

Research Article

Enhancement of Resistance Switching in Electrodeposited Co-ZnO Films

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Received 12 April 2012; Accepted 27 June 2012

Academic Editors: K. S. Coleman and C.-L. Hsu

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High quality Co-doped ZnO films were prepared with electrodeposition. The correlation among the surface morphology, lattice structure, Co-dopant distribution, and resistance switching properties of the as-deposited films were investigated. It is found that resistance switching behaviour could be manipulated by controlling the composition of Co in the ZnO films. The significant enhancement of resistance switching was achieved with 5 at% Co doping in the films, and the possible switching mechanism was also discussed.

1. Introduction

Resistive switching random access memory (RRAM) has attracted enormous interests, due to its simple structure and compatibility with complementary metal oxide semiconductor technology [1–5]. In comparable with the traditional nonvolatile memories (flash), RRAM exhibits unique advantages including much faster writing rate, smaller bit cell size, and lower operating voltages. In particular, the resistive transition induced by applying electric pulses can complete within tenths of nanoseconds at room temperature while the resultant resistance states could be retained for 10 years [2, 6, 7].

RRAM devices are usually structured with an insulating layer sandwiched by two electrodes, which generate reversible electrical field to induce the resistance switching. In this case, the performance of RRAM strongly depends on the resistively switching materials. Therefore, the primary requirement for RRAM is to develop a material that possesses resistive switching effect. To date, a number of materials have been found to have resistive switching behavior, for example, ferromagnetic oxide ($\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$), doped perovskite oxide (SrZrO_3), and binary transition metal oxide (TiO_2 , NiO , ZnO , and Cu_2O) [1, 2, 4, 6, 8–11]. Among these materials, only the transition metal oxides are transparent to the visible light due to their large optical band gap. More importantly, their compositions are easier to be controlled

compared to the ferromagnetic or perovskite oxides. Hence, such materials have a great potential for the applications of transparent RRAM devices [12, 13].

In this work, high quality Co-doped ZnO films were prepared with electrodeposition at low temperature, and their resistive switching behaviors were characterized. The morphology and size of metal oxide crystals were optimized by manipulating the potential, current, and concentration of the reactant. Co was strategically doped into ZnO to enlarge the memory window via increasing the resistivity of the high resistance state.

2. Experiment

Electrodeposition was carried out in an Autolab 302N electrochemical workstation. A standard three-electrode setup in an undivided cell was applied. ITO ($9.3\sim 9.7\ \Omega$, Asahi Glass Corporation, Japan, $1.1\ \text{mm} \times 26\ \text{mm} \times 30\ \text{mm}$) was used as the working electrode while platinum foil ($0.2\ \text{mm} \times 10\ \text{mm} \times 20\ \text{mm}$) was employed as the counter electrode. The two electrodes were separated with a distance of 30 mm. Ag/AgCl electrode was used as a reference electrode in 4 M KCl solution.

The ITO substrates were first cleaned with ethanol and acetone sonication/ultra violet ozone, and the electrodeposition was implemented in a solution of 0.1 M



FIGURE 1: Schematic of setup used to measure I - V curves on Co-ZnO films using an electrochemical workstation. The working electrode (WE) and sensor electrode (SE) leads from the workstation were connected to the top Au electrode, while counter electrode (CE) and reference electrode (RE) leads from the workstation were connected to the bottom Au electrode.

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with Co in different composition at 1 mA for 30 min, at 75°C . The crystal structure of the as-deposited materials was determined by X-ray powder diffraction (Philips X'pert Multipurpose X-ray Diffraction System (MPD) with $\text{Cu K}\alpha$). The morphologies of the as-deposited materials were characterized using scanning electron microscopy (SEM, Hitachi S3400). To measure the electrical property of the materials, Au top electrodes were patterned and deposited by DC magnetron sputter with a metal shadow mask. Voltage-current curves of the films were measured using an Autolab 302N electrochemical workstation controlled with Nova software. During the measurement, the working electrode and sensor electrode were connected to the top Au electrodes while the reference and counter electrode were connected to the ITO substrate. A schematic of the setup for I - V measurement is shown in Figure 1.

