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Article

ZnO Doped with Bismuth in case of In-Phase Behavior for Solar Cell Application

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Abstract. Zinc Oxide (ZnO) nanostructure thin films doped with bismuth atoms were initially achieved by spin coating preparation from zinc acetate gel on the fused quartz substrate. The optical and structural properties have been preliminary studied in order to obtain more understanding the optimized factors for transparent conductive oxides (TCOs) of thin film solar cell. The optical transmittance was higher than 90% in the visible range for all films. In addition, the optical band gap of the prepared films calculated by Tauc plot showed the change of lightly blue shift but no significantly changed with increasing of Bi doping concentration. The glancing incident X-ray diffraction result showed that the Bi doped in ZnO nanostructure thin films after annealing have polycrystalline hexagonal wurtzite structure and good preferential orientation along c-axis. This chemical characterization indicated that in-phase behavior occurred in low Bi dopant content between 0.2 – 1.0 at.% Bi content, hence 1 atomic percentage of Bi content was uppermost to obtain preferential orientation in this study. However, the quality of the films surface was improved due to the larger number of coating layers but the electrical properties was improved. The tentative study in term of electrical behavior was investigated for application in TCO film of solar cell. The electrical property showed that more multi ZnO layers affected on an increase in the electrical conductivity of the films.

Keywords: Bi doped ZnO, ZnO thin film, TCO film, photovoltaic.

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1. Introduction

In the recent, Zinc Oxide is a semiconductor material that is interested and applied in many applications, such as solar cells, transparent electrode, gas sensor, photo catalysts, transducers, laser diodes and acoustic wave devices [1-5]. Due to its properties such as n-type semiconductor with wide direct energy band gap (3.37 eV), high exciton binding energy (60 meV) [6] and the electrical resistivity can be adjusted between low and high which depend on the processing, annealing temperature and doping concentration [7-9]. Furthermore ZnO is stable in hydrogen plasma and environment, low cost material and transparent in visible light region. Therefore ZnO is interested and approached to replacement of indium tin oxide (ITO) which is widely used for transparent conducting electrode.

Nowadays, doped n-typed ZnO thin films has been prepared by various deposition techniques e.g. r.f. magnetron sputtering, pulsed laser deposition (PLD), chemical vapor deposition (CVD), evaporation, metal organic chemical vapor deposition (MOCVD), sol-gel, and spray pyrolysis [10-17]. Sol-gel technique is very low-cost effective due to nanostructural preparation under low-temperature, and it is simple to control the dopant composition. M. Jiang et.al (2009) [11] studied the effect of the annealing condition on the Bi-doped ZnO films prepared by r.f. magnetron sputtering. The Bi-doped ZnO films possessed high transmittance (about 85%) in the visible region and resistivity value with high carries density of the film. Furthermore, F. Chouikh *et al.* (2011) [18] studied the structural, optical and electrical properties of undoped ZnO and Bi doped ZnO thin films prepared by ultrasonic spray pyrolysis technique. The conductive and transparent Bi-doping ZnO films by sol-gel method have not been reported yet. Moreover, their structural and optical characteristics for this film have not been fully understood.

In this paper, the Bi-doped ZnO thin films were prepared by spin coating of the sol-gel method. The effects of dopant concentration on structural, optical and electrical properties with various Bi doping concentrations of ZnO thin films were investigated. The transmittance of the layers deposited on glass was measured in UV-visible region. Tauc plot was used for estimating the band gap energy of Bi-doped ZnO thin films that was appropriate to apply in TCO film in solar cell.

2. Experimental

2.1. Materials

Undoped and bismuth doped ZnO gel were synthesized from zinc acetate dihydrate $\{Zn(CH_3COO)_2 \cdot 2H_2O\}$, Bismuth nitrate pentahydrate $\{Bi(NO_3)_3 \cdot 5H_2O\}$, ethylene glycol and monoethanolamine (MEA) as starting material for ZnO, bismuth dopant source, solvent and sol-stabilizer, respectively. All materials were purchased from Ajax Finechem, Fluka, CARLO ERBA, Ajax Finechem, respectively.

2.2. Sol-Gel and Thin Film Preparation

Zinc acetate dihydrate was added in the mixed solution of ethylene glycol and monoethanolamine (MEA). Concentration of zinc acetate was 0.7 M and molar ratio of zinc acetate dihydrate to MEA was kept at 1. The solution was stirred at 80°C for 10 minutes and then dropped bismuth dopant solution by varying the bismuth concentrations for 0.0 – 1.2 at.%, and continue stirred at 80°C for 1 hour. The fused quartz substrates in this work were carefully cleaned by Ratio Corporation of America (RCA) method. The undoped and bismuth doped ZnO nanostructure thin films were prepare by spin coating process on the fused quartz substrate by using spinning speed at 2500 rpm for 10 seconds. The films were dried at 100°C for 30 minutes in oven and then repeated coating again as shown in Fig. 1. All films were annealed at 600°C for 2 hrs in furnace with air atmosphere as followed to previous work [19].

