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Temperature influence and reset voltage study of bipolar resistive switching behaviour in ZrO_2 thin films

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Abstract. **We have fabricated ZrO_2 thin films by sol–gel deposition and annealed them at 300, 500 and 700 °C. Reproducible *I–V* curves can be obtained for the device Cu/ZrO_2/ATO which is measured at room temperature (300 K). During the RESET operation, R_L and R_H values can be controlled by the RESET voltage. Moreover, the Cu/ZrO_2/ATO device which the ZrO_2 thin film annealed at 300 °C can be measured as resistive switching sweeps at 200, 100 and 50 K. It was found that the ratio of R_{off}/R_{on} reduced when the measured temperature decreased. When the *I–V* measurement temperature decreases, R_{on} decreases obviously which is typical for electronic transportation in a Cu metal. It is indicated that the Cu metallic conduction filament has been formed in the ZrO_2 films. Besides, the microstructure by high resolution transmission electrical microscopy (HRTEM) was also investigated.**

Keywords. **Resistive switching; TEM; ZrO_2; low temperature.**

1. Introduction

Resistive switching behaviours of thin films which are used in high density resistance random access memories (RRAM) have shown great promise for the next generation nonvolatile memory (NVM) (Ting *et al* 2000; Li *et al* 2011). Types of NVMs are several, such as ferroelectric random access memory (FRAM), RRAM and magnetic random access memory (MRAM). The intensive research and development of RRAM were triggered due to the low power consumption, high density integration and high speed operation. To achieve this controllability and repeatability of resistance, the controllability of switching voltage for both SET and RESET process is a key factor (Gao *et al* 2008). In addition, reducing switching voltage is also a desire for low power consumption for next generation nonvolatile memory. As for the resistive switching mechanism, there are several kinds of switching phenomena like redox effects in the resistance changes, filament formation and the percolation of the defects in the oxide (Choi *et al* 2005; Waser 2009). Researchers have used several techniques to investigate the mechanism such as conductive atomic force microscopy (C-AFM), high resolution transmission electrical microscopy (HRTEM) and scanning electrical microscopy (SEM) (Gopalan *et al* 2007; Guo *et al* 2007).

In the recent study, we have investigated the influence of the temperature on the resistive switching behaviours of the sol–gel deposited ZrO_2 thin film in the metal–oxide–semiconductor structure. The ZrO_2 thin films were annealed at different temperatures: 300, 500 and 700 °C. The bipolar resistive switching behaviour can be observed successfully in this structure. Successful *I–V* sweeps were also observed at room temperature and low temperatures of 200, 100 and 50 K and HRTEM observation was used to study the interface between the layers.

2. Experimental

The whole process of fabrication is shown in the following. The substrate is self-made transparent and conductive $SnO_2:F$ (ATO) thin film on Si substrate (Zhi *et al* 2008). The ATO substrates were cleaned by proponal and acetone step by step. We used zirconium (IV) butoxide and ethanol as starting materials while benzoyl acetone (BzAcH) as chemical modifier. The components zirconium (IV) butoxide, ethanol and BzAcH were mixed in terms of molar ratio 1 : 20 : 0·8. ZrO_2 solution could be obtained after stirring for 8 h in the glove box. Then, a dip-coating process was used to make a ZrO_2 gel film on the ATO substrate. After annealing the gel films for 15 min, organic compounds were evaporated and ZrO_2 thin films were obtained. The ZrO_2 thin films being produced were annealed in air at different temperatures of 300, 500 and 700 °C. Then, ZrO_2 thin film was covered

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by a mask and copper (99·99%) was evaporated by high vacuum thermal evaporation at 2×10^{-4} Pa for 2·5 min at a speed of 20 nm/min. Finally, the metal–oxide–semiconductor structure Cu/ZrO_2/ATO was achieved.

