surface changes its appearance from yellowish to shiny crystalline reflection. After releasing most of amorphous sulfur by sublimation, the surface is covered with very thin layers of sulfur atoms. This as-treated, kept-in-vacuum surface of GaAs, on which exist S-S, S-Ga and S-As bonds, has a less crystalline structure due to an excess of arsenic atoms.

3) On heating the sample, S-S bonds are observed to disappear and other bonds to remain essentially unchanged.

4) Above transition temperature of about 250 °C, the surface is gradually restored by the formation of dominant S-Ga bonds and the disappearance of S-As bonds. Simultaneously, an ordered structure of (2x1) appears, indicating that sulfur atoms occupy near sites for arsenic atoms.

5) On further heating, covering sulfur atoms gradually disappear and, at 600 °C, sulfur atoms on the surface completely desorb.

However, a correlation between surface structure and electronic quality has not been revealed yet. We studied changes in electronic quality with annealing by using an in-situ photoluminescence (PL) technique. In this report, we stress the superiority in electronic quality of (NH₄)₂Sₓ-treated surface after annealing at about 500 °C (Stage 4). Figure 1 shows the changes in a band-gap PL intensity measured at RT in vacuum on n-type GaAs (100) substrates grown by vapor phase epitaxy (VPE). Open and closed circles are corresponding to the initial and final (60 min) intensities determined from a time-dependence of PL signal, respectively. It is clear that the PL intensity of as-treated surface significantly decrease with time. On heating the sample at 200 °C, however, the degradation behavior is not observed. According to the data obtained by synchrotron radiation photoemission spectroscopy (SRPES), this can be interpreted as follows. Excess sulfur of S-S bonds on the surface is so volatile even at RT that it easily desorbs with a photo-excitation during PL measurement and an annealing at 200 °C. This reduction in surface fixed charge caused by the complete sublimation of excess sulfur may lead to a change in surface potential which influences the PL efficiency. Furthermore, it appears that the PL intensity increases as the annealing temperature is raised. For the sample annealed at 520 °C, it is enhanced by a factor of 10², indicating a decrease in surface recombination velocity. This is considered to result from a relaxation of band bending caused by the formation of stable S-Ga bonds. Finally, at 600 °C, the PL intensity considerably degrades, because Fermi-level on the surface is pinned near the midgap, which attributes to the emergence of defective or off-stoichiometric layer of GaAs caused by a prior evaporation of volatile arsenic atoms.
PHOTOEMISSION ANALYSIS OF H2S-TREATED GaAs SURFACES

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Introduction

The chemistry of sulfur-passivated GaAs surfaces has been intensely studied. It was found that (NH₄)₂Sₓ treatment is effective in increasing the photoluminescence intensity and in improving the I-V and C-V characteristics of the devices. 1) The photoemission analysis revealed that the Ga-S, As-S, and S-S bonds are formed on the (NH₄)₂Sₓ-treated GaAs surfaces. 2) This report investigates the bonding states of the H₂S-treated GaAs surfaces, which show higher photoluminescence intensity than (NH₄)₂Sₓ-treated GaAs surfaces.3)

Experiment

H₂S treatment of the n-GaAs (001) surfaces was carried out at 650°C for 20 min in an MOCVD system. Prior to the H₂S treatment, the surfaces were pre-annealed at 670°C for 10 min in AsH₃ ambient. Photoemission spectra of the core levels of the H₂S-treated n-GaAs surfaces were measured before and after annealing at 360°C for 10 min in a vacuum at BL-1A. Photon energy was adjusted to about 210 eV to obtain surface sensitive information about S 2p core electrons. The MgKα characteristic x-ray was also used to confirm the SR photoemission spectra.

Results and Discussion

S 2p and Ga 3d photoemission spectra for the H₂S-treated n-GaAs surfaces are shown in Fig. 1. For the (NH₄)₂Sₓ-treated GaAs, S-As and S-S components are observed in S 2p spectrum,2) and they disappear by 360°C annealing. However, no such peaks are observed in both S 2p and As 3d for the H₂S-treated GaAs. This may be due to the relatively high temperature of the H₂S treatment. Based on the above results, we deconvoluted the S 2p spectrum of the H₂S-treated GaAs into three S-Ga components, namely S-Ga (1a), S-Ga (1b), and S-Ga (2). Although it is difficult to assign them, we think that they correspond to the Ga₂S-, GaS-, and Ga₂S₃-like bonds, respectively, judging from the amount of the peak shift. The previously reported S-Ga (1) peak2) in the S 2p spectrum of the (NH₄)₂Sₓ-treated GaAs corresponds to the convolution of the S-Ga (1a) and S-Ga (1b). The Ga-S (1) shoulder peak in the Ga 3d spectrum is also interpreted as the convolution of the Ga₂S and GaS components.

The thickness of the sulfur layer for the H₂S-treated GaAs (001) surfaces was estimated to be about 0.3 nm by the intensities of the photoemission spectra. The H₂S-treated surfaces showed a 2x1 LEED pattern, suggesting that a rearrangement of the sulfur atoms occurs at the surface. The fact that the GaS-like bonds become dominant after annealing at 360°C suggests that the sulfur atom ordering takes place at the bridging site4) of the GaAs (001) surfaces, where the GaS-like bonds are formed.

In summary, it was found that the Ga₂S-, GaS-, and Ga₂S₃-like Ga-S bonds are formed on the H₂S-treated n-GaAs (001) surfaces. The increase in the photoluminescence intensity is thought to be related to the Ga-S bond formation.

References

Interface structures of S-passivated GaAs(111) with CaF₂ overlayers studied by X-ray standing wave technique

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INTRODUCTION

Recently, it has been found that a well stabilized GaAs surface is produced by (NH₄)₂Sₓ treatment(1). This treatment has been shown to be very effective in improving the surface/interface electronic properties of GaAs.

The structures of (NH₄)₂Sₓ-treated GaAs(111)A and (111)B with CaF₂ overlayers studied by the X-ray standing wave technique(2) are presented.

EXPERIMENTAL

(NH₄)₂Sₓ-treated GaAs(111)A and (111)B substrates were used. These samples were pre-annealed at 480°C for 10 minutes followed by deposition of a CaF₂ about 100Å. Finally the samples were post-annealed at 480°C for 10 minutes in vacuum.

The X-ray standing wave experiment was carried out at the Photon Factory BL-1A in Tsukuba. The XSW data were taken by scanning the incidence angle(3) around the GaAs 111 Bragg reflection at a photon energy of 3.1 keV. S Kα fluorescence yields were measured by a Si(Li) detector.

RESULTS AND DISCUSSION

S Kα fluorescence yields and rocking curves for (NH₄)₂Sₓ-treated GaAs(111)A and (111)B with CaF₂ overlayer are shown in Figure 1. The points represent experimental data, while the solid lines represent the theoretical fitting curves.

The structure models for S-GaAs(111)A and B based on parameter P(coherent position) determined by XSW are shown in Fig.2. It was found that on the GaAs(111)A substrate S atoms are located on top of the first layer Ga atom, however, on the (111)B substrate S atoms replace the top layer As atom. In both cases, S is bonded to Ga. These models agree with the photoemission studies which revealed that (NH₄)₂Sₓ-treated GaAs surfaces are terminated by Ga-S bonds after annealing(4).

The XSW results on CaF₂/S/GaAs(111)B are characterized by a high coherent fraction (F=1.0). This indicates that the S inter-layer on GaAs(111)B is completely ordered. It seems that S atoms on GaAs (111)B are more stable than on GaAs(111)A. On the other hand, the XSW measurement on S/GaAs(111)B without an overlayer results in F=0.55 and P=0.00. It is thought that on GaAs(111)B, deposition of CaF₂ induces S inter-layer order.

REFERENCES

(2) B.W.Batterman; Phys.Rev.133(1964)A759
(3) S.Maejama et al; to be published Rev.Sci.Instrum.

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Fig.1 S Kα fluorescence yields and rocking curves
(a) for CaF₂/S/GaAs(111)A, (b) for CaF₂/S/GaAs(111)B

Fig.2 Positions of S atoms in cross-sectional view
(a) on GaAs(111)A, (b) on GaAs(111)B
Effects of a Se interlayer at the Pd/GaAs(100) interface.

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Introduction
As an important consideration in Schottky barrier formation and ohmic contact preparation, the behaviour of metal overlayers on semiconductor materials has received much experimental attention.

Earlier investigation of the effect of a Pd overlayer on GaAs[1] concluded that As (and Ga to a small extent) reacts with and diffuses into the metal overlayer. We are interested in the effect of an interlayer at the metal-semiconductor interface in reducing substrate surface disruption and possible segregation.[2]

In this report we present preliminary results of a study involving a Se interlayer at the Pd/GaAs(100) interface.

Experimental
Experiments were performed at BL-1A at the Photon Factory. SR photoemission spectra were recorded using a photon energy of 88.9 eV. X-ray photoelectron spectroscopy was performed using a photon energy of 1253.6 eV.

GaAs(100) wafers were rinsed in acetone and then etched in a commercially available alkaline etchant. The wafers were then cleaned in an MBE chamber by heating to 600°C before being exposed to a Se flux at 450°C (source temperature 140°C) for 5 minutes. Surface structure was monitored by RHEED. Se thickness was estimated to be 1-2 ML.

Subsequently Pd was evaporated from a tungsten basket and SRPES spectra were recorded for various metal layer thicknesses up to 14Å. Both Se and Pd thicknesses were calculated from the attenuation in the Ga3d SRPES and XPS peak intensities after deposition[3].

Results and Discussion
If a non-reactive, uniform Pd overlayer is deposited onto GaAs, the Ga3d and As3d peak intensities are expected to decrease exponentially as a function of the thickness of Pd deposited[3]. However, as shown in Fig. 1, we observe that the As3d peak intensity recedes more slowly than for Ga3d. As SRPES analysis is surface sensitive, this suggests that As must remain close to the surface of the Pd layer.

RHEED patterns observed during Se deposition confirm the Se interlayer as a thin crystalline film and not of amorphous or islandic nature.

It is observed in Fig. 2 that before Pd deposition takes place the As peak intensity is diminished with respect to a clean, untreated GaAs surface. This is probably due to Se substitution for As at the high deposition temperature of 450°C.

In comparison with Fig. 1, the decrease in As peak intensity in Fig. 2 is markedly different. The similar attenuation slope for As3d and Ga3d peak intensities suggests that the Se interlayer is an important factor in preserving the GaAs stoichiometry at the interface.

The reason for the successful reduction of substrate surface disruption and subsequent As segregation is probably due to the fact that Se itself seems to react with Pd and remains close to the surface. The Se3d peak intensity in Fig. 2 remains almost unchanged regardless of Pd layer thickness.

In substituting for As[4], Se can be expected to assume different bonding configurations depending upon the substrate crystal face it bonds to. Hence the behaviour of the Se interlayer at the GaAs(111)B and GaAs(111)A/Pd interfaces is presently under investigation.

References
Application of Multilayer Mirrors to Grating/Crystal Monochromator

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Introduction

In order to realize a monochromatic beam for both the VUV and soft x-rays regions, a grating/crystal monochromator(GCM)\(^1\) was installed at beamline 1-A in the Photon Factory. For grating monochromatization mode of the GCM, a Pt-coated plane mirror(Pt mirror) and grating are employed as the first and second optical elements, respectively. This report describes transmission functions of the GCM using multilayer-coated mirrors for the first optical element in combination with a 24001/mm grating.

Experimental

W/B\(_{12}C\) multilayers with 95Å and 123Å d-spacings were deposited onto optically flat SiC substrates(60x70x5mm) by sputtering\(^2\). These mirrors were loaded on the first carousel of the GCM. Transmission functions of the grating monochromatization using the multilayer mirrors as well as the Pt mirror were measured by photocurrent output from a metal grid. In addition, 0 Ka fluorescence x-ray spectra excited from a SiO\(_2\) film by these monochromatized beams were measured by means of a gas scintillation proportional counter\(^3\).

Results

Figures 1-(a) and (b) show comparisons of transmission functions for using the W/B\(_{12}C\) multilayer mirror and the Pt mirror with an incident angle of 86 degrees in combination with the 24001/mm grating. Increases of the photocurrent relative to that for the Pt mirror were observed at about 500eV and 1000eV in the transmission functions for the W/B\(_{12}C\) multilayer mirrors of d=95Å and d=123Å, respectively. According to the calculated reflectivities of these W/B\(_{12}C\) multilayers, these increments are attributed to the diffraction effect of the multilayer. Figure 2 shows a comparison of 0 Ka fluorescence x-ray spectra above the 0 K-edge for a SiO\(_2\) film of 70Å thickness. These spectra were not corrected by the transmission functions shown in Fig.1-(b). A broad peak near 1000eV in Fig.2 corresponds to the increased incident beam intensity due to the diffraction effect of the multilayer. Since the grazing incident angle limit of the GCM is 86 degrees, utilizing the multilayer mirror instead of the Pt mirror as the first optical element of the GCM is considered to be an effective method for obtaining a monochromatic beam of high intensity in the 500-1000eV energy region.

References

Deposition of CaF$_2$ and GaF$_3$ on Sulfur passivated GaAs(111)A, 100 and (111)B surfaces

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Introduction

While GaAs appears to be an excellent candidate for a variety of electronic devices, commercial development of GaAs technology has been hampered by the existence of surface states and pinning of the Fermi level near the midgap. Recently, treatment of the GaAs surface by (NH$_4$)$_2$S$_x$ treatment has been shown to reduce the GaAs surface states as well as unpin the Fermi level$^{1,2}$. The work presented here is directed towards the deposition of CaF$_2$ and GaF$_3$ on sulfur passivated GaAs(111)A, 100 and (111)B surfaces in order to correlate the CaF$_2$/S/GaAs and GaF$_3$/S/GaAs interface chemistry with the macroscopic MIS characteristics.

Experimental

The CaF$_2$/S/GaAs interface was performed at the Synchrotron storage ring facility located at Tsukuba. A photon energy of 210 eV was used to excite the S 2p electrons. The GaAs wafers were treated with a (NH$_4$)S$_x$ solution for 1 hour at 60°C before being placed in the analysis chamber. Deposition of CaF$_2$ and GaF$_3$ was performed by thermal evaporation in a W basket.

Results and discussion

In the deposition of CaF$_2$ on the S passivated GaAs surface, S segregation(Rs) to the surface was observed and found to depend on the crystal face. This is shown in fig. 1. The surface segregation is found to correlate well with the S-Ga coordination number as well as the S-Ga binding energy$^{3}$. The sulfur surface segregation is greater for the GaAs(111)A surface where the S-Ga coordination number is 1 and the S-Ga bond is relatively weak. In contrast, there is very little sulfur surface segregation for the GaAs(111)B surface where S is coordinated to three Ga atoms and the S-Ga binding energy is relatively high.

A measure of the GaAs band bending can be obtained by measuring the Ga 3d binding energy shift. In this case, the Ga 3d binding energy shift is plotted as a function of annealing and CaF$_2$ deposition in fig. 2 for both CaF$_2$ and GaF$_3$ deposition. In all cases, a decrease in relative binding energy indicates an increase in band bending since the GaAs is n doped. Thus, unfavorable increases in band bending are observed for the 100 and (111)B surfaces for CaF$_2$ deposition while there is a slight band flattening for the (111)A surface. In contrast, there is band flattening for all three surfaces for the GaF$_3$ deposition case. This favorable band flattening is in accord with the favorable MIS macroscopic characteristics obtained by Richard et al. for the GaF$_3$/S/GaAs(100) system$^{4}$. Another difference between these two systems is that there is a reduction of Ca from Ca$^{2+}$ to Ca$^0$ during the final annealing. This reduction does not take place for GaF$_3$. From the coverage dependent substrate photoelectron intensity and SEM images, CaF$_2$ is believed to grow in an island mode while GaF$_3$ growth is better characterized as layer by layer growth$^{3}$.

References

Temperature-dependent changes on the Sulfur passivated GaAs(111)A, 100 and (111)B surfaces

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Introduction

Passivation of the GaAs surface by (NH₄)Sₓ has been shown to significantly reduce the GaAs surface state density. Nevertheless, wet chemical treatment alone is not sufficient in preparing a well ordered monolayer S passivated GaAs surface. To do this, one needs to place the S treated surface in vacuum and heat it in the 300°C - 500°C temperature range. The object of this study is to understand the temperature dependent chemical bonding of the GaAs(111)A, 100 and (111)B surfaces by in-situ SR photoelectron Spectroscopy (SRPES).

Experimental

The experiments were carried out at the Photon Factory on beam line BL-1A which is equipped with a grating/crystal monochromator. A photon energy of 210 eV was used to excite the S 2p electrons. The GaAs wafers were treated with a (NH₄)Sₓ solution for 1 hour at 60°C before being place in the analysis chamber. The temperature of the GaAs surface was measured in-situ by an optical pyrometer.

Results and discussion

The SRPES S 2p spectra for S/GaAs(111)B is shown as a function of temperature in Fig. 1. At room temperature, there are essentially two peaks centered at binding energies of 162.3 and 163.4 eV, which correspond to Ga-S and As-S bonds, respectively. As the temperature is raised, the intensity of the Ga-S bond increases at the expense of the As-S intensity. The significance of this is that the As-S to Ga-S exchange brings about a reduction of surface states and unpinning of the GaAs surface.

At a temperature about 50°C below the S desorption temperature, a pre desorption state is observed. This is also observed for the S/GaAs(111)A surface. One may expect the desorption temperature of sulfur on the three different GaAs surfaces to be different based on the idea that the Ga-S coordination number ranges from 1 for the (111)A surface to 3 for the (111)B surface. The S 2p peak intensity (background subtracted) is plotted in figure 2 as a function of substrate temperature for the three different surfaces. These results are also consistent with the calculated Ga-S bond strength for the three different surfaces which are 4.3, 5.6, and 6.1 eV for the (111)A, 100 and (111)B surfaces respectively.

References

5) T. Ohno, private communication.

Fig. 2 The SRPES S 2p peak intensity is plotted as a function of sample temperature for the S/GaAs(111)A, 100 and (111)B surfaces. The desorption temperatures for the three surfaces are 586°C, 596°C and 618°C, respectively.
Direct Pattern formation of CaF₂ and SrF₂ films with Multilayer-monochromatized SR
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Introduction
In the fabrication process of GaAs MIS devices, CaF₂ and SrF₂ films are used for epitaxial gate insulator. Since these fluoride films cannot be selectively delineated, complicated processes such as Ar ion etching followed by chemical etching were utilized for device fabrication.

In this study, a new technique for pattern delineation through the use of strong synchrotron radiation semi-monochromatized by applying a multilayer is investigated to facilitate the selective etching of fluorides on GaAs and Si substrates.

Experiments
Experiments were performed at Beamline 1A of the Photon Factory in KEK. A W/B₆C multilayer of 123 Å d-spacing was installed in the first crystal holder of the grating/crystal monochromator. Figure 1 shows photon flux as a function of photon energy, where the output includes the reflected light component as well as the diffracted light component. When a SiN filter was used, a semi-monochromatic beam at about 1000 eV of hv was obtained. Samples were CaF₂ and SrF₂ films evaporated on Si(100) substrates at room temperature in UHV from tungsten baskets.

Results and discussion
When CaF₂ and SrF₂ films were irradiated at room temperature with the multilayer-monochromatized beam, the irradiated area was not etched. However, it was found that these films were etched at elevated temperatures. When the substrate temperature was maintained at 400°C, a practical CaF₂ etching rate of about 70 Å/min was obtained without any selective desorption of fluorine. At 500°C and higher, the etching rate decreased down to about 40 Å/min. Since CaF₂ and SrF₂ films are not etched only by heating without SR irradiation, these etching processes are regarded as SR-enhanced evaporation.

Next, the SR irradiation etching technique was applied to direct pattern delineation process of SrF₂ films. A #2000 mesh was used as a mask and placed less than 1mm above the sample. As shown in Fig. 2, clear mesh images were formed, where both SR beams with and without the SIN filter were irradiated. It is found that the etching rate of SrF₂ films with the semi-monochromatic SR beam in Fig. 1 is about one third of that with the SR beam without the filter. This means that the Fis core electron excitation with the soft X-ray is the dominant process of the SR etching process, because the photon flux at 950eV with the filter is about 1/2.5, while the total photon flux is less than one 20th than the SR beam without the filter.

Finally we tried the direct fine pattern formation on the CaF₂ film. Figure 3 shows an AFM image of the fine-pattern-delineated CaF₂ film with a transparent X-ray mask with 0.2 µm to 0.8 µm line & space. Although a clear fine pattern is not formed with the transparent X-ray mask at the present stage, this technique has a good potential for device fabrication applications, because the SR beam does not etch Si or GaAs substrates at all, and many resist processes can be eliminated.

In conclusion, we developed a novel technique for fine pattern delineation of fluoride films through the use of strong multilayer-monochromatized synchrotron radiation beam.

Fig. 1 Monochromatization characteristics without and with a SIN filter obtained by applying a multilayer as the first optical element.

Fig. 2 SR-etched mesh patterns on CaF₂/Si at (a) 400°C and (b) 500°C for 50 min. The etched area is about 6 µm x 6 µm.

Fig. 3 An AFM image of fine-pattern-delineated CaF₂ film with the transparent X-ray mask with 0.2 µm to 0.8 µm line & space.

[References]
Highly-sensitive Auger Electron Spectroscopy using a Multilayer-monochromatized SR Beam
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1. Introduction

Although the total reflection X-ray fluorescence analysis is very powerful for detecting heavy element impurities, there is a drawback in detecting light elements such as fluorine and carbon, since the fluorescence yields for these elements are quite small. The detection limit for the conventional XPS and the grating-monochromatized SR-excited Auger electron spectroscopy is about 10^{17} \text{cm}^{-2}.

In this study, the strong semi-monochromatic SR beam was used for the trace analysis of fluorine in semiconductors, where fluorine contamination is a serious problem in Si wafer cleaning procedures. Furthermore, this SR-excited Auger electron spectroscopy was applied to the real-time process monitor for CaF_2 direct etching.

2. Experiments

Experiments were performed at Beamline 1A of the Photon Factory. A W/B_4C multilayer of 123 Å d-spacing was installed in the first crystal holder of the grating/crystal monochromator to obtain a semi-monochromatic SR beam at about 1000 eV.

Samples were F-implanted Si(100) wafers with 10^{11}, 10^{12}, and 10^{13} \text{cm}^{-2} doses at 50 keV implantation energy. CaF_2 films were also used for the real-time Auger electron monitor for the SR direct etching process. Auger electrons were analyzed with a CLAM analyzer.

3. Results and discussion

3.1 Auger trace analysis

A greater than 20-fold photon flux with about a 50 times wider semi-monochromatic SR beam at 950 eV was obtained with the W/B_4C multilayer. From this, we can expect about 3 orders of magnitude larger F_KLL Auger signal with respect to the grating-monochromatized beam.

Figures 1(a) and (b) show the F_KLL Auger electron spectra from 10^{11} and 10^{13} \text{cm}^{-2} F-implanted Si wafers respectively. Taking into account the Gaussian depth distribution of F in a 125 Å projected range and an escape depth of F_KLL Auger electrons of about 12 Å, the detected F atom concentration in the Si wafer was calculated to be 7.45 \times 10^{17} \text{cm}^{-2} for the 10^{13} \text{cm}^{-2} F-implanted Si case. Although the fluorine contamination during sample transfer and measurements should be considered, about 1 order of magnitude difference in F_KLL Auger peak intensities in (a) and (b) was clearly observed, suggesting that the F_KLL Auger signals come from the implanted F impurities. Furthermore, neither F_KLL Auger signal nor F_ls photoelectron signals were observed by means of a MgK \alpha X-ray excitation source (15 kV and 20 mA) on these surfaces.

3.2 Real-time etching process monitor

The semi-monochromatic SR beam was also used for the process monitor of the SR direct etching of CaF_2 films. The etching process could be simultaneously monitored by SR-excited Auger electron spectra, as shown in Fig. 2. It is found that CaF_2 is etched and almost no selective desorption of fluorine occurs at 400 °C. At 500°C, however, the etching rate decreased drastically, which can be attributed to the fluorine desorption from the surface as shown in Fig. 2(b). This is also confirmed by the fact that the Ca_LVV Auger peak shifted towards higher kinetic energy, indicating that the Ca atoms are in the metallic Ca state. The Ca metallic overlayer is thought to act as a prohibitor of further etching.

In conclusion, a strong semi-monochromatic SR beam has been successfully utilized both for the trace analysis of surface fluorine atoms and the real-time etching monitor of CaF_2.

[References]
**InAs growth on EuBa$_2$Cu$_3$O$_{7-y}$ superconducting films with SrF$_2$ interlayers**

**Analysis of interlayer**

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**INTRODUCTION**

Growth of semiconductor films on high-$T_c$ superconductors has the attractive possibility of combining conventional semiconducting devices and the devices constructed by these superconductors. However, growth of the semiconductor layers on the high-$T_c$ superconductors degrades superconducting properties because oxidation of overlayers and reduction of superconductivity take place at the interface.

In this study, we propose a SrF$_2$ interlayer to prevent interfacial reaction between superconducting EuBa$_2$Cu$_3$O$_{7-y}$ (EBCO) and InAs overlayers, and describe results of effectiveness of the SrF$_2$ interlayer whose lattice parameter is a value between those of EBCO and InAs. The semiconductor material was chosen to be InAs because n-type InAs has advantages of high electron mobility, light electron effective mass and negative Schottky barrier.

**EXPERIMENTAL**

The EBCO films were grown on MgO(O01) using planar-type magnetron sputtering. SrF$_2$ deposition, molecular beam epitaxial growth of InAs and in situ surface analysis were performed at BL-IA. Photoemission spectra were taken with photon energy of 76 eV. First, EBCO surfaces were cleaned by heating the sample up to 300°C under exposure of As$_4$ flux or in vacuum. Then, about one or two monolayers of SrF$_2$ were deposited on the surface at room temperature. After the SrF$_2$ interlayer formation, InAs was grown on the SrF$_2$ surface at various temperatures up to 200°C with thickness in the range from one monolayer to around 10 nm.

**RESULTS AND DISCUSSION**

Figures 1 and 2 show typical O1s XPS spectra of two-monolayer InAs-deposited samples with (Fig. 1) and without the SrF$_2$ interlayer (Fig. 2). As shown in Fig. 1, an additional peak B grows caused by InAs deposition, whereas the O1s bulk emission peak A becomes attenuated. On the other hand, the spectral features shown in Fig. 2 are not changed by either SrF$_2$ deposition or InAs growth. These results indicate the effectiveness of the SrF$_2$ interlayer to prevent the removal of oxygen from the surface region of the EBCO and oxidizing the InAs overlayers.

It is found that InAs cannot be grown on as-deposited SrF$_2$ surfaces because As$_4$ hardly adsorbs on fluorine atoms which lie on the top layer of SrF$_2$. We therefore tried to increase the wet-stability of SrF$_2$ surface by exposing it to As$_2$ flux. Figure 3 shows the As3d SRPES spectra after As$_2$ exposure and after InAs deposition. The peak showing elemental arsenic appears after As$_2$ exposure, and after growing the InAs, there is no sign of an arsenic-oxide peak at around 45 eV binding energy. This result strongly suggests that InAs can be grown on the SrF$_2$ surface, and that the SrF$_2$ interlayer prevents oxidation of the InAs overlayers.

In conclusion, we proposed the use of a SrF$_2$ interlayer to prevent reaction between superconducting thin films of EBCO and semiconductor InAs overlayers. Photoemission spectroscopy showed the effectiveness of the SrF$_2$ interlayer for suppressing these redox reactions.


2) Y. Watanabe, F. Maeda, M. Oshima and O. Michikami, Extended Abstracts of SSDH '91, Yokohama, 429.

InAs growth on EuBa$_2$Cu$_3$O$_{7-y}$ superconducting films with SrF$_2$ interlayers

- Two-step growth procedure -

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INTRODUCTION

Growth of semiconductor films on high-Tc superconductors (HTS) has the attractive feature of combining conventional semiconducting devices with superconducting devices. However, growth of semiconductor films on HTS oxidizes the semiconductor films and reduces the superconductivity of the underlying HTS at the interface because of oxygen instability near the HTS surface region. Recently, we proposed a method to prevent these redox reactions at the interface between superconducting EuBa$_2$Cu$_3$O$_{7-y}$ films (written EBCO hereafter) and InAs overlayers. This method is to deposit a SrF$_2$ thin film (SrF$_2$ interlayer) before growing InAs layers. In this report, we present the results of synchrotron-radiation photoemission spectroscopy (SRPES) and X-ray photoemission spectroscopy studies of InAs deposition on SrF$_2$-coated EBCO thin films. It is found that, by initially growing InAs layers at room temperature (RT), oxidation-free and highly-oriented InAs overlayers can be grown at 200°C.

EXPERIMENTAL

Photoelectrons were measured with a hemispherical angle-integrated type analyzer with an electrostatic lens in the analysis chamber. SRPES and XPS spectra were taken with a monochromatized synchrotron radiation source ($\hbar\nu = 76$ eV) and an Al Ka x-ray source ($\hbar\nu = 1486.6$ eV). The total energy resolution for the SRPES and XPS measurements were 0.3 eV and 1.1 eV respectively. The EBCO thin films were deposited on SrO(001) using planar-type magnetron sputtering with a typical film thickness of about 300 nm. Then, 3-monolayer (ML) thick SrF$_2$ layers were deposited on the clean EBCO surface at RT. InAs was grown at various temperatures up to 200°C with various thicknesses.

RESULTS AND DISCUSSION

Figure 1 shows the O1s XPS spectra for an InAs-grown sample on a SrF$_2$-coated EBCO film. The features of the O1s spectra are not affected by growing an InAs layer at RT, which indicates that the Cu-O bonding is not significantly modified. However, the surface regions of the EBCO are modified chemically or structurally when the sample is annealed at 200°C. Indeed, as shown in Fig. 2, the As-oxide As3d peak at about 44 eV of binding energy appears after annealing at 200°C. These results indicate that, although the interlayer plays an important role of suppressing the interface redox reactions in growing at RT, quality of InAs layers is insufficient. Because the InAs layer grown at RT becomes amorphous and crystalline InAs layers can be obtained by using growth temperatures more than 200°C. To solve this problem, a two-step growth procedure was used to grow InAs layers. Figure 3 compares the results of As3d SRPES spectra. (a) is for the InAs surface grown on a SrF$_2$/EBCO at 200°C, and (b) is for the InAs surface grown by the two-step growth procedure, where an initial InAs layer was grown at RT and then the overlayer was grown at 200°C. With the sample of (a), the As-oxide peak at about 44 eV is mainly observed, whereas with the sample of (b), the As3d5/2 and 3/2 peaks of the InAs state are clearly observed. This result suggests that this two-step growth procedure effectively prevents oxidation of the InAs overlayer grown at 200°C.

In conclusion, it is found that, by initially growing InAs layers at room temperature, oxidation-free and highly-oriented InAs overlayers can be grown at 200°C.

1) Y. Watanabe et al.: Extended Abstracts of SSDM '91, Yokohama, p429.
Interfacial Reaction on GaAs/interlayer/EuBa2Cu3O7-y(001)

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Introduction

In order to apply high-Tc oxide superconductor to three terminal devices, many attempts have been made for growing semiconductor on high-Tc superconductor. We intended to grow GaAs on EuBa2Cu3O7-y (EBCO), because GaAs can be grown at low temperature by MEE technique and because EBCO is comparatively stable for heating. However, it was found that strong interfacial reaction between GaAs and EBCO occurred resulting in the formation of undesirable oxide interlayer, which is composed of reduced EBCO and oxidized GaAs. For reducing this interfacial reaction, AsOx or SrF2 interlayer was formed on EBCO. And then, we verified its effects on the GaAs growth.

Experimental

The experiments were carried out at BL-1A. Photoelectrons were measured with a hemispherical angle-integrated type analyzer. The excitation photon energy was 76 eV. The total energy resolution was determined to be less than 0.3 eV. The substrates for interlayer formation and GaAs deposition are EuBa2Cu3O7-y (001) crystal thin films grown on EuO(001). The interlayer, AsOx or SrF2, was formed on the EBCO surfaces cleaned by heating to 300 °C. And then, GaAs was deposited on this interlayer in the MBE chamber and this surface was analyzed by photoelectron spectroscopy in situ.

Results & Discussion

Figure 1 shows Ga 3d and As 3d SRPES spectra of GaAs deposited on EBCO with an AsOx interlayer. In the spectra of one monolayer GaAs deposited EBCO, oxide states are observed in Ga 3d spectrum since the outermost layer of the AsOx interlayer is composed of oxygen atoms although the GaAs state is observed in As 3d spectrum. After GaAs deposition on the 1 ML deposited surface, GaAs state peak intensities increase in both the Ga 3d and As 3d spectra, whereas the oxide state intensities decrease. These results suggest that there is no oxidation reaction taking place after the second layer deposition.

Figure 2 shows Ga 3d and As 3d SRPES spectra of GaAs deposited on EBCO with the SrF2 interlayer. According to these spectra, Ga and As are deposited entering only the GaAs state from the first deposition of 1 ML. After this deposition, GaAs is deposited without forming oxide states when the substrate is at room temperature.

The results described above verify that the two interlayers have strong effects of suppressing oxidation reactions at room temperature. However, the GaAs films should be annealed at 200 °C in order to crystallize thin films, which might cause the interfacial reaction.

In conclusion, crystalline GaAs layers were grown on EBCO thin films and it was found that the interfacial reactions were more effectively suppressed with the SrF2 interlayer than the AsOx interlayer.

References

THE INDUCTION KINETICS OF CHROMOSOME ABERRATIONS BY X-RAYS WITH RESONANCE ENERGY OF PHOSPHORUS K-SHELL ABSORPTION EDGE

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The biologically relevant effects on organic molecules of the photoelectric absorption are due to ionization by photoelectrons and associated Auger electrons and the dissociation of molecules by electric charge of the photo-absorbed atoms. DNA is a prime target molecule for the radiation-induced mutations, chromosome aberrations and cell killing, and the phosphorus atom is the essential element which constitutes main chain of DNA. The present study was carried out to examine the induction kinetics of chromosome structural aberrations by X-rays with energy corresponding to the K-shell absorption edge of the phosphorus.

Mouse m35S cells were grown in monolayer on plastic sheet, covered with 1.5 um thick Mylar film, set to the irradiation system installed at the beam line BL-1B, and exposed to the monochromatic X-rays with energies of below (2.146 keV), peak (2.153 keV) and above (2.160 keV) the resonance energy of phosphorus K-shell absorption edge. The induced chromosome aberrations were analyzed in the first post-irradiation mitoses [1].

Figure 1 shows the frequencies of dicentrics (chromosome rearrangements resulting in the chromosome with two centromeres) against exposure to X-rays with three different energies. In the experiments using X-rays with off-peak energies (2.146 keV and 2.160 keV), there was no difference in the frequency of dicentrics. However, in the cells irradiated with the X-rays with energy corresponding to the resonance peak (2.154 keV), the dicentric yield was significantly higher than those for off-peak energies. When the dicentric yields were fitted to the linear-quadratic model, Y = αX + βX^2, against exposure (X), the difference was largely due to the increased yield of linear term (Figure 2). These observations indicate that the enhancement of chromosome aberration yield is due to the photoelectric absorption of the phosphorus atoms, and moreover, it is presumed that the induction of chromosome aberrations is largely a consequence of the single absorption event.

Assuming that the difference in the aberration yield was solely due to the difference in the photoabsorption of the phosphorus atoms in the DNA, the quantum efficiency was calculated to be 2.7x10^-3 dicentrics per absorption, which was comparable to that for γ-ray-induced DNA double strand breaks in the cultured diploid mouse cells (1.8-8.9x10^-3 dicentrics per double strand break). How the photoelectric absorption of the phosphorus atom in DNA lead to the DNA double strand breakage? The photoelectric absorption of phosphorus will result in an emission of a low energy K-shell photoelectron and Auger electrons leaving multiply charged atom (P^{3+}). Since the energy of K-shell photoelectrons (about 4 eV) is far below the threshold energy for DNA strand breakage, their contribution may be ignored. Then, a question was raised as to the possibility of the involvement of multiply charged phosphorus atoms and associated Auger electrons which occurred within DNA: dissociation of DNA single strand by charged phosphorus atom associated with occasional hit of complementary strand by Auger electrons. If such is the case, an equal efficiency is expected when the aberration yields are plotted against the absorbed dose to DNA. However, when the dicentric yields were expressed in a function of absorbed dose estimated basing on the elemental composition of the cell nucleus and DNA, the efficiencies were reversed, i.e., the aberration yields for peak energy were far below those for off-peak energies. This indicates that the induction of chromosome aberrations is not all due to the direct consequence of the selective photoelectric absorption of the phosphorus moiety in DNA but that the Auger electrons generated from the phosphorus in DNA as well as those from outside DNA had a significant contribution in the induction of chromosome aberrations.

Figure 1 shows the frequencies of dicentrics (chromosome rearrangements resulting in the chromosome with two centromeres) against exposure to X-rays with three different energies. In the experiments using X-rays with off-peak energies (2.146 keV and 2.160 keV), there was no difference in the frequency of dicentrics. However, in the cells irradiated with the X-rays with energy corresponding to the resonance peak (2.154 keV), the dicentric yield was significantly higher than those for off-peak energies. When the dicentric yields were fitted to the linear-quadratic model, Y = αX + βX^2, against exposure (X), the difference was largely due to the increased yield of linear term (Figure 2). These observations indicate that the enhancement of chromosome aberration yield is due to the photoelectric absorption of the phosphorus atoms, and moreover, it is presumed that the induction of chromosome aberrations is largely a consequence of the single absorption event.

Assuming that the difference in the aberration yield was solely due to the difference in the photoabsorption of the phosphorus atoms in the DNA, the quantum efficiency was calculated to be 2.7x10^-3 dicentrics per absorption, which was comparable to that for γ-ray-induced DNA double strand breaks in the cultured diploid mouse cells (1.8-8.9x10^-3 dicentrics per double strand break). How the photoelectric absorption of the phosphorus atom in DNA lead to the DNA double strand breakage? The photoelectric absorption of phosphorus will result in an emission of a low energy K-shell photoelectron and Auger electrons leaving multiply charged atom (P^{3+}). Since the energy of K-shell photoelectrons (about 4 eV) is far below the threshold energy for DNA strand breakage, their contribution may be ignored. Then, a question was raised as to the possibility of the involvement of multiply charged phosphorus atoms and associated Auger electrons which occurred within DNA: dissociation of DNA single strand by charged phosphorus atom associated with occasional hit of complementary strand by Auger electrons. If such is the case, an equal efficiency is expected when the aberration yields are plotted against the absorbed dose to DNA. However, when the dicentric yields were expressed in a function of absorbed dose estimated basing on the elemental composition of the cell nucleus and DNA, the efficiencies were reversed, i.e., the aberration yields for peak energy were far below those for off-peak energies. This indicates that the induction of chromosome aberrations is not all due to the direct consequence of the selective photoelectric absorption of the phosphorus moiety in DNA but that the Auger electrons generated from the phosphorus in DNA as well as those from outside DNA had a significant contribution in the induction of chromosome aberrations.

Introduction

Silicon photo-epitaxy has been widely attempted in order to realize low-temperature selective growth and efficient selective doping. The irradiation effects of high-energy photons on silicon epitaxy, however, are still far from clear. The investigation of SR-irradiation effects on silicon epitaxy processes is therefore important. In this report, we are primarily interested in observing SR-irradiation effects on silicon gas source MBE and surface oxide elimination using disilane gas.

Experimental

An SR-excited gas source MBE system was positioned downstream of the beam line BL-IC of KEK-PF. The reaction chamber was configured so that it can be evacuated to a background pressure of less than $5 \times 10^{-10}$ Torr. The substrates were 2-inch Si(100) just-oriented wafers (p-type, $1-10 \, \text{ohm}\cdot\text{cm}$). The substrate surface was degreased and oxidized for protection using the conventional chemical treatment, and the surface oxide was thermally evaporated just before film growth by heating it at 950°C for ten minutes. The elimination of the surface oxide was verified by observing the substrate surface 2x1 RHEED patterns. The incident SR-beam irradiated the sample surface perpendicularly while the reaction gas, pure disilane, was simultaneously fed.

Results and Discussion

The RHEED patterns of the film grown on the SR-irradiated area exhibited a 2x1 reconstruction surface for substrate temperatures ranging from 380 to 715°C. The results indicate that two-dimensional growth was realized on the SR-irradiated area. The growth rates of the epitaxial films are shown in Fig. 1 as a function of the substrate temperature. In this figure, thermal growth rates are also shown for comparison. As shown in the figure, the substrate temperature range can be separated into two regions. In the higher temperature region, exceeding about 580-650°C, the difference between SR-excited and thermal growth rates was negligible. In the lower temperature region, the growth rates were enhanced by SR irradiation. In this region, activation energies of SR-excited growth for $3.0 \times 10^{-5}$ and $1.5 \times 10^{-4}$ Torr are 20 and 32 kcal/mole, respectively, while that of thermal growth was 54 kcal/mole, irrespective of the pressure. The growth rate enhancement and activation energy reduction can be explained by hydrogen desorption by SR irradiation from the surface.

At higher than 700°C, epitaxial growth was observed even without thermal pre-evaporation of the surface oxide. The performance of this surface cleaning effect was estimated by observing the RHEED patterns of the grown film. Figure 2 shows the RHEED patterns of the as-grown films in the center and the edge areas of the SR-beam irradiation at a disilane pressure of $1.5 \times 10^{-4}$ Torr at 655 and 700°C. At 700°C, the RHEED pattern on SR-irradiated area presented a 2x1 reconstructed surface, indicating that oxide was perfectly eliminated and that two-dimensional epitaxial growth occurred on the cleaned silicon surface. In the edge area at 700°C and both areas at 655°C, spotty patterns, including sub-spots, appeared. This indicates that the surface oxide was etched, but not perfectly eliminated. SIMS measurement determined that the density of the interface oxygen declined with increasing temperature and with decreasing disilane pressure. These results suggest that SR-enhanced reduction of surface oxide is dominant in the cleaning reaction.

Reference

Crystallinity Improvement by Synchrotron Radiation Irradiation in Low Temperature Si Epitaxial Growth using Disilane

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Introduction
Low-temperature semiconductor processes have recently become more important for future devices such as quantum effect devices. Photoexcited epitaxial growth using synchrotron radiation (SR) is one of the leading candidates for such processes. In the present work, SR irradiation effects on the growth rate and on crystallinity are investigated around the low temperature limit for epitaxial growth in the gas-source MBE systems using disilane.

Experimental
The experimental system is described in detail in ref. (2). The reaction gas 100% Si2H6 was fed into the reaction chamber. Pressures during experiments were 1.5×10⁻² to 1.5×10⁻¹ Torr. Germanium (100) wafers were used as the substrates of the epitaxial growth. The thermal desorption for Ge surface cleaning was carried out at 600°C for 10 min. The average ring current during SR irradiation was 300 mA. The crystallinity of the deposited Si film was evaluated by observing the Reflective High Energy Electron Diffraction (RHEED) patterns and Raman scattering spectrum.

Results and Discussion
Figure 1 shows the observed growth rate of the Si film as a function of the substrate temperature. It is clearly shown that SR irradiation enhances growth rate, especially at lower temperature. The substrate temperature range can be separated into two regions, above and below about 500°C (1.5×10⁻¹ Torr) and 400°C (1.5×10⁻² Torr), respectively. In the higher temperature region, where temperature dependence is steep and a RHEED 2×1 surface reconstruction pattern is observed, hydrogen desorption is considered to be rate limiting. Whereas, in the lower temperature region, where the growth rate depends less on the substrate temperature, adsorption of disilane molecules is assumed to be rate limiting.

The effect of SR irradiation on crystallinity of Si film around the low temperature limit for epitaxial growth was investigated. At around the low temperature limit for epitaxial growth (410°C), the RHEED pattern shows a clear difference between the irradiated (Fig. 2(A)) and the nonirradiated (Fig. 2(B)) areas. This difference was also observed for the temperature range from 410°C to about 470°C. Since the increase of the surface temperature due to SR irradiation was less than 15°C, this phenomenon is caused mainly by the photoexcitation effects. The improvement of crystallinity was also reflected in the Raman scattering spectrum of these samples (3). From these results, it is concluded that SR irradiation is effective for lowering Si epitaxial growth temperature.

References

Fig. 1. Growth rates of Si film as a function of substrate temperature. Open and closed dots represent SR-excited growth. Growth rates of the thermal growth are also shown by the open and closed squares. For comparison, the growth rate for thermal deposition without SR irradiation is also shown in broken lines.

Fig. 2. Comparison of the RHEED patterns between irradiated (A) and nonirradiated (B) areas at around the low temperature limit for epitaxial growth. Substrate temperature and disilane pressure were 410°C and 1.5×10⁻¹ Torr, respectively.
REMOVAL OF MOLYBDENUM NATURAL OXIDE BY SYNCHROTRON RADIATION

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INTRODUCTION

With the progressive miniaturization of VLSI devices, it is becoming increasingly difficult to remove natural oxides from interconnecting metal surfaces by using conventional methods. Because the natural oxides increase contact resistances and obstruct the growth of metal plugs, a new removal method is required. The well-known photoinduced desorption of oxygen from metal surfaces implies that synchrotron radiation (SR) irradiation might remove natural oxides. This paper therefore reports the effects of using SR irradiation on molybdenum natural oxide.

EXPERIMENTAL

Experiments were performed at the beam line BL-IC which was constructed for the study of photochemical processes. The white beam of this beam line was used to excite the substrate surface. The calculated photon flux density was $1 \times 10^{17}$ photons/sec cm$^2$ at a ring current of 300 mA. The substrate was heated by a carbon heater in an ultrahigh vacuum chamber with a base pressure of $1 \times 10^{-9}$ torr. The substrate temperature was monitored with a thermocouple.

A molybdenum film was deposited by magnetron sputtering on a Si wafer covered by thermal SiO$_2$. In air, the surface of a molybdenum film is usually covered with a film of native oxide 5-10 Å thick. After the SR irradiation, the sample was transferred under vacuum to a chamber where the amount of surface oxygen was measured by Auger electron spectroscopy (AES).

RESULT AND DISCUSSION

Figure 1 shows how the oxygen AES (0 KLL) signal intensity depended on substrate temperatures when the irradiation dose (ring current x irradiation time) was about 10 A min. The data were normalized by the value of the initial surface. Because the thickness of the oxide was less than the mean free path of the oxygen Auger electron, the oxygen AES signal intensity was almost proportional to the thickness of molybdenum natural oxide. The reduction of the surface oxide by SR irradiation was observed even at the low temperature near room temperature, and the amount of surface oxygen decreased with increasing substrate temperature. The data from the non-irradiated region show that the oxide was not removed by heating up to only 400°C. For several substrate temperatures, Fig. 2 shows how the intensity of the oxygen AES signal depended on irradiation dose. This figure indicates that the oxygen reduction process involves two kinds of reaction processes. The reaction probability of the first step was greater than $10^{-6}$/photon, and that of the second step was roughly $10^{-7}$/photon. To evaluate the potential of this photochemical process for cleaning metal surfaces, the effects of SR irradiation on the metal silicidation reaction are going to be investigated in succeeding experiments.

REFERENCE

SYNCHROTRON-RADIATION-STIMULATED EVAPORATION AND CRYSTALIZATION OF MICROCRYSTALLINE SILICON

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INTRODUCTION
To understand the fundamental mechanism involved in the photo-etching with etching gases such as SF₆ and XeF₂, irradiation effect for the solid material in UHV should be studied. We have previously discovered that synchrotron radiation (SR) irradiation of an a-SiO₂ film causes continuous photostimulated evaporation at high temperatures even without an etching gas.¹ ² We report here a similar experimental result for microcrystalline Si (μc-Si).

EXPERIMENTAL
The experiments were made at the beam line 1C using a UHV photochemical reaction chamber. The total incident photon was 2x10¹⁵/min per 100 mA of ring current. For μc-Si samples, a 3500-A-thick a-Si:H film was deposited from SiH₄ at 520°C onto a 1000-A-thick SiO₂ film. After annealing the sample at 600°C for 20 min, hydrogen in the film decreased to less than 2x10¹⁵ cm⁻³. Raman scattering showed a sharp peak at 522 cm⁻¹ but the RHEED pattern remained halo. These properties are indicative of μc-Si.

RESULTS AND DISCUSSION
In fact, the bulk of the μc-Si was evaporated without etching gas and the rate is shown in Fig. 1 for the SR dose of 10⁴ mA-min. The rate is about two orders of magnitude less than that for a-SiO₂ at the same temperature.¹ ² This large difference is due to the ionicity of the chemical bonds: An electronic transition breaks a Si-O bond more easily than an Si-Si bond.

The evaporation rate of μc-Si reaches a maximum at around 700°C. The rate increase between 500 and 700°C is caused by the activation of thermal processes involved in the evaporation e.g., enhancement of vibration and displacement of Si atoms. The bond rearrangement, on the other hand, induces recrystallization of the μc-Si film. Above 800°C, all of the surface regions became polycrystal, which was proved by the ring RHEED pattern. As polycrystalization progressed, the surface of the wafer changed from mirror-like to rough. The decrease in the rate above 750°C is closely related to this change in the crystalinity. The stimulated evaporation would occur exclusively at step or kink edges where atoms are loosely bound. Increasing crystalization greatly reduces such defect points, causing the rate to decrease.

Between 730°C and 780°C, a ring pattern appeared only in the irradiated region, whereas the nonirradiated region continued to give a halo pattern (Fig. 2). This observation shows that SR promoted the microcrystal-to-polycrystal conversion similar to the enhancement of solid-phase epitaxy by SR in an x-ray region.³

REFERENCES

FIG. 1. The dependence of the photoevaporation rate of μc-Si on substrate temperature. The rate is given for 100 mA of ring current.

FIG. 2. RHEED patterns demonstrating conversion from microcrystal to ordered-polycrystal in (a) irradiated and (b) nonirradiated regions. The SR dose was 10⁴ mA-min and the substrate temperature was 760°C.
Partial cross sections for production of multiply charged Xe ions under 4.1-8.0 keV X-ray impact

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Previously we determined the mean charges of $\text{Xe}^{1+}$ ions produced in photon collisions with Xe atoms over the L-edge region and observed their stepwise variation at the L-edges and furthermore showed that Monte Carlo simulation could reproduce well the observed behavior as a function of the photon energy. Recent experiments have revealed distinctive structures around the edge regions and just below the photoionization threshold energy, photoabsorption spectrum shows significant increase of the absorption of photons. In addition to smooth decrease, slow variations and sharp enhancement over narrow energy region in total photon production of Xe in L-edges have also been observed.

In order to get more insight in photoionization processes, we have in the present work measured fractional distributions of the produced $\text{Xe}^{1+}$ ions in photon impact and determined their production cross sections over the photon energy range 4.1-8 keV. After normalization of sum of the observed relative intensities of ions with various charges to the known total photoionization cross sections at the energy regions well below each L-edge, the partial cross sections for production of ions with different charges have been deduced as shown in Fig. 1.

Fig. 1 Partial cross sections for production of $\text{Xe}^{1+}$ ions as a function of photon energy

References
MEASUREMENT OF THE MASS OF THE ELECTRON NEUTRINO USING ELECTRON CAPTURE IN $^{163}$Ho

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In the Experiment No. 87-175, we accumulated $^{163}$Ho$^{3+}$, $^{163}$Ho$^{5+}$, and $^{163}$Ho$^{4+}$ spectra having an enough statistics for a thin dysprosium target (10µg/cm$^2$) deposited on a mylar backing, as already described in the page 240 of the Photon Factory Activity Report #7 (1989). However, we could not obtain $^{163}$Ho$^{4+}$ spectra with monochromatic photons from the BL-2B line, because it was found that there exist unwanted photons whose energies are about 1.6 keV in monochromatized photons from the BL-2B monochromator (the 10 m grazing-incidence monochromator).

Therefore we proposed a new experiment where a beryl double crystal monochromator at the BL-2A will be used for $^{163}$Ho$^{4+}$ fluorescence spectra measurements on dysprosium atoms. This proposal (No. 89-200) was approved in October, 1989.

In November 1989, a beryl double crystal monochromator was tested at the BL-2A, finding that this monochromator also did not show a good enough quality as a monochromator for the energy range 1.2 keV to 1.6 keV. We were confronted with the difficulty that there is no suitable X-ray monochromator to be able to measure $^{163}$Ho$^{4+}$ spectra.

At present, some efforts to improve this situation by cooling crystals at the BL-2A, are continued by some P.F. staff, while some people are looking for new materials including Yb:ZnS suitable to a monochromator for the energy range above-mentioned.

Replacing beryl crystals with InSb crystals at the BL-2A line, measurements of the quantity $N$ (see, equation (3) on the page 38 of the Activity Report #8, 1990) were repeated with the improved photon counter, where Kr/iso-butane gas mixture was used.

M-fluorescence spectra measurements on dysprosium atoms are performed using a Si(Li) detector, while the intensity of the corresponding incident photons are monitored with the same Si(Li) detector. (This is called "self-monitoring method" by us). Next, this monitor is calibrated with the photon counter, where a proportional counter and a beryllium absorber array$^{11}$ serves as follows: By adjusting the slit system as shown in Fig. 1 and by using a Be absorber of the photon counter having an appropriate thickness, the intensity of incident photons is reduced so as to be tolerable for counting with the proportional counter. Simultaneous measurements of fluorescence spectra on Dy with the Si(Li) detector and the intensity of incident photons with the photon counter, give the calibration factor for obtaining the quantity $N$. This calibration method is valid if the incident photons are uniformly distributed in the beam profile (~ 1 mm$^2$).

In June 1990, the energy of the 5p-3s X-ray line of the dysprosium atom was measured more carefully. This has the aim to test the possibility of our method for determining $\nu$, as described in the page 38 of the Activity Report #8 1990.

In May 1991, we tried again to look for the possibility of the fluorescence spectra measurement at lower energies at the BL-2B. Finally we found some conditions where the intensity of unwanted photons can be reduced to be able to measure $^{163}$Ho$^{4+}$ and $^{163}$Ho$^{5+}$ spectra, by adjusting some parameters in the undulator, the beam line, and the 10 m grazing-incidence monochromator. This was done in collaboration with Dr. A. Yagishita. We gratefully acknowledge his efforts.

References
1) S. Yasumi, Talk in the Undulator Beam line User Meeting at PF, KEK, May 7 ~ 8, 1990.
SITE SELECTIVE ADSORPTION OF Cl ATOMS ON Ni(111)
STUDIED BY BACK-REFLECTION X-RAY STANDING WAVE METHOD

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Introduction

We have previously studied the surface structure of (7\times 7)R30°C1/Ni(111) by means of surface EXAFS and back-reflection X-ray standing wave (SW) techniques. These analyses revealed that the Cl atom locates at the 3-fold hollow site with the Cl-Ni bond distance of 2.33 Å and the surface relaxation induced by Cl adsorption is negligibly small. For the fcc (111) surface, there are two inequivalent hollow sites, labeled as fcc and hcp sites. The Cl atom is expected to adsorb on either of these sites. In the present study, site selective adsorption was studied for the (7\times 7)R30°C1/Ni(111) system by the SW triangulation method.

Experimental

All the experiments were performed at BL-2A using the newly fabricated UHV apparatus. A (7\times 7)R30°C1/Ni(111) surface was prepared with the same procedure as in the previous study. The SW absorption profiles for the normal incidence 111 and 111 reflections were taken in the energy scanning mode. Cl-K fluorescence yield spectra were obtained by use of a Si(Li) solid state detector (SSD). Total electron yield spectra were also taken and used as the substrate SW profiles. Bragg reflectivity curves were recorded by monitoring the photoelectric current of a Cu mesh placed in front of the sample.

Results and Discussion

From the analysis of the Bragg reflectivity curves, the energy width of the incident X-rays and the mosaic width of the Ni crystal were estimated as 0.68 eV and 0.21°, respectively. Using these values, the SW profiles were analyzed following the theoretical formulation. For the 111 reflection, it was revealed that the Cl atom is located 1.84 Å above the bulk-extrapolated lattice plane, and is in good agreement with the previous result within the experimental error. Fig.1 shows the observed SW profiles (solid lines) for the 111 reflection. In contrast to the previous apparatus equipped with the proportional counter for fluorescence detection, the new one with the Si(Li) SSD enabled us to record the fluorescence data with considerably high S/Bratio (-3600%). The best fit of the Cl fluorescence yield profile (dotted line) gives the result that the Cl atom is located 1.91 Å above the Ni (111) lattice plane.

From the SW result for the 111 reflection, the distance between the Cl atom and (111) lattice plane can be calculated for the fcc and hcp sites, as shown in Fig.2. The SW result (1.91 Å) for the 111 reflection obviously agrees with the distance (1.97 Å) of the fcc site which is directly above the atom in the third substrate layer. This result suggests that adsorbate atoms form chemical bond with the top substrate layer, but are repulsive to the second layer.

Reference

Angular distributions of photofragments emitted following K-shell excitation of \( \text{Na} \) and \( \text{O}_2 \)

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For electric dipole transitions excited by linearly polarized radiation, the transition probability depends on the orientation of molecules relative to the polarization direction of the radiation. In the case of K-shell excitation of linear molecules, for \( \sigma \rightarrow \sigma \ (\Delta \Omega = 0) \) transitions, molecules oriented parallel to the polarization direction of the radiation are selectively excited, while for \( \sigma \rightarrow \pi \ (\Delta \Omega = 1) \) transitions, molecules aligned perpendicular to the polarization direction are selectively excited. The molecular orientation will directly be reflected in the angular distribution of fragment photoions immediately emitted from a repulsive potential of molecular ions reached after a fast Auger decay of K-shell vacancy (\( \tau \sim 10^{-14} \) sec) relative to molecular rotations (\( \tau \sim 10^{-10} \) sec). The angular distribution of the photoions is expressed by the similar formula as that of photoelectrons, and its anisotropic nature is characterized by an asymmetry parameter \( \beta \).

The BL-2B undulator provides us both tunable and linearly polarized exciting radiation over the spectral range near the K-shell thresholds of first-row elements. Combination of the advantages of the undulator radiation with angle-resolved fragment-photoion spectroscopy has enabled us to determine directly the symmetries of the K-shell excited states of \( \text{Na} \) and \( \text{O}_2 \).

Figure 1 (b) shows the obtained \( \beta \) parameters of \( \text{O}_2 \) in the vicinity of the K-shell ionization thresholds. Prominent anisotropic angular distributions of the fragment-ejection have been observed. Detailed results and discussions have been described in elsewhere.\(^1\)\(^-\)\(^2\)

References

Fig. 1. (a) Total-ion yield spectrum and (b) molecular orientation parameters of \( \text{O}_2 \) in the vicinity of the K-shell ionization thresholds.
XAS STUDY OF Cu₂Sb TYPE COMPOUNDS

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I Introduction
The intermetallic Cu₂Sb type compounds have two crystallographically different magnetic sites (we call M(I) and M(II)), and reveal complex magnetic properties. For instance, Mn₂Sb is a ferromagnet (Tₘ = 550K) and shows spin reorientation. In addition, a first order ferri-antiferro magnetic transition occurs when a small part of Mn is replaced by Cr or Co atoms. The values of the magnetic moments are much smaller than those of localized spins, and suggest that the 3d electron states of magnetic atoms have broad band width.

II Experimental
In order to understand these complex magnetic features, we carried out XAS measurements of Cr, Mn and Fe 2p core levels of these materials at BL-2B with 10m Vodar monochromator. We employed an entrance and exit slit of 15μm. The spectra were taken in the total electron yield mode and were normalized by the incident photon flux which was measured simultaneously with use of a stainless mesh placed in front of the entrance slit. The samples were scraped in situ by a diamond file. The base pressure of the analyzer chamber was 1x10⁻¹¹ Torr.

III Results and Discussion
Mn 2p XAS spectra of Mn₂Sb and MnAlGe are shown in Fig.1. Both spectra show broad structures in the 2p₁/₂ as well as 2p₃/₂ region. Thole et al. calculated Mn 2p XAS spectra assuming various ground state configurations and tried to fit the XAS spectra of Mn impurity in Cu and Ag and of Mn metal, where the spectra of CuMn and AgMn were found to be in good agreement with the theoretical spectrum for 3d⁵ 6s⁵/₂ ground state configuration. On the other hand, the experimental Mn metal spectrum with no significant multiplets is interpreted to be due to a delocalized character of Mn 3d electrons. Our Mn₂Sb and MnAlGe spectra are similar to the Mn metal spectrum. The 2p₃/₂ peak is much stronger in Mn₂Sb than in MnAlGe. The 2p₃/₂ peak in MnAlGe (Mn(I)) is rather broad. It seems as if an additional contribution from Mn(II) is overlapping on this peak in Mn₂Sb. This fact may be ascribed to a more delocalized character of the Mn(I) 3d state than the Mn(II) 3d state in Mn₂Sb.

Cr and Fe 2p XAS spectra of Cr₂As and Fe₂As are also measured (not shown in the figure). Slight multiplet structures are recognized in both 2p spin-orbit components. The observed line shapes are qualitatively reproduced by the calculated spectra of Cr^{2+} and Fe^{2+} in high spin configuration performed by Yamaguchi et al. But the calculation does not involve hybridization effects. In order to quantitatively interpret the spectra, however, hybridization effect should be taken into account.

References
Collapse of the Mott-Hubbard framework by hole-doping in Bi$_2$Sr$_2$CaCu$_2$O$_8$ observed by polarized oxygen K absorption spectroscopy

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In this report, we present the first comparative polarized oxygen K absorption spectroscopy on the superconductive and nonsuperconductive Bi$_2$Sr$_2$Ca$_{1-x}$Y$_xCu$_2O$_8$ (x=0.0 and 0.6) single crystals. Comparison of the polarized oxygen K absorption spectrum between the superconductor and the nonsuperconductor would give some insights into the process of formation of the Fermi-liquid-like states and the atomic orbitals involved in the process. The x-ray absorption measurement was performed at BL2B. The oxygen K absorption spectrum was recorded at room temperature with the total-photo-yield method at the energy resolution of about 70 meV.

Figure 1 shows polarized oxygen K absorption spectra of superconductive Bi$_2$Sr$_2$CaCu$_2$O$_8$ (lower panel) and nonsuperconductive Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_8$ (upper panel) single crystals measured at two incidence-angles (0) of 0° and 75°. The parallel component (0=0°) of the spectrum for the superconductor shows a prominent peak at the absorption-threshold at 528.5 eV which is almost equal to the binding energy of the oxygen Is core level, while the intensity of the peak is remarkably reduced in the spectrum of 0=75°. This indicates a dominant O 2px nature of the electronic states at the Fermi level in the superconductor. As for the nonsuperconductor, such a peak is not observed in the spectra. Instead, a large shoulder emerges at about 529.5 eV in the parallel component (0=0°). This shoulder has a strong in-plane symmetry. We ascribe this large shoulder observed only in the nonsuperconductor to the upper Hubbard band projected into the O 2p states through the p-d hybridization. It is clearly seen in Fig. 1 that there is a transfer of weight of the electronic states between the shoulder at 529.5 eV [upper Hubbard band] in the nonsuperconductor and the peak at 528.5 eV [mid-gap states] in the superconductor. This suggests that the hole-doping causes a gradual collapse of the Mott-Hubbard framework of the electronic structure standing in the insulator.

The present comparative polarized oxygen K absorption spectroscopy has revealed the process of the formation of the Fermi-liquid-like states in the high-Tc superconductor. The experimental result has directly shown the existence of the upper Hubbard band with a perfect in-plane symmetry about 1 eV above the Fermi level in the insulator, which indicates that the Mott-Hubbard picture certainly stands in the insulator. We found that the hole-doping into the insulator causes a transfer of weight of the electronic states from the upper Hubbard band to the additional states [mid-gap states] produced in the gap by the hole-doping itself. This suggests that the Mott-Hubbard framework in the electronic structure gradually collapses by the hole-doping and finally the band picture may be recovered in the superconductor.

![Polarized oxygen K absorption spectra of superconductive Bi$_2$Sr$_2$CaCu$_2$O$_8$ (lower panel) and nonsuperconductive Bi$_2$Sr$_2$Ca$_{0.4}$Y$_{0.6}$Cu$_2$O$_8$ (upper panel) single crystals measured at two incidence-angles (0= 0° and 75°) of linearly-polarized synchrotron-radiation light.](image-url)
Angular Dependence of Photoelectric Yield Spectra of CeRuSns

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Distortion of spectral line shape in absorption can be occurred because of the lifetime and the various complicated resonant effects of the excited states. Especially, the deformation could be large in the materials having a strong absorption. Aim of this experiment is to estimate such spectral distortion from the measurement of angular dependence of photoelectric yield spectra with respect to the incident beam. Samples are CeRuSns, which is interesting as a new heavy fermion material. The surface of samples was scraped by diamond files and using the 10° grazing-incidence monochromator at the undulator beam line BL-2B the photoelectric yield spectra were measured. The yield electrons from the sample were directly detected by electrometer at various incident angle in the region of Ce 3d absorption edge.

Figure 1 shows the total yield spectra of Ce Mn, from CeRuSns, at 60° which is of the angle of incidence to the surface normal. The Ce Mn yield spectrum consists of a main peak at 900.5 eV and three weak structures on the both sides of the peak. The Ce Ms shows two high peaks around 883 eV and two weak structures in the low energy side of the two peaks. These structures are due to 3d104f→3d3f transitions. The valence of Ce in the CeRuSns can be estimated to be 3+ from the multiplet structures which were revealed in the yield spectra.

The angular dependence of the yield spectra was measured by rotating the sample respect to the incident beam 10° to 80°. However, contrary to expectation the deformation in the line shape did not be seen in this experiment. This results should be reexamined in the future.

References


Fig 1. Ce Mn, Yield Spectra of CeRuSns.
RESONANT PHOTOREMISSION OF Bi$_2$Sr$_2$CaCu$_2$O$_8$

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Introduction

The valence band resonant photoemission spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$ near Cu$^{2+}$ and O$^{1s}$ absorption edges were measured. The valence band photoemission spectra of this compound was studied by Fujimori et al. They attributed the satellite structure which appeared at the high binding energy side of the main band to d state by their cluster model calculation. The initial state of this compound is essentially d state, so, after direct photoemission process, the final state is d state (d$^0$ —> d$^0$ + e). This d$^0$ state is also formed after Cu$^{2+}$ —> 3d absorption process (2p$^6$3d —> 2p$^5$3d$^0$ —> 2p$^6$3d$^0$ + e). Therefore, we can expect the resonance effect between these two processes.

Experimental

Measurements were carried out with a 10 m grazing incidence monochromator at the undulator beam line BL-2B of Photon Factory. The samples of Bi$_2$Sr$_2$CaCu$_2$O$_8$ were available as single crystals. The sample chamber was evacuated to the vacuum of 7x10^{-9} Torr. Clean surfaces were prepared by cleavage in situ. The total resolution including the DCMA analyser and the monochromator at the Cu$^{2+}$ edge was about 1eV.

Result and Discussion

Figure 1 shows the valence band photoemission spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$ in the photon energy range from 912.2 eV to 962.2 eV. At photon energy of 931.5 eV and 951.2 eV, the resonance energy for Cu$^{2+}$/2 and Cu$^{2+}$/2, respectively, the satellite peaks show the giant resonance near the binding energy about 11 eV. On the other hand, the main bands near the Fermi edge show weak resonance.

In this respect, we consider that the origin of this peak is due to O$^{1s}$ two hole states following O$^{1s}$ —> 2p absorption process (1s$^2$2p$^5$ —> 1s$^2$2p$^4$ —> 1s$^2$2p$^4$ + e).

Reference


Figure 1

...
POLARIZATION DEPENDENCY IN THE Ce 3d-4f XAS OF CeRhaBz

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INTRODUCTION

Polarization dependency in the Ce 3d-4f absorption of CeRhaBz were measured. CeRhaBz is very interesting compound due to its high Curie temperature, Tc=115K and shows a strong valence-fluctuation of n=0.85-0.90. The single crystal of this compound has a Hexagonal structure and has a strong anisotropy along the C axis. The interatomic Ce-Ce distance along C axis is much shorter than that in the C plane. Recently, Kasaya et al.1 reported anisotropic magnetic properties of the compounds. These anomalous properties are attributed to the overlapping of 4f orbital coming from strong crystal field. Therefore, we can expect the polarization dependency in Ce 3d-4f absorption spectra.

EXPERIMENTAL

Measurements were carried out with a 10 m grazing incidence monochromator at the undulator beam line BL-2B of photon factory. The single crystal of CeRhaBz were sliced parallel to the C plane and were crashed to get clean surface. The sample chamber was evacuated to the vacuum of 1x10^-10 Torr. Samples were turned or rotated to the polarization of incident beam parallel and perpendicular to the C axis. The energy resolution was about 0.2eV.

RESULTS AND DISCUSSION

Figure 1 shows the Ce 3d-4f absorption spectra of CeRhaBz. The upper curve was taken for the polarization of electric field parallel to the C axis (E//C) and lower one was taken perpendicular to the C axis (E\perp C). The polarization dependency, so called linear dichroism is clearly seen in the 3d 5/2 absorption peak and in the 3d 3/2 region. Similar linear dichroism was observed by Fujimori et al.2 in the Ce 4d-4f absorption spectra for same crystal. They measured the spectra under 80K. On the other hand, in our study, measurements were performed under room temperature, therefore, only crystal field should be taken into account to analyze the spectra. Recently, Jo3 calculated the linear dichroism for Ce 3d-4f absorption spectra by impurity Anderson model taking into account the crystal field effect and multiplot effect. The difference spectrum (not shown) between the E//C and E\perp C spectra is good agreement with the calculated result by Jo.

REFERENCES

2) A.Fujimori et al., private communication
Dissociation dynamics of inner-shell photoexcited molecules composed of light elements

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Auger-electron—photoion coincidence (AEPICO) measurements are indispensable for studying the ionic fragmentations of core-excited molecules. Recently, we have developed a new apparatus for electron-ion coincidence studies (EICO apparatus). We have performed the Auger-electron—photoion coincidence measurements for SiF₄ using a time-of-flight (TOF) mass spectrometer and a parallel-plate electrostatic analyzers.


As the application of the EICO apparatus, we have developed "symmetry-resolved photoabsorption spectroscopy" using a technique of angle-resolved photoion spectroscopy combined with linearly polarized undulator radiation, and applied it to first-row diatomic molecules in the K-shell excitation regions, and obtained Σ- and Π-symmetry component spectra (Fig.1).


6)"High-resolution and symmetry-resolved nitrogen and oxygen K-edge spectra of NO". N. Kosugi, E. Shigemasa, and A. Yagishita, in preparation for publication.

![Fig.1. Symmetry-resolved K-shell photoabsorption spectra of N₂.](attachment:image.png)
The Ne 1s shake-up structures have attracted the attention of many workers for the fact that a conjugate shake-up structure induced by dipole transitions (1s→3s ionization, 2p→3s excitation) has been firstly observed by means of X-ray photoelectron spectroscopy (XPS). The structures observing by XPS, ordinarily, are normal shake-up structures induced by monopole transitions (1s→3p, 2p→np). The normal shake-up processes are explained well by the sudden approximation but the conjugate shake-up ones are forbidden in the situation of the approximation. Indeed, the Ne 1s conjugate shake-up structure observed by XPS shows very weak intensity only 0.05% of the 1s photo line. However, recent theories and experiments have revealed the fact that conjugate shake-up intensities are enhanced in shake-up thresholds. So, we measured the Ne 1s shake-up structures by means of a threshold electron technique.

Experimental

Experiments were performed using a 10m grazing incident monochromator at the undulator beam line BL—2B2. The monochromator was equipped with a 2400 grooves/mm grating. The spectral resolution was about 0.6 eV at 900 eV. The mass spectrometer used was of time-of-flight type accompanied with a threshold electron energy analyzer. The energy resolution of the analyzer is estimated to be about 0.01 eV from a measurement for Kr 4p outer—shell photoelectrons.

Results and Discussion

Figure 1 shows photoion spectra of Ne$^{2+}$ and Ne$^{3+}$ ions taken in coincidence with threshold electrons. Ne 1s shake-up processes take place in the photon energy region. Some prominent peaks due to the shake-up processes can be seen in the photoion spectra, which are labeled by notation of A—F. Peaks C and D correspond to ones observed by XPS. These peaks are assigned to the normal shake—up structures, 1s→2p$^1$(P, P)3p. Similarly, peaks E and F are assigned to 1s→2p$^1$(P, P)4p. On the other hand, peaks A and B are presumably assigned to the conjugate shake—up structures, 1s→2p$^1$3s or 3d.

References

Ar 2p SHAKE−UP STRUCTURES
STUDIED BY THRESHOLD ELECTRON SPECTROSCOPY

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Introduction

Recently, we have observed the Kr 3d and Xe 4d shake−up structures by means of threshold electron techniques. The observed spectra exhibited not only normal shake−up structures induced by monopole transitions (ex. 3d £p or £f, 4p ^ np in Kr) but also conjugate shake−up structures induced by dipole transitions (ex. 3d £d, 4p ^ ns or nd in Kr). This fact is in agreement with the theoretical prediction that conjugate shake−up intensities increase as photon energies decrease. The shake−up structures, ordinarily, have been observed by means of X−ray photoelectron spectroscopy (XPS). The observed structures are mainly normal shake−up ones, while conjugate shake−up structures are almost unobserved except for the case of Ne 1s shake−up. This work is now extended to the Ar 2p shake−up region such as Kr and Xe of the previous work.

Experimental

Experiments were performed using a 24 meter spherical grating monochromator at BL−3B. The monochromator was equipped with a 1800 grooves/mm gold−coated holographic laminar grating. The spectral resolution was about 0.2 eV at 250 eV. The mass spectrometer used was of time−of−flight type accompanied with a threshold electron energy analyzer.

The threshold electron analyzer is of steradiancy type. The energy resolution of the analyzer is estimated to be about 0.01 eV from a measurement for Kr 4p outer−shell photoelectrons.

Results and Discussion

Figure 1 shows the threshold electron spectrum in the Ar 2p shake−up region. The spectrum exhibits prominent peaks of A−F. To attain tentative assignments of these peaks, we performed by the multiconfigurational Dirac−Fock (MCDF) energy calculations using the code of Grant et al. The calculated energy ranges are indicated in the upper parts of figure 1. Peaks C−F are ascribable to normal shake−up structures (2p ^ 3p ^ nl) which have been observed by XPS, whereas peaks A and B are ascribable to conjugate shake−up structures (2p ^ 3p ^ 4s or 3d) which have not been observed by XPS.

References

The 2s^{-1} 2p^{-1} nl Correlation Satellites in the Outer-Shell Photoionization of Ne Atom

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Introduction

One of recent topics in photoionization studies of atoms and molecules is satellite structure in photoelectron spectra. The satellites associated with ionization by x-rays of outer (valence and subvalence) shell electrons are normally called "correlation satellite" because the occurrence of such satellites is attributed to sudden change in the correlation of many-electron system. In ionization of outer-shell electron by VUV radiation where photoelectrons carry away smaller excess energy, the phenomena become more complex and the sudden-change model is expected not to apply. We have studied correlation satellites of 2p^{-1} nl and 2s^{-1} 2p^{-1} nl types of Ne atom by using synchrotron radiation. The photon energy range investigated is 55~210eV. Satellite spectrum as well as intensities of the parent 2p and 2s peak were recorded at different photon energies. For main satellite peaks, we have examined the energy dependence of their intensities relative to the parent (2p or 2s) peak.

Experimental

The experiment was done at the BL-3B in the synchrotron radiation facility (Photon Factory) of National Laboratory for High Energy Physics (KEK). A monochromatized synchrotron radiation from the 24-meter spherical grating monochromator (24m-SGM) crossed a Ne-atom beam effusing from a gas nozzle. Photoelectrons resulting from the photon-atom interaction were energy analyzed by a spherical electrostatic analyzer with a resolution of about 0.25eV. The energy analyzer is set at the magic angle (54.7°) relative to the polarization direction (horizontal) of the radiation. The control of the radiation monochromator and the electron energy analyzer, the accumulation of the spectral data, and the analysis of the data obtained were made by using personal computers.

Results and discussion

The satellite spectra in the VUV region obtained in this study are fairly different from those in the x-ray region reported by Svensson et. al. The satellite/parent intensity ratio for each 2p^{-1} nl satellite peak (not shown here) varies in a complex manner against photon energy. The variation is especially dominant in the region below 100 eV, indicating that electron correlation plays dominant role here. Figure 1 shows, as an example, the 2s^{-1} 2p^{-1} nl satellite spectrum obtained at photon energy 125eV. It is compared with the corresponding satellite spectrum taken at 1487 eV reported by Svensson et. al. The 2s^{-1} 2p^{-1} nl satellite states relax mainly by autoionization because they lie above the threshold of double ionization (2p^{2}). It follows that each satellite peak accompanies its autoionization peak in the lower kinetic-energy region. One sees in figure 1 that the left part (E_{B}>96eV) of the spectrum consists of such autoionization peak and mirrors the satellite spectrum in the region of E_{B}<96eV. Other marked differences of our spectrum with respect to that of Svensson et. al. are (a) the satellite peak 21 at E_{B}=85eV, assigned 2s2p^{2}(P)3s^{2}P + (^P)3p^{3}P, is largely enhanced and (b) new peaks denoted by x and y appear at about E_{B}=92eV and E_{B}=95eV, respectively. We have assigned these new peak tentatively as 2s2p^{2}(P)np(^P) with n=3 (x) and n=4 (y).

References


![Figure 1](image-url)
Dissociation following the photoexcitation of inner-shell electrons to the discrete resonances has been of much interest because of its site-specific nature. To understand the state-to-state dissociation dynamics, it is indispensable to perform mass spectroscopy of fragment ions taken in coincidence with energy-resolved electrons ejected through the resonance Auger decay processes. We report here the first result of such resonance-Auger-electron-photoion coincidence (RAEPICO) measurement. The results reported here are for BF$_3$.

The experiments were carried out on beamline BL-3B at the Photon Factory using a newly developed electron-ion coincidence apparatus [1]. Figure 1 shows a resonance Auger spectrum of BF$_3$ excited at the B 1s –> $d_2^*$ resonance. The ionization potential scaled on the top abscissa indicates the energy of the resonance Auger-final BF$_3^+$ states relative to the ground state of the neutral BF$_3$. According to the ab-initio analysis [2], the A1 and A2 peaks are assigned as the BF$_3^+$ states having two outer-valence holes at different F atomic sites and at the same F atomic site, respectively, with one excited electron, and the A3 peak is assigned as the BF$_3^+$ states having one outer-valence hole, one inner-valence hole at different F atomic sites, and one excited electron.

The A1, A2, and A3 spectra in Fig. 2 were taken in coincidence with the resonance Auger electrons corresponding to the A1, A2, and A3 peaks, respectively, in Fig. 1. For comparison, we took also the photoelectron-photoion coincidence (PEPICO) spectra. The P1, P2, and P3 spectra in Fig. 2 were taken in coincidence with the outer-valence, inner-valence, and B 1s photoelectrons, respectively, of BF$_3$.

The P1 PEPICO spectrum indicates that fragmentation from the BF$_3^+$ states having one hole in an outer-valence orbital produces only BF$^+$, while the A1 RAEPICO spectrum indicates that fragmentation from the BF$_3^+$ states having two outer-valence holes and one excited electron predominately produces B$^+$, suggesting that the electron excitation from the outer-valence orbital to the unoccupied $d_2^*$ orbital dramatically affects the fragmentation.

The BF$_3^+$ states corresponding to the A3 peak and a higher energy part of the A2 peak lie above the double ionization threshold at ~ 40 eV. (See Fig. 1.) Thus, the autoionization is energetically allowed for these states. If the autoionization occurs, the final states will be the outer-valence two-hole states similar to the normal-Auger-final states. The A2 and A3 RAEPICO spectra is, however, quite different from the P3 PEPICO spectrum that represents mostly the fragmentation from the normal-Auger-final two-hole states. This indicates that there are dissociation channels starting from the resonance-Auger-final BF$_3^+$ states without the autoionization even though these states are above the double ionization threshold.

There are two major decay processes following the photoexcitation of inner-shell electrons to the discrete resonances in molecules. In the first process, which is called the participant Auger, the excited electron participates in the decay process. The final state of this process is the same as one-hole final states after the direct ionization of outer-shell electrons. In the second process, called the resonance (spectator) Auger, the excited electron acts as a spectator during the Auger-like decay. We report here observation of the resonance Auger spectra of BCl₃ in comparison with normal Auger spectra.

The experiments were carried out on beamline BL-3B at the Photon Factory using a 10-cm mean-radius hemisphere electron spectrometer (RIGAKU XPS-7000). The photon bandpass was 1.4 eV while the bandpass of the electron spectrometer was 0.4 eV.

Figure 1 shows electron spectra of BCl₃ taken at six photon energies in the vicinity of the B Is (199.8 eV) and C1 2p (208 eV) thresholds. The bottom spectrum taken below the B Is preedge structure represents outervalence and innervalence photolines that move toward the higher energy side with an increase in photon energy. In the top spectrum taken above the C1 2p threshold, B KVV and C LVV Auger components are superimposed as in the case of the 2-keV electron-excited Auger spectrum [1]. In the second spectrum taken just above the B Is threshold and below the C1 2p preedge structure, the B KVV Auger spectrum is not superimposed with C LVV and two broad peaks are revealed at electron energies of 163 and 155 eV. Based on the theoretical analysis by Cini et al. [1], the 163-eV and 155-eV peaks are assigned to Auger transitions whose final states are two-outervalence-hole states and one-innervalence-hole one-outervalence-hole states, respectively.

The other three spectra represent resonance Auger spectra. The photon energies 192.5, 197, and 198.5 eV correspond to B Is → 2pγ(α₂'), 2pγ*(ε'), and 4pγ(α₂'), respectively [2]. The 188.5-eV and 197-eV resonance Auger spectra are quite similar to the 200-eV normal Auger spectrum besides the energy shifts of 1.5 and 5 eV, respectively, toward the higher energy side relative to the normal Auger peaks. Thus, the high-energy and low-energy broad peaks are assigned to resonance Auger transitions whose final states are two-outervalence-hole plus one-electron states and one-innervalence-hole one-outervalence-hole plus one-electron states, respectively.

In the 192.5-eV resonance Auger spectrum, fine structure can be observed, although its envelope is similar to the 197-eV spectrum. The enhancement of the middle peak of outervalence photolines excited by 192.5-eV and 197-eV photons clearly indicates the participant Auger process. The middle peak is a superposition of 2α₂' and 6ε' photolines and these orbitals can be characterized with the B 2p atomic population [1]. This suggests that the 2α₂' and 6ε' participant processes following the B Is → 2pγ and 2pγ* excitations are closely related to the B 2p atomic population in the 2α₂' and 6ε' orbitals.

STUDIES ON ELECTRON-CORRELATIONS IN INNER-SHELL PHOTOIONIZATION OF ATOMS
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In recent years, excitation and ionization of inner-shell electrons in atoms and molecules and their subsequent Auger decay processes have been studied by each individual experiment such as photoelectron spectroscopy, Auger-electron spectroscopy, and photo-ion spectroscopy. Dynamics of such processes is an issue of great interest.

In order to study the dynamics of electron correlations in inner-shell photoionization of atoms, we proceed at present with the improvement of EICO apparatus and some basic and preliminary measurements as follows.

By changing photon energy, it has been proved that the post collision interaction (PCI) effect in the vicinity of the Kr 3d ionization thresholds, which is due to the electron correlation between the 3d photoelectron and the associated M-NN Auger-electron, make the line shape broadening and the energy shift of the Auger line.

Moreover, photoelectron – photoion coincidence measurements has been tried. Figure 1 (a) shows the time-of-flight (TOF) mass spectrum of Kr taken in coincidence with Kr 4s and 4p photoelectrons. Since, for valence electrons, there are no mechanism to produce multiply charged ions without direct multiple ionization, only Kr* is observed as expected. Figure 1 (b) shows the TOF mass spectrum taken in coincidence with Kr 3d photoelectrons. In the case of the 3d photoionization, the Kr2+ and Kr3+ ions are produced by the normal M-NN Auger decay and double M-NNN Auger decay, respectively. The Kr ions are not observed in Fig. 1 (b).

Angular correlation in coincidence between the photoelectron and the Auger electron will be measured in the course of time ambitiously.

Reference

![Fig. 1. TOF mass spectra of Kr taken in coincidence with (a) 4s and 4p photoelectrons and (b) 3d photoelectrons, obtained at a photon energy of 123 eV.](image-url)
GRAZING INCIDENCE X-RAY SPECTROSCOPY FOR THIN LAYER ANALYSIS

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The reflection curve and the fluorescence intensity profile curve for a stratified material under the grazing incidence conditions have a shape characterizing its layered structure. Modulation in the reflection curve is much affected by the thickness of the layers and the interfacial roughness.

The present paper describes the characterization of sputtered titanium thin film by the analysis of both reflection and fluorescence intensity profile curves. All measurements were performed using synchrotron radiation at the Photon Factory on the beam line 4A. The energy of incident X-rays was 10keV.

Figure 1 shows the experimental reflection curves, where periods of modulation become shorter as the heat treatment temperature is raised. This means that the layer thickness is increasing as the heating proceeds. Since the total Ti amount is not changed, the cause should be sought in the change of metallic titanium into titanium silicide due to the heating, resulting in the increase of layer thickness. New layers must be assumed on the surface and interface in order to fit the experimental results. Titanium oxide was found to be appropriate for the surface layer. As shown in Fig.2, the final results indicate that the composition consists of 42% titanium and 58% oxygen and the density is 4.67g/cm$^3$. The composition is similar to that of Ti$_2$O$_3$ (density = 4.6g/cm$^3$, Ti / O = 40 / 60). The total Ti amount calculated from the above results is 24μg/cm$^2$. This value is in good agreement with that determined by chemical analysis. This confirms the validity of the proposed structure model.

The analysis of the reflection and fluorescence curve for the heat treatment at 500K indicates that the Ti layer reacts with the silicon substrate to form the homogeneous silicide layer 64nm thick. The fluorescence intensity profile suggests that such a high-density surface layer as found in the as-deposited sample does not exist or, even if any, it is so thin that no influence is caused. It is estimated from the calculation that the silicide layer consists of 76% Ti and 24% Si, and its density is 4.41g/cm$^3$.

The authors express their sincere thanks to Dr. A. Iida and Dr. T. Matsushita of the National Laboratory for High Energy Physics for their invaluable support and guidance.

QUANTITATIVE ANALYSIS OF LIQUID SAMPLES USING TOTAL REFLECTION X-RAY FLUORESCENCE

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INTRODUCTION

In total reflection X-ray fluorescence spectrometry (TXRF), quantitative analysis of liquid samples by means of a calibration curve method or a standard addition method often meets with difficulties. In the measurement of energy dispersive spectrometry with monochromatic excitation, fluorescence intensity \( I_i \) and analyte concentration \( C_i \) can be expressed as

\[
C_i = I_i \left/ K e_i \right. \quad (i)
\]

where \( K \) is the parameter determined by experiment such as incident X-ray intensity and detector sensitivity; \( e_i \) is the constant parameter for element such as absorption coefficient and fluorescence yield. For the actual sample analysis, the following relationship was employed in consideration of matrix absorption by the sample:

\[
C_i = \left/ Ke_i \right. \exp (a \lambda_i) (2)
\]

where \( \lambda_i \) is the wavelength; \( a \) is the parameter determined by experiment. The unknown concentrations of three elements, \( C_1, C_2 \) and \( C_3 \) contained in the sample can be expressed as:

\[
C_1 = I_1 \exp (a \lambda_1) / K e_1 \quad (3)
\]

\[
C_2 = I_2 \exp (a \lambda_2) / K e_2 \quad (4)
\]

\[
C_3 = I_3 \exp (a \lambda_3) / K e_3 \quad (5)
\]

The overlap of \( K \alpha \) and \( K \beta \) as well as absorption by the air was corrected.

EXPERIMENTAL

All measurements were performed using synchrotron radiation at Photon Factory on the beam line 4A. NIST SRM 1643b (Trace Elements in Water) is used as the sample for analysis. A 100 \( \mu \)l aliquot of the sample was pipetted onto a silicon wafer (20 \( \times \) 20 mm\(^2\)) and then dried under an infrared lamp. For the calculation of quantitative value, Mn and Zn (50 ng/g) were added. TXRF measurements were performed before and after the addition. TXRF measurement conditions were as follows: excitation energy 12 keV, incident beam angle 2 mrad, beam size 0.15 \( \times \) 30 mm\(^2\), counting time 1000 sec. The peak area of \( K \alpha \) line in the spectrum was employed as the fluorescence X-ray intensity of each element.

RESULTS AND DISCUSSION

Table I shows the quantitative results for SRM 1643b. Good agreement is found except that the values of Fe and Zn are a little higher than the certified values. This is probably because the salt matrix concentration of SRM 1643b is so high that it absorbs moisture at room temperature, falling to form an ideal thin film.

The authors express their sincere thanks to Dr. A. Iida of the National Laboratory for High Energy Physics for his invaluable support and guidance.

REFERENCES


Table 1. Results for NIST SRM 1643b. Certified values are given for comparison.

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified, ng/g</th>
<th>Found, ng/g a</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>45.2 ± 0.4</td>
<td>43</td>
</tr>
<tr>
<td>Cr</td>
<td>18.6 ± 0.4</td>
<td>15</td>
</tr>
<tr>
<td>Mn</td>
<td>28 ± 2</td>
<td>21</td>
</tr>
<tr>
<td>Fe</td>
<td>99 ± 8</td>
<td>114</td>
</tr>
<tr>
<td>Co</td>
<td>26 ± 1</td>
<td>24</td>
</tr>
<tr>
<td>Ni</td>
<td>49 ± 3</td>
<td>47</td>
</tr>
<tr>
<td>Cu</td>
<td>21.9 ± 0.4</td>
<td>20</td>
</tr>
<tr>
<td>Zn</td>
<td>66 ± 2</td>
<td>86</td>
</tr>
</tbody>
</table>

a. For the calculation of \( K \) and \( a \), the fluorescence intensities of Mn, Zn and Ni were used.
A NEW ABSORPTION CORRECTION METHOD FOR TRACE ELEMENT QUANTIFICATION BY SRXRF

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Introduction

Recent advances in x-ray microprobe (XRM) have lead to micro x-ray fluorescence (XRF) analysis, and qualitative information of trace elements in the small region of heterogeneous samples can be discussed. However, when the signal intensity is discussed, differences between micro analysis and conventional bulk analysis makes it difficult to obtain quantitative information.

We have utilized the energy tunability of SR and a new absorption correction method was proposed and examined.

Principles of quantification

Use of SR as an energy tunable x-ray source can realize simplified theoretical description of XRF intensity. Considering the selective excitation of a specific kind of element with the incident beam energy just above the absorption edge energy, elimination of higher order excitation and the optimization of sensitivity can be simultaneously achieved. In this condition, XRF intensity $I_T$ can be expressed by the following equations.

$$I_T = kI_0(E)W_pt/sin\phi F$$

with $F = (1-exp(-ut))/ut$  

and $\mu = \mu(E)/sin\phi + \mu(E_f)/sin\psi$  

where $I_0(E)$ is the intensity of the incident x-rays, $\phi$ and $\psi$ are glancing angle and takeoff angle, $\mu$ is linear absorption coefficient, $E$ and $E_f$ are the energy of the incident x-rays and fluorescence x-rays, $W_p$ is the weight fraction of the element of interest, $t$ is thickness of the sample, $\rho$ is the sample density, and $k$ is constant.

The absorption correction coefficient $F$ in Eq.(2) represents the attenuation of both incident x-rays and fluorescent x-rays in the matrix. Therefore the corrected XRF intensity $I_T/F$ becomes proportional to $W_pt$, and quantification can be performed for intermediate samples in a manner similar for thin samples.

Using an energy tunable SRXRF system, $\mu(E)/sin\phi$ and $\mu(E_f)/sin\psi$ can be independently determined from conventional transmission measurements. The surface density of the element $W_pt$ can be determined by comparing the corrected $I_T$ to that obtained from reference thin samples.

Experimental

Experiments were carried out on the BL-4A. An energy dispersive x-ray fluorescence detection system was used with a Si(Li) detector. The beam size was 1.5 mm(H) 0.95 mm(V) on the sample. Incident x-rays of 9 keV were used for excitation and 6.4 keV x-rays were used to evaluate the transmittance of Fe Ka x-rays. The takeoff angle was set at around 45°.

To evaluate the feasibility of this method, trace Fe in National Institute for Environmental Studies (NIES) certified reference materials #6 Mussel was examined. The certified value of Fe is 158 ppm. A series of pellets(13 mm in diameter) were prepared from the same sample bottle.

Results and discussion

To estimate the inhomogeneity in a sample pellet, $ut$ and $I_T$ were measured at five different positions on the sample. At each position on the sample, $F$ was calculated and the correction of XRF intensity was carried out. Fig. 1 shows the observed Fe Ka XRF intensity $I_T/I_0$ and corrected XRF intensity $I_T/F$ as a function of $ut$. Though the thickness deviation results in the large standard deviation, the corrected data show a linear relationship to thickness.

The surface density of Fe was derived from a comparison between the corrected XRF intensity and XRF intensity with the reference thin films, and weight fraction $W_p$ was calculated using $pt$.

Obtained $W_p$ values agree well with the certified value of 158 ppm for intermediate thick samples of $ut$ ranging from 1.61 to 4.61. The accuracy of the analytical results was limited by sample inhomogeneity in this case. However, the accuracy of this method should be inherently determined by the experimental measurement accuracy.

Figure 1 Observed Fe Ka XRF intensity $I_T/I_0$ (white circles) and corrected intensity $I_T/I_0/F$ (black circles) as a function of $ut$. 

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APPLICATION OF SYNCHROTRON RADIATION TO ARCHAEOLOGICAL OBJECTS (V)

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**Professor Emeritus, Nagoya University, Nagoya 464, Japan

1. Introduction
SR-XRF technique has been applied to various problems in archaeology in our previous studies. In this paper we report XRF imaging of a bronze mirror made in China in the Later Han to demonstrate elimination of overlapping peaks by selective excitation technique. We also report chemical state analysis of a fragment of Temmoku bowl excavated by Prof. J.M. Plumer in 1935 at the kiln site in southern China. There is a spot pattern, so called "oil spots", on the black glaze of the bowl. The origin of this pattern has been a problem of archaeology for long years.

2. Experimental
Measurements were made at BL-4A, PF using the energy dispersive XRF system. The imaging technique used was described in our previous reports. The compositional image is represented by 14 densities from black to white corresponding to the intensity of the fluorescent X-rays of each element.

3. Results and Discussion
Figure 1 shows XRF spectra of the model compound (As2S3+PbF2+Cu) excited at (a) 16.0 and (b) 12.0 keV and of the sample of mirror (c) at 12.6 keV. As K edge (10.542keV) and Pb Lα (10.550keV) lines overlap in conventional EDS-XRF analysis with Si(Li) detector. XANES spectrum was obtained by normalizing the intensity of the fluorescent X-rays by the incident intensity and by plotting the data against the X-ray energy.

Two dimensional chemical analysis of the mirror was made for Fe, Cr, As and Cu based on the selective excitation. The result of As analysis is given in Fig. 2. The distribution of As was relatively uniform compared with those of Fe and Cr. It is known that there are two ways of pouring the charge at the manufacturing process of mirrors: the charge is poured into the mold, which is either kept horizontally or vertically. The distribution of Fe and Cr indicated a vertical way of the pouring. The rather uniform distribution of As is considered to be due to the small amount of As.

Fe K-edge XANES spectra of Temmoku bowl and some reference compounds of iron were measured and are compared in Fig. 3. The spectra of reference compounds, (a) metallic iron (Fe0), (b) olivine (Mg,Fe2)2SiO4, and (c) hematite Fe3+O2 show chemical shift of their absorption edges depending on their oxidation states. The spectrum (d) in Fig. 3 was measured at the surrounding part of the oil spots and that of (e) on an oil spot of the Temmoku bowl. It is found that the absorption edge of the spectrum (d) is close to that of Fe2+ in olivine, while that of the oil spot (e) shifts to hematite (higher energy) side compared with the spectrum (d), hence iron in the oil spot is more oxidized compared with their surroundings. It is thought that the origin of the oil spots may be bubbles formed during the manufacturing process. Our observation could propose the following mechanism of the formation of the oil spots: i.e., thermal decomposion of the source material of the bowl produces gas and the oil spots were formed by bubbles of this oxidizing gas.

The present XRF technique can be used in the two dimensional analyses of chemical state as well as chemical compositions of archaeological objects. This technique is truly nondestructive and does not require any pretreatment of the sample. Besides, the SR facility provides spatial freedom, which allows the analysis of large artifacts such as sculptures, paintings, etc. It can be said that the Synchrotron Radiation is an ideal light source for XRF analysis of archaeological objects.

References:
Simultaneous Detection of X-ray Photoacoustic and Fluorescence Signals for Evaluation of Fluorescence Quantum Yield(2)

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++ Department of Materials Science, Kanagawa University, Tsuchiya, Kanagawa 259-12

Introduction

The authors reported that quantum yield of X-ray fluorescence can be evaluated by analyzing the simultaneously measured photoacoustic(PA) and fluorescent(FL) spectra. Since the photoacoustic spectroscopy(PAS) is based on the measurement of heat generation that is concerned with the non-radiative process, the study combined with the fluorescence measurement enables us to trace the total flow of the energy relaxed in the sample. We have also reported that the self-absorption of the fluorescence may cause an error in the measurement of quantum yield. In this study, the contributions of self-absorption of PA- and FL-signals are estimated and examined for copper samples with various thicknesses.

Theory

The intensities of PA-signal \( I_p(E) \) and fluorescence \( I_f(E) \) (n=1,2, these correspond to \( K_1 \) and \( K_2 \)) by an excitation with intensity \( I_0(E) \) and photon energy \( E \) are given as,

\[
I_p(E) = I_0(E) \beta(E) E - \Sigma E_i \frac{C_{esc,n} Q_{1,n}}{C_{esc,n} Q_{1,n}} \]

where \( \beta(E) \), \( Q_{1,n} \), \( E_i \), and \( C_{esc,n} \) are the absorption coefficient, the quantum yield, the energy of fluorescence and the escape efficiency of fluorescence, respectively. \( C_{esc,n} \) equals 1-self absorption efficiency and is calculated from \( E_i \), \( E_{1,n} \), the sample thickness and the mass absorption coefficient. The ratio \( I_p(E)/I_f(E) \) will be given as

\[
\frac{I_p(E)}{I_f(E)} = \frac{C_T}{} E - \Sigma E_i \frac{C_{esc,n} Q_{1,n}}{} \]

where the \( \beta \) and \( I_0 \) terms vanish. If we plot the experimental \( I_p(E)/I_f(E) \) value as a function of \( E \), and extrapolate the plotted line to the point where it crosses the \( E \) axis, we obtain \( E_{0,n} \) and \( Q_{1,n} \) as follows,

\[
E_{0,n} = \Sigma E_i \frac{C_{esc,n} Q_{1,n}}{} = 0, \quad Q_{1,n} = ( E_{0,n} / E_i \frac{C_{esc,n} Q_{1,n}}{} ) T,
\]

where

\( T = E_{1,n} \frac{C_{esc,n} Q_{1,n}}{} / \Sigma E_i \frac{C_{esc,n} Q_{1,n}}{} \)

\( T \) can be obtained from \( C_{esc} \) and intensity ratio between \( K_1 \) and \( K_2 \) (S:1).

Experimental

The experiment was conducted at BL-4A. A chopped X-ray beam (f=20Hz) was irradiated onto a sample placed in a PA-cell. The photon energy of incident X-rays was in the 8 to 14 KeV region. The fluorescent X-rays were detected by a solid state Si(Li) detector and analyzed with the use of a multichannel analyzer. The PA-signal was detected by a condenser microphone and then amplified by a lock-in amplifier.

Results and Discussion

Fluorescence and photoacoustic spectra of copper foils were simultaneously measured. Fig.1 shows an intensity ratio plotted as a function of \( E \) for a 4 \( \mu \)m thick sample. The \( E_{0,n} \) values obtained by the extrapolation were 2.4 and 2.5 KeV for the \( K_1 \) and \( K_2 \), resulting in \( Q_{1,n} \) value about 0.32 and 0.07, respectively. In this calculation, \( C_{esc} \) was assumed to be constant. The total quantum yield of K-fluorescence is about 0.39. This value is in fair agreement with the reported value(0.4). However, the \( Q_{1,n} \) value obtained for thinner or thicker samples deviated from that for the 4 \( \mu \)m thick sample as shown in Table 1. This is considered to be due to two causes. The first is the background noise in PA-spectra. The second is that \( C_{esc} \) was assumed to be constant. In fact, \( C_{esc} \) is a function of the energy of excitation X-rays.

Table 1. Experimental values of fluorescence quantum yield of copper foils.

<table>
<thead>
<tr>
<th>Thickness/( \mu )m</th>
<th>( C_{esc} )</th>
<th>( E_{0}/\text{KeV} )</th>
<th>( T )</th>
<th>( Q_{1,n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.56 0.89</td>
<td>1.81 1.84</td>
<td>0.814 0.186</td>
<td>0.21 0.04</td>
</tr>
<tr>
<td>4</td>
<td>0.76 0.81</td>
<td>2.40 2.60</td>
<td>0.809 0.191</td>
<td>0.32 0.07</td>
</tr>
<tr>
<td>6</td>
<td>0.68 0.74</td>
<td>2.40 3.00</td>
<td>0.806 0.194</td>
<td>0.35 0.09</td>
</tr>
<tr>
<td>10</td>
<td>0.58 0.64</td>
<td>3.67 2.33</td>
<td>0.804 0.194</td>
<td>0.63 0.08</td>
</tr>
</tbody>
</table>

References

Because it is important to observe small amount of impurities on a surface of silicon wafers, high purity is a vital characteristic for silicon wafers. Iron, one of the impurities in silicon wafers, is a popular element that causes decrease of lifetimes of silicon wafers as well as other elements such as sodium, zinc etc. Total reflection X-ray fluorescence spectrometry (TR-XRF) was applied to characterize iron on surface of silicon wafers.

In the present experiments, quantities, depth profiles, and chemical states of iron on a surface of silicon wafers were measured. Silicon wafers for the experiments were contaminated with standard solution of iron by spin-coating, and annealed at 450°C and 650°C for diffusing iron into the silicon.

In the quantitative analysis, SR-TR-XRF is compared with other analytical methods such as wet analysis using flameless atomic absorption spectrometry (FLAAS) and commercial TR-XRF analysis. Fig.1 shows the intensities of the fluorescent X-ray of iron obtained from SR-TR-XRF and commercial TR-XRF against the concentration of iron measured by wet analysis. Good correlations between SR-TR-XRF and other methods can be found. Table 1 shows the quantitation limits of these methods. One may say that SR-TR-XRF is inferior to other analysis methods, however, there are many points to be improved for the sensitivity in the SR-TR-XRF. We think that SR-TR-XRF methods have the potential as high sensitive methods.

Depth profiles were obtained by changing the glancing angle of incident X-ray around the critical angle of the silicon (3.2 mrad, for the incident X-ray energy, 9.7 keV). Depth profiles of these samples revealed that iron exists on the surface roughly and inhomogeneously. But the quantity of the iron on the silicon wafer is too much to get information of iron inside the silicon wafer.

In order to know the chemical state of the iron, incident X-ray energy was scanned near absorption edge of iron and fluorescent X-ray spectra were obtained. These spectra showed that chemical states of iron of these samples are different from metal state. But it is difficult to identify the chemical state of iron because of less information from the present experiments.

Table 1. Quantitation limits (QL) of three methods

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>QL</td>
<td>$3 \times 10^{-1}$</td>
<td>$1 \times 10^{-8}$</td>
<td>$4 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Unit: atoms/cm$^2$
DETECTION OF DNA DAMAGE IRRADIATED WITH MONO-X-RAY;
PART IV: REPAIR OF DNA DAMAGE

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2) Department of Development, Hamari Chemical Co., Kunijima, Higashiyodogawa-ku, Osaka 553.
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INTRODUCTION

Recently, we have studied the detection of instability of nuclear DNA on acid hydrolysis by fluorescent staining with acridine orange (AO)(1,2). The quantitative detection methods were applied to determine the amount of DNA damages by mono-X-ray radiation in the presence of bromodeoxyuridine (BrdU) and/or hematoporphyrin oligomer (HpO-3000; mean molecular weight = 3000) two years ago(3). From the results, it was found that BrdU and HpO molecules enhanced the nuclear DNA damages irradiated at 0.918 Å which corresponded to the energy level of the K-shell electron of Br atomic nuclei. In the last year, the effect of various porphyrins for the radiation damages of nuclear DNA was examined at 0.918 and 5.763 Å. It was resulted that the values of y0 and k2 increased linearly with increasing of X-ray doses at 0.91 eÅ, furthermore, the slopes of the dose response curves in the presence of the porphyrins were large in the following order: HpO(3.16-4.19 times)>Photofrin II(1.62-2.56 times)>PH-1126(1.64-1.88 times)> Control(1.00 time)(4). On the other hand, the inhibitory effect of the porphyrins were observed at 5.763Å which corresponded to the energy level of the K-shell electron of P-atomic nuclei(4). In this study, The repair of DNA damage irradiated with mono-X-ray was investigated by previous detection method of acid hydrolysis and AO fluorescence staining(1,2).

EXPERIMENTS

Human melanoma flow (HMF) cells were treated with 100 µg/ml BrdU for 6 hr before harvesting. At 30 min before the harvesting, 50 µg/ml various porphyrins (Photofrin II®, HpO-3000 and a pheophorbide derivative (PH-1126) were administered in the cell suspension. The cells were washed with medium RPMI-1640 and were irradiated 5 kR in ice-cold water by mono-X-ray at 0.918 and 5.763 Å, respectively. At 1, 0.5, 1.3 and 6 hr after the irradiation, these cells were smeared on non-fluorescent glass slide and were fixed with 70 % EtOH aqueous solution for 16 hr at 4 °C. The fixed cells were treated by an acid hydrolysis and AO fluorescence staining method mentioned in our previous reports(1,2).

Fluorescence intensities of AO green and red fluorescence were measured by a fluorescence cytophotometry (model QH-2, Olympus). The hydrolysis curves obtained by the micro-photometry were fitted to the Bateman function: \[ y(t) = y_0 \frac{k_1}{k_2 - k_1}(\exp(-k_1t)-\exp(-k_2t)) \] to determine the kinetic parameters; \( y_0 \), the initial yield of apurinic acid or single-stranded DNA; \( k_1 \), the rate constant of depolymerization or the degree of DNA denaturation.

RESULTS

The values of parameter \( y_0 \) and \( k_2 \) obtained at 0.918Å were plotted against the duration time after X-ray radiation in the presence of BrdU as shown in Figs. 1, 2. The values of \( y_0 \) and \( k_2 \) decreased suddenly with increasing of the duration times until 1 hr after the radiation, respectively. At almost immediately after the irradiation, the enhancement of various porphyrins were compared in the parameters \( y_0 \) and \( k_2 \) as shown in Fig.3. HpO-3000 and BrdU enhanced more effectively than that of the other sensitizers in parameters \( y_0 \) and \( k_2 \). On the other hand, the repair of DNA damage irradiated at 5.763Å which corresponded to the energy level of the K-shell electron of P-atomic nuclei was obtained as shown in Fig.4. The value of parameters \( y_0 \) and \( k_2 \) decreased suddenly until 1 hr same as Figs. 1, 2. In conclusion, both parameters of \( y_0 \) and \( k_2 \) may reflect the single-stranded breaks damaged by mono-X-ray radiation to excision repair of the DNA damage.

REFERENCES

NONDESTRUCTIVE SYNCHROTRON RADIATION X-RAY FLUORESCENCE IMAGING OF TRACE ELEMENTS IN HUMAN KIDNEY

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**Department of Chemistry, University of Tsukuba, Ibaraki 305
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Introduction
The knowledge of the importance of trace elements in medical research has increased in the last few years. It is necessary for the study of the physiological role of trace elements to reveal detailed distributions of trace elements in organs or tissues. But fewer data are available concerning the two dimensional distribution of trace elements in organs or tissues. In the present study, we have analyzed zinc, copper, and selenium distribution in human kidney by nondestructive synchrotron radiation X-ray fluorescence (SR-XRF) imaging.

Experimental
The renal tissues examined (a newborn, an infant, and adults (a 22 years old-man, a 44 years old-man, and a 61 years old-man)) were free from occupational metal exposure. The renal tissues were fixed in 10% formalin and were paraffined. Then, the tissues were cut into slices of 2mm thick near the hilus of kidney.

Measurements were made at BL-4A, PF utilizing energy dispersive SR-XRF system with monochromatic X-ray obtained by Si(111) double crystal monochromator. Energy of X-ray used was 16keV. Two dimensional analysis was carried out by placing a sample on a XZ stage under the following condition: beam size = 750x750μm, step size = 750μm/step, counting time = 20sec/point (newborn and infant), 6sec/point (22 years old-man), 6sec/point (44 years old-man), 10sec/point (61 years old-man).

Results and Discussion
Examples of the results are given in Fig. 1, which show the distribution of zinc, copper, and selenium for the adult human kidney (22 and 61 years old). Zinc, copper, and selenium were more accumulated in the renal cortex than in the renal medulla. The same results were obtained from the other samples. This finding is interesting, because the function of the renal cortex is different from that of the renal medulla. For instance, there are glomerulus in the renal cortex, which play important roles in cleaning waste materials from blood. In addition, there are loop of Henle in the renal medulla, which is related with the concentration of urine.

Scott et al.1) found that zinc, cadmium, and calcium concentrations of the renal cortex were higher than that of the renal medulla. Julsham et al.2) also reported that selenium concentration of the renal cortex was higher than that of the renal medulla. Our results agree well with their findings. In their analysis, the renal cortex and the renal medulla were separated, and the trace element concentrations were determined by AAS. On the other hand, we have nondestructively revealed two dimensional distributions of zinc, copper, and selenium in human kidneys for the first time by SR-XRF.

Using the X-ray intensity data of each analytical points, correlation coefficients among the trace elements were calculated (Table 1). High correlation between two elements was observed, particularly, between zinc and copper. Concerning this result, differences depending on age were not observed. It is interesting to find high correlation between zinc and copper, because there is an enzyme which contains zinc and copper; i.e., Cu,Zn-superoxide dismutase.

As the present method does not cause any damage to the samples, we could examine the same sample histologically after the SR-XRF analysis. Therefore, this method will become a new histochemical technique for the analysis of biological tissues.

Reference

Table 1. Correlation coefficients between two trace elements for human kidney.

<table>
<thead>
<tr>
<th>case</th>
<th>Zn-Cu</th>
<th>Zn-Se</th>
<th>Cu-Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>newborn</td>
<td>0.911*</td>
<td>0.271*</td>
<td>0.229*</td>
</tr>
<tr>
<td>infant</td>
<td>0.400*</td>
<td>0.441*</td>
<td>0.582*</td>
</tr>
<tr>
<td>adult(22)</td>
<td>0.945*</td>
<td>0.643*</td>
<td>0.827*</td>
</tr>
<tr>
<td>adult(44)</td>
<td>0.842*</td>
<td>0.316*</td>
<td>0.457*</td>
</tr>
<tr>
<td>adult(61)</td>
<td>0.584*</td>
<td>0.615*</td>
<td>0.473*</td>
</tr>
</tbody>
</table>

*: P<0.01

Fig. 1. Results of chemical imaging of trace elements on the adult human kidneys.

a) Photograph of the sample slice (22 years old) and distribution of Zn, Cu, and Se.
b) Photograph of the sample slice (61 years old) and distribution of Zn, Cu, and Se.
NONDESTRUCTIVE SYNCHROTRON RADIATION X-RAY FLUORESCENCE IMAGING OF TRACE ELEMENTS IN HUMAN KIDNEY TUMOURS.

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Abstract

Introduction

Recently, the study of the physiological role of the essential trace elements has been emphasized in the research for possible causes of cancer. For instance, the blood serum levels of copper and zinc in cancer patients have been the subject of a multitude of investigations, and their possible involvement has been well recognized in many cancerous conditions. But in malignant tissues, few data are available concerning the distributions of trace elements. In the present study, two dimensional distribution of zinc, copper, and selenium in human kidney tumours was clarified by nondestructive synchrotron radiation X-ray fluorescence imaging.

Experimental

Materials of 12 cases examined are shown in Table 1. Cancerous tissues and corresponding normal ones were fixed in 10% formalin and were paraffined, then they were cut into slices of 2mm thick.

Measurements were made at BL-4A, PF utilizing energy dispersive SR-XRF system with monochromatic X-ray obtained by Si(111) double crystal monochromator. Energy of X-ray used was 16keV. Two dimensional analysis was carried out by placing a sample on a XZ stage under the following condition: beam size = 750 x 750μm, step size = 750μm/step, counting time = 10sec/point.

Results and Discussion

Examples of the results are given in Fig. 1, which show the distributions of zinc, copper, and selenium for the sample belonging to the case 3. Zinc, copper, and selenium were more accumulated in the normal tissue than the cancerous ones. Similar results were obtained from the other cases except for the case 8 and case 12.

Karcicoglu et al.5) and Margalioth et al.4) discovered significant decrease in zinc concentrations in kidney tumours. Concerning copper, Margalioth et al.4) reported that Cu concentration in cancerous tissues was lower than that in normal tissues. Our results agree well with their findings. Moreover, we have revealed two dimensional distribution of zinc, copper, and selenium in cancerous and normal tissues.

Using the X-ray intensity data of each analytical points, correlation coefficients among the trace elements were calculated (Table 2). The correlation coefficients between the elements in the cancerous tissues were lower than that in the normal tissues. In particular, the correlation coefficients between zinc and copper were statistically significant.

In recent years, many publications have appeared on the subject of free radicals in malignant disease. For example, the lowest activity of Cu,Zn-SOD (superoxide dismutase) was found in the hepatomas with the fastest growth rates5). Cu,Zn-SOD, which is one of the antioxidant enzymes, contains copper and zinc.

The trace element distribution and the correlation between two elements obtained by the present method agree with their finding. Therefore, it is estimated that these trace elements play important roles in cancer; they are constituents of metal enzymes.

Table 1. Materials of 12 cases examined.

<table>
<thead>
<tr>
<th>case</th>
<th>sex</th>
<th>age</th>
<th>clinical classification</th>
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Table 2. Correlation coefficients between two trace elements for cancerous and normal tissues.

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Fig. 1. Results of chemical imaging of trace elements on cancerous and normal renal tissue of the sample belonging to the case 3. a) the photograph of the sample slice C: cancer, N: normal b) Zn distribution, c) Cu distribution, d) Se distribution.
Development of Dedicated Measurement System
for X-ray Photoacoustic Spectroscopy

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3.Dept. of Applied Phys. Chem., University of Electro-Communications, Chofugaoka, Choufu 182, Japan
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5.Rion Co. Ltd., Higashi-motomachi 3-20-41, Kokubunji 185, Japan

Introduction

In order to apply the X-ray photoacoustic method for practical use, the improvement in sensitivity of the measurement system, i.e. detector and overall system, was inevitable. We have decided to check every factors which are contributing to the noise of photoacoustic signals and developed new sensitive measurement system for X-ray Photoacoustic Spectroscopy as a dedicated apparatus at PF.

Experimental and Results

1) Relation between surrounding air borne noise and X-ray photoacoustic signal

As reported elsewhere[1], air borne noise from air conditioning ducts at the Photon Factory experimental hall was the main source of surrounding noise and it would be included into the photoacoustic signal. The hall was estimated to be a little "hissy" in total as seen in Fig. 1, however, the frequency range of X-ray photoacoustic measurement was usually low as 5-50 Hz. So, the low frequency components are most important to be cut off. Since the quite low frequency noises are always found in signals, both of the photoacoustic cell and detector system were covered and sealed with air-tight box as seen in Fig. 2. This was also suitable for electric shield. Against mechanical noise, special insulating gel rubber and the anti-vibration slab were used on the base in order to cut off the mechanical vibration noise.

2) Improvement in data acquisition system

In place of A/D converter and hand made pulse stage driver, GPR–IB networking system was adopted with new instrumentations of the digital electrometer (Advantest Co. Ltd., model R-8240), 3D pulse controller (Chuo Precision Dev. Co. Ltd.), and Lock-in amp. (NF circuit design Co. Ltd., model 5610AS) The wave form of X-ray photoacoustic signal can be also accumulated by digital oscilloscope (Sony Tektronix Co. Ltd., type 2440).

Using BL4A and 15A, the setup of apparatus was performed for best state and the final S/N ratio was estimated to be improved about 3 times better than before. Super sensitive microphone is still under development. Final goal we set is 10–100 times improvement in S/N ratio.

Reference

1.T.Ohkuma, in this activity report.

Experimental and Results

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Evaluations of Acoustic Surrounding Noise at the Halls of PF and AR

Tsuneyasu Ohkuma

Rion Co. Ltd., Higashi-motomachi 3-20-41, Kokubunji 185, Japan

Introduction

In order to develop a sensitive X-ray photoacoustic measurement system, T. Masujima (Hiroshima Univ.) and M. Ando (PF) had asked Dr. T. Ohkuma (Rion Co.Ltd.) for evaluation of the acoustic circumstance at the Halls of PF and AR. This report is written by T. Masujima according to the Japanese report from Dr. Ohkuma who is now under the hospital care.

We have a feeling that the experimental hall of PF is a little noisy to concentrate on thinking and asked why and what is the cause. This report shows what kind of level and nature our halls of PF and AR can be evaluated on account of acoustic circumstances.

Experimental

High Precision Noise Meter (Rion NA-29E) and Signal Analyzer (Rion SA-77) were used for measurement on July 4, 1990 at time 13:00-17:00.

