

Growth and Electrical Properties of Doped ZnO by Electrochemical Deposition

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Received August 30th, 2011; revised October 6th, 2011; accepted October 7th, 2011

ABSTRACT

In this work, pure and different metal ions doped ZnO thin films were obtained by a facile electrochemical deposition process. Different morphologies of ZnO, such as nanoplates, nanoparticles, as well as dense film can be obtained by doping Cu²⁺, In³⁺, and Al³⁺, respectively. Besides, the electrical properties of ZnO were also dependent on the doping ions. In this work, only pure ZnO shows resistive switching characteristics, indicating that the defects in ZnO is a key role in inducing resistive switching behaviour.

Keywords: ZnO Electrochemical Deposition

1. Introduction

As a wide band gap II-VI semiconductor, zinc oxide (ZnO) has many applications such as transducers, gas sensors, and dye-sensitized solar cells, etc. [1-5]. Specially, ZnO thin films have attracted considerable attention because they can be tailored to possess high electrical conductivity and high visible transmittance by different coating techniques. For example, ZnO films have been deposited for resistive random access memory (RRAM) applications [6-8]. In these cases, ZnO films with well aligned sheets, rods, or wires may exhibit better performance, because of fast and effective path for electron transportation. Therefore, it is essential to control the morphology of ZnO films for potential RRAM applications.

To date, various physical and chemical methods have been developed to fabricate ZnO thin films. For instance, pulsed laser deposition, radiofrequency magnetron sputtering, metal-organic chemical vapor deposition (MOCVD), a vapor-liquid-solid mechanism, spray pyrolysis, sol-gel, and have been reported [9-11]. In most cases, high temperature and special atmosphere are necessary, which go against large-scale and low-cost production of ZnO films. In contrast, electrochemical deposition method represents a simple and effective route to control the morphology and composition of ZnO films [12,13]. Most reports on ZnO films prepared by electrochemical deposition method are focused on their morphology and optical properties, while only a few researches mentioned their electrical

properties [14-16]. For RRAM applications, control of their electrical properties is very important to achieve high performance. Therefore, it is worthwhile to investigate the relationship between the structure, composition and electrical properties of ZnO films prepared by electrochemical method. In this paper, different metal ions doped ZnO films were deposited and the effects of doping ions on the electrical properties were investigated.

2. Experimental

Electrodeposition was carried out using a HA151 Potentiostat (Hokuto Denko Corporation, Japan). A standard three-electrode setup in an undivided cell was used. FTO (9.3 ~ 9.7 Ω , Asahi Glass Corporation, Japan, 1.1 mm \times 26 mm \times 30 mm) was used as the working electrode while platinum foil (0.2 mm \times mm 10 mm \times 20 mm) was used as the counter electrode. The distance between the two electrodes was 30 mm. The reference electrode was an Ag/AgCl electrode in 4 M KCl solution, against which all the potentials reported herein were measured.

The FTO substrates were first cleaned by ethanol and acetone sonication/ultra-violet ozone and electrodeposited in a solution of 0.01 M Zn(NO₃)₂·6H₂O and different amount of dopants at 2 mA for 30 min, at 75°C. The phase composition of the samples was characterized by X-ray powder diffraction (XRD, RINT-2100V, Rigaku, Cu K α). The morphologies of the samples were observed by field emission scanning electron microscopy (FESEM; JSM-6335FM, JEOL, with an accelerating voltage of 5 kV). A Keithley 6517B source meter was used for elec-

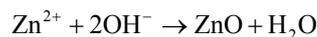
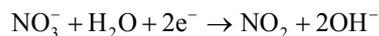
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trical characterization.

3. Results and Discussion

The surface morphology of undoped and doped ZnO films was illustrated by SEM, as shown in **Figure 1**. For undoped ZnO, oriented nanorod arrays with average diameter of 200 nm were obtained under 2 mA, 70°C, 30 min. This is consistent with other reports about ZnO nanorods array from electrochemical deposition. As to 5 at% Cu²⁺ doped ZnO, it is interesting that nanoplates instead of nanorods were found. The average thickness of the nanoplates was 200 nm and their diameter could reach several micrometers. More interestingly, In³⁺ doping resulted in small nanoparticles with size less than 150 nm. Further, continuous film was obtained by 5 at% Al³⁺ doping. It is obvious that doping ions had great effects on the morphology of ZnO films. Usually, electrodeposition of ZnO is based on the generation of hydroxide ions

(OH⁻) at the surface of the electrode by the cathodic reduction of oxygen precursor in a Zn(NO₃)₂ solution. The Zn²⁺ and OH⁻ ions react together, leading to ZnO deposition on the surface of the cathode according the following formulas:



