

# Excellent Resistive Switching Characteristics of Cu doped ZrO<sub>2</sub> and its 64 bit Cross-point Integration

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## Abstract

Excellent nonpolar resistive switching behavior is reported in the Cu doped ZrO<sub>2</sub> memory devices with the sandwiched structure of Cu/ZrO<sub>2</sub>:Cu/Pt. The ratio between the high and low resistance is in the order of 10<sup>6</sup>. Set and Reset operation in voltage pulse mode can be as fast as 50 ns and 100 ns, respectively. Multilevel storage is considered feasible due to the dependence of ON-state resistance on Set compliance current. The switching mechanism is demonstrated to be related with the formation and rupture of Cu conductive bridge. Based on this working cell, 64 bit cross-point array is fabricated and tested.

## 1. Introduction

Resistive Random Access Memory (ReRAM) in the form of metal-insulator-metal (MIM) structure, where the electrical conductance of the insulator can be modulated between different levels by the application of external electric stimuli, is a promising next generation nonvolatile memory candidate due to its low operation voltage, low power consumption, long retention time, multibit storage ability and non-destructive readout. A large variety of solid-state materials seem to be applicable for ReRAM. Among all the choices, binary transition metal oxides (TMO) have attracted special attention owing to the simple structure, easy fabrication process and compatibility with the CMOS technology. However, full understanding of the mechanisms in ReRAM is still lacking. Moreover, uniform and reproducible resistance switching characteristics are eagerly required for real applications.

In this work, we will report the excellent resistive switching of Cu doped ZrO<sub>2</sub> and its 64 bit cross-point integration for non-volatile memory applications. The underlying switching mechanism is also elucidated.

## 2. Experiments

Starting from the SiO<sub>2</sub>/Si substrate, an array of Pt/Ti bottom electrode is transferred onto this substrate using the lift-off method. A second photolithography is performed to pattern the switching layer and the top

electrode. Then Cu doped ZrO<sub>2</sub> switching layer and top Cu electrode (coated with Au protective layer) are evaporated in succession without breaking the chamber. During the evaporation process, the chamber pressure and the temperature are kept at  $5.3 \times 10^{-7}$  Torr and room temperature, respectively. Another lift-off process is used to release the 8×8 cross-point array. The photograph of the fabricated cross-point resistive memory array is shown in Fig. 1.

## 3. Results and Discussion

Fig. 2 shows typical I-V characteristics of the memory cell. No “electroforming” process is needed to induce the resistive switching. The as-deposited devices are normally in OFF state (resistance in the order of GΩ). A current-limited set voltage ( $V_{\text{set}}$ ) is required to turn ON the device, while another reset voltage ( $V_{\text{reset}}$ ) is required for switching back to the OFF state. The ratio between these two states can be as high as 10<sup>6</sup> at 0.3 V, the largest value we have known. The switching exhibits a nonpolar characteristics: both of the switching from ON to OFF and from OFF to ON can be done without changing the polarity (unipolar), while they can also be done by changing the polarity (bipolar).

Fig. 3 shows the result of 10 times DC cycles in the positive voltage range for a specific device. As can be seen,  $V_{\text{reset}}$  is distributed from 0.8 V to 1.5 V, while the  $V_{\text{set}}$  has a wide distribution from 2.1 V to 3.6 V. Though  $V_{\text{set}}$  and  $V_{\text{reset}}$  show some variations,  $V_{\text{set}}$  is always higher than  $V_{\text{reset}}$ .

We have also studied the device-to-device distributions of the  $V_{\text{set}}$  and  $V_{\text{reset}}$ . As shown in Fig. 4,  $V_{\text{reset}}$  also exhibits a more concentrated distribution than the  $V_{\text{set}}$  and no overlap between them is observed. Therefore, for any previous resistance state (either ON or OFF), the Cu/ZrO<sub>2</sub>:Cu/Pt memory devices can be switched into the opposite state by choosing proper voltage and polarity. The programmed resistance state can be read by a voltage less than  $V_{\text{reset}}$  without affecting the stored information.

Fig. 5 indicates the resistive switching speed of the Cu/ZrO<sub>2</sub>:Cu/Pt device. Set and Reset can be achieved through 8 V with 50 ns duration and 2 V with 100 ns duration, respectively. Thus high speed operations are

demonstrated.

Fig. 6 shows the ON resistance ( $R_{on}$ ) and reset current ( $I_{reset}$ , defined as the peak current during the reset process) as a function of the current compliance ( $I_{comp}$ ). The ON resistance decreases, while the reset current rises with increasing the  $I_{comp}$ . Multibit storage is thus thought to be feasible via setting different  $I_{comp}$ .