Electrical measurements were performed by Keithley 2400 analyser at room temperature (300 K). *I–V* sweeps at low temperatures of 200, 100 and 50 K were also carried out by Versa Lab (Quantum design). The microstructural characterization was carried out by HRTEM (JEOL 3010, Japan). A cross-section of Cu/ZrO_2/ATO single unit device was successfully made by the low angle Argon milling machine (Gatan, USA). The milling angle was below 8°.

3. Results and discussion

Figure 1 presents the XRD patterns of ZrO_2 thin films at various annealing temperatures. We observed the formation of amorphous ZrO_2 thin films for annealing up to 700 °C. Figure 1(a) did not show any peaks of ZrO_2. That means the ZrO_2 thin film is amorphous. When the temperature increased to 500 and 700 °C, ZrO_2 thin film showed tetragonal phase occurring at $2\theta = 30{\cdot}1$, 34·6 and 50·1°, which are attributed to (101), (002), (112) reflections, respectively. It is in close agreement with the JCPDS card no. 81-1544. It shows that amorphous ZrO_2 thin films changing to tetragonal phase up on annealing. As to ATO film, it also shows the tetragonal phase according to the card JCPDS no. 88-0287.

We took one unit of sample for TEM observations in which the ZrO_2 thin film in the structure was annealed at 300, 500 and 700 °C, respectively. Microstructural analysis has been done on the basis of TEM observations. Figure 2 shows the interface image of Cu/ZrO_2/ATO structure in which the ZrO_2 thin film was annealed at 300 °C. The bottom electrode (BE) is ATO film and the thickness is about 400 nm. The ZrO_2 work layer is about 200 nm thick and it is amorphous according to the selected area diffraction pattern. Figure 3 shows the interface image of Cu/ZrO_2/ATO structure in which the ZrO_2 thin film was annealed at 500 °C. The ZrO_2 work layer is about 100 nm thick and it is polycrystalline according to the selected

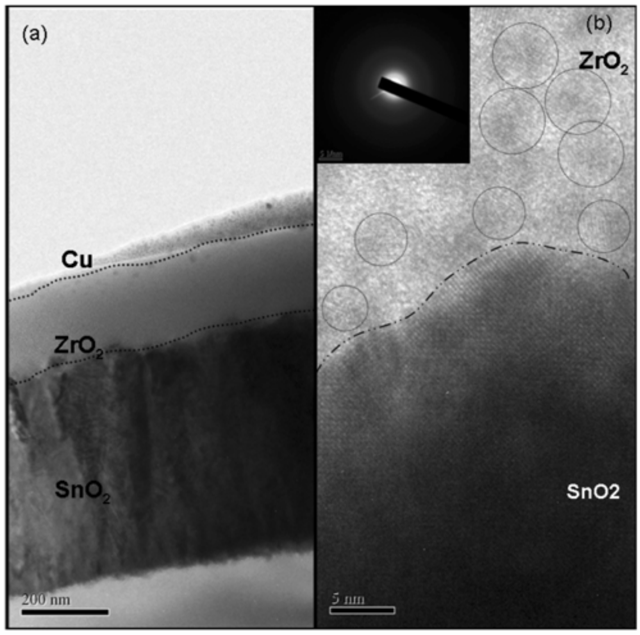

Figure 2. HRTEM images of Cu/ZrO_2/ATO structure in which ZrO_2 thin film was calcined at 300 °C and inset image is selected area diffraction (SAD) pattern.

