# On the resistive switching mechanisms of $Cu/ZrO_2:Cu/Pt$

Weihua Guan,[1] Ming Liu,[1,a)] Shibing Long,[1] Qi Liu,[1] and Wei Wang[2]
[1]*Laboratory of Nanofabrication and Novel Device Integration, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, People's Republic of China*
[2]*College of Nanoscale Science and Engineering (CNSE), University at Albany, New York 12203, USA*

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We use convincing experimental evidences to demonstrate that the nonpolar resistive switching phenomenon observed in $Cu/ZrO_2:Cu/Pt$ memory devices conforms to a filament formation and annihilation mechanism. Temperature-dependent switching characteristics show that a metallic filamentary channel is responsible for the low resistance state (ON state). Further analysis reveals that the physical origin of this metallic filament is the nanoscale Cu conductive bridge. On this basis, we propose that the set process (switching from OFF state to ON state) and the reset process (switching from ON to OFF state) stem from the electrochemical reactions in the filament, in which a thermal effect is greatly involved. © *2008 American Institute of Physics*.
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The efforts of seeking alternative approaches to charge based solid state nonvolatile memories to overcome the scaling limits in the nanoera never stopped.[1,2] Among all of the emerging concepts, resistive random access memory (ReRAM) in the form of metal-insulator-metal (MIM) structure, where the conductivity of the insulator can be modulated by external electrical stimuli, is of great application prospect due to its high operation speed, low power consumption, and multibit storage ability. A large variety of materials seem to be applicable for ReRAM.[2–15] Although various models for resistive switching have been suggested, e.g., alternation of Schottky barrier,[3] filamentary conduction,[4–6] and trap-controlled space-charge-limited current,[7] the underlying physical mechanism of resistive switching and the charge transportations in ReRAM is still not yet understood. It seems difficult to summarize a universal mechanism that can explain the switching behaviors in different types of ReRAM. In our recent study,[8] we have demonstrated a unique nonpolar switching behavior in the $Cu/ZrO_2:Cu/Pt$ devices. Further studies, however, are required to understand the microscopic nature of this nonpolar switching behavior.

In this letter, temperature-dependent switching characteristics, as well as further calculations, reveal that the nonpolar resistive switching in $Cu/ZrO_2:Cu/Pt$ devices comes from the formation and rupture of the conductive filaments, whose physical nature is the Cu conductive bridge. Based on this analysis, the microscopic resistive switching process between the high resistance state (OFF state) and low resistance state (ON state) is discussed, leading to an informative understanding of the MIM based resistive memories.

The detailed device fabrication process is described elsewhere.[8] Figure 1 shows the tilted cross-sectional scanning electron microscopy (SEM) image of the $Cu/ZrO_2:Cu/Pt$ device. This device exhibits satisfying resistive switching behavior. A typical macroscopic *I-V* switching characteristic of $Cu/ZrO_2:Cu/Pt$ memory device is shown in Fig. 2. The fresh devices are generally in the OFF state. By sweeping the voltage from zero in the positive or negative voltage side with a current compliance, an abrupt increase in the current takes place above a threshold voltage. Afterward, by resweeping the voltage in either polarity sides, the resistance of the device is recovered to the original OFF value. This clear reversible and reproducible switching between ON and OFF states are observed over a temperature span from 100 to 420 K. The switching behavior of our devices exhibits a unique nonpolar behavior.[8] This polarity independent switching behavior was also observed in V-doped $SrZrO_3$,[9] $Pt/TiO_2/Pt$,[10] and Cu-doped $SiO_2$ memory devices.[11]

Based on the aforementioned working devices, we study the temperature-dependent switching characteristics, which is informative in understanding the switching mechanisms.[4] Figure 3(a) shows the ON state resistance ($R_{ON}$) as a function of the temperature in the range from 180 to 320 K. Note that this temperature related measurement is carried out in vacuum chamber *after only one set process*, ensuring that the microscopic geometry and the chemical compositions of the formed filament remain the same at different temperatures. As shown in Fig. 3(a), $R_{ON}$ increases linearly with increasing