Results and Discussion

Table 1 shows the noise level and NC (Noise criteria) which were evaluated from the octave-band sound-pressure curves as shown in Table 2, Fig. 1 and 2.

The noise levels indoor of PF and AR were 60 db and 51 db respectively and NC were 55 and 45-50 respectively. These levels were larger than the office room. PF can be equivalent to computer room and AR be drafting room.

The quality of noise was evaluated by FFT analyzer and the noise both of PF and AR has higher frequency components much more than usual case. It can be say to be a little "hissy". The noise source seemed to come from air conditioning ducts, however the sound was not special one. The soundproof for the duct or compartments might be necessary for more quiet circumstance.
Elemental Scanning Analysis across the Muscle of the Antarctic Icefish, Champsocephalus gunnari with a Synchrotron Monochromatized X-ray Microbeam

Masafumi ISHIKAWA, Keiji NAKAMURA*, Atsuo IID*2 and Kenji OKOSHI*3

Div. of Marine Radioecol., Nat. Inst. of Radiol. Sci., Nakaminato, Ibaraki,310, Japan; *Labo. of Environ. Sci., Dept. of Gen. Educut., Ibaraki Univ., Mito, Ibaraki, 310, Japan; *2 Photon Factory, National Labo. for High Energy Physics, Tsukuba, Ibaraki, 310, Japan; *3 Dept. of Biotechnol., Senshu Univ. of Ishinomaki, Miyagi, 986, Japan

The Antarctic icefish, Champsocephalus gunnari, although expressed as bloodless, nevertheless possesses an anti-freeze mechanism for surviving in cold seas.(1) In our previous report(2) we suggested that its blood is completely lacking in haemoglobin.

Since this fish is migratory, its oxygen requirements are as high as those of fishes inhabiting temperate zones. Increased levels of transition metals such as Mn, Fe and Cu in the muscle but not in the gill of this fish have been detected using PIXE, suggesting that oxygen passes through the skin surface.

In the present study we investigated the vertical distribution of the elements S, K, Mn, and Fe in the icefish muscle to determine its physiological characteristics.

The muscles were dissected perpendicular to the axis of the fish into cross-sectional slices 50 μm thickness. The sections were fixed on a 2 μm Makrofol membrane.

Synchrotron white X-rays were monochromatized, with beam size H 200 x W 200 μm and scanning intervals of 150 μm horizontally and 200 μm vertically, forming 3364 pixels. Duration of exposure was 3 sec. for each point.

An X-Z movement system made a comb-like scanning.

Fig. 1-(a), (b), (c) and (d) show the respective scanning patterns for S, K, Mn and Fe on a cross section of the icefish muscle. The deposition patterns of the elements Mn and Fe were specific. In our previous report(2), we indicated that the Mn concentration in the icefish is 200 times higher than that in normal fish.

Fig. 1-(c) shows that Mn is densely distributed on the surface of the fish muscle, and that a comparable amount is also found beneath the surface skin. If oxygen transport in this fish is not initiated in the gill, then cutaneous respiration occurs and that Mn may assist in the oxygen delivery.

The distribution of Fe shows somewhat analogous pattern; deposition gradually decreases in proportion to muscle depth, and in the connective tissue, relatively higher deposition is observed. Oxygen bound with transition metals especially, the Fe present in high amount, may migrate together into the inner layer, where it is available subjecting to cyclic metabolic processes at acceptors.

Should these transition metals be found not to be involved in the transport of oxygen, how this process is accomplished in the icefish. And we still don't know whether or not this oxygen incorporation is equivalent to oxygen consumption of the fish in the cold sea. Roles of Mn and Fe could physiologically be significant in the icefish.

References
(2) M. Ishikawa and K. Nakamura; Nucl. Instr. and Methods, B49, 220(1990)
QUANTITATIVE IMAGING OF TRACE NICKEL IN A SYNTHESIZED DIAMOND

Shinjiro HAYAKAWA
Masao WAKATSUKI, Sadao AOKI, Yohichi GOHSHI and Atsuo IIDA

1) Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Tokyo
2) Institute of Material Science, University of Tsukuba, Tsukuba, Ibaraki
3) Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki
4) Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki

Introduction

An energy tunable x-ray microprobe (XRM) has enabled qualitative and quantitative x-ray fluorescence (XRF) analysis with spatial resolution. We have utilized the XRM for investigating trace impurities in synthesized diamonds.

Experimental

Experiments were carried out on the BL-4A using an XRM composed with an ellipsoidal mirror. The beam size was restricted to be 15 μm in diameter on the sample. An energy dispersive x-ray fluorescence detection system was used with a Si(Li) detector.

A single diamond crystal grown in a Ni-Fe alloy flux under the condition of high temperature and high pressure was polished into a plate of 270 μm in thickness. The sample was fixed on a plastic sheet with the takeoff angle of 45 degree, and both transmitted x-rays and fluorescent x-rays were measured.

Results and discussion

Fig. 1 shows a schematic representation of the sample. The sample was plenary investigated with the optical microscope to check the inclusions which show the strong XRF intensity of both Ni and Fe. The area marked on the figure was measured with 9 keV monochromatic x-rays.

Fig. 2 shows images of Ni Ka, Fe Ka XRF, scattered x-rays and transmitted x-rays. The Ni image clearly shows that Ni is dissolved selectively in {111} growth sector and that Fe is dissolved in neither sectors within the range of detectable concentration.

Fig. 3 shows XRF spectra taken in {111} and {100} sectors, respectively. To evaluate the attenuation of both incident x-rays and fluorescent x-rays, transmission measurements were performed with 9 keV and 7.4 keV x-rays. Utilizing the absorption correction method we have developed, concentration of Ni in {111} sector and in {100} sector were determined about 50 ppm and less than 0.5 ppm, respectively.

Reference

FOURIER ANALYSIS OF INTERFERENCE STRUCTURE OBSERVED IN X-RAY SPECULAR REFLECTION FROM THIN FILMS

Kenji SAKURAI and Atsuo IIDA

* National Research Institute for Metals, Sengen, Tsukuba, Ibaraki 305
Photon Factory, National Laboratory for High Energy Physics, Oho, Tsukuba, Ibaraki 305

Introduction

In grazing incidence X-ray experiments, as is often the case in practical analysis of multi-layered thin films, a complicated oscillating structure is observed in the angular/energy dependence of X-ray reflectivity. This is due to interference caused by multiple reflections of X-rays at each interface, and therefore, such oscillation includes the information on layer thickness and on interface roughness. In the present study, Fourier transform algorithm was first employed to determine the thicknesses of each layer from frequency components of oscillation.

Principle of the present technique

The oscillating part of the reflectivity from a multi-layered thin film is essentially expressed as the sum of cosine functions; they includes the total sum of

\[ A_j \cos(4\pi d_j \left\{ (\theta^2 - 8c_j^2)^{1/2} / \lambda \right\}) \]

where \( d_j \) and \( 8c_j \) are the layer thickness and critical angle of the jth layer; \( \theta \) is the glancing angle; \( \lambda \) is the wavelength of the X-rays; and \( A_j \) is a coefficient. Therefore the oscillating part of the reflectivity data, when plotted as a function of \((8c_j^2)^{1/2} / \lambda \), are converted by Fourier transform to the distribution of \( d_j \).

Experimental and Results

The experiment was done on beam line 4A. The apparatus employed is essentially the same as the one for the grazing incidence X-ray fluorescence analysis. SR beams were monochromatized by a Si(111) double-crystal sagittal focusing monochromator. Reflectivity ranging 1 to \( 10^9 \) was measured by detecting the intensities of incident and reflected X-rays with two ionization chambers. Optical alignment was optimized by the translational/rotational motion of the sample stage. The measurement was done in air.

Figure 1 shows the experimental results of reflectivity of 8 keV X-rays for a SiO\(_2\)/Si sample, which were prepared using the conventional thermal oxidation process. The thickness of the SiO\(_2\) layer obtained from ellipsometry was 501 Å. The critical angle \( 8c_2 \) was 3.81 mrad, which was determined within 0.1 mrad by the direct comparison with the calculated reflectivity curve for SiO\(_2\), and this accuracy is sufficient in this case.

The reflectivity measured was expressed as a function of \((8c_j^2)^{1/2} / \lambda \), and then, to compensate for the attenuation of the amplitude in the higher angle region, was normalized by the average curve obtained from the polynomial equation fitting in the logarithmic plot. After removing the non-oscillating background, the data were Fourier transformed. Figure 2 shows the results of Fourier analysis. A single sharp peak was clearly obtained, which gives the frequency of the oscillation observed in Fig.1. It is important that the peak position (499.5 Å) agrees well with the thickness of the SiO\(_2\) layer (501 Å). The differences are less than 1%.

The present results show that Fourier transform is effective in the analysis of the interference oscillation observed in the X-ray specular reflectivity. The advantages of this technique will become more apparent when applied to cases where the number of layers is increased. Fourier analysis is advantageous to separate the several frequency components, and can determine the thickness of each layer.

The authors would like to thank Dr. K. Saitoh and Dr. K. Honda for preparing samples.

References

3) K. Sakurai and A. Iida, submitted to JJAP.
Grazing Exit X-ray Fluorescence Spectrometry

Takashi Nom, Atsuo Iida*, Kenji Sakurai**

Research Center, Canon Inc., Atsugi Kanagawa 243-01
• Photon Factory, National Laboratory for High Energy Physics, Tsukuba Ibaraki 305.
• National Research Institute for Metals, Tsukuba, Ibaraki 305.

Introduction

X-ray analysis under the grazing incidence condition has been used for studying surfaces and thin films. For example, the grazing incidence X-ray fluorescence (XRF) analysis was used for trace element analysis and elemental depth profiling[1]. It was pointed out that grazing exit XRF might also be useful as a near-surface probe[2], but the validities of the grazing exit XRF have been scarcely investigated.

We have performed XRF experiments on layered structures under the grazing exit condition. The yields of fluorescent X-rays vs. their exit angle were measured with high angular resolution using synchrotron radiation. The experimental curves exhibit the same feature as the ones obtained in the experiments of grazing incidence XRF. The experimental evidence of the interference effect in the thin film was observed.

Experimental

Figure 1 shows the geometry of grazing exit XRF. The experiment was carried out at BL-4A PF. Monochromatic or continuous radiation was used for excitation. Samples were held on a goniometer. Fluorescent X-rays emitted from samples were detected by a Si(Li) solid state detector placed in the horizontal plane at 90 deg. to the primary beam direction. The slit 40 micron wide was placed at 360 mm distant from sample. The angle of incidence was nearly normal so that the beam illuminated the small part of the surface. This geometry enabled to attain an angular resolution less than 0.17 mrad.

Figure 2 shows the angular dependence of fluorescence intensities emitted from Cr/Au/Cr films on SiO2 substrate. Two samples have a difference in thickness of top Cr layer, i.e. (a)20nm and (b)50nm. Two broad peaks in (a) and four narrower peaks in (b) are observed.

Figure 3 shows the angular dependence of Ni and Fe fluorescence emitted from Ni/C/Fe films on Si substrate. The oscillation structure is observed in the curves. The similar oscillation structure was also observed in the experiment of grazing incidence XRF[1].

Discussion

The feature of these curves may be explained in terms of the interference between direct and reflected beams. The angular dependence of intensity can be evaluated by using the reciprocity theorem[3], which dictate that the X-ray propagation process is symmetric with respect to the source and the point of observation. The XRF intensity for each point can be calculated using the formula developed by Parratt[2]. The intensity expected at each angle is given as the integral of contribution from each point in the source region. Theoretical curves in Fig.2 were obtained in this way. Since the angular dependence is sensitive to the near surface structure as shown in Fig.2, this technique can be utilized for depth analysis of layered structures in a small region.

References

1) A. Iida, Adv. in X-ray Anal. 34, 23 (1991)
3) L.G. Parratt, Phys. Rev. 95, 359 (1954)
MICROBEAM SR-XRF ANALYSIS OF TRACE ELEMENTS IN METEORITIC IRONS:
APPLICATION TO THE DIFFERENTIATION TRENDS IN THE RU/Ni DIAGRAM

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Introduction

Meteoritic irons have been studied geochemically to classify them into several groups on the Ni vs. trace element plots and to reveal their differentiation processes. We have been performing detection of trace Rhutenium (Ru) in meteoritic minerals by microbeam X-ray fluorescence analysis using synchrotron radiation (SR-XRF). Only a few data of Ru concentration have been reported, showing large variations within a single subgroup such as IIA and IIB. Our work on microbeam SR-XRF has revealed that a few ppm order of Ru can be detected undestructively within about 0.5 X 0.5 mm region. Such a method can play an important role for meteorite research. Here, we compared our SR-XRF data with newly reported RNAA data to check our analytical data, and also tried to detect variations of Ru abundances between kamacite and taenite (-FeNi) lamellae in meteoritic irons.

Sample and Analytical Methods

The microbeam XRF unit on BL-4A was used for the XRF intensity measurements. The samples were irradiated by X-ray of excitation energy fixed at 22.5 KeV, counting times ranging from 900 to 1000 sec., and the beam diameters range from 0.25 X 0.25 mm to 0.50 X 0.50 mm squares. Standard samples used are Ni-Fe alloy (Fe90:Nil0) doped with Ru (0.1, 0.01, 0.001 wt %, Ru). The specimens of meteoritic irons used include type IIAB irons (Coahuila, Benett County, Negrillos and Scottsville), and IAB irons (ALH77283 and Toluca). The IIAB iron is a member of IIA, consisting mainly of kamacite (ct-FeNi) crystals and the IAB iron is that of IA subgroup, consisting of kamacite and fine taenite (-FeNi) lamellae.

Results and Discussion

Our Ru data of IIA irons are plotted on their Ni/Ru diagram of Hoashi et al. (Fig. 1). The IIA data fall very close to the region of type IIA irons. The comparisons indicate that our SR-XRF techniques can be applied for classification of irons as a speedy and non-destructive analytical technique. In the case of some IA irons, however, the Ru concentration of large kamacite portions fall outside the IA region in Fig. 1. The counting time (about 1000 sec) for Ru in IA irons may be too short to gain enough counts for accurate analysis. Another application of the SR-XRF technique is to analysis of trace elements (ppm order) in localized areas. We also tried to detect differences of the Ru abundance between the kamacite and taenite portions in IA irons. However, the taenite lamellae of the IA irons we used are so fine to be detected selectively using the beam diameter at this time, that no obvious variation between kamacite and taenite are detected.

We thank Dr. K. Ohsumi at PF-KEK for help, Dr. R. S. Clark Jr. of Smithsonian Institution (NMNH), and National Inst. of Polar Res. (NIPR) for meteorite samples, and Tanaka Kikinzoku Co. for the Ru standards.

References


Fig. 1 Our data of IA and IIA irons by SR-XRF plotted in the Ni. vs Ru diagram (after Hoashi et al. (1990)).
Structure Determination of MgSO₄ • 5Mg(OH)₂ • 2H₂O by Means of Ultramicro-Single-Crystal X-ray diffraction

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Crystals of MgSO₄ • 5Mg(OH)₂ • 2H₂O are obtained only in a form of extremely small needles through a hydrothermal procedure. The powder diffraction technique is difficult to apply for structure determination of this compound because of the strong preferred orientation inevitably induced in the process of sample preparation and of the overlappings of reflections in the powder diffraction diagram. On the other hand, the crystals are too small (not larger than 100 x 2.5 x 0.5 μm³) to be used to analyze the structure with the single crystal X-ray diffraction method utilizing a conventional X-ray source. Recently an X-ray diffraction device has been developed for single crystals with dimensions of the μm order by Ohsumi et al.[1]. The device employs SR as incident beam and the imaging plate as detector. The authors have successfully determined the crystal structure of the title compound with the aid of this X-ray camera.

The diffraction experiments were carried out at the BL-4B station. The Weissenberg method was employed for the intensities collection. The Intensities were measured for 419 reflections, of which 105 were independent and corrected for the Lorentz and polarization factors. The crystal is orthorhombic with a C-centered cell. The lattice parameters were determined by the WPPD method[2] from the powder diffraction pattern (Cu Kα λ =1.540562 Å); a=15.8949(5) Å, b=3.1047(1) Å and c=13.3670(5) Å. The measured density, Dm=2.3g cm⁻³ gave Z=2. The structure was solved using the Patterson technique. The scale factor, positional parameters and isotropic temperature factors (a total of 21 parameters) were refined by the least-squares method. Function minimized was Σ (Fₐi-Fₑi)² by allotting unit weight for all reflections. The final cycle of refinements gave R=0.073 (wR=0.083). Hydrogen atoms were not included in the refinement. The space group was found to be Ccmm as a result of the structure determination.

The crystal structure is shown in Fig.1. The structure is based on a chain composed of edge-sharing MgO₆ octahedra running along the b axis (the needle direction). The chains share their octahedral edges to form a zigzag sheet parallel to (100). The sheets are stacked along the a axis probably with hydrogen bonds. The two O atoms of the SO₄ tetrahedra are shared with MgO₆ octahedra. The SO₄ tetrahedra exist statistically with a probability of one half. The edge formed by the unshared O atoms of the SO₄ tetrahedra is parallel to the b axis. The b length corresponds to the O-O distance of MgO₆ octahedra, which is considerably longer than the normal O-O distance of a SO₄ tetrahedra, but shorter than twice of it. Therefore, SO₄ tetrahedra are obliged to be located alternately along the b axis. Although the crystal gives sharp streaks perpendicular to the b axis on the electron diffraction photographs, no superlattice spots were observed. The facts indicate random distribution of the SO₄ tetrahedra along the a and c axes, and support the alternate distribution along the b axis.

Introduction

Many sesquioxides $M_2O_3$ with 3d-transition elements have a corundum ($\alpha - Al_2O_3$) structure (R3c). However, it has been known that $\alpha - Mn_2O_3$ (Pcab) has a slightly distorted structure from the C-type of rare earth sesquioxide structures (1). The C-type structure has a cubic unit cell (Ia3) in which cations are surrounded by six anions. Several rare earth sesquioxides with the C-type structure transform to the B-type structure (C2/m) having cations with a seven-folded coordination at high pressure and temperature. On the other hand, $\alpha$-Ti$_2$O$_3$ and $\alpha$-In$_2$O$_3$, both of which have the C-type structure, transform to the corundum structure at high pressure and temperature. These phase transformations (from the C-type to the B-type, or from the C-type to the corundum) are also confirmed by shock loading experiments (5).

It has been reported that $\alpha$-Mn$_2$O$_3$ recovered from a condition of 6.5 GPa and 1300 °C showed no structural change. In this study, we carried out an in-situ X-ray diffraction analysis of $\alpha$-Mn$_2$O$_3$ under pressure with DAC (Diamond Anvil Cell).

Experimental

Starting material of $\alpha$-Mn$_2$O$_3$ was prepared by heating $\beta$-Mn$_2$O$_3$ (Guaranteed Reagent provided by Nacalai Tesque, Inc.) at 800 °C for 48 hours. Pressure was generated by a clamp screw type DAC up to 10GPa. PTM (Pressure Transmitting Medium) of methanol:ethanol = 4:1 (volume ratio) was used. Pressure was calibrated using the shift of the R$_2$ fluorescence line of a ruby crystal in a sample room. YAG laser was irradiated to the material after loading pressure in order to heat it over 1000 °C. Details of experimental conditions are listed on Table 1. Data collections were performed at BL-4B by energy dispersive X-ray diffraction method using Ge-SSD (Solid State Detector) with $2\theta$ = 15°.

Results

-Compression at ambient temperature
  Hydrostatic compression experiments up to 5GPa were made with PTM. Isothermal bulk modulus of $\alpha$-Mn$_2$O$_3$ was estimated at 154.2 GPa by fitting V/$V_0$ to Birch - Murnaghan's equation of state with the first order approximation. This value is smaller than those of other 3d-transition metal sesquioxides with the corundum structure.

-Laser heating experiments
  While sample heated at 10GPa without PTM (No.1) showed no phase transformation, diffraction patterns of both samples with PTM (No.2, No.4) and without PTM (No.3) compressed to about 5GPa were transformed after heating. Although the observed diffraction patterns were different in the intensity ratios, peak positions were almost the same among these three samples. There were no peaks which belonged to $\alpha$-Mn$_2$O$_3$. Some peaks were identified as MnO. Other peaks, however, remained unindexed. These diffraction patterns were not similar to any other compounds of manganese. These phases were recovered after releasing pressure. We are now analyzing these phases.

Acknowledgements

The authors thank to T.Yagi , I.S.S.P., Univ. of Tokyo, for using YAG laser and giving us useful comments about this study.

References


Table 1. Pressure data of laser heating experiments (Pressure: GPa)

<table>
<thead>
<tr>
<th>cell number</th>
<th>PTM</th>
<th>before heating</th>
<th>after heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>none</td>
<td>10.9</td>
<td>9.8</td>
</tr>
<tr>
<td>No.2</td>
<td>O</td>
<td>5.4</td>
<td>5.2</td>
</tr>
<tr>
<td>No.3</td>
<td>O</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>No.4</td>
<td>none</td>
<td>&gt;5.0</td>
<td>unknown</td>
</tr>
</tbody>
</table>

(Ruby fluorescence from the No.4 cell could not be observed.)

Fig.1 Observed diffraction pattern
A. before heating (No.3)
B. after heating (No.3)
C. after heating (No.2)
Proposal No 89-174

Structural analysis of orthorhombic HfO₂
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1. Introduction

HfO₂ is of interest because of its high melting point and high chemical stability. Its chemical and physical properties are very similar to those of ZrO₂. HfO₂, which has monoclinic symmetry at room temperature under atmospheric pressure, transforms to a high pressure phase with orthorhombic symmetry by compression above about 3 GPa\(^2\). We performed the Rietveld analysis of the X-ray diffraction data to confirm the structure and to compare it with that of the orthorhombic ZrO₂.

2. Experimental

The starting material used for the high pressure synthesis was fine-powdered HfO₂ (grain size was 100 nm) provided by Nacalai Tesque, Inc. The starting material was charged in a platinum capsule and treated at 600°C and 6 GPa for 30 min by a cubic-anvil-type device\(^3\). The product consisted of the almost single phase of the orthorhombic except for a trace of the monoclinic. A powder diffractometer PFPD designed for the high angular resolution study within ±0.0005° was used for the data collection. Using a monolithic Si (111) monochromator with fixed beam position, the incident X-ray source with the precise wavelength of 1.52335 Å, which is similar to the characteristic X-ray of CuKα, was adopted. All optical paths including the sample chamber were evacuated in order to reduce background noise. Sample spinner with 3 rpm was employed for the randomization orientation. The step counting of 0.02°/10 sec was applied.

3. Data Analysis and Result

Least-squares structure refinements were executed with the RIETAN program for the Rietveld analysis of SR diffraction data\(^4\). As a small amount of the monoclinic phase coexisted in the sample, the recorded diffraction pattern was analyzed assuming a two-phase mixture of the monoclinic and the orthorhombic. In the two-phase refinement, a matrix refinement of the orthorhombic structure with the variables of the scale factor, lattice parameters, fractional coordinates and individual isotropic thermal parameters was undertaken along with the refinements of the scale factor and lattice parameters of the monoclinic structure, while fractional coordinates and individual isotropic thermal parameters of this phase were fixed for the reported values\(^5\). On the basis of TEM observations, Raman spectra analyses and comparisons with the monoclinic structure, several structural models were proposed for the orthorhombic HfO₂ and ZrO₂\(^6\). Among these models, the smallest R factors were obtained when a Pbcn model was used. The R factors, the resulting structural parameters and their standard deviations which we have tentatively obtained are listed in Table. As shown in Table, however, the R factors and standard deviations for the structural parameters (especially those of oxygen atoms) are still considerably large. We are now executing further analysis of the data.

This result also indicates that the configuration of oxygen framework is difficult to be fixed by the present X-ray powder diffraction method. As the X-ray scattering factor of oxygen is considerably small compared with that of hafnium, we are planning neutron diffraction experiments of this phase in order to determine the accurate configuration of oxygen framework.

References

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>B(nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>0</td>
<td>0.384(2)</td>
</tr>
<tr>
<td>Be</td>
<td>0.209(4)</td>
<td>0.397(8)</td>
</tr>
<tr>
<td>01</td>
<td>0.209(4)</td>
<td>0.397(8)</td>
</tr>
<tr>
<td>02</td>
<td>0.209(4)</td>
<td>0.397(8)</td>
</tr>
</tbody>
</table>

Table: Space group: Pbcn \(RWP=16.08\) \(RFP=12.65\) \(REL=10.05\)

HAFNIA ORTHO: B=9.98 RF=5.22
HAFNIA MONOCL.: B=8.10 RF=4.72

\(\text{If}^\text{a}=1.00118(1)\) \(\text{b}=0.522470(18)\) \(\text{c}=0.505735(7)\) \(\text{nm}\)
Determination of lattice parameter of Y' precipitate, size of crystallite and distribution of the parameter due to coherency strains in Ni-base superalloy

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National Laboratory for High Energy Physics, 1-1 Oho Tsukuba-shi Ibaragi-ken 305

Nickel-base superalloys "single crystal Ni-base superalloys" for gas turbine blades have an ordered FCC type Y' precipitate based on Ni₃Al in Y-matrix having disordered FCC structure. The creep rupture life strongly depend on the lattice misfit between Y and Y' phases. The purpose of this work was to study the advantages of using strage ring X-rays for analysis of microstructure in the superalloys. Example of the outline of accurate measurements of the diffraction patterns and line-broadening analysis of the patterns for the determination the lattice parameter of Y' precipitate and the distribution of the parameter due to the distorted lattice by the coherency strains.

Powder alloy specimen and Y' precipitate isolated from Y-matrix, which were prepared previously described method[1], were measured with the PFPD. The PFPD was improved to obtain high angular-resolution without losing intensity, on BL-4B in the Photon Factory. The reflection peaks from Y and Y' phases were in a cluster of overlapping peaks because of very small different lattice parameters between both phases and instrumental broadening due to X-ray optics of PFPD.

The equation (1) is a fundamental relation of strains on the diffraction peaks.

$$\frac{\beta \cos \theta}{\lambda} = 2g \sin \theta + \frac{1}{\xi}$$

where \(\lambda\) is the wave length, \(2\theta\) is observed peak angle, \(g\) is integral width.

Thus, random strain \(\eta\) and mean crystallite size \(\xi\) are calculated.

A profile fitting method[3] with a pseudo-Voigt function was used to determine individual profile shapes. Examples of the profile fittings of the powder data obtained from the Y' precipitate electro-chemically isolated from Y-matrix and that in the alloy specimens are shown in Fig. 1.

The Y' crystallite in the alloy was distored by the lattice misfit because the peak angles of the isolated Y' crystallite in the Y-matrix in Fig. 1 were

![Fig. 1 Fitting results for (111) peak profiles reflected from isolated Y' crystallite (a) and overlapped peaks reflected from Y and Y' crystallites in alloy (b).](image)

Table 1 Lattice parameters of Y' precipitate and its distribution of that due to coherency strains in alloy

<table>
<thead>
<tr>
<th>Lattice parameter((A))</th>
<th>(a_{Y'})</th>
<th>(a_{Y})</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in alloy</td>
<td>3.59311</td>
<td>3.58446</td>
<td>0.24</td>
</tr>
<tr>
<td>std.dev.</td>
<td>0.00129</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Isolated</td>
<td>3.59393</td>
<td></td>
<td></td>
</tr>
<tr>
<td>std.dev.</td>
<td>0.00001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Misfit \(\delta(%) = 2(a_{Y'} - a_{Y})/(a_{Y'} + a_{Y})\)
Uniform strain(%) : 0.023

In addition, the FWHM of the Y' crystallite in alloy was significantly larger than that of the isolated crystallite. The large std.dev of Y' crystallite in the Y-matrix in Table 1 are considered to be the distribution of the lattice parameter due to random disortion by interraction of both phases.

This work has been performed under the approval of the Photon Factory Program Advisory Committee(Proposal No. 90-081).

References
Anomalous oscillational structure in X-ray diffraction vector for superstructured heterogeneous Langmuir-Blodgett films

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**Photon Factory, National Laboratory for High Energy Physics, Tsukuba 305, Japan.

The Langmuir-Blodgett (LB) method begins to be applied to fabricate an organic superlattice. We reported the anomalous X-ray diffraction line shift in the heterogeneous superstructured LB films [1]. We extended the X-ray study using high resolution Photon Factory Powder Diffraction system (PFPD) and by scanning diffraction intensity two-dimensionally. We prepared two kinds of samples as for the arrangement of Cd\(^2\+) stearic acid ion CH\(_3\)(CH\(_2\))\(_{17}\)COO\(^-\) and behenic acid ion CH\(_3\)(CH\(_2\))\(_{21}\)COO\(^-\) as shown in Fig. 1; type A and type B. The accumulated film with the A unit is expressed as Am, where m is the accumulation number; similar for Bm.

Table 1. List of parameters for various samples, S denotes Cd stearate, A denotes Cd arachidate and B denotes Cd behenate. d\(_{ave}\) is evaluated from the empirical formula [2].

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (obs)</th>
<th>d(Å)</th>
<th>d(_{calc}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homo(S)</td>
<td>0</td>
<td>±0.002</td>
<td>50.6 50.3</td>
</tr>
<tr>
<td>A4(S-B)+</td>
<td>0</td>
<td>±0.01</td>
<td>110.4 110.6</td>
</tr>
<tr>
<td>B6(S-B)</td>
<td>0.089</td>
<td>±0.002</td>
<td>111.0 110.6</td>
</tr>
<tr>
<td>B7(S-B)</td>
<td>0.041</td>
<td>±0.002</td>
<td>110.7 110.6</td>
</tr>
<tr>
<td>B15(S-B)</td>
<td>0.047</td>
<td>±0.002</td>
<td>110.8 110.6</td>
</tr>
</tbody>
</table>

The obtained values of a(average of a over n) & d are listed in Table 1. The magnitude of d is well described by the sum of the thickness of constituent molecule layers [2]. a is zero for the homogeneous Cd stearate film and for A-type heterogeneous film. On the other hand, a is rather large for the B-type, for example, 0.089 for B6 film, 0.041 for B7 and 0.047 for B15. The shift direction of the diffraction vector was found to lie almost in the accumulating direction of LB films, and the angle between them was less than 0.1 deg.

The coherent length normal to the layer plane \(\xi\) was 185±25Å for B6 film and 240±20Å for B15. In the mean time, the coherent length in the layer plane \(\xi\) was more than (1.0±0.3)×10\(^4\)Å for B6 and (2.4±0.3)×10\(^4\)Å for B15. These values were estimated from the widths of diffraction spots of the even-indices. The diffraction spots of the odd-indices are about twice wider than those of even-indices.

The anomalous shift of the observed diffraction vector represented by eq.(1) indicates the missing of the translational symmetry along the accumulating direction in the B-type films. We checked the possibility of the diffraction vector shift due to the limited number of the accumulated layers by taking account of the peak profiles in the Laue function. However the amplitudes of the calculated shifts are rather small (a < 0.01) and cannot explain the oscillational behavior.

The diffraction pattern of B6 film observed by the PFPD is displayed as Fig. 2. The angular position of the diffraction spot looks to form dimers. The magnitudes of the X-ray diffraction vector \(D\) was expressed experimentally as

\[ D = (M - (-1)^M \cdot a) \times 2\pi / d \]

where \(a\) is amplitude of the shift from \(M\) (integer) for the \(n\)-th diffraction vector; \(d\) is defined as the average periodicity in the real space.

Fig. 1. Schematic representation of the heterogeneously deposited LB films. The long bar represents behenic acid ion and the short bar represents stearic acid ion. The closed circle represents Cd ion. The shaded part represents a substrate.

Fig. 2. Diffraction pattern observed by the PFPD system for sample B6.

Reference:
ACCURATE MEASUREMENT OF UNIT-CELL PARAMETERS FOR POWDERS USING SYNCHROTRON RADIATION

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2) National Research Institute for Metals, Meguro, Tokyo 153, Japan
3) National Laboratory for High Energy Physics, Oho, Tsukuba 305, Japan

Introduction

One of the authors (HT) has conducted experiments on the accurate measurement of unit-cell parameters by using both tube-generated X-ray and synchrotron radiation (SR) sources¹. A previous study using the conventional type powder diffractometer (para-focusing geometry) achieved the accuracy of 1 to 5 p.p.m. in measuring the unit cell parameters of Si, W, and CeO₂, with respect to the internal standard reference material (SRM). Average deviations of observed 2θ were, however, 0.0021°, and the cause of larger deviation compared to the Daresbury SR experiment (0.0003° to 0.0005°)¹ has been ascribed to the inaccuracy of measuring the peak maximum for overlapping Kα₁-Kα₂ doublet of tube-generated X-ray. One of the advantages of synchrotron radiation source is the capability of using the strictly monochromatized beam. The present experiment has been conducted in order to resolve the problem of doublet peaks.

Experimental

A newly designed horizontal parallel slit with an aperture of 0.06° was used to obtain high angular-resolution without losing the intensity. Profile intensities of three mixtures of Si-W, W-CeO₂, and CeO₂-Si powders were measured at the station BL-4B in Photon Factory, Tsukuba. Maximum counts were 41993 (fixed time = 3s), 17204 (2), and 16924 (2) for respective mixtures in the 2θ range of 2θ-128°. The wavelength was determined to be 1.39043Å, although the algorithm for peak-shift correction is wavelength free. Peak maximum positions were determined by using a computer program PRO-FIT for the profile fitting method. The unit cell parameters were calculated with a computer program UNITCELL².

Results and Discussion

Pearson VII function was a better profile representative for peaks in the low angle region, while pseudo-Voigt in high angle region. A typical profile fitting result is shown in Fig. 1. Profile shapes were almost symmetric around the peak maximum, while slightly asymmetric in tails. The FWHM of W peaks varies from 0.062° at 2θ = 36.2° to 0.097° at 122.9°, showing that the new Soller slit system works well for achieving high-resolution. The unit-cell parameters are given in Table 1 together with the previous results¹. The accuracy with respect to the starting value of NIST SRM 640b Si powder [a = 5.430940(35)Å] was 6 p.p.m., and it was close to the range, which was aimed as a goal. The e.s.d.'s of unit-cell parameters in the present experiment were better than the tube-generated X-ray result (Table 1). The smaller e.s.d.'s can be ascribed to the simple profile of SR data. The average deviations were 0.0003° to 0.0006° which were comparable with the Daresbury SR data¹.

<table>
<thead>
<tr>
<th>Step(deg.)</th>
<th>W</th>
<th>CeO₂</th>
<th>Si</th>
<th>Δ</th>
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</thead>
<tbody>
<tr>
<td>0.01</td>
<td>3.16537(6)</td>
<td>5.41134(6)</td>
<td>5.43091(5)</td>
<td>-0.00003</td>
</tr>
<tr>
<td>0.02</td>
<td>3.16537(6)</td>
<td>5.41134(6)</td>
<td>5.43091(5)</td>
<td>-0.00003</td>
</tr>
<tr>
<td>0.01</td>
<td>3.16528(3)</td>
<td>5.41136(7)</td>
<td>5.43095(5)</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

References


Fig. 1. Fitting result for Si 422 and CeO₂ 422 peaks (Solid squares: observed, solid lines: calculated, and the difference plot at the bottom of figure)
We observed nice oscillatory modulations of the X-ray crystal truncation rod (CTR) intensities from CaSrF\textsubscript{2}/GaAs(111)B heteroepitaxial systems [1]. The samples used here have Ca\textsubscript{0.39}Sr\textsubscript{0.61}F\textsubscript{2} epilayers with lattice parameters closely matched to those of substrate GaAs and a film thickness ranging from ca. 100 to 250 Å. The oscillations were observed in the triple-crystal goniometry data transversely integrating the CTR intensities near the GaAs Bragg peaks, and also in Imaging Plate pictures of the CTR scatterings near the 111, 220, 113 and 111 Bragg points. The oscillations are essentially given rise to by the interference of the CTR scattering from the semi-infinite GaAs substrate with the Laue function of the thin epitaxial crystal [2].

A useful feature of the interference pattern is that it contains rich information on the micromorphology and atomic structure of the epitaxial-substrate interface. The observed fringe periods near the GaAs 111 Bragg peak are best explained by 29 and 79 F-(Ca, Sr)-F epilayers present in the thin and thick CaSrF\textsubscript{2} crystals, respectively. The determined layer numbers (N) are slightly less than those from the Fresnel reflectivity measurements [3], indicating the presence of non-diffracting disordered surface layers. To explain the observed intensity profiles we modeled the heteroepitaxial interface by a missing F layer and substrate As-Ga double layers shifted from the bulk positions according to a simple exponential law [4]. Least-squares fits to the observed profiles involved as variables vertical lattice mismatch (γ\textsubscript{111}), interface layer distance (d\textsubscript{r}), substrate top layer shift (S\textsubscript{t}) and interface roughness (σ\textsubscript{1}, σ\textsubscript{2}). Table 1 lists the parameters obtained from the fit. The values for γ\textsubscript{111} and d\textsubscript{r} are in a satisfactory agreement with the XSW results [5]. Also, the obtained rms roughness σ\textsubscript{i} (i = 1, 2) agrees with the Fresnel reflectivity results [3]. Information on the in-plane position of the interface atoms is provided by the X-ray scattering in a region near the GaAs 220 Bragg peak (Fig. 1). A comparison with the calculated profiles clearly favors the T sites over the T4 sites for the interface position of the (Ca, Sr) atoms.

In the structure model shown in Fig. 2 the interface consists of (Ca, Sr)-As bonds with a missing F layer. In Fig. 2(a) the interface (Ca, Sr) atoms occupy the T4 sites above the second-layer Ga atoms while the top-layer As atoms maintain the bulk tetrahedral coordination. In Fig. 2(b) the top-layer As atoms are shifted to the H3 sites located above the forth-layer Ga atoms, creating a stacking fault at the interface to accommodate (Ca, Sr) atoms in the T sites at a short vertical distance. This latter model gives 220 scattering profiles more consistent with the observation (Fig. 1).

Synchrotron X-Ray Diffraction Study of Thue-Morse lattice

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Introduction

One-dimensional quasiperiodic lattice have been studied from viewpoint of the projection of a quasicrystal onto a line. We discussed the diffraction patterns of the one-dimensional second- and third-order Fibonacci lattices grown by molecular beam epitaxy (MBE).1-3 In this report, we discuss the diffraction pattern of one-dimensional Thue-Morse lattice which locates between quasiperiodic and random lattices. The Thue-Morse chain of n-th order is constructed as $S_1=A$, $S_3=AB$ and generated factor is

$$S_n=S_{n-1}S_{n-1}$$  

where $S_{n-1}$ is the complement of $S_n$ obtained by interchanging A and B in $S_{n-1}$.

Experimental

Thue-Morse lattice was grown by MBE on the (001) GaAs substrate at ~550°C following the sequence defined in Eq. (1), where the block species were A=(GaAs)$_{1.0}$ and B=(AlAs)$_{1.0}$. In this work, the order of sample was 10th.

High resolution X-ray measurements was carried out by using synchrotron radiation (SR) available at PF. Radiation ($\lambda=1.54\text{Å}$) was monochromized by pair of Si(111) crystals (beam line 4C).

Result and Discussion

The observed diffraction pattern is shown in Fig. 1, where $q_0$ is $2\pi/5a_0$ and $a_0$ is the average lattice constant of GaAs and AlAs. The peak positions are specified by $(2k+1)/3\cdot2^p q_0$, where $k$ and $p$ are integer. The diffraction pattern is symmetrical with respect to $q=1/2^l q_0$, where $l$ is integer. This implies that the Thue-Morse lattice has no definite periodicity but have a strong correlation.

Figure 2 shows the partial correlation function $C(r)'s^{2,3}$ in Fibonacci lattice and the Thue-Morse lattice of 10th order. In the Fibonacci lattice, the amplitude of correlation function does not decay and is very strong independent of the lattice length. But in the Thue-Morse lattice, the amplitude is varied by varying the distance(r). This is a significant difference between the Thue-Morse and the Fibonacci (quasi-periodic) lattice. The correlation of lattice in the Thue-Morse lattice is smaller than that of the Fibonacci lattice. The Thue-Morse lattice locates between quasi-periodic and random lattices.

*Faculty of Science, Chiba University

references

Metallic sodium undergoes a martensitic transition from the high temperature bcc phase to a hcp or 9R structure at 36 K [1]. Blaschko and Krexner reported pretransitional phenomena connected with the bcc-hcp transition in Na by neutron scattering techniques. They found a softening of the low-lying TA [110] phonons and q-independent diffuse scattering with a marked hysteresis effect [2]. Berliner et al. have performed the structure determination of polycrystalline Na specimens at 80 and 20 K by neutron powder diffraction measurements [3].

In this experiment, we have investigated the phase transition in Na by synchrotron radiation techniques with a single crystal.

Data collection of X-ray scattering was performed on a Huber 5020.4 four circle diffractometer with HOPG crystal analyzer installed at BL-4C.

Fig. 1 shows a series of rocking curves of (110) Bragg reflection from 290 to 14 K. Fig. 2 shows the temperature dependence of the full-width at half maximum (FWHM) from the profile in Fig. 1. It is gradually wider below 200 K and almost constant below 40 K. This change may be reflected from the precursor phenomena of the phase transition in Na.

We are planning to take the temperature dependence of phonon dispersion curve in Na by neutron diffraction.

Measurements of X-ray Diffuse Scattering in a Quenched Copper Single Crystal
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*Faculty of Engineering, Hiroshima Univ., Kagamiyama, Higashi-Hiroshima 724
**College of Liberal Arts and Sciences, Okayama Univ. Tsushima-Naka, Okayama 700
***Faculty of Engineering, Tamagawa Univ., Machida Tokyo 194

Studies of vacancy clustering in quenched metals can contribute to an understanding of more complex point defect cluster problems. For example, the most important radiation-induced defects found in irradiated metals, void and dislocation loops, may be produced easily by quenching. So, of the pure FCC metals studied, aluminum and gold have received most attention and a reasonably clear picture of quenched-in vacancy clustering was built up. However, several inconsistencies and lack of reproducibility reported for copper metals studied has limited progress towards a more general understanding.

In the case of copper, it has been shown that many of the discrepancies arise from the presence of impurities or contaminating gases (particularly oxygen) which strongly influence vacancy clustering. It may have small clusters of vacancies or single vacancies trapped with impurities without forming large clusters. Experimental investigations have proved to be difficult as a result of the small sizes of clusters. X-ray diffuse scattering method has been developed which complement the direct observation methods by electron microscope and are capable of providing detailed information on clustered defects when scattering models are available.

In this study, we have tried to make diffuse scattering measurements for the detection of small vacancy clusters in quenched copper crystal.

The specimens of single crystal plates were spark-cut out of single crystal rods (nominal purity 99.9999%) purchased from Nippon Kogyo Limited. The size of the sample used for X-ray diffraction was 5x7x0.2 mm with their surface parallel to the (111) crystallographic plane. After the annealing, specimens were quenched from 1040 C to 4 C in atmosphere of hydrogen and argon gases.

X-ray diffuse scattering experiments were performed on a Huber 5020.4 four circle diffractometer at room temperature installed at BL-4C. A wavelength of 0.15405 (corresponding to CuKα1) was selected by the double crystal Si 111 monochromator with sagittal focusing.

At first x-ray scattering measurements at (111) reflection in [211] q (ω scanning) are carried out for the quenched and annealed specimens. Fig. 1 shows the Huang diffuse scattering as a function of q in a double logarithmic scale. The intensity is proportional to $q^{-2}$. This means the characteristic features of scattering from single point defects or small clusters.

Diffuse scattering intensity measurements were made on the quenched and annealed specimens around the 111 reflections at room temperature. A large temperature diffuse scattering (TDS) was appeared perpendicular to the 111 direction of reciprocal vector. Detailed analysis is in progress.

Fig. 1 Huang diffuse intensity measured at (111) reflection in the [211] direction for quenched copper.

![Graph](image-url)
Crystal structure of *Streptomyces erythraeus* trypsin at 2.7Å resolution

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**Introduction**

*Streptomyces erythraeus* trypsin (SET) is a bacterial serine protease and consists of 227 amino acid residues. SET is similar to mammalian trypsins as same as *Streptomyces griseus* trypsin (SGT) is, though the sequence homology among these trypsins is rather low. SET is only 36% homologous with bovine trypsin (BT). SET hardly autolyses itself at all at its active pH range between 5 and 10. This marked characteristic provides a good example to study the circumstances around the active sites of serine protease in its neutral state, if crystals of SET can be obtained without any modification of the active sites. Therefore the crystal structure of SET has been determined in order to make clear the precise conformation and the hydrogen bond network of the catalytic triad. The study on the pH stability of SET is another major purpose of this crystal structure analysis.

**Experimental Section**

Crystals of SET belong to the trigonal system, space group P321 with a=47.0Å and c=178.9Å. The unit cell contains 6 molecules, and the solvent content is 47% by volume.

High resolution data for the native crystal were collected with a screenless Weissenberg camera at the BL-6A2 station. The radius of the film cassette was 287mm; in it Fuji imaging plates were mounted. The wavelength was set to 1.038Å. Fuji imaging plates were digitized with a Fuji BA100 at the Photon Factory, and processed with the WEIS system. By the processing of the plates, 48,451 reflections were measured at 1.7Å resolution, of which 17,912 were independent, giving the merging R-factor of 0.061.

The structure was refined by the restrained least-squares refinement method using PROLSQ at 2.7Å resolution. The model building of SET was carried out on a 3.5Å MIR Fourier map. The starting model for refinement was constructed from a new 3.5Å Fourier map calculated with combined phases between MIR and model phases. The current R-factor was 0.272 for 4968 reflections with |Fo| > 5σ(F) between 8 and 2.7Å resolution.

**Results and Discussion**

The overall structure of SET is very similar to that of BT and SGT. The spatial arrangements of the catalytic triad in the three proteins are similar to each other. The distances between Ser195 and His57, and between Asp102 and His57 are in the current model 2.9 and 3.4Å, respectively.

The aromatic rings of Trp89, His91, Trp94, Phe110, and Tyr234 come together closely and form a cluster (aromatic cluster) in SET. BT seems also to form an aromatic cluster, while only Tyr94 and Phe234 are conserved among the residues forming the aromatic cluster in SGT. Therefore an aromatic cluster does not occur in SGT and another factor to stabilize the protein structure must be considered.

The aromatic ring of Trp237 is in van der Waals contact with the hydrophobic side chain of Ile89 and stabilizes the base of the C-terminal α-helix in BT. Though the 237th residue is substituted with Val in SET, the similar contact is kept by side-chain exchanges of a compensatory nature; that is, Trp89 and Val237 in SET in place of Ile89 and Trp237 in BT. It is worth noting that such contact does not occur in SGT, because 89th and 237th residues are substituted by Leu and Ala respectively.

The details of the crystal structure of SET will be described elsewhere.

**References**

ACTIVE-SITE RESIDUE OF THE HEAT-LABILE ENTEROTOXIN

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Introduction

Enterotoxigenic *Escherichia coli* produces heat-labile enterotoxin (LT) which is a causative agent of diarrhea in mammals such as pigs, cows and humans. 1) LT is structurally, functionally and immunologically similar to cholera toxin (CT) produced by *Vibrio cholerae*. LT and CT consist of one A subunit (Mr=28 K) and five B subunit (Mr=11.6 K), forming an AB₅ complex of Mr=86 K in total. 2) The A and B subunits consist of 240 and 103 amino acid residues, respectively. The sequence of both the A and B subunits of these toxins is more than 80 % identical. The A subunit consists of A₁ and A₂ fragments. The A₁ fragment increases cyclic AMP in target cells by catalyzing NAD-dependent ADP ribosylation of the regulatory GTP-binding protein of adenylate cyclase. The A₂ fragment may be bound to the B subunit pentamer. The B subunit has a role to bind the toxin molecule to target cell surface by its specific affinity to the GM₁-ganglioside receptor.

We have studied the relation between structure and functions of heat-labile enterotoxin by mutagenesis. 3-5) We crystallized the pentamer of the B subunit, 6) and measured its diffraction intensities using Weissenberg camera for macromolecular crystals at BL6A. 7) However, recently the structure of the whole toxin has been determined at 2.3 Å resolution by Sixma et al. 8) Thus we abandoned the X-ray analysis of the B subunit pentamer. Here we report biological activities of a mutant LT and its relation to the three-dimensional structure.

Experimental and Results

A plasmid EWD 299 encoding LT gene was treated with 0.1 % hydroxylamine, and transformed into *E. coli* HB 101. A mutant strain of *E. coli* HB 101 produced a low toxic mutant LT, which is cross-reactive with anti-LT antibody. The mobilities of the A and B subunit of the mutant LT in SDS-PAGE were identical to those of the normal LT. The activity of the mutant LT was less than 0.15 and 0.006 % of the normal LT in the rabbit ileal loop test (Fig. 1) and in the rabbit skin permeability test, respectively. The amino acid composition of the mutant LT-B subunit was the same as that of the normal B subunit. Though the A₂ fragment of the mutant LT was identical to that of the normal LT by DNA analysis, glutamic acid at position 112 in the A₁ fragment of the normal LT was replaced by lysine in the mutant LT.

![Fig. 1. Comparison of the mutant LT with the normal LT by the rabbit ileal loop test. O, normal LT; •, mutant LT.](image)

X-ray crystallographic analysis of LT has shown that the toxin consists indeed of one A subunit and B subunit pentamer, and that these are mediated by the A₂ fragment. One remarkable finding is that the active site of LT is superimposable on that of exotoxin A from *Pseudomonas aeruginosa*; the NAD-binding site of the exotoxin A was identified as Glu-553, which corresponds to Glu-112 in LT. Such results indicate that Glu-112 is the active-site residue for ADP-ribosyltransferase activity.

References

Crystal structure of guanine specific ribonuclease from \textit{Fusarium moniliforme} at 1.3Å resolution

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\(^2\)Department of Chemistry, Shimane Medical University, 89-1, En-ya-cho, Izumo, 693 Japan

The ribonuclease from \textit{Fusarium moniliforme}, RNase F1, is a guanylate endoribonuclease, which belongs to the RNase T1 family. RNase F1 is composed of 106 amino acids and it shows 59\% sequence identity to RNase T1, of which an accurately refined crystal structure is available (1,2). The crystal structure was solved by molecular replacement and refined by least-squares methods using stereochemical restraints.

The crystal belongs to the space group \textit{P}_{2_1}2_12_1 and has unit cell parameters of \(a=46.65\,\text{Å}\), \(b=56.26\,\text{Å}\), and \(c=31.60\,\text{Å}\). Intensity data up to 1.3 Å resolution were collected using a Weissenberg camera with an imaging plate which was developed for macromolecules (3) at the BL6A2 station of the Photon Factory. The diffraction data were processed with the program WEIS and gave 13278 independent reflections above a 1.0\(\sigma(F)\) limit with the merging R-factor of 0.059. The structure of RNaseT1-2'GMP complex refined at 1.9 Å was used as a search model for calculating the rotation function with the program PROTEIN and the translation function using T-function (T(t)-function of Crowther and Blow). Both maps showed only one prominent peak. The R-factor at this stage was 0.464 in a resolution range of 10-2.5 Å. The structure was refined using the reciprocal space stereochemically restrained least-squares program PROLSQ in combination with the interactive graphics program FRODO. The structure was converged to an R factor of 0.187 for 13257 observed structure factors at the 1.0\(\sigma\) level between 8.0 and 1.3 Å. The final model contains 107 water molecules and its statistics are given in Table 1.

RNase F1 and RNase T1 adopt the same main chain folding except for the N-terminus, the C-terminus and the loop ranging from Asp30 to Thr37 of RNase F1 (Fig. 1). In particular, the structural homology of a large \(\beta\)-sheet, which comprises important residues involved in the enzyme activity (His40, Glu58, Arg76, His91 (Fig. 2)), is remarkable.

REFERENCES


![Figure 1](image-url)

**Figure 1**: Stereo view of the Ca model of RNase F1 in solid bonds and RNase T1 (free-form, Heinemann \textit{et al}, unpublished result) in open bonds.

![Figure 2](image-url)

**Figure 2**: Comparison of important residues for the enzyme activity. RNase F1 in solid bonds and RNase T1 (free-form) in open bonds.
THREE-DIMENSIONAL STRUCTURE OF RNASE RH, A NEW CLASS OF MICROBIAL RIBONUCLEASE FROM RHIZOPUS NIVEUS


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* Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan
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Introduction

Ribonuclease Rh (RNase Rh) was isolated from Rhizopus niveus by Tomoyeda et al. and purified by Komiyama and Irie[1]. RNase Rh splits the 3',5' phosphodiester linkage of RNA (through 2',3' cyclic phosphodiester as an intermediate) without absolute base specificity. Its base specificity estimated from the time-course of release of nucleotides from RNA is in the order A>G>C>U and is very similar to that of RNase T2 or RNase M. It seems that this new class of RNase involving RNase Rh, T2, M and S-glycoproteins[2] share a common backbone folding, as in the case of the other class of microbial RNases involving a group of much smaller RNases, such as RNase S and RNase T1.

Experimental

After we had overcome the polymorphism difficulty of this protein crystal[3], the intensity data were collected using either one of the following two devices: a Rigaku four-circle diffractometer AFC-5R mounted on an RU-200 rotating anode generator operated at 50kV, 200mA and the macromolecule-oriented Weissenberg camera, devised by Sakabe[4], installed at the Beam Line 6A of the Synchrotron Radiation Source at the National Laboratory for High Energy Physics, Tsukuba. Total number of independent reflections in the resolution range of 10-2.5Å was 7830.

The crystal structure was solved at 2.5Å resolution by the multiple isomorphous replacement method using HgO, 3-chloro mercuri-2-methoxy propyl urea (CMMPU) (2 data sets), Pb(OAc)2 (2 data sets) and (NH4)2Pt(NO2)4 derivatives. The structure was refined by the simulated annealing procedure employing the program X-PLOR. The current R-factor is 0.203 in the 6.0-2.5Å range.

Results

The overall three-dimensional structure of RNase Rh is shown in Fig.1. The molecule has a dimension of 50 X 40 X 25 Å. The structure consists of six alpha-helices and seven beta-strands. On the surface of the molecule, a fairly deep cleft runs along the direction indicated by an arrow in Fig.1. Two histidine (His46 and His109) and one glutamic acid (Glu105) residues which were predicted as the most probably functional residues by chemical modification studies are located on the central beta-sheet consisting of four beta-strands and a helix running parallel to these strands.

References


Fig. 1 α-Carbon chain of the RNase Rh molecule (stereo pair).
The arrow indicates the direction of a cleft on the surface of the molecule.
Crystal Structure Analyses of Aminotransferase and Their Mutants from Microorganisms 2. Aspartate Aminotransferase and Its Complex from Escherichia coli and Thermotable Aspartate Aminotransferase from Thermophilic Bacillus Species


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Introduction

Escherichia coli aspartate aminotransferase (Ec AspAT) takes a dimeric form of identical subunits with total M.W. of about 90,000. X-ray crystallographic studies on several vertebrate isozymes and their complexes with inhibitors revealed that their overall three-dimensional structures are essentially the same and that large conformational changes from "open" to "closed" occur depending on the binding of inhibitors (substrates). Our structure analyses of AspAT-2-methylaspartate (2-MeAsp) complex and K258R mutant from E. coli suggested that some activity toward aromatic amino acids is due to a hydrophobic pocket in the active site region, and that the change from "open" to "closed" conformation may be small in E. coli AspAT. The thermophilic Bacillus aspartate aminotransferase (TsAspAT) has been purified from the E. coli clone cell extracts and crystallized. The X-ray structures of the wild type AspAT and AspAT-2-MeAsp from E. coli and preliminary X-ray characterization of TsAspAT are here reported.

Experimental

X-ray diffraction data for both crystals of AspAT and AspAT-2MeAsp complex (sodium sulfate, pH 7.0) were collected to a resolution of 1.8Å on a screenless Weissenberg type camera equipped with a Fuji imaging plate as a two dimensional detector using synchrotron radiation at the Photon Factory, Tsukuba. The space group was C2221 for both crystals with cell parameters a=155.4, b=87.1, and c=79.4Å for AspAT, and a=157.1, b=85.5, and c=78.9Å for the complex. After refinements for both structures, the R values reduced to 0.22 for AspAT (29267 reflections with Fo>4σ(Fo)) and to 0.22 for the complex (26354 reflections with Fo>4σ(Fo)).

TsAspAT was crystallized in the buffered ammonium sulfate solution by the hanging drop method. The crystals (yellow platelets) are monoclinic with unit cell dimensions of a=121.2, b=110.5, c=81.8Å, and β=97.6, belonging to space group C2, and contain two molecules in the asymmetric unit.

Results

AspAT and the AspAT-2-MeAsp from E. coli exhibited 2 dimeric forms, consisting of two identical subunits, large and small, related by the crystallographic 2-fold axis. Stereoview of the active site for E. coli AspAT and AspAT-2-MeAsp are shown in Fig.1. The enzymatic conformational change from "open" to "closed" was found in AspAT-2-MeAsp from E. coli. The rotation with change is about 5°, compared to 13° found in chicken m-AspAT. By the addition of 2-MeAsp, four water molecules in the active site in the "open" form were replaced, and a new Schiff base was formed through 50 rotation of the pyridine ring of PLP. The TsAspAT is active as a dimer of identical subunits with total molecular mass 85,780 daltons and Vm of 3.3Å^2/dalton. There are two molecules (one dimer) per asymmetric unit. The intensity data of about 2.2Å resolution were collected for TsAspAT-2-MeAsp complex. Preparations of substituted enzymes with heavy metals is in progress.

References

Structure of Antibodies and Antibody-Antigen Complexes

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Parkville, Victoria, AUSTRALIA

Introduction

The surface antigens of influenza virus, hemagglutinin and neuraminidase, provide an ideal system to investigate antigen-antibody interactions, and the structure of protein epitopes.

2/1, is a monoclonal antibody raised against a 24 amino acid synthetic peptide immunogen corresponding to the C-terminal sequence of the influenza virus hemagglutinin heavy chain (residues 305-328). The anti-peptide monoclonal antibody fragment, 2/1 Fab', has been crystallised in the space group P321, a=b=160Å, c=77Å. Isomorphous crystals of 2/1 Fab' complexed with a pentapeptide, LKLAT, have also been obtained, and will allow investigations to be made on the interactions of an antibody with a peptide immunogen.

Considering that the crystal structures of a number of monoclonal antibodies (Fabs), Fab-antigen, Fab-hapten and light-chain dimers have already been determined, this reservoir of information can be utilised in drawing comparisons and in solving the structure of 2/1 Fab' and its complex with an immunogen.

Experimental

Diffraction of the crystals on a rotating anode X-ray generator was poor thereby limiting data collection. The synchrotron facilities at The Photon Factory were ideally suited to collecting data on these crystals.

Data collection using imaging plates on Prof. Sakabe’s screenless Wissenberg camera at beamline BL-6A2. Table 1 shows the experimental conditions for the data collections and the statistics of data processing.

Results and Discussion

It was initially considered to solve the structure of 2/1 Fab' using molecular replacement techniques. This was proving to be difficult, especially since the data for 2/1 Fab' indicates that there are two molecules per asymmetric unit. In order to aid in the structure solution and to confirm any molecular replacement solution, a uranyl acetate derivative of 2/1 Fab' was obtained. It is hoped that a combination of molecular replacement and single isomorphous replacement techniques will be used to determine the structure.

The crystals of 2/1 Fab' complexed with LKLAT appear isomorphous with the native crystals and also possess two molecules in the asymmetric unit. It is hoped that the structure of the complex will be determined by molecular replacement once the native structure has been solved.

Acknowledgements

We are grateful to Professor N. Sakabe and his group at The Photon Factory for assistance during the data collection.

Table 1. Statistics for Photon Factory Data Collections

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<th>Crystal</th>
<th>2/1 Fab'</th>
<th>UA derivative</th>
<th>Complex</th>
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<tr>
<td>Rotation axis</td>
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<td>a*</td>
<td>c*</td>
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<td>2. Data processing results</td>
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<td>65% to 3.9Å</td>
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Phaseolin is the major storage protein in the French bean *Phaseolus vulgaris*. The structure of seed-storage proteins is of particular interest to genetic engineering; goals such as enhanced nutritional value may be contemplated. To this end we have recently determined the structure of phaseolin to 3Å resolution\(^1\). Higher-resolution structural information for phaseolin necessitates synchrotron diffraction data collection. This report details such data collection on beam-line 6A2 at the Photon Factory.

### Table 1 Data Collection statistics for phaseolin

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<th># Refl.</th>
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<th>Resol. (Å)</th>
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<td></td>
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<tr>
<td>C</td>
<td>11/1990</td>
<td>Type II</td>
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<td>to be processed</td>
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<td></td>
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</table>

We are at present refining the Type III structure to high resolution. A number of cycles of molecular dynamics refinement have been performed and we are currently modelling water molecules bound to the protein and endeavouring to build the carbohydrate moieties attached to the protein. The crystallographic R-factor at this stage of the refinement is 21% for reflections in the range 6.0-2.0 Å.

### Acknowledgments

We thank Prof. N. Sakabe and Dr Nakagawa for invaluable assistance with the data collection.

### References

THE ELECTRON DENSITY DISTRIBUTION OF BERYLLIUM METAL.
OBTAINED FROM THE SR POWDER DATA BY THE MAXIMUM ENTROPY METHOD.

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Introduction
The electron density distribution of Be metal has been studied by several authors in the past two decades in order to reveal the feature of a bonding charge density. Brown (1972) measured 27 Bragg reflections up to (sinθ/λ) < 0.88Å⁻¹ on an absolute scale. Larsen et al. (1984) measured them with even higher resolution, i.e. (sinθ/λ) < 1.21Å⁻¹. Hansen et al. (1987) carried out γ-ray diffraction experiment. In these studies, the charge density distributions of Be were analyzed by Fourier method and compared with results of theoretical studies.

Recently, it was found that the Maximum Entropy Method (MEM) is a very powerful method to visualize the detail of an electron density distribution. Sakata et al. (1990) showed that the reliable electron density could be obtained from X-ray powder data by the MEM. The purpose of the present work is to study bonding states of Be in solid states by using newly developed method.

Experiment
In order to study the charge density in Be, a new powder diffraction method, which is composed of the combination of the Synchrotron Radiation (SR) and Imaging Plate (IP), was adopted. This experimental technique is suitable for materials composed of only light elements, because the experiment is carried out in transmission geometry.

The X-ray powder data for Be was collected by the large Debye-Scherrer camera (radius 572mm) at the Photon Factory BL-6A. The wavelength of incident X-ray was 1.04 Å. In order to have a X-ray powder pattern with good counting statistics, the diffracted intensities were accumulated on IP for 5 hours, which is rather long as exposure time for IP experiment. The other detailed experimental arrangements were described elsewhere. After all, 19 Bragg integrated intensities were obtained.

Results and Discussion
The detail of the data analysis was written in the previous works. The MEM density map, which is the electron density distribution map obtained by the MEM, is shown in Fig. 1. This is for Be (110) plane. In the figure, the contour lines are written only for lower electron density region in order to avoid too dense contour lines. Apart from electrons around atomic sites, small peaks of electron density can be seen around the tetrahedral holes. On the other hand, octahedral holes show rather depletion of electrons compared with the tetrahedral holes. This implies that the bonding nature of Be can not be described by a simple metallic bonding. Such a fundamental image of the electron density is consistent with the deformation maps in the previous works.

In this study, only 19 lowest-angle structure factors were used for the MEM analysis. The present results, however, do not affected severely by the termination effects of the Fourier summation. The MEM is basically a method of a statistical deduction. It is, therefore, possible to calculate the deduced structure factors from MEM density map for unmeasured Bragg reflections. In order to demonstrate it, the calculated structure factors from the MEM map are shown together with the observed values by Larsen et al. (1984). For unmeasured reflections, the calculated values show very good agreement with the experimental values. In conclusion, the accurate electron density distribution of Be metal was revealed from SR powder data by the MEM.

The authors thank Prof. N. Sakabe and Drs. A. Nakagawa and N. Watanabe of Photon Factory for their kind help and suggestions in data collection.

References
1) P.J. Brown, Philos. Mag. 28 (1972) 1377.

Fig. 1 The MEM map of (110) for Be between 0.0~1.0[e/A³] with 0.05[e/A³] step.

Fig. 2 The plots of F(hkl)/C(hkl) vs. sinθ/λ. Calculated values (O) and Larsen et al.'s data (X). C(hkl) is the phase factor.
Crystallographic refinement of Bowman-Birk type protease inhibitor B-I from peanut (*Arachis hypogaea*) at 2.2Å resolution

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Introduction

Bowman-Birk type protease inhibitor (BBI) is one of serine protease inhibitor families. BBI has two domains, which are sequentially homologous to each other. The crystal structures of AB-I,1 BBI from adzuki bean, complexed with trypsin and A-II,2 BBI from peanuts, has been determined at 2.3Å resolution, respectively. These structures show that BBI is constructed with two homologous domains which are related by a pseudo 2-fold axis and that significant structural changes does not occur in the reactive site of BBI at the formation of the inhibitor-protease complex.

B-I is one of BBIs obtained from peanuts, with 63 amino-acid residues. Crystals of B-I are isomorphous to those of A-II. Therefore we have determined the crystal structure of B-I in order to obtain the structure-function relationship of BBIs in detail.

Experimental Section

Crystals of B-I belong to the trigonal system, space group P3₁2₁ with a=71.4Å and c=65.1Å. The unit cell contains 12 molecules, and the solvent content is 65% by volume.

High resolution data for the native crystal were collected with a screenless Weissenberg camera3 at the BL6A2 station. Fuji imaging plates were digitized with a Fuji BA100 at the Photon Factory, and processed with the WEIS system.4 A summary of data collection and processing is given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. A summary of data collection and processing.</th>
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<td>Wavelength (Å)</td>
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<td>Total rotation angle (deg.)</td>
</tr>
<tr>
<td>Exposure time (sec./deg.)</td>
</tr>
<tr>
<td>Number of films</td>
</tr>
<tr>
<td>Total reflections</td>
</tr>
<tr>
<td>(independent)</td>
</tr>
<tr>
<td>Resolution (Å)</td>
</tr>
<tr>
<td>Merging R</td>
</tr>
<tr>
<td>Mean intensity difference from A-II</td>
</tr>
</tbody>
</table>

The structure was refined by the restrained least-squares refinement method using PROLSQ at 2.2Å resolution. The starting model for refinement was the structure of A-II.2 The refinement statistics are given in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Refinement statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution range</td>
</tr>
<tr>
<td>No of reflections (&gt;5σ(I))</td>
</tr>
<tr>
<td>R-factor</td>
</tr>
<tr>
<td>No of Protein atoms</td>
</tr>
<tr>
<td>No of Solvent atoms</td>
</tr>
</tbody>
</table>

Results and Discussion

The molecular structure of B-I is very similar to that of A-II, including the orientations of side chains. Both the molecules did not contain several residues at the N- and C-terminals, as the chain tracing was impossible at both the terminals due to very low electron densities. The fractions with high temperature factors or low temperature factors in B-I almost coincide with those in A-II.

Two molecules in an asymmetric unit form a dimer by a β-sandwich type interaction. Two dimers related by a crystallographic 2-fold axis make a tetramer in the crystalline state. The quaternary structure of B-I, however, changed from that of A-II, showing that the packing scheme differs to each other.

References

Crystallographic Study of Bacterial α-Amylase

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Introduction

α-Amylase is an enzyme which hydrolyzes the α-1,4-glucoside linkage in polysaccharides randomly along the molecular chain. It is widely found in bacteria, plants, and animal secretions. But amino-acid sequences of α-amylases from different origins are considerably different one another. The crystal structures of three α-amylases, Taka-amylase\textsuperscript{1}, porcine pancreatic α-amylase\textsuperscript{2}, and Aspergillus niger α-amylase\textsuperscript{3} have been reported, but that of bacterial one has not been determined. In order to reveal the structure-function relationship on bacterial α-amylases, we started X-ray crystal analysis of a bacterial α-amylase from Bacillus amyloliquefaciens by isomorphous replacement method.

Experimental

Crystals are in the space group of P2\textsubscript{1}2\textsubscript{1}2 with the unit cell dimensions of a= 91.4Å, b=149.9Å, and c=77.1Å. Two molecules (Mr=55000) are in an asymmetric unit. A thallium derivative was prepared by soaking crystals in 5mM thallium acetate solution for 3 days. X-ray diffraction data from the native and Tl-derivative crystal were collected at BL6A2 beam line of the Photon Factory with Sakabe's Weissenberg camera\textsuperscript{4}. The crystallographic b axis was parallel to the oscillation axis. An imaging plate was used as a two-dimensional X-ray detector. The diffraction images on the plate were digitized by a Fuji BA100 image reader and processed to intensity data with the program WEIS\textsuperscript{5}. The conditions in the data collection and the statistics of the intensity data are summarized in Table 1.

Results

Using the program PROTEIN, the data from the Tl-derivative were scaled to those from the native crystal, and difference Patterson map were calculated at 5Å resolution. From this map, two major Tl-sites were found. Additional two minor sites were located from the difference Fourier map calculated with the phases obtained from the two major sites. After the refinement of the positions, occupancies, and B-factors of the heavy atoms, low-resolution phases were calculated using isomorphous and anomalous differences. An overall figure of merit is 0.69 for the reflections ranging from 25Å to 5Å resolution. From the electron density map at 5Å resolution, the molecular boundary was not able to be determined. In order to obtain more accurate phases, the intensity data from Pt, Pb, and Ir-derivatives were measured at PF. They are now being processed.

References


Table 1. Summary of data collection

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<th>Native</th>
<th>Tl-derivative</th>
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<tr>
<td>Wavelength (Å)</td>
<td>1.00</td>
<td>1.04</td>
</tr>
<tr>
<td>Film distance (mm)</td>
<td>286.5</td>
<td>429.7</td>
</tr>
<tr>
<td>No. of imaging plates</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Oscillation angle (deg./IP)</td>
<td>6.0-10.0*1</td>
<td>6.5</td>
</tr>
<tr>
<td>ω-scan speed (deg./sec.)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Exposure time (sec./deg.)</td>
<td>10.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Resolution (Å)</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>No. of observed reflections</td>
<td>110815</td>
<td>89899*2</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>39229</td>
<td>51426*2</td>
</tr>
<tr>
<td>Rmerge = Σ(</td>
<td>I&lt;</td>
<td>I&gt;−&lt;I&gt;</td>
</tr>
</tbody>
</table>

*1: optimized to exclude the overlaps of reflections on each imaging plate.
*2: including Bijvoet pairs.
Almost all myoglobins (Mbs) and hemoglobins (Hbs) contain histidine residues (His) at the proximal (F8) and distal (E7) sites of the heme group. Great importance for the formation of the stable iron-oxygen complex in Mb and Hb has been ascribed to His E7, which is located closely enough to interact with the iron-bound oxygen molecule. In fact, the neutron diffraction study on oxy Mb afforded an evidence for the hydrogen bonding between the distal His and the coordinated oxygen. Further support for this view seems to be provided by the behaviour of Aplysia Mb or Glycera Hb, in which the distal His is replaced by other amino acid residue, and the oxygen binding constants are significantly different from those for normal Mb and Hb. These findings have frequently allowed one to suggest that the distal His may play a crucial role in the binding of the oxygen molecule to the heme iron. Recently, novel sperm whale Mb mutants in which the distal His is substituted by other residues were constructed using site-directed mutagenesis to replace the distal His residue. This synthesis and expression of a gene for sperm whale Mb in Eschericha coli have provided the useful materials for proving the functional role of highly conserved distal His.

We have currently interested in a facile way to modify the distal residue of Mb, that is, chemical modification of the His of Mb.[1] We have studied the effect of N-cyanation of the distal histidyl imidazole NH of Mb by cyanogen bromide on the heme environmental structure, and the ligand binding kinetics. With a view to understanding biochemical role of the distal His in Mb we have started the structural study using the SR sources and the macromolecular-oriented Weissenberg camera devised by Sakabe.[2]

The BrCN-modified Mb was prepared by addition of an equimolar amount of BrCN to a metMb solution at pH 7. The O2 complex of BrCN-Mb, BrCN-Mb(O2), was prepared by bubbling of O2 gas to BrCN-Mb solution, and single crystals suitable for X-ray diffraction were obtained from an aqueous solution saturated with (NH4)2SO4. Data collection was carried out by using the Sakabe's screen-less Weissenberg camera at BL-6A2 using the wavelength of 1.04 Å. Each Weissenberg pattern was digitized by BA-100 reader and processed by the computer program WEIS to assign the reflection indices and to integrate the intensities within a certain range around the Bragg peaks. The intensity data thus obtained were then combined into the same file and put on a common scale by the program COMBINE and SCALE.

The crystal structure of BrCN-Mb(O2) was solved by the molecular replacement method with that of native Mb reported previously. The crystallographic refinement of modified Mb structure was done by using the restrained parameters-least-squares technique of Hendrickson and Konnert, in which stereochemical informations of amino acid residues, such as bond length and angle, and so on.

The whole molecular structure of modified Mb are essentially the same as that of the native Mb. The X-ray crystallographic result demonstrates the formation of the novel Mb having imidazole N-cyanide and oxygen to the heme iron as a sixth internal ligand. In previous paper, we reported the reaction mechanism of the formation of stable O2-binding Mb. This result shows the formation of the stable Mb(O2) complex is due to the interaction between CN and O2. The refinement is not finished yet, so that some ambiguities of structure remain for the solvent molecules and the other side chains, and is now being carried out.

We thank Prof. N. Sakabe, and Drs K. Sakabe, A. Nakagawa, and N. Watanabe of the Photon Factory for their technical advice and use of the Sakabe's camera and computer programs.

Crystal Structure Analysis of Blue-Colored Anthocyanin, Commelinin, from Commelina communis (2)
Structure Determination of Cd-Commelinin

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§ Faculty of Agriculture, Nagoya University, Nagoya 464, Japan

Introduction

Commelinin is a kind of anthocyanins from blue-flowers, Commelina communis (Japanese name: Tsuyukusa). We have been trying to solve crystal structure of commelinin to elucidate mechanism of coloration of flowers, and succeeded to solve its atomic structure by X-ray diffraction method.

Data collection of Cd-commelinin has been reported (Nakagawa et al., 1990).

Result and Discussion

After some trials of direct method attempt, one solution of SHELXS-86 (Sheldrick, 1990) showed two highest peaks at positions correspond to positions of cadmium ions which were determined by interpretation of Patterson maps. Interpretation of electron density peaks calculated from a solution of SHELXS-86 was carried out on a three-dimensional graphics system, PS-340 connected with Vax Station 3100, using model building program, FRODO (Jones, 1978). At the initial stage of model building, totals of 63 peaks are assumed as parts of molecule, and R-factor calculated from these positions was 39.8% at 1.0Å resolution. Some trials of interpretations of difference-Fourier maps finally reveal entirely atomic structure of Cd-commelinin.

Atomic parameters are refined using XTAL system (Hall et al., 1980). Present atomic parameters are refined to an R-factor of 13.2% at 1.0Å resolution (10165 reflections) including 30 solvent molecules for structure factor calculation and anisotropic thermal parameters are applied to 207 atoms.

Two cadmium ions are located at center of a molecule, 5.1Å apart, on a crystallographic three-fold axis. Six malonylawobanins and six flavocommelinins surround these two cadmium ions with coordination of oxygen atoms of malonylawobanins. Two malonylawobanin and two flavocommelinin fragments are in an asymmetric unit and others are related by three-fold crystallographic symmetry. Both of malonylawobanin and flavocommelinin fragments in an asymmetric unit are correlated by non-crystallographic pseudo-two-fold axes each other.

Cd-commelinin is a novel type supramolecule which has some kinds of associations, such as self-association, co-pigmentation and intramolecular sandwich type association, in a molecule, and the result supports the suggestions by Goto and Kondo (1990). Once a molecule is formed, not only coordination of metal ions but also strong hydrophobic stacking and hydrophilic interaction make a quite stable molecule.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas No.02250103 from the Ministry of Education, Science and Culture of Japan.

References


Stereoscopic drawing of Cd-commelinin viewing along crystallographic c-axis
X-RAY DIFFRACTION STUDY OF DOUBLE SHELLED SPHERICAL VIRUS, RICE DWARF VIRUS

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1 National Institute of Agrobiological Resources, Tsukuba, Ibaraki 305
2 National Agriculture Research Center, Tsukuba, Ibaraki 305
3 National Institute of Sericultural and Entomological Science, Tsukuba, Ibaraki 305
4 Faculty of Engineering, Tottori University, Tottori 680
5 Faculty of Engineering, Tokushima University, Tokushima 770

Introduction

Rice dwarf virus (RDV) is a spherical virus having double-shelled structure, viz., outer (capsid) and inner (core) shells. Structural information of such larger and more complicated viruses is quite few. Recently, outer and inner shell structures, and interaction between the two shell proteins have been studied by cryo-electron microscopy and image reconstruction using roavirus¹² and reovirus³. In this method, resolution is limited, but the structure model might be useful to initial information for crystallographic structure analysis. The present study is only the case of X-ray crystal structure analysis of such a complicated and large (molecular particle weight; 6.52x10⁷) double-shelled spherical virus.

Experimental

Diffraction experiments were carried out with a Weissenberg camera designed for macromolecules⁴ at BL6A-2. Camera radius (viz., crystal-to-film distance) was either 430, 573 or 860mm. The wavelength was either 1.04 or 1.488Å. The incident beam, focused by double bent mirrors, was collimated to 0.1mm in diameter. Diffraction data were recorded on imaging plates and digitized with a Fuji BAS100 system and processed using "WEIS" program⁵. Weissenberg and oscillation photographs were taken to determine cell parameters and to collect intensity data.

Results

The preliminary diffraction study was recently reported⁶. The intensity data were collected at 20Å resolution using a total of 15 crystals. It is not clear whether a complete data set was recorded, because mirror indices were assigned only partly. This is ascribed to complexity coming from both "no setting photographs" and large lattice parameters of cubic crystal with a=789Å. To solve this problem, rotation search around 8x, 8y, 8z in "WEIS" program is under consideration. The data collection of very low angle reflections are crucial to use molecular replacement method effective for the initial stage of the structure analysis. However, these reflections are usually not observed because of beam-stopper. This difficulty is now cleared with a small beam-stopper(3x3mm) attached manually just close to the imaging plate. Figure 1 shows (2 0 0) reflection of 2θ=0.15° just outside of the beam-stop area. so, according to this method the missing reflection is (1 1 0) only.

Figure 1. Typical oscillation photograph of a crystal. A small beam-stopper(3x3mm) was attached in close proximity to the imaging plate. The oscillation angle was 3.2°. The exposure time was 80sec. The fiducial point at the edge on the right was 30mm from the origin. Crystal-to-film distance was 860mm. Wavelength was 1.04Å. The storage ring was operated at 2.5GeV with a beam current of 320mA. The index of the reflection marked by arrow is (2 0 0) with 2θ=0.15°. The interval between the nearest two reflections (many are observed) corresponds to the spacing based on (1 1 0).

References

CRYSTAL STRUCTURE ANALYSIS OF HUMAN INSULIN MUTANT AT HIGH RESOLUTION

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Institute of Biophysics, Chinese Academy of Sciences, Beijing, China
* NOVO Research Institute, DK-2880 Bagsvaerd, Denmark

INTRODUCTION

It was found a long time ago that insulin in acid solution is unstable. The main reason is that the A-chain C-terminal residue, A21-Asn, is very susceptible to acid hydrolysis[1]. It has brought about some problems in clinical use of insulin preparation. To search for applicable high-stable preparations, J. Markus.sen and co-workers [2] prepared a series of A21-substituted human insulin mutants by protein engineering approach, including A21-Ser, A21-Gly and A21-Asp. They all basically retain the biological potencies but are 5-10 times more stable in an acidic solution than native insulin[2]. But A21-Asn has been conserved throughout the evolution and invariant among the insulin species known today. Therefore it is necessary to know the impact of A21-substitutions on the molecular structure of insulin through X-ray structure at high resolution. Crystallographic studies on all three mutants are undertaken here we report the structure analysis of A21-Ser human insulin(A21S) at 1.5Å resolution.

EXPERIMENT

Crystals of A21S were prepared in a Tris-citric system and belong to the space group R3 with unit cell dimensions aH = bH = 80.61Å, cH = 37.98Å. The diffraction data collection was carried out with a screenless Weissenburg camera[3] at the BL6A2 station in the Photo Factory of KEK. A wavelength of 1.04Å and two film cassettes with radii 287mm and 430mm were used for the lower and high resolution data respectively. 14 IP were collected at 12.46° interval and 10 IP were collected at 18.68° interval to cover 180° of rotation for the aH axis mounting. Intensity data were processed using the WEIS program system[4]. A total of 32879 reflections from one crystal were measured at 1.5Å resolution and 11332 independent reflections with a R-merge of 0.098 were used in the structure analysis.

RESULTS AND DISCUSSION

In the final map at 1.8Å resolution, residue Ser·A21 appeared clearly and the structural changes of A21S mutant mainly occurred near the A21 residue. One of the interesting observations is that the structure mode of A21S takes 4Zn-type, i.e. T3/R3 conformation[5], but the coordination mode of zinc ions may take 2Zn type and OD1 of B3-Asn of molecule 2 takes part in coordination with a zinc ion on the 3-fold axis. That means R3 conformation of insulin molecule could be induced not only by Cl⁻, phenol, but also by other factors. More reliable information will be provided by further analysis at 1.5Å resolution.

The authors thank Prof. N. Sakabe and Dr. A. Nakagawa for their helps in data collection. The project was supported by grants of UNIDO (91/048/cw) and "863" High-Tech Plan of China(103-19-01).

REFERENCES

Crystal structures have been determined for several Fab fragments and or complexes with their antigens. Their basic modes of ligand binding are well characterized. However, the fine details of binding are still uncertain. A whole range of binding interactions have now been observed, including block end types of protein-protein juxtaposition, linear polymers fitting in grooves on the antibody and cavities, depressions or slots on the surfaces of the antibodies fitted with small molecules. Our present studies are designed to exploit the power of synchrotron radiation coupled to Prof Sakabe’s Weissenberg Camera on BL6A2 to produce higher resolution images of the molecules involved in these interactions. We also investigate other novel immunoglobulins and immunoglobulin-type molecules to compare their structures with those that exist in the Protein Data Bank. Discussion and hypotheses regarding evolutionary aspects can also be made. In this report we give the results of data collection and progress toward structure determinations of six immunoglobulin molecules.

The data collection statistics for the six molecules studied are given in Table 1. Data set 1 was taken from a protein that was produced by hybridizing two immunoglobulin light chains from different human sera: one from the patient MCG and the second from patient Hud [1]. Following the same procedure but with the samples interchanged a second crystal was obtained. The structures of both of these have now been determined. Data collected using a sealed tube generator was inconclusive for trying to establish the correct orientation of individual chains.

In a continuation of binding studies involving the Bence-Jones protein MCG with different ligands [2], the structure determination of the MCG molecule bound to a trinucleotide is in progress (Data set 3). The current R is 25% for all data to 2.0 Å resolution.

Data sets 4 and 5 are from two more Bence-Jones proteins SEA and JEN. Their structures are yet to be determined although some progress has been made with the SEA protein.

Data set 6 is from a crystal of the intact MCG IgG molecule in ammonium sulfate. The structure of MCG IgG in water [3] is nearing completion and the new crystal form will provide the basis for comparisons of the crystal structure in different media.

We would like to thank Prof Sakabe and his staff for the use of the camera and expert guidance and assistance. Also we would like to thank Prof Michael James and Dr Bret Church for helping in the data collection procedure.

References

<table>
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<tr>
<th>PROTEIN</th>
<th>NO. OBSERVED</th>
<th>NO. REFLECTIONS</th>
<th>R(mean)</th>
<th>FILMS RES Å</th>
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<tr>
<td>1.MCGXHUD</td>
<td>90,959</td>
<td>26,658</td>
<td>7.9</td>
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<tr>
<td>2.HUDXMCG</td>
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<td>28,764</td>
<td>8.6</td>
<td>19 1.6</td>
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<td>3.MCG TNT</td>
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<td>28,486</td>
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<td>4.SEA</td>
<td>82,146</td>
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<tr>
<td>5.JEN</td>
<td>29,763</td>
<td>12,323</td>
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<tr>
<td>6.MCG IGG</td>
<td>97,295</td>
<td>25,614</td>
<td>9.9</td>
<td>36 2.5</td>
</tr>
</tbody>
</table>

Table 1. Data Collection statistics for six protein crystals collected on BL6A2.
Structural Basis for Oncogenic Mutations of Ras Proteins

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Ras proteins play a pivotal role in the signalling of cell growth and differentiation. Like other signalling proteins, such as G-proteins or transducin, a ras protein in its GTP bound state communicates to effector proteins and is deactivated by hydrolysis of GTP to GDP. The molecular switching from the GDP to the GTP-bound form is accompanied by extensive conformational changes in two parts of the protein, the switch I and switch II regions, which are made up of loop L2/strand β2 and loop L4/helix α2, respectively.

Mammalian ras proteins are made up of 188 or 189 amino acids with an approximate molecular weight of 21,000 daltons, and are hence named p21. Three ras genes have been identified in human cells, H-ras, K-ras, and N-ras, and all show a high degree of sequence homology for the first 165 amino acids, after which the sequences diverge. The p21 proteins are attached to the cytoplasmic side of the membrane through a poly-isoprenoid group which is covalently linked to Cys-186, and possess an inherent GTPase activity that is stimulated by GAP, GTPase Activating Protein and by the GAP-related domain of the neurofibromatosis type 1 protein, NF1 GRD.

Ras oncogenes isolated from human tumor cells often have single point mutations in the codons corresponding to amino acid positions 12, 13, 61, or 146. Both H and K rat sarcoma virus have a ras gene with mutations at codons 12 and 59, and in vitro mutagenesis at positions 12, 13, 59, 61, 63, 116, 117 or 119 endow p21 with cell transforming capabilities. These positions make up part of the guanine nucleotide binding pocket, and these can be mapped to either the phosphate region (12, 13, 59, 61, 63) or base region (116, 117, 119, 146). To date, all of the biochemically characterized phosphate-region mutants show a decrease in the intrinsic GTP hydrolysis rate and are insensitive to GAP and NF1 GRD stimulation. In addition, all of the base-region mutations that have been tested show a decreased affinity for the guanine nucleotide. Either or both of these mechanisms, reduced hydrolysis rates and weakened nucleotide binding, are thought to be the biochemical reasons for cell transformation by oncogenic p21 proteins.

To understand the structural basis for these biochemical effects, we have analyzed the conformational differences between crystal structures of normal and mutant proteins, paying special attention to distinguish changes caused by amino acid substitutions from those caused by crystal packing. To avoid the danger of misinterpretation, we compare crystal structures in several different crystal packing environments whenever possible.

Although all of these mutations lead to cell transformation, the structural basis for each is different. Mutation of glycine at position 12 prevents the p21 GTP hydrolysis reaction by a direct interaction of the residue 12 side chain with the GTP hydrolysis transition state. Gly-13 plays a special role in the formation of a conformationally restricted type II β turn within the phosphate binding loop (residues 10-17), and most other amino acids would distort this highly conserved loop. The side chain of Gln-61 plays a catalytically essential role in stabilizing the pentavalent γ-phosphate intermediate of the GTP hydrolysis reaction. Replacement of Ala-59 with a threonine produces a steric clash with the loop L2 (residues 32-40), and pushes away residues 59-61 so that Gln-61 can no longer function in catalysis. Asn-116, Lys-117, Asp-119 and Ala-146 are directly involved in stabilizing the guanine base interaction, and mutations at these positions would increase the nucleotide exchange rate. Our interpretations of the oncogenic effect for residues 12, 61, and 63 are different than previous hypotheses, and those for residues 13 and 59 are new.
CRYSTAL STRUCTURE ANALYSIS OF ALEURIA AURANTIA LECTIN

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2) Department of Agricultural Chemistry, Chiba University, Matsudo, Chiba 271

Specific interactions between proteins and carbohydrates attract attention from the viewpoint of biological recognition on cell surfaces. Lectins are multivalent carbohydrate-binding proteins, and are found in plants, animals, and microorganisms. A lectin from fruiting bodies of Aleuria aurantia (orange peel fungus) is known to have binding specificity for a GlcNAc\(\beta\)1-4(Fuc\(\alpha\)1-6)GlcNAc residue which frequently exists in the core region of asparagine linked glycoproteins. Recently one of the authors (Y.N.) succeeded in crystallization of the lectin (AAL), and we started the crystallographic study to investigate its ternary structure and the specific interaction with the carbohydrates.

AAL is composed of two identical non-glycosylated subunits. The subunits consists of 312 amino acids, and the sequence shows that AAL includes six internal homologous regions. No significant homology was observed with known lectins from plants or animals except a hemagglutinin from a Gram-negative bacterium, Myxococcus xanthus.

Using the recombinant AAL, which was produced in Escherichia coli, crystallization of AAL was carried out by the vapor-diffusion method using ammonium sulphate as the precipitant. The crystallization conditions are: 13.8 mg protein/ml, phosphate-buffered saline (PBS; 8 mM Na\(_2\)HPO\(_4\), 1.5 mM KH\(_2\)PO\(_4\), 137 mM NaCl, 2.7 mM KCl, pH 7.2), the initial and final concentrations of ammonium sulphate are 10% and 30% saturation, respectively. Crystals of hexagonal bipyramid in shape were grown at 4 °C over a period of one month (size 1.2 mm × 0.8 mm x 0.3 mm).

Crystallographic parameters were determined by X-ray precession photography using Ni-filtered X-ray beam from a Rigaku rotating-anode X-ray generator (50 mA, 50 kV, 14 h exposure). Crystal data are: hexagonal, space group P6\(_3\)2\(_2\)2, a=b=84.1, c=248.7 Å. A \(V_m\) value\(^{17}\) was calculated to be 2.0 Å\(^3\)/dalton, assuming that there are two subunits per an asymmetric unit.

The date collection of a native crystal was performed at the BL6A2 station in the Photon Factory with a Weissenberg camera for macromolecular crystallography and imaging plates (IP).\(^{16}\) Monochromatized beam of 1.00 Å by Si(111) was used. Measurements were performed at 15 °C. The crystal was mounted with the a axis parallel to the spindle axis of the Weissenberg camera. Rotation angle and rotation-streak ratio were changed during a series of measurements to avoid overlapping of reflections due to the long c axis (10.0, 5.0, 3.5 °, and 2.0, 1.0, 0.5 °/mm, respectively). The read-out of IP data was carried out by a Fuji image reader BA-100 system, and the data reduction was made by program system WEIS.\(^7\) Total 32600 independent reflections with up to 2.0 Å resolution were collected. The rotational search will be applied to locate the 2-fold molecular axis of the dimer.

Acknowledgment. We thank Nichirei Co. for generous gifts of recombinant AAL sample. This investigation has been partly supported by Grant for "Biodesign Research Program" from RIKEN to Y. Sugawara.

References
INTRODUCTION

Succinyl-CoA synthetase is an enzyme of the citric acid cycle, catalyzing the "substrate-level" phosphorylation step; it performs a vital function in aerobic metabolism [1]. Succinyl-CoA synthetase, purified from Escherichia coli, is a tetramer with a molecular weight of 1.42 X 10^5. It consists of two different polypeptide chains or subunits, designated α and β, thought to be assembled in an α2β2-tetramer as a dimer of αβ-dimers. Several lines of evidence suggest that although the complete catalytic site is formed by regions in contact from both subunits in the αβ-dimer, these αβ-dimers do not function independently within the active, tetrameric enzyme. The two "halves" of the molecule are thought to work in an alternating fashion. One way to reconcile the catalytic properties of this enzyme with its quaternary structure is to have a clear representation of the conformation of the tetrameric enzyme in three dimensions. Such a determination is in progress. Crystals of succinyl-CoA synthetase suitable for X-ray diffraction study are soft and undergo severe radiation damage when subjected to a beam of X-rays. Their lifetime and utility for data collection to high resolution with conventional X-ray sources is limited. Fortunately, this problem is solvable using synchrotron radiation.

EXPERIMENTAL METHODS

Succinyl-CoA synthetase was purified from Escherichia coli and crystallized as described in a preliminary paper [2]. Tetragonal crystals suitable for X-ray diffraction study were grown by micro-dialysis against ammonium sulfate solutions containing coenzyme A. The space group is P4_12_2 with unit cell dimensions of 98.48 X 98.48 X 400.60 Å and one tetramer per asymmetric unit. Potential heavy-atom derivatives were prepared by soaking native crystals in situ but from which coenzyme A and protein in the surrounding mother liquor had been removed. Following are the heavy-atom salt solutions tried: trimethyl lead acetate, ethyl mercury chloride, mercuric thiocyanate, potassium platinum chloride, and ammonium platinum cyanate. Diffraction data were collected on BL-6A2 using a screenless Weissenberg Camera [3] with a crystal-to-film distance of 430 mm and a wavelength of 1.04 Å. Crystals were mounted with c* aligned perpendicularly to the spindle axis and X-ray beam. A total range of 90° was collected for each data set using 6-7 crystals. Diffraction intensities were recorded on Fuji Imaging Plates and digitized immediately using a Fuji BA-100 scanning system. The "shooting schedule" of oscillation ranges and coupling constants was compiled based on analyzing printed predictions and incorporated an overlap of 0.5° between successive Imaging Plates and 1° overlap between sequential crystals.

RESULTS AND DISCUSSION

Eight full data sets (approximately 30 Imaging Plates each) were collected, three native (with and without coenzyme A) and five potential derivatives, to a measurable resolution of 3 Å. Preliminary processing of the data sets to 5 Å resolution has been completed. The merged and scaled intensity data (90-100 % complete) are of good quality with R(merge)-factors in the order of 5-7%. Moreover, the corresponding R-factors representing differences of the potential derivative sets to native sets range from 8-24%. Difference Patterson maps are presently being calculated to assess the quality of each derivative. Those showing greatest promise will be pursued first and processed further to the limit of resolution.

ACKNOWLEDGEMENTS

This work was supported by a grant to the MRC Group in Protein Structure and Function and by Grant MT-2805, both from the Medical Research Council of Canada. Provision of beam time by Professor Sakabe and assistance by Dr. Nakagawa at the Photon Factory has been greatly appreciated.

REFERENCES

STRUCTURAL STUDIES OF LYSOZOMAL HEXOSAMINIDASE B AND A SITE SPECIFIC MUTANT OF BACILLUS STEAROTHERMOPHILUS LACTATE DEHYDROGENASE

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Introduction

Hexosaminidase B is a lysosomal hydrolase that is important in the metabolism of sphingoglycolipids (1). It is closely related to hexosaminidase A which hydrolyzes N-acetylgalactosamine from ganglioside GM2. An autosomal recessive deficiency in Hex A results in Tay-Sachs disease. Hex B defects result in the related and more rapidly progressing Sandhoff's disease. Crystals of Hex B have been grown in collaboration with Dr. D. Mahuran, Sick Children's Hospital, University of Toronto.

Bacillus Stearothermophilus lactate dehydrogenase (BSLDH) is an NAD/H oxidoreductase that catalyzes the interconversion of C=O and CH(OH) groups. The natural substrates are pyruvate and L-lactate. This enzyme has been selected as a good candidate to explore the possibility of engineering a broad substrate specificity into an important metabolic enzyme. In collaboration with Dr. B. Jones, Department of Chemistry, University of Toronto, crystals of several mutants of BSLDH have been grown. The one studied here is a triple mutant Arg171 Trp, Gln102 Arg and Cys97 Gly.

Experimental Methods

Intensity data collection was carried out at BL6A2 with the Sakabe Weissenberg camera. The wavelength was 1.04 Å. Since both crystals were hexagonal we tried to collect the data from crystals mounted about the a (or b) axis. The unit cell dimensions for Hex B are: a = b = 114.2 Å, c = 402.2 Å; the tentative space group from precession photographs taken in Edmonton is P6i22. The unit cell dimensions of the BSLDH mutant enzyme are: a = b = 102.38 Å and c = 168.6 Å; the space group of these crystals is P62 (determined as a result of the successful molecular replacement solution using wild type BSLDH as search model). The intensity data were recorded on Imaging Plates and scanned by the BA-100 scanner. Imaging plate records were processed by the program Weiss. Intensity data statistics for both crystalline enzymes are shown in Tables 1 and 2.

Results

Many of the crystals of Hex B suffered from very large mosaicity. The better crystals diffracted to 3.2 Å resolution. For the native enzyme crystals (Table 1) we collected data with the c-axis as rotation axis on 21 imaging plates. Processing of the native data and 4 potential heavy atom derivatives to 5 Å resolution has resulted in Rmerge values that range from 0.063 for the native to 0.090 for one of the derivatives. Work on trying to interpret difference Patterson maps is still in progress.

For BSLDH the structure was solved by the molecular replacement method. The search model was that of the wild type BSLDH (2). The rotation function was done with the 10-4 Å data. With the mutant crystals in space group P62 a prominent peak of 13 σ was observed (α, β, γ = 2.9°, 85.4°, 92.5°). Since P62 is a polar space group it was only necessary to define the Z coordinate once the x, y positions were determined by a 2D search. Using the solution for the correctly oriented and translated structure the refinement of the coordinates has been initiated using the program XPLOR. The two molecules in the asymmetric unit have been treated as identical in the initial simulated annealing runs. The R-factor is presently 0.28 for the 10-2.8 Å data with cut-off of IFI > 2 σ IFI. The Ca- atoms of the complete tetramer are shown in Fig. 1.

Table 1 Native crystal of Hex B

<table>
<thead>
<tr>
<th>Rmerge</th>
<th>Measurements</th>
<th>Unique data</th>
<th>Resolution</th>
<th>% complete</th>
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</thead>
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<tr>
<td>0.063</td>
<td>12,144</td>
<td>5,856</td>
<td>5.0 Å</td>
<td>80.0</td>
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</table>

Table 2 Native crystals of BSLDH

<table>
<thead>
<tr>
<th>Rmerge</th>
<th>Measurements</th>
<th>Unique data</th>
<th>Resolution</th>
<th>% complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.085</td>
<td>146,752</td>
<td>30,936</td>
<td>2.5 Å</td>
<td>84.8</td>
</tr>
</tbody>
</table>

Figure. Mutant BSLDH tetramer in the unit cell P62. Present R-factor is 0.2 for the data from 10-2.5 Å resolution.

Structural Studies on HIV Reverse Transcriptase

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† Laboratory of Molecular Biophysics, Rex Richards Building,
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  Nagatsuta, Midori-ku, Yokohama 227

Introduction.
The virus encoded enzyme reverse transcriptase (RT) plays a key role in the replication of human immunodeficiency virus (HIV). The structure of the HIV RT molecule is therefore of particular interest as a basis for the rational design of a second generation of antiviral drugs to combat AIDS.

The HIV-1 RT molecule comprises a 66/51k heterodimer. Extensive studies on the crystallisation of HIV-1 RT (using recombinant material from high level expression in E. coli) have yielded two crystal forms which show diffraction to minimum Bragg spacings of 6Å or better. Type 1 crystals belong to the orthorhombic space group P2₁2₁2₁ with unit cell dimensions of a=147Å, b=190Å, c=182Å. Type 2 crystals result from the co-crystallization of RT heterodimer with double-stranded DNA oligonucleotide and belong to the tetragonal space group P4₂2₂ with dimensions a=b=120Å, c=320Å. Both types of crystals diffract only weakly and are profoundly sensitive to X-rays. For such cases a combination of relatively short X-ray wavelength (1Å) (improved crystal lifetime) and image plate based detector system (high sensitivity coupled with low background noise) is clearly beneficial. Data collection (to date primarily on type 1 crystals) has therefore been pursued on image plates at station BL6A2 of the Photon Factory using synchrotron radiation of wavelength 1.04Å.

Experimental and Results.
Diffraction data were collected from 20 HIV-1 RT crystals, including several of the tetragonal type 2 crystals of RT/oligonucleotide, but mainly the orthorhombic type 1 crystals both native and soaked in a variety of heavy atom solutions. The data were recorded on Fuji BASIII imaging plates mounted on a helium filled Weissenberg camera of radius 430mm using 0.1mm beam collimation, with an oscillation range of 4.8° and a coupling constant of 2° per mm (0.3° overlap between successive images) for exposure times of 30 to 40 seconds per degree. The imaging plates were then digitized on a BA100 IP scanner (Fuji Film Co., Japan) and the data processed via the WEIS program package. Crystals were orientated in the beam on the basis of their macroscopic morphology without recourse to setting stills. For subsequent data processing initial missetting angles were estimated by eye or obtained via autoindexing (algorithm of T. Higashi) a supplementary series of oscillation photographs.

The quality and completeness of the data collected on image plates at the Photon Factory showed a clear improvement over previous data collections by other methods, as illustrated by the statistics for the orthorhombic native crystals presented in Table 1. The additional benefit of the large helium filled camera resulted in a particularly marked increase in the amount of useful data which could be collected from a single position on a crystal (routinely in excess of 25°). Similarly the tight (0.1mm) beam collimation allowed several positions to be separately exposed on each rodlike type 1 crystal. The Photon Factory type 1 native data set is over 87% complete to 6Å resolution with 12.6% merging R factor. Diffraction was observed to minimum Bragg spacings of 4.5Å but these data have not yet been incorporated.

Acknowledgements
We gratefully acknowledge the advice and help of Professor N. Sakabe, Dr K. Sakabe, Dr A. Nakagawa and Dr N. Watanabe at the Photon Factory. EYJ and DIS were supported by the MRC AIDS directed program and the Sasakawa Fund, University of Oxford.

References

<table>
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<tr>
<th>Data set</th>
<th>Res.</th>
<th>xtal</th>
<th>Obs</th>
<th>Unique</th>
<th>R merge</th>
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</thead>
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<td>Xentronics</td>
<td>10Å</td>
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<td>5437</td>
<td>1366</td>
<td>11.1%</td>
</tr>
<tr>
<td>Film</td>
<td>8Å</td>
<td>7</td>
<td>7152</td>
<td>3353</td>
<td>16.1%</td>
</tr>
<tr>
<td>(Daresbury)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imaging plate (DESY)</td>
<td>7Å</td>
<td>1</td>
<td>5467</td>
<td>2265</td>
<td>12.3%</td>
</tr>
<tr>
<td>Imaging plate (PF)</td>
<td>6Å</td>
<td>3</td>
<td>45555</td>
<td>11600</td>
<td>12.6%</td>
</tr>
</tbody>
</table>

Table 1: Data statistics for RT type 1 native data
X-RAY CRYSTALLOGRAPHIC STUDIES OF RECOMBINANT HUMAN LYMPHOTOXIN

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Human lymphotoxin (hLT) is a cytolytic lymphokine produced by lymphocytes\(^1\). It was first purified to homogeneity from a human B lymphoblastoid cell line, and the amino acid sequence was determined\(^3\). hLT is found to be homologous to human tumor necrosis factor (hTNF). Since the primary structure of hLT and hTNF have revealed 30% identity in amino acid sequence\(^3\), they also are called as TNF-\(\beta\) and TNF-\(\alpha\), respectively. Both proteins bind to the same receptor and show similar biological activities against certain tumor target cells, induction of interleukin-1 and release of PGE\(_2\). However, they are not simultaneously produced by the same immunoresponse cells, and their expressions are regulated independently. These results may suggest that the two proteins have distinct physiological roles in an immunodefense.

It has already been reported that TNF is a trimeric molecule\(^5\), each subunit of which consists of an antiparallel \(\beta\)-sandwich\(^6\). In order to clarify further the structure–function relationships of TNF family, we have prepared several crystals of the recombinant human lymphotoxin (rhLT), deletion mutant constructed by \textit{in vitro} mutagenesis and expressed in \textit{E. coli}, and tried to collect the intensity data by Weissenberg camera system for macro molecule in BL6A2.

Crystals of rhLT were grown at 4 °C by the sitting drop vapor diffusion method. The crystal system is hexagonal with unit cell dimensions \(a = b = 64.5 \text{ Å}, \ c = 246.3 \text{ Å}\).

Still, oscillation and Weissenberg photographs with various orientations of the crystal axes were taken. Table 1 shows the conditions of Weissenberg photography.

Table 1. Experimental Conditions

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>1.04 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Lambda_0)</td>
<td>7.5°</td>
</tr>
<tr>
<td>c.c</td>
<td>1.0°/mm</td>
</tr>
<tr>
<td>Speed</td>
<td>2°/sec</td>
</tr>
<tr>
<td>Oscillation times</td>
<td>5 times</td>
</tr>
<tr>
<td>Exposure time</td>
<td>37.5 sec</td>
</tr>
<tr>
<td>Camera residue</td>
<td>429.7 mm</td>
</tr>
</tbody>
</table>

Figure 1 shows Weissenberg photograph of rhLT. Crystal aligned with \(c^*\) along X-ray beam. Diffraction spots separated well beyond 3.0 Å resolution.

The processing of data toward a structure determination are in progress. Comparison with TNF structure should be valuable understanding of binding region to the receptor.

X-RAY STUDY OF PROTEINASE A, A NON-PEPSIN-TYPE ACID PROTEINASE
FROM Aspergillus niger var. macrosporus

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1Department of Biophysics and Biochemistry, Faculty of Science, The University of Tokyo, Tokyo
2The Photon Factory, National Laboratory for High Energy Physics, Tsukuba

Introduction

Proteinase A secreted by Aspergillus niger var. macrosporus is a non-pepsin-type acid proteinase distinctly different in various properties from the family of pepsin-type aspartic proteinases, and so far it remains to be elucidated which residues participate in the catalysis of the enzyme and how the mechanism operates.1 In addition, no proteins homologous with proteinase A have been found in GenBank database except for Scytalidium lignicolum proteinase B that shows about 50 % identity. The spatial structure of A. niger proteinase A may, therefore, be rather different from those of proteins determined so far. It is hoped that the determination of the three-dimensional structure of the proteinase A will make clear the location of the catalytic sites and shed light on the catalytic mechanism of the enzyme.

Experimental and Results

For crystallization, the hanging-drop vapor diffusion method was employed at 25°C with ammonium sulfate as a precipitating agent at pH 2 in the presence of 5 % dimethylsulfoxide (DMSO).

Preliminary X-ray diffraction experiments were performed using a Huber precession camera with Ni-filtered CuKα radiation generated by a Rigaku RU-200 X-ray generator (40 kV, 70 mA, focus size 0.2 x 2 mm). The crystal data obtained are listed in Table 1.2) On the assumption that there is one enzyme molecule in the asymmetric unit, the ratio of volume to unit protein mass (\(V_\text{mol}\)) was calculated to be 1.64 \(\text{Å}^3/\text{dalton}\). The unit cell mass of the proteinase A crystal was among the smallest for protein crystals reported by Matthews.3) The density of crystals was measured in various concentrations of sucrose solutions. Using the volumes of \(V_\text{mol}\), \(V_\text{s}\), crystal density, and the number of asymmetric units per unit cell, the solvent content (\(V_\text{sol}\)) was estimated to be 21 %, indicating that the solvent content of the proteinase A crystal was among the smallest values for protein crystals.

Intensity data were collected by using a data collection system at the BL6A2 station in the Photon Factory, by combining the Weissenberg camera for macromolecular crystallography, an imaging plate, a Fuji image reader BAL100, and a data reduction program WEIS with a synchrotron radiation (\(\lambda=1.04 \text{Å}\)).4,5) The photographs showed that the intact crystals of proteinase A diffract X-rays at least to a resolution of 1.5 Å. The average isotropic temperature factor for the data from 20 Å to 1.5 Å was estimated to be as small as 11.8 \(\text{Å}^2\) by means of Wilson statistics, indicating the crystals of A. niger proteinase A is good for the structural analysis with a high resolution. In order to determine the three-dimensional structure of the acid proteinase A, the crystals soaked in heavy atom solutions were subjected to the collection of intensity data with a radiation of \(\lambda=1.00 \text{Å}\) (Table 2). So far there have, however, been no evidence that heavy atom derivatives are formed. The preparation of crystals of heavy atom derivatives of the enzyme are in progress.

We thank Prof. Noriyoshi Sakabe (The Photon Factory) for his encouragement and interest during the experiments.

References


Table 1. Crystal data of A. niger proteinase A

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P2_12_2_2</td>
</tr>
<tr>
<td>Lattice constants: a=54.7 Å, b=70.4 Å, c=38.0 Å</td>
<td></td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>1.46 (\times 10^5) (\text{Å}^3)</td>
</tr>
<tr>
<td>(V_\text{s})</td>
<td>1.64 (\text{Å}^3/\text{dalton})</td>
</tr>
<tr>
<td>Density</td>
<td>1.29 (\text{g/cm}^3)</td>
</tr>
<tr>
<td>(V_\text{sol})</td>
<td>21 %</td>
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Table 2. Conditions for measurements with Weissenberg camera

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Rotation axis (deg)</th>
<th>Wcc</th>
<th>No.of IP</th>
<th>Total rotation exposure time (deg)</th>
<th>Average Collimator ring size (mm)</th>
<th>IP type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>c</td>
<td>10.5</td>
<td>1.5</td>
<td>12</td>
<td>120.5</td>
<td>8.4</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>c</td>
<td>10.5</td>
<td>1.5</td>
<td>12</td>
<td>120.5</td>
<td>42</td>
</tr>
<tr>
<td>IrCl₃</td>
<td>c</td>
<td>10.5</td>
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<td>LaCl₃</td>
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<tr>
<td>Pb(OAc)₂</td>
<td>c</td>
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<td>1.5</td>
<td>12</td>
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<tr>
<td>K₂UO₂F₅</td>
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<tr>
<td>UO₂(NO₃)₂</td>
<td>c</td>
<td>10.5</td>
<td>1.5</td>
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<td>42</td>
</tr>
</tbody>
</table>
X-ray Crystal Structural Analysis of Manganese Superoxide dismutase from Serratia Marcescens

Michiko KONNO and Momi MURASE

Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112

Introduction
Superoxide dismutases (SODs) are metallo-proteins which catalyze the dismutation of the superoxide radical according to the following reaction:

\[ 2O_2^- + 2H_2 \rightarrow H_2O_2 + O_2 \]

Three classes of SODs have been identified by metal content and sources. Mn SOD from Serratia marcescens constitutes the dimer of identical subunits consisting of 205 amino acid residues and has molecular weight of 4.8x10^4. We initiated X-ray crystal structural analysis of this Mn SOD using the photon factory source in order to interpret the specific property for metals and reactive mechanism by comparing the high-resolution structures between Mn SODs and Fe SODs. Our previous report^1 indicated the results of intensity data for native crystals at wavelengths near an absorption edge of Mn atoms. We report results of the measurements of derivative crystals and the remeasurement of native crystals.

Experimental and Results
Because native crystals are so fragile that they are easily cracked in soaking in the heavy-atom solution, they were lightly crosslinked by the immersion in 0.025 % (v/v) gluteraldehyde for 20 hours at room temperature and transferred to water. The difference of diffraction patterns between native crystals and crosslinked crystals might give rise from the small movement of molecules in the unit cells as observed in native crystals of Mn SOD from B. stearothermophilu^2. Crosslinked native crystals were soaked in 40mM Pb(OAc)_2 solution for 6 days, in 10mM Sm(OAc)_3 for 3 days and in 1mM UO_2(OAc)_2 for 3 days, respectively. Intensity data collections were carried out at the BL6A2 station at the photon factory. Intensities were recorded on the imaging plate in Weissenberg camera^3 with radius of 430mm at 10°C, read out by Fuji film BA100 system and processed by modified WEIS program^4. Experimental conditions are given in Table 1. Previous intensity data of K_2PtCl_6 recalculated by this program reduced Rmerge from 0.10 to 0.073. Difference Patterson maps were calculated by PROTEIN program and the map of Barker section at b=1/2 for Pb(OAc)_2 and Sm(OAc)_3 derivatives showed one strong peak in the same position. Difference Fourier maps of UO_2(OAc)_2 derivative using the Blow and Crick best phases by Pb(OAc)_2 gave the five peaks which do not contradict with the difference Patterson maps. However, electron density maps using the phase from double isomorphous replacement method of Pb(OAc)_2 and UO_2(OAc)_2 derivatives gave obscure border between molecular and solvent regions. This might be due to the different movement of molecules in the unit cells between crosslinked native crystals and derivative crystals. We are trying the molecular replacement method on the basis of molecular structure of Fe SOD from P. ovalis^5 using AUTOMR program written by Y. Mathurua.

Table 1. Experimental conditions and data evaluation

<table>
<thead>
<tr>
<th>Natives</th>
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<td>rotation axis</td>
<td>a</td>
</tr>
<tr>
<td>camera movement (mm)</td>
<td>7.3</td>
</tr>
<tr>
<td>rotation speed (°/sec)</td>
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</tr>
<tr>
<td>coupling const. (°/mm)</td>
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</tr>
<tr>
<td>oscillation angle (°)</td>
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<tr>
<td>repeat of oscillation</td>
<td>2-3</td>
</tr>
<tr>
<td>No. of films used</td>
<td>28</td>
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<tr>
<td>No. of reflections observed</td>
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<td>unique</td>
<td>16616</td>
</tr>
<tr>
<td>Rmerge</td>
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<tr>
<td>resolution (A)</td>
<td>2.2</td>
</tr>
<tr>
<td>derivatives</td>
<td>Pb(OAc)_2</td>
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<td>No.of reflections observed</td>
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<td>unique</td>
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<td>Rmerge</td>
<td>0.061</td>
</tr>
<tr>
<td>resolution (A)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

References
1) M.Konno and M.Murase, Photon Factory Activity Reports 8, 85(1990)
X-RAY CRYSTALLOGRAPHIC ANALYSIS OF CYTOCHROME bc~ COMPLEX

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Department of Biology, Faculty of Science, Osaka University, Toyonaka, Osaka 560

Introduction

The cytochrome bc~ complex (known as ubiquinol-cytochrome c reductase or complex III) is an oligomeric membrane protein which catalyzes electron transfer from ubiquinol to cytochrome c. The reaction is coupled with the translocation of protons across the mitochondrial inner membrane. The proton gradient produced by this enzyme is utilized for ATP synthesis. This enzyme contains two b-type and one c-type hemes and a Rieske-type iron-sulfur center. The functional unit in the bovine heart enzyme consists of 11 subunits, and its molecular weight is approximately 250 K. Although the electron-transfer and proton-translocation mechanisms have been investigated intensively, progress in the mechanistic studies has been slow due to lack of detailed knowledge of its three-dimensional structure. In order to shed light on the mechanism of this enzyme, we initiated crystallization and X-ray crystallographic studies of bovine heart mitochondrial cytochrome bc~ complex.

Experimental and Results

Purification and Crystallization of bovine heart mitochondrial cytochrome bc~ complex have been reported elsewhere. We obtained two crystal forms; crystal I was grown in Tris buffer while crystal II in potassium phosphate buffer. Crystal I is monoclinic, space group P21 with unit-cell constants of a=196 Å, b=179 Å, c=253 Å and β=97°. Assuming that two dimers (four functional units) were present in an asymmetric unit, V_m value is 4.4 Å³/dalton. Crystal II is hexagonal, space group P61 with unit cell constants of a=b=131 Å, c=710 Å. V_m value is 3.5 Å³/dalton for one dimer (two functional unit) in one asymmetric unit.

All the X-ray experiments were done at the BL6A2 using Weissenberg camera for macromolecular crystals. SR-ray was focused by cylindrical-bended asymmetric cut Si(111) monochromater. Each crystal was sealed in a quartz capillary just before the diffraction experiment. After several exposures the crystal was translated to avoid deterioration of diffraction pattern. The diffraction intensities were recorded on the imaging plates (40x20 cm), and read out by a Fuji film BA-100. The experimental conditions are summarized in Table 1.

Table 1. Experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Crystal I</th>
<th>Crystal II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of crystal (mm)</td>
<td>1 x 1 x 1</td>
<td>0.1 x 0.1 x 0.5</td>
</tr>
<tr>
<td>Rotation axis</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.04</td>
<td>1.00</td>
</tr>
<tr>
<td>Collimator (mm)</td>
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<td>0.1</td>
</tr>
<tr>
<td>Radius of cassette (mm)</td>
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<td>859</td>
</tr>
<tr>
<td>Oscillation angle (°/IP)</td>
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<td>2.2</td>
</tr>
<tr>
<td>Overlap of ω (*)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Coupling constant (°/mm)</td>
<td>3.0</td>
<td>.a)</td>
</tr>
<tr>
<td>Exposure time (s/IP)</td>
<td>83</td>
<td>88</td>
</tr>
<tr>
<td>Number of IPs</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>Total range of ω (*)</td>
<td>90</td>
<td>46</td>
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</tbody>
</table>

a) Measured with oscillation mode

Crystal I diffracted X-rays to 7.5 Å resolution, while crystal II to 6.5 Å resolution. Both crystals, in particular crystal I, are fragile; mechanical shock resulted in deterioration of the diffraction pattern.

The diffraction patterns on the imaging plates for crystal II were processed by the program WEIS. At present we processed six imaging plates, and collected 4088 intensities within 6.5 Å resolution. These intensities were merged and scaled to give 2721 independent reflections. The R_merge was 8.4 %.

We thank Prof. Noriyoshi Sakabe and Dr. Atsushi Nakagawa for their kind help in the data collection using the Weissenberg camera.