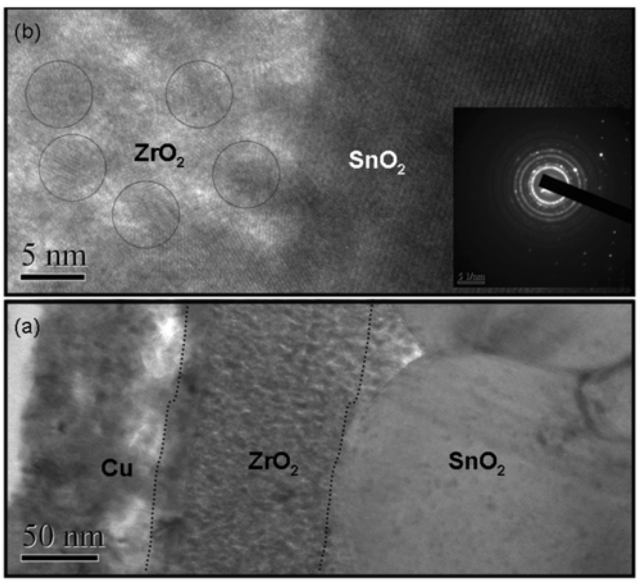

Figure 3. HRTEM images of Cu/ZrO_2/ATO structure in which ZrO_2 thin film was calcined at 500 °C and inset image is SAD pattern.

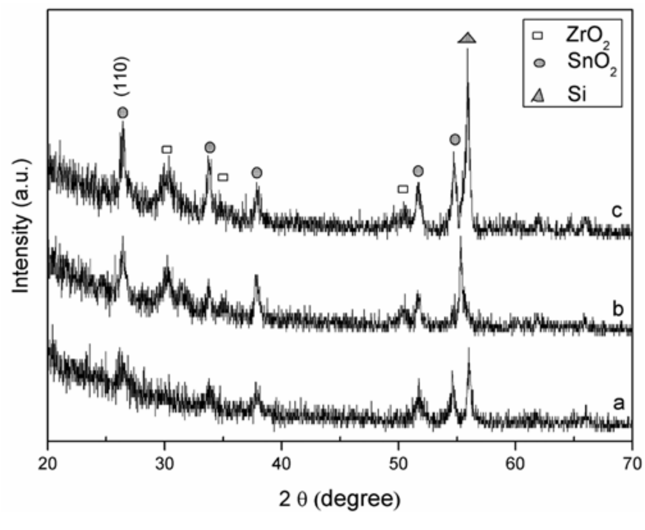

Figure 1. XRD images of annealed ZrO_2 thin films at different temperatures: (a) 300, (b) 500 and (c) 700 °C.

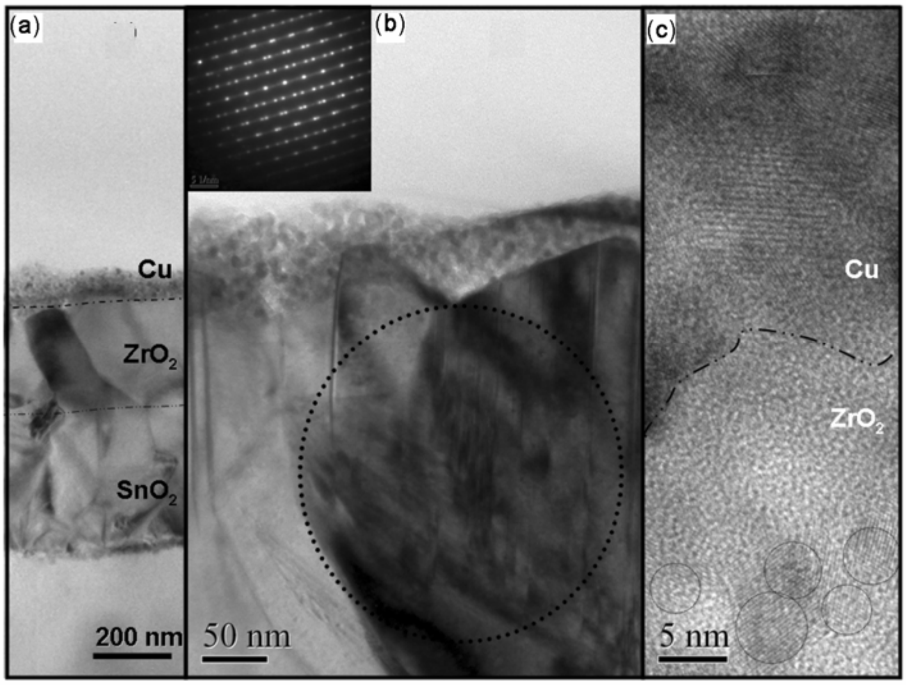

Figure 4. HRTEM images of Cu/ZrO_2/ATO structure in which ZrO_2 thin film was calcined at 700 °C and inset image is SAD pattern.

