

## The Optical and Structural Properties of ZnO Films Prepared by Spray Pyrolysis

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### Abstract

Zinc oxide (ZnO) thin film have been prepared by Spray Pyrolysis technique using zinc acetate dehydrate dissolved in methanol, ethanol and deionized water. A number of techniques including X-ray diffraction (XRD), optical transmission microscope (OTM), Fourier transform infrared (FTIR) spectroscopy, UV-visible were used to characterize and study the obtained ZnO thin films. The evolution of preferred crystalline orientation in the ZnO films was systematically investigated and the (002) reflection was the preferred orientation. The optical measurement reveal that films have a maximum transmittance of about 90% and a direct band gap of 3.2 eV.

**Keywords:** ZnO thin film , The physical properties of ZnO film

### الخصائص البصرية و التركيبية لاغشيه اوكسيد الزنك ZnO المحضرة بطريقة التحلل الكيميائي الحراري

#### الخلاصة

تم تحضير نماذج من اوكسيد الزنك كاغشية رقيقة باستخدام تقنيته التحلل الكيميائي الحراري باستخدام خلات الزنك المذابة في الميثانول ، الايثانول والماء المؤين . عدد من التقنيات التي تتضمن حيود الاشعة السينية ، المجهر البصري المعتمد على النفاذية وطيف الاشعة تحت الحمراء ، وطيف المنطقة المرئية وتحت البنفسجية اخذت لتشخيص ودراسة اغشية من اوكسيد الزنك ، كذلك تم الاستدلال على ان احسن اتجاهية تبلور للاغشية المحضرة كانت عند الانعكاس (002) . القياسات البصرية اشارت الى نفاذية الاغشية هي بحدود 90% واكبر فجوة طاقة مباشرة هي عند 3.2 الكترون فولت.

### 1- Introduction

Zinc oxide (ZnO) is an important multifunctional material with application such as varistors, gas sensors, transparent electrodes, catalysts etc[1]. The variation applications of ZnO are due to the specific chemical, surface and micro structural properties of this material. The micro structural and physical properties of ZnO can be modified by introducing changes into the procedure of its chemical synthesis.

The wide direct band gap of 3.3 eV and large exaction bonding energy ~60 meV at room temperature is essentially attractive for optoelectronic, nonlinear optics and electro-optics applications. ZnO , in general, is an n-type material, with a high electrical conductivity due to lack of oxidation[2,3].

The electrical properties of ZnO are closely related to the composition and the microstructure.

Thin films of ZnO have been prepared by using several deposition

techniques which include chemical vapor deposition, magnetron sputtering, oxidation of an evaporated metallic film, spray pyrolysis, pulsed laser deposition, sol-gel technique, photo deposition, etc[4]. Among these methods, the spray pyrolysis technique has several advantages such as simplicity, safety and low cost of the equipments and raw materials [5]. In this technique, a starting solution containing a soluble salt of the cation of interest is sprayed by means of a nozzle assisted by a carrier gas over a hot substrate. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound [6]. The quality and the physical properties of the films depend on the various process parameters, such as substrate temperature, molar concentration of the starting solution, spray rate, type and pressure of the carrier gas and the geometric characteristics of the spray system [7]. In this paper we study the change in substrate temperature and its effect on the optical and structural properties of ZnO thin film prepared by spray pyrolysis technique.

## 2- Experimental details

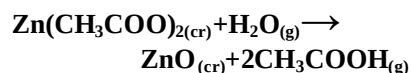
The film were prepared on clean glass substrates, the slides ( 80 x 20x 1 ) mm first cleaned in distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromatic acid (for two day), to introduce functional groups called nucleation and /or epitaxial centers, which formed the basis for layer films growth. Then the samples were washed repeatedly in deionized

water, and finally put in ultrasonic agitation with distilled water for 15 min then dried.

The solution used for the films investigated here had the following amounts: 2.2g  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (Fulka99.9%); 50ml  $\text{H}_2\text{O}$  (deionized); 40ml  $\text{CH}_3\text{OH}$  (Merck 99.5%); 60ml  $\text{C}_2\text{H}_5\text{OH}$  (Merck 99.5%). A small amount of acetic acid was added to aqueous solutions to adjust the pH value to about 4.6 to prevent the formation of hydroxides. Water is the most convenient oxidizing agent. Methanol and ethanol were the obvious choice because of their volatility and thus facilitating quick transformation of the precursor mist into vapor form, which is an important criterion for obtaining good quality films. The molarity of solution is 0.1 M.

The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle with 1 mm inner diameter, with the help of compressed air as carrier gas. During the course of spray, the substrate temperature was monitored using a thermocouple with the help of digital multimeter.

