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Effect of voltage polarity and amplitude on electroforming of TiO₂ based memristive devices

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Pt/TiO₂/Pt/Ti memristive devices were electrically formed to either the ON or OFF state using voltages of the same polarity but with different amplitudes. The forming step dictated the subsequent switching behaviour. A qualitative model based on the creation and migration of oxygen vacancies was proposed to explain the experimental results.

Resistive switching phenomena in metal oxides, first discovered 50 years ago,¹ have again attracted a great deal of interest in recent years due to the potential applications for emerging electronic devices beyond CMOS (complementary metal-oxide-semiconductor).^{2,3} A wide range of materials exhibiting resistive switching behavior have been identified such as binary or ternary transition metal oxides, perovskites and solid state electrolytes.⁴ Devices based on electrical and/or thermally actuated resistance change were recently linked to the memristors or memristive devices that were postulated by Chua in 1971.^{5,6} As non-volatile two terminal resistive switches, memristive devices are promising for applications in non-volatile memory,^{7–9} reconfigurable switches,¹⁰ non-volatile logic,¹¹ and bio-inspired neuromorphic computing.^{12–14} Significant progress has been made in device performance such as high endurance up to 10¹² cycles,¹⁵ faster than 1 ns switch speed,¹⁶ sub-100 fJ energy consumption per switching event,¹⁷ and an extrapolated data retention time longer than 10 years at room temperature.¹⁸ Regarding scaling, crossbar arrays of 8 × 8 nm² devices have been demonstrated with programming currents lower than 600 pA for each cross point.¹⁹

Compared with the achievements in device performance, understanding of the device physics especially the electroforming process is left behind. Electroforming, or so-called 'soft-breakdown' is a one-time step in which a high voltage/current sweep or pulse is used to significantly change the

conductivity of the switching material. The electroforming and switching processes in TiO₂ based bipolar memristive devices were attributed to the creation and motion of positively charged oxygen vacancies under electric fields and subsequent changes to the electrode–oxide interface.^{20,21} It was widely accepted that a negative voltage on the top electrode forms an asymmetric Pt/TiO₂/Pt/Ti device into an ON (low resistance) state while a positive voltage forms the device into an OFF (high resistance) state.²⁰ Previously, effects of applied voltage on unipolar resistive switches were also studied. For example, a Cu doped ZrO₂ unipolar device was found to be able to switch between ON and OFF states using either positive or negative voltages.²²

In this Communication, we report our discovery that a TiO₂ based memristive device can be formed to either the ON or OFF state, depending on the amplitude but independent of the polarity of forming voltages. The switching locations and device performance afterwards, however, are related to the previous forming step. We also propose a qualitative model that satisfactorily explains our observations.

Our 5 μm × 10 μm cross point devices used in this study consisted of 5 nm Ti/10 nm Pt/17 nm TiO₂/10 nm Pt that were fabricated on a silicon wafer with 100 nm thick thermally grown silicon dioxide (Fig. 1). The device fabrication process is as follows. First, a 5 nm thick Ti adhesion layer and 10 nm thick Pt were evaporated to the substrate through a metal shadow mask. A 17 nm thick blank layer of TiO₂ thin film was then deposited at room temperature using RF sputtering (270 W power) with an argon pressure of 4 mTorr. Finally, the 10 nm thick Pt top electrodes were deposited through a metal shadow mask. The base pressure for the electron beam evaporator was better than 2 × 10^{−7} Torr during both the bottom and top electrode fabrication. The finished samples were then annealed at 275 °C in a N₂ protective atmosphere for 1 hour. During electrical characterization, a two-terminal scheme was used: the bottom electrodes were grounded and quasi-DC sweeps were applied to the top electrodes (Fig. 1). All electrical measurements were conducted at room temperature using a Keithley 4200 semiconductor parameter analyzer.

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Fig. 1 Optical micrograph of a typical 5 μm by 10 μm device used for this study. The bottom electrode is 5 μm and the top electrode is 10 μm wide. The device geometry and the measurement set up are shown in the inset. A voltage (V) is applied to the top electrode and the bottom electrode is grounded during electrical characterization.

