Characterization of ZnO thin films grown by chemical bath deposition

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Abstract

The ZnO thin films were prepared by chemical bath deposition technique using glass substrates with bath temperature 80^oC and annealing temperatures 300^oC, 350^oC and 400^oC. The X-ray diffraction analysis shows that the prepared samples are polycrystalline and it exhibits hexagonal structure along with c-axis orientation. The average grain size of ZnO thin films was found to be 36.340nm as calculated by XRD using Debye Scherer's formula. After annealing the films in air the grain size was 32.420nm, 60.993nm and 34.067nm respectively. The optical absorbance of the deposited films was characterized by UV-VIS-NIR spectrometry and shows the presence of direct transition with band gap energy 3.32eV and after annealing, it decreases to 3.12eV, 3.04eV and 3.10eV respectively.

Keywords: Zinc oxide film, Chemical bath deposition, XRD, Optical properties

1. Introduction

We are in a threshold of new era of materials; nano and micro semiconducting materials have attracted a great deal of attention for their size dependent properties and their wide range of applications. ZnO is one of the most interesting semiconducting materials with band gap energy of 3.3 eV and it is being considered as a potential material to use in the fields of solid state emission, solar cells, chemical sensors, piezoelectric transducers, transparent electrodes, photo-catalysts, electroluminescent devices and ultraviolet laser diodes [1-4]. ZnO thin films have been studied as the active channel material in thin film transistors development because of its exhibiting n-type semiconductive characteristic and excellent thermal stability and can be well oriented crystalline on various substrates [5,6]. Numerous methods have already been used to deposit ZnO thin films, among the fabrication methods chemical bath deposition (CBD) was used for the preparation of semiconducting oxide films [7]. CBD is known to be a simple, low temperature and inexpensive large-area deposition technique, it is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions [8,9], such as CdS [10,11], CdSe [12,13], CdO [14,15], ZnS [16,17], ZnSe [18,19] and ZnO [20-26]. CBD results good deposits on suitable substrates by controlled precipitation of the compound from the solution, it offers many advantages over other well-known methods of vapour phase synthetic routes, and could allow us to easily control the growth factors such as, film thickness, deposition rate and crystalline quality by varying the solution PH, temperature and bath concentration [27]. The deposition of metal oxide semiconducting thin films occurs due to substrate maintained in contact with chemical bath containing metal ions, the film formation on substrate takes place when the ionic product exceeds the solubility product [28]. A small amount of the reagents in the solutions are used for film growth and a larger amount of material produces colloidal particles in the solution. Only 2% of reagents in the solution is used during CdS film growth on the substrate [29].
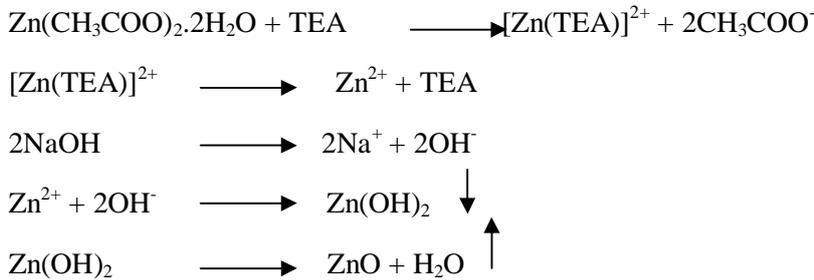
In this work reports, the deposition of ZnO thin films on glass substrates using CBD with the study of the structural and optical properties along with micro structural quantities. Effects of thermal annealing on these properties are also studied.

2. Experimental details

ZnO films were prepared using aqueous solutions of $Zn(CH_3COO)_2.2H_2O$, triethanolamine (TEA) and NaOH [weighed amounts] in de-ionized water to the volume of 100ml. The micro corning glass (35mm x 35mm x 1mm) was used as a substrate. The substrate was cleaned with toothpaste because it is a mild abrasive, then washed in warm soapy water and a water-ethanol (50:50) solution and then dried.