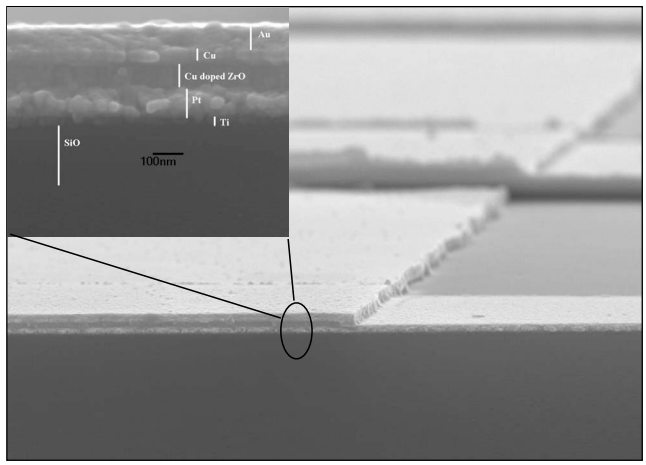


FIG. 1. Titled cross-sectional SEM image of the $Cu/ZrO_2:Cu/Pt$ devices (where the $ZrO_2:Cu$ denotes a ultrathin Cu layer embedded in $ZrO_2$). The inset shows the stacked memory structure in a magnified scale. The coating Au layer is to avoid the atmosphere oxidation of Cu top electrode during testing and to prevent the probe tip from scratching the device surfaces.

a)Author to whom correspondence should be addressed. Electronic mail: liuming@ime.ac.cn. Tel: 86-10-62007699. FAX: 86-10-62055666.

 

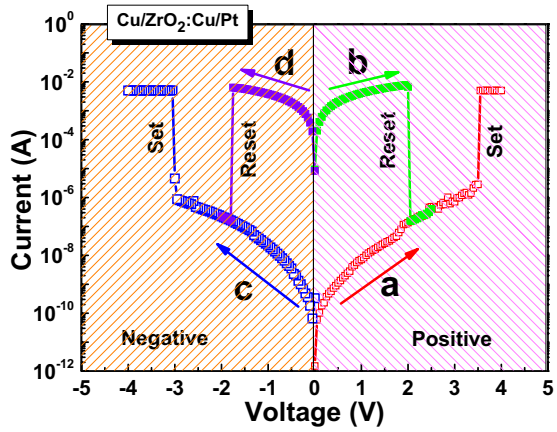


FIG. 2. (Color online) Typical nonpolar *I-V* switching characteristics of $Cu/ZrO_2:Cu/Pt$ memory devices with area of $3\times3$ $\mu m^2$ in voltage sweeping mode. During the set process, the current is limited to a compliance of 5 mA to prevent the permanent breakdown of the memory devices.

temperature, which is typical for electronic transport in metals. The metallic resistance as a function of temperature change can be written as[5] $R(T)=R_0[1+\alpha(T-T_0)]$, in which $R_0$ is the resistance at temperature $T_0$ and $\alpha$ is the resistance temperature coefficient. Thus, we can calculate the temperature coefficient of the ON state resistance for the $5\times5$ $\mu m^2$ samples to be $\alpha=2.98\times10^{-3}$ $K^{-1}$. Moreover, we also obtain this value to be $2.49\times10^{-3}$ $K^{-1}$ for the $10\times10$ $\mu m^2$ samples and $2.39\times10^{-3}$ $K^{-1}$ for the $20\times20$ $\mu m^2$ samples, as shown in the inset of Fig. 3(a). All those results match excellently with the temperature coefficient of the Cu nanowire of diameter $\geq15$ nm($\alpha=2.5\times10^{-3}$ $K^{-1}$).[12] Considering the fact that the temperature coefficients of all other involved elements and compounds are distinctly different from the measured value, we conclude that the metallic behavior of the ON state originates from the conducting Cu filaments with the size around tens of nanometers. This is similar to the physical observations of Ag dendrites through SEM techniques[13] and the Cu precipitate through transmission electron microscope (TEM) method.[14] In contrast to the metallic behavior of the ON state, the device in the OFF state exhibits a clear semiconducting behavior. As shown in Fig. 3(b), the device exhibits a dependence of OFF current on temperature in the form of $I_{OFF}=I_0\exp(-\phi_t/\kappa T)$, where $\kappa$ is the Boltzmann constant and $\phi_t$ is the thermal activation energy. The inset in Fig. 3(b) shows

