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Characteristic modification by inserted metal layer and interface graphene layer in ZnO-based resistive switching structures*

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ZnO-based resistive switching device Ag/ZnO/TiN, and its modified structure Ag/ZnO/Zn/ZnO/TiN and Ag/graphene/ZnO/TiN, were prepared. The effects of inserted Zn layers in ZnO matrix and an interface graphene layer on resistive switching characteristics were studied. It is found that metal ions, oxygen vacancies, and interface are involved in the RS process. A thin inserted Zn layer can increase the resistance of HRS and enhance the resistance ratio. A graphene interface layer between ZnO layer and top electrode can block the carrier transport and enhance the resistance ratio to several times. The results suggest feasible routes to tailor the resistive switching performance of ZnO-based structure.

Keywords: resistive switching, ZnO, graphene, multilayer thin films

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1. Introduction

Resistive switching (RS) has aroused lots of interest for its potential applications in the resistive random access memory devices.[1] The resistive switching phenomenon has been widely observed in the structures based on transition metal oxides, such as TiN/ZnO/Pt,[2] Cu/HfO_2/Pt,[3] TiN/HfO_x/ITO,[4] Pt/TiO_2/Pt,[5] Ag/ZnO/Pt,[6] Ti/CeO_2/Pt,[7] Pt/Mn_3O_4/Nb:$SrTiO_3$,[8] Cu/SiO_x/Al,[9] and Ti/ZrO_2/Pt.[10] The main stream of RS materials is metal oxide. RS mechanisms involve the conductive filaments and interface effects between oxide matrix and electrodes.[11] The existence and roles of conductive filaments in oxide matrix were detected during RS process. Both oxygen vacancies and oxygen ions can form conductive filaments, leading to RS behavior. Metal cations in RS oxide and from the electrochemical process in active electrodes can also constitute conductive filaments.[12]

Most RS devices in previous research are sandwiched structure, and other RS structures, such as core–shell nanowires[13] and stepped oxide films[14] were also reported. The RS structure based on oxide stacked thin films[15] and oxide heterostructure resistive memory[16] were studied recently. The matrix-modified structure by inserted metal layer in oxides[17] and nitrides,[18] were reported with modified RS characteristics. A Ta thin layer between bottom electrode and NiO functional layer were reported as enhancing the ON/OFF ratio significantly.[19] Interface-modified RS structure by graphene in Ta_2O_5[20] and HfO_x[21] were studied and suggested that inserted graphene layer could effectively control the RS performances.

In the present article, we study a ZnO-based RS structure with active Ag top electrodes. RS structures with metal and graphene inserted layer are also studied. The results show that an inserted thin metal layer or a graphene layer can significantly modify the characteristics of this ZnO-based RS structures.

2. Experimental details

The resistive Ag/ZnO/TiN structure is shown in Fig. 1(a). The TiN layers were deposited by ion-beam-assisted deposition on SiO_2/Si substrates as the bottom electrodes; the experimental details of the preparation of TiN layers can be found in Ref. [22]. The functional ZnO layer was deposited by magnetron sputtering using a ZnO target in a pure argon atmosphere; the method and parameters were mentioned in Ref. [23]. The top Ag electrodes were prepared by e-beam evaporation with a thickness of about 50 nm. No post-annealing was performed in the whole process. The metal top electrode (TE) is sized ϕ0.5 mm. Figure 1(b) shows the morphology of the cross section of a sample, which was analyzed by a scanning electron microscope (SEM) of Zeiss Supra55. The ZnO layer is about 70 nm in thickness.

