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The effect of annealing temperature and Al dopant on characterization of ZnO thin films prepared by sol-gel method

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ABSTRACT

In this project, the sol-gel technique was used to prepare Zinc Oxide (ZnO) thin film and deposited on glass substrate by dip coating method. Zinc acetate dihydrate was used as a source of Zinc ions. The effect of annealing temperature temperatures (300, 400 and 500) °C, Aluminum dopant concentration (3 wt% and 5 wt%) on the properties of ZnO thin film were investigated and analyzed by using X-ray diffraction for structural properties, SEM for morphological properties, UV–VIS for optical properties. X-ray diffraction result has confirmed the formation of hexagonal wurtzite ZnO structure. And the film crystallinity increases with increase the annealing temperature while it decreases with increase Al dopant concentration. The SEM revealed to the formation of a uniform compact surface with ganglia-like hills. The energy band gap (3.28–3.22 eV) found to be decrease with increase the annealing temperature and increase with Al dopant concentrations.

Introduction

The semiconductor nanostructures have attracted much interest due to uncommon mechanical, optical and electrical properties compared with their bulk counterparts [1]. Semiconductors metal oxide are used in many applications due to small size, inexpensive, simple fabrication technique, etc [2]. The zinc oxide (ZnO) thin film is one of the II-VI group semiconductor materials and is composed of hexagonal wurtzite crystal structure, and used as the transparent conductive oxides (TCO) in thin films [3,4].

Undoped and doped (ZnO) thin films have much interesting properties, such as, transparency in the high and visible infrared reflectivity, excellent piezoelectric properties, etc. All these properties make them widely employed in many fields, such as, solar cells, transparent conductors, electrical, piezoelectric or luminescent devices, gas sensors, chemical sensors, surface acoustic wave devices (SAW), UV laser and catalysts [4]. The physical properties of the thin film, such as thickness, crystal phase and orientation, composition, and microstructure, are controlled by the deposition conditions, whereas the annealing temperature plays important rule on the structure properties and so on other physical properties.

Many elements were used as dopant source to change the physical properties of pure ZnO thin films, among which is Aluminum [5].

There are many different physical methods to synthesis thin films such as:laser ablation, ion-beam sputtering, rf-sputtering, and beam epitaxy. on the other hand, chemical methods are widely used for thin films preparation [6,7].

The chemical methods give a good stoichiometric compound, and the dip-coating is one simplest method to deposit the sol-gal solution on the substrate.

This work presents the method of synthesis of undoped and doped (aluminum) ZnO thin films prepared by sol-gel and using dip-coating technique to deposit it on glass substrate and investigate the effect of Aluminum dopant on the structure and morphology and optical properties. Also, the effect of annealing temperatures, to be used as gas sensor. Two concentrations of Al used (3 wt% and 5 wt%). Three annealing temperatures used 300,400 and 500 °C.

Experimental work

The Zinc Oxide films were prepared over glass substrate used sol-gel technique dip coating method. We used the Zinc Acetate Dihydrate as precursor and Monoethanolamine as a stabilizer. The Methanol, Isopropanol are used as solvents. The substrates were cleaned by rinsing them with soap solution, dilute sulfuric acid, ultrasonically cleaned into distilled water and alcohol for (10 min), then rinsed with distilled water and dried with an oven at (100 °C) for (10 min) to remove containments (water or solvent) on the substrate. To prepare (0.2 M) of pure ZnO seed solution, zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was dissolved in a mixture of methanol and isopropanol (IPA) solvents, respectively. The mixture was stirred at room temperature for (30 min) to completely dissolve the solute into the solvents subsequently. Monoethanolamine

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(MEA) which was used as a stabilizer to avoid the formation of milky precipitate of hydroxides was added drop wise into the solution under constant stirring at (65 °C) for (4 h) to yield a clear, transparent, and homogeneous solution. Then the solution was aged at room temperature for 24 h. In order to dope the Aluminum element to ZnO, Aluminum chlorid-6-hydrate ($AlCl_3{\cdot}6H_2O$) was selected as a source material. ($AlCl_3{\cdot}6H_2O$) with percentage (5 wt%) and zinc acetate dihydrate were added to the mixture of methanol and IPA and stirred at room temperature for (30 min). (MEA) which was added drop wise into the solution under constant stirring at (65 °C) for (4 h). Then the solution was aged at room temperature for 24 h. The aged pure and Al doped ZnO (5 wt%) solutions were deposited on to cleaned glass substrates by using a dip coating technique with a controlled withdrawal speed of (0.4 cm/s) and the deposition time (5 min) at room temperature. The films dried at (150 °C) for (20 min) to evaporate the solvent and remove organic residuals. Then the films were annealed in a furnace under ambient air for (2 h) to get crystallized ZnO and AZO. The equations of the reactions shown below:

$$Zn(CH_2COO)_2{\cdot}2H_2O + 2(NH_2CH_2CH_2OH)$$
$$\rightarrow 2H_2O + CH_3CONHCH_2CH_2OH_2 + Zn(OH)_2Zn(OH)_2$$
$$\xrightarrow{\Delta} ZnO + H_2O$$

The thickness of the film was measured using the weight method. The thickness found equals to (4.8 µm for ZnO, 7.5 µm for AZO).

Characterization

The structural properties of prepared ZnO and AZO films was investigated by X-ray diffraction using Philips PW 1050 X-ray diffractometer of (λ = 1.54 Å) from Cu-kα. The crystallite size can be estimate by the using the Debye-Scherer's formula [8]:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where D is average crystallite size, β the full-width at half-Maximum (FWHM), λ the X-ray wavelength of Cu-Kα radiation (λ = 1.54 Å) and θ the Bragg angle [8].

The morphological characteristics of the thin films were examined by scanning electron microscope type (INSPECT S50 (FEI)-Netherlands). In order to determine the band gap energy of the thin films, optical transmission study was carried using UV–VIS-1650 PC Shimadzu ultraviolet spectrophotometer-Japan.

The optical band gap of the films was evaluated from the transmittance spectra. The absorption coefficient calculated by, using the following formula [9].

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \tag{2}$$

where t is the thickness of the thin film, T is the transmittance.

The Optical energy gap E_g and absorption coefficient α are related by the equation

$$\alpha h\upsilon = A(h\upsilon - E_g)^{\beta} \tag{3}$$

where A = constant, hυ = the incident photon energy (in eV units) and β is a number which characterizes the nature of electronic transition between valance band and conduction band. For direct transition band gap β = 1/2 and 2/3 and, it is known that ZnO is a direct band gap semiconductor.

Results and discussion

Structural properties

The X-ray diffraction patterns recorded for the dip coated ZnO thin films on to glass substrates at various annealing temperatures are shown in Fig. 1a–c. All the diffraction peaks of these XRD patterns are in good agreement with the (JCPDS data Card No. 36-1451). ZnO thin films are polycrystalline in nature having hexagonal wurtzite structure. The presence of prominent peaks three diffraction peaks for the planes (1 0 0), (0 0 2) and (1 0 1) were observed. Increasing of annealing temperature makes (1 0 1) more higher, more sharper and dominance over others.

