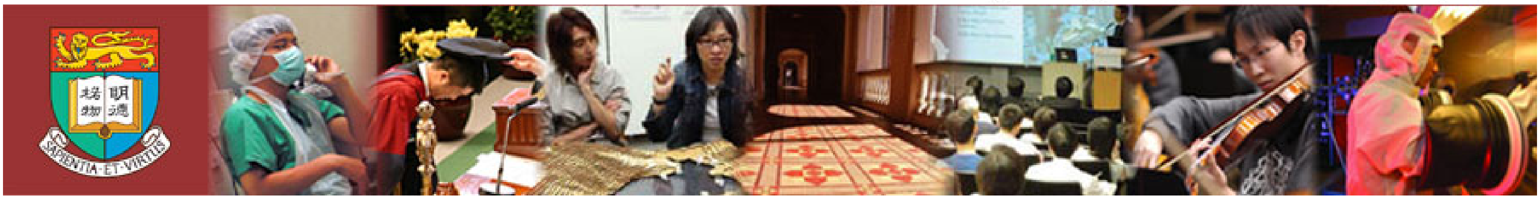

Resistive Switching in Perovskite-Oxide Capacitor-Type Devices

Zhi Luo[1], Hon Kit Lau[2], Paddy Kwok Leung Chan[3], and Chi Wah Leung[2]

[1]Department of Electronic Engineering, Jinan University, Guangzhou 510632, People's Republic of China
[2]Department of Applied Physics, Hong Kong Polytechnic University, Hung Hom, Hong Kong, People's Republic of China
[3]Department of Mechanical Engineering, University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

Resistive switching effect was demonstrated in the Ti/$Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO)/$LaNiO_3$/Ti top-down device structure. A high resistance state was activated by a forming process. Hysteretic current–voltage (I–V) characteristic was observed by applying potential differences in the order of 5 V across the electrodes. I–V characteristics with different combinations of top and bottom electrodes suggested that the forming process changed the interface between the oxides and Ti electrodes, with the active region for resistive switching located at the Ti electrode/PCMO interface region. Such results show the possibility of high-density and nonvolatile memory applications based on the resistive switching effect.

Index Terms—**Nonvolatile memories, $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO), resistive switching.**

I. Introduction

Resistive switching effect is hailed as one of the candidates for the next-generation nonvolatile memories [1]. Upon the application of a voltage pulse, the sample resistance can be changed and retained. This effect has been manifested in various materials and device geometries [2]–[4]. Some of the advantages of the effect include the fast writing time (<10 ns) [5], low operating voltage [6], and potentially high data storage densities [7].

$Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO), for example, is one of the promising materials, which shows resistive switching in thin-film device structures [8]. Switching ratio over 3000% and switching voltage below 2 V have been achieved [6], [8], [9]. However, further advancement of the performance in such devices requires thorough understanding of the working mechanism, which is still under debate [10], [11]. A few schemes have been proposed, involving either bulk or interface effects, with the interfacial contribution considered to be more important in perovskite-based resistive switching devices [4], [12]–[14]. Some of the most common explanations include the presence of trap states within the Schottky barrier, trapped-charges-induced space-charge-limited current, as well as formation of oxides at the electrode/oxide interfaces [4], [9], [14]–[17].

In this paper, we study the current–voltage (I–V) characteristics and resistive switching behavior of epitaxially grown PCMO with $LaNiO_3$ (LNO) and Ti as bottom and top electrodes, respectively. By investigating the I–V characteristics for various electrode combinations, we argue that the active region for resistive switching is located at the Ti/PCMO interface. The highly localized nature of the switching effect highlights the possibility of simplifying the device fabrication process using a common bottom electrode.

