



RESEARCH ARTICLE

Effect of substrate temperature studies on spray pyrolysis deposited ZnO thin films

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Abstract

In the present work and in the order to obtain conducting transparent layers, ZnO thin films were deposited by pyrolysis spray technique, zinc acetate was used as starting solution with a molarity of 0.1 M. The glass substrate temperature was varied in the range of 250 °C–400 °C to investigate the influence of substrate temperature on the structure and optical properties of ZnO films. Optical film characterization was carried by using UV–visible transmission spectroscopy in the spectral range 300–1100 nm; the optical gap was deduced from absorption. From X ray diffraction (XRD) analysis, we have deduced that ZnO films are formed with nanocrystalline structure with preferential (002) orientation. The grain size is increased with the substrate temperature (300 to 350 °C) from 12.5 to 15.5 nm, and then it is decreased to 14 nm (400 °C). However the optical gap is varied from 3.12 to 3.32 eV.

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INTRODUCTION

Zinc oxide (ZnO) thin film is a promising material for its use in various application devices. In opto-electronics, it can be used as light emitting diode in the blue to ultraviolet spectral region due to its wide band gap of 3.3 eV at room temperature [1]. It is extensively studied because of its potential applications in various fields, such as solar cells, gas sensors, piezoelectric sensors, waves guides... ZnO films are prepared by several methods such as reactive thermal evaporation [1,2], pulsed laser deposition [3,4], the sol-gel process [5,6], magnetron sputtering [7,8] and spray pyrolysis [9]. Spray pyrolysis method is an inexpensive and simple technique, it has low toxicity and it does not require a high vacuum apparatus. Another advantage of spray pyrolysis technique is that the thin films can be deposited in air at different temperatures [7].

Among these techniques Spray ultrasonic pyrolysis [10,11] has many advantages such as high growth rate, large area uniformity, and easy doping processes.

In the present work reports on the investigation of the substrate temperature on the structural and optical properties of ZnO thin films prepared by spray pyrolysis.

2. Experimental

The solution involves 0.1 M, zinc acetate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$) diluted in methanol. Well cleaned glass substrates in methanol were used for the optical characterization. The deposition temperature was 250 °C–400 °C,

the distance between the substrate and the nozzle was fixed at 10 cm, the deposition time was maintained at 5 min for each sample. The structural properties were determined by X-ray diffraction (XRD) using a Philips X' Pert system with Cu K α radiation ($\lambda=1.5418$ Å). The optical transmittance of the deposited films was measured in the range of 300–1100 nm by using an ultraviolet-visible spectrophotometer (SHUMADZU UV-1601).

3. Results and discussion

3.1. Structural properties

X-ray diffraction profiles of ZnO thin films prepared at different substrate temperatures ($T_s=250$ – 400 °C) are shown in (Fig. 1). As shown in the figure, the pattern diagrams are composed of several peaks identified as (100), (002) and (110). This suggested that the deposited films are polycrystalline and have a hexagonal wurtzite structure with (002) as preferential orientation. With increasing substrate temperature from 300 to 400 °C the (002) peak becomes more intense and sharper, indicating the film crystallinity improvement [5,7].

The increasing substrate temperature generally improves the crystalline structure of thin films. Film characterization using Fourier Transform Infrared Spectroscopy (FTIR), photoluminescence spectroscopy (PL), and ultraviolet–visible (UV–Vis) optical transmission spectroscopy suggests the onset of ZnO growth at temperatures as low as 100 °C as well as the transformation to a polycrystalline phase at deposition temperatures > 200 °C reported by Adamopoulos et al [8].

