Influence of Annealing Temperature on the Structural, Optical Properties Dispersion Parameters of ZnO Thin Films and

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Received : 14 January 2016 ; Accepted : 29 February 2016

Abstract

Zinc oxide ZnO thin films were prepared by chemical spray pyrolysis technique on glass substrates at (450℃) temperature. The prepared films were annealed at different temperatures (550and600 ℃) in air for 2h to study the effect of annealing on the structural and optical properties of ZnO thin films. As-deposited and annealed films were characterized by X-ray diffraction (XRD) and UV-Vis-NIR spectroscopy. X-ray diffraction patterns indicated that the ZnO films had a polycrystalline wurtzite structure and crystallite size increases with the increase of annealing temperature. The optical properties and dispersion parameters of ZnO films have been studied over a wavelength range(400-900)nm. The optical band gap, refractive index, extinction coefficient, single-oscillator energy, dispersion energy, moments of the optical spectra (M_{-1}) and (M_{-3}), average oscillator strength, average oscillator wavelength, high frequency dielectric constant, the ratio of carrier concentration to the effective mass N/m*, static dielectric constant and static refractive indices of the ZnO thin films were investigated. It was shown that the annealing temperature has significant effect on the properties of ZnO thin films.

Keywords: ZnO, Thin films, Spray pyrolysis, Annealing, Structure, Optical properties, Dispersion parameters.

Influence of Annealing Temperature on the Structural, Optical Properties and Dispersion Parameters of ZnO Thin Films

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تأثير درجة حرارة التلدين على الخصائص التركيبية والبصرية ومعلمات التفريق لأغشية ZnO الرقيقة

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الخلاصة

حضرت اغشية اوكسيد الخارصين بطريقة التحلل الكيميائي الحراري على قواعد زجاجية وبدرجة حرارة 450°C وقد تم تلدين الاغشية المحضرة بدرجات حرارة 550°C , 600°C ولمدة ساعتين لدراسة تأثير التلدين على التركيب والخصائص البصرية للأغشية المحضرة. وصفت خصائص الاغشية باستخدام حيود الاشعة السينية وجهاز مطياف الاشعة فوق البنفسجية – المرئية – تحت الحمراء القريبة، وبينت دراسة حيود الاشعة السينية ان تركيب اغشية اوكسيد الخارصين هي من نوع متعدد التبلور وان الحجم البلوري يزداد بزيادة التلدين. درست الخصائص البصرية ومعلمات التفريق لأغشية ZnO ضمن الاطوال الموجية nm(400-900). وقد بينت الدراسة تأثيرالتلدين على خواص اغشية ZnO، طاقة الفجوة البصرية، معامل الانكسار، معامل الخمود، طاقة التذبذب المنفردة، طاقة التفريق، معاملات العزم للطيف المرئي، معدل قوة التذبذب، معدل التذبذب للأطوال الموجية، ثابت العزل للترددات العالية، نسبة تركيز الحاملات الى الكتلة الفعالة، ثابت العزل الأستاتيكي، ومعامل الانكسار الأستاتيكي للاغشية.

الكلمات المفتاحية: ZnO، الغشاء الرقيق، التحلل الكيميائي، التلدين، التركيب، الخصائص البصرية، معلمات التفريق

Introduction

Transparent conducting oxide (TCO) thin films are of great interest due to their variety of applications. Consequently, thin films with high electrical conductivity and optical transparency have been a subject of investigation since last century. ZnO belongs to the important II–VI semiconductor class of transparent conductor oxide materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum. high chemical and thermal stability at room temperature (27°C) with direct energy wide band gap (3.2-3.3 eV) and a large exciton binding energy of 60 meV[1]. Due to these unique characteristics it is expected ZnO's efficient utilization in different commercial applications such as integrated optics, antireflection coatings, solar cells

[2,3], laser diodes [4],light emitting diodes [4,5], chemical sensors [6,7], etc. ZnO is also a strong candidate for high temperature electronic devices that can reliably be operated in space and other harsh environments [8,9]. ZnO thin film has been prepared by various techniques such as spray pyrolysis[10], magnetron sputtering [11], electron beam evaporation [12], sol gel coating [13], chemical vapor deposition [14], etc. Among them chemical spray pyrolysis technique is one of the most widely used because it is an inexpensive and safe method for producing highly transparent and conductive zinc oxide film. In this work, the effect of annealing treatment on the structure, optical properties and dispersion parameters of ZnO thin films prepared by chemical spray pyrolysis technique has been investigated.