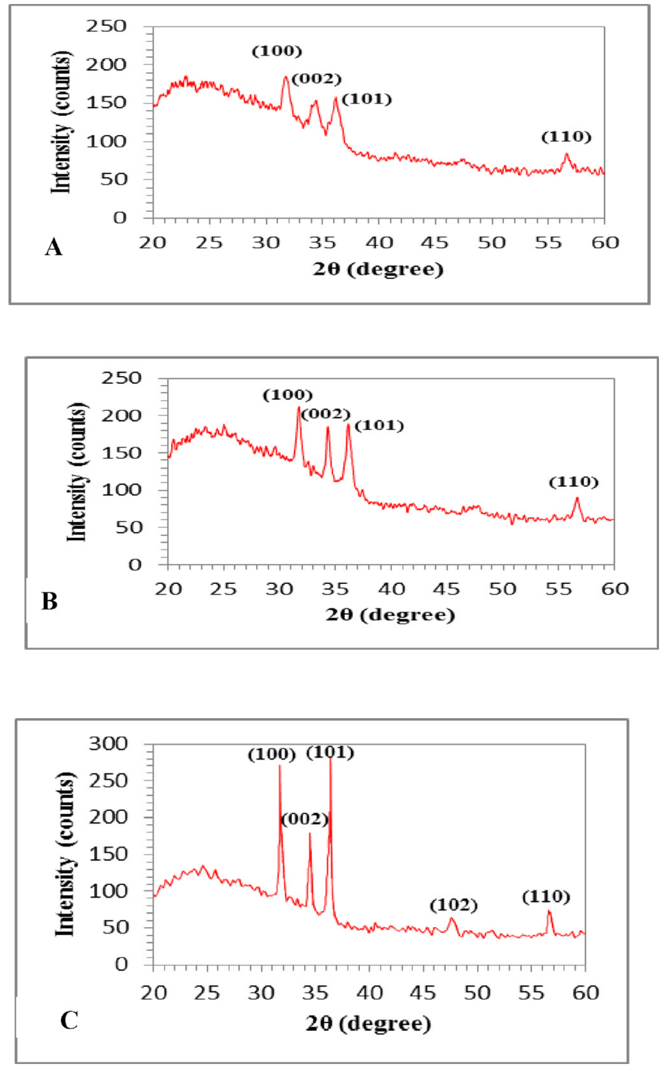

Fig. 1. XRD spectra of ZnO thin films at different annealing temperatures (A) 300 °C. (B) 400 °C. (C) 500 °C.

The intensity of these peaks increases as the annealing temperature increases and the crystallite of the films are improved, this means that the thin films become more crystalline and there are change in crystallite size. The intensity along the (1 0 1) plane is highlighted in this discussion and crystallite size along this plane calculated.

It was found that the crystallite sizes for three orientations are enhanced when the highest annealing temperature was used, thereby indicating an improved crystallinity of the films with higher annealing temperature.

Furthermore, we can see that the (1 0 1) peak intensity increases and also the full-width at half maximum (FWHM) for the (1 0 1) peak decreases with increasing annealing temperatures as shown in Fig. 1. The quality of the ZnO film improved when annealed at higher temperature.

The crystallite size is 8.66 nm at annealing temperature 300 °C and becomes 15.381 nm when the annealing temperature is 500 °C. The results are summarized in Table 1.

These results agree with Ref. [10].

Table 1
The XRD results for ZnO thin film at different annealing temperatures for [1 0 1] plane.

Annealing temperature	2Θ (deg.)	FWHM (deg.)	d (A°)	D (nm)
300 °C	36.200	0.965	2.479	8.661
400 °C	36.220	0.635	2.478	13.163
500 °C	36.325	0.544	2.471	15.381

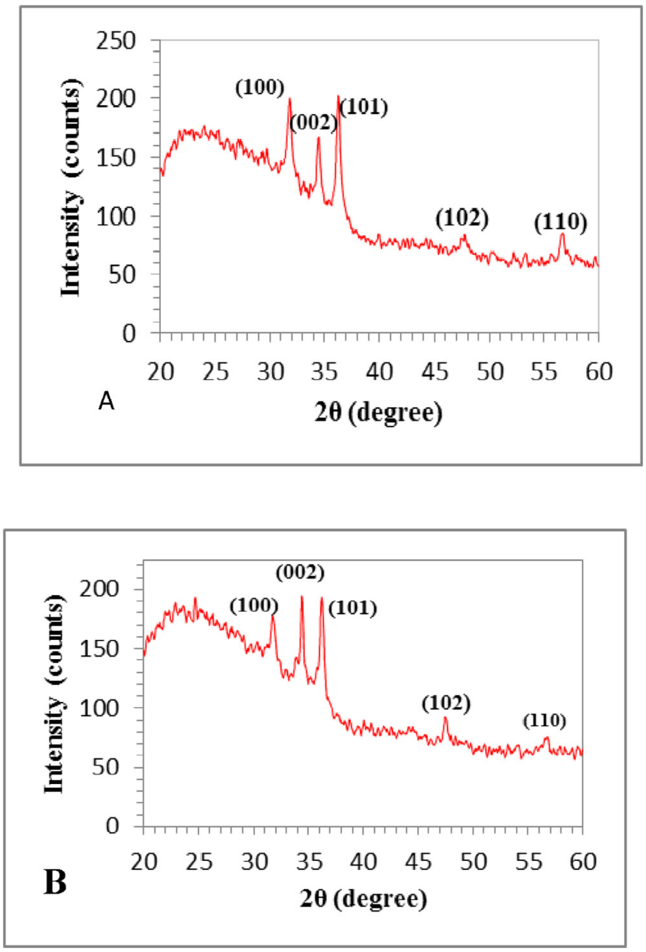

Fig. 2. XRD spectra of AZO thin films, annealed at 500 °C (A) 3 wt% AZO (B) 5 wt%.

Fig. 2 shows the XRD spectra of AZO thin films and the annealing temperature was 500 °C.