Prior to the deposition, the beaker containing the deposition solution was placed in the water bath at 80 °C for about 5 minutes to stabilize the temperature of the solution, then the beaker was kept in the water bath. At the end of the deposition time ($\approx$ 2.15 hours), the slides were taken out, rinsed with distilled water and allowed to dry with warm air. The slides were observed to have been coated with milky white deposits. The equation of the reaction is shown below:

$$Zn(CH_3COO)_2.2H_2O + TEA \longrightarrow [Zn(TEA)]^{2+} + 2CH_3COO^-$$

$$[Zn(TEA)]^{2+} \longrightarrow Zn^{2+} + TEA$$

$$2NaOH \longrightarrow 2Na^+ + 2OH^-$$

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O \uparrow$$

They were later annealed at different temperature (300°C, 350°C and 400°C) for 12 minutes. The optical absorbance and transmittance measurements were made on ZnO thin films by UV-VIS-NIR spectrophotometer at normal incident of light in the wavelength range of 250-1100nm. The optical absorption coefficient α was calculated for each film using the Lambert's formula [30]:

$$\alpha = \left(\frac{1}{t}\right) ln \left(\frac{1}{T}\right) \quad (1)$$

Where, t = is a thickness of the film.

T = is a transmittance of the film.

The absorption coefficient α is related to the incident photon energy hv as [31]:

$$\alpha = k (hv-E_g)^{n/2}/hv \quad (2)$$

Where, k is a constant, E_g is the optical band gap and n is equal to 1 for direct band gap material such as ZnO. The band gap was determined for each film by plotting $(\alpha hv)^2$ versus hv and then extrapolating the straight line portion to the energy axis.

The structure of ZnO thin films was carried out using a Philips X'pert ProMPD diffractometer unit (PANalytical Company), with 40KV and 20mA CuKα radiation (λ=1.5406 Å). The sample was scanned from 20° to 70° in step of 0.01° with a scan rate of 1.2° min⁻¹.

3. Result and discussion

3.1 Structural analysis

The as-deposited and annealed ZnO thin films were analyzed for their structural properties by recording X-ray diffraction pattern. Figure 1(a, b, c and d) shows the XRD pattern of ZnO films which was deposited on glass substrates at bath temperature 80 °C and annealed at 300°C, 350°C and 400°C for 12 minutes. According to this figure, the films are polycrystalline and the diffraction peaks of ZnO exhibited hexagonal plane (crystals have hexagonal structure) with preferred orientation of the grains along (100), (002), (101), (102) and (110). In addition the prominent peak (002) indicates preferential c-axis orientation of the crystals [32]. The lattice parameters have been calculated using the relation.

$$\frac{1}{d^2} = \frac{3}{4}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

(3)

A comparison of XRD data for standard hexagonal ZnO with the XRD data of as-grown and annealed films is shown in table 1.

Table1. A comparison of XRD data for standard hexagonal ZnO with the XRD data of prepared ZnO films.

Sample										
ZnO(Hexagonal)[33]		As-grown film		Annealed film						
				300°C		350°C		400°C		
2θ(°)	d(Å)	2θ(°)	d(Å)	2θ(°)	d(Å)	2θ(°)	d(Å)	2θ(°)	d(Å)	(hkl)
31.766	2.8147	31.642	2.8277	31.668	2.8254	31.670	2.8253	31.489	2.8411	(100)
34.419	2.6036	34.298	2.6146	34.325	2.6125	34.310	2.6115	34.116	2.6281	(002)
36.250	2.4761	36.116	2.4870	36.148	2.4849	36.145	2.4850	35.961	2.4974	(101)
47.535	1.9113	47.441	1.9164	47.476	1.9151	47.493	1.9144	47.224	1.9247	(102)
56.590	1.6251	56.446	1.6302	56.564	1.6270	56.569	1.6269	56.313	1.6337	(110)
62.851	1.4774	62.751	1.4807	62.836	1.4789	62.802	1.4796	62.688	1.4808	(103)
67.941	1.3786	67.814	1.3819	67.900	1.3793	67.903	1.3803	67.814	1.3819	(112)
69.006	1.360	69.007	1.3598	69.012	1.3597	69.062	1.3589	69.007	1.3598	(201)

The mean crystallite (grain) size of ZnO thin films D; can be estimated by the Debye-Scherer's formula [33].

$$D = 0.9\lambda/(\beta\cos\theta)$$

(4)

Where, λ = wavelength of the X-rays (1.5406 Å).

