Nonpolar Nonvolatile Resistive Switching in Cu Doped ZrO_2

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***Abstract*—In this letter, the unique reproducible nonpolar resistive switching behavior is reported in the Cu-doped ZrO_2 memory devices. The devices are with the sandwiched structure of Cu/ZrO_2:Cu/Pt. The switching between high resistance state (OFF-state) and low resistance state (ON-state) does not depend on the polarity of the applied voltage bias and can be achieved under both voltage sweeping and voltage pulse. The ratio between the high and low resistance is on the order of 10^6. Set and Reset operation in voltage pulse mode can be as fast as 50 and 100 ns, respectively. No data loss is found upon continuous readout for more than 10^4 s. Multilevel storage is considered feasible due to the dependence of ON-state resistance on Set compliance current. The switching mechanism is believed to be related with the formation and rupture of conducting filamentary paths.**

***Index Terms*—Cu doping, nonvolatile memory (NVM), resistive random access memory (ReRAM), resistive switching, ZrO_2.**

I. Introduction

Resistive random access memory (ReRAM) in the form of metal–insulator–metal structures, where the conductance of the insulator can be modulated by external electrical stimuli, is a promising next generation nonvolatile memory (NVM) candidate due to its high-speed operation, low power consumption, long retention time, simple structure and nondestructive readout [1]. A large variety of solid-state materials seem to be applicable for ReRAM, including ferromagnetic materials [1], perovskite oxide [2], [3], polymer [4], and binary transition-metal oxides [5]–[14]. Among all the choices, binary transition-metal oxides have attracted special attention owing to the simple structure, easy fabrication process and compatibility with CMOS technology [14]. Recently, zirconium oxide (ZrO_2), one of the promising high-κ dielectrics in advanced CMOS devices, was investigated by several groups for ReRAM applications [9]–[13]. However, the ZrO_2-based switching memory devices exhibit puzzling polarity-dependent characteristics [9]–[13]. In our previous study [13], we demonstrated that the intentionally introduced external traps in ZrO_2 films can significantly improve the device yield due to more uniform and homogeneous trap concentrations. However, a full understanding of the switching mechanisms in ZrO_2-based ReRAM is still lacking.

In this letter, we will report a unique reproducible nonpolar resistive switching behavior in the Cu-doped ZrO_2 (ZrO_2:Cu) memory devices with the structure of Cu/ZrO_2:Cu/Pt. The reproducibility, switching speed, retention, and nondestructive readout properties of the memory devices are investigated. The physical origin of this switching phenomenon is also suggested. Therefore, this letter may lead to a better understanding of the ZrO_2-based ReRAM.

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II. Experimental Setup

Starting from the SiO_2/Si substrate, horizontal stripes of Pt/Ti (100/20 nm) bottom electrode, grown by e-beam evaporation, are transferred onto this substrate through a lift-off process. Then, a second photolithography is performed to pattern the switching layer and the top electrode vertically. After that, the resistive switching layer, consisting of three sequential layers of $ZrO_2/Cu/ZrO_2$ (with thickness of 20/3/20 nm, respectively) is e-beam evaporated. Thereafter, the top Cu electrode (70 nm) and the protective Au layer (30 nm) are deposited in succession. The Au layer is to avoid the oxidation of Cu electrode during testing and to prevent the probe tip from scratching the device surfaces. All these steps are completed without breaking the chamber. During the evaporation process, the chamber pressure and the temperature are kept at 5.3×10^{-7} torr and at room temperature, respectively. Then, another lift-off process is used to release the Cu/ZrO_2:Cu/Pt memory devices. We have fabricated the devices with an area ranging from 9 μm^2 (3×3 μm^2) to 400 μm^2 (20×20 μm^2). The dc current–voltage (I–V) characteristics of the fabricated ZrO_2-based resistive memory devices are analyzed by Keithley 4200 Semiconductor Characterization System. The dynamic resistive switching behavior is evaluated with Agilent 81110A Pulse Pattern Generator and Tektronix DPO 7000 Oscilloscope. All the measurements are performed at room temperature and under dark condition.

III. Results and Discussion

Fig. 1 shows typical I–V characteristics of the Cu/ZrO_2:Cu/Pt memory cell, in which bias polarity is defined with

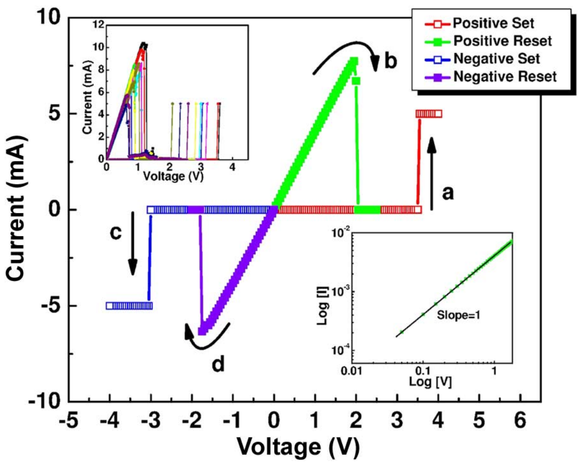

Fig. 1. Typical nonpolar I–V switching characteristics of Cu/ZrO_2:Cu/Pt memory devices with area of $3 \times 3\ \mu m^2$ in voltage sweeping mode. The upper inset shows the reproducibility of the resistive switching in dc sweeping mode (10 times cycles). The bottom inset shows the I–V fitting result in log–log scale, demonstrating a linear correlation.

