

## Impact of oxygen vacancy on interfacial band diagram of Ti/Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> resistive switching junctions

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### 1. Introduction

Resistive switching (RS) effects of transition metal oxides (TMOs) have attracted great attention because it can be utilized for nonvolatile memory, i.e., resistance random access memory (ReRAM), which is one of the promising candidates for the next generation nonvolatile memory. Concerning the mechanism of RS effect, it becomes clear that an electrochemical migration of oxygen vacancy at the interface of TMOs plays a crucial role[1,2], but the definitive mechanism has not been clarified yet. Since RS behaviors vary with materials such as binary oxides and ternary perovskite oxides, the driving mechanism may depend on materials[3,4].

In this study, to elucidate the mechanism of the RS effect for perovskite manganites, we have investigated the carrier concentration dependence of RS characteristics and the impact of oxygen vacancies on the interfacial band diagram of Ti/Pr<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub> [PCMO(*x*)] RS junctions. Because a vacancy acts as a hole-carrier scavenger in PCMO(*x*), the change in oxygen vacancy concentration alters carrier concentration. In the correlated electron material of PCMO(*x*), the electronic structures such as a band gap (charge-transfer gap) and Fermi level depend on carrier concentration. Therefore, the oxygen vacancies can be expected to change the interfacial band diagram, resulting in a change in interfacial transport properties, i.e. resistive switching.

### 2. Experiments

To evaluate the carrier concentration dependence of the RS characteristics, Ca-composition-spread PCMO(*x*) films with *x* = 0 - 1 were deposited on epitaxial SrRuO<sub>3</sub> (SRO) electrodes on (100) SrTiO<sub>3</sub> substrates by using a combinatorial pulsed laser deposition technique. Here, the SRO electrode realized the Ohmic contact on PCMO(*x*). The thicknesses of PCMO(*x*) and SRO layers were 30 nm and 50 nm, respectively. After Au(180 nm)/Ti(20 nm) top electrodes were deposited on PCMO(*x*)/SRO, the layered structures were patterned into mesa structures with 100 × 100 μm<sup>2</sup> in size at 100 μm intervals. Current-voltage (*I-V*) characteristics were measured to determine the RS ratio ( $R_H/R_L$ ), where  $R_H$  and  $R_L$  are resistance values of high and low resistance states, respectively.

PCMO(*x*) films with *x* = 0, 0.5, and 1 were also prepared on STO and SrTi<sub>0.9998</sub>Nb<sub>0.0002</sub>O<sub>3</sub> (Nb:STO) substrate, where Nb:STO is an *n*-type semiconductor which has the band gap of ~3.2 eV. From optical absorption spectra of the PCMO(*x*) films on STO substrates, we

evaluated a band gap. Au electrode was deposited on the PCMO(*x*)/Nb:STO, and then the layered structures were patterned into mesa structures with 100 × 100 μm<sup>2</sup>. Independently of the Ca composition *x*, the PCMO(*x*)/Nb:STO junctions showed rectifying *I-V* characteristics, indicating that depletion layers form at the interfaces. We evaluated the difference of the work functions between PCMO(*x*) and Nb:STO, i.e. built-in potential, from capacitance-voltage (*C-V*) characteristics of the PCMO(*x*)/Nb:STO junctions.

Cross-sectional transmission electron microscope images of Au/Ti/PCMO(*x*)/SRO junctions were observed to evaluate structural properties at the Ti/PCMO(*x*) interfaces which show the RS effect. For the as-prepared junctions, there was at most 1-nm thick of amorphous TiO<sub>y</sub> layer between the Ti and PCMO(*x*). After applying electric fields, the thickness of the TiO<sub>y</sub> layer increased to ~10 nm. This result suggests that oxygen ions were diffused into the Ti electrode from PCMO(*x*) layer due to an electrochemical migration. The electrochemical migration of oxygen ion can be also expected to reduce the PCMO(*x*) in the vicinity of the interface.

### 3. Results and Discussions

Figure 1 shows typical *I-V* characteristics of Ti/PCMO(*x*) with *x* = 0, 0.4, 0.6, and 1. We defined the resistance values in the low and high resistance states measured at *V* = +1 V as  $R_L$  and  $R_H$ , respectively, and the RS ratio ( $R_H/R_L$ ) is plotted as a function of *x* in Fig. 2. We measured 2 - 5 junctions for each Ca composition.  $R_H/R_L$  apparently depends on the Ca composition, i.e. carrier concentration, and it has a maximum value (> 30) around *x* = 0.4. In the case of PCMO(1), i.e. CaMnO<sub>3</sub> (CMO), the RS effect is negligibly small. These results suggest that the carrier concentration plays a crucial role in determining the RS characteristics.

Optical absorption spectra of the oxygenated and reduced PCMO(*x*) with *x* = 0.5 and 1 are shown in Fig. 3(a). To prepare the reduced PCMO(*x*) films which have a large amount of oxygen vacancies, the films were annealed at 600 °C in ~10<sup>-7</sup> Torr for 1 hour. In both of PCMO(0.5) and CMO, the reduced films have a larger band gap as compared to the oxygenated ones. Figure 3(b) shows *I/C*<sup>2</sup>-*V* characteristics in the reverse bias of oxygenated and reduced PCMO(*x*)/Nb:STO junctions. The built-in potential  $V_{bi}$  is determined from the intersection of *V* at *I/C*<sup>2</sup> = 0.  $V_{bi}$  of the reduced junctions is smaller than that of the oxygenated ones in both of PCMO(0.5) and CMO. This

result suggests that the work functions of the reduced PCMO(0.5) and CMO are smaller than those of the oxygenated ones. Since the work function of Nb:STO is  $\sim 3.9$  eV, the work functions of the oxygenated and reduced PCMO(0.5) can be estimated to  $\sim 4.8$  eV and  $\sim 4.7$  eV, respectively, and those of the oxygenated and reduced CMO are  $\sim 5.3$  eV and  $\sim 5.2$  eV, respectively. These results of the optical absorption and  $C-V$  characteristics suggest that the formation of the oxygen vacancies alters the band diagram of the PCMO( $x$ ).