The TiO_2 device was electrically formed at negative voltages. Fig. 2a shows a typical forming curve when a -8 V sweep was applied to the top electrode. A sudden jump of current occurred at -6.7 V , indicating the formation of a conductive channel. The device stayed at the ON state after the forming voltage was removed. We call this the forming ON process. After negative forming ON, the device exhibited a repeatable nonvolatile switching behavior. For example, it was switched OFF with a positive voltage sweep from 0 to 10 V and ON again with a negative voltage sweep of 0 to -5 V (Fig. 2b). The ON/OFF conductance ratio at -0.5 V was 110. Interestingly, the device with the same geometry and dimension was formed to the OFF state using a negative voltage of higher amplitude. We applied a voltage sweep of -10 V to the device. Although the resistance suddenly decreased at -5.2 V , it increased again and stayed high after experiencing the -10 V sweep, leading to a forming OFF scenario (Fig. 2c). The device was also readily switched ON

Fig. 2 Typical I/V curves for electroforming at negative voltages and the subsequent switching. (a) A negative voltage (-8 V) forms the device to the ON state, and the device exhibits repeatable switching behavior between 10 and -5 V (b). (c) The device can also be formed to the OFF state using a larger negative voltage (-10 V). After forming OFF, the device is switched ON and OFF between 6 and -10 V . The arrows indicate the switching directions.

and OFF afterwards between +6 and -10 V (Fig. 2d), with an ON/OFF ratio of 2500 at +0.5 V.

On the other hand, the TiO_2 device can be formed to ON or OFF states with positive voltages. Fig. 3 shows typical I - V curves for such positive forming and subsequent switching behavior. With a 0 to +8 V sweep, the device was formed to the ON state (an abrupt resistance change at 5.8 V) (Fig. 3a). The device was then switched OFF and ON between -10 and +7 V (Fig. 3b). Similarly, the device was formed OFF with a higher positive voltage (+10 V) (Fig. 3c). There was also a temporary drop to low resistance at around +8 V, but the device eventually went to high resistance after 10 V was removed. After forming OFF, the device was then switched to ON and OFF states between -6 and +10 V.

It is noticeable that for either positive or negative forming, the forming OFF process needed a higher voltage than the forming ON process. And for a forming OFF process (Fig. 2c and 3c), there was an abrupt but temporary resistance decrease

before a higher voltage brought the device to the OFF state. To explain the dependence on the forming voltage polarity and amplitude, we proposed a qualitative model based on the creation and migration of mobile ions in the TiO_2 layer. As schematically illustrated in Fig. 4, a certain amount of oxygen vacancies were generated at the TiO_2 -bottom electrode (BE) interface after device annealing. This was a result from the Ti adhesion layer that diffused through grain boundaries of the bottom Pt wire and reacted with the TiO_2 at the interface, as has been experimentally observed previously.²³ The positively charged oxygen vacancies will be attracted towards the top electrode that was negatively biased, building a conductive channel that bridged the two electrodes (Fig. 4a). In the following OFF/ON switching cycles, a positive voltage pushed the oxygen vacancies away from the top electrode (TE)-oxide interface (also known as a rupture process), while a negative voltage re-bridged it together. When a negative voltage with

Fig. 3 Typical I - V curves for electroforming at positive voltages and the subsequent switching. (a) A positive voltage (8 V) forms the device to the ON state, and the device exhibits repeatable switching behavior between -10 V and 7 V (b). (c) The device can also be formed to the OFF state using a 10 V sweep. (d) After forming OFF, the device is switched ON and OFF between -6 and 10 V. The arrows indicate the switching directions.

Fig. 4 Schematic illustration for negative forming and the subsequent switching mechanisms. (a) Oxygen vacancies (V_{O}^{2+}) inside TiO_2 are attracted by a negative voltage ($-V_1$) to the top electrode (TE), forming the device ON. The switching then takes place at the TE-oxide interface. (b) With a larger negative voltage ($-V_2$), all the oxygen vacancies are driven towards the oxide and TE, leaving an oxygen vacancy depletion region at the BE-oxide interface where the subsequent switching events take place. This corresponds to a forming OFF process. The double red arrows indicate the location (interface) for the subsequent switching.

higher amplitude was used during the electroforming process, a temporary conductive channel was formed first, corresponding to the sudden current increase in Fig. 2c. However, further increasing the voltage led to an electric field that was strong enough to take all oxygen vacancies away from the BE-oxide interface. Consequently, the oxygen vacancy reservoir was depleted at the BE-oxide interface, resulting in an OFF state after forming (Fig. 4b). The subsequent switching events then took place at the BE-oxide interface with a positive voltage switched the device ON and a negative voltage switched it OFF.

