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Structural and Optical Properties of ZnO Thin Films Prepared by Sol-Gel Method

Anup Kumar Das[1]
[1]*Department of Physics, P. K. College, Contai, India.*

Abstract: ***The structural and optical properties of ZnO thin films prepared by sol-gel spin coating process are investigated. Zinc acetate dehydrate is used as the precursor material. The thin films of ZnO are deposited onto glass substrate in room temperature and as-grown film is sintered at 100 ^{o}C for 5 minutes and then post annealed in air at 600^{o}C for 1 hour. The optical properties like absorbance; extinction coefficient and electronic energy band gap are measured by double beam spectrophotometer. X-ray diffraction (XRD) studies on the films show the polycrystalline nature with hexagonal wurtzite structure. The crystallite sizes of the films are estimated using the Debye-Scherer's formula and have shown 47 nm for 002 plane. The method is used to obtain the lattice parameters a, c for wurtzite cell types as well as cell volume and the ratio c/a of the sample. The calculated value of a, c and c/a of ZnO are respectively, 3.262 Å, 5.222Å and 1.60.The optical band gap energy of the films is found to be direct allowed transition at~3.21eV.Theaverage crystallite size of the ZnO nanoparticles is observed to be greater than 33 nm in high resolution transmission electron microscope (HR-TEM) and clearly indicate that ZnO nanoparticles are crystalline with hexagonal wurtzite structure.***

Keywords: Thin films, ZnO, Spin coating, Sol-gel, XRD, HR-TEM, Band gap.

I. INTRDUCTION

Zinc Oxide film is one of II-IV inorganic compound semiconductor of inexpensive white powder that is insoluble in water and having direct band gap of 3.37eV which crystallizes in hexagonal wurtzite structure(c=5.215Å and a=3.253 **Å**).The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type. This semiconductor has several favourable properties, including good transparency, high electron mobility, wideband gap and strong room temperature luminescence those are valuable in emerging applications. ZnO thin films have been widely used for many devices application such as optoelectronic devices like window layer in polycrystalline solar cells [1]-[3],light emitting diodes [4], nanolasers [5] and have been recognized as spintronic material [6].Also various biological, chemical and gas sensors [7] are based on ZnO thin film. Thin films of ZnO can be prepared by various techniques; among them are sputtering [8]-[9],metal-organic chemical vapour deposition (MOCVD) [10],pulse laser deposition (PLD) [11],spray pyrolysis [12] and sol-gel method [13]-[17] have studied structural and optical properties of nano crystalline ZnO thin films derived from clear emulation of nano-crystallite ZnO nano crystals. Compare to the other processes, the sol-gel process has the advantages of control ability of chemical compositions due to its simplicity in processing and cost effective. Properties of ZnO thin films show dependence on the technique used apart from doping to increase the functionality of ZnO thin film, the effect of preparation conditions on the properties have to be considered for its effective technological applications. Relatively few works have been done in this direction of ZnO film prepared by sol-gel process. In the present work sol-gel spin coating process is employed for film preparation. Zinc acetate dehydrate was used as the precursor material. The effects of annealing the ZnO thin film on its structural and optical properties at 600 ^{o} Care studied. XRD and HR-TEM were used for structural properties and double beam spectrophotometer was used for optical properties.

II. EXPERIMENTAL

ZnO thin films were prepared on glass substrate (5X2.5cm^2) by sol-gel spin coating technique. The glass substrates were cleaned with soap solution followed by ultra Zsonication in water for 1 hour. Then the substrates were cleaned successively in distilled water and in acetone. In order to deposit, 0.5 M high purity zinc acetate dihydrate (ZAD) [$Zn(CH_3COO)_2.2H_2O$] solution was prepared in ethanol [C_2H_5OH]. Mono-ethanolamine (MEA) [C_2H_7NO] and ethanol were used as stabilizer and solvent, respectively. Appropriate quantity of ZAD was mixed in 25 ml of ethanol and was stirred by magnetic stirrer at 60 ^{o}C about 15 minutes until the solid ZAD was completely dissolved. Then the MEA was dropped to the whitish solution until a clear sol was appeared and the as-prepared solution was stirred at same temperature for 1 hour until a homogeneous sol was obtained. Then the freshly prepared sol was dropped onto a pre dried clean glass substrate using spin coating technique in room temperature with a rate of 3000 rpm in 30 sec. The as-coated film was sintered at 100^{o}C for 5 minutes immediately to evaporate the solvent. The process was repeated to