References

STRUCTURAL STUDIES ON GLUTATHIONE SYNTHETASE FROM ESCHERICHIA COLI B

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Institute for Protein Research, Osaka University, 3-2 Yamadaoka, Suita, Osaka 565; and †Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611, Japan

INTRODUCTION

Glutathione synthetase catalyzes the synthesis of glutathione from \( \gamma \)-L-glutamyl-L-cysteine and glycine in the presence of ATP. The enzyme of *Escherichia coli* B is a tetramer of four identical subunits with 316 amino acid residues. We crystallized the enzyme from potassium phosphate buffer (pH 6.0) and the structure was solved at 2.2 Å resolution with crystallographic R-factor was 20.3 % (P-NATIVE) (1, 2). The binding sites of ATP and \( \gamma \)-L-glutamyl-L-aminobutylate (a substrate analogue) have already been determined. To elucidate the structure-function relationship of the enzyme in more detail, it is important to analyse the structure of the enzyme-substrate complex or the enzyme-intermediate complex. Therefore, we carried out structure analysis of complexed crystals with the substrates. Firstly, we prepared the crystals complexed with ATP and \( \gamma \)-L-glutamyl-L-aminobutylate by soaking method using phosphate buffer system. However, the occupancy of the substrates was low because phosphate ion inhibits the binding of them competitively. Then, we try to obtain enzyme-ATP complexed crystals by cocrystallization in Tris buffer solution to raise the ATP occupancy. Obtained crystals were isomorphous with the crystals from phosphate buffer solution but the dimension of c-axis were elongated about 6 Å (a=87.85, c=170.26 Å). Native crystals were also obtained from Tris buffer solution (T-NATIVE) and have almost same cell dimensions (a=87.86, c=170.20 Å).

EXPERIMENTAL and RESULTS

Both the T-NATIVE and the ATP-complexed crystals were obtained by microdialysis using the same procedure reported previously (1). Enzyme solution was dialyzed against the outer solution containing 5 mM ATP used for the preparation of the complexed crystals. Diffraction patterns of the T-NATIVE crystals in the one a- and two c- axis crystal settings were recorded on imaging plates by using a large Weissenberg camera installed at the BL-6A2 station of Photon Factory (4). For ATP-complexed crystals, one crystal for the each setting was applied. The diffraction images were processed to intensity data with the programs WEIS and COLLECT up to 1.9 Å resolution (5). All frames of the data in each crystal were scaled together into a single data set by the program SCALE. Statistical data of the data collections are listed in Table-1. The refined structure model of P-NATIVE without the water molecules was used as the starting model of T-NATIVE structure. The center of the P-NATIVE tetrameric molecule was set on \((x, y, z) = (1/2, 0, 0)\) in the unit cell of the T-NATIVE crystal with the same molecular packing scheme as that of the P-NATIVE crystal. The reflections phased with the initial model. Refinement of the T-NATIVE structure was carried out using the Hendrickson & Konnert program (6). The initial value of a crystallographic R-factor for the structure was 35 % for diffraction data ranging from 5.0 Å to 3.0 Å resolutions. The R-factor was reduced to 22.5 % at 2.5 Å resolution \((F_{o}>3.0 \sigma)\). For the refinement of ATP-complexed structure, we use the same model with ATP molecule as the starting model of T-NATIVE refinement. ATP molecule was fitted on the difference Fourier map computed using the diffraction data of both the P-NATIVE and ATP complexed crystal which were prepared by soaking, and was fitted to the T-NATIVE cell. An R-factor was fallen down from 43 % to 22.1 % at 2.5 Å resolution now \((F_{o}>3.0 \sigma)\). Further refinements of both the crystals are in progress.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Number of observed reflections</th>
<th>Number of independent reflections</th>
<th>( R_{merge} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-NATIVE</td>
<td>67534</td>
<td>33088</td>
<td>0.073</td>
</tr>
<tr>
<td>ATP complex</td>
<td>41469</td>
<td>30849</td>
<td>0.045</td>
</tr>
</tbody>
</table>

REFERENCES

(2) Yamaguchi et al., Photon Factory Activity Report (1989),7, 109
(3) Yamaguchi et al., Photon Factory Activity Report (1990),8, 87
(4) Sakabe, J.Appl.Cryst.,(1983),16, 542
An X-ray study of hydrogenase and rubredoxin from sulfate reducing bacterium, *Desulfovibrio vulgaris* Miyazaki F

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Introduction

Hydrogenase is an enzyme which catalyzes reversible dehydrogenation of molecular hydrogen, and characteristic for the sulfate-reducing bacteria. We have been engaged in an X-ray structural study of hydrogenase and related proteins found in the species Desulfovibrio. This period we have carried out the diffraction experiments of hydrogenase and rubredoxin in the Photon Factory. The solubilized hydrogenase (hydrogen : ferricytochrome o oxidoreductase, EC 1.12.2.1) from *Desulfovibrio vulgaris* Miyazaki F (DVMF) has 89000 of molecular weight and has two or three 4Fe-4S or 3Fe-4S type clusters as the active center. Rubredoxin is a small protein and it is well known that rubredoxin serves as an electron carrier to omega-hydroxylase in aerobic Pseudomonas oleovorans, but it is not still unclear in anaerobic bacteria. In this report, we describe the collection of intensity data from DVMF hydrogenase crystal at multiple wavelengths, and also the diffraction experiments on rubredoxin.

Experimental and Results

Membrane-bound hydrogenase was solubilized by trypsin digestion from the wet cells of DVMF bacterium cultured by Ajinomoto Co. The protein was isolated and purified before. Single crystals of freshly prepared hydrogenase were obtained by sitting-drop vapor diffusion method from 15-20% (w/w) polyethylene glycol 1000 buffer solution (25mM Tris-HCl, containing 0.05% NaN3 pH=7.5). X-ray intensity data were collected at 5°C using a Weissenberg camera designed for macromolecular crystallography by Sakabe et al1 (r=430.5 mm) installed in BL-A2. The wavelengths of x-ray used were 1.000, 1.488, 1.730, 1.741 and 1.748 A (these wavelengths were selected near absorption edge of Fe atom and imaginary component (f) and f component of atomic scattering power are comparably large or small) from SR of National Laboratory for High Energy Physics. The diffraction patterns were recorded on Fuji Film 'Imaging Plate' (20 X 40cm), and read out by a Fuji Film BA-100. The beam pass from collimator to film was filled with He gas to reduce air scattering. The hydrogenase crystals were sealed in glass tubes, and mounted on goniometer head, being one crystal axis visually parallel to the spindle axis of the camera. Then the axes of crystals were exactly aligned manually to the spindle axis considering the diffraction cones of small angle oscillation photographs recorded on Polaroid film (exposure time : 20s/film, oscillation angle : 1 degree). The collected intensity patterns on Imaging Plate were processed by program WEIS developed by Higashi et al.2 in order to obtain indexed F-data. Hydrogenase crystals showed distinct decay during data collection at room temperature. Decreasing temperature down to 5°C, however, showed great improvement to reduce radiation damage of the crystals.

The difference of Bijvoet data and that of intensity data from two different wavelengths of x-ray were significantly observed. Patterson functions calculated with these difference have given the information on the possible locations of Fe-S clusters. Further data processing, evaluation of Bijvoet differences and comparison with data obtained by 4-circle diffractometer using rotating anode are now in progress.

X-ray diffraction data of rubredoxin are also collected by Weissenberg camera in Photon Factory. Crystal data: Trigonal, space group P3121, a = b = 43.7 A, c = 50.7 A, V = 83800 A^3, Z=6. Wavelength of 1.00 A was used. Crystal of dimensions 1.2X0.2X0.2 mm, camera length 430 mm, oscillation angle 12.9°, oscillation speed 1°/sec, exposure 60sec/frame. A total of 10630 reflections were collected up to the resolution range of 2.5 A.

The structure of rubredoxin from Desulfovibrio vulgaris Hildenborough has been reported by Adman, Sieker and Jensen. The homology of it with the present protein is rather high, only five out of fifty-two amino acids being different. Thus the molecular replacement method seems the best way to solve the structure, and the calculation is under way.

We are indebted to Prof. Noriyoshi Sakabe, Dr. Kiyoko Sakabe and Dr. Tsuneyuki Higashi for their technical advice and use of computer programs.

References

Lactoferrin is an iron-binding protein found in milk and many other secretions, as well as white blood cells. It performs an important function in controlling iron levels in body fluids, has pronounced antibacterial properties and has a postulated role in iron absorption by infants. It is a glycoprotein, molecular weight 80,000 Da, with the capacity to bind, very tightly but reversibly, two Fe$^{3+}$ ions together with two CO$_3^-$ anions. The three-dimensional structure of human lactoferrin has been determined crystallographically [1] but the factors which determine the strength of iron binding, and the differences in the characteristics of iron binding and release between different species, are not understood. Accordingly, we undertook an X-ray structure analysis of bovine lactoferrin.

Crystals of bovine lactoferrin, obtained by dialysis of a 200 mg/ml protein solution against 0.025 M Tris buffer, pH 7.7, containing 7% MPD (2-methyl-2,4-pentanediol) and 6% methanol, are radiation sensitive and diffract weakly. Data to only 4 Å resolution could be obtained using a conventional diffractometer on a sealed-tube generator.

Diffraction data to 2.5 Å resolution, could, however, be obtained by Weissenberg photography using imaging plates [2] with the synchrotron radiation source of the Photon Factory. The crystals, with unit cell dimensions a = 138.4, b = 87.1, c = 73.6 Å, space-group P2$_1$2$_1$2$_1$, were mounted along their [a] and [b] axes. Data sets covering 90° of rotation were collected in each case, using oscillation ranges of 9.0° and 12.0° respectively. After processing using the program WEIS, a total of 128046 reflections were obtained; these were then merged and scaled to give a final data set of 27299 reflections to 2.5 Å resolution, with a merging R value for redundant measurements of 0.075. These synchrotron data also merged well with the original 4 Å diffractometer data (merging R 0.077).

The present protein model is 99% complete and gives very good agreement with the observed X-ray data (R = 0.201). Density for solvent molecules and three of the four carbohydrate chains can be seen, but these have yet to be added. The polypeptide chain of 689 amino acids is folded into two globular lobes (N- and C-lobes), each of them further subdivided into two domains (N1 and N2, C1 and C2) with the iron sites in the interdomain clefts (Fig. 1).

When compared with human lactoferrin, the polypeptide chain folding is the same but the relative orientations of the lobes and domains are somewhat different. If the N-lobes of the two proteins are superimposed, the C-lobes differ in orientation by 12°. Likewise the N-lobe of bovine lactoferrin is slightly more closed than that of human lactoferrin. Differences in metal and anion binding properties may also be related to:

(i) the presence of carboxyde attached to Asn 545 near the back of the iron site in the C-lobe,
(ii) the loss of an iron pair, Asp 217...Lys 296, linking domains N1 and N2 (Asp 217 becomes Asn in bovine lactoferrin), and
(iii) differences in interdomain interactions in the N-lobe resulting from the substitution of Arg 210 by Lys.

Refinement of the structure is continuing, together with further analysis of its functional implications.


Fig. 1 Ribbon diagram showing polypeptide chain conformation of bovine lactoferrin. Iron atoms shown as filled circles.
DNA topoisomerases are the enzymes responsible for maintaining and controlling the topological state of DNA in the cell. They play an important role in replication, transcription, and genetic recombination. Despite their importance, their structure and detailed mechanism of action are still unknown ([1]).

The best studied and characterized of all topoisomerases is *E. coli* DNA topoisomerase I. It is the product of the topA gene which has been cloned, sequenced, and mapped. The protein is made of 864 amino acids and has a molecular weight of 97,413 daltons. The only divalent required for activity is Mg**++.** The protein has three or four zinc atoms bound and removal of these results in loss of activity. The enzyme catalyzes the breakage and rejoining of one strand of the DNA through a mechanism that involves a transient covalent bond between a tyrosine in the enzyme and DNA. The bond energy is conserved and thus there is no requirement for an external source to reform the break.

*E. coli* DNA topoisomerase I is known to catalyze the following reactions: relaxation of negatively supercoiled DNA, interconversion of simple and knotted single stranded DNA rings, catenation of a pair of double stranded rings, provided that one of them has a single stranded nick or gap, and linking of a pair of complementary circular DNA rings into a double stranded ring.

We have obtained crystals of two fragments of the enzyme, of 30 kD and 67 kD molecular weight. Both contain the catalytic tyrosine, cleave single stranded DNA, and bind short oligonucleotides. The larger fragment comprises 70% of the intact molecule. The crystal of the larger fragment belong to space group P2₁2₁2₁, with unit cell constants a = 63.7 Å, b = 79.1 Å, c = 142.3 Å. Typically the crystals are only 50-150 μm thick. The crystals are radiation sensitive. In a conventional rotating anode source they diffract to 2.3-2.5 Å for 20 minutes before starting to deteriorate and then diffract to only 3.2 Å. We cannot see diffraction beyond 3.2 Å in a conventional rotating anode source. Due to the sensitivity and size of our crystals we needed to collect data on a synchrotron beamline BL6A2 using the Weissenberg camera of Professor Sakabe [2]. We used a wavelength of 1.0 Å and a crystal to film distance of 430 mm. The data was recorded using 20 x 40 cm imaging plates and scanned on a BA100 Fuji scanner. Indexing and integration was done using the program WEIS [3] on the FACOM computer at the Photon Factory. Some images were reprocessed on a Silicon Graphics using a version of WEIS provided by G. Prive of Berkeley University. Data from different films were scaled and merged using the CCP4 suite of programs [4].

The crystals were mounted with either a* or b* along the spindle axis. For the former case, we collected 5.5° per film, in the latter case we collected 7.5° per film. In both cases we overlapped the oscillation ranges by 0.5°. Exposure varied with the size and quality of the crystals; it was between 2-3 minutes per film. In all cases, the crystals were aligned using short oscillation photographs recorded on Polaroid film. As our crystals deteriorated rapidly we collected native data from several crystals starting at different points. Only the first few films recorded from each crystal showed high resolution diffraction.

The native data set is complete to 3.2 Å and partial to 2.8 Å. Analysis of native gives an R<sub>free</sub> of 10.6% to 3.2 Å and with 80% of the measurements greater than 3σ. The need to align the crystals before actual data collection prevented us from collecting more high resolution data as the crystals start decaying as soon as they are exposed for alignment purposes. We would like to collect more data at high resolution using the same system but without pre-alignment of the crystals.

Aside from the native data, we also collected partial data sets on crystals that had been soaked with two different oligonucleotides. The two oligonucleotides are identical except that one was chemically modified to have a mercury covalently attached at a specific position. Analysis of both data sets show clear differences both with the native and between themselves. We expect to use the mercurated oligonucleotide as a derivative. Unfortunately, these data sets are too incomplete to use for phasing. We hope to be able to collect data on these crystals soon in order to solve the structure.

We are very grateful to Professor N. Sakabe for allowing us to use his Weissenberg camera and for his help and suggestions. We thank A. Nakagawa and S. Iwata for their help at the Photon Factory. We also thank J. Smith and J. Bolin for their help during data collection and G. Prive and G. Lange for their UNIX versions of WEISS.

Of all organelles in the living cell, only the ribosome, the supramolecular assemblies facilitating the translation of the genetic code into proteins, has thus far been crystallized. A typical bacterial ribosome is of a molecular weight of 2.3 million daltons, is composed of 3 chains of RNA (a total of about 5500 nucleotides) and 57 different proteins. These facilitating the translation of the genetic code into proteins, has thus far been crystallized. Of particular interest are those of unequal size (m.w. 1.45 and 0.85 million daltons) which associate upon initiation of protein synthesis. Although ribosomes are notoriously unstable and flexible, diffracting crystals from each ribosomal particle have been grown. Of particular interest are those of complexes mimicking defined stages in the process of protein biosynthesis, and those that diffract to almost atomic resolution, 2.9 Å.

Due to the weak diffracting power and the large unit cells, virtually all the crystallographic studies have to be performed with synchrotron radiation. At ambient temperatures all ribosomal crystals decay upon irradiation so rapidly that the reflections beyond 18 Å decay before they can be detected. Therefore, a procedure was developed to collect data at cryo-temperature from shock frozen crystals.

During 1991 we focused on collecting quality data at the highest possible resolution from crystals of large subunits from Halobacterium marismortui. A significant improvements in the quality of these crystals has been obtained recently, by the addition of 1 mM Cd++ to the crystallization medium, which contained more than 2 M of other salts. The improved crystals are isomorphous (C2221, a=210, b=300, c=581 Å) with the previously reported ones, which diffracted to 4.5 Å (see 1990 report). Their superior internal order is reflected not only in their high resolution (2.9 Å), but also in their mosaicity (around 0.3 °) and in their adequate mechanical strength. Thus, the severe splitting problem reported earlier (Photon Factory Activity Report 1990) was virtually eliminated.

Using our well established cryotemperature procedures, data could be collected from the same crystal for days without detectable decay. However, as our measuring period was in July, a very humid period in Japan, and as four days were needed for collecting a (almost) complete diffraction data set, the formation of ice around the cooled crystal became a severe problem. Water-rings have been detected on diffraction patterns with increasing magnitudes as a function of measuring time and obscured the very weak reflection of spacings of 3-4.7 Å. Diffraction data were collected on the new generation Weissenberg camera build by Prof. Sakabe. The data collection parameters were: crystal to detector distance: 573 mm (equipped with a helium path), detector total area: 40x40 cm (provided by two plates, each 20x80cm; collimator=.1 mm; wavelength=1.00 Å).

A new type of Imaging Plate (blue) with a spatial resolution of less than a 100 micron (compared with app. 180 micron for the regular, ones) was used. The data were scanned on RUI RA100, with a raster of 100 micron, although theoretically it could be finer. We found that the main drawback of the new (blue) plate is their lower sensitivity. 24 minutes of exposure were needed for a 2° rotation (compared with 8 min. on the regular type). Since there were only two of the new plates, collecting a frame required around an hour (including scanning and erasure), and the net calculated time for collecting a complete set was 60 hour. Together with the time spent for alignment, etc., the actual time spend for this crystal was 4x24 hours (we used the scanning and erasure period for collecting a parallel 180° set on the regular IP's).

Thus, although the total allocation for our experiments seems to be rather long (5x25 hours), we could collect only 90% of a data set. For comparison, a complete 1.5 Å data set of Spinach Rubisco was collected in 2 hours on the same beamline (Anderson, 1990 Photon Factory Activity Report). This stresses the necessity for extended beam periods for useful crystallographic studies of ribosomal particles.

Unfortunately we were not able to exploit the advantage of the Weissenberg camera, namely large rotation ranges. As the reflections at high resolution are very weak, to obtain a measurable peak to background ratio, we reduced the rotation to the minimum required to measure fully recorded reflections on each frame.

Processing of the data is in progress. Further improvement of the WEIS-display version has been implemented. We have found that interactive procedures with a visual inspection of the diffraction pattern overlaid on the predicted one, was crucial for correct indexing of the reflections, since due to the large cell dimensions the distance between the centers of reflections was less than 1 mm.

Though sharp reflections to 3 Å resolution were easily detected in several directions, preliminary results of the data evaluation showed that the diffraction of the crystal was, as often seen for crystals of ribosomal particles, rather anisotropic. An example for the quality of the data, using only the left half of one exposure is given below:

<table>
<thead>
<tr>
<th>Sigma Cutoff</th>
<th>Total refl.</th>
<th>R-sym.</th>
<th>Num.</th>
</tr>
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<tr>
<td>0</td>
<td>4060</td>
<td>61</td>
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<td>3</td>
<td>1151</td>
<td>0</td>
<td>7.91</td>
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Crystallographic studies on *Mirabilis* Antiviral Protein (MAP)


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**Introduction**

*Mirabilis* Antiviral Protein (MAP) was found in *Mirabilis jalapa* L. plants as a systemic anti-plant-viral agent\(^1\). The monomeric basic protein (molecular weight 28kDa) was revealed to be a family of ribosome-inactivating protein (RIP) which is a widely distributed cytotoxin in plants\(^2\).

To facilitate the protein engineering for MAP, its total synthetic gene was constructed\(^3\). The site-directed mutagenesis of invariant amino acid residues among RIPs has been performed\(^4\). In the way of the structure and function relation studies, the crystallographic studies on MAP is going. Promising crystals of MAP for the protein crystallography were obtained, and they are trigonal P3\(_1\)21 or P3\(_2\)21 space group with \(a=b=103.9\text{Å},\) and \(c=134.6\text{Å}\)^\(^4\).

We report the data collection statistics of the diffraction data of MAP crystal using imaging plate on Sakabe's Weissenberg camera at Beam Line 6A2\(^5\) in comparison with that of the data collected with different Xuong-Hamlin Multi-wire area systems on a conventional X-ray source\(^6\).

**Experimental**

MAP was purified from *Mirabilis jalapa* L. tuber as described\(^7\). The crystals were grown from ammonium sulfate as a precipitant with hanging drop vapor diffusion at room temperature. The crystals belonged to the same crystallographic characteristics in spite of their various forms\(^8\). The size of the crystals were 0.3 x 0.4 x 0.8 mm and 0.2 x 0.2 x 0.6 mm for rotating anode and SR X-ray sources, respectively.

The diffraction data up to 2.5Å resolution were collected on Sakabe’s Weissenberg camera at Beam Line 6A2\(^5\) in comparison with that of the data collected with different Xuong-Hamlin Multi-wire area systems on a conventional X-ray source\(^6\).

**Results and Discussions**

The merging statistics shows in Fig. 1 after scaled with the combined isotropic s-shell scaling program\(^8\). These results seems to be comparable with the native mouse adenosine deaminase data sets by Quiocho and Wilson\(^9\) while the sizes of the measured crystals were different.

![Merging statistics of MAP data sets.](image)

<table>
<thead>
<tr>
<th>Rmerge (%)</th>
<th>(number of refractions)</th>
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</thead>
<tbody>
<tr>
<td>KEK-PF</td>
<td>Xuong at UCSD (2.8Å)</td>
</tr>
<tr>
<td>9.41</td>
<td>(65099)</td>
</tr>
<tr>
<td>Xuong at JT</td>
<td>13.53*</td>
</tr>
<tr>
<td>4.40</td>
<td>(22676)</td>
</tr>
<tr>
<td>Xuong at JT</td>
<td>13.97*</td>
</tr>
<tr>
<td>5.08</td>
<td>(13371)</td>
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</table>

* using all paired refractions.

We thank to Prof. N. Sakabe and Dr. A. Nakagawa for their technical advice. We also thank to Dr. F. Takusagawa for the preparation of his Multiscale programs prior to the publication.

**References**

EXAFS STUDY OF (Mg0.9Fe0.1)SiO3 PEROVSKITE

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Introduction

It is widely accepted that the (Mg, Fe)SiO3 perovskite is the most abundant constituent in the Earth's lower mantle. Its crystal structure is, therefore, of fundamental importance in understanding the physical and chemical properties of the lower mantle.

It is generally considered that Mg and Fe occupy A site (8-12 coordinated) and Si occupies B site (6 coordinated) in the perovskite structure. The EXAFS study carried out by Jackson et al. suggested, however, that Fe substitutes for Si in the B site in (Mg0.88Fe0.12)SiO3 perovskite. They claimed that this is the first evidence for Si occupying an 8-12 coordinated site in an oxide material.

However, their results were not reliable because the amount of their specimens was very small (thirty micrograms), and they measured fluorescence X-ray absorption spectra instead of transmission X-ray absorption spectra. In this study, we examined transmission X-ray absorption spectrum using sufficient amount of sample (2-3 milligrams) and check the results given by Jackson et al.

Experimental

The (Mg0.9Fe0.1)SiO3 perovskite was examined together with (Mg0.9Fe0.1)O magnesiowustite for calibration. The Perovskite was synthesized from synthetic orthoenstatite with composition of (Mg0.9Fe0.1)SiO3 at 25 GPa and 1800°C using a uniaxial split-sphere apparatus installed at Institute for Study of the Earth's Interior, Okayama University (USSA-5000 ℤ). The magnesiowustite was synthesized from oxide mixture of hematite and periclase at the atmospheric pressure and 1400°C under controlled oxygen fugacity.

Transmission Fe K-EXAFS and K-XANES spectra (6611-8211eV) were measured at the KEK. The samples were loaded in a small hole (3mm diameter) of an aluminum plate. Data were collected on a high intensity photon factory beam line (BL-6B) using an ion chamber and a double crystal Si (111) monochrometer.

The EXAFS spectra is modeled in the single scattering approximation as the sum of scattering contributions from each shell(3), and the coordination number of Fe and the Fe-0 bond lengths were calculated for (Mg0.9Fe0.1)SiO3 perovskite. The phase shift, the Deby Waller factor and the electron mean free path were calibrated by setting the coordination number and Fe-0 bond distance at 6 and 2.155Å for magnesiowustite (Mg0.9Fe0.1)O.

Results and discussion

There are three kinds of O atoms around Fe in the perovskite structure, whose Fe-O bond lengths are 1.99Å, 2.14Å and 2.55Å. The numbers of the O atom in each shell are 4.14±1.1, 10, 5.33±0.89, and 1.21±1.18, resulting on the total number of the O atom around Fe of 10.68±2.36. These results suggest that Fe occupies A site but not B site. The Si is not substituted by Fe, and the coordination number of Si should be 6.

References


Figure 1 K edge X-ray absorption spectrum of Fe in (Mg0.9Fe0.1)SiO3 perovskite
DETERMINATION OF THE ENVIRONMENTAL STRUCTURE AROUND A SPECIFIC ATOM IN DISORDERED ALLOYS BY THE ANOMALOUS X-RAY SCATTERING

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Introduction
Quite new type of amorphous alloys with a wide supercooled liquid region at temperatures below onset temperature of crystallization ($T_s$) have been found in some rapidly solidified systems, such as, La-Al-TM, La-Mg-TM, Zr-Al-TM, and so on, where 'TM' indicates the 3d-transition metals. In the La-Al-Ni alloy system, the value of $T_s$ is about 70K in La$_{55}$Al$_{25}$Ni$_{20}$ amorphous alloy. Such a very large $T_s$ indicates a high thermal stability of supercooled liquid against the precipitation of a crystalline phase, which enables us to produce a bulky amorphous phase with various shapes.

In the present study, the AXS method was employed to determine the environmental structures around Ni in La$_{55}$Al$_{25}$Ni$_{20}$ amorphous alloys as-quenched, annealed in the supercooled liquid region and crystallized.

Experimental
An ingot of the ternary alloy of 50 at%Mg, 30 at%Ni and 20 at%La was prepared by induction-melting a mixture of pure magnesium (99.99 mass%) and a binary Ni-La alloy made from pure nickel (99.9 mass%) and pure lanthanum (99.7 mass%) in a purified argon atmosphere. From the master ingots, ribbons of about 0.02 mm thickness and 1 mm width were produced by a single-roller melt-spinning technique. The ribbons were cut into small pieces of about 20 mm length, closely arranged and placed one upon another in an aluminum frame of about 15 mm width and 10 mm height for the x-ray diffraction measurements.

Results
The ordinary RDF and the environmental RDF around Ni of the amorphous samples are shown in (a) and (b) of Fig.1, where the solid and dotted curves correspond to the as-quenched sample and the sample annealed in the supercooled liquid region, respectively. If may be noted that the ordinary RDFs of both of the samples show almost identical patterns. The first peak at about 3.6 nm in the total RDF has a shoulder at 2.8 nm. For convenience, these shoulder and peak are labeled $r_1$ and $r_2$. The first peak in the environmental RDF around Ni has a single peak at $r_1$ and there is no peak at $r_2$. Taking account of the definition of the environmental RDF around Ni that represents only the pairs including Ni and the concentrations of the constituent elements, the peak at $r_1$ is mainly attributed to the atomic correlations of La-Ni pairs. Similarly, the peak at $r_2$ is attributed to La-La and La-Al pairs. From the present study alone, the contributions of these two pairs cannot separately be determined. However, since the contribution of La-La pairs to the ordinary RDF which is estimated from the coefficient of the partial RDF of La-La pairs is about 4 times larger than that of La-Al pairs in the present system, it was assumed that the peak at $r_2$ is ascribed to La-La pairs.

The ordinary RDF and the environmental RDF around Ni of the fully crystallized La$_{55}$Al$_{25}$Ni$_{20}$ alloy are shown in Fig.2. The profile in the near-neighboring region is different from that of the amorphous phase in Fig.2. an additional shoulder appears at a larger-$r$ side of the first peak in the environmental RDF and an extra peak is observed at a larger-$r$ side of the first peak in the environmental RDF around Ni. By comparing these RDFs of the crystallized sample in Fig.3 with those of the amorphous samples in Fig.2, it is found that the shoulder at a lower-$r$ side of the first peak in the ordinary RDF and the extra peak is located at a lower-$r$ side of the first peak in the environmental RDF of Fig.3. On the other hand, the shoulder at a larger-$r$ side of the first peak in the ordinary RDF and the second peak in the environmental RDF of Fig.3 are located at almost the same distance labeled by $r_3$. 

Fig.1 The ordinary (a) and environmental (b) RDFs for as-quenched La$_{55}$Al$_{25}$Ni$_{20}$ alloy. Dotted line: annealed sample.

Fig.2 The ordinary (a) and environmental (b) RDFs for crystallized La$_{55}$Al$_{25}$Ni$_{20}$ alloy.
Determination of the Environmental Structure Around a Specific Atom in Oxide Superconducting Glasses of Bi-Sr-Ca-Cu-O System

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Introduction

The BiSrCaCu2O8 glass compound which was reported by Maeda et al.[1] as a high-transition temperature (Tc) superconductor without containing any rare earth element was a mixture of the low- and high-Tc phases, which were ascertained to be Bi2Sr2CaCu2O8 with Tc near 80K and Bi2Sr2Ca2Cu3O10 with Tc near 105K, respectively. Most of the recent works for the Bi-Sr-Ca-Cu-O glass have focused on the crystallization process in order to obtain single high Tc phase. Within our best knowledge, the atomic structure has not quantitatively been studied by X-ray diffraction, although the X-ray diffraction profiles were mainly used for checking whether any crystalline phase is present in the as-quenched glass.

The main purpose of this paper is to present the structural information of Bi2Sr2Ca2Cu2O8 glass which was obtained by determining the environmental structures around Bi and Cu atoms, using the anomalous X-ray scattering (AXS) technique.

Experimental

The sample of Bi2Sr2Ca2Cu2O8 glass was prepared by melting thoroughly mixed reagents of Bi2O3 (99.9%), SrO (99.9%), CaO (99.9%) and CuO (99.9%) in an alumina crucible for 600 s at 1423 K and by pouring the melts on a brass plate, followed by immediately pressing them by another brass plate to quench the sample. The obtained glass plate of about 2 mm thickness was used for the X-ray scattering measurements. Its density measured by a pycnometer is 5.4 kg/m3.

Results and Discussion

Coherent intensity profiles (100h) of the Bi2Sr2Ca2Cu2O8 glass below Bi LIII- and Cu K-absorption edges are shown in Figs. 1 and 2, respectively. No crystalline phase is observed in the present sample. In the bottom of Fig. 1, the full and dotted curves indicate the profiles at 13.399 and 13.124 keV, respectively, which correspond to the energies of 27 and 302 keV below the Bi LIII-absorption edge (13.426 keV). The energy derivative profile 1Bi that is, the difference between these two profiles, which is multiplied by a factor of 2 is shown in the top of the figure. Similarly, the scattering intensity profiles at 8.955 and 8.680 keV which are 25 and 300 eV below the Cu K-absorption edge (8.980 keV) and their difference A1Cu multiplied by 2 is shown in Fig. 2. The fundamental features of these profiles are classified into the typical non-crystalline system. The position of the first peak in A1Cu of Fig. 2 slightly shifts to a higher Q-value. This peak shift is explained by smaller atomic size of Cu than the other elements. Namely, the scattering intensity due to atomic correlations including Cu mainly contributes to the high-Q side of the first peak in the scattering profile. The scattering power of Bi is at least about 4.5 times larger than other elements. Therefore, the ratio of the contribution of pairs with Bi to the total scattering intensity is very high. As a result, the profile of the first peak is dominated by the atomic correlations including Bi. This is a reason why such a shift of the first peak as in A1Bi of Fig. 1 is not observed in A1Cu of Fig. 1. More detailed RDF analysis is now under investigation.

References

PRESSURE-INDUCED MOLECULAR DISSOCIATION IN BROMINE AND STRUCTURAL SCALING RULES IN HALOGENS

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INTRODUCTION

Solid iodine I2 and iodine monobromide IBr undergo the first order structural phase transition associated with molecular dissociation at pressures of 21GPa1 and 39GPa2, respectively. The purpose of the present study is to investigate the structural behavior of solid bromine Br2 under pressure which has the same molecular structure (D2h-Cmc2) as iodine. We explore its transition pressure and the empirical structural scaling rule to understand the mechanism of the molecular dissociation in halogens.

EXPERIMENTAL

Bromine was solidified at liquid N2 temperature and ground into fine powder. The specimen was mounted in a diamond anvil cell(DAC) with an 80μm gasket hole. SR x-ray powder diffraction experiment was performed on BL-6B. We employed an imaging plate(IP) to sensitively detect weak signals from a small specimen. The incident beam was monochromatized by a Si(111) sagittally-focusing double-crystal-monochromator (2θ=93.4°). After a flat IP was exposed for 6 hours and two-dimensional image was digitized, intensities of the Debye-Sherrer ring were integrated along each arc by a specially-developed computer program. Thus high quality diffraction patterns with the high signal-to-noise ratio were obtained.

RESULTS AND DISCUSSION

Figure 1 shows the pressure dependence of the diffraction patterns near 80GPa. New peaks indicated with arrows appear at 80GPa and become stronger at the higher pressures. These new reflections can be explained by a body centered orthorhombic lattice(D2h-Cmc2) as indexed in figure, which is identical to the high pressure (HP) monatomic phase of iodine.1) It is therefore concluded that the molecular dissociation in bromine begins at 80GPa. In our previous study,1) it was found that the intramolecular distance rgs in a crystalline state could be a relevant parameter to scale the molecular structure. The scaled lattice constants of I2, IBr, and Br2 in their low pressure (LP) molecular phase revealed the similarity for the shape of unit cells3). This result further implied the similarity of the molecular arrangement. In Fig.2 we plot the atomic parameters y, z obtained by our reliable intensity data against the scaled volume V. Two solid vertical lines represent T of I2 and Br2 at atmospheric pressure while the dashed one does the molecular-to-monatomic transition point. One can see the universal behavior of both y and z in I2 and Br2. This fact strongly suggests the existence of the similarity of the crystal structure scaled by rgs in halogens.

REFERENCES

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Cesium metal is very compressible. Its volume decreases to about 25% at 20 GPa. The large compressibility is closely related to the 6s to 5d electronic transition. Cesium has one 6s electron in the conduction band under normal condition. At high pressures, however, the initially unfilled 5d state becomes progressively stable relative to the 6s state, and electrons are transferred from the 6s to 5d bands. This s-d transition in cesium has been extensively studied both experimentally and theoretically and found to terminate around 15 GPa. If we further apply pressure to cesium, the next step expected is the approach of the inner 5p core bands to the Fermi level and eventual delocalization of the 5p core electrons into the conduction bands: the pressure ionization. We have performed high pressure powder x-ray diffraction experiments up to about 100 GPa looking for an evidence for the pressure ionization [1].

Cesium was pressurized in a gasketed-diamond anvil cell at room temperature. Pressure was determined by the ruby luminescence method. Angle-dispersive powder x-ray diffraction patterns were obtained on the beam-line 6B of Photon Factory using an imaging plate. A new structural phase transition to the phase Cs(VI) was found at around 72 GPa. Figure 1(a) shows the observed diffraction pattern at 92 GPa. The pattern can be indexed either as a hexagonal close packed (hcp) or a double hexagonal close packed (dhcp) structure [Fig. 1(b) and (c)]. The ambiguity comes from the remaining diffractions of the low-pressure phase Cs(V). The lattice parameters for hcp are a=3.011(7), and c=4.855(16) Å with c/a=1.612(9) at 92 GPa.

The transition from the open-packed Cs(V) structure [2] to the close-packed Cs(VI) structure implies a qualitative change in the bonding property. According to the band structure calculation [3], the hcp structure is most stable in this pressure range because of the large repulsion between the ion cores. The present results agree with this theoretical result. The calculated volume for the onset of the pressure ionization is $V/V_0=0.13$, whereas the smallest volume achieved in the present experiments is $V/V_0=0.16$. The calculation predicts a transition from hcp to bcc structure around the pressure ionization. Hence the transition to the close packed Cs(VI) structure cannot be directly related to the pressure ionization. However, the strong core repulsion in Cs(VI) indicates the close approach of ion cores and we hope to obtain an evidence for pressure ionization at still higher pressures.

EXAFS studies of Cu/carbon catalyst for NO removal
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Introduction
For the purpose of removal of nitric oxide (NO) from diesel exhaust, the reduction of NO has been attempted using reducing gases like hydrocarbon gases. Carbon would be another candidate as a reducing agent. Previously, we have found that Cu-loaded carbon (brown coal char) is effective to remove low concentration of NO in the presence of O2 [1,2]. In the present study, EXAFS studies of the structural change of Cu/char during the reaction with NO in the presence of O2 were investigated.

Experimental
Loy Yang brown coal from Australia was used as a precursor of carbon. Cu has been introduced by impregnation with copper acetate solution (2 wt% as metal). The Cu-loaded carbon were devolatilized in N2 at 650°C. The NO decomposition reaction was carried out in a conventional fixed-bed reactor under an atmospheric pressure. The reaction temperature was 300°C and a gas mixture (NO: 1000 ppm, O2: 5 %) was used at a flow rate of 100 ml min⁻¹. EXAFS spectra at Cu K-edge were recorded in a transmission mode on a beam line BL-6B at room temperature using a Si(311) monochrometer.

Results and Discussion
Fig. 1 shows the effect of O2 concentration on the NOx conversion with Cu/char. The NOx conversion in the presence of even 1 % O2 was much higher than that in the absence of O2. The reaction temperature was 300°C and a gas mixture (NO: 1000 ppm, O2: 5 %) was used at a flow rate of 100 ml min⁻¹. EXAFS spectra at Cu K-edge were recorded in a transmission mode on a beam line BL-6B at room temperature using a Si(311) monochrometer.

Pressure - Induced Structural Phase Transition of Indium

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Indium metal has a face-centered tetragonal (fct) structure. Recent high-pressure x-ray diffraction experiment [1] showed an evidence for a structural phase transition around 45 GPa. We have extended the pressure range to 100 GPa and determined the crystal structure of the high pressure phase.

Indium powder was pressurized directly in a gasketed-diamond anvil cell without pressure medium. Angle-dispersive powder x-ray diffraction patterns were obtained on the beam-line 3A and 6B of Photon Factory using an imaging plate.

Figure 1(a) shows the diffraction pattern taken at 93 ± 5 GPa. The pattern resembles that of the low-pressure fct phase, but consists of more number of peaks. The crystal structure of the high-pressure phase is thus thought as a distortion from the fct structure. Figure 1(b) shows the diffraction profile calculated for a face-centered orthorhombic (fco) structure with the lattice constants of \(a=3.771\), \(b=3.841\), \(c=4.142\) Å. The observed and calculated peak positions agree within ± 0.1%. Figure 1(c) shows the diffraction profile calculated for the same orthorhombic cell but including a plastic deformation.

Figure 2 illustrates the model, in which the atoms in the (111) plane move successively to the [01\(\bar{1}\)] direction. This type of plastic deformation is common to the fcc metals subjected to a uniaxial stress. The characteristic features of the observed pattern are now well reproduced, including the broad background between the 002 and 020 reflections as well as the tail of the 113 reflection. The estimated volume change at the fct-fco transition is close to zero, offering a possibility that the transition is of the second order. The transition was reversible with respect to pressure.

The present results are in good accord with this theoretical consideration.

EXAFS Study on Hydrodesulfurization Catalysts for Ultra low Sulfur Distillate

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INTRODUCTION

Recently, environmental pollution has become a serious social issue. For diesel engines in the 1990s, particulate control is an important problem. Analysis of tests concluded that fuel sulfur was one of the most important factors. It is worthwhile to produce gas oil which contains few sulfur compounds.

One method for producing very low-sulfur fuel is to deeply hydrodesulfurize distillate, in which the sulfur content is about 1wt%. It has been reported that a Ni-W catalyst is one of the most active catalysts for such a reaction. In this work, we tried to study the effect of support composition on metal dispersion.

EXPERIMENTAL

The catalysts were prepared by impregnating extruded SiO₂-Al₂O₃ with an aqueous solution of ammonium metatungstate and nickel nitrate. After impregnation, they were dried and calcinated.

The SiO₂/Al₂O₃ ratios were 100/0, 70/30, 50/50, 0/100 by weight. NiO loading was varied from 4wt% to 11wt%. WO₃ loading was 20wt% or 25wt%.

The Ni K-absorption and W L-absorption were measured at room temperature using the EXAFS spectrometer at BL-6B of KEK-PF.

RESULTS AND DISCUSSION

Figure 1 shows the radial distribution functions from Ni-EXAFS of Ni-W/SiO₂-Al₂O₃ catalysts. The Ni of Ni-W/SiO₂ catalysts is found to be easily sintered during calcination from the fact that the Ni-Ni peak is much higher than the Ni-O peak. This pattern is quite similar to that of NiO. On the other hand, the Ni on SiO₂-Al₂O₃ is more highly dispersed than that on SiO₂. There is also a similar tendency for W. From these facts, it is suggested that the dispersion of loaded metal depends on the compositions of the supports.

Figure 2 shows the relationship between the SiO₂/Al₂O₃ ratio and the Ni-O/Ni-Ni peak height ratio that indicates the Ni dispersion. The Ni dispersion has a maximum at SiO₂/Al₂O₃ = 70/30 (weight ratio).

Figure 1 Radial distribution functions from Ni-EXAFS of Ni-W cataysts.

Figure 2 Effect of support composition on metal dispersion.
EXAFS STUDY ON HYDRODESULFURIZATION CATALYSTS FOR ULTRA LOW SULFUR DISTILLATE
II. EFFECT OF TEMPERATURE OF PRESULFIDING ON THE STRUCTURE OF ALUMINA SUPPORTED NICKEL-TUNGSTEN CATALYSTS

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Introduction

Alumina supported nickel-tungsten catalysts are used for hydrodesulfurization reaction. But the structure of nickel-tungsten catalysts have not been known well compared with that of cobalt-molybdenum and nickel-molybdenum catalysts. Especially, the structure of sulfided nickel-tungsten catalysts have not researched well yet. It is important to know the relation between the condition of presulfiding and the structure of catalysts. In the present report, we investigate the effect of temperature of presulfiding on the structure of nickel-tungsten catalysts by EXAFS spectroscopy.

Experimental

The catalyst studied in the present report was prepared by an impregnation method with a solution of ammonium paratungstate and nickel nitrate. Then the catalyst was dried at 110°C for 16 hours and calcined at 500°C for 4 hours. Nickel and tungsten contents were 2.6wt% and 15.1wt%, respectively. The atomic ratio of Ni/W was 0.54. The catalyst was presulfided in a stream of 5 vol% of H₂S/H₂ at 400, 500 and 600°C for 4 hours. The tungsten L-III absorption EXAFS spectra were measured at BL6B of the Photon Factory.

Results and Discussion

Figure 1 shows the Fourier transformations of the tungsten L-III edge EXAFS data for the catalysts presulfided at 400, 500 and 600°C. The peak at 1.9Å observed in the Fourier transformation of the EXAFS of the catalyst presulfided at 400°C is corresponding to the W-O. This peak is not observed in the Fourier transformations of the EXAFS of the catalysts presulfided at 500 and 600°C. It indicates that the catalyst is not sulfided completely at 400°C. The peaks at 2.5Å and 3.2Å are corresponding to the W-S and W-W, respectively. Table 1 shows the results from EXAFS for tungsten on the catalysts presulfided at 400, 500 and 600°C and WS₂. The distance from absorbing atom (R) was corrected by use of the distance of standard samples (WS₂ and WO₃). The average number of coordinating atoms (N) was calculated from the intensity of the peak. Table 1 shows the difference between the average number of coordinating atoms of W-W(N(W)) of the catalyst presulfided at 400°C and that of the catalysts presulfided at 500 and 600°C. Table 1 shows that the value of N(W)/(N(O)+N(S)) increases with an increase in temperature, too. The value of N(W) and N(W)/(N(O)+N(S)) show the degree of sintering of tungsten. It indicates that sintering of tungsten occurred under the condition of presulfiding at 500 and 600°C. Sintering of metal decreases the catalytic activity.

We conclude that the catalysts can be sulfided completely at 500 and 600°C, but under these conditions sintering of tungsten occurs, too.

The relationship between the structure of catalysts and the catalytic activity is not clear yet. Further experiments are now in progress.

This work was a part of cooperative research between Petroleum Energy Center and National Laboratory for High Energy Physics.

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<th>W-S R(Å)</th>
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<th>W-W R(Å)</th>
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Table 1. Results of analysis of EXAFS.

This work was a part of cooperative research between Petroleum Energy Center and National Laboratory for High Energy Physics.
X-RAY DIFFRACTION OF LOW-DIMENSIONAL METAL \( K_3Cu_8S_6 \) AT HIGH PRESSURE AND LOW TEMPERATURE

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Introduction

\( K_3Cu_8S_6 \) has a low-dimensional crystal structure\(^1\) and has two phase transitions at 153K and 55K, respectively.\(^2,3\) The first transition at 153K is accompanied by a weak incommensurate superstructure originated from a charge-density wave (CDW). On the other hand, the second transition at 55K is accompanied by a strong commensurate superstructure whose origin is not clear. Recently, M. Raghu et al. have reported that an incommensurate (IC) to commensurate (C) transition was induced by pressure\(^4\) from the measurement of resistivity. However, there is a considerable discrepancy between their data and ours\(^5\). We carried out the structural study at high pressures up to 20GPa and low temperatures down to 77K using diamond anvil cell.

Experimental

The experiment was carried out at BL-6C in photon factory. The powder of \( K_3Cu_8S_6 \) and NaCl was placed in a diamond anvil cell. As the pressure medium, a mixture of n-pentane and i-pentane was used. Pressure was monitored by the change of lattice parameter of NaCl.

Results and Discussion

Fig. 1. shows the diffraction pattern under several pressures. The basic pattern does not change under pressures up to 12GPa. No peaks originated from the incommensurate superstructure was detectable because the diffraction of the superstructure of CDW is generally very weak compared to that of host lattice. On the other hand, the diffraction of the commensurate superstructure below 55K was reported as strong as that of the host diffractions\(^5\). Therefore, the pressure induced IC-C transition reported by M. Raghu et al. is expected to be detectable enough. However, we found no change in the diffraction pattern at 200K under 2.2GPa where they found an anomaly in the resistivity.

Table 1. shows the compressibility of \( K_3Cu_8S_6 \) from the analysis of the present experiment. Clearly, the crystal is more compressible along the axis perpendicular to the b-axis than along the b-axis. This reflects the crystal structure\(^1\) composed of the copper-sulfur layers including Cu4S4 chain structure along the b-axis.

References

1) C. Burschka, Z. Naturforsch, 34b, 675 (1979)

Table 1. Linear isothermal compressibility of \( K_3Cu_8S_6 \). (10\(^{-3}\)GPa\(^{-1}\))

<table>
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<th>Ka</th>
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Fig. 1. Powder diffraction pattern of \( K_3Cu_8S_6 \) under pressure.
Near the absorption edge, X-ray resonant scattering becomes conspicuous and shows a large variation. By the large variation, Pendellosung fringes are induced in the integrated reflection intensities in the Laue case. The fringe is called Pendellosung fringe due to X-ray resonant scattering (PFXRS).

PFXRS was first observed for GaAs 600 reflection near the Ga K-absorption edge by Yoshizawa et al.1 It was then applied to determination of anomalous scattering factor f' from the experiment. In a previous work,2 we measured PFXRS for high index reflection of Ge near the K-absorption edge and determined f'. We found that f' could be determined within the error of 1% at an optimum condition.

There are two commonly used values of anomalous scattering factors. One is based on an empirical formula by Parratt and Hempstead3 and the other is determined by using wave functions including the relativistic correction by Cromer and Liberman.4 The latter values are 2.5% larger than the former near the absorption edge. The values determined by using PFXRS in our previous work was in better agreement with the latter except for very near the edge.

In this paper, we report on the determination of f' values by using PFXRS from 40eV below to just the Ge K-absorption edge by improving the precision in the experiment. For measuring PFXRS for Ge, it is easier to measure a high index reflection. In this case, it is important to use a crystal with homogeneous thickness of several tens of micrometers and measure the thickness precisely. In a previous work, we used a micrometer to measure the thickness, which was not precise enough. In the present experiment, we measured the X-ray absorbance for MoKa line and determined the thickness. The value was 39.3μm.

The observed PFXRS in 844 reflection by using KEK-PF BL6C is shown in Fig. 1. The X-ray intensity is higher for the low energy side and smaller near the absorption edge. It shows small oscillations due to PFXRS. At the point marked 'A', the condition f° + f' = 0 is satisfied, which was determined by measuring the intensities in the Bragg case. Here f° is the normal scattering factor for 844 reflection. The value of f' at this point is determined by this relation.

In Fig. 2, the f' values determined from PFXRS are shown by open circles. The filled circle is the value determined by the relation f° + f' = 0. The solid line is the calculated values based on Parratt and Hempstead formula. The dashed line is the calculated values by Cromer and Liberman approach. The measured values are smaller than the calculated values for the X-ray energy between -20eV to 0 eV. We could not sort out the origin of the difference, which should be studied in future.

References

![Fig. 1](image1.png) Fig. 1 The measured 844 integrated intensities in the Laue case very near the Ge K-absorption edge.

![Fig. 2](image2.png) Fig. 2 The experimental and calculated f' values of Ge.
Phase Transitions of Phosphorus-Arsenic Alloys at Low Temperatures and High Pressures

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Black phosphorus (black P) is transformed from an orthorhombic structure to a rhombohedral one at around 5 GPa and then further to a simple cubic one at around 10 GPa at room temperature (1). The orthorhombic form of a phosphorus-arsenic alloy (P 0.95 As 0.05) transforms to successively the rhombohedral form at about 5 GPa and the simple cubic one at about 10 GPa at room temperature (2). By using synchrotron radiation, the pressure-induced phase transitions of black P and P 0.95 As 0.05 are studied at low temperatures (2, 3). The pressures of both transitions increase with decreasing temperature. The phase transitions of P 0.95 As 0.05 have been studied at about 30 K and high pressures. A new diamond-anvil cell was developed for X-ray diffraction measurement which makes possible a continuous change in the pressure at low temperature (4). The diffraction patterns of P 0.95 As 0.05 and NaCl were recorded at 2θ = 2θ. The diffraction lines of NaCl were used to determined the pressure value according to Decker's scale.

Figure 1-a and 1-b show energy dispersive X-ray diffraction profiles of P 0.9 As 0.1 at 30 K and high pressures. A single phase pattern of the orthorhombic form was found at around 6.1 GPa. The alloy began to transform from the orthorhombic structure to rhombohedral one at around 8 GPa and then to the simple cubic one at around 18 GPa at 30 K. The pressures of both transitions of P 0.9 As 0.1 are higher than those of P 0.95 As 0.05. As pressure was decreased at 30 K, the simple cubic form of P 0.9 As 0.1 was transformed to rhombohedral form at around 11 GPa.


Figure 1-a and 1-b Energy dispersive X-ray diffraction profiles of P 0.9 As 0.1 at 30 K and high pressures: O: orthorhombic, R: rhombohedral, C: simple cubic.
ANALYSIS OF PHOTOELECTRON DIFFRACTION PATTERN


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*Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113

Introduction

The study of the two-dimensional angular distribution pattern of photoelectrons is a powerful tool to analyze the atomic structure of bulk crystals or thin films. We have developed a new display-type spherical mirror analyzer® for a simultaneous measurement of angular distributions. Using this analyzer, a photoelectron diffraction pattern of Si 2p core emission from Si(lll)7x7 surface was obtained® and analyzed with a single scattering cluster calculation.

Experiment

The experiment was made at BL-7A. The electric vector of the photons are linearly polarized about 85 - 90% in a horizontal plane.

Figure 1(a) shows the bulk photo-electron diffraction pattern of Si 2p core from clean Si(lll) 7x7 surface at the kinetic energy of 270 eV. Almost six-fold symmetrical peaks are clearly observed.

Analysis

Calculational method used here was similar to the usual cluster calculations. About 100 atoms in five Si layers, the spherical nature of the emitting wave, and the anisotropy of the final state wave were considered®. Figure 2(a), (b), (c), (d), and (e) show the calculated patterns for the photoelectrons emitted from first, second, third, fourth, and fifth layer Si atoms, respectively. Figure 2(f) is the sum of (a), (b), (c), (d), and (e), which is the expected pattern from Si(111) surface. In Fig. 1(b), the peaks in Fig. 2(f) were enhanced by the same method with the experiment®. This figure agrees well with the observed one, Fig.1(a).

Qualitatively, the observed peak positions can be explained simply by considering the directions of the strong scatterers from the emitter.

Conclusions

The peak positions in the pattern were well reproduced by the calculation and they are explained well considering the directions of strong scatterers from the emitter. The inclusion of the final state anisotropy in the calculation worsen the agreement with the experiment. This suggests that there is little anisotropy in the final state.

References


Fig. 1 (a) Observed photoelectron diffraction pattern of Si 2p core from Si(lll) 7x7 surface at the energy of 270 eV. (b) Calculated pattern.

Fig. 2 (a), (b), (c), (d), and (e) shows the calculated patterns from first, second, third, fourth, and fifth layer Si atoms, respectively. (f) is the sum of them.
NITROGEN ADSORPTION INDUCED RECONSTRUCTION OF Ni(111)
STUDIED BY NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE

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Faculty of Science, the University of Tokyo, Bunkyo-ku, Tokyo

Introduction

Reconstruction induced by adsorption is one of characteristic phenomena of solid surfaces. For understanding their origins, it is important to know atomic arrangements of reconstructed surfaces. We expected that adsorption of nitrogen atoms would induce reconstruction of Ni(111) surfaces. Near Edge X-ray Absorption Fine Structure (NEXAFS) is a useful technique to determine local structure of the surroundings of an adsorbed atom, and provides an important information to determine surface reconstruction. In this report, we applied NEXAFS and LEED to the structural study of the adsorption of nitrogen atoms on Ni(111), and found that the substrate was reconstructed to give a Ni(100)-like structure.

Experimental

Measurements were performed at the soft X-ray beam line BL-7Ai. NEXAFS spectra were recorded in Auger detection mode using an angle resolved electron energy analyzer. All measurements were done at room temperature.

Chemisorption of nitrogen atoms was performed at room temperature by exposing a clean surface to N* or N* which was produced by electron bombardment of nitrogen gas.

Results and Discussion

The adsorption of nitrogen atoms at room temperature resulted an increase of the background intensity of LEED without showing any extra spots. By heating this sample to temperature of 400°C, extra spots appeared as shown in Fig.1, though the background intensity was still high.

We assign this pattern to (110). Fig.2 shows nitrogen K-edge NEXAFS spectra of N/Ni(111) before and after heating to temperature of 400°C. Remarkable polarization dependence of the spectral profile is observed. At normal incidence, a strong peak is observed at room temperature at the edge position, and the peak height is reduced by heating. It has been reported that, at normal incidence, oxygen occupying 3-fold site on a Ni(lll) surface and 4-fold site on a Ni(100) surface shows a large and a small peak at the edge, respectively. Under the assumption that the characteristic feature of NEXAFS spectrum would be similar for a N/Ni system, we conclude that nitrogen atoms adsorb on 3-fold sites at room temperature, and on 4-fold sites after heating. By heating the sample, the atomic arrangement of the top layer of the substrate is reconstructed to give a Ni(100)-like structure.

In conclusion, at room temperature, nitrogen atoms adsorb on the 3-fold sites of Ni(111) randomly. After heating to temperature of 400°C, the substrate was reconstructed to give a structure like $c(2\times2)$ N/Ni(100).

Fig.1 LEED pattern of N/Ni(111) after heating to temperature of 400°C.

Fig.2 NEXAFS spectra of N/Ni(111).
(a) Adsorption at R.T.
(b) After heating to temperature of 400°C.

References

PHOTODECOMPOSITION OF AMMONIA ADSORBED ON Si(100) BY SYNCHROTRON RADIATION

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**Kuroda Solid Surface Project, Japan Society for the Promotion of Science, Tokodai, Tsukuba City, Ibaragiken 305, Japan

Dynamical behavior of intermediate species created by photoexcitation of adsorbates on surfaces is not only a fascinating subject in surface chemistry and physics but also important in technology of material design. Microscopic aspects of photochemical processes on surfaces revealed by modern techniques of surface science such as electron spectroscopy can give a new sight in both of fundamental and technological researches.

We studied photodecomposition of ammonia dissociatively adsorbed on Si(100) at room temperature in the photon energy range from 10 to 50 eV by ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction, Auger electron spectroscopy (AES) and photon stimulated desorption (PSD). In this energy range, valence and N 2s electrons can be excited, but silicon has no core electron. Ammonia molecules are dissociatively adsorbed to form Si-NH2 and Si-H at surface dimer sites of a Si(100) surface.1

Photoelectron spectra as a function of irradiation time of monochromatized synchrotron radiation (SR) of 35 eV and a difference spectrum are shown in the figure. In the spectrum recorded before irradiation, emission peaks of nitrogen lone pair electrons overlapped with Si-N bonding electrons and of N-H bonding electrons are seen at -5 and -10 eV measured from the Fermi level, respectively. After the irradiation, a small increase of the intensity at the intermediate region between two peaks is detected, which is clearly distinguishable in the difference spectrum. This increase around -7 eV is accompanied by the intensity decrease of N lone pair, Si-N bonding and N-H bonding electrons. This new peak is fitted to the Si-H bonding level.

By the irradiation of SR, the decrease of N-KLL Auger peak intensity is confirmed. In PSD, desorption of protons and hydrogen molecular ions are detected above the ionization threshold of N 2s (about 27 eV), but no nitrogen containing ion is not confirmed.

The results of AES and UPS suggest that the sample surface becomes nitrogen deficient and Si-H bond rich by photodecomposition of surface amino groups. The ionic fragments are produced by photoionization of N 2s. An excited complex of adsorbate-substrate with multi-holes in valence levels created by Auger decay of a N 2s hole decomposes to a proton or a hydrogen molecular ion. Desorption of nitrogen containing species may be neutral which was not detectable in the present measurement. In this model, it is not necessary to neglect a possibility that diffusion of NH or N into a bulk opens a reaction channel of silicon nitride formation.

Reference


UPS spectra

a: before irradiation, b: after 3.3 hr. of irradiation, c: after 5.8 hr. of irradiation, d: difference of c-a.
Monolayer Structures of Niobic-Acids supported on SiO₂
Masayuki Shirai, Kiyotaka Asakura and Yasuhiro Iwasawa
Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

Introduction

New one atomic layer niobic acid catalysts were prepared by the reaction of Nb(OC₂H₅)₅ with surface OH groups of SiO₂. These catalysts showed activities twenty times as large as a niobic-acid bulk catalyst and three times as large as an one atomic layer Nb oxide catalysts for the esterification of acetic acid with ethanol up to 8.0 v/t% Nb loadings. The surface structures were characterized by means of EXAFS to reveal the high activity.

Experimental

SiO₂-attached niobic acid catalyst were prepared by reaction of Nb(OC₂H₅)₅ with the OH groups of SiO₂. Nb K-edge EXAFS spectra were measured at BL-7C of Photon Factory. The spectra were taken at 80 K or 293 K.

Result and Discussion

The curve-fitting results were shown in Table 1. The number of Nb-Si bond contained in 1 g of the catalyst was plotted against Nb loadings in the catalyst. It shows that there was a linear relation between the number of Nb-Si bond and the Nb loading in the catalyst. There was a break at 8.0 wt% of Nb loading, followed by a line with a different slope. These results suggest the monolayer-growth mode of niobic acid deposited on SiO₂ surface up to 8.0 wt%. 8 wt% is corresponding to the full coverage of Nb(OC₂H₅)₅ on SiO₂ surface. The size of the bulky Nb(OC₂H₅)₅ is almost twice as large as that of [Nd₆O₂₋₈]. Consequently, half of SiO₂ surface was uncovered with niobic acid species. The proposed structure from 0 to 8.0 wt% was shown in Fig. 2. Comparing to the structure of one atomic layer Nb oxide catalyst, one atomic layer Nb acid has a longer Nb-O-Nb linkage to which the high activity of esterification can be assigned.

<table>
<thead>
<tr>
<th>Loading/wt%</th>
<th>Bond Distance / nm</th>
<th>Coordination Number</th>
<th>Nb-O</th>
<th>Nb-0</th>
<th>Nb-Nb</th>
<th>Nb-Nb</th>
<th>Nb-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.191</td>
<td>0.336</td>
<td>0.392</td>
<td>0.327</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.194</td>
<td>0.335</td>
<td>0.339</td>
<td>0.328</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>0.190</td>
<td>0.336</td>
<td>0.390</td>
<td>0.328</td>
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</tr>
<tr>
<td>7.0</td>
<td>0.193</td>
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<td>0.193</td>
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<tr>
<td>15</td>
<td>0.194</td>
<td>0.333</td>
<td>0.394</td>
<td>0.329</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 1. Curve-Fitting analysis for the EXAFS data of Nb₂O₅/SiO₂

Fig. 1. The number of Nb-Si bonds contained in 1 g of the SiO₂-attached niobic acid catalyst as a function of function of the Nb loading.

Fig. 2. A proposed structure for the SiO₂-attached niobic acid catalyst.
AN EXAFS STUDY ON THE STRUCTURES OF V₂O₅/TiO₂ AND V-Ti COMPOSITE OXIDES PREPARED BY A CVD METHOD

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There have been some studies on the structures of V₂O₅ supported on TiO₂(V₂O₅/TiO₂) and supported V₂O₅-TiO₂ composite oxides which are active for selective oxidation of aromatic hydrocarbons. Catalytic active species of supported vanadium oxide catalysts are influenced structurally and electronically by supports and composite components. EXAFS/XANES experiments were carried out to elucidate the structures for highly dispersed V₂O₅/TiO₂ and V₂O₅-TiO₂ composites prepared by a CVD method.

Experimental

V₂O₅/TiO₂(CVD) was prepared by the following method: vaporized VO(OPr)₃ was reacted with OH groups of Ti(OPr)₄ at 423K which had been evacuated at 673 K for 2 h and then isopropoxy-vanadyl-TiO₂ was evacuated for 1 h followed by heating in O₂ at 673 K for 2 h. V₂O₅/TiO₂(IMP) was prepared by impregnating TiO₂ in an oxalic solution containing vanadyl species followed by drying at 383K and heating in air at 773K for 3h. Supported V₂O₅-TiO₂ composite oxides were prepared by a successive CVD of Ti(OPr)₄ and VO(OPr)₃ (or vice versa) onto supports(SiO₂ and Al₂O₃) at 423K and room temperature, respectively, followed by heating in O₂ at 673K. X-ray absorption experiments was run at room temperature at the BL-7C by using SSD and fluorescence detectors.

Results and discussion

An EXAFS analysis for V₂O₅ supported on TiO₂ is very difficult since absorption of abundant Ti species overlaps that of low amount of V species. SSD and fluorescence detectors were used to overcome it. Their EXAFS spectra, especially those by SSD are too noisy to be analyzed.

The V K-edge XANES spectrum of V₂O₅/TiO₂(CVD) is different from those of SiO₂- and Al₂O₃-supported V₂O₅ which are analyzed to be tetrahedral,1) and V₂O₅ bulk which is distorted square pyramidal. (Fig. 1)2) The spectrum resembles to those of low loaded V₂O₅/TiO₂(IMP). The XANES spectrum of 10% V₂O₅/TiO₂(IMP) is similar to that of V₂O₅ indicating that multi-layers of V₂O₅ are formed at more than 5% loading. The XANES spectra of V₂O₅/TiO₂(CVD) and low-loaded V₂O₅/TiO₂(IMP) are somewhat similar to that of octahedral decavanadate.

The V K-edge XANES spectra of V₂O₅-TiO₂ composite oxides prepared by a CVD method have been reported elsewhere in this Report.3)

1) S. Yoshida et al., Catalysis Today, in press.
3) H. Kanai et al., Photon Factory Activity Report, #9(91-002).

![Fig. 1 V K-edge XANES spectra of supported V₂O₅ and reference compounds.
A: Fluorescence, B: SSD, C: Authentic sample](image)
Mechanical alloying (MA) has been successfully employed in recent years as a method to synthesize amorphous alloy. While many metal-metal systems have been studied in this regard, only a few attempts have been made to amorphize metal-metalloid alloys by MA. However, recently an Fe$_x$C amorphous alloy was prepared by MA[1]. The main purpose of this work is to observe the structural change during the solid state amorphization reaction of an Fe-C alloy by EXAFS measurement, and to discuss the mechanism of amorphization.

Fe$_x$C$_y$ alloy powder was prepared in a laboratory ball mill using stainless steel vials with hardened stainless steel balls. The starting material was a mixture of iron powder and carbon powder.

EXAFS measurements were carried out at the beam-line 7C of Photon Factory in KEK. Energy scanning was carried out around the iron K-edge (7.1112 keV).

X-ray diffraction patterns of Fe$_x$C$_y$, alloy as a function of milling time show that the structure is mostly amorphous but with a small amount of α-Fe remaining at 700 h milling. Figure 1 shows the radial distribution functions around an iron atom provided by the Fourier transform of the EXAFS spectra (4.1-14.1 Å$^{-1}$) as a function of MA time. It clearly shows the disintegration process of the crystalline structure. The arrows indicate the first, second, third and fourth nearest neighbors around an iron atom in the crystalline phase. The height of the peaks corresponding to the long range order of the crystalline phase are reduced with MA time and almost vanish at 700 h. Only the main peak, corresponding to the short range order of the amorphous phase, remained. The small peak (1.59 Å), which indicates the solution of carbon in crystalline iron, appeared and grew with MA time. As the amount of carbon solution in crystalline iron increased, the long range order of crystalline iron disintegrated. To determine the structural parameters, curve-fitting analysis for the spectra (1-3 Å) was performed using a theoretical amplitude and phase function. The interatomic distances (Fe-C, Fe-Fe:1st, Fe-Fe:2nd) of the Fe$_x$C$_y$ alloy by MA became closer to the values of the short range order in Fe$_x$C cementite with MA time, and they became almost the same values as those for cementite at 700 h. The amorphous Fe$_x$C$_y$ alloy prepared by MA has a short range order analogous to the Fe$_x$C cementite.

EXAFS study of zeolite-encaged cobalt clusters
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Pohang 790-600, Korea

*Photon Factory, KEK, Oho 1-1, Tsukuba-shi, Ibaraki-ken 305, Japan

It is known that iron or cobalt-exchanged zeolite is hardly reduced to form zeolite-encaged metal clusters by the conventional reduction with hydrogen gas [1]. We employed a simple alkali-injection method to reduce ion-exchanged cobalt ion in zeolite, and succeeded in obtaining highly reduced cobalt clusters encaged inside zeolite. In this report, the successful formation of cobalt clusters was confirmed by EXAFS.

Fourier-transformed EXAFS spectra for ion-exchanged CoY(A) and NaOH-treated CoY-NaOH(B) are shown in Fig. 1. CoY shows Co-Co and Co-O scattering peaks which correspond to oxidized CoO while CoY-NaOH shows that a large portion of Co-Co scattering peaks which correspond to reduced cobalt. As shown in table 1, the alkali-treatment yielded high degree of reduction compared with that of CoY.

These alkali-treated highly reduced CoY-NaOH catalysts showed higher yield of 1-olefins and suppressed formation of branched hydrocarbons [2]. It was assumed that the reduced cobalt of CoY-NaOH is within cluster size since either X-ray diffraction or TEM measurement could not detect cobalt particles located on zeolite. Table 1 shows peak heights of 3 successive EXAFS peaks for samples oxidized at 400°C. The peaks were located at radial distance of about 1.4, 2.4 and 3.0 Å respectively. The decreasing tendency of peak height with radial distance is more prominent in the NaOH-treated CoY, when compared with bulk Co$_3$O$_4$. This confirms that particle size of cobalt in CoY-NaOH is very small so that the number at atom decreases abruptly with distance in the shell.


Table 1. Ratios of the peak heights of Co$_3$O$_4$ EXAFS peaks.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%R*</th>
<th>peak1</th>
<th>peak2</th>
<th>peak3</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk Co$_3$O$_4$</td>
<td>tr</td>
<td>1.000</td>
<td>1.260</td>
<td>0.897</td>
</tr>
<tr>
<td>5.6 CoY</td>
<td>75.4</td>
<td>1.000</td>
<td>1.143</td>
<td>0.807</td>
</tr>
<tr>
<td>8.5 CoY-NaOH</td>
<td>43.7</td>
<td>1.000</td>
<td>0.939</td>
<td>0.541</td>
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<tr>
<td>4.8 CoY-NaOH</td>
<td>74.0</td>
<td>1.000</td>
<td>0.735</td>
<td>0.545</td>
</tr>
</tbody>
</table>

* degree of reduction for the reduced sample.
Structural Studies on the Al2O3-Supported PtMo6O24 Heteropoly Acid Catalyst with Various Temperatures by Means of EXAFS

Yousuke NAGASAWA, Kiyotaka ASAKURA and Yasuhiro IWASAWA
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

INTRODUCTION
Using the AndersOn-type heteropoly anion, which possesses unique structure, as a precursor of catalysts will make well-defined bimetallic sites. We already investigated [PtMo6O24]8- heteropolyanion catalyst supported on SiO2 and Al2O3, and found that the catalysts reduced by hydrogen at 773 K formed the specific site with platinum particle surrounded by molybdenum, which showed much higher activity on ethene hydrogenation than conventional Pt-Mo coimpregnation catalysts. However, the decomposition of the unique structure took place by reducing at 773 K with hydrogen. In this study, we performed oxidation pretreatment with alumina supported [PtMo6O24]8- catalyst to take advantage of the specific structure of the heteropoly acid, and investigated the structures after the oxidation at various temperatures.

EXPERIMENTAL SECTION
PtMo6O24 / Al2O3 catalyst was prepared from aqueous solution of (NH4)4[PtMo6O24] and Al2O3 (Allon-C) by conventional impregnation method: the catalyst contained 1 wt% of platinum. The Pt LIII-edge and Mo K-edge EXAFS spectra at room temperature were collected at BL-7C of Photon Factory. The EXAFS analysis was performed by a curve-fitting method. Pt foil and (NH4)4[PtMo6O24] were used as model compounds for Pt-Pt and Pt-Mo, respectively. Prior to the measurements, the catalyst was pretreated under 100 Torr of O2 for an hour at the denoted temperatures.

RESULTS AND DISCUSSION
Fig. 1 shows the Fourier-transform of k3-weighted EXAFS spectra: a: precursor, b: after impregnation, c: oxidized at 423 K, d: oxidized at 773 K. Each spectrum except fig.1d possessed the strong peak around 0.17 nm corresponding to Pt-O. Additional weak broad peak was observed at 0.29 nm attributed to Pt-Mo as shown in fig. 1b. The peak at 0.28 nm shown in fig.1d was assigned to Pt-Pt bond. The curve-fitting results for Pt-LIII edge were summarized on table 1. Low coordination number of Pt-Mo in b suggests that Mo was still around Pt, though the structure of heteropoly acid was extremely deformed after impregnation. When it was treated at 423 K, the peak at 0.29 nm disappeared, indicating the distortion of the heteropolyacid framework, and treated at 773 K, Pt was aggregated to Pt metal particle as shown in fig.1c and 1d. Prepared from the precursor, we found that the heteropoly acid structure was distorted after impregnation, and was decomposed after oxidizing at 423 K.

Table 1. Results of curve fitting for the PtMo catalysts.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>r/nm</th>
<th>ΔE/EV</th>
<th>σ/rm</th>
<th>R/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a*</td>
<td>Pt-O</td>
<td>6.0</td>
<td>0.200</td>
<td>0</td>
<td>0.0060</td>
</tr>
<tr>
<td></td>
<td>Pt-Mo</td>
<td>6.0</td>
<td>0.334</td>
<td>0</td>
<td>0.0060</td>
</tr>
<tr>
<td>b</td>
<td>Pt-O</td>
<td>6.9</td>
<td>0.200</td>
<td>2.99</td>
<td>0.00707</td>
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<td>3.4</td>
<td>0.332</td>
<td>-2.47</td>
<td>0.00654</td>
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<tr>
<td>c</td>
<td>Pt-O</td>
<td>9.0</td>
<td>0.205</td>
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<td>Pt-Pt</td>
<td>10.3</td>
<td>0.276</td>
<td>-0.395</td>
<td>0.00647</td>
</tr>
</tbody>
</table>

*: reference compound

![Fig. 1](image-url)
EXAFS study on the structure of Pd-Pt bimetallic cluster supported on SiO₂

Y. Yamazaki¹, K. Asakura¹, K. Kuroda¹, M. Harada², and N. Toshima³.

[¹] Department of Chemistry, Faculty of Science, and [²] Department of Industrial Chemistry, Faculty of Engineering, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

Introduction

In order to understand the catalyses of bimetallic clusters, it is necessary to obtain their structures. EXAFS spectroscopy is thought to be the established method. But in EXAFS analysis of the structure of bimetallic catalysts, it still remains the serious problems. The first problem is that we cannot obtain suitable amplitude and phase functions for the different metal pair in the absence of reference material. The second is that we have to determine the many structural parameters simultaneously which were strongly correlated with each other. In this studies we estimated the errors of the structural parameters and determined the structure of the PtPd small bimetallic clusters.

Experimental

PtPd bimetallic clusters were prepared by alcohol reduction method and stabilized by the polymer protection. They were deposited on the SiO₂ surface from the PtPd alcohol solution. After being dried under vacuum at room temperature, they were oxidized at 473 K for 1 hour, reduced at 473 K for 1 hour and evacuated at the same temperature for 30 min. The atomic ratio of Pt and Pd was 1:4. Then the sample was transferred to the air-tight EXAFS cell without exposure to air. The EXAFS measurements were carried out at BL-7C and BL-10B. The measurement temperature was low temperature.

Results and Discussion

In order to check the validity of the backscattering amplitude and phase shift functions used here, we measured EXAFS spectra of PtPd=1:1 foil which has a well-defined fcc structure. The curve fitting results of the EXAFS oscillations of Pt L₃-edge and Pd K-edge of PtPd 1:1 foil based on the several backscattering amplitude and phase shift functions showed that the interatomic distances were not so different from the different backscattering amplitude and phase shift functions. But the coordination numbers estimated from the McKale's theoretical parameters [¹] were smaller than those expected from the PtPd=1:1 sample structure. We can get more accurate coordination numbers when the backscattering amplitude and phase shift functions were empirically derived from the PtPd foils whose compositions were 1:9 and 9:1, respectively.

Thus hereinafter we use the empirically-derived backscattering amplitude and phase shift functions. Table 1 shows the curve fitting results of PtPd/SiO₂. The errors for coordination numbers and Debye-Waller factors were estimated using the R-factor contour mapping as shown in Fig.1. We adopted coordination numbers and Debye-Waller factors which give the R factor √2 times as large as that of the local minimum. The results of the estimated coordination numbers indicated that the Pt and Pd were miscible. The PtPd cluster in alcohol solution is composed of Pt core and Pd outer shell [²]. This difference between PtPd on SiO₂ and PtPd in solution might arise from the oxidation and reduction treatment at 573 K after the deposition.

Table 1. Curve fitting results of Pd₄Pt₁ cluster/SiO₂ using amplitude and phase functions empirically derived from pure metal foil or 10% composition foil.

<table>
<thead>
<tr>
<th>Coord. No.</th>
<th>distance/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Pt</td>
<td>2.1 ± 1.1</td>
</tr>
<tr>
<td>Pd-Pd</td>
<td>7.0 ± 1.3</td>
</tr>
<tr>
<td>Pt-Pd</td>
<td>6.8 ± 1.8</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>3.4 ± 1.3</td>
</tr>
</tbody>
</table>

Fig.1. R-factor contour maps of Pd₄Pt₁ cluster for the correlations between N₁₄-Pd and N₁₄-Pt. Local minimum (x), √2 times as large as the local minimum value (solid line).

EXAFS STUDIES ON THE CLUSTER-DERIVED Co/SiO2 CATALYST FOR VAPOR PHASE HYDROFORMYLATION OF ETHENE

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Introduction

Vapor phase hydroformylation of olefins has been attracted much attention of researchers to develop a new alternative process to the present homogeneous hydroformylation systems. It is also a good model reaction for a CO insertion step in oxygenates formation in syngas reaction. Recently, we found that Co/SiO2 catalyst prepared from Co2(CO)g (Co(CO)/SiO2) is very active for vapor phase hydroformylation of ethene 1). Its hydroformylation activity was higher than that of Rh/SiO2. On the other hand, the conventional Co/SiO2 derived from cobalt(II) nitrate or chloride were almost inactive for hydroformylation. In this report, we will describe a structure of surface Co species of this Co2(CO)g derived cobalt catalyst.

Experimental

Catalysts were prepared by an impregnation method using silica gel (Davison grade 57) support as described previously 1). EXAFS of catalysts was measured at the BL-7C of the Photon Factory of KEK using an in situ EXAFS glass cell with Capton windows. The Co(CO)/SiO2 catalyst was prepared in situ in this cell under a nitrogen atmosphere. All catalysts were treated with hydrogen at 673 K for 3 h in the cell just before the measurements. EXAFS of Co2(CO)g powder was measured using a nitrogen sealed plastic bag.

Results and discussion

Figure 1 shows the k^2-weighted Fourier transforms of Co K-edge EXAFS oscillation of Co foil, Co2(CO)g powder, and cobalt catalysts. The peaks at 0.255 and 0.210 nm in the Fourier transform of the absorption spectrum of Co2(CO)g powder (a) are accepted as Co-Co and Co-C bondings, respectively (phase shift uncorrected). The peak at 0.142 nm is accepted as a Co-O bonding of the partially oxidized Co2(CO)g during the experiment.

When dark orange Co2(CO)g was supported on SiO2, it turned to dark brown. The Co species of this supported Co2(CO)g can be assigned to Co4(CO)12 like species by the Fourier transform of EXAFS (c) as reported by Iwasawa and Yamada 2).

After being treated at 673 K in hydrogen, the catalyst became black. The Fourier transform of EXAFS exhibits two peaks at 0.214 and 0.159 nm. One at 0.214 nm is attributed to Co-Co bondings of cobalt metal (d). The amplitude of this peak, which is much lower than that of Co-Co bondings of Co foil (b), gave 2.6 of a coordination number of cobalt atom of the metal particle. The size of this cobalt metal particle was estimated to about 1 nm in diameter. The peak at 0.159 nm is assigned to a Co-O bonding of the partially oxidized Co2(CO)g during the experiment.

By exposing this catalyst to air, the Co(CO)/SiO2 catalyst turned to blue. The peak of Co-Co bonding at 0.214 nm was quickly disappeared and the Co-O bonding at 0.159 nm became a main peak (e). This oxidized Co(CO)/SiO2 was inactive for hydroformylation of ethene.

The conventional Co/SiO2 catalysts derived from cobalt(II) nitrate and chloride gave similar EXAFS spectra with that of Co foil. The peak amplitudes and the distance of particles were much bigger than that of Co/SiO2 derived from Co2(CO)g. The size of Co metal particles of these conventional catalysts were estimated about 10 to 20 nm in diameter by an XRD line broadening technique.

These results indicate that Co2(CO)g supported on silica gel provides highly dispersed cobalt particles on Co/SiO2 and this fine cobalt metal particle is the active site for hydroformylation of ethene. Hydrogenation of ethene proceeds predominantly on the big cobalt metal particle.

References


Fig. 1 Fourier transforms of k^2(k) of Co K-edge EXAFS (a) Co2(CO)g powder, (b) Co foil, (c) Co(CO)/SiO2 just after impregnated, (d) Co(CO)/SiO2 after treated in H2 at 673 K, and (e) Co(CO)/SiO2 after exposed to air. Catalyst; metal loading 5 wt%.
STRUCTURAL ANALYSIS OF ACTIVE PHASE OF V-P POLYOXO COMPOUNDS

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INTRODUCTION

As for V-P oxides (P/V=1), crystalline phases such as α- and β-VOPO₄, and (VO)₂P₂O₇ are known. Among them, single crystalline phase of vanadyl pyrophosphate, (VO)₂P₂O₇, in which the oxidation state of V is +4, is selective for the production of maleic anhydride from n-butane.¹⁻³ Pretreatments of (VO)₂P₂O₇ affected strongly the microstruture of particles and the catalytic performance.

In the present study, the local bonding around the vanadium centers of these (VO)₂P₂O₇ and its change upon the heat treatment in the presence of O₂ and washing with H₂O (O₂-wash) were examined using EXAFS.

EXPERIMENTAL

Three kinds of (VO)₂P₂O₇ (C-1, C-3 and amorphous) were used. C-1 was obtained from H₃PO₄, NH₄OH·HCl, and V₂O₅.¹ C-3 was prepared in organic solvent.³ The bulk structure of these samples were confirmed by XRD and IR to be VOPO₄ and (VO)₂P₂O₇, respectively. SEM showed that C-1 has plate-like structure (thickness: 39nm), and C-3 has rose-like one (thickness: 8nm). After the treatment in a N₂ flow at 500°C, this will be denoted as e.g., C-1-N₂. Then it was oxidized with O₂ at 500°C (2 h) and was washed with water. This is denoted as e.g., C-1-O₂-wash.

EXAFS and XANES were measured at the Photon Factory (BL-7C) at the room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the schematic structure of (VO)₂P₂O₇. In (VO)₂P₂O₇, pairs of edge-sharing VO₅ linked to pyrophosphate group, having distance of 1.57-1.73, 1.92-2.09, and 2.17-2.37 A for V=O, V-O, and V-P, respectively. The distances of V-V were determined to be 3.18-3.20 and 3.86 A.⁴ In the case of P-VOPO₄, VO₆ octahedra is surrounded by VO₄ tetrahedra. The bond lengths of V=O and short V-O are 1.57 and 1.85-1.89 A, respectively.⁵

Figure 2 shows the Fourier transforms of K-edge EXAFS data of (VO)₂P₂O₇ (C-1, C-3 and amorphous). Besides a broad peak around 1.88 A (V=O and V-O), two peaks appeared at 3.24 and 3.90 A. The former is assigned to V-V or V-P bond and the latter V-O bond.

As shown in Figs. 2a and 2b, O₂-wash of C-1 and C-3 affected the spectra. For C-3-N₂, small peak due to V-V (V-P) (>3 A) appeared, showing the low crystallinity. It should be noted that the intensity of the V-V peak (6.8 Å) increased after O₂-wash treatment. This is well consistent with the increase in the crystallinity (XRD). In the case of amorphous phase, the intensity of the V-V peak was small, which supports the changes in the Fourier transform of (VO)₂P₂O₇ upon the O₂-wash. The catalytic performance was enhanced appreciably by the O₂-wash. Therefore, the differences in the local bonding of V between the crystalline V-P oxides having different catalytic performance were confirmed by EXAFS.

Figure 1 Coordination polyhedra around V in the crystal structure of (VO)₂P₂O₇.

Figure 2 Fourier transforms of K-edge EXAFS of (a) C-1, (b) C-3, (c) Amorphous. --- O₂-wash, --- N₂

EXAFS studies of Ca catalyst for carbon gasification
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Introduction
Calcium compounds are very useful catalysts for the gasification of coal and carbon. In the present study, XAFS spectra were obtained with calcium-carbon samples containing different metal contents. The objective is to analyze the evolution of the local structure and the calcium dispersion in samples which were submitted to heat treatments at different temperatures under an inert atmosphere.

Experimental
A char from phenolformaldehyde polymer resin has been oxidized with HNO₃. Calcium has been introduced by ion-exchange with calcium acetate solution (A-2.9 wt%). Impregnation has been used to obtain other calcium contents (B-9.4 wt%). The Ca-loaded carbon were devolatilized in N₂ at atmospheric pressure in a small fluidized bed reactor. EXAFS and XANES spectra at Ca K-edge were recorded in a transmission mode on a beam line BL-7C at KEK-PF at room temperature using a Si(111) double crystal monochrometer. Mirror was used to remove higher harmonics.

Results and Discussion
Figure 1 and 2 show the XAFS spectra (XANES and FT-EXAFS) of (A-2.9) and (B-9.4) samples after heat treatment, respectively. XANES spectrum of dried A-2.9 sample (Fig. 1a) presents a broad main peak without any shoulder. The presence of a small pre-edge peak (I) in XANES spectrum (Fig. 1b,c) indicates that coordination of oxygen atoms around calcium atom is somewhat distorted from an ideal octahedral symmetry. FT-EXAFS oscillations of samples heated at -550°C (Fig. 1A,B,C) exhibit only one Ca-O peak at ~2.0 Å and no Ca-Ca peak is present, indicating that calcium is still linked to carboxylic groups. FT-EXAFS spectrum of samples heated at 950°C (Fig. 1D) presents a Ca-O peak ~2.0 Å beside a very weak Ca-Ca peak, indicating that most of the calcium species are highly dispersed and/or forming amorphous small cluster with spectra characteristics similar to those of CaO. In the case of B-9.4, XAFS spectra obtained after a treatment at 550°C (Fig. 2c,C) exhibits characteristics of CaCO₃. A heat treatment at 950°C produces CaCO₃ decomposition to yield CaO (Fig. 2d,D).

In conclusions, the evolution of the local structure and the calcium dispersion in samples depends on the calcium contents. The calcium contents below and above the saturation of carboxylic groups on the carbon bring about the different transformation of calcium compounds with heating.
The coprecipitates were filtered off, washed with diluted HNO₃, and shapes of the Zn K-XANES spectra of the Bi-Zn coprecipitate are standard ZnS, which is known to have two forms of crystal structures: i.e. wurtzite and sphalerite types. However, their differences in the shapes of the XANES spectra are too slight to be distinguished by the spectra (Fig. 1).

Coprecipitation, which sometimes occurs in the precipitation reactions, is defined as the contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation. Although the distinction between the various types of coprecipitation is not sharp, they may be classified according to the following mechanisms: mixed crystal formation, surface absorption, mechanical occlusion and inclusion.

It is known that zinc sulfide does not precipitate under the acid conditions. However, coprecipitation of zinc with metal sulfides, whose solubility products are small enough to precipitate from acidic solution like mercury sulfide, occurs even under acid conditions. The purpose of this work is to elucidate the details of coprecipitation reaction of Zn under acid conditions from structural point of view by means of EXAFS/XANES technique.

2. Experimental

Coprecipitates of Zn with sulfides of Hg, Cd, and Bi were prepared as follows. First, Zn(NO₃)₂ solution was mixed with each solution of Hg(NO₃)₂, Cd(NO₃)₂, Bi(NO₃)₃ in the ratio of 1 : 1, and the mixed solutions were acidified with HNO₃. Next, Na₂S solution was slowly added to each mixed solution, to form coprecipitates. The coprecipitates were filtered off, washed with diluted HNO₃, and dried at room temperature. In addition, precipitate of zinc sulfide was prepared separately for comparison.

The Zn K-edge spectra were measured in a fluorescence transmission mode at BL-7C using a Si(311) channel-cut crystal monochromator. On the other hand, Hg L₃-edge, Cd K-edge, and Bi L₃-edge spectra were measured in a transmission mode at BL-10B using a Si(311) channel-cut crystal monochromator.

3. Results and Discussion

The Zn K-XANES spectra of a series of standards of Zn and pure ZnS precipitate are shown in Fig. 1, and those of coprecipitates in Fig. 2. The shapes of the spectra of Hg-Zn and Cd-Zn coprecipitates have a strong resemblance to that of crystalline standard ZnS, which is known to have two forms of crystal structures: i.e. wurtzite and sphalerite types. However, their differences in the shapes of the XANES spectra are too slight to be distinguished by the spectra (Fig. 1).

In contrast, both positions of the absorption edge and the shapes of the Zn K-XANES spectra of the Bi-Zn coprecipitate are different from those of other coprecipitates, and appear to be similar to ZnSO₄. The chemical shift toward higher energy side is observed in the spectra of the Bi-Zn coprecipitate.

The positive shift in the energy of absorption edge can be understood conceptually to be due to an increase in the attractive potential of the nucleus core Coulomb interaction with all other electrons in the compound. For example, the position of absorption edge of ZnS is lower than that of ZnSO₄, in which ligand atom around Zn is oxygen.

The strong peak, so-called white line, has been assigned as dipole-allowed transition 1s→4p, and then the chemical shifts in the spectra are due to a combination of valence, electronegativity of the bonding ligands, coordination number, and other structural features. Since oxygens is more electronegative than sulfur, ligand electronegativity effects can be seen in the case of ZnS and ZnSO₄. Consequently, ligand atom around Zn in the Bi-Zn coprecipitate may not to be sulfur but oxygen.

It is considered that the coordination structures around Zn in the coprecipitates of sulfides are affected by the structures of the crystals. HgS (metacinnabar) and sphalerite, CdS (greenockite) and wurtzite are isomorphous, but Bi₂S₃ and ZnS of both forms are not. As a result, in the case of coprecipitates of Zn with sulfides of Hg and Cd, that the two coprecipitated phases may form a solid solution. In practice, the ligand atom around Zn is sulfur. On the other hand, in the case of the Bi-Zn coprecipitate, Zn has little possibility of forming a solid solution with Bi₂S₃. Therefore, the structure of Zn in the coprecipitate is different from that of ZnS of both forms.

References:

Fig. 1. The Zn K-XANES spectra of ZnS standards and pure ZnS precipitate

Fig. 2. The Zn K-XANES spectra of coprecipitate
MONOCHROMATIC LAUE DIFFRACTION OF Cs MONOLAYER ON GRAPHITE USING IMAGING PLATE TECHNIQUE

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Introduction

The cesium monolayer on graphite has some different two-dimensional (2D) superstructures: \( \sqrt{7} \times \sqrt{7} \), \( 2 \times 2 \) and \( \sqrt{3} \times \sqrt{3} \) depending on coverage. \(^1\) These systems can be regarded as two-dimensional 7-, 4- and 3-state Potts model, respectively. In two-dimensional q-state Potts model the melting transition is predicted as first order for \( q > 4 \) and continuous one for \( q < 4 \). \(^2\) Our aim is to verify this theory, we have studied the critical behavior of melting transition in Cs monolayer by using the X-ray monochromatic Laue method.

Experimental

X-ray diffraction measurements were carried out by using synchrotron radiation at Photon Factory (BL-7), KEK. The X-ray radiation were monochromatized at \( \lambda = 1.004 \) Å by Si(111) double monochrometer. The reciprocal lattice of two-dimensional system is like a rod perpendicular to the plane. So, the Ewalt sphere can cross the rod. The imaging plate was used for the detection.

A single crystal Kish graphite (about 2mm x 2mm) was sealed into glass tube with cesium metal. After setting the glass tube in a cryostat, cesium metal was adsorbed on the graphite at \( T = 330 \) K and then the temperature of the sample was decreased down to \( T = 95 \) K.

Results and Discussion

Figure 1 shows a monochromatic Laue photograph of Cs monolayer at room temperature. The diffraction spots (11) and (21) of \( \sqrt{7} \times \sqrt{7} \) structure were observed. These appear in two equivalent sets of spots, which come from two different kinds of domains shown in Fig.2: the angle between the two domains is about 21.8°. The spot position does not change at \( 95 \) K \( \geq T \geq 329 \) K. Namely, the \( \sqrt{7} \times \sqrt{7} \) structure does not melt up to \( T = 329 \) K. This melting temperature is very high compared with that of high stage Cs-graphite intercalation compound (\( T_m = 228 \) K). \(^3\) This may attributed to the strong interaction with graphite substrate.

In this experiment we have observed successfully the 2D structure of Cs monolayer by using the monochromatic Laue method and an imaging plate.

Acknowledgement

We thank Prof. Amamiya and Mr. Fujihisa for teaching us to use an imaging plate.

References


Figure 1
A monochromatic Laue photograph of Cs monolayer on single crystal Kish graphite. Closed circles are observed spots of \( \sqrt{7} \times \sqrt{7} \) structure and open spots are not observed spots in the present experiment.

Figure 2
Two kinds of domains (O and X) for the \( \sqrt{7} \times \sqrt{7} \) structure is superposed.
Polarized Total Reflection Fluorescence EXAFS spectroscopy is powerful technique for the determination of surface structure. This technique enables us to get an information of angularly selected structure information.

In order to acquire the information about the surface reaction mechanism, it is necessary to study the surface structures under in-situ conditions (pressure 0-10 atom, temperature 100-873 K).

The design of an apparatus for in-situ Polarized Total Reflection Fluorescence EXAFS spectroscopy using synchrotron radiation is reported here. The in-situ cell for Polarized Total Reflection Fluorescence EXAFS is shown in Fig. 1. This cell is designed to satisfy the following necessities.

1. The cell is composed of two sections.
   For sample preparation, the cell is divided into two sections, one is for sample preparation and the other is for measurement of x-ray absorption under reaction conditions. Each section is pumped by rotary and diffusion pumps and is isolated by gate valve when the sample is prepared. The sample is transferred easily by the sample holder shown in Fig. 2.

2. X-ray spot is invariable as orientation is changed about all three axis transfer.
   Rotation about the x-ray is achieved by a cylinder which is mounted on two bearings with the rotation range being ca. 100 degree shown in Fig. 2.
   For Total Reflection EXAFS, accurate location of sample is of utmost importance. The total reflection condition for p polarization is achieved by movement of the rotation table under the cell, while for s polarization the total reflection condition is achieved by three jacks which allow 3 dimensional movement under the cell (Fig. 1). All tables and micro jacks are remotely controlled by computer.

3. Large solid angle
   It is important to obtain a large solid angle for fluorescence which detected by scintillation counters. The detection window is equipped with Be (diameter ca. 20 thickness 25 \( \mu \)m). Large solid angles are achieved by placing the detector in a close proximity to the sample.

4. In-situ conditions
   Heterogeneous catalysis is usually carried out high pressure and high temperature. We used of Be windows, diameter ca. 10 mm and thickness 25 \( \mu \)m for the entrance and exit of synchrotron beam and fluorescence exit port to measure EXAFS under high pressure. The measurement temperature can be varied from 100 K to 873 K using liquid Na and Ta heater.
ADSORBED STATE OF THE COPPER AND CALCIUM DIPIVALOYL METHANATES
[Cu(DPM)$_2$ AND Ca(DPM)$_2$] REACTED WITH HYDROXYLS ON OXIDE SURFACE

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Copper and Calcium dipivaloylmethanates (Cu(DPM)$_2$, Ca(DPM)$_2$), which are volatile β-diketonate complexes, are reacted selectively and stoichiometrically with surface hydroxyl groups (OH) on oxide surfaces. By infrared spectroscopy, both for Cu and Ca(DPM)$_2$, it was clarified that (1) the stoichiometric ratio of reacted complexes and OH is approximately 1:2, (2) the adsorbed species no longer have )>CH structure but )CH$_2$ structure, and (3) the structure around Cu does not change after adsorption.

The above model was supported as to the system Cu(DPM)$_2$ / SiO$_2$ by the curve fitting analysis of the Cu K-edge EXAFS spectra, which is comparing the bond length and the coordination number of Cu-0 (first coordinated atoms) and of Cu''''C (second coordinated atoms) between the model compounds (A) [Cu(DPM)$_2$] and the adsorbed Cu(DPM)$_2$ on SiO$_2$ (B)$^3$. It was found that bond length Cu-0 and also Cu''''C are identical between (A) and (B). In addition, the coordination numbers were identical as well. Therefore, it can be concluded that after the adsorption, Cu-0 bond length and the ring structure of the ligand remains unchanged.

Recently, we have measured the EXAFS spectra of the system Ca(DPM)$_2$ / SiO$_2$ and comparing it with the model Ca(DPM)$_2$ complex.

The samples were prepared as previously.$^{2,3}$ The EXAFS and XANES spectra were taken at BL-7C by transmission method for the model complex [Ca(DPM)$_2$] and by the fluorescence method for the Ca(DPM)$_2$/SiO$_2$.

Figure 1 shows the raw fluorescence spectrum for adsorbed Ca(DPM)$_2$ on SiO$_2$. Carefully alignment of two parallel quartz mirror can eliminate the effect of higher harmonics. The EXAFS oscillations are shown in Fig.2 (the model Ca(DPM)$_2$) and Fig.3 (Ca(DPM)$_2$/SiO$_2$). The curve fitting analysis of these spectra is now in progress.

References
XAFS STUDY ON ACTIVE INTERMEDIATES OF CYTOCHROME P-450 MODELS POSSESSING THIOLATE AXIAL LIGAND

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The elucidation of the role of axial thiolate ligand on the chemistry of cytochrome P-450 is an important subject on the study of heme enzymes and also metalloporphyrin chemistry [1]. We have already succeeded in the synthesis of an unique iron porphyrin coordinated by a thiolate anion (SR) which can keep its structure during catalytic oxidations. SR complex has high structural similarity to the active site of cytochrome P-450 [2]. Therefore the oxidized form of SR must be a good model of the active intermediate of P-450 that has never been observed in the native enzyme. The analysis of structure of the peroxo-iron form of SR complex in organic solution was examined with fluorescence XAFS method at low temperature in order to contribute to the clarification of the mechanism of cytochrome P-450 reactions.

The fluorescence Fe-K edge X-ray absorption measurements have been carried out at the Photon Factory BL-7C. 10 mg of KO2 and 5 ml of 3-mM SR in acetonitrile were mixed and sonicated for 3 min to start the reaction. The reaction mixture was then transferred to a polyethylene bag and freeze-dried rapidly with liquid nitrogen to stop the reaction at the transition state, followed by the measurements. Temperature of the sample was kept below 200 K during the measurements by using a dry-ice/methanol freezing mixture.

Figure 1 depicts the X-ray absorption spectra of 3-mM SR (a), the freeze-dried reaction-mixture of SR and KO2 (b), and the mixture of post-reaction which was obtained by leaving the mixture at room temperature (c). Intensity of the shoulder peak around 7110 eV of (a) is increased according to the stage of the reaction, indicating that the surroundings of the central Fe atom of SR have been changed. The energy position of pre-edge peak due to 1s-3d transition of (b) shifts by ~1 eV toward higher energy compared to those of (a) and (c). This suggests that valence of Fe atom at the transition state is higher than that (+3) of at pre- and post-reaction state.

EXAFS STUDY ON THE STRUCTURE OF HIGHLY ACTIVE COBALT SULFIDE CATALYSTS PREPARED FROM COBALT CARBONYL

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Introduction

Cobalt-molybdenum alumina catalysts have been widely employed for hydrotreating petroleum feed stocks. Recently, development of deep desulfurization catalysts is eagerly desired to protect environment, e.g. acid rain. In order to exploit highly active hydrotreating catalysts, we have investigated the preparations of highly dispersed cobalt and molybdenum sulfide catalysts. With molybdenum catalysts, it has been found that sulfidation of Mo(CO)$_5$ anchored on zeolite or Al$_2$O$_3$ provides molybdenum sulfide catalysts with higher dispersions (super-dispersed) than in conventional sulfided MoO$_3$/Al$_2$O$_3$ catalysts and that the structure of super-dispersed molybdenum sulfide species is described as amorphous MoS$_3$ or sulfido Mo-dimer complexes, since a direct Mo-Mo bonding is observed by EXAFS.

In the present study, we examine preparations of super-dispersed cobalt sulfide catalysts by using cobalt carbonyl. In addition, we try decoration of super-dispersed molybdenum sulfide species with cobalt using cobalt carbonyl to design highly active hydrotreating catalysts and to obtain some insights into the genesis of synergy in cobalt-molybdenum sulfide catalysts.

Experimental

Cobalt carbonyl Co$_2$(CO)$_8$ was adsorbed at r.t. from a gas phase on Al$_2$O$_3$ and SiO$_2$, which had been dehydrated at 673 K. The loading of cobalt was controlled by varying adsorption time. After evacuation at r.t., cobalt carbonyl/Al$_2$O$_3$ or SiO$_2$ was sulfided in an atmospheric stream of H$_2$S/H$_2$ (0.1) by increasing the temperature from r.t. to 673 K (6 K min$^{-1}$), followed by a further treatment at 673 K for 90 min.

Cobalt-molybdenum catalysts were prepared by adsorbing cobalt carbonyl on sulfided Mo(CO)$_5$/Al$_2$O$_3$ or sulfided MoO$_3$/Al$_2$O$_3$. The catalysts were sulfided again as stated above.

The EXAFS studies of Co-K and Mo-K edges for the catalysts were measured at r.t. by using BL-7C and 10B instruments, respectively, at Photon Factory in KEK. The spectra were obtained without exposure to air by using an in situ cell with Kapton windows.

Results and Discussion

Fourier transforms (FT) of Co-K edge for Co$_3$S$_7$ and sulfided Co-carbonyl/Al$_2$O$_3$ (13.7 wt % Co) are compared in Fig.1. It is apparent that with the Co-sulfide catalyst, a relative peak intensity due to a Co-Co bond at 0.2 nm (not corrected for the phase shift) is considerably weak compared to that for Co$_3$S$_7$ and that no Co-Co peak is observed at 0.3 nm. A similar FT was obtained for a Co-sulfide/SiO$_2$ catalyst prepared from Co-carbonyl. These EXAFS results suggest that highly dispersed cobalt sulfide is produced on these supports by using Co-carbonyl adsorption. Further EXAFS works and precise analyses are required for detailed description of the structure of cobalt sulfide and for comparison with cobalt sulfide catalysts prepared by conventional impregnation.

Figure 2 shows FTs of Mo-K edge for cobalt-molybdenum catalysts prepared by the carbonyl adsorption method. It is evident that the Mo-Mo direct bond (0.277 nm) in super-dispersed molybdenum sulfide (a) is cleaved, forming a microcrystalline MoS$_2$-like structure. The transformation of Mo-sulfide structure may suggest direct interactions between cobalt and molybdenum. The suggestion is consistent with the observation of catalytic synergy in hydrodesulfurization of thiophene over the present catalyst system.

References


Fig.1 FTs of Co-K edge for a) Co$_3$S$_7$ and b) sulfided Co-carbonyl/Al$_2$O$_3$.

Fig.2 FTs of Mo-K edge for a) sulfided Mo(CO)$_5$/Al$_2$O$_3$ and b) catalyst (a) modified by cobalt.
EXAFS STUDIES ON LOCAL STRUCTURE OF HYDROGENATED AMORPHOUS LaNi$_5$$_0$ FILMS

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Introduction

An Amorphous LaNi$_5$$_0$ film is a promising material for hydrogen separation membranes and negative electrodes on batteries, because the film exhibits good resistance to hydrogen embrittlement. The difference of characteristics between the amorphous and crystalline LaNi$_5$$_0$, especially as for the structure, has not been clarified sufficiently. We have studied on the local structure of the amorphous LaNi$_5$$_0$ film by means of EXAFS. In this report, the change in the local geometry around metal atoms due to absorption of hydrogen in LaNi$_5$$_0$ amorphous films in contrast to crystalline samples is investigated.

Experimental

The amorphous and 80% crystallinity LaNi$_5$$_0$ films were prepared using sputtering. The LaNi$_5$$_0$ crystalline powder and pure Ni foil were used as reference materials. The detailed procedure of preparation and characterization of these LaNi$_5$$_0$ samples were described in a previous paper$. The hydrogenation of the samples were performed in the stainless steel cell with X-ray transparent polyimide membrane windows.

The measurement of XAS was performed by using the EXAFS facilities of BL-7C. EXAFS spectra were collected at the Ni K- and La L$_{III}$-edges. The total thickness of the LaNi$_5$$_0$ films used for the X-ray absorption measurements were about 35 and 20 μm for the La and Ni edges respectively. The XAS data were obtained in vacuo and at a hydrogen pressure of 8.0×10$^{-5}$ Pa. The EXAFS data were analyzed with a "KABO" program$^2$.

Results and Discussion

Fourier transforms of EXAFS related to before and after hydrogenated amorphous and crystalline LaNi$_5$$_0$ samples are shown in Fig.1. No remarkable change in profiles was observed between before and after hydrogenated samples for both amorphous and crystalline samples, indicating that the local environment of La and Ni atoms was not strongly influenced by the absorption of hydrogen.

Table 1 gives the interatomic distances of Ni-Ni and La-Ni pairs. The lengthening of interatomic distance which was caused by hydrogenation was smaller for the amorphous film than for the crystalline film and bulk. This appears to suggest that the hydrogen content is smaller in the amorphous film than in the crystalline samples.

References


Fig. 1 Ni K- and La L$_{III}$- edge Fourier transforms of EXAFS in the 80% crystallinity and the amorphous sputtered LaNi$_5$$_0$ films.

--- before hydrogenation

| Central Sub- | Before | After hydrogenation |
| atom | shell | | |
| | | | |
| | | | |
| Crystalline bulk | | | |
| Ni | 2.45±0.01 | 2.49±0.01 | |
| Ni | 2.51±0.01 | 2.54±0.01 | |
| La | 2.89±0.01 | 2.93±0.01 | |
| 80% crystallinity sputtered film | | | |
| Ni | 2.46±0.01 | 2.49±0.01 | |
| Ni | 2.56±0.01 | 2.61±0.01 | |
| La | 2.90±0.01 | 2.94±0.01 | |
| Amorphous sputtered film | | | |
| Ni | 2.46±0.01 | 2.47±0.01 | |
| Ni | 2.57±0.01 | 2.61±0.01 | |
| La | 2.92±0.08 | 2.95±0.08 | |

Table 1. Interatomic distances for LaNi$_5$$_0$ before and after hydrogenation.
EXPERIMENTAL DETERMINATION OF THE DISPLACEMENT CORRELATION FUNCTIONS
IN THE TETRAHEDRALLY COORDINATED BINARY CRYSTALS

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Toshihiro MORIGA(5) and Kichiro KOTO(6).

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6) Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770.

Introduction

The Debye-Waller factor determined by EXAFS for the first-shell is sensitive to short-range correlations of the atomic motion; the mean-square relative displacement (MSRD) of the backscatterer atoms with respect to the absorber atom is determined by EXAFS. The mean-square displacement (MSD) of each atom from crystallographically equivalent position is determined by diffraction methods. The MSRD contains the contribution from the MSD of both absorber and backscatterer atoms and the displacement correlation function (DCF)\. In this study, the thermal behaviour of atoms in binary crystals of AgI has been investigated as a function of temperature by the EXAFS and diffraction method and the DCF of the local mode of vibration has been determined.

Experimental and analysis

The fine powder samples of AgI, CuCl, CuBr, CdSe, CdS and ZnO were pressed with powder of boron nitride into pellets of 0.5 mm in thickness and 13.0 mm in diameter. The X-ray absorption measurements near Ag, Cu, Cd, Zn, Br and Se K-edges in the temperature range 20-973 K were made using the EXAFS facilities installed at the beam lines 7C and 10B of Photon Factory in KEK. EXAFS interference function was extracted from the measured absorption data using standard techniques\. The Fourier filtered EXAFS data were fitted using the least-squares minimization technique with analytical EXAFS formula. The amplitude and the phase function employed here were the theoretical curves tabulated by Teo and Lee\. Details of the data processing procedure were already given in references 2 and 4. We have calculated the MSD of each atom in AgI, CuCl, CuBr, CdSe, CdS and ZnO with the published temperature factors\-10).

Results and discussion

Table 1 shows the DCF of the local modes of vibration derived from the MSRD and the MSD of the both absorber and backscatterer atoms in order of ionicity based on the Phillips scale (f)\. The ionicity is increasing from ZnO to AgI. It is well known that the elastic properties of the covalently bonded tetrahedral compounds show a systematic tendency towards lattice instability as the ionicity increases. The lattice vibrations dependent on the bonding force and the tendency toward the lattice instability result in increasing magnitude of MSRD and MSD. Table 2 shows the temperature dependence of the MSRD, MSD and DCF for CuBr. We have also evaluated the ratio of the DCF to the MSD. The magnitude of the DCF term amounts to about 70% of the MSD in tetrahedrally coordinated covalent crystals; the large contribution of the DCF to MSD is revealed.

References


Table 1. The MSRDs (\sigma_1^2), the MSDs (\sigma_2^2) for the cation and anion, the DCFs and the ratios of the DCF to the MSD in binary crystals of AgI.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>f_1</th>
<th>\sigma_1^2 (\AA^2)</th>
<th>\sigma_2^2_{cation} (\AA^2)</th>
<th>\sigma_2^2_{anion} (\AA^2)</th>
<th>DCF</th>
<th>(DCF/MSD_{cation})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI</td>
<td>0.77</td>
<td>0.018(1)</td>
<td>0.074(1)</td>
<td>0.043(1)</td>
<td>0.050</td>
<td>0.68</td>
</tr>
<tr>
<td>CuCl</td>
<td>0.746</td>
<td>0.013(1)</td>
<td>0.056(1)</td>
<td>0.030(1)</td>
<td>0.037</td>
<td>0.65</td>
</tr>
<tr>
<td>CuBr</td>
<td>0.735</td>
<td>0.012(1)</td>
<td>0.044(1)</td>
<td>0.028(1)</td>
<td>0.030</td>
<td>0.68</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.699</td>
<td>0.006(1)</td>
<td>0.020(1)</td>
<td>0.016(1)</td>
<td>0.015</td>
<td>0.75</td>
</tr>
<tr>
<td>CdS</td>
<td>0.685</td>
<td>0.004(5)</td>
<td>0.018(1)</td>
<td>0.014(1)</td>
<td>0.014</td>
<td>0.77</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.616</td>
<td>0.0018(5)</td>
<td>0.0073(2)</td>
<td>0.0073(2)</td>
<td>0.0064</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 2. The temperature dependences of the MSRD, MSD and DCF.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>f_1</th>
<th>\sigma_1^2 (\AA^2)</th>
<th>\sigma_2^2_{cation} (\AA^2)</th>
<th>\sigma_2^2_{anion} (\AA^2)</th>
<th>DCF</th>
<th>(DCF/MSD_{cation})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr(100K)</td>
<td>0.006(1)</td>
<td>0.015</td>
<td>0.009</td>
<td>0.009</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(200K)</td>
<td>0.009(1)</td>
<td>0.030</td>
<td>0.018</td>
<td>0.020</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>(300K)</td>
<td>0.012(1)</td>
<td>0.044</td>
<td>0.028</td>
<td>0.030</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>(400K)</td>
<td>0.016(1)</td>
<td>0.059</td>
<td>0.038</td>
<td>0.041</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>(500K)</td>
<td>0.018(1)</td>
<td>0.073</td>
<td>0.046</td>
<td>0.051</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>
Amorphization process by solid state reaction was investigated by means of EXAFS study to get informations of atomic scale configurations. Amorphous samples were prepared by mixing elemental Cu and Ti powders using a high energy ball mill mixer (mechanical alloying: MA) or grinding intermetallic compound Cu₅Ti₃₀ using the same apparatus (mechanical grinding: MG).

EXAFS measurement was performed in transmission mode at Cu K-edge at BL-7C, 10B of KEK and data was analyzed using a program "EXAFS1"[1]. Amorphization was confirmed by halo X-ray diffraction patterns after milling 50hr (MA) and 80hr (MG).

Fig.1 shows radial distribution function (RDF) of MA and MG samples of Cu₅Ti₃₀ of various milling time. The maximum of the first coordination shell shifted to shorter distance from that of fcc Cu (MA) and of Cu₅Ti₃₀ (MG) as the milling time is prolonged. In case of MA, the periodicity of fcc Cu disappears after 80hr milling, whereas for MG, the periodicity of Cu₅Ti₃₀ is modified after the same milling period. The peak position of the first shell at long milling amorphous state were almost the same irrespective of MA and MG.

The results of curve fitting are listed in Table.1. In case of MG, coordination number of Ti immediately decreases and bond lengths of Cu-Cu and Cu-Ti extend at milling 20hr. With further milling, say 80hr, both Cu-Cu and Cu-Ti bond lengths tend to decrease and reach values which are larger than that of intermetallic compound Cu₅Ti₃₀. Coordination number changes slightly after 80hr milling. This behavior is likely a feature of amorphization by MG. In case of MA, bond length of Cu-Cu contracts from that of fcc Cu (2.556Å). A difference of amorphous states obtained MA and MG is found in shorter Cu-Cu and Cu-Ti bond lengths of MA samples compared to MG ones.

Table.1. The results of curve fitting of MG and MA samples.

<table>
<thead>
<tr>
<th>milling time(hr)</th>
<th>bond length(Å)</th>
<th>coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu-Cu</td>
<td>Cu-Ti</td>
</tr>
<tr>
<td>MG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.453</td>
<td>2.618</td>
</tr>
<tr>
<td>20</td>
<td>2.543</td>
<td>2.724</td>
</tr>
<tr>
<td>80</td>
<td>2.500</td>
<td>2.674</td>
</tr>
<tr>
<td>200</td>
<td>2.473</td>
<td>2.663</td>
</tr>
<tr>
<td>320</td>
<td>2.431</td>
<td>2.681</td>
</tr>
<tr>
<td>900</td>
<td>2.468</td>
<td>2.661</td>
</tr>
<tr>
<td>MA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.536</td>
<td>--</td>
</tr>
<tr>
<td>20</td>
<td>2.479</td>
<td>2.683</td>
</tr>
<tr>
<td>80</td>
<td>2.469</td>
<td>2.644</td>
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<td>200</td>
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<tr>
<td>320</td>
<td>2.486</td>
<td>2.684</td>
</tr>
<tr>
<td>900</td>
<td>2.477</td>
<td>2.655</td>
</tr>
</tbody>
</table>

In case of MG, the decrease of coordination number of Ti was significant, together with the larger change of Cu-Ti bond length. Preferred decomposition of Cu-Ti bond is a possible amorphization process of MG. In case of MA, alloying will give rise to the formation of compound-like bond. The observed shift of Cu-Cu bond length, and formation of Cu-Ti bond may reflect this situation.

[1] N.Kosugi and H.Kuroda, Program EXAFS1, Research Center for Spectroscopy, The University of Tokyo (1985)
EXAFS STUDY ON CRYSTALLIZATION OF AMORPHOUS Cu_{80}Ti_{20} ALLOYS PREPARED BY MECHANICAL ALLOYING AND GRINDING

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Department of Materials Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169

Crystallization behaviors which reflect the amorphous state were examined with mechanically alloyed (MA) and ground (MG) Cu_{80}Ti_{20} by means of EXAFS. Experiments were described in the preceding report, and the crystallization was conducted by annealing the samples in a differential scanning calorimeter furnace.

Fig. 1 (left) shows RDF of MG samples of various milling time heated up to 993K. Long time milled samples, especially 320 hr, show asymmetric shoulder distribution of the first coordination shell at long distance side, while short time milled samples remain gaussian distributions. This behavior is also seen in case of MA samples. Fig. 1 (right) is RDF of MG 320 hr sample of various annealing temperatures, and shows that the asymmetric distribution is formed during the progress of crystallization.

Fig. 2 shows curve fitting results of the first coordination shell of F(R) of MG 320 hr sample. The upper figure is by a two bond (Cu-Cu, Cu-Ti) simulation, while the lower one is by a three bond (Cu-Cu, short Cu-Ti, long Cu-Ti) one by extending the range of inverse Fourier transformation to the observed k^2 x (k) spectrum. Fitting is better by the latter method.

X-ray diffraction spectra of crystallized samples showed formation of several binary Cu-Ti compounds. The occurrence of asymmetry in the first coordination shell and better fitting by the three bonds simulation are in accord with a relative increase in CuTi_3 and Cu_Ti phases. The newly formed long Cu-Ti bond may be assigned to the nearest Cu-Ti bond of CuTi_3.

Since the F(R) of amorphous state can be fitted by two bonds simulation, it is likely that nearest Cu-Ti bond in the amorphous state is separated to two bonds accompanying with the crystallization; long one forms Cu-Ti bond of Cu_Ti_3 and short ones of CuTi and Cu_Ti.
Amorphization process by mechanical alloying was investigated from composition dependence of EXAFS of Cu$_x$Ti$_{1-x}$ alloys ($x=25, 33, 40, 50, 57, 60, 75$). Experimental procedures are described in the preceding report, and milling time was fixed at 300 hr.

Fig. 1 shows RDF of various composition amorphous samples. Periodicity of metallic Cu disappears in the present compositional range except the $x=75$ sample, and the maximum of the first coordination shell of $F(R)$ contracts from these of the crystalline materials. For $x=75$, RDF is similar to that of metallic Cu while partial amorphization is evident from DSC (Differential Scanning Calorimetric) study.

A feature of composition dependence is found in the coordination number obtained from the curve fitting analysis.

$N_{Cu}/N_{Ti}$ increases in a monotonous way with $x$ as shown in Fig. 2. Noteworthy is a slight minimum in Cu-Cu and Cu-Ti bond lengths. Cu-Cu bond length increases after $x=60$. These behaviors are in accord with the composition dependence of the crystallization temperature at DSC measurement.

These facts suggest that the framework of the amorphous state is the same for various composition, while Cu and Ti atoms tend to be randomly distributed. Amorphization is likely to proceed by the diffusion of Ti into Cu. The contraction of Cu-Cu and Cu-Ti bond length near $x=57$ may be resulted from a compound-like configuration corresponding to such as Cu$_{14}$Ti$_3$, Cu$_{13}$Ti$_4$, and Cu$_9$Ti$_4$, which have strong bonding.

Fig. 2. The results of curve fitting analysis. The upper figure shows the ratio of coordination number of Cu to that of Ti around Cu. The lower one shows bond lengths of Cu-Cu and Cu-Ti bond.
STRUCTURE OF BALL-MILLED POWDERS OF THE IMMISCIBLE SYSTEM Cu-V

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Introduction

Mechanical alloying (MA), which is a new amorphization process by means of solid-state reaction, has usually been applied to the systems with a large negative heat of mixing (ΔHmix), since the ease of interdiffusion between different atomic species is considered to be an indispensable factor. Recently, however, we have found that MA also facilitates the amorphization of Cu-Ta system, which has a positive ΔHmix. For further understanding of reaction mechanism of MA, it is important to investigate the structural change during MA in the systems with a positive ΔHmix, other than Cu-Ta. In this report, the Cu-V powders were studied by EXAFS.