The reaction leading to the formation of ZnO is as follows [8].



The slides then were placed on the surface of a substrate heater when sprayed. The nozzle-to-substrate distance was 25 cm and the spraying period was (5 s) with flow rate as (3 ml/min). The substrate heater was an electrically controlled block furnace, thickness

of ZnO thin film is calculated using gravimetric method through weighing the substrate before and after deposition as in relation (1):

$$t = \Delta m / \rho A \quad \dots\dots(1)$$

Where  $\Delta m$  is the mass difference (before and after deposition),  $\rho$  is the density of ZnO and A is the area of deposited film.

Film thickness was determined by the weight–difference method using an sensitive electrical balance of Metler AE-160), with preciseness reaches  $10^{-4}$  gm. ZnO thin film were deposited onto glass substrates ( $30 \times 12 \times 1 \text{ mm}^3$ ) in the temperature range ( $300^\circ\text{C}$ – $400^\circ\text{C}$ ). The substrate temperature was monitored with a thermocouple and controlled electronically. The various process parameters used in the film deposition are listed in table (1). The film morphology was examined using a Nikon optical transmission microscope (OTM) of digital camera, model: ME600. The structural analysis of the ZnO thin films is done by powder x-ray diffraction (XRD) data collected on SHIMADZU diffract meter model: XRD6000, using  $\text{CuK}\alpha$  with  $\lambda = 1.540598$  nm radiation with range from 30-50 degree with step of 0.0500 degree, Japan. The optical transmission spectra of the films of different condition were obtained in the ultraviolet (uv/visible near infrared (nir) region up to 1100 nm using SPECTRO UV/VIS spectrophotometer, model: SP 300. The infrared transmittance modes of these samples were obtained from FTIR transmittance measurements takes at room temperature. The FTIR

measurements are performed with a SHIMADZU spectrometer model (IR Prestige-21) of range 250-4000  $1/\text{cm}$  with resolution of  $4[1/\text{cm}]$ .

### 3- Result and Discussions

#### 3.1 Structure and morphology

The films morphology was examined using a transmittance optical microscope as it shown if figure (1:a,b,c), these films show different morphology of surface grains, which are depend on deposition of the substrate temperature. X-ray diffraction analysis, obtained for  $2\theta$  scan between  $30^\circ$  and  $50^\circ$  at  $0.0500^\circ$  glancing angle, indicated that the deposited ZnO films on the glass substrate were polycrystalline and retained a hexagonal structure type wurtzite. The diffraction peaks are easily indexed on the basis of the hexagonal structure of ZnO ( $P6_3mc$  (186),  $a=3.24982\text{\AA}$ , and  $c=5.20661\text{\AA}$  JCPDS v.1.30. ).

A set of samples were deposited at temperatures at  $300^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $400^\circ\text{C}$ . In order to explore the dependence of structural properties on the substrate temperature, we investigate the changes in structural characteristics such as the full width half maximum (FWHM), average grain size (G.S) and micro strain ( $\delta$ ). From figure (2: a,b,c), Miller indices are indicated on each diffraction peak. It can be seen that a set of peaks with strong intensity can be obtained and its position refers to a crystalline ZnO phase, It is seen that the reflection for the parent residual organic compound disappear completely, whereas the (002) and (101) reflections for hexagonal ZnO show up. The films exhibit strong (002) orientation in the three samples

, when  $T_s = 400^\circ\text{C}$ , it is clear from the figure(2a) that as  $T_s$  increased the thin films adopts a preferred orientation, with the c-axis (002) perpendicular to the substrate, beside that the intensity of peaks became strongest and disappeared of some plans with increasing the substrate temperature. In growing ZnO thin films, it is of primary importance to control the prefer orientation for each application. ZnO having the (002) orientation normal to the substrate is especially important for piezoelectric applications whereas the one with (100) orientations is of benefit to transparent conductive oxide application [8]. The deposition conditions should be optimized for the particular application of interest in every case. The most important structure parameters which we are studying it are:

#### (A) FWHM ( $\Delta$ )

The FWHM is an indication of the existence of dislocation in the material [9]. From tables (2) we can conclude the following: in our samples which are prepared in pyrolysis method the effect on FWHM are limited.

#### (B) Average grain size (G.S)

The average grain size is determined from the full width at half maximum (FWHM) for the most intense peak using the Scherrers

$$G.S = \frac{(0.91)}{\Delta_{2\theta} \cos \theta} \dots\dots\dots (2)$$

formula [9]:

The increasing of the substrate temperature is likely to drive the modification of grain boundary configuration. It is well known that the shape and size of inorganic functional materials have an important influence on their

electrical and optical properties[2]. Table (2) shows the variation in the average grain size with substrate temperature, we can conclude that average grain size increase with increasing substrate temperature.

