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Microstructure and optical properties of nanocrystalline ZnO and ZnO:(Li or Al) thin films

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Abstract

Zinc oxide thin films (ZnO, ZnO:Li, ZnO:Al) were deposited on glass substrates by a sol–gel technique. Zinc acetate, lithium acetate, and aluminum chloride were used as metal ion sources in the precursor solutions. XRD analysis revealed that Li doped and undoped ZnO films formed single phase zincite structure in contrast to Al:ZnO films which did not fully crystallize at the annealing temperature of 550 °C. Crystallized films had a grain size under 50 nm and showed *c*-axis grain orientation. All films had a very smooth surface with RMS surface roughness values between 0.23 and 0.35 nm. Surface roughness and optical band tail values increased by Al doping. Compared to undoped ZnO films, Li doping slightly increased the optical band gap of the films.

Keywords: Doped zinc oxide; Sol–gel; Thin film; Transparent-conductive oxide

1. Introduction

ZnO is a wide band gap semiconductor. It crystallizes in hexagonal wurtzite structure (zincite) [1]. In this structure, Zn atoms are tetrahedrally coordinated to four O atoms, where the Zn d-electrons hybridize with the O p-electrons [2]. The n-type semiconductor behavior is originated by the ionization of excess zinc atoms at interstitial positions and by the ionization of oxygen vacancies forming defect levels approximately 0.01–0.05 eV below the conduction band [2].

ZnO is used in many applications such as surface acoustic wave devices (SAW), laser devices, gas sensors and MEMS [3]. In addition, there is interest in integrating ZnO with other wide band semiconductors such as AlInGaN due to the lattice match between them [2].

ZnO thin films have been prepared by various techniques such as rf sputtering [4,5], spray pyrolysis [6,7], chemical vapor deposition (CVD) [8–10], pulsed laser deposition [11–13], molecular beam epitaxy [14] and sol–gel processing [3,15–17]. When sol–gel is used, there are two principal routes used to obtain oxide thin films: the alkoxide route using organometallic precursors and the none-alkoxide route using water or alcohol solutions of metal salts [18].

Doped zinc oxide (ZnO) thin films have attracted much attention because of their potential for being used as transparent conducting electrodes after doping with group IIIB elements or fluorine, Furthermore, they can be used as insulating or ferroelectric layers after doping with Li or Mg in opto-electronic devices [19]. Transparent ZnO thin films doped with Al, In, or Ga show good electrical conductivity [20]. Currently, conductive zinc oxides replace indium-tin-oxide (ITO) thin films in the area of transparent conducting electrodes due to their inertness under hydrogen plasma atmosphere [21].

It is generally accepted that doping of ZnO with Al decreases its resistivity contrasted with Li, which is known to increase resistivity in ZnO [22]. Al acts as a donor when it is substitutionally incorporated on zinc lattice sites [23]. Accordingly, Musat et al. [24] fabricated low resistivity Al doped ZnO films when segregation of aluminum (as Al_2O_3) at the grain boundaries was avoided. Then, substitution of the Al atoms effectively took place in Zn sites of the ZnO structure according to the following equation:

$$Al_2O_3 \rightarrow 2Al_{Zn^\bullet} + 2O_0 + \tfrac{1}{2}O_2 + 2e'$$

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where Al_{Zn} is Al in zinc lattice site and O_0 is oxygen on lattice site.

Generally, Li introduces a deep acceptor level and induces ferroelectric behavior [2]. According to Fujihara et al. [25], chemical defect formation due to Li-doping mainly occurs as follows:

$$Li_2O \rightarrow Li'_{Zn} + Li_i^{+} + O_0$$

where Li_{Zn} represents lithium on zinc lattice site and Li_i^+ lithium in interstitial position. In fact, some Li atoms in interstitial sites may later replace Zn atoms as follows:

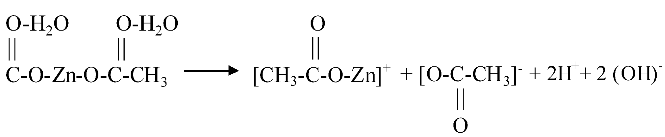
$$Li_i^{+} + Zn_{Zn} + e^{-} \rightarrow Li'_{Zn} + Zn_i^{+} \quad \text{or} \quad Li_i^{+} + e^{-} \rightarrow Li'_{Zn} + V_O^{+}$$

where Zn_{Zn} represents zinc in zinc site and Vo^+ oxygen vacancy on lattice site.