β = FWHM of the observed peak.

θ = diffraction angle.

The dislocation density was calculated by the relation [34]:

$$\delta = 1/D^2$$

(5)

Where, D is the grain size.

The micro strain was calculated by the formula [34]:

$$\varepsilon = \beta \cos\theta/4$$

(6)

3.2 Effect of thermal annealing

Thermal annealing of ZnO thin films deposited at bath temperature 80°C was carried out at 300°C, 350°C and 400°C in air. We can show from table 2, the best temperature of annealing (T_a) is 350°C that occurs in this temperature increase in grain size (60.993nm) and decreases the dislocation density and micro strain, also the mean values of lattice parameters have been found as a = 3.257 Å, c = 5.213 Å that agree with standard values. However, no change in the orientation of the films is observed. The strong and sharp diffraction peaks indicate the formation of well crystallized sample. The variation of crystallite size and strain with bath temperature 80°C and annealing temperatures is shown in Figure 2. It is observed from Fig.2, that at T_a =350°C the crystallite size reaches the maximum value and at the same time strain decreases (minimum value). Figure 3 represents the variation of dislocation density with annealing temperature.

3.3 Optical properties

The variance of absorbance (A) of ZnO films deposited at bath temperature 80°C and annealing temperatures 300°C, 350°C and 400°C are shown in Figure 4. This spectrum reveals that all ZnO films have low absorbance in visible region, which is a characteristic of ZnO.

The optical energy gap E_g could be obtained from the intercept of $(\alpha h\nu)^2$ vs $h\nu$ for direct allowed transitions (equation 2). The $(\alpha h\nu)^2$ vs $h\nu$ plots for typical sample deposited at optimized preparative parameters (deposition time 2.15 hour, bath temperature 80°C) and annealed samples are shown in Figure 5. When straight portion of $(\alpha h\nu)^2$ is extrapolated to the point of intercept in the X-axis (photon energy) gives the band gap (E_g). The band gap of ZnO films was found to be 3.32eV (as-deposited at 80°C), 3.12eV (at T_a=300°C), 3.04eV (at T_a=350°C) and 3.10eV (at T_a=400°C) respectively.

Table 2. Some calculated quantities of micro structural for ZnO thin films.

