Real time observation of nanoscale multiple conductive filaments in RRAM by using advanced in-situ TEM

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Abstract: In this letter, we dynamically investigate the resistive switching characteristics and physical mechanism of the ZrO_2-based device. Using in-situ transmission electron microscopy, we observe in real time that multiple conductive filaments (CFs) are formed across the ZrO_2 layer between top electrode and bottom electrodes after forming. Various top electrode materials have been used, such as Cu, Ag, and Ni. Contrary to common belief, it is found that CF growth begins at the anode, rather than having to reach the cathode and grow backwards. Energy-dispersive X-ray spectroscopy results confirm that metal from the top electrode is the main composition of the CFs.

Keywords – Transmission electron microscopy (TEM), in-situ, resistive random access memory, conductive filaments

I. INTRODUCTION

The efforts of seeking alternative approaches to replace conventional charge-based nonvolatile memories (NVM) is one of the most attractive topics for satisfying the requirements of ultra-density storage, high-speed and low-power consumption in nowadays information era [1-6]. Solid-electrolyte-based resistive random-access memory (RRAM) has been extensively studied in recent years as a promising nonvolatile memory technology because of its excellent scalability, high density and superior memory performances. The device consists of a solid electrolyte layer sandwiched between an oxidizable electrode and an inert counter electrode, and its resistance switching is related to the formation of conductive filaments (CFs) inside the solid electrolyte layer. The CFs involve the metal ions transferring from the oxidizable electrode to the counter electrode through the electrochemical metallization effect [7,8].

In this study, *in-situ* transmission electron microscopy (TEM) observation directly confirms that the bipolar resistive switching in ZrO_2-based RRAM devices with various metal electrodes, such as Cu, Ag, and Ni. Obtaining these pieces of information could help elucidate the underlying nature of the RS phenomenon and guide the design of ReRAM devices with desirable properties.

II. METHDOLOGY

ZrO_2-based RRAM devices with various metal electrodes: Cu, Ag, and Ni. devices are respectively prepared on the platform of a W probe and a SiO_2/Si substrate by successively depositing a 10 nm thick Ti adhesion layer, a 50 nm-thick Pt bottom electrode layer, a 40 nm thick ZrO_2 film and a 70 nm metal top electrode layer using electron beam evaporation.

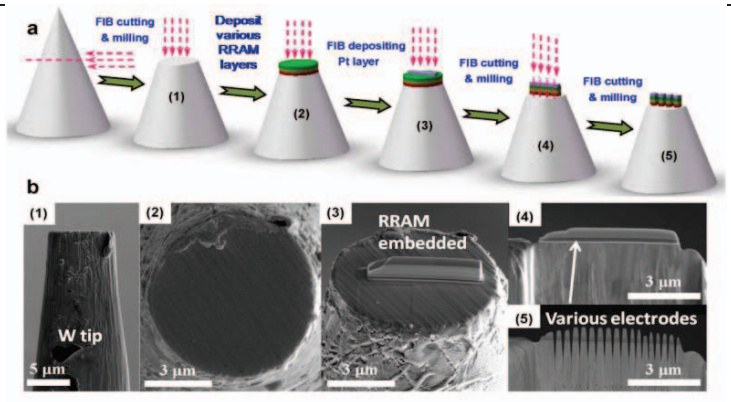

Figure 1. *In situ* fabrication technique used to produce RRAM TEM specimen. (a) Schematic of the methods used to fabricate the Ag (or Cu, Ni)/ZrO_2/Pt TEM specimen. (b) Corresponding SEM images in each of the TEM specimen fabrication processes. Images (1)-(2) show a cross-sectional of W platform and a top-view of the platform with RRAM multi-layer, indicating the platform has a smooth surface to meet the requirement for fabricating the RRAM device. Images (3)-(5) confirm that multiple TEM specimens with small size RRAM structure can be achieved through this method.

The device structure is shown in the inset of Fig. 1a. The Cu(or Ag, Ni)/ZrO_2/Pt stacked films on the platform of the W probe is fabricated to multiple TEM specimens with small lateral sizes (~200 nm) by using a dual-beam focused ion beam (FIB) system. Multiple ReRAM devices can be fabricated on one W probe, which not only reduces the lateral size but also greatly enhances the fabricating efficiency of TEM specimens. This method can also be used to fabricate other two-terminal electronic devices for in situ TEM experiment.

The W probe with the TEM specimen and another W probe with a sharp-tip were inserted into the fixed and movable contacting terminals of TEM holder, respectively. During the electrical testing, the TEM specimen was clamped by the two W probes, and the voltage applied to the fixed contacting terminals and the movable terminal was grounded. This method could achieve real-time visuliation of the nanoscale structureal changes with high spatial resolution inside TEM under applied electrical bias.