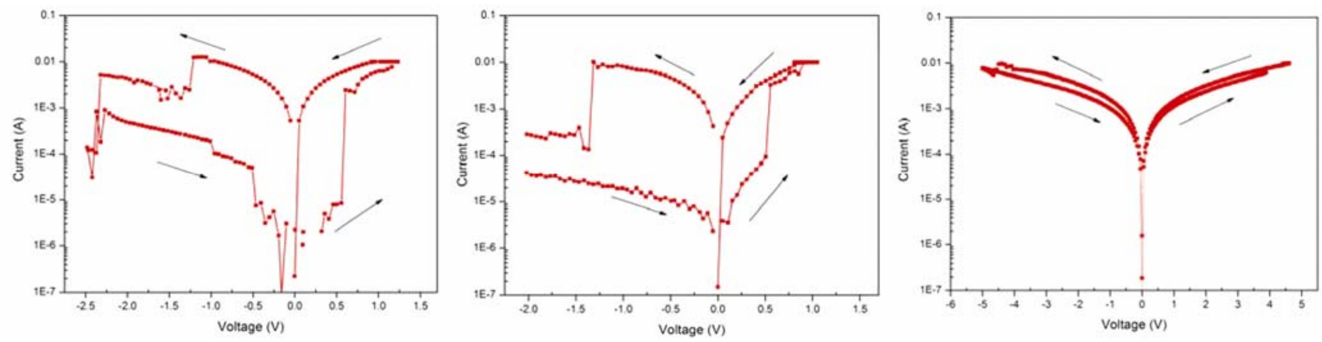

Figure 5. Typical *I*–*V* characteristics of Cu/ZrO_2/ATO device: (**a**) 300, (**b**) 500 and (**c**) 700 °C.

area diffraction pattern. Figure 3(b) shows that the grain size of ZrO_2 is about 5 nm. Figure 4 shows the interface image of Cu/ZrO_2/ATO structure in which the ZrO_2 thin film was annealed at 700 °C. The microstructure of ZrO_2 grains in figure 4(b) shows twin crystalline due to the selected area diffraction pattern. The interface between ZrO_2 and ATO films is obscure. In figure 1, ZrO_2 and ATO are all showed tetragonal phases. It can be deduced that ZrO_2 and ATO grains are grown together. Figures 2–4 show that Cu ions are penetrated into the ZrO_2 layer. It can be proved by the fast Fourier transform (FFT) patterns. According to the filament formation mechanism, resistance reduction in the devices is due to the existing Cu forming conducting Cu-rich pathways. An opposite bias takes the existing Cu back to the Cu electrode to its high-resistance state (Guo *et al* 2007).

The thickness of ZrO_2 thin film formed ranges from 100 to 200 nm depending on the annealing temperature. It shows that film thickness decreased with an increasing temperature of anneal. It is reported that the thickness of thin film reached a saturation value of 63 nm at 400 °C (Korkmaz *et al* 2012; Soo *et al* 2012). At the highest temperature of 700 °C, it is deduced that at this temperature the thickness of thin film is no longer affected by densification, but the phase formed to tetragonal ZrO_2. ZrO_2 and ATO grains grow together. Therefore, the interface between ZrO_2 and ATO films is obscure.