obtain the workable thickness of the film up to seven coating layers. Then, the film is annealed in air at 600 ^{o}C for 1 hour in a tube furnace to reach the crystal phase. The flow chart is shown in Fig. 1.

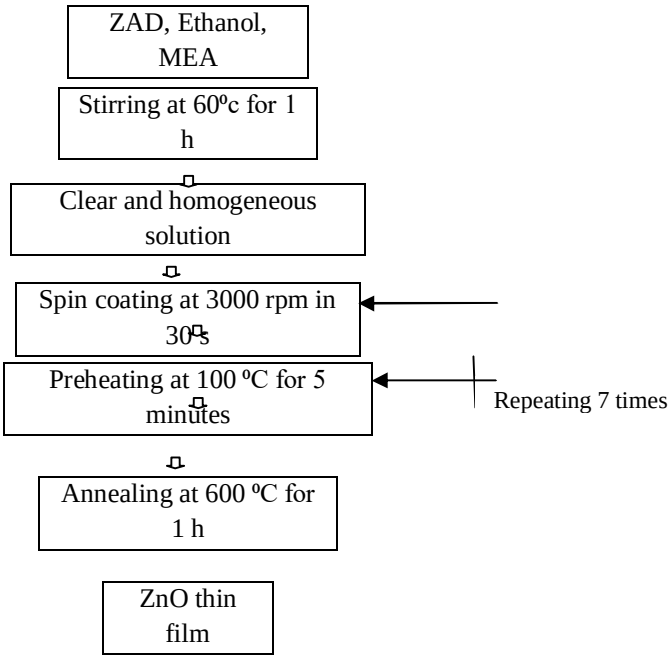


Fig1: The flow chart of methodology for preparation of ZnO thin film.

The XRD [X'Pert High score plus, PANalytical] pattern was obtained with CuK_{α} radiation (λ=1.5406Å) and the HR-TEM [JEM-2100F, Japan] images of ZnO nanoparticles cluster were obtained from powder scratched from as-grown thin film sample that was dropped (1-2 drops) on carbon grid after ultrasonication in acetone. The UV measurements were carried out at room temperature using UV-VIS double beam spectrophotometer (Systronics 2202) in the wavelength range of 210nm – 500nm.

III.RESULTS AND DISCUSSION

A. Structural

Structural characterization of ZnO nanoparticles has been carried out by XRD and HR-TEM. The XRD spectrum for scanned angle (2θ) varying from 10 ^{o} to 90 ^{o}of ZnO thin films grown at 600 ^{o}C is shown in Fig. 2. From this figure as-grown sample gives strong diffraction peaks at 2θ = 31.65^{o}, 34.31 ^{o}and 36.06 ^{o} which corresponds to (100), (002) and (101) peaks and showing growth of ZnO crystallites of hexagonal wurtzite structure with higher degree of preference along the c-axis perpendicular to the substrate. The presence of prominent peaks shows that the film is polycrystalline in nature. The lattice constants a and c of the nanocrystalline ZnO film can be calculated using the following relations.

From (100) plane $$a = \sqrt{\frac{1}{3}}\frac{\lambda}{\sin\theta} \quad (1)$$

and from (002) plane $$c = \frac{\lambda}{\sin\theta} \quad (2)$$

Where, λ is the wavelength of X-ray and θ is the Bragg angle. The grain size (D) of ZnO nano crystals annealed at 600 ^{o}C was calculated using the Debye-Scherrer's formula,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Where, K is constant and taken to be 0.94 [18] and β is the full width at half maximum (FWHM).

