

WET CHEMICAL GROWTH OF ONE DIMENSIONAL ZnO FILM

**P. L. Meena^{1,✉}, Yogesh Kumar¹, Pooja Bhardwaj², Mahaveer Genwa³,
Dinesh Kumar Arya⁴, Asha Verma⁵ and Surinder P. Singh⁶**

¹Department of Physics, Deen Dayal Upadhyaya College (University of Delhi), Sector-3, Dwarka, New Delhi, India, 110078.

²Department of Applied Physics, Amity School of Applied Sciences Amity University, Manesar, Gurugram, Haryana, India, 122413.

³Department of Chemistry, Deen Dayal Upadhyaya College (University of Delhi), Sector-3, Dwarka, New Delhi, India, 110078.

⁴Department of Chemistry, Acharya Narendra Dev College (University of Delhi), Govindpuri, Kalka ji, New Delhi, India, 110019.

⁵Department of Chemistry, University of Rajasthan, Jaipur, India, 302004.

⁶CSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi, India, 110012.

✉Corresponding Author: plmeena@gmail.com, plmeena@ddu.ac.in

ABSTRACT

The present work focuses on the growth of ZnO films vertically on indium tin oxide substrate using a wet chemical method. The morphological and structural study of the prepared films confirmed the formation of one-dimensional growth with a polycrystalline single-phase hexagonal wurtzite structure. The computed texture coefficient indicates the c-axis growth of the film. The optical spectra study exhibited a strong and sharp characteristics absorption band. The numerical derivative method and the Tauc plot method for the different transition values have been used to compare energy bandgap calculations.

Keywords: ZnO Film, SEM, XRD, Rietveld Refinement, UV-Visible Spectroscopy, Tauc Plot Method

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INTRODUCTION

In the recent era, metal oxide nanostructures showcase many applications in every field that exists, mainly biosensors, solar cells, photocatalysis, bio-imaging, UV-light emitters, piezoelectric transducers, chemical sensors.¹ There are many metal oxide nanostructures existing in nature, out of which ZnO is the most promising nanostructures (nanomaterial) due to its wide bandgap, thermal stability, high electron mobility, conductance variability, etc.² According to the literature, these ZnO nanostructures can be subdivided into various categories such as nanodots, nanoflowers, nanowires, nanopores, nanotubes, nanorings, nanorods, etc.¹ Among these, nanorods and nanowires are being extensively used for practical applications, such as nanowires are used for field-effect transistor (FET) devices, nanogenerators, and nanorods are used for heterojunction devices such as varistors, four-probe electrode systems, sensing applications, etc.³⁻⁶ In addition to these applications, ZnO nanorods in the form of films are being used in FET, dye-sensitized solar cells (DSSCs), light emitters, light detectors, biosensors, gas sensors, etc.⁷⁻⁸ Various methods are reported in the literature for synthesizing these nanorods, such as electrochemical deposition technique, hydrothermal method, sputter chemical deposition, etc.⁹⁻¹⁰ However, certain criteria need to be met to use these methods, mainly high reactant concentration, and high reaction temperature. On similar grounds, these processes are complex and expensive. Therefore, the more accessible approach to synthesize ZnO nanorods is by using the wet chemical method due to its easy processing and cost effectiveness.¹¹⁻¹²

As per the literature, ZnO nanorods possess a hexagonal wurtzite structure with c-axis texturing along the (002) plane. The c-axis texturing is usually confirmed from the texture coefficient (TC) value. If the value of $TC(hkl) = 1.0$, the sample has random crystallites orientation, and for $0 < TC(hkl) < 1$ indicates the deficiency of grains orientation in that direction, for $TC(hkl) > 1.0$, then the sample has the preferred direction growth along that particular plane. The texture coefficient $TC(hkl)$ represents the distribution of crystallites orientation of polycrystalline materials. As the value of $TC(hkl)$ enhances, the favored growth of small crystals increases in the perpendicular direction to (hkl) plane.¹³