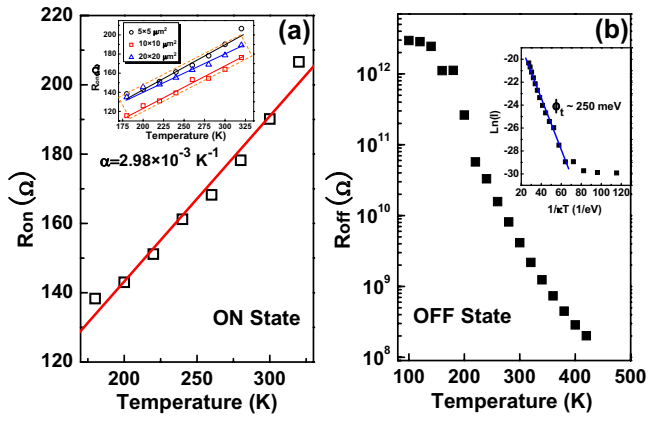


FIG. 3. (Color online) Impact of the temperature on (a) the ON state resistance and (b) the OFF state resistance.

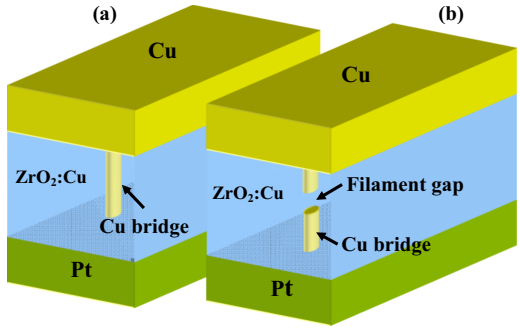


FIG. 4. (Color online) Schematic structure of the filamentary conduction in $Cu/ZrO_2:Cu/Pt$ devices. (a) ON state and (b) OFF state. Note that the geometrical shape and distribution in this picture are simplified to be an ideal column for clarity. The real filamentary conduction is believed to be more complicated.

the plot of $\ln(I)$ versus $1/\kappa T$, from which we can calculate the thermal activation energy $\phi_t$ as 250 meV.

Based on the above analysis, we are able to draw an intuitive scenario of the resistive switching in our $Cu/ZrO_2:Cu/Pt$ devices, as shown in Fig. 4. On one hand, once the nanoscale conductive Cu filament is built in the $ZrO_2$ films [Fig. 4(a)], the resistance of the device drops abruptly, leading the switching to the ON state. Under this circumstance, the current that flows through the device is mostly confined within the low impedance Cu channels. As a result, the ON state shows a metallic transportation behavior. The OFF state, on the other hand, is reached when the filamentary Cu channel is ruptured [Fig. 4(b)] no matter the reasons and locations. The carriers at this time can only transport through the insulated $ZrO_2$ film with a semiconductorlike behavior. Although the relation between the formation/rupture of the filament and the set/reset process is easy to understand from a macroscopic point of view, microscopic pictures are more useful for understanding the resistive switching processes.

Here we propose a microscopic model to describe the switching process between ON and OFF states. For the positive set process, when the Cu electrode is applied with a positive voltage, there is an electrochemical reaction in this anode, which oxidizes the Cu atoms to Cu ions according to $Cu\rightarrow Cu^+ + e$ or $Cu\rightarrow Cu^{2+}+2e$. If the electrical field in the $ZrO_2$ film is strong enough, these Cu ions will migrate toward the Pt electrode (cathode), where they are reduced back to metallic Cu according to $Cu^+ + e\rightarrow Cu$ or $Cu^{2+}+2e\rightarrow Cu$. As this process continues, metallic Cu filament finally reaches the Cu top electrode eventually, leading to the switching into ON state. This is essentially the same as the redox process in the memory devices based on the solid state electrolyte.[13,15] The switching to the ON state can also be achieved by a nearly symmetric negative voltage. This suggests that there exists some kind of oxidizable Cu source near the Pt electrode. In the unipolar switching for the $Cu/SiO_2:Cu/W$ device, Schindler *et al.*[11] assumed that sufficient Cu would diffuse through the $SiO_2$ during annealing and accumulated at the W layer to form a source of oxidizable material. This is, however, not the case for our devices since there is no annealing process involved. We believe that the most possible origin of the Cu source near the Pt electrode is the physical diffusion during the deposition process. When 3 nm Cu doping layer is deposited directly onto the first $ZrO_2$ layer, there is a certain possibility for the Cu atoms