We have noticed that the intensities of diffraction peaks tended to decrease with entry of Al dopant. This indicates that doping with Al has decreased the crystallinity of ZnO films. In XRD patterns of both (3 wt %, 5 wt%) AZO no new peaks appeared. That is indicates that there is no AlO_3 in the structure of the films, in other words the additive of Al, has no effect on the structure of ZnO though the concentration of Al is low.

Table 2 shows the X-ray diffraction result of AZO thin films for peak (1 0 1).

From the Table 2 we have noticed that there is small shift in peak position.

In XRD patterns of both (3 wt% and 5 wt%) AZO no new peaks appeared. This could be caused by interaction between Al and ZnO. It may be due to the fact that Al upon entering the ZnO structure did not form a crystalline phase or solid solutions with ZnO system or that the concentration of Al is too low. Also, from Table 2 we can see the variation of the crystallite size (D) and (FWHM) of Aluminum doped ZnO at various Aluminum concentrations (0 wt%, 3 wt% and 5 wt%).

Table 2
The XRD results for AZO thin film at 500 °C annealing temperatures for [1 0 1] plane.

Al concentration	2Θ (deg.)	FWHM (deg.)	d (A°)	D (nm)
0 wt%	36.200	0.965	2.479	8.661
3 wt%	36.320	0.565	2.472	14.798
5 wt%	36.260	0.581	2.476	14.388

It is clearly seen that the FWHM of the reflection peaks decreases with increased Aluminum concentration, reflects the decreasing of improvement thin film quality. This means that an increase in Al doping content decreases crystallite size of the films. It seems that Aluminum which exists in ZnO structure as a dopant may tend to create more nucleation centers during the deposition process and as a result the increase in Al content, may cause a decrease in crystallite size [11].

As the ionic radius of Zinc is greater than ionic radius of aluminium by (0.07 Å); Therefore, the Al atom is interstice between oxygen and zinc atoms. This means that the aluminium atom take place in interstitial configuration.

Morphological properties

Fig. 3 shows the SEM image of ZnO thin films annealed at different temperatures. The SEM image shows a uniform compact surface. The surface morphology of the samples was represented by different ganglia-like hills with typical width of about 1 μm and a height of 5–10 μm. The surface of the thin film, annealed at 300 °C, contained some cracks while no crack was observed after annealing at 400 °C, and 500 °C. The highest density thin film was achieved after annealing at 500 °C. As the annealing temperature of ZnO films increased from 300 °C to 500 °C, the volume and size of ganglia-like hills increased and the films became denser.

Fig. 4 shows the SEM image of AZO at two Al concentrations and annealed at 500 °C. It seems that the ganglia are looking more distorted and branched at their ends. The ganglia-like hills are of typical width 0.1–0.5 μm, and height about 2.5–3 μm. The increase of Al dopant decreases the size and volume of ganglia-like hills. The wrinkles are smaller and the morphology was not homogenous.

Optical properties

The optical transmittance variations with wavelength for ZnO and AZO thin films deposited at different parameters were obtained. Ultra Violet Visible (UV–VIS) Spectrophotometer was used to record the optical transmission for pure and doped ZnO/glass thin films under different conditions within the wavelength range of (300–700 nm). The data from transmission spectrum can be used in the calculate of the absorption coefficient (α). We used it to calculation energy gap. These results were obtained by using: UV/VIS-1650 PC Shimadzu ultraviolet spectrophotometer – Japan.

It can be seen from Fig. 5 that the film has low transparency in the vicinity of (55%) in the visible region at (300 °C) and then increase with increased annealing temperature to reach (64%) and (78%) in the annealing temperature (400 °C) and (500 °C) respectively. The increase in annealing temperature leads to an increase in the transmittance of thin films as seen in the figure. This result is inconsistent with those published researches [11]. The increase in transmittance of the films was related to an increase in crystallinity of the films. The improvement of crystallinity leads to decrease in optical scattering.

The optical transmission spectra of AZO thin film on glass substrate annealed at 500 °C in air and doped with different Aluminum concentrations (0 wt%, 3 wt% and 5 wt%) are shown in Fig. 6. The films have high transparency in the visible region and the transparency of the

