Charge transport and bipolar switching mechanism in a Cu/HfO_2/Pt resistive switching cell*

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Bipolar resistance switching characteristics are investigated in Cu/sputtered-HfO_2/Pt structure in the application of resistive random access memory (RRAM). The conduction mechanism of the structure is characterized to be SCLC conduction. The dependence of resistances in both high resistance state (HRS) and low resistance state (LRS) on the temperature and device area are studied. Then, the composition and chemical bonding state of Cu and Hf at Cu/HfO_2 interface region are analyzed by x-ray photoelectron spectroscopy (XPS). Combining the electrical characteristics and the chemical structure at the interface, a model for the resistive switching effect in Cu/HfO_2/Pt stack is proposed. According to this model, the generation and recovery of oxygen vacancies in the HfO_2 film are responsible for the resistance change.

Keywords: HfO_2 film, resistive switching mechanism, chemical structure

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1. Introduction

Recently, resistive random access memory (RRAM) devices have attracted considerable attention as nonvolatile memories.[1–3] An oxide sandwiched between two metal electrodes exhibits reversible electric field induced resistance switching behavior. In most cases, the resistance switching effect has its origin in the creation, dissolution, and recovery of conductive filaments (CF). Depending on material combination of a large variety of metal oxides and electrodes, filament compositions are generally classified into two categories: metal filament (MF) comprising metal precipitation from electrochemically active electrodes, such as Ni, Cu, and Ag,[4,5] and oxygen vacancy filament generated by redox of metal oxides.[6,7] Understanding the nature of the CF is of great important to control the performance, variability, and reliability of these devices and to improve their characteristics in the application.

Since hafnium based oxides are now being integrated into today's complementary metal–oxide–semiconductor technology, it is appealing to investigate this material for potential RRAM applications.[8] In this work, the resistive switching properties of Cu/HfO_2/Pt memory cell were investigated and a model was proposed to explain the resistive switching mechanism of Cu/HfO_2/Pt structure.

2. Experiments

The HfO_2 films were fabricated by RF magnetron sputtering. Before deposition, the Pt/Ti/SiO_2/Si substrates were cleaned by deionized water, alcohol, and acetone sequentially. Then, HfO_2 films were deposited on Pt substrates at room temperature by using metal Hf target (99.995%). During the sputtering process, the ratio of Ar:O_2 was 4:1, the working pressure was 0.3 Pa and the RF power was 80 W. The HfO_2 film thickness was measured by ellipsometer and determined to be 20 nm. To measure the electrical properties, the 20-nm Cu top electrodes of 1 mm in diameter were deposited on HfO_2 film by evaporation technology using a metal shadow mask with diameters of 1 mm, 1.5 mm, 2 mm, 2.5 mm, 3 mm, respectively. The chemical structure of Cu/HfO_2 interface was measured by XPS. The electrical properties of the samples were characterized by a two-probe measurement system with a semiconductor device analyzer.

3. Results and discussion

Figure 1 shows the typical current–voltage (I–V) characteristic of the Cu/HfO_2/Pt structure. The measurements were performed by a dc voltage sweep mode and all the bias voltages were applied on the Cu electrode with Pt grounded. Before getting reversible bipolar resistive switching from the pristine device, electroforming process was needed for the memory structure, which was shown in the inset of Fig. 1. During the electroforming process, soft breakdown occurred at a voltage ($V_{\rm form}$) of 0.8 V with a current compliance of 10 mA. In this process, some of Hf–O bonds in HfO_2 film may break and create oxygen vacancies (V_O). After the first reset, the memory structure shows successive bipolar resistive switching properties with small set/reset voltage and the ON/OFF ratio of approximately 5×10^2 at room temperature. As can be seen, the transition from HRS to LRS occurs under posi-

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tive bias (arrow: 1→2), while the change from LRS to HRS can be obtained by applying negative bias (arrow: 3→4). To investigate the current conduction mechanism, the *I*–*V* curves of Cu/HfO_2/Pt structure under both positive and negative voltages were replotted in a double-log scale, as shown in Fig. 2. The *I*–*V* curves in LRS can be fitted as a straight line, which corresponds to ohmic conduction. The curves in HRS can be described in the model of space charge limited current (SCLC),[9] indicating that the resistive switching behavior was controlled by the traps in the HfO_2 film.