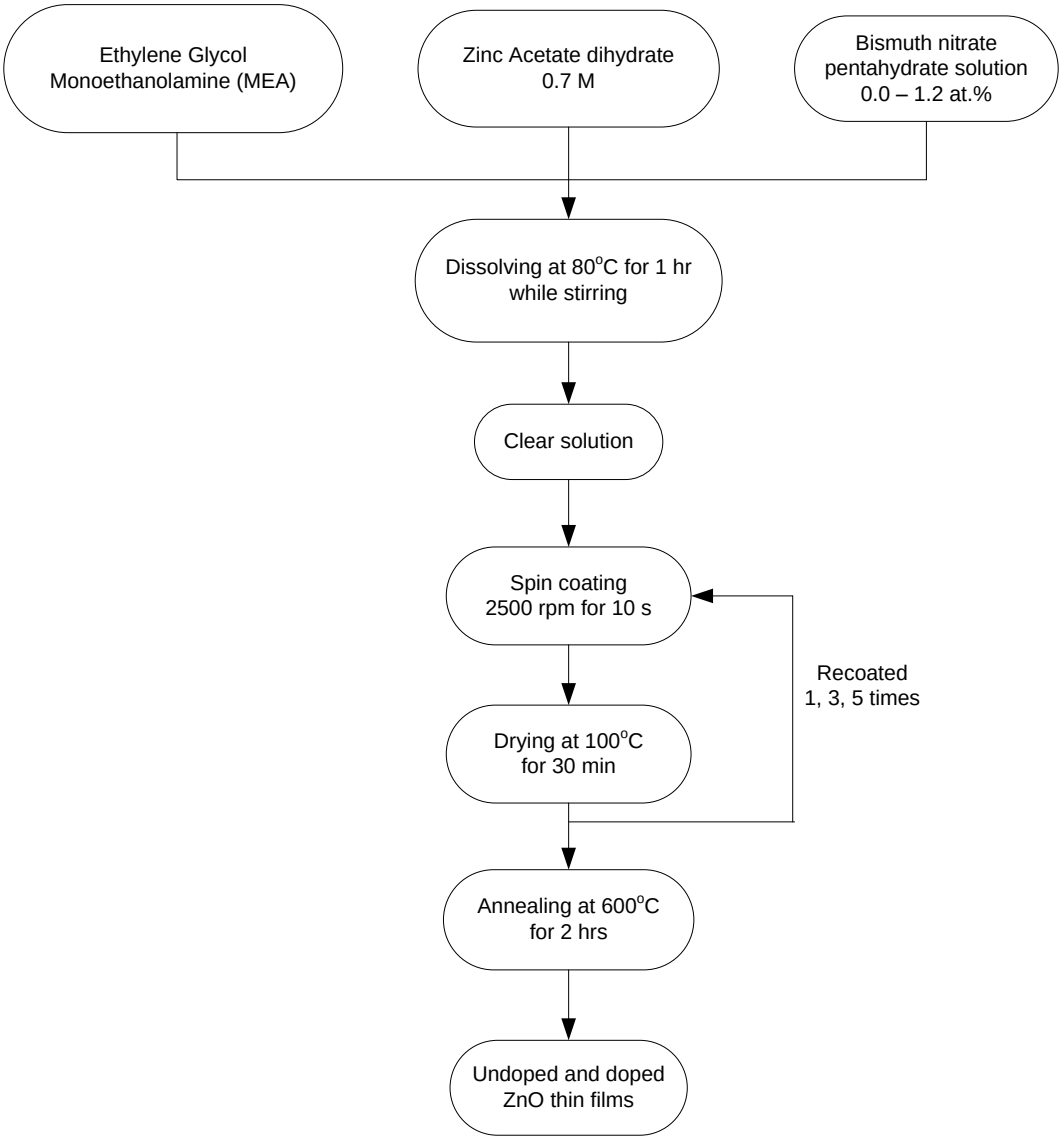

Fig. 1. Flow chart of Bi doped ZnO thin film preparation.

2.3. Characterization of Bi-doped ZnO Thin Films

The phase and structural characterization of thin films were determined by using Glancing X-ray diffractometer (RIGAKU TTRAX III) with a Cu-$K_{\alpha 1}$ (1.54059 Å) as an X-ray source at 40 kV and 300 mA. Surface morphology was observed by using scanning electron microscope (Neo-1450VP). The optical transmittance and reflectance were measured by UV-Vis spectrophotometer (AJUK SPECORD 250+222P133) in the range of 300-1100 nm wavelength. The film thickness was measured by optical profiler (Veeco WYKO NT1100). The average grain size (d) of ZnO thin films was calculate by using Scherrer formula as Eq. (1) [20].

$$d = \frac{0.9\lambda}{B\cos\theta_B} \tag{1}$$

where λ , B, θ_B are wavelength of the X-ray radiation (1.54059 Å), full width at half maximum (FWHM), and the Bragg diffraction angle of the most intense peak in this study (002), respectively. Tauc plot method is used for estimating the band gap energy (E_g) of ZnO thin films by an extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $(h\nu)$ curve from Eq. (2) [21]:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \tag{2}$$

where C is a constant for a direct transition and photon energy. The optical absorption coefficient (α) of ZnO thin films can be calculated by Eq. (3) [21]:

$$\alpha = \frac{1}{t}\ln\left(\frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2}\right) \tag{3}$$

where t, T, R are the thickness, the optical transmittance, the optical reflectance of the film, respectively.