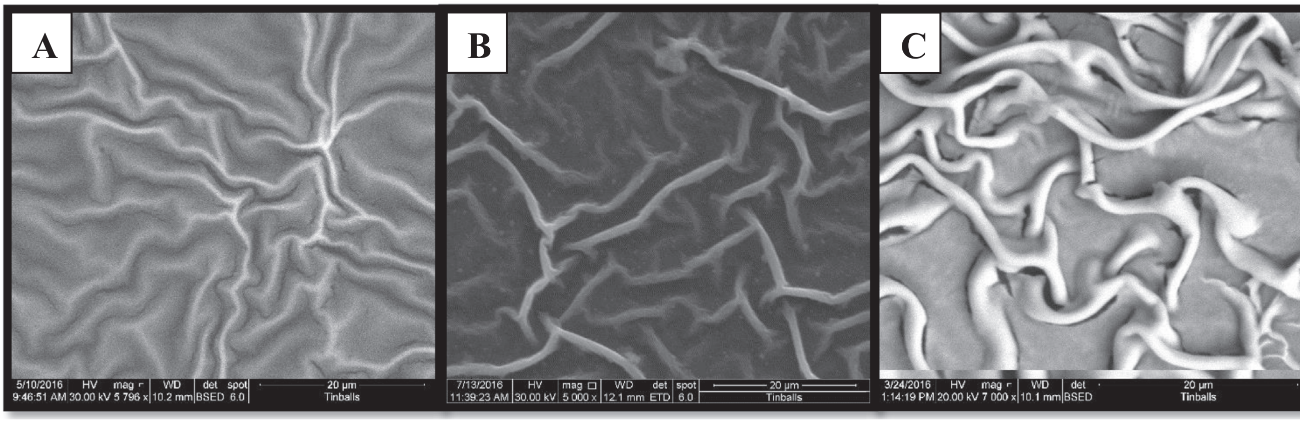

Fig. 3. SEM image of the ZnO thin films at different annealing temperature (A) 300 °C (B) 400 °C (C) 500 °C.

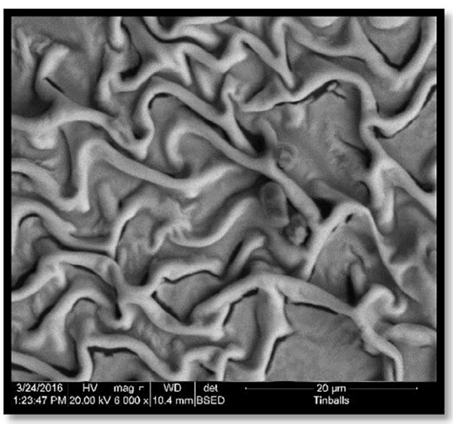

Fig. 4. SEM image of the AZO thin films annealed at 500 °C with Al concentration 5 wt%.

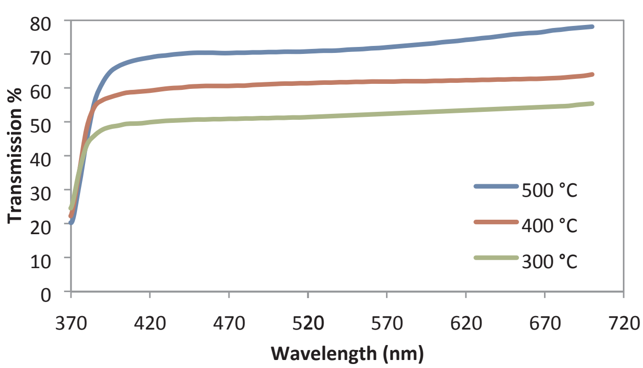

Fig. 5. Transmittance as a function of wavelength for ZnO thin film annealed at different temperatures.

films decreases when the dopant content is raised. The transmittance decreases from (78%) to (66%) and (59%) when adding Al content to the film with (3 wt%) and (5 wt%) respectively. The decrease in transmittance of the thin film was mainly attributed to the increase in free electrons with the increase in Aluminum concentration and due to reduce crystallization of the films.

The energy gap (Eg) values depend, in general, on the film crystal structure, the arrangement and distribution of atoms in crystal lattice. The Direct band gap of ZnO films calculated from the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (according to Eq. (3), the determination of (E_g) was made by extrapolating the linear portion of the curves until they intercept the photon energy axis. The plot of $(\alpha h\nu)^2$ against ($h\nu$) shows a

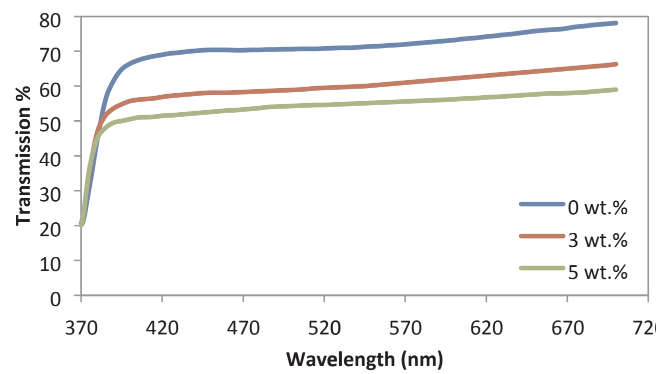

Fig. 6. Transmittance as a function of wavelength for AZO thin films annealed at 500 °C with different Al concentrations.

