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Effect of Precursor Concentration and Annealed Substrate Temperature on the Crystal Structure, Electronic and Optical Properties of ZnO Thin Film

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ABSTRACT

This study carried out on the effect of precursor concentration and annealed substrate temperature on the crystal structure, electronic and optical properties of ZnO thin film. An aqueous solution of Acid Nitrite was used as precursors and its concentration was varied from 0.1 M to 0.4 M. The ZnO thin film was deposited on the glass substrate by Spray Pyrolysis Deposition and annealed with different temperature from 300 ºC to 600 ºC. The crystal structure, electronic and optical properties were investigated by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and UV-Spectrometer. XRD result showed that all thin films have amorphous hexagonal wurtzite crystalline. Particle sizes ranging from 21.83 to 43.67 nm were calculated through Debye-Scherer Method. It showed that the concentration of the precursor had slightly impact on the particle size. Meanwhile, the increase in particle size with increasing annealed temperature is found to be gradual. The average transparent of all thin film was more than 80%. The bandgap of the ZnO thin films was estimated by Tauc Plot Relation. It showed that the bandgap values were increased with the increasing of precursor concentration due to Burstein-Moss Effect. In addition, the decrease in band gap values was found with increasing annealed temperature. Our results demonstrated that the varying precursor concentration and annealed substrate temperature can enhance the structure, electronic and the optical properties of ZnO thin films.

Keywords: ZnO thin films, concentration precursors, annealed temperature, spray pyrolysis

INTRODUCTION

ZnO (Zinc Oxide)-based semiconductor materials is a promising material for electronic devices application due to high transmittance in visible light and have low resistivity (10^{-2} to 10^{-4} Ω cm) [1], [2]. ZnO in Nano size is very useful in the development of solar cell panels [3]. The characteristics of ZnO such as high electron mobility, high conductivity, wide bandgap and energy that ZnO is very clear for being a Transparent Conductive Oxide (TCO) material

[4]. Therefore, further research and development of ZnO material for TCO applications should be developed.

There are various techniques that can be used in the synthesis process of thin-film zinc oxide such as, thermal evaporation, sputtering, pyrolysis spray, organic chemical vapor deposition (MOCVD), pulsed laser deposition, molecular beam epitaxy (MBE) and chemical synthesis including hydrothermal, solvothermal, sol-gel, electrochemical, chemical deposition bath. From the various techniques of ZnO materials deposition above, the pyrolysis spray technique has many advantages such as easy deposition process, low cost, lower deposition temperature, wide deposition area and uniform results with the excellent coating with a specific composition and also good properties between the substrate and the deposited layer [5]. Tarwal et. al, conducted a study of thin-film ZnO with spray pyrolysis method and produced a thin film ZnO with an average value of transmittance about 85% and bandgap energy of 3.25 eV [6]. In addition, Mani et. al., also used the pyrolysis spray method by varying the annealed time in the ZnO-oriented surgical method. The results showed that the transmittance of the ZnO thin film was about 75% [7].

In this paper, we demonstrate that the electronic and the optical properties of ZnO thin films can be improved by using different precursors concentration and annealed temperature. We made different kinds of ZnO samples with varied of precursors concentration at 0.1 M to 0.4 M and annealed the sample from 300°C, 400°C, 500°C and 600°C, which has not been previously reported. We investigated the effect of different precursors concentration and annealed temperature treatment on the microstructure, energy band gap and optical properties.

EXPERIMENT

Chemicals and instrumentation

In this study, Zinc Oxide was deposited on a quartz substrate using a pyrolysis spray method with substrate temperature is 50 °C. The precursor solution was prepared by using 99.9% pure zinc oxide powder and nitric acid. The deposition time was used for 3 minutes and the annealed process was done for an hour in air atmosphere. In order to find the effects of precursor concentration and temperature of annealed, the thin films were varied for both parameters.

