Correlation between diode polarization and resistive switching polarity in Pt/TiO$_2$/Pt memristive device

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We have investigated the correlation between diode polarization and switching polarity in electroformed Pt/TiO$_2$/Pt memristive device. Before forming, the diode direction of the Pt/TiO$_2$/Pt device is reversible under the current pulses with varying current amplitude. The diode polarization arises from oxygen vacancy migration in fully depleted Pt/TiO$_2$/Pt films. The measurement results indicated that only the polarized diode can be electroformed and the metallic suboxide filament is created in parallel to the diode with a switching polarity dependent on the polarization of stack prior to forming. The non-polar state inhibits field concentration at either end of the device at the specified current, preventing the electroforming. On and off state currents are measured at 0.2 V for $5 \times 10^4$ s showing good retention, which is promising for non-volatile memory application.

1 Introduction

Resistive switching random access memory devices (RRAM) have attracted extensive attention due to promising applications in next generation nonvolatile memories, programmable logic, hybrid circuits with CMOS, and neuromorphic computing [1]. Indeed, due to the simple structure and ionic nature of the memory mechanism, RRAM devices have excellent scaling prospects, which are combined with fast and low energy switching and high retention. Many insulating materials have been reported to show resistive switching behaviors, including metal oxides, e.g., HfO$_2$ [2] TiO$_2$ [3] and Ta$_2$O$_5$ [4] and solid state electrolyte materials, such as chalcogenides [5, 6], a-Si [7–9]. Among them, TiO$_2$ is a model system for studying resistive switching. Metal oxide resistive switches are favored for nonvolatile memory and neuromorphic applications due to their superior properties, such as good scalability and CMOS processing compatibility. In addition, we recently found that TiO$_2$ can be switched continuously by applying electrical bias (current or voltage pulses) with gradually increasing amplitude and/or duration, which is promising for analog computing circuit application [10–12].

A deeper understanding of the resistive switching mechanism from the atomic scale point of view is helpful to overcome endurance and yield problem. Recently, many groups’ investigation indicated that the switching behavior is due to the oxygen vacancy migration in the switching layer and a resultant change in the electronic barrier at the metal/oxide interface [13–24]. For example, Shima et al. [16] have shown that the Pt/TiO$_2$/Pt device shows switchable rectification behavior at the interface region. Yang et al. [17] found the interaction between the resistive switching behavior and rectification properties at the two interfaces of Pt/TiO$_2$/Pt crosspoint devices after electroforming. Nieh et al. [20] proposed that the resistive switching behavior in a single SnO$_2$ nanowire device is attributed to the switchable diode effect, which is induced by external bias. Wedig et al. [21] concluded that the resistive switching in Ta$_2$O$_5$, HfO$_2$, and TiO$_2$ can be caused by both the diffusion of oxygen vacancies and the migration of cations. Jaemson et al. [22] suggested that hydrogen ions could be the source of resistive switching along with oxygen vacancies. Messer-schmitt et al. [23] demonstrated that moisture has impact on the resistive switching behavior of oxygen

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anionic-electronic switching metal-oxides and this behavior is fully reversible. Lubben et al. [24] found that moisture is playing a significant role in the redox process of resistive switching in valence change memories cell. However, there are no reports on identifying the correlation between the diode polarization and oxide resistive switching polarity in Pt/TiO2/Pt memristive device. The forming polarity (and therefore its polarization) of a pristine device is critical for achieving good performance and high uniformity especially since it determines the nature of the conducting pathways in the switching layer [25–27]. For example, Tsai et al. [26, 27] reported an IrOx/TaOx/WOx/W resistive memory stack to control the formation polarity, resulting in improved resistive switching memory characteristics. However, the multilayer film deposition has extra steps and hence increases cost. In this paper, we correlate programmable rectification in virgin devices with post electroformed switching polarity in the Pt/TiO2/Pt devices.

