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EFFECT OF ANNEALING ON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS BY SOL GEL TECHNIQUE

ALI FATIMA ABDUL RAZAK*, SUGANTHI DEVADASON, C.SANJEEVIRAJA[a], V. SWAMINATHAN[b]
Department of Physics, Karunya University, Coimbatore-641114, India
[a]Department of Physics, Alagappa University, Karaikudi-630003, India
[b]School of Physical and Mathematical Sciences, Nanyang Technological University,Singapore-637371

Zinc oxide thin films were prepared by sol gel spin coating technique using zinc acetate as precursor solution on glass substrate**.** The prepared films were annealed at three different temperatures 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), UV-Vis-NIR spectroscopy and photoluminescence spectroscopy. The XRD pattern shows that ZnO films are polycrystalline in nature and crystallite size increases with the increase in annealing temperature. Optical transmittance measurements were taken using UV-Vis-NIR spectrophotometer and the calculated values of the direct band gap energy, E_g was between 2.6 -3.13 *eV*. Photoluminescence spectra of films exhibit a huge band edge emission at ~383 nm. It was shown that the annealing temperature has significant effect on the properties of ZnO thin films.

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1. Introduction

The preparation of zinc oxide (ZnO) thin films via sol-gel process has been the subject of intense research during the past decade. Zinc oxide has received much attention due to its direct wideband gap of 3.31 eV with a hexagonal wurzite structure. ZnO thin film is a promising material in the applications of UV light devices, light emitting diodes (LEDs) and laser systems [1], and is used in antireflection coatings, transparent electrodes in solar cells, piezoelectric devices, gas sensors [2], etc. Several techniques were used to prepare ZnO thin films namely: spray pyrolysis [3-5], thermal evaporation [6], RF/DC magnetron sputtering [7], chemical vapour deposition (CVD) methods [8], Molecular beam epitaxy [9], pulsed-laser deposition (PLD) [10], chemical bath deposition technique [11], hydrothermal method [12] and sol–gel [13,]. The present paper describes the effect of post-deposition annealing on structural and optical properties of ZnO films.

2. Experimental detail

ZnO films were prepared on glass substrates by sol gel spin coating technique. Before the deposition of the films, glass substrates were cleaned using soap solution, dilute acid, deionised water and acetone. The precursor of 0.5 M of $Zn(CH_3COO)_2 \cdot 2H_2O$ (zinc acetate dehydrate) is dissolved in ethanol and Diethanolamine (DEA) and the molar ratio of zinc acetate to DEA was taken in the ratio of 1:1. The prepared solution was stirred for 60 min at 50°C. The solution was

* Corresponding author: alif41070@gmail.com

left for ageing for 24 hours at room temperature after which the sol was used for spin coating for thin film preparation.

ZnO films were spin coated on glass substrate which was placed on the sample holder rotating at a speed of 3000 rpm for 30 s. After each spin coating the substrates were dried for 1 min in an open air furnace kept at 200°C to evaporate the solvent. The process was repeated 8 times to increase the thickness of the film. The samples were annealed at 350, 450 and 550°C in order to study the effect of annealing on their physical properties.

The structure and lattice parameters of ZnO films were analyzed by a X-ray diffractometer (XRD) with Cu (Kα) radiation with λ = 1.5405 Å (40 kV, 30 mA). The surface of the films was observed by scanning electron microscope (Model- JSM-6390).The optical transmittance and absorption were measured using Ocean Optics HR 2000 UV-Vis -NIR spectrophotometer in the wavelength range of 300-1000 nm. Room temperature photoluminescence (PL) was carried out by a Varian Cary Eclipse Fluorescence spectrophotometer.

3. Results and discussion

3.1 Structural properties of the crystalline ZnO thin film

The crystal structure and orientation of the ZnO thin film of the as prepared and annealed samples at 350, 450 and 550°C were investigated using X-ray diffraction (XRD) patterns. The X-ray diffraction patterns for the crystalline ZnO thin films are shown in Fig. 1 which indicates that the films are of polycrystalline in nature and exhibit single phase hexagonal wurtzite structure. It is clearly seen from the figure that the crystallanity of ZnO films increases with the increase in annealing temperature.

