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### Regular Article

# An influence of bottom electrode material on electrical conduction and resistance switching of $TiO_x$ thin films

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**Abstract.** We investigated the electrical conduction and resistance switching mechanisms of  $\text{TiO}_x$  thin films grown on three kinds of bottom electrode at room temperature (an inert Pt, an active Ti and fluorine tin oxide FTO electrodes). The bottom electrode materials strongly affect the *I-V* characteristics and switching parameters. The *I-V* characteristic is explained through the presence of interface states in the metal electrode devices (Pt and Ti) and the work function in the metal oxide device (FTO). The Pt device has the smallest  $V_{\text{SET}}$  and largest switching ratio, while the Ti device shows the largest  $V_{\text{SET}}$  and smallest switching arises from formation and rupture of filament paths, generated by the movement of oxygen vacancies. All devices depict the same electrical conductions, trap-controlled space-charge-limited, FN tunneling and Ohmic conductions for a high resistance state and a low resistance state, respectively. In this study, the rarely reported FN tunneling conduction in published TiO<sub>x</sub>-based ReRAM device was found, which can be attributed to an influence of the bottom electrode on the electronic distribution in devices.

# 1 Introduction

Resistive switching in  $TiO_2$  thin films has attracted significant attention for possible application in nonvolatile memory devices. Some works reported the role of electrode on the resistance switching of TiO<sub>2</sub> thin films. Park et al., reported the bipolar resistance switching of  $Ir/TiO_x/TiN$ structure due to a variation of oxygen vacancy concentration at top  $Ir/TiO_x$  interface [1]. Choi et al., found that the resistance switching of TiO<sub>2</sub> films significantly depended on a bias polarity to the top electrode (Al, Pt) [2]. Jung et al., presented the switching in the Al/a-TiO<sub>x</sub>/ITO structure, which results from the migration of the oxygen vacancies in the a-TiO<sub>x</sub> [3]. Yang et al., compared the role of different top metal electrode on the resistance switching of a-TiO<sub>2</sub> films in the top electrode (Pt, Au, Ag, Ni, W and Ti)/a-TiO<sub>2</sub>/Pt structure. The resistance switching is controlled by the chemical reaction between the top electrode materials and  $TiO_2$  layer [4].

However, there is a lack in work regarding the role of the bottom electrode. In this study, we aim to compare the role of three kinds of electrode: an inert Pt electrode, an active Ti electrode and a fluorine tin oxide FTO electrode on electrical conduction and resistance switching behavior of  $Ag/TiO_x/bottom$  electrode device.

# 2 Experiments

In this study, fluorine tin oxide/glass (FTO) and  $Pt/TiO_2/SiO_2/Si$  substrate are commercial samples. The other electrodes (Ti and Ag) and  $TiO_x$  thin films were fabricated from metallic (Ti, Ag) targets by using the dc sputtering technique at room temperature. 100-nm-thick metallic Ti and Ag layers were deposited as bottom and top electrodes at a pressure of 2 mTorr in an Ar environment. The 100-nm-thick TiO<sub>x</sub> thin film was prepared in a mixture of Ar + O<sub>2</sub> (6%) gases at a pressure of 7 mTorr. During the deposition of the top Ag layer, a mask was used

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Fig. 1. XRD pattern of TiO<sub>2</sub>/glass substrate.

for top electrode patterning. The crystalline phases and microstructures of the thin films were characterized in the  $\theta - 2\theta$  mode by using a D8 advance (Bruker) X-ray diffractometer (XRD) with CuK $\alpha$  radiation ( $\lambda = 1.54$  Å). The chemical state of TiO<sub>x</sub> composition was determined by X-ray photoelectron spectroscopy (XPS). Current-voltage (*I-V*) measurements were carried out using a Semiconductor characterization system (Keithley 4200 SCS) and probe station.