Although there exist extensive researches on the origin of resistive switching phenomena and various models have been proposed, full understanding of the underlying switching mechanisms in ReRAM is still in debate. According to the experimental observations, filament conduction is suitable to explain the resistive switching behavior in Cu/ZrO<sub>2</sub>:Cu/Pt memory devices.

First of all, the above mentioned ON-state resistance dependence on  $I_{comp}$  gives clues to relate the physical origin of resistive switching of Cu/ZrO<sub>2</sub>:Cu/Pt devices with filament conduction. According to this mechanism, the set and reset of the memory devices originate from the formation and rupture of filaments inside the ZrO<sub>2</sub> matrix. As can be expected, the larger the  $I_{comp}$ , the stronger filaments (better percolation of conducting elements) will come into being. Therefore, better conductive capacity of the ON state (thus smaller ON-state resistance) can be expected with larger  $I_{comp}$ , consistent with the result in Fig. 6. On the other hand, the stronger the filaments form, the harder these filaments rupture. As a result, reset current rises with increasing the  $I_{comp}$ . The filamentary mechanism is further confirmed by the log-log scale I-V fitting for the ON state, which is shown in Fig. 7. The current of ON state clearly exhibits ohmic characteristics, since the log-log curve is a straight line with slope equal to 1.

The active area dependence of the resistance value is shown in Fig. 8. The resistance of the OFF state exhibits obvious dependence on the device area and increases with decreasing the area, but the ON state resistance shows little dependence on device area. The size insensitive property of ON state resistance is attributed to the highly localized filament formed in ZrO<sub>2</sub> matrix.

To obtain a deeper insight into the physical nature of the conductive filament in our devices, we investigate the temperature-dependent switching characteristics.

Fig. 9 shows the ON state resistance ( $R_{on}$ ) as a function of the temperature in the range from 180 to 320 K. When the temperature increases,  $R_{on}$  increases obviously with a linear correlation. This correlation is typical for electronic transport in a metal. We further calculate the temperature coefficient of the ON state resistance to be  $\alpha=2.98\times10^{-3} \text{ K}^{-1}$ , which matches excellently with that of the Cu nanowire of diameter  $\geq 15 \text{ nm}$  ( $\alpha=2.5\times10^{-3} \text{ K}^{-1}$ ). Therefore, we deduce that the filament formed in the ON state is the Cu conductive bridge.

The temperature dependence of the OFF state

resistance, different from that of the ON state, shows a clear semiconductor-like transportation characteristic. So far, we have not obtained a clear image of the carrier transportations in the OFF state. We believe the Poole-Frenkel emission, and hopping through trap sites etc. will be all involved in a sophisticated way. The most dominant mechanism may be dependent on the variation of the temperature, applied electrical field and microscopic structure (oxygen vacancies, Cu impurities etc.) of the ZrO<sub>2</sub> film.

Fig. 10 demonstrates the retention performances. After turning the device ON or OFF, a continuous readout voltage is applied. The read voltage samplings the resistance value of the device every 100 seconds. The resistance values of both ON and OFF are stable and show no detectable sign of degradation more than  $10^4 \text{ s}$ , confirming the nonvolatility and the non-destructive readout property.

Fig. 11 depicts the crosstalk effect of the adjacent cell due to the lack of rectifying elements connected to the memory cells. Fig. 11 (a) shows the resistance of four cells before turn ON the cell A2, B1 and B2. Fig. 11 (b) shows the misreading of A1 cell. Fig. 12 describes the unexpected current route. Therefore, incorporating of rectifying elements in the memory cell or searching for the rectifying resistive switching is very important.

## 4. Conclusion

We have investigated the resistive switching of Cu doped ZrO<sub>2</sub> for nonvolatile memory applications. Excellent switching performances of the ZrO<sub>2</sub>:Cu films are demonstrated. Moreover, for the integration of the ZrO<sub>2</sub>:Cu films into cross-point memory array, additional rectifying mechanisms should be taken into serious consideration.

## Acknowledgments

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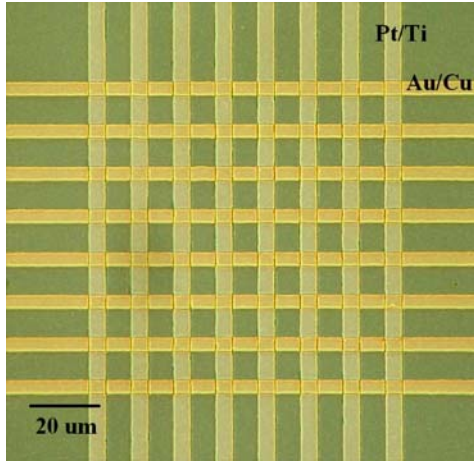


Fig.1 Optical image of the fabricated 64 bit cross-point resistive memory array.