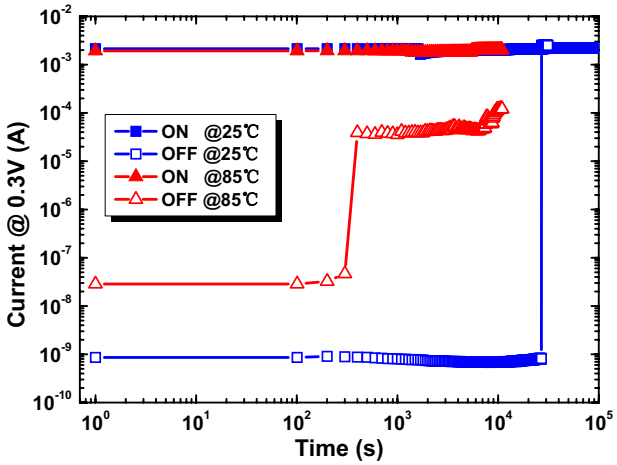


FIG. 5. (Color online) Thermal and time-dependent stability of the ON and OFF state current. The ON state current exhibits a stable behavior at both 25 and 85 °C. The OFF state shows a time-dependent set behavior which is accelerated by high temperatures.

to penetrate toward the Pt electrode due to the energy release in the agglomeration process and the radiation generated in the chamber.

Now we consider the reset process, which occurs when the pre-existing metallic Cu filament is ionized and dissolved in the $ZrO_2$ film. It has been reported that the reset process is greatly influenced by the thermal effect.[5] Supposing that the diameter of the conductive Cu filament produced during the set process is in the range of tens of nanometers,[6] the 1 mA reset current means a current density above $10^9$ $A/cm^2$ passing along the conductive path, which will generate an extremely high local Joule heating. This local heating is able to facilitate and accelerate the oxidation process.[16] According to the simulation results for thermal dissolution by Russo *et al.*,[5] the filament will be ruptured in the middle, where there is a peak temperature, as sketched in Fig. 4(b). Therefore, by adopting both the electrical current heating effect (Joule heating) and the electrochemical reaction in the filament, we propose that the reset process is caused by the Joule heating assisted electrochemical reaction. Since there are no current direction issues involved in this model, both the positive and negative reset can be achieved as long as the reset current reaches a critical value, as shown in Fig. 2 (arrows b and d).

To further confirm this model, current versus time experiment at a constant voltage is performed for both the room temperature (25 °C) and 85 °C thermal stress (note that this experiment is carried out in vacuum). Figure 5 shows the time evolution of the current for a constant applied voltage of +0.3 V. For the room temperature case (blue symbol), ON state current is very stable while the OFF state current has a steep increase at 27000 s, indicating a decrease in resistance. Similar trend is also observed in the 85 °C thermal stress case (red symbol), in which ON state is very stable while an abrupt rise in current in OFF state occurs at an accelerated time of 300 s. This phenomenon can be understood as follows. For the OFF state [Fig. 4(b)], due to the random vibrations, there is a certain chance for the Cu ions to touch the residual Cu filament under the constant electrical field and get reduced into Cu atoms. This process will shorten the gap in the residual Cu filament. As can be expected, the random vibrations will be accelerated under thermal stress conditions. Therefore, the possibility for the closeup of the filament gap increases at higher temperatures. Once the filament gap is closed, the device is switched to the ON state. Since the structure of the Cu filament rebuilt under this way is similar to the filament formed by normal set process, this time-dependent change into the ON state is expected to be recovered back into the OFF state by applying a proper reset voltage, which is consistent with the experimental observation.

In conclusion, we employ experimental evidences to demonstrate that the reversible and reproducible resistive switching observed in $Cu/ZrO_2:Cu/Pt$ memory devices is due to a filament formation and annihilation mechanism. Temperature-dependent switching characteristics provide a clue for the microscopic nature of the conductive filament. Detailed analysis reveals that the highly localized metallic Cu conductive bridge is formed during the set process as a result of the electrochemical reactions. The reset process is believed to be caused by the localized Joule heating assisted oxidation reaction, which dissolves the pre-existing Cu conductive bridge.

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