III. RESULTS AND DISSCUSSION

Figures 2a-2e show the growth dynamics of CFs between the Cu and Pt electrodes under a -4 V constant voltage stress, with a 1.1 μA compliance current (I_{CC}) applied to the Pt electrode. These images were extracted from a 140 s video, with images a-e representing frame times at 0, 60, 110, 120 and 130 s, respectively. In the video images, a first CF suddenly emerged across the ZrO_2 film between the two electrodes at ~60 s. The sudden appearance of the first CF was accompanied by an equally sudden increase in the electrical current through the device (Figure 2k). However, the low resistance state was only maintained for a short time, probably because of the instability of this particular CF, which led to a spontaneous rupture. When the stress time reached 110 s, the second CF began to form inside the ZrO_2 film and appeared to be connected only to the Cu electrode. From 110 s to 130 s, the second CF continued to grow until reaching the Pt electrode (Figure 2c-2e). During this process, the electrical current continued to increase and finally jumped to the value of I_{CC} (Figure 2k).

Similar uncorrelated multiple filaments formations have been observed in Ni based ZrO_2 RRAM devices. Figure 3a shows a typical cross-section TEM image of a fresh Ni/ZrO_2/Pt device, which exhibits the Ni, ZrO_2 and Pt triple-stacked films with clear interface. The fresh TEM specimens are generally in the high resistance state. Then, when a positive voltage with 100 nA I_{CC} is applied to the Ni electrode, the device transits from the initial OFF-state to the ON-state (the data are not shown here). After the forming process, some nanoscale dark-regions appear inside the ZrO_2 layer, as can be seen from Fig. 3b. By enlarging these dark-regions, several complete CFs can be clearly observed to connect the Ni electrode with the Pt electrode across the ZrO_2 layer (Fig. 3c and 3e). The results directly confirm that the formation and dissolution of multiple CFs dominate the resistive switching

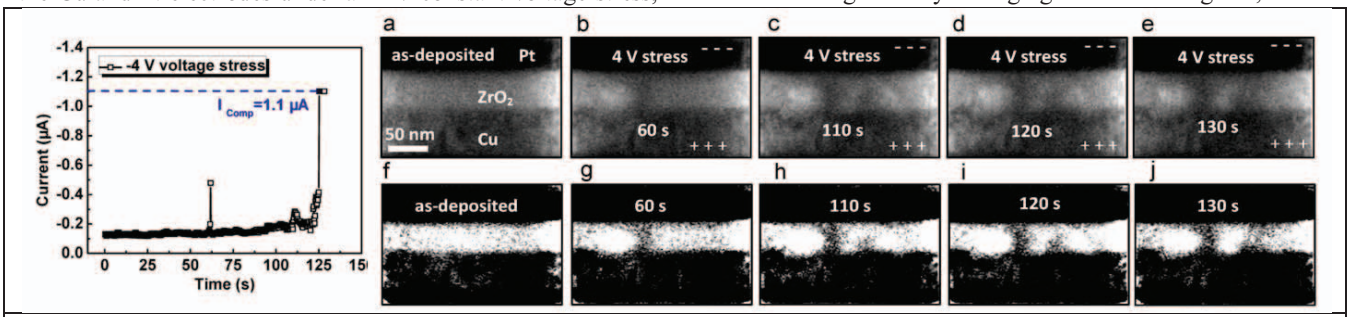

Figure 2. Left: Current versus time curve of the TEM specimen under a -4 V constant stress. Dynamics of CF growth. (a)-(e) A series of TEM images capturing the dynamic CF growth processes in the Cu/ZrO_2/Pt TEM device. (f)-(j) Black-and-white images converted from the raw TEM images of the (a)-(e) to highlight the filaments.

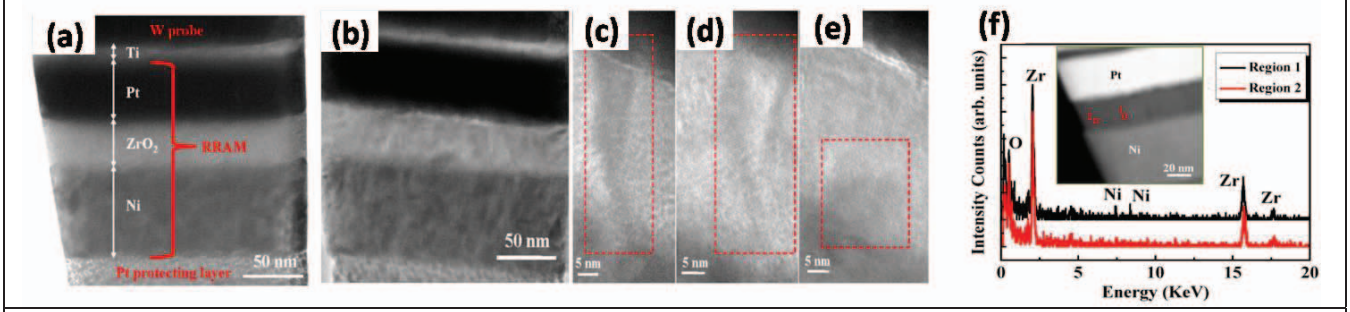

Figure 3. (a) Cross-sectional TEM micrograph of a fresh Ni/ZrO_2/Pt device. (b) Cross-sectional TEM micrograph of the device after the electroforming process. Some nanoscale dark-regions inside ZrO2 film appear after forming. (c) - (e) show the enlarged TEM images of these nanoscale dark-regions. (f) EDX spectrums of the ON-state device collected at two locations as indicated in the inserted STEM micrograph. Compared to the region away from filament (marked as "2"), Ni signal is obviously observed in the filament region (marked as "1").