Manuscript received October 29, 2013; revised November 25, 2013; accepted December 25, 2013. Date of current version July 7, 2014. Corresponding author: C. W. Leung (e-mail: dennis.leung@polyu.edu.hk).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TMAG.2013.2297408

II. Experiment

Thick (200 nm) epitaxial LNO layers were grown by pulsed laser deposition on $LaAlO_3$ (LAO) substrates at a temperature of 650 °C and oxygen pressure of 150 mtorr [18], [19]. The laser pulse energy was around 250 mJ, with a pulse repetition rate of 5 Hz. A 100-nm-thick PCMO film was then deposited on the LNO layer through a stainless steel shadow mask at the same temperature and oxygen ambient, with a laser pulse energy of 200 mJ. Afterwards, the epitaxial layers were cooled down to room temperature at a rate of 10 °C min^{-1} under the same oxygen pressure. The chamber was then pumped down to 3×10^{-5} torr, before the Ti electrodes with diameter 100 μm were defined and deposited on top of the PCMO using another shadow mask.

Structural analyses of the samples were performed by X-ray diffractometry (XRD), and electrical measurements (I–V characteristics and resistive switching measurements) were done at room temperature by a Keithley 2400 sourcemeter. A current passing from the top Ti electrode through PCMO into the LNO layer was defined as a positive current.

III. Results and Discussion

A. Structural Characterization

Fig. 1 shows the θ-2θ scan of a PCMO/LNO sample. The PCMO (002) and LNO (002) peaks are basically overlapping with one another. The rocking curve of the PCMO/LNO film (upper inset, Fig. 1) at the (002) peak shows the oxide layers are textured with a full-width at half-maximum (FWHM) of 0.67°. The small FWHM shows that the PCMO film deposited on LNO has good crystallinity. φ-scan (lower inset) further confirms the epitaxial cube-on-cube growth of the multilayer on the LAO substrate.

B. Electrical Characterization

Resistive switching measurements were performed with the circuit shown in Fig. 2(a). Reproducible changes in sample resistances, after the application of voltage pulses, are shown in Fig. 2(b). The measurement procedure is as follows. After applying a pulse at +4.5 V for 1 ms, the sample resistance

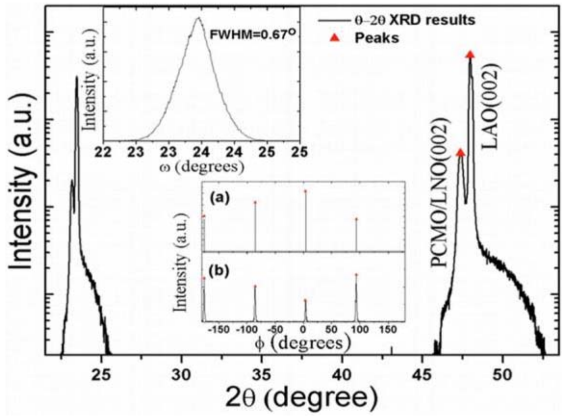

Fig. 1. XRD pattern of a PCMO/LNO/LAO device. Upper inset: ω-scan of the PCMO thin film. Lower inset: φ-scans of (a) LAO substrate and (b) LNO/PCMO film.

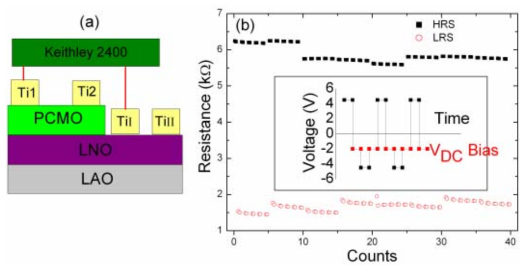

Fig. 2. Schematic diagram and measurement setup of Ti/PCMO/LNO/LAO/Ti switching devices. (b) Resistance switching measurements of the device, with open circles (solid squares) correspond to LRS (HRS). Inset: voltage sweeping profile of the measurement.

was measured with a bias of −2 V. Subsequently, a −4.5 V pulse was applied to switch the sample to the low resistance state (LRS), and the resistance was measured again at −2 V [see inset of Fig. 2(b) for the voltage profile during the measurement cycle]. Switching properties were stable over at least 40 switching cycles, and an averaged switching ratio of 230% was obtained, a resistance variation that is easily observed by conventional means of measurements.

