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Solid State Communications

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Effect of defect content on the unipolar resistive switching characteristics of ZnO thin film memory devices

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ARTICLE INFO

Article history:

Received 28 November 2011

Received in revised form

21 March 2012

Accepted 27 April 2012

by M. Wang

Available online 3 May 2012

Keywords:

A. Zinc oxide

A. Thin film

D. Resistive switching

ABSTRACT

In this study, unipolar resistive switching (URS) characteristics in ZnO thin film memory devices were systematically investigated with variable defect content. ZnO films displayed typically URS behavior while oxygen-deficient ZnO_{1-x} films did not show resistive switching effects. The devices with two intentional Ohmic interfaces still show URS. These results show that appearance of URS behavior can be dominated by initial oxygen vacancy content in ZnO thin films. Modest increase in oxygen vacancy content in ZnO films will lead to forming-free and narrower distributions of switching parameters (set and reset voltage, high and low resistance states). It indicates that controlling the initial oxygen vacancy content was an effective method to enhance the URS performance.

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1. Introduction

Resistance random access memory (RRAM) is considered as a very promising candidate for next generation nonvolatile memory due to its fast switching speed, high density, and low power consumption [1,2]. External electrical bias or pulse induced reversible resistive switching effect is generally utilized in these devices [1,3,4]. With the dependence on the polarity of applied voltage, the resistive switching effect is classified into unipolar and bipolar resistive switching behaviors (URS and BRS) [4,5]. Compared with BRS behavior, the URS exhibits faster reset speed, larger OFF/ON ratio, and require simpler peripheral circuit [6,7]. Up to now, resistive switching effect has been reported in many perovskite oxides and binary metal oxides thin films [4]. Interestingly, almost all the reported resistive switching oxides could display URS behavior, even previously reported BRS multinary oxides (LCMO [8], PCMO [9], and STO [10]). Lee *et al.* [11] also developed a material-independent scaling theory to explain the URS behavior. Although the URS may be a material-independent behavior, few works focused on the determining factor for the URS behavior.

It has been widely accepted that URS behavior was attributed to the rupture and recovery of percolating defect filament initialized by

forming process [12–15], which was also well simulated by the random circuit breaker model [7] with a defects network. It is reasonable that the defects forming the filament could be divided into the initial defects and new-generated defects in the forming process. Besides, both the interfacial state and the resistance state of the sandwich structure devices are related with the initial defect content [4,16]. So it is necessary to investigate the effect of the initial defect content on URS characteristics. For ZnO-based RRAM devices, ZnO is a typical n-type semiconductor owing to oxygen vacancy and interstitial zinc ion and many studies have indicated that electrons' hopping on oxygen vacancy filaments is responsible for its URS behaviors [17–20]. Based on above consideration, we systematically investigated the effect of initial oxygen vacancy content on URS characteristics of ZnO thin film memory devices. The results demonstrated that appropriate oxygen vacancy content in its initial state was a determining factor for the appearance of URS behavior, and control the initial oxygen vacancy content of ZnO films is an effective method for the improvement of the URS performance.

2. Experimental details

ZnO thin films were deposited by pulsed laser deposition (PLD) on Pt/Ti/SiO₂/Si substrates at 200 °C using a ceramic ZnO target. For comparative investigation, three types of ZnO samples with

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different deposition condition were fabricated; Oxygen-deficient ZnO_{1-x} was deposited for 80 min under vacuum. Nearly stoichiometric ZnO thin films were deposited for 80 min under an oxygen partial pressure of 2 Pa and oxygen plasma was used for assisting growth. Stacked $\text{ZnO}_{1-x}/\text{ZnO}/\text{ZnO}_{1-x}$ thin films were firstly deposited for 20 min under vacuum and then for 40 min under an oxygen partial pressure of 2 Pa (oxygen plasma), subsequently deposited for 20 min under vacuum. The thickness of ZnO_{1-x} , ZnO, and stacked $\text{ZnO}_{1-x}/\text{ZnO}/\text{ZnO}_{1-x}$ thin films were all approximately 120 nm. XPS measurements (Thermo Scientific ESCALAB 250) were performed in ultra-high vacuum with a base pressure of 10^{-10} mbar and were using the VG Avantage4.53 software system. The measurement chamber is equipped with a monochromatic Al (K_{α}) X-ray source providing photo with $h\nu=1486.6$ eV and a FLOOD GUN to avoid surface charging. Its energy resolution is 0.49 eV. In order to examine the chemical state of each element, the samples were etched by Ar^+ bombardment ($\sim 10^{-5}$ Torr) with the energy of 1 kV and a current of 1 μA . The position of the C 1s peak was taken as a standard (with a bounding energy of 280.50 eV).

