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Indium-doped ZnO Transparent Thin Films Deposited by Sol-gel Dip Coating Method

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Abstract

Indium-doped zinc oxide (IZO) thin films were deposited onto glass substrates by sol-gel dip coating method with variation of doping concentration from 0.5 to 5% using Indium (III) acetate and Zinc(II) acetate as starting precursors for In and Zn sources, respectively followed by calcinations. Effect of doping concentration on the structural, morphological, and optical properties of IZO transparent thin films were investigated by relevant characterization including X-ray diffraction (XRD), scanning electron microscope (SEM), and optical spectroscopy. XRD spectra show the polycrystalline of hexagonal wurtzite structure of as-prepared films. IZO films with high doping concentration condition exhibit significant deterioration in their crystallinity. The crystalline size of the deposited thin films can be estimated by the calculation of the broadening of characteristic XRD peaks. IZO thin films show high optical transmittance in visible range without significant change in their optical band gaps with variation in In doping composition. Possible mechanisms taking responsibility on these features are mentioned and discussed.

Keywords: In-doped ZnO thin film, Sol-gel dip coating, Indium doping

1. Introduction

In recent years, optoelectronic devices such as touch screens, solar cells and flat panel displays have been widely implemented. Transparent conducting oxide films (TCOs) have been widely used in optoelectronic devices with its high transparency and low resistivity [1, 2]. Meanwhile, ZnO is one of interesting candidate materials due to its resource abundance, nontoxicity, high transparency, ease of doping to improve electrical conductivity and wide band gap of 3.37 eV possessing good optical transparency in visible region. However, bare ZnO generally has rather high resistivity that is not well applicable for specific applications in optoelectronics. Great number of researches have recently reported the pioneered works to enhance both optical and electrical properties of ZnO by doping with both metal and non-metal elements. It has been proven

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that tri-valent dopants such as Al, Ga, and In have been widely employed as effective donors to improve the electrical properties of ZnO films [2-6]. Among many available thin film deposition processes, sol-gel based process typically benefits considerable advantages such as high homogeneity of starting precursors, readiness of adding dopant, ease of compositional control, and relatively low process temperature [7].

The main propose of this work focuses on the preparation of In-doped ZnO thin films via sol-gel dip coating process on a glass substrates. Structural, and optical properties of as-prepared films were extensively characterized and investigated.

2. Materials and Methods

To prepare the starting precursor, 0.2 M zinc acetate dihydrate ($(CH_3COO)_2Zn•2H_2O$) chosen as Zn source and 0.2M indium(III) acetate ($In(OOCCH_3)_3$) selected as In source were dissolved in absolute ethanol solvent. The In dopant concentration were varied from 0 to 5 at. %. Diethanolamine (DEA, HN $(CH_2CH_2OH)_2$) acting as sol-stabilizer was consecutively added into the solution. Each solution was vigorously stirred at 75°C for 3 h and then aged for 24 h at room temperature. In doped ZnO thin films were deposited onto glass substrates by sol–gel dip coating at drawing speed of 60 mm/min. During each dip-coating the film was mildly baked at 250°C for 5 min in air to evaporate the solvent. The coating was repeated several times before annealing process in air at 500°C for 2 h. The crystal structures of ZnO thin films were measured by X-ray diffraction (BRUKER AXS: D8 DISCOVER) while their surface topography and thickness was monitored by a field emission scanning electron microscope (JEOL:JSM-634OF). Optical properties of the films were investigated by a UV–Vis spectrophotometer (Thermo Electron: Helios Alpha).