The Current-Voltage (I-V) curve of ZnO thin films was measured by using Keithley 2400 source meter and plot a J-V curve as a function of ZnO thin film thickness. Silver plate was used as electrode on 0.2 at.% Bi doped ZnO thin films with varying film layers.

3. Result and Discussion

3.1. Structural Characterization

3.1.1. X-Ray Diffraction

The undoped and Bi doped ZnO thin films were first coated on clean fused quartz substrate and annealed at 600°C. The effect of Bi doping concentration on the chemical structure of ZnO thin films was studied. Figure 2 shows X-ray diffraction patterns of ZnO thin films and undoped ZnO thin film which are polycrystalline with hexagonal wurtzite structure. The diffraction peaks are identified to (100), (002), (101), (102), (110) and (103) in the scanning angle (2θ) from 25 – 65°, compared with ICDD JCPDS pattern no. 36-1451 (the powder diffraction of ZnO structure). The evaluated structure parameters of thin films are presented in Table 1. ZnO thin films with 0.2 – 1.0 at.% Bi contents showed preferential orientation along (002) and (103) peaks. However, the diffraction patterns of ZnO thin film with 1.2 at.% Bi content were same as that of undoped ZnO thin film. It indicated that Bi atom was not in-phase of ZnO but it was probably separated in Bi_2O_3 phase into the grain boundary. However, it could not detect the diffraction peaks of Bi_2O_3 due to its small concentration. The lattice parameters can be calculated by using the following formula [22]:

$$d_{hkl} = \frac{1}{\sqrt{4(h^2 + k^2 + hk)/3a^2 + l^2/c^2}} \tag{4}$$

where a and c are the lattice parameters and d_{hkl} is the crystalline surface distance of hkl indices. The lattice parameters of undoped ZnO thin films are closed to the parameters of a_0 = 3.250 Å and c_0 = 5.207 Å (JCPDS 36-1451). As can be seen in table 1, the different Bi doping concentrations give higher c values than undoped ZnO thin film. Bao *et al.* [23] have reported that slightly higher c values for ZnO thin films prepared on quartz glass substrates by a sol-gel method. The c-axis preferentially oriented ZnO thin film can be suggested that the value of the surface free energy is minimum for the ZnO (002) plane at the growth stage [24]. The increasing of parameter c value is possible to substitute Bi dopants into the Zn sites. The parameter c value slightly increased with increasing the Bi doping concentrations until 1.0 at.% and with further increasing in doping level, the parameter c value decreased to lower its value in undoped one at 1.2 at.% Bi dopant. Therefore, 1.0 at.% Bi concentration is the upper limit content for in-phase ZnO film in this study. The grain size of the different doping concentrations was determined using the XRD spectra and the Dybye-Scherer formula. The average grain size of doped ZnO decreased as compared to undoped ZnO film. The grain size slightly increased with increasing Bi doping contents until 0.6 at.% and decreased to 8.5 μm at 1.2 at.% Bi concentration as shown in Fig. 3.

Table 1. Lattice parameters and Crystallite size of ZnO thin films.

Bi dopant concentration (at.%)	Annealing temperature (°C)	Lattice parameters		Relative intensity of (002) peak
		a (Å)	c (Å)	
0.0	600	3.254	5.213	0.228
0.2		3.250	5.220	0.769
0.4		3.246	5.219	0.720
0.6		3.252	5.218	0.673
1.0		3.237	5.223	0.705
1.2		3.268	5.179	0.320