The structure of the thin film of zinc oxide was observed with the characterization of X-Ray Diffraction (XRD). Surface morphology was investigated by using a scanning electron microscope (SEM). The absorbance value, transmittance and energy band gap of the ZnO thin films were measured by using a spectrophotometer UV-Vis.

Procedure reaction

The precursor concentrations were varied at 0.1 M, 0.2 M, 0.3 M and 0.4 M. Meanwhile, the annealing temperatures of 300°C, 400°C, 500°C and 600°C were used in the experiment. After the pyrolysis spraying process, the characterization of the induced sample for zinc oxide thin film was performed.

RESULT AND DISCUSSION

In order to reveal the effect of precursor concentration and annealed substrate temperature, SEM characterization was performed. The result of SEM characterization was shown in Fig. 1. It shows that the thin film with precursors concentration of 0.1 M and 0.4 M at the annealed temperature of 400 °C and 500 °C tend to have homogenous surface. By comparing the thin film with the same precursor concentration, we know that the effect of annealed temperatures on the results obtained in this study is very dominant. It demonstrated that the annealed substrate temperature has a great effect to the surface morphology of the thin films due to the increase of the particle size of the films. The growing size of the atom proved able to cover the parts that have not been coated properly by ZnO material. Meanwhile, it was found the non-homogeneous surface of the thin film with precursors concentration of 0.4 M at the annealed temperature of 600 °C. The non-homogeneous surface was appeared to form the islands due to the effects of "mother droplets". Chen et. al., [8] reported that there are "mother droplets" in the thin film due to the evaporation of the solvent before the droplet reaches the surface of the substrate during the process of deposition. Hence, the particles resulting from "mother droplets" will form a dry particle when reaching the surface of the substrate. This will lead to the formation of clumps on the surface of the coating. Meanwhile, the effect of concentration precursors could be known by comparing the films with similar annealed temperature. It was implied that the precursors' concentration was not affected by the surface morphology of the thin films.