3. Results and Discussion

X-ray diffraction (XRD) measurement was carried out on all after-annealed IZO thin films and their corresponding results are exhibited in Figure 1. The In-doping content was varied from 0%(undoped) to 5%. All films showed three prominent peaks positioned at 2θ=31.8°, 34.5°, 36.2° that are nicely indexed to (100), (002) and (101) of hexagonal wurtzite structure of ZnO, respectively [8]. The other peaks at higher diffracted angles labelled with (102), (110) and (103) are also attributed the orientation planes of ZnO. These strong XRD diffraction peaks suggest that the films deposited by this technique are in single-phase polycrystalline structure without any preferable orientation and without any secondary impurity phases. As the In dopant was introduced into the ZnO films, the position of three signature peaks of (100), (002) and (101) orientation planes still situate at the same position angle, implying that the doped films have such good stability of hexagonal crystalline as deposited on glass substrates. As observed in doped films with increasing In doping content up to 3%, the deterioration in peak intensity of these diffraction patterns was noticed. This feature is generally the indication of the reduction in crystallite size and increment of amorphousity of the films. At light doping level, the incorporated In into the films may preferably substitute at Zn site and obstruct the crystal growth of ZnO matrix due to the microstress generated from the difference in ion radius between In^{3+}(80 pm) and Zn^{2+}(74 pm). Further increasing in In doping content beyond this certain soluable limit value could initiate the formation of secondary phase of In_xO_y and the film becomes composite films of In_xO_y/ZnO mixture phases. At this point, crystal growth of ZnO could still proceed without interruption. However, In_xO_y phase were undetectable by XRD measurement that may due to amorphousity and small amount of this phase.

Surface morphologies of sol-gel diped-coated In-doped ZnO films with 0-5% In doping content are illustrated in Figure 2 (a-f). It is obviously noticed that all films are composed of densely- and well-distributed grains with uniformity in size and shape. The grain size of thin films are less than 100 nm. It is evidently seen that the grain size of the doped film were significantly decreases with increasing Al-doping content up to 3% thereafter increases. These features monitored by SEM measurement are in harmony with the interpretation from the XRD results.

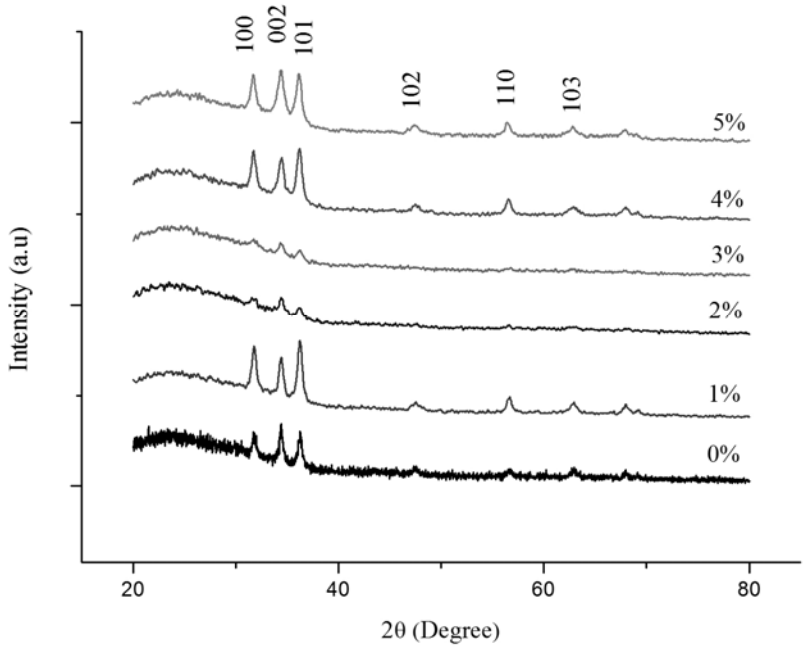

Figure 1. XRD patterns of sol-gel dip-coated In-doped ZnO thin films prepared at different In doping compositions.