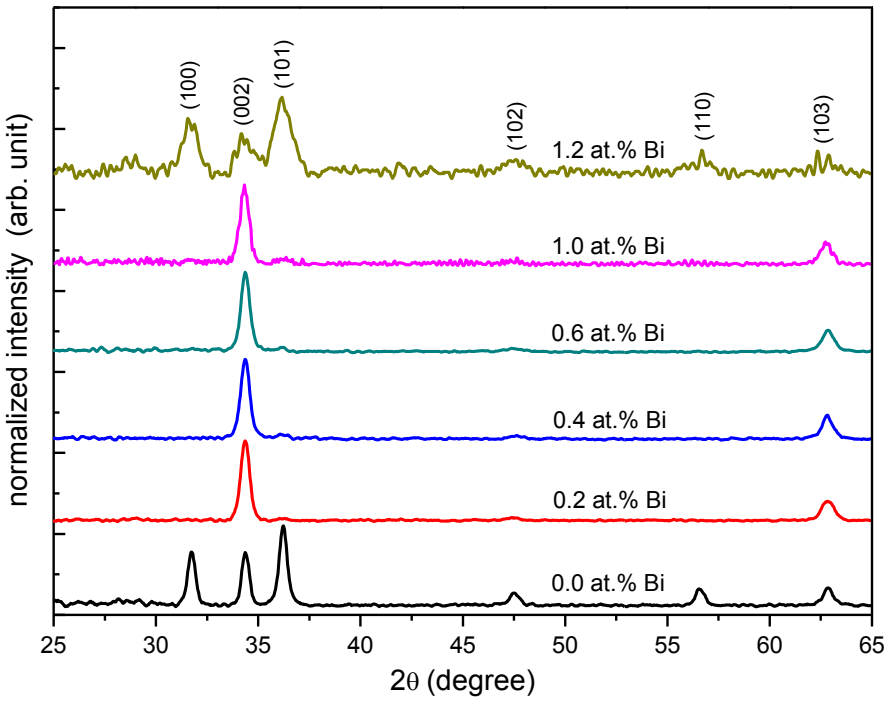

Fig. 2. X-ray diffraction patterns of Bi doped ZnO thin films annealed at 600°C with various Bi concentrations.

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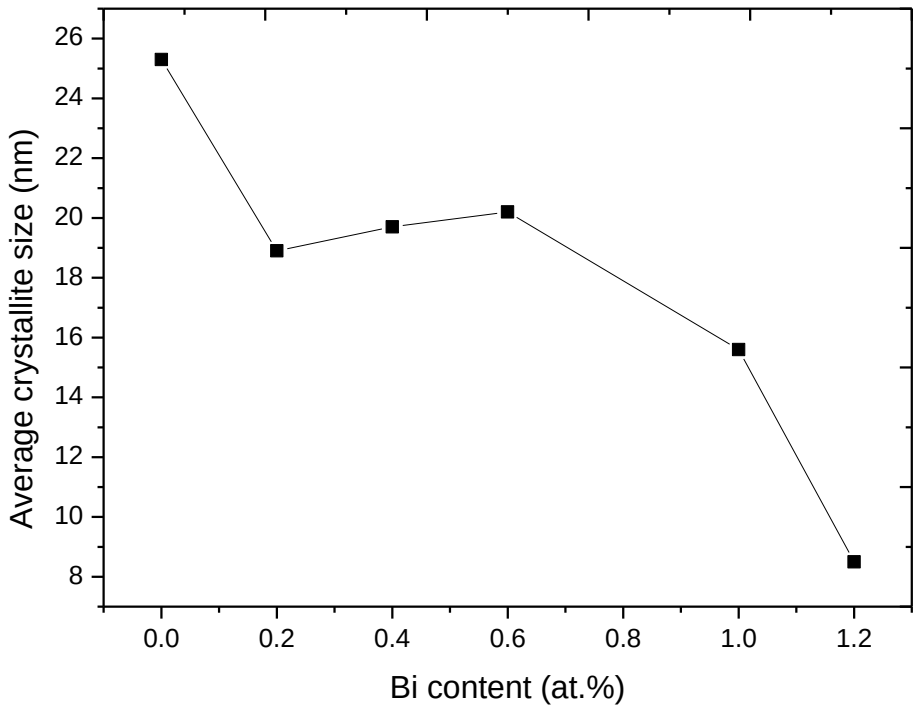

Fig. 3. Variation of average crystallite size of Bi doped ZnO thin films annealed at 600°C with Bi dopant concentrations.

3.1.2. Surface Morphology

From the previous work [18], 0.2 at% Bi doped ZnO thin film had the best preferential c-axis orientation. The surface morphology of this film with various dopant concentrations and coating layers was observed by using SEM as shown in Fig. 4 and 5, respectively. Figure 4(a)–(e) show the surface morphology of 1 layer ZnO thin films with various dopant concentrations. Pores and many small cracks appeared on surface for all films resulting in the low electrical conductivity of thin films. Figure 5(a)–(c) show the SEM micrographs of 0.2 at.% Bi doped ZnO nanostructure thin films annealed at 600°C with various repeat coatings at 1, 3 and 5 layers, respectively. From these figures, the morphology of the film at 1 layer coating appeared cracks more than other films. In the other hand, the crack and porous defects were improved with increasing coating layers, but it appears higher roughness.

