Improved Magnetism in Mn-doped ZnO Thin Films by Inserting ZnO Layer

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Abstract. Compared to Ti/Mn doped ZnO/Pt (Ti/MZO/Pt) device, the Ti/MZO/ZnO/Pt device exhibits more excellent resistive switching (RS) performances and larger magnetic variation behaviors. The RS behavior is attributed to formation and rupture of oxygen vacancy (Vo) based conductive filaments (CFs), and magnetic variation was demonstrated by bound magnetic pole (BMP) model. Here ZnO buffer layer contribute to improve the RS and magnetism.

1. Introduction
Extensive studies have been investigated ferromagnetism (FM) at room temperature in many transition metal (TM) doped and undoped binary metal oxide structures, such as ZnO, NiO, TiO2 [1-3]. However their room temperature FM is still too weak to practically apply in spintronics. It is generally believe that oxygen vacancies (Vos) played an important role in the FM of binary metal oxides. Many techniques, such as annealing in argon or vacuum and doping TM [4], have been used to enhance Vo density. Unfortunately those methods have no significant improvements in FM at room temperature. Recently it was reported that Vos migrate easily in binary oxides under an electric field, generating Vo-based conductive filaments (CFs) during resistive switching (RS) process [5]. It is the Vos with high density in CFs that coupled each other, resulting in a large magnetism in a resistive state [6, 7]. It has been proven that inserting oxide buffer layer between metal electrodes and insulator is an effective method to improve the RS performances [8, 9]. So, it is interesting to study magnetism by inserting buffer layer. In this paper, we fabricate Ti/Mn doped ZnO/Pt (Ti/MZO/Pt) and Ti/MZO/ZnO/Pt memory devices for investigating the RS performances and magnetic variation.

2. Material and Methods
The 4 at.% Mn doped ZnO films (MZO films) with and without a ZnO buffer layer were deposited on a commercially available Pt/Ti/SiO2/Si substrate at 400°C using pulsed laser deposition (PLD) under an oxygen pressure of 5 Pa. The thicknesses of MZO films about 115 nm. ZnO buffer layers were deposited at 400 °C under a background pressure of 1.0×10⁻⁷ Pa in vacuum atmosphere. Top electrodes (TE) of Ti (diameter 200 μm) were deposited through a metal shadow mask onto the MZO films by using magnetron sputtering.

The crystalline structure was determined by X-ray diffraction (XRD, X’pert PRO MPD). The current-voltage (I-V) characteristics were performed using a Keithley 2612A sourcemeter, and Schematic of the device layout and the current-voltage (I-V) measurement configuration, as shown Figure 1 (a). Hysteresis loops (M-H curves) at room temperature were measured by Quantum Design PPMS-6700.
3. Results and Discussion

Figure 1 (b) shows XRD spectra of the MZO films with and without a ZnO buffer layer. It can be seen that a sharp (002) peak of ZnO wurtzite structure appear in both the as-prepared films except for the diffraction peak form the substrate, and no peaks related to Mn metal was determined. Compared to MZO films, the crystalline quality of MZO films with a ZnO buffer layer (MZO/ZnO) have improved.

![Figure 1](image)

Figure 1. (a) Schematic of the device layout and the current-voltage (I-V) measurement configuration. (b) XRD patterns of the MZO films with and without a ZnO buffer layer.