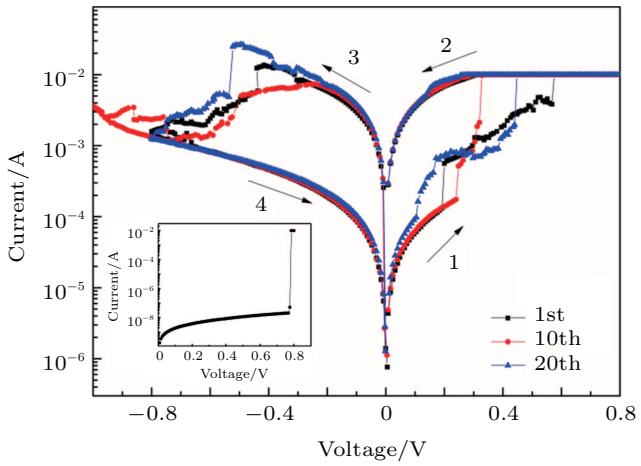


Fig. 1. (color online) Typical current-voltage (*I*–*V*) curves of Cu/HfO_2/Pt resistive switching structure. The inset shows the electroforming process.

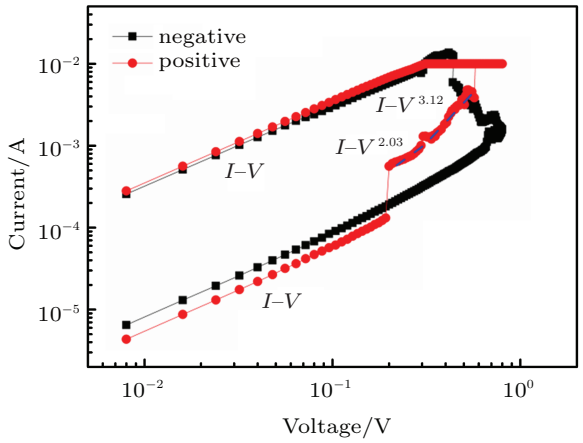


Fig. 2. (color online) Current–voltage curves under both positive and negative voltage re-plotted in a log–log scale.

Understanding the dependence of the resistance on the temperature is an effective way to reveal the transport properties and conduction mechanism. Figure 3(a) shows the resistance of the Cu/HfO_2/Pt device under different temperatures. The HRS can be related with a semiconducting-like behavior, in which the resistance decreases as the temperature increases. Meanwhile, the LRS exhibits a metallic-like characteristic, in which the resistance increases slightly as the temperature increases. A similar observation has been observed for TiN/HfO_2/Ti/TiN devices in Ref. [10] and they considered that the resistance change in LRS was related to the scattering centers inside or outside the filament path. In this work, it may be related to the diffusion of Cu into HfO_2 film, which was proved by XPS analysis later. Figure 3(b) shows the dependence of the HRS and the LRS on the device area. The LRS displays no obvious change with the increase of device area, suggesting the presence of localized conducting filaments. Moreover, the HRS exhibits a decreasing trend as the device area is increased. The switching mechanism may be governed by the formation and rupture of conducting filaments comprised of oxygen vacancies. Besides, it is worth noting that the ON/OFF ratios of resistance are decreased when the device area is increased, which indicates that the devices have excellent characteristics of scaling down and have potential for exploring high-density RRAM.

