

EFFECTS OF GROUP III DOPANTS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF SOL-GEL DERIVED ZnO THIN FILMS

Somtop Santibenchakul¹, Russameeruk Noonuruk², Kamonchanok Ruangon³, Warut Khamon³, and Wisanu Pecharapa^{3*}

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Abstract

In this research, the effect of group III dopants on the structural and optical properties of zinc oxide (ZnO) thin films was investigated. Undoped, Al-, Ga-, and In-doped ZnO thin films at a constant 3 at. % doping content were fabricated by the simple route of a sol-gel spin coating process followed by an annealing technique in an ambient pressure at 500°C. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), and indium (III) acetate ($\text{In}(\text{CH}_3\text{COO})_3$) were used as the starting materials for Zn, Al, Ga, and In sources, respectively. The structural properties of undoped and group III-doped ZnO thin films agreed with the hexagonal wurtzite crystal structure. Moreover, incorporation of group III dopants into the ZnO lattice was able to decrease the grain size and deteriorate the crystallinity of the ZnO. The transmittance phenomena in the visible region of all thin films was shown to be higher than 92%. Furthermore, the optical band gap of ZnO doping with group III dopants is higher than for purified ZnO. In the same way, the morphology of ZnO has a sharp distinction with various types of group III dopants.

Keywords: Group III dopants, sol-gel, ZnO thin films

¹ Department of Science and Mathematics, Faculty of Science and Technology, Rajamangala University of Technology Tawan-ok, Chonburi, 20110, Thailand.

² Division of Physics, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Pathumthani, 12110, Thailand.

³ College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520, Thailand. E-mail: kpewisan@gmail.com

* Corresponding author

Introduction

In general, several transparent conductive oxides (TCO) were fabricated as thin film structures on substrates for optoelectronics applications. The conductivity and transparency of thin films play important roles in increasing the performance of the corresponding devices (Muhammad *et al.*, 2012). In general, indium tin oxide (ITO) is one of most widely employed TCO materials because of its high electrical conductivity and optical transparency (Her and Chang, 2016). However, it is well known that ITO has several disadvantages such as low stability, high toxicity, and expensive cost (Jun *et al.*, 2012). In this case, zinc oxide (ZnO) with different doping materials has attracted much attention because of its low toxicity, low resistivity, and high transmittance in the visible region (Haga *et al.*, 2001; Look *et al.*, 2003; von Wenckstern *et al.*, 2009). Many kinds of dopants, especially for group III, were introduced to ZnO for enhancement of the electrical and optical properties, such as aluminium (Musat *et al.*, 2004), gallium (Thambidurai *et al.*, 2014), and indium (Djessas *et al.*, 2014). Group III elements can act as either interstitial elements or as a substitutional one in the ZnO lattice to form n-type ZnO that can improve its physical properties (Karakaya and Ozbaz, 2015; von Wenckstern *et al.*, 2009). Doping ZnO with group III dopants enhances the transmittance and the band gap of materials. Moreover, the resistivity of doping materials is decreased at low dopant concentrations (Khuili *et al.*, 2016). Finally, the obtained product of doping ZnO with group III dopants acts as an n-type semiconductor (Paul *et al.*, 2016). It should be noted that group III elements-doped ZnO thin films have been fabricated by various techniques such as chemical-vapor deposition (Haga *et al.*, 2001), rf-magnetron sputtering (Djessas *et al.*, 2014), spray pyrolysis (Karakaya and Ozbaz, 2015), electrochemical deposition (Chen *et al.*, 2014), or sol-gel method (Musat *et al.*, 2004). In all of the above, the sol-gel method is a wet chemical method which is normally utilized to fabricate various kinds of functional ZnO films because of its uncomplicated equipment, inexpensive cost,

and ease of preparation of a homogeneous precursor.

In this work, Al-doped ZnO (AZO), Ga-doped ZnO (GZO), and In-doped ZnO (IZO) thin films were fabricated by the sol-gel method. The effects of the Al, Ga, and In dopants with a certain concentration on the microstructure and optical properties of the AZO, GZO, and IZO thin films were compared and investigated.

Materials and Methods

The sol-gel method was utilized to synthesize ZnO thin films doped with 3 group III elements, Al, Ga, and In. The starting precursors of Zn, Al, Ga, and In are derived from zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), and indium(III) acetate ($\text{In}(\text{CH}_3\text{COO})_3$), respectively. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) and diethanolamine ($\text{NH}(\text{CH}_2\text{CH}_2\text{OH})$) were used as a solvent and stabilizer, respectively. Firstly, the Zn precursor solution was prepared by dissolving the starting precursor in a solvent mixture between absolute ethanol and diethanolamine to obtain zinc ion of 0.2 mol/dm^3 in the solution.