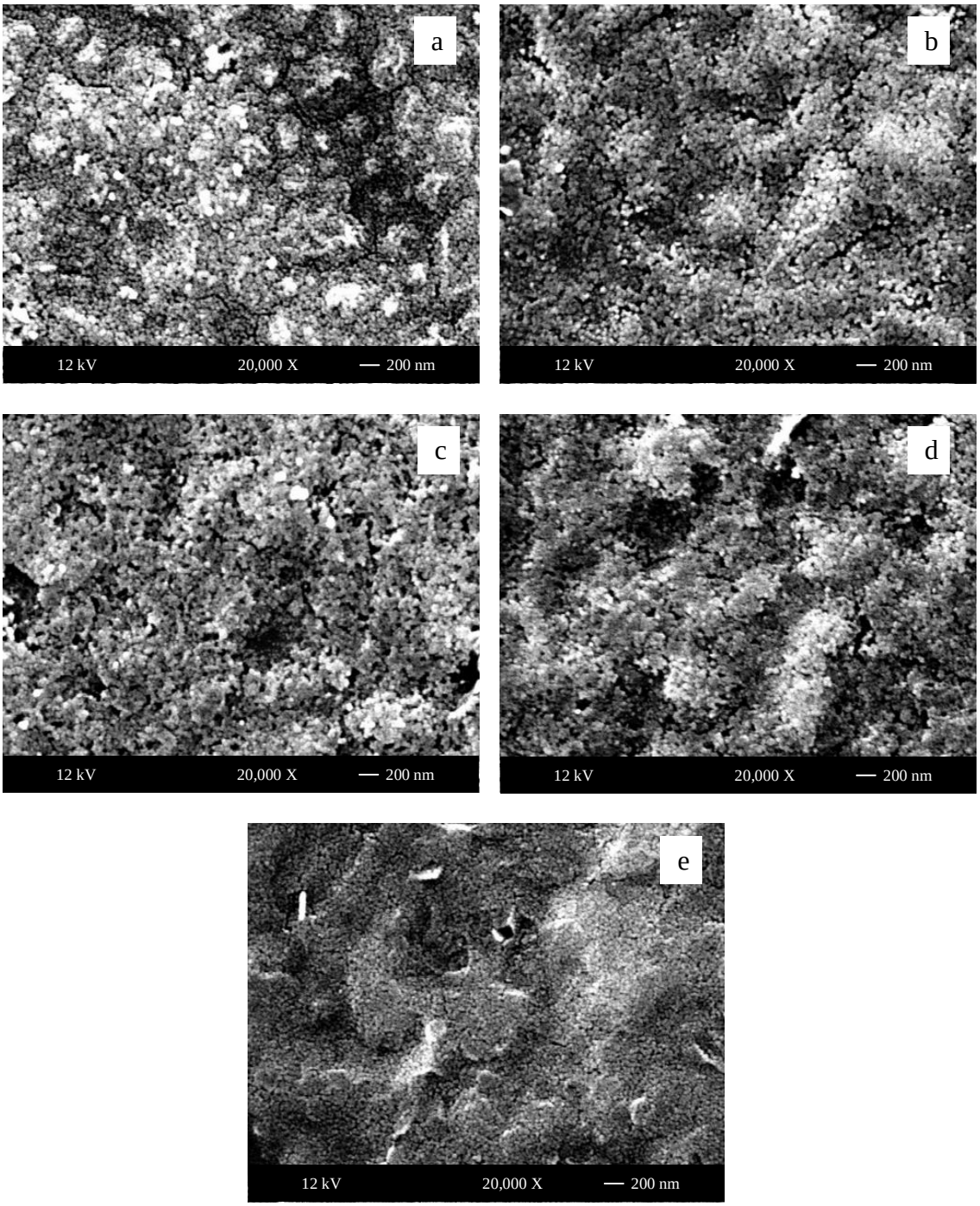

Fig. 4. SEM micrographs of Bi doped ZnO thin films annealed at 600°C with various Bi concentrations for 1 layer films (a) 0.0 at. %, (b) 0.2 at. %, (c) 0.4 at. %, (d) 0.6 at. %, (e) 1.0 at. %.