Experimental Details

Thin films of ZnO with thickness of 0.5 μm were deposited on to cleaned glass substrates at 450 ℃ using spray pyrolysis technique as described in our previous paper [15]. The prepared ZnO films were annealed in air ambient for 2h at different temperatures 550℃ and 600℃. The structure of ZnO films were analyzed by X-ray diffractometer (XRD) instrument type (Rigaku company – Miniflex 2) with Cu-Kα radiation with λ = 1.5406 Å. The optical transmittance and absorbance spectra were recorded in the wavelength range (400 – 900) nm, using double beam (SCHIMADZU UV/VIS-160 Å), all measurements were carried out at room temperature.

Results and discussion

1. Structural properties

X-ray diffraction patterns for the crystalline ZnO thin films are shown in fig.(1). Three diffraction peaks of the ZnO thin films can be indexed to (100), (002) and (101) diffraction planes. The films produced were polycrystalline, in nature and exhibit hexagonal wurtzite phase structure, the prepared ZnO thin film has (100) as a preferred orientation while the other orientations like (101) and (002) were also seen comparatively with lesser intensities. It could be stated that annealing causes an increase in intensity of planes. The values of lattice constants a and c for the as prepared and annealed films at various temperature were calculated using equation (1) [13,16] and the calculated values are given in table(1), it can be noticed that the calculated values were in good agreement with the standard values for ZnO wurtzite structure(ICDD No. 01-075- 0576).

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

Where d is the interplanar spacing and *h*, *k*, and *l* are the Miller indices.

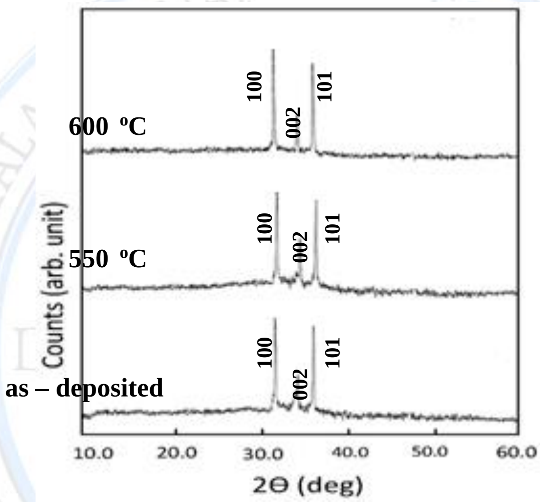


Fig (1) XRD patterns of ZnO films annealed at different temperatures.

The size of crystallites is calculated using the well-known Scherrer's formula as given in following equation [13,16]:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (2)$$

Where D is the size of crystallite, λ (=1.5405 Å) the wavelength of X-rays used, β is the full width at half maximum(rad) and θ is the Bragg diffraction angle of the XRD peak(degree). The crystallite size varies from (29.95 – 34) nm can be noticed from table (1), which is well supported in literature [13,17]. This implies that annealing enhances crystallinity of thin film.

Improvement in crystal structure could be attributed to the increase in crystallite size as the small crystallites join each other in the planes by increasing heat treatments.

Table (1) The crystallite size and the lattice parameters (*a*, *b*, and *c*) of the ZnO thin films.

parameters / samples	Calculated			(ICDD) No.01-075 -0576	
	D nm	a=d Å	c Å	a=d Å	*c* Å
As-deposited	29.95	3.25	5.21	3.243	5.195
Annealed at 550˚C	31.24	3.246	5.206		
Annealed at 600˚C	34	3.248	5.213		

2. Optical properties

Transmittance spectra observed of as-deposited and after annealing of ZnO thin films are presented in fig.(2),using the measured values of transmission (T) the absorption coefficient (α) can be written in the form [13,16].

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \qquad \textbf{(3)}$$

Where d is the film thickness.

