Ghazi Y. Nasser

Department of Physics,
College of Education,
Al-Iraqia University,
Baghdad, IRAQ

Effect of Heat Treatment on the Optical Properties of ZnO Thin Films Prepared by Chemical Spray Method

ZnO is one of transparent conducting oxide materials whose thin films attract much interest because of typical properties such as high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region. Due to these properties ZnO is a promising material for electronic or optoelectronic application such as solar cells (anti-reflecting coating and transparent conducting materials), gas sensors, liquid crystal displays, heat mirrors, surface acoustic wave and bulk acoustic devices (piezoelectric devices), multilayer photo-thermal conversion systems, etc.

In this research, thin films of ZnO of thickness 5200±30 prepared using chemical spray method. The films deposited on Crown glass substrates Optical studies show that in these films the electronic transition is of the direct transition type. The optical energy gap for the films of as deposited and for those heat treated for an hour at different temperatures is estimated to be in the range 3.05-3.2 eV. Results analysis exhibits the dependence of optical energy gap on the temperature of heat treatment.

Keywords: ZnO thin films, Chemical spray, Optical properties, Heat treatment

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1. Introduction

In the last decade, Zinc Oxide (ZnO) thin film attracts much interest due to valuable properties such as it is high resistance to chemical attack, chemical stability and good adherence to many substrates. High optical transparent in the visible region and the index of refractive is ~1.8 enables them to act as a antireflection coating in solar cells applications. Also, its abundant in nature makes it a lower cost material when compared with ITO and SnO₂ materials.

Zinc oxide (ZnO) is a widely used functional material with wide and direct band gap, large exciton binding energy, and excellent chemical and thermal stability. ZnO is a semi-conducting material widely used as transparent electrodes in solar cells, chemical and gas sensors, spintronic devices, and light emitting diodes. Nowadays, the sol-gel method has been extensively used to obtain various kinds of functional oxide films due to its simplicity and low cost. It has been found that post-annealing plays an important role on the properties of ZnO films, and the optical transmittance and photoluminescence are very sensitive to the quality of crystal structure and to the presence of defects.

Also, ZnO is one of transparent conducting oxide materials whose thin films attract much interest because of typical properties such as high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region [1-3]. Due to these properties ZnO is a promising material for electronic or optoelectronic application such as solar cells (anti-reflecting coating and transparent conducting materials), gas sensors, liquid crystal displays, heat mirrors, surface acoustic wave and bulk acoustic devices (piezoelectric devices), multilayer photo-thermal conversion systems, etc [4-8].

Thin films of ZnO have been prepared by using several deposition techniques which include chemical vapor deposition, RF/DC magnetron sputtering, oxidation of evaporated metallic film, spray pyrolysis, pulsed laser deposition, sol-gel technique, etc [9-13]. Among these methods, the spray pyrolysis technique has several advantages such as simplicity, safety, and low cost of the equipments and raw materials. With the spray process, the solution is sprayed directly onto the substrate by means of a nozzle assisted by a carrier gas. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound. The quality and physical properties of the films depend on the various process parameters, such as substrate temperature, molar concentration of the starting solution, spray rate, pressure of the carrier gas and the geometric characteristics of the spray system.

In this research work, we report a study on optical properties of ZnO thin films prepared by spray pyrolysis technique.

2. Experiment

ZnO films were prepared on crown glass substrates by spray pyrolysis technique. The spray
solution used was of 0.2M of high purity zinc acetate dehydrate \( \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \), isopropyl alcohol and distilled water (Volume ratio 3 to 1).

The solution was stirred at 300K for 1 hour by a magnetic stirrer to get a clear homogeneous solution. The atomization of the solution into a spray of fine droplets was carried out by the nozzle, with the help of compressed air as carrier gas. The flow rate of solution was 8 ml/min and the substrate temperature was held constant at 473K using a chromel-alumel thermocouple with the help of a digital multimeter supplied by Pasco. The nozzle to substrate distance was 50 cm and the diameter of nozzle was 0.3 mm.

The substrates were cleaned by acetone, alcohol and finally with distilled water before coating. Each coated substrate was dried at 473K for 10 min to evaporate the solvent and remove the organic residuals. The process repeated many times to obtain the desired thickness. The heat-treated films placed into evacuated tube furnace and annealed under low pressure of 10^-1 torr using a mechanical rotary pump for 1 hour.

Film thickness determined by the weight–difference method \( d=M/\rho A \), where \( A \) is the area of the film, \( M \) its mass, \( d \) its thickness and \( \rho \) its density, 5.61 g/cm³ using an electronic precision balance. The optical transmission and absorbance of the films were obtained in the Ultraviolet/visible/near infrared region up to 1100 nm using 800 Philips double beam spectrophotometer.