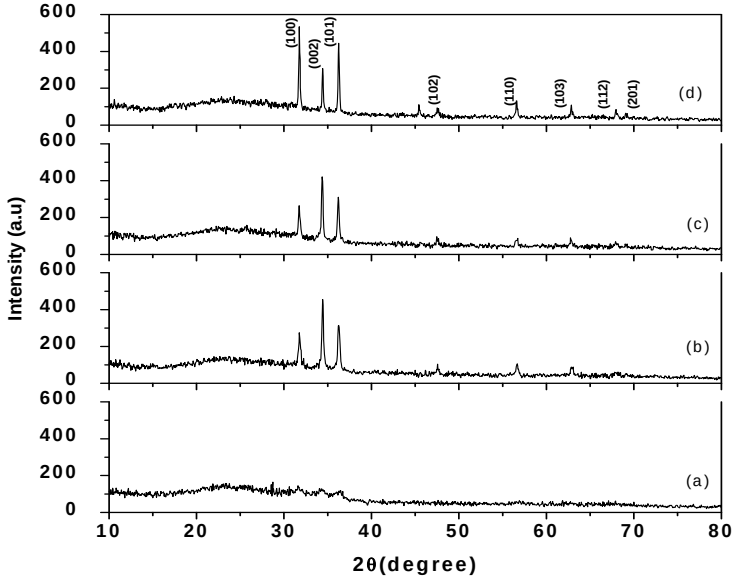


Fig.1: XRD patterns of ZnO thin films. (a) as prepared, annealed (b)at 350°C (c)at450°C (d)at550°C.

Three peaks appear on the XRD pattern for the as-deposited film. As seen in Fig.1(a), the as prepared ZnO thin film has (101) as the preferred orientation while the other orientations like (100) and (002) are also seen comparatively with lesser intensities. However, most of the ZnO thin films which grow with wurtzite structure have (002) preferential orientation. The annealing temperature plays an important role on the surface reactions and species mobility.