Experimental and Results

Pure metallic copper (fcc) and vanadium (bcc) powders were mixed to give the starting composition of Cu$_{50}$V$_{50}$ and Cu$_{30}$V$_{70}$ and were milled with the Cu-B6 vial and balls in an argon atmosphere. EXAFS above the V K (5876.6 eV) and Cu K (8980.3 eV) absorption edges were measured with a Si(111) double-crystal monochromator on BL-7C. For V K EXAFS measurement, a platinum coated mirror was employed to reject higher harmonic reflections on the monochromator. Measurement was carried out at 30 K, in order to sharpen EXAFS spectra by attenuating the thermal oscillation of the system.

Figures 1 and 2 show the magnitude of Fourier transforms of $k^2x(k)$ above the Cu and V K edges, respectively. A significant structural change around the copper atoms was observed as the milling time increased, while the vanadium K EXAFS did not change so much.

As for Cu$_{50}$V$_{50}$ (30h), the higher order peaks around copper atom are relatively weakened, indicating the gradual destruction of the long range order of fcc copper crystal. This is apparently like to an amorphization process. However, it is fairly difficult to explain it as amorphization, since a bcc crystal structure is almost remained around vanadium as shown in Fig.2. For the Cu$_{30}$V$_{70}$ samples after 60 h and 120 h of milling, some new peaks are observed in the region of 3 to 6 Å. The peak position marked with the asterisk in Fig.1 coincide with that of the 4th neighboring atoms when assuming the bcc lattice of copper crystal. On the contrary, the structure around vanadium atom does not change so much during MA.

From the fact that bcc structure was observed around both copper and vanadium atoms, it is concluded that a bcc solid solution was formed through the dissolution of copper atoms into a bcc vanadium lattice. The solution limit in the solid state is far more extended (possibly a few tens of at. % Cu) by MA than that shown in the phase diagram (4 at. % Cu).

The data for the Cu$_{30}$V$_{70}$ are also consistent with the formation of a bcc structure. The difference between them is explained by the formation rate of the solid solution.

The authors gratefully thank Prof. T. Fukunaga of Nagoya Univ. for his valuable discussion and cooperation to this work.

References
2) K. Sakurai et al., APL 57(90)2660.
3) K. Sakurai et al., PF Activity Rep. #8(90)133.
Catalytic active species of supported metal oxide catalysts are influenced structurally and electronically by supports and preparation methods. EXAFS/XANES experiments were carried out to elucidate the structures of supported highly dispersed composite TiO\textsubscript{2} oxides prepared by a CVD method which are known to be active for photooxidation of hydrocarbons.

Experimental

TiO\textsubscript{2}/SiO\textsubscript{2}: vaporized Ti(OPr\textsuperscript{i})\textsubscript{4} was reacted with OH groups of SiO\textsubscript{2} at 423 K which had been evacuated at 673 K for 2 h. Isopropoxytitanium-SiO\textsubscript{2} species were evacuated for 1 h followed by heating in O\textsubscript{2} at 673 K for 2 h. TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}: vaporized Ti(OPr\textsuperscript{i})\textsubscript{4} was similarly reacted with Al\textsubscript{2}O\textsubscript{3} at 423 K which had been heated in vacuo at 623 K for 2 h. Isopropoxytitanium-Al\textsubscript{2}O\textsubscript{3} was hydrolyzed with water vapor at 423 K for 0.5 h to regenerate OH groups followed by being further treated with Ti(OPr\textsuperscript{i})\textsubscript{4} vapor and calcined at 623 K for 2 h. X-ray absorption measurements were carried out at the BL-7C by using a fluorescence detector.

Results and discussion

1. XANES and EXAFS of TiO\textsubscript{2}/SiO\textsubscript{2}

The XANES spectrum of Ti K-edge of TiO\textsubscript{2}/SiO\textsubscript{2} (Dry) prepared by a CVD method (Fig. 1) is different from rutile and anatase TiO\textsubscript{2} which are in octahedral.\textsuperscript{1} A sharp pre-edge peak is characteristic for tetrahedral and pentagonal structures.\textsuperscript{2} The XANES spectrum is similar to that of tetrahedral Ti(OPr\textsuperscript{i})\textsubscript{4} which is the source of CVD. The structure is very different from those of TiO\textsubscript{2}/SiO\textsubscript{2} prepared by impregnating SiO\textsubscript{2} in a hexane or toluene solution of TiOPr\textsuperscript{i})\textsubscript{4} which are shown to be in an anatase-like structure from EXAFS studies.\textsuperscript{3} The spectrum resembles the XANES of TiO\textsubscript{2} (2-6 wt%)-SiO\textsubscript{2} glass prepared by a flame hydrolysis process.\textsuperscript{4} The FT spectrum gives a peak attributed to the Ti-O bond and no further peaks. When the sample was exposed to the moist air, both XANES and FT spectra changed similarly to the case of V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2}.\textsuperscript{5} The pre-edge peak becomes less due to the coordination of water molecule changing from four-fold to five- or six-fold coordination. A water molecule makes a bridge between isolated vanadium species. However, no further peaks over Ti-O bond appears.

2. XANES and EXAFS of TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}

The XANES spectrum of TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} (Dry) is different from that of TiO\textsubscript{2}/SiO\textsubscript{2} and the pre-edge peak is less. (Fig. 1) The spectrum is also different from those of rutile and anatase TiO\textsubscript{2}. Wetted with moist air the spectrum scarcely changed differing from the case of TiO\textsubscript{2}/SiO\textsubscript{2}. The precise structure should be determined by the curve fitting.

The behavior of TiO\textsubscript{2} on supports prepared by a CVD method is very similar to that of V\textsubscript{2}O\textsubscript{5}.

Many compounds of Ce exhibit a variety of interesting features resulting from the hybridization between the 4f and conduction electrons. It is known that the hybridization is mainly influenced by the Ce-Ce spacing in the compounds, but the details are not clarified as yet. The present authors found that Pd₅Ce alloy has a one-dimensional long period superstructure (L-Pd₅Ce) and the antiphase domain size changes with temperature [1]. In this work, the changes in electrical resistivity and valence of Ce in L-Pd₅Ce were measured as a function of quenching temperature (Tq) in order to investigate the influence of local arrangements of Ce atoms upon physical properties.

A Pd₅Ce ingot was prepared by arc melting under argon atmosphere. The ingot was filed to powder specimens for X-ray experiments and sliced to rod-specimens for electrical resistivity measurements, followed by annealing in vacuum at various temperatures between 673 K and 985 K, and quenched into iced brine. X-ray powder diffraction experiments were carried out to examine the volume of atoms in each specimen. Electrical resistivity was measured by a D.C. four-probe technique in the temperature range between 10 K and 300 K. XANES spectra were measured at BL-7C of KEK-PF to evaluate the valences of Ce in the specimens [2].

Figure 1 shows the temperature-changes in electrical resistivity as a function of Tq. One can see that the temperature coefficient of resistivity (TCR) decreases with increasing Tq. Especially, the TCR decreases rapidly in the range of Tq=898–923 K. One can also notice that the absolute value of resistivity increases with Tq, and the increment of the absolute value in Tq=898–923 K is very large. Since the antiphase domain size changes due to the variation of degree of order [1], these resistivity anomalies are thought to be caused by the local changes in atomic configuration. However, the degree of order does not show a rapid change at the temperature range of 900–920 K [1]. Besides, the volume of atoms which is analyzed from X-ray diffraction changes only ±0.2% with changing Tq [3]. We also found that the volume of L-Pd₅Ce decreases by 5% under an external pressure of 80 kbar, but such a small change of volume hardly affects the electrical resistivity [4]. Therefore, the large changes of electrical resistivities shown in Fig. 1 are not attributable to the change in atom-volume with the variation in degree of order.

Figure 2 shows the XANES spectra for the specimen quenched from Tq=873–973 K. The values for Ce valences are estimated to be Vs 3.37–3.38. One can see that there are little differences in the shape of these spectra, and the valence changes hardly with Tq. The value for Ce valences in L-Pd₅Ce is about 3.3 which is a saturated value for Pd-Ce alloy system [5], and thus L-Pd₅Ce is found to have a strongly mixed valence state as similarly as Pd₅Ce [6].

As above mentioned, the atomic volume and the Ce-valences averaged over the alloys change little with Tq. However, since the degree of order changes with Tq, the local circumstances e.g. the number of Ce(Pd) atoms in the nearest neighbor coordinates, of individual Ce atoms also change with Tq. Therefore, there is a more inhomogeneity in special distribution of Ce-valence in an alloy with a lower degree of order. The inhomogeneity can account for Tq-dependence of electrical resistivity observed in the present.

![Fig. 1](image1)

**Fig. 1** Changes in electrical resistivity with temperature for Pd₅Ce quenched from Tq.

![Fig. 2](image2)

**Fig. 2** XANES spectra for Pd₅Ce quenched from Tq.

References

An EXAFS study of the active site of hydrogenase from Desulfovibrio vulgaris Miyazaki F

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Introduction

Hydrogenase has iron-sulfur clusters, and is also believed to contain nickel atom. We have carried out an EXAFS study of hydrogenase solution, and wish to report preliminary results of the experiments.

Hydrogenase is an enzyme which catalyzes reversible dehydrogenation of molecular hydrogen. The solubilized hydrogenase (hydrogen : ferricytochrome c oxidoreductase, EC 1.12.2.1) from Desulfovibrio vulgaris Miyazaki F (DvMF) has 89000 of molecular weight and has two or three 4Fe-4S type clusters as the active center. It is also reported to contain nickel atom near the active site. In order to investigate the local structure of the active site of hydrogenase, we have carried out an EXAFS study. We have been engaged in an X-ray diffraction study of hydrogenase in Photon Factory. Both studies seem to be helpful each other.

Experimental and Results

Membrane-bound hydrogenase was solubilized by trypsin digestion from the wet cells of DvMF bacterium cultured by Ajinomoto Co. The protein was isolated1 and purified2 as described before. Specimen solutions of hydrogenase were carefully prepared in order not to be contaminated metal ions from the environment. The concentration of the solution was as high as 1.5mM. Low molecular weight model compounds were also used for calibration purpose. They include FeS, NiS, (Et4N)2 [Fe4S4(SCH2Ph)4] and (Ph4P)2 [Fe4S4(SCH2(CH3)4)]. The latter two compounds were kindly supplied Dr. N. Ueyama of Osaka University. They are dispersed in polyethylene powder and used for the experiments. The measurement were carried out in the stream of nitrogen gas at 10 degree centigrade. X-ray absorption spectra of Ni K-edge and Fe K-edge were measured in the fluorescent mode as well as in the absorption mode at the BL7C of the Photon Factory.

Results and Discussion

Absorption spectra of the Ni K-edge as well as Fe K-edge of hydrogenase solution could be observed. The ratio of the content of Ni atom to Fe atom was estimated to be 10% considering the jump in the absorption edge. Thus the presence of Ni atom has been confirmed by an EXAFS study. The Fourier transform of the Fe K-edge spectra of hydrogenase is shown below. Further analysis in terms of the model compounds are being carried out.

References

EXAFS study on reduction process of Pauri-paramagnetic LaNiO$_3$ to antiferromagnetic LaNiO$_2$.5

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INTRODUCTION

Recently, double oxides with perovskite-related structure have been spotlighted in terms of interesting electrical and magnetic properties. Their oxygen amounts directly affect these properties. LaNiO$_3$ has a rhombohedrally-distorted perovskite-type structure with metallic conductivity and Pauri-paramagnetism. Crespin et al. reported that low-temperature reduction of LaNiO$_3$ under H$_2$ flow led to a new compound La$_2$Ni$_2$O$_{5+1/2}$. We have clarified its structure by using Rietveld analysis and its magnetic property. A presence of new ferromagnetic phase was detected in a reduction of LaNiO$_3$ to antiferromagnetic LaNiO$_2$.5. However, structural variation under reduction did not become apparent because of poor crystalinity of the intermediate phases. In this report, EXAFS data on the reduction process of LaNiO$_3$ to LaNiO$_{2.5}$ are shown.

EXPERIMENTAL PROCEDURE

Fine powder specimens of LaNiO$_{3-x}$ (0<x<0.5) were prepared by reducing LaNiO$_3$ in an atmosphere of H$_2$ flow at 275°C for various periods. Successively, only in case of LaNiO$_{2.5}$, the reducing product was annealed in 1%H$_2$/N$_2$ gas flow for 30 hours. Their oxygen amounts were determined by reducing them in carbon crucible on a carrier gas of He with Horiba EMGA-2800. X-ray absorption spectra measurements near Ni K-edges were carried out at the BL-7C station using a Si(111) double monochromator. The samples were dispersed in h-BN and pressed into pellets. Analyses of the EXAFS data were performed with the program developed in Yokoyama Lab., Faculty of Science, Osaka University.

RESULTS AND DISCUSSION

Fig. 1 shows the Ni K-edge XANES spectra of LaNiO$_{3-x}$ (0<x<0.5). The XANES spectra of the specimens reduced for more than 1 hour have a smaller and gentler peak at about 8333eV compared to the spectrum of LaNiO$_3$. This style of absorption can generally be assigned to 1s->3d electron transition in 4-folded square-planar Ni$^{2+}$ rather than to that in 4-folded tetrahedral or 5-folded pyramidal Ni$^{3+}$ because of its weak intensity. The specimen reduced for 1 hour was found to already have the square-planar coordination present in LaNiO$_{2.5}$.

Table 1 represents Ni-O distances of the reduced samples by EXAFS versus the reducing times and their oxygen amounts. The Ni-O distance decreases with an increase of reducing time in spite of the enhancement of the ionic radius accompanying a valence reduction from Ni$^{3+}$ to Ni$^{2+}$. From the results of Rietveld analysis, in LaNiO$_{2.5}$, the Ni-O distances in the ab-plane and along the c-axis of NiO$_6$ octahedron were 1.87 Å and 2.02 Å, respectively. Similarly, the distance in NiO$_4$ square-planar was 1.88 Å. In LaNiO$_3$, that was 1.92 Å, which agrees well with EXAFS result. EXAFS data of reduction product LaNiO$_{3-x}$ (x<0.5) can be interpreted as showing the first-neighbour Ni-O distance lying in the ab-plane. These results indicate that, even in an early step of the reduction, most of apical oxygens deintercalate from half of NiO$_6$ octahedra in LaNiO$_3$ so that the NiO$_4$ square-planar is formed, and simultaneously, the Ni-O distance along the c-axis in the other NiO$_6$ octahedra stretches. Afterward, the residuary interstitial oxygens which are considered to affect a magnetic property of the intermediate ferromagnetic phase eliminate gradually. Consequently, the antiferromagnetic LaNiO$_{2.5}$ is formed.

REFERENCES


Table 1. Ni-O distances of the reduced samples by EXAFS versus the reducing periods and their oxygen amounts.

<table>
<thead>
<tr>
<th>No. reducing period x in LaNiO$_{3-x}$</th>
<th>Ni-O distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 hour</td>
<td>0.09 (LaNiO$_3$) 1.92 Å</td>
</tr>
<tr>
<td>0.5</td>
<td>0.31 1.89</td>
</tr>
<tr>
<td>1.0</td>
<td>0.41 1.87</td>
</tr>
<tr>
<td>2.0</td>
<td>0.43 1.87</td>
</tr>
<tr>
<td>5.0</td>
<td>0.46 1.87</td>
</tr>
<tr>
<td>8.0</td>
<td>0.49 1.86</td>
</tr>
<tr>
<td>16 + 30 anneal</td>
<td>0.52 (LaNiO$_{2.5}$) 1.85</td>
</tr>
</tbody>
</table>
L_{III} XAFS STUDIES OF HEXACHLORO-COMPLEXES OF IRIDIUM (III) AND (IV)

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Introduction

The absorption threshold resonance (white line) in the L-absorption spectrum gives information on the chemical combination and environment of the absorbing atom. The white line has been attributed to transitions from a core level to vacant d states of the absorbing atom. In a series of compounds of platinum, iridium or gold, the relationship between the intensity of the white line and the ionicity of the bonds or the d orbital occupancy has been reported. In this work, we have investigated the white line intensities and interatomic distances of octahedral hexachloro-complexes of iridium(III) and (IV) both in solution and crystalline state.

Experimental

The crystal samples used in this work were K$_2$IrCl$_6$, K$_3$IrCl$_6$ and IrO$_2$. The 0.1 M solution samples of [IrCl$_6$]$^{3-}$ and [IrCl$_6$]$^{2-}$ were prepared by dissolving K$_3$IrCl$_6$ and K$_2$IrCl$_6$ in 4 M NaCl solution, respectively. The Ir L$_{III}$ XAFS spectra were taken with Si(111) double-crystal monochromator at the BL-7C station. Data analysis was performed using the program EXAFS2 developed by the University of Tokyo.

Results

The iridium L$_{III}$ absorption spectra of K$_2$IrCl$_6$, K$_3$IrCl$_6$ and IrO$_2$ in crystalline state are shown in Fig. 1, where the absorption intensities are normalized at the threshold peak of the three spectra. The absorption spectra of [IrCl$_6$]$^{3-}$ and [IrCl$_6$]$^{2-}$ in solution are shown in Fig. 2, where the absorption intensities are also normalized as stated above and the spectrum of K$_2$IrCl$_6$ is reproduced for comparison. As can be seen in Fig. 1 and 2, the intensity ratio of the white line to absorption in the EXAFS region is greater in Ir(IV) than in Ir(III), and is greater in solution than in crystalline state. The intensity ratio in IrO$_2$ is greater than in K$_2$IrCl$_6$, although the valence of Ir in the both compounds is +4.

The Ir-Cl distances determined are listed in Table 1. The Ir(III)-Cl distances are longer than the Ir(IV)-Cl distances both in solution and crystalline state. In comparing the distances of complexes of the same valency in crystal and in solution, there is no significant difference between the Ir-Cl distance in solution and that in crystalline state. It is interesting that the white line intensity of the hexachloroiridate in solution is different from that in crystalline state although their Ir-Cl distances do not differ.

References

1) F. W. Lytle et al., J. Chem. Phys. 70, 4849 (1979)

Table 1. EXAFS results of iridium hexachlorides. The K$_2$IrCl$_6$ crystal is employed as the model compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Distance(Å)</th>
<th>Δσ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_3$IrCl$_6$</td>
<td>2.507</td>
<td>0.001</td>
</tr>
<tr>
<td>K$_2$IrCl$_6$</td>
<td>(2.470)</td>
<td>(0)</td>
</tr>
<tr>
<td>[IrCl$_6$]$^{3-}$ (solution)</td>
<td>2.506</td>
<td>0.006</td>
</tr>
<tr>
<td>[IrCl$_6$]$^{2-}$ (solution)</td>
<td>2.476</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Enhancement of photo-stimulated O\(^+\) desorption by atomic hydrogen

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As the dimension of large-scale integrated circuits approaches the nanometer level, semiconductor processes with low temperature, low damage, low contamination are becoming necessary. Recently, synchrotron excited reactions have been studied actively as new processing techniques[1-2]. Photo-stimulated desorption (PSD) is one of important mechanisms of the reaction. This report presents experimental results of PSD from naturally oxidized Si surface exposed by atomic hydrogen beam.

The experiments were carried out using beam line BL-8A. BL-8A has the monochromator equipped with three mirrors and one varied-space plane grating[3]. Zeroth-order light (hv < 2 keV) from the monochromator was used as a SR irradiation. The photon flux is about 10\(^{13}\) photons/s/cm\(^2\)/100mA.

Mass analysis of photo-stimulated desorbed ions under SR irradiation was performed using a quadrupole mass analyzer (QMA) operated in a pulse counting mode. The monochromatic light and a spherical sector electron energy analyzer were used for x-ray photoelectron spectroscopy (XPS).

The cross-sectional view of an atomic hydrogen source is shown in Fig.1. By the atomization of molecular hydrogen at a hot inner surface (~1700°C) of the tungsten pipe, an intense atomic hydrogen beam was obtained. The pipe was heated by electron bombardment.

The specimen used here was an Si\{111\} wafer dipped in an aqueous 50% HF solution. The exposure to atomic hydrogen beam was performed under the condition of the H\(_2\) filling pressure of 1.33x10\(^{-4}\)Pa and exposure time of 180 s. The temperature rise during exposure was about 20 °C.

The PSD ion mass spectra with and without atomic hydrogen exposure are shown in Fig. 2. Desorption of H\(^+\), O\(^+\) and F\(^+\) ions was primarily detected during SR irradiation. The yield of O\(^+\) ions was increased by 30 times by atomic hydrogen exposure. From the Si-2p photoelectron spectra of the surface without atomic hydrogen exposure, the Si surface seems to have an intermediate oxidation state partly terminated with H and F atoms as shown in Fig. 3(a). The Si-O-Si bonds are broken by the atomic hydrogen and Si-OH bonds are formed as shown in Fig. 3 (b). The oxygen atoms in Si-OH bond are thought to be desorbed easily by SR irradiation.

In conclusion, the enhancement of O\(^+\) PSD ions was observed by atomic hydrogen exposure on a naturally oxidized Si surface. The breaking of Si-O-Si bond and formation of Si-OH bond is thought to be a mechanism of the enhancement by the exposure of H atoms.

THE EFFECTS OF SR IRRADIATION ON POLYDIACETYLENE LB FILMS

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Introduction

The possibility of using polydiacetylene thin films as optical waveguides has attracted much attention. We have studied the possibility of using SR irradiation to fabricate optical waveguides made of polydiacetylene LB films. Here we report the bleaching and degradation that white SR irradiation induces in polydiacetylene LB films.

Experimental

Poly-[dibutyl-4,17-dioxo-5,16-diaxa-3,18-diaza-9,ll-eicosa-diynedioate] (poly-3BCMU) was used in this study. Fabricating LB films using poly-3BCMU has been described elsewhere [1]. Poly-3BCMU LB films about 110 nm thick were deposited on optically polished quartz substrates and were irradiated with white SR irradiation at BL-8A. The change in film thickness was determined by measuring the reflection of monochromatized soft x-ray [2]. We used a Hitachi U-3000 spectrometer and a Digilab FTS-50C FT-IR spectrometer to measure absorption spectra in the UV-visible and infrared regions, respectively.

Results and Discussion

White SR changed the UV-visible absorption spectra and decreased the thickness of poly-3BCMU LB films. Figure 1 shows change of absorption spectrum of poly-3BCMU LB film. The absorbance of the LB films, which is due to π-conjugated system of poly-3BCMU, gradually decreased in intensity and shifted to higher energies. These changes indicate a decrease in π-conjugation length, which indicates cross-linking [3] caused by white SR irradiation in the π-conjugated polymer chain. This phenomenon differs from the bleaching seen when photo-induced oxidation is induced by Ar ion laser [4]. Figure 2 shows decrease in thickness of the poly-3BCMU LB films against white SR dose. Film thickness gradually decreased with further irradiation, and this decrease is independent of spectral change. FT-IR analysis indicates radiation-induced dissociation of C-N and C-O bonds. This decrease in film thickness thus results from the decomposition of poly-3BCMU side-chains. Neither spectral change nor decrease in film thickness could be observed when we evaluated film thickness using soft x-ray with a wavelength less than several nm. These reactions probably result from the excitations of C2s and/or C2p. These reaction mechanisms are under investigation with evaluating the dependence of excitation energy.

References


Figure 1. UV-visible absorption of poly-3BCMU LB film as a function of incident dose. (a) 0, (b) 550, (c) 4700, and (d) 11100 min mA.

Figure 2. Decrease of poly-3BCMU LB film thickness as a function of incident dose.
Proposal No. 90-Y001

Detection of Line Patterns Using Microscopic X-ray Photoelectron Spectroscopy

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Microscopic X-ray photoelectron spectroscopy (μ-XPS) uses a focused X-ray to achieve a high lateral resolution in XPS analysis. This analytical technique is expected to provide detailed chemical and electronic information useful for understanding heterogeneous surface phenomena observed in material and surface science. In our previous studies, XPS spectra could be clearly observed using a focused X-ray with a beam size ranging from a micrometer to a few tens of micrometers. The present study demonstrates that fine line patterns can be detected by monitoring energy-filtered photoelectrons.

The experiments were performed in a soft X-ray beamline (BL-8A) equipped with a varied-spacing plane grating monochromator. For generating a focused X-ray beam, a Wolter type X-ray mirror, which was made from Pyrex by vacuum replication technique,^5^ was located behind the exit slit of the monochromator. The peak-to-valley roughness value of the mirror surface was 10 - 15 nm. The mirror had a demagnification value of 1/29.8, and the average grazing incidence angle of the X-ray to the mirror surface was 19 mrad for the ellipsoid and 25 mrad for the hyperboloid of the mirror. Two pinholes with diameters of 1000 and 100 μm were used to determine the X-ray source size for the mirror.

The intensity profile of a focused 150 eV X-ray was measured for each pinhole by knife edge scanning (Fig. 1). The beam size defined as the full width at half maximum (FWHM) of the profile is 12 μm for the 1000 μm pinhole and 4 μm for the 100 μm pinhole. The former beam size is smaller than the value predicted from the pinhole diameter and the demagnification value of the mirror. This difference probably results from the X-ray intensity distribution within the pinhole.

![Fig. 1. Intensity profiles of focused 150 eV X-ray beam observed for (a) 1000 and (b) 100 μm pinholes.](image)

The focused beam was scanned across gold line patterns (10 - 50 μm wide) delineated on a Si wafer by moving a sample stage at intervals of 5 μm. The Si(2p) photoelectrons from surface oxides were monitored for detecting the line patterns since the Si(2p) photoionization cross section is larger than the Au(4f) cross section at the present photon energy. In this monitoring, the photoelectron was counted with a double-pass cylindrical mirror electron energy analyzer whose energy window was fixed at 103 eV with an energy resolution of 1.1 eV.

![Fig. 2. Silicon (2p) photoelectron count rates as a function of beam position on a Si wafer with a 10 μm-wide pattern.](image)

Figure 2 shows the change in Si(2p) photoelectron count rate when the beam was scanned across a 10 μm pattern. The dashed line represents an average count rate in a surface region with no Au patterns. As shown in the figure, the count rate becomes small when the focused beam hits the pattern. The pattern width observed is about 11 μm (the FWHM of the count rate drops), which is nearly equal to the actual pattern size. Judging from this agreement, a micrometer-size pattern would also be detected if the 4 μm focused beam (Fig. 1(b)) is used as a probe beam for μ-XPS analysis.

References

A method for measuring density depth-profiles of light elements in thin films is tested using soft X-rays (λ ~ 3 nm). While a soft X-ray beam irradiates a thin film, a standing wave is formed in the film under nearly total reflection condition. The standing wave moves in a direction perpendicular to the film surface by varying the wavelength and/or the grazing angle of the incident beam. Atoms excited by the standing wave emit soft X-ray fluorescence and secondary-electrons, the intensities of which depend on the strength of the standing wave at the locations (depths) of the atoms. Therefore, by measuring the fluorescence or secondary-electron yield varying wavelength or grazing angle of the incident soft X-rays, the depth-profile of specific elements is determined. Standard samples were prepared using the LB method taking advantage of the high controllability of organic film thickness to angstrom scale, and the secondary-electron yield from nitrogen was measured. The results correspond to the sample structures and indicate the method's potential.

Experiments and Results

LB films consisting of cadmium arachidate (C_{20}Cd) and poly-dibutyl-1, 17-dioxa-5, 16-dioxa-3, 18-diazao-3, 11-ecosadiynedioate (P3BCMU) were used. Only P3BCMU contained nitrogen, whose density was 1x10^{15} cm^{-2} monolayer^{-1}. Five monolayers of C_{20}Cd were deposited on a glass substrate and two monolayers of P3BCMU were further deposited on it. The thickness of the film was about 19 nm, derived from reflectivity. The C_{20}Cd and P3BCMU monolayers are 2.75 nm and 2.9 nm thick, respectively. Fluorescence intensity should be measured because of its non-surface sensitivity, whereas the escape depth of secondary-electrons is several nanometers. However, the intensity of N-K fluorescence was quite weak, and the total electron yield was measured using a channel electron multiplier. In order to extract the secondary-electrons emitted from nitrogen, the data obtained using soft X-rays of an energy level just below the K-shell absorption edge (399 eV) of nitrogen was subtracted from the data just above the edge. In Figure 1, electron yield from nitrogen (•) and reflectivity (o) measured at BL-8A are plotted against the soft X-ray grazing angle. The calculated intensity of the soft X-ray field at the film surface is also shown.

Discussions

Fig. 1 shows that the electron yield varied in a way similar to the intensity of the standing wave at the surface. Because nitrogen was located in the surface lamella (～ 6 nm thick), it can be seen that qualitatively, the data reflects the film structure. This ensures that the predicted standing wave was formed at the near surface. The determination of the depth profile of the atom density is not successful because of the following problems, (a) low S/N, (b) poor stability of detection system, (c) error due to the data subtraction, and (d) unknown escape depth of secondary electrons from organic films. (a) and (b) are solved by improving the performance of the detection system and by using brighter soft X-ray source. As for (c), elements are distinguished by detecting Auger electrons, and no subtraction is necessary. (d) is rather crucial because the secondary-electron escape depth limits the depth analysis to within a several-nanometer-thick surface lamella. Although secondary-electrons are partially available for the depth analysis, for wide applications, it is still desirable to detect fluorescence.
XAFS study on GeO₂ glass synthesized under high pressure.

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College of General Education, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560

INTRODUCTION

A XAFS spectrum of amorphous germanium dioxide synthesized under high pressure was measured using beam line BL-8B under ambient condition. Melt glass and two types of polymorphs, i.e., α-quartz type (hexagonal) and rutile type (tetragonal), were also measured for references. A thermodynamical behavior of the germanates is known to be similar to that of silicates. An interesting feature is that a given germanate structure will often undergo the same pressure-induced transitions as the corresponding silicate at lower pressure. Therefore, germanates make it easier to model by laboratory study, phase transitions of silicate at higher pressure.

EXPERIMENTAL

Instrument: The XAFS spectra were measured from 10.9 to 12.1 keV by using a double crystal (Si(311)) monochromator. Incident and transmission X-ray intensities were measured by ionization chambers.

Sample preparation: Germanium dioxides of (a) α-quartz type (low pressure form), (b) rutile type (high pressure form), (c) melt glass and (d) high pressure glass were prepared for XAFS measurements. Sample(a): A commercial powder of α-quartz type GeO₂ was heat-treated at 1353 K. Sample(b): Rutile type was made by phase transition from α-quartz type powder under high temperature (773 K) and high pressure (3.0 GPa) for 2 hours and cooled to the room temperature. Sample(c): GeO₂ melt at 1573 K was quenched to the room temperature. Sample(d): α-quartz type powder was processed in a tetrahedral anvil cell under high pressure (13.0 GPa) and room temperature and returned to the atmospheric condition in 10 hours. All GeO₂ samples and powder of lithium oxide, which is almost transparent to X-ray, were ground and pressed into thin pellets of about 200μm in thickness and 14mm in diameter by pelletizer.

ANALYSIS AND RESULTS

Measured EXAFS spectra were analyzed by pattern fitting of χ(k) using least-squares method. Calculated values of f(k) and χ(k) by Mackale et al. were used in the analyses. Fig. 1 shows the radial distribution functions (RDF) of high pressure glass and high temperature glass. The largest peak is assigned to the nearest neighbor oxygen. Analyzed interatomic distances are listed in Table 1. The Ge-O distance of α-quartz type is smaller than that of rutile type. According to the in-situ study by Itie et al., a Ge-O distance of GeO₂ glass increases from 0.174 nm at ambient pressure to 0.184 nm above 10 GPa. It means that a local structure of GeO₂ transforms from GeO₂ tetrahedron to GeO₂ octahedron with increases in pressure. In this study, high pressure synthesized glass(d) was observed in ambient condition. As shown in Table 1, the Ge-O distance of high pressure glass(d) is slightly larger than that of melt glass(c). And the Ge-O distances of two types of glass is larger than that of α-quartz type. However, the difference are small and seemed to be within a error of this analysis.

Table 1. Ge-O and Ge-Ge distance of crystal and amorphous GeO₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R(Ge-O) (nm)</th>
<th>R(Ge-Ge)(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-quartz type</td>
<td>0.1682(2)</td>
<td>0.3147(1)</td>
</tr>
<tr>
<td>rutile type</td>
<td>0.1819(2)</td>
<td>0.3450(1)</td>
</tr>
<tr>
<td>melt glass</td>
<td>0.1686(2)</td>
<td></td>
</tr>
<tr>
<td>high-p glass</td>
<td>0.1693(2)</td>
<td></td>
</tr>
</tbody>
</table>

Ge-K absorption edges of the samples were observed to shift as shown in Fig. 2. To emphasize the shifts, the observed absorption coefficients were differentiated by x-ray energy. The energies at the maximum differential value, i.e. the absorption edges, of sample (a), (c) and (b), (d) shift to higher energy respectively. And the differential profile of high pressure glass(d) is broader than that of high temperature glass. Considering the Ge-O distance of high pressure glass(d), 6-coordinated glass is seemed to be unstable under ambient condition. The slight difference of Ge-O distances and the differential profile between high temperature and high pressure glass suggest that a reconstruction of GeO₂ tetrahedra in the high pressure glass was not performed sufficiently under the quenching process from high pressure.

Micro X-ray Diffractometer Using SR
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INTRODUCTION
Crystal structure analysis is indispensable in development of new materials such as high Tc superconductors and high temperature alloys and there are strong demands for analysis of as-received sample in the micron-order specific region. X-ray diffraction is the most suitable method for these purposes. Several micro-X-ray diffractometers with a one-dimensional detector, such as PSPC, have been developed. However, it is very difficult to obtain both a large enough number of diffracted peaks and diffraction intensity to get reliable analysis due to the following reasons:

1. When the X-ray beam is simply collimated with a small pinhole, the incident X-ray intensity decreases drastically.
2. Debye rings become discontinuous due to a decreased number of crystallites which contribute to diffraction.
3. Diffracted intensity decreases owing to decrease of the number of atoms which contribute to diffraction.

Considering the above, a micro-X-ray diffractometer with incident X-ray focusing mirrors and two-dimensional detector using SR has been developed. In this report, the developed apparatus and its performance results are described.

APPARATUS
The developed micro-X-ray diffractometer (1) forms a fine and intense beam by focusing the incident X-rays on a sample using two spherical mirrors which are placed at Kirkpatrick-Baez type (K-B type spherical mirrors) and (2) it improves the detection efficiency of the diffracted X-rays by two-dimensional recording with an imaging plate.

Figure 1 shows a schematic drawing of the developed apparatus. It is installed at the BL8C2 experimental station. The SR formed by a slit is monochromatized and reduced to the horizontal beam width by a double crystal monochromator which consists of symmetrical Si(111) and asymmetrical Si(111) crystals. The asymmetrical factor of 100 at 10 keV photon energy is used. The monochromatized X-rays are focused by the K-B type spherical mirrors. The vertical mirror is designed assuming that the source point is on the SR storage ring, while the horizontal one is designed assuming that it is on the asymmetrical Si(111) crystal. The diffracted X-rays from a sample are recorded on the cylindrical imaging plate and are read out by He-Ne laser. The radius of the imaging plate is 150 mm and the X-rays diffracted within the diffraction angle of 2θ=20°-140° and the azimuthal angle of φ=-40° to 40° can be detected. The Debye rings of the diffracted X-rays become straight lines on the imaging plate due to the adoption of a cylindrical type imaging plate. It allows us to analyze the recorded diffraction lines/spots easily.

The optical microscope is set on the sample stage and the specific point of the sample can be set within 5 μm by coincidence of the X-ray focusing point with the crosshairs in the microscope.

PERFORMANCE RESULTS
The vertical and horizontal widths of the focused X-ray beam at 10 keV were measured by the knife-edge method and they were both about 10 μm at FWHM. The intensity was \(1.4 \times 10^7\) photons/s at 300 mA storage ring current. The increase of the intensity per unit area was about 270 times larger than that without the focusing mirrors.

Figure 2 shows an example of measured diffraction patterns and the optical image of the sample. The sample was the metal superconducting wire of NbTi fine wires buried in the Cu matrix. The diffraction patterns were integrated along the 2θ constant lines. The diffraction patterns from NbTi wires could be observed clearly and distinctly from Cu matrix. However, very weak peaks from the Cu matrix appeared in the diffraction pattern from the #2-NbTi wire. This was caused by expansion of the foot of the focused X-ray beam. This was not so serious for the determination of lattice constants but became a problem for qualitative analysis. Therefore, it was necessary to produce a sharp profile beam.

![Figure 1. Schematic drawing of micro-X-ray diffractometer.](image1)

![Figure 2. Diffraction patterns of NbTi superconducting wire.](image2)
X-RAY IRRADIATION EFFECTS ON A MICROWAVE-PLASMA-CVD DIAMOND MEMBRANE

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Introduction
Diamond is one of the most attractive materials for X-ray mask membranes owing to its unique characteristics, such as high transparency to the both soft X-ray and visible light, high Young's modulus and high thermal conductivity. The major issue in applying the diamond membrane mask for the industrial use is the X-ray irradiation stability. From this point of view we have investigated X-ray irradiation effects on the MPCVD polycrystalline diamond membranes.

Experimental
Diamond films were deposited on 2 mm thick, 75 mm diameter (100) silicon wafers by Microwave Plasma CVD (MPCVD) using a methane-hydrogen gas mixture. The films were nominally 2 μm thick and the thickness uniformity was ± 5% in 25mm diameter. The diamond films are smooth, small-grained, polycrystalline films having tensile stress of 0.7 - 1.5 x 10^7 dyn/cm^2. The average grain size was calculated from the X-ray diffraction data and was typically 50-100 nm. After fabricating Ta patterns on the diamond film with pitches of 2 mm both in rows and columns, the silicon wafer was selectively etched from the back to fabricate a 20 mm square diamond membrane.

The X-ray irradiation for the diamond membranes was carried out using the beam line 9A. Major beam-line components affecting the SR beam spectrum are a 15 μm thick Be-window and a cylindrical SiC oscillating-mirror which not only collimates the SR-beam in horizontal direction but also enlarges the SR-beam exposure area in vertical direction and cutting off hard X-rays. The SR beam irradiated on the diamond membrane is ranging 5-14 Å peaked at 7 Å. The X-ray irradiation for X-ray masks has been carried out in a vacuum. In order to measure the X-ray irradiation effect on the in-plane-distortion most clearly, only a half area of the membrane was irradiated to the SR beam by shielding the other half with a 500 μm thick Si-wafer. The maximum X-ray energy absorbed in the diamond membrane was 15 MJ/cm^2 corresponding to the dose required for 5000 6-inch wafers with 100 mj/cm^2 sensitivity resist.

Results and Discussion
In-plane distortion of the diamond membrane masks were measured before and after X-ray irradiation, using a laser interferometric coordinate measurement system (Nikon 3i). Pattern displacement in the 25mm square diamond membranes having absorbed 15 MJ/cm^2 X-ray in the left half area are shown in Fig. 1. Small (<0.07μm) but rather systematic distortion due to shrinkage of the X-ray irradiated area is observed in both the membrane.

Spin density in the diamond membrane corresponding to carbon dangling bond (g-value; 2.003) increased with X-ray exposure, and was approximately twice as high as that of unirradiated membrane at 15 MJ/cm^2 dose.

Raman spectra were taken by using 488nm laser from the both unirradiated diamond membrane and an X-ray irradiated membrane. After the X-ray irradiation intensity of the diamond peak at 1332cm^1 increased to approximately 150% of that before irradiation. Visible transmission of the membranes was improved 4.5% - 6.1% at 633nm after irradiation.

From these results, it is thought that hydrogen residing in the as deposited diamond have been dissociated by X-ray irradiation, resulting in increase of the spin density. Some of the created carbon dangling bonds have combined with neighbor dangling bonds, leading to shrinkage of the membrane. The change in the Raman spectra suggests that a part of the non-diamond structure has been transformed into diamond after the X-ray irradiation.


Sample : A

Window (25mmx25mm)

Sample : B

Fig.1 In-plane distortion in 25 mm square diamond membranes induced by 15MJ/cm^2 X-ray irradiation on the left half area of each individual samples.
Structural Study of the Si/B(V3 x V3)R30°/Ge,2i,.,(111) Interface  
by Diffraction Anomalous Fine Structure (DAFS)


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Introduction

Although XAFS is well known for chemical specificity, it is neither site specific nor spatially specific; i.e., it cannot distinguish between atoms in different sites or in different parts of the sample. However, by combining the techniques of x-ray diffraction and XAFS, such site and spatial specificity can be realized. This combined method we refer to as DAFS.

Experiment

We have applied DAFS to the (V3 x V3)R30° reconstructed interface in Si/B(V3 x V3)R30°/Ge,2i,.,(111). This is an important material which may exhibit delta-doping, in which the boron-produced holes are trapped at the interface. Our goal is to determine the role of Ge in the reconstruction.

The experiment consists of measuring the integrated peak intensity (Fig. 1) and background (not shown) of the (2/3,2/3) reconstructed peak as a function of x-ray energy across the Ge K-shell absorption edge. Since the background is dominated by Ge fluorescence, the oscillations which are observed in the background level are simply the usual XAFS signal. This gives information about the average environment of all the Ge atoms in the Ge,2i,., layer.

The oscillation in the integrated peak intensity (Fig. 1) is the DAFS signal. Since this peak comes from the reconstructed interface, only those Ge atoms which participate in the reconstruction contribute; thus, the DAFS signal can be analyzed to understand the local structure surrounding just the Ge atoms which are at the interface. We can thereby separate the interfacial Ge from the Ge in the rest of the sample. DAFS is thus spatially specific.

Results and Discussion

Spline-fitting the DAFS data (in Fig. 1) and the XAFS data results in χ(k) for DAFS and XAFS as shown in Fig. 2. The DAFS curve has been multiplied by a factor of 5.0 for easier comparison with the XAFS curve. The magnitude of the Fourier transforms of both χ(k) are plotted in Fig. 3, in which the DAFS values have been scaled up by a factor of 4.5.

Although we are somewhat limited by the quality of the data from this first experiment, the Fourier transforms for XAFS and DAFS appear to show strong differences in the first and third shells. This would indicate that Ge at the interface has a different environment from Ge in the rest of the sample. Further experiments are being conducted, but this initial demonstration of the spatial selectivity of DAFS is very encouraging. We are especially optimistic about the future usefulness of DAFS when the next generation of synchrotron sources become available.

References


Fig. 1 Integrated Peak Intensity versus Energy: DAFS

Fig. 2 DAFS and XAFS χ(k) Data

Fig. 3 Fourier Transforms of DAFS and XAFS
Oxidation Effects on Si(111)-7x7 Superstructures

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Introduction

We are greatly interested to study oxidation process of Si. Previously we have reported on SiO$_2$/Si(111) interface structure prepared at room temperature by molecular beam deposition (MBD) method. However, usually oxide layers are grown above 700°C. Therefore, in this report, a GID investigation on initial oxidation process of Si(111)-7x7 surface at 700°C is presented.

Experiments

To investigate the process of oxidation of Si(111)-7x7 at 700°C, two types of samples were prepared. One was a slightly oxidized sample, the other was a highly oxidized one. These two samples were prepared by the following procedure. After cleaning P' type Si(111) wafers, epitaxial buffer layers of Si were deposited. One sample was then exposed to oxygen up to 15L (slightly oxidized sample), the other one was exposed up to 450L (highly oxidized sample). Then these surfaces were covered with 100Å of amorphous Si. The experiments were performed at BL-9C using incident X-rays of 1.5Å from a Si(111) double-crystal monochrometer. The size of incident beam was 12mm x 1mm and the glancing angle was set to 0.22'.

Results and Discussion

7x7 interface superstructures were observed in both samples. The partial Patterson map of the slightly oxidized sample has several features different from that of the clean Si(111)-7x7 surface observed by Takayanagi. This Patterson map suggests that stacking fault layer and dimer layer are preserved. Existence of ordered layers extending into the a-Si region is also suggested. Through model refinement procedures using Fourier difference map, the atomic arrangements of this sample was obtained as shown in Fig.1. The R-factor of this model is 24% and chi-square is 0.98. This structure is nearly the same as that of the MBD-SiO$_2$/Si(111)-7x7 interface mentioned above. These results indicate that the faulted half is more easily oxidized that the unfaulted half.

As for the highly oxidized sample, the partial Patterson map indicates quite a different structure from that of the slightly oxidized one. First of all, there is no indication of the stacking fault layer and dimer layer, there seems to be several regions whose oxidation stages are different from one another. Therefore it is difficult to derive a unique structure model from our observations. One typical model of this sample is shown in Fig.2. The R-factor and chi-square of this model are 30% and 0.49, respectively. According to this model, there is a remarkable loss of atomic ordering around corner hole. Therefore this model suggests that oxidation advances from the corner hole to the center region of the unit cell. Since it is thought that the region near to corner holes is strained, it may be that oxidation of Si(111)-7x7 occurs preferentially at highly strained regions.

*) 1 Langmuir (L)=10$^{-6}$ Torr sec.

References

INTRODUCTION
There is a great deal of current interest in growing single-crystal films of iron, because they are thought to be attractive candidates for magnetic head materials. In the study of the films grown on GaAs the coercivities were on the order of 50 Oe\(^1\) whereas those grown on ZnSe were on the order of 2 Oe\(^2\). It has not been clear yet why there was a large difference in the two coercivities, but possible reasons include the effect of the different lattice constant of the substrates on the lattice of the iron films. Therefore, we have studied the template effect of the underlayer of MBE-grown Fe\((001)\) films on the Fe\((001)\) crystal structure and the coercivities. Fe\((001)\) films were epitaxially grown on three kinds of underlayers, Ag\((001)\), Cr\((001)\) epilayers which are both grown on MgO\((001)\) substrate and MgO\((001)\). The lattice mismatch of \((001)\) face between Fe and these underlayers are 3.8\%, 0.8\% and 0.45\%, respectively. The lattice constant of Fe\((001)\) face is smaller than those of underlayers.

EXPERIMENTAL
Epitaxial Fe\((001)\), Ag\((001)\) and Cr\((001)\) films were grown on the MgO\((001)\) substrate in the Molecular Beam Epitaxy chamber under the base pressure of \(10^{-9}\)Torr. The thickness of Fe films was 2000 Å in each sample and the buffer layers of Ag and Cr grown on MgO substrate were 2000 Å and 1000 Å in thickness, respectively. One sample of Fe films grown on MgO directly was covered with Cr films of 1000 Å in thickness. The diffraction experiments were carried out at BL-9C with a Huber 5020.4 four-circle diffractometer. 1.488 Å of X-ray wavelength was selected by Si\((111)\) double crystal monochromator.

RESULTS
The lattice constant of \(c\)-axis was obtained with a \((002)\) diffraction position and that of \(a\)-axis was obtained with \((022)\), \((022)\), \((202)\), and \((202)\) diffraction positions. The lattice constant of the \(a\)-axis calculated with these diffractions was in good agreement with each other within 0.03\%. Figures 1 and 2 show the lattice constants of the \(a\)- and \(c\)-axes, and the coercivities of these samples measured utilizing a vibrating sample magnetometer, respectively. The coercivities were measured with a \((100)\) and a \((110)\) directions of magnetic field. As seen in Fig. 1, the crystal structures of all of the Fe films except for the films on MgO were not bcc, but bct. This is because the lattice constants of Ag and Cr are both larger than that of Fe, then, the in-plane lattice constant of Fe was expanded and it’s lattice constant along the growth direction was compressed as compared the bulk bcc Fe. On the other hand, the lattice mismatch between Fe and MgO is so much that the critical thickness for a pseudomorphism must be less than 2000 Å. Therefore, the crystal structure of Fe films of 2000 Å in thickness grown on MgO was the same as that of bulk \(\alpha\)-Fe. From Fig. 2, we can see a relation between the lattice constant and coercivity and it seems to be an optimum lattice constant to get the lowest coercivity of Fe.

EXAFS STUDY ON Tl$_2$Ba$_2$CuO$_{6+\delta}$ COMPOUNDS

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Introduction

Many different types of Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2201) compounds have been prepared by various heat treatments. It has been found that the appearance of superconductivity is independent of the structural symmetry, but is affected by oxygen content[1]. Crystal structures of Tl-2201 compounds have been well-characterized by neutron and X-ray diffraction methods[2,3]. Two structures with different symmetries, orthorhombic and tetragonal, have been reported for these Tl-2201 compounds[1,4]. Hewat et al. prepared a non-superconducting Tl-2201 compound with an orthorhombic symmetry. They discussed the appearance of superconductivity in this compound in terms of its structural symmetry and degree of ordering; that is, the non-superconducting orthorhombic phase is ordered over a long distance, while the superconducting tetragonal phase is ordered at only short range[4]. Thus, it is very interesting to examine the relation between superconductivity and local structure in the CuO$_2$ plane. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a useful probe for investigating short range pair-distribution functions in solids.

Experimental

The EXAFS measurements were carried out at BL-9C. The measurements were done on the Cu K-edge at room temperature in the transmission mode. Four kinds of Tl-2201 compounds were studied: superconducting tetragonal, non-superconducting tetragonal, superconducting orthorhombic and non-superconducting orthorhombic. These were prepared by the standard method[1]. Superconductivity was tested by AC susceptibility measurements and structural studies were carried out by X-ray powder diffraction. The samples for EXAFS measurements were prepared by powdering, and filtering through a 20µm sieve. The powdered samples were deposited uniformly onto Scotch tape.

Results and Discussion

In the EXAFS analysis to determine local structure parameters, the standard procedure was adopted[5]. Figure 1 shows the Fourier transform of k$^2$ weighted EXAFS spectra around Cu atoms in the tetragonal non-superconducting sample.

The best-fit results of the EXAFS analysis are tabulated in Table I. Among the various Tl-2201 compounds, no differences in the Cu-O interatomic distances in the CuO$_2$ plane are observed by our EXAFS analysis, within our experimental resolution of ±0.01Å. In the CuO$_2$ plane the EXAFS results, which are based on short-range order, are in good agreement with the results from X-ray diffraction, which are based on long-range order.

To confirm this results and determine the local structure parameters in the axial Cu-O bonds, we plan to measure polarization-dependent EXAFS using a single crystal in the near future.

Table I. Local structure parameters in CuO$_2$ plane at 300K : the least-Square refined, Cu-O interatomic distance, MSD($\sigma$ (2)) and coordination number(N).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-O (Å)</th>
<th>$\sigma$ (2) (Å$^2$)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal super</td>
<td>1.931</td>
<td>0.0035</td>
<td>4.00</td>
</tr>
<tr>
<td>non-super</td>
<td>1.934</td>
<td>0.0027</td>
<td>4.16</td>
</tr>
<tr>
<td>Orthorhombic super</td>
<td>1.938</td>
<td>0.0036</td>
<td>3.99</td>
</tr>
<tr>
<td>non-super</td>
<td>1.931</td>
<td>0.0077</td>
<td>3.84</td>
</tr>
</tbody>
</table>
The rubber-like behavior in Au-47.5at% Cd alloy has been known for 60 years and occurs by a reversible twin boundary movement after stabilization. The mechanisms of the rubber-like behavior in atomic scale are proposed by many researchers. However, there is no experimental proof for those mechanisms. One of the most interesting mechanisms proposed by Lieberman is that the structural change occurs after twin boundary movement. We measured the integrated intensities to detect the structural change after the twin boundary movement and found that there is no change in intensities after the twin boundary movement; that is, no structural change occurs. For further study, reflection profiles were examined precisely in this study to try to explain the rubber-like behavior.

Experimental

The BL-10A was utilized to detect the profile changes after the twin boundary movement. The PSPC was attached on a 2θ arm to measure precise changes of the profiles with a situation that a scintillation counter can be available also. The crystal was mounted on a tensile jig to move the twin boundary with tension. The crystal orientation was preliminary determined and the reflection was firstly refined by the scintillation counter. The 2θ was shifted to place a reflection at a center of the PSPC counter. The profile change was measured for 500 sec by the PSPC and a multi channel analyzer. The ω axis was moved by 0.2 degree to measure a whole profile of the reflection. To use the synchrotron radiation with strong intensity and the PSPC is helpful to measure a small change of the profile.

Results and Discussion

A small change in profile was found by the measurements. The profile of 040 reflection is shown in Fig. 1. The profile was reversed about the peak position and subtracted from the original one to see the main reason of the change. It will be easy to see what happened after the twin boundary movement. The profile becomes asymmetry after the twin boundary movement.

A schematic picture of the profile changes in reciprocal space was shown in Fig. 2. The Ewald sphere and reciprocal axes projected on the equator are shown.

Two possibilities were considered on this profile change. One is a Huang scattering from defects. The effect from the Huang scattering appears symmetrically. However, the profiles become asymmetry. Another is a size effect of atoms. In general, the size effect appears asymmetrically. The profiles now measured become asymmetry after the twin boundary movement; that means twin boundary movement may induces a rearrangement of atoms which have different atomic radii.

References

X-RAY SINGLE-CRYSTAL STUDY OF A SUPERCONDUCTIVE Tl$_2$CaBa$_2$Cu$_2$O$_8$
AT 296 K AND 104 K

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Introduction

A Tl-Ca-Ba-Cu-O system with 120 K superconductivity was found soon after the report of the Tl-Ba-Cu-O system.\(^1,2\) In contrast with the Y-Ba-Cu-O system, the Tl-Ca-Ba-Cu-O system is rather simple because there are no Cu-O chains and the $T_c$ increases with a rise in the number of Cu-O layers in the unit cell.

Since the discovery of high-$T_c$ superconductors, much effort has been devoted to understand the mechanism of superconductivity. Partially filled 3d orbitals of the transition metal are affected by a strong crystal field with a symmetry and also considered to influence the superconductivity. Therefore, we have examined single crystals with good quality of a Tl$_2$CaBa$_2$Cu$_2$O$_8$, based on the electron density in crystals. The 110 K superconductor makes possible the use of low-temperature equipment of a cold-gas-flow type at BL-10A.\(^3\) This is a preliminary report to study crystal structures and electron distributions around Cu and the other atoms below the $T_c$.

Experimental

Single crystals of Tl$_2$CaBa$_2$Cu$_2$O$_8$ were grown from an oxide melt of Tl$_2$O$_3$-2CaO-3BaCuO$_2$ by a slow-cooling method. A single crystal of 370 x 250 x 100 mm was cut into four pieces which were used for the x-ray and magnetization measurements. The SQUID magnetometer measurement showed that the crystal has diamagnetism below 108 K.

A single crystal was ground into a sphere of 120 mm in diameter and used for crystal structure analyses. The x-ray precession photographs showed the space group $I4/mmm$. Integrated intensity data up to $\sin \theta/\lambda = 1.37$ were collected at the $\omega$-2$\theta$ scan mode at temperatures of 296 K (Mo $K\alpha$) and 104 K ($\lambda = 0.6$ Å; monochromatized by Si(111) at BL-10A). After Lorentz, polarization and absorption corrections ($\mu = 518.2$ cm$^{-1}$ for Mo K$\alpha$; $\mu = 317.1$ at $\lambda = 0.6$ Å), all parameters were refined simultaneously using a full-matrix least-squares program RADY.\(^4\) Final $R$ and $R_w$ values for refinements are 0.023 and 0.014 at 296 K and 0.016 and 0.021 at 104 K, respectively.

Results and discussion

The final positional and thermal parameters obtained in refinements are listed in Table 1 together with cell parameters. The two pyramid Cu-O layers alternately stack with a layer of Ba-O and double layers of Tl-O. The O(3) atoms occupy fully 4e sites (1/2, 1/2, z) instead of 16n sites.\(^5\) The site-occupancy refinement shows that the Tl sites are occupied by 1.70(5) Tl + 0.30 Cu, while the Ca sites are occupied by 0.839(2) Ca + 0.161 Ba. The Ba, Cu and O sites are fully occupied by the respective atoms. The above results well coincide with the chemical formula obtained by EPMA. Difference-Fourier maps are currently analyzed using the data measured at two temperatures.

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Crystal chemical role of Mg cation in anorthite

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The last few decades have seen a vehement controversy about the extent of chemical deviation from the \( \text{AT}_{2}\text{O}_{5} \) ideal formula of feldspar[1]. The importance of Mg cation in plagioclases has been extensively debated for the past ten years. To develop penetrating insights into crystal chemical role of MgO composition in anorthite synthesized along the join \( \text{CaAl}_{2}\text{Si}_{2}\text{O}_{8}-\text{CaMgSi}_{2}\text{O}_{8} \) was a major focus of the present works.

X-ray reflection data for Mg-bearing anorthites were collected using an automated four-circle diffractometer combined with synchrotron radiation at the BL-1OA station, KEK. Chemical compositions of synthetic anorthites with a length of several tens micron were determined using JEOL JXA-8621 electron microprobe. Lattice constants of their Mg-bearing anorthites, as represented in Table 1, gradually enlarge with increasing MgO concentration.

Chemical shift of MgKα lines pointing to the coordination state of Mg in silicates was accurately estimated by wavelength dispersive technique of EPMA. Majorite, \( \text{[\text{Mg}_{8}\text{Si}_{6}\text{O}_{18}]^{3-}} \), with the garnet structure [2] has three magnesiums eight-coordinated and one six-coordinated, and akermanite, \( \text{[\text{Ca}_{2}\text{MgSi}_{2}\text{O}_{8}]^{10-}} \), with the melilite structure [3], has one magnesium tetrahedrally coordinated. Fig. 1 goes to prove that the wavelength range of \( ^{5}\text{Mg} \) does not coincide with that of \( ^{56}\text{Mg} \) and that the present anorthites are plotted within the range of \( ^{57}\text{Mg} \). Structural behaviour of MgO in anorthites leads to solubility of \( \text{CaMgSi}_{2}\text{O}_{8} \) endmember rather than \( \text{MgAl}_{2}\text{Si}_{2}\text{O}_{8} \). The role in crystal chemistry establishes Tschermak substitution, \( \text{Mg}+\text{Si} \rightarrow \text{2Al} \), in only tetrahedral sites.


Table 1. Cell dimensions chemical composition of anorthites

<table>
<thead>
<tr>
<th>Synthentic Anorthite</th>
<th>Cell Dimensions ( (\text{CaAl}<em>{2}\text{Si}</em>{2}\text{O}<em>{8} \cdots \text{CaMgSi}</em>{2}\text{O}_{8}) \text{ system} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (( \text{A} ))</td>
<td>8.177(1) 8.169(1) 8.171(5) 8.178(1)</td>
</tr>
<tr>
<td>( \beta ) (( \text{A} ))</td>
<td>12.867(1) 12.860(1) 12.856(9) 12.863(2)</td>
</tr>
<tr>
<td>( \gamma ) (( \text{A} ))</td>
<td>7.083(1) 7.073(1) 7.072(4) 7.072(4)</td>
</tr>
<tr>
<td>( \rho ) (( \text{deg} ))</td>
<td>93.214(8) 93.213(9) 93.19(6) 93.170(9)</td>
</tr>
<tr>
<td>( \phi ) (( \text{deg} ))</td>
<td>115.835(1) 115.848(1) 115.77(5) 115.860(7)</td>
</tr>
<tr>
<td>( \omega ) (( \text{deg} ))</td>
<td>91.192(2) 91.184(2) 91.33(8) 91.259(8)</td>
</tr>
<tr>
<td>( \chi ) (( \text{deg} ))</td>
<td>98.8(2) 98.7(2) 98.7(2) 98.7(2)</td>
</tr>
<tr>
<td>Number of measurement points</td>
<td>62 82 105 40</td>
</tr>
</tbody>
</table>

Fig. 1. WD spectra and intensity for the Kα emission peaks of Mg in akermanite, majorite and synthetic Mg-bearing anorthite.
THE INTERSITE DISTRIBUTION OF A SMALL AMOUNT OF Mn ION IN OLIVINE

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Introduction

Olivine (MgSi2O4), one of the most popular minerals in the upper mantle, contains non-equivalent M1 and M2 sites and their intersite distribution of cations is of importance in geoscience. Various cation-systems have been investigated[1-2] and an anomalous scattering factor with synchrotron radiation is effective for determination of intersite distribution. But when the existence of one component of ternary cation system is very small, determination of distribution of the small amount of ion by ordinary X-ray diffraction method remains much difficulty. We tried to give a statistical inspection of intersite distribution of only 1.4 mol% of Mn ion in (Fe,Mg,Mn)2Si2O4 by repeated data collection of particular reflections, and introduction of order-disorder structural models.

Experimental

The sample of natural crystal was shaped into an ellipsoid with the dimension of 200x150x150 mm³. Data collection was made by two wave length of 1.8983Å and 1.9093Å, which are close to the Mn-absorption edge(1.8964Å) and monochromated by Quartz(110) crystal. After assuming an order and a disorder models about M1-M2 site distribution of Mn ion, seven reflections were selected and summarized in Table 1. In former three refractions, the difference of calculated F between two wave length with both models were almost zero, while in the later four ones, the differences are large in ether models. Integrated intensities were repeatedly collected about 14 times with the seven reflections set.

Result and discussion

Intensity data were corrected by Lorentz-polarization factor and damping effect of the beam current against time, regarding themselves as standard reflections. From the comparison of R-factors with two structural models, any remarkable difference between the two models were observed. The reasons are assumed as below and now preparing for next experiment.

1) The crystal size was too large for exact correction of extinction factor.
2) The scintillation counter used so many times seem to have not good sensitivity against long wave length radiation.
3) Ensuring the confidence of the data, more numbers of the reflections are needed.

References


Table 1. Measured seven reflections and their calculated structure factor.

<table>
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<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>F(s)</th>
<th>F(l)</th>
<th>DF</th>
<th>F(s)</th>
<th>F(l)</th>
<th>DF</th>
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<td>.00</td>
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<td>.00</td>
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<td>8</td>
<td>1</td>
<td>2</td>
<td>21.83</td>
<td>21.82</td>
<td>.01</td>
<td>21.63</td>
<td>21.60</td>
<td>.03</td>
</tr>
<tr>
<td>9</td>
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<td>1</td>
<td>8.70</td>
<td>8.76</td>
<td>.06</td>
<td>8.25</td>
<td>8.26</td>
<td>.01</td>
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</table>

s - λ = 1.8993Å, 1 - λ = 1.9093Å
Diffuse X-ray Scattering Study on Sublattice Ordering in In_{x}(Al_{y}Ga_{1-y})_{1-x}P

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2) Institute of Applied Physics, University of Tsukuba, Tsukuba 305:
3) Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Midori-ku, Yokohama 227:
4) Photon Factory, National Laboratory for High Energy Physics, Tsukuba 305

Studies on the ordered structure in In_{x}(Al_{y}Ga_{1-y})_{1-x}P, grown on a (001) GaAs substrate, were motivated by an unexpected bandgap variation depending on the growth temperature and on V/III molar ratios in the gas phase composition.\(^1\)

Super-structure reflections due to the ordered structure are occasionally associated with straight or wavy diffuse scattering rods. This scattering intensity distribution provides information on ordering among the atoms. In analyzing the ordering of the column-III atoms, a hypothetical crystal which has the f.c.c. lattice occupied by these column-III atoms is assumed.

A diffuse scattering rod has reasonably good axial symmetry. A set of intensity distributions in a repeating unit of the reciprocal space was completed according to this symmetry, using the data measured in the plane where the diffuse scattering rods lie. After conversion into absolute values\(^2\), the intensity distribution was Fourier-transformed to obtain the Warren-Cowley short-range-order parameters in the real space.

Figure 1 shows a map of scattering intensity in the reciprocal space, obtained for the [111] ordered structure. Table 1 lists some of resultant Warren-Cowley short-range-order parameters. The structure derived using these parameters is the same as the one for the ordered structure proposed on the basis of electron diffraction and TEM studies.\(^3\) The tendency for the same kind of atoms to exist in the [110] direction is significant, reaching as far as the 10th neighbor. Correlation between atoms of different kinds is observed up to the 4th neighbor in both [110] and [001] directions. After that, however, the same kind of atoms tend to align in the [001] direction. It is considered that a trace of the [110] ordering is left. Different values of the correlation length obtained in different directions indicate the mechanism whereby the column III atoms are piled up to form the ordered structure. Consequently, studies on diffuse X-ray scattering are able to reveal the ordered structure and the mechanism that forms it in semiconductor alloys.

Acknowledgements
The authors would like to thank Dr. Y.Ohba and Mr. H.Sugawara for supplying samples. They also thank Ms. E.Yamamoto for her assistance with the computer calculations. Finally, they thank Dr. A.Hojo for his continual encouragement during this study.

References

Fig.1. Scattering intensity on an arbitrary scale in the (110) reciprocal lattice plane.

Table 1. Warren-Cowley short-range-order parameters.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>r</th>
<th>c</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>0.086</td>
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<td>0.024</td>
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<td>0</td>
<td>0.016</td>
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<td>-6</td>
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<td>0</td>
<td>0.012</td>
<td>1</td>
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<td>-8</td>
<td>-8</td>
<td>0</td>
<td>0.009</td>
<td>0</td>
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<td>-10</td>
<td>-10</td>
<td>0</td>
<td>0.007</td>
<td>3</td>
</tr>
<tr>
<td>-20</td>
<td>-20</td>
<td>0</td>
<td>0.001</td>
<td>2</td>
</tr>
<tr>
<td>-30</td>
<td>-30</td>
<td>0</td>
<td>0.000</td>
<td>1</td>
</tr>
</tbody>
</table>
EXAFS STUDIES ON OXIDATIVE DISRUPTION OF SUPPORTED RHODIUM CATALYSTS BY O₂ AND CO
Takakazu FUKUSHIMA
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Introduction
In the previous studies 1, 2) we have shown the oxidative disruption of alumina- and silica-supported Rh catalysts by O₂ and CO. In comparison of the results from IR with EXAFS studies, we come to the conviction that the presence of di-carbonyl species in IR spectra on CO adsorption experiments stands for rhodium particles on the catalyst surface being oxidatively disrupted. Among the additives to Rh/SiO₂, Zn is the unusual element producing only tiny di-carbonyl and bridged bands in IR spectra when CO was introduced over Rh-Zn/SiO₂.

In the following we report the effect of Zn addition to Rh/SiO₂ on the disruption of Rh particles by O₂ and CO.

Experimental
The catalysts were prepared and reduced by the method described elsewhere 3). The sample powder was pressed into wafer and mounted in a glass cell. The EXAFS measurements were carried out in appropriate gas atmospheres at r.t. by use of the EXAFS spectrometer at the Beam Line 10B.

Results and Discussion
Fourier transforms of the Rh K-edge EXAFS of 0.5wt% Rh/SiO₂ and Rh-Zn(1:1)/SiO₂ catalysts are shown in Fig. 1. All of the EXAFS parameters obtained by curvefitting for Rh/Al₂O₃, Rh/SiO₂, and Rh-Zn/SiO₂ catalysts, carried out in this project are summarized in Table 1.

By the results of IR studies, it could be conclude that Rh particles dispersed on Al₂O₃ are disrupted much easily than on SiO₂ by CO chemisorption and this is confirmed by EXAFS technique showing the smaller coordination number for Rh/Al₂O₃ than Rh/SiO₂ when CO is introduced on the reduced state. Although Rh particle in the reduced state on SiO₂ is not disrupted to atomic state perfectly by CO adsorption, one in the oxidized state is easily converted to di-carbonyl species.

In contrast to these results, Rh-Zn/SiO₂ sample shows the presence of small Rh particles even after O₂ adsorption while no di-carbonyl bands are observed by the IR studies where the content of Zn is increased. The presence of no di-carbonyl bands tells us the evidence that it is hard for Rh-Zn/SiO₂ catalyst to be disrupted to the atomically dispersed state because Zn plays the role of glue for Rh particles. Indeed, as described in the previous sentence, the bridged carbonyl species are not produced by the addition of Zn to Rh/SiO₂. These results indicate that Zn covers over Rh particle at least partially and blocks CO to adsorb on the ensemble site of Rh and eventually prevent Rh particle from being disrupted to atomically dispersed state.

References

Table 1. Curvefitting results for supported Rh catalysts.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>1wt% Rh/Al₂O₃</th>
<th>0.5wt% Rh/SiO₂</th>
<th>0.5wt% Rh-Zn/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂, at 400 C</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>H₂ at r.t.</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>Passivation, H₂ at r.t.</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>Passivation only</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>H₂, at 400 C, CO at r.t.</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>H₂, at r.t., CO at r.t.</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
<tr>
<td>Passivation, CO at r.t.</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
<td>R(A) R(A)</td>
</tr>
</tbody>
</table>

- As the peak height is so low that the parameters can't be obtained by the curve fitting.
EXAFS STUDY ON THE MODULATED (Ca,Sr)\(_2\)(Mg,Co,Zn)Si\(_2\)O\(_7\)  MELILITE SOLID-SOLUTION

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Hironobu Maeda\(^3\), Shuichi Emura\(^4\), and Kichiro Koto\(^5\)

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\(^2\)Faculty of Science, Yamaguchi University, Yamaguchi 753
\(^3\)Faculty of Science, Okayama University, Okayama 700
\(^4\)The Institute of Scientific and Industrial Research, Osaka University, Osaka 567
\(^5\)Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770

Introduction

The structure of melilite X\(\text{T'}\)\(\text{T}^\text{g}\)\(\text{O}_{8}\) is a tetragonal lattice (space group \(\text{I}4\text{I}2\_\text{m}\)). The \(\text{T}^\text{g}\) cations are tetrahedrally coordinated by four oxygens all of which are shared by adjacent \(\text{T}^\text{g}\)\(\text{O}_{4}\) double tetrahedra. The linkage of \(\text{T}^\text{g}\) and \(\text{T}^\text{g}\) tetrahedra forms five-membered rings forming sheets parallel to (001). These sheets are linked together by large X cations. Iishi et al. found that the Ca\(_2\)Co\(_{1-x}\)Sr\(_{x}\)Si\(_2\)O\(_7\) solid-solution with Sr/(Sr+Ca) ratio between 0.0 and 0.3 and the Ca\(_2\)Co\(_{1-x}\)Mg\(_{x}\)Si\(_2\)O\(_7\) and Ca\(_2\)Zn\(_{1-x}\)Mg\(_x\)Si\(_2\)O\(_7\) solid-solution with a whole range at room temperature exhibit an incommensurate phase with rectangular modulation in the [110] direction. And also Armbruster et al. proposed explanation concerning the X-0 and T-0 distances in the average model compared to the actual structure by means of the libration of the cation both X and T sites. In this study, local structure around the X and T' site cations have been investigated by the EXAFS method in order to interpret the modulated melilite structure.

Experimental and analysis

In this study the PXE method was applied to synthesize single crystals of the Ca\(_{2-x}\)Sr\(_x\)Co\(_{1-x}\)Mg\(_x\)Si\(_2\)O\(_7\), Ca\(_{2-x}\)Co\(_{1-x}\)Mg\(_x\)Si\(_2\)O\(_7\), and Ca\(_{2-x}\)Zn\(_{1-x}\)Mg\(_x\)Si\(_2\)O\(_7\) compositions. The X-ray absorption measurements near the Sr K-, Co K-, and Zn K-edge were made with synchrotron radiation at the beam line 10B of Photon Factory in KEK. EXAFS interference function was extracted from the measured absorption data using standard techniques. The structure parameters were determined by the least-squares parameter fitting with analytical EXAFS formula. The amplitude and the phase function employed here were the theoretical curves tabulated by Teo and Lee. Details of the data processing procedure were already given in references.

Results and Discussion

Fig. 1 shows the tendency of anisotropy of thermal ellipsoids determined by averaged structural refinement in the melilite with modulated structure. The actual bond-distance determined by EXAFS method for X site is shorter and that for the T' site is longer than the mean bond-distance determined by X-ray diffraction methods. These facts obtained by EXAFS method clarify the libration of X site and T' tetrahedron by X-ray diffraction method. Examination of these values yields a conclusion that the modulated structure in melilite is caused by the simultaneous and mutual interference of the libration of ions at the X and T' sites and that the cation in X site and oxygen atoms around T' site is located at off-center of the average position determined by diffraction and the libration of the X polyhedron and T' tetrahedron is anticipated.

References

2) T. Armbruster et al., Am Miner., 75:847 (1990)

Table 1. The X-0 (Sr-O) and T'-0 (Co-O and Zn-O) distance determined by both of the EXAFS method and the X-ray diffraction method.

<table>
<thead>
<tr>
<th></th>
<th>EXAFS</th>
<th>X-ray</th>
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<tbody>
<tr>
<td>Sr-O</td>
<td>2.619</td>
<td>2.625A</td>
</tr>
<tr>
<td>Co-O</td>
<td>1.936</td>
<td>1.948A</td>
</tr>
<tr>
<td>Zn-O</td>
<td>1.974</td>
<td>1.976A</td>
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Fig. 1. The tendency of anisotropy of thermal ellipsoids determined by averaged structural refinement in the melilite with modulated structure.
CHARACTERIZATION OF HYDROFORMYLATION-SELECTIVE STRUCTURE OF SiO₂-SUPPORTED [Ru₆C(CO)₁₆(CH₃)]

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•The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan

Introduction

Metal clusters have metal ensemble, and can be good models for catalysis on multimetal site which never proceeds on single metal complexes. There have been lots of researches for supported cluster catalysts, but the aggregation of metal cluster or transformation to smaller cluster on support make it difficult to observe the reaction mechanism. We prepared a supported cluster from ruthenium carbido-carbonyl cluster, [Ru₆C(CO)₁₆(CH₃)]⁻ which has an interstitial carbon inside Ru₆ framework with the expectation that the cluster framework is retained under catalytic reaction with the stabilization by the interstitial carbon.

Experimental

[BTMA][Ru₆C(CO)₁₆(CH₃)]⁻ (BTMA = PhCH₂N(CH₃)₃) (Fig. 1) was supported on SiO₂ (#952, Fuji-Davison Chem.) in CH₂Cl₂ which was refluxed and distilled before use. The EXAFS of Ru K-edge were observed at BL 10B.

Results and Discussion

At the process of impregnation no gas was desorbed and prepared cluster showed very similar EXAFS oscillation to [Ru₆C(CO)₁₆(CH₃)]⁻ crystal. Such EXAFS pattern was retained at 473 K in CO + H₂ (26.6 kPa, 1:1) (Fig. 2, Table 1). These results show the retention of octahedral cluster framework because of the stabilization by the interstitial carbon.

The methyl ligand was reacted to form mainly acetaldehyde (82%) at 373 - 473 K in CO + H₂. This CO insertion reaction proceeded on octahedral Ru₆C, Table 1. Curve fitting results for the EXAFS data in Figure 2.

(a) Ru-C

<table>
<thead>
<tr>
<th>T/K</th>
<th>R/Å</th>
<th>σ/Å</th>
<th>Rf</th>
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<tbody>
<tr>
<td>473</td>
<td>2.6</td>
<td>1.92</td>
<td>0.065 0.051</td>
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</tbody>
</table>

X-ray

(b) Ru-Ru (Ru-Ru first coordination) + Ru(-C)-O

<table>
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<tr>
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<th>Ru-Ru</th>
<th>Ru(-C)-O</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>3.7</td>
<td>2.91</td>
<td>0.047 0.031 0.020</td>
</tr>
</tbody>
</table>

X-ray

(c) Ru(-C)-Ru (Ru-Ru second coordination)

<table>
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<th>T/K</th>
<th>N</th>
<th>R/Å</th>
<th>σ/Å</th>
<th>Rf</th>
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</thead>
<tbody>
<tr>
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<td>1.1</td>
<td>4.10</td>
<td>0.069 0.032</td>
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</table>

X-ray

*1: The results of X-ray analysis for [BTMA][Ru₆C(CO)₁₆(CH₃)]⁻ by X-ray measurement.

Figure 1. The structure of [Ru₆C(CO)₁₆(CH₃)]⁻ by X-ray measurement.

Figure 2. EXAFS spectra for Ru K-edge of [Ru₆C(CO)₁₆(CH₃)]⁻/SiO₂ in CO + H₂ (26.6 kPa, CO : H₂ = 1:1) at 473 K; (a) k²-weighted EXAFS oscillation, (b) its associated Fourier transform, and curve fitting analyses for Ru-C (c), Ru-Ru + Ru(-C)-O (d), and Ru(-C)-Ru (e); : observed, -----: calculated.

not on decomposed cluster, from previous data of EXAFS. As a probe catalytic reaction through CO insertion process we observed ethene hydroformylation (C₂H₄ : 17.3, CO : 3.3, H₂ : 10.6 kPa, 398 K) after acetaldehyde formation at 398 K in CO + H₂. The propional selectivity was 100% and we suppose similar mechanism to CO insertion process to ligand CH₃ also for this catalytic cycle after ethyl species are formed on Ru₆C site.
STRUCTURE OF BIMETALLIC COLLOIDAL CATALYSTS

—Pd/Au Bimetallic Clusters Prepared by the Simultaneous Reduction—

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The University of Tokyo, Hongo Bunkyo-ku, Tokyo 113

Introduction

The colloidal dispersions of noble metals protected by polymers can be prepared by reducing the noble metal ions by refluxing the solution of alcohol or alcohol/water containing water-soluble polymers such as polyvinylalcohol and poly(N-vinyl-2-pyrrolidone). The colloidal dispersions thus obtained are stable and composed of the fine metal particles with uniform size, and work as catalysts with high activity and selectivity for the hydrogenation of olefins and dienes,\(^1,2\) the light-induced hydrogen generation from water, and so on.

Bimetallic colloidal dispersions are interesting from a viewpoint of a model for a heterogeneous catalyst of multi-components. However, few have been reported on the bimetallic clusters. Here we would like to report the structure of Pd-Au bimetallic clusters which can work as the catalysts for the selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctene. The extended x-ray absorption fine structure (EXAFS) associated with the K-edge of palladium and the L\(_g\)-edge of gold is a useful tool for the structure determination.

Experimental

The bimetallic clusters at the various ratios of gold and palladium were prepared by refluxing the mixed solution of the corresponding ions in water-ethanol under nitrogen. These bimetallic clusters were concentrated by evaporating the solvent under reduced pressure, and the concentrated solutions were sealed in the 50 mm (for palladium) and 5-10 mm (for gold) cells under nitrogen. The EXAFS spectra were measured at a BL-10B station of the Photon Factory, KEK.

Results and Discussion

Palladium cluster is an active catalyst for hydrogenation of 1,3-cyclooctadiene, while colloidal gold is inactive for the hydrogenation. When palladium-gold bimetallic clusters at different molar ratio were used as the hydrogenation catalysts, it was found that the activity varies with the ratio of Pd to Au and the Pd/Au(4/1) bimetallic clusters have the highest activity. Figure shows the Fourier transforms of the Pd K-edge EXAFS of the colloidal dispersions of the Pd/Au bimetallic clusters at the various ratio. Decreasing the Pd content, the main peak splits into two. This can be attributed to a Pd-Au bond as well as a Pd-Pd bond because of the phase shift arising from the interference between the Pd and Au atoms. The EXAFS data of these bimetallic clusters can provide informations on the structure of the Pd/Au bimetallic clusters. The EXAFS data are shown in TABLE. The coordination number of Au atoms around the Au atom suggests that the Au atoms are located at the center of the cluster (Au core structure), and that the coordination numbers are different both from those calculated for the random model and from those of the mixture of the monometallic Pd and Au clusters.

Reference


![Distance R(A)](image)

**Fig.** The Fourier-transformed EXAFS spectrum at K-edge of Pd of the Pd/Au bimetallic clusters at the various Pd/Au ratios.

**TABLE :** Coordination Numbers around the Pd and Au Atoms of the Pd/Au = 4/1 Bimetallic Cluster Determined from EXAFS Data

<table>
<thead>
<tr>
<th>Absorbing metal</th>
<th>Scattering metal</th>
<th>Interatomic distance r/A</th>
<th>Coordination number N</th>
<th>Observed</th>
<th>Au core</th>
<th>Random</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Pd</td>
<td>2.76±0.03</td>
<td>4.1±1.2</td>
<td>5.4</td>
<td>6.9</td>
<td>5.4±2.8</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>Au</td>
<td>2.75±0.03</td>
<td>3.1±1.7</td>
<td>1.4</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>Au</td>
<td>2.81±0.03</td>
<td>6.2±2.7</td>
<td>8.3</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>Pd</td>
<td>2.77±0.03</td>
<td>4.4±1.7</td>
<td>5.7</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
QUANTITATIVE ANALYSIS BY MEANS OF X-RAY ABSORPTION EDGE SPECTROMETRY

Masaharu NOMURA
Photon Factory. National Laboratory for High Energy Physics
Oho 1-1. Tsukuba, 305 JAPAN

The concept of X-ray absorption edge spectrometry was developed in 1925 by Glocker and Frohmayer. They measured absorbances at several energies above and below an absorption edge. This method has many advantages compared with other spectrochemical methods. Elemental selectivity, absence of matrix effect and little interference are the most important ones. But its sensitivity was rather low compared with X-ray fluorescence method.

On the other hand, X-ray fluorescence analysis has become popular because of its fairly high sensitivity, but it suffers serious matrix effect and interferences. Also it is not so easy to analyse small amount of an element in a large amount of slightly lighter elements: such as zinc in copper. By using the methods developed for X-ray absorption fine structure experiments and analyses, the sensitivity of X-ray absorption edge spectrometry has much improved. This method realize a quantitative analysis free from working curve, matrix effect and interferences.

Experimental

Silver-cadmium test solutions were prepared by mixing weighed amounts of silver and cadmium standard solutions for atomic absorption analysis (1000 ppm). X-Ray absorption spectra were measured at BL10B using a Si(311) channel-cut monochromator. Although apparent absorbance, $\ln (I_0/I)$, is different from true one, the variation of absorbance at an absorption edge (hereafter called as edge-jump) is the same as that of true absorbance.

Results and Discussion

Spectra were analyzed according to usual manner used in data analysis of EXAFS. The large variation of absorbance is directly obtained from the extrapolation of $\mu k^{-1}$. However, minute one is obtained from $\langle k^2 \chi(k) \rangle_{10}/k^2$. Theoretical mass absorption coefficients were obtained from references 2-4. They agreed within 10%.

Two methods were tested. One is the direct comparison of observed and calculated edge jumps (edge-jump method). If the density and the thickness of a sample is already known, the concentration can be calculated from eq.1.

$$\Delta \ln (I_0/I) = \Delta \mu_{\text{Cd}}, \frac{\rho d}{W_i}$$

Here $\Delta \ln (I_0/I)$, is the observed edge-jump, $\rho$ the density (g/cm$^3$), $d$ the thickness (cm). $\Delta \mu_{\text{Cd}}, W_i$ is the variation of authentic mass absorption coefficient at the absorption edge (cm/g) and weight fraction of $i$-th element, respectively. Accurate information on $\rho$ and $d$ is inevitable in this method.

The second method is to get the ratio of edge-jumps of minor and major elements in a solution then calculate the concentration of the minor element according to eq.2 (ratio method).

$$\frac{\Delta \mu_{\text{Cd}}}{\Delta \mu_{\text{Ag}}} = \frac{\Delta \mu_{\text{Cd}}, W_i}{\Delta \mu_{\text{Ag}}, W_i}$$

As the concentration of the major element, $W_i$, can be determined easily by means of other analytical methods, that of the minor element is determined easily. In the latter method, no information on the density and thickness of the sample is not required.

Both methods showed good agreement with the results calculated from authentic mass absorption coefficients and known concentrations as shown in Figures.

References


![Working curve of Cd-Ag solution by edge-jump method.](image1)

![Working curve of Cd-Ag solution by ratio method.](image2)
CHARACTERIZATION OF RhIr BIMETALLIC CLUSTERS IN ZEOLITE BY EXAFS

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Catalysis Research Center, Hokkaido University, Kita11,Nishi 10, Kita-ku, Sapporo 060

Introduction

Surface organometallic chemistry and intra-zeolite synthesis of organometallics such as metal carbonyl clusters have been a recent subject of interest, because they offer many promises for molecular approaches in heterogeneous catalysis and rational preparation of tailored metal catalysts having a uniform distribution of discrete Rh₆, Ir₆, and Rh₄Ir₂ clusters grafted on amorphous metal oxides and entrapped inside zeolite pores. EXAFS is a useful method to get the structural information of bimetallic RhIr clusters entrapped in the zeolites, especially its metal frameworks, which are incorporated into catalysis e.g., hydrogenolysis of n-butane.

Experimental

Zeolite-entrapped RhIr clusters were synthesized from co-ion-exchanged [(6-x)Rh³⁺ + xFe⁴⁺]/NaY in CO + H₂ reaction, [Rh₆₋ₓ Feₓ(CO)₁₆]/NaY (x=1,2,3), by using Ship-in-bottle technique. We also prepared the reduced material, [Rh₃Fe₃(CO)₁₆]/NaY which was derived from [Rh₃Fe₃(CO)₁₆]/NaY. The sample were charged under He, CO, and H₂ in a specially designed cell with Kapton films as a window to avoid the exposure to air and moisture. EXAFS measurements were performed at room temperature at BL10B in KEK-PF. The program "EXAFS2" were used for analysis.

Result and Discussion

The precursors for the RhIr bimetallic cluster catalysts were similarly prepared in CO + H₂ at 1 atm and 473 K from the double-ion-exchanged NaY: [Rh³⁺ + Ir⁴⁺]/NaY with the different metal compositions. The resulting species inside NaY gave a carbonyl IR spectra characteristic of hexanuclear carbonyl clusters consisting of linear CO (2099-2096 cm⁻¹) and face-bridging CO (1756,1752, and 1744 cm⁻¹) for Rh/Ir atomic ratio = 5/1, 4/2, and 3/3, respectively. The face-bridging CO ligands of the series of RhIr bimetallic clusters gave sharp Ir bands with a similar half width, the positions of which systematically shift to lower frequency on increasing the Ir content from Rh₆(CO)₁₆ (1760 cm⁻¹) to Ir₆(CO)₁₆ (1734 cm⁻¹). The result suggest that the homogenous hexanuclear RhIr bimetallic carbonyl clusters Rh₆₋ₓIrₓ(CO)₁₆ are uniformly distributed inside the zeolite cages and have a well-defined Rh/Ir metal ratio (x) associated with the of the starting [Rh³⁺ + Ir⁴⁺]/NaY.

Studies of Rh K-edge and Ir L-edge EXAFS on the resulting bimetallic carbonyl samples prepared from [Rh³⁺ + Ir⁴⁺]/NaY (Rh:Ir=1) have been conducted, and the preliminary results after the curve fitting analysis, as shown in Table 1, revealed the preferential formation of Rh₃Ir₃(CO)₁₆ based on coordination numbers around Rh₆₋ₓIrₓ(CO)₁₆. The reduced bimetallic RhIr catalysts [Rh₆₋ₓIrₓ(CO)₁₆]/NaY (x=2,3, and 4) were obtained by procedures similar to those for the reduced Rh₆ and Ir₆ catalysts.

Table 1 EXAFS evaluation of CN and R values for NaY-entrapped Rh₆(CO)₁₆, Ir₆(CO)₁₆, and Rh₃Ir₃(CO)₁₆ which were prepared by CO + H₂ reaction with Rh³⁺/NaY, Ir⁴⁺/NaY and [Rh³⁺ + Ir⁴⁺]/NaY (Rh:Ir = 1)

<table>
<thead>
<tr>
<th>Clusters</th>
<th>Rh K-edge CN</th>
<th>Rh Ir-CN</th>
<th>Rh Ir-R (Å)</th>
<th>Ir K-edge CN</th>
<th>Ir-R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh₆(CO)₁₆]/NaY</td>
<td>3</td>
<td>2.74</td>
<td>-</td>
<td>3.8</td>
<td>2.70</td>
</tr>
<tr>
<td>[Ir₆(CO)₁₆]/NaY</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td>2.72</td>
<td>1.4</td>
</tr>
<tr>
<td>[Rh₃Ir₃(CO)₁₆]/NaY</td>
<td>2.4</td>
<td>2.72</td>
<td>1.4</td>
<td>2.74</td>
<td>2.4</td>
</tr>
</tbody>
</table>

reference:
1) M. Ichikawa, Polyhedron, 1,2351(1988)

References
There are two types of spatial correlations in molecular liquids: intra- and intermolecular correlations. Recently we have suggested that the intramolecular correlations can be selectively extracted by EXAFS measurements, because the EXAFS signal is unusually large where the photoelectron is backscattered by the covalently bonded neighboring atoms. In this paper we discuss the intramolecular correlations in liquid Se-Cl and Se-I mixtures.

EXAFS spectra for the Se-halogen mixtures were taken on the K-edge of Se using the spectrometer installed at the BL-10B. Specially designed sample cells made of fused quartz were used.

The average coordination numbers of Se, $N_{Se}$, and Cl, $N_{Cl}$, around a central Se atom have been estimated from the observed EXAFS oscillations for $1$-Se$_x$-$\chi$Cl$_x$, and shown in Figs. 1(a) and (b). The value of $N_{Se}$ decreases with increasing Cl concentration $\chi$, being about 1 at $\chi=0.5$ and nearly 0 at $\chi=0.67$. On the other hand, $N_{Cl}$ increases from 0 to nearly 0.67.

If we assume that every halogen(X) atom acts as a chain terminator to form the molecules X-(Se-)$_n$-X, where $n=2/x-2$, then $N_{Se}$ and $N_{X}$ are given

$$N_{Se} = \frac{2n-2}{n} = \frac{2-3\chi}{1-\chi}, \quad (1)$$

and

$$N_{X} = \frac{2}{n} = \frac{x}{1-x}, \quad (2)$$

The calculated values are shown in Fig.1 by the dashed lines. The agreement between the observed and calculated values is good, implying that $1$-Se$_x$-$\chi$Cl$_x$ is composed of the molecules Cl-(Se-)$_n$-Cl, as assumed.

Figure 2(a) and 2(b) display the coordination numbers of Se, $N_{Se}$, and I, $N_{I}$, around a central Se atom for $1$-Se$_x$-$\chi$I$_x$, as a function of $\chi$. With increasing $\chi$, $N_{Se}$ decreases and $N_{I}$ increases. The dashed line in Fig. 2 represents the concentration variation of $N_{Se}$ and $N_{I}$ described by eqs. (1) and (2). The $N_{I}$ curve deviates downwards from what it would be if all I atoms were chain terminators, and the $N_{Se}$ does not tend to zero even for high $\chi$. Therefore I atoms are not always incorporated into the chain molecules in contrast to Cl atoms which have large electronegativity. The excess I atoms may form I$_2$ molecules. A more detailed description including the intermolecular correlations are given elsewhere.
LOCAL STRUCTURE OF HIGHLY DISPERSED MOLYBDENUM SULFIDE CATALYSTS PREPARED FROM MOLYBDENUM HEXACARBONYL

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Introduction

Metal carbonyl complexes anchored on metal oxide have been employed with the hope of preparation of novel catalyst systems.1) In our previous studies,2,3 it was shown on the basis of NO adsorption and EXAFS that highly dispersed molybdenum sulfide is formed by a reaction at 373 K between molybdenum subcarbonyl species Mo(CO)3 encaged in zeolite and H2S. In the present study, preparation of molybdenum sulfide catalysts highly dispersed on Al2O3 was examined by using Mo(CO)5/Al2O3. The local structure and dispersion of molybdenum sulfides thus prepared were studied by using EXAFS. The hydrodesulfurization (HDS) of thiophene was carried out over molybdenum sulfides supported on Al2O3 and NaY.

Experimental

Mo(CO)5 was anchored on Al2O3, which had been dehydrated at 673 K, by adsorption at 300 K from a gas phase. Resultant Mo(CO)5/Al2O3 was sulfided in a stream of H2S/H2 (1 atm, 0.1) by uniformly increasing the temperature from r.t. to 673 K (6 K min−1), where the sample was kept for 90 min. Conventional sulfided MoO3/Al2O3 catalyst (10 wt % Mo) prepared by impregnation was also studied for comparison. The HDS reaction of thiophene and the hydrogenation of butadiene were conducted over sulfided molybdenum catalysts at 673 K and 423 K, respectively, by using a closed circulation system.

The EXAFS spectra of Mo K-edge for molybdenum catalysts were measured at BL-10B instrument of the Photon Factory in the National Laboratory for High Energy Physics using synchrotron radiation. The spectra were obtained without exposure to air by using an in situ cell with Kapton windows.

Results and Discussion

Figure 1 shows the Fourier transforms (FT) for polycrystalline MoS2 and Al2O3-supported catalyst systems. With MoO3/Al2O3 catalyst, Mo-S and Mo-Mo bondings are observed at the distances of 0.240 and 0.315 nm, respectively. These values are very close to those of MoS2 (0.241 and 0.316), indicating a formation of MoS2 on the sulfided impregnation catalyst. The coordination numbers of the Mo-S and Mo-Mo bonds were calculated to be 4.8 and 3.5, respectively. These values suggest that the crystalline size of MoS2 is 1-2 nm.

As regards the molybdenum sulfide catalyst prepared from Mo(CO)6, the Mo-S bond was observed at 0.237 nm, this being slightly shorter than the Mo-S for MoS2. Surprisingly, a Mo-Mo bond was observed at 0.277 nm. The bond distance is much shorter than that for MoS2, indicating a formation of a direct Mo-Mo bond in sulfided Mo(CO)6/Al2O3 (1.9 wt %). The coordination numbers were estimated to be 2.8 and 0.7 for the Mo-S and Mo-Mo bonds, respectively. On the basis of the EXAFS results, the structure of molybdenum sulfide species is completely different from that of MoS2 and may be described as amorphous MoS3 or sulfido Mo-dimer complexes. Essentially identical EXAFS results were obtained for sulfided Mo(CO)6/NaY catalyst (ca. 6 wt % Mo).

It was found that sulfided Mo(CO)6/Al2O3 and NaY catalysts show 1.5 times higher HDS activity per Mo (TOF) and 5-10 times higher TOF for the hydrogenation of butadiene than the conventional molybdenum sulfide catalyst. These enhanced activities of sulfided Mo(CO)6/NaY or Al2O3 catalyst are considered to result from increased dispersion and specific structure of molybdenum sulfide species.

References

1) "Tailored Metal Catalysts" (Y.Iwasawa Ed.), Reidel, 1986.

Fig.1 FT for molybdenum sulfide catalysts. a) MoO3/Al2O3, b) Mo(CO)6/Al2O3, and c) MoS2
TEMPERATURE DEPENDENCE OF EXAFS SPECTRUM IN Bi-Pb-Sr-Ca-Cu OXIDE SUPERCONDUCTOR

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INTRODUCTION

In oxide high-\(T_c\) superconductors experimental and theoretical attentions have been focused on an apical oxygen formed the CuO\(_6\) square pyramidal structure.[1,2] We have previously found an anomalous increase of mean square relative displacement (MSRD: \(\sigma^2\)) of the axial Cu-O bonds around \(T_c\) on the powdered YBa\(_2\)Cu\(_3\)O\(_y\).[3] It has been ascribed to a softening of lattice vibrations relating with the apical oxygen. In this report, we study the temperature dependence of the EXAFS spectrum at the Cu K-edge in Bi-Pb-Sr-Ca-Cu oxide superconductor, to confirm whether the anomaly of thermal vibrations around \(T_c\) exists independently of material or not.

EXPERIMENTAL

The sample of Bi\(_{0.87}\)Pb\(_{0.07}\)Sr\(_{0.95}\)Ca\(_{0.05}\)Cu\(_3\)O\(_y\) compound (BPSCCO) was prepared from coprecipitated oxalates containing the relevant cations. The superconducting transition temperature was determined to be \(T_c=107\)K by the resistance measurement with four probe method. The sample for the EXAFS measurements was prepared by grinding the sintered pellet into fine powder, which was dusted uniformly onto Scotch tapes. The EXAFS spectrum at the Cu K-edge was obtained in the transmission method by using the beam line 10-B in the temperature range 26.9-300K.

The BPSCCO has three Cu-O sheets in the unit cell: The Cu atoms occupy one square planer site and two tetragonal pyramidal sites. We treat the nearest-neighbor distance as the average of the equatorial bond length Cu-O\(_e\) and the axial bond length Cu-O\(_a\). The equatorial and axial components of MSRD are \(\sigma^2_e\) and \(\sigma^2_a\), respectively. These four parameters were determined by a two-shell model.

The temperature variation of the equatorial and axial Cu-O bond lengths is shown in Fig.1. The Cu-O\(_e\) bond length is almost independent of temperature in the present measurements, and does not indicate any anomalous behavior around \(T_c\). The Cu-O\(_a\) bond also shows little temperature variation as a whole except where it becomes short just around \(T_c\).

In order to examine the temperature dependent part of \(\sigma^2\), the difference \(\Delta \sigma^2(T)=\sigma^2(T)-\sigma^2(T_0)\) between the values at temperature \(T\) and reference temperature \(T_0\) was studied. Figure 2 shows the temperature dependence of \(\Delta \sigma^2(T)\) with respect to the data at \(T_0=26.9\)K. (a) for the equatorial and (b) for the axial components. As seen in these figures, \(\sigma^2_e\) gradually decreases with decreasing temperature, and shows a normal behavior. On the other hand, \(\sigma^2_a\) indicates an anomalous increase below \(T_c\). The solid line is the result calculated by the Einstein model. This anomaly is qualitatively similar to our previous results for Y-Ba-Cu-O superconductor. It is likely that this anomaly is common phenomenon relating to the superconducting transition in oxide compound.

REFERENCES

The Structure of PtRh Particle in NaY

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\textsuperscript{1)}Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.
\textsuperscript{2)}J.R.D.C, Tokodai, Tukuba, Ibaraki 300-26, Japan.

Introduction

In order to improve and modify the catalytic properties, bimetallic particles supported on inorganic oxides were often used. NaY has two types of pores, supercage and sodalite cage which have different pore sizes (1.2 nm for supercage and 0.66 nm for sodalite cage). M. S. Tzou et al., reported that the activity for NO reduction and CO oxidation are improved in the PtRh/NaY catalysts prepared in the similar way. In this study we have investigated the structure of PtRh in NaY using EXAFS spectroscopy.

Experimental

PtRh/NaY was prepared by ion exchange of NaY with an aqueous solution of Pt(NH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2} and Rh(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{3} at 353 K. The sample was heated in the flow of oxygen with a rate of 1000 ml/min./g-zeolite from 293 K to 573 K at a heating rate of 0.5 K/min and the temperature was held at 573 K for 2 hours. The sample was treated under hydrogen from 293 K to 673 K with a heating rate of 10 K/min and at 673 K for 3 hours. The loadings of Pt and Rh were both 1.9 wt%.

Result

The EXAFS oscillations were extracted from the absorption coefficients by subtracting the background estimated from the cubic spline method and were Fourier transformed. Fig. 1 showed the Fourier transforms of Pt and Rh EXAFS oscillations of PtRh/NaY. The first peaks were inversely Fourier transformed to k-space and the curve fitting analyses were carried out. The results of curve fitting were listed in Table 1. Table 1 contained the curve fitting results of PtY and RhY prepared in the same way.

Discussion

The Pt-Rh and Rh-Pt interaction were found from the analysis of EXAFS, indicating the production of the PtRh alloy particles. The total coordination numbers around Pt and Rh were 7.6 and 6.3, respectively. The average coordination number is about 6, indicating the PtRh alloy still stay in the pore of the NaY. The bond length of Rh-Rh was similar to that of Rh bulk metal. The bond length of Pt-Pt (0.278 nm) was quite shorter than those of the bulk Pt metal (0.278 nm) and PtNaY (0.276 nm). The distance of Rh-Pt was also shorter than that expected from the metallic radii of Rh and Pt. The shorter metal-metal distance of monometal particles in the zeolite was when the sample was evacuated. On the other hand, when the H\textsubscript{2} gas remained around the metal particle in NaY, the distance was reported to be similar to that of the bulk metal. Since the H\textsubscript{2} gas remained in this RhPtNaY, the metal-metal distance should not be reduced. In reality Pt-Pt and Rh-Rh distances were similar to those of the bulk metal in PtNaY and RhNaY. Thus the shortening of the Pt-Pt distance might cause by the alloying effect of PtRh particle in Zeolite.

<table>
<thead>
<tr>
<th>Table 1 Curve fitting results</th>
</tr>
</thead>
<tbody>
<tr>
<td>A B N ( r/nm )</td>
</tr>
<tr>
<td>Pt/NaY Pt Pt 6.4(1.0) 0.276(2)</td>
</tr>
<tr>
<td>Rh/NaY Rh Rh 5.4(1.0) 0.267(2)</td>
</tr>
<tr>
<td>PtRh2/NaY Pt Pt 4.1(0.8) 0.269(2)</td>
</tr>
<tr>
<td>Pt Rh 3.5(0.7) 0.269(2)</td>
</tr>
<tr>
<td>Rh Pt 2.3(0.6) 0.270(2)</td>
</tr>
<tr>
<td>Rh Rh 4.0(0.9) 0.268(2)</td>
</tr>
</tbody>
</table>

Fig. 1 Fourier transforms of Rh k-edge (a) and Pt L\textsubscript{3}-edge of PtRh2NaY

\textsuperscript{157}
EXAFS STUDIES ON RhSn/SiO₂ CATALYSTS PREPARED BY
THE REACTION OF (CH₃)₄Sn WITH Rh/SiO₂

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Introduction

The catalytic properties of bimetallic catalysts can be controlled by the structures of catalysts. We prepare the catalysts by the reaction between organometallic compound (CH₃)₄Sn and Rh metal particles on SiO₂. The catalysts thus obtained have higher selectivity on hydroformylation reaction and much higher activity on NO reduction reaction than conventional co-impregnation catalysts. We investigate the structural difference between two catalysts by EXAFS.

Experimental

Rh/SiO₂ (1wt%) catalyst was prepared by the conventional impregnation of SiO₂ with a methanol solution of RhCl₃ • 3H₂O. RhSn/SiO₂(1:0.3)(B), conventional co-impregnation catalyst, was prepared by the impregnation of SiO₂ with a methanol solution of RhCl₃ • 3H₂O and SnCl₂. After impregnation, the catalysts were dried in air at 393K for 12h. And RhSn/SiO₂ (1:0.3)(A) catalysts were prepared by the reaction at 423K between (CH₃)₄Sn vapor and Rh/SiO₂ reduced at 573K. After this procedure, they were reduced at 573K. EXAFS spectra of Rh/SiO₂ and RhSn/SiO₂(A), (B) were measured at BL10B. Some data of Sn K-edge were measured on BL14A.

Results and discussion

Fig.1 shows the Fourier transforms of k²x(k) for both catalysts: (a) RhSn/SiO₂(A) after reduction and (b) O₂ exposure to (a) at r.t. In (c), Sn atoms in RhSn/SiO₂(B) are oxidized, since Sn-Rh bondings disappear. In contrast to (c), in Fig.1 (d), a part of Sn atoms in RhSn/SiO₂(A) are oxidized, and Sn-Rh bondings remain. From these results, more Sn atoms in RhSn/SiO₂(A) are located on the surface or near-surface of bimetallic particles than RhSn/SiO₂(B).

Table 1 shows the one shell CF results of Rh K-edge EXAFS for Rh-Rh bond in RhSn/SiO₂ and average particle size by TEM measurement. Rh-Rh C.N. decreases though the particle size is the same as that of Rh/SiO₂ because of Rh metal lattice distortion by addition of Sn. The Sn located on the surface of the Rh particles, the surface lattice of the Rh particles is mainly distorted. On the other hand, Sn atoms in the RhSn/SiO₂(B) distorts the bulk lattice, because the Sn atoms are mainly located in the bulk of Rh particle. The distortion of the surface lattice of the Rh particles may cause the high activity of NO reduction on RhSn/SiO₂(A).
XANES STUDIES ON MIXED VALENCE COMPOUNDS IN (R, R'-DCNQI): Cu (R, R'=CH₃, CH₃O, Cl, Br)

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Introduction

In single crystal (R, R'-DCNQI): Cu system, organic x-acceptor molecules R, R'-DCNQIs (R, R'=CH₃, CH₃O, Cl, Br) uniformly stack along the tetragonal c axis and Cu atoms coordinate to the terminal N atoms of R, R'-DCNQI molecules. (Fig. 1) There are two groups, one exhibiting sharp metal-insulator (M-I) transition (group I) and the other keeping stable metallic states (group II).

The Cu K-edge x-ray absorption spectra probe the unoccupied partial (of p-type symmetry) and local density of states at the Cu sites. At the absorption threshold, information on the p-type unoccupied states close to the Fermi level can be extracted. The 1s-4p transitions of the 3d transition metal compounds are modified by electronic environments such as the ligand field and the chemical bonding in the initial state through the core-hole screening effect in the final state.

Experimental investigations by Cu K-edge X-ray absorption near edge structure (XANES) has been performed to determine the electronic states of Cu atoms using strong polarized X-ray.

Experimental

The measurements were performed by the BL-10B of Photon Factory at the National Laboratory for High Energy Physics (KEK-PF, Tsukuba). The XANES spectra of the Cu K-edge was recorded in the transmission mode. X-ray synchrotron radiation from the 2.5 GeV Storage ring is monochromatized using a Si(311) channel-cut crystal. Gas mixing conditions in the ion chamber X-ray detectors were selected for the optimum signal to noise ratio (N₂: 100% for Iq chamber and N₂: 75%, Ar: 25% for I chamber). The step energy to take XANES spectrum was about 0.5 eV in the present study. Aligned single crystals, group I (DMe- and DMeO-) and group II (MeBr, DBr- and MeCl-) salts, were measured for the polarization parallel with crystal c axis from 300 K down to 20 K. Samples were fixed using vacuum grease on aluminum foil connected to the cold finger.

Results and Discussion

Figure 2 and 3 show Cu K-edge XANES spectra of the present compounds at room temperature and 100K. These profiles are considerably similar each other. We assigned those peaks in fig.2 and 3 as follows. The pre-edge structure A is assigned to the 1s-3d transition. The peak intensity originates mainly in electric quadrupole transitions, and it is correlating with 3d hole densities, in addition, B, C, D and E peaks are assigned to dipole-allowed 1s-4p transitions. In (DMe-DCNQI): Cu and (DMeO-DCNQI): Cu (group II), the peak D seems too weak to recognize. In the 100K spectra, we should note that the peaks A and D have grown in group I salts. We can consider that the Cu 3d holes have increased through M-I transition in the insulating state. On the other hand, the group II salts spectra show no marked change. A recent discussion on the valence state of Cu in (R, R'-DCNQI): Cu insists the value 1.3+, but another report using the samples carefully grown under the exclusion of oxygen shows the value nearly 1+ from XPS measurements. When we observe the peaks A, the peak intensities for group II salts are weaker than those for other two compounds of group I. It is clear that the 3d hole populations, which affect for 1s-4p transitions, between group I and group II salts are different. It is likely that these differences originate in the different physical properties between two groups of R, R'-DCNQI salts. We will discuss the electric states and local structure in the other article.

Reference

4) T. Doi et al. in preparation.
PHASE TRANSITION AND LOCAL STRUCTURE IN Cd\(_{1-x}\)Zn\(_x\)Te

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INTRODUCTION

Recently, the ferroelectricity of the cadmium zinc tellurium Cd\(_{1-x}\)Zn\(_x\)Te, one of the II-VI mixed semiconductor crystal, was reported by Weil et al.,\(^1\) In their report, the transition temperature varied from 363K to 518K with the Zn content x varying from 0.04 to 0.45. The spontaneous polarization appeared along the \langle 1 1 1 \rangle direction, except for the pure compounds. They suggested that this ferroelectric phase transition was an order-disorder type with the double-well potential of Zn atom owing to the difference between the covalent radii (Cd=1.48Å, Zn=1.31Å) or the ion radii (Cd\(^{2+}\)=1.03Å, Zn\(^{2+}\)=0.83Å).

It is well known that the average structure of this mixed crystal is the zinc-blende structure at room temperature. The lattice parameter a(x) fulfills the Vegard's law,\(^2\) i.e., it varies almost linearly between the values of pure compounds. EXAFS measurement around Te L\(_{III}\)-edge was performed at room temperature by Balzarotti.\(^3\) The two kinds of anion-cation distances (Cd-Te, Zn-Te) were almost independent of the x and the same values as in those pure compounds.

As the results from the X-ray diffraction study and the EXAFS study,\(^3\) Cd\(_{1-x}\)Zn\(_x\)Te mixed crystal is the zinc-blende structure as the average structure, but the local structure distorted. We intend EXAFS study at wide temperature ranges to examine the change of the local structure through the ferroelectric transition.

EXPERIMENTAL AND RESULTS

The powder specimens were prepared from the single crystals, which were grown from the Bridgman technique. The Zn content x was determined by the lattice parameter from the X-ray diffraction measurements. Conventional EXAFS measurements around the Zn K-absorption edge and Cd K-absorption edge were carried out at BL10B. EXAFS signal and Fourier transformed radial distribution functions were obtained. The filtering technique was made to determine the nearest neighbor distance, Debye-Waller factor, mean free path of photo-electron, the energy of the absorption edge and the scale factor. In this stage, one-shell model in which the tetrahedron undistorted, and two-shell model in which the tetrahedron distorted were assumed as the local structure. The two-shell model was not converged to the reasonable values. Figure 1 shows the anion-cation distances as function of Zn content x from the result of the one-shell model. Open circles represent the Zn-Te distances and closed circles Cd-Te ones. Solid line is the calculated values from the Vegard's law.

CONCLUSION

We carried out the EXAFS measurements around Cd K-edge and Zn K-edge at room temperature as the preliminary experiment. Our results are almost similar of ones by Balzarotti.\(^2\) Cd\(_{1-x}\)Zn\(_x\)Te crystal is the ferroelectricity with a spontaneous polarization along \langle 1 1 1 \rangle direction. It is expected that there are two different bond lengths of Zn-Te. One is a shorter bond length than that of the undistorted Zn-Te tetrahedron and the rests are longer than that ones. In this study, it is not observed. This reason is, now, considered as follow:

1) The displacement of the Zn atom is smaller than the resolution of EXAFS experiment.
2) The disorder state of Zn atom is included in the Debye-Waller factors.

To be clear the above equations, more detailed EXAFS experiments are required at the wide temperature ranges.

References

2) L. Vegard; Z. Phys. 5 17 (1921)
3) A. Balzarotti; Physica 146B 150 (1987)
EXAFS studies on amorphous Gd$_{22}$Y$_{46}$Cu$_{32}$

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*Department of Chemistry, Faculty of Science, Okayama University, Okayama 700

Introduction

Amorphous Gd$_{68-x}$Y$_x$Cu$_{32}$ system shows the following magnetism: ferromagnetism ($X>65$), reentrant spin glass ($38<X<65$), spin glass ($10<X<38$) and paramagnetism ($X<10$) [1]. These behaviors are interpreted from the nearest neighbor Heisenberg model with fluctuations in the exchange interaction $\Delta J/J_0$, in which the structural parameters, that is, the coordination number, the interatomic distance and the Debye-Waller factor between Gd-Gd pairs play an important role in determining the properties.

In the previous work [2] we have estimated $\Delta J/J_0 \sim 0.75$ for an amorphous Gd$_{52}$Y$_{16}$Cu$_{32}$ from magnetic and EXAFS measurements. In the report we will show the EXAFS result for a Gd$_{22}$Y$_{46}$Cu$_{32}$ spin glass.

Experimental technique and data analysis

The alloy ingot was prepared from 3N Gd, 3N Y and 4N Cu by argon arc melting. Amorphous ribbons of Gd$_{22}$Y$_{46}$Cu$_{32}$ was made by a melt spinning technique.

The EXAFS measurement was performed at BL-10B station of Photon Factory (KEK, Tsukuba). The X-ray absorption spectra were taken in the transmission mode at 34 K near a Gd L$_{III}$ absorption edge. We made the least squares analysis [3] for EXAFS spectra to obtain the structural parameters.

Results and discussion

Figure 1 shows an EXAFS spectrum $k^3 \chi (k)$ around Gd for the amorphous Gd$_{22}$Y$_{46}$Cu$_{32}$. The Fourier transform of Fig.1 is shown in Fig.2, where the distance is not corrected for the phase shift. The best fit for a Fourier filtered EXAFS spectrum gives the following result on the structural parameters. The interatomic distance of Gd-Cu (2.89 Å), Gd-Y (3.64 Å) and Gd-Gd (3.76 Å) are nearly equal to those of amorphous Gd$_{52}$Y$_{16}$Cu$_{32}$. A large value of 0.15 Å at 34 K for the Debye-Waller factor between Gd atoms comes from a structural disorder of amorphous structure. A central Gd atom is surrounded by 3.8 Cu atoms, 5.7 Y atoms and 3.4 Gd atoms. The total coordination number is slightly larger than that of fcc structure. The measurements for Cu K and Y K absorption edges are in progress.

References

XAFS STUDY ON THE SOLUTION FOR IMPREGNATION OF MULTI-COMPONENT SUPPORTING CATALYSTS

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INTRODUCTION

Cobalt–molybdate and nickel–molybdate catalysts have been commonly used to get clean fuels from the petroleum and unconventional feedstocks. Dispersion and geometric configuration of MoS$_2$-like crystallites on the supports as well as location of Co and Ni on those crystallites influence their catalytic activities, such as hydrodenitrogenation (HDN) and hydrodesulfurization (HDS). Liganding agent such as citric acid influenced the size of Mo structure in the impregnating solutions, and also the MoS$_2$-like structure on the γ-Al$_2$O$_3$ support for the sulfided NiMo catalysts. In this paper, we prepared the Co–Mo impregnating aqueous solutions using citric acid and investigated the Mo structure by extended X-ray absorption fine structure (EXAFS) method. Further, the structure and dispersion of these metal sulfides on the sulfided Co–Mo/γ-Al$_2$O$_3$ catalysts were investigated by EXAFS and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

The molybdate catalysts were impregnated to incipient wetness on γ-Al$_2$O$_3$ support with the impregnating aqueous solutions; Co–Mo solution containing (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O and Co(N0$_3$)$_2$.6H$_2$O with ammonia; Co–Mo solution containing MoO$_3$ and Co carbonate, with citric acid. The impregnated catalysts were dried at 393K for 3 hours and then calcined at 773K for 3 hours. The calcined catalysts were sulfided with a gas consisting of 5 volume % H$_2$S and 95 volume % H$_2$ at 673K for 2 hours prior to the HDN and HDS runs. The structure of metals in the impregnating solutions and on the parent sulfided catalysts was analyzed by a EXAFS at the Photon Factory (BL–10B).

RESULTS AND DISCUSSION

Figure 1 shows the Fourier transform of EXAFS spectra (Mo K-edge) for the impregnating Co–Mo(am), Co–Mo(cit) and Ni–Mo(cit) solutions. A sharp peak was observed at 0.182 nm for the Co–Mo(am) solution, which correspond to the Mo–O(first shell) distance in the monomeric MoO$_4$$^{2-}$ tetrahedra. On the other hand, two distinct peaks were observed at 0.175 nm and 0.35 nm, for the Ni–Mo(cit) and Co–Mo(cit) solutions. Primary peak might correspond to the Mo–O(first shell) distance in the Mo octahedra. The distance of long–range peak(0.35 nm) was far from 0.32 nm of the Mo–O$_6$ distance at room temperature, but shorter than 0.36 nm of the Mo–O distance in crystalline MoO$_2$ made of the distorted MoO$_6$ octahedra. This increase in the distance of long–range coordination might be attributed to some coordination of Co–citrate/citric–acid ligands to the polymerized octahedra(MoO$_4$) and formation of some Co–Mo complexes. Intensity of the long–distance peak for the Ni–Mo(cit) solution was about twice that of the Co–Mo(cit) solution, which indicated the higher agglomeration of the Mo octahedra in the Ni–Mo(cit) solution than in the Co–Mo(cit) solution.

Figure 2 shows the Fourier transform of EXAFS spectra (Mo K-edge) for the sulfided Co–Mo catalysts. Two main peaks were observed at 0.24 nm and 0.32 nm for both of the catalysts, which corresponded to the Mo–S and Mo–Mo distances in MoS$_2$ crystallites. Both peak intensity was higher in the sulfided catalyst using citric acid than those in the sulfides catalyst using ammonia. The average coordination numbers for the nearest(first shell) S(N(S)) and Mo(N(Mo)) atoms around a particular Mo atom were calculated from the above EXAFS spectra,[2] N(Mo)=1.6 and N(S)=4.0 for the Co–Mo(am) catalyst, N(Mo)=1.9 and N(S)=4.8 for the Co–Mo(cit) catalyst. Agglomerated Mo structure in the Co–Mo(cit) solution influenced the dispersion of MoS$_2$-like sulfides on the sulfided Co–Mo(cit) catalysts, i.e. lower dispersion than that of Co–Mo(am) catalyst and higher dispersion than that of Ni–Mo(cit) catalyst. Breakage of MoS$_2$-like crystallites on the sulfided catalyst was marked after Co addition than Ni addition independent of the kind of ligands.

REFERENCES

2) N.Matsubayashi et al. PF Activity Report, No.6, 48(1988).

![Fig.1](image1.png)  
**Fig.1** Fourier transform of molybdenum EXAFS spectra for the Co–Mo and Ni–Mo impregnating solutions; Co–Mo(am) solution using ammonia ( ), Ni–Mo(cit) solution ( ) and Co–Mo(cit) solution ( ) using citric acid.

![Fig.2](image2.png)  
**Fig.2** Fourier transform of molybdenum EXAFS spectra for the sulfided Co–Mo/γ-Al$_2$O$_3$ catalysts prepared by using ammonia ( ) and citric acid ( ).
An EXAFS study on Pd-Cu metal particles formed in Y-zeolite and mordenite

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*Department of Industrial Chemistry, Kitami Institute of Technology, Kitami 090

It is possible to introduce two kinds of transition metal cations into zeolite pores by a cation exchange procedure. We have prepared samples of mordenite and Y-zeolite containing both of Pd$^{2+}$ and Cu$^{2+}$ cations. For understanding the catalytic behavior of the Pd-Cu/zeolites, it seems to be important to characterize metal particles formed. The purpose in the present study is to characterize the metal particles formed on the Pd-Cu/zeolites by means of EXAFS technique.