The main characteristic of a nanomaterial for various applications is wide bandgap energy. Mostly used method to compute the bandgap energy value from UV-Vis. spectrum is to find the dA/dE from the given UV data and subsequently locate the point of maxima at lower energy sides.¹⁴ There is one more method "Tauc plot", can be used to find the bandgap energy.¹⁵ Tauc equation is used to fit the UV-Visible data where the type of transition (n) in a given sample can be determined. For $n = 0.5$ (direct allowed transition), $n = 1.5$ (direct forbidden transition), $n = 2$ (indirect allowed transition) and $n = 3$ (indirect forbidden transition). This method is widely used in amorphous and crystalline thin films for determining absorption characteristics.¹⁶ This method is quite appropriate. Still, it has some inadequacies relevant to the semi-classical model, such as assuming the zero coulomb attraction at low temperature, unexpected origin of extrinsic absorption, etc.¹⁷ In comparison to the Tauc plot, a numerical derivative method is preferred, may be due to its identification of peaks in a small wavelength range.

Here we have synthesized, cost-effective ZnO film using a wet chemical route. The structural and optical studies were analyzed through SEM, XRD, and UV-Vis. spectroscopy. In addition to this, comparative analysis between Tauc plot and numerical derivative method has been discussed for bandgap energy calculations.

EXPERIMENTAL

ZnO nanoparticles (NPs) were synthesized using zinc acetate dihydrate ($ZnAc_2 \cdot 2H_2O$) (Sigma-Aldrich with purity 98.0%), lithium hydroxide monohydrate ($LiOH \cdot H_2O$) (Sigma Aldrich with purity 98.0%) as a precursor, and absolute ethanol (EtOH) (Alfa Aesar with purity > 99.9%) as a reducing agent via modified Spanhel Anderson method.¹⁸⁻¹⁹ The detailed procedure has been depicted in Fig.-1.

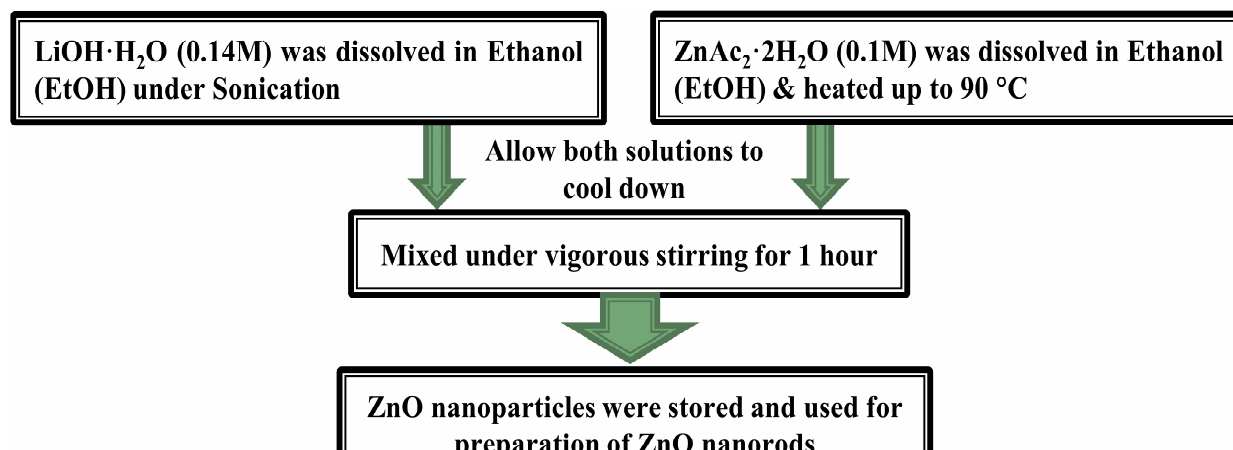


Fig.-1: Flowchart for the Synthesis of ZnO Nanoparticles.

