Resistive Switching Characteristics of Al₂O₃/ZnO Bilayer Thin Films for Flexible Memory Applications

Zhi-Peng Wu, Jun Zhu, and Li-Bin Fang

Abstract—Unipolar resistive switching behaviors of the ZnO and Al₂O₃/ZnO films fabricated on flexible substrates by pulse laser deposition were studied in this paper. The films were deposited at room temperature without post-annealing treatment during the process. X-ray diffraction results indicated that ZnO film has a dominant peak at (002). Scanning electron microscopy observation showed a columnar grain structure of the ZnO film to the substrate. The bilayer device of Al₂O₃/ZnO films had stable resistive switching behaviors with a good endurance performance of more than 200 cycles, high resistive switching ratio of over 10⁵ at a read voltage of 0.1 V, which is better than that of the single oxide layer device of ZnO film. A possible resistive switching filamentary mode was demonstrated in this paper. The conduction mechanisms of high and low resistance states can be explained by space charge limited conduction and Ohmic’s behaviors. The endurance of the bilayer (BL) device was not degraded upon bending cycles, which indicates the potential of the flexible resistive switching random access memory applications.

Index Terms—Flexible, pulsed laser deposition, resistive switching, ZnO thin film.

1. Introduction

Resistive random access memory (RRAM) is one of the most promising emerging nonvolatile memories due to its simple structure, high operational speed, and high density integration, which uses a material(s) that changes the resistance between a high resistance state (HRS) and a low resistance state (LRS) when an electric field (voltage or current) is induced[4]. The type of these memory devices is metal-insulator-metal (MIM) structure. According to the dependence of the electric field polarity, the resistive switching (RS) can be classified into two types: Bipolar resistive switching (BRS) and unipolar resistive switching (URS). For the BRS, the switching from HRS to LRS occurs at one electric polarity, whereas the reverse switching takes place to the opposite field. In contrast, the URS does not rely on the electric polarity. Up to now, many binary transition metal oxides such as TiO₂[7], CuO[8], and NiO[9], perovskite oxides[10],[11], and some organic materials[12] have been reported for the applications to RRAM because of their excellent characteristics.

Recently, flexible electronics, which possess favorable qualities including light weight, low cost, and good endurance under bending conditions have drawn attention from researchers in the past years[10]-[12]. As the memory is the fundamental component of all modern electronic systems, the information storage components require advanced research on flexible memories. Until now, lots of research works for the applications of flexible RRAM devices at low temperatures or without post annealing were carried out to investigate the performance of the devices under bending conditions[13]-[15], the RS characteristics were not degraded upon bending and some of them were improved.

ZnO film has been widely studied as the active layer because of its good performances of the RS behavior such as the coexistence of unipolar and bipolar switching behaviors and the transparent and flexible applications aspect[16]-[19][20]. However, there are large obstacles in ZnO single layer for practical applications including the poor endurance, low memory window, and non-uniformity in the distribution of resistance states[11],[16],[17]. To improve the RS behavior, doping and multilayer are two effective methods[18],[19],[20]. For the multilayer structure, heterostructure and interface play important roles in the resistance switching effect. The Al₂O₃ thin film has many advantages, such as complementary metal oxide semiconductor (CMOS) compatibility, high breakdown voltage, and easy formation of a stable oxide thin film at low temperatures. RS characteristics have also been observed in Al₂O₃[20]. In this paper, ZnO single oxide layer (SL) and Al₂O₃/ZnO bilayer (BL) as the functional layers in the MIM structure are fabricated on a flexible substrate at room temperature (RT). The current-voltage (I-V) characteristics, retention, and endurance are analyzed.
2. Experimental Details

The experiment started with the fabrication of the 200-nm Au/20-nm Ti bottom electrode (BE) on cleaned polyethylene terephthalate (PET) substrate by electron beam evaporation. After that, a 180-nm ZnO thin film was deposited on the Au-coated PET substrate by pulse laser deposition (PLD) with ceramic ZnO target at RT for the SL device. A following 5-nm Al\textsubscript{2}O\textsubscript{3} thin film was deposited on the ZnO film for the BL device. For electrical measurement, 200-nm Au/20-nm Ti with an area of about 2.5×10\textsuperscript{-4} cm\textsuperscript{2} was deposited by electron beam evaporation through a metal shadow mask as the top electrodes (TEs).

The crystalline orientation and microstructure of these thin films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Endurance characterizations were measured using an Agilent 4156C semiconductor parameter analyzer in the direct current sweep mode at RT. The retention time was carried out with 8×10\textsuperscript{4} s at the thermal stress of 60 °C. During the electrical measurements, the bias voltage was applied on the TE while the BE was grounded. To make the resistance switching possible, a forming process was indispensable, as our devices were HRS initially. In this work, 5 V and 7 V forming voltages were applied to achieve this process for the SL and BL devices. All these measurements were carried out at RT.

3. Results and Discussion

The XRD pattern of Al\textsubscript{2}O\textsubscript{3}/ZnO films deposited on the Au-coated PET substrate is shown in Fig. 1 (a). The ZnO films exhibit a polycrystalline pattern with a highly (002) preferred orientation. There is no peak of the Al\textsubscript{2}O\textsubscript{3} film, which reveals that the Al\textsubscript{2}O\textsubscript{3} film was amorphous at RT\textsuperscript{[31]}. The cross-section SEM image of the Al\textsubscript{2}O\textsubscript{3}/ZnO structure is shown in Fig. 1 (b); the result shows that the ZnO film has a columnar grain structure to the substrate. The Al\textsubscript{2}O\textsubscript{3} layer is too thin to be observed in the SEM image.