Zeolite samples containing Cu$^{2+}$ and Pd$^{2+}$ (Pd/Cu = 1.0, 1.6x10^{-4} mol(Pd,Cu)/g) were prepared from Na-form zeolites (Na/Y—zeolite, Na/mordenite) and an ammonia solution containing Cu(NH$_3$)$_4$^{2+} and Pd(NH$_3$)$_4$$^{2+}$. After cation exchange the solid was thoroughly washed with distilled water or diluted ammonia water (0.02 mol/dm$^3$). The solid was then dried at 383 K overnight in an oven.

The reduction behavior of Pd$^{2+}$-Cu$^{2+}$/zeolites with H$_2$ has been studied by using a temperature-programmed reduction (TPR) technique. The TPR spectra are shown in Fig.1. On both kinds of zeolite, Y-zeolite and mordenite, the sample washed with distilled water (denoted by -(W)) was reduced much easier than that washed with diluted ammonia water (denoted by -(A)). The difference between TPR patterns for the samples -(W) and -(A) is due to the difference in the concentration of NH$_3$ ligand in the samples (the concentration of NH$_3$ on the sample -(W) was lower than that on the sample -(A)).

In order to characterize Pd-Cu metal particles formed on the four samples, EXAFS measurements of them were carried out (Beam Line 1OB). Analysis of the EXAFS data was performed with Program EXAFS1 and EXAFS2. A Typical EXAFS spectrum for Pd K-edge on Pd-Cu/Y-zeolite-(W), $\chi(k)k^3$ vs. R is shown in Fig.2. The spectra on the four samples are found to be very similar, and they were interpreted by the contribution of two backscatters, i.e., Pd and Cu. The interatomic distances for Pd-Pd and Pd-Cu were found to be 0.270 nm and 0.257 nm, respectively. The distance for Pd-Pd was close to that observed on Pd-foil or Pd/zeolites (0.272 nm). Thus, there was no appreciable difference among the EXAFS spectra on the four samples, whereas the TPR patterns were very different from each other.

Consequently, EXAFS spectra of the Pd-Cu/zeolite samples clearly showed the presence of Pd-Cu bond as well as Pd-Pd bond in all samples studied. The TPR results showed that Pd$^{2+}$ loaded on the sample was completely reduced to metallic Pd. On the other hand, Cu$^{2+}$ in zeolite was hardly reduced to Cu$^0$. The predominant species in the samples after TPR were considered to be Cu$^+$. On the basis of the results obtained by EXAFS and TPR techniques, formation of Pd metal particles, which were coated with Cu$^+$, may be proposed.

1) N.Kosugi and H.Kuroda, Program EXAFS1/V04 and EXAFS2/V03, Research Center for Spectrochemistry, Univ. Tokyo, Japan, 1987.
EXFAS STUDIES ON HOMODINUCLEAR MERCURY(II) PORPHYRIN IN SOLUTION

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** Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840

Introduction

Large metal ions such as mercury(II), cadmium(II), and lead(II) can not incorporate well into porphyrin core, and just sit on the porphyrin plane. Lead(II) is 117 pm above the plane formed by the four nitrogen groups of the porphyrin macrocycle in crystal1 and these metalloporphyrins are very unstable. The formation constants of lead(II)- and cadmium(II)porphyrin are 10^10 times smaller than that of zinc(II)porphyrin. However, mercury(II) is unique in that it forms thermodynamically very stable complex with N-donor ligands. The characteristic feature of mercury(II) encourages us to study the structure of mercury(II) porphyrin in aqueous solution by the EXAFS method because the large stability of the mercury(II) complex may be reflected in its structure in solution. In this report, we describe the molecular structure of mercury(II) porphyrin of tetrakis(4-sulfonatophenyl)-porphyrin (H2tpps6-) in aqueous solution.

Experimental

Four test solutions were prepared as shown in Table 1 for EXAFS measurements. Solutions A and B are aqueous mercury(II) nitrate solutions and used as the structure standard for an Hg-0 atom pair.2) Solutions C and D were prepared by dissolving Hg(NO3)2 and H2tpps6- in water at different Ctpps/Ctug ratios and then adjusting to suitable hydrogen ion concentrations by sodium hydroxide. In these solutions Hg2(tpps)2- is the main species from the equilibrium constant. EXAFS spectra were measured around the Hg L3-edge at the BL10B of the Photon Factory, KEK.

Results and Discussion

Figure 1 depicts the Fourier transforms (uncorrected for the phase shift) of the sample solutions. The first intense peaks at 180 pm in the curves of solutions A and B are due to the Hg-0 bonds in the first coordination sphere within Hg(H2O)62+.2) The main peaks, which are due to the Hg-N (tpps) and Hg-0 (H2O) bonds, shift to significantly shorter r (160 pm) in the | F(r) | curves of solutions C and D involving dinuclear Hg2(tpps)2-. This may be ascribed to the shorter Hg-N bonds within the porphyrin complexes. Small peaks are observed around 280 pm in the | F(r) | curves of solutions C and D. These peaks may consist of peaks due to the nonbonding Hg-C and Hg-Hg pairs within Hg2(tpps)2-. We could not separate the peak into components and no direct information on the nonbonding Hg-Hg pair could be obtained.

The structure parameters of the complexes in the first coordination sphere were finally determined by a curve fit applied to the filtered k^2|F(k)| values. The lengths and Debye-Waller factors of the Hg-N and Hg-0 bonds and the number of Hg-0 bonds were optimized in the least-squares calculation, while the number of the Hg-N bonds were kept constant on the basis of structure models of the two-, three-, and four-coordination (model I, 11, and III) of pyrrole nitrogens. As seen in Table 2, no definite conclusion was drawn for the number of the Hg-N and Hg-0 bonds since no drastic change in error-square sums U was found. However, the Hg-N and Hg-0 bond lengths are 215(2) and 255(4) pm, respectively, regardless of the structure models examined. It is also obvious that the Hg-N bond length is much shorter than the Hg-0 one within the hydrated ion and complexes. The Hg-N length almost corresponds to the sum of the covalent radii and the strong Hg-N bonds are formed upon the complexation. The fact may correspond to the large stability of the mercury(II) complex with N-donor ligands.

Table 1. The composition of solutions (mol dm^-3).

<table>
<thead>
<tr>
<th>Solution</th>
<th>Hg2t</th>
<th>tpps^6-</th>
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<td>A</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
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<td>0.100</td>
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<tr>
<td>D</td>
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<td>0.0250</td>
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Table 2. Results of the least-squares refinements.

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<th>Species</th>
<th>Model</th>
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<th>r/pm</th>
<th>a/°pm</th>
<th>n</th>
<th>U</th>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(tpps)2-</td>
<td>I</td>
<td>Hg-O</td>
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<td>10.4(2)</td>
<td>6(4)</td>
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<td>(Solution C)</td>
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<td>Hg-N</td>
<td>215(1)</td>
<td>7.3(1)</td>
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<td>0.47</td>
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<tr>
<td></td>
<td>III</td>
<td>Hg-N</td>
<td>257(2)</td>
<td>15(1)</td>
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<td>22(2)</td>
<td>11(1)</td>
<td>1.12</td>
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<td>9.0(1)</td>
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<td>0.47</td>
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<tr>
<td>(Solution C)</td>
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<td>Hg-O</td>
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<td>22(2)</td>
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a) Fixed. b) Ref. 2.
EXAFS STUDIES ON THE STRUCTURE OF $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$/$\text{SiO}_2$ AND STRUCTURAL CHANGES AFTER VARIOUS TREATMENTS

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INTRODUCTION

It is important to know the structure of active site in order to investigate the mechanism of catalysis. Active site prepared from metal cluster can have a similar structure to the original metal cluster. In this work, we used platinum tetramer $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ to obtain a square framework of Pt active site. We studied the structure and the surface behavior of the Pt catalyst derived from $[\text{Pt}_4(\mu-\text{CH}_2\text{COO})_8]$ by EXAFS measurement.

EXPERIMENTAL

Precursor platinum cluster $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ was synthesized by the method described in the literature. Catalyst was prepared by impregnation of SiO$_2$ (Fuji-Davison #952) with CH$_2$Cl$_2$ solution of $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ in Ar atmosphere, followed by the solvent removal. EXAFS spectra were measured in vacuum at 70K at BL-10B.

RESULTS AND DISCUSSION

Fig. 2a is the Fourier transform of Pt EXAFS oscillation of precursor $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ and Fig. 2b is of $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ supported on silica ($\text{Pt}_4/\text{SiO}_2$). There is little difference between two spectra. FT-IR spectra also show that precursor cluster (solution) and supported platinum cluster are completely the same. Thus we concluded that the supported platinum tetramer has the same structure as the precursor cluster.

Fig. 2c is the Fourier transform of EXAFS data of $\text{Pt}_4/\text{SiO}_2$ exposed to H$_2$ gas for 1 hour at room temperature and followed by evacuation. Distances (R) are almost the same both for Pt-Pt and Pt-O as those before treatment. But Pt-Pt peak intensity has reduced to about half of that of original catalyst. This implies partial cleavage of Pt-Pt bond.

Curve fitting results are shown in table 1. The coordination number of Pt-Pt suggests Pt dimer. IR studies indicate all acetate ligands removed after H$_2$ treatment, though the C.N. of Pt-O remains four after treatment. New ligands such as hydroxyl group or lattice oxygen might be coordinated to Pt atom. Further studies are now in progress.

REFERENCES

1) C. Skapski et al., J.C.S. Chem. Comm., 1976, 410
2) T. Yamaguchi, Dr. thesis, Tohoku University (1989)

<p>| Table 1. Results of curve fitting for the (a) $\text{Pt}_4/\text{SiO}_2$ (untreated) and (b) H$_2$ treated $\text{Pt}_4/\text{SiO}_2$ catalysts. |
|-------------------|-------------------|------------------|-------------------|</p>
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<th>C.N.</th>
<th>r/nm</th>
<th>R/%</th>
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<tr>
<td>(a)</td>
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Fig. 1 Structure of $[\text{Pt}_4(\mu-\text{CH}_3\text{COO})_8]$ \(^1\)

Fig. 2 Fourier transforms of EXAFS oscillation of (a) precursor, (b) $\text{Pt}_4/\text{SiO}_2$ (untreated) and (c) H$_2$ treated $\text{Pt}_4/\text{SiO}_2$. 
ACCUMULATION AND FUNCTIONAL DEVELOPMENT OF METAL COMPLEXES - XAFS STUDY OF Ni(II) COMPLEXES CONTAINING N-GLYCOSIDES DERIVED FROM SACCHARIDES AND POLYAMINES

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*** Department of Chemistry, Faculty of Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162.

Introduction

In our laboratory, we have extensively studied the synthesis and characterization of transitional metal complexes containing N-glycosides derived from the reaction of saccharides and diamines. Recently we have succeeded in preparation of nickel(II) complexes containing disaccharides. These complexes are very interesting in connection with metal containing enzymes. In fact during our investigations, we found that aldoses treated with \( [\text{Ni(H}_2\text{O)}_2(\text{N,N,N'-Me-en})_2]Cl_2 \) (SCC, 3-4 min) in methanol were rapidly epimerized at C-2 to give the mixtures of C-2 epimers. In addition a stereo selective complexation of the mannosetype aldoses having a cis arrangement of C-2 and C-3 hydroxyl groups was observed. The molecular structures of some complexes were determined by X-ray crystallography. However most of the complexes obtained are powder samples which are unsuitable for X-ray crystallography.

X-ray absorption fine structure (XAFS) includes extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES), has provided structure information on a number of metal complexes. Recently we investigated the nickel(II) complexes containing N-glycosides derived from monosaccharides and disaccharides were investigated by XAFS spectroscopy. In this report, we wish to discuss the results concerning the XANES study.

Experimental

Beam lines BL-7C and 10B at the Photon Factory of the National Laboratory for High Energy Physics (2.5 GeV, 90-150 mA) was used with a Si(311) channel-cut monochromator. The experiments were done in the transmission mode at room temperature for the polyethylene pellets of [Ni(en)(D-Fru-en)]Cl, CH OH (a), [Ni(en)(L-Sor-en)]Cl, CH OH (b), [Ni(L-Rha-tren)]Cl, CH OH (c), [Ni(D-GlcN-en)]Br • 4H 0 (d), (N,N'-CH(OH))(N-(D-Man)-N,N'-Me2-en)Cl • 4H 0 • 2CH OH (f), where en = ethylenediamine, tren = tris(2-aminoethyl)amine, D-Fru = D-fructose, L-Sor = L-sorbose, L-Rha = L-rhamnose, D-GlcN = D-glucosamine, D-Man = D-mannose. Edge energies were calibrated with Ni foil.

Results

The edge region of the Ni K edge X-ray absorption spectrum generally reveals considerable information about the electronic and molecular structure of the Ni site. Figure 1 shows the experimental XANES for six nickel(II) complexes containing N-glycoside(s). In every case three peaks are observed. The features labeled A - D in Figure 1 could be assigned to various origins. Feature A (8332 eV) has been identified as originating from a 1s - 3d transition. The features C and D have generally been understood as arising shape resonance involving multi-scattering effects. The absorption heights of XANES main peaks after extraction were normalized with respect to the XAFS background absorption at 839 eV, which is about 60 eV higher than the edge energies. The peak position of A is fixed at 8332 eV. It has been generally accepted that the peak A is the fingerprints of the coordination geometry around the central metal. However, the correlation between the C and D peaks and the coordination geometry has not been well established. The normalized peak heights and peak positions are summarized in Table 1. These peak heights and peak positions are distributed in a narrow range. The molecular structures of the present nickel(II) complexes have been determined by X-ray crystallography. Therefore, the great similarity of the feature C and D for every complexes are significantly corresponding to the coordination geometry of nickel(II) complexes as well as the feature A. Thus the coordination geometry around the nickel(II) ion is well discussed by the XANES spectra.

References

Local Structures of $\text{RbBr}_x\text{Cl}_{1-x}$ and $\text{CuBr}_x\text{Cl}_{1-x}$ Solid Solutions

Studied by Temperature-Dependent $\text{Br}$ K-Edge EXAFS Spectroscopy

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1. Introduction

Local structures of binary solid solutions have been extensively investigated by EXAFS spectroscopy, and these works have denied the virtual crystal approximation (VCA), and remarked that a bonding pair of atoms is likely to retain its natural bond distance. Recently, we measured temperature-dependent $\text{Br}$ K-edge EXAFS spectra of $\text{AgBr}_x\text{Cl}_{1-x}$ solid solution [1], and found that the $x$-dependence of the $\text{Br}-\text{Ag}$ distance, $\alpha_{\text{Br}-\text{Ag}}(x)$, is significantly temperature-dependent, becoming noticeably smaller as temperature increases. In the present study, we have measured $\alpha(T)$ in $\text{RbBr}_x\text{Cl}_{1-x}$ and $\text{CuBr}_x\text{Cl}_{1-x}$, and compared with the results of $\text{AgBr}_x\text{Cl}_{1-x}$.

2. Experimental

$\text{RbBr}_x\text{Cl}_{1-x}$ and $\text{CuBr}_x\text{Cl}_{1-x}$ were prepared for $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and $0.9$ by mixing appropriate amounts of corresponding bromides and chlorides, followed by repeated treatments of grinding and melting ($\sim 1023\text{K}$ for $\text{RbBr}_x\text{Cl}_{1-x}$ and $\sim 873\text{K}$ for $\text{CuBr}_x\text{Cl}_{1-x}$). The homogeneity of solid solutions was confirmed by the X-ray diffraction measurement. $\text{Br}$ K-edge EXAFS spectra of the solid solutions diluted with boron nitride powder were measured at $77\text{K}$, $150\text{K}$ and $295\text{K}$ at BL-10B.

3. Results and Discussion

Figure 1 gives the $x$-dependence of the first nearest neighbor $\text{Br}-\text{Rb}$ interatomic distance, $R_{\text{Br}-\text{Rb}}(x, T)$, at each temperature, determined by the present EXAFS analysis. This clearly shows that for all the temperatures investigated, the VCA is discrepant from the observation. Furthermore, $\alpha_{\text{Br}-\text{Rb}}(x, T)$ is independent of temperature in contrast to the results of $\text{AgBr}_x\text{Cl}_{1-x}$ [1].

Figure 2 gives the $R_{\text{Br}-\text{Cu}}(x, T)$, of $\text{CuBr}_x\text{Cl}_{1-x}$ at each temperature, which shows a noticeably different behavior from $\text{RbBr}_x\text{Cl}_{1-x}$. $R_{\text{Br}-\text{Cu}}(x, T)$ is almost independent of $x$, and $\alpha_{\text{Br}-\text{Cu}}(T)$ is also temperature independent. Although the VCA cannot explain the results, the Pauling's concept of the constant ionic radii seems adequate in $\text{CuBr}_x\text{Cl}_{1-x}$ as observed in other covalent solid solution [2,3]. Temperature dependence of $\alpha(T)$, which was observed in silver halides, was not found in $\text{RbBr}_x\text{Cl}_{1-x}$ and $\text{CuBr}_x\text{Cl}_{1-x}$, indicating the abnormal character of of silver halides. These different behaviors can be understood by taking account of the competition between the long-range force and short-range force which determine the crystal structure. The long-range force which suppresses the crystal distortion is comparatively large in $\text{RbBr}_x\text{Cl}_{1-x}$ but is not important in $\text{CuBr}_x\text{Cl}_{1-x}$ for all the temperature range investigated. In silver halide solid solutions, the long-range force at low temperature is as large as that in $\text{RbBr}_x\text{Cl}_{1-x}$, and it become less significant as temperature increases, leading to the large crystal distortion.

references


![Figure 1. The $\text{Br}-\text{Rb}$ interatomic distance $R_{\text{Br}-\text{Rb}}(x, T)$ of $\text{RbBr}_x\text{Cl}_{1-x}$ at 77K, 150k and 295k. The dashed line corresponds to the averaged linear function which gives $\alpha_{\text{Br}-\text{Rb}}(T)$ as y intersection, and the solid line corresponds to the VCA.](image)

![Figure 2. The $\text{Br}-\text{Cu}$ interatomic distance $R_{\text{Br}-\text{Cu}}(x, T)$ of $\text{CuBr}_x\text{Cl}_{1-x}$ at 77K, 150k and 295k.](image)
A STUDY ON ANHARMONIC VIBRATIONS IN AgI BY EXAFS

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Introduction

β-AgI (the wurtzite-type structure) exhibits a negative thermal expansion, and undergoes a first-order phase transition at 420 K to α-AgI with higher density. The α-phase of silver iodide is a classical and typical superionic conductor of Ag ions. In the structure of α-AgI, the iodine ions form a regular body-centered cubic lattice with a statistical distribution of the highly mobile Ag ions.

In this study, the thermal behaviour of atoms in β- and α-AgI has been investigated by the EXAFS method in the temperature range 73-815 K. The EXAFS data were analyzed using a formula expressed by the cumulant-expansion up to the fourth-order terms.

Experimental and analysis

The fine powder samples identified to be β-AgI by X-ray diffraction were pressed with powder of boron nitride into pellets of 0.6 mm in thickness and 10.0 mm in diameter. The X-ray absorption measurements near Ag K-edge were made with synchrotron radiation at the beam line 10B of Photon Factory in KEK, at 73, 173, 293, 373, 473, 573, and 815 K. The temperature was controlled within a stability of 1 K. EXAFS interference function was extracted from the measured absorption data using standard techniques1). The radial structure function (RSF) around Ag ions at various temperatures are shown in Fig. 1, where no phase shift correction is made, and the same k range (k = 4.5 - 11.0 Å⁻¹) is used in each case. The simulation of the RSF around Ag ions of AgI is made using theoretical amplitude and phase functions2) and hypothetical structure parameters of a harmonic model (N=4, r=2.81 Å, \( \sigma^2=0.5 \times 10^{-2} \) Å²), and is also shown in Fig. 1. The Fourier filtered EXAFS data were fitted using the least-squares minimization technique with analytical EXAFS formula expressed by the cumulant-expansion up to the fourth-order terms3,4). The amplitude and the phase function employed here were the theoretical curves tabulated by Teo and Lee2). Details of the data processing procedure were already given in references 1 and 5.

Results and discussion

The experimental results can be explained satisfactorily by the anharmonic model which has a set of reasonable values of the local structure parameters. The Ag ions in α-AgI occupy only the 12(d) tetrahedral sites of space group Im3m. The reduction of peak height with increasing temperature results from the Debye-Waller type broadening between Ag and I nearest-neighbors. The third and fourth cumulants are significant even at 73 K. The position of each peak in the RSF around Ag ions observed in both β- and α-AgI (Fig. 1) is significantly shorter than that of the simulation, and shifts apparently to a shorter distance with increasing temperature due to the contributions of third-order terms. The temperature variations of the cumulants are shown in Fig. 2. The temperature dependence of these values are different between β- and α-AgI, which may be correspond to the result obtained from diffraction experiments6).
EXAFS STUDY OF MoO₃ CATALYSTS ON COMPOSIT SUPPORTS PREPARED BY CVD METHOD

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INTRODUCTION
Supported molybdena are some of the most important catalysts in the petroleum industry. For example, sulfided molybdenum catalysts are widely used for hydrodesulfurization of petroleum fractions. It is known that supports affect the catalytic activities. In present study, three kind of supported molybdenum catalysts were prepared and their structure was investigated by EXAFS.

EXPERIMENTAL
The supports employed TiO₂(P-25 from Degussa), γ-Al₂O₃(JRC-ALO-4) and TiO₂-Al₂O₃. TiO₂-Al₂O₃ was prepared by repeated vapor deposition of TiCl₄ on γ-Al₂O₃. The detail procedure was described by Foger and Anderson(1). Supported molybdena catalysts were prepared by impregnation method. For sulfiding treatments, the catalysts was sulfided with a gas flow using a mixture of H₂S, H₂, N₂(3/20f77) at 673K for 2h. Mo K-edge EXAFS spectra were measured at room temperature, using BL-10B.

RESULT AND DISCUSSION
Figure 1 shows the Fourier transformed EXAFS spectra of the sulfided catalysts. For the all catalysts, the two peaks were observed at 0.24nm and 0.32nm. These peaks based on Mo-S and Mo-Mo distance, respectively. This results suggested that the catalysts formed a MoS₂-like structure. The peak intensity of MoO₃/Al₂O₃ corresponded to that of MoO₃/TiO₂-Al₂O₃. The oxidized catalysts also demonstrated the same result. Therefore, these catalysts have the local ordered structure. The peak intensity of MoO₃/TiO₂ is smaller than others because the concentration of Mo in this catalyst is lower. The results of EXAFS analysis didn't show a remarkable difference of the structure in the catalysts. Therefore, support did not affect the structure of the catalysts but interact with metal-oxide or sulfide.

REFERENCES
CHARACTERIZATION OF THE Cu(II)-S(ALIPHATIC THIOLATE) BOND IN LOW MOLECULAR-WEIGHT COMPLEX: TERNARY COMPLEXES FROM Cu(II), GLYCYLGLYCINE, AND CYSTEINE OR PENICILLAMINE

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Cysteinyl residues are important metal binding sites in enzymes and proteins that contain copper or iron as prosthetic groups. Chemically stable Cu(II)-S(cysteinyl thiolate) bond is found in blue copper proteins and oxidases, e.g., plastocyanin and laccase, and non-blue copper enzymes, e.g., cytochrome c oxidase. It is of much interest that the Cu(II)-S bond, which is chemically unstable in low molecular-weight complexes, is conserved in those proteins. We have been studying on peptide complexes with Cu(II)-S(cysteinyl thiolate) bond, and reported their coordination structures and spectroscopic properties [1]. In this paper, are described characterization by EXAFS of the Cu(II)-S bond in the ternary complexes from Cu(II), glycylglycine (GlyGly), and cysteine(CySH) or penicillamine(PaSH).

The ternary complexes were unstable undergoing rapid oxidoreduction. Therefore, preparation of the complexes were done by a rapid-mixing and rapidfreezing technique. Solutions of Cu(II)-(H\textsubscript{2}GlyGly) and the thiol(RSH) were mixed by using a rapid-mixing apparatus [2] to yield the complex, (RS)Cu(II)-(H\textsubscript{2}GlyGly). The solution of ternary complex coming out from jets of the mixer were rapidly frozed and trapped as thin films on the inner surface of a copper cylinder cooled at about -200 °C. The frozed sample thus prepared was collected and transferred to an aluminum observation cell.

Measurements of X-ray absorption spectra were carried out on the EXAFS port, BL 7C. The spectra were measured at -200 °C in the range of photon energy from 8520 to 9980 eV and registered in a transmission mode.

The ternary complexes are shown to have a coordination structure Cu(II)-(N\textsubscript{2})(NS); the nitrogen ligands are derived from amino group and deprotonated peptide-bond of GlyGly, and amino group of RSH. The Cu(II)-S distance in the complexes was determined as 2.27 Å.

Introduction
Formazan compounds are one of the most active reagents to form various complexes with metal ions. The color of the copper with 1-(2-pyridyl)-3-phenyl-5-(2-hydroxyphenyl)formazan (PHF) changes markedly depending on pH of the solution, i.e., red in acid media and blue in neutral to alkaline media, respectively. Similar color change is also observed for the nickel-PHF complexes. The present XAFS studies have been performed to investigate the structural changes of metal-PHF complexes due to pH of the solution.

Experimental
The measurements of X-ray absorption spectra near K-edges have been carried out at the Photon Factory BL-10B. All the spectra were obtained in transmission mode. Each sample for measurement was formed by pressure with an appropriate amount of the powdered sample into a disk which adjusted its thickness to make the X-ray absorption coefficient fall within the range of 1 and 2 at the absorption edge.

Results and discussion
Figure 1 depicts the postulated structures of Cu-PHF complex at pH 2.15 and pH 5.2 and the corresponding radial distributions. The radial distributions were obtained by the Fourier transform of the k^2-weighted EXAFS oscillation of the Cu-PHF complex by taking correction of the theoretical phase shift of the Cu and N contributions into consideration.

At pH 2.15 the complex indicates a peak at 1.9 Å and a shoulder peak at 2.4 Å. These two peaks were assigned to the scatterings due to the nitrogen atoms and the oxygen atom at the nearest-neighbor of the copper atom, respectively. The complex at pH 5.2 shows only one large peak at 2.0 Å, which is close to the bond distance of the Cu-N bond in Cu-porphyrin compounds, indicating that the Cu-N and Cu-O bond distances of the complex at pH 5.2 are almost similar to each other. XANES spectra suggested that the planer structures are maintained for the both compounds. These show that the undissociated -OH of PHF takes part in the complex formation with copper by Cu...OH bond at pH less than 2.15 and that the dissociated -O~ forms Cu-O bond of the complex at pH above 5.2, as shown in Fig. 1.

The structural changes for Ni-PHF complexes were found to be different from that for Cu-compounds. The radial distribution of the Ni-PHF formed at pH 8.0 was similar to those of Ni(acac)_2 and Ni-TPP, whereas that of the complex formed at an acidic condition showed a peak approximately two times larger than that formed at a higher pH for the 2nd nearest neighbor scattering peak. These suggest that two PHF molecules form the Ni-PHF complex at the acidic conditions.

![Figure 1. Postulated structures of Cu-PHF complex at pH 2.15 and pH 5.2 and the corresponding radial distributions obtained from the EXAFS data.](image-url)
EXAFS Study on The Structure of The Photoprodut Produced by The Irradiation of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ Adsorbed on Silica

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INTRODUCTION

Coordinatively unsaturated surface species with metal-metal bonding have a potential to show high activity for industrially important reactions. A photochemical approach for preparing of such surface species may have several advantages over thermal process, because very clean photochemical transformation without declusterification is expected to be carried out on polynuclear metal carbonyl clusters adsorbed on inorganic oxide. In this paper, we report the preparation of coordinatively unsaturated Ru carbonyl by using the photochemical reaction of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ adsorbed on $\text{SiO}_2$ and its structure analysis by means of EXAFS.

EXPERIMENTAL

$\text{H}_2\text{Ru}_4(\text{CO})_{13}$ was prepared according to the method given in the literature. Two kinds of silica (Nippon Aerosil) was used as a support. The one is Aerosil 380 with surface OH groups (“normal”), the other is RY200 where all silanol groups have been replaced by methyl groups (“surface modified”). $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ was supported on silica by putting dried silica into a n-hexane solution of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ followed by solvent removal. The 313nm-irradiation was performed by using a ultra high pressure Hg-lamp (WACOM DLM-500D, 500W). EXAFS data were obtained by use of the EXAFS spectrometer at BL-10B.

RESULTS AND DISCUSSION

Upon UV-vis light irradiation, the FT-IR absorption spectrum changes with clear isosbestic points, indicating that a single product is produced. The gas evolved during the light irradiation composed of CO. No indication was found for the evolution of $\text{H}_2$. UV-vis light irradiation leads to a slight change of the Fourier Transform of the Ru K-edge EXAFS for $\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{SiO}_2$ (“normal”) but its main feature remains unchanged as shown in Figure 1. The curve fitting analysis shows that Ru-Ru distance and its coordination number of the photoproduct are 2.80Å and 2.3 respectively, which are 2.81Å and 3.0 for $\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{SiO}_2$ (“normal”). Hence, the Ru-Ru distance and coordination number for both $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and the photoproduct on $\text{SiO}_2$ (“normal”) are almost the same within the experimental error. This means that original metal framework, $\text{Ru}_4$, of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ is retained in the photoprodut. The FT-IR absorption spectrum of the product agrees well with that of the coordinatively unsaturated species, $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ in polystyrene film at 77K. From these results the photoproduct is assigned to the coordinatively unsaturated species $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ and the photochemical reaction can be formulated as

$$\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{SiO}_2(\text{normal}) \rightarrow \text{H}_2\text{Ru}_4(\text{CO})_{12}/\text{SiO}_2(\text{normal}) + \text{CO}$$

Since light irradiation leads $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ to decompose on $\text{SiO}_2$ (“surface modified”), the surface hydroxyl groups are essential for the photoirradiation represented by eq.1. The role of hydroxyl groups is supposed to make $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ in a well dispersed state and trap the coordinatively unsaturated $\text{H}_2\text{Ru}_4(\text{CO})_{12}$.

CONCLUSION

The possibility of preparing unstable polynuclear metal carbonyl by utilizing photochemical reaction was demonstrated. UV-vis light irradiation of $\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{SiO}_2$ (“normal”) leads to selective loss of one CO ligand, yielding $\text{H}_2\text{Ru}_4(\text{CO})_{12}$. The coordinatively unsaturated $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ is stabilized by the interaction with surface OH groups and the dissociated CO is lost from the surface. These situations may prevent a secondary reaction. This might be the reason why $\text{H}_2\text{Ru}_4(\text{CO})_{12}$ is efficiently formed upon UV-vis light irradiation of $\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{SiO}_2$ (“normal”).

REFERENCES


1098 737.3 604 303.0 202.0 101.0 002.0 000.0 60 50 40 30 20 10 0 Distance/Å

Fig.1 Fourier Transform of Ru K-edge EXAFS oscillation of $\text{H}_2\text{Ru}_4(\text{CO})_{13}/\text{silica(‘normal’)}$

(A) before irradiation (B) after irradiation at 313nm
A STRUCTURAL STUDY FOR THE ROLE OF INTERSTITIAL CARBON FOR OXYGENATES FORMATION ON SUPPORTED [Ru6C(CO)16(CH3)] CATALYSTS

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Metal ensembles are expected to have catalytic properties which are never observed with single metal complexes. In this point of view supported metal clusters have extensively been studied, but there are few examples which exhibit specific catalytic performance of supported clusters. We have found specific catalysis of supported Ru-carbido-carbonyl clusters for the formation of oxygenates (CH3OH, H2CO, (CH3)2O) from CO/H2 (Fig. 1). This particular cluster has an interstitial carbon inside the Ru6 framework. Conventional Ru catalysts or supported Ru6 clusters without interstitial carbon (precursor: [Ru6(CO)16]^+) formed mainly methane. Therefore, we examined the role of the interstitial carbon inside the Ru6 framework in oxygenates formation by means of EXAFS.

[BTMA][Ru6C(CO)16(CH3)] (BTMA = PhCH2N(CH3)3) (Fig. 1 in No.89016) was supported on oxides (MgO, ZnO, La2O3, TiO2, ZrO2, Al2O3, SiO2), followed by treatment at 623 K. The EXAFS of Ru K-edge were observed at BL 10B. For supported [Ru6C(CO)16(CH3)] after impregnation all catalysts showed similar transforms of EXAFS oscillation to that of [Ru6C(CO)16(CH3)]- crystal in consistent with no gas desorption at the preparation of catalysts. Methane formations from methyl ligand were observed on MgO and La2O3 (basic oxides) in catalyst preparation, and the EXAFS of [Ru6C(CO)16] crystal was similar to that of [Ru6C(CO)16(CH3)]-. After pretreatment at 623 K all the samples showed only one peak at the distance of Ru-Ru. The low coordination number (N) of Ru-Ru by curve fitting procedure for all the supported clusters (3.0 - 5.4) was specific. Carbido-clusters are known to be stable because of the support by an interstitial carbon. In our case interstitial carbon is supposed to stabilize Ru6 unit on oxides, and prevent to aggregate to metal particles. After CO/H2 reaction at 523 K, only little changes of EXAFS were observed with the adsorption of CO on La2O3 and TiO2 (Fig. 2, N = 3.5, 2.63 Å for Ru-Ru), but a peak around 3.1 - 4.1 Å (phase shift is not corrected) emerged in Fourier transform for [Ru6C(CO)16(CH3)]/MgO. This can be well curve-fitted by the parameter of Ru-C=1Ru bond in EXAFS of [Ru6C(CO)16(CH3)]- crystal with N = 1.0 and distance (4.11 Å). We suppose that the high activity and selectivity for oxygenates can be attributed to Ru6 units on oxides.

Figure 1. The selectivity in CO/H2 reaction on supported Ru6C, Ru6 and conventional Ru catalysts; CO 14.6 kPa, H2 14.6 kPa.

Figure 2. EXAFS spectra for Ru K-edge of [Ru6C(CO)16(CH3)]/TiO2 after CO/H2 reaction at 523 K; (a) k^-weighted EXAFS oscillation, (b) its associated Fourier transform, and (c) curve fitting analysis (---: observed, ------: calculated).
STRUCTURE OF BIMETALLIC COLLOIDAL CATALYSTS
— Reduction Process of the Pd/Au Bimetallic Clusters —

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Introduction

The colloidal dispersions of the poly(N-vinyl-2-pyrrolidone)-protected palladium/gold bimetallic clusters were obtained by preparing both by simultaneous and successive reductions. The catalytic activity of the bimetallic clusters prepared by the simultaneous reduction is examined for the selective partial hydrogenation of 1,3-cyclooctadiene and compared with that of the mixtures of the monometallic clusters. The initial rate of hydrogenation depends on the metal composition and the maximum catalytic activities were achieved at Pd/Au = 4/1.

In the case of the mixtures of the Pd and Au monometallic clusters, the catalytic activity is higher than that expected for the mixture of the two kinds of the monometallic clusters without interaction. The EXAFS data of the Pd/Au(4/1) bimetallic clusters prepared by simultaneous reduction indicate that the surface of the cluster consists entirely of palladium atoms and the core consists of gold atoms (core structure). On the other hand, the mixtures of the Pd and Au monometallic clusters become bimetallic with time in solutions on the basis of the TEM observation and the electronic spectra. Here we will discuss the process to form the Pd/Au(4/1) bimetallic cluster by the simultaneous reduction by comparing the EXAFS measurements of the clusters prepared by the simultaneous and successive reductions.

Experimental

The Pd/Au(4/1) bimetallic clusters were prepared by refluxing the mixed solution of the corresponding ions in water-ethanol under nitrogen (simultaneous reduction). On the other hand, the Pd/Au(4/1) clusters were also prepared by the successive reduction, in which the solution of HAuCl₅ was reduced at first, and then the ethanol solution of PdCl₂ was added and the successive reduction was followed (Au → Pd). In the other sample the sequence was reversed (Pd → Au). These bimetallic clusters were concentrated under reduced pressure, and the solutions were sealed in the 50 mm (for palladium) and 5-10 mm (for gold) cells under nitrogen. The EXAFS spectra were measured at a BL-10B station of the Photon Factory, KEK.

Table 1. Coordination Numbers around the Pd and Au Atoms of the Various Pd/Au(4/1) Bimetallic Clusters Determined from EXAFS Data

<table>
<thead>
<tr>
<th>Absorbing metal</th>
<th>Scattering metal</th>
<th>Au-Pd</th>
<th>Pd-Au</th>
<th>Simul.</th>
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<tr>
<td>Pd</td>
<td>Pd</td>
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<tr>
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<td>Au</td>
<td>4.4±2.8</td>
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<tr>
<td>Au</td>
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<td>4.2±1.7</td>
<td>4.4±1.7</td>
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</tr>
</tbody>
</table>

Results and Discussion

Figure 1 shows the Fourier transforms of Au L₃-edge EXAFS of the Pd/Au(4/1) clusters prepared by the simultaneous and the successive reductions. Comparing these samples, the main peaks have nearly the same shape. In the case of the Pd K-edge, these samples have only Pd-Pd bonds similar to those of the monometallic Pd clusters.

Table 1 shows the coordination numbers around the Pd and Au atoms of the Pd/Au clusters. The dispersions prepared by the successive reduction (Au → Pd) consist of large gold particles and the monometallic Pd clusters. So the Au clusters immediately form precipitates. Hence, the edge jump of the sample cannot be observed. On the other hand, the cluster (Pd → Au) has the same structure as the Pd/Au(4/1) bimetallic cluster prepared by the simultaneous reduction. Therefore, it could be concluded that the process to form the Pd/Au bimetallic cluster by the simultaneous reduction consists of both reduction steps, i.e., the first step is the reduction of the Pd ions and the second step, the reduction of the Au ions.

Reference


![Fig.1. The Fourier-transformed EXAFS spectrum at L₃-edge of Au of the Pd/Au bimetallic clusters prepared by the simultaneous and successive reductions.](image-url)
Changes in the Electronic Structure of Bi 2201 Phase Annealing in Absence of Oxygen Studied by Cu K-edge X-ray Absorption Near-Edge Structure

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It has been reported that Tc's of Bi 2201 phase was observed to increase by 5-20 K after annealing in the absence of oxygen. However, it is difficult to determine oxygen positions of the Bi 2201 phase by x-ray and neutron diffraction, under the existence of heavy atoms and with modulated structure.

XANES contains information on the valence state of the X-ray absorbing atoms and the local structure around them. Therefore, it is interesting to investigate changes in geometric and electronic structure arisen from the post annealing in absence of oxygen by Cu K-edge XANES for the Bi 2201 samples.

Powder samples were prepared as previously. Cu K-edge XANES spectra were measured at BL-10B. Powdered sample was pressed into d=13 mm pellets with dry BN.

All the Bi 2201 samples, (a)Bi₂Sr₁₈La₀₂CuO₆+y, (b) Bi₂Sr₁₆La₀₄CuO₆+y and (c) Bi₁₁.₆Pb₀.₄Sr₁₆La₀₄CuO₆+y showed the structure from A to E in XANES. Only the spectrum for sample (c) is shown in Fig. 1(A). The absorptions of A, B, C, D, and E are assigned to the transitions of ls-3d, ls-4p₇r (3d⁺⁹⁻), ls-4p₇c (3d⁰²⁻), ls-4p₄a' (3d⁰⁻), and ls-4p₄a (3d⁰ respectively, following Kosugi et al.²,³.

Figure 1(B) shows the subtraction spectrum of [sample (c) annealed in N₂] - [sample (c) annealed in O₂]. The increase in absorption between the structures A and B is observed. For other Bi 2201 samples, (a) and (b), similar tendency was observed in subtraction spectra.

To explain the increase of the absorption between the structures A and B, we have carried out the DV-Xα cluster calculation for CuO₂, CuO₅, CuO₆ clusters, and found that Cu 4p states splits into two levels in CuO₅ cluster, where these levels are degenerated in CuO₄ and CuO₆ clusters. This indicates that, the increase of the states between A and B can be assigned to the transition from is to split 4pₓstates, forming a counter pair to the absorption B. Therefore, by the post annealing in absence of oxygen, the apex oxygen of CuO₂ layer in Bi 2201 phase moves into the direction from the CuO₂ plane to BiO, and as a result octahedral symmetry breaks after the annealing.

REFERENCES
Liquid-Liquid Critical Phenomena in Liquid Chalcogenides

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There are many liquid binary systems (e.g., water and oil) which are known to have the miscibility gap. However, a very fundamental question: "Why are they immiscible?" has been so far scarcely answered.

We have studied the physical properties near the miscibility gap of liquid metal-liquid semiconductor mixtures such as Tl-Se, and liquid metal-molten salt mixtures such as Bi-BiBr₃ by measuring the electrical conductivity and the sound velocity under high pressures.* We found that the miscibility gap which appears in the metal-nonmetal transition range in these binary systems at 1 atm becomes small with increasing pressure and eventually disappears when the systems become metallic in whole concentration range.

In this study we determine the precise shape of the liquid-liquid coexistence curve and to study the local atomic arrangements in the liquid chalcogen mixture by means of X-ray absorption measurements.

As shown in Fig.1, when a liquid metal (M)-semiconductor (S) mixture with concentration C is slowly cooled down to the temperature on the coexistence curve, it will separate into two phases A and B. By carrying out the X-ray absorption measurements on both absorption edges of M and S for both A and B phases, we can simultaneously determine the concentration and the density of the both phases from the jumps of absorbance. The accurate determination of the coexistence curve will enable us to deduce the critical exponent β and to know whether the so-called "law of rectilinear diameter" is valid or not.

We show a preliminary result of EXAFS measurement for the liquid Rb-Se system which has a miscibility gap on the Se-rich side with the consolute temperature of 250°C.** The EXAFS spectra were taken on both Se and Rb K-edges with EXAFS spectrometer installed at BL-10B station. Fig.2 shows the EXAFS function χ(k) of liquid Se₉₀Rb₁₀ at 270°C in the homogeneous phase. The partial radial distribution function F(r) obtained by Fourier transform of χ(k) is shown in Fig.3.

Fig.1. The schematic diagram of phase separation for liquid metal - liquid semiconductor mixture.

Fig.2. The EXAFS oscillations, χ(k), near Se K-edge for 1-Se₀.₉₉Rb₀.₁ at 270°C as a function of photo-electron wave number k.

Fig.3. The radial distribution function F(r) around a Se atom, obtained by Fourier transform of χ(k) for 1-Se₀.₉₉Rb₀.₁.
An XAFS Study on Copper(n) Complexes Containing N-Glycosides which Catalyze an Epoxidation of Olefins

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Introduction

The elucidation of interactions between carbohydrates and metal ions has become an important subject in inorganic chemistry as well as organic chemistry. We have studied the synthesis and characterization of nickel(II) complexes containing N-glycosides derived from the reaction of sugars and diamines. Here, we prepared and characterized new copper(II) complexes containing N-glycoside ligands by XAFS analyses, in the hope of exploring some catalytic reactions promoted by transition metal-sugar complexes.

Experimental

Copper(II) complexes of N-glycosides, Cu(N,N-(aldose)-2-en)X2 (2) (aldose = D-Glc, D-Man, D-Xyl, and D-Lyx; X = CF3, Br-) and Cu(N-(aldose)-diamine)X2 (diamine = N,N'-Me2en 3, N,N-Me2en 4) were prepared by the reaction of CuX2·2H2O with aldoses and diamines. Cu{hen(OH)2}Br2 (la) and Cu(henOH)Cl2 (lb) were also prepared as reference compounds (hen(OH)2 = (CH2NHCH2CH2OH)2, henOH=NH2CH2CH2NH-CH2CH2OH). X-Ray absorption spectra near Cu K-edge were measured at room temperature in transmission mode with synchrotron radiation (PF) using EXAFS facilities installed on the Beam Line 10B. EXAFS analysis were carried out by the use of theoretical least-squares curve-fitting techniques for Fourier filtered waves with the program EXAFS1, 2)

Results and Discussion

XANES spectra of the copper(II) N-glycoside complexes (2-4) were similar to those of model compounds (1) except for slight broadening seemingly due to the distortion from an square planar geometry. These indicated that the copper(II) sugar complexes have an almost identical structure around the metal center to that of the model compounds (1).

X-Ray crystallographic studies revealed that la or lb has a square planar structure coordinated by tridentate hen(OH)2 or hen(OH) and a halide anion, as shown in Figure 1e and 2a. In these compounds, the atomic parameters derived from EXAFS analysis are in good agreement with those from crystallographic studies. The Fourier transform and the result of curve-fitting using k^2(χN/O(k)) + χC(k) + χX(k)) for 1b are depicted in Figure 1. By the similar method, the structural parameters of the sugar complexes (2-4) were determined by EXAFS analysis. As a representative result, the Fourier transform and the result of curve-fitting for 3a are given in Figure 1b and 1d. These results strongly suggested that the copper(II) complexes of N-glycosides adopt the square planar structure just like the complexes la and lb, where tridentate N-glycoside, N,N'-aldose,N-aldose, N,N'-aldose,N,N'-aldose, or N-(aldose)-N,N'-aldose, and halide anion (Cl^- or Br^-) attach to the metal center (Figure 1f and 2b).

The copper(II) complexes of N-glycosides interestingly catalyzed an epoxidation of olefins (trans-stilbene, cis-stilbene, β-methylstyrene, and cinnamylacetate with tert-butyldihdroperoxide.

References

2) N. Kosugi and H. Kuroda, EXAFS1, Research Center for Spectrochemistry, the University of Tokyo (1985).
Introduction

Recently, it has been shown the possibility of that MerR, the DNA binding protein which triggers the gene expression when it traps mercury of trace amount, adopts planar HgS\(^3\) geometry for its mercury site. We provided, in the last activity report, the result of the structural analysis for the mercury peptide, (Boc-Cys-Pro-Leu-Cys-OMe) Hg(II) (H\(_2\)O)\(_2\), which has linear HgS\(^3\) coordination unit. In this report, we wish to present the structural analysis of [(Boc-Cys-Pro-Leu-Cys-OMe)Hg(II)(SBu\(^3\))]\(^+\), the mercury peptide model for the HgS\(^3\).

The method of structural analysis used here is the same as the last report, where we combined by distance geometry technique the distance information around metal (from XAS experiment) and that about H- H pairs from NOESY experiment.

Experimental

The linear mercury peptide 2 was synthesized as before, from which the tridentate mercury salt, 2, was prepared by reacting 1 eq. of NaSBu\(^3\) in DMF (or MeOH). Hg L(III) XAS experiment was carried out by using the EXAFS facilities of BL-1OB of PF on transmission mode in DMF solution and analyzed by EXAFS 1. XAS for the other 7 mercury compounds were also measured for comparison. The coordination geometry around mercury was determined comparing the XANES spectrum with those of reference compounds. Hg-S distance was calculated on the basis of both theoretical and experimental parameters. Independently from these XAS experiment, H- H distances of the peptide moiety were estimated from the cross peak intensities of the NOESY spectrum observed on a JEOL JNM-GSX-500 spectrophotometer. From these distance informations, the whole structure of compound 3 was calculated by the distance geometry program, DIANA, equipped with a newly developed simulated annealing method. EXAFS distances were weighted heavily in the calculation, considering the accuracy of the distance informations from XAS and NOE.

Result

Fig. 1 includes the XANES regions of 8 compounds. As is seen in here, the mercury in [(Boc-Cys-Pro-Leu-Cys-OMe)Hg(II)(SBu\(^3\))]\(^+\) is well superimposed to that of [Hg(SBu\(^3\))\(^3\)]\(^+\), suggesting the similarity of the mercury coo of both compounds. The mean distance between Hg and S was calculated as 2.43 Å in DMF. The optimized whole structure of this mercury peptide after distance geometry calculation is given in Fig. 2. This structure overlaps very well with the metal site of rubredoxin and alcohol dehydrogenase. The result is the first example of the peptide including model of the metal sites of these metallo enzymes, as well as probably the metal binding site of zinc finger proteins, which also interact with DNA.

![Figure 1. The Hg L(III) edge XANES spectra of eight mercury compounds.](image1)

![Figure 2. The coordination and the conformation of [(Boc-Cys-Pro-Leu-Cys)Hg (SBu\(^3\))]\(^+\).](image2)
XAFS analysis of halide glass structure
--multi-component zinc halide-based glasses

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Halide glasses, which consist of only fluorides, chlorides, bromides and/or iodides, have been received much attention for the past decade because of their applicability for optical materials in infrared region. Many glass-forming halide systems have been reported. However, the glass structure of these systems has been still open except for some fluoride and chloride glasses. XAFS spectroscopy which gives information about the structure around each element is a very useful method for structural analysis since most halide glasses are obtained only in multi-component systems. Here we report the structure of multi-component zinc halide glasses (ZnX2-CsX-BaX2 where X=Cl, Br and I), focusing on the coordination structure of zinc ions which play a role of glass-forming cation.

The compositions of the glasses are 55ZnX2-40CsX-5BaX2 and 50ZnX2-40CsX-10BaX2 (X=Cl, Br and I). The glass preparation is described elsewhere[1]. The ground samples for XAFS spectroscopy were sealed with polyethylene films in order to prevent hydrolysis. XAFS measurements were carried out at Zn K-edge by use of the EXAFS facilities installed at the beam line 10B. Data analyses were made by the usual manner[2].

Figure 1 shows the Fourier transforms of the multi-component ZnBr2-based glasses along with ZnBr2 and Cs2ZnBr4 crystals and ZnBr2 glass. All the Fourier transforms have peaks at around 2.1 Å which are assigned to the nearest-neighbour Br⁻ ions coordinating to Zn²⁺ ions.

The structural parameters were obtained by means of Fourier-filtering technique and curve-fitting method using theoretically calculated back-scattering amplitudes and phase shifts[2,3] For the crystalline samples the refinements were applied to bond distance (R), Debye-Waller type thermal parameter (σ), mean free path of photoelectron (λ), and energy difference between theoretical and experimental threshold (Δε). For the glasses, the curve-fitting analyses were performed with coordination number (N), R, σ and Δε as variable parameters.

The structural parameters are set out in Table 1. The coordination numbers of ZnBr2 glass and the multi-component glasses are 3.5-3.9. This is consistent with those predicted from Raman spectra of these glasses which have been interpreted with a structural model of four-fold coordination[1]. The bond distance between Zn²⁺ and Br⁻ ions in ZnBr2 glass is similar to that in ZnBr2 crystal. On the other hand, those in the multi-component glasses are shorter that that in ZnBr2 crystal and are close to that in Cs2ZnBr4 crystal. This agrees with the result of Raman spectroscopy which expects that the introduction of CsBr and BaBr2 to ZnBr2 glass forms non-bridging Br⁻ ions in the network structure of the glass[1].

The results for the chloride and the iodide glasses are the same as those for the bromide glasses.

Dispersion and structure of NiO on the surface of Al2O3

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Institute of Physics, the Chinese Academy of Science

Dispersion and structure of active component in heterogeneous catalyst and adsorbent have great significance both on practice and on theory. It has been found that salts and oxides can disperse onto surface of a carrier in monolayer spontaneously[1]. Unfortunately, surface structure is very complicated and has been known very little yet.

In this paper we studied NiO/f-Al2O3 system. NiO has the structure of NaCl with high symmetry. Lytle has studied its structure by XAFS and got a set of good structure data up to 17th shell[2]. So structure change after dispersion of NiO can be observed distinctly by XAFS.

Crystal phase amounts in the system measured by XRD are shown in Fig.1-a. For other samples crystal phase amounts are less 0.185 g/g than NiO load. If the amount is less than 0.185 g/g, there is no crystal NiO phase. It means that at least a part of NiO exists in form of disperse phase in the samples. The maximum dispersion amount is 0.185 g/g for NiO load. If the amount is less than 0.185 g/g, there is no crystal NiO phase. It means that at least a part of NiO exists in form of disperse phase in the samples.

The XAFS data were collected in synchrotron radiation station of Photon Factory in Japan. Proportions or coordinate numbers of Ni ions with different coordinate states in the disperse phase are obtained by XAFS analysis of mixed phase system, of which the principle is proposed by Lu Kunquan[3]. The different coordinate atoms are identified by fitting and APCFT, which is to be sensitive to different atoms and weak signals[4,5].

FT curves of NiO/f-Al2O3 of XAFS are shown in Fig.2. The first peaks corresponding to Ni-O coordinate are all similar to that of NiO, but shoulder peaks, which locate on the lower R side, appear for the samples with lower load of NiO. It is implied that most Ni ions might have 6 neighboring O, similar to that of crystal NiO, while in the samples with lower NiO perhaps there are some Ni ions with 4-coordinate O. It is confirmed by fitting.

There are 4 peaks in FT curves of all NiO/f-Al2O3 samples corresponding to peaks of four Ni-Ni coordinate shells of Ni ions in FT of NiO respectively. Opposite to the first peaks, their magnitude become lower and smaller quickly with the decrease of NiO load, the positions are gradually and regularly changed, such as the distances of 1st, 2nd, and fourth peaks become shorter gradually.

Both curve fitting and APCFT confirm that there are corresponding Ni-coordinate shells around Ni ions in the samples with that of NiO, though the coordinate numbers go down quickly with decrease of NiO load, and show that a part of Ni in these shells is substituted by Al ions of Al2O3, especially, in the samples with low NiO load. The coordinate numbers of disperse phase deduced from mixed phase analysis of EXAFS are shown as in Fig.1-b. It indicated that coordinate numbers rise with the increase of NiO load amount on the surface of Al2O3, until the NiO load reaches at the threshold (0.185 g/g). When NiO load goes beyond this point the coordinate number does not change. The Ni-Ni coordinate numbers are about 4, 3, 0.4, 3.7, respectively, for 1st to 3rd shells. It is in right consistent with XRD results. This arrangement of Ni ions happens to be similar to that of the cations on (111) plane of spinel or /-Al2O3. It is interesting that the disperse amount of NiO on Al2O3 calculated according this arrangement is 0.245 g/g, which is quite close to the experimental value 0.185 g/g.

Reference
1. Xie Youchang, Tang Youqi, Advance in Catalysis, 39, 1, (1990)
EXAFS STUDY ON HYDRODESULFURIZATION CATALYSTS FOR ULTRA LOW SULFIDE DISTILLATE
- EFFECT OF PHOSPHORUS ON STRUCTURE OF MOLYBDENUM SULFIDE IN Ni-Mo/Y- Al₂O₃ -

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2) General Sekiyu K.K., Kawasaki-shi, Kanagawa 210
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4) Photon Factory, National Laboratory for High Energy Physics, Oho-machi, Ibaraki 305

INTRODUCTION

For Ni-Mo catalysts, phosphorus has been reported to improve hydrodesulfurization and hydrogenation activity. However, the role of phosphorus on these activities has not been properly studied with respect to the structure of active species.

We have investigated that the effect of phosphorus on the structure of molybdenum sulfide phase and Ni by means of EXAFS.

EXPERIMENTAL

Catalysts used were prepared by double-stage impregnation method, in which aqueous ammonium heptamolybdate was impregnated first and, after drying at 403 K, aqueous solution of phosphoric acid or, aqueous solution of phosphoric acid and nickel nitrate was added. All catalysts were calcined at 723 K for 1 h and sulfided in a flow of 5 vol% H₂S in H₂ (flow rate: 200 ml/min at 0.5 kg/cm²) at 673 K for 1 hour. The metal content of catalysts impregnated was Mo (10 wt%) and Ni (3 wt%).

X-ray absorption spectra of Mo K-edge and Ni K-edge were measured by the EXAFS facilities at the BL-10B in Photon Factory. Phase corrections in fourier transform were based on NiO for Ni K-edge spectra, and MoO for Mo K-edge spectra.

RESULTS AND DISCUSSION

Dependence of average numbers of coordinating sulfur atoms (N(S)) and nearest Mo atoms (N(Mo)) around Mo on phosphorus content are shown in Fig. 1. N(S) and N(Mo) were calculated by referring to corresponding peak intensities of MoS₂ crystal. Both N(Mo) and N(S) decrease in both cases, no Ni added and Ni added and Ni added, as the content of phosphorus increases, indicating that phosphorus reduces the growth of MoS₂-like structure. It is assumed that phosphorus has a some kind of interaction with Mo which reduces the mobility of Mo during sulfiding. However, no direct evidence of bonding between phosphorus and Mo was observed in EXAFS spectra. N(Mo) and N(S) become larger with the addition of nickel showing larger size of MoS₂-like structure, meaning that Ni also affects the mobility of Mo during sulfiding.

Fourier transform of Ni K-edge EXAFS spectra shows one peak at the distance of 2.17 Å, which is more similar to the distance of Ni-O (2.13 Å) in NiO than that of Ni-S (2.38 Å) in NiS. Intensity of the peak I(Å) also decreases as the phosphorus content increases as shown in

REFERENCES

EXAFS STUDY ON HYDRODESULFURIZATION CATALYSTS FOR ULTRA LOW SULFUR DISTILLATE
IV. INVESTIGATION OF LOCAL STRUCTURE AROUND Ni AND Mo SUPPORTED ON γ-Al₂O₃

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³Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305
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Introduction
Ni-Mo supported catalysts are well used for the hydrosulfurization of petroleum and have been much studied⁵, but the local structure around Mo and Ni is little known. In this report we investigated the effect of the variation of Ni and Mo on the change of the local structure of supported metals and on the hydrosulfurization activity of AH-VGO and Boscan crude oil.

Experimental
NiO and MoO₃ catalysts supported on the γ-Al₂O₃ were prepared by impregnation methods with solutions of nickel nitrate and ammonium paramolybdate. The catalysts were presulfided for XAS measurements in a stream of 5 vol% of H₂S/H₂ at 400°C for 1h. The catalysts were presulfided in a stream of 10 vol% of H₂S/H₂ at 400°C for 2h before activities were measured. XAS measurements were carried out by use of the EXAFS apparatus at BL-10B.

Results and Discussion
Distinct differences are not seen in the results of the Fourier transforms of the Mo K-edge EXAFS on these catalysts. The average numbers of coordinating S atoms (N(S)), nearest Mo atoms (N(Mo)) around Mo and their ratio (N(Mo))/N(S), which is considered a good index for agglomeration⁶, were calculated from the intensities of the Mo-S and Mo-Mo peaks.

Activities and the results of the EXAFS of Mo on the catalysts are shown in Table 1. The distance, R, from absorbing atom was corrected by using standard sample MoS₂. The Ni K-edge XANES spectra are shown in Fig.1. The spectral patterns of catalysts are different from that of NiS. It suggests that most of Ni atoms are not presulfurized. The results of Fourier transforms of the Ni K-edge EXAFS shown in Fig.2 seem to agree with the results of Ni K-edge XANES. Ni-S peak of standard sample NiS is at 2.4 Å, but those of catalysts are at about 2.2 Å. Not showing any corresponding data here, the Ni-O peak of standard sample NiO is seen at 2.2 Å. The XAS results suggest that most of Ni atoms are not presulfurized but remained at oxidic state. It seems that most of Ni atoms are too strongly interacted with Al₂O₃ to be presulfurized and that most of them don't contribute to the active sites. Though definite correlation was not seen between the activity and the local structure of fresh catalysts, it can be seen on used catalysts.

This work was performed by the Petroleum Energy Center.

References

Table 1. Activity data for hydrosulfurization and results of analysis of EXAFS for Ni-Mo/Al₂O₃

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>No-S activity</th>
<th>Mo-S</th>
<th>Mo-Wo</th>
<th>NiS/Mo(S)</th>
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<td>A-2/9</td>
<td>100</td>
<td>2.46</td>
<td>5.2</td>
<td>3.24</td>
</tr>
<tr>
<td>A-4/12</td>
<td>176</td>
<td>2.46</td>
<td>5.5</td>
<td>3.24</td>
</tr>
<tr>
<td>B-4/12</td>
<td>100</td>
<td>2.44</td>
<td>5.0</td>
<td>3.24</td>
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<tr>
<td>B-5/15</td>
<td>147</td>
<td>2.44</td>
<td>5.0</td>
<td>3.24</td>
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<tr>
<td>B-5/20</td>
<td>146</td>
<td>2.44</td>
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<td>3.23</td>
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</tbody>
</table>

Table 1. Activity data for hydrosulfurization and results of analysis of EXAFS for Ni-Mo/Al₂O₃

Catalysts will be denoted as A-x/y here x represents the percentages of the Ni content as NiO, and y represents that of the Ni content as NiO. Relative hydrosulfurization activities of A-cat and B-cat were measured by AH-VGO and Boscan crude oil, respectively.

Fig.1. Ni K-edge XANES spectra of Ni-Mo/Al₂O₃ catalysts and standard sample NiS

Fig.2. Fourier transforms of Ni K-edge EXAFS for Ni-Mo/Al₂O₃ catalysts
EXAFS Study on Hydrodesulfurization Catalysts for Ultra Low Sulfur Distillate

V. Structure Analysis of Active Species on the Co-Mo/Al2O3 Catalysts

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2. National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
3. Photon Factory, National Laboratory for High energy Physics, Tsukuba, Ibaraki 305

Introduction

Recently, in the environmental view, it has become more important to develop highly active desulfurization (HDS) catalyst. Although extensive studies have been carried out concerning conventional HDS catalysts such as Co-Mo, Ni-Mo and Ni-W systems, the structure of their active species have not been clarified yet.

In the present study, EXAFS method was applied to the investigation of the local structure of oxidized state around molybdenum and cobalt in the oxidized Co-Mo/Al2O3 catalysts.

Experimental

The catalysts shown in Table 1 were prepared by impregnation method; ammonium paramolybdate was loaded first, and after calcination (550°C-2h), cobalt nitrate was loaded, then the catalysts were calcined (550°C-2h) again. Mo K-edge and Co K-edge spectra were measured at BL-10B of KEK-PF.

Results and Discussion

The distance, R, from absorbing atom and average number, N, of coordinating atoms obtained from the EXAFS spectra are shown in Table 2. Standard samples, MoO3 and CoO, were used for correction of R and calculation of N (under the assumption that Debye-Waller factor is constant).

Obtained R and N for molybdenum show that there exists almost the same local environment around molybdenum regardless of molybdenum content and addition of cobalt. The Fourier transform of the Mo K-edge EXAFS data measured on cat-F is shown in Fig. 1 together with those of standard samples, MoO3, (NH4)6Mo7O24•4H2O and Na2MoO4. The comparison of these Fourier transforms may lead to the following two interpretations concerning the local structure around molybdenum in the catalysts studied here.

1) Molybdenum forms either MoO3 crystalline or its polymer-like structure, which has octahedral coordination of six oxygen atoms. Four nearest neighboring oxygen atoms (planner) coordinate molybdenum atom with one kind of bond length without any restriction discussed for crystalline. The remaining two oxygen atoms are disordered, which causes absence of the Mo-O(2) peak.

2) Molybdenum forms tetrahedral coordination with one kind of bond length. Although either interpretation makes Fourier transform magnitude larger than that of MoO3 crystalline, this can be explained by highly dispersion of molybdenum atoms, which is consistent with absence of the Mo-Mo peak. Coexistence of both structures can be also possible.

As for the results for Co K-edge spectra, plausible assignment of each peak is as follows: R(Co-O) of cat-B,D (Co 1wt%) and of cat-C,E (Co 5wt%) are assigned to R(Co-O) of CoAl2O4, 1.97 Å, and of CoO4, 1.94 Å, respectively. R(Co-Co) of all catalysts are assigned to R(Co-Co) of CoO4, 2.86 Å. These assignments lead to the assumption about the local structure of cobalt: CoAl2O4 is formed first on the Al2O3 surface remaining after molybdenum loading, and then CoO4 is formed. Thus, CoAl2O4 and CoO4 coexist in the catalysts, and the quantity of CoO4 component increases as content of cobalt increases.

In the catalysts studied here, any Co-Mo bond and the effect of cobalt addition for the local structure of molybdenum cannot be observed. We are planning to investigate the structure of active species by measurement on more systematized series of Co-Mo/Al2O3 system including their sulfurized state.

This work was carried out under the collaboration between KEK and Petroleum Energy Center.

Table 1. Content of Mo and Co in the catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo wt%</th>
<th>Co wt%</th>
</tr>
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<tbody>
<tr>
<td>cat-A</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>cat-B</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>cat-C</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>cat-D</td>
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<tr>
<td>cat-E</td>
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<td>1</td>
</tr>
<tr>
<td>cat-F</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2. Results of analysis of EXAFS data for the catalysts.

<table>
<thead>
<tr>
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<th>Mo-O(2)</th>
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<th>Co-O</th>
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<tr>
<td>cat-A</td>
<td>1.87</td>
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<tr>
<td>cat-B</td>
<td>1.88</td>
<td>4.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>cat-C</td>
<td>1.88</td>
<td>4.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>cat-D</td>
<td>1.86</td>
<td>3.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>cat-E</td>
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<td>4.0</td>
<td>ND</td>
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</tr>
<tr>
<td>cat-F</td>
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<td>4.6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>MoO3</td>
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<td>4.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CoO</td>
<td>1.88</td>
<td>4.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: No significant peak was observed.

Fig. 1. Fourier transforms of Mo K-edge EXAFS data for (a)cat-F, (b)MoO3, (c1) (NH4)6Mo7O24•4H2O, (c2) Na2MoO4.
XAFS STUDIES OF SiO₂–ZrO₂–Na₂O POROUS GLASSES

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Introduction

Porous silicate glasses containing ZrO₂ have a considerable technological interest due to the low solubility in alkaline solution. Recently, we have developed a new method for the preparation of porous silicate glass with SiO₂–ZrO₂–Na₂O composition. The porous glasses with sharp pore size distribution are obtained when the sol-gel derived microspherical SiO₂ gel was heated together with ZrOCl₂ and NaCl at 730 and 760°C for 5 hours. In previous study¹, we have found that the structures measured by X-ray diffraction were different in three samples heated at 700, 730, and 760°C, respectively.

In this investigation, we have tried to apply XAFS to elucidate the local atomic structures around Zr with different heat treatment temperature.

Experimental

Three samples were prepared by heating mixture of SiO₂ gel, ZrOCl₂ and NaCl at 700, 730, and 760°C. Each sample was mixed with cellulose powder, and pressed into a disk. The Zr K-edge XAFS spectra of these samples have been measured in transmission mode at BL10B.

Results and Discussion

The XANES spectra of Zr K-edge are shown in Figure 1. It is found that the intensity of peak A is gradually increasing as heat-treatment temperature increased from 700 to 760°C. It indicates that the structures around Zr are different in three samples.

Figure 2 shows the results of Fourier transform of the EXAFS data. The peaks of Zr-O and Zr-M(M=Zr, Si) can be seen in all samples. The Zr-O peak becomes higher as heat-treatment temperature increased. On the other hand, the Zr-M peak is reduced.

The results of curve-fitting are shown in Table 1. In three samples, the Zr-O interatomic distances show nearly the same values. However, the coordination number becomes larger, close to be 8 as temperature elevated. So we conclude that the porous glass treated at 760°C may have Zr with similar local structure of ZrSiO₄.

More detailed structure analyses, and the analyses of other kind of glasses are in progress.

References


Table 1. The structural parameters from curve-fitting analyses of Zr K-edge EXAFS

<table>
<thead>
<tr>
<th>Sample</th>
<th>R (Å)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>2.18</td>
<td>5.2</td>
</tr>
<tr>
<td>730°C</td>
<td>2.18</td>
<td>5.8</td>
</tr>
<tr>
<td>760°C</td>
<td>2.19</td>
<td>7.5</td>
</tr>
</tbody>
</table>

R: interatomic distance  N: coordination number
Oxidation State Analysis of Metallic Copper Particles by Transmission-Type XAFS Spectroscopy

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Introduction

In the characterization of metallic fine particles, it is important to analyze the surface oxide layers, since they have great influence on the characteristics of the material. XANES spectroscopy using hard x rays is suitable for the analysis of metallic particles readily oxidized in the air, because it is sensitive to the oxidation states and measurements are possible in atmospheric pressure using wide variety of windows. The transmission-type XAFS spectrum of metallic particles with large higher-order diameter is, however, largely distorted by the inevitable unevenness of the sample. A fluorescence detection-type XAFS can solve this problem, but long measurement time prevents common SR users from measuring more than a few samples.

In order to investigate the oxidation process of Cu particles, a transmission-type XANES spectroscopy were applied and the spectral distortion was corrected with a simple procedure. In this paper, the correction procedure and the results of the analysis will be shown.

Experiments

Sample Preparation: Reduced Cu particles were put into degassed waters and partially oxidized by (1) air flow or by (2) introduction of NO$_3^-$ ions. The wet Cu particles were mixed well with warm melted polyethylene glycol (PEG) and then cooled and solidified. All the operations after reduction was performed in a N$_2$ atmosphere. The resulting Cu/PEG solids were triply sealed by N$_2$-filled polyethylene bags and measured.

XAFS Measurements: The XAFS spectra of a Cu foil, Cu$_2$O/BN and CuO/BN pellets, and the samples (1) and (2) were measured around the Cu K-edge at BL-10B in the Photon Factory.

Results and Discussion

Correction Procedure: In the transmission-type XAFS measurements of uneven samples, a part of the primary x rays is detected together with the original transmitted x rays and causes the distortion. The distortion was corrected in the following way: (1) The real values for absorbance were obtained by removing instrumental functions from the raw data. (2) The background absorption was extrapolated using the data of the pre-edge region. (3) The net absorption for the Cu K-edge was corrected according to the procedure below.

For an uneven sample, the observed intensity of the transmitted x rays ($I_{obs}$) is

$$I_{obs} = I + x I_0$$  \hspace{1cm} (1)

where $I$ is the intensity of the original transmitted x-rays, and $x$ is the ratio of the mixing of primary x-rays. Original and observed transmittance ($\mu$ and $\mu_{obs}$) are

$$\mu = -\ln \left( \frac{I}{I_0} \right)$$  \hspace{1cm} (2)

$$\mu_{obs} = -\ln \left( \frac{I}{I_0 + x} \right)$$  \hspace{1cm} (3)

From the equations (1) to (3), we can obtain

$$\ln \left[ \exp(-\mu) + x \right] + \mu_{obs} = 0$$  \hspace{1cm} (4)

The value $\mu$ was acquired from the equation (4), where the value $x$ was determined so that the ratio of (edge jump magnitude) / (Cu weight per a unit area) for the corrected spectrum makes equal to that for the spectrum of a Cu foil.

Oxidation State Analysis: In order to examine small spectral changes, the deviations of the corrected XANES spectra were compared with one another. Figures 1 and 2 show the [1s-4p] (+[1s-3d]) region of the XANES deviation. The former is for a Cu foil [A], Cu$_2$O [B] and CuO [C], while the latter is for a Cu foil [A] and the samples (1) [B] and (2) [C]. In fig. 2, the shoulder peak (a) of curve [B] and the peak (b) of curve [C] will show the existence of Cu$_2$O and CuO, respectively. It can be concluded that reduced copper particles in water forms Cu$_2$O layers by air oxidation, while CuO layers are formed when oxidized by NO$_3^-$ ions.

Conclusion

Transmission-type XANES spectroscopy were applied to the oxidation-state analysis of copper particles by correcting the spectral distortion. It was shown that the surface oxide layers are different between the samples oxidized by air and NO$_3^-$ ions. The correction procedure is applicable to transmission-type XANES and EXAFS spectra of many kinds of uneven samples.

Reference

XAFS STUDIES OF CdS MICROCRYSTALLITES-DOPED POLYMER FILMS

Shigeo KANAYAMA, Hiroshi YAO, Shigeru TAKAHARA, Toyoharu HAYASHI, Kazushi OHSHIMA, Masatoshi TAKEUCHI, Nobuyuki MATSUBAYASHI, Yuji YOSHIMURA, Hiromichi SHIMADA, and Akio NISHIJIMA

Introduction

Semiconductive microcrystallites embedded in matrices of low density are among promising materials for third-order nonlinear optical devices. Use of polymers as the matrix gives advantages of freedom from inorganic impurities, and high workability.

This paper is on a characterization of CdS microcrystallites-doped styrene-acrylonitrile (SAN) copolymer films. A XAFS spectroscopy was applied to the film samples to pursue the CdS precipitation process and to investigate the extent of the progress of sulfurization.

Experiments

Sample Preparation: The samples of CdS/SAN films were prepared in the following way. A dimethylformamide (DMF) solution of a Cd salt and a SAN copolymer was cast and then dried in a low-pressure chamber. The resulting viscous cast film was exposed to H2S at room temperature and CdS microcrystallites were precipitated in the film according to the reaction:

\[ \text{CdX}_n + \text{H}_2\text{S} \rightarrow \text{CdS} + 2\text{HX}. \]

The SAN copolymer prevented the microcrystallites from growing larger. Then the cast film was evacuated to remove residual DMF and H2S.

Morphological Characterization: A TEM image showed that the microcrystallites with diameter of about 40 Å were homogeneously embedded in the film. A lattice image and an electron diffraction image showed that the microcrystallites are CdS in hcp- system.

UV-VIS Luminescence Spectra: The CdS/SAN film synthesized with Cd(NO3)2 showed an emission that can be assigned to a direct electron-hole recombination, while it was not observed for the film synthesized from CdI2. The absence of the emission will be due to some trapped states.

XAFS Measurements and Data Analysis: The XAFS spectra were measured around the Cd K-edge at BL-10B of the Photon Factory. Fourier transforms were obtained from the EXAFS oscillations between \( k = 3.7 \text{ Å}^{-1} \) and \( k = 15.7 \text{ Å}^{-1} \) weighted by \( k^2 \). The phase shifts were corrected using the parameters for CdO.

Results and Discussion

Figures 1 and 2 show the EXAFS Fourier transforms of [A] (raw Cd salt)/SAN, and the samples obtained by [B] 5 minutes and [C] 6 hours sulfurization. The raw Cd salts were Cd(NO3)2 for fig. 1 and CdI2 for fig. 2.

In these figures, the corresponding positions to the lengths of the Cd-S bond of bulk CdS (\( 2.51 \text{ Å} \)), the Cd-O bond of bulk Cd(NO3)2 (\( 2.20 \text{ Å} \)), and the Cd-I bond of bulk CdI2 (\( 2.95 \text{ Å} \)) were marked as “S”, “O” and “I”, respectively. The peak marked “Cd” of the curve [A] in fig. 1 can be attributed to Cd-Cd bonds.

The followings can be concluded from these Fourier transforms: (1) When exposed to H2S, the Cd(NO3)2/SAN film is quantitatively sulfurized, while the CdI2/SAN film is hard to be sulfurized. Some trapped states will be made by the remaining counter ions (\( :I^- \) and/or \( :I_3^- \)) in the CdS/SAN film synthesized from CdI2. (2) CdS nano-particles are in hcp- system similarly to bulk crystallites. (3) Cd(NO3)2 forms clusters in the Cd(NO3)2/SAN film before sulfurization. Additionally, XAFS of annealed CdS/SAN films showed that CdS microcrystallites become larger or smaller by annealing depending on the raw Cd salts, and that there may be some atomistic interaction between the CdS microcrystallites and the SAN copolymer.

Acknowledgements

The authors are grateful to Prof. M. Nomura for his kind help in the XAFS experiments.

References


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STRUCTURE OF THE PROTEOLYTIC FRAGMENT F34 OF CALMODULIN WITH OR WITHOUT MASTOPARAN AS REVEALED BY SOLUTION X-RAY SCATTERING

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3. School of Allied Health Professions, Sapporo Medical College, Sapporo 060

Introduction

The solution X-ray scattering (SAXS) technique has been applied to examine the conformations of proteolytic fragment F34 (78Asp-146 Lys) of calmodulin with or without mastoparan (MP). The purpose of this work is to present a possible molecular model for the interaction of MP with the fragment, based on its result.

Results

From the Guinier plots for F34 fragment over the concentration series, we estimated four parameters of M, A, R, and m following ref. 1, whose values are compiled in Table I. The value of M increases about 191 in the presence of 1 mol MP, whose increment just corresponds to the molecular weight of 1 mol MP, while the values of A, R, and m are almost constant irrespective of the absence or the presence of MP. The result for M suggests that a complex is formed between the fragment and MP. The formation of a tertiary complex with Ca\(^{2+}\) and MP increases the R of fragment by 1.1 \pm 0.3A and M by about 19% in comparison with that of Ca\(^{2+}\)-free F34. Furthermore, the formation of the tertiary complex drastically changes the A\(_2\) parameter to negative value from the positive value in the case of Ca\(^{2+}\)-free F34. On the other hand, the addition of Ca\(^{2+}\) alone hardly changes the values of R, M, A, and A\(_2\).

Discussion

In order to present a molecular model for the structure of the complex, we assumed explicitly that the structure of F34 in the presence of MP holds that of in the absence of MP and that MP in the complex retains an \(\alpha\)-helical conformation.

The radius of gyration of the complex, R, making no assumption about shape is

\[ R_{2} = \frac{(M_{a} R_{a}^2 + M_{R} R_{R}^2)}{(M_{a} + M_{R})} + L_{f} \frac{1}{2} \frac{R_{a}}{A} \]

where M\(_a\), M\(_R\), R\(_a\), and R\(_R\) are the molecular weights and the radii of gyration of F34 and MP, respectively, and L\(_f\) is the center-to-center distance between F34 and MP. Then from above equation the L\(_{f}\) is calculated using the values of R, and R\(_a\), observed here and assuming R\(_m\)=7.6 A, where mastoparan in the resolution of this model may be taken as a cylinder whose radius is about 7 A and the height is about 20 A. Here M\(_a\) and M\(_R\) were evaluated from these primary structures. The value of L\(_{f}\) is about 12.7 A.

It is noted that this estimated value corresponds to the half of the center-to-center distance (L\(_{c}\)) between two lobes of intact CaM. Present estimation may be reasonable, because it is suggested that the distance L\(_{c}\) between F12 and mastoparan almost equal to that of L\(_{f}\), as seen from our previous result in which the value of L\(_{c}\)/2 is about 12.5A in the presence of both MP and 4Ca\(^{2+}\). Therefore the present result is consistent with our previous result for the intact calmodulin-MP complex.

The present model proposed for Ca\(^{2+}\)-MP-F34 complex is consistent with the previous model based on the crystal coordinates and is based on the model for the interaction of CaM and M13\(^{-}\). Based on the present SAXS result, however, it is concluded that the center-to-center distance between fragment F34 and MP was shorter by about 5 A than the corresponding separation in the model of ref. 4.


Table I: Molecular weight M, second virial coefficient A, radius of gyration Re and A\(_2\) coefficient for fragment F34 at pH 7.6.

<table>
<thead>
<tr>
<th>Condition</th>
<th>10(^{-3})M</th>
<th>10(^{2})A</th>
<th>((\text{mol}\cdot\mu\text{l}/\text{g}^2))</th>
<th>10(^{-1})A(_2)</th>
<th>(cm(^{-1})/g)</th>
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<tr>
<td>EDTA</td>
<td>8.25 \pm 0.50</td>
<td>2.3 \pm 0.2</td>
<td>13.2 \pm 0.3</td>
<td>2.9 \pm 0.1</td>
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</tr>
<tr>
<td>2.5Ca(^{2+})</td>
<td>8.25 \pm 0.50</td>
<td>2.2 \pm 0.2</td>
<td>13.5 \pm 0.3</td>
<td>3.3 \pm 0.1</td>
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<tr>
<td>2Ca(^{2+})+MP</td>
<td>9.82 \pm 0.70</td>
<td>2.2 \pm 0.2</td>
<td>14.3 \pm 0.3</td>
<td>-4.4 \pm 0.1</td>
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</tbody>
</table>
On the Determination of Molecular Weight by Means of Small-Angle X-ray Scattering

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INTRODUCTION

Although synchrotron radiation provides a powerful X-ray source for scattering experiments, the absolute measurement of scattered X-ray intensity causes a practical problem. Since the conventional molecular weight determination by small-angle X-ray scattering requires the absolute intensity to be evaluated accurately, no experiment was undertaken so far to determine molecular weight by SR SAXS.

A theory was developed to evaluate molecular weight without knowledge of absolute scattered intensity. Here the theory is based on the fact that no particular interference effect will appear in scattering profile when the magnitude of scattering vector \( q \) exceeds a certain finite value \( q_m \). The molecular weight \( M \) is then given in terms of the relative scattered intensity \( I(q) \) as

\[
M = 2\pi^2 N_A \frac{I(0)}{c} \frac{d}{dc} \int_0^{q_m} \frac{I(q)}{c} \cdot q^2 \cdot dq
\]

with \( c \) and \( N_A \) being the solute concentration and Avogadro’s number, respectively.

Commercially available proteins (lysozyme from chicken egg white and bovine serum albumin) and polysaccharide (pullulan) were employed for present SAXS experiments with the optics and detector system of SASES installed in the BL-10C. The solution temperature was controlled to \( 20 \pm 0.1^\circ C \), and each counting time was set to 600 sec. The Guinier approximation was used to evaluate the radii of gyration of lysozyme and BSA, while the Zimm plot was employed for pullulan solutions.

RESULTS and DISCUSSION

Figure 1 shows an example of SAXS measurements from lysozyme aqueous solutions. The results are summarized in Table 1, where the molecular weights were determined from eq. (1). Here the molecular weights are calculated as 14,000 for lysozyme and 66,100 for BSA from the primary structures, and estimated as 5,800 for pullulan P-5 and 12,200 for pullulan P-10 from GPC.

\( q_m \) was uniquely specified for lysozyme and BSA, which assume a globular shape. Here lysozyme yields a reasonable agreement with the calculated value of molecular weight. BSA on the other hand exhibits 20% larger molecular weight than the calculated value, probably due to some amounts of higher molecular weight materials contained in the present sample (purchased from Sigma).

Since pullulan behaves as an expanded random coil, the scattering profile is characterized by its long tail, and \( q_m \) could not be specified in the present \( q \) range. Thus the estimated molecular weights by the present procedure differ considerably from respective values estimated by GPC.

In conclusion, the present method allows a reliable estimation of molecular weight for compact molecules, but is inadequate to be applied to the system of random coils.
SOLUTION SCATTERING STUDIES OF TRUNCATED MUTANT OF STAPHYLOCOCCAL NUCLEASE

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INTRODUCTION

Protein folding problem is one of the central issues in modern biological science. It is impossible to understand the complete information written in DNA sequences without the knowledge how a primary structure dictates a unique tertiary structure. We stress that the structural information of an unfolded state is as important to understand the folding as that of a folded state which is confirmed by X-ray crystallography, NMR and many other techniques. Solution scattering is the most effective way to describe an unfolded state. Many discussions of protein folding have taken the view that the initial condition of polypeptide in its folding pathway is random coil in solution. However, there are several lines of evidence to suspect that the physiologically relevant unfolded state should not be thought of in this way.

Experimentally, an unfolded state is taken as a denatured state, which is obtained by denaturant, heat, acid etc. These conditions, however, are far from physiological conditions. Shortle et al. have shown that removal of the C-terminal 13 amino acids of Staphylococcal nuclease (SNase) is sufficient to destabilize the protein's native state or stabilize its unfolded state. We have intensively examined the solution structure of the truncated SNase as a model system of an unfolded state under physiological conditions.

EXPERIMENTAL

SAXS measurements were performed with SAXES installed at BL10C. Wild type SNase and SNase fragment were expressed in E. coli.

RESULTS

The fragment of SNase has the Rg of 22Å, while the Rg of wild type SNase is 16.5Å, suggesting that the fragment is in an unfolded state under near physiological condition. The Rg of a fully denatured SNase by 5M urea is larger than 30Å. The dmax derived from the distance distribution function, P(r), is 47Å for wild type SNase, 63Å for the fragment, and more than 80Å for the denatured SNase. These values indicate that the unfolded state under physiological condition is rather compact. Figure 1 shows Kratky plots of the scattering curves for these three states. A globular structure gives a peak in the plot, like wild type SNase. The curve for the 5M urea state (denatured state) is typical for a chain-like polymer with a persistent length, indicating that even the denatured state is not random coil. The curve for SNase fragment shows a broad hump, clearly suggesting that the fragment has some compact structure, and this is neither globule nor random coil.

The inhibitor, pdTp, induces folding in the fragment. The final scattering curve and the P(r), are identical with those of the native wild type SNase (Fig. 2). These results indicate that the SNase fragment is a good model for folding, which is unfolded under physiological condition and turns to the folded state with an inhibitor.

We tried to measure kinetics of the inhibitor induced folding of the fragment. However, since the folding reaction was completed within a dead time of a rapid mixing system (10msec), we could not follow the reaction. The effects of amino acid substitutions to the fragment are now examining.

REFERENCES

Introduction

LiNbO$_3$ single crystals have been used for SAW devices for more than 10 years and now are regarded as promising materials for future electro-optical devices. An extra care is required to secure the quality for such future needs. The major problems are point defects in the grown crystals. Efforts have been paid to improvement of the growth conditions. Now the influence of the structure of the melt, from which crystal is grown, is under focus. An anomalous viscosity change in LiNbO$_3$ melt has been reported$^{1,2}$. The data seem to indicate the existence of some form of clusters in the melt near the solidification.

Due to the high corrosiveness of the liquid and the high melting temperature (1253°C) the existence of these clusters has never been confirmed by a structure study. A handy furnace to keep the thin melt sample upright without container was developed for the present work and a study of the LiNbO$_3$ liquid could be realized by X-ray SAS.

Experiment

The liquid sample of 3 mm in diameter was held vertical (fig.1); its thickness varied between 80 and 150 µm. The exact value was determined by the absorption of the X-ray beam. The temperature was decreasing from 1400°C to 1242°C to include the undercooling. The error was estimated to be less than ±4 °C. The detector was positioned at the short distance to obtain a large Q domain ($0.02-1.37\AA^{-1}$). The beamline 10C was used at KEK with $\lambda=1.2\AA$ and a beam section limited to 1.5x1.5 mm$^2$ to expose only the sample part having parallel faces. To limit the evaporation of the melt, the exposure time was reduced at 1000 s. for each measurement.

Results

Incoherent, multiple and thermal diffusions were evaluated. Air scattering was measured with the background. All parasitic contributions were subtracted. Then the intensities were corrected with respect to absorption by air and sample and normalized by adjusting with the results obtained previously to describe the local order$^3$.

The presence of clusters in liquid LiNbO$_3$ was confirmed. In all the studied temperature region a dense system of microclusters is present giving an interference effect (fig. 2). At a temperature below 1280°C, macroclusters appear, and their size increases rapidly as temperature approaches that of solidification. The most probably cluster form versus temperature has been described from the changes of the radius of gyration (fig. 3), the average size $\bar{1}$ and the length of correlation $l_c$ (fig. 4). At the higher temperatures dimers probably exist in the liquid, then as the temperature decreases, the chains of 3, 4, and 5 octahedron NbO$_6$ and prismatic blocks of Niizeki et al.$^4$ can be retained. At about 1280°C a sudden “macroclustering” appears which would be liable for the large increase of viscosity.

References


![Figure 1. A miniature furnace for SAS of LiNbO$_3$ melt.](image1)

![Figure 2. Experimental scattering intensity of LiNbO$_3$ melt.](image2)

![Figure 3. Radius of gyration of clusters.](image3)

![Figure 4. Correlation length $l_c$ and mean size $\bar{1}$ of clusters.](image4)
SOLUTION STRUCTURAL STUDIES OF CALMODULIN BOUND TO TWO PEPTIDES CORRESPONDING TO PARTS OF THE CALMODULIN-BINDING DOMAIN OF THE PLASMA MEMBRANE Ca\textsuperscript{2+} PUMP

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INTRODUCTION

Calmodulin, a ubiquitous Ca\textsuperscript{2+}-binding protein in eukaryotic cells, modulates various Ca\textsuperscript{2+}-activated processes through Ca\textsuperscript{2+}-dependent binding to target enzymes. Because of the importance of CAM-mediated regulation, much work has focused on the molecular mechanisms underlying the protein-protein interaction. We have shown that CAM undergoes a large, Ca\textsuperscript{2+}-dependent conformational change on binding to melittin\textsuperscript{1}. SANS studies have also revealed the similar conformational change in CAM upon binding of M13\textsuperscript{2} or mastoparan\textsuperscript{3}. These three peptides share a structure consisting of a basic amphipathic helix, and interact with both lobes of CAM.

Peptides corresponding to parts of the CAM-binding domain of the Ca\textsuperscript{2+} pump of human erythrocytes have distinct properties. The full domain consists of 28 residues in a helix plus $\beta$-sheet arrangement\textsuperscript{4}. A shorter, 20-residue, version of the peptide (C20W) interacts only with the C-terminal lobe of CAM. Therefore, these peptides provide a valuable opportunity to study the structural requirements for the formation of the CAM-target complex.

EXPERIMENTAL

CAM was isolated and purified from bovine brain. The peptides, C24W and C20W, were kind gifts from Dr. J. Krebs (ETH, Switzerland). C24W lacks the 4 N-terminal 4 residues of the full peptide (C28W) but otherwise has similar properties. C20W lacks the C-terminal 8 residues of C28W.

SAXS measurements were performed with SASES installed at BL10C. The final data for processing were obtained by extrapolation to zero protein concentration using a series of scattering curves at different protein concentrations in the range of 2 to 25 mg/ml.

RESULTS

In the presence of Ca\textsuperscript{2+}, both C20W and C24W bring about a compaction of the CAM molecule. The observed Rg's are 22.0A for CAM alone, 19.0A for the C24W complex and 19.8A for the C20W complex. The I(0)'s of the peptide complexes relative to CAM alone are slightly higher, and consistent with the molecular weight increase resulting from the binding of one mole of peptide per mole of CAM. Since the CAM-C20W complex has a larger Rg than the CAM-C24W complex, it is evident they are distinct structures. The structural differences are clearly seen in the Guinier plots (Fig. 1). The inflections in the curves at Q<sub>0</sub> 0.01 for CAM alone and for the CAM-C20W complex are apparent and indicative of dumbbell-shape structures\textsuperscript{5}. However, the plot for the CAM-C24W complex is almost linear, suggesting a globular structure. Similar conclusions can be drawn from the related interatomic length distribution functions, P(r) (Fig. 2). CAM alone has a peak near 20A, principally representing interatomic distances within each lobe of the dumbbell, and a shoulder at about 45A, representing interlobe distances. The dmax is about 63A. The CAM-C20W complex has a P(r) with a similar form, indicative of a dumbbell, but with a dmax of only about 58A. The CAM-C24W complex has a very much different P(r). The single peak suggests a globular shape with dmax of about 53A.

REFERENCES

Crystallization Behavior of Poly(ε-caprolactone) Chain in Block Copolymer

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Introduction

It has been well known that block copolymers show a well-ordered microstructure when cast from a solvent. In the case of crystalline-amorphous block copolymers, an additional complexity may intervene, that is, the morphology formation is expected by crystallization, microphase separation, or a cooperative effect of these two factors, and eventually a complicated morphology will appear in the system. In the present study, we investigate the behavior of morphology formation in a crystalline-amorphous diblock copolymer, ε-caprolactone-block-butadiene (PCL-b-PB), by time-resolved small-angle X-ray scattering (SAXS) with synchrotron radiation after the copolymer is quenched from a homogeneous state into a temperature both below T_m (melting temperature of the PCL block) and T_s (spinodal temperature of the microphase separation). The cooperative effect between crystallization and microphase separation was elucidated on the process of morphology formation of this copolymer system.

Experimental Section

The PCL-b-PB copolymers used in this study were synthesized by a successive anionic polymerization under vacuum. The total molecular weight is about 10,000 with the PCL content ranging from 20 % to 45 %. The process of morphology formation was observed by SAXES facility at BL-10C. The wave length used was 0.1448 nm and the distance between the sample and detector was about 2,000 mm. Details of the optics and the instrumentation are described elsewhere. The SAXS intensity was collected as the sum of the intensity during the period of 10 sec from the beginning of the temperature drop, and the measurement was continued until the overall scattering profile has no more changed.

Results and Discussion

Figure shows the time evolution of the SAXS curve measured with PCL-b-PB quenched from a homogeneous melt into 28.7 °C, a temperature both below T_m and T_s. At the melt (t = 0 sec), there appears a diffuse scattering maximum due to the correlation hole effect of the homogeneous block copolymer. This scattering maximum is replaced by a sharp diffraction just after quenching (65 sec), with the angular position of the maximum intensity being slightly smaller than that from the melt. This sharp diffraction comes from the microstructure of the copolymer. In the Figure, there appears second intensity maximum at smaller angle (250 sec), and this maximum intensity grows with time and the sharp diffraction simultaneously reduces in intensity, and finally disappears. The second maximum arises from the crystallization of the PCL block. Following facts can be extracted from the Figure. (1) The induction time of the microphase separation can not be detected, and the copolymer presents the microstructure as soon as it is quenched below T_s. The induction time of crystallization, on the other hand, extremely long. The difference in the induction time suggests an essential difference in mechanism between microphase separation and crystallization in a molecular level. (2) The crystallization of the PCL block occurs spontaneously from the microstructure existing in the system, that is, energetic gain in the crystallization overwhelms that in the microphase separation, so that the microstructure is completely destroyed by the following crystallization.

References

1. S. Nojima et. al., submitted to Macromolecules.

Figure Time-resolved SAXS curve plotted against channel number for PCL-b-PB quenched from c.a. 55 °C into 28.7 °C. Channel number 258 corresponds to the zero angle, and the SAXS intensity is symmetrical against this channel.
STRUCTURE FUNCTION OF PEO/PMMA BLENDS IN CRYSTALLIZATION PROCESS

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Introduction

Form of structure function measured by small angle X-ray scattering (SAXS) contains information about the form and the distribution of periodic structure as well as the value of long period. Therefore, the time evolutions of these quantities can be obtained by measuring the change of structure function in course of pattern formation processes in materials. This study aims at investigating the kinetics of crystallization in crystalline/amorphous polymer blends by small angle X-ray scattering measurement of poly(ethyleneoxide) (PEO) / poly(methylmethacrylate) (PMMA) blends in the crystallization process.

Experimental

PEO used was the products of Wako Pure Chemical Ind. Ltd. with average molecular weight $M=50,000 \pm 10,000$. Five PMMA samples were used. The values of the molecular weight were 22,000, 23,000, 160,000, 170,000 and 770,000. They are denoted as $f_1$, $f_2$, $f_3$, $f_4$ and $f_5$, respectively. Blend samples were obtained by solvent casting. The composition of blends studied here was 20 wt% PMMA. SAXS measurement was carried out by using BL-10C beam line. Crystallization process was induced by temperature jump method, which was made by transferring the sample to the heating block controled at a temperature below melting point. The scattered intensity was detected by PSPC with the sensor length of about 20cm. The temperature of samples was controled within ± 0.1 °C.

Results and Discussion

Fig.1 shows structure functions $F(k,t)$ at $T = 321K$ and various crystallization time $t$ for PEO/f5 blend in double logarithmic scale. Here, we defined $F(k,t)$ as $F(k,t) = I(k,t) - I(k,0)$ from the scattered intensity $I(k,t)$ at time $t$ and wave number $k$. $F(k,t)$ increased with $t$ increased, but the form was almost unchanged. Fig.2 shows the composite master curve of the structure function which was obtained by shifting the structure functions along the ordinate. The superposition is fairly good. The master curve in Fig.2 shows that the structure function $F(k,t)$ has the following functional form

$$F(k,t) = c(t)s(k)$$

where $c(t)$ and $s(k)$ represent the t- and k-dependences of the structure function, respectively. The increase of the total scattered intensity observed in crystallization process seems to correspond with the increase of the crystallinity $X(t)$. Therefore, we can put

$$X(t) F(k,t) = Sc(t)$$

where $S = S(k)dk$. Namely, the function $c(t)$ representing the time evolution of the scattered intensity corresponds with the crystallinity $X(t)$. $X(t)$ was evaluated from the intensity of the maximum peak $(k = k_m)$ by $X(t) = F(k_m,t) / F(k_m,t= \infty)$. The Avrani plot shown in Fig.3 coincides with that obtained by DSC measurement.
Dynamic Process of Siloxane Network Formation
as Observed by Synchrotron Small-Angle X-ray Scattering

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INTRODUCTION

Gel structure can be characterized by means of the scattering method using electromagnetic wave\(^{1}\). For example, the scattered intensity for \(f\)-functional polycondensates is given by

\[
I(q) \sim \frac{(1 + \alpha \phi)}{[1 - (f - 1)\alpha \phi]} \tag{1}
\]

where

\[
\phi = \exp(-q^2 b^2 / 6) \tag{2}
\]

with \(b\) and \(q\) being the segment length and the magnitude of the scattering vector given by \((4\pi/\lambda)\sin(\theta/2)\) (\(\lambda\), the wavelength of the incident beam and \(\theta\); the scattering angle), respectively. Eq.(1) converges as far as \((f - 1)\alpha \phi < 1\), and yields the scattering intensity which diverges in the limit of \(\phi \rightarrow 1/[(f - 1)\alpha]\) in the case of gel though gives a finite value over the whole range of \(q\) for sol\(^{1}\).

EXPERIMENTAL

The time-resolved SAXS was observed with the SASES optics installed at BL-10C from the system forming network by hydrosilylation of VT-M and F4-C in the presence of \(\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}\) as schematically shown in Figure 1. The strong X-ray source of synctrotron radiation enabled to take the scattering data in the \(q\) range from \(6.61 \times 10^{-3} \) Å to 0.33 Å with three-minute resolution. The sample solution (20 wt.% stoichiometric mixture of VT-M and F4-C in toluene) was prepared at 0°C, and the SAXS measurement was started immediately after the solution was put into the cell thermostated in advance. The 3-minute measurement was repeated 98 times with an appropriate interval, and the total measuring time was 5 to 8 hours, depending on the reaction temperature.

RESULTS and DISCUSSION

The system eventually forms gel, and its sol-gel transition can be traced by the upturn of \(q^2 I(q)\) in \(q \rightarrow 0\) as expected from eq.(1) (see Figure 2). Here gelation was found to take place after about 14,400 seconds at 45°C, or after about 6,000 seconds at 50°C. Hydrosilylation proceeds further after gelation to increase crosslinking density, which is confirmed by the shift of the upturning point of \(q^2 I(q)\) in \(q \rightarrow 0\) to higher \(q\). The increase of the slop at higher \(q\) indicates that the chain becomes less flexible in the process of network formation.

In conclusion, the gelation by hydrosilylation can be described in terms of the cascade theory.

REFERENCES

2) H. Urakawa, K. Kajiwara, Polymer Preprints, 39, 2178 (1990)
Small-Angle X-ray Scattering Study of Reconstitution Process of Tobacco Mosaic Virus Particles Using Low Temperature Quenching

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Introduction

Tobacco mosaic virus (TMV) is a rod-like particle that consists of a helical long RNA surrounded by its coat proteins (TMVP) of 2100. The TMV particle can be reconstituted in vitro from its constituents under the physiological condition in two steps: formation of the initial complex by interaction of the double-layered disk of TMVP with the hairpin loop of RNA, and growth of the helical rod by sequential addition of TMVP. This assembly reaction is thought to complete approximately within 20-40 min. A small-angle X-ray scattering (SAXS) method is exceedingly useful for observation of this reaction. The growth of aggregates of TMVP and RNA to rod-like particle is suspended to about 5°C. We shall be able to determine an aggregation state at each reaction time if we quench the sample at 5°C after growing the aggregate by keeping the sample at 20°C for each reaction time (min) and carry out the ordinary static SAXS experiments at 5°C.

Experimental

The experimental procedure was described in details in the previous report1). The TMV reassembly experiments were carried out at three temperatures, 15°C, 20°C and 25°C, and the SAXS measurements were done at 5°C under the condition where the reassembly process was quenched. The experimental station was BL-10C equipped with SAXES.

Results and Discussion

The reconstitution proceeds rapidly in 2 to 10 min, followed by a gradual growth of the aggregates as shown in Fig.1 of Ref.3). The Kratky plot and the distance distribution function are more sensitive than $R_g$ or $J(0)$ to estimate the particle size and shape: The former is a plot of $J(Q) \cdot Q^2$ versus $Q$ and the latter is the Fourier transformation function of $J(Q) \cdot Q^r$ where $r$ is the distance between any pair of points within the scattering particle. Time variation of the Kratky plot and the distance distribution function during TMV assembly at 20°C are shown, respectively, in Fig.1 and Fig.2, where $t_{01}$ is for 1 min, $t_{05}$ for 5 min, $t_{11}$ for 11 min, and $t_{25}$ for 25 min. Comparison of Figs. 1 and 2 with the simulation plot of Fig.2 of Ref.2) suggests that the incubation of TMVP with RNA at 20°C leads to the elongation of the rod assembly.

References

2) Y. Sano et al., PF Activity Report 8, 221 (1990).
MECHANISM OF MICROGEL FORMATION OF CELLOOLIGOSACCHARIDES
BY SMALL-ANGLE X-RAY SCATTERING METHOD

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INTRODUCTION

Oligosaccharides containing sequences of D-mannose or D-glucose linked by different glycosidic linkages are widespread in nature. Oligosaccharide units occur as an inner core in both soluble and cell surface glycoproteins of yeast, fungi, higher plants and animals, and there are ample indications that they play important biological roles, for example, in the stabilization of protein conformation. Properties of the oligosaccharides include a decreasing water solubility with increasing molecular weight, limited solubility in nonaqueous or partially aqueous solvents, and a melting point which increases with increasing molecular weight. The structural characterization of cellooligosaccharide and maltooligosaccharide in solution are, therefore, an important base for elucidation of the spatial arrangement of oligo- and polysaccharide chains.

In the present work, the size and shape of oligosaccharides of cello- and malto-types in solution were determined as a function of the degree of polymerization (DP) by using the small-angle X-ray solution scattering (SAXS) method.

MATERIALS

A series of cellooligosaccharides from dimer to pentamer are prepared by hydrolysis of cellulose. All oligomers of cello- and malto-types are chromatographically pure, confirmed by high performance liquid chromatography, and are lyophylized power.

RESULTS AND DISCUSSION

SAXS experiments were performed with the optics and detector system of SAXS, in the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan (BL10C).

The net scattering intensities were calculated by subtracting the scattering intensities of a blank solution from those of the sample solution. Since the scattered intensity I(Q) at smaller scattering angles is generally approximated in terms of an exponential function of the mean-square radius of gyration of a solute, the radius of gyration Rg can be evaluated from the initial slope of the straight line by plotting the natural logarithm of I(Q) against Q² (the Guinier plot).

The Guinier plots were approximated by almost straight line in smaller DP regions in cellooligosaccharide and in wide DP regions of maltooligosaccharide. In this region, both parameters of I(0) and Rg increased almost linearly with the increase of DP, as shown in Fig.1. However, for higher DP regions of cellooligosaccharide such as cellopentaose, the Guinier plot curved upward in the smaller Q-ranges, which indicates the presence of microgels. The abnormal structural change by the intensive presence of microgel was also observed in cellohexaose. These microgels in cellopentaose and -hexaose may be formed by the entanglement of each oligosaccharide chains structured like cellodextrins. The β-glycosidic linkage appears to be more flexible in the malto- than in the cello-oligosaccharides and the microgel formation occurs more easily in the cellooligosaccharide solutions.
TIME RESOLVED X-RAY DIFFRACTION FROM TENDON COLLAGEN UNDER CREEP

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Introduction

Collagen is considered to be one of the most important candidates when regarding the biomedical application of materials. A number of information about the strength in the dry and swollen state of collagenous tissue have been accumulated by mechanical measurements. Almost all of collagenous tissue have been known to have a hierarchical structure. The detail of the structure relates to the function of the tissue working in the biological system. Only small amount of works have been made for relating the mechanical properties of the tissue with such a hierarchical structure. It is important to know the contribution of each structure in hierarchy to mechanical properties of collagenous tissue as a whole. For this, a separation technique of each structural contribution to the mechanical properties as a collagenous tissue is needed. In this report, we presented the results of creep measurements of tendon collagen as observed by time resolved X-ray diffraction method, by which we were able to make the separation.

Experimental

Collagen used was from bovine Achilles tendon (BAT). The specimen for X-ray measurements was cut in a rectangular plate of the size of 5" × 20" with 1" thick. In order to apply a stress to the specimen, a constant stress applicating equipment was constructed. Small angle X-ray scattering (SAXS) method was employed. The SAXS measurements were made using synchrotron radiation by the instrument BL-10C which was installed at the Photon Factory, Tsukuba. All the measurements were performed for swollen specimen at room temperature.

Results and Discussion

Figure 1 shows the Meridional SAXS pattern from BAT for relaxed state (arrow) and the state under a stress of 5.2 MPa. The intensity of all of the peaks reduced and the D-period increased by the addition of the stress (Figure 2). These changes in intensity and spacing occurred in 15 sec after the application of the stress in the time resolution of this measurement. Over this period, both quantities did not change. The change in D-period was 1.1 % which accorded with the strain value estimated from the static stress-strain curve for BAT collagen D-period. These results indicate that in the conditions of this experiment (time-resolution, applied stress, etc.) BAT collagen fibril is Hookean. However, tendon collagen has been known to show a remarkable viscoelasticity. In order to have a consistency between these results and the viscoelasticity of collagen, such an explanation may be possible as the viscoelasticity of collagen is originated from the movement of something like a "dislocation" in a regular arrangement of collagen molecules in a fibril.

References

2) Kastelic, J. et al., Connect. Tissue Res. 8, 11-23 (1978)

Figure 1. The meridional SAXS pattern from BAT for relaxed state (arrow) and the state under a stress of 5.2 MPa.

Figure 2. D-period plotted against time after the application of stress.
Structural Change of the protein during the hydrolysis of ATP or GTP

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Introduction

The product of the human c-Ha-ras gene, ras p21 is a small guanine-nucleotide-binding protein encoding 189 residues. It hydrolyzes GTP to GDP, and its conformational change is thought to represent molecular switch from the "off" to the "on" state signaling cell growth. The structures of ras p21 in crystalline state have been already solved by two groups.

Our aim of this study is to explore the time resolved change during GTP hydrolysis in solution and to compare the results between crystalline and solution state. As a basic study for this purpose we did the static small-angle scattering experiment.

Experiment

For experiment we used truncated ras p21 devoid of 18 residues from carboxy terminal, which has the same GTPase activity as whole protein.

In order to study the initial and final state of GTP hydrolysis we measured ras p21 with GTP analogue GDPNHP (5'-guanylimido diphosphate) and that with GDP. The single point mutants at the residues of 12, 59 and 61 are often found in some human cancers, which have reduced GTPase activity [11]. We also measured these mutants as a reference.

Results and Discussion

The all samples are very soluble and no aggregation was seen judging from their Guinier plot (Fig.1) and forward scattering. The extrapolation to zero protein concentration gives Rg values of 16.89 Å, 17.46 Å, 17.03 Å, 17.04 Å, and 16.98 Å for GDP bound wild type, GTP bound wild type, Q61L(Gln to Leu), G12V(Gly to Val) and A59T(Ala to Thr). [2] The slight increase of Rg are very small but they are above standard deviation. Like crystalline state distance distribution function from scattering intensity shows globular shape though the structure seems to be a little expanded in solution. Fig. 2 clearly shows the difference between the calculated scattering curve based on crystalline structure and experimental data. The calculated curve is taken into consideration of excluded volume [31]. Rg of crystalline state is 15.4 Å.

We are now verifying whether this difference comes from real structural difference or not.

The over expression vectors and crystal structure coordinates are generous gift from Dr. Nishimura.

Recently, the Si(111)/3\times/3-Sb surface came to attract attention. The authors investigated its structure using X-ray diffraction method. It is the unique method that can determine both the lateral and the normal components of atomic sites.

The experiment was performed at BL-10C using an ultra high vacuum chamber designed for X-ray diffraction measurements. We measured X-ray diffraction intensities along (00) and several fractional order rods.

As described in the former report, it was concluded from the diffraction intensity distributions on fractional order rods that the adsorbed structure of Sb atoms is trimer arrangement. This result agrees with those obtained by photoelectron diffraction and scanning tunneling microscopy.

In order to determine the accurate adsorption site of Sb, we made least squares fitting for all data measured along (00) and fractional order rods taking account of the displacements of Si atoms in the substrate. The calculated fitting curve along the (00)rod is shown in Fig.1. The result of the least squares fitting suggests that Sb atoms are sited in "milk stool" type trimer arrangement centered at T4 site. The calculated side length of the trimer is 2.82Å and the bond length of Sb-Si is 2.74Å. The top and side views of the obtained structure are illustrated in Fig.2.

References
PERFORMANCE OF A WIDE-BAND MULTILAYER POLARIZER FOR SOFT X RAYS. 1

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Introduction

Multilayer polarizers have high throughput and polarizance. However, they are effective only for soft x rays (SXR) of wavelengths in the vicinity of their respective peak wavelengths at an angle of incidence of \( ^\circ 45\). To overcome the difficulties with a multilayer polarizer, we arranged two multilayer polarizers of the same characteristics in a manner similar to a double-crystal x-ray monochromator. Figure 1 shows a schematic of this double-multilayer polarizer (DMP). By means of a cam mechanism \( P_1 \) and \( P_2 \) are rotated and translated simultaneously in such a way that the direction of the beam transmitted through the DMP remains unchanged.

Experiments and Results

A 21-layer Ru/Si multilayer was fabricated on a silicon wafer by magnetron sputtering and was cut into two 20x20-mm\(^2\) pieces for use as \( P_1 \) and \( P_2 \). Their peak reflectance was \( ^\circ 56\) for \( s\)-polarized SXR of 97.5 eV at an angle of incidence of 45\(^\circ\).

The performance of the DMP was evaluated on the beamline 11A at the Photon Factory in terms of throughput and polarizance. The throughput of the DMP was measured with a photodiode (D in Fig. 1). Figure 2 shows the measured throughput of the DMP when the azimuth \( \chi \) of its transmission axis is 0\(^\circ\), \( \chi \) being measured from a plane parallel to the positron orbit. The dashed curves show the throughput at various angles of incidence indicated in the figure. The measured throughput was higher than 5\% over the measured range of 80-120 eV, with a maximum of \( ^\circ 32\) at 99 eV.

Polarization of the light transmitted through the DMP was measured by using a rotating analyzer A (Ru/Si multilayer) and a micro-channel plate D' (Fig. 1). This was done for SXR of 89 and 97 eV at \( \chi = 0^\circ \) and 45\(^\circ\). When \( \chi = 0^\circ \), the contrast factor \( C = (I_{\max} - I_{\min})/(I_{\max} + I_{\min}) \) is equal to the polarizance of the analyzer (0.970 at 89 and 97 eV). When \( \chi = 45^\circ \), the contrast factor is expressed by the product of the polarizance of the DMP and that of the analyzer. We obtain for the polarizance of the DMP 99.6\% and 99.5\%, respectively, at 89 and 97 eV. These values agree well with those calculated with known optical constants. For reference, calculated polarizances at several photon energies are plotted with triangles.

References

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PERFORMANCE OF A WIDE-BAND MULTILAYER POLARIZER FOR SOFT X RAYS. II

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Introduction

In the companion paper we report the performance of the Ru/Si double-multilayer polarizer (DMP). The performance was, however, evaluated at only two energies, 97 and 89eV. In addition, because of the Si L absorption, the throughput was largely suppressed above 100eV, resulting in a narrow effective range of 80-120eV for practical use.

If the incident SXR is almost linearly polarized in a plane parallel to the positron orbit, that is, \( \tan \theta < 1 \) and \( \delta \approx 0 \), the throughput ratio of the two azimuthal angles of the DMP \( \chi = 90^\circ \) and \( \theta = 0^\circ \) is expressed as

\[
T = \frac{R_p}{R_s} \tan^2 \delta + 1
\]

The first term is the intensity ratio of the \( p \)- to the \( s \)-component of the incident SXR. If we know the degree of polarization of incident SXR over an energy range, we can obtain polarizance of the DMP, \( (R_s - R_p)/(R_s + R_p) \).

Experiments and Results

To extend the effective spectral range with practical throughput we employed a Ru/C multilayer polarizer. Its peak reflectance was 34% for \( s \)-polarized SXR of 99eV at an angle of incidence of 45°.

The performance of the DMP was evaluated on the beamline 11A. The state of polarization of the emergent SXR was evaluated by using the rotating analyzer. It was found that \( \tan^2 \delta = 0.010 \pm 0.001 \) and \( \delta \approx 0 \) at 97eV. The throughput of the DMP was then measured for \( \chi = 0^\circ \) and \( 90^\circ \) over a spectral range from 70 to 180 eV. Figures 1 and 2 show the measured throughput of the DMP for \( \chi = 0^\circ \) and \( 90^\circ \), respectively. The dashed curves show the throughput at various angles of incidence indicated in the figures. The measured throughput for \( s \)-polarized light (Fig. 1) was higher than 4% (5%) over a range of 80-150eV (84-140eV) with a maximum of ~11.5% at 100eV. The maximum throughput is, however, lower than that of the Ru/Si DMP, practical throughput ranges over a wider energy region.

By assuming that the state of polarization does not change over the spectral range under investigation, that is, the ratio of intensities along the two elliptic axes of the incident SXR is 0.010 in the 80-150eV range, polarizance of the DMP is calculated using the measured throughputs. They are plotted in Fig. 1 with solid triangles. The polarizance is higher than 94% between 80 and 110eV, with a maximum of 99.0% at ~88eV for an angle of incidence of 40°.

References

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OPTICAL CONSTANTS OF Pt THIN FILMS MEASURED BY THE ANGULAR DEPENDENT PHOTOELECTRON YIELD

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Introduction
For the application like soft x-ray (SXR) multilayers we have so far determined optical constants of very thin films of various materials in the SXR region by means of the reflectance method. To study the consistency of the optical constants, we measured the reflectance and the total photoelectron yield of Pt thin films as a function of the angle of incidence in the SXR region. For the two measurements, the same area of the sample surface is surveyed, which makes it easier to compare directly the optical constants.

Experiments
Five Pt samples were prepared by ion-beam sputtering to film thicknesses from 63 to 153 Å on BK7 glass substrates. The measurements were performed on the beamline 11A in the photon energy range between 70 and 900 eV using the SXR reflectometer. An aluminum electrode, biased to 200 V, was placed close to the sample surface to take off the emitted electrons. The photocurrent of the sample was measured, while changing the angle of incidence from 0 to 90 °. To determine the optical constants the measured data, once normalized to one at normal incidence, was fitted with the Pepper's formula by means of the least squares method. The reflectance measurement is described in Ref. 1.

Results
Figures 1 and 2 show the optical constants \( n \) and \( k \), respectively, determined for the 153 Å thick Pt film by the reflectance (O) and the total photoelectric yield (+) measurements. They show excellent agreement within error of 5% over the measured energy range, showing the consistency between the two. The optical constants determined for the other four samples also agree within error of 5% with those of the 153 Å thick sample. For comparison the data of Henke et al. are also illustrated in the figure with dotted curves. Discrepancy is remarkable between 200 and 400 eV in \( n \) and so is in \( k \) between 150 and 200 eV.

Birken et al. reported remarkable inconsistency between the two measurements for Pt samples above about 300 eV, which result was not found in this study.

References
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DEVELOPMENT OF GSPC DETECTOR FOR P.A SCATTERING OF SOFT X-RAY

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Introduction

The theory of inelastic scattering of soft X-ray by solids of light elements suggests a possibility of detecting the effect of p.a term in the energy range of 80-1000 eV. However, the cross section is very small. We are now developing the spectroscopic analysis using a GSPC detector (Gas Scintillation Proportional Counter) for soft X-ray.

Experiment

Table 1 shows the specification of the GSPC for soft-X-ray.

| drift region | 2~3 mm voltage ~200V |
| scintillation region | 10 mm ~4000V |
| wavelength shifter | p-terphenyl |
| window | mylar 0.6 micron |
| PMT | R580, R980(1-1/2") |
| gas | xenon(99.995%) 1 atm |

The incident beam is monochromatized by a Grasshopper monochromator installed at the BL-11A. The experiments were performed on two photon energy ranges. The one is 100-300 eV for the low energy range and the other 700-900 eV for the high energy range. The resolution of the GSPC is 63, 35, 27, and 20% for 100, 200, 300, and 800 eV, respectively. (Figs. 1 and 2) Xenon gas is not continuously circulating during the experiment in the high energy range.

Discussion

The resolution of the GSPC agrees with the rule of 1/\(\sqrt{E}\), when we assume the value of that at 5.9keV as 8%. However, linearity of energy to pulse height spectra is not so good for the low energy range. We can consider three reasons as follows: 1) effect of higher-order incident beam, 2) instability of drift region, 3) non-linearity of charge sensitivity of the pre-amplifier.

In the experiment of high energy range, pulse height spectra shift toward lower channels during the measurements. This is due to desorption from the surface of the counter cell. The desorption gases absorb electrons and photons in drift and scintillation region. In Fig. 3, a peak shifts at the rate of 20 eV/min. This result gives us the good information about purity of xenon gas in the counter cell.

References


Fig. 1 Pulse height spectra of 200 eV.

Fig. 2 Pulse height spectra of 800 eV.

Fig. 3 Pulse height spectra at t=0 and t=15.5 minutes.

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Soft X-Ray Ellipsometric Study of Multilayer Reflection

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We have developed soft x-ray multilayer polarizers and phase shifters for polarization measurement in soft x-ray region[1]. With the soft x-ray polarizer, the polarization response of the multilayer has been studied for the first time by soft x-ray ellipsometry at 97eV photon energy. The relative amplitude attenuation \( \rho = \tan \psi \exp(i\Delta) = i\rho_p/R_p \) representing the relative phase and amplitude change between p- and s- components has been measured as a function of the angle of incidence.

