In situ photoemission study of metal/Pr_{0.7}Ca_{0.3}MnO₃ interfaces showing electricfield-induced resistance-switching behavior

Ryutaro YASUHARA¹, Taiki YAMAMOTO¹, Isao OHKUBO^{1,2}, Hiroshi KUMIGASHIRA*^{1–3}, Masaharu OSHIMA^{1–3}

¹Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan ²JST-CREST, Bunkyo-ku, Tokyo 113-8656, Japan

³Synchrotron Radiation Research Organization, The University of Tokyo, Bunkyo-ku,

Tokyo 113-8656, Japan

Introduction

Electric-field-induced resistance-switching behavior of Pr_{0.7}Ca_{0.3}MnO₃ (PCMO) has been intensively studied for the application to a next generation nonvolatile random access memory. However, the mechanism of the resistance switching has not been fully understood yet, which has largely hindered the development of future memory devices. It has been reported that the resistance-switching characteristics of metal/PCMO is considerably dependent on electrode materials [1]. This indicates that interfacial structures between electrodes and oxides play an important role in the resistance switching. Thus, we have investigated the interfacial electronic states of resistance-switching metal/PCMO structures by *in situ* photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS).

Experimental

Epitaxial PCMO films with a thickness of about 400 Å were grown on LaAlO₃ (100) single-crystal substrates by pulsed laser deposition. Al and Pt electrodes were deposited on PCMO films by radio frequency sputtering at room temperature. It was confirmed by current–voltage measurements that PCMO films with the Al electrode showed the resistance-switching behavior, while those with Pt electrode ohmic contact. These characteristics are in good agreement with the previous report [1]. PES and XAS measurements were carried out at an undulator beamline BL-2C.

Results and discussion

Figures 1(a) and (b) show the dependence of Al 2p and Mn 2p core level PES spectra on Al deposition thickness for Al/PCMO structures, respectively. A broad peak originated from Al oxide is observed at the first stage of Al deposition, and a sharp peak derived from Al metal suddenly appears at the lower bonding energy above the Al thickness of 4 Å. The relative intensity of the peak from Al oxide to metal is reduced with increasing Al thickness. Finally, the oxide peak disappears for the sample with Al metal of 40 Å. These results indicate that the deposited Al metal is oxidized by oxygen atoms near the surface of the PCMO film. In order to investigate how the chemical states of Mn ions changed at the Al/PCMO



FIG. 1 Dependence of (a) Al 2p and (b) Mn 2p core level PES spectra on Al deposition thickness for Al/PCMO.

interface in connection with the oxidation of Al metal, Mn 2p core levels were also measured as shown in Fig. 1(b). Satellite structures in Mn 2p core level [2] indicative of the existence of Mn^{2+} states are observed for the Al deposition thickness of 1–4 Å. Furthermore, an additional sharp peak appears at the lowest binding energy, suggesting the existence of Mn metal at the interface. From these results, it was evident that a redox reaction between Al metal and Mn oxides occurs at the Al/PCMO. On the other hand, these chemical reactions were not observed at Pt/PCMO interface (not shown) where the resistance switching does not occur. These results suggest that the redox reaction at the electrode/oxide interface is responsible for resistance-switching behaviors.

References

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^{*} yasuhara@sr.t.u-tokyo.ac.jp