#### (C) Texture coefficient (Tc)

Texture coefficient Tc is the best indication of preferred orientation, (which may be defined simply as a condition in which the distribution of crystals orientation is nonrandom), the fabricated film is calculated using relation [10]:

Table (2) shows the influence of different deposition condition on (Tc). We think that our results indicate that for ZnO<sub>there</sub> is a value of preferred orientation produced by the forming process itself, it is due to the tendency of the grains in a polycrystalline aggregate to rotate during their growth in complex way that is determined by imposed force adjoining the grains, the result is a preferred orientation. For samples with different substrate temperature the preferred orientation or Tc is (002) plane and its value increase when the substrate temperature is increased, this means that this case increases the arrangements of preferred orientation or reduces the degree of disorder, this is in agreement with the results for ZnO in [11], and it may decrease the stress which accompanies with formation grain size. this causes more symmetrical or uniform in film smoothness [12].

#### (D)Non uniform strain ( $\Delta d/d$ )

When a polycrystalline piece is deformed by any force effect, slip occurs in each grain causing a change in shape, becoming flattened and elongated in the direction.

Beside each grain retains contact on its boundary surface with its entire neighbor, and because of this interaction between grains, no single grain in a polycrystalline mass is free to deform in the same way as an isolated crystal would, if subjected to the same deformation acts. As a result of this restraint by its neighbors, a plastically deformed grain in a aggregate solid usually has regions of its lattice left in an elastically bent or twisted condition or, more rarely, in a state of uniform tension (+) or compression (-) [13]. The x-ray diffraction data can also

$$Tc(hkl) = [I(hkl)/I_0(hkl)]$$

$$/[N_R^{-1} \sum I(hkl)/I_0(hkl)] \quad \dots\dots(3)$$

be used to determine residual stress or non uniform strains in the film due to structural defect like dislocation, stacking faults etc. The inhomogeneous stress in the film can determined from the line broadening  $\Delta(2\theta)$ , full width at half maximum (FWHM) (where  $\theta$  is the diffraction angle), which is also related to the variations in d-spacing  $\Delta d$  (where d is the distance between any two parallel planes having the same Miller index (h,k,l). In the x-ray diffraction data we can calculate

$$\frac{\Delta d}{d} = \frac{d_{hkl}(Observed) - d_{hkl}(ASTM)}{d_{hkl}(ASTM)} \quad \dots\dots\dots(4)$$

$\Delta d/d$  using the relation below [14]:

The value of  $\Delta d/d$  is referring as the non uniform or strain residual stress parameter [14]. Generally there is increase in the value of the d space for the preferred orientation (002) with the increase of substrate temperature as there ASTM values, which means that increasing

substrate temperature makes the samples under the effect of compression strain (-) as it shown in table (2).

### 3.2 Fourier transforms infrared (FTIR) analysis

FTIR spectroscopy supplements the information obtained from XRD. It is the combination of all data helps us to understand, analyze and refined more effectively the structure of films beside that to be insure of our procedure of preparing ZnO films. Figure (3: a,b) shows the FTIR transmittance spectra of ZnO sample and zinc acetates dehydrate for comparison. Here, signal derived from glass substrate was never detected in these measurements because the measurements were performed with the solid scraped from the substrate.

This spectral region encompasses several important stretch modes involving carbon bonded to hydrogen as well as to oxygen, hydrogen bonded to oxygen and bonding between Zn-O  $\sim(432.05 \text{ cm}^{-1})$ . The broad asymmetrical absorption region that peaks around  $3390.86 \text{ cm}^{-1}$  is likely due to the OH stretching mode of hydroxyl group. Theoretical calculations predict O-H vibrations in ZnO ranging from  $3216 \text{ cm}^{-1}$  to  $3644 \text{ cm}^{-1}$ , depending on the configuration and number of hydrogen atoms in the complex[2].