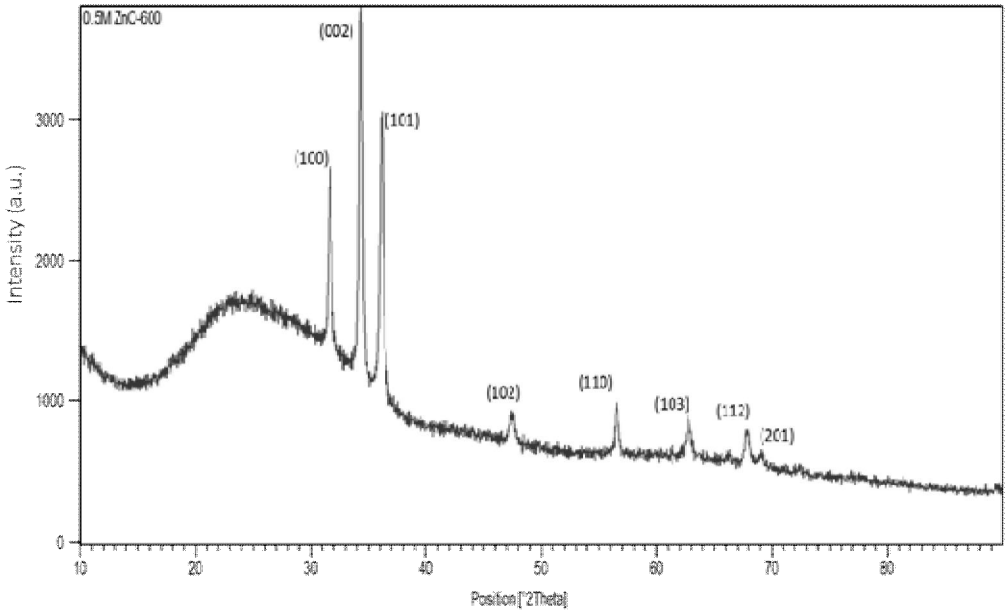


Fig2: XRD Spectrum of ZnO thin film annealed at 600ºC.

Calculation of the lattice parameters (a and c) for hexagonal structure has also been done using the relation (4).

$$sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\left(\frac{h^2+k^2+hk}{a^2}\right) + \frac{l^2}{c^2}\right] \quad (4)$$

The dislocation density (δ) defined as the length of dislocation lines per unit volume is estimated using the relation

$$\delta = \frac{1}{D^2} \quad (5)$$

and the strain (€)of the thin films is estimated using the relation

$$€ = \frac{\beta Cos\ \theta}{4} \quad (6)$$

Table 1 shows the structural parameters as obtained from XRD and calculated lattice parameters in comparison with standard value of nanocrystalline ZnO are shown in Table 2.