3. Results and Discussion

The electrochemical synthesis of ZnO is a four-step process: first, nitrate ions and H_2O are electrochemically reduced at the surface of the working electrode, resulting in an increase of local pH value in the vicinity of the electrode as shown in (1) and (2). Subsequently, the increase of the local pH leads to the precipitation of zinc ions as zinc hydroxide $[\text{Zn}(\text{OH})_2]$, (3) at 75°C and $\text{Zn}(\text{OH})_2$ can be transformed into ZnO eventually. In the presence of Co^{2+} , part of the Co^{2+} ions would be incorporated into ZnO lattices accordingly as follows:

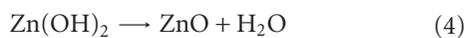
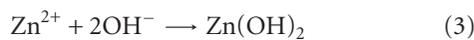
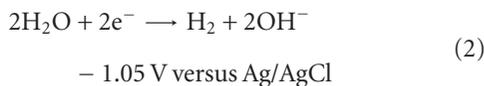
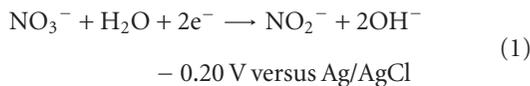


Figure 2 shows the XRD spectra of pure and 5 at % Co-doped ZnO films on ITO substrates. No impurity is detected in these spectra. The predominant (002) peak in the spectra demonstrates that the films grew with the preferential orientation of [001]. It is discernible that the characteristic

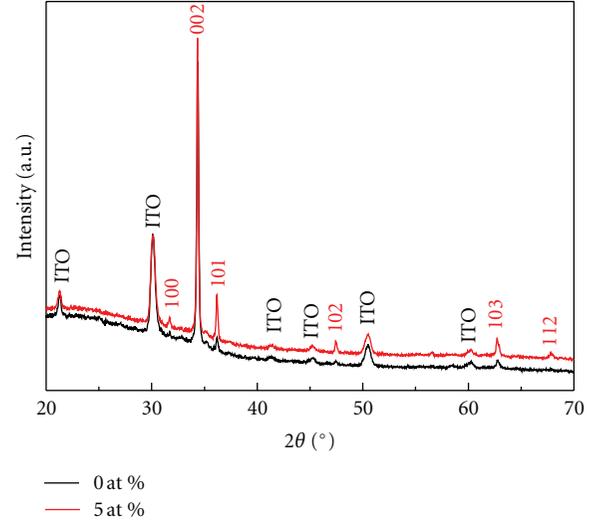


FIGURE 2: XRD patterns of pure and 5 at% Co-doped ZnO films on ITO substrates.

peaks of Co doped ZnO shift to the higher diffraction angles, showing the occurrence of shrinkage induced by Co-doping, which are associated with the different the different ionic radii between Co^{2+} (0.058 nm) and Zn^{2+} (0.060 nm). This finding is in a good agreement with the reported observation in Co-doped ZnO thin films [14].

The SEM surface morphologies of 5 at% Co-doped ZnO films in Figure 3 show that the films are composed of nanorods those grow densely and vertically on the substrate. These nanorods are well crystalline with an average diameter of ~ 250 nm. In addition, Energy Dispersive Spectrometry (EDS) elemental mapping was employed to verify whether the Co has been incorporated into the as-deposited ZnO films homogenously and the results shown in Figures 3(b), 3(c), and 3(d) evidence that the O, Zn, and Co elemental maps have the identical spatial distribution. This indicates that the doped Co has incorporated in ZnO films homogenously.