2 Experiment The Pt/TiO2/Pt memristive device studied here is implemented in the cross-point structure with an overlap area between two electrodes of about 1 μm^2, as schematically shown in the inset of Fig. 1(a). An e-beam evaporated Ti/Pt bottom electrode (5 nm/25 nm) has been patterned by standard optical lithography technique on a Si/SiO2 substrate (500 μm/200 nm, respectively) at a rate of 0.1 nm/s. The 30 nm TiO2 film is then deposited by using atomic layer deposition at 200 °C using titanium isopropoxide (C12H28O4Ti) and water as a pre-cursor and reactant, respectively. The orthogonal Pt/Au (15 nm/25 nm) top electrode is formed on top of the TiO2 blanket layer by using e-beam vaporization and a subsequent lift-off process. The samples are rapidly thermal annealed at 400 °C for 5 min in forming gas. The device structure and fabrication methods are similar to the ones described in Ref. [10]. The current–voltage (I–V) characteristics were carried out with an Agilent B1500A semiconductor parameter analyzer in air at room temperature. First, to reverse the diode direction, a negative polarized current (i.e., compliance current) with sequentially increased magnitude from –0.01 mA to –1.1 mA was applied to the device, followed by a read voltage at –1 V. Then, the reverse diode is switched back to the forward diode by sequentially applying a positive polarized current from 0.01 mA to 1.5 mA to reversed device, followed by a read voltage at 1 V.

3 Results and discussion Figure 1 shows the initial I–V characteristics of Pt/TiO2/Pt device in its virgin state. Both devices before and after annealing exhibit a rectifying characteristic with the forward current under positive voltage (defined as forward diode). Considering the large work function of Pt and the n-type semiconductor of TiO2, the origin of the rectification is thought to be the Schottky barrier at the interface between the TiO2 and Pt layers. In addition, the observed forward diode indicates that the rectification is dominated by the Pt/TiO2 top interface rather than the TiO2/Pt bottom interface. Yang et al. [28] suggested that a Ti adhesion layer can diffuse through the Pt bottom electrode to react with the TiO2 at the bottom interface during hot deposition of TiO2 and form a locally reduced oxide (i.e. TiO2–x), reducing the bottom interface barrier height. The results of I–V measurement show that the resistance of the device after annealing at 400 °C for 5 min in forming gas decreases by two orders compared with that of as-fabricated device, due to the introduction oxygen vacancies under oxygen deficient ambient annealing, as shown in the Fig. 1(b). The introduced vacancies from the Ti adhesion layer during annealing can take the form of isolated oxygen vacancies and clustered segregates [29, 30]. Thus, for a 30 nm TiO2 interlayer dielectric, vacancy concentrations as high as 10^19/cm^3 can reasonably be expected to result in completely depleted films. Such ionized charges could contribute to modulating the internal electric fields, and thus the device polarization. The behavior of such a device, however, is likely different than in an electroformed device with a metallic filament, e.g. based on TiO2 Magnelli phase [31].

To prevent overheating of the devices, current pulses with 10 ms width through a limiting transistor were applied to cause device polarization. Figure 2(b) shows the dependence of read current at –1 V on a polarized current.

**Figure 1** (a) I–V characteristics of the initial state of the Pt/TiO2/Pt device before and after annealing and (b) the corresponding log scale I–V curves. The inset in (a) shows the schematic structure of Pt/TiO2/Pt device.
Figure 2 (a) Schematics of a measurement setup. A PNP or NPN transistor is used as positive and negative current limiters, respectively. (b) Response of the device using a −1 V conductivity read. The device is read after negative polarized current pulses of increasing magnitude from −0.01 mA to −1.1 mA. The top three figures show $I-V$ curves of initial state (N1), peak current (N2), and fully switched rectification (N3). The polarity is continuously programmable with the current pulses. (c) The schematic illustration of oxygen migration between top and bottom interface at initial state (N1), at the peak current state (N2), and switched rectification (N3). (d) Dependence of read current at 1 V on a positive compliance current of increasing magnitude from 0.01 mA to 1.5 mA. The top three figures are $I-V$ curves of reversed state (P1), peak current (P2), and switched back to the forward diode rectification (P3).

with sequentially increased magnitude from −0.01 mA to −1.1 mA (the measurement setup is shown in Fig. 2(a)). The top three figures of Fig. 2(b) show $I-V$ curves of initial state (N1) with forward diode behavior, peak current when the polarized current is equal to −0.8 mA (N2), and fully switched rectification (N3). It is interesting to find that the reverse current shows an increase when the polarized current is below −0.8 mA due to passing through the neutral, nonpolar point in the device. Higher than −0.8 mA, the device begins to enter into the opposing polarization and the reverse current begins to decline.