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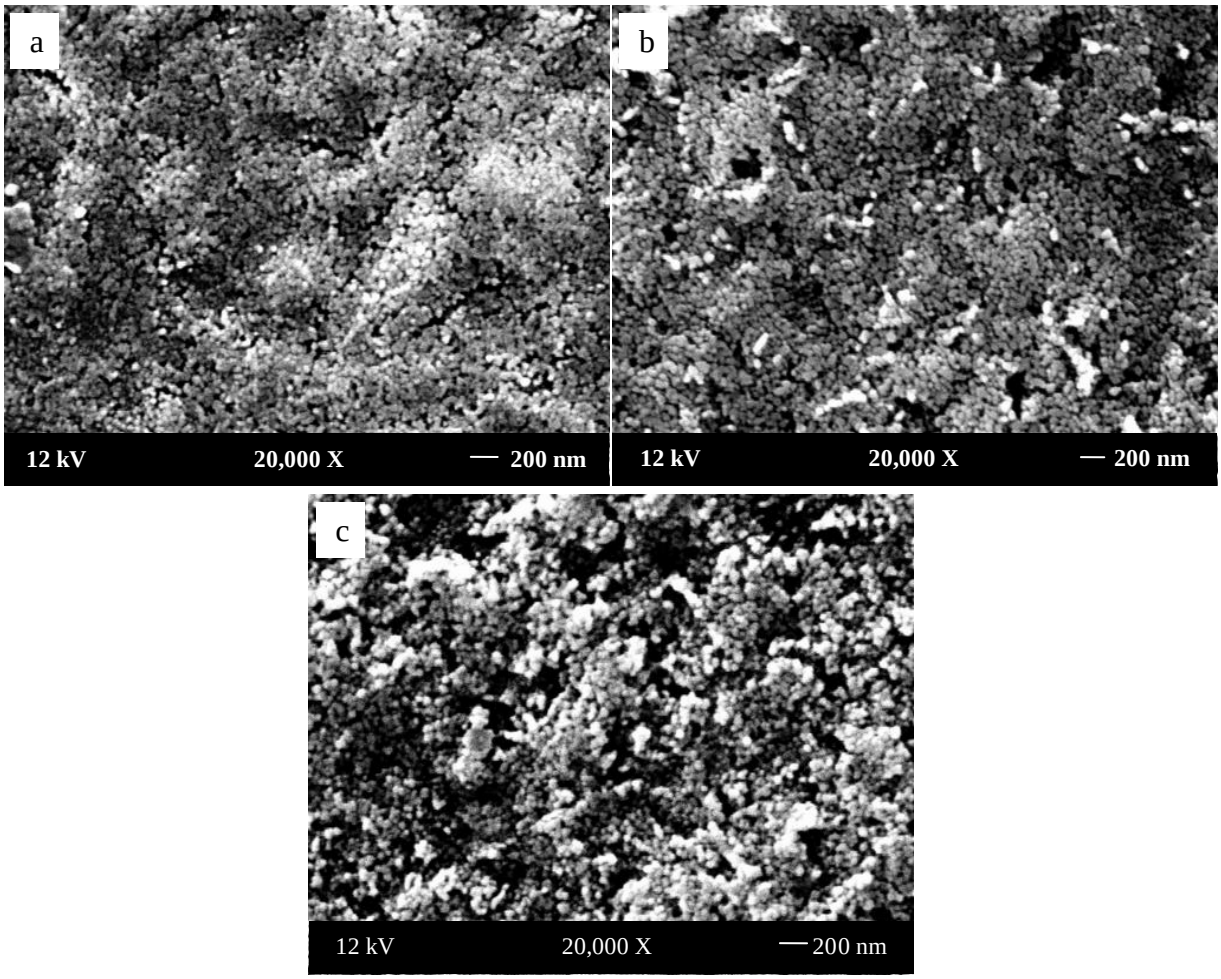

Fig. 5. SEM micrographs of 0.2 at.% Bi doped ZnO thin films annealed at 600°C with varying layers (a) 1 layer, (b) 3 layers, and (c) 5 layers.

3.2. Optical Characterization

Figure 6 and 7 show the transmittance and reflectance spectra of the ZnO thin films (1 layer thin film) in the range of 350 – 800 nm, respectively. It shows low reflectance value in visible light region. It can indicate that the ZnO thin films are transparent and suitable to apply as the TCO. Moreover, the ZnO thin films responded to 350 – 400 nm in blue light wavelength. The optical band gap (E_g) of ZnO thin films can be estimated from the relationship curve between $(\alpha h\nu)^2$ versus $(h\nu)$ by extrapolation of the linear portion (Tauc plot). As can be seen in Fig. 8, the band gap energy of Bi doped ZnO thin films decreased (3.27 eV) as compared with undoped ZnO thin film (3.28 eV) and no significantly change with different Bi doping concentrations as summarized in Table 2. This result is against the report of M. Jiang *et al.* [10] who observed the band gap shift from 3.24 to 3.29 eV for the Bi-doped ZnO thin films prepared by rf magnetron sputtering with increasing the argon pressure from 1.0 to 3.0 Pa. F. Chouikh *et al.* [18] who found that the band gap shift from 3.19 to 3.24 eV for Bi-doped ZnO films deposited by ultrasonic spray pyrolysis (to 5 mol% Bi concentration). They suggested that narrowing of optical band gap might be attributed to the forming of Bi impurity energy level. Therefore, the optical properties of thin films can be attributed to the deposition/ coating process and annealing temperature.