The experiment was carried with synchrotron radiation from a grasshopper monochromator at beamline 11A, Photon Factory, KEK. With the multilayer polarizer[1], the beamline optics were optimized for the best linear polarization with unwanted vertical component less than 1% and used as the linear polarization source for ellipsometry.

Two identical Ru/C multilayer mirror samples are mounted in the double crystal configuration on our double multilayer polarizer unit[2] and double reflection response are measured.

In rotating analyzer ellipsometry, the polarization ellipse is detected as a characteristic sinusoidal signal giving ellipticity and inclination of the ellipse, which can be converted to \( \psi \) and \( \Delta \) easily. Figure 1 shows some examples of such signals plotted in logarithmic scale as a function of the analyzer azimuth. Each symbol marked at the data points represents a set of measurements at each incidence angle indicated above the figure. The dash curves are those of best fit.

The curve 2 measured at 40° has the steepest valley indicating the most linear polarization having been obtained. In contrast, curve 6 measured at 52.8° is very close to DC signal indicating a circular polarization having been obtained. The signal level of the curve 6 is an order of magnitude higher than the noise level around 20. This directly shows that the double reflection gives 90 phase shift and produced a circularly polarized light.

Figure 2 shows the total phase shift \( 2\Delta \) between p- and s- polarization and the total relative amplitude attenuation \( |R_p/R_s|^2 \) of the doubled Ru/C multilayer thus measured. At 40° incidence, the minimum attenuation is recorded where the double multilayer configuration most effectively polarizes incident light as having been designed[2]. The phase shift curve crosses at three angles with the line of \( 2\Delta = 90° \), where circular polarizations were observed. The up-down changes above 49° may correspond the effect of interference. At present, there is a large discrepancy between the observed results and the theories.

References
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Fig. 1 Observed analyzer outputs at various angles of incidence of the doubled multilayer sample. Wide variation in their states of polarization is evident. 2: linear polarization, 6: circular polarization.

Fig. 2 Phase shift and relative amplitude attenuation of the doubled Ru/C multilayer sample measured by the rotating analyzer ellipsometry. At 40°, the multilayer shows smallest p-reflectance and is a good polarizer. At three angles, the total phase shift of 90° is evident.
ION DESORPTION FROM Si(100)-H$_2$O/D$_2$O BY O 1s ELECTRON EXCITATION

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INTRODUCTION

Recently, Auger stimulated desorption (ASD) model$^1$ has been proposed for the photon stimulated desorption (PSD) mechanisms in covalent adsorbate systems by core excitation. But actually after desorption, PSD ions have high probability of neutralization by strong interaction with surface molecules.

EXPERIMENTAL

The experiments were performed at BL11A using a grasshopper monochromator in the energy range of 525–615eV. The PSD ions were detected by a time-of-flight mass spectrometer using a pulsed SR$^2$. The PSD investigation was carried out at a base pressure of $3 \times 10^{-10}$Torr after 10L exposure of D$_2$O and/or H$_2$O with n-Si(100) at room temperature. Under these conditions H$_2$O is dissociated on Si(100)$^3$.

RESULTS AND DISCUSSION

Fig.1 shows relative yields of PSD ions and O(KLL) Auger electrons from Si(100)-H$_2$O/D$_2$O as a function of photon energy. The H$^+$ and D$^+$ yield curves exhibit two broad peaks below (peak A at 535eV) and above (peak B at 558eV) the O K edge, whereas O$^+$ ion exhibits a delayed threshold at 570eV. Oxygen Auger electrons of 503eV are created by the decay of the O 1s core hole, and thus Auger electron yield (AEY) spectra represents the primary absorption cross section of the adsorbed OH and is compared with PSD yield in order to check the deviation of the ASD model. AEY spectra coincides in position with two peaks of PSD yield of H$^+$ and D$^+$ shown in Fig.1. Since the absorption spectrum of OH radical in this energy region has not been reported, AEY spectra is compared with the gas phase EELS spectra$^5$ and recent CI calculations$^8$ of core excitation of H$_2$O. Although AEY spectra is not well resolved, its overall structure resembles that of EELS, and by comparison with the CI calculations, peaks A and B can be roughly assigned. Shake off transition and doubly excitation are possible transitions which suggestively coincide with the threshold energy (570eV) of O$^+$.

Fig.1. Relative yields of PSD ions and O(KLL) Auger electron from Si(100)-10L H$_2$O/D$_2$O

Above 570eV not only O$^+$ but also H$^+$ and D$^+$ have a marked deviation from AEY spectra. As OH is bound with the O atom pointing to the surface, the probability of neutralization of O$^+$ is assumed to be much higher than that of H$^+$. Then, even if O$^+$ is formed by these excitations, it may immediately neutralize and desorb as neutral O atom. Thus, the appearance of O$^+$ above 570eV can be better explained by the highly charged ions such as O$^{2+}$ and O$^{3+}$. As mentioned above, shake off transition and/or doubly excitation can take place in this region and form OH$^{m+}$ (m≥3) through the following auger decay. OH$^{m+}$ may decompose into O$^{m+}$+H$^+$, O$^{m+}$+H, and so on, which can survive the neutralization and desorb as H$^+$, O$^+$ and O$^{m+}$. This interpretation for the appearance of O$^+$ is suggestively supported by preliminary PIPICO (photo ion-photo ion coincidence) measurements which indicate simultaneous desorption of O$^+$ and H$^+$.

REFERENCES

5) N. Kosugi, unpublished results.
Pyrolysis of Polysilazane and Related Polymers Studied by XANES

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Introduction

X-ray absorption near edge structure (XANES) is sensitive to the chemical state and structure around an absorbing atom. In the present study, we measured XANES of poly(dimethylsilylene), poly(silazane), poly(dimethylsiloxane), and also observed the XANES spectral change in the heating process of poly(silazane), which is known as a precursor of silicon nitride.

Experimental

Si-K XANES measurements were performed at BL-11B and Si-L, C-K, N-K, O-K at BL-11A by the total electron yield method. Samples of Si polymers are either powders or thin films. For the experiment of pyrolysis, a thin film of poly(silazane) was prepared by dropping the solution on a Mo substrate and was heated from room temperature to 1000°C in three different conditions: high vacuum (~10^-7torr), 10 torr-N2, and 1 torr-H2 atmosphere.

Discussion

Fig.1 shows Si-L and Si-K XANES spectra of Si polymers. K and L XANES reflect mainly Si3s → Si3p and Si2p → Si3d transition, respectively. In Si-K XANES, sharp peaks suggest that these polymers have ionic character more than covalent one and the peak shifts are roughly in proportion to the electronegativity differences of bonding atoms. On the other hand, Si-L XANES are rather complicated because they consist of L2 and L3 edge components and furthermore around the edge region some peaks appear, possibly by the excitonic effect.

Fig.2 shows Si-K XANES of poly(silazane), heat treated at several temperatures in a high vacuum. Reactant gases did not affect the results. The spectrum began to change at 600°C and gradually shifted to higher energy and broadened. From our results of XPS, IR and mass spectroscopy, above spectral change corresponds to the desorption of hydrogen and formation of Si-O bond as well as Si-N bond. Consequently, the product is not pure silicon nitride, but SiN_xO_y (x ~ 1, y ~ 0.5).

Fig.1. Si-L and Si-K XANES of poly(dimethylsilylene), poly(silazane) and poly(dimethylsiloxane)

Fig.2. Si-L XANES of poly(silazane) heat treated up to 1000°C in high vacuum (~10^-7torr)

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Experimental evaluation of the semitransparent soft X-ray photocathodes and observation of biological samples with the X-ray zooming tube.

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Introduction

It is very useful to increase the sensitivity of the photocathode of a X-ray zooming tube¹², which picks up the output image of X-ray microscope, because X-ray irradiating time to the sample will decrease and it makes X-ray damage of the sample small. In order to find out the most sensitive semitransparent soft X-ray photocathode material, various materials such as CsI, RbI, CuI, Au, etc. have been experimentally evaluated at KEK-PF by changing their thicknesses. In addition, some biological samples have been observed with the X-ray zooming tube. In this paper, the experimental arrangement and the obtained results are described.

Experimental arrangement

Fig.1 shows the experimental arrangement for the observation of biological samples with the X-ray zooming tube. As a X-ray source, the beam line of BL-11A (GRASSHOPPER monochromator; 76~827eV) and BL-6B (double crystal monochromator; 4~22keV) are used. For calibrating input photon number, the opaque Au photocathode (300 Å) is used, and it is calculated based on the data of Henke³.

Results

Fig.2 shows the spectral sensitivity of the various photocathodes. CsI is the best material at this experiment. Fig.3 shows the sensitivity of CsI photocathode depending on film thickness. At the X-ray energy of 76~827eV the thickness of 1k Å is best, and at the region of 4~22keV 3k Å is best. The sensitivity of the lowest X-ray energy is limited to be about 80eV by the transmissivity of the substrate which is made of organic film.

Fig.4 shows the output image of Diatom observed by the X-ray zooming tube, where the magnification factor of the tube is ~200 and X-ray energy is 276eV.

Reference


X-ray Microscopy III (Springer-Verlag, Berlin) in press.
REFLECTIVITY MEASUREMENTS OF Mo/Si MULTILAYER MIRRORS
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Introduction
Mo/Si multilayer mirrors are expected to show high reflectivity for wavelengths between 12.5 and 25nm at near-normal angle of incidence. Therefore they are promising as optical components of many applications in X-ray optics: X-ray microscopy, X-ray projection lithography, etc. To evaluate the performance of the mirrors for these applications, it is primarily important to measure the reflectivity of multilayer mirrors for the wavelength and the angle of incidence to be actually used. We fabricated the Mo/Si multilayer mirrors and measured the reflectivity at near-normal angle of incidence by SR light source.

Experiments
Mo/Si multilayers were coated by RF-magnetron sputtering on the polished quartz glass substrates (roughness < 0.3nm rms). We prepared two kinds of samples of different d-spacings: sample(1) had the period of 7nm with 61 layers stack and sample(2) had the period of 12.5nm with 41 layers stack. These samples are expected to have high reflectivity for wavelengths around 13nm and 24nm and are very useful in optics for X-ray projection lithography[1] and X-ray laser[2].

In our previous study[3], we have found that lower argon pressure in magnetron sputtering suppresses the columnar structure formation and forms smoother interfaces in Mo/Si multilayers, and consequently leads to higher reflectivity. Therefore, we prepared the samples by magnetron sputtering under the condition of low argon pressure: 0.4-1.0 mTorr.

The near-normal incidence reflectivity measurements were carried out with soft X-ray reflectometer[4](PF. BL11A). SR light was wavelength-scanned by the graspermonochromater and entered onto samples at fixed angle of incidence with S-polarization. Since the electron multiplier we used as an X-ray detector had large ununiformity of sensitivity at sensitive face, we aligned the X-ray beam and samples very carefully and precisely; the position difference between direct and reflected beams entered onto the detector was less than 0.5mm.

Results and Discussion
Fig.1 and 2 show measured reflectivity(solid line) of sample(1) and (2) for wavelengths between 10 and 16nm, and 15 and 25nm, respectively. The calculated peak reflectivity for ideal multilayer structures are 75-79% and 44-52% at angles of incidence of 12-30deg. for samples (1) and (2), respectively. Therefore the observed peak reflectivity is 83-90% of ideal values.

The broken lines in Fig.1 and 2 are calculated curves of best fitted to the reflectivity profiles with fitting parameters of layer materials density, \( \rho \), and interfaces roughness, \( \sigma \). In this study, \( \rho \) and \( \sigma \) values are mainly responsible for bandwidth and peak height of reflectivity profiles, respectively. The values of best fitted parameters \( \rho \) and \( \sigma \) are 90% of bulk density for both Mo and Si layers and about 0.8nm rms, respectively in both samples (1) and (2).

The observed values of peak reflectivity of sample(1) are 62-65% at angles of incidence between 12-23deg. which are as good as the world’s best reflectivity obtained up to today[5]. Making use of the sample(2) mirror as an end reflector of Ge soft X-ray laser, the intensity enhancement by a factor of ~50 was obtained in the experiment of X-ray laser at the Institute of Laser Engineering (ILE) in Osaka University[2].

References

Fig.1 Reflectivity of sample(1): \( d \approx 7nm \), 61 layers

Fig.2 Reflectivity of sample(2): \( d \approx 12.5nm \), 41 layers
Reflectivity Measurement of Mo/Si Multilayers

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Introduction

Multilayers of Mo/Si have relatively high reflectivity in the wavelength region longer than the silicon L absorption edge at 123 Å. Therefore they are suitable for the multilayer optical system of x-ray projection lithography.

We prepared Mo/Si multilayers by rf magnetron sputtering and ion beam sputtering. Their properties were investigated.

Experiment

The multilayers, with the layer period of 75 Å and the layer number of 50, were deposited on silicon wafers.

Reflectivity for s-polarized x-ray was measured in 100-160 Å wavelength region using a high-precision reflectometer at the beam line BL-11A. The wavelength resolution was 0.4 Å with a grating of 1200 lines/mm and the slit width of 100 μm. Beryllium filter was employed to cut higher order diffraction.

Results

Figure 1 shows measured reflectivity of the Mo/Si multilayers prepared by rf magnetron sputtering. In this figure \( \Theta \) represents incidence angle measured from normal. In the wavelength region longer than silicon absorption edge they showed high reflectivity of nearly 70%. The reflectivity of the multilayers prepared by ion beam sputtering was shown in Fig. 2. The reflectivity was lower than that in Fig. 1 in the whole wavelength region. Also the reduction of the peak width and the shift of the peak position to shorter wavelength were observed. These two multilayers had almost the same value of reflectivity with Cu Kα radiation. The difference in reflectivity was observed only in the soft x-ray region.

The micro-structure of these multilayers was investigated by transparent electron microscopy and Auger analysis. It has become clear that silicide was formed in each interface of layers and that the thickness of silicide layer was larger in ion beam sputtering than in magnetron sputtering.

The reflectivity of Mo/Si multilayers with silicide(MoSi₂) interface layers was calculated. Optical constants reported by LBL group was used in the calculation. The result was shown in Fig. 3. With the increase of silicide thickness, the reflectivity was lowered. The change of the peak profile was consistent with the experiment.

References

STUDY ON S KLL AUGER ELECTRON SPECTRA BY X-RAY EXCITATION NEAR S K-EDGE

III. S K-EDGE XAFS OF MoS₂

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Introduction

Molybdenum disulfide is an important species as a catalyst, which is often used for hydrotreating of oil. Although S K-edge EXAFS is very important to clarify structure of active sites, there are Mo L-edges on the high energy side of S K-edge in the X-ray absorption spectra. These edges interfere S K-edge EXAFS analysis for MoS₂. A measurement of XAFS by Auger electron yield theoretically enables the separation of a specified edge from others. Experimentally, however, there are some difficulties related to background, photoelectron peaks, and signal to noise ratio. In the present report, we have attempted to obtain S K-edge XAFS spectra of MoS₂ by S KLL Auger electron yield.

Experimental

All the measurements were performed at the BL-11B in the Photon Factory. X-ray excited S KLL Auger electron spectra were taken over the kinetic energy range of 2080–2125 eV (0.2 eV step) with incident X-ray energy range of 2400–3320 eV using a electrostatic hemispherical electron analyzer system (Rigaku Industrial Corp.). The pass energy was set to 40 eV and the acquisition time was 0.4 s/step. It took about 8 hours to measure a whole spectrum.

Results and Discussion

Figure 1 shows S KLL Auger spectra of MoS₂ with changing the incident X-ray energy near S K-edge. No resonancelike phenomena were not observed, which was observed for SO₄²⁻. Figure 2 shows S K-edge absorption spectra obtained by total electron yield (dotted line), peak intensity of S KLL Auger electrons (2110 eV) (broken line), and intrinsic S KLL Auger electron yield extracted from Fig.1 (solid line). Mo L-edges appear beyond S K-edge in the absorption spectra by total electron yield. These edges remain in the absorption spectra by S KLL Auger electron yield monitored by fixing kinetic energy of the analyzer. In contrast, in the absorption spectra obtained by S KLL Auger electron yield monitored by fixing kinetic energy of the analyzer. In contrast, in the absorption spectra obtained by S KLL Auger electron yield extracted these edges are perfectly removed. Figure 3 shows the Fourier transform of S K-edge EXAFS of the MoS₂ obtained by the S KLL Auger electron yield extracted. The phase shift correction was performed as S-S in Fourier transform. Peaks of S-Mo and S-S are observed at 2.1 Å and 3.2 Å, respectively, in the Fourier transform. The signal to noise ratio of spectra for catalyst samples were not good enough for EXAFS analysis. It is expected to be improved by the use of a multi channel plate as a detector.

References

SCISSION OF THE Oligonucleotide BY MONOCHROMATIC SOFT X-RAYS
ON AND BELOW THE K-SHELL ABSORPTION EDGE OF PHOSPHORUS
AS A MODEL OF STRAND BREAK IN DNA

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Introduction

The scission of the pentadeoxynucleotide, d(pT)₅, by monochromatic soft X-rays was studied as a model of strand breaking in DNA. We tried to clarify the effects of the K-shell absorption of phosphorus and the subsequent Auger process on the scission of the oligonucleotide.

Materials and methods

Ten μg of d(pT)₅ on a glass plate was dried in a vacuum and irradiated with monochromatic soft X-rays on (2153 eV) and below (2147 eV) the K-shell absorption edge of phosphorus. The irradiated samples were dissolved in distilled water and analyzed by HPLC.

Results and discussion

The HPLC chromatograms of soft X-ray irradiated d(pT)₅ are shown in Fig.1.

![HPLC chromatograms of d(pT)₅](image)

Table 1 Cross-sections for the induction of the products

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Thy</th>
<th>pTp</th>
<th>5'-TMP</th>
<th>d(pT)₂</th>
<th>d(pT)₃</th>
<th>d(pT)₅</th>
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<td>1.04</td>
<td>1.42</td>
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<td>18.40</td>
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<td>3.73</td>
<td>4.51</td>
<td>4.84</td>
<td>3.50</td>
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<td>Ratio</td>
<td>3.4</td>
<td>3.0</td>
<td>3.6</td>
<td>3.2</td>
<td>3.2</td>
<td>3.0</td>
</tr>
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</table>

The main products induced by 2147 and 2153 eV X-rays were Thy, 5'-TP, pTp, d(pT)₂-4 and three products which were presumed to be pTpTp, pTpTpTp and pTpTpTpTp, respectively. The cross-sections for the induction of the products are listed in Table 1. The 2153 eV X-rays were found to be more effective in the scission of the oligonucleotide by comparing the number of molecules of the products induced per photon. However, the 2153 eV X-rays were more highly absorbed due to the K-shell absorption of phosphorus than 2147 eV X-rays. Each cross section was converted to the corresponding G-value, which is the number of molecules of each product induced per 100 eV of energy absorbed (Table 2). The G₂₁₅₃/G₂₁₄₇ ratios were 1.0-1.2, indicating that the effects of K-shell absorption and the subsequent Auger process did not lead to any serious differences qualitatively or quantitatively concerning the scission of the oligonucleotide.

Table 2 G-values for the induction of the products

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Thy</th>
<th>pTp</th>
<th>5'-TMP</th>
<th>d(pT)₂</th>
<th>d(pT)₃</th>
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<td>Ratio</td>
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<td>1.2</td>
<td>1.1</td>
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Fig.1. HPLC chromatograms of d(pT)₅
Sulfur K-Edge XANES Studies of Merocyanine Dyes Adsorbed on AgCl
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Introduction
In silver halide photography, many sulfur-containing organic compounds called "photoadditives" play important roles. Since they are used in adsorbed states on silver halides, it is important to study their adsorption geometries. Spectral sensitizing dyes, which extend the photosensitive wavelength range form an important class of photoadditives, with merocyanine and cyanine dyes being typical examples. In this work, we studied the adsorbed states of two merocyanine dyes by sulfur K-Edge XANES (X-ray Absorption Near Edge Structure) spectroscopy. Information about the adsorption structure was obtained by comparing the spectra of adsorbed dyes with that of dye solids, which were systematically measured and assigned.

Experimental
Spectra were measured on BL-11B at Photon Factory with a double crystal monochromator. Samples of dye solids were prepared by rubbing dye powder on Ag sheets and were measured in the total electron yield mode. Samples for the adsorbed states were prepared by pressing AgCl powder with adsorbed dyes into disks and were measured in the X-ray fluorescence yield mode.

Result and Discussion
Figure 1 shows S K-Edge XANES spectra of merocyanine dye solids. The structures in the XANES spectra of the dyes can be ascribed to characteristic local chemical structures around the sulfur atoms. Namely, peak A at about 2470eV is assigned to the transition from the Sis state to the \( \pi^* \) level in the thioke-tone(C=S) part. Peak B at about 2473eV is assigned to the Sis \( \rightarrow \sigma^* \) transitions at thioketone S and thia(C=S-C) S (possibly including the Sis \( \rightarrow \pi^* \) transition at thia S). Peak C at about 2500eV is assigned to the transition in the SO3H group. Figure 2 shows the spectra of two simple dye solids and those of the same dyes adsorbed on AgCl. One dye has S of thia type, while the other has S of thioketone type. On adsorption, the spectrum of the thia type dye shows almost no change, but that of thioketone type dye shows a decrease in the intensity of peak A corresponding to the transition to the \( \pi^* \) level. Therefore we conclude that thioketone sulfur acts as an effective adsorption part, while thia sulfur does not.

Fig.1 (left)
S K-edge XANES spectra of merocyanine dye solids

Fig.2 (right)
S K-edge XANES spectra of two simple merocyanine dye solids and those of the same dyes adsorbed on AgCl
SEXAFS STUDIES ON THE STRUCTURE OF P/Ni(7 9 11)

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[3] Department of Material Science, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 724, Japan.

Introduction

Electronegative atoms, such as chlorine, sulfur and phosphorus, on metal surfaces are important as catalyst poisons. The surface structures of sulfur and chlorine are studied by many researchers. On the other hand, those of phosphorus are largely unexplored. A previous SEXAFS studies(1) showed that sulfur was selectively adsorbed on the step 4-fold site of Ni(7 9 11)=5(1 1 1)x(1 0 1) surface. In this paper we studied the surface structure of the phosphorus on Ni(7 9 11) and we found that the phosphorus also was adsorbed onto the step 4-fold site of Ni(7 9 11).

Experimental

Ni(7 9 11) surface was cleaned by repeated cycle of annealing at 1030 K and Ar+ bombardment in UHV chamber whose base pressure was 10^-10 Torr. The phosphorus was adsorbed in the form of PH3 at room temperature. The amount of adsorbed phosphorus was estimated using the AES peak-to-peak ratio of P(120eV)/Ni(59eV){2). When the peak-to-peak ratio is equal to 0.2, the sample was annealed at 873 K. SEXAFS measurements were carried out at BL-11B at room temperature.

Results and Discussion

We observed that the (1x1) pattern of P/Ni(7 9 11) was gradually diffused without any superstructures when PH3 was dosed at room temperature. When the sample with peak-to-peak ratio of P/Ni=0.2 was heated at 873 K, quite complex patterns appeared as shown in Fig.1. The analyses of LEED patterns indicated the production of (1 1 1) facets and (1 3 5)=2(1 1 1)x(1 0 1) facets.

SEXAFS was measured for two azimuthal angles: E parallel to step and perpendicular to step. Fig.2 showed the Fourier transforms of P K-edge EXAFS oscillations which were obtained at incident angles of 15°, 45° and 90° for each azimuthal angles. The curve fitting results were shown in Table 1 which contained the effective coordination numbers N* calculated from the several adsorption models. The effective coordination numbers are close to those of the models of phosphorus onto the step 4-fold site. In this point, it is similar to the case of sulfur on Ni(7 9 11). However, phosphorus induced the surface reconstruction of Ni(7 9 11) to Ni(1 1 1) and Ni(1 3 5) facets.

References


<table>
<thead>
<tr>
<th>Table 1</th>
<th>Polarization dependence of effective coordination number</th>
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<tr>
<td></td>
<td>exp. step 4-fold</td>
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<td>E//step</td>
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<td>N(45°) / N(90°)</td>
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<tr>
<td>E/step</td>
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<td>N(45°) / N(90°)</td>
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Fig.1 Observed LEED pattern 120eV

Fig.2 Fourier transforms of P/Ni(7 9 11)
S K-EDGE X-RAY ABSORPTION AND X-RAY PHOTOELECTRON
SPECTROSCOPIC STUDIES OF CS₂ ADSORPTION ON Ni(100)

Shinya Yagi, Toshihiko Yokoyama, Yasutaka Takata, Hitoshi Sato,
Toshiyuki Asahi, Toshiaki Ohba and Yoshinori Kitajima


INTRODUCTION
The exact knowledge of the adsorption process of simple S-containing molecules on transition metal surfaces is a fundamental subject in surface science and of importance for the understanding of catalysis. Recently, we have investigated thiophenol (C₆H₅SH) adsorption on Ni(100) at various temperatures by means of surface XAFS (EXAFS and XANES) technique, and successfully determined the adsorption geometry of the adsorbed species. It is of great interest to clarify how the adsorption behavior is influenced by the chemical bond of an adsorbed molecule. In the present study, we have investigated CS₂ adsorption on Ni(100) by surface XAFS and XPS techniques.

EXPERIMENTAL
All the experiments were performed at BL-11B by use of the newly fabricated UHV apparatus. Clean and ordered Ni(100) was cooled down by LN₂ to 100 K and was subsequently dosed with 6 L of CS₂. The crystal was gradually heated and the polarization dependence of S K-edge XAFS spectra at each temperature was studied by means of the fluorescence yield mode. S L₃ photoemission spectra were also measured using the synchrotron radiation.

RESULTS and DISCUSSION
At 130–140 K, physisorbed CS₂ is found to desorb, judging from the sudden decrease of the edge jump of S K fluorescence yield and S L₃ photoelectron intensity. In this stage, the polarization dependence of XANES is apparent (Fig.1). We determined the average polar angle of the S-C bond direction ωₑₑ as 68° from the polarization dependence of the absorption intensity of the σ⁺(S-C) resonance (peak a). With the further rise of temperature till 1000 K, σ⁺(S-C) resonance disappears completely and the spectral features approach those of c(2x2)S/Ni(100), implying the complete dissociation of the S-C bond. Figure 2 shows the Fourier transforms of the EXAFS spectra from the 140 K species and from the multilayer CS₂. The empirical curve-fitting analysis for a double shell of the S-Ni and S-S coordinations was performed. As a standard for the S-Ni and S-S pairs, the spectrum of c(2x2)S/Ni(100) at 120 K and of the CS₂ multilayer at 95 K were chosen, respectively. From the polarization dependence of S-Ni effective coordination numbers, it was revealed that 68 % S is atomically-adsorbed species on the 4-fold hollow site of the surface Ni layer with the S-Ni distance of 2.25 Å, and 32 % S is in the state of CS₂ molecules which have no direct chemical bonds with the surface Ni. The results for the S-S coordination indicate the averaged polar angle of molecular axis of CS₂ is 73° and is nearly equal to the ωₑₑ of 68° by XANES. From the SEXAFS analysis, the ratio of molecular CS₂ is also estimated to be 35 %, supporting the results from the S-Ni coordination.

REFERENCE
Damages to Adenosine-Triphosphate in aqueous solution induced by monochromatic X-rays around the K-absorption edge of phosphorus

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Introduction

Some studies of enhanced damages on biological systems due to the Auger cascade initiated by the ionization of the K-shell have been reported in recent years. The purpose of these studies is to clarify the specific radiation effect on biomolecules induced by selected energy absorption in inner shell of component atom. In the present study, Adenosine-Triphosphate (ATP) in concentrated aqueous solution was irradiated with monochromatic X-rays around the K-shell absorption edge of phosphorus and the enhanced damages on ATP induced by ionization in K-shell of phosphorus were examined by the method of high performance liquid chromatography (HPLC).

Materials and methods

Adenosine 5'triphosphate (Fig.1) was dissolved in distilled water at concentration of 155 mg/ml (0.282 mol/l), and was irradiated in a specially designed cell with a mylar film window, stirring with a glass coated iron rod. The absorption spectrum of ATP film in the rage from 2.10 to 2.25 keV was measured and shown in Fig.2. Monochromatic X-rays having energies of resonance absorption peak of phosphorus K-shell, 2.153 keV, and slightly below and above the peak, 2.146 keV and 2.160 keV, were selected for irradiation. The radioproducts from irradiated ATP were analyzed by ion exchange chromatography (HPLC).

Results and discussion

There were no qualitative differences among HPLC elution profiles of ATP irradiated with 2.146, 2.153, and 2.160 keV X-rays. As the main radioproducts, Adenine, Adenosine 5'monophosphate (5'AMP) and Adenosine 5'diphosphate (5'ADP) were determined among several fractions in the HPLC profiles. Adenosine was not obtained as one of the products. G values of these radioproducts calculated on the basis of the absorbed dose were shown in Table 1. When the ATP solution was irradiated with 2.160 keV X-rays which can ionize the K-shell of phosphorus, G-values of Adenine, 5'AMP and 5'ADP were estimated to be 1.4, 0.40 and 0.46, respectively. These values were respectively 1.3, 2.9 and 3.8 times higher than those obtained on the irradiation with 2.146 keV X-rays which cannot ionize the K-shell of phosphorus. These energy dependent enhancements may reflect the difference of energy absorption process. Especially Auger cascade in phosphorus may be suspected to play an important role in these enhancements. Radioproducts induced by the irradiation with 60Co γ-rays were also analyzed and the G values were shown in Table 1. In this case insignificant quantities of 5'AMP and 5'ADP were obtained and G value of produced Adenine was smaller than that for irradiation with X-rays around the K-absorption edge of phosphorus, indicating the much difference in mechanism of radiation action among these radiation sources.

![Fig.2 Absorption spectrum of ATP](image)

![Fig.1 Chemical structure of ATP](image)

<table>
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<th>Radio-products</th>
<th>2.146 keV X-rays</th>
<th>2.153 keV X-rays</th>
<th>2.160 keV X-rays</th>
<th>60Co γ-rays</th>
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<td>5'ADP</td>
<td>0.12</td>
<td>0.47</td>
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</table>
Reflectivity spectra $R(E)$ of $Y_2O_3$ single crystals in Proposal No. 83-068 were not fully satisfiable, because they were measured by a detecting system with poor S/N ratios. In addition, the spectral range from 5 eV to 41 eV adopted there turned out to be insufficient for deriving the loss spectrum $-\text{Im}\frac{\epsilon(E)}{\epsilon_0}$ in the region of a plasma oscillation at $E \approx 36$ eV, i.e., the spectrum showed a spectral dependence of a shoulder instead of a peak at $E \approx 36$ eV.

Figure 1 shows $R(E)$ from $\{111\}$ of $Y_2O_3$ single crystals at 297 K measured at BL 11C and 11D from 5 eV to 110.5 eV by use of a detecting system with improved S/N ratios. The experimental method was detailed in ref. 2). This spectrum is saved from the above two defects: The spectrum is similar in its spectral behaviour to $R(E)$ of ref. 3) shown in the region of $E \lesssim 25$ eV and can yield the loss peak at $E = 38.4$ eV. The spectrum $\epsilon_2(E)$ (full curve) transformed from $R(E)$ by the Kramers-Kronig relation is shown in Fig. 2. The physical interpretation for the features found in $E \lesssim 41$ eV was given in ref. 1). The spectrum of $\epsilon_2(E)$ in $E \gtrsim 60$ eV stands for the free electron-like absorption. The dotted curve in Fig. 2 represents the effective optical dielectric constant $\epsilon_{\infty}(E)$ defined by the next equation:

$$\epsilon_{\infty}(E) = 1 + \frac{2}{\pi} \int_{0}^{E} \frac{\epsilon_2(E')}{E'} dE'.$$

This yields $\epsilon_{\infty}(E) = 3.58$ at $E = 110.5$ eV. The broken line exhibits the optical dielectric constant $\epsilon_{\infty} = 3.578^{4,5}$ obtained by independent measurements on the dispersion curve. The agreement between them is excellent.

References
Ellipsometrical Determination of the Optical Constants of Gold
In the VUV Region

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Spectroscopic ellipsometry is a well-established technique for determining the optical constants (n and k) with high accuracy in the visible and near-UV region.

The present report describes ellipsometric determination of the optical constants of gold in the VUV region.

An ellipsometer was constructed, utilizing three-reflection polarizers. Fig. 1 shows a schematic drawing of the present ellipsometer. P1 and P2 are polarizers with Au coated mirrors. The horizontally polarized SR light is converted to an elliptically polarized light by P1 and is incident to the sample S with 60° near the principal angle. The reflected light is analyzed by P2, detected by a photodiode D.

Fig. 2 shows variation of the detected intensity as a function of the rotation angle of P2; photon energy=22 eV and angle of P1=50°. The intensity varies as $I_0 + I_1 \cos 2\phi + I_2 \sin 2\phi$. In this figure, $I_1/I_0 = -0.418$, $I_2/I_0 = -0.294$. Fig. 3 gives curves of constant $I_1/I_0$ and $I_2/I_0$ as a function of n, k, from which the optical constants are determined: n=1.08, k=0.69.

The same type procedures have been done, obtaining the optical constants of gold in the photon energy from 15 to 28 eV (Fig. 4). Although small discrepancies are observed between the present results and those of ref. 3, the overall agreement is satisfactory. Efforts to extending into higher energy region is in progress.

ANGLE-RESOLVED PHOTOEMISSION SPECTRA OF THE ORGANIC SUPERCONDUCTOR $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$

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Masami Kageshima$^1$, Hiroo Kato$^4$ and Akira Kawazu$^1$

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$^3$Institute for Molecular Science, Okazaki 444
$^4$National Laboratory for High Energy Physics, Tsukuba Science City 305

BEDT-TTF-based organic materials are very attractive because they have very intriguing physical properties: electronic structure varies from insulating to superconducting in accordance with their crystal structure, especially in the molecular arrangement of BEDT-TTF molecules. Attempts have been made to understand these properties through molecular orbital (MO) calculations, and recently, some of the electronic structures of those materials have been examined on an atomic scale by scanning tunneling microscopy [1,2]. In order to confirm these results, we performed angle-resolved photoemission spectroscopy on $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (where BEDT-TTF is bis(ethylene-dithio)tetrathiafulvalene), an organic superconductor with one of the highest $T_c$'s.

Single crystals of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$, surface conditions of which were examined by STM observation, were attached to Ta plates by means of conductive epoxy, with their bc-plane parallel to the substrate. The base pressure of the experimental chamber was below $1 \times 10^{-8}$ torr. Polarization dependence of normal emission was observed for the incident photon energy of 40 eV.

Two dominant structures were observed at the binding energies of $\sim$7.5 eV and $\sim$11.5 eV, as is shown in Fig.1, where they are labeled A and B in the figure. The intensity of "A" decreased and disappeared at 45° with increase of the incident beam angle (measured from the normal axis of the surface, Fig.1), while that of "B" was unchanged.

Figure 2 shows the electronic structure calculated by the extended Hückel method. Two shallow peaks appearing at $\sim$4 eV and $\sim$8 eV below Fermi energy correspond to $\pi$ and $\sigma$ bonds, respectively. The molecular orbitals of the $\pi$ bonds expand almost parallel to the surface, and the $\sigma$ bonds are almost circular in the crystal.

In comparison with the MO structure calculated, peaks "A" and "B" are considered to correspond to the $\pi$ and $\sigma$-bonding states, respectively. These results support the validity of the analysis for the electronic structure of the BEDT-TTF-based organic conductors through MO calculations [3].

References

Fig.1. Normal emission spectra of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ surface as a function of the incident beam angle.

Fig.2. Electronic structure of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ calculated by the extended Hückel Method. The value of horizontal axis is relative to the Fermi level.
Introduction

It is known that the electronic structure of the TiC(111) surface is much different from that of TiC substrate, due to the charge redistribution around the surface, which screens the long-range electric field produced by the polar structure. We report here the angle-resolved photoemission study of the surface state inherent to the TiC(111) surface.

Experimental

The experiments were made on BL 11D. The TiC(111) clean surface was prepared by repeated flashing at \( \sim 1600^\circ \text{C} \).

Results and discussion

Fig. 1 shows normal-emission spectra for the TiC(111) surface taken at various photon energies. A sharp peak is observed at just below \( E_F \), which is not found in the spectra for the TiC(100) surface. By the use of \( H_2 \) adsorption study, the state has been identified as the emission from the surface state. We made detection-angle dependent measurements to study the two-dimensional band structure. The results show that the peak of the surface state emission is decreased in intensity and becomes asymmetric (more steep on the low binding energy side) with the increase of the detection angle. These suggest that the state is located in the vicinity of \( E_F \) around the \( \Gamma - K \) point and disperses upwards for both the \( \Gamma - K \) and \( \Gamma - \bar{K} \) directions, as is expected theoretically by Fujimori et al. \(^1\).

The cross section of the surface state is dependent on the photon energy (Fig. 1). The surface state emission is enhanced alternatively to the C 2s band emission. In Fig. 2a we plot peak intensities of the surface state and C 2s band emissions as a function of photon energy. The intensity maximum of the C 2s band at 35 eV for the (111) surface is not found for the (100) surface, indicating that the maximum is relevant to the polar structure. Since the surface state and C 2s band are localized to the first Ti and second C layers on the TiC(111) surface, respectively, the alternative \( h\nu \)-dependence may be caused from the surface optical response. In Fig. 2b, we display the calculated electric field component perpendicular to the surface just outside and inside the surface. The calculation is made using the complex dielectric constants for the TiC\(_{\text{sub}}\). The calculated curves qualitatively reproduce the alternative feature, however, the observed maximum (C 2s band) and minimum (the surface state) energies are higher than those found in the calculated curves. This may be due to the large charge redistribution around the (111) surface, which results in the increase of the electric density at the surface region.

References

Angle-Resolved Photoemission Study of the Surface State on TiC(111)

Kazuyuki EDAMOTO, Toshihisa ANAZAWA, Atsushi Mochida, Rizo MIYAZAKI, and Hiroo KATO

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Introduction

It is known that the electronic structure of the TiC(111) surface is much different from that of TiC substrate, due to the charge redistribution around the surface, which screens the long-range electric field produced by the polar structure. We report here the angle-resolved photoemission study of the surface state inherent to the TiC(111) surface.

Experimental

The experiments were made on BL 110. The TiC(111) clean surface was prepared by repeated flashing at ~1600°C.

Results and discussion

Fig. 1 shows normal-emission spectra for the TiC(111) surface taken at various photon energies. A sharp peak is observed at just below E_F, which is not found in the spectra for the TiC(100) surface. By the use of He adsorption study, the state has been identified as the emission from the surface state. We made detection-angle dependent measurements to study the two-dimensional band structure. The results show that the peak of the surface state emission is decreased in intensity and becomes asymmetric (more steep on the low binding energy side) with the increase of the detection angle. These suggest that the state is located in the vicinity of E_F around the \( \Gamma \) point and disperses upwards for both the \( \Gamma-K \) and \( \Gamma-H \) directions, as is expected theoretically by Fujimori et al.

The cross section of the surface state is dependent on the photon energy (Fig. 1). The surface state emission is enhanced alternatively to the C 2s band emission. In Fig. 2a we plot peak intensities of the surface state and C 2s band emissions as a function of photon energy. The intensity maximum of the C 2s band at 35 eV for the (111) surface is not found for the (100) surface, indicating that the maximum is relevant to the polar structure. Since the surface state and C 2s band are localized to the first Ti and second C layers on the TiC(111) surface, respectively, the alternative h\( \nu \)-dependence may be caused from the surface optical response. In Fig. 2b, we display the calculated electric field component perpendicular to the surface just outside and inside the surface. The calculation is made using the complex dielectric constants for the TiC, as substrate. The calculated curves qualitatively reproduce the alternative feature, however, the observed maximum (C 2s band) and minimum (the surface state) energies are higher than those found in the calculated curves. This may be due to the large charge redistribution around the (111) surface, which results in the increase of the electric density at the surface region.

References

ULTRA-VIOLET PHOTOEMISSION STUDY OF SrVO₃
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The electronic structure of 3d transition-metal oxides has attracted renewed interest stimulated by the discovery of high-temperature superconductivity and the new information obtained from photoemission spectroscopy. So far, main interest has been focused on the charge-transfer-type compounds, where the band gap is of a ligand-to-metal charge-transfer type, since high-Tc Cu oxides belong to this class. Studies on Mott-Hubbard-type compounds having d-d type band gaps are equally important in understanding the physics of correlated electron systems. In this work, we have studied perovskite-type SrVO₃, a metallic compound which belongs to the Mott-Hubbard regime, and compared the results with those of related oxides on both sides of the metal-insulator transition (Mott transition).

![SrVO₃](image)

We have studied a polycrystalline SrVO₃ sample, which was made by melt-quenching sintered powders of SrCO₃ and VO₂. Photoemission measurements were performed at beamline BL-11D. Angle-integrated spectra were collected using a double-pass cylindrical-mirror analyzer. The sample was cooled down to -35 K using a closed-cycle He refrigerator and was scraped in situ with a diamond file.

In Fig. 1, we show the photoemission spectra of SrVO₃ taken with varying photon energies in the V 3p→3d core absorption region. Above the threshold (hν=40 eV), V 3d-derived photoemission is enhanced due to the 3p-3d resonance photoemission effect. The emission within -3 eV of the Fermi level is thus unambiguously identified with the occupied part of the V 3d conduction band, while the emission between -3 eV and -9 eV is due to the filled O 2p band.

One notices in Fig. 1 that the V 3d band consists of two structures: One is at 0-1 eV with a sharp Fermi edge and the other is a broad peak centered at -1.5 eV. We attribute the former feature to the itinerant d-band states or the "coherent part" of the single-particle spectral density, and the latter feature to a reminiscent of the lower Hubbard band, a satellite (the d↓→d↑ spectral weight) accompanying the itinerant d band, or the "incoherent part" of the spectral density.

Recent theoretical studies on the Hubbard model have suggested the presence of such spectral features in the d-band region and that the coherent part gains its intensity with decreasing strength of electron correlation [1,2]. Indeed, if we compare the present spectra with those of LaTiO₃ [3], which is an antiferromagnetic (weakly ferromagnetic) metal [4] and is therefore expected to be more strongly correlated than the Pauli-paramagnetic SrVO₃ [5], the coherent part is weaker in LaTiO₃ than in SrVO₃. As for YTiO₃, a ferromagnetic insulator, no coherent part is observed, leaving only the lower Hubbard band centered at -1.5 eV.

DETECTION CHARACTERISTICS OF MICROCHANNEL PLATES IN THE VUV REGION (INCIDENT ANGLE DEPENDENCE)

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** Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305

Introduction

Microchannel plates (MCPs) are often used as compact and high gain x-ray detector for plasma diagnostics instruments. We have examined the current response characteristics of MCPs as a function of incident angle in the VUV band. A simple model of MCP detection current, in which the effect of x-ray reflection within a channel is taken into account, is used to predict the incident angle dependence of current response. The comparison between the measurement and calculation will be shown.

Detection Current of MCPs

A parallel monochromatic beam of x-rays illuminates an MCP (diameter d and length L) at an incident angle \( \theta \) with respect to the channel axis. We consider the elemental strip parallel to the channel axis lying between polar angles \( \varphi, \varphi + d\varphi \). A fraction of the flux incident on this strip is reflected with the reflectivity \( R(\theta') \), where \( \theta' \) is given by \( \sin^{-1} (\sin \theta - \cos \varphi) \), and undergoes multiple reflections within a channel. Electrons emitted from the \( n \)-th reflection point are multiplied during the traversal of channel, then the number of output electrons originated from this strip can be written as

\[
Q(\theta') = \sum_{n=1}^{N} \alpha [1 - R(\theta')] R(\theta') \left[ \prod_{i=1}^{n-1} R(\theta') \right] \exp \left[ g (L - z - (n-1) \cot \theta') \right],
\]

where \( \alpha \) is the photoelectron emission coefficient from the channel surface, \( I_0 \) the incident photon intensity, \( g \) the gain coefficient of the MCP, \( z \) the depth of the first interaction point and \( N \) the maximum number of the reflection point within a channel. The reflectivity \( R \) can be calculated using optical constant of SiO\(_2\) glass. Then the number of output electrons from an irradiated microchannel is given by integration over \( \varphi \).

Results

In Fig. 1 are shown the results of calculation of the relative response, \( Q(\theta)/I_0 \), together with that of measurement. In the figure the relative response is normalized at 13° which is equal to the bias angle of the MCP used. The gain coefficient is taken at a low gain regime in which the experiment has been carried out, that is \( g = 0.075 \) (dotted curve), 0.1 (solid curve) or 0.15 (dashed curve). The feature of the measured angle-dependence is well reproduced by the calculation.

References

1) N. Yamaguchi et al., PF Activity Report, 8, 268(1990).
3) N. Yamaguchi et al., to be published in Appl. Optics.
Angular momentum population of H(3\ell) produced through photodissociation of H₂

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Angular momentum population of H(3\ell) produced through the photodissociation of H₂ has been obtained by time-resolved measurements of Balmer-\alpha emission, where \ell is an orbital angular momentum quantum number. This method is based on the fact that natural lifetimes of H(3\ell) are different from each other and are 160 ns, 5.4 ns and 15.6 ns for 3s, 3p and 3d, respectively. The present experiment will be helpful to substantiate precursor superexcited states of H₂ and their dissociation mechanism. The precursor superexcited states to form H(3\ell) have not yet been fully understood. In this report, we describe measurements of the population of H(3\ell) using a pulse character of SR (synchrotron radiation) from PF Ring under a single bunch operation, where the pulse interval is 624 ns and the pulse width is 0.1 ns.

Time-resolved Balmer-\alpha emission intensity was measured through a delayed coincidence technique, where the time correlation was measured between a Balmer-\alpha photon pulse and a RF pick-up pulse. A pulsed SR was dispersed by a 1m Seya-Namioka monochromator. A gas cell was filled with H₂ gas of which pressure ranged from 1 to 50 mTorr. Balmer-\alpha emission was detected with a cooled photomultiplier.

Typical time-resolved intensities of Balmer-\alpha emission are shown in fig.1 for various H₂ gas pressures. Incident wavelength is 73.8 nm, which corresponds to the maximum peak in the excitation function of Balmer-\alpha emission measured in this experiment. Decay of Balmer-\alpha intensity becomes faster with extra-palating the H₂ gas pressure, as can be seen in fig.1. Decay curves are analyzed through fitting a sum of three exponential decay functions and a background. Obtained decay rates depend on the H₂ gas pressure linearly and converge to the inverse of the natural lifetimes of H(3\ell) with decreasing the H₂ gas pressure to zero. This experimental result indicates that H(3\ell) are subjected to collisional deexcitation and \ell-changing collision by H₂. The angular momentum population of H(3\ell) is obtained from the pre-exponential factor for each exponential decay function. A precise kinetic analysis of H(3\ell) makes it possible to obtain the population at zero gas pressure. The results are summarized in Table 1 for two incident wavelengths. The following conclusions are obtained:

(1) The angular momentum populations in Table 1 are much different from each other in spite of a small difference in the incident photon energies. (2) the populations are not very localized, which strongly indicates a wide range of photodissociative excitation processes of H₂ to produce H(3\ell). Further measurements are now in progress as well as more precise discussion of the present experimental results.

Reference

Table 1. Angular momentum populations of H(3\ell) produced from H₂.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>( \sigma(3s) )</th>
<th>( \sigma(3p) )</th>
<th>( \sigma(3d) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>73.8 nm</td>
<td>31%</td>
<td>24%</td>
<td>45%</td>
</tr>
<tr>
<td>74.5 nm</td>
<td>10%</td>
<td>53%</td>
<td>37%</td>
</tr>
</tbody>
</table>

Fig.1. Typical time-resolved intensities of Balmer-\alpha emission produced through the photodissociation of H₂.
OPTICAL THRESHOLD EXCITATION FUNCTIONS OF Xe 5s, 5p PHOTOIONIZATION SATELLITES NEAR THE S^-1 COOPER MINIMUM

M. Ukai, N. Terazawa, Y. Chikahiro, N. Kouchi, K. Kameta, Y. Hatano and K. Tanaka


Introduction

Photoionization of valence s-shell electrons of rare gas atoms manifests the electron correlation by the production of accompanying ionic excited states, namely, photoionization satellites. Because of a photoionization cross section of Xe 5s shell at around the double-ionization limit in its Cooper minimum region, intensity ratios of satellites to the principal s^-1 state in this region were remarkably large in comparison with those well above the threshold. It was proposed that the phenomenon was originated from an intensity-borrowing of oscillator strengths from the outer p-shell electron transition as a result of a strong initial s^-1 and p^-1 states correlation.

Detailed investigations of the Xe 5s^-1, 5p^-1 correlation satellites in their threshold region have been performed using fluorescence detection technique and photoelectron spectroscopy (PES). However, experimental limitations have restricted the investigations in a narrow energy region. Especially a detailed study of the Xe 5s^-1, 5p^-1 satellites near the 5s^-1 Cooper minimum region is greatly needed.

We present here the first measurement of fluorescence excitation spectra (FES) of undispersed VUV and UV emissions of Xe^+ satellites between the 5s^-1 threshold at 23.4 eV and 36.5 eV, in which the 5s^-1 Cooper minimum is located. The purpose of the present investigation is to clarify a general behavior of Xe correlation satellites near the 5s^-1 Cooper minimum.

Experimental

The experiment was performed using a monochromatized extreme-UV radiation from BL-12A. Undispersed VUV (105-180 nm) emissions involving Xe^+ 5s^-1-5p^-1 and optical lines from satellites were detected by a CaF coated microchannel plate behind a LiF window. UV-emissions (200-320 nm) were extracted to outside the vacuum and detected by a UV-sensitive photomultiplier. Signal intensities were not corrected for the optical responses. Special care was taken to eliminate secondary photoelectron impact emissions of neutral species, which showed quadratic pressure dependence. Data sampling was made by 0.6 meV step with 38 meV band pass and a 19 meV step with 96 meV band pass for VUV- and UV-FES, respectively.

Results and Discussion

Fig. 1 presents a FES of VUV emission in the 23.4-31 eV region. The FES shows a sharp onset at 23.4 eV corresponding to the Xe^+ 5s^-1 threshold. The origin of emission is the 5s^-1-5p^-1 resonance lines at the threshold. A variety of satellites are produced with the increase in the photon energy. A general appearance of the FES is in good agreement with the previous undispersed result in the 22.4-25.8 eV region. Energy positions of oscillating peaks well correspond to spectrographically determined absorption lines.

The UV spectrum in Fig. 2 shows a first onset at 28.25 eV, which corresponds to the threshold of ('D) 6p^-1F7/2 satellite. Some other step-like onsets are identified as shown in Fig. 2. The most pronounced increase is recorded at the ('P)7p^-1F5/2 satellite (28.38 eV). A maximum intensity is obtained at around the first double ionization limit of Xe^+(F7/2) at 33.3 eV. This can be understood as a strong initial-ionic-states correlation between 5s^-1 and 5p^-1 states. After the second ('P) and forth ('D) limits small post-threshold enhancements are recognized, which are explained by an inelastic scattering of outgoing electron in the final state to result in partitioned double ionization into shakedown satellites.

PARTIAL PHOTODISSOCIATION CROSS SECTIONS OF O₂ MOLECULES AS PROBED BY VACUUM ULTRAVIOLET FLUORESCENCE

M. Ukai, N. Kouchi, K. Kameta, N. Terazawa, Y. Chikahiro, Y. Hatano and K. Tanaka


Introduction

The neutral dissociation among decay processes of superexcited molecules deserve considerable importance, in which nuclear dynamic behavior is coupled with electronic relaxation. To which fragments and to which excited states the excitation energy will be provided are of special interest. We have studied the photodissociation of molecules in superexcited states by observing fluorescences from electronically excited neutral fragments. Because of an insufficiency of incident photon flux, however, a great difficulty in dispersing secondary fluorescences from individual dissociation fragments has restricted us to the detection of total fluorescences.

In this report we present an attempt to disperse secondary atomic fluorescence from neutral dissociation of O₂. A detailed measurement of an undispersed VUV fluorescence excitation spectrum was made previously. The purpose of the present investigation is to obtain information about partial photodissociation processes in the resonant enhanced formation of O₂ molecules. We have newly constructed a VUV monochromator and employed an integrated detection technique instead of a conventionally employed differential dispersion.

Experimental

The experiment was performed at BL-12A. A monochromatized radiation passes through a gas cell. The secondary fluorescences are dispersed using a holographic 1200 lines/mm grating with 30 cm radius of curvature. As an entrance point of the monochromator a real slit or a source point (interaction region) is selected by moving the image position. The 64° dispersion is employed to achieve a pseudo Seya-Namioka mount. At the image point, instead of an exit slit, placed is a CsI-coated microchannel plate (MCP) coupled with a resistive anode-type position sensitive detector.

Results

VUV fluorescence spectra at the 74, 71, and 69 nm incident photon wavelengths are shown in Fig. 1. At 74 nm only O(3s→S-P) atomic resonance line is observed. At 71 and 69 nm, new atomic lines of O(4s→S-P) and O(3s→D) respectively show up. Because of the geometrical aberration on the image point, a very good resolution of the VUV monochromator is not obtained. Fig. 2 presents excitation spectra (FES) of the total and O(3s→S-P) fluorescences. The inset in Fig. 2 shows the total FES for emission shorter than O(3s→S-P) region. The general features of the total and the O(3s→S-P) FESs are almost identical in the longer incident wavelength region than 74 nm, whereas in the shorter wavelength region than 69 nm, the fluorescence intensity of O(3s→S-P) is much smaller than the total FES. This observation is contrary to the result by Lee et al., that the most essential fluorescence in this region is from O(3s→S-P). This implies that new dissociation channels such as O(4s→S)+O(P) and O(3s→D)+O(P) have a considerable amount to the total dissociation processes.


Fig. 1 Fluorescence spectra at 69, 71, and 74 nm.

![Fluorescence spectra at 69, 71, and 74 nm.](image_url)
EXTREME ULTRAVIOLET PHOTODISSOCIATION OF FREE CO MOLECULE

M. Ukai, K. Kameta, N. Terazawa, Y. Chikahiro, N. Kouchi, Y. Hatano and K. Tanaka


Introduction

An important nature of molecular superexcited states exists in a competitive decay processes of the states into autoionization and neutral dissociation channels. By the measurements of photoionization quantum yields, the absolute probability of ionization on a single photoabsorption, we have shown the strong competition of the state in the extreme-UV region. We remark, however, even for simple molecules, the energy levels of superexcited states are not well known. Conventionally, they have been observed using photoabsorption and photoionization spectrum measurements. However, a good deal of direct ionization involved in these spectra makes the identification of the energy levels quite difficult, especially, well above the ionization threshold. By contrast, observation of fluorescences from neutral dissociation products determines these levels directly. We thus remark that this kind of observation can provide a new spectroscopic technique to clarify excitation processes to molecular superexcited states.

As a typical example, we present here a VUV-fluorescence excitation spectrum (FES) of neutral dissociation fragments of CO in the extreme UV photodissociation.

Experimental

Experimental details at BL-12A were described in the previous report. Briefly, a monochromatized synchrotron radiation from a Seya-Namioka monochromator was introduced into a gas cell filled with CO. VUV-fluorescence from the dissociation fragments was detected by a CsI coated microchannel plate (MCP) behind a LiF window. The detection range was defined to 105-180 nm. The pressure dependence of the VUV intensity was carefully examined. A quadratic dependence in shorter than 54 nm incident wavelength was due to secondary CO(A-X) emission caused by photoelectron impact excitation. In longer wavelength region than 54 nm, linear pressure dependence was obtained.

Results and Discussion

Fig. 1 presents the VUV-FES of CO in the 53-67 nm region obtained with a 0.04 nm incident photon band pass. We observe an onset at 67 nm where the C02*(B2Σu+) dissociation limit for the lowest VUV emitting fragment exists. Below the C02*(B2Σu+) ionization threshold, sharp Rydberg structures show up on a continuum cross section. The peak structures are prominent in comparison with those in the partial ionization cross section and in the previous VUV-FES. In the wavelength region shorter than 62 nm, rich resonance enhanced structures are obtained. These structures well correspond to highly vibrational progressions of 3σg, 3δt, 3δd, 4σd, and 4σt states. Several peaks in the present VUV-FES were not resolved in the previous spectrographical absorption spectrum with nearly one order of magnitude better resolution than in the present experiment. This implies that even with better photon resolution, information from a total absorption spectrum is restricted by a good deal of contribution from the direct ionization. These peaks are identified as those in the above vibrational progressions.

Laboratory absorption spectra of molecules at interstellar cloud temperatures: first measurements on CO at ~97 nm

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Fig. 1. Relative photoabsorption cross sections for the \( L(0) - X(0) \), \( L'(1) - X(0) \), and \( K(0) - X(0) \) bands of CO cooled to about 30 K with a supersonic jet expansion device.

In the 91 - 100 nm spectral region, where absorption of photons by interstellar CO usually leads to dissociation, laboratory spectra obtained at ~295 K show that most CO bands are both overlapped and perturbed. Reliable band oscillator strengths cannot be extracted from such spectra.

We used the supersonic free jet (SSFJ) expansion technique (Levy 1980), first applied to EUV molecular absorption spectroscopy by Huber & Jungen (1990), to produce molecules at very low temperature. Because rotational temperatures down to ~10 K can easily be achieved, the method has two advantages: (i) complex spectra are greatly simplified by the reduction in population of higher rotational levels, and (ii) absorption cross sections that are very similar to those under interstellar conditions can be measured.

Small quantities of CO were added through a needle valve to a flowing supply of He at about 1.0 atm that was then expanded through a 50-μm diameter stainless steel nozzle into a chamber maintained at low pressure. The jet nozzle was mounted approximately 2 mm above the optical axis of the synchrotron radiation and approximately 60 cm from the entrance slit of the 6V0PE on Beam Line 12-B. A differential pumping system isolated the SSFJ chamber from the beam line. Instrumental linewidth was approximately 5.5×10⁻⁴ nm (5.5 mA).

Our relative photoabsorption cross sections for the rotational lines of three bands between 96.8 and 97.1 nm are shown in Figure 1. The intensity distributions within single bands show that we have achieved a rotational temperature of about ~30 K. Because the measurement process effectively involves a convolution of the true spectrum with the instrument function, the peak cross sections for the sharp bands, \( \sigma(L(0) - X(0)) \) and \( \sigma(K(0) - X(0)) \), are lower limits.

Our absorption cross sections are very different in appearance from the synthetic spectrum shown in Fig. 1 of Edlenderg & Rostas (1990). A new synthetic spectrum of \(^{12}C\)CO at 50 K has been calculated by Edlenderg et al. (1991). It reproduces, reasonably well, the main features of our measured 30 K spectrum shown in Fig. 1.

Because the bands are unblended in our spectrum, we can make direct measurements of individual band f-values by determining the integrated cross section for each band. Preliminary analysis gives ratios of cross sections:

\[
\sigma(L(0) - X(0)) : \sigma(L'(1) - X(0)) : \sigma(K(0) - X(0)) = 1.0 : 0.7±0.3 : 2.9±0.5
\]

For the same bands, the integrated cross sections of Letzelter et al. (1987) are in the ratio 1.0 : 1.6 : 2.7, with uncertainties of ±10 percent.

A paper describing this work has been accepted for publication in Astronomy & Astrophysics. Absolute band oscillator strengths for all significant bands in the 91 - 100 nm region will be determined from our absorption spectra of CO at 30 K and published at a later date.

Acknowledgements. The authors thank W. H. Parkinson for his assistance with this project, which was supported by NASA grant NAGW-1296 to Harvard University. GS thanks JSPS for support; PLS, GS, KY, and MHS thank the staff of the Photon Factory for their hospitality.

References

High-Resolution, VUV (147-201 nm) Photoabsorption Cross Sections for C₂H₂ at 195 and 295 K

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Acetylene plays an important role in the photochemistry of the atmospheres of the giant planets because, in part, of its strong absorption features in the 145-200 nm region where there is significant solar flux (Clarke et al. 1982). The identifications of C₂H₂ in planetary VUV spectra required only qualitative knowledge of molecular band strengths. However, detailed models of molecular abundances and excitation conditions in the upper parts of planetary atmospheres require accurate high-resolution photoabsorption cross section data at the relevant temperatures, typically 150-200 K. We undertook this measurement program because of suggestions of some temperature dependence in the VUV photoabsorption cross section for acetylene.

Photoelectric cross sections measurements in the wavelength range 137-175 nm were made with the GEXOPE spectrometer on Beam Line 12-B. Additional measurements in the range 172-201 nm were made at the Harvard-Smithsonian Center for Astrophysics. Gaseous C₂H₂ (99.9%; Takachiho Seiki Company, Ltd.) at a pressure of ~0.4 atm was used for the measurements at the Photon Factory. Absorption cells of length 1.0 and 32 cm and pressures sufficient to give maximum optical depths of 0.5 - 1.5 were used. For the low temperature measurements, the cells were cooled with a dry-ice/methanol slurry (195±1 K).

Our results are shown in Figures 1 and 2. Our peak cross sections in the 144-153 nm range agree with those of Suto & Lee (1984). There are minor differences between our results at 295 K and those of Wu (1991), but larger differences, which are too large to be explained by the difference in the temperatures used (195 vs. 155 K), in the low temperature cross sections. The fact that the cross section ratio r(295 K)/r(195 K) is greater than 1.0 for our work suggests that some hot bands may be present in the region studied. However, we can provide little guidance for the modeling of the absorption cross sections of C₂H₂ at temperatures other than those at which we have made measurements and, therefore, we urge that photochemical models of planetary atmospheres employ cross sections measured at the temperatures of these atmospheres.

This work has been published in J. Geophys. Res. 96 17,529 (1991).

Acknowledgements. The authors thank W. H. Parkinson for his assistance with this project, which was supported by NASA grant NAGW-1400 to Harvard University. PLL gratefully acknowledges additional support from the Japanese Ministry of Education, Science, and Culture as well as the hospitality of the personal at the Photon Factory.

References

High-Resolution Photoabsorption Cross Sections of \(^{13}\text{CO}\) and \(^{12}\text{CO}\)

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2. Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, U.S.A.
3. Photon Factory, National Laboratory for High Energy Physics, Oho, Tsukuba, Ibaraki 305

Photodissociation following absorption of extreme ultraviolet photons is an important factor in determining the abundance and isotopic fractionation of CO in diffuse and translucent interstellar clouds (van Dishoeck & Black 1988). The principal channel for destruction of \(^{13}\text{CO}\) in such clouds begins with absorption in the \((1,0)\) vibrational band of the \(^{13}\Pi - \text{X}^{1}\Sigma^+\) system; similarity, absorption in the \((0,0)\) band begins a significant destruction channel for \(^{12}\text{CO}\). Reliable modeling of the CO fractionation process depends critically upon the accuracy of the photoabsorption cross sections. Therefore, we have measured cross sections for these bands and for the \((1,0)\) band of \(^{12}\text{CO}\).

All measurements were made with the 6V0PE (Beam Line 12-0) in photoelectric mode. A 1200 groove mm\(^{-1}\) grating, used in the fifth spectral order, provided a reciprocal dispersion of approximately 0.025 nm mm\(^{-1}\). With entrance and exit slits of 10 \(\mu\)m, the instrumental full width at half maximum linewidth was approximately 8.0 \times 10\(^{-4}\) nm (8 mA). The spectrometer tank, at a temperature of ~295 K, served as an absorption cell with a path length of 12.61 m.

The \(^{13}\text{CO}\) absorption measurements were made on carbon monoxide in natural abundance (\(^{13}\text{C}^{12}\text{O}\), 98.7%); all \(^{12}\text{CO}\) measurements were made on a sample of ~92% \(^{13}\text{C}^{12}\text{O}\) and ~8% \(^{12}\text{C}^{13}\text{O}\) obtained from MSD Isotopes. A flowing configuration was used. The tank pressure was monitored by an ionization gauge, which was calibrated using a volumetric expansion technique. Molecular flow conditions prevailed at the pressures of interest and the cross-sectional area of the pumping port was a negligible fraction of the total interior surface area of the spectrometer tank. Thus, there was no pressure differential in the absorbing path or between the absorbing path and the ionization gauge. Column densities were kept low - measured optical depths never exceeded 0.25 for \(P\) and \(R\) branches, and 0.50 for \(Q\) branches - in order to minimize systematic underestimations caused by under-resolution of individual rotational lineshapes (cf. Hudson 1971). Values ranged from 3.0 \times 10\(^3\) to 3.6 \times 10\(^3\) cm\(^{-2}\).

The \(P\), \(Q\), and \(R\) branches of each band were scanned separately, typically at five different column densities. Our integrated cross sections and band \(f\)-values, which have uncertainties of about 10%, are given in the Table. Values for the \(^{13}\Pi - \text{X}^{1}\Sigma^+\) bands of \(^{13}\text{CO}\) and \(^{12}\text{CO}\) differ by an amount less than the associated error bars. This is consistent with the expected isotopic behavior of an isolated, and only weakly perturbed, band.

### INTEGRATED CROSS SECTIONS AND BAND \(f\)-VALUES FOR \(E-X\) BANDS OF \(\text{CO}\)

<table>
<thead>
<tr>
<th>Band</th>
<th>Integration</th>
<th>(f_{\text{rad}})</th>
<th>(f_{\text{int}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{13}\text{CO})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((1,0))</td>
<td>107.490 - 0.688</td>
<td>5.0</td>
<td>4.9</td>
</tr>
<tr>
<td>((0,0))</td>
<td>105.075 - 249</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>((1,0))</td>
<td>105.122 - 304</td>
<td>0.29</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Our final integrated cross sections for the \(E - X\) bands are in good agreement with the calculated values of Kirby & Cooper (1989), but are systematically larger than recent experimental results. Our measurements were performed with a resolving power approximately 20 times larger than that of Fock, Gurtler, & Koch (1980), Letzelier et al. (1987), and Eidelsberg & Rostas (1990), and 40 times larger than that of Lee & Guest (1981). We believe these differences result from the moderate resolutions used in previous studies; with inadequate resolution, systematic underestimation of integrated cross sections is difficult to avoid (cf. Hudson 1971).

A paper that describes these results is in preparation for submission to the Astrophysical Journal.

Acknowledgments. The authors thank W. H. Parkinson for his assistance on this project, which was supported by NASA grant NAGW-1696 to Harvard University. GS thanks JSPS for support; GS, PLS, and KY thank the staff of the Photon Factory for their hospitality.

References

SOFT X-RAY INDUCED ION EMISSION FROM PMMA NEAR CARBON K EDGE

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\(^{1}\)Faculty of Engineering, Chiba University, Chiba 260
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Introduction

Photon energy dependence of the photochemical decomposition of polymers was in general investigated by measuring the mass spectra and intensities of neutral species ejected from the surface of sample film as a function of the incident photon energy. A principal drawback of this experiment is that the fragments produced inside the sample by the photochemical decomposition can diffuse to the surface followed by vaporization and the diffusion time depends largely on their structure. Therefore, in general, it is very difficult to obtain meaningful information on the photon energy dependence of the mass pattern of the neutral species from this experiment.

In the present investigation, we observed photon energy dependence of photoemitted ion yield of poly(methyl methacrylate) (PMMA) in SX region in order to study the effect of a core hole on the molecular decomposition.

Experiment and Results

The experiments were performed at the beam line 12C utilizing plane grating monochromator. Thin films (<100Å) of PMMA were spin-cast on gold-evaporated Si wafer. Total ion yield (TIY), total electron yield (TEY) and partial yield of electron (PEY) of kinetic energies greater than 200 eV were measured around carbon 1s edge. Further, time-of-flight (TOF) spectra of photoemitted ions were measured using pulsed synchrotron radiation during single-bunch operation of PF ring.

Figure 1 compares TIY, TEY, PEY and electron-energy-loss spectra (EELS) measured by Ritsko et al.\(^{2}\). The EELS corresponds with the absorption spectrum and shows three resonance transitions at 285 eV, 287.4 eV and 288.4 eV which were ascribed respectively to electron transitions to \(\pi^*\), \(\delta^*\) and some \(\delta^*\) states.\(^{2}\) TIY shows a clear peak at 289 eV corresponding to the mixed 1s – \(\delta^*\) excitations and a weak shoulder at 285 eV corresponding to 1s – \(\pi^*\) excitation, while TEY and PEY show only weak features corresponding to these resonances. The results indicate that the TIY peak is not ascribed to ions produced by the secondary excitations of PMMA by electrons such as secondary and Auger electrons and the ion emission at this energy occurs more effectively by the primary excitation of the polymer chain.

Figure 2 shows an example of ion TOF spectra at photon energy of 300 eV. In contrast to the mass spectroscopy of the neutral species, the time dependence of the TOF spectra which can be ascribed to the difference of diffusion time of ionic species in the PMMA film was not observed. The main ions emitted from PMMA were found to be H\(^+\) and CH\(_3\)\(^+\), although various ions were clearly observed. Measurements of the photon energy dependence of the TOF spectra are now in progress.

References

PHOTOCHEMICAL ETCHING OF Si BY SOFT X-RAY IRRADIATION

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Introduction

The photochemical reaction using synchrotron radiation (SR) draws our attention for potential use in the etching and chemical vapor deposition, because an application to microfabrication at low temperature, with low damage and high accuracy can be expected. In previous report we successfully proposed the simultaneous use of VUV radiation and microwave (2.45GHz) to increase the etching rate of Si which can not be etched only by SR irradiation in the SF6/Ar environment. In this work we investigated the correlation between the etching rate and the absorption coefficient of Si using monochromatic soft x-ray.

Experimental

Experiments were carried out at the beam line 12C equipped with planar grating monochromator. The SR beam is monochromatized in the range of 40-800eV. Details of experimental apparatus were described previously. SF6 and Ar were introduced into reaction chamber through the mass flow controller. The partial pressure of SF6 was 40mTorr and that of Ar was 500mTorr. The etching species were generated in the quartz tube by the microwave discharge and then were transported into reaction chamber. The output power of the microwave was 15W. The experiments were carried out at -25°C. A nickel mesh which has 8μm line and 24μm spacing was used as a photo mask.

Results and discussion

We compared the etching rate with the TEY. The TEY measurement were performed at +1x10^-8Torr and the etching were performed in the gas ambient. The etching rate at the photon energies 50, 85 and 130eV were estimated to be 2.8, 1.6 and 4.1nm/μA per 300μA min respectively, where the incident beam intensity was represented by photocurrent (nA) and the transmittances of incident beam 33. 46 and 63% at each energy through the SF6 and Ar gas before reaching Si surface were taken into account. The ratio 1.8:1.0:2.6 of the etching rates at 50, 85, 130eV are very close to the relative TEY values for the total discharge time 60min shown in Table 1. This result indicates that the etching rate has a correlation to the absorption coefficient of Si substrate.

References

1) S. Terakado et al., PF Activity Report #7 280 (1989).

Fig.1 The optical micrograph of Si surface etched at 130eV.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Photocurrent (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.0</td>
</tr>
<tr>
<td>85</td>
<td>1.8</td>
</tr>
<tr>
<td>130</td>
<td>1.6</td>
</tr>
<tr>
<td>170</td>
<td>1.5</td>
</tr>
<tr>
<td>200</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1 The relative TEY values normalized at 85eV.
Cu Film Deposition by SOR Light Irradiation


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1. Introduction

Cu film is now attracting attention as a new interconnection material to take place of Al because of its high resistivity to electromigration and higher conductivity compared with Al. The fundamental properties and reliability have been studied for this purpose using Cu film deposited by sputtering[1,2]. However, Cu film patterning involves many difficult problems such as heating of the wafer and the selection of an appropriate etching mask material and its removal process, because the vapor pressure of a Cu compound is so low that high temperature above 300°C is required for the reactive ion etching for Cu. On the contrary, one possible approach to Cu patterning is to deposit the Cu film selectively.

This paper reports the chemical vapor deposition of Cu films using a cyclopentadienyl-Cu-triethylphosphin adduct.

2. Experimental

The CVD experiment was carried out using the beam from BL-12C. The samples were Si substrates which n+ and p+ diffusion regions had been preliminarily formed. The samples were placed on a sample holder and heated at 400°C. The source material was a cyclopentadienyl-Cu-triethylphosphin adduct, of which structure is shown in Fig. 1. This Cu complex in a stainless steel vessel was heated at 150°C and its produced vapor was introduced into the deposition chamber and gave a pressure of 0.15 Torr. SOR light was introduced normally to the sample surface.

3. Results and Discussion

3.1 Analysis of deposited material

Figures 2(a) and (b) show the deposition profiles of non-irradiated and irradiated n+ Si regions, respectively. A spherical deposition was observed not only on n+ Si but also on SiO2. The deposition seemed to be not affected by SOR light irradiation. Figures 3(a) and (b) show the XPS spectra of this deposition and Cu film deposited by sputtering, respectively. Cu2p, Cu3p, and CuLMM Auger signals were clearly observed in the spectrum of this spherical deposition. In addition, any differences were not observed between the two XPS spectra. Accordingly, the spherical deposition can be concluded to be Cu.

3.2 Influence of SOR light irradiation

Figures 4 (a) and (b) show the deposition profiles of non-irradiated and irradiated p+ Si regions, respectively. Although any deposition was not observed on the non-irradiated region, a spherical deposition similar to that shown in Fig. 2 was observed on the irradiated region. It can be considered that electrons excited by SOR light gave some influence on decomposition of the Cu complex. Its detailed mechanism is now under investigation.

4. Summary

Cu CVD has been studied using a cyclopentadienyl-Cu-triethylphosphin adduct. Cu was deposited on n+ Si and SiO2 even when SOR light was not irradiated. On the other hand, Cu was deposited only on SOR irradiated p+ Si. It can be considered that electrons excited by SOR light participate in the CVD reaction.

5. References

Synchrotron radiation (SR)-assisted etching of SiO$_2$ using resist mask

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Recently, synchrotron radiation (SR)-assisted etching of semiconductor materials has actively been studied for its low temperature, low contamination, and high selectivity$^{1-2)}$. In this study, SR-assisted etching of SiO$_2$ has been conducted using a single-layer resist mask from a practical process viewpoint. Photo-stimulated desorption (PSD)-ions from the Si-oxide surface adsorbed by etching-gas were also measured to analyze this reaction.

An etching experiment was conducted using the multi-layer mirror line of BL-12C$^3)$. A quasimonochromatic light of 120 eV (AE/E=0.1) with $10^{15}$ photons s$^{-1}$ cm$^{-2}$ was irradiated to the specimens. This line is equipped with the differential pumping system, and the SF$_6$ etching gas at a pressure of 2.5 Pa was maintained during SR-irradiation. The specimens were thermally-oxidized Si (SiO$_2$) at a thickness of 0.3 μm. Novolac resist patterns (SAL-601, Shipley) at a thickness of 0.3 μm and a minimum pattern size of 0.3 μm were delineated on it by EB-writing. The specimen was cooled below -100°C with liq.N$_2$ during SR irradiation to enhance adsorption of the etching gas$^4)$. The PSD-ions from SF$_6$-adsorbed Si-oxide surface were measured using BL-8A$^5)$. BL-8A has a monochromator, and the 0th-order light of the monochromator was used for SR-irradiation. This light had a peak wavelength around 1 nm and supplied $10^{13}-10^{14}$ photons s$^{-1}$ cm$^{-2}$. The SF$_6$ gas was adsorbed on the native oxide of Si surface by cooling it at -150°C with liq.N$_2$. After the SF$_6$ gas was adsorbed, the chamber was evacuated, and SR irradiation was successively performed. Mass analysis of the PSD-ions was conducted using a quadrupole-mass spectrometer (QMS) operated in the pulse-counting mode. A hot filament of QMS was switched off to detect only the PSD-ions from the surface.

In Fig.1, SEM photographs of SiO$_2$ after etching are shown. An SiO$_2$ could be etched at a depth of 0.15 μm. Resist patterns were also etched at a depth of 0.15 μm toward the normal direction. However, it should be noted that the side-etching of SiO$_2$ under the resist was negligibly small. This can lead to ultra-fine etching in a feature size less than 0.1 μm.

The results of mass analysis of PSD-ions are shown in Fig.2. Strong peaks were observed around mass numbers 47, 51, 85, and 123, and these peaks were assigned as SiF$^+$, SF$^+$, SiF$_3^+$, and SiF$_6^+$, respectively. The SF$^+$ fragment was dominantly detected in the dissociated species of SF$_6$, and this is regarded as an effect of its inner-shell excitation reaction$^6)$. The SiF$^+$, SiF$_3^+$, and SiF$_6^+$, which clarify the photo-chemical reaction between the Si substrate and the SF$_6$ molecules, were also detected, while the yield of SiF$_2^+$ and SiF$^+$ was very little. Clarifying the etching-mechanism based on the above ion species is the subject of future study.

References
The Structure Determination of Copper on Quartz by Total Reflection Fluorescence Extended X-ray Absorption Fine Structure

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Introduction

It is important to elucidate for the surface structure of copper on silica catalyst which has high activity for oxidation of propene. EXAFS spectroscopy is a good technique for structure determination of catalyst. However, we can obtain the one-dimensionally average structure around copper atom because the catalyst is powder. We made copper oxide on quartz glass substrate and investigate the surface structure of copper on quartz substrate three-dimensionally by polarized total reflection fluorescence EXAFS spectroscopy.

Experimental

Copper oxide on a quartz glass was made as follows. Following to anneal the quartz (10×30×1 mm) at 473 for 2 hours, Cu(DPM)2 was deposited on the quartz for 5 hours by chemical vapor deposition system (vapor temperature: 373 K, deposition temperature: 473 K, flow rate: 20 ml/min, carrier gas: dry air). It is reported that Cu(DPM)2 reacts with silanol group stoichiometry and that ligand remained copper atom when Cu(DPM)2 reacted to Si-ORi-13. Then, the sample was annealed at 673 K in air. Polarized total reflection fluorescence EXAFS spectra were measured at BL-14A of Photon Factory. Four axis goniometer was used to adjust the sample position. The incident angle was monitored by ion chamber. The fluorescence was detected by scintillation counter. CuO was used as a model compound to extract amplitude and phase shift function for Cu-O.

Result and discussion

S and p polarization EXAFS spectra and Fourier transforms were shown in Fig. 1 and Fig. 2. Table 1 shows Curve-Fitting results of s and p polarized EXAFS. In both s and p polarization EXAFS Fourier Transform, there are one peak between 0.1 and 0.2 nm. It is ascribed to Cu-O bond. It is shown that copper oxide is monomer form on quartz.

STRUCTURE ANALYSES OF PbO-TiO₂-TeO₂ GLASSES BY EXAFS

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Introduction

In recent years, materials with high optical nonlinearity have been studied extensively for use in all-optical devices. The oxide glass is one of the candidates for these materials because of its transparency, chemical stability, formability and so on. In our previous work, it was found that TeO₂-based glasses have extremely high optical nonlinearity compared with SiO₂-based glasses. However, the origin of these high optical nonlinearity in relation to the glass structure have not been made clear yet. As a Te⁻¹⁻ ion is known to be present as both 3- and 4-fold coordinated states in glass structure, determination of its coordination number in TeO₂-based glasses is necessary to clarify the origin of high optical nonlinearity. In the present work, EXAFS studies of Te K-edge were performed in order to obtain information about the coordination state of Te⁻¹⁻ in PbO-TiO₂-TeO₂ glasses which have third order nonlinear optical susceptibility χ(3) of the order of 10⁻⁹ esu.

Experimental

The glasses used for experiments were obtained from reagent grade PbO, TiO₂ and TeO₂ by conventional melting method. Mixture of the starting materials were melted in the air with a Pt-Au crucible for 30 minutes at 900°C, poured on a steel plate and then annealed for 2 hours at 300 ~ 320°C. No crystal phases were observed by X-ray diffraction analysis in these samples. X-ray absorption measurements around Te K-edge were carried out in transmission mode at BL-14A of PF. The α-TeO₂ crystal was used as a reference.

![Diagram](image)

Fig. 1 Fourier transforms of EXAFS k² x(k)

Results

Figure 1 shows the Fourier transforms of Te K-edge EXAFS weighted by k² of α-TeO₂ and the 10PbO-10TiO₂-80TeO₂ glass. Phase shifts were not corrected. The Fourier transforms of other glasses were similar to that of the 10PbO-10TiO₂-80TeO₂ glass. Curve of the glass in Fig.1 has only one peak corresponding to Te-O distance at approximately 1.5 Å in contrast with that of α-TeO₂. This indicates that TeO₂-based glasses have a very random structure over the range of 2 Å. To obtain further information on the coordination state of Te⁻¹⁻ ions in the glasses, curve-fitting analysis was performed. Coordination number, average Te-O distance and Debye-Waller factor were used as fitting parameters. The results were shown in Table 1. It is seen that the coordination number of Te⁻¹⁻ with respect to oxygen decreases with increasing the content of PbO. This indicates that TeO polyhedra change from trigonal-bipyramidal TeO₃ to trigonal-pyramidal TeO₄ as the content of PbO is increased. Both of coordination structures are also found in crystal materials. It is known that each Te⁻¹⁻ ion has one lone electron-pair, and the decrease in coordination number causes the increase of flexibility of the lone electron-pair. Thus, the compositional dependence of optical nonlinearity of PbO-TiO₂-TeO₂ glasses is assumed to be related with the change in coordination state of Te⁻¹⁻ ions discussed above.

References


Table 1 Results of the curve fitting for k² x(k)

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<th>Glass Composition</th>
<th>N</th>
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STRUCTURE ANALYSIS OF FERREDOXIN FROM SULFOLOBUS ACIDOCALDARIUS


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Introduction

Ferredoxins 1) are iron-sulfur proteins which act as electron carriers in various biological metabolic systems. Recently, a new ferredoxin was isolated from an aerobic and thermoacidophilic archaeabacterium, Sulfolobus acidocaldarius 2). It has been suggested that the ferredoxin contain 9.6 molar iron and 5.5 molar sulfide per 1 molar protein 3). It is interesting to determine the three dimensional structure of ferredoxin from S. acidocaldarius for elucidating the architecture of this ferredoxin and the evolutionary position of archaeabacteria.

Experimental

The crystals available for X-ray experiments were produced by a batch method using (NH₄)₂SO₄ as a precipitant. Synchrotron X-ray experiments have been performed with a mirror-monochromator optics at the end of beam line 14A. The X-ray absorption spectra of ferredoxin crystals were recorded as the ratio of fluorescence intensity, I(f1)/I(0), to input beam intensity, I(0)/I(E), monitored by an ion chamber. Spectra were taken from 7000 eV to 7502 ev in steps of 2 eV. In the spectra, strong absorption had started near 7118 eV. It may due to the absorption effect of the Fe atom in ferredoxin. Based on the results of the analysis of absorption spectra and the estimations of anomalous diffraction contribution, we used four wave lengths; 1.740 Å, 1.743 Å, 1.500 Å, 1.800 Å. The diffraction data were collected by the oscillation method. Imaging plates were used as the detector. Imaging plate were processed with the BAS2000 system. The all of X-ray diffraction data with the four wave length were collected from a single crystal.

Results

The space group and unit cell dimensions were determined; it is belongs to tetragonal space group P4₁2₁₂ or P4₃2₁₂ with cell dimensions of a=b=49.8Å, c=69.5Å. Assuming that an asymmetric unit contains one molecule of ferredoxin with molecular weight of 12,000, the Vm value is calculated to be 1.88 Å³/dalton 4).

Figure 1 is a X-ray diffraction patterns from the crystal of ferredoxin. It shows that the diffraction pattern extends to at least 2.0 Å resolution, thus permitting a high-resolution structure determination. Further studies now undergo.

References

3) Minami, Y. et al J. Biochem. 97, 745-753 (1985)

Figure 1. The X-ray diffraction patterns from the crystal of ferredoxin. ϕ = 19.9°-22.1°, Δϕ = 2.2°, λ=1.743 Å. Cut off background O.D. level = 700. The rotation axis was c* axis.
PERFORMANCE OF AN AVALANCHE PHOTODIODE X-RAY DETECTOR

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Introduction

An avalanche photodiode (APD) detector has been developed for X-ray timing measurements with a subnanosecond time resolution. A silicon APD used in the present detector was commercially available device of Hamamatsu S2384. The rise time of the APD’s outputs decreases with decreasing a diode capacitance. Therefore, the time resolution can be expected to be better with decreasing the capacitance, that is, the diameter of the device which has the same structure. Then, we measured time spectra at single-bunch runs with some APD devices, which were the same type but have different sizes in diameter. The intrinsic efficiency and the counting-rate capability were also measured to study the performance in various applications.

Experimental

The timing performance of the APD detector has been tested at BL-14A during single-bunch runs. We used the APD devices of S2383 (1mm in diam., 7pF), S2384(3mm in diam., 40pF) and S2385(5mm in diam., 95pF). The monochromatic X-ray beams of 14.4 keV were defined by slits to 0.2X0.2 mm and were incident on the detector. The electronic system for timing measurements was a normal system using a time-to-amplitude converter (TAC) and a multi-channel analyzer (MCA), which was the same as described in the previous report. The efficiency and the counting-rate capability have been measured with the detector mounted an APD device of S2384. The experiment was performed in multi-bunch runs to use the incident beam as intense as possible and to reduce a pileup effect caused by photons emitted from the same bunch. The X-ray beams of 8.0 and 14.4 keV were selected. The operating condition of the APD was the same as in measuring time spectra. However, the electronic system was changed to be suitable for the counting measurements.

Results and Discussion

The measured spectrum with S2383 is shown in Fig. 1. The best time resolution of 0.23ns (FWHM) was obtained from the width of the main peak. When the Gaussian distribution was assumed to each shape of the observed peak and the bunch profile, the resolution of the detector system was determined as 0.15 ns (FWHM) since the beam width of the main bucket was known as 0.17ns (FWHM). With S2384 or S2385, 0.23ns and 0.43ns were obtained as the resolution of the detector system in each measurement.

The intrinsic efficiencies depending only on the detector properties were obtained from the ratios of the number of the APD’s outputs to that of the scintillation counter’s outputs attenuated by a filter, which was divided by the transmission rate of the filter. As the results, (56±1)% at 8.0 keV and (7.5±0.1)% at 14.4 keV were obtained.

The variations of the observed rates with the APD detector as a function of the true rates at 8.0 and 14.4-keV X-rays were investigated in multi-bunch runs. In both cases, the maximum observed rate of 3.8X10^7cps was achieved. Since the maximum observed rate was found, the behavior of the outputs can be regarded as the paralyzable type. According to the paralyzable model, the dead time of the detector system can be obtained as 9.7X10^{-9}ns from the maximum observed rate of 3.8X10^7cps.

References

Analysis of microstructure of metal ultrafine particles from EXAFS measurements

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The structures of nano-phase ultrafine silver particles were investigated by EXAFS. The ultrafine particles from granular silver (99.999%) were generated with the aerosol process in Helium gas (99.995%) and isolated in organic solvent (Hexane) by means of the heterogeneous nucleation and cold-trap. The colloidal ultrafine particles were concentrated by gelling up to \(10^{13}\) particles/cm\(^3\) or more. To prevent mutual fusion of the particles in the gelling process, the surface of each particle was coated with a surfactant at the point of collection in the organic solvent. The condition of particles in the gel, which was observed with an electron microscopy and examined by a photon correlation spectroscopy for the gel resolved in organic solvent, presented satisfactory isolation of each particle by a surfactant film as shown in Fig. 1. From a technological point of view, this method for particle isolation has various merits as:

1) It can be manipulated even in a room temperature and be handled easier comparing with the method of isolation in Ar matrix,

2) The concentration of particles is easily enhanced by the gelling process and the isolation by surfactant film is superior to that by the usual support system with bulk substrate, and

3) In-situ particle sizing can be performed by a photon correlation spectroscopy for the colloidal particles of nano-meter range in organic solvent.

The measurements of EXAFS both by the transmission and by the fluorescence were performed at the beam line BL-14A of KEK. Several sizes ultrafine silver particles of fairly narrow size distribution, of which diameters ranged from 2 to 56 nm, set in the beam line for the EXAFS measurement with the forms of colloidal particles or the glass-supported gel. The EXAFS from a 10 \(\mu\)m thick silver foil (99.98%) was used as a standard reference.

Figure 2 shows examples of K-edge fluorescence EXAFS of the silver particles of 7 nm in diameter and the silver foil at 295 K. The EXAFS from ultrafine particles shows a good signal-to-noise (S/N) ratio comparing to that of the foil, and atomic distances of silver estimated from the EXAFS function were about 0.29 nm for both cases. Further experiments relating to the size dependence of the structure and the analysis of these EXAFS are in progress.

The two results, a good S/N ratio and the reasonable atomic distance, on the EXAFS of the ultrafine particles prove the availability of the method of particle manipulation by the gelling process with surfactant.

X-RAY ANOMALOUS TRANSMISSION MEASUREMENTS IN SIX-BEAM LAUE DIFFRACTION

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Introduction. An anomalous transmission of X-rays through thick absorbing crystals is one of the fundamental phenomena in dynamical diffraction. Significant enhancement of anomalous transmission in six-beam Laue diffraction (220,242,044,224,202) in comparison with two-beam case is predicted by theory. This effect so far has been studied experimentally by topography only. However, in topographic studies anomalous transmission effect is strongly masked by optical effects which make any quantitative measurements impossible. We have proposed and tested X-ray optics arrangement which allows to perform quantitative experiments. This report presents first experimental results of direct measurements of angular intensity distribution of anomalously transmitted beam in six-beam diffraction case.

Experimental. The main experimental problem is the appropriate preprocessing of the incident beam satisfying condition of monochromatic plane wave as completely as possible. So, good angular collimation in both vertical and horizontal planes as well as a non-dispersive multicrystal arrangement are required.

Experiments were carried out at beamline 14B (vertical wiggler). The experimental setup is shown in Fig.1 X-ray beam after double-crystal Si(111) upstream monochromator was reflected to following collimator and sample crystals. Calculations show that the transmitted beam in the six-beam case demonstrates good two-dimensional angular collimation which increases with the increase of $\mu t$. Therefore, we used X-ray beam transmitted through a thick Si crystal, set in six-beam diffraction condition, as an incident one. The second six-beam diffracting crystal as a sample was mounted on a diffractometer which provides an opportunity of fine $\theta$ and $\phi$ rotations ($\theta$-axis is vertical and $\phi$-axis is perpendicular to (044) diffraction planes).

Results. Two-dimensional ($\theta, \phi$) angular distributions of transmitted beam intensity were measured at wavelengths 0.93Å and 1.15Å with resulting $\mu t/\gamma_p$ values for the sample being 12, 24 and 40. One of them ($\mu t/\gamma_p=12$) is shown in Fig.2. The 220 and 202 diffraction peaks approach each other as we approach multibeam region until only one peak is observed at exact six-beam condition. Experimental curves agree very well with theoretical ones giving enhancement of X-ray transmission of about 3.3 times for this $\mu t$-value. Further studies of much thicker crystals by proposed technique can provide a new sensitive method to test perfection of large crystal volumes. Moreover, new X-ray optical elements to obtain monochromatic beams with excellent needle-shaped two-dimensional collimation can be constructed.

References.
X-RAY STANDING WAVES UNDER CONDITION OF MULTIPLE 111/220 DIFFRACTION: PHOTOELECTRON YIELD MEASUREMENTS.

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Introduction. In X-ray standing wave analysis often more than one reflection should be studied for a thorough examination of the sample. It is expected that structural characterization simultaneously in different crystallographic directions could be obtained if XSW curves are measured when Bragg conditions are satisfied for several sets of diffraction planes1-4. The main experimental problem which must be solved is the proper preprocessing of the incident beam satisfying all necessary conditions of dynamical diffraction for all reflections. This report presents results of multiple diffraction XSW measurement of photoelectron yield with using two possible multicrystal X-ray optics.

Experimental. Double-crystal Si(111) upstream monochromator was used for monochromation ($\lambda=1.54\AA$) and collimation of the X-ray beam in the vertical plane at beamline 15C (Fig.1). A channel-cut Si(220) crystal was used for the collimation in the horizontal plane. For the arrangement to be a nondispersive one for the (220) reflection the channel-cut crystal was rotated about direction of the incident beam so that its diffraction planes were parallel to the (220) diffraction planes of the sample. The second multicrystal arrangement which was used at beamline 14B is based on the phenomenon of anomalous X-ray transmission in six-beam multiple Laue diffraction. An X-ray beam transmitted through a thick ($\mu\tau=40$ at $\lambda=1.15\AA$) Si crystal was used as the incident beam providing two-dimensional angular collimation and additional monochromation5. Integrated over energy photoelectron yield was measured by a gas flow proportional counter.

Results. A set of photoelectron yield and reflectivity angular curves were measured for different azimuthal angles $\varphi$ through the region of multiple diffraction scattering. Some of them are shown in Fig.2 (solid lines is calculated by dynamical theory6).

Two-dimensional ($\theta, \varphi$) photoelectron yield angular dependences can be used for the study of the structure of the standing-wave field excited during multiple diffraction of X-rays. Besides a non-dispersive multiple diffraction arrangement allows the measurement of standing-wave curves outside the range of strong-beam interaction for two reflections during one angular scan making possible to use simpler two-beam dynamical theory for fitting. Such kind of measurements can be used for time-dependent structural characterization of thin surface layers simultaneously in two directions.

References.
4) M.V.Kovalchuk et al., JAP (in press).
5) A.Yu.Kazimirov et al., (these Act.Rep.)
PHASE SENSITIVE MEASUREMENTS IN 111/220 MULTIPLE X-RAY DIFFRACTION

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Introduction. X-ray multiple diffraction (MD) is known as an effective tool to solve the phase problem in X-ray crystallography. If one of the diffracted beams is weak (i.e. on the 'tail' of rocking curve) it can be considered by analogy to optical holography as a reference one and its intensity is determined by phase ratio between amplitudes of incident beam and other diffracted one. Similar effects can be used to study thin surface layer structure of nearly perfect crystals. Proposed recently new method is based on the analysis of 'tail' intensity of g-reflection in angular range of strong diffraction condition for h-reflection in the case of three-beam MD. The thickness of studied layer (i.e. the thickness of weak g-wave formation) as it follows from the scattering theory is small (≤ 0.1 μm) and determined by deviation from exact Bragg angle. The purpose of our experiment was to prove the phase sensitivity of this new method. We present first results obtained on perfect Si crystal.

Experimental. The experiment was carried out at beamline 14B. To obtain two-dimensional angular collimation an X-ray beam transmitted through a thick (μ≈40 at λ=1.58A) six-beam Laue diffracting Si crystal was used as an incident beam. Perfect (111)-oriented Si crystal as a sample was set in 111/220 diffraction condition. Angular distributions of intensities on the tails of rocking curves were measured by precise θ-rotation around vertical axes at different azimuthal (φ) angles.

Results. One set of experimental curves corresponding φ-115 arc sec is shown in Fig.1 Position of φ-scan on (θ,φ) diagram is shown by dashed line in Fig.2. Vertical strip in it represents the range of total reflection for 111 (h) reflection and inclined one - for 220 (g) reflection. The phase sensitivity of measured curves is clearly seen in Fig.1. The right curve in it is determined by the phase of E_h/E_o ratio and the left curve - by the phase of E_g/E_o (solid lines - calculations by dynamical theory of MD). For crystal with modified surface layer structure additional phase shifts due to displacements of surface atoms in h and g directions from their positions in ideal crystal will change the shapes of these curves. Measurement of such curves at different azimuthal angles φ allows to change the thickness of studied layer providing depth selectivity of new method.

Fig.1. Intensity distributions on the tails of rocking curves (upper curves, right scale) and in the ranges of total reflections.

Fig.2. Position of (111) and (220) total reflection ranges on (θ,φ) angular diagram.

References.
2) A.Yu.Kazimirov et al., (these Act.Rep.)
Diffraction of evanescent X-rays has been a matter of some interest since last years. We have given experimental evidences for the dynamical coupling of evanescent X-rays in a perfect crystal under total external reflection conditions. Rocking curves observed from a passivated germanium surface showed characteristic profiles in agreement with the theoretical calculations for the reflected and the reflected-diffracted beams [1]. The GeK emission profiles from the same sample provided information on the X-ray standing waves in a very shallow surface layer [2].

Our previous calculation [3] indicates that for the grazing-angle diffraction conditions the extinction distance is only a few hundreds Å which is of the same order of magnitude as the penetration depth. This means that dynamical standing waves can be produced from epitaxial crystals as thin as 100Å in grazing-angle Bragg reflection.

Experiments carried out to put this prediction in evidence used a Ca₃Sr₀.₆Fe₂/GaAs(111)B heteroepitaxial sample and recorded SrK emission signal from the epilayers as a function of the deviation angle Δθ = θ - θb at fixed grazing-incidence angles φ₀ close to the off-Bragg critical angle of total external reflection for Ca₃Sr₀.₆Fe₂ (= 2.1 mrad). The thickness of the epitaxial film was 99.9 Å and the (220) planes were excited by 17.5 keV X-rays at the BL-14B work station. In Fig. 1 observed SrK signal is compared with the calculations assuming Ca₃Sr₀.₆Fe₂ epilayers with an ideal crystalline perfection. The experiment reproduces the general features of the calculated curves but obvious discrepancies are seen, suggesting a deformation introduced in the epitaxial crystal during the sample preparation at high temperatures [4].

Meanwhile we received an X-ray scattering chamber designed for grazing-angle standing-wave experiments under ultra-high vacuum condition. The chamber is equipped with χ circles compatible with the high-precision rotary tables at the BL-14B station. It will receive samples from a UHV vessel transporting samples from the molecular-beam epitaxy facility at TIT. A first test using a synchrotron beam is planned at December 1991. It is expected that the instruments will allow us to challenge before Summer 1992 the direct determination of the registry of chemisorbed monolayer arsenic atoms on clean silicon surface.

Structural study of Fe-Tb amorphous thin films by X-ray anomalous scattering

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Introduction

Rare-earth transition metal amorphous thin films as magneto-optic recording media have been studied extensively and a few of them come to be in commercial use now. However, the correlation between magnetic properties and atomic structure still remain unexplained and the reliable structural characterization is considered to be one of the essential element in order to improve their characteristics.

In this work, the X-ray anomalous scattering in Fe_{76}Tb_{24} amorphous film was measured using S.R. and the environmental pair distribution function (PDF) of Tb atom was obtained for the first time.

Experimental

Amorphous Fe_{76}Tb_{24} thin films with a thickness of 1μm were RF sputter-deposited onto 7.5μm polyimide film and were coated with 200Å-thick Si_{3}N_{x} to prevent oxidation. X-ray anomalous scattering was carried out by transmission method at BL14C beam line. In order to determine the environmental structure factor of Tb, the scattering intensities of the sample were measured at incident beam energies of 51.8513KeV(E_{1}) and 51.0013 KeV(E_{2}), which are 150 eV and 1000 eV below the K absorption edge of Tb atom, respectively.

Results and Discussion

Figure 1 shows the normalized scattering intensities from the sample at two incident energy of E_{1} and E_{2}. The environmental PDF of Tb atom was calculated by the Fourier transformation of the environmental structure factor, which is evaluated from strong variation of the anomalous scattering term in the vicinity of the K absorption edge. The obtained total and environmental PDF are shown in figure 2. The two first peaks correspond to the distance of Tb-Fe and Tb-Tb pairs, respectively. And the preliminary analysis shows that the local structure of amorphous Fe_{76}Tb_{24} film is similar to that of Fe_{23}Tb_{5} intermetallic compound. Now detailed analysis is under investigation with the structural model of relaxed dense random packing of the amorphous alloy.

References

3) E. Matsubara, Y. Waseda, and S. Takayama, Mat. Trans., JIM, 31, 739 (1990)
SECTION AND TRAVERSE TOPOGRAPHY WITH HIGH-ORDER REFLECTION
AND THEIR APPLICATION TO DEFECTS IN SILICON CRYSTALS

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Introduction

We have been studying defect structures in high quality FZ and CZ silicon crystals using section or traverse topography with high-order reflection. In a previous activity report (1), we reported the observation of a very large strain field at the center of a 100 mm FZ silicon wafer, which is believed to be caused by a group of composite type dislocations running parallel to the growth direction of the crystal boule. In this report, we describe the results of the analysis by the computer simulation method based on the kinematical diffraction theory.

Experimental

The experimental arrangement and procedures for x-ray topography used in this study were described in the previous report (1). Topographs were taken with 0.4 Å x-ray beam and with the 8 8 0 and 14 14 0 reflections.

Results

Fig. 1 is a 14 14 0 traverse topograph showing a strain field caused by a group of "composite type" dislocations normal to the wafer surface. Fig. 2 is a 14 14 0 limited traverse topograph obtained by eliminating with slits the margin effect which takes place at both edges of the diffracted beam. We performed computer simulation of the defect images using the equation representing the effective misorientation of the lattice planes around the defect,

\[ d'/(d\theta) = -(Ksin2\theta)^{-1}d(u,v)/as\]

In this calculation, \( u \), displacement around the defect, is approximated by the displacement caused by a dislocation dipole, as illustrated in Fig. 3, with the Burgers vectors of \( b_1 = 120\times1/2 (110) \) and \( b_2 = 120\times1/2 (1\overline{1}0) \). Fig. 4 shows the calculated shape of the contrast and we may see that this result is in good agreement with the contrast represented in Fig. 1. Further work is in progress on the computer simulation of the defect and will be reported at a later date.

References


Fig. 1. 14 14 0 topograph.

Fig. 2. 14 14 0 limited traverse topograph.

Fig. 3. Defect model used for computer simulation.

Fig. 4. Calculated shape for the same reflection as in Fig. 2.
CINE K-EDGE SUBTRACTION CORONARY ANGIOGRAPHY USING AN IODINE FILTER  
METHOD:SECOND REPORT

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Introduction
Rubenstein et. al. first reported an iodine K-edge energy subtraction coronary angiographic system using synchrotron radiation in 1981[1]. Some human studies have been performed by line scan methods in USA[2,3]. In Japan, two-dimensional image acquisition techniques have been used to study the coronary arteries of rats, rabbits and dogs[4-8]. In this paper, we describe our recent results using a new angiographic system in which an iodine filter is used for energy exchange[9].

Method and materials
A new type of cine K-edge subtraction angiographic system has been constructed at the Wiggler beam line of BL14C of the Photon Factory in Tsukuba. This system consists of an iodine filter for energy exchange, a movable silicon(311) monocrystal, an image intensifier(ll)-TV, and a digital memory system(144 MB). X-ray TV images are digitalized in a 1024x1024 pixel matrix with a 12-bit depth using a 12-bit AD converter. This system has been markedly improved by application of the results of experiments conducted in the Spring of 1990(mechanical vibration and scatter radiation was reduced, and improvement of monochromator crystal).

The energy of the beam is precisely adjusted to be both higher and lower than that of the K-edge energy. Furthermore, to increase the S/N ratio of the image, the component of higher energy contains 75% of the entire energy band width(80 eV). When the iodine filter is not inserted in the SR beam path, a mixed-energy X-ray image is taken. When the filter is inserted, the high energy component of the X-ray is blocked, and only the lower-energy X-ray image is obtained.

Dogs(average weight, 10 Kg) were anesthetized with phenobarbital(0.5 mg/kg), and a 5F catheter(0.8 mm in diameter) was inserted into the inferior vena cava via the right femoral vein. Contrast material(Conraxin H 80%, 0.75 mg/kg) was injected via the injector at the rate of 0.75mg/sec. Angiography was performed in lateral projection and RAO 80 degrees.

Results
As the beam size in this system is small(40X70 mm), all structures of the left ventricle and coronary arteries were not imaged simultaneously. Nevertheless, the proximal right coronary artery, left main trunk, and left anterior descending coronary arteries as well as their arterial branches were imaged(Fig.1). However, the image quality is not sufficient for clinical use, because of insufficient X-ray flux(1x10^9 photons/mm^2/sec, Wiggler 5T, 2.5 GeV 280 mA). We are now in the process of remodeling the vertical wiggler as a 5-pole type wiggler, and hope to obtain clear images of the coronary artery in the next series of experiments planned for 1992.

Reference

Fig.1 Image of coronary arteries
STRUCTURAL PHASE TRANSITIONS IN THE THREE-DIMENSIONAL HALOGEN-BRIDGED MIXED-VALENCE COMPOUND Rb₂Au₂I₆ UNDER HIGH PRESSURES

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M₂Au²⁺AuIII⁺X₀ (M=K, Rb, Cs; X=Cl, Br, I) are known as the three-dimensional halogen bridged Au mixed-valence compounds. Recently, we have found that Rb₂Au₂I₆ undergoes a semiconductor-to-metal transition at 7.0GPa and 150°C, and the resistivity as a function of pressure at r.t. has a minimum and a maximum at 2.8GPa and 4.6GPa respectively. From an interest in the behavior of the resistivity of Rb₂Au₂I₆ under high pressures, we have investigated its crystal structure under high pressures. From an interest in the behavior of the resistivity of Rb₂Au₂I₆ under high pressures, we have investigated its crystal structure under high pressures.

Experimental

The crystal structure of Rb₂Au₂I₆ was investigated by energy-dispersive X-ray diffraction method using high-temperature and high-pressure apparatuses, called MAX80 and MAX90, with synchrotron radiation. The pressure vessel is a cubic anvil type which compresses a boron-epoxy cube with a teflon capsule. As the pressure medium in the teflon capsule, Fluorinert or kerosene was used.

Results and Discussion

The crystal structures of Rb₂Au₂X₆(X=Br,I) are a distorted perovskite structure (I2/m), where the AuX₆ octahedra tilt and the Au-X chains run zigzag. Figures 1 and 2 show the pressure dependence of the lattice constants of Rb₂Au₂I₆ at r.t. When the pressure is applied, a monoclinic-to-tetragonal structural phase transition takes place at about 1.0GPa. Figure 3 shows the axial ratio 2a/c, which indicates the distortion from the cubic lattice. It remains between 0.94 and 0.95 within the pressure range between 1.0GPa and 5.5GPa, and above 5GPa it increases. The contracting rates of the lattice constants a and c also changed slightly around 5GPa. At 9.6GPa, the axial ratio 2a/c suddenly decreases. The lattice constants a and c changes remarkably at the same pressure. From these results, it is considered that Rb₂Au₂I₆ undergoes two kinds of tetragonal-to-tetragonal transitions at 5GPa and 9.6GPa, respectively. The transition at 9.6GPa in Rb₂Au₂I₆ resembles closely the tetragonal-to-tetragonal transition at 5.5GPa in Cs₂Au₂I₆. In Cs₂Au₂I₆, this transition is considered to be a Jahn-Teller transition caused by the realization of the AuII valence state. So that the same origin is supposed for Rb₂Au₂I₆.

At 6.5GPa and 440K, the diffraction pattern of Rb₂Au₂I₆ changed remarkably to simple one which showed a cubic structure of a=6.320Å. This structural phase transition would be equivalent to the semiconductor-to-metal transition. This new phase was stable at 6.5GPa and r.t. in the cooling process, but it was unstable at ambient pressure and returned back to the monoclinic phase. This cubic pattern, however, can not be explained as the cubic perovskite structure, differing from Cs₂Au₂I₆.

References

A structural study of Al-Pd-Mn quasicrystals by a X-ray anomalous scattering method

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A newly discovered quasicrystalline alloy of Al-Pd-Mn is subject to a group of F-type quasicrystals, whose diffraction patterns can be indexed on the basis of quasilattice model generated by projection from 6D FCC lattice to 3D space. Atomic arrangements of F-type quasicrystalline alloys are not known at all although for P-type alloys there are good structure models which consist of Mackay's icosahedral clusters located along the 3D quasi-lattice projected from a 6D simple cubic lattice. It is not easy work to determine a structure of quasicrystal because any crystallographic method on the basis of the periodicity of crystals cannot be applied to the quasi-periodic system. In this study we evaluated a differential structure factor and a pair distribution function (PDF) of the environmental structure of Pd atoms in an Al73Pd18Mn9 alloy by using a X-ray anomalous scattering method (XAS).

Two reflection intensity spectra of the powder sample were measured at BL14C at the energies of an incident beam of 23.948 keV and 24.298 keV, which were 50 eV and 400 eV lower than the K absorption edge of Pd atom, respectively.

Figure 1 shows the diffraction profile for the lower energy and the differential intensity between the lower and the higher energy. As indicated with arrows in the figure, the intensity difference of super lattice peaks which was identified with six odd indices were higher than the other peaks with all even indices. This suggests that modulation of the Pd atom sites were one of origins of the super structure.

The whole PDF is similar to the PDF of a Al-Mn-Si alloys, which are typical P-type alloy. In other word, the local structure of this alloy is similar to that of P-type alloys. The Pd environmental PDF is not similar to the total PDF.

From those results we constructed a new F-type model which consist of two types of the Mackay's icosahedral clusters. The first type clusters were arranged on the twelve fold vertices with even parity, which meant that the sum of indices of the vertex points was even, and the second were on the odd parity vertices. Mackay's cluster having three different symmetrical sites, it is necessary to reproduce the large intensity of the super lattice peaks that an element of atom at each site of the first type cluster is different from that of the second.

Figure 1

Figure 2
1 Introduction

A tungsten single crystal with high crystal perfection can be a promising X-ray monochromator. Recently, tungsten single crystals of large dimensions have been grown by the secondary recrystallization (SRC) method [1]. The crystal perfection of the SRC-grown tungsten single crystals was studied by the X-ray topography and the rocking curve measurements with CuKα radiation [2] and with synchrotron radiation of short wave length [3]. The mosaic spread of the SRC-grown tungsten single crystals was about 40 – 80 arcsec. Although these values were not so large, further improvement on the crystal perfection was desired so as to apply a SRC-grown tungsten single crystal to a monochromator for the synchrotron radiation of the next generation. The present report shows the effects of the doping level of CaO impurity in the raw materials on the crystal perfection of the SRC-grown tungsten single crystal.

2 Experimental

Five specimens were grown by the SRC-method from hot-rolled tungsten plates with different doping level of CaO. X-ray experiments were performed at BL-14C with the similar arrangement as described in a previous report [3].

3 Results and Discussion

The rocking curve of the SRC-grown tungsten crystals was measured by the Si(422)–W(220) nearly parallel (+,−) setting in Bragg case with Cu Kα radiation. The width and peak reflectivity of the rocking curves is shown in Table 1 with the Ca concentration. The specimen E did not show anomalous grain growth. The width of the rocking curve of W 110 reflection, which was measured in Laue case with 60 keV synchrotron radiation, was larger than that shown in Table 1. This difference is probably due to the difference of the penetration depth of both X-rays of different energy, and also due to the depth dependence of the crystal perfection. A study is in progress to improve a crystal perfection of the tungsten crystals by optimizing the growth conditions such as doping level, hot-rolling process and annealing conditions.

Table 1: Width and peak reflectivity of the rocking curve of W 220 reflection and concentration of Ca impurity.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>FWHM (arcsec)</th>
<th>reflectivity (%)</th>
<th>doping level (wt. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>190</td>
<td>18</td>
<td>12.7</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>16</td>
<td>18.9</td>
</tr>
<tr>
<td>C</td>
<td>95</td>
<td>35</td>
<td>43.1</td>
</tr>
<tr>
<td>D</td>
<td>89</td>
<td>20</td>
<td>76.2</td>
</tr>
<tr>
<td>E</td>
<td>−</td>
<td>−</td>
<td>198.3</td>
</tr>
</tbody>
</table>

References

A PRELIMINARY TEST OF THE LAUE METHOD FOR A TIME-RESOLVED STRUCTURAL STUDY OF o-AMINO ACID : PYRUVATE AMINOTRANSFERASE

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Introduction

White synchrotron X-rays can be used to obtain the integrated intensity from a single crystal in Laue geometry. In spite of many inherent limitations, for example, the harmonic problem, wavelength-dependent factors, low signal to background ratio, the use of the synchrotron Laue diffraction technique is believed to have great advantages in time-resolved structural studies on macromolecules on a time scale of milliseconds or less (for a review see, for example, Clifton, 1991). This paper presents results of millisecond Laue experiments using a time-resolved Laue camera which had been already reported2).

Experimental

The broadband Laue experiment was performed at the vertical wiggler beamline 14C with a crystal of o-amino acid : pyruvate aminotransferase3) (o-APT) co-crystalized with its inhibitor DL-α-F-β-alanine. The crystal had cell dimensions of a=124.7, b=137.9, c=61.5Å, and space group I222. No focussing optics or high pass filters, except for beamline beryllium windows (total thickness of 900μm), were used for the experiment. The size of the o-APT crystal was about 0.7 x 0.8 x 2.0mm. The size of the detector Imaging Plate (IP) was 200 x 400 mm, and the distance from the crystal to the IP was 363mm. The crystal was aligned with the c axis along the spindle and the a axis parallel to the X-rays at φ=0°. In order to collect a complete unique data set, ten exposures of 100msec were recorded at φ = 0, 10, 20, 30, 40, 50, 60, 70, 80, 90°. The average ring current was 310mA. The Laue photographs recorded on the IPs were scanned using a Fuji BAI100 readout system. The data were processed using the programs GENLAUE, INTLAUE, and LAUENORM4), modified for the Laue camera.

Results

The nominally estimated maximum resolution was 2.2Å (since the crystals of o-APT can diffract to 1.6Å, we guess the resolution was strongly limited by water background) and the wavelength range was 0.24 to 2.5Å. The non-overlapping 57,480 reflections from the ten photographs gave a total of 13,537 independent reflections. The final merging R-factor was 11%. The overall completeness of the finally accepted data was 51%. The difference Fourier map, Fig.1(a), calculated using the Laue data as the derivative, shows DL-α-F-β-alanine bound at the active site of o-APT. Fig.1(b) is a similar map calculated with a full Weissenberg data set to 2.2Å resolution of 26,442 reflections. The quality of the Laue map is comparable to that of the Weissenberg map.

References


Fig.1. A comparison of difference electron density calculated using Laue and Weissenberg data. The maps were calculated with coefficients [F(DL-α-F-β-alanine complex)-F(Weissenberg, native)]×exp(-iφ(Native)).
(a) Laue, (b) Weissenberg data were used as the data of the complex crystal. The maps were contoured at the 3σ level.
**ENERGY DEPOSITION OF X-RAYS TO MATTERS**

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Photon mass energy-absorption coefficient \( \mu_{en}/\rho \) is widely used in calculations of photon energy-deposition to matters, which is approximately equal to the product of \( \mu_{en}/\rho \) and the photon intensity. Some tabulations\(^{1}\) of calculated values are widely used but are rarely compared with measurements. In this work, \( \mu_{en}/\rho \) of air, nitrogen and argon at 30-keV were measured at BL-14C.

The experimental setup is shown in Fig. 1. The calibrated parallel plate free-air ionization chamber \([IC2]\) was placed in the vacuum chamber \([V2]\) and filled with gases at 0.5-1.0 atm. The ionization current \((I)\) was measured at the position where electrons from the window do not affect. Another free-air ionization chamber \([IC1]\) was used to normalize the results. X-rays intensity \((J)\) was measured using the total absorption calorimeter\(^{2}\) \([CA]\). To monitor higher harmonics content, a Be foil \([Be]\) was placed in a vacuum chamber \([V1]\) and scattered photons were measured using HP-Ge detector \([Ge]\). Then \( \mu_{en}/\rho \) was given from the ionization current \((I)\) and intensity \((J)\) as follows:

\[
\mu_{en}/\rho = \frac{I}{W} \left(1.602 \times 10^{-19}\right) \left(1 + \frac{t}{\rho}\right) \\
\text{where } \frac{1}{W} \text{ is the } W \text{ value, the mean energy required to produce one ion pair in gases and that in ICRU Report 31 were sited, } t \text{ is the length of the collecting region of the current and } \rho \text{ is the density of the gas. Results are shown in Table 1 and are in good agreement with published values}^{1}.

The characteristics of LiF thermoluminescence dosimeters (TLD-100) were studied at 10-40 keV region, which were widely used as personnel dosimeters for X-rays above 50-keV. Their TL response was calibrated by \( ^{60}\text{Co} \) \( \gamma \)-rays. Response in 10-40 keV region were calculated using \( \mu_{en}/\rho \) tables\(^{1}\). LiF TLDs were irradiated at BL-14C and the measured values of TL response were about 10% higher than calculated ones.

The linearity of TL response vs absorbed dose was also studied for \( ^{60}\text{Co} \) \( \gamma \)-rays, 30- and 10-keV photons as shown in Fig. 2. Up to 0.8 Gy, good linearity was seen for all cases. Above 0.8 Gy, supralinearity was seen but it became smaller as the photon energy decreases.

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**Table 1. Photon Mass Energy-Absorption Coefficients at 30 keV. Calculated values by Hubbell\(^{1}\) are also shown.**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Exp. ( [m^2 kg^{-1}] )</th>
<th>Cal. ( [m^2 kg^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.0148±0.0002</td>
<td>0.01501</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0105±0.0002</td>
<td>0.01069</td>
</tr>
<tr>
<td>Argon</td>
<td>0.239±0.006</td>
<td>0.2353</td>
</tr>
</tbody>
</table>

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**Fig. 1** Experimental setup.


**Fig. 2** LiF thermoluminescence response vs absorbed dose. Supralinearity is seen.

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X-ray computed tomography using synchrotron radiation (SR-CT) has been developed to improve resolution and contrast of CT images. The advantages of using the SR are its abilities to give spatial distributions of a specific element and quantitative measurements by subtraction of the CT images below and above the x-ray absorption edge of the element (K-edge subtraction method).

We have been developing monochromatic x-ray CT in an energy range up to 50 keV to observe specimens with large attenuation coefficients with a short inspection time. We use the vertical wiggle beamline (BL14C) at the Photon Factory (PF) of the National Laboratory for High Energy Physics (KEK). This beamline can produce x-rays in an energy range below 100 keV of high intensity compared with other beamlines which use a bending magnet without insertion devices.