In order to study the influence of metal layers in RS devices, we inserted a Zn thin layer in resistive ZnO layer. Figure 1(c) is a diagram of this Ag/ZnO/Zn/ZnO/TiN structure. The thin Zn layers between the two ZnO layers were *in-situ* deposited by DC sputtering. The thickness of the Zn layer is

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about 2 nm and 4 nm, respectively, which is measured by a quartz oscillator. The thickness of either ZnO layer is about 35 nm. Additionally, we studied the effects of the interface graphene layer on the RS behavior. A single-layer graphene was inserted between ZnO layer and Ag top electrode. A diagram of the Ag/graphene/ZnO/TiN structure is in Fig. 1(d). The graphene layer is fabricated by chemical vapor deposition on copper substrates, and then was transferred to the ZnO/TiN/SiO_2/Si substrate. The preparation experiments of graphene follow Ref. [24]. All the RS characteristics in this work were measured by Keithley 2636A system.

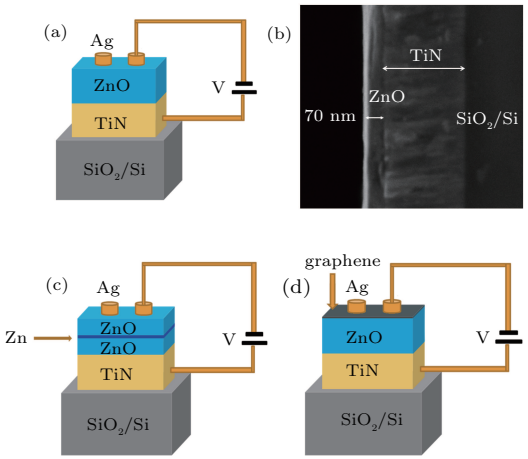


Fig. 1. (color online) Diagrams of RS structures. (a): Ag/ZnO/TiN structure; (b): SEM morphology of its cross section; (c): Ag/ZnO/Zn/ZnO/TiN structure; (d): Ag/graphene/ZnO/TiN structure.

3. Results and discussion

Figure 2(a) shows the surface micrographs of the ZnO films, which were characterized by tapping mode of an atom force microscopy (AFM, Nanoscope IIIa) with a silicon tip. We can see the surface of the films is smooth, continuous, and dense.

Figure 2(b) shows the x-ray diffraction (XRD) patterns of the films. Only ZnO (002) peak appears, and no other diffraction peak emerges, indicating a *c*-oriented hexagonal wurtzite structure of ZnO was exhibited.

As a control group, the RS characteristics of Pt/ZnO/TiN structure with the same sizes were studied. Figure 3(a) shows the *I*–*V* curve of the Ag/ZnO/TiN and the Pt/ZnO/TiN structure. Except for the TE materials, there is no structural difference between the Ag/ZnO/TiN and Pt/ZnO/TiN structure devices. The scanning sequence is indicated with arrows, and the positive voltage is defined from TiN to TE. The scanning speed is 4.0 V/s. We can see a bipolar RS characteristic in both structures. However, the current of the structure with Ag TE is much larger than that of the structure with Pt TE in both high resistance state (HRS) and low resistance state (LRS). Many charged particles, such as V_os, oxygen ions, Zn ions, can possibly serve as carriers. As an active metal, Ag^+s and electrons deriving from electrochemical process can be transported between TE and bottom electrodes as carriers to play an important role in RS behavior. So Ag TE can give larger current than Pt TE.