The hydroxyl results from the hygroscopic nature of ZnO. Three peaks of very weak intensities at  $2856 \text{ cm}^{-1}$ ,  $2927 \text{ cm}^{-1}$  and  $2960 \text{ cm}^{-1}$  are observed which are due to C-H stretching vibrations of alkane groups. These specific peaks correlate well with the observed frequencies of the C-H<sub>2</sub> symmetric

stretch ( $2926 \pm 10 \text{ cm}^{-1}$ ), and C-H<sub>3</sub> asymmetric stretch ( $2962 \pm 10 \text{ cm}^{-1}$ ) of saturated hydrocarbons, respectively [2]. The peaks observed at  $1375.25 \text{ cm}^{-1}$  and  $1508.33 \text{ cm}^{-1}$  are due to asymmetrical and symmetrical stretching of zinc carboxylate ( $-\text{COO}^-$ ), respectively [2]. According to the literature, a unidentate or monodentate acetate ligand usually lies between  $80\text{--}160 \text{ cm}^{-1}$  [15]. Nevertheless, these bands are clearly shifted compared to those displayed for the bidentate acetate ligand in  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  [16]. Figure (3: a,b) compares the infrared wavelength range for the ZnO sample and zinc acetate dehydrate powder. The average separation of these two bands,  $\Delta\nu = 232 \text{ cm}^{-1}$  is typical of unidentate acetate ligand ( $\Delta\nu = 110 \text{ cm}^{-1}$ ) for zinc acetate dehydrate). This confirms that acetate is complex with metal zinc, likely in the surface. The small peak at  $1039 \text{ cm}^{-1}$  represents C=O deformation. The absorption in  $2368.59 \text{ cm}^{-1}$  is due to the presence of  $\text{CO}_2$  molecular in air. The FTIR results strongly support the hypothesis that at least some of the carbon and hydrogen co-exist as defect complex in the undoped ZnO and their absorption bands have no obvious change.

### 3.3 Optical studies

The optical transmission spectra of ZnO films deposited on the glass substrate at  $300^\circ\text{C}$ ,  $350^\circ\text{C}$ ,  $400^\circ\text{C}$  was recorded as a function of wavelength in the range of  $190\text{--}1100 \text{ nm}$  and it shown in the figure(4). These spectra show that for film having  $300^\circ\text{C}$ , the average

transmission over the range  $500\text{--}1100 \text{ nm}$  exceeds 85% with a sharp fall near the fundamental absorption; whereas fall in transmission is gradual for other samples, these result is good agreement with the measurements results with the measurements results obtained by Khedidja et al [2]. The absorption coefficient ( $\alpha$ ) was calculated using Lambert law as follows [3]:

$$\ln(I_0/I) = 2.303A = \alpha d \dots\dots\dots(5)$$

Where  $I_0$  and  $I$  are the intensity of incident light and transmission light respectively,  $A$ , the optical absorbance and  $d$  the sample thickness.

The absorption coefficient ( $\alpha$ ) was found to follow the relation:

$$\alpha = [A(h\nu - E_g)^{1/2}] / h\nu \dots\dots\dots(6)$$

Where  $A$  is a constant and  $E_g$  the optical energy gap. Plots of  $(\alpha h\nu)^2$  versus the photon energy ( $h\nu$ ) in the absorption region near the fundamental absorption edge indicate direct allowed transmission in the film material, as shown in figure (5). The optical energy gap was estimated from the extrapolation of the linear portion of the graph to the photon energy axis [3], and its dependence on film temperature is illustrated in figure (6). It is observed that  $E_g$  decreases with increasing substrate temperature. This may be due to the possibility of structural defects in the films arisen during the time of their preparation and the increase of substrate temperature is likely to be attributed to a change of crystallite size and a modification of the grain boundary configuration



during growth [2], which could give rise to the allowed states near the conduction band in the energy band gap. In case of much higher substrate temperature films, these allowed states could well merge with the conduction band resulting in the reduction of energy band gap. Figure (7) shows variations in refractive index of the films with photon energy. The increase in the film substrate temperature results in the overall increase in the refractive index in the visible/near infrared region. The refractive index of the samples grown at substrate temperature lower than 350 °C are smaller than the samples grown at 350°C and 400°C the reason for this phenomena is from the poor qualities of the films deposited at lower temperatures . The density of such films is also smaller than that deposited at higher temperatures [2, 3]. The peak values of the refractive index for the substrate temperature vary of 2.225 to 2.652.

#### 4-Conclusions

Pure ZnO films were deposited by spray pyrolysis technique using zinc acetate dehydrate dissolved in methanol, ethanol and deionized water, within the substrate temperature values 300°C, 350°C, and 400°C. The X- ray diffraction analysis confirms that undoped ZnO films are polycrystalline, having hexagonal structure. It was seen that the preferred orientation change with a temperature increased. Specific preparation conditions to obtain films having reflection planes in (002) and (101) the prefer orientation was in (002) plane. The optical measurements reveal that films have maximum transmittance of about

90% and a direct band gap of 3.2eV.

