3 Oxide Heterostructure Project

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3-1 Introduction

The goal of this project is to design novel physical properties appearing at the heterointerface of strongly correlated oxides. The physical properties arise from strong mutual coupling among the spin, charge, and orbital degrees of freedom in the interface region between two different oxides [1]. In order to control such properties, it is necessary to clarify the interfacial electronic, magnetic, and orbital structures. We are therefore using synchrotron radiation spectroscopic techniques having elemental selectivity to probe these structures in the nm-scale at the oxide heterointerface. For example, the electronic structure at the interface is determined by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), the magnetic structure by magnetic circular dichroism of XAS, and the orbital structure by linear dichroism of XAS. We aim to design and create novel quantum materials by optimally combining sophisticated oxide growth techniques using laser molecular beam epitaxy (MBE) and advanced analysis techniques using quantum beams.

3-2 Construction of new beamline for surface and interface studies of oxide superstructures

We have constructed and developed a new undulator beamline MUSASHI (Multiple Undulator beamline for Spectroscopic Analysis on Surface and HeteroInterface) at the BL-2 section of the PF-ring. This new beamline has two types of undulator in tandem alignment; one is designed for the vacuum ultraviolet (VUV) region (30–300 eV), and the other for the soft X-ray (SX) region (250–2000 eV). Consequently, relatively wide energy-range light while maintaining both high brilliance and high energy resolution will be available in this beamline by the combination of the two undulators and a variable-included-angle varied-line-spacing plane-grating monochromator. Moreover, an additional double-crystal monochromator is built into this branch beamline (BL-2B) to make available the energy range of 2000–4000 eV using the wiggler mode of the SX undulator. Our developed system "*in-situ* photoelectron spectrometer – laser MBE" has been installed at the new beamline BL-2A as an end station (Fig. 1).

The performance of the new beamline in terms of energy resolution has been evaluated for SX and VUV mode. The resolving power (E/ΔE) of much more than 10,000 is achieved for the SX optics of the new BL-2 beamline. Moreover, the
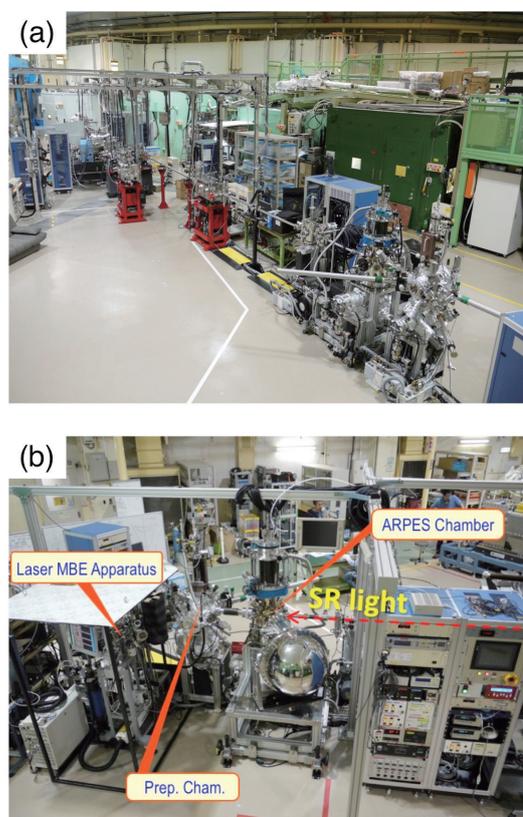
Fig. 1: Photograph of (a) BL-2A MUSASHI beamline and (b) "*in-situ* ARPES – Laser MBE system" which is installed as an end station of BL-2A MUSASHI.

photon flux at the end station is more than 10^{12} photons/sec at the energy resolution of E/ΔE ~ 10,000. For VUV mode, the resolving power is evaluated to be more than 20,000 thanks to the VUV optics of the new BL-2 beamline. This resolving power and the photon flux at E/ΔE ~ 20,000 are comparable to those of the VUV undulator beamline BL-28 at PF [2].

At the new BL-2A MUSASHI, we will perform both VUV and SX spectroscopic measurements at the same time, for the same grown sample, with the same experimental setup. This approach guarantees the quality of the experimental data, and offers numerous benefits to the field of surface science: the newly developed system enables us to obtain complete information on the electronic and chemical structures of samples grown by laser MBE with high reproducibility. For example, the chemical states and band lineup of heterostructures are characterized by X-ray photoemission spectroscopy and/or X-ray adsorption spectroscopy (XAS) using SX light, confirming the quality of the heterostructures, and then their band structures are investigated by angle-resolved photoemission spectroscopy (ARPES) using VUV light.

3-3 Science topic: Spatial distribution of transferred charges across the heterointerface between perovskite transition metal oxides LaNiO$_3$ and LaMnO$_3$

Heterointerfaces between perovskite transition metal oxides have attracted much attention because of their novel electronic and/or magnetic properties. Recently, it has been reported that an unusual spin order occurs in a paramagnetic LaNiO$_3$ (LNO) layer in the heterointerface region with a "ferromagnetic" LaMnO$_3$ (LMO) layer, resulting in the appearance of exchange bias between the two oxides [4]. In order to understand these exotic magnetic properties appearing at the heterointerface of LNO/LMO, it is indispensable to elucidate the relationships between the electronic states at the heterointerface and the interfacial ferromagnetism. In this study, we have investigated the interfacial charge transfer between Ni and Mn ions by utilizing the elemental selectivity and surface (interface) sensitivity of XAS: the changes in valence of both ions caused by the interfacial charge transfer and their spatial distributions are determined by XAS [5].