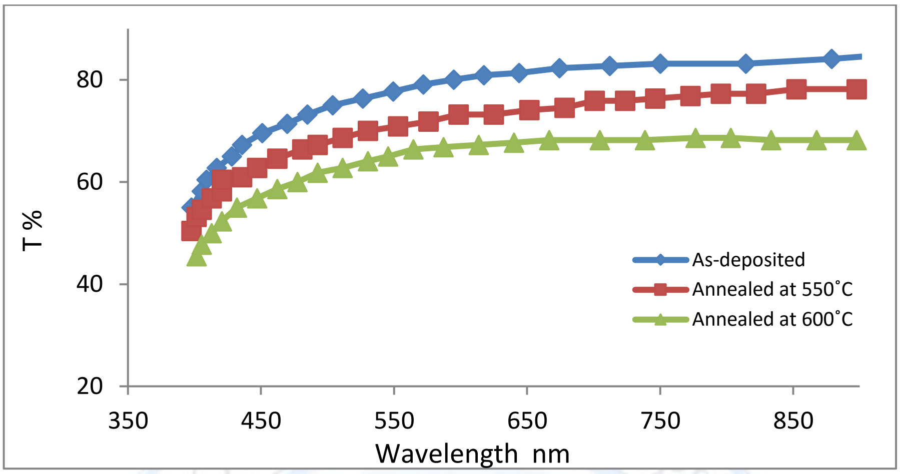


Fig (2) Transmitance versus wavelength for ZnO thin films at different annealing temperatures.

The absorption coefficient can be used to determine the optical band gap Eg following equation [13,16]:

$$\alpha h v = (h v - E_g)^r \qquad \textbf{(4)}$$

Where A is a constant, hν is the photon energy and r is a constant which depends on the type of the electronic transitions, where r is equal to 1/2, 3/2, 2 and 3 for allowed direct, forbidden direct, indirect allowed and indirect forbidden transitions, respectively. The optical band gap can be obtained by extrapolating the linear portion of the plots of $(\alpha h\upsilon)^r$ versus hυ to $(\alpha h\upsilon)^r = 0$. Using the value r = 1/2, the relation found to be straight line as shown in fig.(3) indicating a direct optical transition. The values of allowed direct band gaps calculated from the graphs are listed in the table (2). The results show a decrease in the band gap with increasing annealing temperature due to the crystallite growth and decreases in defect states near the bands.