ZnO film was grown in the reaction flask consisting of 40.0 ml of 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar with purity > 99.9%) and $C_6H_{12}N_4$ (HMTA) (Sigma-Aldrich with purity > 99%) with reflux condenser using ZnO NPs as seed layer particles via wet chemical route.¹⁹ The seed layer of ZnO NPs was coated on the cleaned conducting indium tin oxide (ITO) surface through spin coating methods. Then this ZnO seed layer coated on ITO film was dipped in a reaction flask containing $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA solution. This solution was heated on the hotplate at a constant reaction temperature of 90 °C for 8 hours, and the film was annealed for 3 hours at 300 °C for the formation on the ITO substrate, as shown in Fig.-2.

The surface morphology of the prepared film was characterized by a scanning electron microscope (SEM) Zeiss EVO MA 10 in the scanning mode at room temperature. These observed SEM micrographs were

analyzed through freely downloadable software Fiji ImageJ (Version 1.53g 4 December 2020 window-based software).

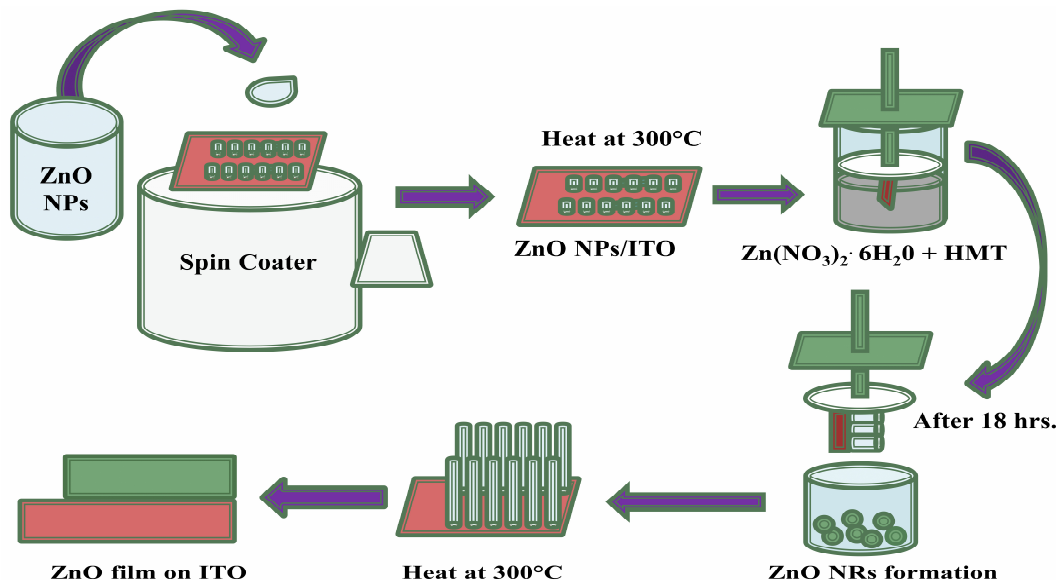


Fig.-2: Schematic Representation of Fabrication of ZnO Film.

For structural analysis of the synthesized film, diffraction measurements were performed at room temperature in the 2θ range of $20^\circ - 80^\circ$ by step scan mode with step size $\Delta(2\theta) = 0.02^\circ$ through Rigaku Ultima IV Powder X-ray diffraction (XRD) system with copper K_α radiation ($\lambda = 0.15406$ nm). These observed XRD data were initially analyzed through a window-based Powder X-ray Data Analysis System and then freely downloadable Fullprof Suite version September 2020.

UV-Vis. spectroscopy was performed on the prepared film in the wavelength range 300 - 800 nm through a computer interfaced Cary 5000 UV-Vis-NIR spectrophotometer of Agilent Technologies.