For electrical testing, 50 nm-thick Pt top electrodes with a diameter of 100 μm were deposited on these films by electron beam evaporation with a metal shadow mask. All the resistance values of initial state (before forming process, R_{initial}), high resistance state (HRS, R_{off}) and low resistance state (LRS, R_{on}) were measured at 0.01 V. The current–voltage (I – V) curves of these devices were examined by a Keithley 2410c source meter unit with the bottom electrodes being grounded.

3. Results and discussions

Fig. 1(a) and (b) show the initial I – V characteristics of Pt/ ZnO_{1-x} /Pt devices and Pt/ZnO/Pt devices in their pristine states. The resistance values of the sandwich structure devices could be regarded as two interfacial resistances in series with bulk resistance of the films. The Pt/ ZnO_{1-x} /Pt devices have a large leakage current with a low R_{initial} of 11 Ω and do not display any resistive switching behavior. The linear I – V curve [Fig. 1(a)] indicates Ohmic contacts at both Pt/ ZnO_{1-x} interfaces. On the contrast, the Pt/ZnO/Pt devices show dual rectifying I – V curve [Fig. 1(b)], revealing Schottky contacts at both Pt/ZnO interfaces. Typical URS behavior was observed, as shown in Fig. 1(c). The R_{initial} of the Pt/ZnO/Pt devices was $3 \times 10^6 \Omega$ and the forming process switched the device to a low LRS of 30 Ω . Then the URS behavior was observed.

In order to investigate the nature of different resistance states and the resistive switching for the ZnO and ZnO_{1-x} films, X-ray photoelectron spectroscopy (XPS) was employed to examine the chemical composition and the existence of defects. The film surface was etched for 5 s to avoid interference of surface absorbed oxygen. Fig. 2 shows the XPS spectra of O 1s peak and its Gaussian fitting results for ZnO_{1-x} and ZnO thin films. O 1s of ZnO thin films were fitted by three Gaussian components at ~ 529.7 eV, ~ 530.5 eV and ~ 532.0 eV [21,22]. 532.0 eV is usually attributed to chemically absorbed oxygen at the surface. The component of lowest bounding energy at 529.7 eV is associated with O^{2-} in ZnO structure. For ZnO films, O^{2-} content was increased compared with ZnO_{1-x} films. Approximate composition (Zn/O in at%) of ZnO films was 51:49 while it was 58:42 in ZnO_{1-x} films. The component of medium bounding energy at 530.5 eV is related to O^{2-} of oxygen deficiencies. Changes in the intensity of this component mainly connected in part to the variations in the content of oxygen vacancies. ZnO films exhibited a distinct reduction in the signal for oxygen vacancies. Considering ZnO was a typical n-type semiconductor owing to oxygen vacancies and interstitial zinc ion, all the interfacial and bulk resistances could be determined by the oxygen vacancy

Fig. 1. (Color online) The I – V curves of the (a) Pt/ ZnO_{1-x} /Pt device and (b) Pt/ZnO/Pt device in their pristine states. (c) Forming and URS I – V curves for Pt/ ZnO_{1-x} /Pt device.

Fig. 2. (Color online) XPS spectra of O 1s core levels for ZnO_{1-x} and ZnO thin films.

content [4]. For Pt/ ZnO_{1-x} /Pt devices, it is clear that the large quantity of oxygen vacancies would eliminate the Schottky barrier (Pt/ZnO) and decreased the bulk resistance dramatically. The reduction in quantity of oxygen vacancies in ZnO films would increase the bulk resistance and cause the depletion layer wider, resulting in a large R_{initial} and the dual rectifying I – V curve.