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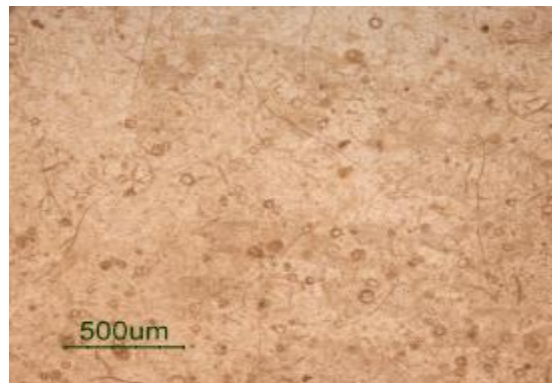
Table (1) Summary of deposition condition

| Spray parameters                          | Optimum values/Item                                        |
|-------------------------------------------|------------------------------------------------------------|
| Nozzle                                    | Glass                                                      |
| Nozzle-substrate distance                 | 25cm                                                       |
| Solution molarity                         | 0.109M                                                     |
| Aqueous solutions pH value                | 4.6                                                        |
| Carrier gas                               | Compressor air                                             |
| Spraying period                           | (5 s)                                                      |
| Flow rat                                  | 3 ml/min                                                   |
| Film thickness with substrate temperature | 0.22mm,0.27mm,0.31mm at 300°C,350°C and 400°C respectively |

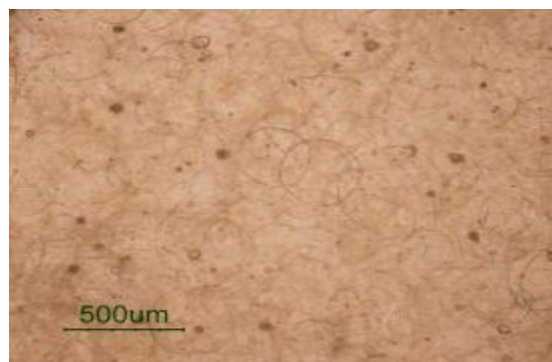
Table (2) Summary of X-ray diffraction data of films  
with different substrate temperature

| Sample | 2q<br>(deg) | d <sub>Observed</sub><br>(Å°) | d <sub>ASTM</sub><br>(Å°) | hkl | FWHM<br>(deg.) | Average<br>G.S(nm) | Tc     | Δd/d   |
|--------|-------------|-------------------------------|---------------------------|-----|----------------|--------------------|--------|--------|
| 300 °C | 34.4147     | 2.6038                        | 2.602                     | 002 | 0.2753         | 30.2               | 1.9082 | 6.9177 |
| 350 °C | 34.4512     | 2.6011                        | 2.602                     | 002 | 0.2995         | 32.2               | 2.4055 | -3.458 |
| 400 °C | 34.4417     | 2.6018                        | 2.602                     | 002 | 0.2931         | 32.8               | 2.4594 | -7.686 |

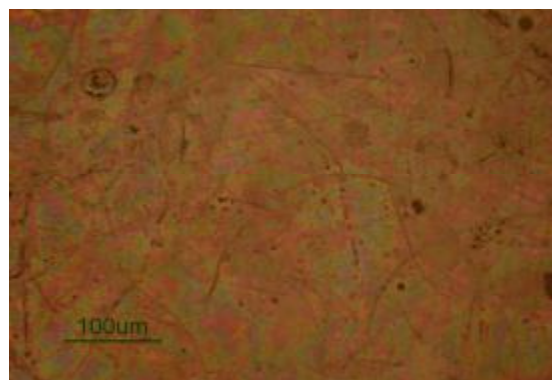




(a) ZnO thin film at 400 °C (thickness : 0.31mm)



(b) ZnO thin film at 350 °C (thickness : 0.27mm)



(c) ZnO thin film at 300 °C (thickness : 0.22mm)

Figure ( 1: a,b,c ) Optical transmission microscopic showing ZnO films at different substrate temperature using spray pyrolysis technique on glass substrate(x=500)