Fig. 2 shows the typical URS characteristics of the ZnO SL and Al\textsubscript{2}O\textsubscript{3}/ZnO BL devices. For the SL device, when the sweep voltage reaches 1.7 V (V\textsubscript{SET}), the current increases to the compliance current and the device switches to the LRS, then the device maintains at LRS. With the following sweep at the same positive bias voltage, the current decreases abruptly and the device switches from the LRS to HRS at 0.6 V (V\textsubscript{RESET}). The RS characteristics of the BL device are similar to the SL device, which shows the set voltage and reset voltage of 1.2 V and 0.3 V, respectively. It is worth pointing out that during the set process, a compliance current of 5 mA was setup to protect the device from the permanent breakdown, while there was no need of compliance current in the reset process.

Endurance is one of the most important properties for memory applications. Endurance cycles of both SL and BL devices were performed as shown in Fig. 3. The resistance states during the endurance cycles were measured with a readout voltage pulse at 0.1 V. Fig. 3 (a) shows the poor endurance and unstable distribution of the SL device. Both the two resistance states were large fluctuations, especially for HRS. The device was permanent breakdown after 33 cycles. The stability of the BL device was improved as shown in Fig. 3 (b), although some fluctuations in HRS, the dispersion of the resistance value is larger than three orders. The inset of Fig. 3 (b) demonstrates the distribution of the resistance at HRS and LRS taken from the endurance cycles. Both resistance states distributed within narrow ranges, which suggested that
the BL device had a good uniformity. Retention time is another important property of RRAM devices. For typical nonvolatile memory devices, the basic require of retention time is at least 10 years. The retention test usually needs to carry out with continual thermal stress at least up to 85 °C. While in this paper, the memory devices were fabricated on PET substrate, which has a glass transition temperature about 67 °C to 81 °C. A thermal stress up to 85 °C could lead to an irreversible shape change, which leads to devices failure directly. Therefore, the retention time of the BL device was measured at 60 °C with a stress voltage of 0.1 V as shown in Fig. 3 (c) and the retention time is extended to 10^8 s by linear extrapolation. The resistances of the HRS and LRS show no sign of deterioration over 8×10^8 s.

Compared with the SL device, the BL one demonstrated a higher HRS/LRS ratio, more slightly resistance variations of both LHS and HRS, and lower operation voltages of set and reset procedures. This indicates that the BL device has great potential for flexible memory applications.

Fig. 4 shows the mechanical flexibility of the BL flexible RS memory device, which demonstrates the feasibility of the applications for flexible nonvolatile RS memory devices with continuous bending up to 200 cycles. The substrate with the BL devices was bent from flat to surface with a radius of curvature about 6 mm (strain of ~1.5%). During the bending process, the resistance ratio between the HRS and LRS was maintained. The excellent endurance against continuous bending may be due to the columnar structure of the ZnO thin film [3] and the high ductility of the Au layer. These results indicate that the BL device shows the URS behavior with good electrical reliability, which is independent of the strain effect of the film.

For the mechanism of the URS, the model of conductive filaments (CFs) may explain the resistance switching behavior. In this model, the reset switching is a result of the rupture of the CFs in the insulator layer by Joule heat, while the mechanism for set switching is assumed to be the recovery of the ruptured CFs. For the SL device, the CFs are recovered and ruptured randomly during the set and reset processes. The improvement of RS characteristics of the BL device can be attributed to the Al₂O₃ layer. The dissociation energy for Al-O bond is 501.9 kJ/mol [22], which is much higher than the Zn-O bond of 284.1 kJ/mol [23]. It suggests that the bond between Al and O are much stronger than the Zn-O bond. The possible filamentary model of the BL device is shown in Fig. 5, which is similar to [23]. After the forming process, the generated oxygen vacancies take place to form the conductive filaments. The CFs connect the TE and BE, and the device switches from the initial HRS to the LRS as shown in Fig. 5 (a). Due to the different dissociation energy between Al₂O₃ and ZnO, the physical dimension of the CFs in Al₂O₃ should be narrower than that in ZnO. The reset process is dominated by the competition between the diffusion force by the oxygen ions concentration gradient and the drift force by the electric field. During the reset process, as there is
no compliance current, the large current flows through the CFs and causes the local Joule heat. The heat is enough to stimulate the thermal diffusion of oxygen ions and some oxygen vacancies in CFs will be filled, the CFs are ruptured[20]. As the CFs in Al₂O₃ are narrower than that in ZnO, the rupture is easily taken place in the Al₂O₃ layer, as shown in Fig. 5 (b). For the set process, the oxygen vacancies are created to form the CFs in the Al₂O₃ layer and the device is switched to LRS.

![Fig. 5. Schematic diagrams to understand the possible filamentary model of the device of TE/Al₂O₃/ZnO/BE structure. The states of (a) LRS and (b) HRS.](image)

To clarify the conduction mechanisms of the two kinds of devices, I-V curves for both LRS and HRS states were plotted with double logarithmic. As shown in Fig. 6, the I-V characteristics of both SL and BL devices in the HRS and LRS are similar. At the LRS, both slopes are close to 1, in which regions are believed to be the Ohmic behavior. At the HRS, the slopes are also close to 1 in the low voltage region but around 2 in the high voltage region, which can be well explained by space charge limited conduction (SCLC) mechanism[3].

![Fig. 6. Log-log scale curves of the URS characteristics in the LRS and the HRS.](image)

### 4. Conclusions

In summary, the performances of ZnO-based RS devices with SL and BL devices were demonstrated in this paper. RS characteristics were analyzed and the BL device has a more excellent switching performance. The BL device shows stable and reliable RS behaviors with 100 switching cycles and excellent mechanical durability upon the bending test. The conduction mechanisms of LRS and HRS are consistent with Ohmic conduction and SCLC, respectively. The results of this study indicate that our BL device has the potential of the flexible memory devices.

### References


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