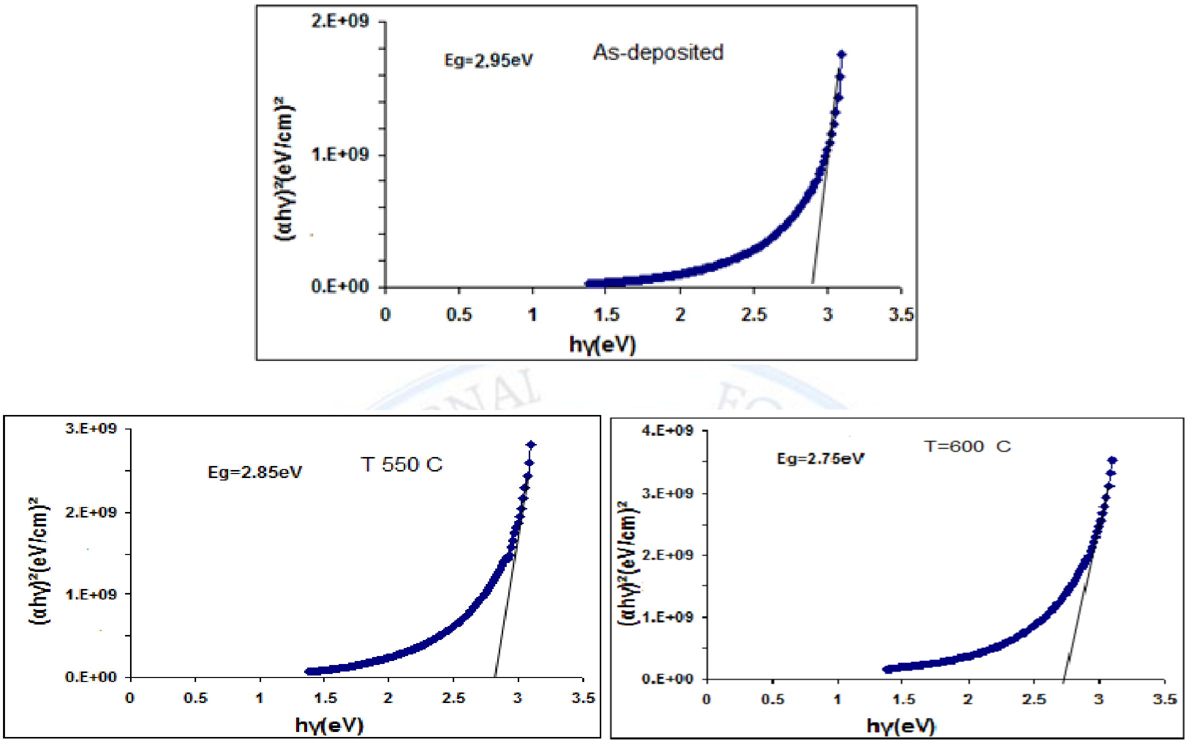


Fig (3) Allowed direct energy gap for ZnO thin films at different annealing temperatures.

3. Optical constants and dispersion parameters

The optical parameters, refractive index (n) and extinction coefficient (k), have been determined from the following relations [13,15,16]:

$$n=\left[\left(\frac{1+R}{1-R}\right)^{2}-\left(k^{2}+1\right)\right]^{\frac{1}{2}}+\frac{1+R}{1-R} \qquad \textbf{(5)}$$

$$k=\frac{\alpha\lambda}{4\pi} \qquad \textbf{(6)}$$

The refractive index and extinction coefficient were plotted in fig.(4) and fig.(5) respectively as a function of the wavelength. It can be noticed that both refractive index as well as extinction coefficient of the ZnO films were increased as a result of annealing. This can be attributed to the decrease in optical energy gap with the annealing temperature.

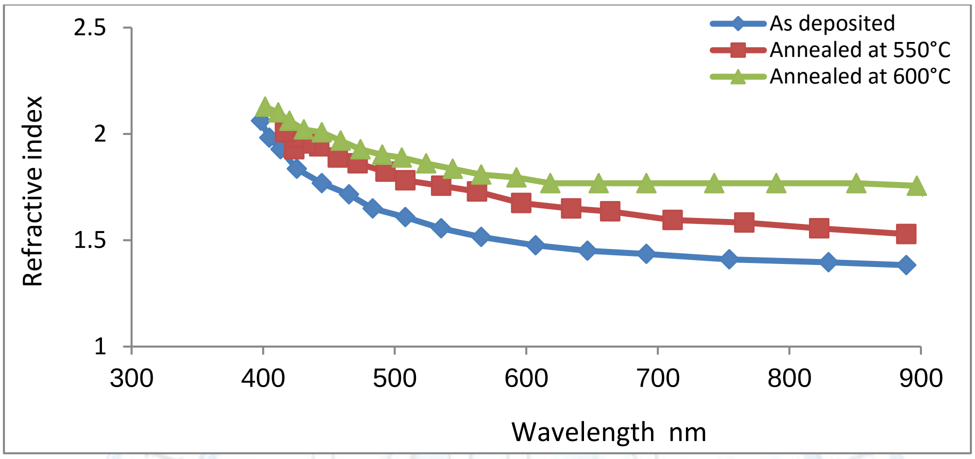
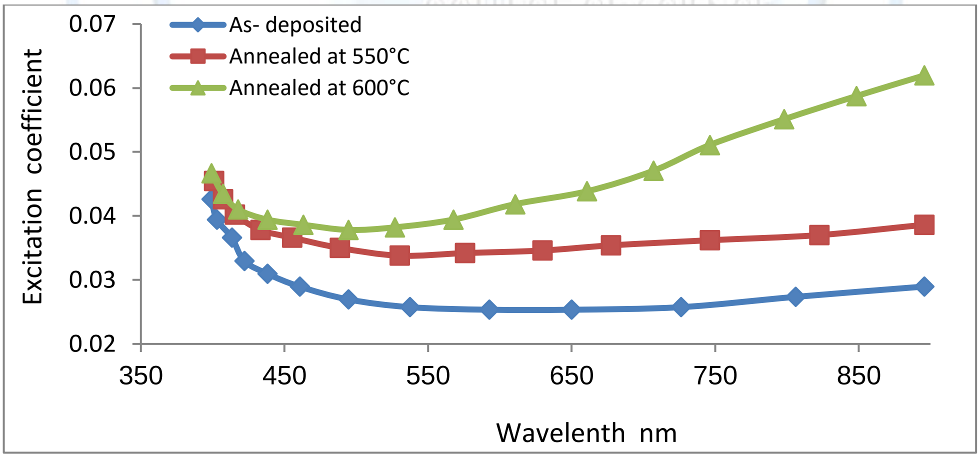


