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The unification of filament and interfacial resistive switching mechanisms for titanium dioxide based memory devices

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Reversible and controllable conversion between unipolar and bipolar resistive switching (URS and BRS) was observed in Pt/TiO2/Pt memory devices. The URS and BRS of this device exhibited different low resistance states but shared the same high resistance state. The conduction mechanisms of low resistance states in URS and BRS are Ohmic conduction and electrons tunneling, respectively, while the high resistance state is controlled by Schottky barrier formed at the top interface of Pt/TiO2. The temperature dependence of resistance states indicates Magnéli phase filaments formed in URS. A unified model was then proposed to demonstrate the unification of filament and interfacial switching mechanisms. © 2011 American Institute of Physics. [doi:10.1063/1.3583669]

I. INTRODUCTION

Resistive switching (RS) effect has been extensively investigated for almost ten years aiming at the application in next generation nonvolatile memory.1,2 The “0” and “1” could be realized through switchable high and low resistance states (HRS and LRS) for storage. In terms of its dependence on the polarity of bias voltage, the RS effect was generally clarified into unipolar and bipolar resistive switching (URS and BRS).3,4 Up to now, the switching behaviors have been found in lots of perovskite oxides and binary metal oxides thin films.4 Among them, titanium dioxide thin film has been widely studied, displaying both URS and BRS behaviors. The mechanisms of the RS behaviors have been explained well by the filament (URS) and interfacial models (BRS): The formation and rupture of localized filament5,6 lead to URS behavior, while the modulation of Schottky barrier at the metal/insulator interface by the drift of oxygen vacancies7,8 is responsible for the BRS behavior.

Recently, the researches on the switching mechanisms for titanium dioxide have achieved significant progress. Nanoscale Magnéli phase (Ti nO2n−1 n = 4,5) filament ruptured and recovered at the anode interface was directly observed by Kwon et al.6 in URS devices, while the Magnéli filament was also indentified by Strachan et al.7 in BRS TiO2 thin films. The difference between them was whether the filament spans the two electrodes completely. Besides, Jeong et al.8 reported the coexistence of URS and BRS in Pt/TiO2/Pt devices. So, a thorough understanding of the correlation between the two models is still necessary. In this work, both URS and BRS have been observed in the same Pt/TiO2/Pt device. Moreover, the reversible conversion between URS and BRS can be achieved by applying deliberate voltage sweeping operation. A unified model was proposed to clarify the unification of filament and interfacial resistive switching mechanisms.

II. EXPERIMENTAL DETAILS

The TiO2 thin film was obtained by thermal ozidization. First, the metallic Ti thin film was deposited on Pt/Ti/SiO2/Si substrate by electron beam evaporation. Then the Ti film was thermally oxidized under an oxygen pressure of 10 Pa at 600 °C for 40 min. For electrical measurement, Pt top electrodes with a diameter of 200 μm were deposited by electron beam evaporation with a metal shadow mask. A sandwiched structure of Pt/TiO2 (150 nm)/Pt was formed and the schematic configuration was shown in Fig. 1(a). All the current-voltage (I-V) characteristics of the fabricated devices were measured by a Keithley 2410c source meter unit using a DC voltage sweeping mode, in which the positive bias was defined by a current flow from top to bottom electrode and the negative bias was defined by the opposite direction.

III. RESULTS AND DISCUSSIONS

The initial state of top and bottom interfaces (Pt/TiO2) has significant roles on the carrier transport and switching characteristics of the memory devices.8 The I-V curve of the initial state revealed a rectifying characteristic, as shows in Fig. 1(b). Considering gradient oxidation during the preparation of TiO2 thin film, a high and a low Schottky barrier were respectively expected at the top and bottom interfaces.

After a positive forming voltage applied to the top electrode with a compliance current (CC) of 20 mA, the memory
device exhibited URS and could be reversibly switched between HRS (~200 kΩ) and LRS (~30 Ω), as shown in Fig. 2(a). When the device was switched to HRS, by controlling the sweeping voltage into negative range, the current decreased suddenly at the voltage of ~0.5 V [arrow 4 in Fig. 2(b)]. Subsequently, an asymmetry BRS curve was obtained [Fig. 2(c)]. The resistance of HRS and LRS are about 200 kΩ and 300 Ω, respectively. The set process (change from HRS to LRS) occurs only under negative voltage bias and the reset process (change from LRS to HRS) only occurs under positive voltage bias. The above operation was similar with that reported by Lee et al.11 Specially, by increasing the magnitude of positive bias [arrow 5 in Fig. 2(d)] after the reset process in BRS, instead of swept back to the negative bias, the device can reach LRS and display URS. As described above, the URS and BRS can be reversibly converted for many times without degradation by applying above-mentioned deliberate voltage sweeping operation.

Both the URS and BRS can be activated from the other one’s HRS.