RESULTS AND DISCUSSION

SEM Analysis of ZnO Film

The SEM micrographs of ZnO film with size distribution are shown in Fig.-3. The inset of Fig.-3 indicates the maximum number of ZnO nanorods grown, having a diameter in the range of 80-100 nm. These dispersed rods indicate c-axis growth due to the decrease in Gibbs free energy that may attribute to the low supersaturation.²⁰ Surface morphology of the grown rods seems to be a hexagonal type structure²¹ with an average diameter of 102.5 nm. For this size distribution, the fitting criteria were based on reduced chi-square and adjacent reduced-square with the maximum standard error of (± 4.4) using the Gaussian model. Regarding the previously reported results on ZnO films, it can be seen from the inset of Fig.-3 that the size distribution of the prepared films seems to be non-uniform. However, Nimalkar et al., 2017 and Amakali et al., 2020 reported the grain size for ZnO films in the range of 34-37 nm with uniform size distribution. The difference between the reported and observed values for ZnO films may be due to the larger grain size of NPs used as seed layer particles for the growth of the film. In addition to this reasoning, the non-uniformity can be attributed due to the difference in the reflux temperature.²²⁻²³

Room temperature XRD data of the prepared film is shown in Fig.-4, where observed Bragg peak positions are indexed, and all the prominent peaks match with the XRD data reported in the literature by other researchers²² and standard JCPDS card number: 89-0510 [Fig.-4 (a)]. The observed XRD spectra indicates polycrystalline hexagonal wurtzite structure with single-phase formation of the prepared film along (002) orientation. The Bragg law of diffraction is closely related to the inter-planar spacing d_{hkl} and diffraction angle (θ) by the following equation:²⁴

$$2d_{hkl}\sin\theta = n\lambda \quad (1)$$

Where, n is the order of diffraction and $\lambda = 0.154056$ nm is the wavelength of Cu K_α radiation.¹⁶ For 1st order diffraction ($n = 1$), lattice parameters $a = b, c$ and the miller indices follow the known relationship:²⁴

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

The lattice constant $a = \lambda/\sqrt{3}\sin\theta$ and $c = \lambda/\sin\theta$ corresponding to the (100) and (002) Bragg planes were used to compute $a = b = 0.322$ nm and $c = 0.520$ nm for the prepared film. These values of lattice parameters were further refined by using Powder X-ray Data Analysis System for the Rietveld profile refinement method.²⁵ In addition to these lattice parameters, overall B-factor, scale factor, FWHM, shape, ten background polynomials ($a_0 - a_9$), two instrumental (Zero and displacement), and two preferred orientations (G1 and G2) parameters also were refined.¹⁹ The excellency of XRD data refinement was considered on the basis of 1) Goodness of Fit ($1 \leq \text{GOF} \leq 1.3$), 2) Durbin Watson Statistic ($d = 2.0$ or $\rightarrow 2.0$) and 3) weighted-profile R-value ($\text{Rwp} \sim 10\%$ for laboratory XRD data) in order to calculate précised lattice structure. Good profile agreement between the experimental and calculated data was achieved, as depicted in Fig.-4 (c). The hexagonal crystal system with 6/mmm, point group 6mm, and Bravais lattice P with space group number (186) was confirmed from the refinement.

The synthesized ZnO film on the ITO substrate was polycrystalline, confirmed by the Rietveld refinement with a strong signal centered at $2\theta = 34.78^\circ$, showing preferential growth along the (002) plane.²⁶ This crystallographic condition indicates some kind of c-axis texturing. The quantitative information about the TC(hkl) concerning the preferential crystallite orientation or texturing for the film can be computed for various prominent planes using the following expression:²⁷

$$TC(hkl) = \frac{I_F(hkl)}{I_{Ref}(hkl)} \left/ \left[\left(\frac{1}{N} \right) \sum \frac{I_F(hkl)}{I_{Ref}(hk)} \right] \right. \quad (3)$$

Where $I_F(hkl)$ represents X-ray intensity observed on the ZnO film, ' $N = 5$ ' represents the number of diffraction peaks considered for calculations, and $I_{Ref}(hkl)$ represents the intensity of reference [JCPDS data card (89-0510)]. The degree of preferred orientation represented by texture coefficient was calculated using equation three and presented in Table-1 for different Bragg planes. The value of TC(hkl) for the film concerning the JCPDS file was found 3.84 for the (002) plane, and for other planes, it is less than unity, indicating preferred growth along the (002) plane along with deficiency of grains orientation.