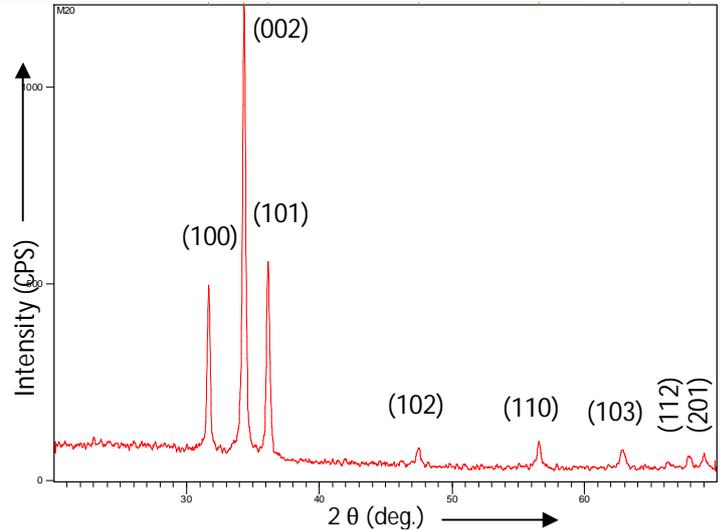| Sample	Grain size (nm) D	Lattice parameters a(Å)	c(Å)	Dislocation density δ (Line^2/m^2)	Micro strain (ε) x10^{-3}
As-grown	36.340	3.263	5.218	0.75723x10^{15}	0.97131
T_a=300°C	32.420	3.258	5.214	0.95138x10^{15}	1.12150
T_a=350°C	60.993	3.257	5.213	0.26880x10^{15}	0.90901
T_a=400°C	34.067	3.272	5.235	0.86162x10^{15}	1.73741
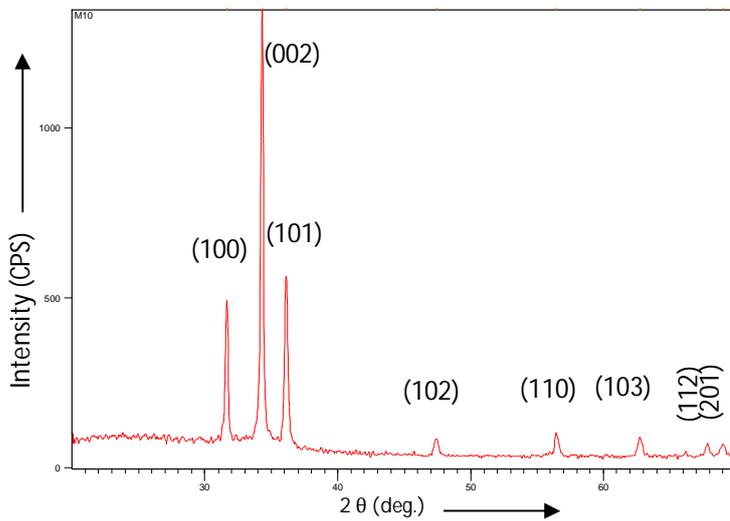
Fig.1(a) XRD pattern of ZnO thin film deposited at 80°C.

Fig.1(b) XRD pattern of ZnO thin film annealed at Ta=300°C.

Fig.1(c) XRD pattern of ZnO thin film annealed at Ta=350°C.
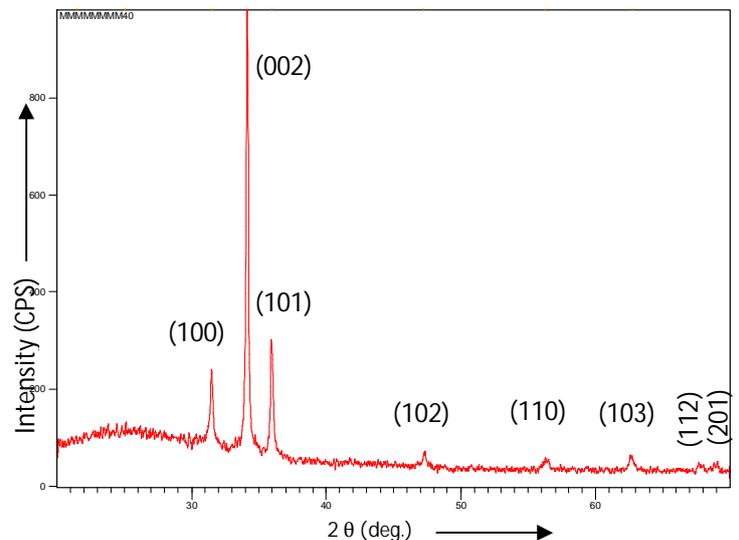
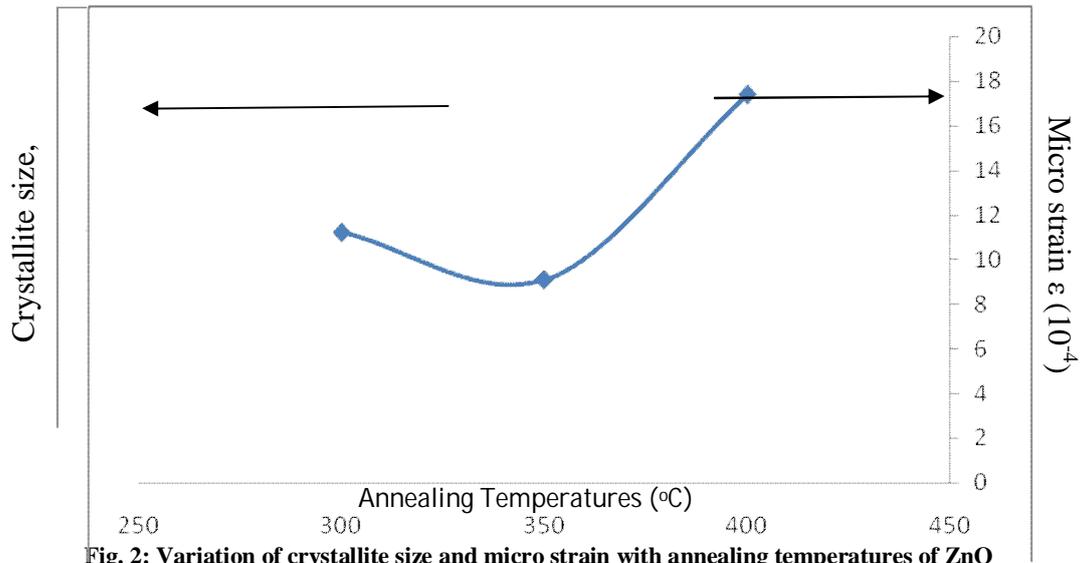Fig.1(d) XRD pattern of ZnO thin film annealed at Ta=400°C.