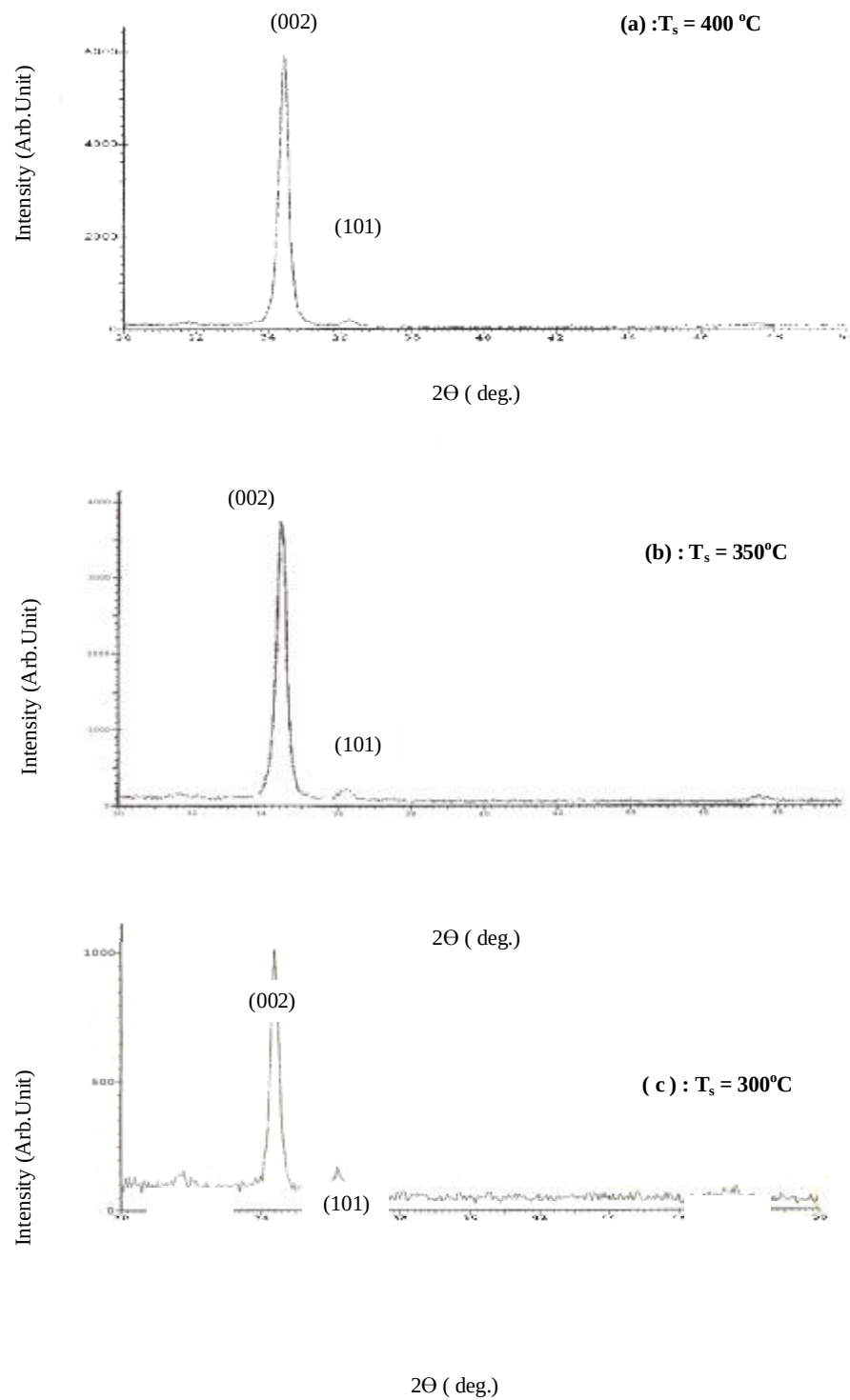


Figure (2: a,b,c) : X-ray diffraction (XRD) of films obtained at different substrate temperatures : (a)  $T_s=400^\circ\text{C}$ ; (b)  $T_s=350^\circ\text{C}$ ; and (c)  $T_s=300^\circ\text{C}$ .