For *I*–*V* measurements, probes contact top electrode (Cu) and bottom electrode (ATO), respectively. The bottom electrode was grounded. Stable and repeatable *I*–*V* curves can be observed in devices in which ZrO_2 thin films were annealed at 300, 500 and 700 °C. All samples

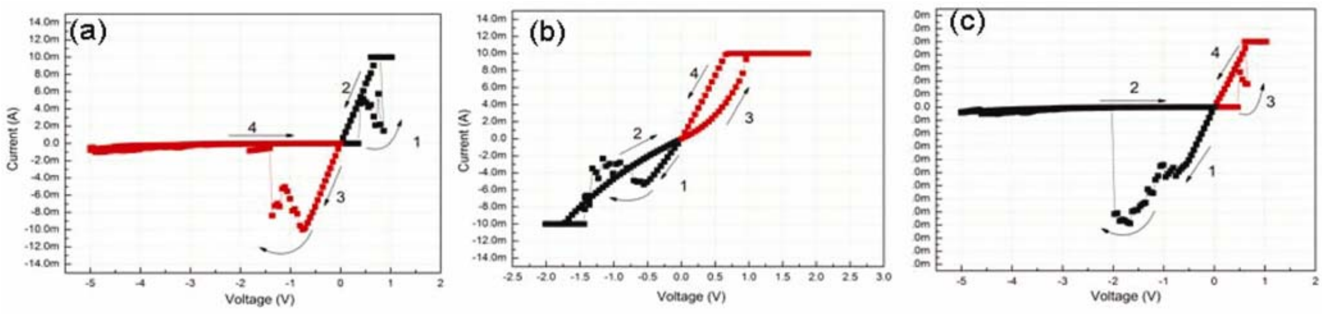

Figure 6. Typical *I–V* curves of Cu/ZrO_2 (300 °C)/ATO device with different RESET voltages: RESET voltages at (**a**) –5 V, (**b**) –2 V and (**c**) –5 V after recovery.

can show stable bipolar resistive switching at room temperature (300 K). Figure 5 shows the repeated *I–V* curves after thirty cycles of Cu/ZrO_2/ATO structure in which the ZrO_2 thin film which was annealed at 300, 500 and 700 °C. The bipolar resistive switching behaviour was observed and the ratio of R_{off}/R_{on} can be reached to 700 °C. For figure 5(a) *I–V* curve, when the SET voltage reaches 0·55 V, the current increases rapidly which shows switching from the OFF state to the ON state. During the second *I–V* sweep at the negative side, when the RESET voltage reaches –1·2 V, the current decreases rapidly which shows switching from the ON state to the OFF state. In figure 5(b), when the SET voltage reaches 0·50 V, the current increases rapidly. It shows switching from the OFF state to the ON state. During the second *I–V* sweep at the negative side, when the RESET voltage reaches –1·3 V, the current decreases rapidly which shows switching from the ON state to the OFF state. When compared these two curves in figure 5(a and b), for the SET voltage, it is almost the same while for the reset voltage, the value increases when the annealing temperature increased. For figure 5(c) *I–V* curve, when the SET voltage reaches 3·8 V, the current increases which shows switching from the OFF state to the ON state. During the second *I–V* sweep at the negative side, when the RESET voltage reaches –4·4 V, the current decreases rapidly which shows switching from the ON state to the OFF state. When compared these (a), (b) and (c), (a) and (b) curves are similar. However, for the curve (c), the ratio of R_{off}/R_{on} decreases to 1·4. The reasons for the higher voltage could be the existence of grain boundaries and more defects (like twin crystals) in structure because of higher annealing temperatures. This can also be proved by the HRTEM image in figure 4. An increase in the annealing temperatures between 300 and 700 °C led to the electronic disorder due to oxygen deficiency at a higher oxidation temperature (Ting *et al* 2000; Korkmaz *et al* 2012).

