Hysteretic current-voltage characteristics and resistance switching at a rectifying Ti/Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ interface

A. Sawa,$^{a,b)}$ T. Fujii,$^{b,c)}$ M. Kawasaki,$^c$ and Y. Tokura$^d$

Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562, Japan

(March 23, 2022)

We have characterized the vertical transport properties of epitaxial layered structures composed of Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ (PCMO) sandwiched between SrRuO$_3$ (SRO) bottom electrode and several kinds of top electrodes such as SRO, Pt, Au, Ag, and Ti. Among the layered structures, Ti/PCMO/SRO is distinct due to a rectifying current-voltage ($I$–$V$) characteristic with a large hysteresis. Corresponding to the hysteresis of the $I$–$V$ characteristics, the contact resistance of the Ti/PCMO interface reversibly switches between two stable states by applying pulsed voltage stress. We propose a model for the resistance switching at the Ti/PCMO interface, in which the width and/or height of a Schottky-like barrier are altered by trapped charge carriers in the interface states.

Perovskite manganites have attracted considerable interest due to unusual electronic and magnetic properties, such as colossal magnetoresistance (CMR), half metallicity, and electric field induced switching of resistance, i.e. colossal electroresistance (CER). Among these characteristics, CER has recently been explored in detail. Liu et al., reported that reversible resistance change can be induced by applying pulsed voltage at room temperature for Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ (PCMO) sandwiched between Ag top electrode and YBa$_2$Cu$_3$O$_7$ or Pt bottom electrode. Similar resistance switching phenomena have also been reported in a wide variety of perovskite oxides, such as titanates and zirconates.

Here, we report on the interface properties between PCMO and several kinds of metallic electrode such as SrRuO$_3$(SRO), Pt, Au, Ag, and Ti, in detail, through vertical transport measurements of metal/PCMO/SRO layered structures grown on (100) SrTiO$_3$ (STO) single-crystal substrates. The Ti/PCMO/SRO layered structure, which has the largest interface resistance among the tested layered structures, is the only one that shows the resistance switching. The switching behavior can be understood by a model for the interface considering the Schottky contact with charge-trapping interface states.

The epitaxial PCMO/SRO layered structures were deposited on buffered-HF treated STO substrates by a pulsed laser deposition technique. Because the SRO film can be epitaxially grown on the STO substrate in a step-flow growth mode, the surface of the SRO bottom layer is atomically flat. This allows us to obtain structurally well-defined PCMO/SRO interfaces. During the deposition, a substrate temperature was kept at 700 °C under an oxygen pressure of 100 mTorr. The thickness of PCMO and SRO layers was 100 nm and 80 nm, respectively. For the sample with an epitaxial SRO layer as the top electrode (TE), 20 nm-thick SRO layer was subsequently deposited on the PCMO layer. After the depositions, the layered structures were annealed at 400 °C for 30 minutes under an oxygen pressure of 500 Torr, and then cooled down to room temperature. The crystal structure was analyzed by a four-circle x-ray diffractometer. The full-width at half of maximum of the rocking curves for all epitaxial layers in a heterostructure measured together is as narrow as 0.06 °.

The device structure is depicted in the inset of Fig. Normal metal TE layers were ex-situ deposited by electron beam or thermal evaporation under a base pressure of $< 4 \times 10^{-7}$ Torr. The thickness of the Au and Ag layers is 400 nm, and that of the Pt and Ti layers is 20 nm. For the TE's of SRO, Pt and Ti, a 380 nm-thick Au cover layer was subsequently deposited. The layered structures were patterned into mesa structures by conventional photolithography and Ar ion milling.