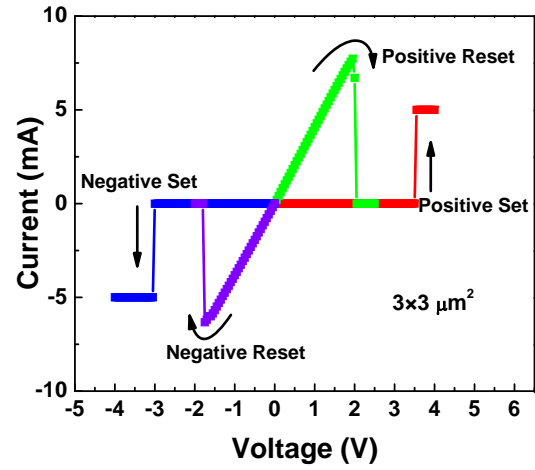


Fig.2 Nonpolar resistive switching behavior of the Cu/ZrO<sub>2</sub>/Cu/Pt device.

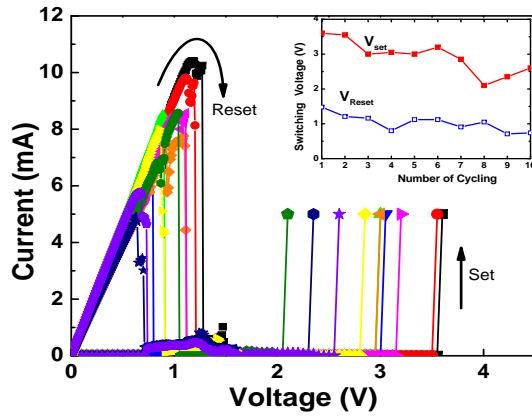


Fig.3 Reproducibility of the resistive switching in DC sweep mode.

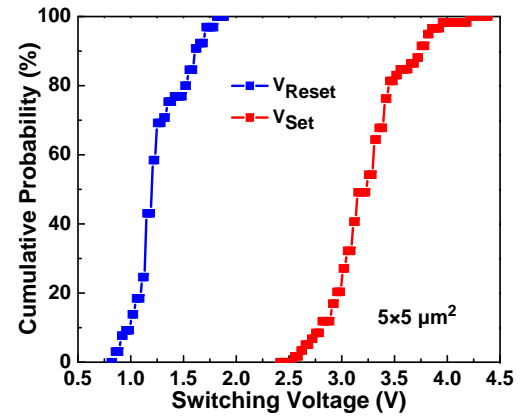


Fig.4 Distribution of the switching voltage for the Cu/ZrO<sub>2</sub>/Cu/Pt device with active area of  $5 \times 5 \mu\text{m}^2$

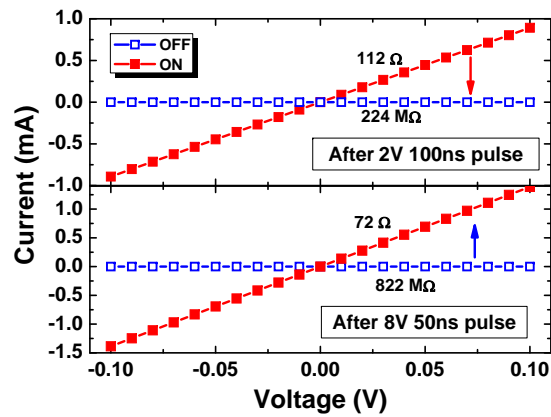


Fig.5 Resistive switching speed of the memory cell with active area of  $5 \times 5 \mu\text{m}^2$

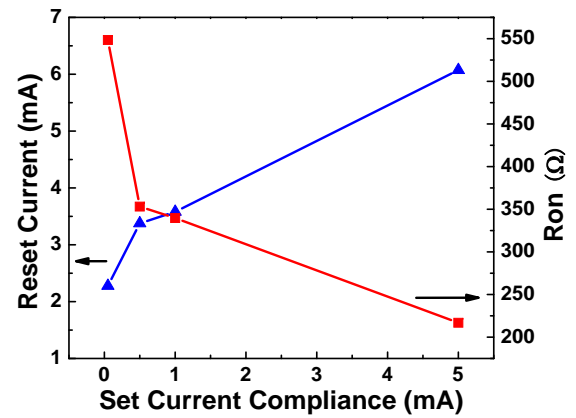


Fig.6 The dependence of ON resistance and Reset current on the set current compliance.