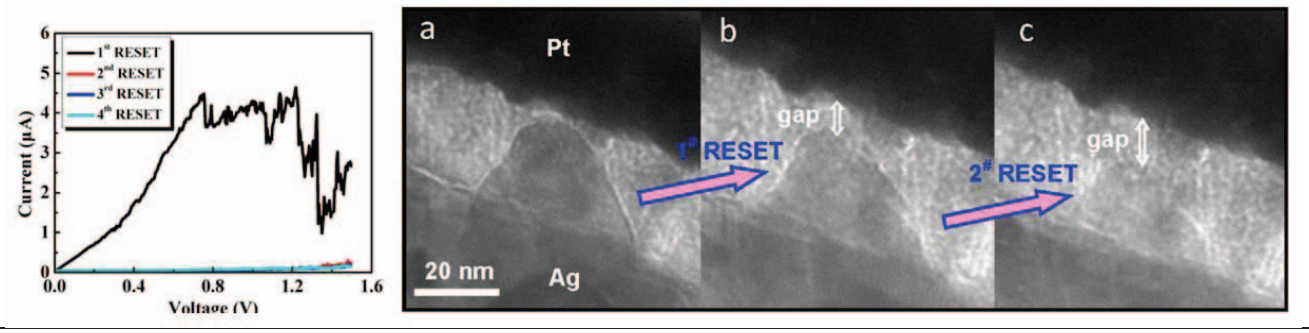

Figure 4. Dynamic of the CF dissolution images was observed in another Ag/ZrO_2/Pt device. (a) High-resolution TEM images of a CF region in a Ag/ZrO_2/Pt TEM specimen after SET process. The CF has a cone shape, and the narrowest point is near the Pt electrode. (b)-(c) Continuous high-resolution TEM images clearly showing that the CF dissolved from anode (Pt) to cathode (Ag) terminals when RESET sweeping voltages (0→2.0 V) were successively applied to the Ag/ZrO_2/Pt TEM specimen several times. These results indicate that the CF dissolution direction is from the anode (Pt) to cathode (Ag) terminals during RESET process.

phenomena in the Ni/ZrO_2/Pt devices. In addition, an incomplete CF connected to the Ni electrode is observed inside the ZrO_2 layers (Fig. 3e), implying that the CF starts to nucleate and grow from the Ni electrode [9]. The number and shape of the CFs observed in the Ni/ZrO_2/Pt device are similar to those in the Ag/ZrO2/Pt. To verify the chemical composition of the CF, the EDS composition analysis is carried out in scanning TEM (STEM) mode, as shown in Fig. 3f.

The dynamics of the CF dissolution process was also investigated by *in situ* TEM. Here, a Ag/ZrO_2/Pt device was first set to the ON-state, and then reset to the OFF-state with a voltage sweep (0→2 V, repeated for several times). The TEM observation window was positioned in the CF region. During the first RESET voltage sweep, the electrical current passing through the device suddenly decreased from ~ 1 μA to ~ 40 nA. Meanwhile, the CF region near the Pt electrode was substantially weakened after the first RESET process as indicated by the increase of the brightness of the dark region in TEM image (Figure 3b). Additional voltage sweeps eventually led to the gradual decrease of the dark region along the direction from the anode (Pt) surface to the cathode (Ag) terminal (Figure 3c). During these repeated RESET processes, the current across the device remained almost constant (Figure 4f), implying that the conductive path in the CF was already disrupted after the first RESET process, whereas further disruptions of the CF by the subsequent RESET actions did not lead to appreciable changes of current that can be detected by the instrument. These results indicate that the CF dissolution direction was from the anode (Pt) to cathode (Ag) terminals, which can be explained by thermal-assistant electrochemical reaction model. The CF residues may serve as the nuclei in the subsequent SET process, which explains why the CF formed, ruptured and re-formed in the same region in the ZrO_2 film during repetitive switching cycles.

IV. Summary

In conclusion, we directly demonstrate that multiple CFs are formed across the ZrO_2 layer between the top and bottom electrodes inside RRAM device after forming process by *in-situ* TEM observation. Based on EDS analysis and temperature-dependent switching characterization, we confirm that the observed CFs consist of metallic top metal electrode atoms as a result of the Cu, Ag, or Ni electrochemical reactions. The formation and rupture of the multiple CFs are spatially uncorrelated.

Acknowledgment

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