Fig. 2: Variation of crystallite size and micro strain with annealing temperatures of ZnO thin films.
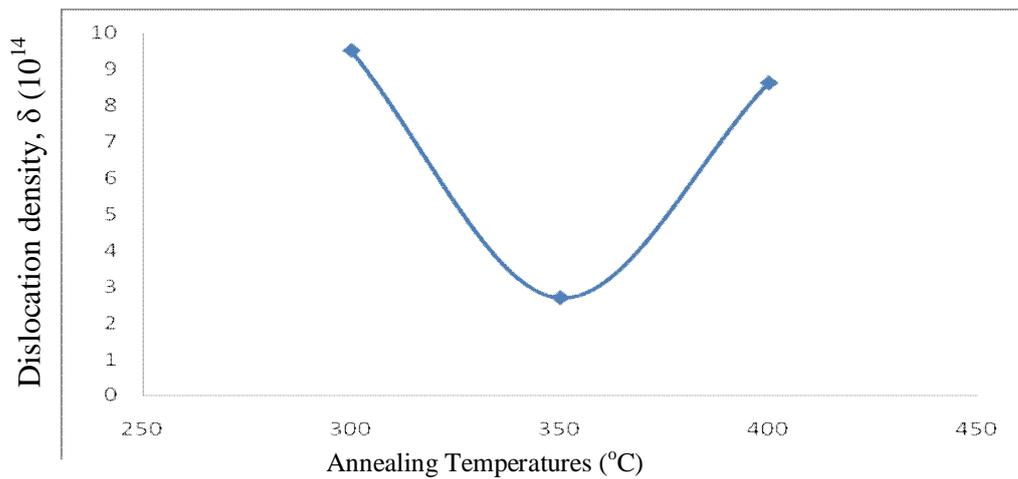