#### 3 Results and discussions

Figure 1 shows the XRD pattern of the  $TiO_x/glass$  substrate. There are not any crystalline peaks in the XRD pattern. Since the  $TiO_x$  thin films were deposited on glass, FTO, Ti and Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates at room temperature, we believe that the grown  $TiO_x$  thin films exist in an amorphous phase. This result is consistent to the published literatures [5,6]. Huang et al., stated that the  $TiO_2$  thin films deposited on the Pt bottom electrode at room temperature result in amorphous phase [5]. In addition, the TiO<sub>2</sub> thin films grown on Pt/Ti/SiO<sub>2</sub>/Si substrate is reported to be amorphous phase in spite of the post-annealing treatment at 250 °C for 1 h [6]. Figure 2 shows XPS spectra of  $TiO_x$  films deposited on various electrodes. The core level spectra of O 1s can be deconvoluted into two peaks corresponding to lattice oxygen (LO,  $\sim$ 530 eV) O-Ti and non-lattice oxygen (NLO,  $\sim$ 531.7 eV). The presence of non-lattice oxygen ions might play an important role in the electrical conduction and resistance switching mechanism. Figure 3 shows that the XPS spectra consist of Ti<sup>4+</sup> (Ti  $2p_{3/2} \sim 458.4 \text{ eV} - 458.8 \text{ eV}$  and Ti  $2p_{1/2} \sim 463.3 \text{ eV} - 464.3 \text{ eV}$ ). This indicates that Ti<sup>4+</sup> ions are dominant in those devices. However, both the peaks at the lower binding energy, 529 eV and 457.4 eV, are observed in the XPS spectra of the  $TiO_x/Pt$  devices,



Fig. 2. XPS spectra of the O 1s of (a) FTO, (b) Pt and (c) Ti devices.

as shown in Figures 2b and 3b. Both peaks might correspond to the occurrence of  $Ti_2O_3$  phase [7,8].

Figure 4 shows the *I-V* characteristics of devices with various bottom electrodes (FTO, Pt and Ti). All the *I-V* curves show the bipolar switching characteristic. For all devices, the as-prepared state is a high resistance state (HRS). The HRS is changed to a low resistance state (LRS) in the negatively biased process (0 to -2 V) to the bottom electrode, whereas HRS is not changed by a positive bias. The LRS is progressively changed to the HRS only by a voltage sweep in the positive voltage region (0 to +  $V_{\rm max}$ , + 1.65 V for Ti and +2.5 V for the other bottom electrodes). The *I-V* characteristics do not change even after repeated stress cycles.

It should be noted that I-V characteristic (the inset of Fig. 4) of the Ti and Pt devices cannot be explained uniquely through the difference in work function. Among those devices, the I-V curve of the Ti device shows the asymmetric characteristic, even though there is a small difference in work function between Ti (4.33 eV) and Ag (4.26 eV) [4]. In theory, the small difference between work function of Ti and Ag cannot induce a significant asymmetry. Therefore, this observed behavior might originate from the high reactivity of Ti with oxygen during TiO<sub>x</sub> film deposition, which will be discussed in the remainder



Fig. 3. XPS spectra of the Ti 2p of (a) FTO, (b) Pt and (c) Ti devices.

of the paper. In case of the Pt device, the symmetric *I-V* curves of Pt device is obtained although the top Ag electrode and the bottom Pt electrode have a large difference in work function, Ag (4.26 eV) and Pt (5.65 eV) [4]. Since Pt is an inert electrode, which leads to high accumulation of oxygen vacancies at the  $Pt/TiO_x$  interface during the  $TiO_x$  deposition, lowering the barrier height or decreasing the difference between two interfaces [4]. As a result, the *I-V* curve of Pt devices is symmetric. It is reported that a polarization discontinuity can induce the formation of oxygen defects and interstitials at oxide interface [9]. Therefore, the further study on the  $TiO_x/FTO$ interface is under investigation. In this report, we suggest that the symmetry of the *I-V* curve of the FTO device might be the consequence of a small difference in the work function between the top Ag (4.26 eV) and bottom FTO (4.5 eVe) electrodes [10]. The differences in the *I-V* curves of those devices obviously stem from the bottom electrode materials.