It should be pointed out that the forming process is needed to prepare the device for resistive switching applications [18], [20], [21]. During the forming process, a voltage of +7 V was applied across a particular device, meaning that the electric current passed from the top PCMO to the bottom LNO layer. Initially, the sample exhibited a relatively low resistance. When the voltage was ramped up +6 V, the resistance suddenly increased to the order of a few kΩ. Afterward, the resistance of the sample was kept at the same order of magnitude and did not return to its initial state. After forming, an asymmetric and hysteretic I–V was observed, with a sharp current increase occurring in the negative voltage bias regime [Fig. 3(a) black square line (Ti$_1$-Ti$_\text{I}$)]. The bias voltage for resistance switching to occur was about −4 V in this case. This confirms that, in our resistance switching measurements, ±4.5 V was sufficient to switch the sample between high resistance state (HRS) and LRS.

A simple analysis of the top-down geometry device can be made by considering a model with three interfacial (Ti/PCMO, PCMO/LNO, and LNO/Ti) and two bulk (PCMO and LNO) resistors connected in series. Various works on perovskite-based resistive switching devices suggested that switching occurs predominantly at interfaces [13], [18], [20], [22]. We have previously studied planar perovskite-based resistive switching devices, and have eliminated the bulk contribution to the switching effect [19]. Thus, there are three interfaces, which may contribute to the resistive switching in our top-down geometry devices.

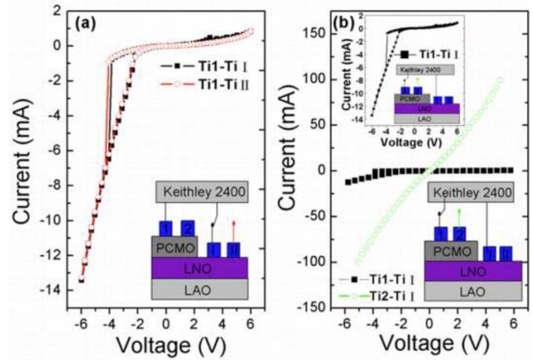

Fig. 3. I–V characteristics of PCMO top-down resistive switching devices with different bottom electrodes, after forming with Ti$_1$/PCMO with Ti$_\text{I}$/LNO pair. (a) Ti$_1$/PCMO with Ti$_\text{I}$/LNO pair (closed squares) and Ti$_1$/PCMO with Ti$_\text{II}$/LNO pair (open circles). (b) Ti$_1$/PCMO with Ti$_\text{I}$/LNO pair (closed squares) and Ti$_2$/PCMO with Ti$_\text{II}$/LNO pair (open circles). Data for Ti$_1$/PCMO/LNO/Ti$_\text{I}$ is magnified in the upper inset. Insets: the schematics of measurement setups.

To locate which interface(s) was modified during the forming process, electrode-swapping measurements were performed. During such measurements, the forming process was conducted on a fixed pair of electrodes Ti$_1$ (on the PCMO layer) and Ti$_\text{I}$ (on the LNO layer) (Fig. 3), with the current path be represented by Ti$_1$/PCMO/LNO/Ti$_\text{I}$. Subsequently, I–V characteristics were measured by fixing Ti$_1$ on PCMO while switching between two Ti electrodes on LNO (Ti$_\text{I}$ and Ti$_\text{II}$). The results for such measurement procedures are shown in Fig. 3(a). For the measurement with the Ti$_1$/PCMO interface paired with LNO/Ti$_\text{I}$ (Process 1), the junction shows hysteretic I–V behavior after the forming process. After that, connection to Ti$_1$ was fixed while the bottom electrode was switched to Ti$_\text{II}$ (Process 2). In Process 1, the interfaces Ti$_1$/PCMO, PCMO/LNO, and LNO/Ti$_\text{I}$ were involved, the last of which was replaced by LNO/Ti$_\text{II}$ in Process 2. If the change induced by forming process mainly occurred at LNO/Ti$_\text{I}$, I–V characteristics should be different in these two processes, as LNO/Ti$_\text{I}$ did not experience forming process. The present result suggests that the change induced by the forming process did not occur at the LNO/Ti interface.