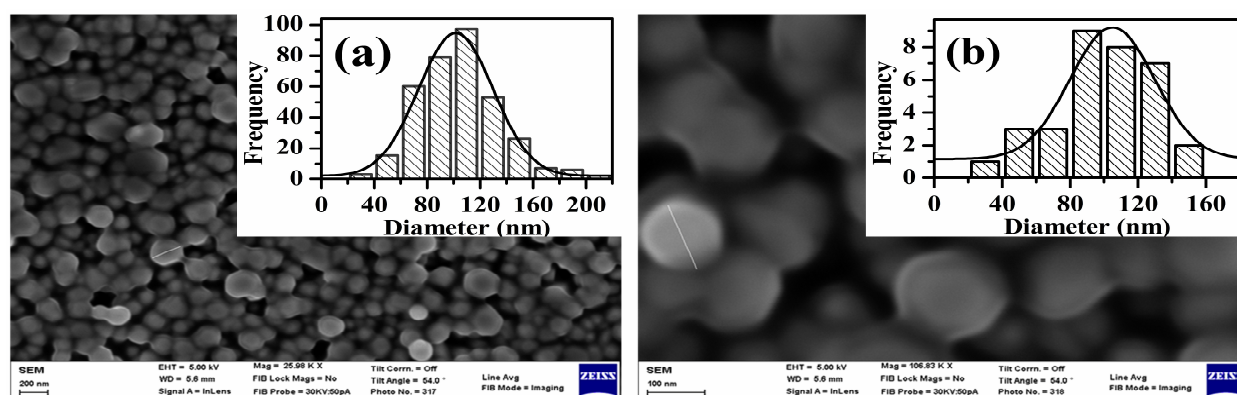


Fig.-3: SEM Micrographs for ZnO Film at Resolution (a) 200 nm and (b) 100 nm. Inset of Micrograph indicating its Size Distribution.

X-Ray Diffraction Measurements and Rietveld Analysis

The hexagonal wurtzite structure of ZnO consists of Zn and O atoms bonded together by tetrahedral and octahedral bonds. These atoms have been assigned specific atomic positions, i.e., for Zn, the position coordinates are (1/3, 2/3, 0), and for O, the position coordinates are (1/3, 2/3, u). In this case of the O atom, u is termed as oxygen or u parameter. The u parameter for ZnO film was 0.385, and c/a is 1.600, estimated from Rietveld refinement. The estimated u value for the prepared film was conceded approximately with the reported result, $u = 0.383$.²⁸ The structure has followed a known relationship

between u and c/a ratio equivalent to uc/a , which remains constant at or near its ideal value $(3/8)^{1/2}$. For this structure, $uc/a = 0.616$ was found, which is less but very close to the ideal value.