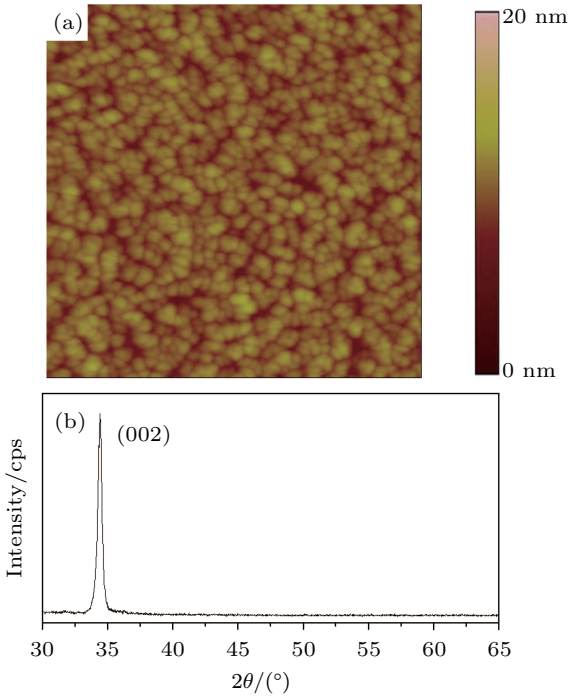


Fig. 2. (color online) The 1.0 μm × 1.0 μm AFM surface morphology (a) and XRD pattern (b) of the ZnO layer.

Figure 3(b) shows the comparison of the *I*–*V* characteristics under positive bias with that under negative bias. We can see the RS hysteresis loop is asymmetric. In low voltage region, the positive and negative *I*–*V* characteristics are similar to each other in both LRS and HRS. To clarify the RS mechanism, the *I*–*V* curve of the Ag/ZnO/TiN structure was also plotted using a log–log scale, as shown in Fig. 3(c). In the low-voltage region of the HRS, the slope is approximately 1, which corresponds to Ohm's law ($I \propto V$). This Ohmic characteristic may be caused by the hopping of thermally generated point defects dominated by V_os and Zn ions.[25] In the larger voltage region of the HRS, the structure is more conductive under negative bias than that under positive bias as shown in Fig. 3(b). The increment of the current under negative bias can be contributed to Ag^+s, considering Ag^+s infiltrated into ZnO layer under negative voltage. For the existence of interface barrier, Ag^+s can enter ZnO layer only under relatively higher voltage. Based on these results, the active TE is an effective method to tune the RS behavior of the ZnO-based structure. A steep increase in current was suddenly observed according to the increase of the voltage, as shown in Fig. 3(c). This behavior corresponds to Child's law ($I \propto V^2$), which is consistent with a space charge limited current (SCLC) mechanism.[26] On the other hand, in the almost entire voltage region of the LRS, the slope is approximately 1, which corresponds to Ohm's law,

and this RS mechanism can be explained by a metallic conductive filament model. For the ZnO layers prepared in the oxygen-absent environment, the main component of conductive filaments are interstitial Zn ions and oxygen vacancy V_os.