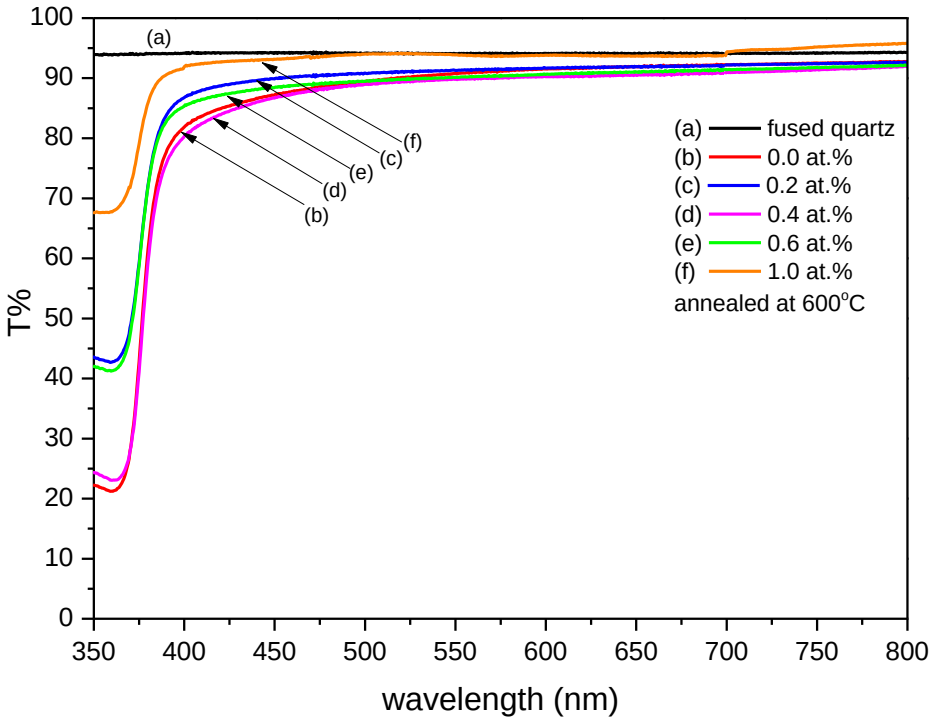

Fig. 6. Transmittance spectra of Bi doped ZnO thin films annealed at 600°C with varying Bi concentrations for 1 layer films.

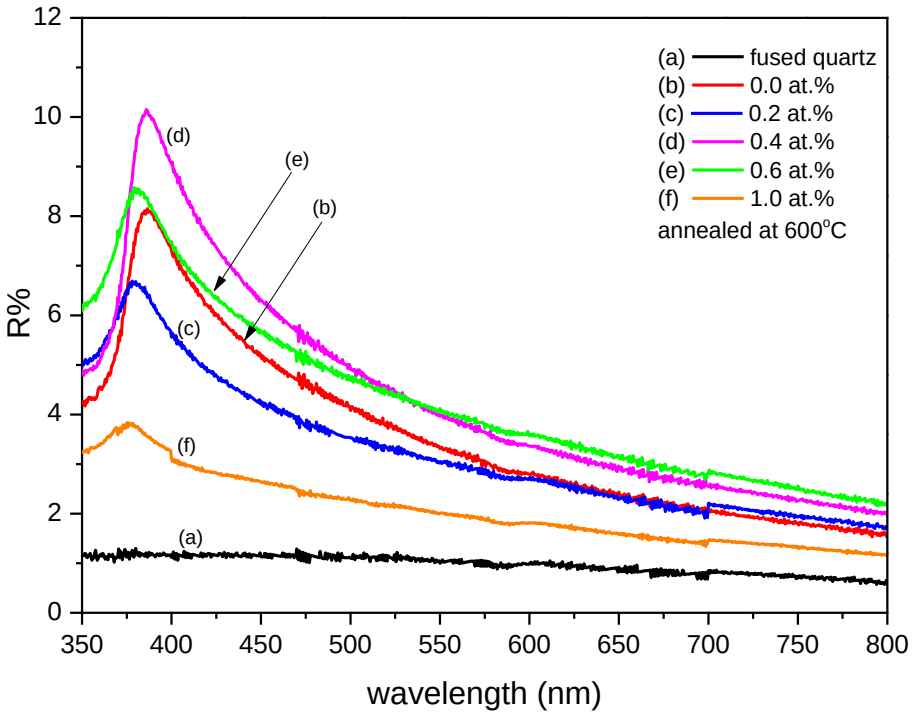

Fig. 7. Reflectance spectra of Bi doped ZnO thin films annealed at 600°C with varying Bi concentrations for 1 layer films.

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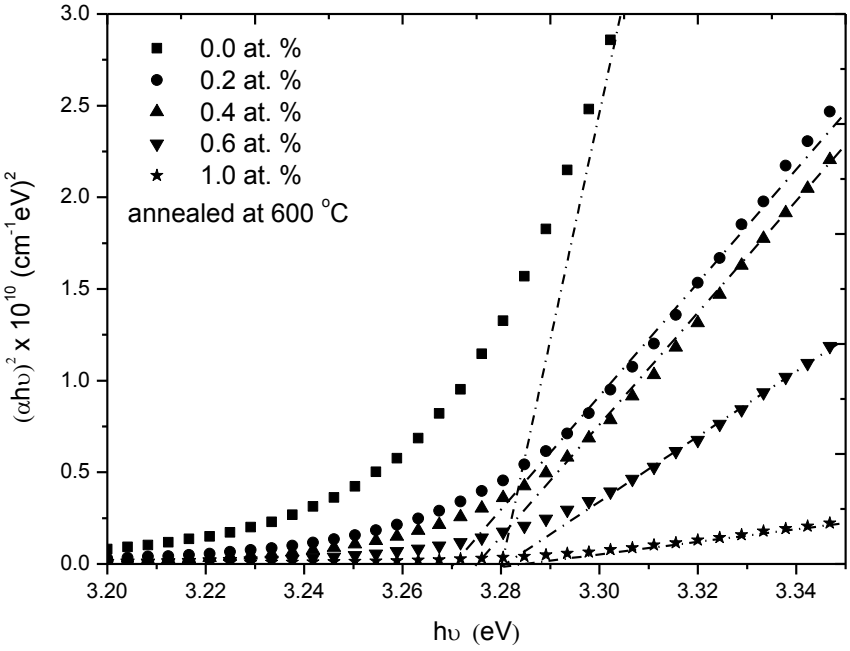

Fig. 8. $(\alpha h\nu)^2$ versus $(h\nu)$ curve of Bi doped ZnO thin films annealed at 600°C with varying Bi contents for 1 layer films.