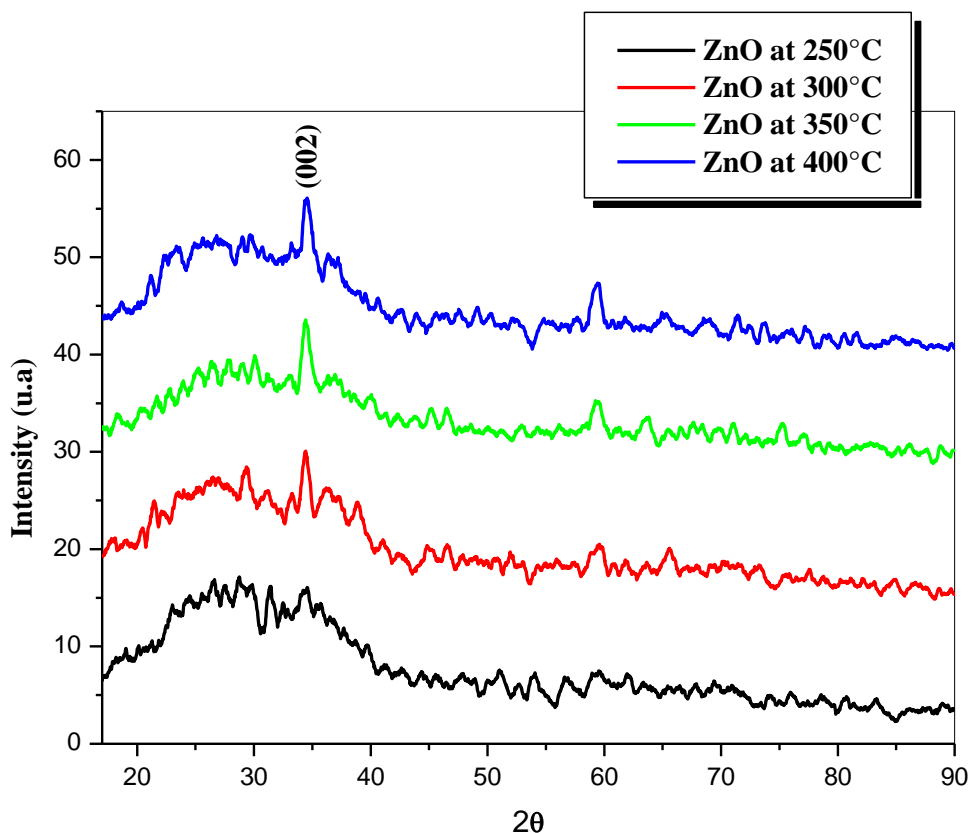


Fig. 1. X-ray diffraction spectra of ZnO thin films deposited by the spray pyrolysis at different substrate temperature.

The lattice constants a and c (hexagonal structure) can be calculated for the high intensity peaks using the following relation [9,10]:

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

d_{hkl} (interplanar spacing) is calculated from Bragg's formula ($2d_{hkl} \sin \theta = n \lambda$).

The internal stresses can be calculated from the following expressions [11]:

$$\sigma = \left(2C_{13} - \frac{(C_{11} + C_{12})C_{33}^{thin\ film}}{C_{13}} \right) e_{zz}$$

$$C_{33}^{thin\ film} = \frac{0,99C_{33}^{crystal}}{(1 - e_{zz})^4}, \quad e_{zz} = \frac{c_0 - c}{c_0}$$

where:

- C_{ij} are the elastic constants of ZnO which have the following values: $C_{11} = 209,7$ GPa, $C_{12} = 121,1$ GPa, $C_{13} = 105,1$ GPa, and $C_{33} = 210,9$ GPa.
- $c_0 = 5.206 \text{ \AA}$ is the theoretical value of lattice parameter c (JCPDS file: zinc oxide, 36-1451).

The stress values of the ZnO thin films as a function of the substrate temperature is shown in Table.1.

Table.1. The stress values in the ZnO thin film as a function of the substrate temperature.

	$a_{\text{calculated}} (\text{\AA})$	$C_{\text{calculated}} (\text{\AA})$	σ (GPa)
ZnO (300 °C)	3,285	5,214	+ 0,7649 (extensive stress)
ZnO (350 °C)	3,294	5,220	+ 1,2663 (extensive stress)
ZnO (400 °C)	3,281	5,191	- 1,2213 (compressive stress)

The grain size (D) of the wurtzite phase of these films was estimated from the high intensity peak (002) in the XRD patterns using the Scherrer's formula [12,13]:

$$D = \frac{0,9\lambda}{\beta \cos \theta_{hkl}}$$

Where β is the full width at half maximum of the high intensity peak, λ is the wave length of the X-rays and θ is the Bragg's angle in radians.

The variation of grain size with substrate temperature for these films is presented in the fig. 2. The grain size increases with the substrate temperature (300 to 350 °C) from 12.5 to 15.5 nm, and then it decreases to 14 nm (400 °C). The first behaviour is logical because the increase of the substrate temperature is always accompanied by the increase of the grain size. In the second behaviour the decreasing of grain size (350°C - 400 °C) may be explained by the decrease of the crystalline quality due to the increase of disorder during film growth (see Fig.4) .