Fig (4) Refractive index versus wavelength for ZnO thin films at different annealing temperatures.



Fig(5) Extinction coefficient versus wavelength for ZnO thin films at different annealing temperatures.

It is well known that, dispersion behavior, plays an important role in the research for optical materials, because it is a significant factor in optical communication and devices design for spectral dispersion. According to the single effective-oscillator model proposed by Wemple–DiDomenico used to analyze experimental data of refractive index, which usually provides physically significant quantities such as the oscillator energy in the interband transition region. The optical data can be described to an excellent approximation by the relation [18]:

$$n^2 - 1 = \frac{E_d\, E_o}{E_o^2 - h\upsilon} \qquad (7)$$

Where E_o is the energy of the effective dispersion oscillator, E_d is the dispersion energy or single oscillator constant, which is a measure of the intensity of the interband optical transitions. The curves of $(n2\ -1)^{-1}$ versus$(h\nu)^2$ for the ZnO films are plotted in Fig. (6) and the data are fitted into straight lines, indicating the W–D dispersion model is applicable to the ZnO films in the present work. The values of E_0 and E_d can be determined from the slope ($1/E_0E_d$) and intercept (E_0/E_d) on the vertical axis. It is clear that E_0 decrease with increasing annealing temperature, and has the same behavior of energy gap. While the values of E_d increased. We found that E_o was related to the direct band gap by $E_o \approx (1.4\text{-}1.5)Eg$, this is good agreement with the result of other workers [19,20].

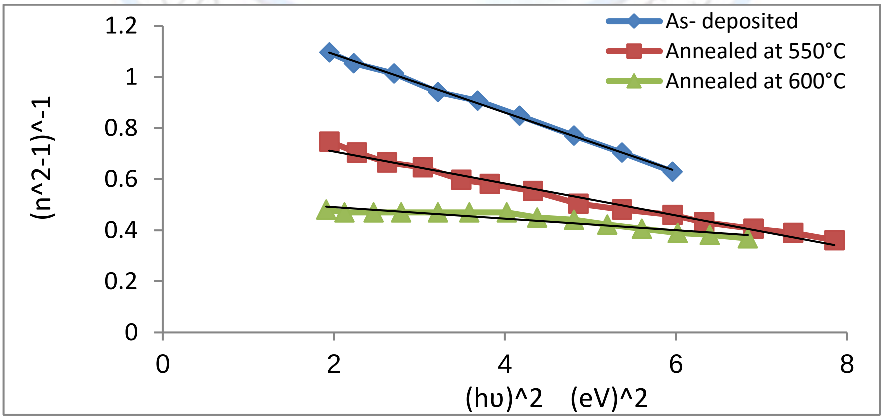


Fig (6) plot between (n^2-1)$^{-1}$ and (hυ)^2

The values of the static refractive index (n_s) can be calculated by extrapolating the Wemple-DiDomenico dispersion equation (7) to hυ → 0[21]

$$n^2_s = 1+Ed/Eo \qquad \textbf{(8)}$$

Then the values of static dielectric constant are equal to the square of the values of static refractive index and they listed in the table (2)

$$\varepsilon_s = n_s^2 \qquad \textbf{(9)}$$

According to the single-oscillator model, the moments of the optical spectrum M_{-1} and M_{-3} can be calculated from the following relations and their values are listed in table (2) for all samples[18]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad \textbf{(10)}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad \textbf{(11)}$$