Since ZnO films displayed typically URS behavior while ZnO_{1-x} films did not show any resistive switching effects, we could conclude that the initial oxygen vacancy content was a determining factor for appearance of URS behavior. Nevertheless, whether the Schottky interfaces in the Pt/ZnO/Pt devices play an essential for URS behavior remains unclear. In this regards, we further

Fig. 3. (Color online) (a) The I - V curves of the Pt/ZnO_{1-x}/ZnO/ZnO_{1-x}/Pt device in its pristine states. Inset is schematic configuration of stacked Pt/ZnO_{1-x}/ZnO/ZnO_{1-x}/Pt structure. (b) Forming and URS I - V curves for the Pt/ZnO_{1-x}/ZnO/ZnO_{1-x}/Pt device.

fabricated the stacked Pt/ZnO_{1-x}/ZnO/ZnO_{1-x}/Pt devices to eliminate the Schottky interfaces. The schematic picture was shown in the inset of Fig. 3(a). Due to the Ohmic contact at Pt/ZnO_{1-x} interface, the Pt/ZnO_{1-x}/ZnO/ZnO_{1-x}/Pt devices exhibit an Ohmic behavior [Fig. 3(a)] and have much lower R_{initial} (2000 Ω). URS behavior was still observed, as shown in Fig. 3(b). It indicates that the Schottky interface is not an essential condition for URS behavior. For the Pt/ZnO/Pt devices, the initial existed oxygen vacancies and the new generated oxygen vacancies would drift and accumulate at the cathode in the forming process, changing the cathode Schottky interface to Ohmic contact. After the oxygen vacancies filament formed, the anode Schottky interface was also changed to Ohmic contact and the device was switched to LRS.

In order to further investigate the effect of oxygen vacancy content on the URS characteristics of ZnO thin film memory devices, the ZnO films were annealed at vacuum (600 $^{\circ}\text{C}$, 20 min) to increase the oxygen vacancy content and annealed at oxygen atmosphere (600 $^{\circ}\text{C}$, 40 min) to decrease the oxygen vacancy content. The oxygen annealed, vacuum annealed, and as prepared (unannealed) ZnO thin films are respectively mentioned as ZnO-Oxy, ZnO-Vac, and ZnO-As in the following discussion.

Wide distribution of resistive switching parameters is considered as one of major obstacles for the application of RRAM [7,23]. The distribution of resistive switching parameters for the Pt/ZnO-Oxy/Pt, Pt/ZnO-Vac/Pt and Pt/ZnO-As/Pt devices was measured, as shown in Fig. 4(a)–(d). The data was obtained from 50 times continuous sweeping cycles. Compared with unannealed sample, the Pt/ZnO-Vac/Pt devices show narrower distribution of switching voltage while the Pt/ZnO-Oxy/Pt devices exhibit wider, especially the set voltage. Importantly, the set voltage and reset voltage of Pt/ZnO-Vac/Pt device shows an evident window, which

Fig. 4. (Color online) Measurement of Pt/ZnO-As/Pt, Pt/ZnO-Vac/Pt and Pt/ZnO-Oxy/Pt devices for continuous 50 cycles in DC sweeping mode. (a), (b) and (c) Set and Reset Voltage distributions. (d) R_{off} and R_{on} distributions.

is essential to avoid wrong operation. Fig. 4(d) shows the distributions of R_{off} and R_{on} . Although the ratio of $R_{\text{off}}/R_{\text{on}}$ is decreased for the Pt/ZnO-Vac/Pt device (higher R_{on} and lower R_{off}), both fluctuations of R_{off} and R_{on} for the Pt/ZnO-Vac/Pt devices are narrowed down greatly compared with Pt/ZnO-Oxy/Pt and Pt/ZnO-As/Pt devices. In

Fig. 5. (Color online) Statistics of resistive switching parameters in Pt/ZnO-As/Pt, Pt/ZnO-Vac/Pt and Pt/ZnO-Oxy/Pt devices, respectively.

a word, narrower distributions of switching parameters (set and reset voltage, R_{HRS} and R_{LRS}) were obtained in the Pt/ZnO-Vac/Pt devices.