Figure 2 (a) and (b) shows typical I-V curves of MZO and MZO/ZnO film. Compared to Ti/MZO/Pt device, the Ti/MZO/ZnO/Pt device presents more stable and larger switching ratio. The top inset in Figure 2 (a) and (b) shows distributions of the set (V_SET) and reset (V_RESET) voltage. For Ti/ZMO/Pt device, the V_SET/V_RESET varies from 1.08V/-0.76V to 1.72V/-0.96V, and the ΔSET/ΔRESET reach up to 0.64 V and 0.2 V, respectively. Compared to the above Ti/ZMO/Pt device without ZnO inserting layer, the V_SET/V_RESET was small in the Ti/ZMO/ZnO/Pt device, changing from 0.49V/-0.50V to 0.52V/-0.54V, and ΔSET/ΔRESET are only 0.03V/0.04V. Obviously, MZO/ZnO bilayer films displays centralized distribution of V_SET and V_RESET. Figure 2 (c) and (d) shows the endurance of the above device with 300 cycles. It should be noted that the R_HRS/R_LRS ratio of Ti/MZO/ZnO/Pt device approximately attained 133, which is far higher than 3 of Ti/MZO/Pt device without a ZnO buffer layer. According to the sudden jump at V_SET and V_RESET in the both devices, it can be speculated that RS behavior may originate from the formation and fracture of CFs [10, 11]. It is confirmed by log-log scale plot in low resistance state (LRS), as shown in the Figure 2 (e) and (f). The fitting curve display Ohmic behavior with a slope close to 1 in the LRS.
To clarify the change of magnetism in the process of RS process, the M-H curves of MZO and MZO/ZnO films in the initial state (IS), LRS and HRS are determined at room temperature, as shown in Figure 3 (Signal from the substrates have been subtracted from the all M-H curves). The saturation magnetism ($M_S$) are only $0.87 \mu\text{emu}$ (in the IS), $2.47 \mu\text{emu}$ (in the HRS) and $3.93 \mu\text{emu}$ (in the LRS) for Ti/ZMO/Pt device without a ZnO buffer layer. While for Ti/ZMO/ZnO/Pt device with a ZnO buffer layer, the $M_S$ value increase to approximately $2.44 \mu\text{emu}$ (in the IS), $6.00 \mu\text{emu}$ (in the HRS) and $16.08 \mu\text{emu}$ (in the LRS), respectively. Especially the ratio of $M_{LRS}/M_{IS}$ reached up to 8.51, which

Figure 2. Typical I-V curves of Ti/ZMO/Pt (a) and (b) Ti/MZO/ZnO/Pt devices, endurance of Ti/ZMO/Pt (c) and Ti/MZO/ZnO/Pt (d) devices at a read voltage of +0.5 V; the Log-Log plot I-V for Ti/ZMO/Pt (e) and Ti/MZO/ZnO/Pt (f) devices.
is much higher than 4.78 of Ti/ZMO/Pt device. The above results show that ZnO buffer layer is favorable for improving magnetism and it variation of MZO film during the RS process.

![Figure 3. M-H curve of Ti/ZMO/Pt device (a) and substrate (inset) and Ti/ZMO/ZnO/Pt device (b) in the IS, HRS, and LRS.](image)

The main view put forward at present is the bound magnetic pole (BMP) model about origin of ferromagnetism in binary metal oxide [7, 12]. The neighboring BMPs are overlapped to form BMPs clusters, thus showing the macroscopic ferromagnetism. In this paper, ZnO buffer layer was deposited in no-oxygen ambient, which is equivalent to introduce enough $V_{OS}$ which increase the thickness (or $V_{O}$ density) of the formed CFs in the MZO films in the LRS. This makes more BMPs clusters overlapped each other, resulting in a stronger FM at room temperature.

4. Conclusions

In summary, Mn doped ZnO-based resistive switching devices with and without ZnO buffer layer are demonstrated in this paper. Compared to Ti/MZO/Pt device without ZnO buffer layer, the Ti/MZO/ZnO/Pt device exhibits more excellent resistive switching performances and larger magnetic variation behaviors. The $R_{HRS}/R_{LRS}$ ratio (approximately 133) of Ti/MZO/ZnO/Pt device is far higher than 3 of Ti/MZO/Pt device, and the ratio of $M_{LRS}/M_{IS}$ of the former reached up to 8.51, which is much higher than 4.78 of the latter. The ZnO buffer layer plays a prominent role in resistive switching and magnetic variation. We speculate the main reason is that buffer layer contribute to increase $V_{O}$ density in the CF$_{S}$ as well as reduce the randomness of filament formation.

5. References

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