The refractive index can also be analyzed using Sellmeir dispersion formula that is given by[18]:

$$n^2 - 1 = \frac{\lambda_o^2 \ S_o}{1-\left(\frac{\lambda_o}{\lambda}\right)^2} \qquad \textbf{(12)}$$

Where S_o is the oscillator strength, and λ_o is the average oscillator wavelength. Fig.(7) shows the relation between $(n^2 -1)^{-1}$ versus $1/\lambda^2$ for the ZnO films. Values of S_o and λ_o can be estimated from the slope ($1/S_o$) and the infinite wavelength intercept ($1/S_o\lambda_o^2$).The value of S_o and λ_o are given in table(2).

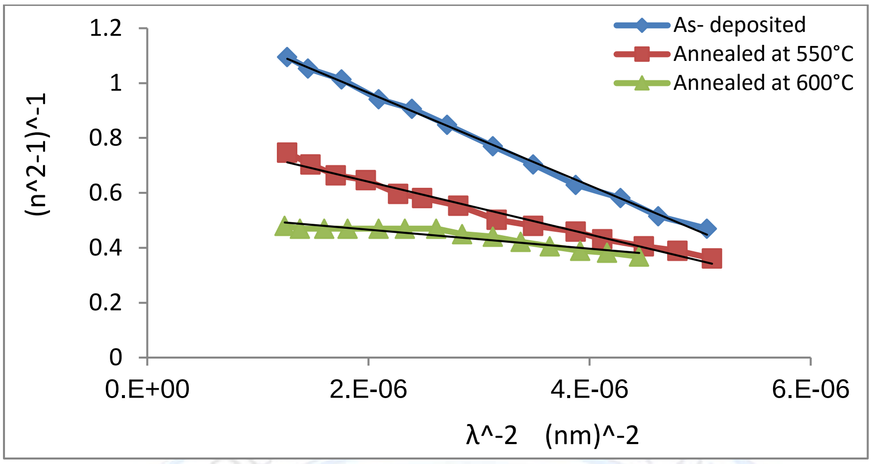


Fig (7)plot between (n^2-1)$^{-1}$ and λ^{-2}

Table (2) Optical parameters of ZnO thin films.

Parameters / Samples	Eg eV	E_o eV	E_d eV	M_{-1}	M_{-3} $(eV)^{-2}$	$S_o x10^{12}$ m^2	$\lambda_o x10^{-7}$ m	ε_s	n_s
As deposited	2.95	4.32	35.5	8.2	0.44	5.8	3.60	9.2	3.03
Annealed at 550˚C	2.85	4.25	36.8	8.65	0.48	10.4	3.39	9.65	3.1
Annealed at 600˚C	2.75	4.12	38.2	9.2	0.54	28.8	2.54	10.2	3.2

The complex dielectric function $\varepsilon = \varepsilon_r + i\varepsilon_i$ characterizes the optical properties of any solid material. The real part of the dielectric constant shows how much the material will slow down the speed of light, whereas the imaginary part shows how a dielectric material absorbs energy from an electric field due to dipole motion.

Using Drude's theory of dielectrics, the real dielectric constant (ε_r) can be written as[18,22]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_\infty - \left[\frac{e^2 N}{4\pi^2 c^2 \varepsilon_o m^*}\right]\lambda^2 \qquad \textbf{(13)}$$

Where ε_r is the real part, ε_∞ is the high frequency dielectric constant , N/m^* is the ratio of carrier concentration to the effective mass, e is the elementary charge, c is the velocity of light, ε_o is the permittivity of free space.

The variation of real part of dielectric constant with λ for different values of annealing temperatures is shown in fig.(8). It can be noticed that ε_r increases as the annealing temperature increases. The variation of real part of dielectric constant with λ^2 for different values of annealing temperature is shown in fig.(9). It can be noticed that the dependence of ε_r on λ^2 is linear at longer wavelengths. Extrapolating these linear parts to zero wavelength gives the value of ε_∞ and from the slopes of these linear parts the ratios N/m* were obtained and listed table(3). It is clear that N/m* decreases with increasing the annealing temperature which can be attributed to decrease of optical energy gap.