The current–voltage ($I$–$V$) characteristics were measured by a three-point contact method. The size of current and voltage contact pads for the SRO bottom electrode (left and right ends in the inset of Fig. respectively) is $0.5 \times 4$ mm$^2$ and that of tested junctions (middle) is $200 \times 200$ $\mu$m$^2$. The use of the separate current and voltage contacts for the SRO bottom electrode allows us to extract the voltage drop between the SRO bottom electrode and
the TE of the tested junction. The reason for using TE/PCMO stack for voltage contact pads is merely to simplify the device fabrication process. The positive bias is defined by the current flowing from the SRO bottom electrode to the TE. The voltage bias was scanned as $0 \rightarrow +V_{\text{max}} \rightarrow 0 \rightarrow -V_{\text{max}} \rightarrow 0$ V. All measurements were performed at room temperature. Figure 2 shows typical I–V characteristics of the layered structures for five different TEs. The I–V characteristic of the epitaxial SRO TE sample shows an ohmic behavior, and the resistance ($R_{\text{SRO}} \approx 6.8 \Omega$) is the smallest among the samples. For the normal metal TE samples, the resistance ($R_{\text{TE}}$) of the samples increases in the order of $TE = \text{Pt, Au, Ag, and Ti}$. From the device configuration and the resistivity of PCMO and TE metals, the resistance of PCMO and TE layers along vertical direction is estimated to be less than 0.1 $\Omega$ and 10 $\mu\Omega$, respectively. Thus, most of the measured resistance comes from a sum of contact resistances at the TE/PCMO and PCMO/SRO interfaces and the spread resistance of 80 nm-thick SRO bottom electrodes (roughly 10 $\Omega$). Therefore, the resistance for the SRO/PCMO/SRO junctions is dominated by the spread resistance and the contact resistance at PCMO/SRO interface is negligibly small. In order to estimate the contact resistance for TE/PCMO interfaces, the difference of the resistance $\Delta R_{\text{TE}} (= R_{\text{TE}} - R_{\text{SRO}})$ between the normal metal TE and the SRO TE samples is evaluated, and is shown in the inset of Fig. 1. The $\Delta R_{\text{TE}}$ provides a lower bound for the contact resistances for the normal metal/PCMO interfaces. For the Ti TE layered structure, we define $R_{\text{Ti}}$ as the dynamic resistance at $V = 0$ V because of the nonlinear I–V characteristic. The results clearly show that the contact resistances of TE/PCMO ($TE = \text{Pt, Au, Ag, and Ti}$) interfaces are much larger than the resistance of PCMO and TE metal layers themselves, and transport properties are dominated by that at the TE/PCMO interfaces.

In addition to the nonlinearity, the I–V characteristic of the Ti/PCMO interface exhibits at the initial state a hysteresis in a negative bias region but not in a positive bias region. When the voltage ($|V_{\text{max}}| = 2$ V) was repeatedly biased, the current gradually decreased and a hysteresis started to be observed both in positive and negative bias regions, as shown in Fig. 3. The decrease of the current is remarkable in a negative bias region, as shown in the inset, and finally the Ti/PCMO interface shows a rectifying characteristic. When much larger voltage ($|V_{\text{max}}| = 5$ V) was applied to the virgin Ti/PCMO interface, the current suddenly decreases at a certain voltage in a negative bias region, i.e., the I–V characteristic has a negative dynamic resistance, as denoted by the triangle (△) in Fig. 3 (a). After applying a large negative voltage bias, the Ti/PCMO interface shows a rectifying characteristic and a large hysteresis is observed both at positive and negative bias, as shown in Fig. 3 (b). We call hereafter such a bias stress process to get the stable state with rectifying and hysteretic characteristics as the forming process.