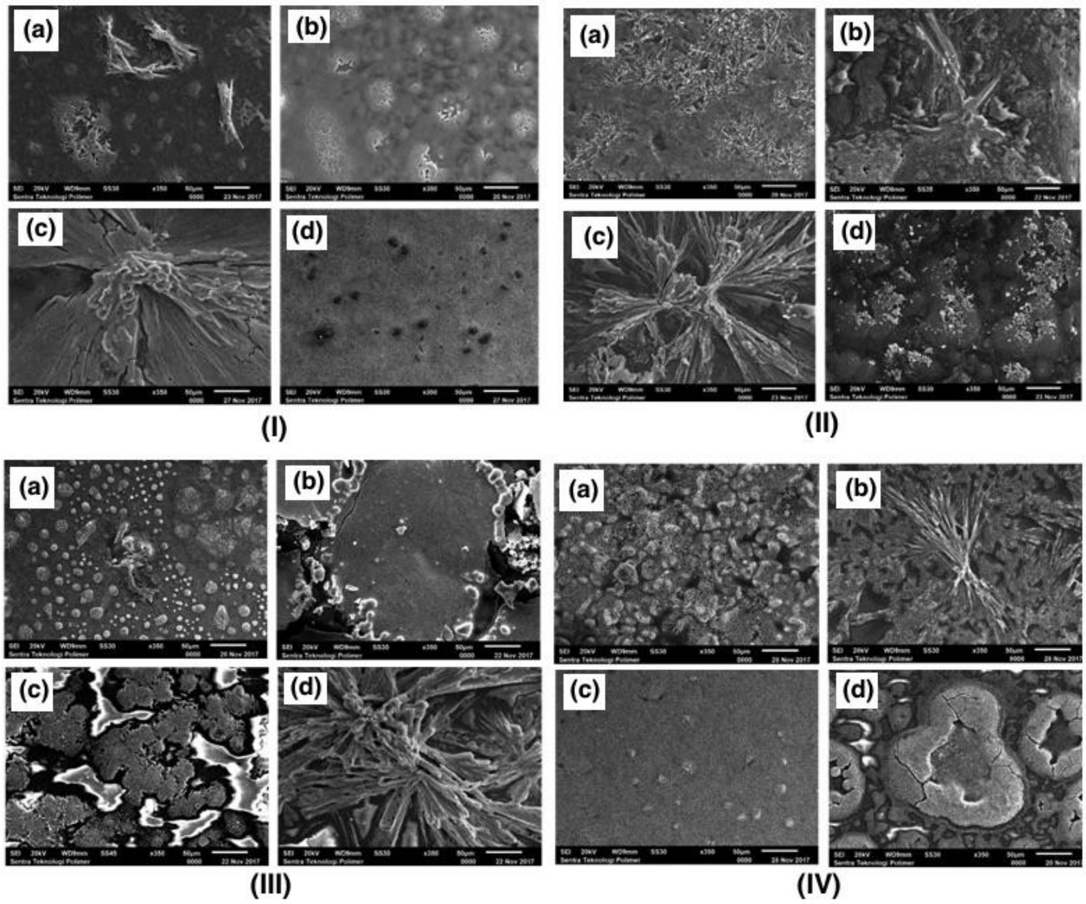

Figure 1. The layer surface morphology at each concentration of precursor varied by annealing temperature. (I) 0.1 M, (II) 0.2 M, (III) 0.3 M and (IV) 0.4 M where the (a-d) code are respectively variations of temperature: (a) 300°C, (b) 400°C, (c) 500°C and (d) 600° C.

Figure 2 shows the peak results of XRD characterization on the ZnO thin film with variations of precursor concentration and annealed temperature. The results showed that all thin films of ZnO have amorphous hexagonal wurtzite crystalline system with the orientation of [010], [002], and [011]. There is no significant difference was found for thin films with different precursor concentration. However, the intensity of the [002] tends to increase with increasing annealed temperature for the film with precursor concentration of 0.3 M and 0.4 M. In addition, the average size of crystalline were calculated from the full width at half maximum of the diffraction of [002] direction through Debye Scherer method. The method as described in [9], and the result were shown in Figure 3.