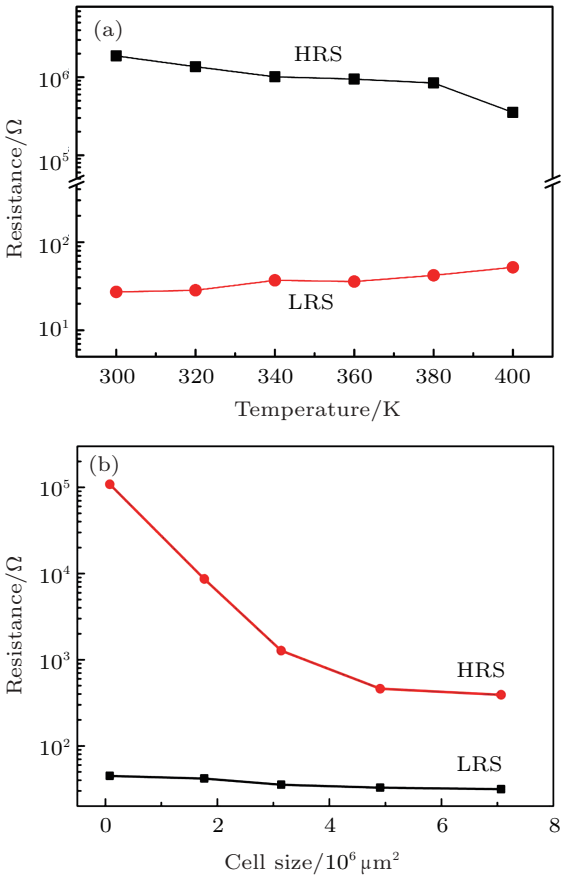


Fig. 3. (color online) (a) The temperature dependence of the HRS and the LRS. (b) The device area dependence of the HRS and the LRS.

To investigate the structural and compositional changes at the Cu/HfO_2 interface, XPS depth analysis were performed in LRS after forming process. Figure 4 displays the Hf 4f and Cu $2p_{3/2}$ core levels spectra with different etching time by Ar^+ at the Cu/HfO_2 interface region, respectively. As shown in Fig. 4(a), the binding energy of Cu $2p_{3/2}$ locates at 932.6 eV for the etching time of 20 s, which corresponds to metallic Cu electrode.[11,12] For etching time of 60 s and 80 s (close to the interface), Cu $2p_{3/2}$ core level spectra are observed at 932.6 eV and 933.5 eV, which are attributed to metallic Cu

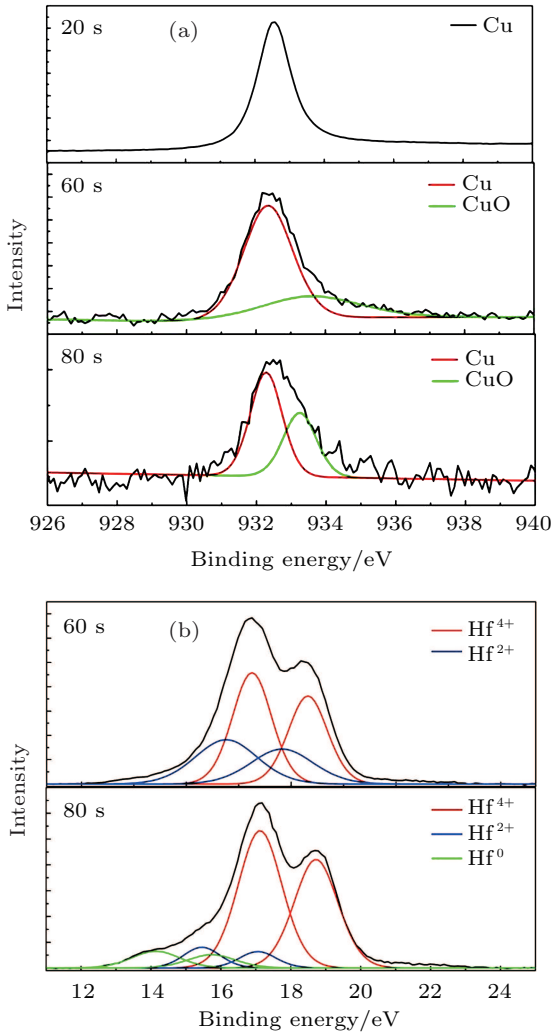


Fig. 4. (color online) The XPS depth profiles of the Hf 4f and Cu $2p_{3/2}$ at the Cu/HfO_2 interface region. (a) Cu $2p_{3/2}$ peaks and (b) Hf 4f peaks.