Figure 4(a) presents a typical I - V character of RRAM cell with the as-prepared structure of Au/5 at % Co-ZnO/ITO/Au capacitor, which was measured by sweeping voltage, at a speed of 0.01 V/s, in the sequence of $0 \rightarrow 5 \rightarrow 0 \rightarrow -5 \rightarrow 0$ V. During the measurements, the bias voltages were applied on the TE with BE grounded, and neither a forming process nor a current compliance was necessary for activating the memory effort. For the Co-doped ZnO, with the increase of the positive bias, a sudden jump in resistance occurs at 2.6 V, indicating the switching to a low-resistance state (LRS). The sample remains in the LRS with increasing bias while a drop of current is observed at 4 V and the backward transition to a high resistance state (HRS) for subsequent bias descending. Sweeping the voltage to negative region exhibits a symmetrical behaviour, as expected from the symmetric stack structure. For comparison, I - V behaviours of the pure ZnO and 2 at% Co-doped ZnO are also measured. Figure 3(b) shows that the pure ZnO has a much smaller memory window compared with 2 at% and 5 at% Co-doped ZnO, demonstrating

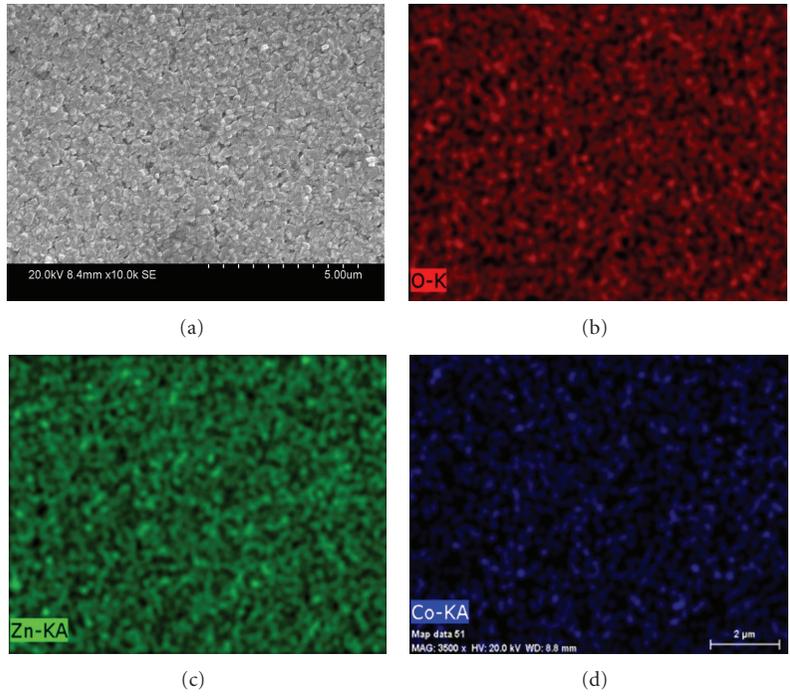


FIGURE 3: SEM (a) and EDS mapping (b, c, and d) images of 5 at% Co-doped ZnO films.