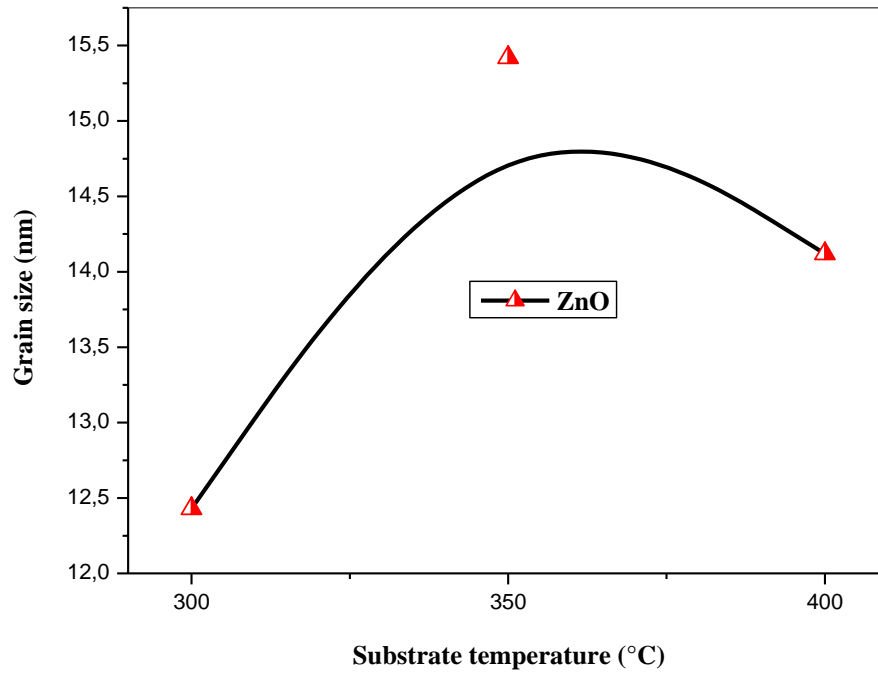


Fig. 2. Variation of grain size with substrate temperature.

3.2. Optical properties

Fig. 3 shows the optical transmission spectra recorded in the range from 300 to 1100nm obtained in films prepared with different substrate temperature. As can be seen, a region of strong transparency is located between 400 and 1100 nm. As can be seen, an increase in the substrate temperature improves the films optical transmission. It passes from 40% to 70%. Generally, the film transmittance is increased with the reduction of film thickness. However, in our case, the transmittance improvement cannot be explained in terms of films thickness, since with increasing the substrate temperature films became thicker (the thickness is varied from 120 nm to 200 nm with increasing temperature). Thereafter, the transmittance improvement may originates from the film structure.

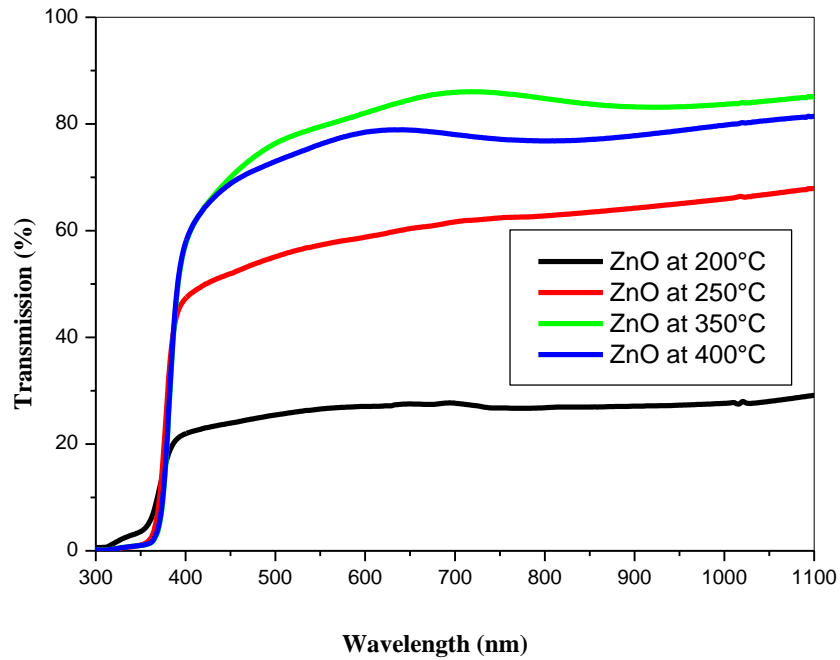


Fig. 3. Optical transmission spectra of ZnO thin films prepared at different substrate temperatures.