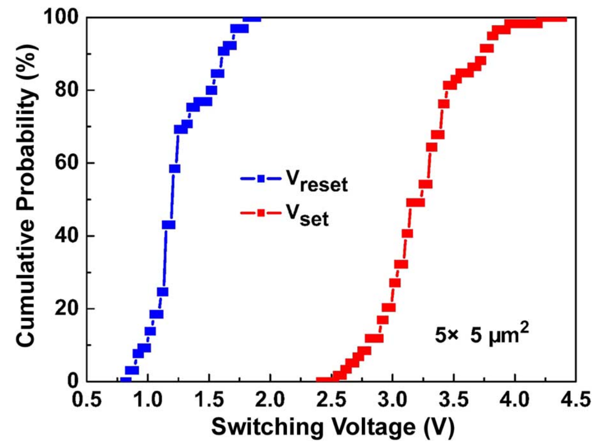

Fig. 2. Distribution of the switching voltage ($V_{\rm set}$ and $V_{\rm reset}$) for the Cu/ZrO_2:Cu/Pt device with area of $5 \times 5\ \mu m^2$.

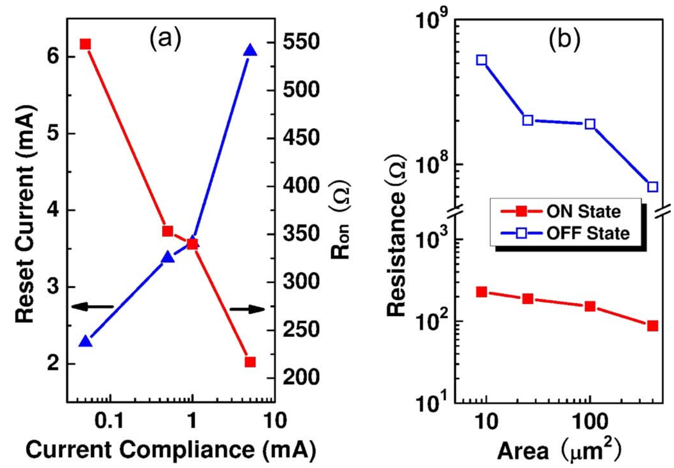

Fig. 3. (a) Dependence of ON-state resistance ($R_{\rm on}$) and $I_{\rm reset}$ on the rest current compliance ($I_{\rm comp}$), and (b) the device area dependence of ON-state and OFF-state resistance.

reference to the bottom Pt electrode. Different from the previous results on ZrO_2-based ReRAM [9]–[12], no "forming" process is required to induce the resistive switching of our devices. The as-deposited devices are normally in the OFF-state (resistance on the order of gigaohms). A current-limited set voltage ($V_{\rm set}$) is required to turn on the device (curve a or c), while another reset voltage ($V_{\rm reset}$) is needed for switching the device back to the OFF-state (curve b or d). The switching behavior of the devices exhibits a unique nonpolar behavior: both of the switching from ON to OFF and from OFF to ON can be done without changing the voltage polarity (unipolar, e.g., curve a and b), while they can also be achieved by changing the polarity (bipolar, e.g., curve a and d). This nonpolar switching behavior is also observed in V-doped $SrZrO_3$ [2] and Cu doped SiO_2 [15] memory devices. The typical resistances of the ON- and OFF-states at 300 mV are on the order of $10^2\ \Omega$ ($R_{\rm on}$) and $10^8\ \Omega$ ($R_{\rm off}$), respectively. The ratio between these two states can be more than 10^6. Resistive switching under voltage pulse mode is also feasible. Set and Reset operation can be as fast as 50 and 100 ns, respectively (data not shown).

The upper inset of Fig. 1 shows the result of ten times dc cycles in the positive voltage range for a specific device. As can be seen, $V_{\rm reset}$ is distributed from 0.8 to 1.5 V, while the $V_{\rm set}$ has a wide distribution from 2.1 to 3.6 V. Though $V_{\rm set}$ and $V_{\rm reset}$ show some variations, $V_{\rm set}$ is always higher than $V_{\rm reset}$. Moreover, we have also studied the device-to-device distributions of the $V_{\rm set}$ and $V_{\rm reset}$. As shown in Fig. 2, $V_{\rm reset}$ also exhibits a more concentrated distribution than the $V_{\rm set}$ and no overlap between them is observed. Therefore, for any previous resistance state (either ON or OFF), the Cu/ZrO_2: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 $V_{\rm reset}$ without affecting the stored information.