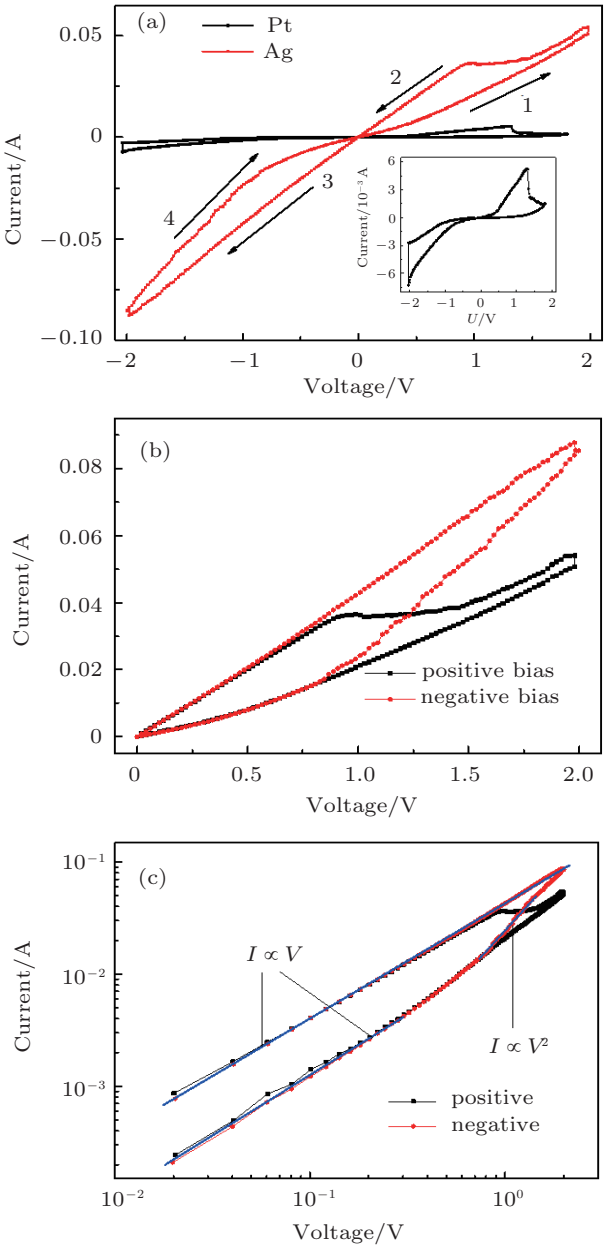


Fig. 3. (color online) Properties of Ag/ZnO/TiN and Pt/ZnO/TiN structures. (a): *I–V* characteristics of the structure, the inset indicating that of the Pt/ZnO/TiN structure, the arrows indicating the scanning directions; (b): the comparison of positive bias with negative bias; (c): *I–V* characteristics in the log–log plot.

The RS behavior can be influenced by inserting a metal layer or nano particles in oxide matrix. Figure 4 shows the RS properties of the Ag/ZnO/Zn/ZnO/TiN structure. The lowest point of the *I–V* curves with an inserted Zn shifts from the zero voltage to negative bias. This shift can be attributed to the effects of the Schottky junction. We can see that the current in LRS of the structure with 2-nm thick Zn layer (blue curve) is larger than that without Zn layer (red curve). However, the HRS current of the device with inserted Zn layer is much lower. The Zn layers play two roles in the RS process. First, the reaction of Zn with oxygen from the interface produces Zn ions and more V_os in the ZnO layer.[17] Under the action of the bias voltage, these V_os and Zn ions constitute much more conductive filaments in the two ZnO layers, increasing the current in LRS. Therefore, the whole device can be regarded as two series metallic resistors. On the other hand, a thicker Zn layer builds a barrier with condensed Zn ions to block the charged carrier. A Zn layer of 2 nm is too thin to form a blocking barrier in LRS, and the former role of the inserted Zn layer is dominating. The 2-nm thick Zn layer is not necessarily a film, but Zn nano particles. These nano particles become centers connecting and strengthening the conductive filaments,[25] which hence enlarge the current. For the Zn layer with 4-nm thickness, the barrier forms and charge carrier transport is blocked to some extent. Therefore, the LRS current of the device inserted with 4-nm Zn layer is lower than that with 2-nm Zn layer. In the Pt/Ta_2O_5/Ta/Ta_2O_5/Pt structure,[17] the RS behavior is also dominated by Zn and V_o filaments, and the thickness of Ta layer can also cause different effects on its RS characteristics.[17]

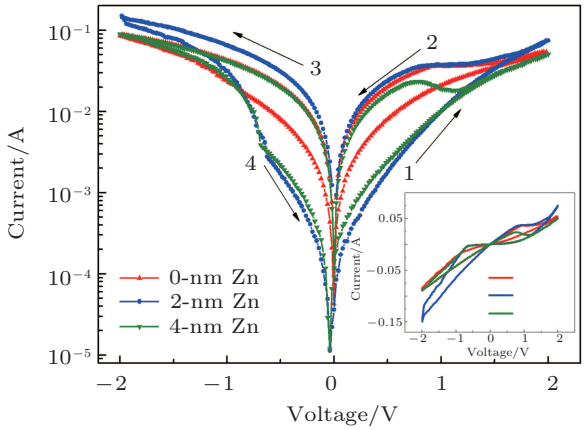


Fig. 4. (color online) The *I–V* characteristics of the Ag/ZnO/Zn/ZnO/TiN structure inserted with Zn layer in different thicknesses, the inset shows its *I–V* characteristics plotted in linear scale.