The mechanism of the switchable diode behavior in Pt/TiO$_2$/Pt device is schematically shown in Fig. 2(c). Metal–semiconductor contacts are more conductive under heavy doping, and more rectifying (Schottky-like) under low doping, so the concentration of $V_o$ at an interface determines its electrical transport behavior. The $I-V$ curve of the initial state (N1) shows forward diode behavior because of the heavily doped $V_o$ at bottom interface, resulting from Ti diffusion into the TiO$_2$ as well as alloying with the Pt during the hot deposition of TiO$_2$ [28]. However, the concentration of $V_o$ can be electrically controlled by a large electric field. The application of a negative bias in the top electrode diffuses $V_o$ into the TiO$_2$ layer, and lowers the resistance of the device (N2). With the negative bias increase, $V_o$ moves to the top interface and finally the $V_o$ concentrates on the top interface. At the same time, $V_o$ depletes due to conservation of mass. Consequently, the rectification at the top electrode is activated (reverse diode, N3), while it is eliminated at the bottom interface. Moreover, the distribution of $V_o$ and the corresponding diode polarity can be switched back when the positive bias is applied to the top electrode (i.e., from N3 to N1 in Fig. 2(c)).

The original rectification can be restored, as shown in the Fig. 2(d). When the positive polarized current from 0.01 mA to 1.5 mA is sequentially applied to reversed device (P1), the forward current (read at 1 V) shows an increase when the polarized current is below 1 mA. With the further increase of the polarized current, forward current begins to decrease. Finally, the reverse diode is switched back to the forward diode (P3). Similarly, the $I-V$ curves of reversed state (P1) with reversed diode behavior, peak current when the polarized current is equal to −1 mA (P2), and switched back to the forward diode (P3).

Figure 3 shows the correlation between diode polarization and following electroforming and switching polarity. When the rectification of the pristine Pt/TiO$_2$/Pt device is reversed (i.e., reverse diode), as shown in Fig. 3(a), the device can only be formed at positive bias, and the SET voltage is also positive, as shown in the Fig. 3(b) and (c), respectively. In this process, the $V_o$ would be created by electro-reduction and drift to the bottom interface and uli-
ultimately create a conducting channel (i.e., conductive filament) between electrodes. A metallically doped filament would cause a large reduction in the total resistivity, as observed experimentally. However, for the forward diode (Fig. 3(d)), the polarity of the forming process and SET process is switched accordingly, as shown in Fig. 3(e) and (f). This can be explained by collapse of the top Schottky interface resulting from the conductive channel growth towards the top interface [32]. The device is not able to be formed when the rectification of the device is switched to the non-polar state, see Fig. 3(g), and the vacancies can be moved back and forth based on the bias polarity, as shown from Fig. 3(h) to (k). In this particularly non-polar state case of Fig. 3(g), firstly, the –4 V was applied to the top electrode (Fig. 3(h)), resulting in the \( V_o \) moves toward the bottom interface (i.e., the reverse current increased, as shown in Fig. 3(i)), while applying +4 V to the top electrode (Fig. 3(j)), resulting in the reverse current decrease (Fig. 3(k)). The non-polar state inhibits field concentration at either end of the device at the specified current, preventing dielectric breakdown from occurring, at least within the same range of voltages used for forming in the other two cases.

Figure 4 shows on and off currents for the devices with positive SET, and negative SET were measured at read voltage of 0.2 V every 60 s for a total test time of \( 5 \times 10^4 \) s at room temperature. Both the electroformed devices show good retention capability after \( 5 \times 10^4 \) s of testing, suggesting both are due to oxygen migration instead of trapping-de-trapping/charging–discharging process, a mechanism that can lead to improved device performance.

Figure 3  (a) \( I-V \) curve for the device with reversed diode behavior (at the point N3 in Fig. 2b), (b) its corresponding forming and (c) switching \( I-V \) curves. (d) \( I-V \) curve for the device with forward diode behavior (at the point P3 in Fig. 2d), (e) its corresponding forming and (f) switching \( I-V \) curves. (g) \( I-V \) curve for the device with neutral behavior (at the point N2 or P2), (h) shows negative forming process and (i) its corresponding \( I-V \) curve, (j) shows positive forming process and (k) its corresponding \( I-V \) curve, indicating the device could not be electroformed. The insets in panels (a), (d) and (g) show schematically the corresponding distribution of oxygen vacancies with reverse, forward, and neutral polarities respectively.

Figure 4  Retention test for the formed devices with reverse-diode state (D1), and forward-diode state (D2).
with intrinsically low retention times [16]. It worth to note that we have tested more than 10 devices, all of them show the programmable rectification in virgin devices, and the correlation between diode polarization and resistive switching polarity, indicating the good endurance, uniformity.

4 Conclusions In summary, oxygen vacancy migration in depleted films can contribute to the modulation of built-in electric fields. In addition to controlling the device polarization and forward bias direction, the movement of vacancies can determine the location at which the dielectric breakdown preceding electroformation occurs. Consequently, this effect will determine the switching direction and orientation of the device during filamentary switching.

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References