Characterization of Resistive Switching States in W/Pr_{0.7}Ca_{0.3}MnO₃ for a Submicron (ϕ 250 nm) Via-Hole Structure

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Analysis of asymmetric current–voltage (I – V) of low resistance state (LRS) and high resistance state (HRS) in a W/Pr_{0.7}Ca_{0.3}MnO₃ (PCMO) submicron (ϕ 250 nm) resistive memory device revealed the formation of a Schottky-like contact in both states. Raman spectroscopy analysis was used to measure the concentration of oxygen vacancies in LRS and HRS. A significant intensity difference at ~ 610 cm^{−1} for HRS and LRS indicates that a higher number of oxygen vacancies are created in HRS than in LRS. Based on material analysis, modulation of the oxygen vacancy concentration at the PCMO layer in relation to the redox reaction between W and Mn proposed to be responsible for resistive switching phenomena. © 2011 The Japan Society of Applied Physics

1. Introduction

Resistive random access memory (RRAM) based on electric field induced resistance change in a metal–insulator–metal (MIM) structure possesses the advantages of low power consumption, high operation speed, nondestructive readout, simple structure and good scalability. These characteristics make it a highly competitive candidate for next-generation nonvolatile memories.^{1–3)} Of several transition metal oxides being investigated, perovskite manganites such as Pr_{0.7}Ca_{0.3}MnO₃ (PCMO) have been intensively studied as a typical RRAM material showing bipolar RS behavior.^{4–11)} Metallic top electrodes (TE) are crucially important for the resistive switching (RS) properties of manganite-based RRAM. In particular, the redox reaction that takes place between a chemically reactive metal and the manganite interface is considered to be an essential condition for RS.^{6–10)} Interfacial oxide layer formation was previously confirmed by transmission electron microscopy (TEM).¹⁰⁾ Although many models have been proposed to elucidate the RS mechanism, such as the space charge limited current (SCLC),^{12,13)} oxygen migration,⁵⁾ and the Schottky barrier,^{3,6,7)} none of them can provide a fully self-consistent explanation of all the observed physical phenomena. Recently Yasuhara *et al.* proposed that the interfacial transition layer due to the redox reaction between Al and Mn ions at the Al/PCMO interface is responsible for RS behavior.⁹⁾ However, the basic switching mechanism is still a controversial issue.

In this study we investigated the RS properties of PCMO at the submicron level (ϕ 250 nm) via hole structure with W as a TE. Based on the Gibb's free energy of formation of oxide (−533 to −764 kJ/mol) and electronegativity (2.36), W can be considered as a potential TE for PCMO-based RRAM.¹⁴⁾ Furthermore, since the work function of W (4.55 eV) is lower than the electron affinity of PCMO films (4.9 eV), a Schottky barrier, which is usually required for RS in chemically reactive metal/PCMO devices,^{6–10)} is expected to be formed at the W/PCMO interface. Based on asymmetric current–voltage (I – V) and Raman spectroscopy analysis, we proposed a model where, RS behavior is explained by the formation and dissolution of an oxygen

deficient PCMO layer in relation to the redox reaction between W and Mn.

2. Experimental Procedure

First, 400 nm W bottom electrode (BE) was deposited by the chemical vapor deposition (CVD) process on TiN/SiO₂/Si substrates. After 100 nm SiO₂ was deposited on W, ϕ 250 nm holes were patterned by lithography and the subsequent etching process. A thin (~ 5 nm) Pt was deposited by E-beam evaporation to protect the W bottom electrode (BE) from oxidation. Polycrystalline PCMO film (~ 40 nm) was deposited on the substrate by RF magnetron sputtering at 600 °C. The PCMO film was then annealed for 10 min at 650 °C in oxygen ambient. W TE was then deposited by RF magnetron sputtering. Finally after conventional photolithography TEs were patterned by reactive ion etching (RIE). The electrical characteristics of the memory devices were evaluated using an Agilent 4155C semiconductor parameter analyzer. Raman spectroscopy was carried out using a 514 nm Ar laser in air ambient for 50 $\times$ 50 μ m² active area device.