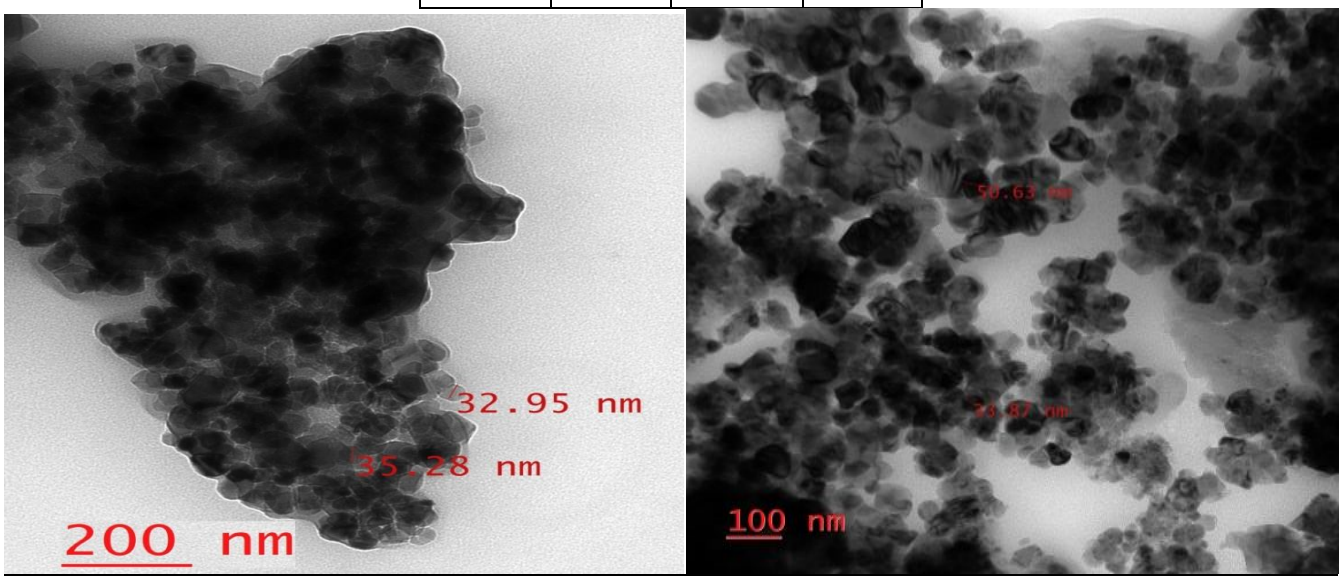
TABLE I
Structural parameters of ZnO thin films:

Planes	Inter-Planer Spacing d (Å)	FWHMβ ($\times10^{-3}$) (rad.)	Grain Size D (nm)	Dislocation Density δ ($\times10^{14}$) (lines/m^2)	Strain € ($\times10^{-4}$)
(100)	2.827	1.458	103.21	0.938	3.50
(002)	2.613	3.209	47.22	4.486	7.67
(101)	2.491	2.918	52.20	3.672	6.94

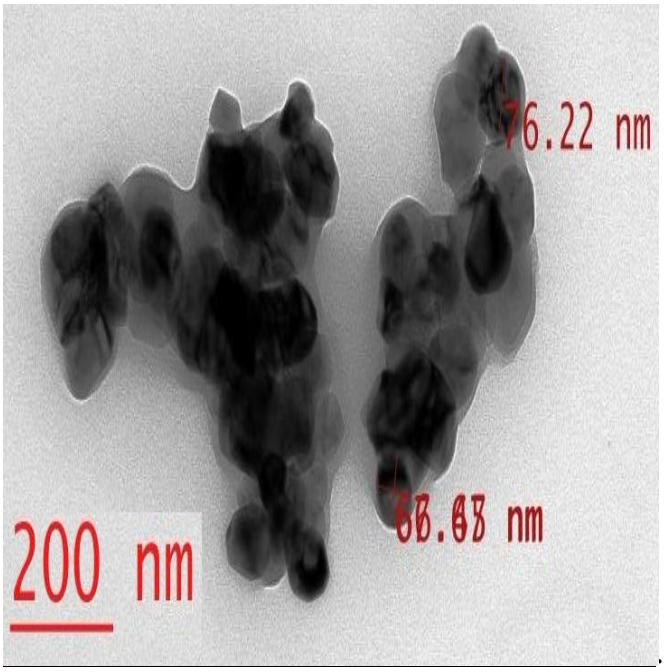
TABLE II
Lattice parameters of the ZnO thin film:

a in Å		c in Å	
Calculated	Standard	Calculated	Standard

3.262	3.253	5.222	5.215



(a) (b)