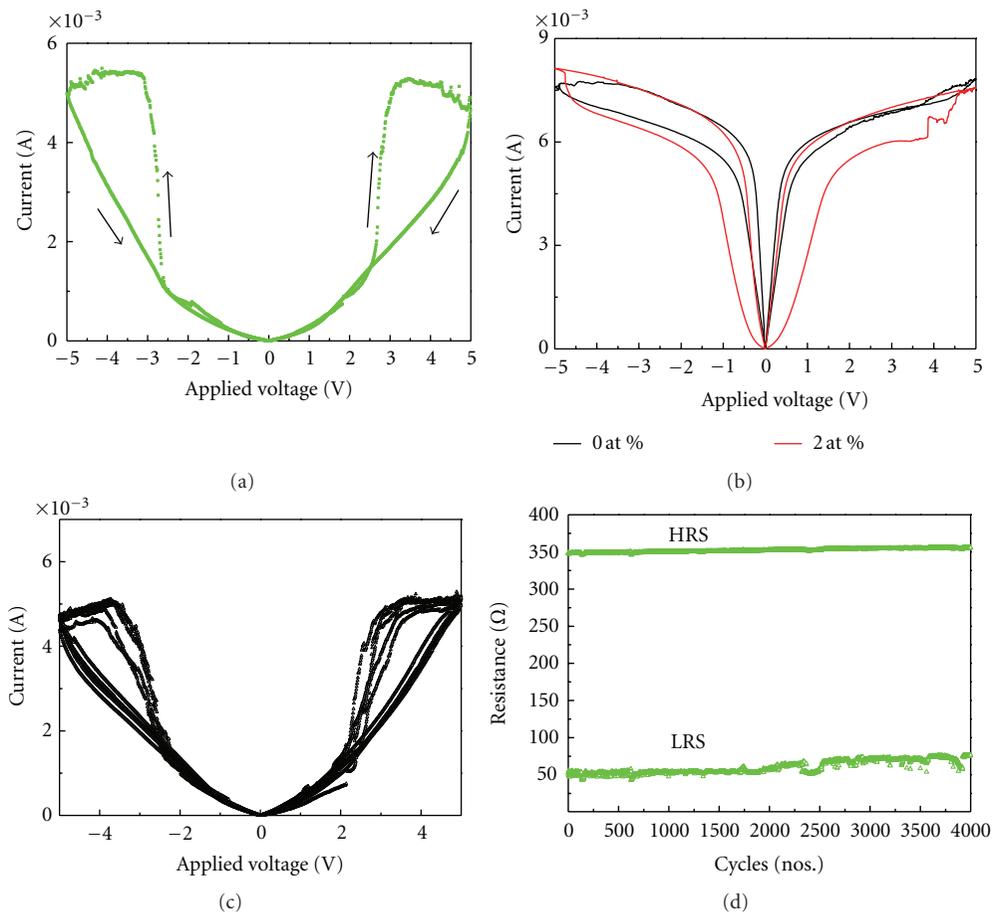


FIGURE 4: *I-V* curves of pure and Co-doped ZnO films. (a) 5 at % Co-doped ZnO film, (b) 0% and 2 at % Co-doped ZnO films, (c) switching cycling test of 5 at % Co-doped ZnO film, and (d) the evolution of resistance of HRS and LRS over 4000 cycles of 5 at % Co-doped ZnO film.

that the Co-doped ZnO is an excellent candidate for RRAM applications. Moreover, the reliability of the memory effects is evaluated by performing a switching cycling test. As shown in Figure 3(c), the bistable resistance switching behaviour is reversible and steady after 10 cycles. To evaluate the resistive switching characteristics of 5 at% Co-doped ZnO film, the evolution of HRS and LRS over 4000 cycles was measured, which is shown in Figure 3(b). From the distributions of HRS and LRS in Figure 3(d), the two well-resolved states provide a clear memory window of the device.

The mechanisms for resistance switching in metal oxides are interesting but still controversial. The filamentary mechanism has been reported to explain the resistance switching behaviour in the pure and doped ZnO films [13]. According to filament theory, defects might condense in the metal oxide to form tiny conducting filament at HRS, and these tiny conducting filaments could gather and align to form a long conducting filament, thus leading to transition to LRS [15]. In this work, the conducting filaments in ZnO may be created and enhanced by the alignment of the structural defects due to Co doping.

4. Conclusion

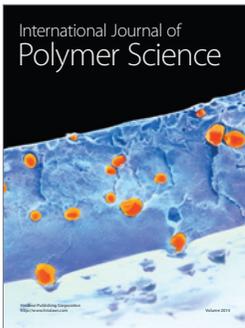
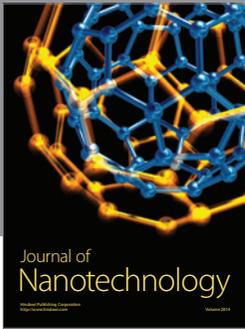
High (002) oriented pure and Co-doped ZnO thin films were prepared by a facile electrochemical deposition method. EDS mapping indicates that ZnO films are homogeneously doped with Co. Reliable and reproducible bipolar resistance memory switching performance is achieved in 5 at % Co-doped ZnO films. The present work demonstrates that Co-ZnO films have the potential for next generation non volatile memory applications.

Acknowledgment

This research was sponsored by Australian Research Council (ARC) Discovery Project (DP 110102391).

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