

TEMPERATURE DEPENDENCE OF $\text{Zn}_{1-x}\text{In}_x\text{O}$ ($x = 0.1$ and 0.2) THIN FILMS PREPARED BY SOL-GEL METHOD

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ABSTRACT

In this work we present a study on the effect of annealing temperatures on the structural, morphological and optical characteristics of In doped $\text{Zn}_{1-x}\text{In}_x\text{O}$ ($x = 0.1$ and 0.2) films, were deposited at room temperature by sol-gel method. Zinc acetate dehydrate was used. 2-methoxyethanol and monoethanolamine were used as the solvent and stabilizer, respectively. The dopant source was Indium chloride. All films were annealed at temperatures of 400, 500 and 600 °C for 1 h. Structural investigation including surface morphology and microstructure was carried out by XRD and SEM measurements. The results show that In built into the crystal lattice of the ZnO and the surface of the particles enriched in In ions. The optical properties were determined by UV-VIS spectrum analyses. Value of band gap were obtained is slightly increased as concentration of In increase. It was proposed that annealing temperature plays a key role in the formation of defects, which is strongly related to the nonradiative recombination centers.

INTRODUCTION

ZnO has received extensive attention in recent years due to its wide direct band-gap energy of 3.37 eV and large exciton-binding energy of 60 meV. Therefore, ZnO is widely used in various optoelectronic devices [1]. ZnO thin films have been prepared by a variety of deposition techniques, such as RF magnetron sputtering [2], molecular beam epitaxy (MBE) [3], metal organic chemical vapor deposition (MOCVD) [4], pulsed laser deposition (PLD) [5] and the sol-gel process [6]. Among these techniques, the sol-gel process has several advantages because of its simplicity, safety and low cost. In addition, relevant reports for ZnO with various metal dopants (In^{3+} , Al^{3+} , Mn^{2+} , Zr^{2+} , Ga^{+} , etc.) improved the optical and electrical properties of ZnO [7]. Among these ZnO-based films, In doped ZnO (IZO) thin films have been considered as the possible alternative to transparent conducting oxide films. Because of IZO film have good conductivity, higher optical transmittance and excellent surface roughness than the other dopants ZnO films [9]. Notably, studies involving In doped ZnO thin film are few and far between. Especially, the crystallization at high temperatures (more than 600 °C) and higher doped content (>4 at.%) has still not been investigated [8]. In this project,

we focus on temperature dependence of structural and optical studies of nanostructure ZnO:In.

EXPERIMENTAL DETAILS

ZnO thin films were prepared by the sol-gel method. As a starting material, zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was used. 2-methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The dopant source of tin was indium chloride (InCl_3). Zinc acetate dehydrates and dopants were first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) was maintained at 1.0 and the concentration of zinc acetate was 0.5 M. The solution was stirred at 60°C for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The solution was dropped onto quartz substrates, which were rotated at 1000 rpm for 30 s. After depositing by spin coating, the films were dried at 150°C for 10 min over a hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated three times until the thickness of the sintered films was approximately 200 nm. The films were then inserted into a furnace and anneal in air at different temperatures which are 400, 500 and 600°C for 1 h. The crystallinity of each ZnO film was measured using an X-ray diffractometer (XRD) with CuK_α radiation. The surface morphology of the films was observed with a scanning electron microscope (SEM) and the changes in the optical properties by UV-Vis.

RESULTS AND DISCUSSION

Figure 1 shows the surface morphology images of In doped ZnO thin films with a crystallization temperature of 400 °C, 500 °C and 600 °C. A large amount of particle-like structures and a few micro pores were found on the surface. This particle-like structures was similar to the data of Lee et al. [10]. The micro-pore structure was particularly apparent on the sol-gel synthesized ZnO thin films. The surface morphology of the In doped ZnO thin film had a thin overlay structure and the micro-pore structures disappeared due to In doping. At $x = 0.1$, the surface morphology exhibited rougher than In-doped at $x = 0.2$. We found the In^{3+} residual had not dispersed uniformly and could not increase the contribution of In_2O_3 phases.