3. Results and Discussion

Figure (1) shows the optical transmission spectra of ZnO thin films of thickness 5200±30 for as deposited sample S3 (RT) and heat treated samples S2 (423 K) and S1 (523 K).

These spectra show that for film S1 which heat treated at 523 for 1 hour, the average transmission over the range 500-1100 nm exceeds 80% with a sharp fall near the fundamental absorption; whereas fall in transmission is gradual for the sample S2 which heat treated at 423 K for 1 hour and for the sample S3 which is left at room temperature (300 K).

It is clear from Fig. (2) for the absorption spectra that the films have low absorbance in the visible/infrared region while absorbance is high in the ultraviolet region. The absorption coefficient (\( \alpha \)) was calculated using Lambert law as follow [14].

\[
\alpha = \frac{2.303 A}{d}
\]  

where, \( d \) is the thickness of the films, and \( A \) is the optical absorbance

![Fig. (2) Transmission spectra of the sprayed ZnO thin films of as deposited and heat treated samples](image)

These absorption coefficients values were used to determine optical energy gap. Figure (3) shows the plot of \( (\alpha h\nu)^2 \) vs. \( h\nu \) where \( h\nu \) is the energy of the incident photon. The energy gap was estimated by assuming a direct transition between valence and conduction bands from the expression:

\[
(\alpha h\nu)^2 = K(h\nu - E_g)^2
\]  

where \( K \) is a constant, \( E_g \) is determined by extrapolating the straight line portion of the spectrum to \( \alpha h\nu = 0 \).

From this graph, the optical energy of as deposited sample S3 (300 K) is 3.05 eV, the optical energy gap of heat treated sample S2 (423K) is 3.08 eV and the optical energy gap of heat treated sample S1 (523K) is 3.2 eV. These values are slightly smaller than the bulk value of 3.31 eV [15] and in good agreement with previously reported data of ZnO thin films [16]. The optical absorption edge has been observed at a wavelength of about 385 nm corresponding to band gap of about 3.05 eV for non-annealed sample S3.
The UV emission peak originates from excitonic recombination as shown by other researchers, and the UV peak intensity varies with annealing temperatures. Defect-related green emission is believed to come from oxygen vacancies [17]. Generally, it is thought that the quality of ZnO films improve with increasing annealing temperatures. However, it is noteworthy that the ZnO film annealed at 450°C shows strong excitonic related UV emission, and the UV emission intensity monotonically increases at annealing temperatures beyond 500°C. This behavior can be understood phenomenally by considering the formation of defects. While the ZnO film was annealed at 450°C, the rate of formation point defects, which is responsible for radiative recombination, is low at low temperature. Accordingly, efficient excitonic emission can be easily achieved. For the temperature higher than 450°C, more defects responsible for the nonradiative transition will be introduced into the films. This is why film annealed at temperatures higher than 500°C would show poor UV emission than that annealed at 450°C. Furthermore, higher annealing temperatures facilitate the migration of grain boundaries and promote the coalescence of small crystals, and thus favor a decrease of the concentration of nonradiative recombination centers [18]. Annealing at temperatures higher than 500°C may be the subject of future studies on zinc oxide thin films.

The observed band gap energy of the heat treated sample S3 (523K) which is 3.2 eV correspond to a wavelength of about 370 nm, which is close to that of single crystal. These results show that the band gap energy of ZnO thin films shits to higher energy values after annealing (Fig. 4). The increase of the band gap energy after annealing is consistent with some of the following studies in the literature. For example, Bouhsira et al. have shown that the band gap energy increases from 3.3 eV in as grown up to 3.7 eV after systematic annealing experiment at temperatures from 373 K to 873 K [19]. Xue et al. has observed almost no change, a little 10 meV increase in the band gap energy up to 1023 K annealing temperature and a decrease of about 10 meV at annealing temperatures between 1023-1223 K [20]. They attribute the blue shift of the optical absorption edge to the increasing crystallinity of the ZnO films. Furthermore Zou et al. showed the increase in the band gap energy from 3.18 eV to 3.2 eV after annealing as well [21].

The increase in transmittance with higher annealed temperature may be due to deceasing optical scattering caused by the densification of grains followed by grain growth and the reduction of grain boundary density [22].

**4. Conclusion**

ZnO thin films of as deposited and heat treated at different temperatures prepared by spray pyrolysis technique have been studied for their optical properties. Analysis of UV/VIS spectra of the films reveals that the materials to be of direct electronic transition with an energy gap in the range 3.05 to 3.2eV. The optical characterization on both as deposited and heat treated samples have shown that the heat treatment carried out at 523K has a great influence on the optical energy gap. It has been observed that the direct band gap was increased from 3.05 eV for as deposited sample to 3.2 eV after
annealing at 523K for 1 hour. We think that this increase in band gap energy may be due to the low oxygen content of the sample surface after heat treatment.

References