Usually, ZnO grows preferentially along [0 0 1] direction in aqueous solution because of the lowest surface energy of (0 0 1) facet. And the growth velocity along [0 1 0] directions is slower than that of [0 0 1] direction, resulting in nanorod morphology. In the presence of doping ions, then can serve as structure-directing agent to adsorb selectively on ZnO basal planes and modify this surface chemistry properties. For example, Cu²⁺ ions might be adsorbed on the (0 0 1) facets of ZnO crystals and significantly decrease the growth rate of these facets,

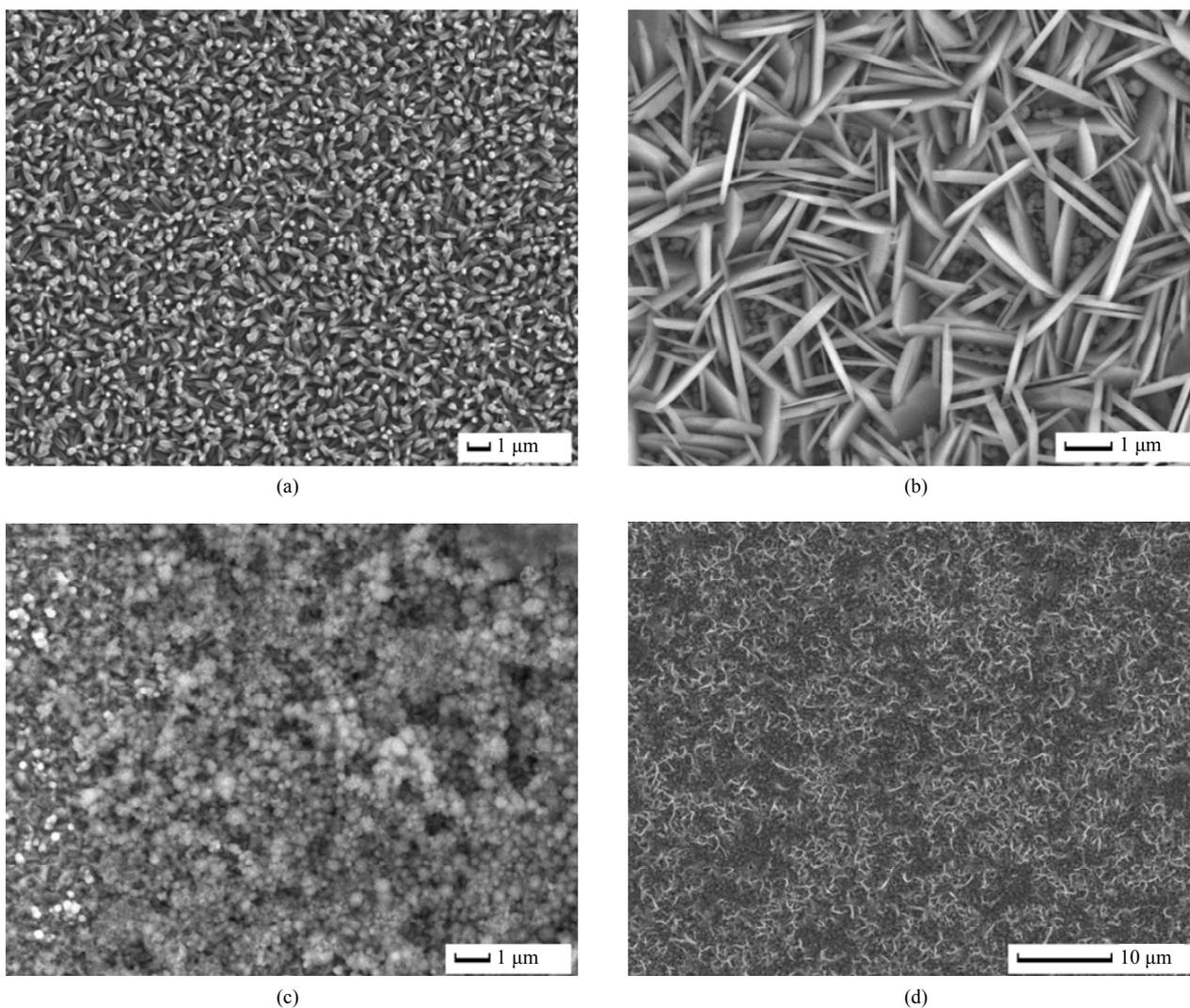


Figure 1. SEM images of pure and different ions doped ZnO: (a) Pure; (b) 5 at% Cu²⁺; (c) 5 at% In³⁺; and (d) 5 at% Al³⁺.