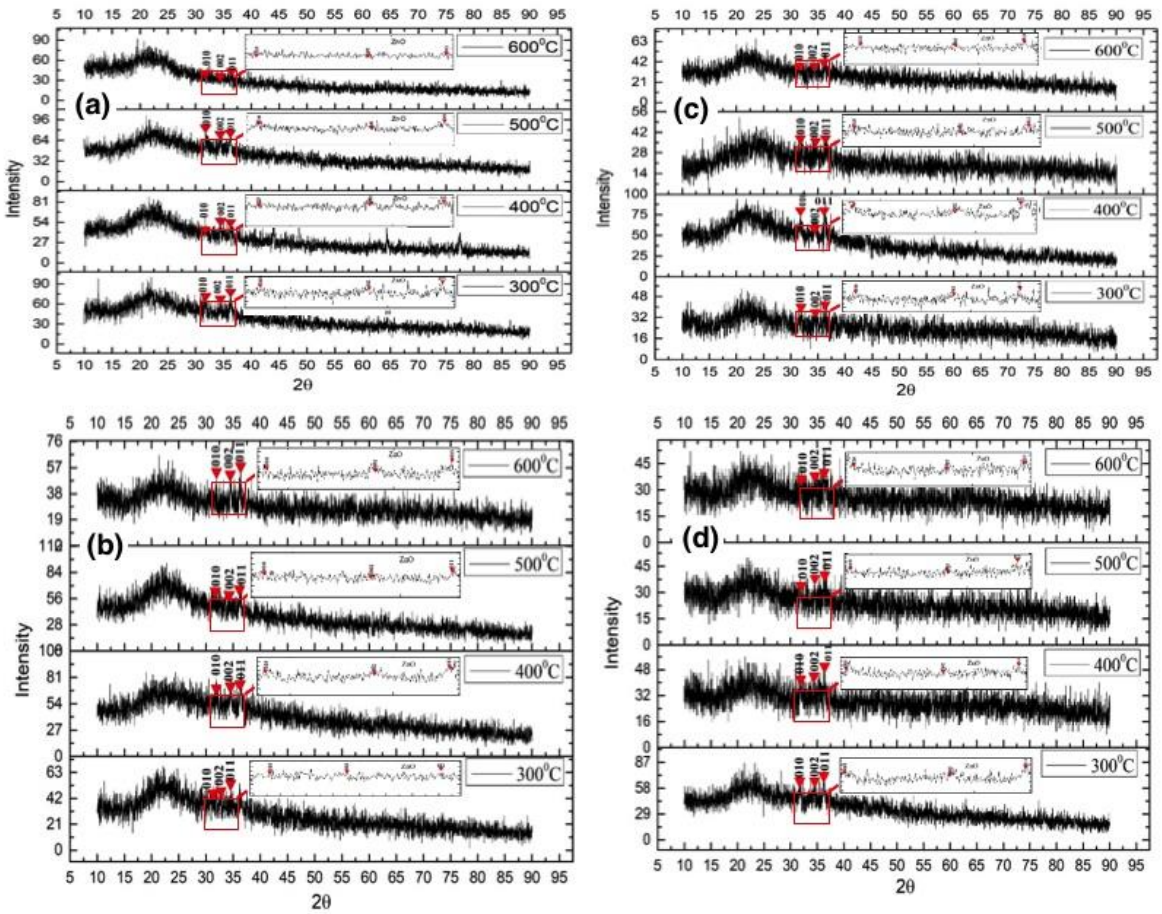

Figure 2. The results of XRD characterization of ZnO thin film with the variation precursors concentration of (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, and (d) 0.4 M for different annealed temperature.

Figures 3(a-b) shows the particle size data of ZnO thin films with varied of different precursors concentration and annealed temperature variations. As shown in Figure 3(a) that the particle size's thin films from the variation of annealed temperature were ranged from 21.83 to 43.67 nm. It showed that the particle size in the ZnO thin films becomes larger with higher annealed temperature. The result implies that the annealed temperature plays a role in improving the surface quality of the ZnO thin film through the increasing of this particle size. Growing grain size will directly reduce the defects found on the surface of the coating [3]. However, Figure 3(b) shows that no significant differences were found of the grain size from the ZnO thin films with different precursors concentration. The results showed that particle size was about 70.12, 46.23, 84.38 and 11.55 nm, for precursors concentrations of 0.1

M, 0.2 M, 0.3 M, and 0.4 M, respectively. It showed that the increased concentration did not sequentially cause the increased particle size of the ZnO thin films. This can be the basis of the reference that the precursor concentration does not significantly affect increasing of grain size of the ZnO thin film.

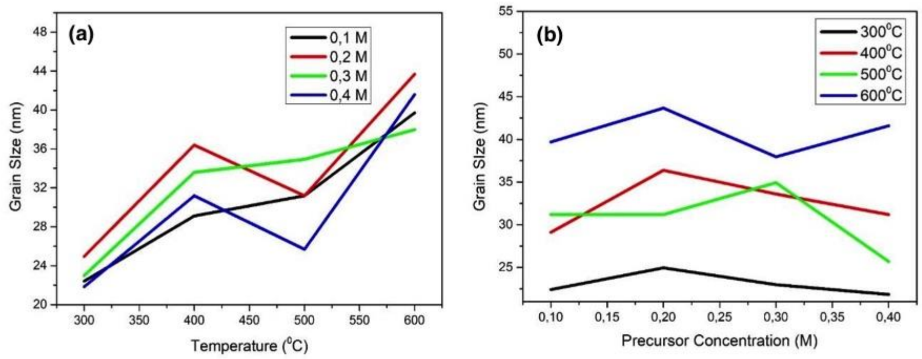

Figure 3. The grain size of ZnO thin films with varied of (a) annealed temperature variations and (b) different precursors concentration.