The electroforming under positive voltages, however, is not as straightforward. When a positive voltage was applied on the TE, oxygen ions (O^{2-} , not a conductor since the outer shells are fully filled) at the TE-oxide interface were oxidized into oxygen atoms that escaped away from the lattice, leaving behind positively charged oxygen vacancies (Fig. 5a). As a result, an oxygen vacancy reservoir was created at the TE-oxide interface. Under a positive voltage, these oxygen vacancies moved into the oxides, met the oxygen vacancies at the BE-oxide interface and formed a conductive channel when the electroforming was completed. After electroforming, the switching events took place at the BE-oxide interface, with a positive voltage switched it ON and a negative one switched it OFF. If the positive forming voltage was much larger, after a temporary ON state, all the oxygen vacancies created at the TE-oxide interface were driven away, leading to a forming OFF scenario (Fig. 5b). The device then exhibited switching behavior at the TE-oxide interface with negative ON and positive OFF.

The device forming history had a significant impact on the device performance, such as the ON/OFF conductance ratio. Table 1 lists the typical ON/OFF ratio read at 0.5 V (or -0.5 V) for ON and OFF switching after different forming processes. Most had high ON/OFF ratios ranging from near 100 to over a couple of 1000. However, devices that were formed ON using positive

Fig. 5 Schematic illustration for the positive forming and the subsequent switching mechanisms. Under a positive bias, oxygen ions (O^{2-}) are oxidized into oxygen atoms (which may combine into oxygen gas and escape), leaving behind oxygen vacancies (V_{O}^{2+}) near the TE-oxide interface. (a) Under the positive voltage (V_3), oxygen vacancies inside near the TE-oxide interface are pushed inside the oxide, meeting the V_{O}^{2+} at the BE-oxide interface, forming the device ON. The switching then takes place at the BE-oxide interface. (b) With a larger positive voltage (V_4), all the oxygen vacancies are driven towards the oxide and BE, forming the device to the OFF state. The following switching events occur at the TE-oxide interface. The double red arrows indicate the location (interface) for the subsequent switching.

voltages only exhibited an ON/OFF ratio lower than 10. This lower ratio was due to the high oxygen vacancy concentration near the BE-oxide interface where the switching took place. After positive forming ON (Fig. 5a), a conductive channel bridged the TE and BE. Dragging all the oxygen vacancies far away from the BE-oxide interface during the following OFF switching was very difficult, hence a high ON/OFF ratio was hard to be achieved. This was very different from a negative forming ON scenario where the subsequent switching events took place at the TE-oxide interface (Fig. 4a), where the concentration of oxygen vacancies was much lower due to the asymmetric device structure. This explains why a high ON/OFF conductive ratio was more feasible for a negatively formed ON than a positively formed ON device.

Finally, for all switching events, the threshold voltage for the OFF switching (V_{RESET}) was larger than that for the ON switching (V_{SET}). This resulted from the two-wire scheme we used for the measurements (inset in Fig. 1), in which the series resistance from the electrodes ($\sim 2 \times 10^3 \Omega$) was included. During the SET process, the series resistance was much smaller than the junction resistance ($> 3 \times 10^5 \Omega$) so that most of the applied voltage dropped on the junction. While during the RESET process, the junction resistance was comparable to the electrode series resistance. As a result, a larger V_{RESET} was necessary

Table 1 Representative ON/OFF ratios for devices that experienced different types of forming processes

Forming process	ON/OFF ratios (read at 0.5 or -0.5 V)	
	ON switching	OFF switching
Negative forming ON	110	95
Negative forming OFF	2500	2000
Positive forming ON	5	3
Positive forming OFF	473	70

in order to deliver a high enough voltage to the junction itself. It has to be noted that both the V_{SET} and V_{RESET} were higher than previously reported values for TiO_2 based memristive devices.²⁰ This was likely due to two reasons. First, a two-terminal measurement scheme was used in the current study, and there was a voltage drop on the metal wire electrodes due to the series resistance. Second, the TiO_2 thin film deposition process was different. For example, in ref. 20, the substrate was heated during the TiO_2 deposition process. The *in situ* annealing process could have produced a higher concentration of oxygen vacancies than the post-annealing process, and hence lower programming voltages than in the current study. The relatively high programming voltages might have also introduced a temperature change at the junction and affected the motion of oxygen vacancies. Physical characterization of the distribution and migration of the oxygen vacancies is needed to confirm the model.

In summary, we discovered that TiO_2 based memristive devices can be electrically formed under either a negative or a positive voltage. The amplitude of the forming voltage dictates the initial ON or OFF state of the device after electroforming. The device behavior is significantly affected by the forming history. We also proposed a model based on the creation and motion of oxygen vacancies that is consistent with our experimental observations. Similar effects have also been shown to cause complementary resistive switching in TaO_x based devices.²⁴ The current study advances our understanding of a switching mechanism and hence helps us to design better devices and testing protocols for memristive devices in a wide variety of applications.

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