The variation of Urbach energy with different substrate temperatures is plotted in Fig. 4. From this figure, we see that the temperature affects the organization of the deposited thin films. Indeed, the substrate temperature influences the mobility of the atoms arriving at the surface during film growth. At high substrate temperature, the atoms arriving at the surface have enough energy to move and find a favorable site, and this effect leads to a better organization of the film. One can see that a minimum Urbach energy was reached at 350°C, which means the adequate temperature for less disorder (less of defects), which may be attributed to the similar ionic radius between O^{2-} and Zn^{2+} , as it was expressed in the literatures [13,14].

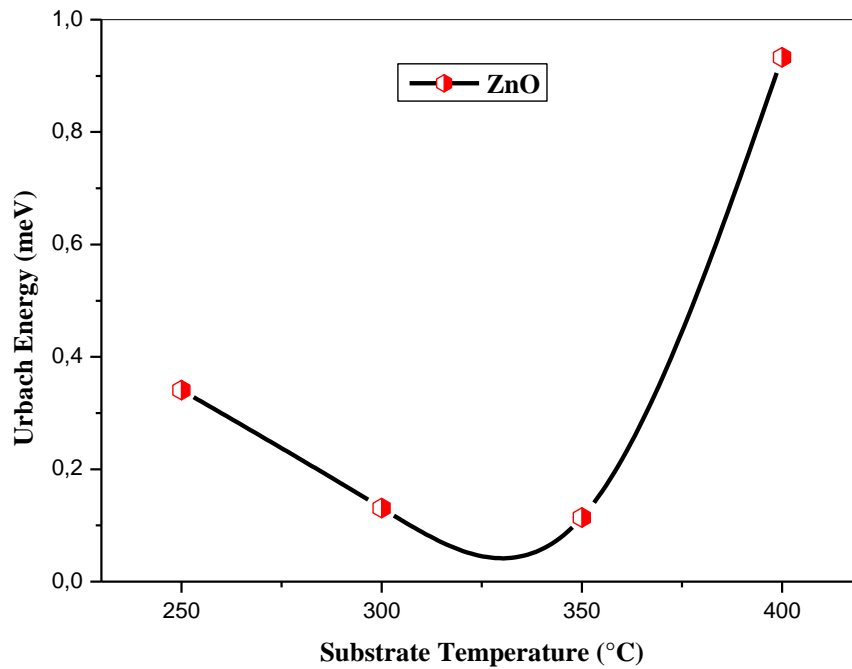


Fig. 4 .Variation of Urbach energy with different substrate temperatures.

The variation of the deduced optical gap of films with substrate temperature is reported in figure 5. As seen, at substrate temperature of 250°C, 300°C and 350°C the values of optical gap are 3.12 eV, 3.2 eV and 3.32 eV respectively. These values are in good agreement with ZnO band gap values reported by other authors [15]. Higher substrate temperature 400°C the value of optical gap is 3.17 eV.

The increase in optical gap with increasing substrate temperature can be due to improvement in the films crystallinity as shown in fig 1.

