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Bipolar and unipolar resistive switching in $Zn_{0.98}Cu_{0.02}O$ films

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Abstract
We report the coexistence of bipolar and unipolar resistive switching (BRS and URS) in a $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ structure. The resistance ratio between the high-resistance state (HRS) and the low-resistance state (LRS) is about 10^6 for the BRS. The URS is observed with a positive bias applied on the ITO electrode, which is more stable than the BRS. The resistance ratio between the HRS and LRS of the URS is about 10^4. The Schottky barrier at the $Zn_{0.98}Cu_{0.02}O/Ag$ interface plays an important role in both the BRS and URS processes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Resistance random access memory (RRAM) has been considered to be one of the potential solutions for the next-generation nonvolatile memory application, and has attracted considerable attention [1, 2]. In a resistive switching (RS) process, an electrical field switches the resistance reversibly between a high-resistance state (HRS) and a low-resistance state (LRS) [3]. Based on the dependence on the operation voltage polarity, RS can be classified as bipolar resistive switching (BRS) and unipolar resistive switching (URS) [4]. RS has been observed in a large variety of materials, including simple binary transition metal oxide materials, perovskite oxide materials, as well as organic materials [5].

ZnO is a wide band gap semiconductor, which has wide applications in optoelectronic applications [6]. Recently, URS and BRS have been observed in ZnO and doped ZnO [1–5, 7–9]. URS is of particular interest for its much larger resistance change and great simplification of the process of reading the memory state [10]. ZnO is intrinsically n-type conducting due to the existence of O vacancies and interstitial Zn atoms [6]. The conducting filament model has been widely accepted to explain the observed URS in ZnO, which includes the formation/rupture of conductive filaments in an insulating matrix [3, 9]. Cu is generally considered as acceptor dopants, which will compensate for the intrinsic donors, thus increasing the resistivity of ZnO [11]. Increasing the resistivity of the insulating matrix will effectively increase the ratio between the resistance of HRS and LRS [3]. In this paper, we report the URS in $Zn_{0.98}Cu_{0.02}O$ films with a resistance ratio between the HRS and LRS of about 10^4. Furthermore, BRS is also observed with a resistance ratio between the HRS and LRS of about 10^6. The mechanisms of BRS and URS are discussed.

2. Experimental details

$Zn_{0.98}Cu_{0.02}O$ films were deposited on ITO/glass substrates at room temperature by pulsed laser deposition using a KrF excimer laser from an analytically pure $Zn_{0.98}Cu_{0.02}O$ target in O_2 ambient with a pressure of 3 Pa, and *ex situ* annealed in air at 450 °C for 30 min. The film thickness was controlled by the number of laser pulses (5000 in this paper) with a pulse energy of 250 mJ, and *ex situ* determined by a scanning electron microscope (SEM, FEI Quanta200) to be about 80 nm. The structure of the film was studied by x-ray diffraction, as shown in figure 1. All the diffraction peaks can be indexed to wurtzite ZnO without any impurity phases. The current–voltage (I–V) measurements were carried out using a Keithley 2400 SourceMeter and 2182A Nanovoltmeter at room temperature. Silver glue dots with a diameter of about 1 mm were used as top electrodes. The schematic $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device structure is illustrated in the inset of figure 1. During the voltage sweep mode, the bias was defined as positive when the current flowed from the top Ag electrode through the film to the bottom ITO electrode.

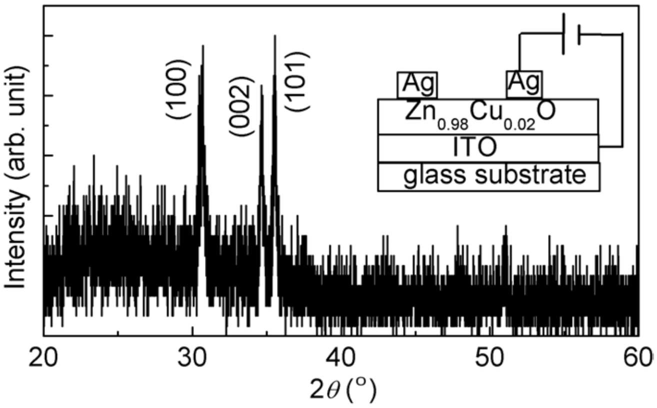

Figure 1. XRD pattern of the $Zn_{0.98}Cu_{0.02}O$ film annealed at 450 °C in air for 30 min. The inset shows the schematic $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device structure.