From the estimated band gaps and work functions of the PCMO(0.5) and CMO, we can describe possible band alignments of the Ti/PCMO(0.5) and Ti/CMO interfaces, as shown in Figs. 4(a) and (b), respectively. Here, it should be noted that the PCMO(0.5) is a  $p$ -type semiconductor and the CMO is an  $n$ -type one. On the basis of these band for

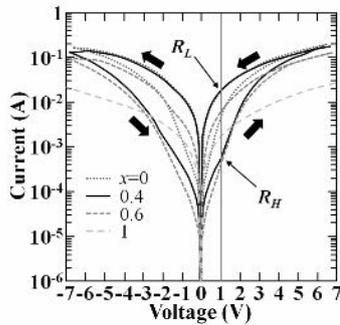


Fig. 1  $I$ - $V$  characteristics of Ti/PCMO( $x$ ) junction with  $x = 0$ , 0.4, 0.6, and 1.

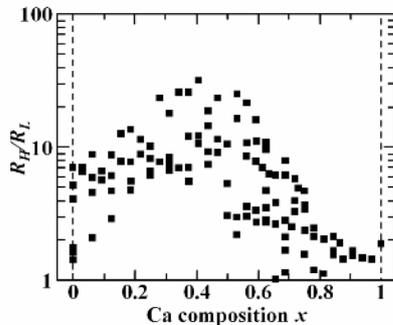


Fig. 2 Ca composition  $x$  dependence of RS ratio ( $R_H/R_L$ ) of Ti/PCMO( $x$ ) junction.

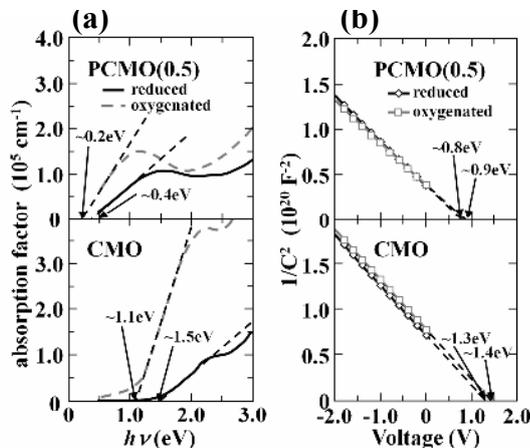


Fig.3 (a) Optical absorption spectra of PCMO( $x$ )/STO thin films ( $x = 0.5$  and 1) and (b)  $1/C^2$ - $V$  characteristics of PCMO( $x$ )/Nb:STO ( $x = 0.5$  and 1) junction.

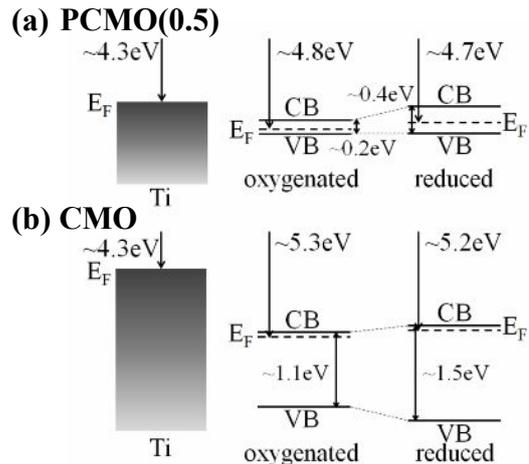


Fig. 4 Band alignments of oxygenated and reduced PCMO( $x$ ) and Ti electrode of (a)  $x = 0.5$  and (b)  $x = 1$ . PCMO(0.5) and CMO are considered as  $p$ -type and  $n$ -type semiconductors, respectively.

alignments, we propose a possible model of the RS effect for the PCMO( $x$ ). According to the voltage polarity of the RS from a low resistance state (LRS) to a high resistance state (HRS) and the formation of an amorphous  $TiO_y$  layer, the reduced PCMO(0.5) layer with a larger band gap can be expected to form in the vicinity of the interface in a HRS. Moreover, since an oxygen vacancy acts as a hole-carrier scavenger in the  $p$ -type PCMO(0.5), an effective acceptor concentration in the reduced PCMO(0.5) is smaller than that in the oxygenated one. Therefore, if the  $Ti(TiO_y)$ /PCMO(0.5) junction can be regarded as a  $p$ -type Schottky junction, the depletion layer width of the  $Ti(TiO_y)$ /reduced PCMO(0.5) is wider than that of the  $Ti(TiO_y)$ /oxygenated PCMO(0.5). Because a wide depletion layer acts as a barrier to hole-carrier conduction, the resistance of the  $Ti(TiO_y)$ /reduced PCMO(0.5) interface is larger than that of the  $Ti(TiO_y)$ /oxygenated PCMO(0.5) interface.

In the  $n$ -type CMO case, we can also expect that the reduced CMO layer forms at the interface, when a negative voltage is applied to the Ti/CMO interface. Although the reduction of the CMO alters the band diagram at the interface, the conduction-band minimum of the oxygenated and reduced CMO locates below the Fermi level of the Ti electrode, as shown in the possible band alignment of the Ti/CMO interface [Fig. 4(b)]. Therefore, the change in the band diagram of the CMO induced by the formation of oxygen vacancies has little influence on the electron-carrier conduction at  $Ti(TiO_y)$ /CMO interface, resulting in the small RS effect.

#### References

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