At the present stage we can obtain monochromatic x-rays in an energy range up to 74 keV and CT images with a pixel size of a few μm in an energy range up to 50 keV. This enabled us to observe fine structures of materials which could not be previously observed with SR-CT because of their large attenuation coefficient. We also used the image subtraction method and demonstrated it with the K-absorption edge of an iodine solution. Since the relative CT values are linearly proportional to I concentration, it is possible to evaluate the concentration distribution of the iodine quantitatively.

This report shows the typical results which were obtained using our system shown in the previous paper1.

A schematic figure of a sintered iron ore specimen and the CT image of three-dimensional images constructed from 6 slices are shown in Figs. 1 (a) and (b), respectively. Each image has a pixel size of 6.3 μm and slice width of 20 μm with monochromatic x-rays of 40 keV using the <333> and <440> Bragg planes of Ge. Pores and other fine structures in the specimen are visible. The specimen is mainly iron oxide and includes some elements such as calcium. Three-dimensional images allow analysis of the inner-pore connectivity, the pore distributions, and the proportions of constituent elements.

A schematic diagram of the specimen used for the subtraction method is shown in Fig. 2 (a). The specimen is a bundle of three glass capillaries (outer and inner diameters 1.6 mm and 0.9 mm). The three capillaries were filled with different solutions, iodine solution 10 wt%, tungsten solution 5 wt%, and platinum solution 5 wt%. Two images obtained above and below the iodine K-absorption edge (33.17 keV) are shown in Figs. 2 (b) and (c). The subtraction image corresponding to the images in Fig. 2 (b) and Fig. 2 (c) is shown in Fig. 2 (d). Although the glass capillaries, the W solution, and the Pt solution became invisible due to the negligible change in absorption above and below the iodine K-absorption edge energy, the I solution can be clearly observed because of the large change at the iodine K-absorption edge. The subtraction method can therefore improve the sensitivity of an element and extract the distribution of a particular element.

In future we intend to extend the energy range up to 100 keV and improve the resolution to ~1 nm. The system will be applied to evaluate advanced materials such as fine ceramics, composites, and other fine structures made by precise engineering.

TIME-RESOLVED X-RAY DIFFRACTION AND CALORIMETRIC STUDIES ON THE FINE STRUCTURE OF THE PHASE TRANSITIONS IN HYDRATED DIPALMITOYLPHOSPHATIDYLETHANOLAMINE

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Due to their frequent occurrence in biological membranes, phosphatidylethanolamines (PEs) have received much attention in model studies. Fully hydrated PEs undergo a gel (Lp)–to–liquid-crystalline (Lθ) phase transition in contrast to fully hydrated phosphatidylcholines, in which a ripple gel phase (Pp) appears between the gel (Lp) and liquid-crystalline (Lθ) phases. However, measurements by high-sensitivity differential scanning calorimetry (HSDSC) have led to the conclusion that the Lp–Lθ transition of PEs is not a single-peak transition but has a fine structure [1]. It has been suggested that the Lq–Lθ phase transition of PEs consists of "pretransition" (Lq–Pp) and "main transition" (Pp–Lθ) and two transitions can be resolved into separate peaks. Since the detection of the fine structure and/or existence of intermediate phases have not been reported in previous X-ray diffraction studies, we reexamined this transition by low-angle X-ray diffraction technique under precise temperature control [2].

DPPE (1,2-dipalmitoyl-sn-glycero-3-phosphoryl-ethanolamine) was purchased from Avanti Polar Lipids. The lipid was dispersed in doubly distilled deionized water by vortexing at room temperature. The lipid concentration was 20 wt%. Time-resolved low-angle X-ray experiments were carried out with a small-angle X-ray diffractometer at station 15A. The experimental arrangement and precise temperature control are described in detail in the previous paper [2]. HSDSC measurements were performed using Privalov DASM-1M and DASM-4 microcalorimeters.

Temperature dependence of a low-angle diffraction profile through Lq → Lθ transition at a scan rate of 0.1 °C/min is shown in Fig. 1(top). No other phases, except coexisting Lq and Lθ phases, appear in the transition region, since there are only two lamellar spacings corresponding to the Lq and Lθ phases. There is no evidence for the existence of intermediate states with lamellar spacings different from those of the Lq and Lθ phases. While, the temperature dependence of the intensity in Fig. 1(bottom) shows that the cooling Lθ → Lq transition is not a simple two-state transition, since there are at least two inflection points in the intensity. On the other hand, a multi-peak thermogram of this transition observed by HSDSC became distinct with increasing incubation time in the Lq phase (data not shown). These data suggest that the equilibrium state of the Lq phase of hydrated DPPE is a mixture of domains that differ in thermal behavior, but their structural difference is too small to be distinguished by low-angle X-ray diffraction technique.

STRUCTURAL ANALYSIS OF THE SQUID PHOTORECEPTOR BY X-RAY DIFFRACTION

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Introduction

The initial step of the visual process is the absorption of light by the visual pigment. The squid visual pigment is located in microvilli which are cylindrical extensions of the cell membrane, arranged hexagonally within the rhabdomes. Until now, only a few papers have been published on the structural study of invertebrate rhabdomes by x-ray diffraction. In those, however, the retina fixed by glutaraldehyde was used, because this tissue disintegrated within 1 hour of dissection. In the previous reports, it was described that we could succeed in a recording of the x-ray diffraction pattern from unfixed retina by the use of the synchrotron radiation and a storage phosphor screen, the imaging plate^1), and that the structural analysis of the photoreceptor has been done based on the model Patterson function^2). In this report, we will present the improved model of the photoreceptor.

Results

Figure 1 shows the Patterson function calculated from the observed x-ray diffraction intensity^1). The Patterson functions were also calculated based on the models, in which the microvillar membrane was assumed to have the bilayer electron density distribution and the radii and electron density of the microvilli and the microvillar cytoskeleton were varied. The previous analysis suggested the existence of inter-microvillus materials, which was thought to be the membrane junction ^3). A fairly good agreement was obtained between the observed and the model Patterson maps by assuming the inter-microvillus materials, except the region around the lattice corner^2^). The significant improvement was found in structure analysis by introducing the rather complicated structure as the model of the inter-microvillus materials, which is shown in figure 2(A). The Patterson map calculated from this model is also shown in figure 2(B).

References

2) T. Hamanaka et al., PF Activity Report, No.8; 296 (1990).

Figure 1. The Patterson map calculated from the observed x-ray diffraction intensity. The lattice constants are a=60 nm, b=60 nm and γ=120°. Negative contours are shown as dashed lines.

Figure 2. The Patterson map (B) calculated based on the model shown in A. The large circle in the model structure represents the cross-section of photoreceptor microvilli, which contains a cytoskeleton core (filled circle) at the center. The others correspond to the membrane junction. The discrepancy factor is 16% for this model.
Allosteric transition of aspartate transcarbamylase (ATCase) has been extensively investigated by stopped-flow X-ray scattering (SFXS) technique. Observation of structural kinetics from T to R transition by SFXS was reported [1], as well as effects by allosteric effectors, CTP, ATP and CTP + UTP on the kinetics [2].

In the present note we report experimental results on allosteric transition induced by carbamyl-L-phosphate and a substrate analogue, succinate. Experiments were done at -8°C with 30% ethylene glycol as antifreeze. Concentration of carbamyl phosphate was kept constant at 44 mM with various concentration of succinate. ATCase was 39 mg/ml. All the measurements were carried out at BL-15A with 1-D PSPC.

On mixing the enzyme with a substrate analogue, scattering subpeak (s values from 0.0143 to 0.0226 Å⁻¹) increased. Integrated intensity between the two s values shows a single exponential increase. Typical curves are shown in Figs. 1 and 2. Apparent rate constants of the allosteric transition were obtained, and shown in Fig 3.

These kinetics show several different aspects from native substrates [1]: (1) integrated intensity increases and never goes down; (2) initial rise rate was remarkably faster than that of the native substrate. The kinetics of aspartate show both T to R and R to T conversion, with a steady state at which the enzyme is not always in complete R state in terms of scattering pattern. In contrast, the kinetics of succinate show a simple T to R transition. Then, the reaction with succinate is a good system to investigate allosteric transition in a simple way.

References
In aqueous dispersion of dipalmitoylphosphatidylcholine (DPPC), the non-rippled gel phase $L_\alpha$ exists below the pretransition temperature $T_p$ (=about 34 °C), the rippled gel phase $P_g'$ between $T_p$ and the main transition $T_m$ (=about 41.5 °C) and the liquid crystalline phase $L_d$ above $T_m$. It has been found that this system has a temperature hysteresis at the $P_g'$ temperature region such that the structure of the system heated from $L_g'$ to $P_g'$ and that cooled from $L_d$ to $P_g'$ are different from each other. For the sample cooled from $L_d$ to $P_g'$, it takes over 24 hours of relaxation time to reach the stable $P_g'$ phase from the metastable $P_g'$ phase, which is denoted as the $P_g'$ (mst) phase (1).

Time resolved small-angle X-ray scattering study from lipid-water bilayer structure have been performed using a small angle camera at the synchrotron radiation source in order to investigate the structure relaxation process with phase transition. In this report we will report one of the results in the case of the the relaxation process for the sample quenched from the stable $P_g'$ phase to the $L_g'$ phase temperature region to reach an equilibrium. We have studied the ordering process below $T_p$ in this system by means of small-angle X-ray scattering (SAXS) using a conventional X-ray source. The result shows that the relaxation time amounts several tens of minutes in the relaxation process for the sample quenched from the $P_g'$ (mst) phase to the $L_g'$ phase temperature region to reach an equilibrium and that there is a minimum in the relaxation time at about 25 °C as a function of the final quenching temperature (2). On the other hand, it is found that the relaxation time amounts several tens of seconds in the relaxation process for the sample quenched from the stable $P_g'$ phase to the $L_g'$ phase temperature region to reach an equilibrium. Since this relaxation process is too fast to measure by means of a conventional X-ray small angle camera, we have undertaken to measure the growth of the $L_d$ structure quenching from the stable $P_g'$ phase using a small angle camera at the synchrotron radiation source.

Synthetic 1,2-dipalmitoylphosphatidylcholine was purchased from Sigma Chemical Co. and was used without further purification, and was dispersed in aqueous solutions. The lipid concentration was 30 wt % in all the samples, which were always in excess water. SAXS experiments were carried out with a mirror-monochromator optics with a position-sensitive proportional counter (PSPC) at BL-15A in Photon Factory, KEK. The wavelength of the radiation was 1.5Å. The sample-to-detector distance was 1.113 m. The temperature of the samples was controlled by a water-circulating thermostat (±0.1 °C) and was monitored using a thermocouple dipped in the cell. The samples were heated from the room temperature ($L_g'$ temperature region) to the $P_g'$ temperature region, and after keeping for 10 minutes, they were quenched to the $L_g'$ temperature region. We measured the SAXS profiles before quenching these samples and sequentially during 10 minutes after quenching.

Figure 1 shows a bird-eye-view of the time-resolved SAXS profiles in initial 300 seconds from the sample as mentioned above. It was quenched from 37.7 °C to 23.2 °C. Each profile was measured for 7 seconds. The initial 20 profiles were measured with an interval of 8 seconds and the last 5 profiles with an interval of 30 seconds. The temperature of the initial 4 profiles was above $T_p$. In the $L_g'$ temperature region the profiles changed very quickly. The first, second and third Bragg peaks at $Q = 0.05, 0.11, 0.15$ Å⁻¹ corresponding to the $P_g'$ ripple structure and those at $Q = 0.09, 0.18, 0.27$ Å⁻¹ corresponding to the $P_g'$ repeat distance of the lamellar disappear soon and those at $Q = 0.095, 0.19, 0.285$ Å⁻¹ corresponding to the $L_g'$ repeat distance of the lamellar structure appear and grow. We have plotted the intensity of the 1st Bragg peak $I$ of each profile below $T_p$ as a function of time in figure 2. The relaxation time of this system has been calculated and appeared to be 150 seconds at about 23 °C. It is a very fast relaxation compared to that quenched from the $P_g'$ (mst) phase to the $L_g'$ phase temperature region as mentioned above.

(2) S. Ueno et al, J. Appl. Cryst., to be published.

![Fig.1 Time resolved SAXS profiles for DPPC-water system quenched from 37.7 °C (stable $P_g'$) to 23.2 °C ($L_g'$ temperature region).](image1)

![Fig.2 The evolution of the first Bragg peak intensity from DPPC-water system quenched from 37.7 °C ($P_g'$) to 23.2 °C ($L_g'$ temperature region).](image2)
SYNCHROTRON RADIATION SMALL-ANGLE SCATTERING STUDY
ON THE REVERSION PROCESS OF AL-LI BINARY ALLOYS

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INTRODUCTION

The reversion process of delta prime precipitates in Al-Li binary alloys has been investigated by means of in-situ small-angle scattering measurements. The delta prime precipitates formed by pre-aging have the ordered structure of Li₁₂ type. In the previous in-situ SAXS experiments on the reversion process of Al-Zn binary alloys, which have a rather simple phase-separation phase diagram, we found that there are two stages in the reversion process of G.P. zones formed by pre-aging at 313K.

The comparison of the reversion process of Al-Zn binary alloys with that of delta prime precipitates in Al-Li binary alloys give us the information how the ordering feature of the precipitates affect the reversion kinetic.

EXPERIMENTAL PROCEDURE

The reversion experiment was performed at Beam-Line 15A. The samples used in the present experiments were Al-8.1at%Li and -11.8at%Li alloys. The samples were solution-treated at 823K for 1.8ks and preaged at 423K for 86.4 ks to form delta prime precipitates of about 6nm by Guinier radius.

In-situ SAXS measurements were performed at several temperatures between 473K and 673K.

RESULTS AND DISCUSSION

Change of the integrated intensity, Q, for Al-8.1%Li is shown in Fig.1. Since the reversion temperatures are above the delta prime solvus, it is seen that Q decreased monotonically to vanish within 20 seconds, corresponding to the dissolution of delta prime precipitates.

Change of the Guinier radius, R₀, for Al-8.1%Li is shown in Fig.2. The most remarkable feature is that the Guinier radius decreased monotonically throughout reversion. In contrast, the Guinier radius increased monotonically during reversion of G.P. zones in Al-Zn binary alloys.

The increase in the Guinier radius was explained in terms of the distribution of solute atoms around the precipitate/matrix interface, which suggests the diffusion-limited dissolution process. The Guinier radius always decreased in the present experimental conditions. It suggests that there is no appreciable gradient in the concentration of lithium around the precipitate/matrix interface, and that the rate determining process of the reversion is the dissolution reaction at the interface. Assuming that the dissolution rate is constant throughout reversion, then the relation between Q and the time is expressed by radius:

\[ f(Q) = \left( \frac{u}{Q} \right)^{1/3} = kt \] (1)

which was found to fit well for the present experimental results.

![Fig.1 Change of Q for Al-8.1%Li.](image1)

![Fig.2 Change of R₀ for Al-8.1%Li.](image2)
SMALL-ANGLE SCATTERING FROM GaAs/Si EXPITAXIAL LAYERS

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INTRODUCTION

The structure and the stability of epitaxial layers and their interfaces grown by vapor phase deposition are important subjects in the evaluation of semiconductor/semiconductor or semiconductor/metal interface. During the experiments on the small-angle x-ray scattering from GaInP epitaxial layers grown on GaAs/Si substrates, we observed small-angle scattering intensity which should be attributed to the GaAs/Si substrate layers^1. In order to examine the origin of the SAXS intensity, we carried out SAXS measurements for GaAs/Si layers and Si substrates.

EXPERIMENTAL PROCEDURE

Small-angle scattering experiments were performed at Beam Line 15A and 17A. The samples used in the present experiment were GaAs/Si grown by metalorganic vapor phase deposition. The sample orientation was (001) with 4 degrees off towards (011). They were polished down to about 100 microns to obtain good transmission. SAXS measurements were performed in the transmission geometry, and two dimensional intensity profile was obtained by imaging plate.

RESULTS AND DISCUSSION

Figure 1 shows the contour map of the SAXS intensity obtained for a GaAs/Si film. It is seen that one set of streaks run along [111], which agrees with the previous results.

The intensity profile taken along the streak is shown in Fig.2 as a function of the scattering vector, k, by the logarithmic scale. Since three dimensional profile of the scattering intensity is not known yet, the substance that cause small angle scattering may be either rod-like (one-dimensional) or plate-like (two-dimensional). From the Guinier fitting of the measured intensity, the Guinier approximation equation for a plate-like substance showed better linearity than that for rod-like substance. The Guinier radius obtained as the thickness of the plate was 1.0nm, and that obtained as the radius of the rod was 1.6nm.

In order to determine the shape of the scattering substance, three-dimensional SAXS measurements in vacuum chamber is now under way.

REFERENCES

Studies on the structure of spiny lobster (Panulirus japonicus) hemocyanin with solution X-ray scattering

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Arthropod hemocyanins (Hc) are generally known to be multimers of fundamental submultiple which comprises six subunits, by means of immunoelectron microscopy. We have been studying the molecular architecture of Limulus polyphemus Hc with solution X-ray scattering [1]. Scattering patterns of the native hemocyanin (48-mer), its half molecule (24-mer) and quarter molecule (12-mer) indicated that the radii of gyration for three molecular species were 110.7, 91.3 and 77.3 Å, respectively. The models constructed by 8, 4, 2 spheres with a radius of 58 Å, fitted well with the experimental data. In this report, X-ray scattering pattern of Panulirus japonicus Hc consisted of single submultiple (6-mer) was analyzed in comparison with the theoretical pattern simulated from two kinds of the model.

Figure 1a shows the scattering pattern of P. japonicus Hc. On the scattering curve, there observed one minimum at h = 0.073 Å⁻¹ and two maxima at h = 0 Å⁻¹ and h = 0.09 Å⁻¹. The radius of gyration (Rg) calculated from the Guinier plot, was 48.44 Å. Fig. 1b shows the p(r) function of this molecule from the experimental result. Maximum dimension (Dmax) and maximum distance distribution of Hc were found to be 125 Å and 65 Å, respectively.

We constructed two models for the Hc molecule, one was approximated by a sphere having a radius of 58 Å, in the same fashion as previously reported (one sphere model). The other was a six spheres model where 2 trigonal layers composed of 3 spheres with a radius of 29 Å were superimposed in a staggered configuration. Fig. 2 shows the calculated X-ray scattering pattern according to the one sphere model. The theoretical scattering pattern was essentially similar to the experimental result while the radius of gyration for the model was 44.9 Å which was smaller than the experimental data slightly. However, the minimum of the model scattering pattern at h = 0.073 Å⁻¹ was distinct from the experimental data. The scattering pattern of the six spheres model was shown in Fig. 3a. Although the theoretical pattern was very similar to the experimental result, the p(r) function (Fig. 3b) showed a shoulder at 30 Å differing from Fig.1b. We are attempting to develop a new multisphere model by using the atomic coordinates of P. japonicus.

ANALYSIS ON STRUCTURAL CHANGE OF PURPLE MEMBRANE ON REGENERATION

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INTRODUCTION

Bacteriorhodopsin (bR) is the sole protein found in the purple membrane of Halobacterium halobium. The bR is composed of 248 amino acid residues and the chromophore retinal. BR is folded into seven α-helices spanning the lipid bilayer and additional segments in the aqueous regions. BR forms trimers which arrange in a hexagonal lattice in purple membrane.

On absorbing light, bR undergoes a photoreaction cycle. Coupling with M intermediate in the cycle, bR actively transports a proton from the inside of the bacterial cell to the outside. We found a treatment with arginine, where M intermediate could be stabilized without alteration of the structure of bR and the membrane or the sequence of the photo-reaction cycle of bR and analyzed the possible structure of M intermediate by X-ray diffraction.

In the process of regeneration of bR from apoprotein and retinal an intermediate appears. This intermediate has an absorption maximum different from bR and intermediates appearing in the photo-cycle. The structural changes of regenerations of bR from the intermediates was studied.

EXPERIMENTAL

Purple membrane was isolated from H. halobium. The apoprotein of bR was prepared by irradiation of bR in the presence of hydroxylamine. The intermediate was produced by the mixing of apoprotein and 14-methyl retinal. M intermediate was produced by irradiating the arginine-treated bR with yellow light.

X-ray diffraction experiments were performed with the MUSCLE Diffractometer installed at BL-15A. The X-ray wavelength was tuned to 1.5 Å. The sample was mounted on a sheet of myler with its plane normal to the incident X-ray beam.

RESULTS AND DISCUSSION

The X-ray diffraction profiles from apoprotein of bacteriorhodopsin, the intermediate produced from 14-methyl retinal and the apoprotein, and bacteriorhodopsin were measured. However the differences among them have not been detected yet. Next the X-ray diffraction profiles during the regeneration of bacteriorhodopsin from M-intermediate. We have already clarified the difference in X-ray diffraction profiles between bacteriorhodopsin and M-intermediate.

Owing to the intense synchrotron radiation and the arginine treatment, we could record the regeneration kinetics from the M-intermediate with time-resolved measurement (Fig. 1). The results showed the simple change of the profiles from M-intermediate to bacteriorhodopsin indicating that the hexagonal arrangement of the bR trimer in the membrane was not distorted during the regeneration of bacteriorhodopsin from M-intermediate. Hence, we concluded that no global structural changes in the membrane occurred during the photo-cycle of bR and that the proton translocation could be achieved by local small structural changes.

REFERENCES


Fig 1. Time-resolved X-ray diffraction diagrams recorded during the regeneration of bacteriorhodopsin from M-intermediate. Whole period (200 sec) was divided into 10 frames of 20 sec. Recordings were repeated 10 times for one sample and the obtained profiles were added. In each cycle, samples were exposed to X-ray after complete accumulation of M-intermediate and the illumination light was turned off at third frame (indicated by arrow). The dotted line shows the maximum intensity of (2 0) reflection at the first frame.
BILAYER/NON-BILAYER PHASE TRANSITION IN GLYCOLIPIDS

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Introduction

Many lipids such as phosphatidylethanolamine or glycolipids show the bilayer (Lα or Lβ)/non-bilayer (Qα or Qβ) transition. This process is more complicated than bilayer/nonbilayer transition. According to the Kirk's theory\(^1\), the d-spacing of the non-bilayer phase decreases with increasing temperature. If the non-bilayer phase coexists with the bilayer phase below the transition temperature, the d-spacing should be equal to the d-spacing at the transition temperature.

The present report shows the temperature dependence of the d-spacing in the non-bilayer phase coexisting with the bilayer phase.

Experimental

The aqueous dispersion of racemic dihexadecyl-(β-D-glucopyranosyl)glycerol (abbreviate as rac16Glc) and 1,2-dodecyl-(β-D-glucopyranosyl)glycerol (abbreviate as 12Glc) were used.

X-ray diffraction study was carried out at BL-15 A station.

Results and Discussion

Rac16Glc shows the direct transition between the Lβ phase and the Hβ phase without through the Lα and Qα phase. Fig.1 shows the d-spacing of the Lβ phase and the Hβ phase.

Measurement was carried out on the cooling process. The midpoint of transition was 62.1°C. The d-spacing of the Hβ phase above the transition temperature increased on cooling. On the other hand, the d-spacing of the Hβ phase coexisting with the Lβ phase decreased on cooling. Such behavior did not observed in the non-bilayer/non-bilayer transition of 12Glc. 12Glc shows the Lα/Qα/Hβ transition. Fig.2 shows the d-spacing of the Qα phase and the Hβ phase. Measurement was also carried out on cooling process. The midpoint of transition was about 69.2°C. The d-spacing of the Hβ phase coexisting with the Qα phase did not depend on temperature. While the d-spacing of the Qα phase showed the same temperature dependence as the Hβ phase of 16Glc.

The temperature dependence of the d-spacing in the non-bilayer phase coexisting with the bilayer phase is not contradictory to the Kirk's theory, however, it requires some amendments.

References

Scanning X-ray Photoacoustic Imaging for Elemental Analysis

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Introduction
For the imaging by absorption method, K-edge subtraction method is quite suitable for elemental analysis. In case of X-ray photoacoustics, images of both signal amplitude and phase were obtained. We present that not only the amplitude image but also the phase subtraction image can show the location of elements. In addition, the phase value can reflects how deep the location is.

Experimental
Using BL15A and 4A(for setup of apparatus), measurements were performed with new apparatus noted elsewhere in this report[1]. The spatial resolution was determined by the aperture with pinhole at size 0.6 and 1.2 mmφ. Chopping frequency was set at 9 Hz.

Results and discussion
Figure 1 shows the scheme of model samples. For the signal amplitude image, simple and no-coverage type sample was chosen(Fig.1 left). Figure 2 shows the calculated subtraction image of this sample at above minus below Ni K-edge at resolution 0.6 mm. Ni region was clearly highlighted. This calculation were come to simple by our newly developed software. Due to the improvement of S/N ratio, imaging at 0.6mm can be done with good reproducibility. It should be noted that the phase values of this image on Ni, Cu, Sn area were obtained to be 5.0, 1.2, and 3.4 degree (see above the left image of the picture of Fig.2). The difference of the X-ray penetration depth is biggest for Ni than two other case because of the drastic change in absorption coefficient at two X-ray wavelength.

Figure 3 shows the subtraction image of the phase at above minus below Ni K-edge at resolution 1.2 mm for the model sample shown in Fig. 1(right). The phase value in this case show how differ the phase between two X-ray energies at above and below K-edge. Ni region of low half is highlighted in clear difference while top half is similar. Furthermore, the phase values are 3.2, –3.6, –9.8 degree for no PET, 25μm and 75μm PET coated regions respectively, which reflect how thick the surface is in each area. This also show the phase subtraction can also be useful for elemental analysis with additive image of the depth. Now several criteria were under investigation to establish this methodology.

Reference
1.T.Masujima, H.Kobayashi, T.Hinoue et al. in this activity report.

Fig.1 Scheme of model samples for imaging.

Fig.2 Subtraction amplitude image of the model sample 1 at Ni K-edge X-ray energy (aperture: 0.6mm φ).

Fig.3 Subtraction phase image of the model sample 2 at Ni K-edge X-ray energy (aperture: 1.2mm φ).
Scanning X-ray Photoacoustic Imaging for Depth Profiling

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Introduction
In contrast to the elemental analysis, subtraction imaging by photoacoustic method has unique advantage that it can be applied for nondestructive depth profiling. Using PET coated model sample, the establishment of this method is under progress. Recent results with newly developed sensitive apparatus are reported.

Experimental
This measurement was performed at BL15A with new apparatus developed. Other conditions are the same as previous report\cite{1}. Figure 1 shows the model sample for this experiment. Metal foils of Ni and Cu are the base of X-ray absorbing material and part of these surfaces were covered by polyethylene terephthalate (PET) films at 25μm and 75μm thick. Modulated (chopped at 9 Hz) and focused X-ray beam of 1.2 mm size was irradiated on the sample in the photoacoustic cell.

Results and Discussion
Figure 2 and 3 show the photoacoustic signal amplitude image and phase image for a model sample at above Ni K-edge. The average values of amplitude and phase in each area are as follows.

Table I  Average of signal amplitude and phase values

<table>
<thead>
<tr>
<th>Area</th>
<th>25 μm PET</th>
<th>without PET</th>
<th>75 μm PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Amp.(mV)</td>
<td>6.7-7.1</td>
<td>11.0-11.4</td>
<td>3.2-3.3</td>
</tr>
<tr>
<td>Phase(deg.)</td>
<td>-27- -28</td>
<td>-5-- -7</td>
<td>-53</td>
</tr>
<tr>
<td>Cu Amp.</td>
<td>5-5.5</td>
<td>5.4-6.2</td>
<td>2.6-2.9</td>
</tr>
<tr>
<td>Phase</td>
<td>-19- -23</td>
<td>-9</td>
<td>-46- -52</td>
</tr>
</tbody>
</table>

It is consistent that the thicker the covered surface is, the smaller amplitudes and more delayed phases were observed. The phase values are more or less the same for both Ni and Cu areas. Slight difference should come from the difference in the average absorption depth depending on the absorption coefficients. From these delay in phase, the depth of each PET area was estimated to be 15-30 μm and 65-80 μm thick for 25 μm and 75 μm PET respectively using calibration curve. Now it is possible for the layered model like samples to answer "What, Where and How Deep", however, in order to apply this method to practical sample, much more improvements are still needed to be established.

Reference
1.T.Masujima, H.Kobayashi, T.Hinoue et al., in this activity report.

Fig.1 Scheme of a model sample for imaging.

Fig.2 Amplitude image of the model sample at above Ni K-edge energy (aperture: 1.2mm φ).

Fig.3 Phase image of the model sample at above Ni K-edge energy (aperture: 1.2mm φ).
SHAPE CHANGE OF THE MYOSIN HEAD INDUCED BY MgATP, STUDIED BY SMALL-ANGLE X-RAY SCATTERING IN SOLUTION

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Introduction

Because of their possible role in energy transduction of muscle contraction, it is important to know the magnitude and extent of the conformational changes of a head portion of myosin molecule during hydrolysis of ATP. We have investigated the conformational change of the myosin head (subfragment 1 (SI)) in the presence of Mg-ATP by small-angle X-ray scattering in solution. The change was detected and compared with those taking place in various nucleotide bound SIs which mimick intermediate states of ATP hydrolysis.

Experimental

Myosin SI was isolated from chicken pectoralis muscle and cleaved with papain. This SI preparation has both classes of light chains and a heavy chain for a total molecular weight of 130 kD. Nucleotide-free and various nucleotide-bound SIs were prepared and purified by an HPLC just before X-ray experiments. Small-angle X-ray scattering was performed by using the diffractometer at BL-15A1. Measurements were done using a 1D-PSD (and/or an IP) at protein concentrations of 3 to 7 mg/ml at 18.5°C. The specimen-to-detector distance was 240 cm and the exposure time was set 180 s.

Results and Discussion

A Guinier plot of the net scattering data from SI in the presence of MgATP (5 mg/ml) solution was compared with those from free SI and various nucleotide-bound SIs (Fig. 1). The deviation from the straight line was smaller in SI in the ATP solution than in free SI. That of ADP+V (vanadate) bound SI (SI.ADP.Vi) was similar to that in the ATP solution and those of ATPY bound (SI.ATPYS) or ADP trapped SI by pPDM crosslinking (SI.ADP-pPDM) and ADP bound SI (SI.ADP) were quite similar to that of free SI with slight differences. Figure 2 shows the values of the radius of gyration (Rg) when extrapolated to zero protein concentration. The Rg of free SI was 47.8 ± 0.4 Å (see Garrigos et al. and Mendelson et al.). The Rg of SI in the ATP solution decreased by about 3 Å, being slightly smaller than but closer to that of SI.ADP.Vi. On the other hand, the Rg of SI.ADP-pPDM was almost the same as that of free SI and the one of SI.ADP was slightly smaller than but closer to that of free SI.

The pair distance distribution function (P(r)) calculated from the free SI scattering data had a highly asymmetric profile with a peak at 37 Å and a distinct shoulder around 80 Å, giving the maximum particle dimension (Dmax) of about 170 Å. The P(r) of SI in the ATP solution showed the peak at the same position, with a less distinct shoulder and intersected the free SI curve at 80 Å, decaying with smaller values than in free SI. Dmax became shorter by about 10 Å. The P(r)s of SI.ADP-pPDM or SI.ATPYS and SI.ADP were similar to that of free SI.

These results strongly indicate that the shape of SI becomes compact or rounding in the presence of MgATP, supporting the recent studies by electron microscopy (e.g., Tokunaga et al.). It has been considered biochemically that SI.ATPYS and SI.ADP-pPDM are an analogue of SI bound ATP state and SI.ADP.Vi is an analogue of SI bound ADP+Pi (phosphate) state. Thus, the shape change of SI in the ATP solution probably occurs in the SI.ADP.Pi intermediate state of the ATP hydrolysis cycle.

Fig. 1 The Guinier plots of net scattering data from free SI and various nucleotide bound SIs.

Fig. 2 The values of Rg of various nucleotide bound SIs at zero protein concentration.

References

In the anterior byssus retractor muscle of Mytilus edulis (ABRM), Ca\(^{2+}\) regulation of contraction is mediated by myosin\(^6\), and structure change of the actin filament appears to be caused by attachment of cross-bridges to actin. For X-ray studies of the structure change in the isometrically contracting ABRM, it is desirable to raise tension as high as possible so that the actin filaments are activated almost in the whole length by actin-myosin interaction. In this work, it is attempted to increase tension by stimulation with acetylcholine solutions of high concentrations, and to compare reflections from the actin filaments between the resting state, the active state during stimulation, and the tonically contracting state after the end of stimulation\(^2\) by taking X-ray patterns in the three states from the same part of a muscle bundle cut from an ABRM. The muscle bundle is fixed at a natural length at which actin filaments fully overlap myosin filaments of the right polarity\(^7\).

Figure 1 shows small angle X-ray patterns in the three states which were recorded on imaging plates by 10 s X-ray exposure using the point-focusing camera at BL-15A. The muscle was stimulated by 10 M acetylcholine in artificial sea water at 8 C. The tension was maintained at 12 Kg/cm during X-ray exposure in the active state, and at 10 Kg/cm in the tonically contracting state. The 195 A layer line which characterizes the actin filaments in the contracting muscle appeared almost at the same intensity in the active, and tonically contracting state. In the resting state, the intensity is partially sampled at 0.009 A\(^{-1}\) due to interfilament interaction. The sampling peak was leveled according to the law of intensity conservation (truncated line)\(^4\). Then, the intensity almost agrees with the intensities in the two contracting states. Intensity increase in the contracting states, if any, is less than 5 %. The layer lines from the actin filaments become sharper with increase in the intensity maximum in the order, the resting, tonically contracting, active state, indicating increase in the persistent length of the helical order in the filaments.

Because the 59 A layer line overlaps the adjacent 51 A and 70 A layer line, it cannot be assumed that the intensity falls to the level of the background in between the layer lines. The intensity gap from the background decreases with decrease in the width of the layer lines. If the intensity of the 59 A layer line is measured assuming nonoverlap between the layer lines, it seems as if the intensity increased about 20 % when the muscle changes from the resting state to the tonically contracting state.

An equatorial intensity peak due to interfilament distance distribution is at (118 A)\(^{-1}\) in the resting state. It moves to the meridian, and becomes broad in both contracting states, but much more in the tonically contracting state than in the active state. The peak is at (119 A)\(^{-1}\) in the active state, and at (126 A)\(^{-1}\) in the tonically contracting state. Probably, arrangement of actin filaments is different between both states.

An X-Ray diffraction study of the age-dependence of skin collagen and hair keratin on humans and primates

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In an earlier study [1] on the role of collagen type III in altering the gap-overlap or d-spacing of mixtures of types I and III, it was reported that there was a definite and progressive reduction of the d-spacing with increase in age for normal human mitral heart valves, in which collagen III comprised 24% of the total collagen content. This had been prompted in part by reports [2,3] that skin collagen, with 15% type III, gave d-spacings of 65 nm from a number of animals, compared with 67 nm for pure type I.

It was then decided to investigate further the properties of skin as revealed by X-ray diffraction, using the Synchrotron at the Photon Factory at Tsukuba, Japan. At the same time the opportunity was taken to combine this project with a related investigation involving the diffraction from the skin and hair of both humans and baboons, some of which had been suffering from diabetes. This latter project is an extension of work reported earlier [4] on the effects of diabetes and sugar absorption on the equatorial X-ray pattern of collagen.

The examination of the results are not yet complete, mainly due to the necessity to produce appropriate computer software to display all facets of the large volume of data recorded. However, sufficient results are already at hand to indicate the submission of at least two papers to scientific journals. Moreover, the results so far have formed the basis for further exposures during our planned visit to Tsukuba in December, 1991.

The skin specimens, from humans aged between 3 weeks and 78 years and from baboons aged between 2 and 13 years, were obtained from punch biopsy samples, and prepared by carefully scraping away the epithelial and epidermal layers, exposing the dermal layer. Strips of this were cut, not in any preferred direction, stretched slightly and mounted in a sealed holder which permitted exposure while the samples were kept moist. The hair specimens consisted of 5 to 10 pieces, slightly stretched so as to ensure that all of the fibre axes were parallel.

Beam line 15-A at the Photon Factory was assigned for this work, and yielded a spot size at the specimen position of width 2 mm and height 1 mm with a wavelength of 0.15 nm. Recording of the patterns was by an imaging plate system [5], which had a dynamic range of sensitivity of 1 to 100,000, up to 60 times greater than X-ray film. The stored image was read by scanning with a He-Ne laser beam. The luminescence was converted into a time-series of digital signals by means of a photomultiplier, amplifiers and an A/D converter, and images were stored and reconstructed by computer. For our experiments the plates were placed at distances of 2.4m, 0.6m and 0.4m from the specimens. The first distance allowed the observation of all low-order reflections, while the second permitted the recording of meridional reflections as far out as the 74th order for collagen and the 67th order for keratin, as well as equatorial patterns out to 0.9 nm.

For collagen, it has been definitely confirmed that the d-spacing is about 65 nm for all specimens, and there is no apparent age-dependence in the d-values. There appears to be some slight variations in the spacings of the diffuse equatorial spot around 1.5 nm, but these are minor and well within the margin of error of measurement.

For keratin, preliminary experiments on the baboon hairs, carried out at the University of New South Wales, had already verified the alpha-pattern of mammalian hair. The results from the Photon Factory confirmed this to a high degree of accuracy, with a d-spacing of 46.8 nm. A significant observation was a definite, progressive increase with age in the spacing of an equatorial reflection.

An X-ray Diffraction Pattern from Frog Skeletal Muscle during Unloaded Shortening

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Structural studies on muscles which are actively shortening at high velocity have been of increasing importance because of the current interest in the sliding mechanism (Harada et al., 1990). However, shortening muscles are more difficult for X-ray diffraction experiments because shortening with low load lasts only less than 100 msec. We have recorded a two-dimensional X-ray diffraction pattern from frog skeletal muscle during shortening with small load on imaging plates.

Methods: An imaging plate exchanger (Amemiya & Wakabayashi, 1991) was used. This mechanism can replace an imaging plate at the position for X-ray exposure within a time of 200 msec. The specimen was frog sartorius muscle which was stimulated electrically for 1 sec (20 Hz stimulation) at 4 °C. The sarcomere length was adjusted to 2.6 µm in a resting state. The tendon end of the specimen was connected to a solenoid with a stainless-steel thread on which a small LED was fixed. The LED was used to monitor length of the muscle. The solenoid was activated to make the thread slack at 280 msec after the first stimulus. Then the muscle shortened about 16 % of its length until the thread became taut again. The load, which included weight of the thread and LED, was small (about 1 gram) compared with the tension the specimen developed (300 - 500 grams). Thus the specimen shortened with virtually no load, with a velocity of about 6 µm per sarcomere per sec. The shortening lasted for about 70 msec.

We made exposures at 5 different phases with 300 msec separations: (1) in a resting state before contraction, (2) during isometric contraction before shortening, (3) during shortening (4) during isometric contraction 330 msec after shortening, (5) during isometric contraction 630 msec after shortening. For each exposure, a fast-acting shutter was opened for 30 msec. In (3), to avoid the transient phase immediately after the release, the shutter was opened at 30 msec after the muscle was released.

Each specimen was subjected to 20 contractions and the diffraction patterns were accumulated on the plates. Thus the total exposure on each imaging plate was 600 msec. Further, patterns from four muscles were summed before intensity of each reflection was measured.

Results: Following intensity and spacing changes were observed during shortening (Fig.1): (1) The intensity of the (1,1) equatorial reflection decreased during shortening, and that of the (1,0) reflection also showed slight decrease making the intensity ratio slightly increase. (2) The 14.3-nm and 7.2-nm meridional reflections decreased in intensity. These reflections moved away from the origin by about 0.5 % during shortening. (3) The off-meridional part of the myosin layer-lines did not change in intensity. (4) The meridional reflection at 1/21.4 nm⁻¹ increased in intensity during shortening. (5) The intensities of the actin layer-lines at 1/5.9 and 1/5.1 nm⁻¹ decreased during shortening.

References

Figure 1
An X-ray diffraction pattern from frog sartorius muscle during unloaded shortening. Total exposure was 2.4 sec.
AN IMPROVED TECHNIQUE TO RECORD ORDERED DIFFRACTION PATTERNS FROM VERTEBRATE SKELETAL MUSCLES.
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Introduction
Whatever the material is, the most important basis of X-ray structure analysis is a diffraction pattern of high quality. Vertebrate striated muscles have an ordered structure in a resting state. This is evident in the myosin layer-lines of frog and rabbit skeletal muscles which are sampled by the superlattice, a lattice larger than the basic hexagonal lattice of the thick filaments. Thus, there must be a reason for the poorly ordered rigor structure. One possibility is that the tension muscle develops on going into rigor distorts the filament lattice. To test this possibility, frog skeletal muscle was put into rigor either after treatment by NEM (N-ethylmaleimide) or in the presence of BDM (2,3-butanedione monoxime). In both cases, rigor tension was suppressed.

Methods
Sartorius muscle from a Japanese frog (Rana nigromaculata) was skinned by 1 mg/ml saponin in a relaxing solution containing 10 mM Mg(methanesulphonate)2, 10 mM Na2ATP, 10 mM EGTA, 20 mM PIPES (pH=7.0). For the NEM-experiment, it was treated by 1 mM NEM in the relaxing solution for 1 hour and then transferred to a rigor solution containing 45 mM K(methanesulphonate), 10 mM EDTA, 5 mM glucose, 20 units/ml hexokinase, 20 mM PIPES (pH=7.0). For the BDM-experiment, the muscle was put into rigor in a rigor solution containing 40 mM BDM. X-ray diffraction patterns were recorded on imaging plates at BL15A.

Results and Discussion
The NEM-treated muscle did not develop tension on going into rigor, while a small rigor tension developed in the presence of BDM (3-4 % of the normal rigor tension). The change in the diffraction pattern from relaxed to rigor completed within 2-4 hours.

NEM is known to label cystein residues (SH-1, SH-2) on the myosin head (Reisler, 1982). When SH-2 is labelled, the myosin head loses MgATPase completely (Reisler, 1982). BDM also inhibits ATPase but in a way different from NEM because it is not a sulfhydryl reagent (Higuchi & Takemori, 1989).

The diffraction pattern recorded from rigor muscles produced by either of these two methods (Fig.1) showed strong samplings on the 36-, 23-, and 14.5-nm layer-lines. The lateral positions of the samplings coincided with those of equatorial reflections, showing that there is no influence of the superlattice. This suggests that the myosin heads have an extensive freedom in the azimuthal direction when forming the rigor bond.

The present result shows that better-ordered rigor structure can be obtained by reducing the rigor tension. The diffraction pattern thus obtained will be useful in a detailed structure analysis of the rigor cross-bridges.

References
Investigations of interaction between poly(L-lysine) and phosphatidic acid bilayers by high resolution X-ray diffraction

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Introduction

In studies on interaction between watersoluble proteins and membranes, poly(L-lysine) is frequently used as a typical model of peptide, because the poly(L-lysine) binds electrostatically to the surface of negatively-charged lipid bilayers. Poly(L-lysine) became a β-sheet conformation when it bound to phosphatidic acid (PA) bilayers [1]. We have studied the detail interaction mechanism between poly(L-lysine) and PA bilayers by X-ray diffraction [2].

Experimental

Dipalmitoylphoshatidic acid (DPPA) and Dimyristoylphoshatidic acid (DMPA) were obtained from Avanti Polar Lipids, Inc. (Birmingham, AL, USA). Poly(L-lysine) of about 20,000 mol. wt. was obtained from Sigma Chemical Co. (St.Lous, Mo, USA). Samples were prepared as described in Ref.2. X-ray diffraction measurements were carried out at the station 15A. X-ray diffraction patterns were recorded with a PSPC and an imaging plate.

Results and Discussion

The X-ray diffraction pattern for DPPA/poly(L-lysine) are shown in Fig.1. The sharp and symmetric single reflection at 0.419 nm indicates that the hydrocarbon chains are packed in a hexagonal lattice. A weak but sharp peak also appears at 0.476 nm. This reflection corresponds to the periodicity between adjoining polypeptide chains in the β-sheet structure. From these observed lattice constants we calculated the surface areas of a DPPA headgroup and a lysine residue of poly(L-lysine) in DPPA/poly(L-lysine). As a result, the ratio of the number of lysine residues to DPPA headgroups per unit area was found to be greater than unity. This fact suggests that there are no specific site-to-site interaction between lysine residues and PA headgroups.

In order to check this conclusion we have examined temperature dependence of these lattice constants for DMPA/poly(L-lysine) (Fig.2). The lattice constant of poly(L-lysine) in the β-sheet hardly depends on temperature. On the other hand the lattice constant of hydrocarbon chains in DMPA bilayers linearly increases with to temperature. From these results we conclude that the two-dimensional lattice formed by lysine residues of poly(L-lysine) on surface PA bilayers.

References

1) G. Loroché, D. Carrier and M. Pézolet, Biochemistry, 22, 6220 (1988)
Introduction

Adenosine triphosphate synthase (ATPase) is an enzyme that uses transmembrane proton motive force to play a role in ATP synthesis and hydrolysis. It is composed of a proton channel portion, Fo and a catalytic portion, Fi. The enzyme can be purified from various sources, but ATPase from the thermophilic bacterium PS3 (TFoFi) is unique because its catalytic portion (TFi) shows considerable stability against both heat and dissociating agents. Solution structure of the TFi portion, which is composed of five subunits with a stoichiometry of 3a, 3b, γ, δ, and ε, was studied by small-angle X-ray scattering (SAXS) method, giving results that showed these three a and three b subunits were hexagonally arranged with one located below the others on a 6-fold axis.

Most recently, Kagawa et al. demonstrated that a reconstituted a3β3 complex without a γ subunit showed ATPase activity. Also the reconstitute a3β3 complex was found to dissociate into three aβ hetero-dimers in the presence of Mg-AT(D)P by means of both SAXS and gel permeation chromatography. The present study shows the dynamical structure of the complex caused by nucleotide binding from the measurement of time-resolved SAXS of the complex.

Experimental

The experiment was undertaken at BL-15A that installed a SAXS camera. 20 mg/ml, 15 mg/ml and 10 mg/ml of a3β3 complex solutions were rapidly mixed with equal volumes of 2 mM Mg-ATP and Mg-ADP solutions in a stopped-flow cell at 13°C, and successive 95 frames of SAXS spectra were recorded at 1 sec/frame with a 10-PSFC (λ = 1.502 Å, camera length = 2538mm).

Results and Discussion

The SAXS spectra were corrected for background scattering and a time-dependent decrease of incident X-ray, and then subjected to a Guinier analysis to derive the radii of gyration, Rg, and zero-angle intensity, I(0). Fig. 1 shows in (a) and (b) the time courses of the I(0) in the presence of Mg-ATP and Mg-ADP, respectively, similar time courses also being observed in Rg.

In the reaction of the a3β3 complex with Mg-ATP, a plateau phase, which depends on Mg-ATP conc. in its time period, were observed just after the reaction started, then I(0) decreasing gradually. This is strongly indicative of the fact that a steady state of an excited state of the a3β3 complex was maintained during the course of ATP hydrolysis until all the added ATP was converted to ADP. In contrast, when the a3β3 complex was mixed with Mg-ADP, the hexamer dissociated into dimer following a simple dissociation reaction kinetics. These results show the capability of being successfully analyzed by a model based on a nonlinear chemical dynamics, which leads to formation of a dissipative structure.

References

1) Y. Kagawa, Biochim. Biophys. Acta, 265, 297 (1972)
CHANGES IN X-RAY EQUATORIAL DIFFRACTIONS UPON PHOTOLYSIS OF CAGED-ATP IN SKINNED FIBERS FROM RABBIT PSOAS MUSCLE

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Caged compounds are useful for studies on kinetics of rapid reactions in skinned muscle fibers. Combining the technique of the flash photolysis of caged ATP and that of the time-resolved X-ray diffraction, we have been studying the structural changes of the cross-bridges following binding ATP in muscle fibers.

Materials and Methods

Bundles of fresh rabbit psoas muscle fibers were skinned by treatment with 1% Triton X-100 in a relaxing solution. A segment of the bundles (200-400 μm wide, 4 mm long, sarcomere length about 2.3 μm) was placed horizontally on a pedestal (2 mm wide, 5 mm long), one end of the bundle being tied to a force transducer (AE801). A rigor solution (10 mM MgCl₂ with no ATP) was put on the muscle pedestal several times to induce the rigor state in the muscle fibers. Several minutes after the development of the rigor force, the rigor solution was replaced with the caged-ATP solution (2.2 mM NPE-caged ATP, 10 mM MgCl₂, 10 EGTA, 10 DTT, pH 7.0 with 50 PIPES-KOH, γ/2=200 mM with KCl). A light guide from a xenon flash lamp (200 J) was then placed perpendicularly against the pedestal surface, the muscle bundle being sandwiched with the light guide window and the top of the pedestal. A single flash of the lamp (300-370 nm) released ≈0.7 mM ATP from the caged ATP in the muscle fibers. X-ray equatorial reflections were recorded at BL15A using the small-angle camera and the linear X-ray detector(1). The experiments were carried out at room temperature, 24°C.

Results and Discussion

As is shown in Fig. 1, the time course of force relaxation upon photolysis could be divided into 3 phases: (1) the initial, slight but rapid decrease from the rigor level, (2) the following increase with a peak, and (3) the final, slow decrease back to the resting level. The change in the equatorial [1,1] intensity upon photolysis was monotonic decay but seemed to have three phases which corresponded to those in force: At the initial relaxation phase (1) the [1,1] intensity rapidly fell to almost half of that in rigor. At the following phase (2) the intensity stayed at this level while force was developing. At the final, slow relaxation phase (3) it decreased gradually to the resting level in parallel with force.

Our results were similar to those previously reported(2) and consistent with the hypothesis(3) that, despite of the absence of Ca ion, on binding ATP, some of the rigor cross-bridges enter the state of active contraction before coming to the final state of relaxation. At the phase of force development, a small number of cross-bridges are probably still formed, and the observed force development is likely due to activity of these bridges.

References


Fig. 1 Changes in force (smooth curve) and equatorial [1,1] intensity (filled circles with lines) upon photo-release (short vertical bar) of ≈0.7 mM ATP in rabbit psoas muscle fibers at 24°C. The calibration bar for time indicates 50 msec. Sum of 25 runs obtained from 5 preparations. The short horizontal bars attached to the end of the records indicate the force and intensity levels 1 sec after photolysis.
EFFECTS OF HYPER- AND HYPO-THYROIDISM ON CROSS-BRIDGE MOVEMENT IN FERRET PAPILLARY MUSCLE

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It is known that the types of myosin isomers in the heart are changed by thyroid hormone. In ferret ventricular muscle, three myosin isomers exist: V1 with a high, V3 with a low, and V2 with an intermediate ATPase activity. In the euthyroid state of adult ferret V3 is dominant in ferret ventricular muscles. In the hyperthyroid state, the myosin isomer is mostly V1, but V3 is dominant in the hypothyroid state. These changes in myosin isomers make it possible to investigate the relationship between myosin’s biochemical properties and its physiological functions. Thus it is interesting to study how the cross-bridge movement in cardiac muscle is modified by the hyper- and hypo-thyroidism.

For hyperthyroidism, L-thyroxine, 0.3 mg/kg, was injected subcutaneously daily for 2 weeks. To induce hypothyroidism, 0.2 g/l of methimazole was added to the drinking water for 4 weeks. Papillary muscles with a diameter of 200 - 500 μm were dissected from the right ventricle. X-ray diffraction experiments were made at the beam line 15A. The equatorial diffraction patterns were recorded by a linear position sensitive detector with a time resolution of 10 msec.

In normal ferret papillary muscle, the time-to-peak of a twitch was about 150 msec at 30 °C. The X-ray equatorial intensity ratio, I_{1,0}/I_{1,1}, decreased from 2.6 to 1.1 at the peak of the twitch. When the tension and the intensity ratio were normalized by their maximum changes, the change in the intensity ratio was found to precede the tension development by about 10 - 20 msec. In hyperthyroid muscle, the time-to-peak of a twitch decreased to about 110 msec (Fig.1). The change in the intensity ratio preceded that in tension by 10 - 20 msec. In hypothyroid muscle, the time-to-peak was 210 msec (Fig.2). The change in the intensity ratio preceded that in tension by 10 - 20 msec.

The present study shows that the change in the myosin isomer types affects the time courses of both tension development and the equatorial intensity changes. In hyperthyroid muscle, the most dominant myosin isomer type is V1, which has a high ATPase activity, and the time-to-peak of a twitch is faster than that in normal muscle. On the other hand, in hypothyroid muscle, in which V3 is dominant, the tension development was slower and the equatorial intensity ratio also changed more slowly than that in normal muscle.

References


MacKinnon et al., Circ. Res. 63 1080 (1988)
A TWO-DIMENSIONAL X-RAY DIFFRACTION PATTERN FROM A FROG SINGLE SKINNED FIBER

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Single skinned fibers and bundles made of a few skinned fibers have been used in many muscle experiments both with physiological and biochemical purposes. The advantage in the use of skinned fibers over intact muscles is that it is possible to change the cytoplasmic environment. For this reason, it is desirable to use a single fiber rather than whole muscle because the diffusion of ions or molecules may not be complete in thick specimens. Especially when the molecule is consumed in the muscle (for example ATP), it is difficult to keep its concentration at a fixed value throughout the specimen. Thus single skinned fibers have many important applications.

To investigate the structural changes that accompany physiological and biochemical experiments, an X-ray diffraction study on the same sample is necessary. However, the size of a single muscle fiber especially its diameter (40-200 μm) makes X-ray studies difficult. On the small angle camera at BL-15A, the size of the X-ray beam at the sample position is about 8 mm in width and 1 mm in height with a camera length of 2400 mm. This implies a single muscle fiber occupies less than 10% of the cross section of the beam. Nevertheless, using imaging plates, it is possible to record two-dimensional diffraction patterns from single muscle fibers in various conditions.

The figure shown below shows X-ray diffraction patterns from single fibers from frog sartorius muscle in various states. These were obtained by summing 3 to 6 patterns from different fibers. An exposure on each fiber in one state was 30 sec.

The upper-left figure is a pattern from fibers in a relaxing solution. The myosin layer-lines, meridional reflections and the 5.9-nm actin layer-line are visible. The upper-right figure is a pattern from fibers activated at a pCa of 5.5; the fiber developed about 35% of its maximum tension. The myosin layer-lines are markedly weakened. The lower-left one is from fibers developing maximum tension at a pCa of 4.4. The myosin layer-lines almost disappeared but the third (at 1/14.5 nm⁻¹) and sixth (at 1/73 nm⁻¹) are strong and broader in the lateral direction. The intensity changes seen in these diffraction patterns from activated skinned muscle fibers are similar to those observed in intact whole muscles that are electrically stimulated. Indications of rigor patterns, namely enhancement of the first actin layer-line at 1/36 nm⁻¹ and the shift of intensity distribution along the 5.9-nm actin layer-line, were not evident when the ATP-regenerating system was included in the activating solution. Without the regenerating system, a layer-line was observed at 1/36 nm⁻¹.

One disappointing finding in X-ray experiments using single skinned fibers was that the diffraction pattern never recovers to the original relaxed image after activation. The lower-right figure shows the diffraction pattern in relaxing solution after activation at pCa 4.4. The myosin layer lines and meridional reflections are weaker. This is probably the result of mechanical damage due to the contraction: skinned muscle fibers are more fragile than intact fibers because of the loss of sarclemma. Also, the activation may not be uniform throughout the fiber at the early stage of activation, although the fiber was incubated in a relaxing solution containing low concentration of calcium buffer before activation.

Considering the contribution of skinned single muscle fibers in understanding the regulation and mechanism of muscle contraction, the necessity for X-ray diffraction experiments using single fibers is obvious. It is now possible to make X-ray diffraction experiments that have been previously done in skinned whole muscles or bundles of skinned fibers using single muscle fibers. Examples of such experiments are: (1) antibody labeling (2) changing fiber volume using PVP or Dextran (3) changing ionic strength (4) ATP-analogues (5) chemical modifications using sulfhydryl-reagents (6) labeling of actin with myosin subfragment-1. Since most of these experiments do not cause the muscle fiber to contract, the difficulties accompanied with the activation experiment will not be serious.

X-ray diffraction pattern recorded from single skinned fibers of frog sartorius muscle.

The number of patterns summed for upper-left (relax) was 4, 3 for upper-right (pCa 5.5), 5 for lower-left (pCa 4.4) and 4 for lower-right (relax after maximal contraction at pCa 4.4). The four quadrants were averaged.
DISLOCATION MOBILITY FOR BASAL GLIDE IN ICE CLOSE TO THE MELTING TEMPERATURE

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Introduction

There have been many discussions on pre-melting phenomena of the dislocation core in ice. Nye [1] first proposed this idea and Perez et al [2] developed this to explain their data on dislocation velocities which gave a non-linear relationship between applied stresses and the velocities. However, such non-linearity was not found in the recent experimental results [3,4]. Since pre-melting phenomena, if it may occur, must be enhanced in great deal at a temperature approaching to the melting point, we intend the velocity measurements close to the melting temperature in the present study.

Experimental

A small compressive deformation apparatus was used in the present study, and its detail was given in the previous report [5]. Specimen with a dimension of 3x6x25mm were prepared from large single crystals grown by the Czochralski’s method. Dislocation densities prepared were in a range of 10-10 cm^-2. Dislocation motion was observed by the TV topography system [6], and was recorded on a video tape. Displacement of a dislocation was measured by comparing two images taken before and after a deformation using an image memory.

Results and Discussion

Fig.1 shows an example of dislocation motion observed. From these images, dislocation displacements were easily measured. Since a wide distribution of the velocities was observed under a same experimental condition, the velocity data were averaged over several tens dislocations. The average velocities were plotted against shear stresses on basal planes (0001), which were inclined to the compression axis. Non-linear relationship predicted by Perez et al [2] was not found in temperatures between -18.8°C and -0.6°C and in stresses between 0.02 MPa and 0.51 MPa. Then, dislocation mobilities M were calculated from the inclination of the plot assuming a linear relationship.

It was found that the mobilities above -2°C were much higher than those extrapolated from the data at lower temperatures, as shown in Fig.2. The activation energy for the data at the lower temperatures was 0.63eV, which agreed well with our previous experiments [7] but not with those by Shearwood and Whitworth [3]. Although we need more experiments to confirm this, the liquid like core may affect the velocity at subzero temperatures.

Fig.1 A real time observation of the dislocation motion and multiplication in ice.

Fig.2 Temperature dependence of dislocation mobility close to the melting point.
X-RAY RESONANCE EXCHANGE SCATTERING IN FERROMAGNETIC Nd2Fe14B COMPOUND

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INTRODUCTION

X-ray resonance exchange scattering (XRES) is sensitive to orbital magnetic moment and spin polarization near Fermi level. At L2,3-edges of rare-earth elements, it will give information on 5d and 4f electronic states due to the dipole (E1) and quadrupole (E2) transitions. In this report, we present (i) the angle dependence and (ii) the temperature dependence of XRES in the Nd2Fe14B compound.

EXPERIMENTAL

The sample is a single crystal of ferromagnetic Nd2Fe14B which has tetragonal symmetry (P4/2/mmm). The Curie temperature and spin reorientation temperature Tg are 588 K and about 135 K, respectively. The magnetic moments are canted from the c-axis to [110] direction below Tg. The measurements were made on beam line 15B equipped with a Si(220) channel-cut monochromator. The XRES were measured at the Nd L2,3-edges by using a linearly polarized X-ray beam with its polarization vector lying in the scattering plane. The external magnetic field (2.5 kOe) was applied parallel to the [001] easy axis of the magnetization, which is perpendicular to the scattering plane. The effect of XRES is manifested by the asymmetry ratio defined by $R = (I_T - I_U)/(I_T + I_U)$, which is extracted as a function of photon energy, where $I_T$ (U) show the intensity of Bragg reflection for the magnetization parallel (antiparallel) to the cross product $(k \times k')$ of the wave vectors of the incident and scattered beams.

RESULTS AND DISCUSSION

(i) The asymmetry ratio $R$ was measured on three different (hh0) Bragg reflections (h=3,4 and 5) at the Nd L2,3-edges, which are shown in Figs.1(a) and 1(b). The vertical dash-dotted line indicates the Fermi energy, $E_F$. According to the E1 contribution, $R$ should become large in proportion to $\tan^2 \theta$, where $2\theta$ is the scattering angle. However, the results are not proportional to $\tan^2 \theta$. This may be attributed to the polarization factor. The ratio of the scattering intensity from a Nd atom to the total scattering intensity varies with lattice plane. The profile of $R$ at the L2-edge is in qualitative agreement with the spin polarization estimated from the calculated density of states of Nd 5d-bands in Nd2Fe14B. It is considered that $R$ at the L3-edge results from the E1 contribution and reflects the spin polarization of the unoccupied 5d-bands of Nd.

(ii) The asymmetry ratio on (330) and (440) reflections was measured from 20 up to 300 K at the L2-edge. The peak value of $R$ at each temperature is normalized by that at room temperature to compare with Nd magnetic moment obtained by Mossbauer measurements. The R spectra on (330) and (440) are proportional to the Nd magnetic moment at 4g site and at both 4g and 4f sites, respectively. From the difference in temperature dependence of $R$ between (330) and (440), canting angles of Nd magnetic moment below Tg are deduced. Nd magnetic moment at 4f site tilts from the c-axis with the angle $\approx 58^\circ$ at low temperature, however, that at 4g site is along the c-axis even below Tg.

REFERENCES

FORMATION OF VACANCY TYPE DISLOCATION LOOPS IN NEARLY PERFECT A1 CRYSTALS

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It is well known that a lot of dislocation loops are observed in quenched metals by electron microscopy. These loops are formed by a condensation of vacancies supersaturated by rapid quenching. However, in metal crystals with a low dislocation density, vacancy type dislocation loops (V-loop) are formed even by a fairly slow cooling. Such a process is interesting from a standpoint of nucleation mechanism.

In the present work the formation process of V-loop during the cooling from 300°C is investigated by SOR topography. Details of the specimen preparation and the experimental procedures are described in our previous report (No.6 P.201). The temperature of specimen was raised from room temperature to 300°C by several temperature steps, and then cooled down to 240°C at the rate of 80°C/h. After keeping at 240°C for 13 minutes, it was cooled down further at the rate of 20°C/h. Topographs taken at 270°C, 240°C and 230°C are shown in Fig.1. Small V-loops are observed at 270°C, and the loop density increases suddenly around 240°C as seen in Fig.2. The maximum number density of V-loop is 10^6 cm^-2. Considering the original dislocation and the generated dislocation loops as sinks for vacancy, the degree of supersaturation of vacancy was estimated. The degree of supersaturation is about 3 at 240°C. Above experimental results show that vacancy cluster is able to grow in spite of such a low degree of supersaturation. This possibility is proved thermodynamically, too. Therefore it is not able to decide which mechanism, homogeneous nucleation mechanism and heterogeneous one, control the vacancy clustering process in the low concentration at present.

Furthermore, growth rate of a V-loop is estimated from change of the diameter. The growth rate decreased rapidly with time. This may come from the localized decrease in vacancy concentration around V-loops and some repulsion between vacancy and dislocation.
Synchrotron X-ray topographic studies of dislocations in laser crystals
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Dislocations in laser crystals, which can potentially be generated either during crystal growing or subsequent to the growth processing, can lead to undesirable degradation of the laser performances [1]. Therefore, it is very important to be able to clarify the dislocation generation and propagation as well as the dislocation multiplication and reaction so as to effectively control and reduce the dislocation density in such crystals. For this purpose several observation techniques such as optical microscopy, transmission electron microscopy and X-ray topography have been used to reveal the dislocations [2-4].

X-ray topography is in principle a non-destructive technique which is well suited to such studies. However, when conventional radiation is employed, such as in the Lang technique, exposure times can be long, and rates of data requisition can be very low. Typical such systems are designed to accept crystals roughly 3-4 cm in diameter, Lang cameras especially suited for the studies of for example 5 cm or larger diameter wafers can be designed but exposure times will necessarily be increased even further.

Topographic imaging techniques employing area filling white beam synchrotron radiation, on the other hand retain the strain sensitivity of the conventional X-ray topography, while at the same time, by the virtue of the high source brightness require much shorter exposure times, enabling rapid coverage of large crystal volumes [5].

In the present report, we would undertake an investigation into the origin, sort and arrangement of the grown-in dislocations and the post-growth dislocations in Cr:BeAl2O4, Ti:Al2O3 and Nd:Y3Al5O12 laser crystals grown by Czochralski technique (CZ) and Temperature Gradient Technique (TGT). Wafers with different thickness are cut from the bulk crystals so as to make the surface normal of parallel to the growth axis of crystals. The details of the samples are summarized in Table 1. In order to ensure that no surface effects would be recorded, samples were chemically polished in molten borax (900-950°C).

High temperature treatment (HTT) experiments were conducted in the heating unit. The HTT processing involved a temperature holding period of 30 min. at 1600-1800°C. The cooling cycle consisted of 10 min. to 800°C and 20 min. to shutoff.

The synchrotron X-ray topography is a powerful tool for surveying the dislocations, the reliable information of dislocation properties in as-grown crystals can be achieved by analysis of the topographs and can lead us to effectively control the dislocations in crystal growth further.


Table 1 Linear absorption coefficient \( \mu \), thickness \( l \) and orientation \( n \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \mu ) (cm(^{-1}))</th>
<th>( l ) (mm)</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr:BeAl2O4</td>
<td>8.4</td>
<td>0.7</td>
<td>(010),(001)</td>
</tr>
<tr>
<td>Ti:Al2O3</td>
<td>14</td>
<td>0.5</td>
<td>(0001),(1T20)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1TO0),(10T2)</td>
</tr>
<tr>
<td>Nd:Y3Al5O12</td>
<td>335</td>
<td>0.06</td>
<td>(111),(100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(110),(101)</td>
</tr>
</tbody>
</table>
X-RAY TOPOGRAPHS OF DISLOCATIONS IN BENZOPHENONE SINGLE CRYSTALS

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The crystal defects, especially dislocations, in organic crystals influence on their physical properties, similarly as in inorganic crystals. These dislocations are mainly introduced during the crystal growth. Therefore, the understanding of the grown-in dislocations in organic crystals is a very important subject for basic research of their properties. X-ray topography is one of the most powerful methods for characterizing individual dislocations in nearly perfect crystals.

This paper shows the characterization of the grown-in dislocations in Czochralski-grown benzophenone single crystals by X-ray topography.

The conventional Lang method and the white beam synchrotron radiation method are employed for X-ray topography. Particularly, synchrotron radiation method with Laue technique allows the simultaneous recording of a number of X-ray topographs in reflection planes in one exposure on one film.

The experimental results are as follows. The colour of benzophenone crystals changed from transparency to pale pink during synchrotron radiation. No accompanying change in the defect structure was observed. Figure 1(a) and 1(b) show X-ray topographs taken in (121) and (120), respectively. The extinction of images of the predominant grown-in dislocations was observed on the topographs taken in some reflection planes with the (001) zone axis. This indicates that the direction of Burgers vector of the dislocations is a [001] direction. Furthermore, the double images of the predominant grown-in dislocations were found on the topographs in some reflections. The widths of double images were estimated from kinematical theory [1]. Table 1 shows observed and estimated image widths for various reflection planes. The good agreement can be seen between observed and estimated values. From these results, it is concluded that the Burgers vector of the predominant grown-in dislocations is in a [001] direction and is equal to 7.88 Å in magnitude [2].

References


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PRESSURE DEPENDENCE OF SELF-INTERSTITIAL PARAMETERS OF ICE I_
MEASURED BY THE METHOD USING X-RAY TOPOGRAPHY

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Introduction

The purpose of the present study is to clarify pressure dependence of the quantities relating to self-interstitials in ice by the use of a high speed x-ray topography camera [1]. The quantities to be determined are the equilibrium concentration \( C_e \), the diffusion coefficient of the self-interstitials \( D \) and the self-diffusion coefficient \( D_g \). The method used has been developed by the present authors, and has an advantage to determine these quantities independently [2]. From pressure dependence of \( C_e \) and \( D \), the formation volume of the self-interstitial \( V_f \) and the activation volume for migration of the self-interstitial \( V_a \) can be determined which are the most important parameters to understand the atomistic structure of the defects.

Experimental

In order to carry out the XRT observations under pressure, the apparatus shown in Fig.1 was used. Details of the high pressure apparatus were given in the literature [3]. Pressure was automatically kept constant by the motor driven actuator. A single crystal of ice was fixed in a pressure cell together with pressure-transmitting liquid, and the cell was compressed by a specially designed oil actuator with a hollow piston. The whole apparatus is schematically shown in Fig.1. The cell was cooled by blowing cold nitrogen gas evaporated from liquid nitrogen.

In-situ X-ray topographic observations were carried out by an X-ray TV camera using [1010] reflection under pressure up to 200MPa.

Results and Discussion

We have successfully observed a dynamic change of dislocation loops and dipoles caused by a pressure change. Fig.2 shows an example. From such observations, we found that behavior of those dislocation loops was different from that caused by a temperature change. This suggests that we have to take the existence of vacancies into consideration, although we have neglected it so far. By the experiments made by temperature changes, we obtained the preliminary results of \( V_f \) and \( V_a \) as \(-0.26V \) and \(+0.40V \), using a molar volume of ice \( V_m \), respectively.

References


Fig.1 An apparatus for SR X-ray topographic observations under hydrostatic pressure.

Fig.2 Shrinkage and extension of dislocation dipoles caused by sudden decrease in pressure.
INVESTIGATION OF HEAVY ATOMS DISTRIBUTION IN ULTRA-THIN L-B FILMS BY FLUORESCENCE STUDY UNDER X-RAY TOTAL EXTERNAL REFLECTION

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Introduction
Organic layers prepared by the Langmuir-Blodgett technique are the main elements of molecular electronic devices as well as models of biomembranes. In both cases the problem of heavy ion penetration through multilayer is of particular importance. In the present work the distributional arrangement of heavy atoms inside the L-B films has been studied by registering fluorescence yield excited by X-ray evanescent/standing wave fields in L-B film under total external reflection (TER) conditions.

Experimental
The experiment was performed at the beam line 15C with Si (111) crystal used as monochromator. The fluorescent intensity as a function of the glancing angle was measured by Ge solid state detector.

Results and discussion
The first sample under investigation - an L-B film containing 8 monolayers of a stearic acid (4 periods of about 50Å each) deposited on flat hydrophobic Si was inserted twice in the solution of lead stearate PbSt2. In fact there is a finite possibility for Pb ions to penetrate inside an acid film and to occupy the head groups of organic molecules. The problem is how many layers of an L-B film have trapped Pb ions.

Fig.1 shows experimental Pb-fluorescence data and theoretical fluorescence curves, calculated for various distributional arrangement of Pb ions inside the L-B film at 13.5 keV radiation. Curve (1) corresponds to the situation, when Pb ions are only at the head groups of the upper bilayer; curves 2,3,4,5 - at the "heads" of two, three, four and five bilayers, respectively. As can be seen the experimental results are in good agreement with the curve 5, so we conclude that Pb ions penetrate inside a stearic acid film and occupy the "heads" of all the L-B bilayers.

The second sample under investigation - an L-B film containing 12 monolayers of PbSt2 deposited on Si substrate was inserted during 1 hour in the solution of Mn(NO3)2.

In this case L-B bilayers contain heavy ions in the headgroups, but due to the substitution process Mn ions can occupy this positions during the insertion of L-B film into the solution of manganese nitrate.

Pb- and Mn- fluorescence results along the best theoretical fits are shown in fig.2. The Pb-fluorescence curve (fig.2a) is sharply peaked at the critical angle of Si substrate \( \theta_{Si} \), indicating that Pb ions occupy the head groups of all the L-B bilayers. Good agreement between the experimental and theoretical Mn-fluorescence results (fig.2b) is obtained by assuming, that Mn ions are randomly distributed inside the L-B film.

As a result it has been demonstrated how fluorescence measurements under TER can be used to obtain direct information about distributional arrangement of heavy atoms in L-B multilayers.

![Fig.1](image1)

![Fig.2](image2)
High Angular-Resolution Study of X Rays Scattered by Phonons and Transmitted Anomalously through Germanium Crystals

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Introduction
In the Laue geometry study of perfect crystals, black diffraction lines in TDS patterns were observed and these are attributed to dynamical Bragg reflection and absorption of x rays subsequent to TDS. In the theoretical prediction, diffraction lines appears as black, black-white or white lines according to the x-ray absorption quantity. Kashiwase et al. has preliminarily reported the black line in detail using monochromatized synchrotron radiation and a triple-crystal diffractometer. They decisively proved that the intensity peak was caused by the anomalous transmission of TDS consistent with the predicted patterns qualitatively. The purpose of the present proposal is to observe absorption and angular dependences of the anomalous transmission of TDS x rays in absorbing perfect germanium crystals with high angular-resolution in detail.

Experimental
The measurement was performed at room temperature using the 3-crystal diffractometer installed on BL-15C. The first Si(111) monochromator crystal selected the desired energy from continuous synchrotron radiation spectrum. Grooved silicon crystals, made tailless by 5-times-consecutive 220 Bragg reflections, were used as the collimator (analyzer). Perfection of the specimen was ascertained from the FWHM value of the rocking curves.

Comparison and Discussion
The experimental result is compared with a calculation based on the dynamical theory after a correction. To make the calculation simple, we assume that the incident radiation is the monochromatic x ray from a far point source and tailless reflectance function of collimator (analyzer) is convoluted. We had 3 parameters; background, reflectance of collimator (analyzer) and the central angle of the diffraction profile. Figure shows the convoluted theoretical (solid line) and experimental curves (marked).

The result of this study is as follows. (1) The observed angle $\Delta(2\theta)$ of the diffraction peak is equal to the offset angle. (2) The intensity profile of each diffraction peak, which strongly depends on the offset angle, is in good agreement with the calculation. (3) The intensity profile varies from black-white to black as the specimen thickness increases. The thickness dependence in the calculated intensity profile explain the experimental result. (4) The intensity profile of the diffraction peak is asymmetric like as a black-white line. The white part in the black-white intensity profile appears at scattering angle slightly higher than the black part.

Both calculated and experimental profiles are in excellent agreement for any offset angles. Speaking out compulsorily, slight disagreement points can be described: The dependence of the experimental peak intensity on the offset angle is less than that of the calculated (TDS) intensity and the peak width becomes broader than the calculated for the higher offset angle.

References

Figure. Observed (marked) and calculated (solid line) intensity profiles of diffraction peaks across 220 TDS with specimen thickness 0.10mm for offset angles -180°, -90°, -30°, 60° and 120°.
OBSERVATION OF THE X-RAY ENERGY RESPONSE OF
A SILICON SURFACE-BARRIER DETECTOR IN THE 5-20 KEV ENERGY RANGE


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National Laboratory for High Energy Physics, Ibaraki 305

1. Introduction

Developments in controlled thermonuclear fusion research require detailed analyses of plasma electron behavior using x-ray diagnostics (1,2). Recently, x-ray energy responses of silicon surface-barrier (SSB) detectors in the keV energy range were pointed out to be contrary to the commonly held belief that the x-ray sensitivity of an SSB detector is determined by the thickness of the depletion layer (3). This important problem was found using isotopes at 8 and 17.5 keV. Such SSB detectors are widely utilized for the measurements of x rays from plasmas so as to analyze plasma electron physics. Therefore, this ambiguous property of SSB detectors should be clarified for precise x-ray analyses.

In this report, we represent the x-ray response of an SSB detector in the 5-20 keV energy range using fairly strong x-rays from the PF storage ring (see also the SSB response data in the 0.06-0.9 keV region (4)); this intense x-ray beam provides fairly good signal-to-noise ratio data as compared with γ rays from isotopes.

2. Experimental Apparatus

The experiments are carried out at the beam line 15C; x-ray energy (5-20 keV) changes by automated control of a double-crystal Si(111) monochromator. The incident x-rays are monitored by ionization chambers with Kapton windows. N₂ or Ar gas is used as working gas for monitoring the photon beam intensities in the energy range below or exceeding about 10 keV, respectively, with an overlapped energy region each other.

An SSB detector with a depletion layer of 218 µm (the test data value; the nominal catalog value of 100 µm), an aluminum entrance window of 45 µg/cm² (the test data value) and an SiO₂ dead layer of a nominal value of 100 Å, an active area of 300 mm² (Tennelec, CR-300-100-21-CB); the detector is operated in a current mode.

The output currents from the detector and the monitors are processed with 10 s of accumulation so as to obtain good signal-to-noise ratio data. A drastic reduction of higher harmonic stray x-rays is confirmed using an NaI(Tl) detector.

3. Experimental Results

The detection efficiency data of the SSB detector for a unit incident photon flux, \( \eta_{SSB} \), are plotted as dots in Fig. 1. A remarkable feature is summarized as follows: The data points are not fitted by either the thickness of the depletion layer alone or of the silicon wafer alone (3). A new theoretical model, which well fits these detailed data, is based on the collection of charge created by x rays in both of the depletion layer and the silicon substrate (existing behind the depletion layer) which has a thermal charge diffusion length of about 75 µm. This new theoretical model will be reported in a journal (5).

References

(5) T. Cho et al., to be submitted.
CONTRAST FORMATION MECHANISM FOR THE SURFACE DEFECTS IMAGED BY X-RAY
TOPOGRAPHY UNDER THE CONDITION OF SIMULTANEOUS SPECULAR AND BRAGG
REFLECTIONS

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INTRODUCTION

X-ray topography under the specular reflection condition, using the tunability of synchrotron radiation in conjunction with an asymmetric reflection, is effective for imaging a short-range strain field near the surface[3]. Although many kinds of surface defects were observed in the topographs of CZ-silicon, including striation, scratches and layers damaged by mechano-chemical polishing, the contrast formation mechanism still remained unclear. In the present work, the contrast obtained under the specular reflection condition is discussed.

EXPERIMENTAL

The experimental arrangement, shown in Fig.1, was set up on Beam line 15C. The X-rays from synchrotron radiation were monochromatized by symmetric Si 111 reflections of the double-crystal. The sample used in this study was a commercial p-type Si epitaxial layer on Czochralski-grown p-type Si crystal. This sample, which was placed horizontally on a sample holder, was set up to give a 084 asymmetric reflection. As the wavelength of the X-rays was decreased by adjusting the double crystal, the Bragg angle for the 084 reflection became smaller. Consequently, the angle of incidence became smaller. At last, specular reflection occurred simultaneously with Bragg diffraction. The glancing angle to the surface was adjusted near the critical angle of 6c=0.16 degrees, corresponding to a selected wavelength equal approximately to 0.11 nm. The X-ray topographic observations were made under this condition, with nuclear emulsion plates (Ilford L4).

RESULTS AND DISCUSSION

Figure 2 shows a series of X-ray topographs taken at the Bragg peaks for glancing angles near the 6c. The X-ray wavelengths are decreased from Figs.2(a) to (c). The reduction of glancing angle, corresponding to the decrement of the X-ray wavelength, is in steps of ca. 0.05 degrees. The glancing angle for Fig.2(b) corresponds to the 6c. No defect images are observed in Fig.2(a), except for the scratch images originated from the monochromator crystals. In Fig.2(b), on the contrary, the surface defect images are faintly detected, and are clearly detected in Fig.2(c). As the glancing angle becomes small near the 6c, the penetration depth becomes extremely shallow up to a few tens nm, and the intensity of the dynamically diffracted beam becomes much weaker[7]. The detection of the surface defect images, shown in Figs.2(b) and (c), is due to the fact that kinematical diffraction from the surface defects is comparatively enhanced, as a result of the reduction of dynamically diffracted background from the highly perfect bulk crystal.

Other experimental results, which support the contrast formation mechanism described above, are shown in Fig.3. A series of X-ray topographs were taken around the Bragg peak for the glancing angle of Fig.2(b). When the diffraction condition is off-Bragg, the surface defect images are clearly detected, as shown in Figs.3(a) and (c). This is because the dynamical diffraction effect is more suppressed by use of X-rays deviated from the Bragg condition. In this way, the specular reflection arrangement, combined with the off-Bragg geometry, is more effective for suppressing the dynamical diffraction effect, and is suitable for imaging the surface defects sensitively.

REFERENCES

SURFACE-SELECTIVE X-RAY TOPOGRAPIC OBSERVATIONS
OF MECHANO-CHEMICAL POLISHED Si SURFACES

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Introduction

X-ray reflection topography using an asymmetric reflection has a great possibility to be one of the most powerful means of imaging the distribution of surface strains over an entire wafer. However, usual asymmetric reflection topography is not sensitive enough to the small strains near the surface.

In order to measure such shallow damage, therefore, it is necessary to reduce the penetration depth to less than 100 nm. This is accomplished by lowering the glancing angle of the incident x-rays to nearly the critical angle of total reflection. Consequently, extremely asymmetric reflection with a glancing angle of about a few mrad is required.

In the present work, mechano-chemical (MC) polished surfaces of silicon wafers were examined using extremely asymmetric reflections. Furthermore, we numerically calculated the diffracted intensity, specularly reflected intensity and penetration depth as functions of glancing angle based on the theory given by Kishino and Kohra. These calculations explain the image formation mechanism very well.

Experimental

The experimental arrangement, set up on BL-15C, is schematically shown in Fig. 1. Using wavelength tunability in conjunction with proper selection of the diffraction vector, the glancing angle to the sample surface, \( \theta_g \), indicated in Fig. 1, can be set near the critical angle of total reflection.

Two highly perfect FZ Si wafers with a thickness of about 8 mm were chosen for samples. The surface of one sample is parallel to (001) and the other to (111). Both surfaces were etched chemically, and then finished by MC polishing.

In the x-ray topographic observations, the (001) sample was imaged with the 555 reflection, and the (111) sample was imaged with the 008 reflection. The topographs were recorded on a nuclear emulsion plate (Ilford L4), and exposure times were between 1 – 30 minutes.

Results

As an example of the results, Fig. 2(a)–(c) show topographs of the (001) sample, which were taken at the glancing angles of (a) 2.94 mrad, (b) 2.72 mrad and (c) 2.60 mrad, respectively. In Fig. 2(a), no clear defect image is observed. However, as the glancing angle becomes smaller, images with a size of a few hundred \( \mu \)m become visible, as shown in Figs. 2(b) and 2(c). This experiment shows that sensitivity to surface strains is improved by making the glancing angle close to the critical angle of total reflection, \( \theta_g = 2.60 \) mrad.

In order to explain the above results, theoretical explanation of the topographic images was made by using the exact theory given by Kishino and Kohra. This theory takes the effect of specular reflection into account. As a result, it was found that as the wavelength becomes shorter, the angular position of the 555 diffraction peak tends to \( \theta_g \) and the 555 diffraction intensity decreases. Furthermore, the penetration depths at the angular positions of the 555 diffraction peak are (a) 267 nm, (b) 172 nm and (c) 67.3 nm, respectively. Notice that in the case of (c), the penetration depth is only one fourth of that for case (a). This is why the images due to polished strains can be clearly observed in case (c). As the glancing angle of the incident x-rays becomes close to \( \theta_g \), the dynamical diffraction from the perfect region of the matrix crystal decreases. Thus the weak, but constant, kinematical images of surface strains due to MC polishing come to dominate the overall image.

References


Fig. 1 Schematic diagram of the experimental arrangement set up on BL-15C of the Photon Factory.

Fig. 2 Topographs of the Si(001) sample.
RELATIONSHIP BETWEEN OXYGEN CONCENTRATION FLUCTUATION IN SILICON AND LATTICE SPACING VARIATION DETERMINED BY PLANE-WAVE X-RAY TOPOGRAPHY

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Introduction
We have studied the local lattice distortion of growth striations in MCZ silicon by plane-wave x-ray diffraction topography. In our previous work,(1,2) we measured the local change of the lattice spacing (Δd/d) and the misorientation of the lattice plane (Δα) separately with a detection limit of 10⁻⁶ order. This report describes the relationship between the variation in Δd/d along the crystal growth direction and oxygen concentration fluctuation measured by micro FT-IR.

Experimental
The sample used was a 10 mm-thick, [100]-oriented silicon plate parallel to the growth direction [001] which was prepared from an MCZ silicon crystal with an oxygen concentration of 14 x 10¹⁰ atoms/cm³ (JEIDA). Topographs were taken using the plane-wave x-ray optics (2) at intervals of 0.05° at the slope of the low angle side of the 200-diffraction peak on Ilford nuclear plates.

Strain analysis was made on the topographs taken in the two cases where the relative position of the sample towards the direction of the incident x-ray beam was reversed at 180° each other. We applied the method proposed by Kikuta et al.(3) in order to separate the lattice distortion of growth striations into Δd/d and Δα.(1,2).

After the x-ray topographic observation, a 2 mm-thick silicon plate for IR measurement was prepared from the test sample used for the x-ray topography. Micro FT-IR measurement was carried out using a JIR-MICRO 6000 to determine the fluctuation of oxygen concentration (Δ[O]i) along the crystal growth direction.

We assumed that Δd/d = β Δ[O]i where β is a constant parameter. The determination of β was performed by rocking curve measurements for a silicon crystal consisting of both CZ and MCZ regions which have different oxygen concentrations (4). Finally, we compared the variation in Δd/d measured by x-ray topography and the variation in Δd/d calculated from oxygen concentration measured by micro FT-IR.

Result
Figure 1 shows the variation in Δd/d along the crystal growth direction which was determined by plane-wave x-ray topography. The range of Δd/d was within 2 x 10⁻⁶. Rocking curve measurements for a silicon crystal having both CZ and MCZ regions gave a β-value of 5 x 10⁻⁶(4). Figure 2 shows the variation in Δd/d calculated from oxygen concentration which was measured by micro FT-IR. The two graphs shown in Figs. 1 and 2 are in good agreement. This result indicates that oxygen concentration fluctuation in silicon can be determined by x-ray topography, and variation in lattice strain can be determined by micro FT-IR measurements to the contrary.

References
1) I. Maekawa et al., PF Activity Report 1990, p.323.
4) I. Maekawa et al., in preparation for publication.

Fig.1 Variation in Δd/d measured by x-ray topography.
Fig.2 Variation in Δd/d calculated from oxygen concentration fluctuation.
INTRODUCTION

Recently, there has been increasing interest in the chemical state of light elements such as Be, B, C, N, and O doped in semiconductor materials. Although soft X-ray emission (SXE) spectroscopy is an attractive method for chemical state analysis, bulk work has been limited due to the low fluorescence yield of light elements and strong absorption of the emitted X-ray in bulk materials. To solve this problem, we have adopted very bright undulator radiation as the incident excitation beam, and devised a high efficiency spectrometer. In this paper, the optical design of the undulator radiation excited X-ray fluorescence analysis system and its performance test evaluated with boron compounds are described.

OPTICAL DESIGN

The undulator radiation excited X-ray fluorescence analysis system shown in Fig. 1 was designed to achieve high efficiency and was constructed with a simple scanning mechanism. Undulator radiation emitted from a 26-period multipole wiggler/undulator and monochromatized by a 2 m-grazing incidence VUV/soft X-ray monochromator at BL-16U is focussed on a sample with the spot size of 8 mm x 0.2 mm. Fluorescent X-rays emitted from the sample are diffracted by a 2400 - mm~^1 variable spacing grating, and then monochromatized and focused vertically on a straight focal plane. Scanning is carried out simply by straight transfer of a gas-flow proportional counter with a polyester window.

PERFORMANCE TEST

Due to the high photon flux of the incident undulator beam, SXE spectra as well as XANES (X-ray absorption near edge structure) spectra with X-ray fluorescence detection can be measured even by a wavelength dispersive detection system. Figure 2 shows the SXE and XANES spectra for the following boron compounds: B, B4C, BN, and B2O3. The first harmonic peak of undulator radiation was fixed at 215 eV so as to maximize the background subtracted B-Ka fluorescent X-ray signal. Energy resolution of the fluorescent X-rays was tuned to less than 3 eV with a 500-μm slit in the SXE measurements. The incident undulator beam was adjusted to a resolution of 0.5 eV with a 100-μm slit for the XANES measurements. In the XES spectra, chemical shifts of B-Ko emission line (B(2p)→B(1s~1)) were observed, and BN and B2O3 satellite peaks were clearly separated from the main peak. In the XANES spectra, chemical shifts of the K-absorption edge were also clearly observed. These spectra indicate the different chemical states among the boron compounds. These results are good agreement with the results previously published by D. M. Koffman et al.

In conclusion, the undulator excited X-ray fluorescence analysis system capable of chemical state analysis has been performed.

INTRODUCTION

Recently, high-concentration doping of light elements such as boron, carbon, and nitrogen in semiconductor materials have been studied. Diffusion of boron doped in silicon or silicon oxide has received interest in the fabrication of submicrometer complementary metal-oxide-semiconductor (CMOS) with very large scale integrations (VLSIs). Thus chemical state analysis of the boron atoms is necessary to analyze the chemical state of light elements, an undulator radiation excited X-ray fluorescence analysis system was developed. Soft X-ray emission (SXE) and X-ray absorption near edge structure (XANES) spectra with wavelength dispersion detection of boron doped in Si(100) were measured. In this paper, the SXE and XANES spectra of B-Kα fluorescent X-rays are described, and the chemical bonding state of the boron atoms is discussed.

EXPERIMENTAL

Boron fluoride ions (BF$_2^+$) were implanted into Si(100). Considering the escape depth and counting rate of B-Kα fluorescent X-rays, injection energy and dose of BF$_2^+$ ions were tuned to be 18 keV and 2.3 x 10$^{15}$ ions/cm$^2$, respectively. A depth profile of B and F atoms in this sample measured by secondary ion mass spectroscopy (SIMS) is shown in Fig. 1. Before the SIMS measurement, a 200 Å-thick hydrogenated amorphous silicon (a-Si:H) film was deposited on the sample to avoid secondary ion yield surface effects on the Si surface. Boron atoms with a maximum concentration of about 8 x 10$^{20}$ atoms/cm$^3$ were implanted at an average depth of 160 Å. The depth distribution of fluorine atoms was similar because of the low-energy injection. Samples of non-doped Si(100) and sintered boron pellets were also prepared as references. Undulator radiation excited X-ray fluorescence measurements were carried out at the 26-period multipole wiggler/undulator BL-16U beamline. The first harmonic peak of the incident undulator beam was tuned at 215 eV so as to maximize the background subtracted B-Kα fluorescent X-ray signal. In the SXE measurements, the sample was exposed to a quasi-monochromatic undulator beam and the X-ray fluorescence spectrometer was scanned with a 500-μm slit. In the XANES measurements, the X-ray fluorescence spectrometer was fixed at the zeroth-order-light position with the undulator beam monochromatized by a 2-m grazing incidence VUV/soft X-ray monochromator.

RESULTS AND DISCUSSION

Figure 2 shows the SXE and XANES spectra of the B-doped Si(100), the sintered boron pellet and non-doped Si(100). The SXE and XANES spectral shapes were nearly the same for B and B-doped in Si(100). If B-F bonds were formed in Si(100), chemical shifts and spectral shape changes would be observed in both the SXE and XANES spectra. Therefore, it is estimated that boron does not bond with fluorine and the chemical state of boron atoms in Si(100) is nearly metallic, despite the high concentration of fluorine atoms (1 x 10$^{21}$ atoms/cm$^3$) in Si. This result is in agreement with the LSS (Lindhard-Scharff-Schiott) theory.

CHARACTERIZATION OF THIN FILMS WITH X-RAY GRAZING INCIDENCE DIFFRACTION

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Introduction

X-ray grazing incidence diffraction is very useful for characterization of crystalline structure of thin films. There are two different scattering geometries which allow to observe the Bragg diffraction under the total reflection. One is the geometry at which the diffraction vector is out of the incident plane between the incident and reflect x-ray, and one can detects diffractions for lattice planes perpendicular to the surface. The other is the geometry at which the diffraction vector is in the incident plane, and one can detects diffractions for lattice planes inclined to the surface. Then, the latter requires free choice of the x-ray wave length in order to vary the incident angle at the Bragg condition. And, this technique can be applied to x-ray reflection topography.

In this article, we will focus on the x-ray grazing incidence diffraction with the latter geometry, and report primary data for a Si(001) wafer and GaAs thin layers under the grazing incidence.

Experimental

Experiments were performed at BL-17A. X-ray wave length is selected with a Si(111) double crystal monochrometer. The goniometer with the horizontal rotating axis is used, and the incident angle at the Bragg condition is controlled by varying x-ray wave length. GaAs thin layers were grown on Si substrates by atomic layer epitaxial growth technique.

Results

Rocking curves for (224), (404), (333), and (555) of a Si(001) crystal have been measured under the grazing incidence in a function of x-ray wave length. The results for the (224) are shown in fig.1. When x-ray wave length decreases, the incident angle at the Bragg diffraction approaches gradually to the critical angle, the profile becomes to be antisymmetric and the full width at the half maximun (FWHM) increases, and the peak intensity decreases rapidly. In Fig.1, the solid line shows the extrapolation from results in a region far from the critical angle according with the relation of \(2\sin\theta = \frac{\lambda}{\lambda'}\). The similar dependences were also observed for the other planes of (404), (333), and (555).

The ultra-thin GaAs layer (20 mono-layers) on a Si substrate was also measured, and the \(\theta-2\theta\) diffraction curves for (224) are shown in Fig.2. The peak of GaAs is clearly observed near the total reflection of Si. When x-ray wave length decreases, the peak of GaAs shifts and reaches the critical angle, while that of Si shifts linearly since far from the critical angle. However, the profiles of GaAs are complicated and broad in contrast to the results for a Si wafer. It is well known that defects such as dislocations and twins can easily generate in GaAs layers on Si substrate because of large lattice mismatch. So, the broad diffraction profiles of GaAs may be caused by defects.

Reflection topography has been tried for the (224) diffraction of GaAs layers. For the GaAs layer with 100 mono-layers, exposure for 30 minutes was needed, but the intensity for the GaAs layer with 20 mono-layers was too weak. In addition, there were many extra line-like images coursed by optics in this beam line. Therefore, a few improvements are required for obtaining good topographic images for thin films.

References

X-RAY ABSORPTION FINE STRUCTURE STUDY OF Ni-Fe
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INTRODUCTION
In the decade, since double-layered Co-Cr/Ni-Fe media were developed for perpendicular magnetic recording, Co-Cr films have been widely studied, but details on the underlying Ni-Fe (~80 wt. % Ni)-on-glass substrate remain to be clarified, despite the influence their structures may have on the magnetic properties in the system. In the present report, our purpose is to clarify exactly what XAFS measurement can clarify about a solid solution with a small disorder such a Ni-Fe film.

EXPERIMENTAL PROCEDURE
5-μm Ni-Fe film, leave from the glass substrates, was put between two pieces of Scotch tapes and 2 to 4 sheets of such tape and film were stacked to get enough XAFS signal above the absorption edge. The resulting sample had μ = 2 above the Ni K-edge and =1.3 above the Fe K-edge. A spectrum of Scotch tape had particularly no glitches during a photon energy range of 6500 to 9500 eV. X-ray absorption spectra were taken at both Ni and Fe K-edge in the transmission mode on an XAFS spectrometer at BL-17A in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PP). The XAFS facility is equipped with a Si(111) double-crystal monochromator in nondispersive (1,1) parallel mode at pressures around 10^{-7} Torr. The finest obtainable angular step of the monochromator is 10^{-5}° for both crystals and their rotations are monitored by a laser rotary encoder with an angular resolution of 2x10^{-5}°. The beam size at the sample position was 5 mm wide and 2 mm high. A typical incident photon flux of 5x10^{20} photons/s with an energy resolution of less than 2 eV was obtained at 2.5 GeV and 300-350 mA in the current storage ring. The influence of higher energy X-ray harmonics was eliminated by slightly detuning the second crystal in obtaining the Fe K-edge spectra.

RESULTS AND DATA ANALYSIS
Extended X-ray absorption fine structure (EXAFS)

The Fourier transforms of k^{2}χ(k) into r-space are shown in Figs. 1 (a) and 1 (b). The program for extracting the structural information from the EXAFS function is developed on a workstation. The results of the best fits based on theory (BFBT) for relevant parameters {ΔR_0, r_j, B_j, G_j} are tabulated in Table 1. The amplitude function, F_j(k, π) and phase shift φ_j(k) function employed here are the theoretical curves tabulated by Mckale et al.\(^2\) For each k value in the experimental EXAFS function, k^{2}χ(k) (φ_j(k) and F_j(k, π), were interpolated from associated with that parameter.\(^1\) In curve fitting procedure, the additional fits with one parameter constrained at various values around its optimal position, then the points where the resulting fit has a value of R^2, R-factor in the crystallography, double the optimal value are taken as the end points for the error bars in the atomic number of components. The BFBT interatomic distances were further refined by the fine adjustment based on models (FABM) technique\(^3\). ΔE_0 vs Δr correlation curves, ΔE_0=Δr=α_1Δr, can be used to improve the accuracy of the EXAFS structural determination with a good model. Here, we used pure nickel. The results of the FABM technique are tabulated in Table 2. The FABM-refined data for the Fe K-edge are in good agreement with those for the Ni K-edge, showing that experimental data and its analysis are sufficiently precise.

REFERENCES

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X = absorber; Y = backscatterer

* Calculated according to ΔE = (ΔE_0 - ΔE_0) / μ, where ΔE_0 was the characteristic threshold energy difference, 10.916 eV.
** This value is crystallographic.
THERMAL STABILITY OF IMPLANTED ARSENIC ATOMS IN SILICON BY FLUORESCENCE XAFS TECHNIQUE

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INTRODUCTION

Ion implantation is one of the most popular techniques of impurity doping for fabrication of electronic devices and integral circuits. As implanted into Si acts as a donor. Depth profile of As concentration is well investigated after thermal treatment by secondary ion mass spectroscopy (SIMS) and other electronic measurements. But few works have been done on the change of the structure around As atoms during thermal treatment. Now we report here the structure and the changes of environment around As atoms under some thermal treatment condition by fluorescence X-ray absorption fine structure (XAFS) technique.

EXPERIMENT

Specimens were prepared from p-type boron-doped Si wafers with resistivity of approximately 10 Ωcm. As⁺ was implanted at room temperature with a dose level of 5 × 10¹⁶ cm⁻², and implanted energy was 70 KeV. In order to investigate thermal stability of As atoms, specimens were annealed at 800° and 1000°C for 30 minutes. This experiment was carried out at beam line 17A. A Si(111) double crystal monochromator was used and fluorescence XAFS was measured between 500 eV lower and 1000 eV higher than As K edge at room temperature. The incident X-ray intensities were measured by the ionization chamber filled with N₂ gas of atmospheric pressure. The fluorescence yield was measured by a Ge solid state detector.

RESULTS

Figure 1 shows the XANES spectra of As implanted into Si. Figure 1-(a), (b) and (c) are the XANES spectra of as-implanted specimen, specimen annealed at 800°C for 30 minutes and specimen annealed at 1000°C for 30 minutes, respectively. In the region of near absorption edge, large difference of XAFS spectra is observed between specimens before and after annealing. Before annealing, there is no shoulder peaks around 11870 eV. After annealing, it is observed. Tyliszczak et al. studied XAFS spectrum of As doped Si grown by MBE method. Their result was that the shoulder peak was observed in XANES spectra of As which dominated substitutional lattice site. Therefore, our experimental result is interpreted that As atoms are in random sites in as-implanted specimen and dominate substitutional sites after annealing.

The analysis of EXAFS spectra is now in progress.

Reference

1) T. Tyliszczak, A.P. Hitchcock and T.E. Jackman

Figure 1. XANES spectra of 5 × 10¹⁶ cm⁻² As implanted specimens; (a) as-implanted, (b) after 800°C annealed for 30 minutes and (c) after 1000°C annealed for 30 minutes.
Characterization of Photo-Excited Cleaning of a Silicon Surface Using Total-Reflection X-ray Fluorescence (TRXRF)

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INTRODUCTION

The LSI density of components in integrated circuits is becoming higher and higher. It is well known that contamination by heavy metals causes threshold voltage instability and increases the leakage current through junctions. For this reason, highly effective cleaning techniques are required for Si wafer surfaces. We investigated more effective cleaning and characterization techniques for silicon wafer contamination. Furthermore, as integrated LSI circuits become denser, lower levels of contamination will be required.

In this report contains the results of UV photo-excited cleaning of silicon wafer surfaces in a Cl₂ atmosphere characterized with TRXRF.

EXPERIMENTAL SYSTEM

The experiments were performed at BL-17A, with a Si(111) double crystal monochromator. We chose an X-ray energy of 12.4 keV for excitation. Fig. 1 shows the experimental system. The beam size was 0.01 mm (high) x 20 mm (wide). The sample was mounted on rise-fall and tilt stages with stepper motors. We monitored reflected intensity using ionization chambers, as a function of the glancing angle. We detected X-ray fluorescence using a pure-Ga solid state detector (SSD), measured in air.

EXPERIMENTAL SAMPLES

Experimental samples were four-inch silicon wafers. We used wet cleaned the sample surfaces and then contaminated them by immersion in an ammonium solution (NH₄OH-H₂O₂-H₂O) containing iron. The iron concentration in the contaminating ammonium solution was 50 ppb. We measured the iron contamination of wafers using flameless atomic absorption spectrometry (AAS). AAS showed a contamination density of 5 x 10¹² atoms/cm². After contamination, samples were cleaned by UV light excitation in a Cl₂ atmosphere for 30 sec and 60 sec.

RESULTS

The intensity of Fe-Kα fluorescence from a 5 x 10¹² atoms/cm² contaminated sample, and X-rays reflected were measured as a function of glancing angle. This is shown in Fig. 2. Our experiments showed that the maximum intensity of Fe-Kα fluorescence occurs at a glancing angle of 0.11 degrees. After this, the glancing angle was fixed at 0.11 degrees. In general, if the surface is contaminated, the intensity of fluorescence is maximum at the critical angle. The critical angle for silicon was calculated as 0.14 degree for a wavelength of 0.1 nm. We compared our results with theory.

We used water samples that we photo-excited cleaned for 30 sec and 60 sec. The result of a quantitative analysis, using several UV photo-excited cleaned times was a contamination density of 1/10 (5 x 10¹¹ atoms/cm²) after cleaning for 30 sec, and 1/100 (5 x 10¹⁰ atoms/cm²) after cleaning for 60 sec. We can conclude that UV photo-excited cleaning in a Cl₂ atmosphere is highly effective in removing iron contamination.

Measurements of contamination using TRXRF are highly sensitive and able to provide a surface analysis, whether made in air or not in air.

REFERENCES

In-Situ Auger Electron Analysis of Silicon and Aluminum
Irradiated with Broadband Synchrotron Radiation

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We studied Auger electron spectroscopy (AES) for samples under broadband synchrotron radiation (SR).

Figure 1 shows experimental setup and typical in-situ SR-AES spectra observed for Si and Al samples. Broadband SR (1-7A) was used to illuminate samples at BL-17 beam line, and a CMA was used to analyze the generated Auger electrons.

The high-energy peaks of the KLL transition are far more intense than the low-energy (LVV transition) peaks. The two separate KLL profiles seem to include several oxide peaks. These peaks have sufficient resolution to allow Si and Al compositions to be monitored. The resolution of the Auger LVV transition is so superior that oxides can be distinguished from pure atoms.

We also used electron beam (EB) AES to compare the excitation efficiency of core electrons with SR. Figure 2 shows AES peaks for Si and Al samples excited by typical electron energies within the SR spectrum (3 and 10 keV). It should be noted that SR is overwhelmingly efficient for exciting inner-shell electrons. This is the important feature of material modifications with the above SR-energy spectrum.

Figure 3 shows relative peak intensities for Si in a 10^-3 Torr hydrogen as a function of SR-exposure time. Carbon and oxygen reduction on the surface was monitored in real time. The high-energy KLL peaks were not influenced much by surface contaminants such as carbon and oxygen, and thus can be inner material indicators, whereas the low-energy LVV peaks were sensitive enough to monitor surface contaminants. This contrast must reflect the escape-depth differences for both energies. For the Al surface, the Al2O3 layer was also assured to be slightly etched in partial SF6 pressure. However, we found SR-exposure with the strong KLL transition to be more suitable for solid-phase material modifications such as photon annealing, rather than surface cleaning or etching.

In summary, SR-AES technology is valuable for in-situ monitoring of compositions and chemicals as well as of inner-shell electron excitation strength during material modifications.

Estimation of SR power at BL-17B for x-ray lithography
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INTRODUCTION

The possibility of low energy x-ray lithography has been shown using synchrotron radiation (SR) in a photon energy range of 500 to 1000 eV at station BL-17B.

We estimated SR power by calculating the reflectivity and focusing gain of a Pt-coated toroidal mirror and compared it with previous results from x-ray lithography.

SR POWER CALCULATION

A Pt-coated toroidal mirror is installed at the beamline to converge the SR beam. We must account for reflectivity reduction due to surface roughness and use a ray-tracing technique to calculate power distribution.

The rms surface roughness of a vacuum-evaporated mirror is estimated to be a few nanometers and the energy range of our interest (500 to 1000 eV) is near the critical energy of the mirror (700 eV at a glancing angle of 87 mrad). Because of this, SR power spectrum is significantly affected by surface roughness. We used the graded index model to calculate the reflectivity.

To calculate the SR power distribution accurately, we developed a ray-tracing program, in which the electron-beam size, divergence, and the asymmetry parameters are simulated. The parameters used in the ray-tracing calculation are listed in Table 1.

RESULTS

Figure 1(a) shows the absorbed power in the CMR resist and mask contrasts as a function of the Be-filter thickness. A 2-μm-thick SiN was used for a mask membrane. Figure 1(b) shows the absorbed power and mask contrasts as a function of the SiC-membrane thickness. A 3.7-μm-thick Be was used for a filter. To derive experimental values for the absorbed power, we used a CMR resist sensitivity of 700 J/cm² which gives a dissolution rate of 250 nm/min (MIBK 2 min, 23°C).

Assuming the surface roughness of 4.8 nm gives good fit of the calculated power to the experimental power. Though this value is slightly larger than our previous measurement for a Pt layer on a fused quartz substrate, it seems possible for a mirror substrate of SiC.

Calculated mask contrasts with a Ta absorber thickness of 170 nm almost agreed with experimental values. This value is thinner than the nominal thickness (200 nm) measured using SEM. The difference can be explained by measurement error or density reduction of the Ta film deposited by sputtering.

In summary, we were able to explain our experimental results with a few assumptions and calculated the SR power spectra and power distributions at BL-17B more accurately. The calculated power spectra with the surface roughness of 4.8 nm is shown in Fig. 2. The calculated power distribution that passes through a 3.7-μm-thick Be filter 28 m from the source is shown in Fig. 3.

Table 1. Parameters used for ray-tracing calculation.

Source parameters:

| Source parameters: | $σ_x$ = 0.48 mm, $σ_y^m = 0.30$ mrad, $γ_x = -0.37$ | $σ_y = 0.22$ mm, $σ_y^m = 0.015$ mrad, $γ_y = -0.09$ |

Acceptance of SR beam: 8 mrad (horizontal) × 1 mrad (vertical)
Distance between source and mirror: 12 m
Radii of the toroidal mirror: 1126 mm × 155590 mm
Glancing angle: 87 mrad
Aperture of differential pumping system
Distance between source and aperture: 26 m
Size: 2 × 2 mm²
Wafer position: 28 m

REFERENCES


Figure 1. Absorbed power in the CMR resist and mask contrasts. Lines show calculated values and symbols show experimental values.

Figure 2. Calculated spectra at BL-17B.

Figure 3. Calculated power distribution.
In-situ measurement of photo-emitted current during SR-assisted etching of SiO₂ film on silicon

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Introduction
Silicon dioxide (SiO₂) film is a material widely used in semiconductor fabrication process. Concerning SiO₂ etching, Akazawa et al. have reported photostimulated evaporation by synchrotron radiation (SR)\(^1\). In SR-assisted etching of SiO₂ film it is important to develop in-situ endpoint detection methods as the etching rate is thought to vary according to the SR-irradiation parameters, such as storage current, electron (positron) energy, photon intensity, and photon energy.

Experiment
Experiments were performed at BL-17B at the Photon Factory. SR with wavelengths between 1 and 100nm was irradiated to the substrate with a photo intensity of about \(10^{16}\) photons/cm\(^2\)/s. The substrates were thermally oxidized silicon wafers (SiO₂ thickness: 10, 20, and 50nm). In order to measure a photo-emitted current from the substrate surface, the substrate was set on a sample holder which was electrically isolated from the vacuum chamber. The pressure during exposure was about \(10^{-9}\) Torr.

Results and discussions
Figure 1 shows the variation of photo-emitted current from SiO₂ film on Si at 645°C. The photo-emitted current for each exposure was normalized by the storage ring current and initial photo-emitted current. With the increase of the SR exposure, photo-emitted current showed three characteristic regions as follows.

1) rapid decrease at the initial stage of exposure
2) almost constant current region
3) gradual decrease starting at the end of region 2

Region 1 could be related to the change in surface conditions such as adsorbed water or hydrocarbon. If we define the SR exposure at the end of region 2 as a critical exposure (indicated vertical arrows in Fig. 1), these exposures become about 100, 200, and 560A·s for the SiO₂ thickness of 10, 20, and 50nm, respectively, showing almost proportional relation between the critical exposure and SiO₂ thickness. The critical exposure decreased as the substrate temperature increased, which was the same as the etching rate dependence on the substrate temperature. After these experiments, SiO₂ film at the irradiated region was completely removed. From the experimental results, we presume that critical exposure may correspond to the end point of SiO₂ etching. The decrease in photo-emitted current at the critical exposure would be explained by the larger absorption coefficient of SiO₂ than that of Si for E<100eV.

Figure 2 compares the substrate temperature dependence of the measured and predicted etched SiO₂ depth at the SR exposure of 370A·s. The predicted values were calculated using the assumption that SiO₂ etching was finished at the critical exposure. Predicted etched depths agree well with the measured depths.

In conclusion, we found that the photo-emitted current from SiO₂ film on Si showed a characteristic change during SR-assisted SiO₂ etching. Therefore, in-situ measurement of photo-emitted current can be useful method to detect the endpoint of SiO₂ etching.

SR-induced surface deoxidation of SiO₂ film at room temperature

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Introduction
Synchrotron radiation (SR) is a promising light source for low-temperature semiconductor fabrication process. It seems important to investigate SR irradiation effects onto SiO₂ film because SiO₂ is the insulator widely used in silicon processes. Furthermore, the mechanism of photostimulated evaporation¹ of SiO₂ film could be studied by analyzing the qualities of the film irradiated at room temperature.

Experiment
The experiments were performed at BL-17B at the Photon Factory. The substrates were thermally oxidized silicon wafers (SiO₂ thickness: 88nm). White SR light (λ>1nm) was perpendicularly irradiated to the substrate at room temperature (without intentional heating). The pressure during exposure was less than 2x10⁻⁶Torr. The SR exposure was varied from 0 to 2015A-s. Some samples were annealed at 850°C for 22min. in vacuum (in the order of 10⁻⁶Torr) after SR irradiation. Samples were analyzed by angle-resolved X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed around Si 2p photoelectron spectra (binding energy~100eV).

Results and discussions
Figure 1 shows XPS spectra of various SR exposures. In these spectra, signal of oxidized Si (E~104eV) and elemental Si (E~100eV) were observed. At the SR exposure as low as 123A-s, the signal of elemental Si was not observed. So the spectrum was the same as non-irradiated SiO₂ film surface. At SR exposures more than 534A-s, the signals of elemental Si were observed. The appearance of elemental Si was caused by the following processes.
1)Bond-breaking of Si-O network by SR irradiation
2)Desorption of oxygen atoms from SiO₂ surface (deoxidation)
3)Formation of Si-Si bonds at the irradiated surface
The amount of deoxidation saturated at a SR exposure around 1000A-s. From the take-off angle dependence of the XPS spectra, the deoxidized thickness was estimated to be about 2nm. The saturation in the deoxidation process and thin deoxidized thickness are due to the small escape depth of oxygen atom from the SiO₂ film at room temperature.

Figure 2 compares an XPS spectrum of as-irradiated sample with that of post-annealed (at 850°C for 22min. in the same chamber as SR irradiation) sample. SR exposure was 534A-s. The signal of elemental Si observed in as-irradiated one disappeared after the post-annealing. SiO₂ thickness at SR irradiated region decreased about 2nm after the post-annealing. This decrease in thickness was the same as the value obtained by take-off angle dependence of XPS measurements. Deoxidized silicon rich layer was etched by the post-annealing.

In conclusion, we found that the SiO₂ film surface is deoxidized by SR exposure at room temperature and the deoxidized layer was etched by the post-annealing. These experimental results will give useful information on the mechanism of photostimulated evaporation¹ of SiO₂ film.

SR-excited low-temperature silicon epitaxy using Si$_2$H$_6$/H$_2$ mixture

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Introduction
In silicon film growth, hydrogen coverage of the growing surface is an important factor as the surface mobilities of adatoms are expected to increase on the hydrogen-terminated surface$^{1,2}$. Therefore, hydrogen dilution of the source gas is an interesting parameter especially in low-temperature silicon epitaxy.

Experiment
Experiments were performed at BL-17B at the Photon Factory. The substrates were Si(100) cleaned by the conventional wet treatment. Before growing silicon film, the substrates were heated at 800°C in vacuum until Si(100) 2x1 surfaces appeared. Si$_2$H$_6$ (5%) and H$_2$ (95%) mixture was used as a source gas. The partial pressure of Si$_2$H$_6$ was kept at 10$^{-3}$Torr. White SR light (λ>$\lambda_{nm}$) was perpendicularly irradiated on the substrate. SR exposure was 2000A·s. The substrate temperature was varied from room temperature (without heating) to 500°C. Temperature increase by SR irradiation was estimated to be 180°C when the heater was off and 40°C when the temperature was set at 400°C. In this report, we use the set temperature, excluding the effect of temperature rise by SR irradiation.

Results and discussions
Figure 1 shows the substrate temperature dependence of the deposited film thickness. From 300 to 500°C, the grown film thickness was thin (about 6 nm) and there was no difference between the irradiated and non-irradiated regions. At low substrate temperature (below 300°C), the grown film thickness increased with the decrease of substrate temperature. This tendency was the same for both irradiated and non-irradiated regions. Thermal decomposition of Si$_2$H$_6$ gas doesn’t occur at this low temperature region and SR irradiation efficiently decomposes the gas to deposit film. This temperature dependence at low-temperature region is probably related to the adsorption characteristics of the source gas and/or radical generated by SR irradiation.

Below 300°C, the film thickness of the irradiated region was several factors larger than that of the non-irradiated region. This means that the direct photo-activation of the substrate and/or adsorbed species is effective for the film deposition. In the non-irradiated region, however, a 10-20 nm thick silicon film could be grown by lowering the substrate temperature. In this case, gas-phase activation of Si$_2$H$_6$ molecules and diffusion of photo generated radicals seem to be effective.

Figure 2 shows the RHEED patterns after the silicon film growth. Clear spots were observed for substrate temperatures from 100 to 500°C. For the room temperature growth, a ring pattern was observed, showing the grown film was polycrystal. Above 300°C, reconstructed 2x1 pattern was observed. Crystallinity in this temperature region was fairly good and was of the same grade as the single-crystal substrate. When the substrate temperature was lowered toward 100°C, the sharpness of the pattern and 2x1 reconstruction were weakened.

In conclusion, we have succeeded to grow epitaxial silicon film at as low as 100°C. Adsorption of source gas and/or photo generated radicals on the growing surface and their activation by SR seem to be important.

Infrared Spectroscopic Study of Silicon Dioxide Film Modified by SR Irradiation
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Introduction
Soft X-ray irradiation induces the excitation of core electrons of materials, in which the irradiated materials are highly excited compared to conventional light sources having longer wavelength. Therefore, Synchrotron Radiation (SR) seems to be efficient light source for low-temperature semiconductor process. Investigation of qualities of SiO₂ film irradiated by SR gives us fundamental information for the application in semiconductor processes.

Experiments
The experiments were performed at BL-17B. The SR beam from the storage ring was reflected by a Pt coated toroidal mirror with the incidence angle of 85°. The reflected beam was continuous light from UV to soft-Xray region, and the maximum energy was about 1 keV. The total photon flux was about \(10^{15}\) photons/cm²/s. The samples were thermally oxidized silicon wafers with oxide thickness of 90 nm. The SR beam perpendicularly irradiated the samples in UHV (below \(10^{-6}\) Pa) without heating. During irradiation, the temperature of samples went up to 185°C. Some samples were annealed at 400-850°C after irradiation in UHV. The irradiated films were analyzed by wet etching properties using HF solution (1:20) and IR absorption measurements.

Results and discussion
Figure 1 shows the wet etching properties of irradiated samples. The gradient of the film thickness curve equals the etch rate. The etch rate increase as the SR irradiation time increases. It is noticeable that the etch rates are almost constant throughout the film thickness for each exposure. This means SiO₂ film quality is changed uniformly in depth. Considering the absorption coefficient of light by SiO₂, the changes in the films are caused through the excitation of Si-2p and/or O-1s electrons.

Detail change in film qualities of SR irradiated SiO₂ film is analyzed by infrared absorption spectroscopy. Figure 2 shows the Si-O stretching vibration absorption spectra. Stoichiometric SiO₂ has a stretching absorption band near 1075 cm⁻¹. The Si-O stretching absorption peak shifts to a lower wavenumber with increasing exposure time. It is known that the similar phenomena occur when the oxide stoichiometry becomes oxygen deficient. The Si-O stretching absorption peak shifts to a lower wavenumber with increasing exposure time. It is known that the similar phenomena occur when the oxide stoichiometry becomes oxygen deficient. Figure 2 also shows that the peak intensity decreases with exposure. Because the film thickness did not change after SR irradiation, decrease in the peak intensity means a decrease of Si-O bonds in the films. These structure changes in SiO₂ may be induced by the ionization of atoms followed by the bond breaking and the atoms displacements.