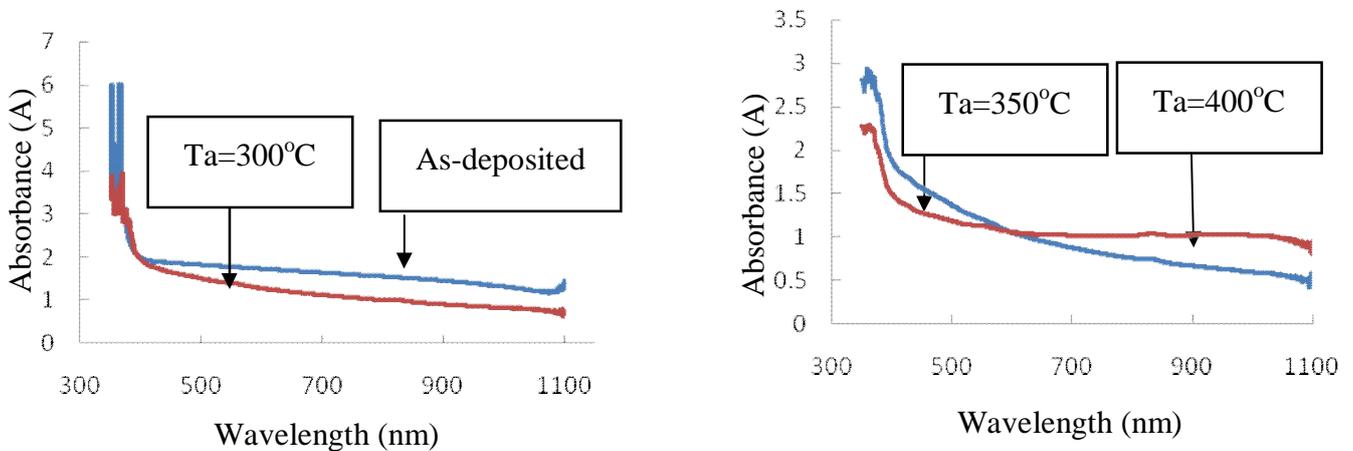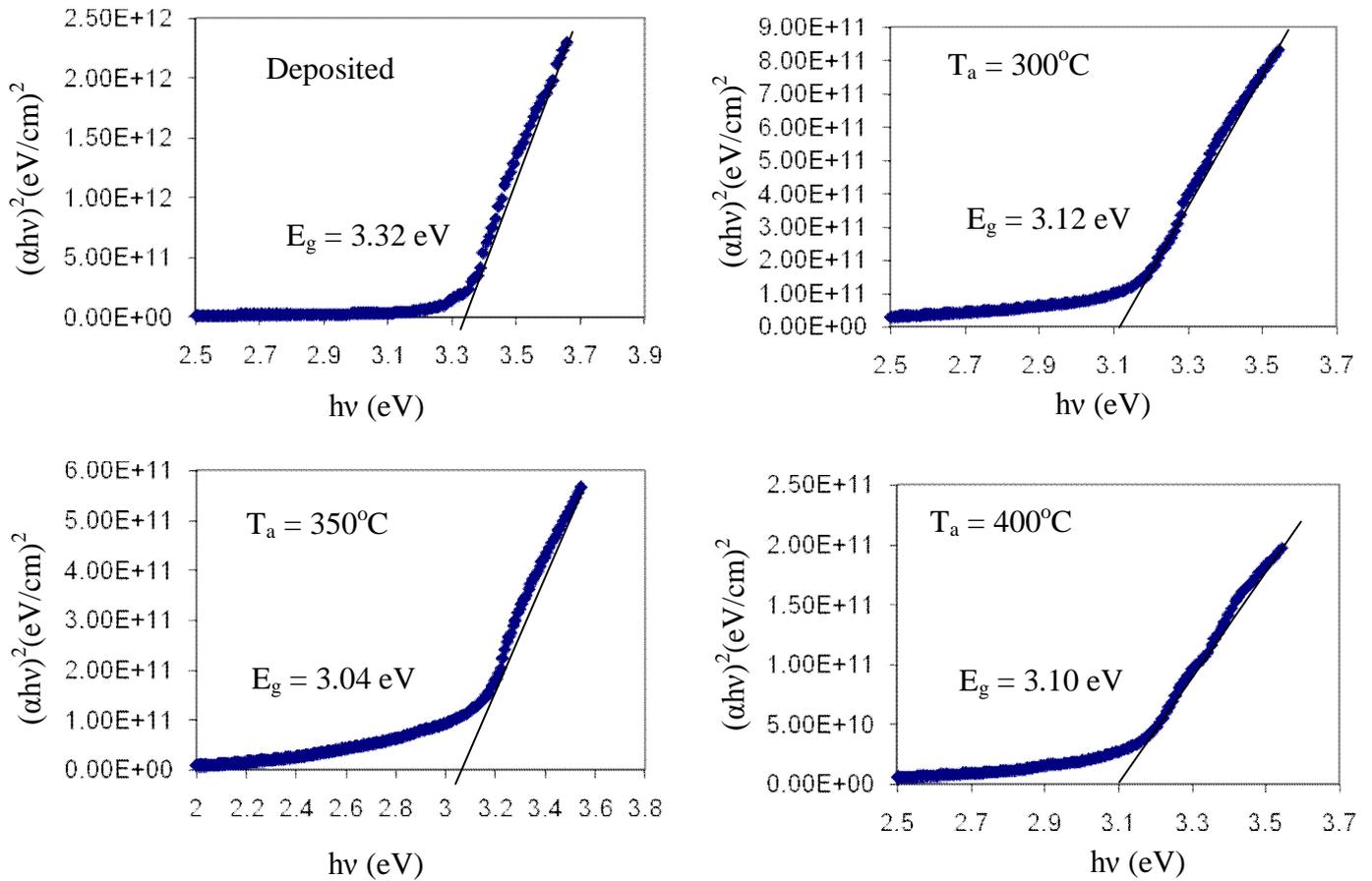**Fig. 3: Variation of the dislocation density with annealing temperatures of ZnO thin films.**