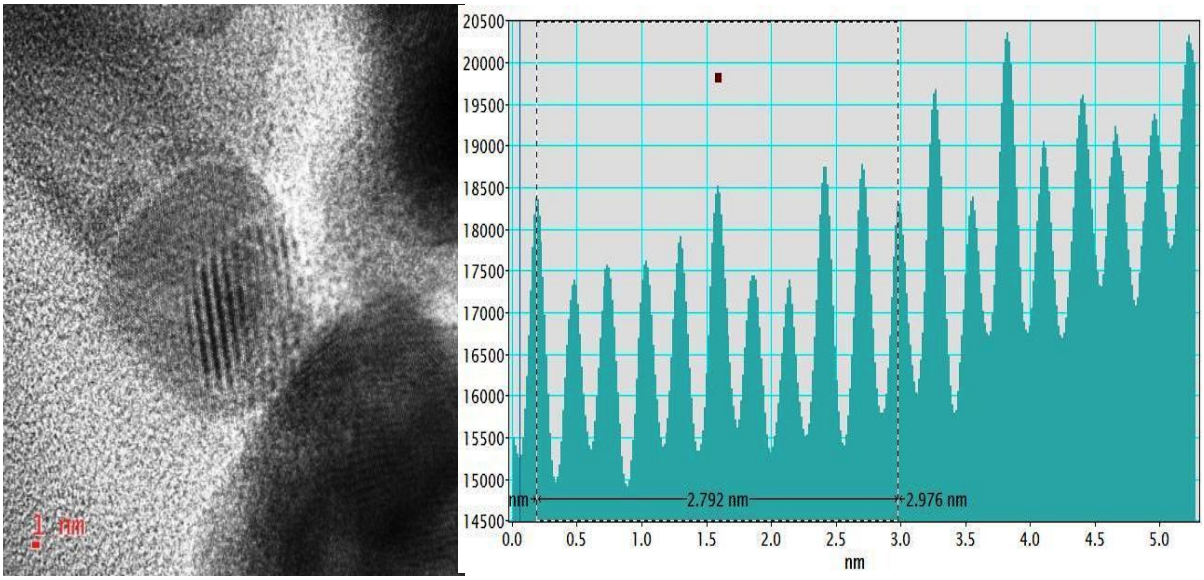
(c)

Fig. 3: The cluster of low magnification TEM images of ZnO nanoparticles: (a) and (c) show 200 nm scale, (b) shows 100 nm scale