Additionally, each of the group III precursors was added into the above solution with a composition of 3 at.% doping content. Each of the precursor solutions was stirred at 75°C for 2 h and kept at room temperature for 24 h. Afterward, undoped ZnO, AZO, GZO, and IZO thin films were deposited on the glass substrates by sol-gel coating. Finally, the deposited films were dried at 100°C for 10 min in the air followed by annealing in the air at 500°C for 2 h.

The crystallinity of the undoped ZnO, AZO, GZO, and IZO thin films were measured by X-ray diffraction using a D8 DISCOVER diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), while their morphologies were monitored by a field emission JSM-6340F scanning electron microscope (JEOL Ltd., Tokyo, Japan). The optical properties of the

thin films were investigated by a UV-Vis T90+ spectrophotometer (PG Instruments, Ltd., Lutterworth, UK).

Results and Discussion

The XRD patterns of the undoped, Al-, Ga-, and In-doped ZnO thin films at a constant 3 at. % doping content and after being annealed at 500°C in air for 2 h are shown Figure 1. All of them show the notable diffraction peaks which are indexed to the hexagonal wurtzite crystal structure of ZnO and agree well with the JCPDS no. 89-1397 (Thanigainathan and Paramasivan, 2013). The 2θ values of the plane (100) for the un-doped ZnO, AZO, GZO, and IZO thin films are found to be 31.25°, 31.24°, 31.24°, and 31.65°, respectively. It can be found that the angle of the diffraction peak of the ZnO is higher than that of the AZO and GZO but lower than that of the IZO thin film. This result is the same relative to an earlier report (Sim *et al.*, 2010) which can be explained by the difference of the ionic radius dopants. The ionic radii of the Al^{3+} (0.53 Å) and Ga^{3+} (0.62 Å) dopants are smaller whereas the value of the In^{3+} (0.81 Å) dopant is bigger than the Zn^{2+} in the lattice. Moreover, doping with group III elements into the ZnO lattice could induce the decrease in the crystallite size compared with

the undoped ZnO. The average crystallite sizes of the undoped ZnO, AZO, GZO, and IZO were evaluated from the major (100), (002), (101) peaks by Scherrer's formula (Sengupta *et al.*, 2010).

Their values were found to be approximately 16.9, 11.8, 13.1, and 9.2 nm, respectively. It can be suggested that incorporation of group III dopants into the ZnO film was able to increase the nucleus number (Thambidurai *et al.*, 2014) resulting in the decrease in grain size and deterioration in crystallinity of the ZnO (Hong *et al.*, 2006).

Figure 2 shows the transmittance spectra in the region of 350-700 nm. It can be observed that the undoped ZnO and doped ZnO thin films exhibit quite low transmittance in the UV region ($\lambda < 400$ nm) due to the typically high photon absorptivity of ZnO beyond its optical band gap. Nevertheless, the large transmittance of all matter appears in the visible region ($\lambda = 400$ -700 nm), indicating the excellent transparency of the prepared films. The average values of transmittance in the visible region for the undoped ZnO, AZO, GZO, and IZO thin films are found to be 95%, 92%, 94%, and 98%, respectively.

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

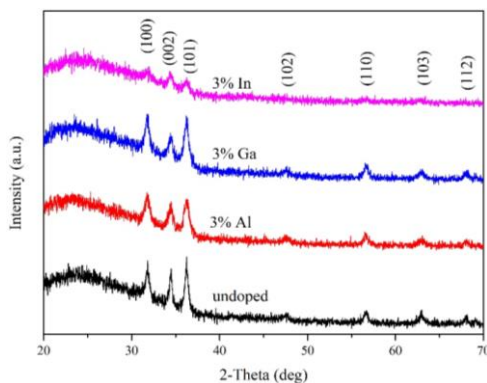


Figure 1. XRD patterns of undoped ZnO, AZO, GZO, and IZO thin films annealed at 500°C

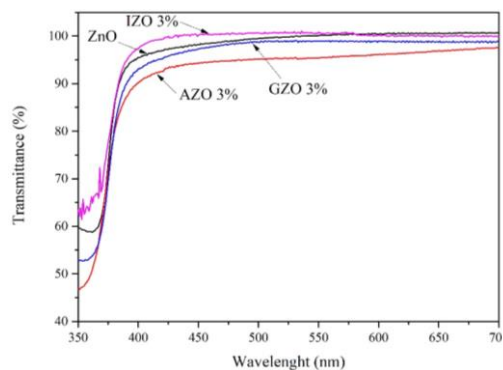


Figure 2. Transmittance of undoped ZnO, AZO, GZO, and IZO thin films annealed at 500°C

The equation shows the relationship between the photon energy ($h\nu$) and the square of the absorption coefficient (α)², whereas A and E_g are a constant and the band gap, respectively. Figure 3 shows the Tauc plot of the ZnO, AZO, GZO, and IZO materials.