Figure 3 shows IR spectra of annealed samples. The shifted peak and decreased peak intensities recovered completely after annealing at 850°C for 22 min. It is known that dangling bonds induced by irradiation in SiO₂ almost disappear by 600°C annealing. The SR irradiation mainly creates defects which do not consist of dangling bond but include atoms displacements. As the annealing out of that changes needs a long time and a high temperature, the atoms displacement caused by the irradiation may be large.

In conclusion, the 90 nm thick thermally grown silicon dioxide is changed uniformly throughout the film thickness by SR irradiation. IR absorption study reveal that the changes are caused by Si-O bonds breaking following the excitation of core electrons of Si-2p or O-1s. The defects introduced by irradiation do not mainly consist of dangling bonds but include atoms displacements.

NEW TURBOMOLECULAR PUMP FOR PRESSURE CONTROL IN BEAMLNE

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1. Introduction
In the medium-wavelength (λp=1-2nm) X-ray lithography, the thickness of the mask absorber can be reduced due to a higher absorption coefficient, so that the absorber patterns can be defined accurately by dry etching and the distortion of the mask membrane can be reduced. The absorption coefficient of the Be window, however, increases for the medium wavelength, too. So, the isolation between the storage ring in 10^-9 Pa and the exposure station that is filled with atmospheric He to cool the mask is an essential subject. We have modified a conventional turbomolecular pump to allow the medium wavelength SR light pass through and investigated its possible utilities in maintaining the pressure difference.

2. New Turbomolecular Pump
A conventional turbomolecular pump having a pumping speed of 400 l/s was modified as shown in Fig. 1. Every other blade of the rotor as well as two blades in each stage of the stator were eliminated, so that a light path having a 20 x 20 mm crossection was realized. The opening rate determined by the shape of the rotator blades was approximately 40%. Although the SR light is chopped, the original spectrum can be brought out unchanged.

This new pump was tested in the beamline BL-17B as shown in Fig. 2. The maximum rotation was 48000 rpm. The compression ratio, defined as a backing pressure P1 divided by a high-vacuum side pressure P2, was measured for P1 from 10^-2 to 10 Pa. The intensity of light passed through the pump was evaluated by exposing a 0.5 µm-thick CMR resist.

3. Results
The compression ratio was plotted as a function of the backing pressure in Fig. 3. A ratio as high as 3 x 10^4 was obtained for N2. For He and H2, the ratios were 200 and 50, respectively. These compression ratios could be maintained at backing pressures up to 1 Pa.

The critical doses at which a residual resist thickness reached zero after development were determined to be 20 A-s for the incident light, and 50 A-s for the light passed through the pump. The ratio of these critical doses gave a transmission of 40%, equal to the opening rate.

As a result, the new pump was found to be operated at backing pressures up to 1 Pa. The compression ratio was moderate and not satisfactory for replacing the conventional Be window. This pump will be effective in lowering residual gas level occupying a small area in the beamline.

References
Total reflection of x-rays from vacuum-evaporated platinum mirrors in photon energy from 1.8-8 keV

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INTRODUCTION

The graded refractive index model has been used to explain reflectivity of grazing incidence mirrors in the hard x-ray region. In the model, surface roughness introduces a local variation in the refractive index near the surface. The fit with data from experiments was very good but no actual measurement of surface roughness was conducted to check the model.

This paper describes the results of reflectivity measurements for platinum-coated mirrors, compared with calculation using the graded index model, and compared with surface roughness measured using scanning tunneling microscopy (STM).

REFLECTIVITY MEASUREMENTS

We studied two types of the platinum-coated mirror. Types A and B were made by the same manufacturer (Toshiba Denko). Each mirror was made of fused quartz 500 mm long, 130 mm wide, and 40 mm thick, coated with chromium and platinum by electron-beam evaporation. The thicknesses of chromium and platinum films are 20 and 100 nm for type A, and these for type B are ~10 and ~20 nm, respectively.

We measured the x-ray reflectivity at station BL-17C. A pair of mirrors was placed 15.5 m from the source. We used an energy dispersive method with a Si(Li) detector to find reflectivity. Each reflectivity was derived as the square root of the spectral ratio of the reflected beam to the direct beam.

RESULTS

We derived the roughness by fitting the calculated reflectivity to measured ones in photon energy from 1.8-8 keV and glancing angles of 10-34 mrad using a graded index model. In the calculations, we treated the surface variation in the refractive index as an error function. Derived rms roughness are 3.4±1.0 nm for type A and 1.6±0.6 nm for type B. Figure 1 shows a good fit between the measured and calculated reflectivity.

To confirm the validity of the model, we measured the surface roughness directly using an STM (Nanoscope II). Figure 3 shows histograms of the surface depth measured using STM. Each histogram was calculated from data in a 1 x 1 µm² area. We found the histograms can be well fitted as Gaussian. The roughness derived by the curve-fitting are 3.8±0.2 nm for type A and 1.6±0.2 nm for type B.

Our results showed a close agreement between the surface roughness estimated using the graded index model and surface roughness measured using STM.

REFERENCES


Figure 1. Measured reflectivity (symbols) and calculated reflectivity (full lines) at 10-, 18-, and 26-mrad glancing angles. Reflectivity is calculated assuming a surface roughness of 3.4 nm for type A and that of 1.6 nm for type B.

Figure 2. Histograms for height distributions for platinum surfaces (symbols) and fitted Gaussian distribution (full lines). The rms roughness of type A and B derived by fitting are 3.8 and 1.6 nm, respectively.
DEEP-ETCH LITHOGRAPHY IN RESIST LAYER USING SYNCHROTRON RADIATION

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Introduction

Synchrotron radiation (SR) is a light source whose photon energy can be changed. With a suitable photon energy, it can be used for fine pattern replication, and for deep-etched pattern fabrication.

In this report, we describe preliminary results of deep-etch lithography in resist layer using hard X-ray SR.

Experiments

We used a positive-type electron beam resist (CMR) in this study. The resist was dripped or spin coated, or both, onto silicon wafers, then prebaked at 200°C for 60 minutes in N₂ atmosphere. A several tenths of μm-thick CMR was obtained.

We carried out SR exposure at beamline BL-17C, equipped with a pair of Pt-coated plane mirrors and a Be window, served as a bandpass filter. The glancing angle of the mirrors was changed to adjust the photon energy. Fig. 1 shows the calculated power spectrum that passes a 200 μm-thick Be and air (17 mm), at the glancing angle of 10, 14 mrad². The resists exposed to SR were developed in MIBK for 120 s, and then rinsed in isopropanol for 30 s. The developed depth was measured with a DEKTAK profilemeter. Pattern replication on the resist was done using a tungsten mesh as a mask.

Results and Discussion

Fig. 2 shows the developed depth in resist layer as a function of the exposed dose. The developed depth (d) can be expressed as, d=kD⁰, where D is the exposure SR dose. This relation is derived from the dissolution characteristics of the resist. The gradient of the developed depth versus exposure dose, a, is 2.3, from the graph. Figure 3 is an SEM image of the pattern replicated resist layer, using a 100 mesh tungsten as a mask. We obtained 35 μm-thick resist pattern with a very sharp edge profile, as can be seen from the figure.

In summary, we demonstrated that it is useful to make deep-etch patterns in a thick resist layer using hard X-ray SR.

References

Angle-Resolved Resonant Photoemission of Ni Single Crystal

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After the first observation of the resonant enhancement of the valence band satellite at about 6 eV binding energy in Ni,\(^1\) many experimental and theoretical works have appeared to explain the origin of the satellite and its resonant behavior near Ni 3p core electron excitation threshold. So far, the resonance is explained as the auto-ionization of an excited quasi-discrete atomic configuration 3p^3d^4s into a continuum of excitations with two holes in the 3d shells and the 6 eV satellite is interpreted as electrons emitted from atoms which are left with two correlated 3d holes and a low-lying excited electron.\(^2\) On the other hand the satellite was also considered as the conventional interband transition effect due to a peak in the density of states in the final energy band.\(^3\) Although the existence of the two 3d holes and their important role in the resonant behavior are seemed to be confirmed by the spin polarized photoemission experiments,\(^4\) the relation between the interband transition effect and the resonance behavior of the 6 eV satellite in Ni is still remains to be clarified by a systematic investigation of the angle-resolved photoemission experiment in 3p-3d resonance region. The aim of this report is to investigate the angle-resolved resonant photoemission of Ni single crystal and to clarify the relation between the resonance enhancement of satellite and those of the interband transition effects.

Figure 1 shows the angle-resolved photoemission spectra of Ni valence band near 3p core electron excitation threshold. Photoelectrons are collected normally to Ni(100) surface. In the figure, the 6 eV satellite, c, shows resonance, whereas two different structures in the main band, a and b, show antiresonance near 3p threshold. We have observed another broad structure at higher binding energy side of the main 3d band and its binding energy varies with the exciting photon energies as is indicated dashed line in the figure. This feature is assigned to the interband transition and its intensity variation is attributed to the photon energy dependence of the photoexcitation cross section of the valence electrons. In the photoemission spectra of Ni(110) surface, we have observed the other valence band satellites at binding energies of 9.5 and 13 eV, which have been considered to be 3d\(^7\) final state configuration.\(^5\)

**Introduction**

The atomic and electronic structures of Si(001)\(2\times1\) surfaces saturated with alkali metal have been the subjects of numerous studies. Recent ARUPS studies showed semiconducting characters contrary to a long-believed notion of metallic character of these surfaces. Recent XPD studies, a new model called double layer (DL) model has been proposed. Electronic structures calculated recently based on the DL model showed qualitative agreement with those of the ARUPS results but no quantitative agreement was reached. The purpose of the present experiment is to improve the previous ARUPS measurements taking advantage of the high quality of the synchrotron-radiation (SR) photoemission.

**Experimental**

The experiments were performed on the ISSP (Institute for Solid State Physics) beam line BL-18A at the Photon Factory, which is equipped with a constant-deviation angle grazing-incidence monochromator and an angle-resolved photoelectron spectrometer (VG ADES 500). The overall instrumental energy and angular resolutions selected were 140 meV and \(\pm 1°\) at \(hν=22\) eV, respectively. A mirror-polished Si(001) substrate was initially cleaned in the spectrometer chamber and a single-domain \(2\times1\) surface was prepared as before. Alkali metal was deposited from a chromate dispenser under a pressure of \(\approx10^{-9}\) mbar and the formation of alkali saturated Si(001)\(2\times1\) surface was confirmed by LEED and XPS.

**Results and discussion**

![Figure 1](image_url)

Figure 1 shows \(E_b-k_{11}\) (binding energy vs. \(k_{11}\)) diagram for the Si(001)\(2\times1\)-K surface along the symmetry directions in the \(2\times1\) surface Brillouin zone (SBZ) as deduced from ARUPS spectra. Solid circles stand for strong or clear peaks and solid triangles for weak or broad structures in actual spectra at \(hν=22\) eV. Open-circles and -triangles are for \(hν=28\) eV, and open-rectangles stand for either strong or weak structures of the results at \(hν=35\) eV. The bands S\(_1\) and S\(_2\) are surface-states (SS) that were reported previously. The weak metallic band E is a state due to a small amount of excess K. A new SS band S\(_1\)' appears between S\(_1\) and S\(_2\). Symmetries of the three states under the mirror reflection about the \(\Gamma-J\) and \(\Gamma-J'\) mirror planes are marked in Fig. 1. The symmetries were determined using the linear polarization of SR. The obtained symmetries of S\(_1\) and S\(_1\)’, respectively are in agreement with those of anti-bonding (\(\pi^*\)) and bonding (\(\pi\)) states of the otherwise dangling-bonds of the dimer structure of the Si(001)\(2\times1\) surface. Dispersions of states other than the three SS bands are noticeable at larger binding energies.

The resulting dispersions and symmetries of the SS bands are in accordance with those expected for the DL model of the alkali-metal-saturated Si(001)\(2\times1\) surface.

**References**


![Figure 1](image_url)
Photoelectron Effect on Photodesorption due to Synchrotron Radiation.

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Introduction
Photodesorption in storage rings is mainly caused by photoelectron which is produced by synchrotron radiation [1,2]. The production of photoelectron depends on incidence angle of synchrotron radiation.

The focus of this experiment has been to study the relation between incidence angle and production of photoelectron. The effect of electric field on the reduction of photodesorption has also been studied.

Experimental
Experiments have been performed at BL-21 which is a white light beam line [3]. Copper block made of oxygen free copper (ASTM Class-1 OFC) has been installed into a chamber which had been irradiated by synchrotron radiation for $2 \times 10^8$ mAh before. Synchrotron radiation is collimated in 5 mm x 5 mm by a slit which also works as an orifice to measure outgas. The copper block which is cooled by water has two incident surfaces for irradiation of synchrotron radiation. One incident angle is normal and the other is ten degree for glancing angle. The irradiated areas are 25 mm² and 144 mm² respectively. Both surfaces are divided by a wall which works to eliminate (or to minimize) the influence due to irradiation of synchrotron radiation to other surface. The copper block can be moved and the irradiated surface can be changed in situ from outside vacuum chamber. Bias voltage can be applied to the block. Photodesorption and photocurrent have been measured through experiments.

Results
Figure 1 shows photocurrents against bias voltage applied to the copper block. The photocurrent at the glancing angle of 10 degree is more than that at normal incidence. This is because photoelectrons are produced in shallow area of copper surface at incidence of glancing angle, then more photoelectrons are emitted as compared with normal incidence. Photocurrent are affected by bias voltages in both incident angles. Photoelectrons are collected by copper block with positive bias voltage. Photoelectron yield due to irradiation of synchrotron radiation can be calculated by photocurrent and photon flux. Photoelectron yield at normal incidence is 0.026 electrons photon⁻¹ and that at the glancing angle of 10 degree is 0.12 electrons photon⁻¹ from the condition with no bias applied. Photoelectron yield at the glancing angle of 10 degree is almost five times higher than that at normal incidence. The discrepancy at the glancing angle of 10 degree from $1/\sin \theta$ law [4] is 20%.

Figure 2 shows photodesorption yields for both incident angles. The beam dose is rearranged for each incident angle. B1-B6 in figure 2 indicate that bias voltage has been applied to the copper block. The photodesorption yield at glancing angle is two times higher than that at normal incidence. The discrepancy of photodesorption yields between glancing incidence and normal incidence is smaller than that of photoelectron yields. It is because photodesorption also occurs at inner surface of chamber same as copper block. The bias voltages of 500 V which collects photoelectrons to copper block increase photodesorption yields. Photodesorption yield at glancing incidence is influenced more than that at normal incidence by bias voltage. Bias voltage is continuously applied to the copper block at B5 which is irradiation of synchrotron radiation to glancing surface for $9 \times 10^8$ mAh. Even though photodesorption increases at first, it comes down with increase of beam dose. Then normal incident surface has been irradiated and bias applied, but the yield shows low value. This probably suggests that "photoelectron cleaning" controlled by bias voltage is effective to reduce photodesorption.

Reference
1. O. Grobner et al., JVST, A7(2), 223 (1989)
4. O. Grobner et al., Vacuum, 33, 7 (1983)
MAGNETIC COMPTON PROFILES OF Fe-Ni SINGLE CRYSTALS

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Introduction

Magnetic Compton scattering is an established method to get the direct information only about magnetic electrons in ferromagnetic materials. The magnetic Compton profile (MCP) method using 13-segmented Ge-Solid-State detector (SSD) with circularly polarized x-rays has been developed to achieve good statistics and been successfully applied to 3d-transition metal system and 4f-rare earth system.

The Fe-Ni alloy system has been extensively studied to investigate the nature of the so-called invar properties which is found around the composition of Fe₆₅Ni₃₅ but there are still big arguments about its origin. In order to investigate the magnetic properties of Fe-Ni alloy system, the MCP's were systematically measured using the single crystals of this alloy system, and the anisotropic behaviors of momentum distribution of magnetic electrons will be discussed.

Experimental

The MCP of Fe-Ni single crystals were measured at the beam line AR-NE1 using circularly polarized x-rays of 59.38keV (Tm K-absorption edge). All measurements were carried out at room temperature.

The Fe₉₀₋ₓNiₓ single crystals (x=30.9, 34.9, and 75.0) were shaped into a circle (10mm in diameter) with thickness of about 250µm. The MCP's of these samples were measured by a transmission mode except the MCP of Fe₆₃.₅Ni₃₆.₅ alloy which the MCP was measured by a reflection mode using thicker sample of 2mm thickness.

Results and Discussion

Figure 1 shows the MCP's of Fe-Ni single crystals along [100], [110] and [111] directions. The dip at P₂=0 of the MCP along the direction [100] becomes deeper with increasing the concentration of Ni, while the dips along the direction [110] and [111] don't change appreciably. Furthermore, it seems that a bump in the dip appears at P₂=0 in the MCP of the invar alloy, Fe₆₅Ni₃₅. This suggests the alloy dependence of s-p-d hybridization is changed and reflected particularly in the direction [100]. However, it is not clear why this tendency is sensitive to the direction along [100].

Reference

5) Y.Tanaka et.al.; private communication.
First observation of magnetic Compton scattering under a standing wave field

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INTRODUCTION
Magnetic Compton scattering by using circularly polarized X-rays gives the information of the spin dependent electron density in a momentum space [1], and magnetic Compton profiles of many ferromagnetic materials has been observed[2]. On the other hand, in a case of Ferri-magnetic materials, there are two positions for Magnetic atoms, and the directions of the spin are opposite to each other. The deference of the amplitudes brings a total magnetization. An usual magnetic Compton scattering only gives the Information of this total magnetization. If a standing wave field is applied In a crystal by using a Bragg diffraction, there Is a possibility to get a so called off-diagonal momentum density of magnetic electrons which was pointed out by Schülke and Mourikis[3] in a case of a normal Compton scattering under a standing wave field. In the present experiment, we only measured the magnetic effect (not magnetic Compton profile) from YIG [Y_{3}Fe_{2}(FeO_{4})_{3}] single crystal under a standing wave field, thus we demonstrate that we can get the information of the magnetic form factor which corresponds to the integrated value of the off-diagonal momentum density of magnetic electrons.

THEORY
According to Schülke and Mourikis[3], the integrated intensity of the normal Compton scattering under a standing field is expressed as a following equations at a simplified case;

\[
\frac{\partial I}{\partial \omega} = \frac{\partial I}{\partial \omega} = \frac{1}{2} (N_{\text{total}})_{\text{eff}} F_{g} \tag{1a}
\]

\[
(N_{\text{total}})_{\text{eff}} = N_{\text{total}} + (2RC/R^{2}) \cos(T) F_{g} \tag{1b}
\]

where \(\omega\) and \(\omega_{0}\) are the energies of scattered and incident X-rays, respectively, \(r_{0}\) is a classical electron radius R and T are the reflectivity of the Bragg diffraction and the phase difference between the Bragg diffracted and the incident X-rays, and \(N_{\text{total}}\) and \(F_{g}\) are a total electron number and the structure factor for g diffraction. We introduce an additional parameter of C, which is so called coherent fraction. The above equation indicates that \((N_{\text{total}})_{\text{eff}}\) contributes to the integrated Compton scattering intensity under a standing wave field. According to the similar consideration, the effective number of the magnetic electrons, which contributes to the magnetic Compton profile under a standing wave field, \((N_{\text{mag}})_{\text{eff}}\), should be expressed as;

\[
(N_{\text{mag}})_{\text{eff}} = N_{\text{mag}} + (2RC/\pi^{2}) F_{g}^{M} \tag{2}
\]

where \(F_{g}^{M}\) is the magnetic structure factor. Consequently, the magnetic effect under a standing wave field is expected as;

\[
\Delta I_{M} = P_{C} F_{C} \frac{(N_{\text{mag}})_{\text{eff}}}{(N_{\text{total}})_{\text{eff}}} \tag{3}
\]

where \(P_{C}\) is the degree of circular polarization, and \(F_{C}\) is the geometrical coefficient[4].

EXPERIMENTAL AND RESULT
The experiment was curried out at the AR-NE1 beamline. Circularly polarized X-rays were obtained from the elliptical multipole wiggler (E-MPW). Figure 1 shows the experimental arrangement. Circularly polarized X-rays were pre-monochromated and sagittally focused by a double crystal monochromator. We chose the monochromatized energy of 15 keV. The monochromatized X-rays were again led to Si(220) main-monochromator in order to realize approximately (+,-) parallel setting between the monochromator and the sample reflection (YIG(444)) to get a non-dispersive condition. The sample crystal was mounted between pole pieces of an electric magnet, so that the magnetization of the sample could be reversed. The intensity of the Bragg reflection was measured by an ion chamber, and Compton scattered X-rays are measured by a Ge-solid-state detector, whose active area was 1000 mm^2. The scattering angles of the Compton scattered X-rays from the incident and the (444) diffracted X-rays were 148 and 142 degrees, respectively. The magnetic effect of the Compton scattering has been estimated by measuring the change of the intensity of Compton scattering under reversing the magnetization of the sample. Figure 2(a) and (b) show the rocking curve of (444) diffraction and the obtained angular dependence of the magnetic effect. Figure 3(a) and (b) show the theoretical calculation of them by using eq.(3), where the value of parameter C is 0.5. The calculated angular dependence qualitatively well explains the experimental data. The relatively small value of C (0.5) is caused by the imperfection of the sample crystal.

Fig. 1:
Fig. 2:
Fig. 3:

References
ELECTRON MOMENTUM DISTRIBUTIONS IN SODIUM AND LITHIUM

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Introduction

From a viewpoint of band theory, valence electrons in sodium and lithium are considered as nearly free electrons, while from the viewpoint of many-body theory, they are considered as an interacting electron gas. Thus, measurements of Compton profiles of sodium and lithium, and comparison of the measured Compton profiles with predictions of band theory and those of many-body theory will provide useful information about the effect of electron-electron correlation in real electron systems.

Experimental

The measurements of the Compton profiles were performed using an X-ray spectrometer at AR-NE1 beamline. The incident X-ray energy is 59.38 keV and the scattering angle is set at 160 degrees. The overall momentum resolution is 0.12 a.u. at 59.38 keV. The samples have a thickness of 4 mm. In order to prevent the samples from oxidizing, the sample chamber was evacuated to 2 x 10^-6 torr.

Results and discussion

After the correction of the measured profiles, valence-electron parts were obtained by subtracting theoretical core-electron parts from the total profiles. Figures 1 and 2 show the valence-electron Compton profiles of sodium and lithium along the [100] direction, respectively. In the figures, the theoretical profiles including the effects of the electron-electron correlation for the free electron gas model are shown for comparison. Agreement between the experiment and theory is very good for sodium, which indicates that the effect of the lattice potential is small as already shown theoretically. Contrary to sodium, the agreement is not so good for lithium. This fact indicates that the effect of the periodic lattice potential is much larger in lithium than in sodium.

For comparison, angular correlation curves of positron-electron annihilation radiation are plotted in the corresponding figures. In both sodium and lithium, the high momentum tail of the angular correlation curve is falling off faster than that of the Compton profile.

References

Three-dimensional Momentum Density of Magnetic Electrons in Ferromagnetic Iron


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Introduction
Three-dimensional (3D) momentum density of magnetic electrons $\rho_{\text{mag}}$ in ferromagnetic iron has been reconstructed for the first time from experimental fourteen directional magnetic Compton profiles (MCP). Previous results on ferromagnetic iron showed that the three measured MCPs were in good agreement with the result of the parametrized FLAPW calculation except slight difference about the negative spin polarization of s,p-like conduction electrons. The present 3D momentum density is directly compared with the results of the same calculation, and makes clear the origin of the discrepancy. It should be mentioned that an elliptical multipole wiggler (EMPW) installed at the 6.5 GeV Accumulation Ring and a segmented Ge solid-state detector (SSD) system only made it possible to carry out the present experiment within a practicable accumulation time.

Experimental
The experiment was made at the beamline AR-NE1. Circularly polarized x-rays emitted from the EMPW were focused and monochromatized with a quasi-doubly bent Si(111) monochromator. The incident x-ray energy was 59.38 keV. A sample of single crystalline Fe+3wt.%Si was 20x20x0.2 mm$^3$ in size. Energy spectra of Compton scattered x-rays were measured with the thirteen segmented SSD. Fourteen MCPs along the (100), (110), (111), (311), (211), (322), (332), (315), (310), (210), (320), and (321) directions were measured. The accumulation time was about 8 h per profile. The average momentum resolution at the Compton peak is 0.76 a.u.

Results and Discussion
The reconstruction procedure developed by R.Suzuki$^8$ was used. A cross-section of the experimental 3D $\rho_{\text{mag}}$ in the (001) plane including the $\Gamma$ point is shown in Fig.1. There is a deep hollow around the $\Gamma$ point, and the $\rho_{\text{mag}}$ is negative in the area $|p| < 1.3$ a.u., which can be ascribed to the negative spin polarization of s,p-like conduction electrons and the negligible contribution of 3d electrons. There are four peaks at $p_x, p_y = \pm 1.9$ a.u. on the (100) axes. In Fig.2 is shown the same cross-section calculated with the FLAPW method. The density is convoluted with a Gaussian of FWHM 0.75 a.u. Although the shapes are qualitatively in good agreement with each other (the symmetry and the region of the negative spin density), the calculated $\rho_{\text{mag}}$ has higher four peaks and a shallower hollow than the experimental $\rho_{\text{mag}}$. This results implies that the theoretical momentum density should have more negatively polarized spin density around the $\Gamma$ point.

References

X-RAY MAGNETIC CIRCULAR DICHOISM AT Pt L$_{2,3}$-EDGES IN ORDERED AND DISORDERED Fe-Pt ALLOYS

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INTRODUCTION

X-ray magnetic circular dichroism (XMCD) has been received considerable interest as a new method to study magnetism. It is convenient for the study of the magnetic local environment effect in 3d-transition metal alloys from the electronic states viewpoint. The Fe-Pt alloy is an appropriate system for this purpose, because it has three ordered phases, Fe$_2$Pt, FePt, and FePt$_3$, whose magnetic ordering is ferro-, ferri- and antiferromagnetic. On the other hand, the disordered alloys show ferromagnetism through overall content. We present the XMCD spectrum at the Pt L$_{2,3}$-edges and the dependence of the spectrum on the content and chemical ordering.

EXPERIMENTAL

The Fe-Pt alloys were prepared by arc melting under Ar atmosphere. The ordered specimens were prepared by a suitable thermal treatment. The degree of order was estimated to be more than 0.9. The disordered samples were obtained by quenching in water.

The XMCD spectrum at the Pt L$_{2,3}$-edges was measured by using circularly polarized X-rays emitted from an elliptical multi-pole wiggler installed on beam line AR-NEI[1]. The measurements were done by the transmission method on the powdered sample dusted uniformly onto Scotch tape. A magnetic field of 2.5kOe was applied and the sample was tilted by 45 degrees away from the direction of the incident beam. The transmitted X-ray intensity was measured by an ion chamber upon reversal of the direction of the magnetic field. The incident beam intensity was monitored using a separate ion chamber. The data were accumulated for a preset time of 2 sec: and, the reverse of the magnetic field was repeated 2 times for each energy point; moreover, the spectrum was collected 4-10 times; so that, the statistical error was less than 10$^{-4}$.

RESULTS AND DISCUSSION

Figures 1 and 2 show the XMCD spectrum $\Delta \mu t$ at Pt L$_2$- and L$_3$-edges, respectively, in the ordered 23.6at%Pt-Fe alloy. The origin of the energy scale was determined from the first inflection point in the absorption spectrum and was regarded as the Fermi level. From the present measurements, the following features are found: (1) the magnetic effect appears just around the Fermi level: (2) $\Delta \mu t$ of the L$_2$ (L$_3$)-edge is positive (negative); (3) the intensity ratio is deviated from the ratio $I(L_2):I(L_3)=1:1$ expected theoretically. These spectra are in good agreement with the results of Schutz et al. [2], and indicate a positive spin polarization and a spin-orbit interaction in the unoccupied 5d-states of Pt atom.

From dependence of the XMCD spectra on Pt concentration, the energy integrated intensity shows a maximum at near 30at%Pt in the disordered alloy; on the other hand, in the ordered alloy, it shows a minimum at 50at%Pt. The intensity in the disordered alloy is significantly larger compared to that in the ordered alloy, which is contrary to the results of magnetization measurements. Therefore, the intensity of the XMCD spectrum does not reflect directly the characteristics of the magnetic moment carried by the 5d-electrons of Pt atom.

REFERENCES


Fig. 1. The XMCD spectrum at the Pt L$_2$-edge in the ordered 23.6at%Pt-Fe alloy.

Fig. 2. The XMCD spectrum at the Pt L$_3$-edge in the ordered 23.6at%Pt-Fe alloy.
XANES SPECTRUM AND X-RAY MAGNETIC CIRCULAR DICHIROISM AT Fe K-EDGE IN Ho-IRON-GARNET

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INTRODUCTION

It is well known that K-edge XANES spectrum of 3d transition-metal oxides is generally characterized by a sharp absorption peak located at pre-edge region at threshold. The absorption has been widely attributed to dipole-forbidden 1s-3d transitions. [1] It has been suggested that quadrupole transitions contribute significantly to the pre-edge feature. Recently, it is predicted that the quadrupolar contribution could be discriminated from the dipolar contribution by the angular dependence of X-ray magnetic circular dichroism (XMCD). [2] This method permits to clarify the origin of the pre-edge absorption in 3d metal oxides.

EXPERIMENTAL

The single crystal of holmium-iron-garnet (HoFe5O12) was grown by liquid phase epitaxial method on the gadolinium-gallium-garnet substrate. The <111> easy direction of magnetization is perpendicular to the surface.

The XMCD spectrum was measured by using circularly polarized X-rays emitted from an elliptical multi-pole wiggler installed on beam line AR-NE1[3]. The spectrum at the Fe K-edge was taken by the fluorescent method for the single crystal. The fluorescent X-ray intensity was measured by a fluorescent ion chamber (Lytle detector) upon reversal of the direction of the magnetic field. The data were accumulated for a preset time of 2 sec; and the reverse of the magnetic field was repeated 2 times for each energy point in order to minimize any time-dependent drift; furthermore, the spectrum was collected 6-10 times; so that, the statistical error was about 10. The XMCD spectrum was measured as a function of the angle $\omega$ between the magnetic field and incident X-ray beam directions in the range of 45-75 degrees.

RESULTS AND DISCUSSION

Figure 1 shows the XANES (upper) and XMCD (lower) spectra at the Fe K-edge. The origin of the energy scale was determined as the point at half the absorption step maximum. The sharp magnetic effect is just located at the pre-edge peak being characteristic of the K-edge XANES of 3d metal oxide. Since the pre-edge feature is attributed to the 1s-3d transitions, the XMCD spectrum reflects the unfilled 3d electronic states and/or the spin-orbit interaction of the trivalent Fe ions in tetrahedral and octahedral sites.

The intensity of the XMCD peaks labeled A, B and C is plotted as a function of $\cos\omega$, as shown in Fig.2. Generally speaking, the intensity varies linearly with $\cos\omega$. According to the theory in Ref.[2], it leads to the result that the dipolar transitions contribute dominantly to the pre-edge absorption. It is likely, however, that the intensity of the peak B deviates from the linear relation. More detailed analysis is in progress.

REFERENCES


Fig.1. The XANES (upper) and XMCD (lower) spectra at the Fe K-edge in Ho-iron garnet.

Fig.2. The angle dependence of the intensity of each XMCD peak.
MAGNETIC XANES SPECTRA OF Fe-Ni ALLOY AT K-ABSORPTION EDGES USING CIRCULARLY POLARIZED X-RAY

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Introduction

Magnetic X-ray absorption near edge structure (MXANES) spectrum measurements can give selective information about the net spin density of empty band above the Fermi level due to the selection rule of the X-ray absorption around a specified kind of atoms even in alloys.

The MXANES spectra of pure Fe and Ni at K-absorption edges have been observed1,2, and have suggested a strong hybridization of 4p-states with 3d-states in transition metals. However, it has not been fully understood what information can be exactly obtained from the MXANES spectra.

In this report the MXANES spectra of Fe-Ni alloys are shown. The Fe-Ni alloy system was chosen because this alloy system is ferromagnetic over the whole composition range and has been extensively studied not only from the fundamental interest about the origin of magnetisms but also of the invar phenomena.

Experimental

The MXANES experiments using circularly polarized x-rays were carried out at the beamline ARNENL. The instrumental facilities were described in another paper3.

The samples of Fe_{100-x}Ni_{x} (X = 20.4, 26.4, 30.4, 35.4, 40.2, 50.0, 69.5, 75.0, and 89.8) alloys were prepared in following procedures; the mother alloy was crushed into fine powder with diameter less than 25 μm, and were annealed at 800 °C for 24 hours in vacuum to remove vacancies and dislocations, and these powder alloys were dispersed on the scotch tape uniformly. All the measurements were carried out at room temperature by a transmission mode.

Results and discussion

Figure 1 shows the normalized MXANES spectra of Fe-Ni alloys at Fe K-edge and Ni K-edge. The spectra of pure Fe and pure Ni are included for comparison4. The Fermi energy E_0 was determined from the first inflection point of the XANES spectra. Two features are to be noted. The first point is the similarity of the MXANES spectra between Fe and Ni K-edge in the same alloy. The second is the concentration dependence of spectra; the positive peak around the Fermi level characteristic of pure Fe is observed up to the Ni concentration of 50.0 % but this positive peak disappears above the Ni concentration of 69.5%. It is also clear that the intensities of the MXANES spectra show a minimum at the absorption edge around the concentration of 26.4 % Ni where Fe-Ni alloy system shows the so-called invar properties.

It is not clarified the reason why the above mentioned features appears. Theoretical calculations are highly desired in order to understand the MXANES in this alloy system.

![Fig. 1 MXANES of Fe-Ni alloy](image)

Reference

X-RAY MAGNETIC CIRCULAR DICHROISM IN CRYSTALLINE AND AMORPHOUS Fe-Dy ALLOYS

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INTRODUCTION

X-ray magnetic circular dichroism (XMCD) has been received considerable interest as a new method to study magnetism. A combination of XMCD and EXAFS will permit to study the correlation between local structure and magnetic ordering. In particular, it is a useful approach to amorphous magnetic materials composed of 3d transition and rare-earth metals. Amorphous 80at% Fe-Dy alloy shows ferrimagnetism with a compensation temperature $T_{\text{comp}} = 210$K. Although the crystalline sample (Fe$_{0.6}$Dy$_{0.4}$) compound also shows ferrimagnetism, no compensation phenomenon is observed. In this report we present the dependence of the XMCD spectrum on morphology and temperature.

EXPERIMENTAL

The amorphous sample of 80 and 45at% Fe-Dy alloys was prepared by rapid quenching method in an Ar atmosphere. The crystalline sample with the same concentrations was made as the reference material. The sample preparation and characterization were given in Ref.[1].

The XMCD spectrum at the Dy $L_2$-edges and the Fe K-edge was measured by using circularly polarized X-rays on beam line AR-NE1. The measurements were done by the transmission method for the ribbon-shaped amorphous sample (0.8mm in width, 10nm in thickness) and for the powdered crystalline sample. A magnetic field of 3.5kOe was applied and the sample was tilted by 45 degrees away from the direction of the incident beam. The transmitted X-ray intensity was measured by an ion chamber upon reversal of the magnetic field. The data were accumulated for a preset time of 2 sec; and the reverse of the magnetic field was repeated 4 times for each energy point, and the spectrum was collected 3 times.

RESULTS AND DISCUSSION

Figure 1 shows the XMCD spectrum at the Fe K-edge, (a) in the amorphous and (b) crystalline 80at%Fe-Dy alloys. In the amorphous alloy, the following features are found near $E_{\text{F}}$ determined from the first inflection point in the XANES spectrum: (1) the XMCD spectrum shows a positive peak at $E_{\text{F}}$; (2) it changes immediately from positive to negative, then reaching a sharp negative peak at $(E-E_{\text{F}})$ 3eV. These features are very similar to the K-edge XMCD spectrum of pure Fe. Therefore, the magnetic moment of Fe atom is parallel to the direction of the bulk magnetization.

Figure 2 shows the temperature variation of the XMCD spectrum at the Dy $L_2$-edge in the amorphous 80at%Fe-Dy alloy. The XMCD intensity decreases apparently with decreasing temperature, which results from non-saturation due to the rapid increase of magnetic anisotropy. It seems, however, that the spectrum changes sign from positive to negative at low temperatures, which is consistent with the magnetic compensation phenomenon at about 210K.

REFERENCES

It has been theoretically predicted that electric quadrupole transitions have a large contribution to X-ray magnetic circular dichroism (XMCD) at the L_{2,3}-edges of rare-earth elements in magnetic materials.[1,2] The quadrupole transitions (2p→4f) have been comparably taken into account in addition to the dipole transitions (2p→5d) in the theories. The dependence of the quadrupole contribution on the angle $\omega$ between magnetic field and incident X-ray beam directions will be appreciably different from that of the dipole one. We present the preliminary result of analysis to verify the existence of the quadrupole contribution to the XMCD spectrum at the Ho L_{2,3}-edges in holmium-iron-garnet (Ho-IG: Ho_3Fe_5O_12).

**EXPERIMENTAL**

The Ho-IG single crystal was grown by liquid phase epitaxial method on the gadolinium-gallium-garnet substrate. The (111) easy direction of magnetization is perpendicular to the surface. With the atomic configuration 4f$^{10}$ Ho$^{3+}$ ion has three f-electrons outside a half filled shell. The quantum numbers of the ground state are $S=2$ and $L=6$, and spin-orbit coupling leads to a total angular momentum $J=8$ ($^{7}I_{8}$). It is expectable to be observed large magnetic effect on the trivalent Ho ion.

The XMCD spectrum was measured by using circularly polarized X-rays emitted from an elliptical multi-pole wiggler installed on beam line AR-NE1[3]. The spectrum at the Ho L_{2,3}-edges was measured by the transmission method for the powdered sample dusted uniformly onto Scotch tape. The transmitted X-ray intensity was measured by an ion chamber upon reversal of the direction of the magnetic field. The XMCD spectrum was taken as a function of the angle $\omega$ in the range of 45-90 degrees.

**RESULTS AND DISCUSSION**

Figure I shows the XMCD spectrum at the Ho L_{3}-edge. The origin of the energy scale was determined from the first inflection point in the absorption spectrum. The spectrum indicates a complicated profile consisting of the peaks labeled A-G. The sharp magnetic effect is observed not only at the white-line region but also at higher energy region. The XMCD spectrum seems to involve the quadrupolar contribution in addition to the dipolar one. The quadrupolar part would be attributed to the large 4f angular momentum, a resulting influence of spin-orbit interaction and the hybridization effect between 5d and 4f electronic states.

The intensity of the XMCD peaks labeled A, B, D and G is plotted as a function of cos$\omega$, as shown in Fig.2. Generally speaking, the intensity varies linearly with cos$\omega$. According to the theory in Ref.[2], it leads to the result that the dipolar transitions contribute dominantly to the XMCD spectrum. It is likely, however, that the intensity of the peak B significantly deviates from the linear relation. More detailed analysis is in progress.

**REFERENCES**

MAGNETIC PROPERTIES OF GADOLINIUM ATOMS IN Gd-Fe MULTILAYERED FILMS BY MAGNETIC X-RAY DICHROISM ON Gd L- AND Fe K- EDGES

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Introduction
Magnetic X-ray absorption near edge structure (MXANES) is a new method to investigate the magnetism of ferromagnetic materials. This method is unique because it can give selective informations about the net spin density of empty band around a specified kind of atoms due to the benefit of well-known selection rule in the absorption process of circularly polarized X-rays.

Fe/Gd multilayered film is known to have a spin-flop-like magnetization in low magnetic field which is one of interesting phenomena in multilayered films such as Fe/Gd. In this study we report MXANES measurements of Fe/Gd multilayered films in order to get informations about the magnetic properties of each layers and/or interfaces between them.

Experimental
Multilayerd films of Ge/Fe were deposited on aluminum substrate using an alternative sputtering method under a vacuum of 10^-6 Torr. Thickness of layer were controlled by each deposition time and confirmed by a traditional X-ray analysis to be 1/1, 5/5, 10/10, 15/15, 20/20 and 40/40 (Å/Å). The MXANES spectra of Gd L edge and L edge and Fe K-edge were observed at AR NE-1 station using the circularly polarized X-rays emitted from the elliptical multipole wiggler. Energy dependence of MXANES in Gd(40Å)/Fe(40Å) film were tried but no significant change was observed in both shape and amplitude. This observation seems to deny the possibility of spin-flop magnetization reported in low field region in this specimen.

Results and Discussions
Figure 1 shows MXANES spectra of Gd L edge and Fe K-edge observed in the magnetic field of 250 Gause. In specimen equal to or less than 5 Å, the spectra of Gd L edge in multilayered film is similar to that in pure Gd while the spectra of Fe is opposite in sign. On the other hand, in specimens with layers equal to or thicker than 10 Å, the above situation is completely reversed; the spectra of Fe in multilayered films are similar to that in pure Fe while spectra of Gd is opposite in sign to that in pure Gd. This means that the coupling of magnetic moment of Gd and Fe in multilayered films is anti-parallel and the magnetic moment of Gd increases as the layer thickness decreases, and even exceeds that of the Fe moment in 1Å/1Å and 5Å/5Å films.

The temperature and magnetic field dependence of MXANES in Gd(40Å)/Fe(40Å) film were tried but no significant change was observed in both shape and amplitude. This observation seems to deny the possibility of spin-flop magnetization reported in low field region in this specimen.

References
SYNCHROTRON RADIATION COMPUTED TOMOGRAPHY FOR BIOMEDICAL USE: PRELIMINARY REPORT WITH PHANTOM


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Introduction

X-ray computed tomography is an important diagnostic modality. Tunable monochromatic X-ray CT with synchrotron radiation, is being constructed in the several experiments. Excellent images with high spatial resolution (2-10um) have been obtained in the material science [1-3]. Using desirable characteristics as a sufficient X-ray flux, parallel beam without beam hardening, we attempted to construct a biomedical diagnosing system evaluating the CT value of tissue and the concentration of contrast agent. In this report, the preliminary results obtained by our line scanning CT system [4], is described.

Method and Materials

A proto-type of the computed tomographic system is now being constructed at a beam line of NE-5 of Tristan Accumulation Ring in Tsukuba (6.5 Gev, 20-30 mA). This system consists of a rotating X-ray shutter, a silicon (111) channel-cut monochromator, X-ray slits system, and an imaging plate (IP) (Fig.1). The energy of monochromatic X-rays was set at 33.2 KeV by the monochromator. Exposure time of each projection was 25 msec and scan projection number was temporarily 18. Line data obtained by IP, were digitized 1024x1024 pixel matrix with a12 bit depth. Cylindrical acrylic phantom with small hole (1, 2, 3, 5mm) (Fig.2) was scanned (beam width: 30 mm, slice thickness: 1 mm). 2.5% contrast material was filled in each hole. This data was reconstructed into a CT image by post-processing computer (HP 9000).

Results and Discussion

Basic phantom examination with contrast material (iodine) was performed. 2 mm hole contained 2.5% contrast material was identified (Fig.3). Image quality was not sufficient because of small number of projection, scatter contamination, fluctuation of X-ray attenuation and regional sensitivity of sensor, and 99 KeV contamination (8%). In the preparing experiments, markedly improvements is expected by increasing scan projection (10 times), decrease the scatter, and so on.

References

STRUCTURE OF LIQUID TELLURIUM UNDER PRESSURE

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Introduction
The phase diagram for tellurium [1] is shown in Figure 1. The structure of Te I is a trigonal one consisting of spiral chains of two-fold atoms, while that of Te II consists of layers of four-fold atoms. The latter can be assumed as the former with additional two interchain covalent bonds. The phase Te III has an almost same structure as of Te II with slightly higher symmetry.

The pressure dependence of the melting temperature of tellurium shows a maximum point. This phenomenon is interpreted in terms of a two-species model [2, 3] which assumes the liquid as a mixture of high- and low-pressure solid phases, and that the concentration of the high-pressure phase in the liquid increases gradually with increasing pressure.

Thus, it is expected that the coordination number of liquid tellurium increases gradually with raising pressure. Previously we confirmed the increase of the coordination number of liquid selenium with pressure, which is also a group Vlb element whose melting curve has a maximum point [4, 5].

Experimental
The high-pressure experiment was carried out using MAX80, a cubic-type high-pressure apparatus installed on an AR bending-magnet line. Details of experiment and data analysis are described elsewhere [6].

Results and Discussion
Figure 2 shows obtained structure factor $S(Q)$ for liquid tellurium at various pressures [7]. The $S(Q)$ at pressures below 2.6 GPa show rather continuous change, while one at 5.1 GPa shows a totally different pattern from those at lower pressures.

Calculated pair distribution functions $g(r)$ are shown in Figure 3. At 1.6 GPa, the second peak of $g(r)$ is nearer to the first peak than that at 0.2 GPa. And at 2.6 GPa, the first and the second peak are almost bound together and make a new peak. This means that the second neighbors approach the center atom, and covalent bonds are formed between them: the structure of liquid tellurium becomes Te II- or Te III-like one with increasing pressure. This result is consistent with the two-species model.

The structure at 5.1 GPa is assumed to be rather simple one, but obtained $S(Q)$ is too poor to calculate $g(r)$. Further measurements are needed to understand this structure.

References

Figure 1: Phase diagram for Tellurium. Dots indicate the experimental points.

Figure 2: Structure factor $S(Q)$ for liquid tellurium.

Figure 3: Pair distribution function $g(r)$ for liquid tellurium.
High Pressure in situ X-ray Diffraction Study on the Phase Transformation from Graphite to Hexagonal Diamond at Room Temperature

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Recently, several studies on the behavior of graphite under high pressure at room temperature using diamond anvil cell have been made, and these optical investigation strongly indicate the existence of a pressure induced phase transformation of graphite at room temperature. In order to determine the structure of this high pressure phase, we carried out an in situ X-ray observation under high pressure.

Experimental. First, we tried to carry out an experiment using a combination of a diamond anvil cell and Imaging Plate at BL-6B. However, high quality data could not be obtained by this system, because the intensity of the X-ray diffraction from the light material such as carbon embedded in a small chamber of the diamond anvil cell was very small. Therefore, we selected a Drickamer type high pressure apparatus with sintered diamond anvils, which could compress large amount of the sample. The powder X-ray diffraction experiment was carried out by the energy dispersive method using the white beam from the Accumulation Ring. In order to obtain the information on the preferred orientation of the sample, we observed the diffraction in two different directions. Crashed single crystal of synthetic kish graphite was used as a starting material.

Results. Fig.1 shows variation of the diffraction profiles of graphite under high pressure observed in the vertical(a) and horizontal(b) directions. In the vertical observation, because of the preferred orientation of the sample, (002) diffraction peak of graphite was observed strongly (this peak is not shown in this Figure), while (100) was weak. When the pressure was increased to 14 GPa, a new diffraction peak began to appear which has a slightly larger d-value than (100) of graphite. By increasing pressure, 3 more diffraction peaks of the high pressure phase were clearly observed. On the other hand, in the horizontal observation, most intense peak of the high pressure phase was observed between (100) and (110) of graphite. All the new diffraction peaks of the high pressure phase were successfully indexed by a hexagonal unit cell, thus it became clear that hexagonal diamond was formed by the room temperature compression of graphite. The diffraction profiles from two different directions support the orientation relationship of the martensitic transformation from graphite to hexagonal diamond previously proposed. The bulk modulus of this hexagonal diamond obtained by the present study is about 400 GPa, which is comparable to the cubic diamond.

Fig.1 Variation of the X-ray diffraction profiles of graphite under high pressure

2. W.Utsumi and T.Yagi, Proc. Japan Acad. 67(B) in press
DENSITY OF LIQUID SELENIUM AND TELLURIUM UNDER PRESSURE

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INTRODUCTION

X-ray diffraction measurements for liquid Se and Te indicated that there was a drastic change in the structure factor under high pressure[1]. To understand these structural changes, the pressure dependence of the density will provide valuable information. In this study, we planned a new X-ray absorption method using synchrotron radiation. To test the validity of the method, we measured the density of crystalline Te[2].

EXPERIMENTAL

Experiments were carried out using MAX80, a cubic-anvil apparatus installed in a bending magnet line on AR. The energy of the X-ray passed through a Si(111) double-crystal monochromator was 45 keV. The intensities of incident beam (I0) and transmitted beam (I) were measured by an ion chamber(IC) filled with Ar gas and a scintillation detector, respectively. The size of the incident X-ray beam at sample position was 0.1 x 0.1 mm². The typical intensity of the current from IC was about 10 nA.

The specimen was placed in a 2-mm-o.d., 1-mm-i.d. BN capsule together with a sapphire ball 0.5 mm in diameter. The internal pressure calibrant of NaCl was placed at the lower part of the assembly.

By moving press, I was measured at various sample positions without changing the beam position. The counting rate for I varied from 10⁶ to 10⁷ cps. All measurements were performed at 298K.

RESULTS AND DISCUSSION

Figure 1 shows the logarithm of I/I₀ at 3.1 GPa as a function of the press height, x. The curvature of the sapphire ball is clearly observed. We fitted the data using the following formula:

\[ I/I₀ = C \exp(-\mu_i \rho_i (3/2 - l(x))) \exp(-\mu_{AB_1} \rho_{AB_1} l(x)) \]

where C is a constant, \( \mu_i \) is a mass absorption coefficient of i, \( \rho_i \) is the density of i, and l(x) is the length of the path in the ball. The solid line in Fig. 1 represents the result of the parameter fitting. The simulation well reproduced the experimental values.

Figure 2 shows the density of crystalline Te as a function of pressure. Open circles represent the value obtained from the present experiment and the solid line represents the result of an X-ray diffraction measurement for reference[3]. The agreement is reasonably well.

The transition from Te I to Te II was observed. Unfortunately, the transition pressure is not accurate since there was a large error in the positions of the NaCl diffraction lines in this experiment.

This method can be applied to disordered systems such as liquid metal. The measurement for liquid Te is in progress.

REFERENCES

STRUCTURE OF LIQUID BISMUTH UNDER PRESSURE

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Introduction

In previous work we found that on increasing pressure the structure factor $S(Q)$ of liquid bismuth changes drastically between 4.7 GPa and 7.3 GPa into a simple pattern with extremely sharp peaks [1, 2]. It is interesting to investigate the structure of the liquid and boundary of the drastic structural change.

In this work, we have carried out diffraction measurement at about 5.9 and 6.8 GPa, and examined a structural model for the liquid at 7.3 GPa.

Experimental

The experiments were carried out by using MAX80, a cubic-type high-pressure apparatus installed in AR-NE5-C. Details of experiments and data analysis are described elsewhere [3].

Results and Discussion

Figure 1 shows a phase diagram for bismuth with the experimental points of both present and previous work as dots. Structure factor $S(Q)$ at these points are shown in Figure 2.

Figure 1: Phase diagram for bismuth. Dots indicate the experimental points.

The pattern at 5.9 GPa can be qualitatively considered as the same pattern as those below 4.7 GPa. The growth of the first peak in intensity and the shift of the second peak towards high-Q side are seen continuously from 0.2 to 5.9 GPa.

At 6.8 GPa, however, the second peak shifts toward the low-Q side. By the further compression to 7.3 GPa, the pattern becomes very sharp.

To interpret the pattern at 7.3 GPa, we assume that the liquid has a distorted crystalline structure so that we can probe a crystalline structure on which the liquid structure is based by comparing the diffraction pattern with the structure factor of liquid. The positions of the sharp peaks of the $S(Q)$ at 7.3 GPa are shown in Table 1. The peaks are located at regular intervals in Q. This cannot be described by a bcc model, which is the structure of Bi V.

One possibility is the structure of pyrolytic graphite, whose diffraction pattern consists of peaks with (001) only. This structure can be assumed as that of graphite with random layer stacking keeping the interlayer distances constant.

Taking a layer structure model, the interlayer distance $d$ is calculated as $d = 2.67 \text{ Å}$. If the structure were close-packed one like hcp, the number density would be 0.040 Å$^{-3}$ while that estimated from compression data of solid is 0.036 Å$^{-3}$.

References


Table 1: Peak positions of $S(Q)$ at 7.3 GPa

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X-RAY DIFFRACTION ANALYSIS OF IONIC LIQUIDS UNDER HIGH PRESSURE

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Introduction

Molten AgCl, CuCl and TiCl shows some different physical properties from simple ionic melts such as NaCl, KCl and so on. According to the analysis of transport properties, thermal properties, NMR or volume change at melting points, these molten salts are seemed to be both ionic and covalent characters. Neutron diffraction with isotopic substitution [1] and X-ray diffraction analysis [2] show that the Ag-Cl bond has more covalent character at low temperature region and has tendency to be glassy state. In this study, X-ray diffraction for molten AgCl has been examined at pressures to 4.5 GPa and temperatures to 823K by transmission and energy dispersive method. The equipment of X-ray diffraction for high pressure and high temperature, MAX80, was used. The results were also compared with those of computer simulation with molecular dynamics calculation.

Experimentals

The equipment of X-ray diffraction for high pressure and high temperature, MAX80, installed in KEK was used. Experimental procedures and analysis of the observed intensities are identical to those described in ref. [3].

For molecular dynamics simulation, the pair potential functions are assumed to consist of a simplified Coulombic and a repulsive term. The number of particles within a basic cell was 500(250Ag, 250Cl). The time increment Δt was 2.5x10⁻¹⁵ sec which corresponds to a mean fluctuation of the internal energy smaller than 0.1 per cent.

Results

Figure 1 shows the structure factor S(Q) of molten AgCl at 0.1 MPa (753K) and 4.5 GPa (823K). New strong peak at around Q=3.3 Å⁻¹ was observed under high pressure condition. This peak was considered to be the enhanced one of the shoulder of the 1st peak which was observed at low temperatures just above the melting point at 0.1 MPa [4]. The intensity of S(Q) at high Q region for molten AgCl at 4.5 GPa was much larger than that at 0.1MPa and the ripple was not decayed under high pressure condition. These results indicate that AgCl has strong tendency to make strong short range ordering and the covalent character of the nearest Ag-Cl pair was enhanced under high pressure. These tendency were also analyzed by the molecular dynamics calculation.

References

COMPRESSIBILITY MEASUREMENT OF $\beta$- AND $\beta''$-ALUMINA USING MAX-80

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Introduction

Na ions which are existing in a conduction plane of $\beta''$-Alumina can be easily exchanged for the optically active ions such as rare earth or transition metal elements. The $\beta''$-Alumina containing such optically active ions has recently attracted special interest as the new optical devices. To develop its applicability, it is important to clarify the site symmetry of the exchanged optically active ions. The pressure dependence of the fluorescence spectra from $\beta''$-Alumina is an useful method to investigate the site symmetry of the exchanged ions.

In this study, the compressibility of $\beta$ and $\beta''$-Alumina which is necessary to analyze the pressure dependence of the fluorescence spectra was measured by using the multi-anvil type high-pressure X-ray diffraction system (MAX-80) installed at KEK.

Experimental

The higher energy synchrotron radiation emitted from Accumulation Ring was used as an X-ray source for the energy dispersive type X-ray diffraction to decrease an absorption by the pressure transmitting medium and to determine the lattice constants more precisely using X-ray diffraction peaks with smaller d-values.

The sample assembly is presented in Fig. 1. Two 6 by 6 by 3 mm blocks of 4:1 boron-epoxy mixture were used as a pressure transmitting medium, a cylindrical hole (2 mm in diameter) being drilled through the center of each block. The $\beta$- and $\beta''$-Alumina single crystals were grown by flux method at 1700°C. These synthetic single crystals were ground and put into the teflon tube with 4:1 methanol-ethanol mixture. The teflon tube was set into the central hole of the higher block. The central hole in the lower block was filled by NaCl powder that was used as a pressure marker. Pressure was determined from the volume change of NaCl using Decker's equation of state.

Results and Discussion

The pressure dependence of X-ray diffraction pattern for $\beta$- and $\beta''$-Alumina is presented in Fig. 2. With increasing pressure, the diffraction peaks shift to the smaller d-value side. The relative intensity change in the diffraction pattern with increasing pressure is considered as the result of a rotation of crystals in the compressed pressure-transmitting medium.

The compressibilities of a- and c-axis determined from the pressure dependence of X-ray diffraction were presented in Fig. 3.

As a-axis, $\beta$ and $\beta''$-Alumina have the same compressibility. Their compressibilities are larger than that of $\alpha$-Alumina as shown in Fig. 3. This phenomenon is explained from the large lattice constant in a-axis for $\beta$- and $\beta''$-Alumina crystal. As c-axis, the compressibility of $\beta$-Alumina is larger than that of $\beta''$-Alumina.
Storage and Lifetime Measurements of Multiply Charged Ions
Produced by Synchrotron Radiation

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The use of inner-shell photoionization is known to be the best method to produce very cold multiply charged ions (MCI). Ion traps can confine ions of very low energy in a small space, and are useful tools for both high-resolution spectroscopy and low-energy collision experiments on MCI. Technical development of the production and storage of MCI using synchrotron radiation (SR), therefore, is a key step in realizing such studies on MCI. In the present study, we tried the storage of MCI created through photoionization and the detection of trapped ions.

We used white radiation on the NE9 beamline of the accumulation ring (AR) of TRISTAN to produce MCI of rare gases (Kr and Xe). The vacuum chamber comprises an rf ion trap, a time-of-flight (TOF) mass spectrometer and a gas handling system. The intensity of the photon flux at the ionization region in the trap was estimated as 10^{13} photon s^{-1} mm^{-2}. The MCI created inside the trap electrode were confined under various trapping conditions. We measured the number of ions confined in the trap by extracting the ions from the trap and conducting them to a particle detector. Charge state distribution of ions in the trap was determined from the TOF mass spectra. The ultimate pressure after baking for 8 hours at 330K was 1x10^{-7} Pa. Introduction of rare gases into the chamber brought the background pressure to a range of 2x10^{-6} to 1x10^{-4} Pa.

Figure 1 shows the average ion intensity at the trapping condition for Xe^{8+} as a function of storage time. The pressure of Xe was 3x10^{-5} Pa. At the beginning of the storage period, the ion signal increases with storage time. It saturates, however, after a transit time of about 1 ms. This tendency is explained as follows; the ions are created continuously through photoionization, while MCI which collide with the background neutral gases and capture electrons are lost from the trap because of the deviation from the trap condition.

Figure 2 shows the TOF spectrum at the trapping condition for Xe^{5+}. For both Xe^{4+} and Xe^{5+} trap conditions, peaks of Xe^{2+} and Xe^{3+} were also present in the TOF spectra. Although the charge states higher than Xe^{4+} were not resolved, probably because of the rather wide energy distribution of the ions extracted from the trap, the TOF signal peaked at around the predicted position for Xe^{6+}. The spatial distribution of stored ions results in energy broadening during the extraction, leading to the lower energy resolution.
In the plasma wakefield accelerator, a high-intensity driving bunch excites a large amplitude plasma wave which, in turn, accelerates a low-intensity trailing bunch. One method to attain a high acceleration field is the use of a driving bunch-train with a triangular envelope. Preparatory experiments for this method were conducted at the KEK on a 500MeV linac. The linac provides us with a sequence of 5-6 electron bunches which generate wakefields in a plasma to accelerate or decelerate trailing bunches. Analyzing the energy of each bunch, we can observe the energy transfer between the bunches without a test beam. The theory tells us that the plasma wakefields are enhanced at certain plasma frequencies resonant with the linac bunch frequency, 2856MHz. We can probe the resonance by controlling the plasma density. The previous paper reports an energy shift of 12MeV in a less dense plasma.

The plasma chamber had a diameter of 50mm and a length of 1m with a 0.5-1kG solenoid magnetic field. A helicon wave, excited by a 5-10MHz and 0.5-1kW rf wave and fed through a helical antenna, ionized argon gas. The plasma density ranged 2-8 x 10^{12} cm^{-3}, the plasma temperature ranged 2-5eV, and the rms plasma radius was around 5mm. Combination of a bending magnet and a streak camera enabled us to measure the energy spectrum of each bunch.

Barycenter differences between experimental energy spectra with and without the plasma were calculated for all the bunches as a function of the plasma density. Two facts were taken into account in comparing them with the theory. First, the bunch length was comparable to, or even longer than, the plasma wavelength. Figure 1 shows the theoretical time evolution of the wakefield with the bunch positions. Let us pay attention to, for example, the third bunch. Its head and tail feels acceleration, while its main body feels deceleration (~13MeV).

Second, a bunch had a broad energy distribution; the fwhm amounted to 50MeV in the absence of a plasma.

The specific data processing was as following. In the phase space of energy and longitudinal position, a bunch was assumed to have an experimentally-obtained energy distribution and the Gaussian longitudinal distribution, respectively. A wakefield was operated, which is a function of both the longitudinal position and the plasma density as given in Fig.1, onto this two-dimensional distribution. The plasma density was finely adjusted to minimize the squared sum of the differences between calculated and experimental energy shifts for six bunches.

Figure 2 shows the density dependence of the energy shifts of the third bunch thus obtained, together with the theoretical prediction. Comparing Figs. 2 and 1, we find the effect of the finite bunch length. First, it averages the wakefield, making the apparent field in the decelerating direction. Second, the resonance becomes broader as the plasma wavelength becomes shorter. Though the directly-observed energy shift was a few MeV, the agreement with the experiments and theory suggests that the energy shift inside the bunch amounted to 13MeV at the maximum in this case of the third bunch, as shown in Fig. 1.

References
Scintillating plate calorimeters with wavelength shifting fiber readout (tile/fiber calorimeters) have been developed as a candidate for precision calorimetry in the SSC experiment [1]. Radiation hardness is an important issue for calorimeters running in the high radiation environment in SSC detectors. The maximum radiation dose that is induced by mainly minimum-bias π°s at electromagnetic shower maximum is estimated to be 58 krad at pseudorapidity \( \eta = 1.5 \) and 5.7 Mrad at \( \eta = 3.0 \) for 10 years of operation at a design luminosity of \( 10^{33} \text{ cm}^{-2}\text{s}^{-1} \).

Radiation damage to scintillating tiles and fibers has been studied so far using radioactive sources or low-energy beam of several MeV. These tests are adequate to investigate radiation damage to scintillating tiles and fibers themselves, but do not provide complete test of a calorimeter. In order to investigate systematic effects of radiation damage on the performance of a calorimeter, we have constructed real electromagnetic test modules and irradiated them with 2.5-GeV electron beam at the KEK linac.

The test module consisted of 21 layers of 6.35-mm thick lead and 3-mm thick scintillating tile. The tile was 11.1 cm square in cross section, made of Kuraray SCSN-81 scintillator, in which Kuraray Y-7 wavelength shifting fiber was embedded. The irradiation took place at the beam dump area of the KEK linac, from May 23 to July 20, 1991. The linac was operated at repetition rates of 1 to 6 Hz. The beam spot was roughly 8 cm and was swept over the module surface with two steering magnets.

The performance degradation of two test modules was measured in an electron beam at the \( \pi \rightarrow 2 \) test beam line of the KEK 12-GeV electron synchrotron. The pulse height peak for 2-GeV electrons was found to decrease by 19.3 ± 1.3% (14.9 ± 2.7%) for the module irradiated to 0.61 Mrad (0.33 Mrad). The response map across the calorimeter surface was also measured before and after irradiation. No significant change was observed.

In addition to these measurements, we irradiated several tile/fiber assemblies with the electron beam up to 4.8 Mrad by placing them at various depths of a lead absorber stack. The light yield of these tile/fiber assemblies was measured before and after irradiation with a Ru source. From these measurements we determined the radiation damage as a function of dose.

We made a GEANT simulation using the measured relationship of damage vs dose. The simulation reproduced the \( \pi \rightarrow 2 \) test beam results well, and was used to predict effects of radiation damage for electrons of higher energy, which are of central interest in the SSC experiment. It is shown that the tile/fiber calorimeter using existing plastics is a candidate for precision calorimetry in the barrel region \( \eta < 1.5 \). For the endcap \( 1.5 < \eta < 3.0 \), we need to develop new plastics which is more resistant to radiation and an engineering design allowing for replacement.

The results of this experiment were presented in the SDC meeting at LBL in August, 1991, and were regarded as one of the most convincing work on radiation damage of the tile/fiber calorimeter. For more detail, see Ref. 2.


Introduction

A wavelength dispersive type X-ray fluorescence (WDXRF) analysis has been developed using a flat crystal analyzer in combination with a position sensitive proportional counter (PSPC), which can obtain XRF spectra with higher energy resolution than the energy dispersive (Si(Li) detector) XRF.

In this report, the results of two types of experiment are described: 1) elemental mapping with medium (0.1 mm) spatial resolution, and 2) the high energy resolution XRF analysis which enables the chemical state analysis in the small region.

Results

Elemental Mapping: Experiments were carried out at BL-4A. The experimental detail was reported elsewhere. For the elemental mapping, the signal intensity was crucial. Effects of excitation modes and analyzer crystals were studied. The efficiency of the continuous spectrum of SR from a bending magnet was about 100 times stronger than the monochromatic excitation obtained with a synthetic multilayer monochromator (W/Si, 2d=61.2 Å), while the signal to background ratio is higher for the monochromatic excitation than the continuous excitation. The mosaic analyzer crystals, i.e., a lapped Ge and a graphite, were effective for the strong signal intensity but the energy resolution was determined by the mosaic spread and geometrical factors.

Fig. 1 shows the elemental mapping of the peridotite obtained with the continuous SR excitation and the lapped Ge analyzer crystal (111 reflection). The incident beam size was about 0.1 mm². The Fe signal was so strong that the weak Co K signal was difficult to separate in the Si(Li) detector measurement. It was confirmed that Co has the same distribution as Cr. This demonstrates the capability of the WDXRF imaging with spatial resolution.

High resolution XRF spectrum: For the high energy resolution XRF spectra measurement, higher order reflection of nearly 90 degree Bragg angle is favorable. A flat crystal of Si 444 reflection (θB=81.4°) was used for the Cu Ka spectra measurement. Fig. 2 shows the Cu Ka spectrum from a Cu metal. The energy resolution of this arrangement is expected to be about 0.2 eV which is narrower than the natural line width of Cu Ka radiation. This type of measurements is important for both spectroscopy and spectrometry. Since the irradiation area was about 0.1 X 0.5 mm², it is possible to measure the chemical effect in the XRF spectrum in a small region or a small amount of the sample.

1) K.Ohashi et al., Adv. in X-Ray Anal. vol.35 In press
HIGH SPATIAL RESOLUTION X-RAY FLUORESCENCE IMAGING

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Introduction

The development of the X-ray imaging technique which has the chemical sensitivity is essential for the material science, biology and geology. In the hard X-ray region, the X-ray fluorescence (XRF) imaging with high spatial resolution is pursued by many researchers using an X-ray microprobe technique (microprobe XRF) as well as a line-beam technique in combination with an image reconstruction algorithm (line-beam XRF)(1).

In this report, two types of the XRF imaging techniques were applied to the analysis of the elemental distribution in the cross section of the human hair.

Experimental

Experiments were performed at the beamline 4A. An experimental configuration is schematically shown in Fig.1 for the line-beam XRF. For the line-beam XRF, an elliptical mirror (Pt coated fused quartz) was used for the vertical focusing to obtain the higher throughput than an asymmetrical reflection. A bent crystal monochromator was used for the horizontal focusing. For the microprobe XRF, SR was monochromatized by a double crystal monochromator and focused with a modified Kirkpatrick-Baez configuration in which a spherical mirror (upstream) and an elliptical mirror (downstream) were used for the vertical and horizontal focusing respectively. The incident X-ray intensities at the sample were about 1 x 10^6 and 1 x 10^7 photons/sec for the line-beam and microprobe XRF respectively. Both systems have the spatial resolution of around 6 μm. The higher photon flux density (about 4 x 10^7) was obtained with a multilayer (Si/W, 2d=61.2 A) monochromator for the microprobe XRF.

A single strand of human scalp hair was washed, embedded in the epoxy resin and cut in thin sections of 10 μm to 40 μm thickness perpendicular to the hair strand.

Results and Discussion

Fig. 2 shows the Zn, Ca and S K fluorescence intensity distribution from a section of human hair obtained with the line-beam XRF. As is shown in the optical micrograph of the sample, the hair consists of an innermost medulla and an outer cuticle, with a cortex in between. At the medulla, Ca signal is strong while Zn signal is weak. The Zn concentration is also high at the periphery. Another hair without medulla showed that the Zn distribution was relatively constant but Ca was strong at the outer edge. Considering the homogeneous distribution of S, incorporation of trace element Zn and Ca is different from the behavior of S.

The line-beam XRF is superior to the microprobe XRF in the incident X-ray intensity for bending magnet SR, but the capability of the point analysis is obtained only with the microprobe XRF. Both methods seem to be complementarily in the XRF imaging.


Fig.1 The experimental arrangements of the line-beam XRF imaging.

Fig.2 The elemental mapping of the cross section of the human hair. The intensity distributions of Zn (upper right), Ca (lower left) and S (lower left) K fluorescence signal obtained with the line-beam XRF. 3.2 μm x 61 translational steps and 3° x 60 rotational steps. 6 sec collection time for each projection step. An optical micrograph is also shown in the upper left.
SAMPLE THICKNESS AND CHOPPING FREQUENCY DEPENDENCE IN X-RAY PHOTOACOUSTIC SIGNAL INTENSITY OF PURE Cu

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Introduction

When materials are irradiated with X-rays, several effects such as absorption, scattering, fluorescence, electron release, and heat production occur. Heat production by X-ray absorption had been thought not to include any spectroscopic information because of its secondary or multi-process character. Recently, the heat production by X-ray absorption has been detected by a photoacoustic method using synchrotron radiation with Cu alloys and compounds in the Cu K-edge regions. The purpose of the present report is to present detailed experimental results concerning the sample thickness and chopping frequency dependence in X-ray photoacoustic signal intensity of pure Cu.

Experimental

The monochromatic X-rays were obtained from the Beam Line 4A. The X-ray beam intensity was modulated by a rotating lead plate chopper with frequencies from 5 Hz to 50 Hz. The photoacoustic cell has a sample chamber with a volume of 0.16 cm³ at the center and two beryllium windows together with an electret microphone. Pure Cu foils between 5 μm and 300 μm were used as specimens.

Results and Discussion

Fig. 1 shows the sample thickness dependence of photoacoustic signal at each chopping frequency. The maximum peaks are seen at 10 μm thickness region. Fig. 2 shows the chopping frequency dependence at each sample thickness. Fig. 3 shows the power of frequency dependence at each samples. For the samples less than 20 μm, the value of the power is -1.0 which is in good agreement with RG theory. However, the value of the power more than 20 μm samples shows -0.5, which does not agree with the predicted value by RG theory.

Fig. 1 Sample Thickness Dependence of the photoacoustic signal intensity.

Fig. 2 Chopping frequency dependence of the photoacoustic signal intensity.

Fig. 3 The values of the power of chopping frequency.
CHARACTERIZATION OF ONE GALIUM LAYER DOPED SILICON CRYSTAL
BY X-RAY STANDING WAVE ANALYSIS.

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Recently atomic layer doping, introduced by Wood\(^1\), is investigated by several method because the electronic structure is useful for electric devices. However because the preparing the ideal one layer structure is difficult, it is important to characterize this crystal structure. Most of investigation is carried out for Sb atomic layer doped crystal because it is easy to prepare the epitaxial structure. However in the case of high amount of Sb it is difficult to make ideal crystal structure. As for Ga atoms the epitaxial structure can be deposited for rather high amounts although the diffusion of Ga in Si substrate is considerable. In this work we characterized the Ga atomic layer doped crystal in Si(111) by X-ray standing wave method. This sample was observed by TEM\(^2\), from which observation the structure around the Ga layer is epitaxially grown and upper layer of Si deposited as amorphous structure.

We used wavelength of 0.78\(\AA\) of incident X-ray because it needs to avoid the Compton peak and the aditional peak generated by exciting the Ge K-shell in the pure germanium detector used for measuring the Ga K-fluorescence X-ray. The cross section of the incident X-ray was limited by slit system to 0.1mm wide and 0.5mm high. We also measured the X-ray standing wave with the incident beam of 0.04mm wide and 0.3mm high to check the effect of bent of the sample, however the results were not changed.

The experimental results are shown in figure. The opened and closed circles are correspond to the diffracted and Ga K-fluorescence X-ray respectively. The data were normalized by intensities of incident X-ray monitored by ionization chamber in front of the sample. The reflectivity was decided by fitting the experimental data with calculated curve with mean least square method. The reflectivity of asymmetric monochromator is taken account of in calculation by convolution. From the fitting we obtained the coherent ratio \(f_C\) of 1.00 and extension \(d/d_{111}\) of 0.95. the \(d\) is the distance between Ga layer and Si layer and \(d_{111}\) is the distance of Si(111) planes. The high coherent ratio suggests that the sample is perfect crystal.

References
CHARACTERIZATION OF ANTIMONY ATOMIC LAYER DOPED CRYSTAL BY X-RAY STANDING WAVE METHOD

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We applied X-ray standing wave method to characterization of the atomic layer doped Si crystal containing the small amount of Sb atoms.

Experiments were carried out at BL-14B vertical wiggler beam line. The wavelength of 1.304Å of X-ray was selected by the premonochromator system of Si(111) double crystal set in vacuum. After diffracted by this premonochromator, we used the Si(400) crystal of the asymmetric factor of 3.5 for the nondispersion scheme. The size of the X-ray beam was limited to 4mm wide and 1mm high by the slits before the sample. The sample used in this study is the Si(100) wafers containing one Sb atomic layer, which is grown by solid phase epitaxy. The top Si amorphous layer is about 800Å thick. The whole thickness of the sample is about 500μm.

In the case of small intensity of the fluorescence yield, the angular dependence of the Compton tail can not be neglected. The signal to noise ratio is about 1/7. In order to subtract the Compton effect we measure the angular dependence of Compton tail simultaneously. The opened and the closed circle are the intensities of diffracted beam and the Sb L-fluorescence X-ray yields respectively. The counting rate of the fluorescence signal is less than 1 cps. The solid lines of the figure are the calculated curves for the diffracted beam and the fluorescence yield. The vertical scale of the experimental data is decided by fitting with the calculated ones using the least mean square method for the both of the diffracted X-ray and the fluorescence yield. The origin of the horizontal coordinate presents the position of the center of the diffracted X-ray peak. The effect of the angular distribution of the incident beam due to the asymmetric monochromator is introduced to the calculation by making the convolution and the thermal vibration is taken account of in the calculation as the Debye factor. For fitting the curves we use also the parameters of the electric noise level and the efficiency of the detectors. From the calculation the best fitting was obtained with the extention \((d_{SB} - d_{400})/d_{400}\) of 0.03 and the coherent ratio \(f_c\) of 0.86. Where \(d_{SB}\) is the distance between the layer of Sb and that of Si and \(d_{400}\) is the distance between Si(400) planes. The \(f_c\) of 0.86 is rather low value. This is considered that some of Sb atoms diffuse in the Si crystal. From the figure the full width at half maximum for the diffracted beam of about 3.4 arcsec is consistect with the calculation. This suggests that the sample has high perfectivity.
Small-angle X-ray scattering study on the deformation processes of toughened nylon-6/poly(phenylene ether) blend and high-impact polystyrene

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Introduction
When polymer materials are deformed, energy-absorbing occurs during deformation. Crazing, shear yielding and cavitation are known as main deformation processes in polymers. For the investigation of microstructural changes during deformation, electron microscopy have been used. Recently, by using intense synchrotron radiation (SR), dynamic studies on crazing of styrenic polymers have been carried out. In the present study, SR was applied to investigation of cavitation as well as crazing.

Experimental
Nylon-6/poly(2,6-dimethyl-1,4-phenylene ether)/rubber blend (nylon/PPE/rubber blend) and high impact polystyrene (HIPS) were used as samples. Tensile specimens, which were 64mm long, 14mm wide, and 2mm thick with two U-notches as stress concentrators, were stretched at a speed of 0.5mm/min. The time-resolved scattering profiles were measured by imaging plate (IP) using an IP rapid exchanger on BL-15A. The wavelength of monochromatized X-rays was 0.150nm.

Results
Two dimensional SAXS patterns of the nylon/PPE/rubber blend during a tensile test are shown in Figure 1 together with the stress-strain curve. The patterns (A), (B), and (C) were measured at the points A, B and C in the stress-strain curve. The tensile direction is horizontal. In the elastic deformation region, the pattern (A) was same as the undeformed SAXS pattern (isotropic). At the point slightly exceeding the yield point, the pattern (B) increased in intensity and, however, was still nearly isotropic. The pattern (C) further elongated beyond the yield point became anisotropic, perpendicular to the tensile direction, as the elongation further proceeded.

Figure 2 shows the SAXS patterns and the stress-strain curve of the HIPS. In the elastic deformation region, HIPS also showed an isotropic pattern (A). Just before yields point, SAXS pattern (B) first showed a streak parallel to the tensile direction resulting from crazes growing in the perpendicular direction. At this point the fibrils within the craze were not oriented. When the specimen was further stretched (the SAXS pattern (C)), the streak perpendicular to the tensile direction arose, showing a cross pattern. In the cross pattern, the perpendicular streak is caused by stretched fibrils parallel to the tensile direction within the craze.

By utilizing SR, the deformation processes of polymers, such as cavitation and crazing, can be examined dynamically and microscopically. We are applying this technique to nylon/PPE blends with different kinds of rubbers in order to find what causes the differences of mechanical properties between these materials.

References
The aim of this work is to study the effect of the electron-electron correlation on the band structure and the geometry of the Fermi surface of vanadium. For this purpose we have measured high resolution Compton profiles of vanadium. The Compton spectrometer is essentially a set of four Cauchois type X-ray spectrometers which are arranged on the surface of a cone and share a scattering angle of 160°. The Compton profiles associated with all four directions can be acquired simultaneously on imaging plates. Using 60keV X-rays and with a momentum resolution of 0.12 atomic units the profiles were taken along 36 separate crystallographic directions in order to reconstruct the 3-dimensional electron momentum density. The figure 1 shows the profiles of the valence electrons along the [111], [110] and [100] directions together with the band theoretical predictions by Wakoh and Matsumoto[1]. The area under the profiles are normalized to the number of electrons in the valence bands. The fine structures mainly due to the jungle-gym structure of the hole surface in the 3rd band are clearly observed in the present experiment. The experimental and theoretical directional differences among the profiles along the three directions are plotted in Fig.2. As seen from Figs. 1 and 2, although the theory reproduces the general features of the experiment qualitatively, there is a quantitative disagreement between the experiment and theory; the theory underestimates the higher-momentum components, and overestimates the fine structures and the directional differences. This is because the effect of electron-electron correlation is incompletely included in the theory.

The authors have found that high-quality silicon single crystal films can be epitaxially grown from its amorphous phase with irradiation of brilliant X-rays at lower temperatures around 500°C using synchrotron radiation [1]. This solid-phase epitaxy with X-ray irradiation is called "SPEXI". However, it has not been clear how the growth processes of SPEXI differ from those in the conventional solid-phase epitaxy (SPE) by thermal annealing.

Especially in liquid or gas phase epitaxy, incorporation of impurities into the crystal during growth strongly depends on the growth temperature, growth rate, structure of growth interface, growth direction, etc. Therefore, growth processes can be understood through the impurity distribution of the grown crystal.

The purpose of this report is to clarify differences between SPEXI and SPE of the implantation-induced amorphous Si (a-Si) by observing segregation of implanted impurities.

Phosphorus ions were implanted into (100)p-type (8-10^15 cm^-2) Si single crystal substrates by multi-acceleration scheme. The substrate holder was kept at LN2 temperature for amorphization. The as-implanted profile of phosphorus has a region of uniform concentration (3.7x10^19/cm^2) extending from the surface down to a depth of ~350nm (Fig.1).

For SPEXI, the specimens were irradiated with brilliant X-rays through three beryllium windows with a thickness of 0.2 mm from the 54-pole wiggler (BL-16 line) which had photon energies larger than 4keV. The irradiation was performed in vacuum (10^-2 torr) using a water-cooled holder. The storage ring was operated at an acceleration voltage of 2.5 GeV and a ring current of 300mA.

The temperature of the specimen was measured by a radiation thermometer. The average growth rate was estimated by monitoring the He-Ne laser beam intensity reflected by the surface of the specimen during SPEXI. The crystallinity of the grown layer was investigated by laser Raman spectroscopy with an Ar ion laser(514.5nm). Phosphorus concentration was measured by secondary ion mass spectroscopy (SIMS).

Figure 1 shows the depth profiles of phosphorus before and after SPEXI about 800°C where regrowth of the amorphized layer was completed for 1 second in the region having nearly uniform concentration, phosphorus concentration of SPEXI film is about 15% higher than that of as-implanted specimen, whereas the situation is opposite in deeper region. Moreover, a spike can be seen in near surface region of SPEXI film. The Raman peak intensity for SPEXI film showed the same polarization vector dependence as that for single crystal; the amorphized region is fully transformed to the epitaxially grown single crystal. Therefore, redistribution of phosphorus after SPEXI can be considered as a result of segregation at the growth interface during SPEXI with a segregation coefficient less than unity. (Segregation coefficient of phosphorus between liquid and solid has been reported to be 0.35 in the dilute case.)

In the conventional SPE of implanted a-Si, concentration profile of the impurity remains with almost the same as the implanted one or implanted atoms always diffuse into the deeper region. (The concentration of impurities after SPE can never overcome the as-implanted level except with the case where regrowth is largely retarded by certain implants like In.) Therefore, the observation of impurity segregation in SPEXI means that SPEXI is essentially different from growth in the thermal SPE. This difference can be attributed to more than 3 orders of magnitude faster diffusion caused by X-ray irradiation [1].


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**Figure 1.** Depth profiles of phosphorus atoms before and after SPEXI.
There has arisen a renewed interest in the structural transition sequence in close-packed metals in connection with novel concepts like the "devil's staircase". In the rare-earth metals, the successive structural change \( \text{hcp} \rightarrow \text{Sm-type} \rightarrow \text{dhcp} \rightarrow \text{fcc} \) with increasing pressure and decreasing atomic number has been observed. Recently Bruinsma and Zangwill showed that several long-period stacking structures of hexagonal close-packed layers observed in the Mg-based alloys can be stabilized by an additional contribution of the strain energy to the electronic energy of the system. In this context, this study has been started primarily to investigate whether in the rare-earth metals polytypic structures with longer period appear upon the pressure and temperature changes or not.

In situ, energy-dispersive, synchrotron powder x-ray diffraction measurements were carried out up to 8 GPa and 700°C using the multi-anvil press MAX80 on beamline NE-5 at the TRISTAN accumulation ring in KEK. We chose Gd as a sample since Gd is known to exhibit the \( \text{hcp} \rightarrow \text{Sm-type} \rightarrow \text{dhcp} \) sequence within the pressure and temperature ranges accessible to MAX80. Two out of fifteen specimens were capsulated together with silicon oil in a nickel container and compressed hydrostatically at a temperature below 300°C. Others were enclosed in vanadium foil to avoid unfavorable reaction and pressurized in solid medium.

Since the 8H structure has the shortest stacking period in terms of the "hexagonality(H)-cubicity(K) lattice", namely HHHK, among an infinite number of possible polytypes in-between the hcp(H) and Sm-type(HHK) structures, we expected that the 8H structure could have the widest stability field being observable. The experimental results, however, led us to a negative conclusion. Key reflections of the 8H structure were never found in the diffraction patterns obtained. All of the patterns consist of reflections from the hep, Sm-type, and dhcp phases of Gd and from the nickel capsule. Throughout the present study, only three structures of hep, Sm-type, and dhcp were observed. It is concluded that long-period structures are not stable beyond a pressure interval of a few tenths of a GigaPascal, even if they exist.

All data obtained for increasing pressure and temperature above 250°C are summarized in Fig. 1. Both the hcp-Sm-type and Sm-type-dhcp transitions proceeded very sluggishly and accompanied a large transition hysteresis, which made it difficult to identify the stable structure somewhat. Nevertheless the present results clearly demonstrate that the hcp-Sm-type phase boundary with a positive slope terminates at the triple phase point located at 6.1 GPa and 600°C. It is noteworthy that the phase diagram for Gd shown in Fig. 1 has striking similarities in both the location of each phase and the presence of a triple phase point to that for Sm proposed by Evele et al. These new aspects of the structural stability would result in slight modifications of generalized phase diagrams for the rare-earth elements. Duthie and Pettifor recognized that the d-band occupancy plays an essential role in determining the crystal structure in the rare-earth elements. The present results imply that there are additional mechanisms giving rise to destabilization of the Sm-type structure at high temperatures.

Investigation of the Structure of Colloidal Dispersions by Bonse-Hart Type Ultra-small-angle X-ray Scattering on Synchrotron Radiation Source.


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Introduction

In 1966, U. Bonse and M. Hart developed a small-angle X-ray scattering apparatus having a very high angular resolution by using two grooved single crystals as a monochromator and an analyzer. [1] In principle, this apparatus can cover a structural investigation of the order of micron, and has such an advantage that applications to three dimensional analysis of turbid systems and liquids, solutions and dispersions are possible, whereas could not be studied by the optical microscope, and light scattering techniques. However, no systematic investigation by this system has been reported except a few examples [2]. Last year, we constructed a Bonse-Hart type Ultra-small-angle X-ray Scattering (USAXS) apparatus by using a rotational anode X-ray generator as a light source, and had succeeded to investigate the ordered structure of colloidal dispersions [3,4]. In the present study, we have tried to investigate colloidl dispersions of much lower concentration and polymer solution using the Bonse-Hart geometry on the synchrotron radiation light source.

Experimental

The apparatus was constructed at the beam line BL-3A of Photon Factory, Tsukuba. The schematic of the optical systems is shown in Fig.1. Two kinds of latices were used; SS-80 powder and MSC-14 dispersion. SS-80 was polystyrene-based and MSC-14 was polymethylmethacrylate-based latex. Both of latices were synthesized in Kyoto University. MSC-14 latex dispersion was purified by ultra-filtration and ion-exchange resin. The dispersion after purification showed iridescence, indicating that the latex particles arranged in ordered manner in the dispersion. The powder sample was sandwiched by Scotch tape, and the sample dispersion was pipetted into metal-flat cell [5].

Results and Discussion

The scattering pattern of SS-80 latex powder showed 7 maxima which are characteristic for an isolated sphere at a suitable position for the sphere of diameter 2800Å. The efficiency of our instrument is now guaranteed.

Figure 2 shows the scattering pattern of MSC-14 latex dispersion in ordered state. In the scattering profile, the distinct Bragg peaks (thin arrow) are observed in addition to the particle scattering. The vertical bars are the peak position expected for cubic lattice systems. Obviously, the lattice system of the arrangement of latex particle in dispersion is concluded to be a face-centered cubic (fcc) lattice. The interparticle distance calculated from peak position is found to be close to the one calculated from concentration with assuming uniform distribution, which is reasonable at this relatively higher concentration range studied here.

Measurements for the dispersions of polystyrene-based latices in ordered state were also tried. However, although the interference peaks could be observed, the scattered intensity was not strong enough to enable us to extract definite results. Some additional device, such as focusing, to increase the beam intensity may be necessary for further applications especially to detail structural analysis of the solution, which we try in near future. Finally, we like to emphasize that Bonse-Hart camera can become a very powerful technique for the investigations not only of colloidal dispersions but also polymer and metal alloy systems, fiber systems, and many other systems having fluctuation in the order of micrometers.

References

Anomalous behavior of hydrogen bond length of K₃H(SO₄)₂ under pressure

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Introduction
Hydrogen bond materials are one of the most attractive and widely studied system to investigate phase transition phenomena because of the existence of a large isotope effect on a phase transition temperature $T_c$. The material group K₃H(SO₄)₂ has the following unique points: 1) The phase transition temperature of K₃D(SO₄)₂ is $T_c(\text{D})=84\text{K}$, while the hydrogen compound does not show the phase transition, $T_c(\text{H})<0$. 2) There is a critical concentration $x_c$ at which $T_c$ of K₃(HD)(SO₄)₂ tends to zero. 3) Only one hydrogen atom takes place in a dimer of SO₄ molecules, and the hydrogen net work is essentially zero dimensional. Recent works concerning the structure analysis of K₃(HD)(SO₄)₂ indicate that the hydrogen bond length $R_{00}(\text{H})$ is accidentally very close to the so-called critical bond length $r_c(\text{H})$, and that $R_{00}(\text{H})$ gradually decreases and crosses $r_c(\text{H})$ accompanied by the lattice contraction when temperature is decreased.

The purpose of the present experiment is to reveal the behavior of the hydrogen bond length under external pressure which causes the lattice contraction at room temperature.

Experimental and Results
X-ray powder diffraction experiments with a diamond anvil cell were carried out on the 8C beam line at room temperature. Imaging plate was used as a detector. Obtained intensity data were analyzed by a Rietveld method with a program RISTAN. Shown in Fig. 1 is the observed and calculated intensity at various pressures. Fitting of Rietveld analysis seems to be reasonably good. Lattice parameters decrease as a function of pressure, and the distance between atoms such as K-K decreases ordinary when pressure is increased. On the other hand, the bond lengths which are related to the hydrogen bonding shows anomalous behavior. In Fig. 2, bond lengths $R_{00}$ and $R_{0g}$ of a SO₄ dimer are shown. In spite of the lattice contraction, these bond lengths increase at high pressure region. Triangle marks in the figure indicate the data given by the conventional structural analysis of single crystals.

We conclude that the hydrogen bond length of K₃H(SO₄)₂ does not decrease even when the unit lattice contracts. This behavior is extraordinary compared with other hydrogen bond system such as KDP, SQ-acid etc., and we speculate that this behavior relates to the characteristics of the zero dimensional hydrogen net work.


Fig. 1 Obtained and calculated intensity.
Fig. 2 Hydrogen bond length 04-04 and distance between two molecules S-S as a function of pressure.
PRESSURE-INDUCED PHASE TRANSITION FROM CRYSTAL TO AMORPHOUS STATE IN Si AND Ge

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National Research Institute for Metals, Sengen, Tsukuba, Ibaraki 305

Introduction

The amorphous-crystalline transition of evaporated amorphous silicon (EV a-Si) is reversible while that of evaporated amorphous germanium (EV a-Ge) irreversible. To study the difference in the reversibility of the phase transition in more detail, X-ray diffraction measurements were carried out at various pressures and temperatures for amorphous silicon-germanium alloys, crystalline silicon (c-Si) and crystalline germanium (c-Ge). In course of these studies, an amorphization from quenched high-pressure crystalline phase was observed even in the case where the starting materials were crystalline samples (c-Si and c-Ge). Since depressurization at room temperature of high pressure phase of c-Si and c-Ge results in transformation to metastable crystalline phases, it has been found that 1-atm state after pressure-temperature (P-T) cycles depends on paths in the P-T diagram. The potential barrier between each phases plays important roles to explain the difference in the 1-atm state through the P-T cycles. This is because that these phase transitions are those between the metastable phases in a finite time. Since thermal energy needed for surmounting the potential barrier changes with temperature, informations about the potential barriers can be obtained by observations of the phase transitions at various temperatures. In this work, we report phase transitions of c-Si and c-Ge in the heating process from 90K up to 330K at various constant pressures.

Experimental

X-ray diffraction measurements were carried out by a transmitting energy-dispersive method using a synchrotron radiation. Powdered samples and pressure marker (NaCl) were compressed together with a ethanol-methanol fluid in a diamond-anvil cell which allowed a continuous pressure control at low temperatures.

Results and Discussion

Figures 1 (a) and (b) show the phase diagram of c-Ge and c-Si, respectively. With increasing pressure at 100K, c-Ge transforms into the β-Sn phase. The β-Sn phase is quenched even when pressure is reduced down to 2 GPa. This quenched β-Sn phase undergoes amorphization when heated around 2 GPa. Similar amorphization from quenched β-Sn phase was also observed in c-Si. On the other hand, the quenched β-Sn phase of c-Ge changes into BC-8 phase predominantly when heated at 4.0, 5.5, 7.5 GPa. The BC-8 structure is one of metastable crystalline form of c-Ge, which is closely related to the ST-12 structure. The quenched β-Sn phase of c-Si also transforms into the BC-8 phase when heated at 4.0 and 6.5 GPa. From these results, it is found that the heating at different pressures results in the different states at 300K. These results were discussed in relation to the pressure variations of the potential barrier height between the β-Sn and the amorphous phases and that between the β-Sn and metastable crystalline phases. The amorphous germanium obtained through the amorphization from the quenched β-Sn phase of c-Ge is called pressure-induced amorphous germanium (PI a-Ge) to distinguish from that prepared by other methods. Peak position in the X-ray diffraction pattern of PI a-Ge are listed in table 1 together with those of EV a-Ge and liquid Ge. The peaks of PI a-Ge locate more closely to those of EV a-Ge than those of liquid Ge. It is expected, therefore, the coordination number of PI a-Ge is about four as that of EV a-Ge is.

References

3) M. Imai, T. Mitamura, K. Yaoita and K. Tsuji, Proc. 4th Intern. Conf. on High Pressure in Semiconductor Physics, Port Garras, Greece, (1990) p. 188.

TABLE 1.

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<tr>
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<td>1.9</td>
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Q₀ : position of i th peak.
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Session of the 15th IUCr Congress

Y. Amemiya
Report on the 3rd International Conference on
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Int. Conference Sci. Tech. Defect Control
Semiconductors. (1990) 673.

T. Kobari, S. Ueda, O. Satoh, M. Matsumoto and
M. Kobayashi
Outgassing Rate of the Stainless Steel Chamber
After Low Temperature Bakeout

T. Koizumi
Multiple Photoionization of Metal Atoms: d-Shell
Photoionization of Alkali, Alkaline-Earth and
Rare-Earth Atoms.

N. Kosugi
Cu K-Edge X-Ray Absorption Spectroscopy of High
T. Superconductors

K. Koto
EXAFS and Its Application in Mineralogy
Japanese).

C. Li, K. Lu and Y. Zhao
An EXAFS Study of the Structural Morphology of Ni
in Synthetic Diamond

E. Matsubara, K. Okuda and Y. Waseda
Anomalous X-Ray Scattering Study of Aqueous
Solutions of YCl₃ and ErCl₃

E. Matsubara, K. Okuda, Y. Waseda, S. N. Okuno and
K. Inomata
Structural Study of Amorphous Co-Ferrite Film by
Anomalous X-Ray Scattering

H. Matsubara, K. Fukuyama and T. Tsuji
Heat-Labile Entrotoxin of Toxinogenic E. coli
Nihon Ouyou Sanso Kyokaishi, 25 (1990) 27. (in
Japanese).

M. Matsumoto, M. Kobayashi, Y. Horii, T. Kobari,
T. Ikekuchi and S. Ueda
Photodesorption from Stainless Steel, Aluminum
Alloy and Oxygen Free Copper Sample Ducts

S. Matsuoka and I. Hatta
Recent Developments of the Structural Study of
Phospholipid Membrane by Synchrotron X-Ray
Scattering II. Oriented Multilayers and
Monolayers

C. Miyake, M. Hirose, Y. Yoneda and M. Sano
The Third Phase of Extraction Process in Fuel
Reprocessing.(II) EXAFS Study of Zirconium
Monobutylphosphosphate and Zirconium Dibutylphosphosphate

Y. Nagahara, N. Konishi, Y. Yokoo and N. Hirayama
Crystallization and Preliminary Diffraction
Studies of Recombinant Human
Granulocyte-stimulating Factor KH2228

T. Nagata, M. Yoshino, T. Hayashi, Y. Itikawa,
T. Koizumi, T. Matsuo, Y. Sato, E. Shigemasa,
Y. Takizawa and A. Yagi-shita
4d-Shell Photoionization of Xe, Cs, Ba, Sm, Eu
and Yb Atoms Studied by Photoion Yield Spectra

M. Nagura, Y. Hi-ragi, K. Kaji-ara and M. Tsukada
Small Angle X-Ray Scattering of Native Liquid Silk
Fibron in a Silkgland and of Dilute Aqueous
Solution of Silk Fibron
J. Sericultural Sci. Jpn., 59 (1990) 475. (in
Japanese).

N. Nakamura
Present Status of Beam Position Stabilization at
Photon Factory Storage Ring

N. Nakamura, A. Araki, K. Haga, Y. Kamiya, T. Katsura
and Y. Inoue
Influence of the Building Distortion on the Closed
Orbit at the Photon Factory Storage Ring

Y. Nannichi and H. Ogawa
The Effect of Sulfur on the Surface of II-V
Compound Semiconductors

M. Niibe, M. Hayashida, T. Iizuka, A. Miyake,
Y. Watanabe, R. Takahashi and Y. Fukuda
Suppression of Columnar-Structure Formation in
Mo-Si Layered Synthetic Microstructures
X-Ray/EUV Optics for Astronomy, Microscopy,
Polarimetry. Projection Lithography, 1343 (1990)
2.

Y. Noda
Structure of CsCl-Type Alloy -Average Structure
and Local Structure in Alloys-

K. Oda, N. Kondo and K. Shibata
X-Ray Absorption Fine Structure Analysis of
Interstitial (C, N)-Substitutional (Cr) Complexes
in Austenitic Stainless Steels
ISIJ Int., 30 (1990) 625.

K. Ohno, H. Harada, T. Yamagata and M. Yamazaki
Numerical Resolution Enhancement of X-Ray
Diffraction Patterns

350

H. Oigawa, J. Fan, Y. Nannichi and M. Kawabe
Epitaxial Growth of Al on (NH₄)₂Si-Treated GaAs

A. Rajalakshmi, M. Seshasayee, G. Aravasudan,
T. Yamaguchi, M. Nomura and H. Ohtaki
Structural Studies on Superionic Glass
AgI-AgO-MoO₃

H. Sakane, I. Watanabe, K. Ono, S. Ikeda, S. Kaizaki
and Y. Kushi
Structures of Fe(III) Complexes with EDTA and
EDDDA in Aqueous Solution by EXAFS and XANES

S. Sasaki
Crystal Structure Analysis of Single
Microcrystal-KBSiO₃ Examplified-

S. Sasaki
Local Structure Study by X-Ray Anomalous
Scattering :An Example on Orthopyroxene

S. Sudoh, T. Miyanaga, S. Ohta, Y. Nagao, S. Katagiri
EXAFS Study on Chloranilate Complexes of Lanthanid (II)

T. Takeda, M. Akisada, I. Anno, T. Nakajima, K. Ueda,
K. Umetani, and C. Yamaguchi
SR Cine k-Edge Subtraction Angiography of the
Rabbit Coronary Arteries

N. Toshima and M. Harada
Structure and Catalytic Function of Metal Clusters
in Dispersed Solution

K. Tsukimura, S. Sasaki and H. Ohashi
Determination of Ternary-System Cation
Distribution in (Co, Ni, Zn)SiO₃ Pyroxene
Employing Two-Wavelength Anomalous Dispersion
with Synchrotron Radiation

S. Ueda, M. Matsumoto, T. Kobari, T. Ikeguchi,
M. Kobayashi and Y. Hori
Photosorption from Stainless Steel Aluminum
Alloy and Oxygen Free Copper Test Chambers
Vacuum, 47 (1990) 183.

K. Umeo, M. Itakura, N. Kuvano and K. Oki
Anomaly in Electrical Resistivity of PdCe
Intermetallic Compound under High Pressure

K. Usuda, S. Yasuami, Y. Higashi, H. Kawata and M. Ando
Lattice Parameter Measurement of GaAs Crystals
Using Monochromatic Synchrotron Radiation

Y. Waseda and E. Matsubara
Structural Investigation of Amorphous and
Quasicrystalline Al-Base Alloys by the Anomalous
X-Ray Scattering (AXS) Method

T. Yamaguchi
Diffraction and X-Ray Absorption Studies of
Electrolyte Solutions

T. Yamaguchi, T. Morita, T. M. Salama and K. Tanabe
Surface Properties of ZrO₂ Dispersed on SiO₂

H. Yamashita and A. Tomita
Relation between Chemical Form and Activity of
Iron Catalyst for Coal Gasification

H. Yamashita, Y. Ohtsuka, S. Yoshida and A. Tomita
Change in Local Structure of Iron Species During
Pyrolysis of Iron-Loaded Brown Coal

A. Yonath, W. Bennett, S. Weinstein and H. G. Wittmann
Crystallography and Image Reconstruction of
Ribosomes and Biochemistry in Structural Studies of
Ribosomes

A. Yoshizawa, H. Maeda, T. Ishii and K. Koto
EXAFS Studies on Anharmonic Thermal Vibrations in

H. Yoshino and Y. Izumi
Calmodulin-Molecular Shape Change and Expression of Function

1991

Y. Amemiya and K. Wakabayashi
Imaging Plate and Its Application to X-Ray
Diffraction of Muscle

M. Ando
More Students and Young members

K. Asakura
Techniques of EXAFS Measurement -Sample

K. Asakura and Y. Iwasawa
Synthesis, Characterization and Catalytic
Properties of SiO₂-Attached One-Atomic-Layer
Niobium Oxide Catalysts

K. Asakura, K. Bando, Y. Iwasawa, H. Arakawa and
K. Isobe
Metal-Promoted Hydroformylation on SiO₂-Supported
Rh Dimer: A Direct Observation of the Structure
Change of Active Site in Working conditions

Two-Dimensional Photoelectron Diffraction Patterns by Display-Type Spherical Mirror Analyzer


X. M. Ding, T. Miyahara, H. Okumura, S. Muto, H. Namba and H. Kuroda

Existence of Ga Dangling Bonds on As-Stabilized GaAs(100) (2×4)-c(2×8) and Al1Ga1-As(100) Surfaces


Anomalous Temperature-Dependent Local Structure in κ-(BEDT-TTF)2Cu(NCS)2


J. Dong and K. Lu

Noncubic Symmetry in Garnet Structures Studied Using Extended X-Ray Absorption-Fine-Structure Spectra


K. Edamatsu, Y. Takata, T. Yokoyama, K. Seki, M. Tohama, T. Ohashi and T. Ohta

Local Structures of Carbon Thin Films Synthesized by the Hot Filament Chemical Vapor Deposition Method: X-Ray-Absorption Near-Edge Structure and Raman Spectroscopic Studies


Oxygen Adsorption on a NbCo3(111) Surface: Angle-Resolved Photoemission Study


S. Emura, T. Moriga, T. Murata, H. Maeda, A. Koizumi and M. Nomura

Local Structure Around Cu Impurities in Sodium Chloride


T. Fujii, H. Moriyama, A. Takeyama, N. Tanaka, T. Wakagi and T. Oshima

Cristallization and Preliminary X-Ray Studies on Sulfolobus Acidocaldarius Ferredoxin


Y. Fujinaga, K. Kusaba, Y. Syono, H. Iwasaki and T. Kikugawa

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M. Funahashi, T. Yokoyama, T. Takata, T. Ohta, Y. Kitajima and H. Kuroda

Surface Structure of Cl/Na(111) Determined by Surface EXAFS Spectroscopy and Soft X-Ray Standing-Wave Method


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Enhanced Killing Effect on 5-Bromodeoxy-Uridine Labelled Bacteriophage T1 by Monoenergetic Synchrotron X-Ray at the Energy of Bromine K-Shell Absorption


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Y. Hatano

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T. Hondo, R. Hoshi, A. Goto and H. Yamagami

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Preparation and Catalytic Properties of a New SiO2-Attached b-Bimer Catalyst; Regulation of Acidity-Basicity by the Number of Metal Atoms in Surface Active Sites


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Analytical Applications of Synchrotron Radiation

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Semiconductor Surface Characterization by Synchrotron X-Ray Fluorescence Analysis

M. Imai, T. Mitamura, K. Yaoita and K. Tsuji
Reversible Phase Transition from Amorphous State to Crystal Induced by Pressure in Silicon-Germanium Alloys

Preliminary Crystallographic Study of a Pseudoazurin from Methylo-trophic Bacterium, Methylo-Bacterium Extorquens AM1

H. Ishii, K. Asakura, H. Namba, N. Kosugi, H. Kuroda, Y. Kitajima, M. Funabashi and T. Ohta
Surface EXAFS Studies of Sulfur Adsorbed on Stepped Surface: Si/Ni(7911)

M. Ishikawa, A. Iida, T. Ishii, S. Hayakawa and K. Okoshi
Elemental Distribution on the Scale of the Red Sea Bream Chrysophrys Major Scanned by a Synchrotron Monochromatized X-Ray Microbeam

M. Itakura, K. Umeo, N. Kuvano and K. Okiki
Influence of Disordering upon Concentrated Kondo Effect for PtCe Alloys

M. Itoh, S. Tohno, M. Adachi, T. Yamamoto and S. Tsukui
Study of Local Structure of Ultratine Silver Particles in Mesoscopic Regime by SOR (2) Fluorescence EXAFS

M. Itoh, S. Tohno, M. Adachi, T. Yamamoto and S. Tsukui
Study of Local Structure of Ultratine Silver Particles in Mesoscopic Regime by SOR (1) Transmission EXAFS

H. Iwasaki
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Y. Iwasawa
EXAFS Studies on SiO2-Attached Nb-Oxide Catalysts and Catalysis

Y. Izumi, K. Asakura and Y. Iwasawa
Promoting Effects of Se on Rh/ZrO2 Catalysis for Ethene Hydroformylation

T. Izumi, T. Kurihama, T. Douzaka, R. Isomura, M. Yamazita, H. Mori and T. Nakajima
Effects of Sr Irradiation of High-Tc Superconductors and Effects of Substituting Elements in the Materials

H. Kageyama and N. Kamijo
High Temperature XAFS Study of Perovskite Type La2-xSrxCuxOy (X=0.2, 0.5)

K. Kajiwara, S. Kohjiya, M. Shibayama and H. Urakawa
Characterization of Gel Structure by Means of SAXS and SANS

A. Kajiwara, M. Kamachi and H. Maeda
Structural Insights from the Extended X-Ray Absorption Fine Structure of Polycrystalline with Paramagnetic Tetraphenylporphyrato-Silver(II) and -Erbium(III) Derivatives.

K. Kameta, M. Ukai, R. Chiba, Y. Hatano and K. Tanaka
Absolute Measurements of Photoabsorption Cross Sections, Photoionization Cross Sections, and Photoionization Quantum Yields of Silane in the 13-40 eV Region

Y. Kashiwase, M. Kogiso, M. Mori, M. Minoura, T. Ishikawa and X. Zhang
Dynamical Diffraction Effect on X-Ray Inelastic Scattering in Absorbing Perfect Germanium Crystal in the Laue Geometry

M. Kataoka, J. F. Head, T. Vorherr, J. Krebs and E. Carafoli
Small-Angle X-Ray Scattering Study of Calmodulin Bound to Two Peptides Corresponding to Parts of the Calmodulin-Binding Domain of the Plasma Membrane Ca2+-Pump

M. Kataoka, J. F. Head, A. Persechini, R. H. Kretsinger and D. M. Engelman
Small-Angle X-Ray Scattering Studies of Calmodulin Mutants with Deletions in the Linker Region of the Central Helix Indicate that the Linker Region Retains a Predominantly α-Helical Conformation

M. Kataoka, N. Sato, T. Hamamana, Y. Amemiya and F. Tokunaga
Properties of the Disorder Induced in the Purple Membrane Structure by Iodination

Y. Katayama, K. Maruyama, M. Yao and H. Endo
Spatial Correlations and Defects in Isolated...
Selenium-Sulfur Mixed Chains

M. Katayama, M. Aono, H. Oigawa, Y. Nannichi, H. Sugahara and M. Oshima
Surface Structure of InAs (001) Treated with (NH₄)₂ S Solution

K. Kato and Y. Sugitani
X-Ray Photoacoustic Imaging of Surface Subsurface Layers of Structured Materials

S. Kawado, S. Kojima, I. Maekawa and T. Ishikawa

S. Kawado, S. Kojima, I. Maekawa and T. Ishikawa
Synchrotron X-Ray Topography of Growth Striaions in Magnetic-Field-Applied Czochralski Silicon

S. Kawado, S. Kojima, I. Maekawa and T. Ishikawa
Influence of Crystal Imperfection on High-Resolution Diffraction Profiles of Silicon Single Crystals Measured by Highly Collimated X-Ray Beams

High-Resolution Measurements of Nuclear Bragg Scattering from a Synthetic α-Fe₂O₃ Crystal

Static and Kinetic Studies on the Dissociation of Limulus Polyphemus Hemocyanin with Solution X-Ray Scattering

S. Kishimoto
An Avalanche Photodiode Detector for X-Ray Timing Measurements

A. Kita, N. Kasai, S. Kasai, T. Nakaya and K. Miki
Crystallization and Preliminary X-Ray Diffraction Studies of a Flavoprotein, FP₃₉₀ from a Luminous Bacterium, Photobacterium phosphoreum

M. Kitajima, K. Nakamura, M. Fujitsuka, H. Shinno, H. Katoh and T. Miyahara
UV Photoemission Study on the Valance Band of Mo(110) during Argon Ion Bombardment

T. Kitano, J. Mizuki and J. Matsu
XAFS Study of Cu Precipitates on Microdefects in FZ-Si Crystals

T. Kitano, T. Ishikawa and J. Matsu
Lattice Spacing Measurements Around Dislocations in an Undoped GaAs Crystal Grown by the Liquid-Encapsulated Czochralski Method

K. Kobayashi, K. Hieda, H. Maeda, Y. Furusawa, M. Suzukii and T. Ito
Effects of K-Shell X-Ray Absorption of Intracellular Phosphorus on Yeast Cells

T. Koide
Elliptical-Polarization Analyses in the UHV and Soft X-Ray Regions: Determination of the Stokes Parameters with a Reflection Polarimeter

T. Koide, T. Shidara, M. Yuri, N. Kandaka and H. Fukutani
Production and Direct Measurement of Circularly Polarized Vacuum-Ultraviolet Light with Multireflection Optics

S. Koide, T. Shidara, M. Yuri, N. Kandaka, K. Yanaguchi and H. Fukutani
Elliptical-Polarization Analyses of Synchrotron Radiation in the 50 eV Region with a Reflection Polarimeter


T. Koyano, E. Kita, K. Ohshima and S. Emura
EXAFS Study of Superionic Conductor A-Bi₂O₃ at High Temperature

T. Koyano, E. Kita, K. Ohshima and S. Emura
Synchrotron X-Ray Diffraction Study of Fe/MgO Multilayered Films with an Enhanced Magnetization

H. Kubo
Spectroscopic Studies in JT-60

T. Kubota, M. Kawamoto, K. Fukuyama, K. Shinzawa-Itoh, S. Yoshikawa and H. Matsubara
Crystallization and Preliminary X-Ray Crystallographic Studies of Bovine Heart Mitochondrial Cytochrome bc1 Complex

N. Kuriyama, H. Nasu and K. Kamiya
EXAFS Study on the Local Structure around Cu in the Nitrogen-Annealed Bi₁₃Pb₁₀Sr₃Ca₂Cu₂O₉ Superconductor

J. Lee, L. Wei, S. Tanigawa, H. Oigawa and Y. Nannichi
Evidence for the Passivation Effect in (HK₄)₂ S₂
Treated GaAs Observed by Slow Positrons

J. Lee, L. Wei, S. Tanigawa, H. Oigawa and Y. Nannichi
The Effect of Surface Oxides on the Creation of Point Defects in GaAs Studied by Slow Positron Beam

H. Li, Z. Ju and K. Lu
EXAFS and Diffraction Study on the Structure of Ba$_2$Sr$_1$Nb$_2$O$_9$

T. Liu, Y. Matsui, U. Lee, K. Asakura and Y. Iwasawa
Structures and Catalysis of Plane [PtMo$_6$O$_{24}$]$^-$
Polyanion Supported on Al$_2$O$_3$ and SiO$_2$

Transmission Anisotropy of Circularly Polarized X-Ray Absorption on Fe and Ni Metals and Nd$_3$Fe$_4$B Compound

H. Maruyama, T. Iwazumi, H. Kawata, A. Koizumi, H. Maeda and T. Ishii

Discommensurations and Diffraction Patterns of Thiourea

T. Maruyama, Y. Sakisaka, H. Kato, Y. Aiura and H. Yamashita
Angle-Resolved Photoemission Study of Hydrogen Adsorbed on Fe(110)


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Characterization of Earth and Planetary Minerals by Synchrotron Radiation Induced X-Ray Fluorescence Analysis

I. Nakai
Local Structure of Amorphous Gd$_6$Ni$_3$ Alloy

I. Nakai, S. Honma, N. Shimojo and A. Iida
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M. Nakasako, M. Kataoka, Y. Amemiya and F. Tokunaga
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H. Nakashima, S. Tanaka, M. Yoshizawa, H. Hirayama, S. Dan, Y. Namito and N. Nariyama
Development of a Microcalorimeter for Measuring Absolute Intensity of Synchrotron Radiation

Y. Nara, Y. Sugita, N. Nakayama and T. Ito
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Design and Performance of Beamline 7C at the Photon Factory

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Y. Ogawa, T. Shidara and A. Asami
Direct Observation of the Multibunch Instability Caused by a Transverse Wake Field

K. Ohno, K. Ohsumi, H. Harada, T. Yamagata and M. Yamazaki
Determination of Lattice Parameter and Strain of C Phases in Nickel-Based Superalloys by Synchrotron Radiation Parallel Beam Deffractometry

H. Ohno, N. Iwaga, T. Mukita, K. Igarashi, T. Kikegawa and O. Shimomura
X-Ray Diffraction Analysis of Molten AgCl under Ultra High Pressure

H. Ogawa, J. Fan, Y. Nannichi, H. Sugahara and M. Oshima
Universal Passivation Effect of (NH4)2S Treatment on the Surface of III-V Compound Semiconductors

K. Okabe, N. Matsubayashi, K. Sayama, H. Arakawa and A. Nishiijima
EXAFS Investigation of Pentasil-Structured Gallium-Containing Metallosilicates

Y. Okamoto, T. Imanaka, K. Asakura and Y. Iwasawa

S. Okamura, E. Miyauchi and T. Hisatsugu
Outgassing Measurement of Finely Polished Stainless Steel

K. Oki, Y. Saito, H. Sato, M. Itakura, N. Kuwano, S. Yamashita, T. Yamaguchi and H. Wakita
Intermediate Valences of Ce and Electrical Resistivity Changes of Pd-Ce Intermetallic Compounds

K. Okoshi, M. Ishikawa and A. Iida
Elemental Distribution on the Growth Front of Oyster Shell Measured by Synchrotron Monochromatized X-Rays

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Structure of Copper(II)-bp and -phen Complexes: EXAFS and Spectrophotometric Studies on the Structure of Copper(II) Complexes with 2,2'-Bipyridine and 1,10-Phenanthinoline in Aqueous Solution

K. Ozutsumi, Y. Miyata and T. Kawashima
EXAFS and Spectrophotometric Studies on the Structure of Mono and Bis(aminocarboxylato) Copper (II) Complexes in Aqueous Solution

N. Sakai, N. Ito, H. Kawata, T. Iwazumi, M. Ando, N. Shiotani, F. Itoh, Y. Sakurai and Y. Nanao
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Storage and Lifetime Measurements of Multiply Charged Ions Produced by Synchrotron Radiation

K. Sakurai, Y. Yamada, C. Lee, T. Fukunaka and U. Mizutani
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XANES Spectra of Co(aba)3 and Co(acac)3 in Solid and Solution

Y. Sano and T. Sasaki
Mechanism of Microgel Formation of
Cellooligosaccharides by Small Angle X-Ray Scattering Methods

K.Seki, T.Yokoyama and T.Ohta
Polarized Inner-Shell Absorption Spectroscopy of Oriented Organic Films

K.Shibata, K.Oda, N.Kondo and B.Chi
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High-Resolution Absorption Cross Sections of Carbon Monoxide Bands at 295 K between 91.7 and 100.4 nm.

H.Sugahara, M.Oshima, R.Klauser, H.Oigawa and Y.Nannichi

H.Sugahara, M.Oshima, H.Oigawa, H.Shigekawa and Y.Nannichi

Y.Sugita, Y.Nara, N.Nakayama and T.Ito
Synchrotron-Radiation-Induced Modification of Silicon Dioxide Film at Room Temperature

Thermstable Aspartate Aminotransferase from Wintersiella species

S.Suzuki, T.Takahashi, T.Kusunoki, T.Morikawa, S.Sato and H.Katayama-Yoshida
Polarized Cu L III Absorption Study of a Bi2Sr2CaCu2O8

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T.Takahashi
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H.Takahashi, S.Matuoka, S.Kato, K.Oki and I.Hatta
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T.Takahashi, S.Nakatani, N.Okamoto, T.Ishikawa and S.Kikuta
A Study of the Si(111)√3×√3-Ag Surface Transmission X-Ray Diffraction and X-Ray Diffraction Topography

N.Takasue, M.Morinaga, N.Yukawa, M.Kato, K.Oshina, J.Harada, S.Sasaki and S.Hanada
Computer Simulation of Local Atomic Displacements in Diffuse Oegea Phase

T.Takeda, Y.Ikita, H.Yoshioka, M.Akisada, K.Ueda and K.Umetani
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K.Takemura, O.Shimosura and H.Fujihisa
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S.Tohno, M.Itoh and K.Takahashi
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M. Ukai, K. Kameta, R. Chiba, K. Nagano, N. Kouchi, K. Shinohara, Y. Hatano, H. Umemoto, Y. Ito and K. Tanaka
Ionizing and Non-Ionizing Decays of Superexcited Acetylene Molecules in the Extreme-UV Region

Y. Ukisu, A. Kazusa and M. Nomura
Oxidative Dimerization of 1-Propyne on a 2-Pyridylethyl Copper Complex Fixed Silica Catalyst

K. Umetani, K. Ueda, T. Takeda, M. Akisada, T. Nakajima and I. Anno
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