After the forming process, the resistance switching takes place upon the application of pulsed voltage stress ($V_p$), as shown in Fig. 4 (b). The resistance switching characteristic depends on the initial resistance state ($R^0_h$ or $R^0_l$) and the pulsed voltage duration ($\tau_p$). We first define the respective high and low resistance values at a voltage bias ($V_{\text{bias}}$) of 0.1 V, which were obtained after the I–V measurements of $0 \rightarrow +5 \rightarrow 0 \rightarrow -5 \rightarrow 0$ V and $0 \rightarrow +5 \rightarrow 0$ V, as $R^0_h$ and $R^0_l$ (Fig. 4 (a)). These correspond to the limiting values for $\tau_p \rightarrow \infty$. Figure 4 (c) shows $\tau_p$ dependence of the values ($R_h$ and $R_l$) for the high and low resistance states after the application of $V_p = -5$ and $+5$ V, respectively. When the resistance switching is started from $R^0_h$, the resistance is switched between the $R_h \approx R^0_h$ and the $R_l$, the latter of which decreases with increasing $\tau_p$. When the resistance switching is started from the $R^0_l$, both of the $R_h$ and the $R_l$ increase with increasing $\tau_p$ and finally overlap with those started from the $R^0_l$. As shown in Fig. 4 (d), the ratio of the resistance change ($R_h/R_l$) increases with increasing $\tau_p$, but the value of $R_h/R_l$ even at $\tau_p = 0.1$ s is less than the one third of $R^0_h/R^0_l$ ($\approx 220$ kΩ/20 kΩ = 11). These results suggest that the high resistance state is much more stable than the low resistance one, and that this resistance switching is dominated by some slow process.

Here, we first discuss a possible origin of the rectification at the Ti/PCMO interface. The rectifying interface, first of all, reminds us of a Schottky contact. Assuming that the Ti/PCMO interface is a Schottky contact, as shown in the inset of Fig. 3, from the I–V characteristic PCMO can be considered as a p-type semiconductor. According to a p-type Schottky contact model, a Schottky barrier height increases with decreasing the work function of metal electrode. Because the work function of metals used for TE in this study decreases in the order of Pt, Au, and Ag, as the TE metal dependence of the contact resistance seems to be consistent with a p-type Schottky contact model. However, since Ag and Ti have the almost same work function of $\sim 4.3$ eV, the difference of the interface property between Ag/PCMO and Ti/PCMO cannot be understood by a conventional Schottky contact. Thus, we consider an interface-state-induced band bending at the Ti/PCMO interface. It is well-known that when a density of interface states is high, electronic band in a semiconductor bends at an interface, independently of a work function of an electrode metal. In this model, the degree of band bending, i.e., barrier width and height, depends on a net charge in the interface states and an energetical distribution of those in the band gap, and this band bending also causes a rectification. Because Ti is a getter for oxygen and has a small electronegativity, the Ti layer possibly extracts a large amount of oxygen atoms from the surface of the PCMO layer. The high density of the interface states induced by the oxygen vacancies may cause a large degree of the band bending at the Ti/PCMO interface, as compared with the Ag/PCMO interface.

Next, on the basis of the interface-state-induced band bending picture, we propose a possible model of the resistance switching. By applying large voltage at the Ti/PCMO interface, a large amount of electrons is accumulated (extracted)
into (from) the interface states upon reverse (forward) bias. Accordingly, a variation of a net charge in the interface states leads to a modification of a Schottky-like barrier width and/or height, because the degree of the band bending depends on a net charge in the interface states. This model is similar to the one proposed for a resistance switching in a layered structure of a ferroelectric oxide. The sandwich structure of Au/PbTiO$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$, where PbTiO$_3$ was a ferroelectric $n$-type semiconductor, showed a resistance switching. The mechanism of the resistance switching was explained by the change of the Schottky barrier width at the Au/PbTiO$_3$ interface caused by a polarity alternation of a space charge in the ferroelectric PbTiO$_3$ layer.

A remaining open question is what happens in the forming process. One possible candidate is the electrochemical migration of oxygen atoms. Oxygen gettering by Ti at the Ti/PCMO interface may generate the oxygen-defect-induced interface states, resulting in a Schottky-like barrier. However, further study is needed for elucidating the origin of the forming process. A way to avoid such chemical problems is to employ heteroepitaxial Schottky junctions made of oxide semiconductors and oxide metals.