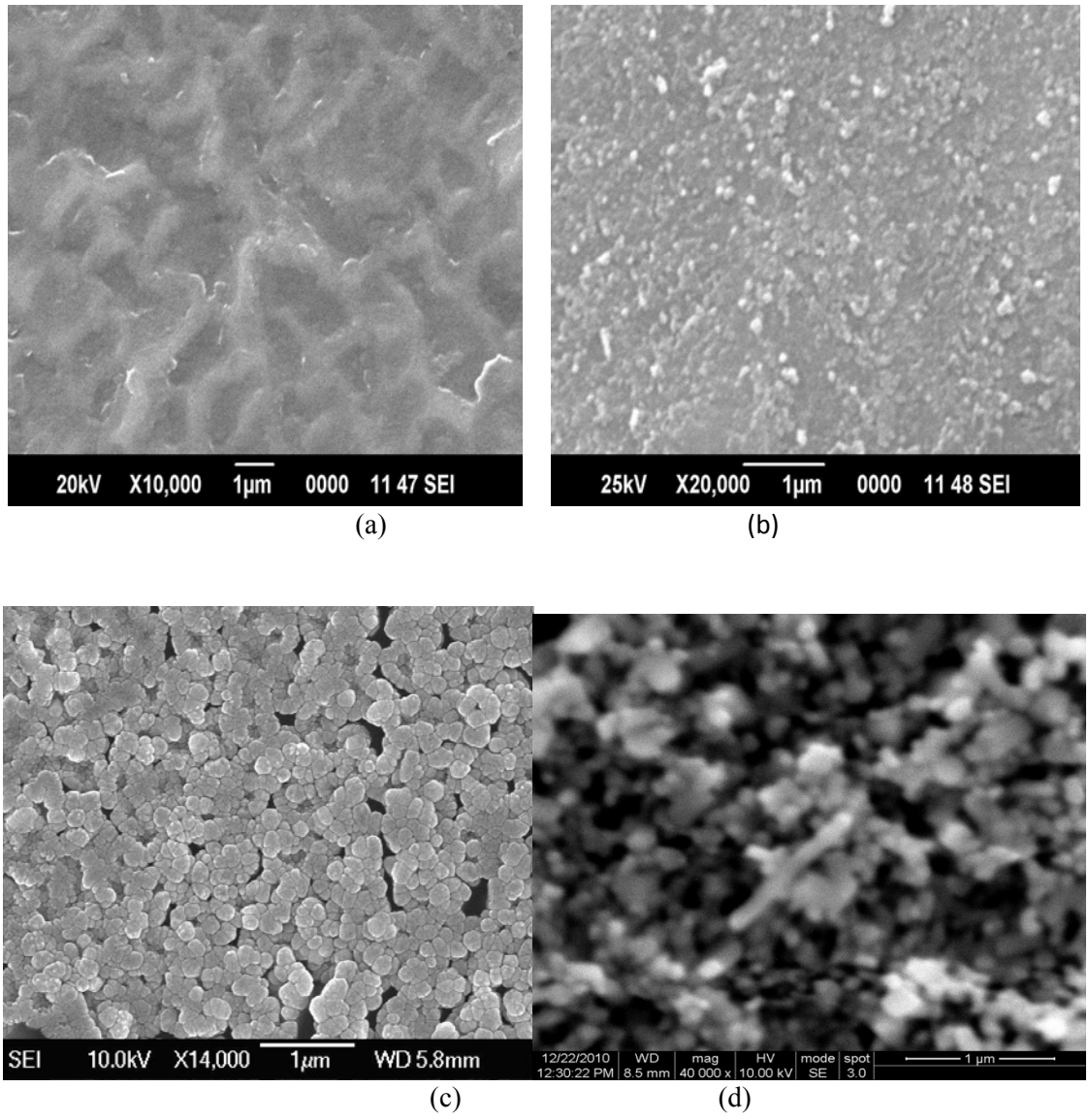
In Fig.1.b & c, it is seen that the ZnO films have (002) planes as the preferred orientation and other intense peaks correspond to the orientations of (100) and (101) planes. Again, some low intensity peaks corresponding to the orientations (102), (110) and (103) are also present. It is observed that in Fig.1.d which corresponds to the XRD pattern of the ZnO thin film annealed at 550°C, the prominent peak of (100) orientation plane and peaks of other orientations also appear. Thus it could be stated that annealing causes increase in intensity and reorientation of planes and a similar behavior is also reported by others [15]. An analytical method [16] was used to calculate the lattice constants *a* and *c* for the spin coated ZnO thin films. The values of lattice constants *a* and *c* for the as prepared and annealed films at various temperature are calculated using equation (1) and the calculated values are given in Table 1. Comparing with the lattice constants for hexagonal ZnO crystal given in JCPDS standard data file *a* = 3.2498 Å and *c*= 5.2066 Å [17], it is seen that the calculated values are in good agreement with the standard values for ZnO wurtzite structure.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l}{c^2}^2 \quad \text{----------(1)}$$

where 'd' is the interplanar spacing and *h*, *k*, and *l* are the Miller indices.
The relative percentage error for the observed and JCPDS standard d –value for all the films is calculated using the formula [18],

Table .1 Lattice constant values of ZnO thin films.

Lattice Parameter	Standard value (Å)	As prepared (Å)	At 350°C (Å)	At 450°C (Å)	At 550°C (Å)
a	3.2498	3.2536	3.2508	3.2543	3.2525
c	5.2066	5.2233	5.2089	5.2111	5.2097



(a) (b)

(c) (d)

Fig. 2. SEM micrographs of ZnO thin film of(a) as prepared, and calcined at (b)350°C, (C)450°C ,and (d) 550°C for 1h.

Relative percentage error,

$$d\,\% = \frac{|Z_H - Z|}{Z} \times 100 \text{----------(2)}$$

where Z_H is the observed d-value and Z is the standard d-value from JCPDS data file. The values of 2θ, d-values, and d% error calculated using equation (2) for all the films for various planes are presented in Table 2.