I–V characteristics for swapping the top electrodes (i.e., measuring with different top electrodes Ti$_1$ and Ti$_2$ with fixed bottom electrode Ti$_\text{I}$, Processes 3 and 4) were also obtained [Fig. 3(b)]. Note that no previous measurements have been performed on Ti$_2$ before the swapping test. Similar to the above analysis, if the Ti/PCMO interface was modified by the forming process, the Ti$_2$/PCMO and LNO/Ti$_\text{I}$ interface pair should not show hysteretic behavior but should be observable

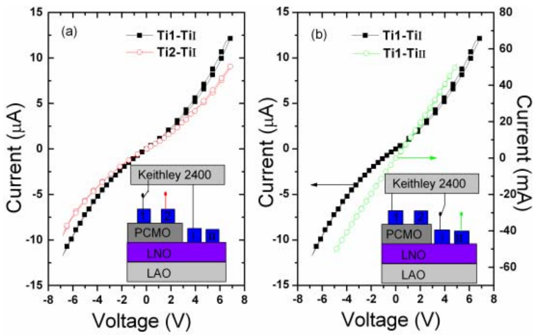

Fig. 4. *I–V* characteristics of PCMO sample with different top electrodes after −9 V voltage bias at Ti_1/PCMO with LNO/Ti_I pair. (a) Ti_1/PCMO with LNO/Ti_I pair (closed square) and Ti_2/PCMO and LNO/Ti_I pair (open circle). (b) Ti_1/PCMO with LNO/Ti_I pair (closed square) and Ti_1/PCMO with LNO/Ti_{II} pair (open circle). Inset: schematic measurement setup, where a switch was inserted between the top electrode connection.

in the Ti_1/PCMO with LNO/Ti_I interface pair. This was actually observed at this paper. Owing to these results, it can be concluded that the changes mainly occurred at Ti/PCMO interface in the forming process. It can also be concluded that Ti/PCMO interface contribute to the switching effect in the formed devices, as the forming process is necessary to activate the switching behavior.

As mentioned previously, the forming voltage must be positive, in which the current passes from the top Ti electrode through PCMO into the LNO layer. Fig. 4 shows the *I–V* characteristics of the same device structure after forming with a *negative* bias of −9 V. In contrast with the case of positive bias-formed devices, no clear resistive switching effect is observed; attempts of sweeping over wider voltage ranges easily led to breakdown of devices. On the other hand, it can be noticed that formed devices have higher resistances, as evidenced by the low current values (in microampere ranges) displayed by the measurements for Ti_1/PCMO/LNO/Ti_I devices [Fig. 4(a) and (b)]. Similar resistance value can be observed when the top electrode is switched to Ti_2 [Fig. 4(a)]. The results of Fig. 4 clearly signals that changes did occur also at the LNO/Ti interface under negative bias. Unlike the case of positive forming process, however, no hysteretic switching was observed. Comparing the *I–V* characteristics with and without forming process, one can also find that devices with forming process (positive and negative) have much higher resistances, implying that a high-resistance interfacial layer was formed during the forming process.

The observed phenomenon can be explained by the migration of oxygen ions under electric field and the formation and disruption of TiO_x layer at the interface. Recently, Borgatti *et al.* [23] investigated the role of the forming process. They found that the reduced PCMO layer dominated in the LRS (initial resistance state). After forming, as a result of oxygen diffusion, TiO_x layer was formed at the interface, leading to an anisotropic n-p junction between the Ti and the PCMO layers. The n-p junction became dominant and the device switched to a high resistance value. Similar process should also occur in the present devices. Once a negative voltage bias is applied, oxygen ions migrate into the PCMO layer, the TiO_x layer dissociates, and the device switches back to the LRS.