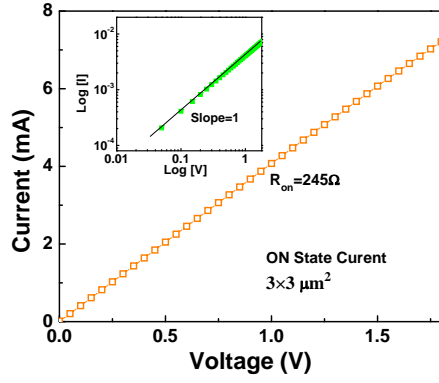


Fig.7 I-V fitting of the ON resistance which shows a linear correlation

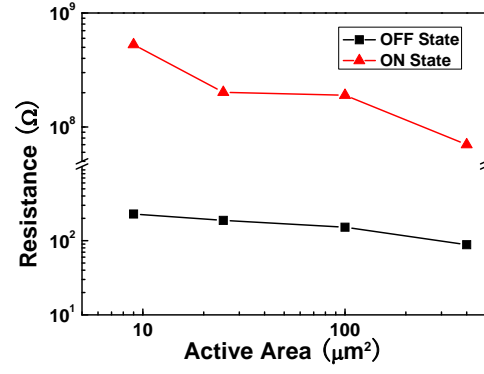


Fig.8 Dependence of ON and OFF resistance on active device area

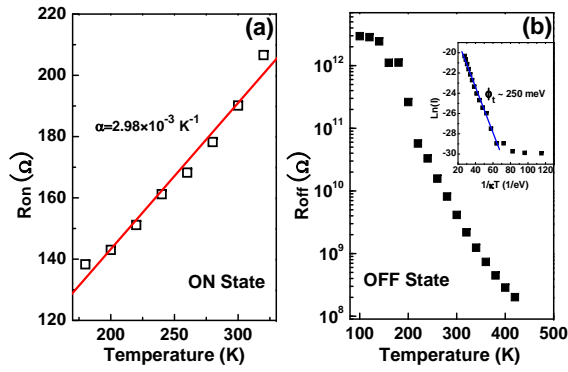


Fig.9 (a) ON state resistance and (b) OFF state resistance as a function of the temperature.

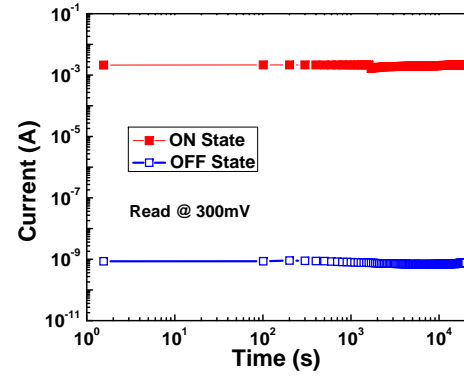


Fig.10 Retention performance and the non-destructive readout property.

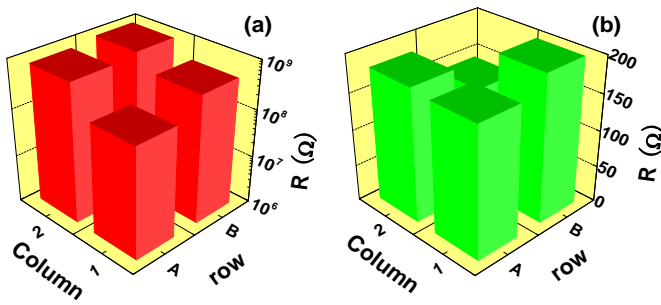


Fig.11 The measured resistance value of the adjacent four cells. (a) before turning on the A2, B1 and B2. (b) after turning on the A2, B1, and B2. The resistance status of A1 cell is misread.

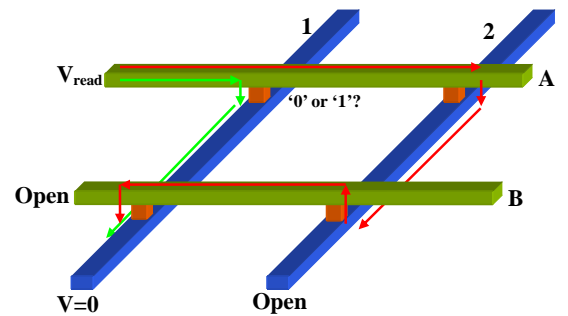


Fig.12 The current route explaining the misread effect. The green arrows indicate the intended measurement path while the red arrows represents the unexpected leakage path.