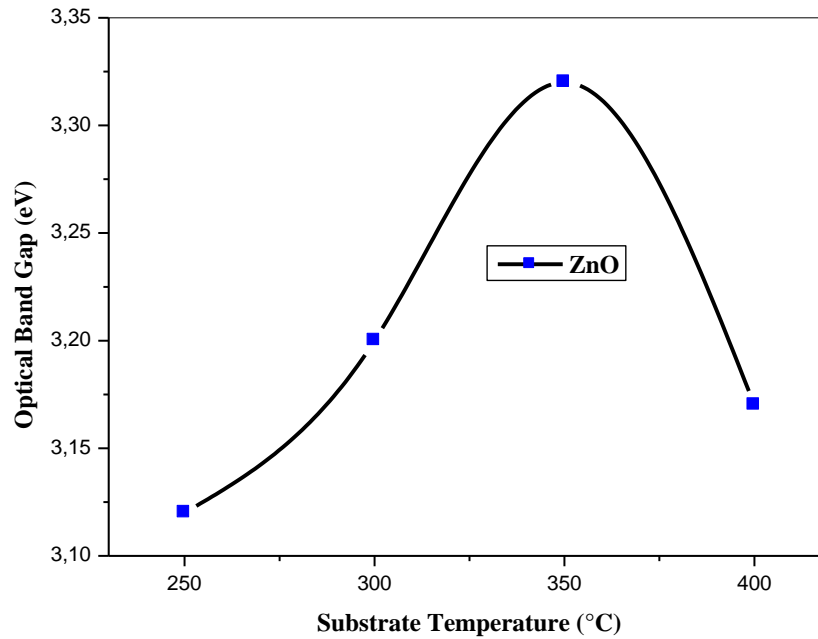


Fig. 5. Variation of the optical gap as a function of the substrate temperature.

In Fig. 6. we have reported a comparison between the variation of the optical gap (E_g) and Urbach energy (E_u) as a function of the substrate temperature. As seen, the variations of both E_g and E_u correlate very well. This effect indicates that the optical gap variation is mainly controlled by the disorder in the film. The increasing of the substrate temperature (250°C to 350°C) can improve the organization and the crystallinity of films (decrease of the disorder), and therefore improves the optical transmission of the films (increasing of optical gap). The best transparency of ZnO thin films deposited by spray pyrolysis is obtained at the temperature 350°C (less of disorder).

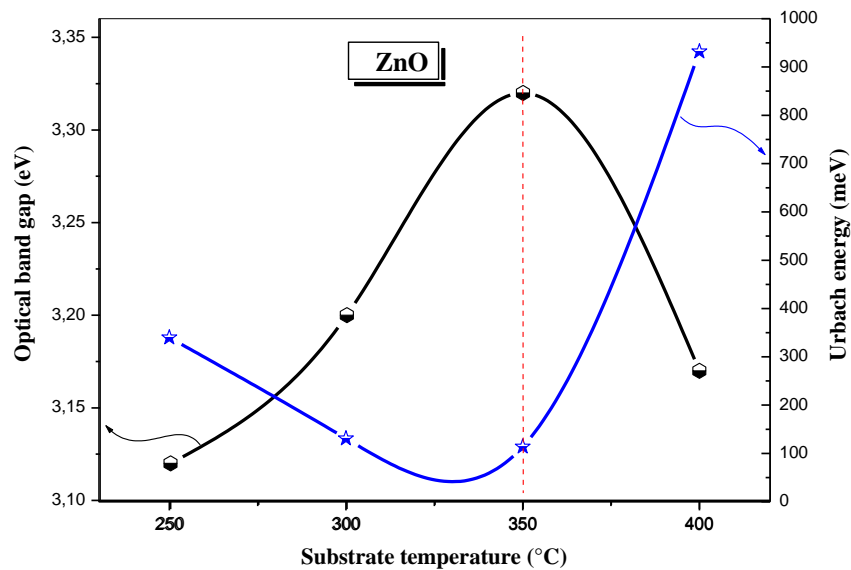


Fig. 6 . Variation of the optical gap and Urbach energy as a function of the substrate temperature

4. Conclusion

ZnO thin films were deposited by spray pyrolysis technique with a non aqueous solution. This technique is simple and inexpensive method to prepare the ZnO thin films and it is useful for large area applications. The effect of substrate temperature (250°C, 300°C, 350°C and 400°C) on the structural and optical properties of films was investigated. The increasing of the substrate temperature improves the crystalline structure of films. The film deposited at 250 °C is amorphous structure. The other films are nanocrystalline structure wurtzite and (002) oriented. The increasing of the substrate temperature (250°C to 350°C) decreases the disorder (decrease of the defects) and it therefore increases the optical gap. The Urbach energy decreased reaching to minimum at 350 °C. The optical gap values of thin films deposited at substrate temperatures 250 ° C, 300 ° C and 350 ° C are 3.12 eV, 3.20 eV and 3.32 eV respectively. At the high substrate temperature (400 ° C), the value of optical gap is 3.17 eV. The optical transmittance of polycrystalline films was varied from 60% to 85% in the near-infrared and visible region. ZnO Thin film prepared on the substrate heated to 350 °C has the best transparency (≈85%).

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