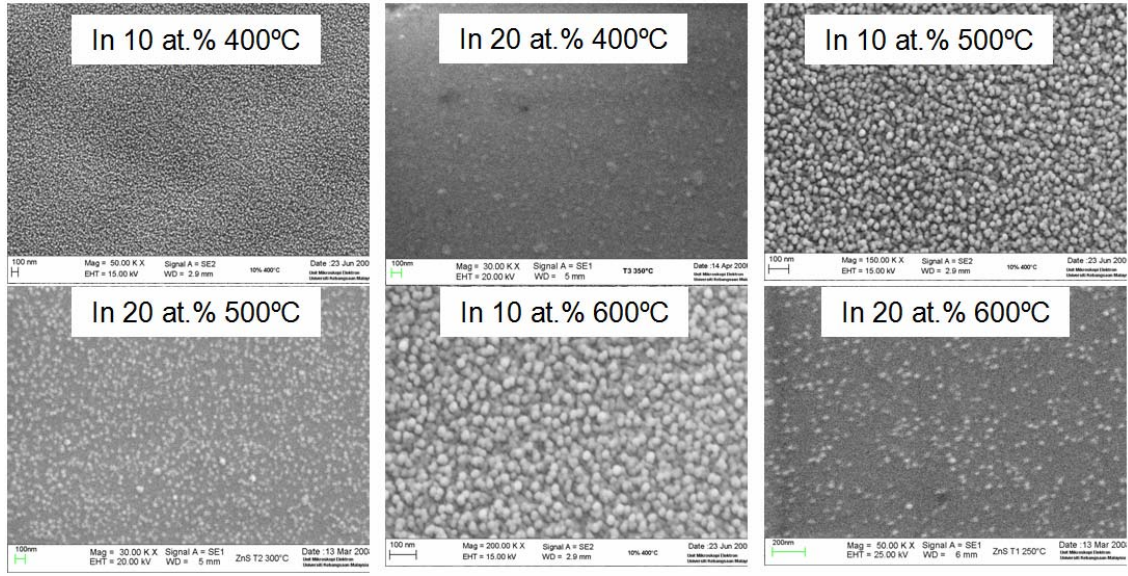


Figure 1: The surface morphology of undoped, 10 and 20 at.% In doped ZnO

Table 1: Estimation of grain sizes by SEM

Annealing Temperature (°C)	Grain Sizes (nm)	
	10 at.% In	20 at.% In
400	24.72	25.30
500	27.80	32.22
600	48.26	50.13

X-ray diffraction patterns of In-doped ZnO films are presented in Figure 2. For the as-prepared ZnO nanoparticles, there are many dangling bonds related to the oxygen vacancies of the grain boundaries. Those grains tend to merge during the annealing process. The doping of In into ZnO thin film destroys the crystallinity of the thin film. It is uncoverable even after annealing at 400, 500 and 600°C. The doped ZnO thin films provide the diffraction peaks for (100), (002) and (101). Similar effect was not observed for the doped ZnO.