3. Result and Discussion

A schematic of the device and measuring condition is shown in Fig. 1(a). The composition of the PCMO film was confirmed by X-ray photoelectron spectroscopy (XPS) [Fig. 1(b)]. The figure shows that no WO_x formed at the bottom interface and elemental distributions were very uniform throughout the film. Very stable RS can be obtained in the W/PCMO device [Fig. 1(c)]. A low resistance state (LRS) and high resistance state (HRS) can be obtained by applying −6 and +6 V, respectively. The I – V hysteresis loop was measured in the sequence 0 $\rightarrow$ V_{max} $\rightarrow$ 0 $\rightarrow$ $-V_{\text{max}}$ $\rightarrow$ 0 (indicated by arrows). All the bias was applied with respect to the TE while BE was grounded. A positive bias was defined as a flow of current from the TE to the BE. Pulse endurance and retention characteristics of the W/PCMO memory device are depicted in Figs. 1(d) and 1(e), respectively.

To further elucidate the RS characteristics, the conduction mechanism of the nanoscale W/PCMO/Pt/W devices was also investigated. In LRS the oxide produced at the metal/PCMO interface is believed to reduce to metal, and the devices can have a metal–semiconductor (MS) structure, exhibiting Schottky diode-like behavior. We fitted the linear

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Fig. 1. (Color online) (a) Schematic structure. (b) Depth profiles of atomic concentrations in PCMO. (c) Typical I - V hysteresis curves. (d) Pulse switching and (e) Retention characteristics for 10^4 s of W/PCMO device.

Fig. 2. (Color online) I - V fits for the W/PCMO memory devices. (a) LRS fitted by thermionic emission theory. The inset shows I - V characteristics in linear scale. (b) $\ln I$ - $V^{0.5}$ plot in the LRS. (c) HRS fitted by thermionic emission theory. The inset shows I - V characteristics in linear scale. (d) $\ln I$ - $V^{0.5}$ plot in the HRS.

region (low voltage region) of the negative-biased LRS using the thermionic emission theory; the best fit to the experimental data at the low voltage region (dark yellow

line) provides a good approximation of Schottky diode, as shown in Fig. 2(a).¹¹⁾ The Inset of the Fig. 2(a) shows the linear plot of the LRS region.

$$I = I_s \exp\left(\frac{qV}{nkT} - 1\right).$$

In the above equation, I_s is the saturated current density dependent on the temperature, and n is the ideality factor. However, the real n value (~ 3.5) deviated from the ideal value of 1, which indicates that an inhomogeneous barrier was formed at the W/PCMO interface. This inhomogeneity may have originated from the residual WO_x layer that is, oxygen vacancies at the interface. In the $\ln I-V^{0.5}$ plot [Fig. 2(b)], LRS is a linear function at the higher voltage region, which also indicates a Schottky-like barrier.¹⁴⁾

For HRS when WO_x is formed, the Schottky barrier is expected to collapse due to the accumulation of oxygen vacancies at the interface,^{1,2)} and the resistance change is explained by the voltage drop across the interfacial oxide layer.¹⁵⁾ Interestingly, in our case, the HRS region can also be fitted well by the thermionic emission equation. The best fit to the experimental data at the low voltage region (green line) in this case also provides a good approximation of the Schottky diode, as shown in Fig. 2(c); this is also shown in the $\ln I-V^{0.5}$ plot [Fig. 2(d)]. The only significant difference between the HRS and LRS region was a higher n value (~ 5) for HRS. The increase in n for HRS indicates that the amount of WO_x or vacancies increased at the interface, but the Schottky barrier did not collapse. Thus even when WO_x is formed at the interface, the device still has a MS structure. These results presume localized oxidation and reduction at the interface. So we can infer that, oxide formation at the interface is not the only phenomenon that leads to RS behavior. However, interfacial properties are much more crucial for explaining RS phenomena than bulk properties as no significant structural change was observed during *in-situ* TEM analysis.¹⁶⁾

In order to explain the RS phenomena, understanding of PCMO properties is very crucial. PCMO is a doped oxide; divalent Ca is doped on PrMnO_3 perovskite. The partial substitution of trivalent Pr^{3+} by Ca^{2+} is balanced by the conversion of Mn valance states and the creation of oxygen vacancies as well.¹⁷⁾ The Kröger Vink notation of the substitution can be written as¹⁸⁾

The ionic structure of PCMO can be written as

where V_y^{O} is the fraction of oxygen vacancies.