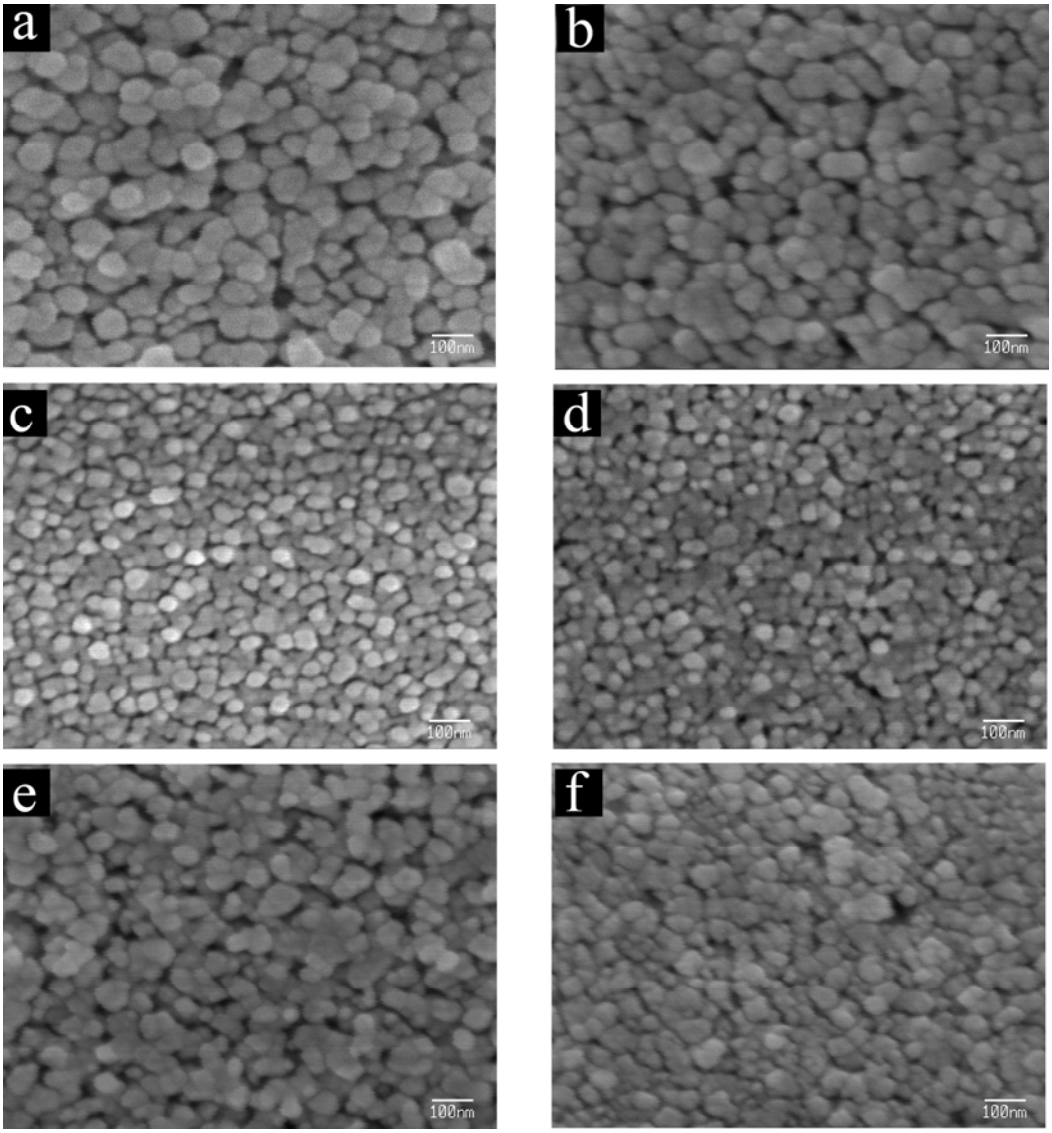

Figure 2. SEM micrographs of In-doped ZnO thin films prepared with different In doping concentration; (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 4%, and (f) 5%.

