

Real-Time Observation of Cobalt Surface Oxidation Reactions Proceeding in the Depth Direction by Wavelength-Dispersive Soft X-Ray Absorption Spectroscopy

The real-time observation of the oxidation process of a Co thin-film surface under exposure to air up to 10 Pa was realized by a fluorescence-yield wavelength-dispersive X-ray absorption spectroscopy (XAS) method in the soft X-ray region, which also has subnanometer depth resolution. The series of Co L-edge XAS spectra shows that the oxide increases from the surface to deeper regions. It is anticipated that this method can be used to analyze various systems and paves the way for real-time observation, such as surface chemical reactions with higher gas pressure, as well as magnetic and electric fields.

It has long been a challenging task to observe surface chemical reactions proceeding in the depth direction without stopping the reaction, with subnanometer depth resolution. For conventional measurements of X-ray absorption spectroscopy (XAS) in the soft X-ray region, a block of time is needed, preventing real-time observation of the chemical reaction. To overcome the drawback of the measurement time, a method to illuminate the sample with dispersed soft X-rays was developed, in which the fluorescence soft X-rays emitted at each position on the sample are separately collected [1]. The method enabled the simultaneous detection of the

signal from a range of energies. Furthermore, the detection of fluorescence soft X-rays has been realized to extend the range of applicable gas pressures, and this method enabled observation under a gas pressure of ~100 Pa. Although we have already developed a non-destructive depth-resolved XAS measurement method, depth-resolved analysis in real time has not been actualized as a simultaneous measurement. In this study, real-time observation with a fluorescence-yield wavelength-dispersive XAS method was realized, which can also analyze the depth profile of chemical composition with subnanometer resolution at the same time. The Co oxidation process of thin-film surfaces during exposure to air was focused on as one example application. We measured Co L-edge XAS, whose absorption peak is at ~780 eV during exposure to air while increasing the pressure up to ~10 Pa, and analyzed the depth profile of the surface area simultaneously.

Figure 1 [2] shows schematic illustrations of the wavelength-dispersive XAS measurement from the side view (a) and top view (b). The wavelength-dispersed soft X-rays, in which the wavelength (energy) continuously changes depending on the position, illuminate the sample surface, and fluorescence X-rays emitted from each position on the surface are separately focused to each position on the soft X-ray detector by an imaging optics. The x-direction of the detector is used for acquiring the energy spectrum, and the y-direction is used for depth-resolved analysis by the angle-resolved method [1, 2].

Prior to the measurement, an ultrathin 1-nm layer of Co was deposited on an Al₂O₃ (0001) substrate at 10⁻⁵ Pa. Subsequently, we measured the XAS of the Co surface continuously while air was gradually introduced into the chamber up to ~10 Pa from 10⁻⁵ Pa.

Figure 2(a) shows depth-integrated Co L-edge X-ray absorption spectra changing with time from bottom to top while introducing atmospheric air. In the initial stage of the measurement, the peak of the spectrum is at ~779 eV, which is the same position as Co and CoO standard sample, then the peak gradually shifts to higher energy, the same peak position as Co₃O₄, and

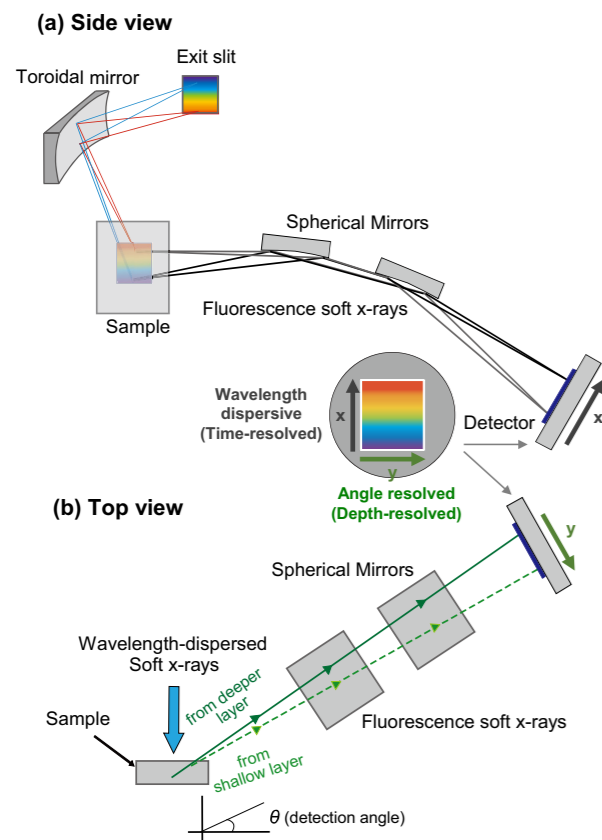


Figure 1: Schematic illustration of the optical configuration of the fluorescence-yield wavelength-dispersive XAS measurement in this study from (a) side view and (b) top view [2].