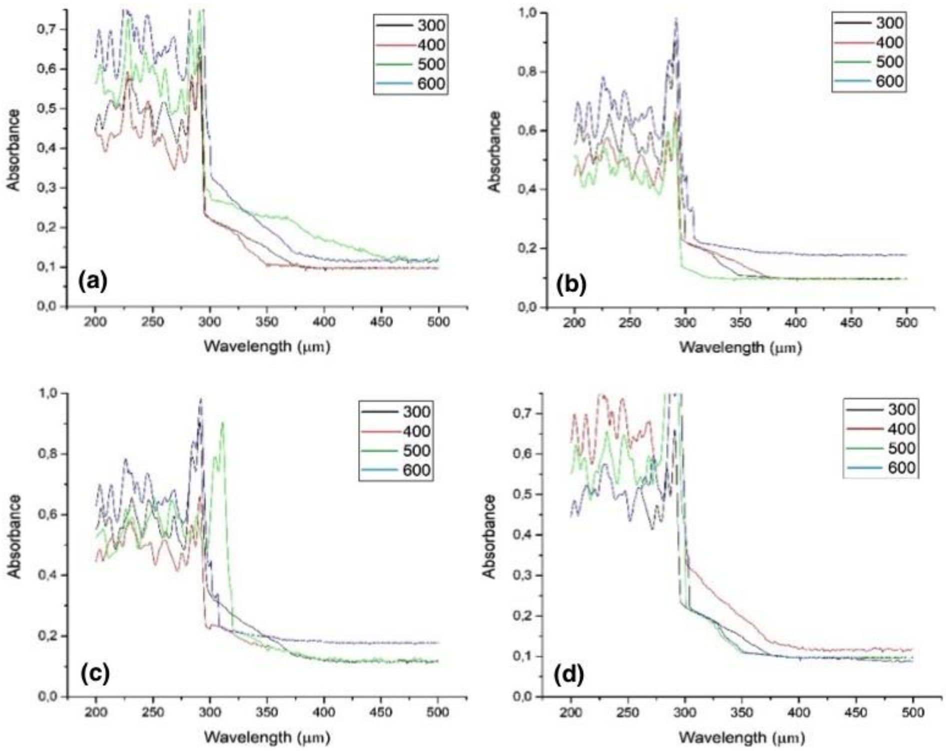

Figure 4. The absorbance spectrum of ZnO thin films in the variation of precursor concentration (a) 0.1 M, (b) 0.2 M, (c)) 0.3 M and (d) 0.4 M.

The optical properties of ZnO thin films were investigated by means of UV-Spectrometer for the films prepared with different precursors concentration and annealed temperature variations. Figure 4 shows that all thin films have a low absorbance value of visible light and infrared light in regions with a wavelength of 380 nm to 500 nm. However, high absorbance values in ultraviolet light areas were shown at wavelengths of 200 nm to 300 nm. The high absorbance value of ultraviolet light is due to the nature of the ZnO material that is sensitive to ultraviolet light.

In addition, the transmittance spectra of ZnO thin films were showed in Figure 5 with different precursor's concentration and annealed temperature variations, and the data were tabulated as shown in Table 1. In the visible light region, the transmittance coefficients are approximately 80% for all films without a change due to the precursor's concentration. However, the highest transmittance value is owned by the thin films at the annealed temperature of 600ºC (the transparency is about 80%). This happens for all variations of precursor concentrations due to improved crystalline quality and reduced defects in the surface layer of ZnO [7], [10].

