Unipolar resistance switching and abnormal reset behaviors in Pt/CuO/Pt and Cu/CuO/Pt structures

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ABSTRACT

The effects of Pt and Cu top electrodes on resistance switching properties were investigated for CuO thin films with Pt/CuO/Pt and Cu/CuO/Pt sandwich structures. Typical unipolar resistance switching (URS) behaviors and two different kinds of resistance changes in the reset process were observed in both structures. When voltages were applied to the film, the low-resistance state (LRS) with relatively low resistance value ($<30\ \Omega$) was switched to the high-resistance state (HRS), exhibiting normal reset behavior. For LRS with relatively high resistance value ($>50\ \Omega$), the resistance first decreased then increased to HRS, showing abnormal reset behavior. The former variation of LRS could be ascribed to the decrease in filament size induced by Joule heating, while the latter one could be ascribed to the growth of disconnected filaments induced by high electric fields. This study indicates that the switching modes and the abnormal reset behaviors in CuO thin films are not due to Pt and Cu top electrodes, but the intrinsic properties of CuO film.

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1. Introduction

Resistance random access memory (RRAM) has attracted great interests due to its potential applications in next-generation non-volatile memory [1–6]. The switching between the high-resistance state (HRS) and low-resistance state (LRS) can be achieved simply by applying an appropriate voltage. On the bias of the polarity of voltage, the switching behavior was generally clarified into unipolar and bipolar resistance switching (URS and BRS) modes [7,8]. Until now, URS and BRS behaviors have been reported in many oxides. Among them, the binary metal oxides have attracted extensive attention owing to their great advantages including simple fabrication process and good compatibility with complementary metal–oxide–semiconductor (CMOS) technologies. CuO-based RRAM has been widely studied due to its full compatibility with the Cu interconnection process [2,9,10]. The reported studies indicate that the CuO-based devices with electrochemically inert metal electrodes generally show the URS behavior, while the ones with electrochemically active metal electrodes generally show the BRS behavior due to the electrochemical metallization (ECM) [11–13].

While several theoretical models have been proposed to explain the resistance switching (RS) effect, the filamentary mechanism [3] is widely accepted in explaining the RS behavior in binary metal

oxides, and switching based on the filamentary mechanism has several advantages such as high-speed operation and a large resistance ratio [14,15]. However, the instability of conducting filaments [16,17] must be overcome before practical applications. Recently, abnormal reset behaviors caused by unstable filaments have been found in some memory devices [18,19]. Li et al. [19] ascribed this instability to the diffusion of active top electrodes. Therefore, it is worth to investigate the effect of the type of top electrode on the instability of resistance switching.

In this work, we chose two types of top electrodes: the electrochemically inert Pt electrode, and the electrochemically active Cu electrode, and fabricated the Pt/CuO/Pt and Cu/CuO/Pt structures, to investigate the effects of Pt and Cu top electrodes on the resistance switching properties in CuO thin films. We investigated the switching modes and different kinds of resistance changes in the reset process, and discussed the mechanism of the abnormal reset behavior.

2. Experiments

CuO thin films were deposited on Pt/Ti/SiO₂/Si substrates by plasma-enhanced pulse laser deposition using a CuO ceramic target at 400 °C under an oxygen pressure of 2 Pa. The thickness of the CuO thin film is 150 nm. Fifty nm-thick top electrodes M (M = Pt and Cu) with a diameter of 100 μ m were deposited on the CuO thin films by electron beam evaporation and thermal

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evaporation with a metal shadow mask. The 10-nm-thick Pt cover layers were subsequently deposited on Cu top electrodes to prevent oxidation of Cu metal. To obtain the electrical properties of CuO thin films, the current–voltage (I – V) characteristics were examined by the Keithley 2410c source meter unit. During the electrical measurements, DC bias was applied to the top electrode while the bottom electrode was grounded.

3. Results and discussion

To obtain the resistance switching effect, a positive electroforming voltage (~ 3.6 V) with a current compliance of 0.01 A was employed to activate the structures (not shown in the paper). Fig. 1a and b shows the resistive switching I – V characteristics of the Pt/CuO/Pt and Cu/CuO/Pt structures after electroforming, respectively. Unlike the devices with electrochemically active Cu electrodes that generally show the BRS behaviors [11,20], the devices with Pt and Cu top electrodes both show typical URS behaviors in our measurements. As the applied voltage increases to the threshold voltage (~ 1.22 V), the current increases suddenly, and the devices switch from HRS to LRS (set process). As the applied voltage sweeps from zero to positive again, the devices switch from LRS to HRS (reset process).

In order to investigate the switching mechanisms in the Pt/CuO/Pt and Cu/CuO/Pt structures, the resistance–temperature (R – T) curves of LRS with the temperature ranging from 200 K to 300 K were measured. The resistance of LRS in the two structures increases with increasing temperature, as shown in Fig. 2. The positive temperature characteristics could be ascribed to a typical metallic behavior. The resistance can be written as $R(T) = R_0[1 + \alpha(T - T_0)]$, where R_0 is the resistance at temperature T_0 and α is the resistance temperature coefficient. We calculated the temperature coefficients to be about $2.32 \times 10^{-3} \text{ K}^{-1}$ and $2.78 \times 10^{-3} \text{ K}^{-1}$ for Pt/CuO/Pt and Cu/CuO/Pt structures, respectively. Both results match well with the temperature coefficient

of Cu nanowires ($\alpha = 2.5 \times 10^{-3} \text{ K}^{-1}$) [21], implying that Cu filaments are formed in the devices.