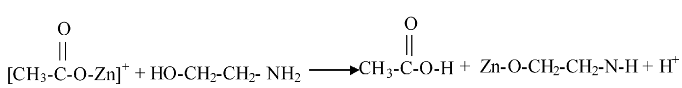
The aim of this work is to evaluate the effects of doping (Li or Al) on the microstructure, optical properties, and grain orientation of ZnO thin films prepared by sol–gel spin coating.

2. Experimental

The basic solution was prepared by dissolving ZnAc ($Zn(CH_3COO)_2{\cdot}2H_2O$) in 2-propanol and monoethanolamine (C_2H_7NO, EA) (EA:ZnAc = 1:1). It is generally accepted that



ZnAc transforms to mono acetate in 2-propanol by the reaction above. Then the following reaction was estimated to occur between monoethanolamine and zinc mono acetate (below).



The resulting solution was stirred by using a magnetic stirrer at 50 °C until it became clear. Afterwards, water (H_2O:ZnAc = 1:2) was slowly added to obtain optimum wettability between the precursor film and the substrate. Finally, a solution with a concentration of 0.4 M was obtained (Fig. 1). Similarly, Li doping solution was prepared from lithium acetate (($CH_3CO_2{\cdot}Li$), LiAc) with a concentration of 0.2 M

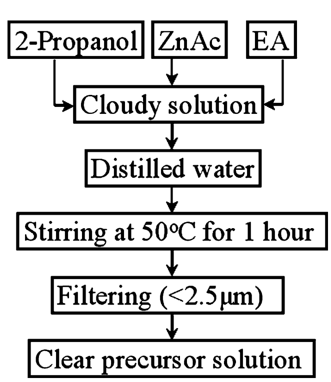


Fig. 1. The flow diagram of the ZnAc precursor solution preparation.

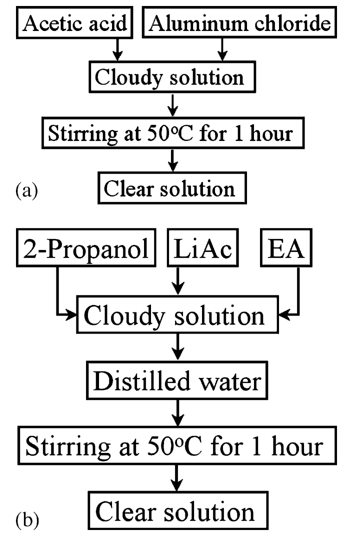


Fig. 2. The flow diagram of: (a) $AlCl_3$ solution preparation; (b) LiAc solution preparation.

(Fig. 2a). Aluminum chloride solution (0.1 M) was prepared by dissolving aluminum chloride ($AlCl_3$) in acetic acid (Fig. 2b). Proportional amounts of doping solutions were added to ZnAc solutions in such a way that final ratio of Zn:(Li or Al) was 99:1, respectively, in each solution.

The microscope glass substrates were cleaned with HCl and distilled water. Deposition was carried out in air at three steps with different spinning speeds, which are 2000 rpm for 30 s, 4000 rpm for 30 s, and 6000 rpm for 60 s. A precursor film formed following the spin coating process. The film was then dried at 250 °C for 1 min on a hot plate. After the deposition of the last layer, the resulting films were annealed in air at 550 °C for 1 h (Fig. 3).

The crystal structure and grain orientation of ZnO films were determined by X-ray diffraction (XRD-Rigaku Dmax 2200) with Cu Kα radiation. The surface morphology of the films was characterized by field emission scanning electron microscope (FESEM, Philips 30XL SFEG) and atomic force microscopy (Digital Instrument Nanoscope IV). Optical transmission and absorbance spectra of the films were analyzed by using a UV–visible spectrophotometer (Shimadzu-2101PC).

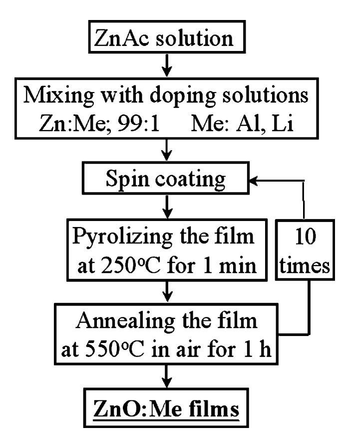


Fig. 3. The flow diagram of ZnO:Me film fabrication.