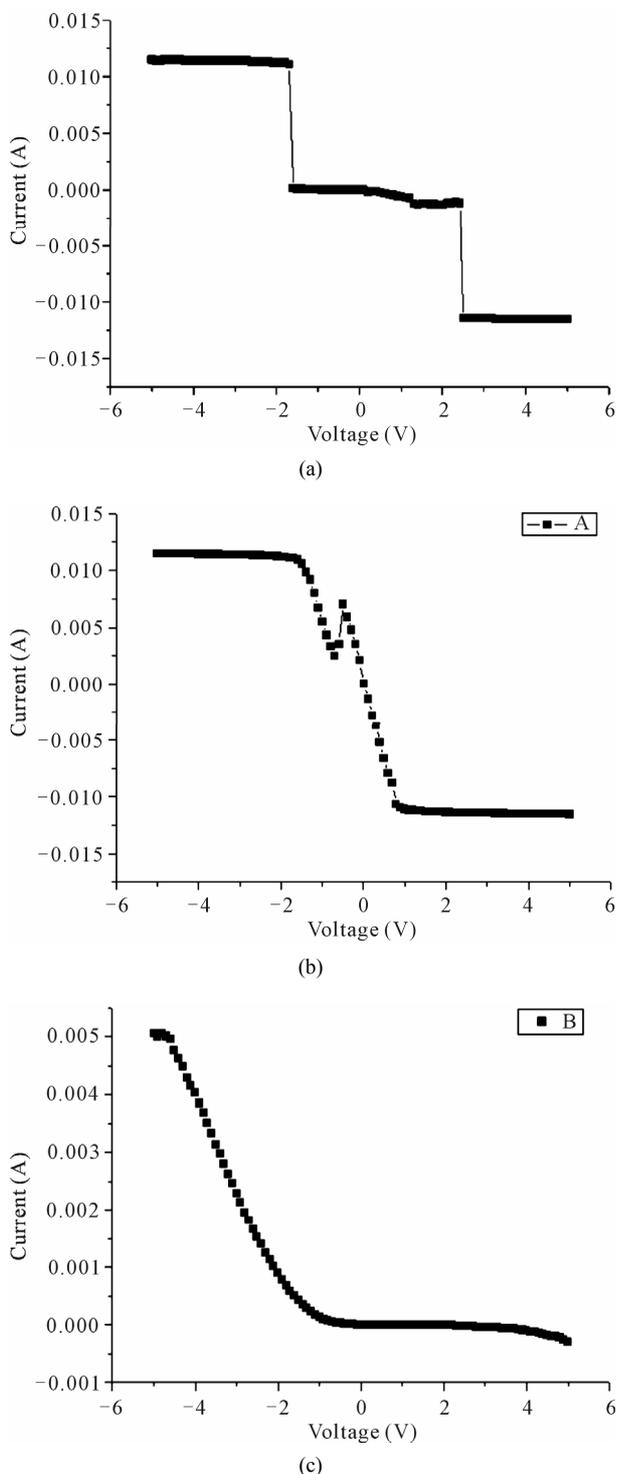


Figure 2. Typical I-V characteristics of (a) Pure ZnO; (b) In³⁺ doped ZnO; and (c) Al³⁺ doped ZnO based on the FTO/ZnO/Pt structure.

resulting in plate-like structure. As to In³⁺ ions doped ZnO, In³⁺ ions might be adsorbed on the different surfaces and small nanoparticles were then obtained.

The typical I-V characteristics of pure and doped ZnO

were shown in **Figure 2**, where the voltage was swept from -5 V to 5 V. For pure ZnO, by sweeping the voltage from -5 V to a certain voltage of about -1.8 V, a sudden drop of leakage current is observed, indicating the resistance has switched to high resistance state, and non-volatile off state is achieved. While sweeping the voltage to positive regions, an abrupt jump of leakage current appears at a higher voltage of 2.5 V is found. Interestingly, for In³⁺ and Al³⁺ doped ZnO, they do not show resistance switching behaviour, as indicated in **Figures 2(b)** and **(c)**. Specially, In³⁺ doped ZnO shows a rectifying behaviour, indicating formation of a ZnO/Pt diode heterojunction. As to Al³⁺ doped ZnO, a linear I-V curve in the region of -2 V to 1 V can be observed and the current was saturated at higher voltage, which suggested that the conductivity has been increased by Al³⁺ doping.

The mechanism for resistive switching related properties of doped ZnO is interesting but still controversial. Among many proposed models, the filamentary mechanism may explain the resistance switching effect in this work. According to this model, the filaments are composed of defects such as oxygen vacancies. Therefore, these defects are essential to the electrical properties, which can be controlled by selective doping.

4. Conclusion

In summary, pure and doped ZnO thin films were prepared by electrochemical deposition at low temperature. ZnO nanoplates, nanoparticles, as well as dense film can be obtained by doping Cu²⁺, In³⁺, and Al³⁺, respectively. Besides, the electrical properties of ZnO were also dependent on the doping ions. In this work, only pure ZnO shows resistive switching characteristics, indicating that the defects in ZnO is a key role in inducing resistive switching behaviour.

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