Moreover, the optical band gaps of all samples are listed in Table 1. From these results, the optical band gap of the undoped ZnO, AZO, GZO, and IZO are 3.26, 3.31, 3.35, and 3.39 eV, respectively. It can be found that doping ZnO with group III dopants can significantly heighten the optical band gap of the ZnO. It can be proposed that Zn²⁺ may be replaced with the A³⁺ and then given oxygen vacancies and a free electron. The Fermi level is shifted to the conduction band by the electrons which inhabit the lowest level of the conduction band.

After that, an electron from the valence band can be excited to the conduction band above the Fermi level (Khuili *et al.*, 2016). Furthermore, upon doping, the group III dopants may improve the ionized impurity scattering and the carrier concentration of the ZnO matrix could be increased, leading to the increasing optical band gap of the ZnO thin film (Nunes *et al.*, 2002; Khuili *et al.*, 2014). Therefore, the band gap of the doping material would be increased which is known through the Moss-Burstein effect.

The surface morphology and particle size distributions of the undoped, Al-, Ga-, and In- doped ZnO materials are illustrated in Figure 4. It can be seen that the microstructures of the AZO and GZO thin films are more homogeneous than the undoped ZnO and IZO films. It can be proposed that group III dopants

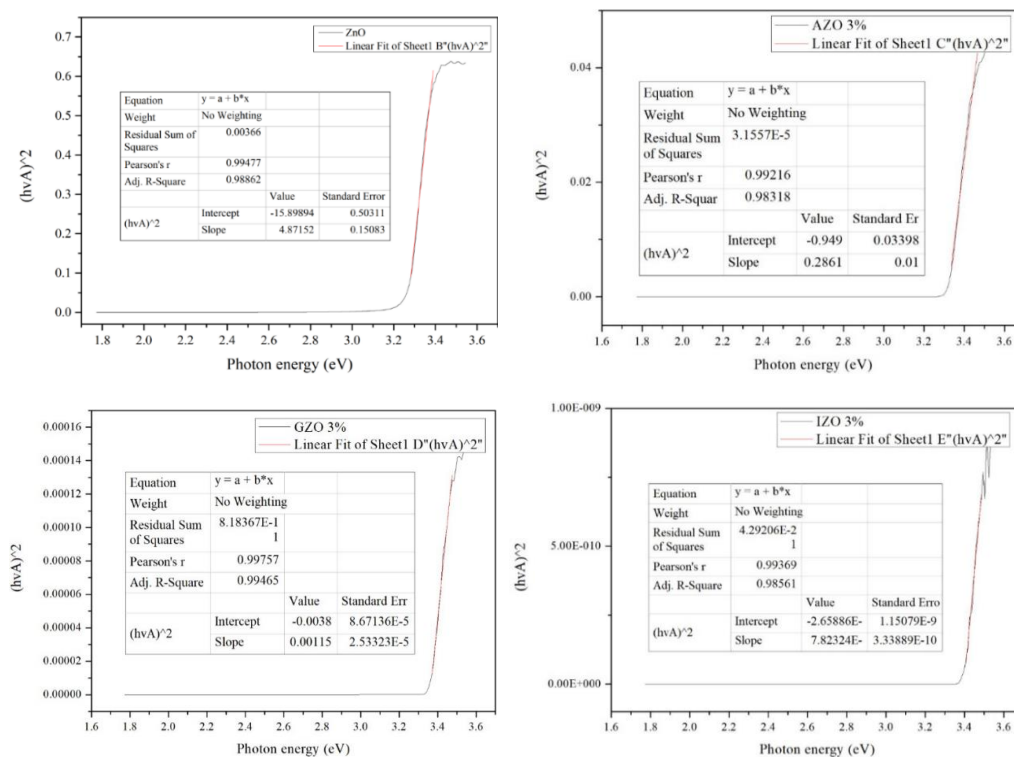
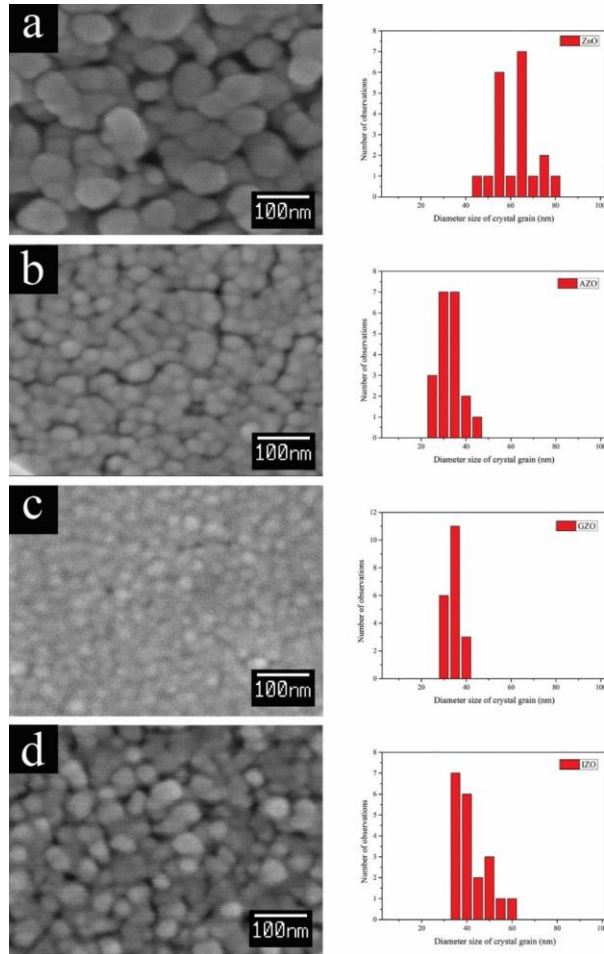