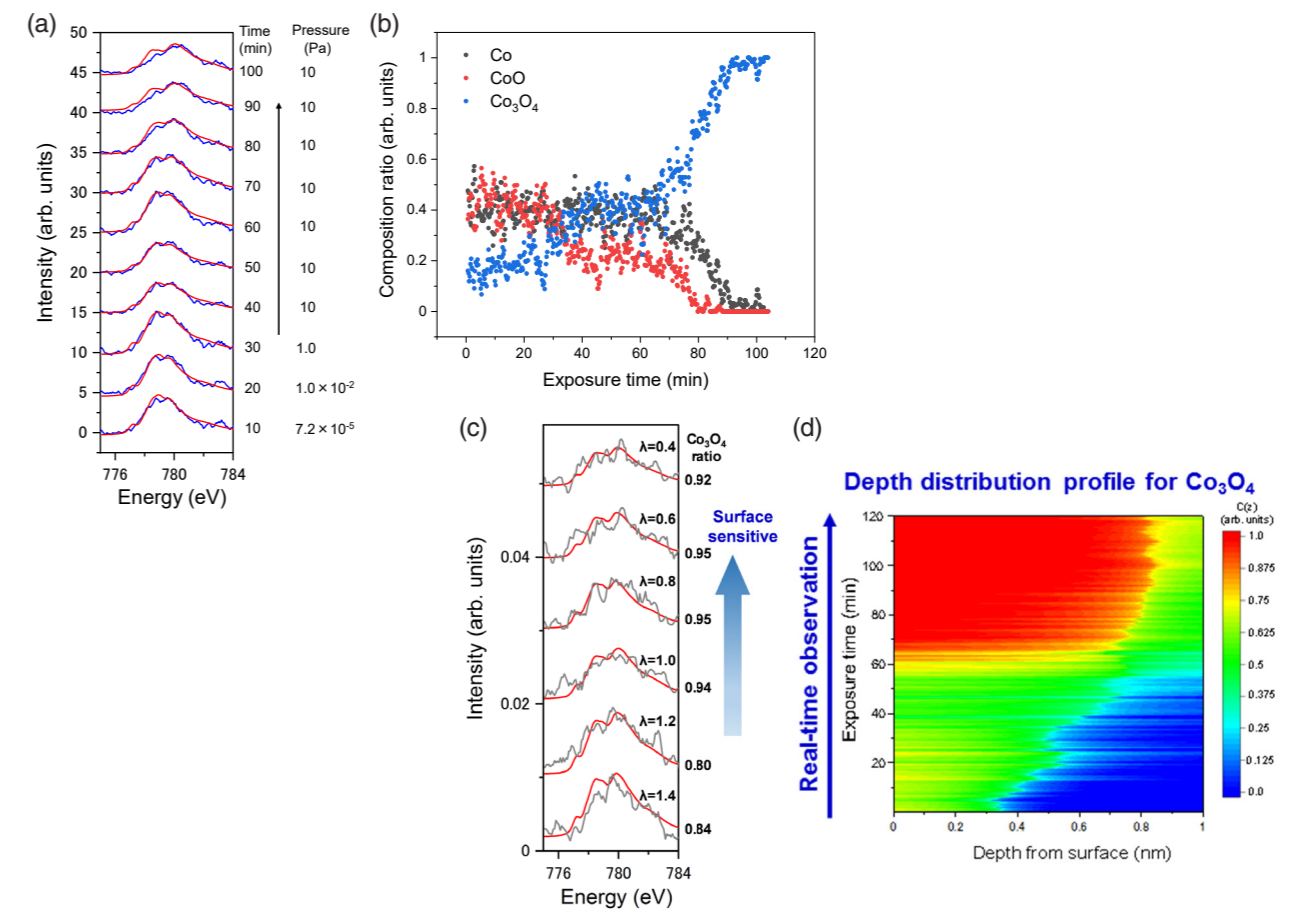


Figure 2: (a) A series of Co L-edge X-ray absorption spectra for CoO/Al₂O₃ was sequentially recorded (from bottom to top) by the wavelength-dispersive method. The interval of each spectrum is 10 min, and all the spectra were obtained with an exposure time of 10 s for each spectrum. Red line spectra are fitted using reference spectra of Co, CoO, and Co₃O₄. (b) Composition ratio of Co (black dots), CoO (red dots), and Co₃O₄ (blue dots) in the fitted spectra of the Co thin film oxidation process corresponding to the process time. (c) Typical depth-resolved spectra fitted by a linear combination of Co, CoO, and Co₃O₄ reference spectra (at 70 min). The Co₃O₄ ratio in the figure is derived from the fitting factor of each spectrum. (d) Contour map of the C(z) profile for Co₃O₄ corresponding to exposure time [2].

they show a remarkable shift, especially when the pressure in the chamber is 10 Pa. To quantify the degree of oxidation, the ratios of Co, CoO, and Co₃O₄ in the fitted spectra were analyzed, as shown in **Fig. 2(b)**. At the beginning of the measurement, Co and CoO are dominant at ~0.6–0.4. This suggests that the Co surface is partially oxidized in the initial stage, and then oxidation gradually proceeds, i.e., the ratio of Co₃O₄ increased. We also obtained the depth-resolved spectrum as shown in **Fig. 2(c)**. We fitted each spectrum with probing depth from $\lambda = 0.4$ to 1.4, and the ratio of Co, CoO, and Co₃O₄ of the fitted spectra was obtained corresponding to the processing time. A gradual peak shift towards higher energy can be found with decreasing probing depth, which suggests that the degree of oxidation is higher around the surface. Therefore, the chemical component C(z), e.g., that for Co₃O₄, as a function of depth profile was assumed in order to analyze the depth-dependent oxidation; details of the analysis are described elsewhere [2]. In **Fig. 2(d)**, the depth profile C(z) for Co₃O₄ vs. exposure time is shown in the con-

tour map. It is clear that the position of the boundary of different chemical components gradually shifted as time elapsed.

These results show that we succeeded in observing Co oxidation proceeding in the depth direction in real time by using wavelength-dispersive XAS together with depth-resolved analysis, which can follow the change in the depth profile of the chemical reaction as time elapses, with subnanometer depth resolution.

REFERENCES

- [1] K. Amemiya, K. Sakata and M. Suzuki-Sakamaki, *Rev. Sci. Instrum.* **91**, 093104 (2020).
- [2] K. Sakata, M. Suzuki-Sakamaki and K. Amemiya, *Nano. Lett.* **21**, 7152 (2021).

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