Nonvolatile information storage mechanisms commonly employed these days rely on either charge storages (as in flash memories) or the orientation of individual magnetic domains (as in magnetic hard disks). Both of these schemes face fundamental obstacles (such as charge leakages or superparamagnetism) as the bit sizes shrink. The current resistive switching memory scheme, which relies on changes in the interfacial states between the oxide and metal electrodes, does not have these problems. Together with the simplicity of data retrieval and read/write operations, we suggest that such a memory scheme has much potential for future high-density nonvolatile memory applications.

IV. Conclusion

PCMO-based top-down geometry resistive switching devices with Ti electrodes were studied. Ti/PCMO/LNO/LAO resistive switching devices were obtained after the forming process. Experiments with different electrodes suggested that the resistive switching region was located at the Ti/PCMO interface, and the effect was explained through the oxidation and dissociation of interfacial TiO_x.

Acknowledgment

This work was supported by UGC of HKSAR (PolyU-5013/08P, PolyU-5112/08E), PolyU (A-PM21, G-YN08) and Canaan Semiconductors Ltd (H-ZDAC). The work of Z. Luo was supported in part by the Central Universities under Grant 21612416 and in part by the National Science Foundation of China under Grant 11204105.

References

[1] (2010). *International Technology Roadmap for Semiconductors* [Online]. Available: http://www.itrs.net/
[2] R. Dong, W. F. Xiang, D. S. Lee, S. J. Oh, D. J. Seong, S. H. Heo, *et al.*, "Improvement of reproducible hysteresis and resistive switching in metal-$La_{0.7}Ca_{0.3}MnO_3$-metal heterostructures by oxygen annealing," *Appl. Phys. Lett.*, vol. 90, no. 18, pp. 182118-1–182118-3, 2007.
[3] M. Fujimoto, H. Koyama, Y. Nishi, and T. Suzuki, "Resistive switching properties of high crystallinity and low-resistance $Pr_{0.7}Ca_{0.3}MnO_3$ thin film with point-contacted Ag electrodes," *Appl. Phys. Lett.*, vol. 91, pp. 223504-1–223504-3, Nov. 2007.
[4] A. Ruotolo, C. Y. Lam, W. F. Cheng, K. H. Wong, and C. W. Leung, "High-quality all-oxide Schottky junctions fabricated on heavily doped Nb:$SrTiO_3$ substrates," *Phys. Rev. B*, vol. 76, pp. 075122-1–075122-5, Aug. 2007.
[5] N. Xu, L. Liu, X. Sun, X. Liu, D. Han, Y. Wang, *et al.*, "Characteristics and mechanism of conduction/set process in the TiN/ZnO/Pt resistance switching random access memories," *Appl. Phys. Lett.*, vol. 92, pp. 232112-1–232112-3, Jun. 2008.
[6] X. Liu, K. P. Biju, E. M. Bourim, S. Park, W. Lee, J. Shin, *et al.*, "Low programming voltage resistive switching in reactive metal/polycrystalline $Pr_{0.7}Ca_{0.3}MnO_3$ devices," *Solid State Commun.*, vol. 150, pp. 2231–2235, Deec. 2010.
[7] H. K. Lau and C. W. Leung, "Nonvolatile multilevel memory effect by resistive switching in manganite thin films," *J. Appl. Phys.*, vol. 104, pp. 123705-1–123705-4, Dec. 2008.
[8] S. Q. Liu, N. J. Wu, and A. Ignatiev, "Electric-pulse-induced reversible resistance change effect in magnetoresistive films," *Appl. Phys. Lett.*, vol. 76, no. 19, pp. 2749–2751, 2000.
[9] A. Odagawa, H. Sato, I. H. Inoue, H. Akoh, M. Kawasaki, Y. Tokura, *et al.*, "Colossal electroresistance of a $Pr_{0.7}Ca_{0.3}MnO_3$ thin film at room temperature," *Phys. Rev. B*, vol. 70, pp. 224403-1–224403-4, Dec. 2004.

[10] R. Oligschlaeger, R. Waser, R. Meyer, S. Karthauser, and R. Dittmann, "Resistive switching and data reliability of epitaxial (Ba,Sr)TiO_3 thin films," *Appl. Phys. Lett.*, vol. 88, no. 4, pp. 042901-1–042901-3, 2006.