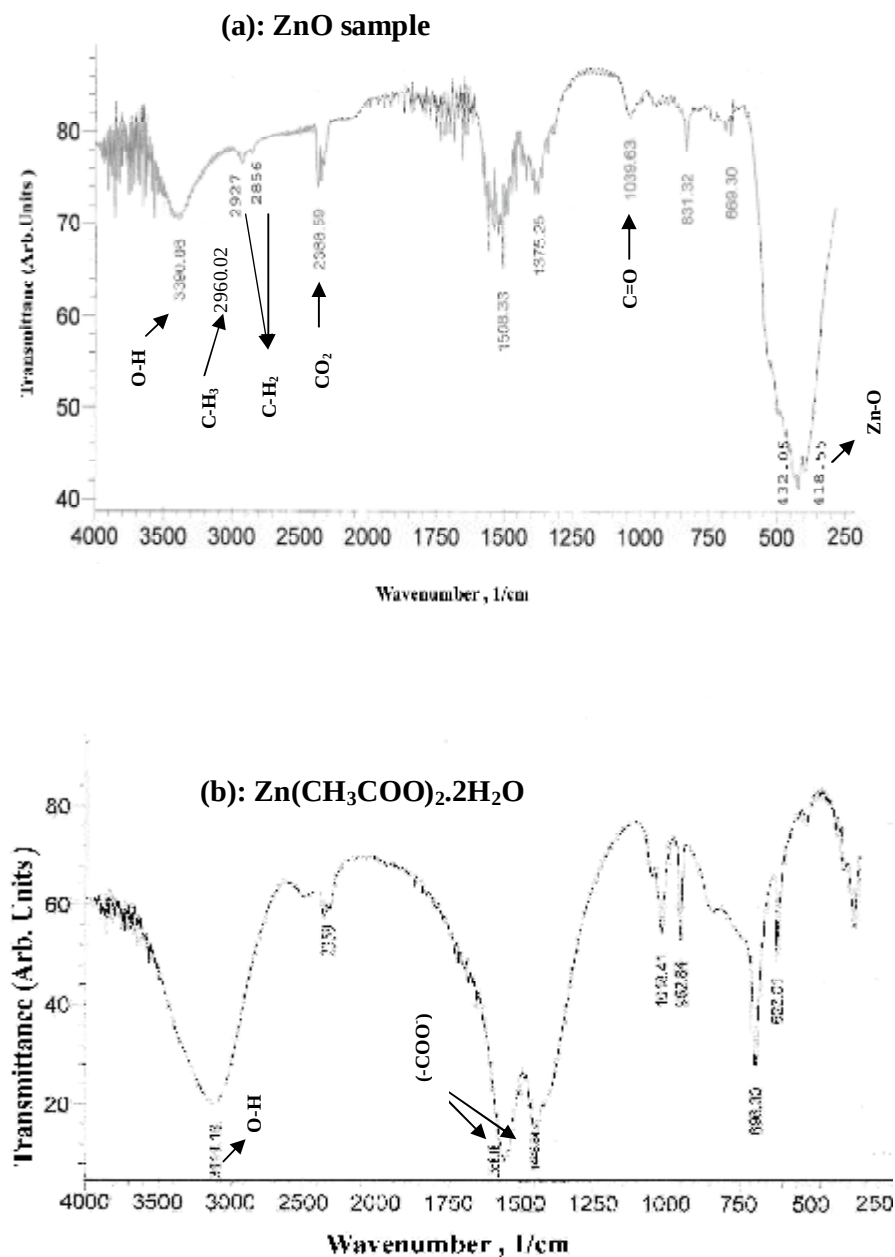


Figure ( 3: a,b ) : FTIR transmission spectra of ZnO sample deposited by pyrolysis method together with zinc acetate dehydrate powder for comparison .

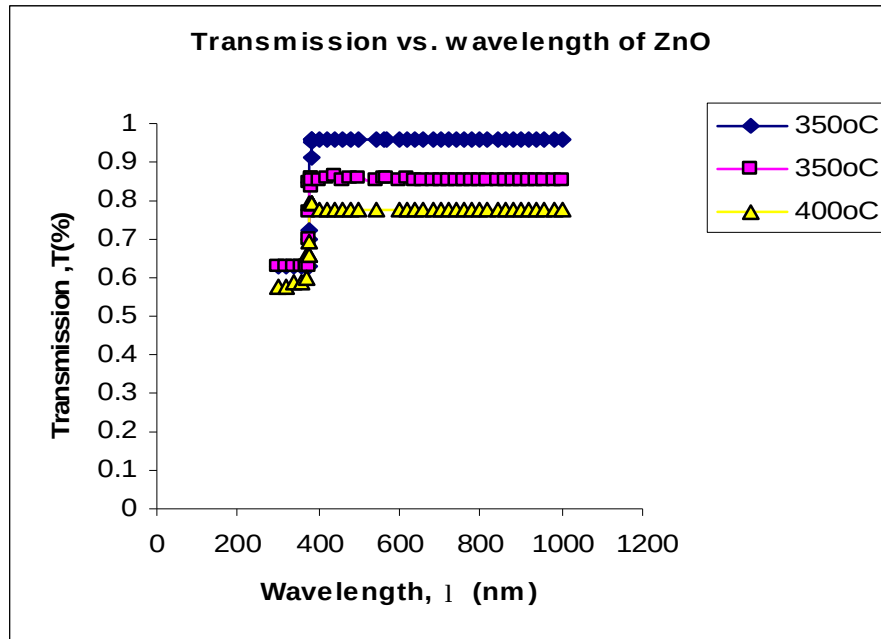


Figure (4) Transmission spectra of the sprayed ZnO thin films at different substrate temperatures