Bipolar resistive switching characterization was stable for ZrO_2 thin film in the structure unit. Figure 6(a) shows the typical *I–V* characteristics of the Cu/ZrO_2/ATO structure unit. Normally the voltage sweeps starting from 0 V and goes to the positive side (5 V) and goes back to 0 V. Resistance switches from high resistance state (R_H) to low resistance state (R_L) and it is called SET process. And then the voltage sweeps from 0 V to the negative side (–5 V) and goes back to 0 V. Resistance switches from R_L to R_H and it is called RESET process. When the voltage swept at –0·5 V, R_L was 70 Ω and R_H was 100 KΩ. This behaviour can be repeated several times. The current compliance (CC) is applied with 10 mA. The highest ratio of R_H/R_L can be reached to 10^4.

During the RESET operation, we found an interesting thing, i.e. R_H varied when we changed the RESET voltage. R_H decreased when the RESET voltage value decreased. For *I–V* curve in figure 6(b), voltage sweep started from 0 V to –2 V and then from –2 V to 0 V during the RESET process. When the voltage swept at –0·5 V, R_L was 100 Ω and R_H was 250 Ω. This behaviour can be repeated several times. The current compliance is applied with 10 mA. The highest ratio of R_H/R_L can be reached to 4.

When the RESET voltage value goes back to –5 V, the bipolar resistive curve recovered. In figure 6(c), during the RESET process, voltage sweep started from 0 V to –5 V and then from –5 V to 0 V. When the voltage swept at –0·5 V, R_L was 65 Ω and R_H was 100 KΩ. This behaviour can be repeated more than thirty times. The current compliance is applied with 10 mA. The highest ratio of R_H/R_L can be reached to 10^4. With the controllability of the RESET voltage, R_L and R_H values are recovered. Therefore, R_L and R_H value can be controlled by the RESET voltage.

We want to characterize the thermal and electrical properties of the Cu filament. The conductive filament resistance changes with device's temperature (Russo *et al* 2009; Peng Gao *et al* 2010). For low temperature *I–V* measurement, however, the device Cu/ZrO_2/ATO, whose ZrO_2 was annealed at 300 °C shows a stable bipolar resistive switching characterization even at low temperature for *I–V* measurements. *I–V* sweeps were operated at 200, 100 and 50 K, respectively. With the Versa Lab system, the voltage compliance was set and it swept the current starting from $0 \rightarrow 70$ mA $\rightarrow 0 \rightarrow -100$ mA $\rightarrow 0$. The

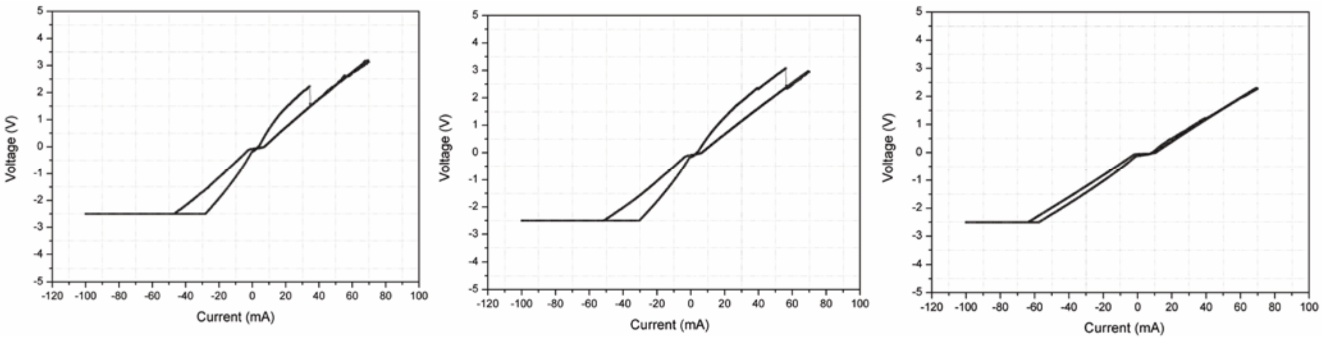

Figure 7. Low temperature *I–V* characteristics of Cu/ZrO_2 (300 °C)/ATO device: (**a**) 200, (**b**) 100 and (**c**) 50 K.