Importantly, the current of the high resistance state in the Ag/ZnO/Zn/ZnO/TiN devices is significantly lower than that of the device without inserted layer, which is also attributed to the barrier effect of the Zn layer. This barrier is enough to block the hopping of charged point defects and reduce the current in HRS, though it cannot seriously block the transport along the filaments in LRS. Figure 5 shows the repetition of the resistance switching of Ag/ZnO/Zn/ZnO/TiN structure between HRS and LRS. We examined the devices up to 100 times. The resistance values were determined by the reciprocal of the slope of the *I–V* curves at 0.5 V. We can see the switching properties are stable within the experimental range. The resistance ratio is 3, 19, 8 for the device of ZnO, 2-nm Zn inserted ZnO, and 4-nm Zn inserted ZnO, respectively. A consequent result of the inserted Zn layer is enhancement of the

resistance ratio, especially in the device with very thin inserted layer.

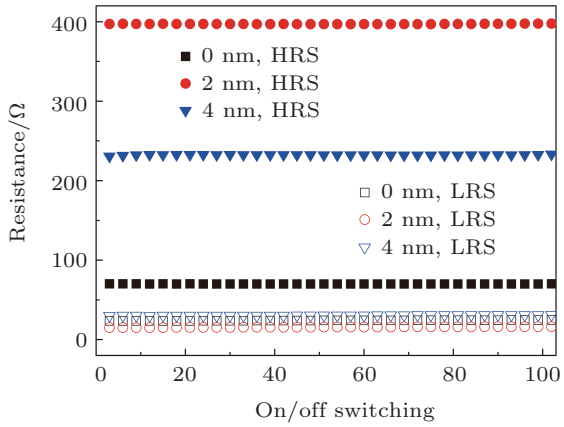


Fig. 5. (color online) The repetition of the resistance switching of the Ag/ZnO/Zn/ZnO/TiN structure between HRS and LRS; only one is indicated each three times for the purpose of clarity.

Graphene could also serve as a blocking barrier layer in RS devices. Figure 6 shows the RS characteristics of the Ag/graphene/ZnO/TiN structure. A shift from the zero voltage to negative bias of the lowest point of the graphene-modified device resulting from the Schottky junction can also be seen. It can be seen that the current of the structure is smaller than that without the graphene layer, in both LRS and HRS. The resistance ratio Ag/graphene/ZnO/TiN structure is several times larger than that in Ag/ZnO/TiN structure. Graphene was used as a barrier to prevent charged particles from further migrating deep into the metal electrodes,[27] because of its high out-of-plane resistance and high interfacial resistance of the graphene/oxide interface. Furthermore, graphene is chemically stable, and can effectively block the redox reaction between electrodes and oxide layer. Therefore, graphene can reduce the V_o quantity. Inserting the graphene into this RS structure limits the migration of oxygen and Zn ions further into the top electrode and serves as a monitor of the carrier movement during SET and RESET programming. The inserted graphene layer also provides a high built-in series resistance to reduce RESET current and power consumption. In this graphene-modified structure, oxygen plays the main role in the RS process. The oxygen-related RS process in this structure can be modelled as reported in Ref. [21]. The process includes movement of oxygen ions to graphene during SET, capture of oxygen ions by graphene, movement of oxygen ions laterally on graphene, formation of covalent bond with graphene, followed by movement of oxygen ions back to ZnO during RESET. The migration of the oxygen ions are aided by the Joule heating generated during the programming event. The influences of the inserted graphene layer on the chemical reaction and migration of carrier were also found in TaO_x-based[20] and NiO-based RS structures.[28]