Figure 3. Tauc plot of ZnO, AZO, GZO, and IZO thin films

Table 1. The optical band gap of the undoped, Al-, Ga-, and In-doped ZnO thin films

Material	Optical band gap (eV)
undoped ZnO	3.26
AZO	3.31
GZO	3.35
IZO	3.39

**Figure 4. SEM images and size distribution plot of grain size: (a) ZnO, (b) AZO, (c) GZO, and (d) IZO materials**

can increase the amount of nucleation of ZnO. After that, the formation of small grains was achieved during incorporation of the group III dopants into the ZnO lattice. Therefore, the

grain size of the undoped ZnO thin film is much larger than that of the AZO, GZO, and IZO thin films. In the same way, the size distribution of the undoped ZnO microstructure

has a wide range of 40-85 nm. In the case of the AZO thin film, Al^{3+} may occupy either substitutional or interstitial sites in the ZnO lattice because the ionic radius of Al^{3+} is normally lower than that of Zn^{2+} . As a result, association of the AZO grain occurred, so that the surface morphology of the AZO was smooth with the existence of noticeable pores. On the other hand, Ga^{3+} seemed to be the only substitutional dopant because the ionic radius of Ga^{3+} is close to that of Zn^{2+} . Consequently, the grain size of GZO is equalized and rearranged in a regular form. As seen in the SEM image of the GZO thin film, the condensed film is achieved with a narrow size distribution of the microstructure. Additionally, In^{3+} could be introduced into the ZnO lattice only by substitution at the Zn^{2+} sites due to the ionic radius of In^{3+} being greater than that of Zn^{2+} . Therefore, the grain size of the IZO is found to be bigger than that of the AZO and GZO microstructure as observed in Figure 4. It can be concluded that the difference in the ionic radius between the group III dopants and zinc could disturb the grain growth of particles. However, the grain size as measured from the SEM images is higher than the values calculated from the XRD measurements. This phenomenon suggests that these grains probably aggregate to form a cluster of particles (Hong *et al.*, 2006; Jun *et al.*, 2012).

Conclusions

Undoped and ZnO with group III elements (Al, Ga, and In) doped into ZnO thin films have been successfully deposited onto glass substrates by a sol-gel method. It was found that the average grain size of the ZnO thin films doped with group III elements was obviously reduced while their optical band gaps were slightly increased. All the doped ZnO thin films exhibited transmittance values over 92.0%, and the optical band gaps were in the range of 3.31-3.39 eV.

The surface morphologies of the prepared films were found to be highly influenced by the type of dopant. In this case, the ionic radius of the dopants plays a key role in their surface

morphologies. As a result, the structural, optical, and morphological properties of ZnO thin films can be modified by different doping elements from group III.

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