Table.2.Interplanar spacing of various planes for the ZnO thin films.

Samples	As prepared			Annealed at 350°C			Annealed at 450°C			Annealed at 550°C		
(hkl)	2θ	d(Å)	d%	2θ	d(Å)	d%	2θ	d(Å)	d%	2θ	d(Å)	d%
(100)	31.7575	2.81772	0.12	31.7588	2.81528	0.03	31.7259	2.81813	0.14	31.7416	2.81677	0.08
(002)	34.3086	2.61166	0.3	34.4060	2.60449	0.04	34.3510	2.60854	0.20	34.4008	2.60487	0.06
(101)	36.2506	2.47608	0.4	36.2406	2.47674	0.4	36.1936	2.47985	0.57	36.2376	2.47694	0.4

The size of crystallites is calculated using the well-known Scherrer's formula as given in equation (2) [19].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{----------(3)}$$

where *D* is the size of crystallite, λ (=1.5405 Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The grain size varies from 9 to 72 nm. The grain size values of all the films are given in Table 3. The grain size of the as-prepared ZnO thin film is very small compared to the annealed films. The grain size increases as the annealing temperature increases which is well supported in literature [20]. The variation of the grain size of ZnO crystallites with annealing temperature is given in Table.3.

Table.3. Variation of grain size of ZnO cryatllites with annealing temperature

Plane (hkl)	Grain size of ZnO crystallites (nm)			
	As prepared	Annealed at 350°C	Annealed at 450°C	Annealed at 550°C
(100)	14	28	41	66
(002)	10	39	47	72
(101)	9	33	46	71

Fig.3 shows the SEM micrographs of as prepared and ZnO nanocrystalline thin films calcined at 350, 450, 550ºC for 1h, respectively. It is observed that film annealed at 450º C shows good homogeneity of grains of hexagonal shape well dispersed on the surface of the film. The morphology of sample annealed at 450ºC is better compared with the other films.

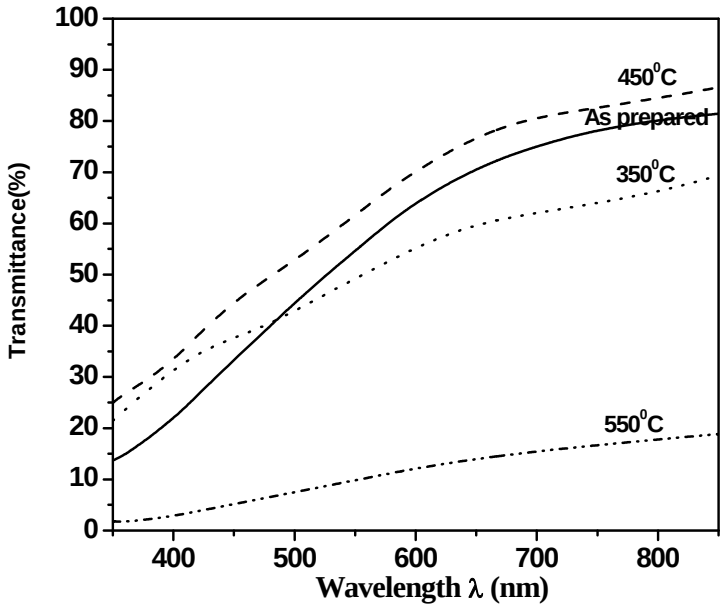


Fig.3. Optical transmittance spectra of ZnO thin films.

3.2 Optical properties

The transmittance spectra (Fig.3) of ZnO thin films, taken in the wavelength range of 350 to 850 nm is shown in Fig 3. The films are highly transparent in the visible range of the electromagnetic spectrum with an average transmittance value up to 80 %. The ZnO film annealed at 450°C shows a high transmittance whereas the film became hazy and the transmittance is dropped drastically low for the ZnO film annealed at 550°C [21].

The absorption coefficient (α) of ZnO films was determined from transmittance measurements. Since envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient (α) of the film in this region was calculated using the following expression

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{t} \text{----------(4)}$$

where T is the normalized transmittance and t is the film thickness. Thickness of the film was measured using digital micrometer(Mitutoyo ,Japan). The thicknesses of the films were 962,844,811 and 934nm for the as prepared and annealed at 350,450 and 550^{0}C respectively.