Figure 5 shows the switching voltages with the various bottom electrodes. The switching voltages ( $V_{\text{SET}}$  and  $V_{\text{RESET}}$ ) vary with sweep cycles. The values of the switching voltages are listed in Table 1. In comparison, the two metal electrode devices show an opposite switching voltages. The inert Pt electrode has the smallest  $V_{\text{SET}}$  and the larger  $V_{\text{RESET}}$ , while the active Ti electrode induces the



**Fig. 4.** Semilogarithmic *I-V* character of (a) FTO, (b) Pt and (c) Ti devices. The inset is the linear plot *I-V* curve.



Fig. 5. Switching voltage of (a) FTO, (b) Pt and (c) Ti devices.



Table 1. The switching voltages of FTO, Pt and Ti devices.

Fig. 6. Switching ratio of (a) FTO, (b) Pt and (c) Ti devices.

largest  $V_{\text{SET}}$  and the smallest  $V_{\text{RESET}}$ . The value of  $V_{\text{SET}}$  of both the Pt and Ti devices supports the above arguments of interface states induced at the bottom interface. Among those devices, the oxide FTO electrode has an intermediate  $V_{\text{SET}}$  and the largest  $V_{\text{RESET}}$ . Figure 6 depicts the switching ratio of those devices. The Pt device shows the largest switching ratio, while the Ti device has the smallest switching ratio.

In order to understand the role of the bottom electrode on conduction behavior in the devices, we examined the transport characteristics for each device. Figures 7 and 8 depict the I-V behaviors in the log-log scale. All the I-Vcurves of the LRS in both the positive and the negative biases follow the linear I-V dependence with a slope of one, which is a typical characteristic of Ohm's law.

The leakage current of the HRS of the devices follows a non-linear I-V dependence where one or more of the conduction processes may be involved. Because of this, all the I-V curves of the HRS were examinated in terms of some potential leakage mechanisms such as space-charge-limited conduction (SCLC), interface-limited Schottky emission conduction (SC), interface-limited Fowler-Norheim tunneling (FN) and bulk-limited Poole-Frenkel emission (PF) [11–15].

There is an abrupt change of current with voltage of the HRS in the negative voltage bias as shown in Figure 7. The leakage currents linearly depend on voltage below the  $V_{\text{SET}}$  ( $I \sim V$ ), and then increase steeply on voltage ( $I \sim V^s$ , s > 2 with  $s \sim 5$ , 7.5, 8 for FTO, Pt and Ti, respectively). The leakage conduction is consistent with the trap-controlled space-charge-limited conduction. The change from the SCLC of the HRS to the Ohmic conduction of the LRS could be ascribed to the occurrence of metallic filaments as noted in the remainder of the paper.



**Fig. 7.** Log-log plot of the *I-V* of (a) FTO, (b) Pt and (c) Ti devices in the negative bias.

In contrast to an abrupt change of current with voltage of the HRS in the negative biases, the current of the HRS in the positive bias, as shown in Figure 8, which is controlled by the  $Ag/TiO_x$  interface, does not suddenly vary with voltage. Those *I-V* curves fit well to FN tunneling conduction with a negative slope, as shown in Figure 9. The inset in Figure 9 shows that the slope m of the fitting line of the devices follows the sequence  $m_{\rm Pt} >$  $m_{\rm FTO} > m_{\rm Ti}$ . It is well known that FN tunneling conduction is dominant in thin dielectric films at high electric field, where the charge carriers are injected from the electrode to the insulator by tunneling through a high potential barrier [15]. It is also noticed that the FN tunneling conduction is rarely reported in the published  $TiO_x$ based ReRAM device. However, in this study we found the FN tunneling conduction in the three investigated devices. Since the Ag and  $TiO_x$  layers of those devices were deposited on the bottom electrodes with the same depositing conditions, the different slope m can be attributed to the different electronic distribution in the devices due to the different bottom electrode materials.