The conduction in PCMO is believed to occur by electron hopping from Mn^{3+} to Mn^{4+} with the assistance of the oxygen anion along $-\text{Mn}-\text{O}-\text{Mn}-\text{O}-$ chains by the double exchange method.⁵⁾ The absence of oxygen atoms in the chain is also believed to disrupt the conduction process as the vacancies acts as a strong scatters for the hole polarons. Depending on the oxygen concentration, it is already shown that oxygen rich PCMO shows lower resistance (100–800 Ω) than oxygen deficient PCMO (1–200 M Ω).¹⁹⁾

Schematic of the proposed switching mechanism is shown in Fig. 3(a). The RS phenomena can be explained as follows: under the application of positive voltage, oxygen ions at the interface react with W to produce WO_x and/or

Fig. 3. (Color online) (a) Proposed switching mechanism for W/PCMO memory device. (b) Raman spectroscopy analysis for LRS and HRS.

oxygen ions moves into the previously formed WO_x region; simultaneously, valance of Mn ions in PCMO also reduced ($\text{Mn}^{3.3+}$ to Mn^{2+}) which is called electron doping.⁹⁾ As oxygen ions are removed from the surface of PCMO and reduce the number of holes, more oxygen deficient and insulating layer is created. Even though MS contact still persists, the presence of a higher amount of oxygen vacancies disrupts the conduction chain $-\text{Mn}-\text{O}-\text{Mn}-\text{O}-$ in the PCMO layer; thus, the resulting state is called HRS.

Conversely under the application of negative voltage, WO_x is reduced to W and/or oxygen ions from WO_x moves back to PCMO; simultaneously, Mn in PCMO is also oxidized, thus increasing the amount of holes. In addition, the oxygen ions moved back rebuild the conduction chain to produce LRS.

Modulation of oxygen vacancy concentration in relation to the redox reaction at the interface seems to play a key role in the switching process. Using low frequency noise (LFN) analysis, Jo *et al.* showed that the normalized power spectrum density (PSD/I^2) of LFN in the HRS of a Pt/Al/PCMO device is higher than that of LRS; this also indicates a higher oxygen vacancy concentration at the interface in the HRS condition.^{11,20)}

Raman spectroscopy is also a very good tool to study the oxygen concentration in perovskite manganites. The relative intensity of disorder induced Raman features due to lattice defects driven by oxygen deficiency $\sim 610 \text{ cm}^{-1}$ serves as a good indicator of oxygen concentration at PCMO.²¹⁾ $50 \times 50 \mu\text{m}^2$ area sample was fabricated for Raman spectroscopic analysis. Figure 3(b) shows the Raman spectroscopy of LRS and HRS. Raman spectra of the crystal were mainly characterized by two vibrational modes of A_g ($\sim 200 \text{ cm}^{-1}$) and

B_g ($\sim 450\text{ cm}^{-1}$) symmetries. Better resolved spectra can be found at low temperature.²¹⁾ However, intensity of the band at about 600 cm^{-1} band is considered as disordered induced feature due to the oxygen deficiency. The significant intensity difference at $\sim 610\text{ cm}^{-1}$ for HRS and LRS reveals that a higher number of oxygen vacancies are created in HRS than LRS. This analysis also supports that the modulation of oxygen vacancy concentration at the PCMO layer is responsible for the RS phenomena in PCMO based RRAM.

4. Conclusions

Based on the I - V analysis and ideality factors of LRS and HRS where both states showed MS contact, localized oxidation and reduction at the interface is presumed. It can be considered that WO_x formation at the interface may not be the only phenomenon for RS effect in PCMO-based resistive memory device. Raman spectroscopy analysis was performed to measure the oxygen vacancy concentration in LRS and HRS, intensity difference at $\sim 610\text{ cm}^{-1}$ for HRS and LRS indicates that a higher number of oxygen vacancies are created in HRS than LRS. As PCMO changes its resistance value depending on the oxygen concentration, based on the experimental results, modulation of oxygen vacancy concentration at the PCMO in relation with the oxide formation at the W/PCMO interface is suggested to be responsible for the RS.