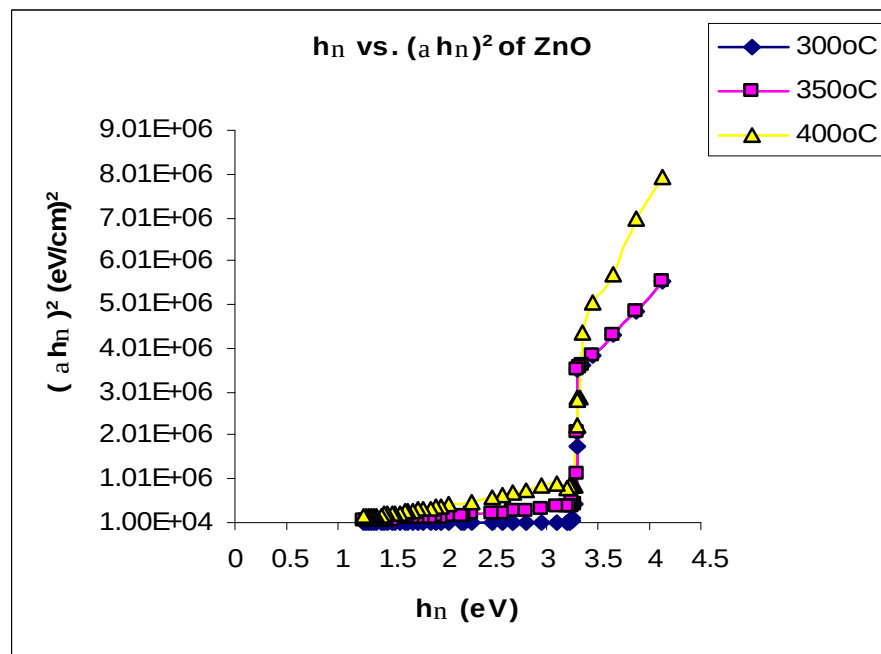


Figure (5) Plots of  $(\alpha h\nu)^2$  vs  $h\nu$  for different substrate temperatures

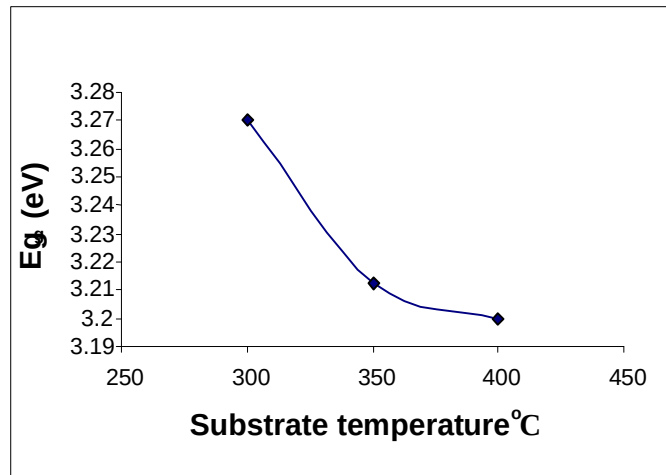


Figure (6) Optical energy gap vs substrate temperature of ZnO thin films

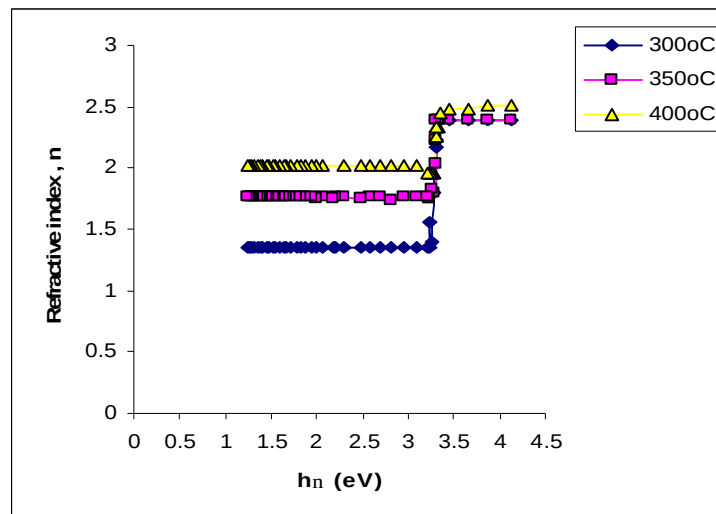


Figure (7) Variations in refractive index of the films with photon energy