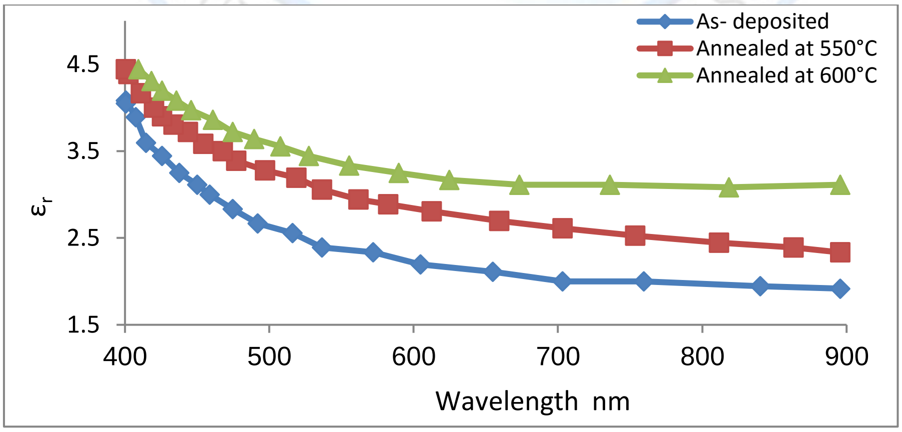


Fig (8) Real part of dielectric constant versus wavelength for ZnO thin films at different annealing temperatures.

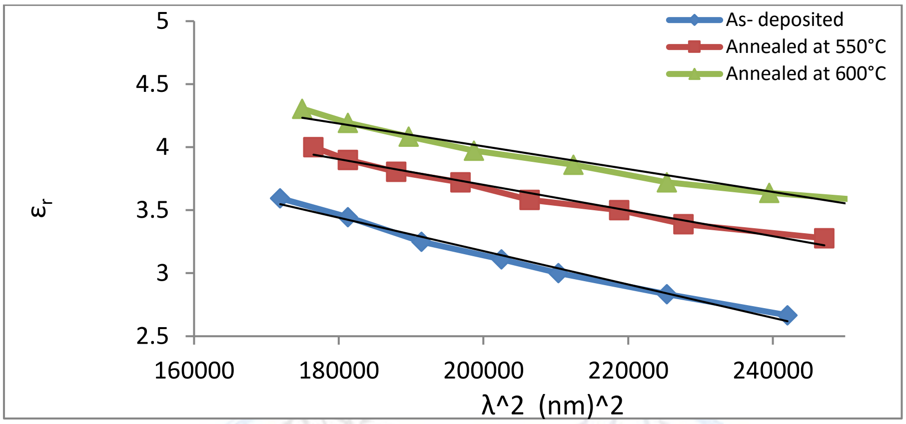


Fig (9) plot between ε_r and λ^2

Also we can calculate the values of static dielectric constant ε'_S and static refractive index n'_s from the following relations and they are listed in table (3) for all samples [17]:

$$\varepsilon'_S = 18.52 - 3.08E_g \quad \textbf{(14)}$$

$$n'_s = \sqrt{\varepsilon'_s} \quad \textbf{(15)}$$

Table(3) Dielectric parameters of ZnO thin films

Parameters / Samples	N/m^* $kg^{-1}.m^{-3}$ $x10^{40}$	ε_∞	n	ε'_s	n'_s
As deposited	1.427	5.83	2.41	9.43	3.07
Annealed at 550˚C	1.272	5.74	2.39	9.74	3.12
Annealed at 600˚C	1.104	5.82	2.41	10.05	3.17

It is clear from table (2) and table (3) that the values of static dielectric constant and the static refractive index obtained from the relations (8,9) and relations (14,15) are approximately equal.

Conclusions

The effects of annealing on the structural and the optical properties of ZnO thin films prepared by chemical spray pyrolysis technique on glass were investigated. The size of the crystallites was found to be in the range of (29.95 – 34) nm. The optical energy gap was found to decrease with increasing the annealing temperature. The single oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model. From structural and optical measurements, it was observed that ZnO thin films were mostly suitable for opto-electronic devices fabrication as the window layer in solar cells applications.

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