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- 1) R. Waser, R. Dittmann, G. Staikov, and K. Szot: *Adv. Mater.* **21** (2009) 2632.
- 2) J. J. Yang, M. D. Pickett, X. M. Li, D. A. A. Ohlberg, D. R. Stewart, and R. S. Williams: *Nat. Nanotechnol.* **3** (2008) 429.
- 3) A. Sawa: *Mater. Today* **11** [6] (2008) 28.
- 4) S. Q. Liu, N. J. Wu, and A. Ignatiev: *Appl. Phys. Lett.* **76** (2000) 2749.
- 5) Y. B. Nian, J. Strozier, N. J. Wu, X. Chen, and A. Ignatiev: *Phys. Rev. Lett.* **98** (2007) 146403.
- 6) A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura: *Appl. Phys. Lett.* **85** (2004) 4073.
- 7) S. Asanuma, H. Akoh, H. Yamada, and A. Sawa: *Phys. Rev. B* **80** (2009) 235113.
- 8) Z. L. Liao, Z. Z. Wang, Y. Meng, Z. Y. Liu, P. Gao, J. L. Gang, H. W. Zhao, X. J. Liang, X. D. Bai, and D. M. Chen: *Appl. Phys. Lett.* **94** (2009) 253503.
- 9) R. Yasuhara, T. Yamamoto, I. Ohkubo, H. Kumigashira, and M. Oshima: *Appl. Phys. Lett.* **97** (2010) 132111.
- 10) D. Seong, J. Park, N. Lee, M. Hasan, S. Jung, H. Choi, J. Lee, M. Jo, W. Lee, S. Park, S. Kim, Y. H. Jang, Y. Lee, M. Sung, D. Kil, Y. Hwang, S. Chung, S. Hong, J. Roh, and H. Hwang: *IEDM Tech. Dig.*, 2009, p. 101.
- 11) M. Jo, D. Seong, S. Kim, J. Lee, W. Lee, J.-B. Park, S. Park, S. Jung, J. Shin, D. Lee, and H. Hwang: *VLSI Tech. Dig.*, 2010, p. 53.
- 12) D. S. Shang, Q. Wang, L. D. Chen, R. Dong, X. M. Li, and W. Q. Zhang: *Phys. Rev. B* **73** (2006) 245427.
- 13) T. Harada, I. Ohkubo, K. Tsubouchi, H. Kumigashira, T. Ohnishi, M. Lippmaa, Y. Matsumoto, H. Koinuma, and M. Oshima: *Appl. Phys. Lett.* **92** (2008) 222113.
- 14) X. Liu, K. P. Biju, El M. Bourim, M. Jo, W. Lee, J. Park, S. Park, J. Shin, and H. Hwang: *Solid State Commun.* **150** (2010) 2231.
- 15) Z. L. Liao, Z. Z. Wang, Y. Meng, Z. Y. Liu, P. Gao, J. L. Gang, H. W. Zhao, X. J. Liang, X. D. Bai, and D. M. Chen: *Appl. Phys. Lett.* **94** (2009) 253503.
- 16) T. Fujii, H. Kaji, H. Kondo, K. Hamada, M. Arita, and Y. Takahashi: *IOP Conf. Ser.: Mater. Sci. Eng.* **8** (2010) 012033.
- 17) Z. L. Wang, J. S. Yin, Y. D. Jiang, and J. Zhang: *Appl. Phys. Lett.* **70** (1997) 3362.
- 18) M. Cherry, M. S. Islam, and C. R. A. Catlow: *J. Solid State Chem.* **118** (1995) 125.
- 19) X. Liu, K. P. Biju, El M. Bourim, S. Park, W. Lee, D. Lee, K. Seo, and H. Hwang: *Electrochem. Solid-State Lett.* **14** (2011) H9.
- 20) M. Rajeswari, A. Goyal, A. K. Raychaudhuri, M. C. Robson, G. C. Xiong, C. Kwon, R. Ramesh, R. L. Greene, T. Venkatesan, and S. Lakeou: *Appl. Phys. Lett.* **69** (1996) 851.
- 21) V. B. Podobedov, D. B. Romero, A. Weber, J. P. Rice, R. Schrekkala, M. Rajeswari, R. Ramesh, T. Venkatesan, and H. D. Drew: *Appl. Phys. Lett.* **73** (1998) 3217.