Figure 6 tells that the current of HRS was reduced more by graphene layer than that of LRS. In the LRS, conductive filaments are the main conductive mechanism. The distance between the filament tips and top electrodes is very small, and a strong electrical field is established. Metal and oxygen ions can pass through the graphene layer with considerable possibility, which is similar to the phenomena of point discharge. Therefore the current in LRS is not reduced very much. In HRS, the main conductive mechanism is the hopping diffusion of charged point defects. The diffusion is blocked by the compact graphene and the current in HRS is reduced significantly, leading to excellent performance for the application of this RS structure. Figure 7 shows the repetition of the resistance switching of Ag/graphene/ZnO/TiN and Ag/ZnO/TiN structure between HRS and LRS. We can see the switching properties are stable within the experimental range. The resistance ratio is 3 and 15 for the device of ZnO and graphene/ZnO respectively. Resistance ratio can be enhanced several times by graphene.

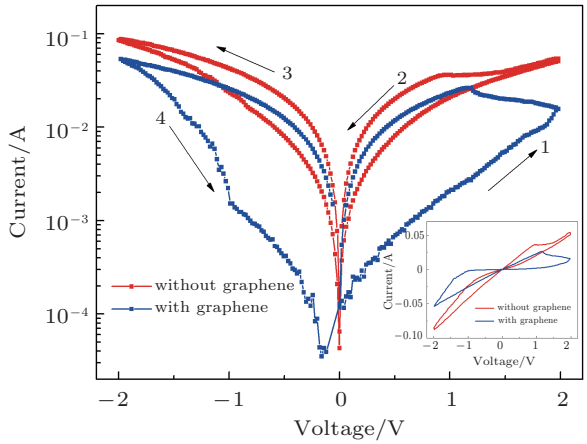


Fig. 6. (color online) The *I*–*V* characteristics of the Ag/graphene/ZnO/TiN structure. The inset shows its *I*–*V* characteristics plotted in linear scale.

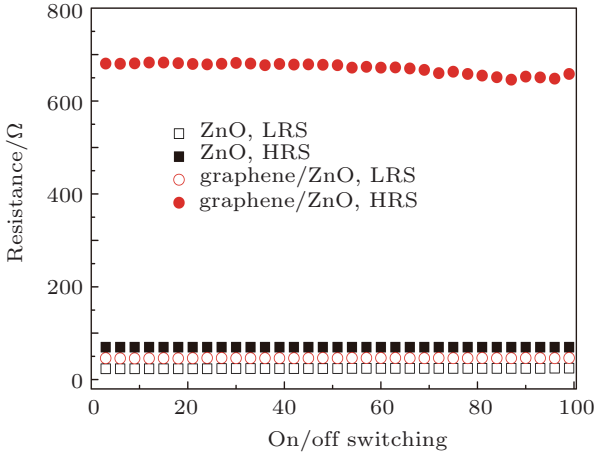


Fig. 7. (color online) Repetition of the resistance switching of the Ag/graphene/ZnO/TiN and Ag/ZnO/TiN structures between HRS and LRS; Only one is indicated each three times for the purpose of clarity.

However, the resistance ratio values in the work are much lower than those reported in references of ZnO-based devices.[29,30] We think the ZnO matrix properties limited the RS performance of the devices. Much work can be put on

the deposition process of ZnO layers to improve the performance of the ZnO matrix. Anyway, the enhancement of the resistance ratio resulting from the modification by thin metal inserted layer and interface graphene layer, provides routes to excellent performance of this RS structure.

4. Conclusions

We studied the influences of active Ag electrodes, inserted metal layers, and graphene interface layers on the RS properties of the ZnO-based structure. The conductive filaments and hopping of point defects are the main RS mechanisms in LRS and HRS, respectively. Metal ions and oxygen are the main carriers of the RS process. The migration of Ag^{+}s from electrodes also contribute to the RS behavior. A thin inserted metal layer and an interface graphene layer can increase the resistance in HRS and enhance the resistance ratio consequently. Interface graphene layers can enhance the resistance ratio several times. The results suggest a feasible route to tune and enhance the RS performance of the ZnO-based structure by inserted and interface layers.

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