

Interfacial electronic states of resistance-switching metal/Pr_{0.7}Ca_{0.3}MnO₃ interfaces

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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_{0.7}Ca_{0.3}MnO₃ (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). 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.

Figure 1 shows the Mn $L_{2,3}$ XAS spectra for Al/PCMO, Pt/PCMO, and PCMO films. For the PCMO film, the XAS spectrum indicates the mixed valency of Mn ions between 3+ and 4+, which is consistent with the fact that the Mn ions of PCMO have a nominal valency of 3.3+. Almost the same shape is observed for the Pt/PCMO structure exhibiting no RS, indicating that the valency of Mn ions in PCMO remains unchanged even after the deposition of Pt. On the other hand, the shape of the XAS spectra dramatically changes after the deposition of Al exhibiting RS: the sharp peak derived from Mn²⁺ states is dominantly observed at the photon energy of 641 eV. The detailed analysis of the XAS spectra reveals that the valency of Mn ions is almost 2+ in the interface region. 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 [3].

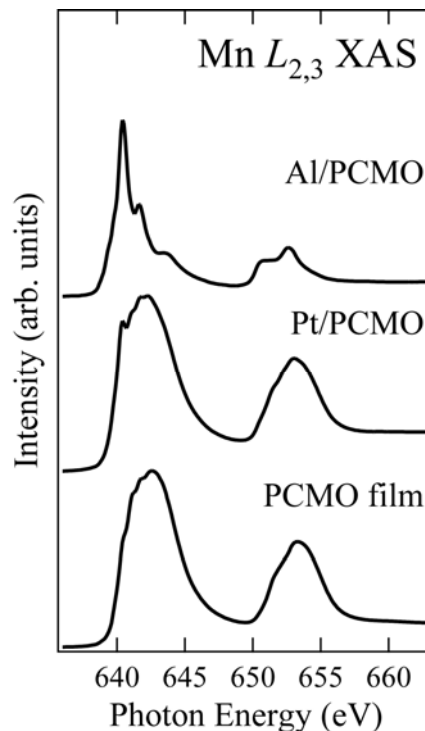


FIG. 1. Mn $L_{2,3}$ XAS spectra for Al/PCMO and Pt/PCMO interfaces, together with that of PCMO film as a reference.

[1] K. Tsubouchi *et al.*, Adv. Mater. **19**, 1711 (2007).

[2] Z. L. Liao *et al.*, Appl. Phys. Lett. **94**, 253503 (2009).

[3] R. Yasuhara *et al.*, Appl. Phys. Lett. **97**, 132111 (2010).