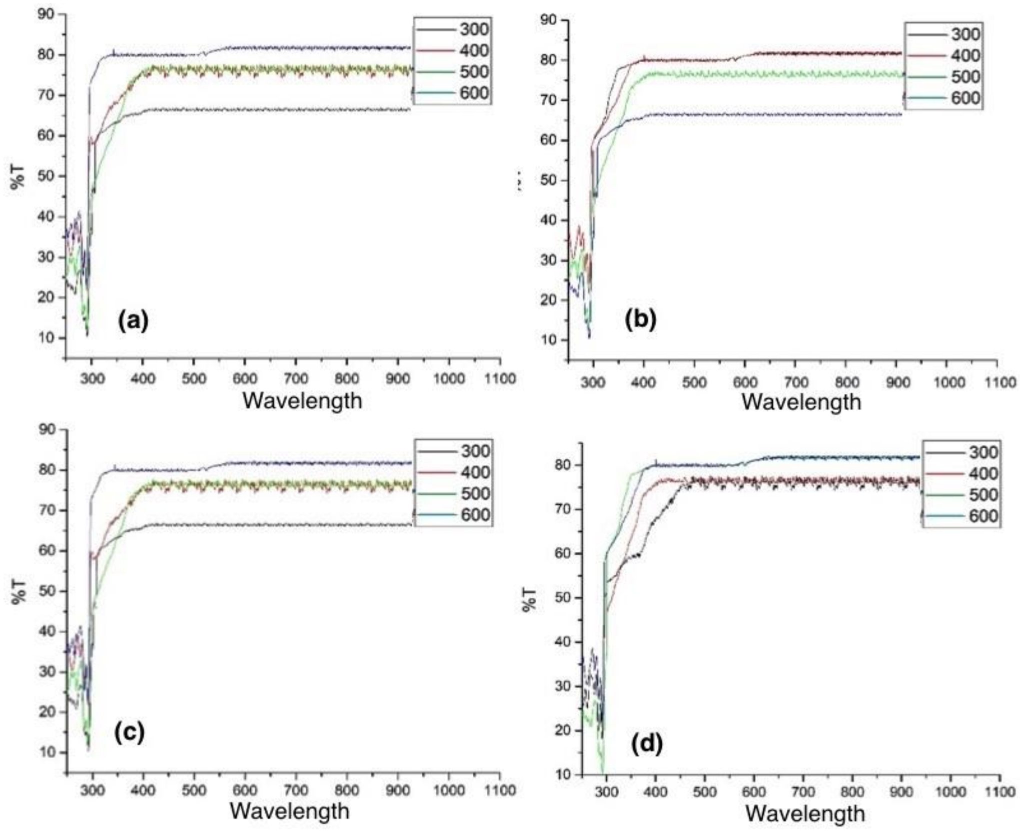

Figure 5. The transmittance spectrum of ZnO thin film for annealed temperature of 300ºC, 400ºC, 500ºC and 600ºC at the precursors concentration of (a) 0.1 M, (b) 0.2 M, (c) 0.3 and (d) 0.4 M, respectively.

The bandgap was determined from the UV spectroscopic measurements by using the Tauc relation [11] (which is valid only for amorphous thin films). The optical band gaps were calculated on the basis of the optical spectral absorption and they can be determined by extrapolating the best fit line between $(\alpha h\upsilon)^2$ and $h\upsilon$, where α, h, and υ are the absorption coefficient, the Planck's constant (6.626×10^{-34} m^2kg/s), and the frequency of incident photons, respectively [12]. The results showed in Figure 6 and tabulated in Table 1. It showed that the optical band gaps of the ZnO thin films tended to decrease as the increasing of annealed temperatures and increase as the increasing of precursors concentration. The decrease of bandgap energy value is due to the effect of ZnO grain size magnification. In addition to the magnification effect of ZnO grain size, the decrease of bandgap energy value is also influenced by the amorph-shaped morphology layer. The bandgap value of the ZnO thin films in this study was similar to those reported by others work [13]–[15].