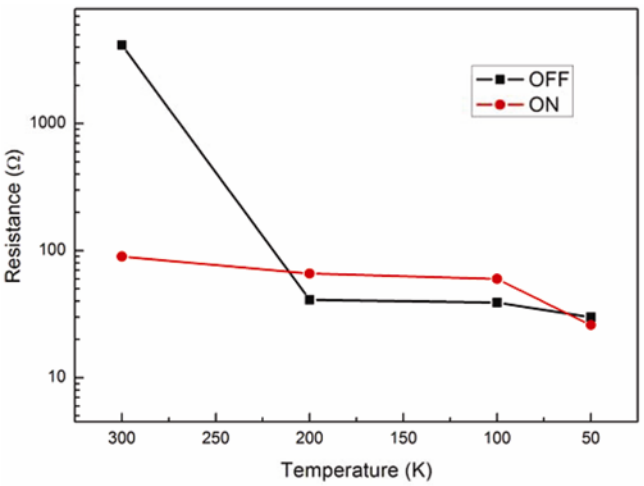

Figure 8. Diagram of temperature impact on ON and OFF resistance.

current swept starting from low resistance state. Figure 7 shows the *I–V* sweep cycles at low temperature (a) 200, (b) 100 and (c) 50 K. For these curves, it still shows the typical bipolar resistive switching curves even when temperatures decrease to below zero. Therefore, when the temperature decreased, the ratio of R_{off}/R_{on} decreased from 1·7 at 200 K down to 1·1 at 50 K. The reset process of this device is also possible under negative bias, indicating that Joule heating may be responsible for the rupture of the conductive filaments (Schindler *et al* 2007; Li *et al* 2010). Figure 8 shows resistances of ON (R_{on}) and OFF state (R_{off}) in the range from 50 to 300 K. When the temperature decreased, more Joule heating may be needed. On the other hand, when the temperature decreased, the Cu ions mobility also decreased (El Kamel *et al* 2006; Russo *et al* 2007). The resistance of ON state increases owing to the decreasing Cu which penetrates into ZrO_2. When the temperature decreases, R_{on} decreases obviously which is typical for electronic transportation in a Cu metal. It is indicated that the Cu metallic conduction filament has been formed in the ZrO_2 films. The metallic resistance as a function of temperature can be written as (Russo *et al* 2007; Liu *et al* 2010):

$$R(T) = R_0[(1 + \alpha(T - T_0)], \quad (1)$$

where R_0 is the resistance at temperature T_0 and α the resistance temperature coefficient. Figure 8 also shows the temperature dependence of R_{off}. It is different from the R_{on}. For the R_{off} curve, it changes slightly when the temperature decreases. In the OFF state, the carrier transportation is complicated. Multi-conductive mechanisms may be included.

4. Conclusions

We fabricated through sol–gel deposition of ZrO_2 thin films post-annealed at 300, 500 and 700 °C. Reproducible *I–V* curves can be obtained with these samples at room temperature (300 K). The ZrO_2 thin film annealed at 300 °C in Cu/ZrO_2/ATO device can also be operated resistive switching sweep cycles at 200, 100 and 50 K. The reasons for the higher leakage current could be the existence of grain boundaries and more defects (like twin crystals) in the structure because of higher annealing temperatures. An increase in the annealing temperatures between 300 and 700 °C led to the electronic disorder due to oxygen deficiency at a higher oxidation temperature. It was found out the ratio of R_{off}/R_{on} reduced at this low temperature. When the *I–V* measurements temperature decreases, R_{on} decreases obviously which is typical for electronic transportation in a Cu metal.

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