It is noted that the SCLC conduction implied the trapping levels within the band gap and the linear *I-V* dependence of the LRS in both negative and positive biases gives clues to the physical origin of the resistive switching with the filament model [16]. A combination of these two above observations rules out the trapping/detraping process controlled resistance switching. Therefore, it is reasonable to



**Fig. 8.** Log-log plot of the *I-V* of (a) FTO, (b) Pt and (c) Ti devices in the positive bias.



Fig. 9. Conventional FN tunneling plot  $\ln (J/E^2) vs (1/E)$  for the HRS of (a) FTO, (b) Pt and (c) Ti devices in the positive bias.

suggest that the mechanism of the formation and rupture of filament paths consisting of oxygen vacancies controls the observed bipolar switching behavior in the  $\text{TiO}_x$  thin films. When a negative voltage is applied to the bottom electrodes (Pt, FTO, Ti), existing oxygen vacancies are driven to the bottom electrode. As a negative voltage increases, the injected carriers begin to fill the trap sites and the conduction follows the SCLC. Once the electric field through the  $\text{TiO}_x$  film reaches a value at which the filament path of oxygen vacancies connect both electrodes throughout the  $\text{TiO}_x$  film and the HRS to LRS transition occurs. Then, large current flow along the filament path and the conduction in the LRS follows the Ohmic behavior. In contrast, the migration of these oxygen vacancies far away the bottom electrode caused by the reverse bias could induce the rupture of the filament path, resulting in the LRS to the HRS transition.

The presence of Ti<sub>2</sub>O<sub>3</sub> phase as a semiconductor or a semimetal [17] embedded in the TiO<sub>x</sub> film of the Pt device in addition to high oxygen vacancy concentration at the TiO<sub>x</sub>/Pt interface result in a low interface resistance, leading to the easy filamentary formation or the smallest  $V_{\text{SET}}$ . With the Ti electrode, Ti is easily oxidized in the presence of oxygen and forms a stable oxide layer TiO<sub>y</sub> between Ti and bulk TiO<sub>x</sub> films during the TiO<sub>x</sub> deposition. It is also probable that Ti<sup>3+</sup> ion in the TiO<sub>y</sub> layer acts as a trap and captures an electron, resulting in a high interface resistance or the largely asymmetric *I-V* curve. This might result in the largest  $V_{\text{SET}}$  value of the Ti device. For the case of the FTO bottom electrode, the absence of reduction of TiO<sub>x</sub> thin film seems to be attributed to the abundant oxygen at the TiO<sub>x</sub>/FTO interfaces. It may lead to the intermediate value for  $V_{\text{SET}}$ .

### **4** Conclusions

In conclusion, the  $TiO_x$  thin films grown on different bottom electrodes at room temperature are in an amorphous phase with the presence of non-lattice oxygen concentration and dominant  $Ti^{4+}$  ions. Especially, the  $Ti_2O_3$  phase nucleated only in the  $TiO_x$  films of the inert Pt device. The I-V characteristic of Ti and Pt devices can be explained based on the interface states induced at the bottom interface rather than the work function. The interface states were originated from the reactivity of the electrode with oxygen during the  $TiO_x$  film growth and significantly affected the switching voltages. The inert Pt device shows the smallest  $V_{\text{SET}}$  and the largest switching ratio, while the active Ti device has the largest  $V_{\text{SET}}$  and the smallest switching voltage. Since the FTO electrode does not react with the  $TiO_x$  film, the FTO device gives an intermediate value of the switching parameter among the devices. The resistance switching is controlled by formation and rupture of filament paths consisting of the oxygen vacancies due to the migration of the oxygen vacancies under the polarity bias. The responsible electrical conduction of the devices is governed by the FN tunneling conduction for the HRS in the positive bias, trap-controlled SCLC conduction for the HRS in the negative bias, and Ohmic conductions for the LRS in both the positive and negative biases.

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