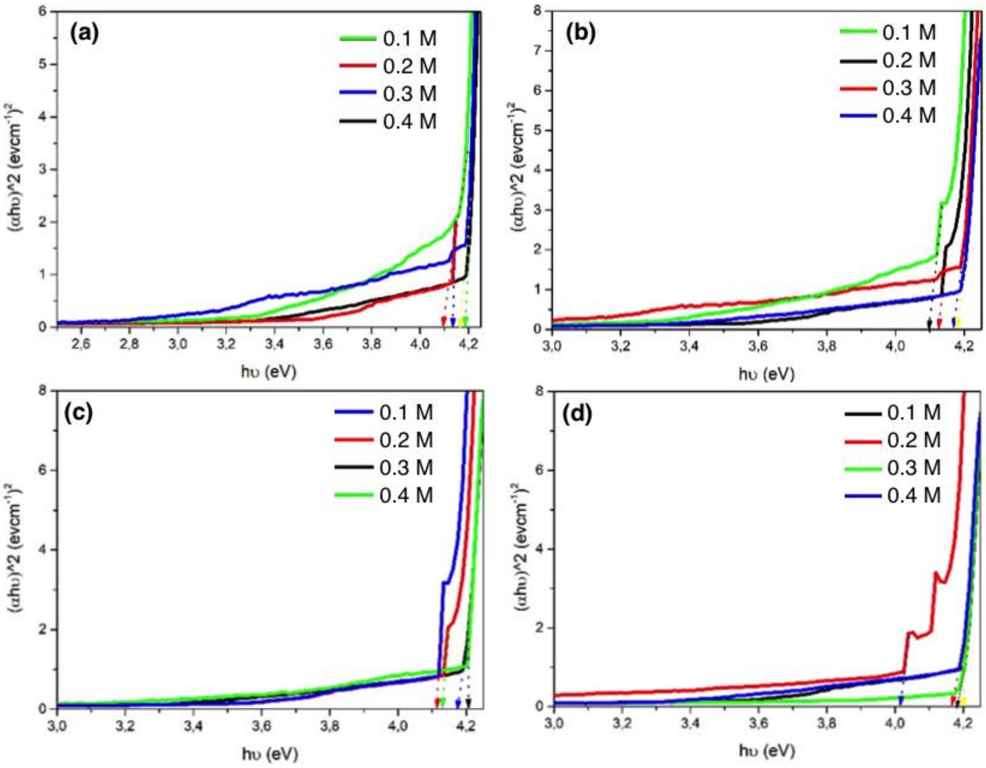

Figure 6. Plot of *(αhυ)*^{2} versus *hυ* of IZTO thin films for different precursors concentration and annealed temperature of ZnO thin film (the a-d code sequentially refers to the variation of annealed substrate temperature of (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C).

CONCLUSION

In this study, we investigated the structure, optical and electronic properties of ZnO thin films with different precursor concentration and substrate temperature. It showed that the concentration of the precursor had slightly impact on the particle size. However, the increase in particle size with increasing annealed temperature is found to be gradual. The average transparent of all thin film was more than 75%. The bandgap of the ZnO thin films was estimated by Tauc Plot Relation. The decrease in band gap values was found with increasing annealed temperature. However, the bandgap of the thin films was not found to be different with varied concentration precursors. Our results demonstrated that the varying precursor concentration and annealed substrate temperature can enhance the structure, electronic and the optical properties of ZnO thin films.

Table 1. The optical band gap of Zinc Oxide Thin Film for different concentration precursors and annealed substrate temperature.

No	Annealed Substrate Temperature (^{o}C)	Concentration Precursor (M)	Optical band gap (Eg)
1.	300	0.1	4.090
		0.2	4.138
		0.3	4.167
		0.4	4.189
2.	400	0.1	4.115
		0.2	4.128
		0.3	4.175
		0.4	4.209
3.	500	0.1	4.135
		0.2	4.145
		0.3	4.193
		0.4	4.206
4.	600	0.1	4.097
		0.2	4.128
		0.3	4.170
		0.4	4.180

CONFLICT OF INTEREST

Authors declare there is no competing interest.

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