In summary, we have demonstrated pulsed voltage induced resistance switching at the Ti/PCMO interface, which is accompanied by hysteretic and rectifying $I$–$V$ characteristics. The resistance switching can be explained by a model of the interface with trapping states which have sufficiently high density to form a Schottky-like barrier.

We would like to thank T. Shimizu, I.H. Inoue, A. Odagawa, H. Yamada, J. Matsuno, and H. Akoh for useful discussions.

---

FIG. 1. $I$–$V$ characteristics of $TE$/PCMO/SRO layered structures with five different $TE$s. Here, $TE$, PCMO, and SRO stand for top electrode, Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, and SrRuO$_3$, respectively. The upper panel of the insets shows a schematic of the samples. The lower one shows $\Delta R_{TE} (= R_{TE} - R_{SRO})$ for $TE = Pt$, Au, Ag, and Ti.

FIG. 2. $I$–$V$ characteristics of a Ti/PCMO/SRO layered structure measured with repeated voltage scan ($|V_{max}| = 2$ V) up to 45th cycle. The inset shows the time chart of the current.

FIG. 3. $I$–$V$ characteristics of a Ti/PCMO/SRO layered structure drawn in (a) linear and (b) semilogarismic current scales. Insets schematically show electronic band diagrams for a rectifying Ti/PCMO interface.

---

a) Electronic mail: a.sawa@aist.go.jp
b) Also at: CREST-JST, Japan.
c) Also at: Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.
d) Also at: Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan.

1. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
2. Y. Tokura and Y. Tomioka, J. Magn. Magn. Mater. 200, 1 (1999).
3. J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) 392, 794 (1998).
4. A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature 388, 50 (1997).
5. V. Ponnambalam, S. Parashar, A.R. Raju, and C.N.R. Rao, Appl. Phys. Lett. 74, 206 (1999).
6. H. Oshima, K. Miyano, Y. Konishi, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. 75, 1473 (1999).
7. S.Q. Liu, N.J. Wu, and A. Ignatiev, Appl. Phys. Lett. 76, 2749 (2000).
8. A. Baikalov, Y.Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y.Y. Sun, Y.Y. Xue, and C.W. Chu, Appl. Phys. Lett. 83, 957 (2003).
9. P.W.M. Blom, R. M. Wolf, J.F.M. Cillessen, and M.P.C.M. Krijn, Phys. Rev. Lett. 73, 2107 (1994).
10. A. Beck, J.G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. 77, 139 (2000)
11. Y. Watanabe, J.G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S.J. Wind, Appl. Phys. Lett. 78, 3738 (2001).
12. A. Schmehl, F. Lichtenberg, H. Bielefeldt, J. Mannhart, and D.G. Schlom, Appl. Phys. Lett. 82, 3077 (2003).
13. J.R. Contreras, H. Kohlstedt, U. Poppe, R. Waser, C. Buchal, and N.A. Pertsiev, Appl. Phys. Lett. 83, 4595 (2003).
14. M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, Science 266, 1504 (1994).
15. S.M. Sze, Physics of Semiconductor Devices, 2nd ed. (Wiley, New York, 1981).
FIG. 4. (a) Forward bias $I-V$ characteristic of a Ti/PCMO/SRO layered structure. Low and high resistance states ($R^0_l$ and $R^0_h$) after voltage scans of $|V_{\text{max}}| = 5$ V (see text) are defined at the filled and open stars, respectively. Each resistance value was evaluated by measuring current at a $V_{\text{bias}}$ of 0.1 V. (b) Resistance switching behavior (bottom) started from the $R^0_l$ state, by applying a sequence of pulsed voltage stress (top) of $V_p = \pm 5$ V. (c) Pulsed voltage duration ($\tau_P$) dependence of the low (square) and high (circle) resistance states. The filled and open symbols represent the data started from $R^0_l$ and $R^0_h$, respectively. (d) $\tau_P$ dependence of the resistance ratio ($R_h/R_l$).