Table 2. Optical band gap of ZnO thin films (1 layer).

Bi (at. %)	Annealing Temp (°C)	E_g (eV)
0.0		3.28
0.2		3.27
0.4	600	3.275
0.6		3.28
1.0		3.28

3.3. Electrical Characterization

The 0.2 at.% Bi doped ZnO thin films with various repeat coating times as shown in Fig. 9. The J-V curve in dark condition of the ZnO thin films shows the ohmic behavior and the conductivity increased with increasing repeat coating times. The film quality was improved due to pores and crack defects were reduced and became homogenous. The resistivity of 5 layers ZnO thin film is 20.48 Ω-cm which is very high as compared to other reports [10, 18]. Bi-doped ZnO thin films deposited by ultrasonic spray pyrolysis have the electrical resistivity varies within four order of decade level (from 0.1-1000 Ω-cm) with increasing Bi doping level. Usually, the grain boundary and surface defect caused a large effect on the electrical properties. In this study, the electrical resistivity decreased with decreasing surface defects. As can be seen in surface morphology (Fig. 5), porosity and surface cracks decreased with increasing coating layers.

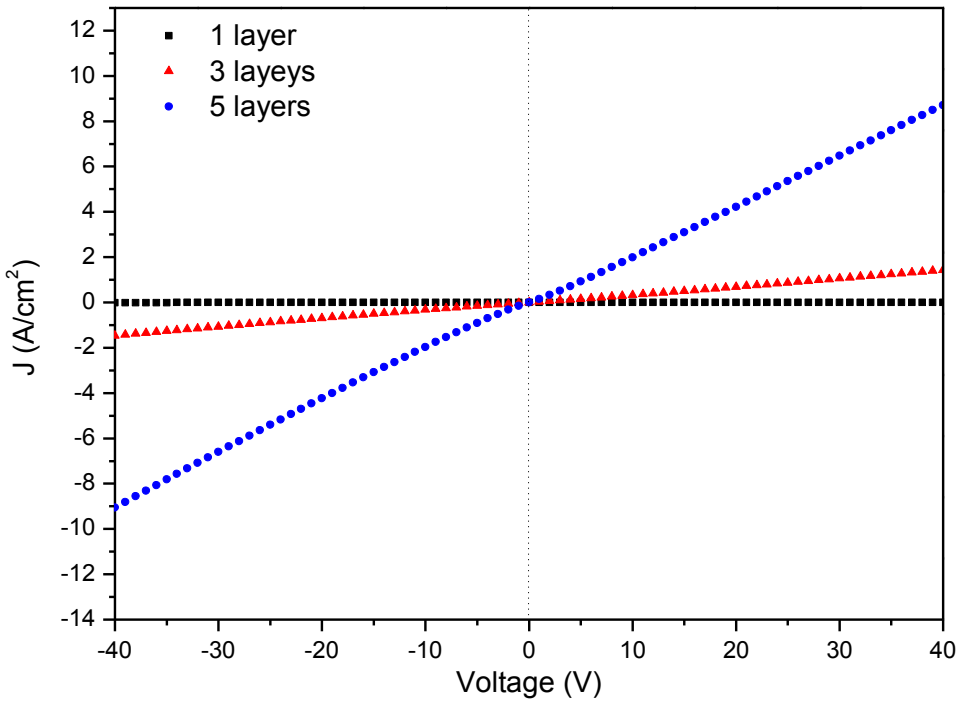

Fig. 9. J-V curve of 0.2 at.% Bi-doped ZnO thin films with varying coating layers.

4. Conclusions

In summary, undoped and Bi doped ZnO thin film on the fused quartz substrates have been prepared by a simple sol-gel spin coating method. XRD pattern of ZnO thin films with 0.2-1.0 at% Bi showed polycrystalline wurtzite structure with a preferential c-axis orientation. However, with 1.2 at.% Bi doped ZnO thin film, it occurred out-of phase ZnO. The optical characteristic showed that Bi doped ZnO thin films were excellent transmission in visible light region. Moreover, the transmittance showed sharp absorption edge shift in blue wavelength. The reflectance spectra showed low reflectance value which will be brought high photon energy to attack solar cell structure. The energy band gap was not affected by Bi incorporation with different concentrations. The surface morphology of 0.2 at.% Bi doped ZnO thin film was improved with increasing the number of layer. Furthermore, the electrical conductivity increased with increasing the number of layer as well.

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