The calculated absorption coefficients values are used to determine the optical energy band gap of the prepared ZnO thin films. Fig. 4(a-d) shows the plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient and $h\nu$ is the energy of the incident photon. Assuming a direct transition between valence and conduction bands, the energy band gap (E_g) was determined by from the expression

$$\alpha h\nu = K\left(h\nu - E_g\right)^{1/2} \tag{3}$$

where K is a constant. E_g is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. The deduced optical energy band gap, E_g is slightly smaller than the bulk value of 3.3 eV [22] and is in good agreement with previously reported results of ZnO thin films.

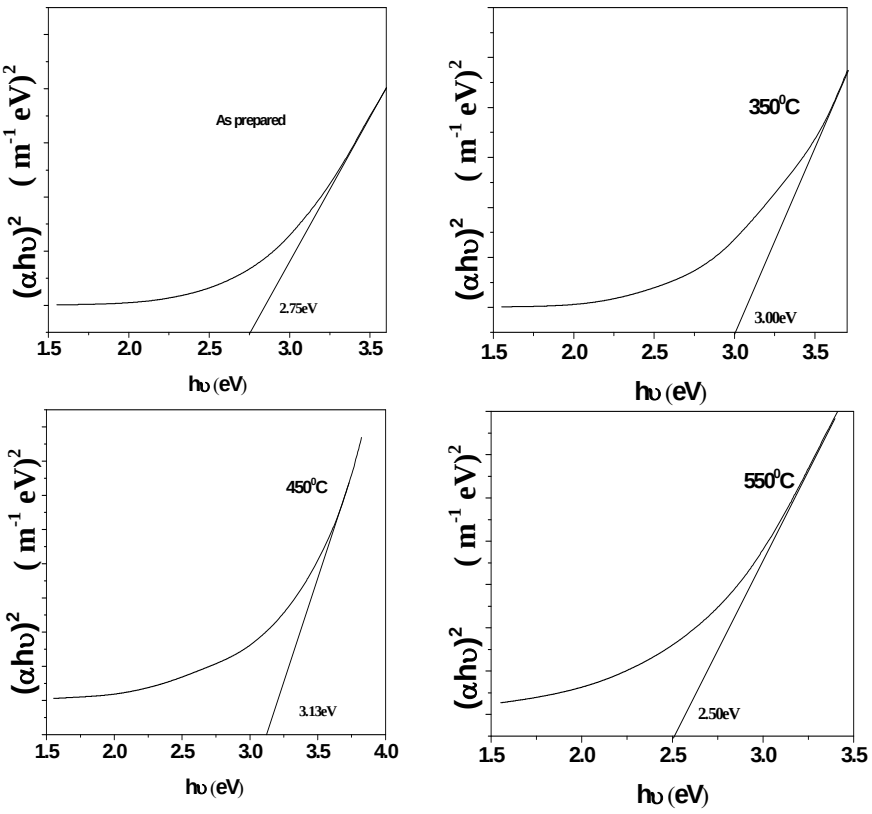


Fig.4. Plots of absorption against photon energy for ZnO thin films.

3.3 Photoluminescence studies of ZnO thin films

Photoluminescence measurements were used to evaluate the optical and crystalline quality of the ZnO layers deposited at different annealing temperatures. The excitation spectra shown in Fig.5 was obtained for the maximum emission wavelength indicated in Fig.6. All spectra show a peak around 383 nm (3.24 eV) resulting due to electron transfer from valence band (V_B) to conduction band (C_B) that could be the origin of any emission.

There are two emission peaks for the as prepared film namely the defect peak which is of lower intensity compared with the strong near band edge (NBE) emission peak. The defect peak of as prepared film has disappeared with the increase in annealing temperature, indicating the better crystalline quality of the samples deposited at higher temperatures. PL intensity increases as the annealing temperature increases till 450°C. PL intensity decreases for the ZnO thin film annealed at 550°C as the film became hazy which is true for the transmission spectra also.