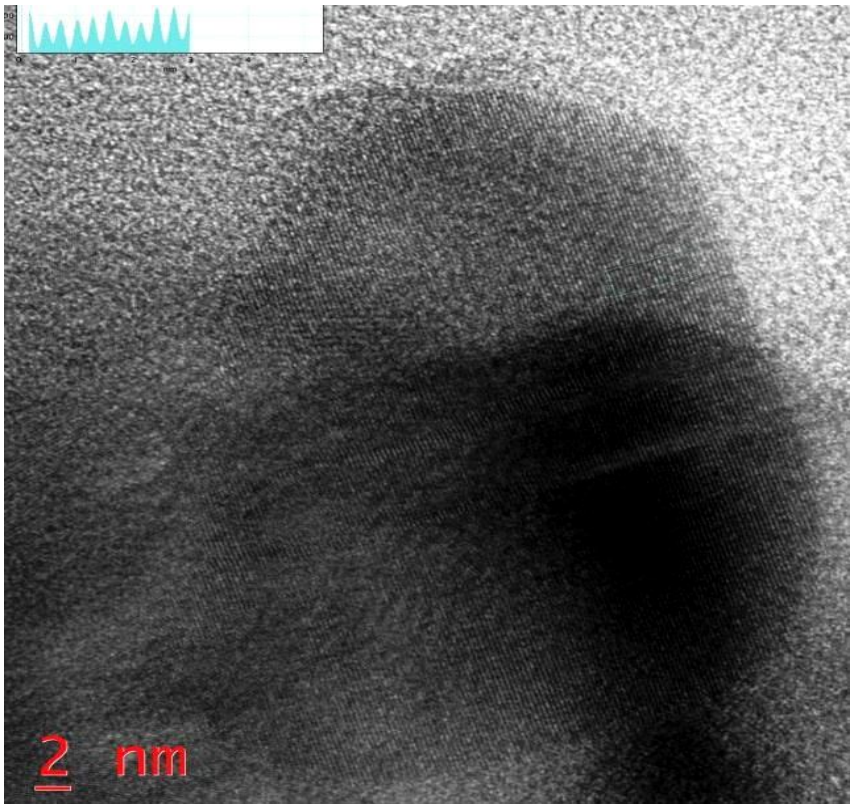
B. HR-TEM analysis

Structural characterization through TEM is a direct way that provides demonstration to estimate grain size, size distribution and morphology exactly. Figures 3(a), 3(b) and 3(c) show the low magnification TEM micrograph of cluster of ZnO nanoparticles annealed at temperature of 600 ^{o}C. These micrographs show broad particle size distribution having the diameter of particles in nanometric regime ranging from 32.95 nm to 76.22 nm. The average particle size is found to be greater than 33 nm. High resolution TEM images of the lattice planes of ZnO sample are shown in Fig. 4(a) and 4(b). The corresponding equal spacing peaks arising

from those parallel planes is shown in Fig. 4(c) which suggests the (100) plane with inter planer spacing d= 2.792 Å and that was confirmed by the XRD data in Table I.



(a) (c)



(b)

Fig. 4: An atomic level lattice image of a magnified ZnO nanoparticles and histogram of d-spacing: (a) 1 nm regime (b) 2nm regime and (c) corresponding peaks showing (100) plane of inter planer spacing d= 2.792 Å.

Crystallinity of each nanoparticles of ZnO sample is confirmed from selected area electron diffraction (SAED) pattern as shown in Fig. 5. In this pattern bright spots make concentric rings that reveal the ZnO nanoparticles are polycrystalline nature.

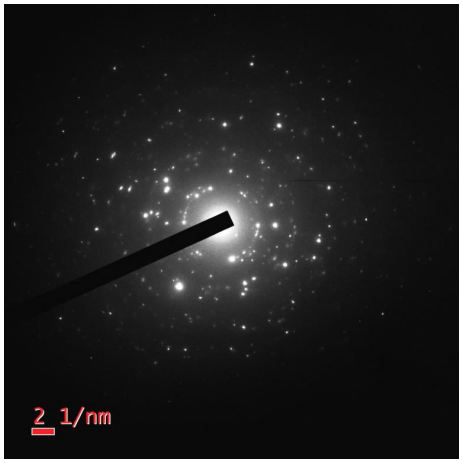


Fig. 5: SAED Pattern showing the polycrystalline ZnO nanoparticles.

C. Optical Properties

Fig. 6 shows the optical absorbance spectrum of nanocrystalline ZnO film after annealing at 600 ^{o}C. It can be seen in this graph that the excitonic absorption peaks at 356.3 nm and 378 nm lie much below the absorption edge located at 386.91nm. The absorption peak is also very sharp which indicates the mono-dispersive nature of the nanoparticles distribution. The absorption coefficient (α) at the corresponding wavelength λ is calculated using Beer-Lambert's relation –

$$\alpha = 2.303 \log_{10}(\tfrac{1}{T})/d \qquad (7)$$

Where d is the thickness of the film and T is the transmittance. The absorbance (A) is the$\log_{10}$of inversion of T and related by

$$A = \log_{10}(\tfrac{1}{T}) \qquad (8)$$

Thus the absorption coefficient α is measured by the relation

$$\alpha = 2.303\frac{A}{d} \qquad (9)$$

and also A is defined by log (I_0/I), where I_0 and I be the intensities of the incident and transmitted beam, respectively. The α is also related with extinction coefficient (k) by the formula