and CuO, respectively. According to previous studies, copper oxide has two different electronic numbers of +1 (Cu_2O) and +2 (CuO), and the Cu $2p_{3/2}$ core level of CuO is about 1.2 eV higher than that of metallic Cu.[11] As the etching time increases, the intensity ratio of CuO/Cu increases, indicating that the CuO interfacial layer was formed at the interface region. In Fig. 4(b), the Hf 4f spectra can be deconvoluted as two double–peak components after 60 s Ar^+ etching, one doublet is at 16.9 eV and 18.5 eV associating with the Hf oxide bond, and the other doublet at 16.1 eV and 17.7 eV are originated from the Hf suboxide bond.[13,14] As the etching time increases to 80 s, the Hf oxide bond, Hf suboxide bond and metallic Hf can be identified out after the curve-fitting process. The low energy side of the Hf 4f doublet peaks at 14.2 eV and 15.8 eV are associated with the metallic Hf-Hf bond, the doublet peaks at 15.4 eV and 17.1 eV are assigned to the Hf suboxide bond, and the high energy side of the doublet peaks can be attributed to Hf oxide bond. In addition, there was no longer any signal of Cu-related compound for the Ar^+ etching time of 100 s (not shown in this paper), and only HfO_2 can be observed. The results provide evidence that copper and oxygen diffuse towards the interface to form a CuO interfacial layer, leaving a lot of oxygen vacancies in HfO_2 film. It can be concluded that the filament is comprised of oxygen vacancies rather than the diffusion of Cu ions.

On the basis of the above analysis, the switching mechanism of Cu/HfO_2/Pt is governed by the formation and rupture of conducting filaments comprised of oxygen vacancies, illustrated schematically in Fig. 5. When a positive voltage is applied on Cu TE, the oxygen ions (O^{2-}) migrate toward Cu TE and are gathering at the interface. The active Cu electrode can be partially oxidized by absorbing O^{2-}s from HfO_2 film as Cu + O $\rightarrow$ CuO, leading to the CuO interfacial layer. After a sufficient electric field is reached, the oxygen vacancy filaments form in HfO_2 film and bring the device from HRS to LRS, as shown in Fig. 5(a). On the other hand, when negative voltage is applied on Cu TE, the oxygen ions move from the Cu/HfO_2 interface toward HfO_2 film and recombine with oxygen vacancies (V_Os). As a result, the filaments rupture and the device goes back to HRS, as shown in Fig. 5(b).

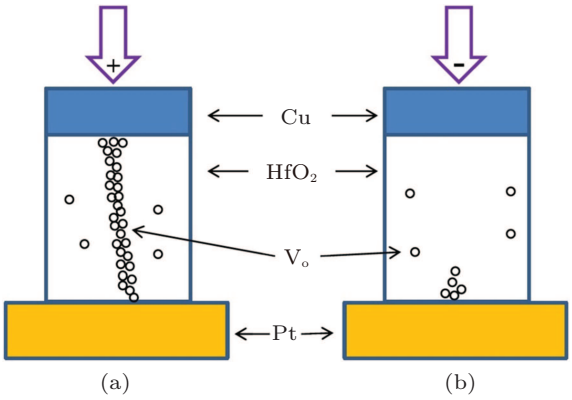


Fig. 5. (color online) Schematic diagram for the mechanism of the resistive switching effects in the Cu/HfO_2/Pt memory device. (a) Low resistance state and (b) high resistance state.

4. Conclusion

In summary, reproducible bipolar resistive switching behaviors are observed for the Cu/HfO_2/Pt device after electroforming process. The memory device exhibits good switching properties with small set/reset voltage and a large resistance ratio at room temperature. The current conduction of the device is governed by the trap-controlled SCLC conduction mechanism. The CuO interfacial layer is observed at the Cu/HfO_2 interface region, which leads to the increase of oxygen vacancies in HfO_2 film. Thus, the bipolar resistance switching characteristics of Cu/HfO_2/Pt device can be described based on the formation and rupture of conducting filaments related to the electrically-induced migration of oxygen vacancies.

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