Changes in relative intensities of the dominant peaks are observed. The intensity of the peak at 383 nm decreases with the annealing temperature. Strong near band edge (NBE) emission

dominates for all samples in the PL spectra taken at room temperature. Though the emission energy of the PL spectra does not change with increasing annealing temperature (Fig. 5), the PL intensity varies with annealing temperature.

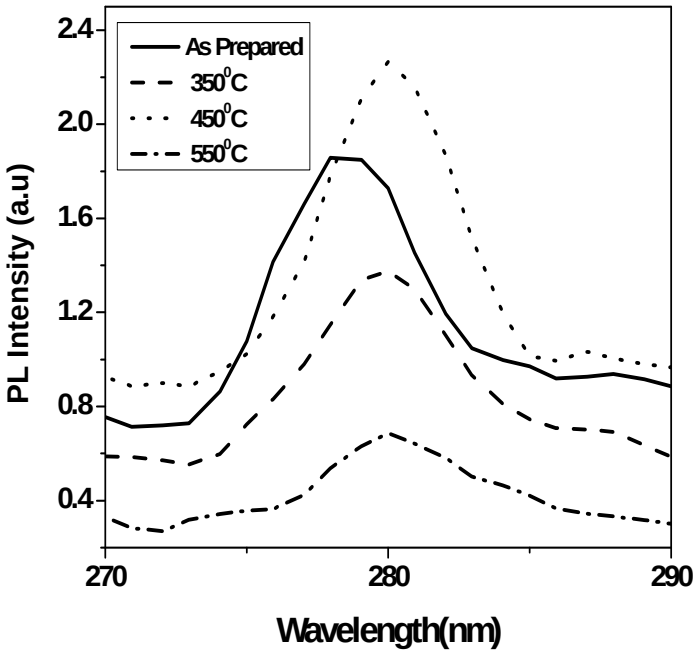


Fig.5.PL excitation spectra for ZnO thin films.

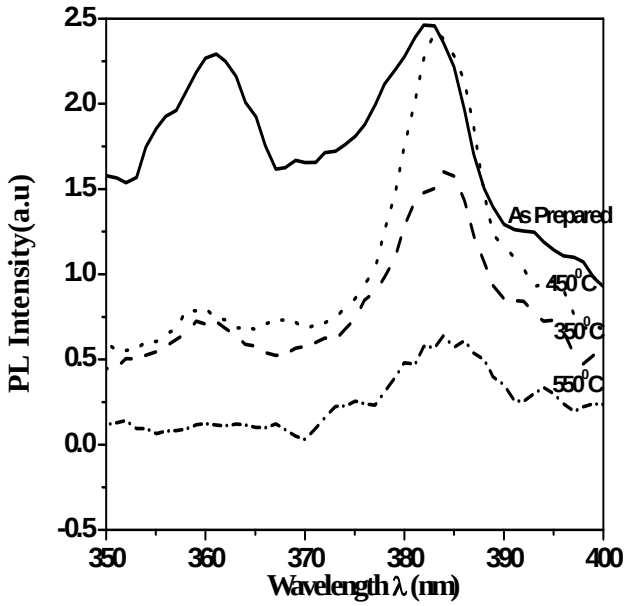


Fig.6. PL emission spectra for ZnO thin films.

4. Conclusions

Highly transparent ZnO thin films were successfully prepared by the spin coating technique on glass substrate. The impact of annealing on structural, optical and photoluminescence properties was systematically studied. XRD studies indicate that the crystallanity is enhanced on annealing and the average crystalline grain size also increases with annealing. The magnitude of the optical band gap determined from optical result is in agreement with the reported works . The photoluminescence spectra of ZnO thin films exhibit a strong UV excitonic peak.

Consequently, it was seen that the effect of annealing makes a significant change on the structural and optical properties of ZnO spin coated thin films. A high optical quality of the deposited ZnO films would potentially allow their application for UV light emission. From the above results, it may be concluded that the ZnO thin films could be annealed at 450^0C is of good quality and it could be used for application purposes.

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