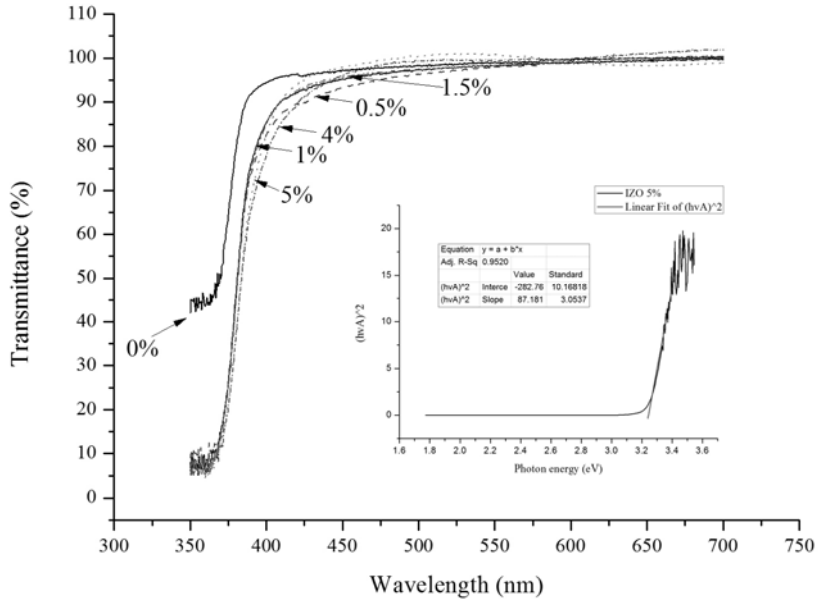

Figure 3. Optical transmittance spectra of In doped ZnO thin films prepared with different In-doping concentrations and (inset) Tauc plot.

Figure 3 shows optical transmittance of after-annealed bare ZnO and In-doped ZnO thin films measuring in the wavelength range of 300-800 nm. The spectra of the films exhibit sharp absorption edge at 375-380 nm, implying good formation of films obtained by dip coating technique. Furthermore undoped film, the spectra of the doped films display noticeably enhancement in the sharpness of absorption edge and transparency in visible wavelength region of 400-800 nm with 85-95% of transmittance. This enhancement could be due to the increase in denseness of the doped films as monitored by SEM images. The increasing denseness of the film results to the better propagation of light through the film without any losses due to light scattering at grain boundary, residue porosity and existence of secondary phases [9]. Corresponding optical band gap of all thin films were estimated by Tauc's using following equation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

where A is a constant parameter, $h\nu$ is photon energy, α is an absorption coefficient and E_g is the optical band gap energy of the film. The variation of optical band gap of all thin films as a function of In doping content is shown in Fig. 4. From the calculation, the band gap of the IZO thin film is found to be varied ranging from 3.23 to 3.27 eV, indicating insignificant change of the band gap as In doping content varies. This feature implies the stability of ZnO films obtained from sol-gel derived coating method.

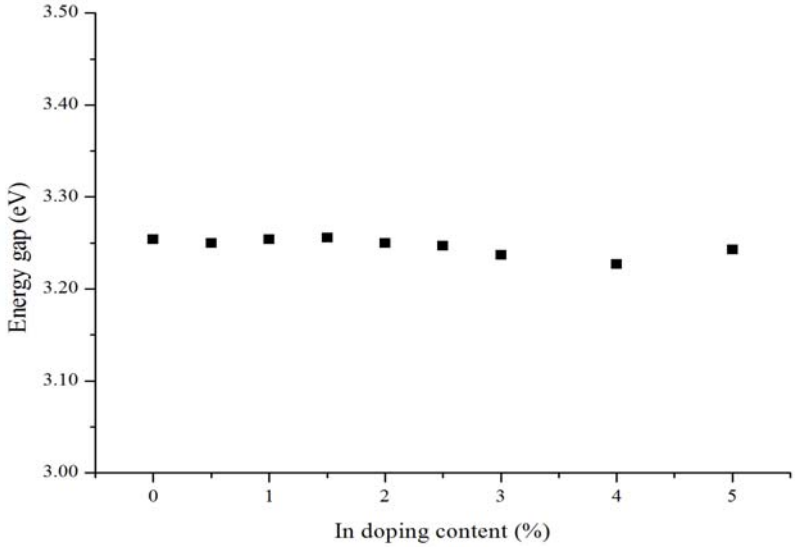

Figure 4. Optical band gap of In-doped ZnO thin films prepared at different doping concentration.

4. Conclusions

Sol-gel derived polycrystalline In-doped ZnO thin films with hexagonal wurtzite structure were prepared onto glass substrates by dip coating method together with annealing process. The XRD and SEM results revealed that the crystallinity and grain size of IZO films were highly affected by In doping with specific content. Moreover, the optical transparency of the films can be enhanced by the incorporation of small amount of In dopant. The In doping insignificantly induced the variation of band gap of the films.

5. Acknowledgement

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