As mentioned above, the current compliance ($I_{\rm comp}$) during set process is necessary to prevent permanent breakdown of the memory devices. It has been reported that the $I_{\rm comp}$ is a key parameter which influences the value of reset current ($I_{\rm reset}$, defined as the peak current during the reset process) and the ON-state resistance ($R_{\rm on}$) for NiO- and TiO_2-based ReRAM [5], [6]. Fig. 3(a) shows the ON-state resistance and $I_{\rm reset}$ as a function of the $I_{\rm comp}$, ranging from 50 μA to 5 mA. It is observed that the ON-state resistance decreases, while the reset current rises with increasing $I_{\rm comp}$. Based on the correlation between $R_{\rm on}$ and $I_{\rm comp}$, multilevel storage is believed to be feasible via setting different $I_{\rm comp}$.

Although there exist extensive researches on the origin of resistive switching phenomena and various models have been proposed, a full understanding of the underlying switching mechanisms in ReRAM is still in debate. Even within the class of ZrO_2-based ReRAM, the possible switching mechanisms seem to be surprisingly diverse, including electron trapping and detrapping [9], [13], formation and rupture of conducting filament [10], and the motion of oxygen vacancy/ion [12]. According to the experimental observations, filament conduction is suggested to explain the resistive switching behavior in Cu/ZrO_2:Cu/Pt memory devices. The reasons are as follows.

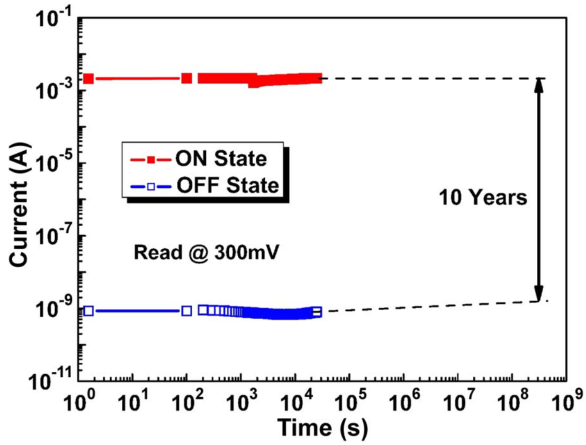

Fig. 4. Long term stability of device resistance upon continuous readout voltage at room temperature.

First of all, the aforementioned ON-state resistance dependence on I_{comp} gives clues to relate the physical origin of resistive switching of Cu/ZrO_2:Cu/Pt devices with filament conduction [5], [6]. According to this mechanism, the set and reset of the memory devices originate from the formation and rupture of metallic filaments inside the ZrO_2 matrix. As can be imagined for filament mechanism, the larger the I_{comp}, the stronger the filaments (better percolation of conducting elements) will form. 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. 3(a) (square red curve). On the other hand, the stronger the filaments form, the harder these filaments rupture. As a result, reset current rises with increasing I_{comp}, as shown in Fig. 3(a) (triangle blue curve). This is similar to the power-driven filament formation process in TiO_2 films [6]. The filamentary mechanism is further confirmed by the log–log scale I–V fitting for the ON-state, which is shown in the bottom inset of Fig. 1. The current of ON-state clearly exhibits ohmic characteristics, since the curve of $\log I$–$\log V$ is a straight line with slope equal to 1.

The active area dependence of the resistance value is shown in Fig. 3(b). The resistance of the OFF-state exhibits obvious dependence on the device area and increases with decreasing area, but the ON-state resistance shows little dependence on device area. Similar correlation between resistance and area is also reported in Cu-doped MoO_x films [8]. The size insensitive property of ON-state resistance is attributed to the highly localized filament formed in ZrO_2 matrix. This result also provides promising scaling down prospect of Cu/ZrO_2:Cu/Pt devices. The detailed filament origin in Cu/ZrO_2:Cu/Pt devices, we believe, may be related to the migration of Cu ions inside the ZrO_2, which is similar to the Cu doped MoO_x [8] and Cu doped SiO_2 [15]. However, further studies are required to understand the detailed process of Cu ions diffusion in ZrO_2 film and their transportations.

Fig. 4 shows the capability of the devices to retain both resistance states. During this measurement, the device is first turned ON or OFF by dc voltage sweep and then a continuous readout voltage (300 mV) is applied. The read voltage samples the resistance value of the device every 100 s. As shown in Fig. 4, the resistance values of both ON- and OFF-state are stable and show undetectable signs of degradation over 10^4 s, confirming the nonvolatile nature and the nondestructive readout property of the devices. Moreover, the extrapolation method is employed to give a long-term prediction result, as shown in Fig. 4, which demonstrates a ten-year retention ability under room temperature.

IV. Conclusion

The Cu/ZrO_2:Cu/Pt resistive switching memory devices are fabricated and investigated for the NVM applications. This memory device possesses the properties of high resistance ratio $(> 10^6)$, reproducible resistive switching, high-speed operation, long retention time, nondestructive readout, and multilevel storage potential. According to the experimental observations, the filament conduction is considered to be the most reasonable mechanism to explain the resistive switching in the Cu/ZrO_2:Cu/Pt devices. The area dependence of ON- and OFF-state guarantees the sufficient sensing margin when the device is scaling down. Considering the excellent memory switching behavior and reliability performances, Cu-doped ZrO_2-based ReRAM shows strong promise for future NVM applications.

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