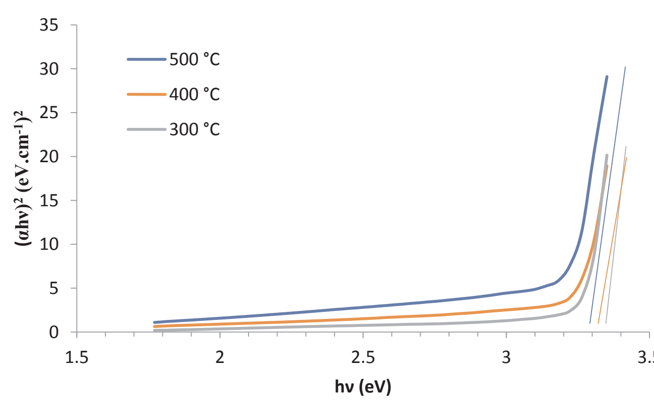

Fig. 7. The effect of annealing temperature on the energy band gap of ZnO thin film.

linear dependence. This means that the films have direct and allowed transition [12]. Fig. 7 shows the variation of energy gap for ZnO thin films with annealing temperature as function of photon energy. The values of band gap agree nearly with band gap of bulk ZnO (3.37 eV). It is observed that the values of band gap decrease with the increase the annealing temperature. This may be due to the decrease of defects, which could be the number of oxygen vacancies and/or grain boundaries. Increasing annealing temperature will result in decreasing oxygen vacancies which lead to a decrease in the carrier concentration in the conduction band [13]. On the other hand, annealing process improves crystallinity and increases average grain size that result in decreasing defects, and also, reduce, the strain in the films; therefore, the band gap energy decreased [14]. The values of energy gap of ZnO thin film with

Table 3
The energy band gap of ZnO thin film at different annealing temperatures.

Annealing temperature (°C)	Energy band gap (eV)
300	3.28
400	3.25
500	3.22

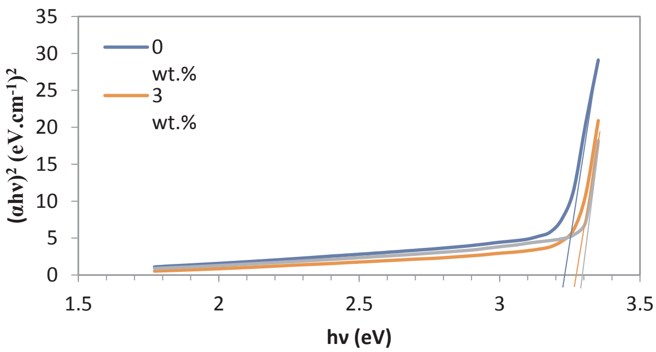

Fig. 8. The effect of Al dopant concentration on the energy band gap.

Table 4
The energy band gap of thin films at different Al concentrations.

Al dopant concentration	Energy band gap (eV)
0 wt%	3.22
3 wt%	3.26
5 wt%	3.28

different annealing temperature are given in Table 3.

The effect of Al dopant concentration on band gap of ZnO thin films annealed at 500 °C and doped with Al at (5 wt%) are shows in the Fig. 8 and Table 4. The band gap increases with doping due to increasing of free electron caused by doping [6]. The crystallite size plays important role in the value of band gap [15].

Conclusion

This study was focused on the ZnO thin films synthesized by sol-gel dip coating method. The films are polycrystalline having hexagonal wurtzite structure.

As the annealing temperature increase, the crystallinity and crystallite size increase. Also, the optical band gap decreases as the increasing of annealing temperature. The Morphology of ZnO thin films are change with annealing temperature and SEM image represented by different ganglia-like hills. Also; the increasing in the annealing temperature decreases the optical band gap of thin film doped with Al.

The dopant by Al has many effects on the ZnO thin films, it does not change the crystal structure, but decrease the crystallinity and crystallite size. The optical band gap increases with respect to the concentration of Al dopant. These properties are useful in using these dopant films as gas sensor.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2018.05.033.

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