$$\alpha = \frac{4\pi k}{\lambda} \qquad (10)$$

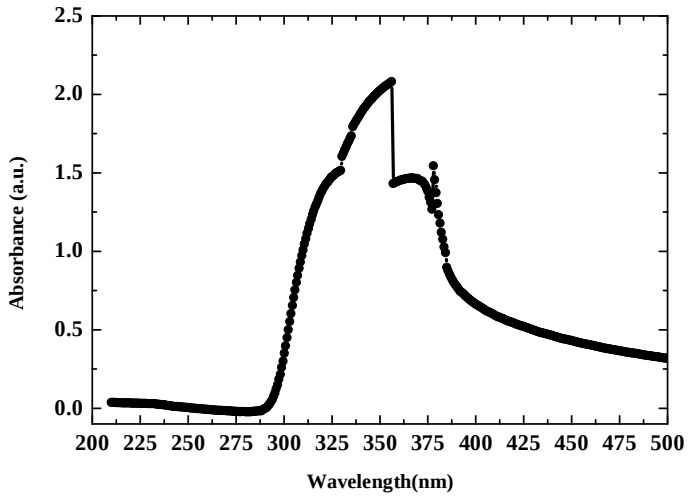


Fig. 6:Variation of Absorbance (A) with wavelength (λ).

The optical band energy gap (E_g) and α related by the Tauc equation

$$\alpha h\gamma = B\left(h\gamma - E_g\right)^n \quad (11)$$

Where B is a constant and h is the Planck constant. $h\gamma$ be the incident photon energy and n is a number which characterized the nature of electronic transition between valence band and conduction band.

Now, the E_g can be estimated by assuming a direct allowed transition for n=1/2 between the valence band and conduction band using the relation

$$\left(\alpha h\gamma\right)^2 = C\left(h\gamma - E_g\right) \quad (12)$$

Where C = $B^2$is another constant. The variation of $\left(\alpha h\gamma\right)^2$ with respect to $h\gamma$ as obtained using equation (12) is shown in figure 7 for ZnO films annealed at 600ºC.The corresponding$E_g$of the sample was evaluated from the intercept of the extrapolated linear portion of the curve with the $h\gamma$ axis and found to be 3.21 eV.

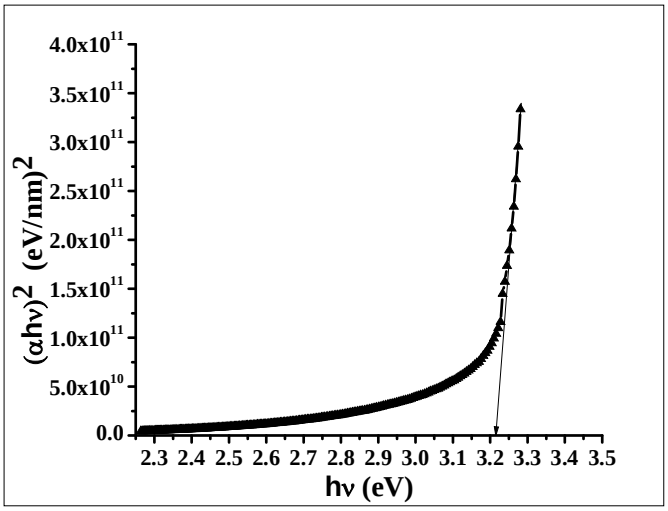


Fig. 7:Plot of $(\alpha h\nu)^2$ vs. Photon energy (hν) of ZnO thin film at 600 ºC.

IV. CONCLUSIONS

The structural and optical characterisation of nanocrystalline ZnO thin films grown by sol-gel spin coating using X-ray diffraction, HRTEM and UV-VIS double beam spectrophotometer have been investigated. From the XRD spectrum, the characteristic planes and lattice constants were verified those agreed with that of bulk ZnO. The nanocrystalline size and lattice planes with inter planer spacings are also obtained by the HRTEM analysis. The optical band gap of 3.21 eV is obtained at band edge wavelength of 386.91 nm in absorbance spectrum.

