

In-situ photoemission spectroscopic studies on Al/perovskite oxides interfaces showing resistive switching

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Introduction

Resistive switching (RS) occurring in metal/insulating oxide/metal structures has attracted much attention because of its potential applications to new nonvolatile memory devices. It has been suggested that the RS is associated with the interfacial transition layer formed by the redox reactions at the metal/oxide interface, since the RS characteristics strongly depend on the difference of redox potential between electrode materials and transition metal ions in oxides [1]. In order to investigate the relationship between the RS phenomena and the formation of transition layers due to interfacial redox reactions, we have studied the interfaces that consist of the Al electrodes and the perovskite oxides with different transition metal ions: Al/La_{0.7}Ca_{0.3}MnO₃ (LCMO) and Al/La_{0.33}Sr_{0.67}FeO₃ (LSFO), where RS behaviors are clearly observed [2, 3].

Experimental

LCMO and LSFO thin films were grown on Nb-doped SrTiO₃ substrates by laser molecular beam epitaxy. During deposition, the substrate temperatures and the ambient oxygen pressures were kept at 1050 °C and 1 × 10⁻⁴ Torr, respectively. Al metals were deposited on films by radio frequency sputtering at room temperature. Both Al/LCMO and Al/LSFO interfaces exhibited similar RS behaviors each other. Photoemission spectroscopy (PES) and X-ray adsorption spectroscopy (XAS) measurements were performed at undulator beamline BL-2C. These growth and characterization of electronic states cycles were carried out *in situ*.

Result and discussion

Figures 1 (a) and (b) show Al thickness dependences of Mn-2p and Fe-2p XAS spectra for Al/LCMO and Al/LSFO interfaces, respectively. As can be seen in Fig. 1(a), sharp peaks appear at lower photon energy around 640 eV after Al deposition. These peaks are derived from divalent state of Mn ions [4]. This result indicates that Mn ions in LCMO reduce from Mn^{3.67+} to Mn²⁺ at the interface. By the same token, chemical states of Fe ions in LSFO are also reduced. As shown in Fig. 1(b), shapes of peak Fe-2p XAS spectra get sharper with increasing the amount of Al deposition. The observed spectral behavior

is similar to that of hole-doped La_{1-x}Sr_xFeO₃ from x = 1 (Fe⁴⁺) to x = 0 (Fe³⁺) [5]. The similar spectral behavior between the two strongly suggests that Fe ions in LSFO reduced from Fe^{3.67+} to Fe³⁺ owing to Al deposition. The difference in valence state of transition metals after reduction reflects the difference of free energy for oxidation.

In addition, it was revealed from Al 2p PES spectra for both Al/LCMO and Al/LSFO that Al metal was oxidized along with the reduction of transition metal ions (not shown).

Thus, redox reactions occur at the Al/transition metal oxide interfaces showing RS. These results strongly suggest that the interfacial transition layer formed by redox reactions is responsible for the RS behavior in metal/oxide interfaces.

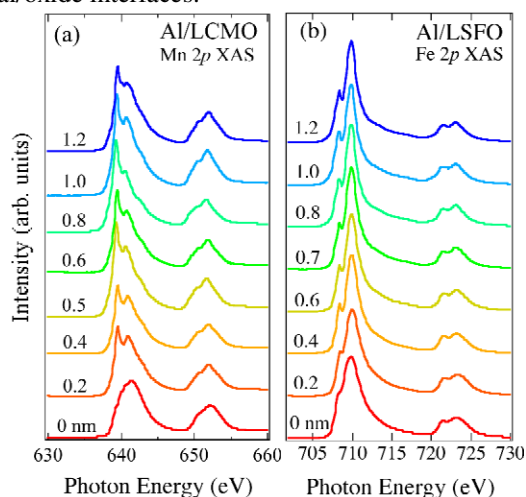


Fig.1 The dependence of (a) Mn-2p XAS and (b) Fe-2p XAS spectra on Al thickness for Al/LCMO and Al/LSFO, respectively

References

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