# Electrode dependence of electronic structures at metal/ Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> interfaces

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# **Introduction**

Electric-pulse-induced resistance-switching (RS)behaviors in transition metal oxides have recently attracted much attention because of its potential applications to resistance random access memory (ReRAM). It has been reported that the RS characteristics of metal/Pr<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> (PCMO) interfaces strongly depend on their electrode materials [1]. Furthermore, Liao et al. have reported that RS behaviors are observed only for PCMO with an electrode metal whose free energy for oxidation is less than that for Mn metal [2]. This experimental fact indicates that the RS in PCMO is associated with the redox reactions at metal/PCMO interfaces, rather than the properties of bulk oxides. Therefore, it is important to reveal the electronic states of the electrode/oxide interface for understanding of the RS mechanism in PCMO. In this study, we have investigated the electrode dependence of the electronic states at the metal/PCMO interfaces by photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS).

# **Experimental**

Epitaxial PCMO films with a thickness of about 40 nm were grown on LaAlO<sub>3</sub> (100) single-crystal substrates by pulsed laser deposition. Al and Pt electrodes were deposited on PCMO films by radio frequency sputtering at room temperature. The RS behavior in the Al/PCMO interface was confirmed by current-voltage measurements, while the Pt/PCMO interface did not show RS. Spectroscopic measurements were carried out at an undulator beamline BL-2C. In order to observe the intrinsic chemical reactions at the interface, we performed the whole experiments in situ: PCMO film growth, electrode deposition, and subsequent spectroscopic measurements.

# **Results and discussion**

Figures 1 shows the electrode dependence of Mn-2*p* XAS spectra of Al/PCMO and Pt/PCMO structures, together with those of as-grown PCMO films. At the Al/PCMO interface, a sharp peak derived from  $Mn^{2+}$  states is observed at the photon energy of 641 eV [3]. This indicates that Mn ions in PCMO layer in the interface region are reduced from  $Mn^{3.3+}$  in as-grown PCMO to  $Mn^{2+}$  states. The detailed analysis of PES and



FIG. 1 Electrode dependence of Mn-2p XAS spectra for metal (6 Å)/PCMO structures.

XAS results reveals that the thickness of the reduced Mn oxide layer is about 4 nm. On the other hand, the shape of XAS spectrum for Pt/PCMO is almost the same as that for as-grown PCMO, indicating that there are no chemical reactions at Pt/PCMO interfaces. These results strongly suggest that the interfacial transition layer due to the redox reactions during the metal deposition is responsible for the RS behavior at metal/PCMO interfaces.

#### **References**

- [1] K. Tsubouchi et al., Adv. Mater. 19, 1711 (2007).
- [2] Z. L. Liao et al., Appl. Phys. Lett. 94, 253503 (2009).
- [3] C. Mitra et al., Phys. Rev. B 67 092404 (2003).

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