Figures 3(a) and 3(c) show the fitting results for the LRS in URS and BRS, respectively. From Fig. 3(a), the linear I-V curve with a slope close to 1 clearly revealed that the transport behavior of LRS in URS is Ohmic conduction, which was supported by conducting filament formed in forming process. From Fig. 3(c), the symmetrical I-V curve for LRS in BRS can be well fitted by the formula of \( I = A \sinh(BU) \), which is consistent with electron tunneling model.7,12 A similar rectifying characteristic as the initial state was observed in the I-V curves of HRS in BRS and URS, as shown in Figs. 2(c) and 2(d), indicating the top Schottky interface (Pt/TiO₂) dominating the conduction behavior. This speculation was confirmed by linear \( \ln(I) - V^{1/2} \) plot at high voltage range of HRS in URS and BRS, as shown in Figs. 3(b) and 3(d), in agreement with the Schottky barrier model.13 In order to confirm the Schottky type electron injection at the top interface of Pt/TiO₂, the current voltage (I-V) curves of HRS in BRS at positive bias was measured at temperatures ranging from 288 to 348 K. Figure 4 shows the temperature-dependent Schottky emission fitting results. The extracted Schottky barrier height is plotted as a function of the square root the applied voltage. By extrapolating to \( V = 0 \), the Schottky barrier height was determined to be ~0.62 eV. An optical dielectric constant of 7.1 was also obtained. These fitting results indicate that the filament and the Schottky interface both play important roles for the observed conversion.

In order to further investigate the conducting and switching mechanisms of the different resistance states in URS and BRS, temperature related measurement was carried out under air atmosphere. Figure 5 shows the temperature dependence of resistance for different resistance states in URS and BRS. The resistance of HRS in URS and BRS shows a
decreasing trend with increasing temperature, the same as the resistance of LRS in BRS. These negative temperature characteristics could be ascribed to typical semiconducting behavior. However, the resistance of LRS in URS increases with increasing temperature, implying a metallic behavior. That may be ascribed to the nanoscale Magnéli phase filament formed in the TiO$_2$ thin films. It has been proved that Magnéli phase filament has a metallic conductivity at room temperature.$^{14}$

Formation and rupture of filament at anode interface$^{5,6,15}$ is usually employed to elucidate the URS behavior, while the variation of Schottky barrier at the metal/insulator interface$^{7–9,16}$ is employed to explain the BRS behavior. Based on the existing filament and interfacial models, a unified model for the conversion between URS and BRS (Fig. 6) could be depicted as below. After the forming process, the conical shape$^{17}$ nanoscale Magnéli phase filament (Ti$_4$O$_7$) [as indicated in Fig. 6(a)] formed in the TiO$_2$ thin film.$^{6,18}$ which exhibited URS behavior. In the reset process in URS, the filament ruptured at the anode interface$^{15}$ by joule-heating effect and the memory device was switched to HRS, as shown in Fig. 6(b). If negative voltage was thereafter applied on the top electrode, the positive oxygen vacancies will drift from the Magnéli phase filament and move toward the top interface,$^{9}$ resulting in the decrease of Schottky barrier.$^{7,8}$ Meanwhile, the filament with high concentration of oxygen vacancies$^{19}$ will contract, leading to smaller electric intensity on the gap between the top of filament and electrode. Maybe the electric intensity on the gap decreased a little but the Schottky barrier decreased a lot. Therefore, once the residual

![FIG. 3. (Color online) Linear fitting results of (a) LRS with Ohmic conduction mechanism and (b) high voltage range of HRS with Schottky emission conduction mechanism in URS. (c) The I-V curve of LRS in BRS fitted by $I = A \sinh(BV)$ formula. (d) Linear fitting results of high voltage range of HRS in BRS with Schottky emission conduction mechanism.](image1)

![FIG. 4. (Color online) Temperature dependent Schottky emission fitting of the memory devices at positive bias. Insert shows the extracted Schottky barrier height as a function of the square root of applied voltage.](image2)

![FIG. 5. (Color online) The temperature dependence of resistance for different resistance states in URS and BRS.](image3)
Schottky barrier was small enough, the electrons would easily tunnel through it and the memory device switched to LRS with a BRS behavior, as shown in Fig. 6(c). On the contrary, when positive voltage was applied on the top electrode, the oxygen vacancies will drift from the top interface into the Magnéli phase filament. The filament will expand and the Schottky barrier will be enhanced. The higher Schottky barrier was hard to tunnel through for electrons and would recover at last. The device was therefore switched back to LRS in URS, as shown in Fig. 6(a).

Thus, it can be seen that the filament model for URS and interfacial model for BRS, not contradictory, but can reversibly convert and coexist. The unified model also implied the role of Schottky barrier for filament dominated URS devices and the role of filament for Schottky interface dominated BRS devices.

The unified model could also be used to explained the earlier reported coexistence of URS and BRS in ZnO, SrTiO$_3$, and TiO$_2$ thin films, in which the BRS and URS behaviors were obtained under different magnitude of CC during the forming process. According to the above unified model, large CC would result in unbridged filament (URS) and small CC would result in unbridged filament (BRS). Recently, URS has been demonstrated universal and independent with materials, while BRS behavior can be observed in the devices with variable Schottky barrier. Therefore, it can be deduced that reversible and controllable conversion between URS and BRS may be realized in those devices with Schottky interface formed between the oxide thin films and electrode. Further investigation on reversible conversion between URS and BRS in other material systems is on progress.

IV. CONCLUSIONS

Reversible and controllable conversion between URS and BRS has been observed in the same memory device of Pt/TiO$_2$/Pt. A unified model for the conversion between URS and BRS was proposed, which demonstrated the unification of filament and interfacial model. In addition, for individual URS or BRS, the Schottky interface and filament both play important roles on resistive switching.

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