Electronic states and Ni valencies in LaNiO₃ epitaxial films studied by synchrotron radiation photoemission spectroscopy and X-ray absorption spectroscopy

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Introduction

Perovskite-type oxides show various and novel electric properties. In order to realize high-performance devices composed of these functional oxides, electrode materials should have both sharp interface formation and metallic behavior especially in the surface and interface regions. LaNiO₃ is a paramagnetic metal [Ref. 1] and one of the most promising candidates for electrode materials. However, under the low oxygen pressure formation conditions, LaNiO₃ contains Ni²⁺ and is not a metal [Ref. 2]. In order to evaluate valency of Ni and valence band structure of LaNiO₃ thin films especially in the surface and interface regions, we performed x-ray absorption spectroscopy (XAS) and photoemission study on LaNiO₃ thin films and LaAlO₃-covered LaNiO₃ films.

Experimental

Epitaxial LaNiO₃ thin films and LaAlO₃/LaNiO₃ bilayer structures were fabricated on LaAlO₃(100) substrates by a pulsed laser deposition technique. The film growth temperature and oxygen pressure were 650 °C and 30 mTorr, respectively [Ref. 3]. Atomically flat surface of the films were confirmed by reflection high energy electron diffraction and atomic force microscope. The photoemission spectra were taken at room temperature with the total energy resolution of about 200 meV at the photon energy of 600 eV. The XAS measurements were performed by a total-electron-yield mode.

Results and discussion

Figure 1 (a) shows XAS spectra of the LaNiO₃ thin film. Ni-derived spectra ("Ni peaks") were extracted by subtracting La-derived spectra ("La peaks") from the XAS spectra. The shape of Ni $2p_{3/2}$ peaks is almost the same as reported spectra of Ni³⁺ in NdNiO₃ and different from that of Ni²⁺ in NiO [Ref. 4]. Ni $2p_{1/2}$ peaks were reported to be a single peak for Ni³⁺ and double peaks for Ni²⁺. In this study, Ni $2p_{1/2}$ peaks are made up of a single peak. These results indicate that the valence state of Ni in the LaNiO₃ thin film is mainly high valence state Ni³⁺.

In order to investigate the metallic behavior in the surface and interface regions, photoemission spectroscopy measurements of LaNiO₃ films and LaAlO₃

 $(0.8 \text{ nm})/\text{LaNiO}_3$ (20 nm) films layer were carried out. The results are shown in Fig. 1 (b). The presence of density of states at the Fermi level reflects the metallic nature of the films. Since probing depth at this photon energy is approximately 1-2 nm, it is found that these LaNiO₃ thin films maintain metallic behavior even in the surface region or the interface region between LaNiO₃ and insulator.



Fig. 1: XAS spectra of $LaNiO_3$ thin film and reported spectra of NdNiO₃ and NiO (a). Valence-band photoemission spectra of $LaNiO_3$ thin films (b).

References

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