The variation of URS switching parameters for Pt/ZnO-Oxy/Pt, Pt/ZnO-Vac/Pt, and Pt/ZnO-As/Pt devices were shown in Fig. 5, each result was examined from measurements on 30 devices. As shown in Fig. 5(a), significantly reduced $R_{initial}$ (2500 Ω) was observed in Pt/ZnO-Vac/Pt devices and increased highly $R_{initial}$ ($5 \times 10^8 \Omega$) in the Pt/ZnO-Oxy/Pt devices. Since oxygen vacancies in ZnO are known to act as n-type dopants, it is reasonable that the device with more oxygen vacancies shows a better conductivity. The forming voltage of these devices has the similar trend with that of $R_{initial}$. As shown in Fig. 5(b), the Pt/ZnO-Oxy/Pt devices have the highest forming voltage which is about 4.9 V; the Pt/ZnO-As/Pt devices have a moderate value of 3.8 V; while Pt/ZnO-Vac/Pt devices have the lowest forming voltage among the three, which is about 2 V. It is worth noting that the forming voltage of 2 V in Pt/ZnO-Vac/Pt devices is low enough and has the same magnitude with set voltage. In another word, the Pt/ZnO-Vac/Pt devices can initially switch from HRS without forming process. However, it should be noticed that if we continue to increase the annealing time at vacuum, the invalid storage points will increase dramatically due to large leakage current. Fig. 5(c) and (d) shows the variation of reset current and R_{on} . The Pt/ZnO-Vac/Pt devices show lower reset current and higher R_{on} , while the Pt/ZnO-Oxy/Pt devices exhibit higher reset current and lower R_{on} . Therefore, by increasing the oxygen vacancy content in the Pt/ZnO/Pt device, better URS properties (forming-free and lower reset current) could be obtained.

According to the existing switching mechanisms in ZnO thin films, a possible explanation for the improvement (vacuum-annealed samples) and degradation (oxygen-annealed samples) of URS characteristics in ZnO thin film memory devices could be depicted as follows. The vacuum annealing will increase oxygen

vacancy content and oxygen annealing will decreasing oxygen content. For the low oxygen vacancy content films (ZnO-Oxy), more new generated oxygen vacancies are required to form the filament in the forming process so it need a higher forming voltage. Besides, due to the large contact resistance at the two Schottky interfaces in the low oxygen vacancy content devices, the forming voltage would drop a lot at the Schottky interfaces and the switching layer is distributed a part of the forming voltage. So the Pt/ZnO-Oxy/Pt devices require a higher forming voltage to generate enough oxygen vacancies while Pt/ZnO-Vac/Pt devices demand lower forming voltage (even as low as the set voltage). Correspondingly, the small forming voltage will generate small size filaments and little numbers of filaments in ZnO matrix. This may be the cause of small R_{on} and reset current in Pt/ZnO-Vac/Pt devices, which means the small size filaments and little numbers of filaments require fewer quantity of heat to rupture them [24]. The small size filaments are easy to control [25] and fewer filaments could suppress random formation and rupture of filament for memory switching. So the Pt/ZnO-Vac/Pt devices exhibited narrow distribution of switching parameters. Based on above results and analysis, controlling the initial oxygen vacancy content should be an effective way to enhance the URS characteristics.

4. Conclusions

In summary, the effect of oxygen vacancy content on unipolar resistive switching characteristics of ZnO thin film memory devices was investigated. The content of oxygen vacancy is not only a crucial factor that governs the appearance of URS behavior, but also has significant influence on the URS characteristics. This indicated that controlling the initial oxygen vacancy content was an effective method to enhance the URS performance.

Acknowledgments

This work was financially supported by Major Program of National Natural Science Foundation of China (Grant No. 90922026), Major State Basic Research Development Program (Grant No. 2009CB623304), and National Natural Science Foundation of China (Grant No. 51072216).

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