Multilayer structures composed of LNO and LMO layers were fabricated on 0.1 at. % Nb-doped SrTiO$_3$ (001) substrates in a laser MBE chamber installed at the beamline BL-2A MUSASHI. The XAS measurements of LMO/LNO and LNO/LMO bilayer structures were carried out in total electron yield mode at 300 K without exposure of the samples to air.

Figure 2 shows Ni-$L_{2,3}$ and Mn-$L_{2,3}$ XAS spectra of LNO/LMO heterostructures, as well as those of constituent films as references for trivalent Ni and Mn ions. The valence of Ni ions in the original LNO layers changes from Ni^{3+} to Ni^{2+} at the heterostructures, while that of Mn ions changes from Mn^{3+} to Mn^{4+}. These results indicate that the electron transfer occurs from LMO layers to LNO layers in the interface region, which is consistent with the case of double perovskite La$_2$NiMnO$_6$ [6].

The spatial distributions of transferred charges in the LNO and the LMO layers have been investigated by systematic thickness-dependent XAS measurements: by probing the spectral change of the *underlayer* (buried interface) as a function of overlayer thickness, the length of the charge spreading in the *overlayer* oxides can be determined as the critical overlayer thickness at which the spectral change in the underlayer oxides is saturated [5]. Figure 3 shows the results of the thickness-dependent XAS measurements on the underlayers for LNO/LMO and LMO/LNO bilayers. As can be seen in Fig. 3, the spectral change of Mn-$L_{2,3}$ XAS is totally saturated by 1-ML LNO deposition on the LMO layer, while that of Ni-$L_{2,3}$ XAS seems to continue up to 3−4 ML deposition of the LMO overlayer on LNO. These results demonstrate that the spatial distribution of the interfacial charge transfer is significantly different
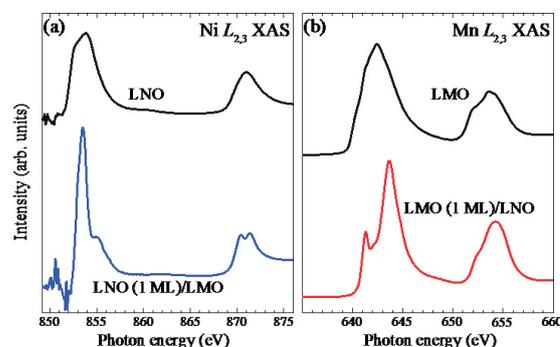
Fig. 2: Ni-$L_{2,3}$ XAS spectra of an LNO film and the 1-ML LNO *overlayer* of an LNO/LMO bilayer structure. (b) Mn-$L_{2,3}$ XAS spectra of an LMO film and the 1-ML LMO *overlayer* of an LMO/LNO bilayer structure.
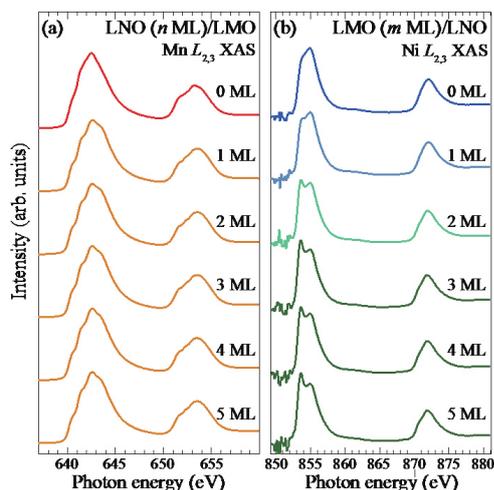
Fig. 3: (a) Mn-$L_{2,3}$ XAS spectra of the LMO *underlayer* of LNO/LMO bilayers. (b) Ni-$L_{2,3}$ XAS spectra of the LNO *underlayer* of LMO/LNO bilayers.

between the two layers. Judging from the saturation thicknesses of overlayers, the interfacial region subject to the charge transfer is evaluated to be about 1 ML for the LNO side, and 3–4 ML for the LMO side. It has been found that the observed spatial distribution is well described by a recent theoretical model treating the strongly correlated nature of both the oxides [7], suggesting that the transfer integral between neighboring transition-metal ions and the Coulomb interactions are important parameters for understanding the charge-transfer phenomena across the heterointerface of perovskite transition metal oxides.

References
[1] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nat. Mater. **11**, 103 (2012).
[2] K. Horiba, H. Ohguchi, H. Kumigashira, M. Oshima, K. Ono, N. Nakagawa, M. Lippmaa, M. Kawasaki, and H. Koinuma: Rev. Sci. Instrum. **74**, 3406 (2003).
[3] http://pfwww.kek.jp/users_info/station_spec/bl28/ bl28.html
[4] M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez, and J.-M. Triscone, Nat. Mater. **11**, 195 (2012).
[5] M. Kitamura, K. Horiba, M. Kobayashi, E. Sakai, M. Minohara, T. Mitsuhashi, A. Fujimori, T. Nagai, H. Fujioka, and H. Kumigashira, Appl. Phys. Lett. **108**, 111603 (2016).
[6] N. S. Rogado, J. Li, A. W. Sleight, and M. A. Subramanian, Adv. Mater. **17**, 2225 (2005).
[7] C. Lin, S. Okamoto, and A. J. Millis, Phys. Rev. B **73**, 041104(R) (2006).