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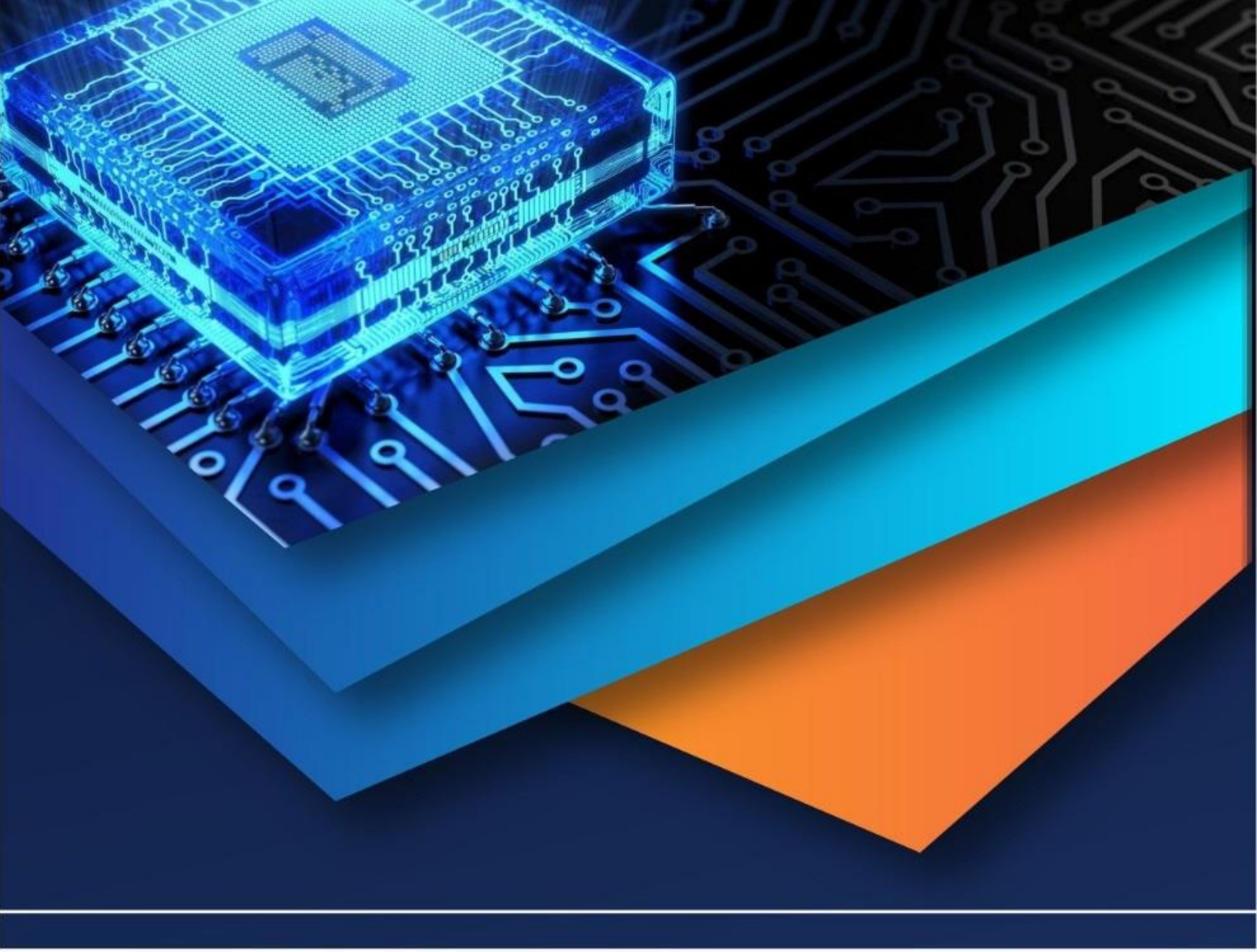

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