Fig. 4: Absorption Spectrum of ZnO thin films.

Fig. 5: Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for ZnO thin films, deposited and annealing at temperatures of a) 300°C, b) 350°C and c) 400°C.

4. Conclusions

The chemical bath deposition of ZnO thin films and the effect of annealing temperature have been studied. The structural and optical analysis of prepared and annealed films have been done. The crystallite size and band gap were found to change with the annealing temperature (T_a), the maximum grain size of the film is 60.993 nm at T_a=350°C. From the X-ray diffraction analysis, all the films show hexagonal structure along with c-axis oriented (002) plane. The energy gap of the synthesized material is found to vary between 3.32eV and 3.04 eV.

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الخلاصة

حضُرة (رُسبت) الأغشية الرقيقة لمركب ZnO على القواعد الزجاجية باستعمال تقنية الترسيب الكيميائي CBD بدرجة حرارة ترسيب 80°C، بعدها تمت معاملة تلك الأغشية حراريا بدرجات حرارية مختلفة (عملية التلدين) 300°C و 350°C و 400°C في الهواء. تم تحليل التركيب البلوري للأغشية المحضرة والملدنة عن طريق حيود الأشعة السينية XRD وتبين ان الأغشية متناسقة وناعمة ومتعددة التبلور وتمتلك طوراً واحداً فقط وهو التركيب البلوري السداسي Hexagonal بدون حدوث اي تغيير في التركيب البلوري على طول فترة التحضيرات والتي رافقتها عملية التلدين. أن معدل الحجم الحبيبي لتلك الأغشية هو 36.340nm والمحسوب عن طريق استعمال علاقة ديباي-شيرر وذلك من خلال حيود الأشعة السينية، وبعد أجراء عملية التلدين فأن معدل الحجم الحبيبي أصبح 32.420nm و 60.993nm و 34.067nm على التوالي. قيست الامتصاصية الضوئية للأغشية باستعمال مدى المطيافية UV-VIS-NIR من الضوء وتبين ان لها سمة الأنتقال المباشر مع فجوة طاقة 3.32eV للأغشية المرسبة بدرجة حرارة 80°C وللأغشية الملدنة كانت 3.12eV و 3.04eV و 3.10eV على التوالي.