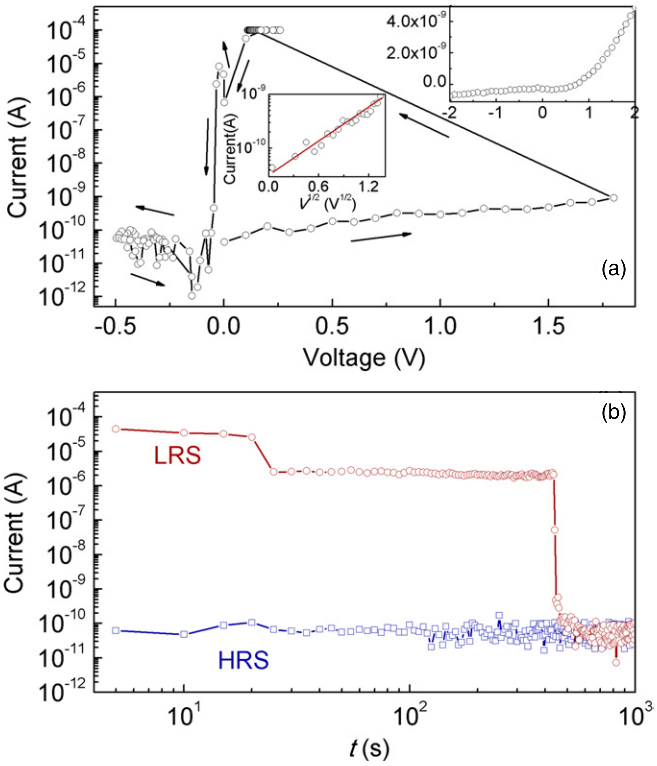

Figure 2. (*a*) Typical BRS characteristics of $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device. The top right inset shows the I–V curve of the device before the forming, and the middle inset shows the Log(I)–$V^{1/2}$ plot for HRS in the positive bias region. (*b*) Retention of the HRS and LRS at room temperature with a reading voltage of 0.2 V.

3. Results and discussion

A typical BRS was observed in the $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device, as shown in figure 2(*a*) after the initial forming process. To protect the device, a current compliance of 10^{-4} A was set. The device was initially in the HRS. On increasing the voltage to 1.8 V, the device switched to the LRS abruptly. A sudden jump of the current to the current compliance of 10^{-4} A happened, and the voltage on the device dropped abruptly, due to the fact that more voltage was divided by the series resistor. The current remained at the compliance level until the downward sweep reached around 0.2 V. The device switched back to the HRS at approximately −0.02 V. The top right inset of figure 2(*a*) shows the I–V curve of the device before the forming. The rectifying characteristic shows that a Schottky-like contact formed at the $Ag/Zn_{0.98}Cu_{0.02}O$ interface, which is due to the different work functions of ZnO (4.5 eV) [12] and Ag (4.7 eV) [13], and an Ohmic contact might be expected due to the nearly same work function of ITO (4.4–4.5 eV) [14]. The BRS showed the directionality of the switching; the resistance state changed from the HRS to LRS when a positive voltage was applied on the top Ag electrode, which is the forward bias on the $Ag/Zn_{0.98}Cu_{0.02}O$ Schottky interface, and vice versa [15]. Furthermore, the linear relationship between Log(I) and $V^{1/2}$, as shown in the middle inset of figure 2(*a*), confirms the Schottky conducting mechanism [16, 17]. Thus we conclude that the Schottky barrier at the $Ag/Zn_{0.98}Cu_{0.02}O$ interface is responsible for the observed BRS in the device.

Under the positive bias, the O ions will be attracted and will accumulate at the $Ag/Zn_{0.98}Cu_{0.02}O$ interface. However, it is demonstrated that the oxidation of Ag at the interface can be neglected [18–20]. Thus the accumulated O ions will locate at the $Zn_{0.98}Cu_{0.02}O$ layer, which will increase the work function of $Zn_{0.98}Cu_{0.02}O$ [12], leading to a decrease in the Schottky barrier height of the interface [21]. Then the device switches to the LRS. By applying a negative bias, the O ions will be pushed away from the interface, or O vacancies will be attracted and will accumulate in $Zn_{0.98}Cu_{0.02}O$ close to the interface, leading to a decrease in the work function and an increase in the Schottky barrier height. The device switches to the HRS. As no oxidation/reduction chemical reaction occurs at the $Ag/Zn_{0.98}Cu_{0.02}O$ interface, the accumulation of O ions at the interface is not stable [3]. Without the positive bias, the concentration gradient of O ions cannot be maintained, and O ions will diffuse away from the interface and the device will switch from the LRS to HRS. The current will decay very fast with a time constant of about 3 s due to O migration [3]. Indeed, without applying the negative bias, the device switches from the LRS to HRS, as can be seen in the retention property of the BRS in the $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device in figure 2(*b*). With a reading voltage of 0.2 V, the initial resistance ratio between the HRS and LRS is around 10^6. It should be noted that BRS is not stable, since after several switches, the device will be permanently broken, similar to the BRS in $Au/SrTiO_3/Pt$ [22].