[11] A. Sawa, "Resistive switching in transition metal oxides," *Mater. Today*, vol. 11, no. 6, pp. 28–36, 2008.

[12] A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, *et al.*, "Field-driven hysteretic and reversible resistive switch at the Ag–$Pr_{0.7}Ca_{0.3}MnO_3$ interface," *Appl. Phys. Lett.*, vol. 83, pp. 957–959, Aug. 2003.

[13] A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura, "Hysteretic current–voltage characteristics and resistance switching at a rectifying Ti/$Pr_{0.7}Ca_{0.3}MnO_3$ interface," *Appl. Phys. Lett.*, vol. 85, no. 18, pp. 4073–4075, 2004.

[14] T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, and Y. Tokura, "Hysteretic current–voltage characteristics and resistance switching at an epitaxial oxide Schottky junction $SrRuO_3/SrTi_{0.99}Nb_{0.01}O_3$," *Appl. Phys. Lett.*, vol. 86, no. 1, pp. 012107-1–012107-3, 2005.

[15] K. Shono, H. Kawano, T. Yokota, and M. Gomi, "Origin of negative differential resistance observed on bipolar resistance switching device with Ti/$Pr_{0.7}Ca_{0.3}MnO_3$/Pt structure," *Appl. Phys. Exp.*, vol. 1, pp. 055002-1–055002-3, Apr. 2008.

[16] S. L. Li, Z. L. Liao, J. Li, J. L. Gang, and D. N. Zheng, "Resistive switching properties and low resistance state relaxation in Al/$Pr_{0.7}Ca_{0.3}MnO_3$/Pt junctions," *J. Phys. D, Appl. Phys.*, vol. 42, no. 4, p. 045411, 2009.

[17] D. S. Shang, Q. Wang, L. D. Chen, R. Dong, X. M. Li, and W. Q. Zhang, "Effect of carrier trapping on the hysteretic current-voltage characteristics in Ag/$La_{0.7}Ca_{0.3}MnO_3$/Pt heterostructures," *Phys. Rev. B*, vol. 73, no. 24, pp. 245427-1–245427-7, 2006.

[18] H. K. Lau, C. W. Leung, W. H. Hu, and P. K. L. Chan, "Interfacial defects in resistive switching devices probed by thermal analysis," *J. Appl. Phys.*, vol. 106, pp. 014504-1–014504-4, Jul. 2009.

[19] H. K. Lau, C. W. Leung, and Y. K. Chan, "Resistance switching properties of epitaxial $Pr_{0.7}Ca_{0.3}MnO_3$ thin films with different electrodes," *Phys. Stat. Sol. A*, vol. 206, no. 9, pp. 2182–2186, 2009.

[20] K. Tsubouchi, I. Ohkubo, H. Kumigashira, M. Oshima, Y. Matsumoto, K. Itaka, *et al.*, "High-throughput characterization of metal electrode performance for electric-field-induced resistance switching in metal/$Pr_{0.7}Ca_{0.3}MnO_3$/metal structures," *Adv. Mater.*, vol. 19, no. 13, pp. 1711–1713, 2007.

[21] Y. H. Do, J. K. Kwak, and J. P. Hong, "Resistive switching characteristics of TiO_2 films with embedded Co ultra thin layer," *J. Semicond. Technol. Sci.*, vol. 8, no. 1, pp. 80–84, 2008.

[22] A. Ruotolo, C. W. Leung, C. Y. Lam, W. F. Cheng, K. H. Wong, and G. P. Pepe, "Unification of bulk and interface electroresistive switching in oxide systems," *Phys. Rev. B*, vol. 77, no. 23, pp. 233103-1–233103-4, 2008.

[23] F. Borgatti, C. Park, A. Herpers, F. Offi, R. Egoavil, Y. Yamashita, *et al.*, "Chemical insight into electroforming of resistive switching manganite heterostructures," *Nanoscale*, vol. 5, no. 9, p. 3954, 2013.