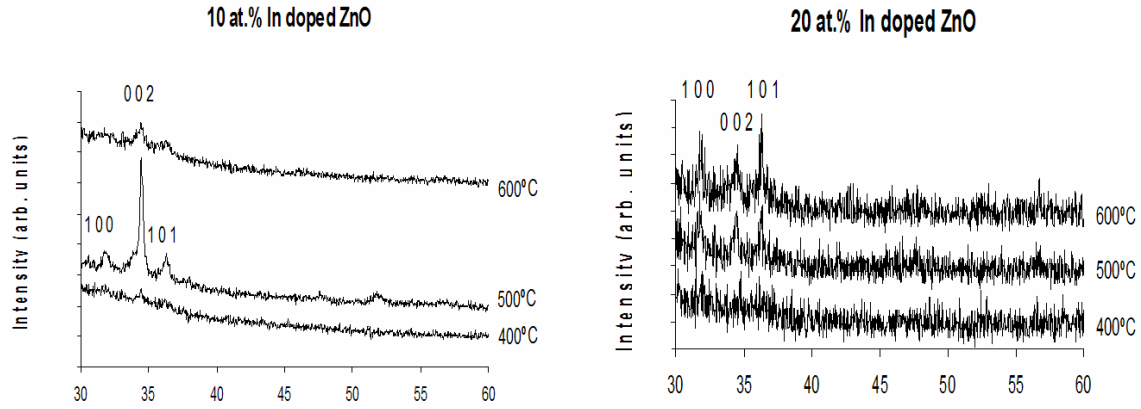


Figure 2: XRD of ZnO and In doped ZnO at different annealing temperatures

The absorption coefficient (α) is calculated by using the following equation [11]:

$$\alpha = \frac{\ln(1/T)}{d} \quad (1)$$

where T is the transmittance index and d is the film thickness. In the direct transition semiconductor, the optical band-gap dependence on the absorption coefficient is given by the following equation [12]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where A , E_g and $h\nu$ are constant, optical band gap, and photo energy, respectively. The E_g can be determined by plotting the curve of $(\alpha h\nu)^2$ versus photo energy $h\nu$ and extrapolating the linear portion of the curve to the $h\nu$ -axis. Band-gap energy estimated from the absorption edge of the films is shown in Fig. 3. The band gap increased from 4.163 to 4.189 eV with increasing of In from $x = 0.1$ to 0.2, respectively. There was not much variation in the peak position of the absorption band on In doping at different annealing. We can see the background absorption at the higher concentration increased drastically. Such an increase in background absorption is due to higher scattering of light at the rough surfaces of the doped nanostructures.

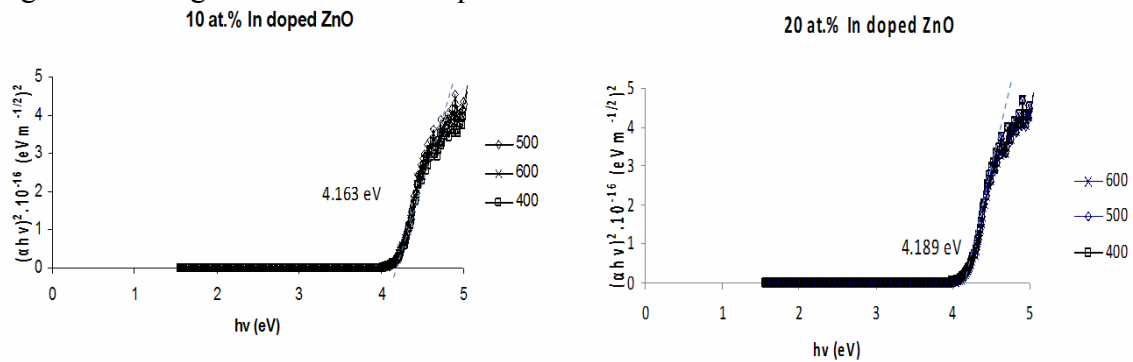


Figure 3: Plot of $(\alpha h\nu)^2$ as a function of photo energy for the undoped and In doped ZnO

CONCLUSIONS

We have discussed the effect of post-annealing temperature on the structural and optical properties of In doped ZnO thin films. The crystal quality of the films is highly dependent on the annealing temperature: it can be improved along with the films annealed from 400 °C to 600 °C. The morphology of ZnO nanostructures changed drastically on the incorporation of In. The band gap increased from 4.163 to 4.189 eV with increasing of In from $x = 0.1$ to 0.2, respectively. The increase of the band gap is attributed to the decrease of the tensile strain in the films and a linear increment of the optical band gap with the strain was obtained.

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