Generally, URS has no polarity dependence, and RS should be observed in both positive bias and negative bias. However, in the $Ag/Zn_{0.98}Cu_{0.02}O/ITO$ device, URS can only be observed with the negative bias (positive voltage on the bottom ITO electrode). With a positive bias, after the forming process from the HRS to LRS, the device is permanently destroyed and cannot be switched back from the LRS to HRS. Figure 3(*a*) shows the URS with a negative bias after the forming. In the set process, a current compliance of 10^{-3} A was set to protect the device. The device is initially in the HRS. With increasing voltage up to −15 V, a sudden jump of the current to 10^{-3} A was observed, and the device switched to the LRS. With increasing voltage to −3.5 V in the reset process, the current dropped suddenly, and the device switched from the LRS to HRS. To gain more insight into

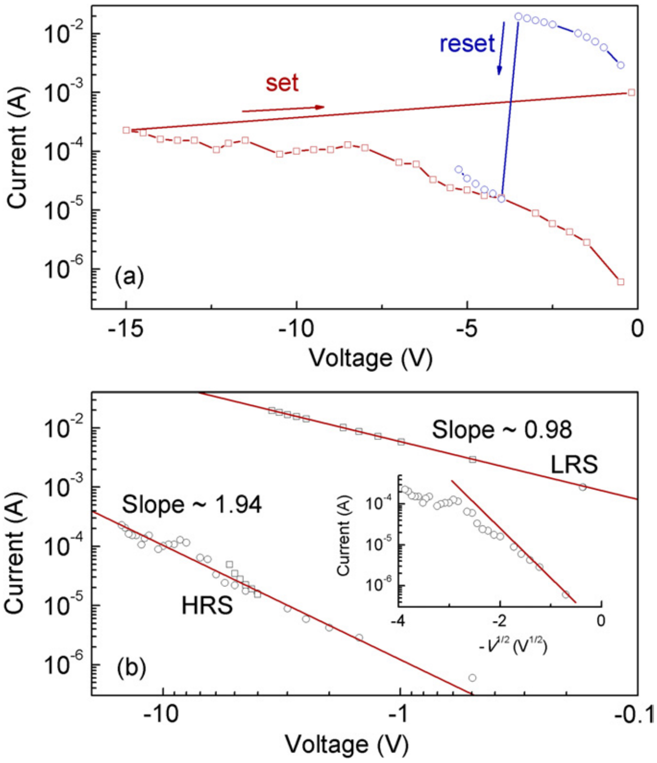

Figure 3. (*a*) Typical URS characteristics of Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO device. (*b*) The log–log plot of I–V curves of the Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO device; the inset shows the Log(I)–$V^{1/2}$ plot for HRS.

the URS, the conduction mechanisms for the HRS and the LRS were analysed, and the typical I–V curves of the set and reset processes are plotted in the log–log scale, as shown in figure 3(*b*). The I–V curves exhibit a linear Ohmic behaviour with a slope of 0.98 in the LRS, while a current square dependence on voltage with a slope of 1.93 can be observed in the HRS at high voltages, corresponding to the typical trap-controlled space charge limited conduction (SCLC) [16, 23]. As shown in the inset of figure 3(*b*), at low voltages, a linear relationship between Log(I) and $V^{1/2}$ can be observed, indicating the Schottky conduction [16, 17]. The different conduction behaviours in the LRS and HRS suggest that the high conductivity in the LRS should be a confined filamentary effect, rather than a homogenously distributed one [2].

The polarity dependence of the URS in the Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO device can be understood by the conducting filaments and the Ag/Zn$_{0.98}$Cu$_{0.02}$O Schottky interface. As discussed in the BRS, the Schottky barrier height of the Ag/Zn$_{0.98}$Cu$_{0.02}$O interface will increase with the increasing negative bias, and decrease with the increasing positive bias. It has been reported that stable RS can only be observed with a high Schottky barrier height [17, 21]. Thus, stable URS can only be observed with a negative bias due to the higher Schottky barrier height. Ag$^+$ might migrate from the Ag electrode to the counter-electrode and get reduced there, and the successive precipitation of Ag metal atoms will form the conducting filaments [2]. However, the metal ions will migrate to the counter-electrode with a positive voltage applied on the metal electrode [2, 24]. In our device, the filaments were formed with a negative voltage applied on the Ag electrode, thus the formation of conduction filaments by Ag can be excluded. The formation of the conducting filaments in the bulk of Zn$_{0.98}$Cu$_{0.02}$O can be attributed to the diffusion of O vacancies, then the device switched to the LRS. In the reset process, the Joule heating induced by the large current ruptured the conducting filaments, and the device switched to the HRS [25].