For the Pt/CuO/Pt structure, the resistance switching is ascribed to the rupture/recovery of Cu metal filaments which are induced by local reduction/oxidation process. In the forming process, the oxygen ions can move towards the top electrodes under high electric fields and release to the air at the surface. The remained Cu ions get reduced forming the Cu conducting filaments. Fujiwara et al. [10] described this reduction as the dielectric-breakdown-like phenomenon, just like the reduction of CuO by plasma induction, a method used in metallurgy. In the reset process, Cu can be oxidized to CuO due to Joule heating [10]. The subsequent set process is similar to the forming process. The Cu metal filaments in the devices have been directly observed by Yasuhara et al. [9] in the Pt/CuO/Pt structure using photoemission electron microscopy. It is noted that the devices with electrochemically active Cu electrodes generally show BRS behaviors due to the electrochemical metallization (ECM) [11]. However, for our Cu/CuO/Pt structure, the resistance switching shows the URS behaviors. We believe that the redox reaction of CuO thin films plays a dominate role in the resistance switching, while the ECM plays a secondary role. Therefore, both the Pt/CuO/Pt and Cu/CuO/Pt structures show the URS behaviors, indicating that the resistance switching is the intrinsic properties of CuO thin films.

In order to investigate the instability of conducting filaments, we studied the reset I – V curves. We observed two different kinds of reset I – V curves in both the Pt/CuO/Pt and Cu/CuO/Pt structures. For LRS with relatively low resistance value ($< 30 \Omega$), the slope of reset I – V curve decreases slightly with the increasing voltage (curve 1 in Fig. 3a and b), implying normal reset process. While for the LRS with relatively high resistance value ($> 50 \Omega$), the slope of reset I – V curve significantly increases at ~ 0.38 V (curve 2 in Fig. 3a and b), showing typical abnormal reset process. In order to investigate the statistical data of LRS that show different reset behaviors, we measured the I – V curves for 100 cycles. The distribution of LRS in both structures that exhibit different reset behaviors is shown in Fig. 4. LRS with resistance value R_1 ($< 30 \Omega$) and R_2

Fig. 1. I – V characteristics of (a) Pt/CuO/Pt and (b) Cu/CuO/Pt structure.

Fig. 2. Resistance–temperature (R – T) curves of LRS with relatively high and low resistance in (a) Pt/CuO/Pt and (b) Cu/CuO/Pt structure.

Fig. 3. Normal reset (curve 1) and abnormal reset (curve 2) I - V curves of (a) Pt/CuO/Pt and (b) Cu/CuO/Pt structure.

Fig. 4. The distribution of LRS in both structures that exhibit the normal and abnormal reset behavior: LRS with resistance value R_1 ($<30 \Omega$) and R_2 ($>50 \Omega$) exhibit the normal reset behavior and abnormal reset behavior, respectively.

Fig. 5. A schematic picture of normal reset process (a–c) and abnormal reset process (d–f) in CuO-based memory devices.

($>50 \Omega$) exhibit the normal reset behavior and abnormal reset behavior, respectively.

The normal reset behavior could be ascribed to the decrease in the filament size at first and subsequent rupture induced by Joule heating [22], as schematically shown in Fig. 5a–c. While for the abnormal reset behavior, Li et al. [19] ascribed it to the increase in the filament size resulting from the diffusion of active top electrodes. However, we observed the abnormal reset behaviors in both the Pt/CuO/Pt and Cu/CuO/Pt structures. Pt is an electrochemically inert metal, which has a large potential barrier. It is quite difficult for the Pt atoms to diffuse to the surroundings. For this reason, we believe that the abnormal reset behavior in the CuO-based memory devices is not due to the diffusion of top electrode, but the intrinsic properties of CuO film. The resistance switching in the CuO-based memory devices is associated with self redox reaction as expressed by

This is equilibrium of oxidation and reduction, and there is a competition between the two reaction directions during the switching process. The high electric field triggers the reduction reaction, while the large Joule heating induces the oxidation reaction. The LRS with relatively high resistance value means that some filaments do not entirely bridge the bottom and top electrodes, as shown in Fig. 5d. In the subsequent reset process, electric fields in the gap of disconnected filaments get enhanced due to the local field concentration effect [23], so the reduction reaction could be induced there. The reduction reaction causes the residual disconnected filaments to bridge the bottom and top electrodes (implying the decreasing resistance), as shown in Fig. 5e. When the LRS resistance is relatively low, more filaments bridge the bottom and top electrodes. After that, the oxidation reaction initiated by Joule heating plays a dominate role, resulting in the decrease in the filament size until the full reset process occurs (Fig. 5f). The phenomena of abnormal reset behaviors indicate that the conducting filaments are unstable in the resistance switching. Further studies are needed to improve the stability of the filaments.

4. Conclusions

The effects of Pt and Cu top electrodes on resistance switching properties have been investigated for CuO thin films with Pt/CuO/Pt and Cu/CuO/Pt sandwich structures. Both structures showed typical URS behaviors and the abnormal reset behaviors. The URS behaviors can be ascribed to the local reduction/oxidation of Cu metal filaments. The abnormal reset behaviors could be ascribed to the growth of disconnected filaments, not due to the diffusion of top electrodes. The URS and abnormal reset behaviors in both structures indicate that the resistance switching properties in CuO thin films are not due to Pt and Cu top electrodes, but the intrinsic properties of CuO film.

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