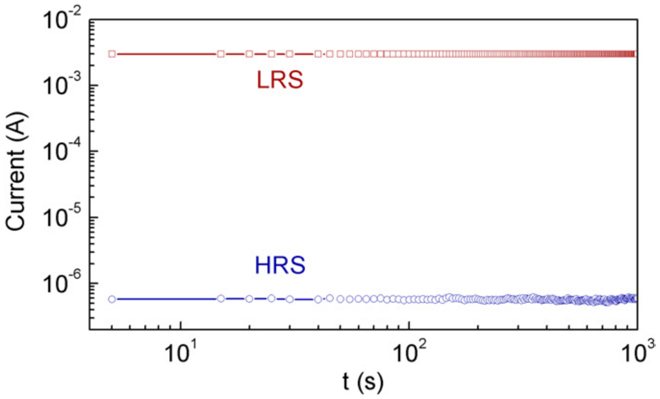

Figure 4. Retention of the HRS and LRS at room temperature with a reading voltage of −0.5 V.

The retention property of the URS in the Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO device at room temperature is shown in figure 4. Both the LRS and HRS are very stable, and no switching between the LRS and HRS is observed, indicating that the URS is more stable than the BRS, which is consistent with a previous report [3]. The resistance ratio between the HRS and LRS of the URS is about 10^4, which is about 1–2 orders larger than that of the device based on ZnO [1, 5, 7–9]. This is due to the increase in the resistivity of ZnO by Cu doping as acceptor dopants which will compensate for the donor defects [11], and increase the ratio between the resistivity of the HRS and LRS [3]. The temperature dependence of the resistance in the LRS and HRS is shown in figure 5. As can be seen, the resistance in the HRS continues to decrease with increasing temperature, indicating the semiconductor conductivity. A sudden jump from HRS to LRS is observed when the temperature is increased to about 70 °C. A gradual increase in the resistance with increasing temperature up to 120 °C is observed in the LRS, indicating the metallic properties of the conducting filaments.

4. Conclusions

In summary, Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO devices are prepared, and the coexistence of BRS and URS is observed. The resistance ratio between the HRS and LRS is about 10^6 for the BRS with a smaller current compliance of 10^{-4} A. The BRS is attributed to the variation of the Schottky barrier height of the Ag/Zn$_{0.98}$Cu$_{0.02}$O interface due to the migration of the O ions or O vacancies. The URS is observed with a positive bias applied on the bottom ITO electrode with a current compliance of 10^{-3} A, which is more stable than the BRS. The resistance ratio between the HRS and LRS of the URS is about 10^4. The model of the formation and rupture of conducting filaments

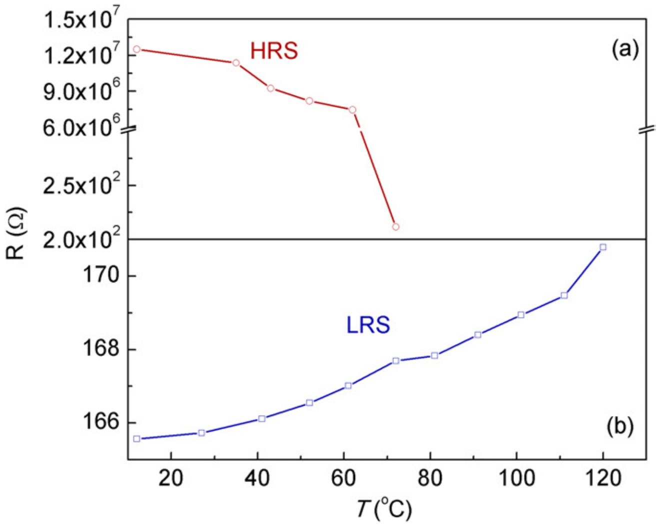

Figure 5. Temperature dependence of the resistance in the HRS and LRS.

formed by the O vacancies is applied to explain the polarity-dependent URS in Ag/Zn$_{0.98}$Cu$_{0.02}$O/ITO devices.

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