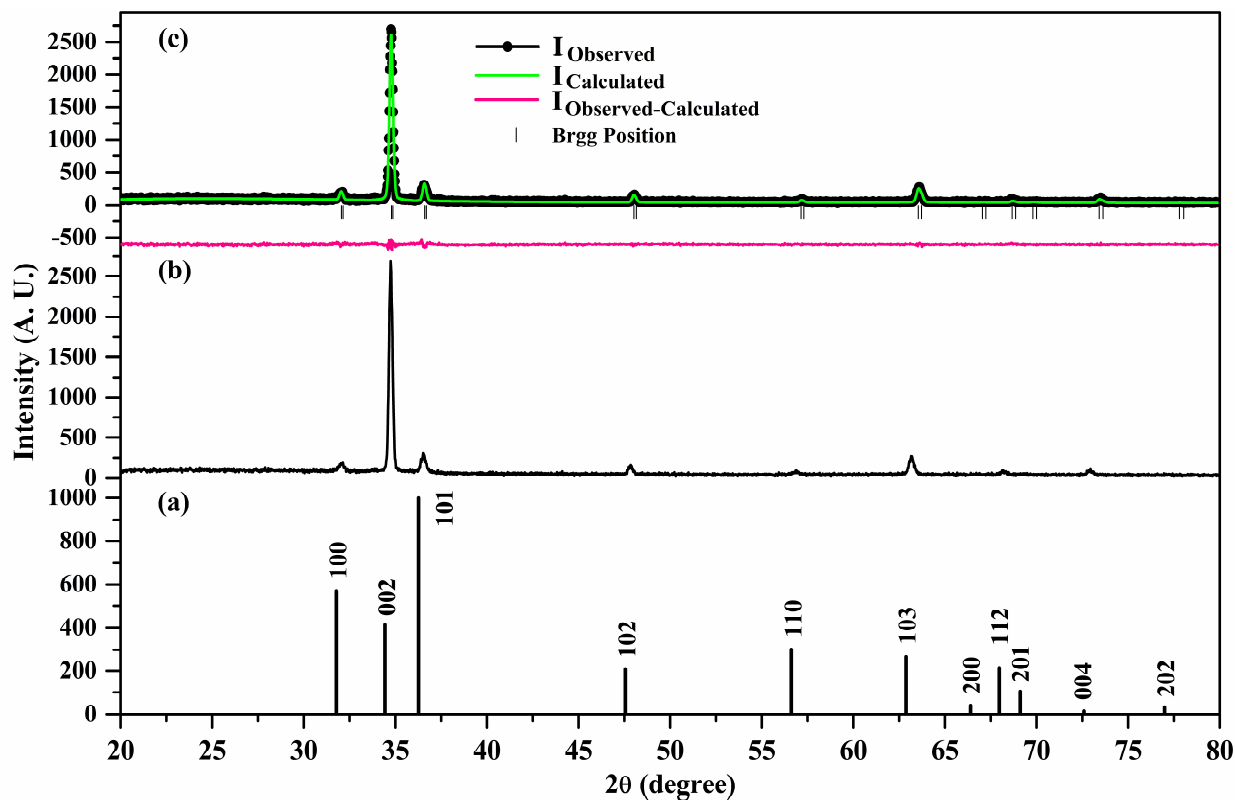


Fig.-4: (a) JCPDS Card Number 89-0510 (b) powder XRD pattern and (c) Rietveld refinement pattern of ZnO film. Black dots represent experimental patterns, continuous green lines represent calculated patterns, and continuous pink lines represent the difference between the experimental and calculated patterns. Vertical markers indicate the positions of the calculated Bragg reflections.

Table-1: Bragg diffraction positions (2θ), Miller indices (hkl), peaks intensity, and texture coefficients (TC) for ZnO film referencing JCPDS card number 89-0510.

(hkl)	Intensity (A.U.)		TC (hkl) (Film)
	JCPDS	Films	
100	570	55	0.15
002	414	999	3.84
101	999	123	0.20
102	210	58	0.44
110	301	23	0.12

The packing diagram of ZnO film was drawn using freely downloadable VESTA (Visualization for Electronic and Structural Analysis) software, version 3.4.4, 64-bit edition, as shown in Fig.-5. The nearest-neighbor bond lengths along the c -axis ($\text{Zn-O} = L_1$) and off the c -axis ($\text{Zn-O} = L_2$) were calculated from the packing diagram. In addition to the nearest-neighbor bond lengths, the second nearest-neighbor distances, one along the c -axis ($\text{Zn-O} = L_1'$), six of them ($\text{Zn-O} = L_2'$), and three of them ($\text{Zn-O} = L_3'$) was also calculated from the packing diagram. The bond angles with reference to c -axis ($\text{O-Zn-O} = \alpha_1$) and off c -axis ($\text{O-Zn-O} = \beta_1$) were also calculated from the packing diagram. These calculated values of bond length (L_1 , L_2 , L_1' , L_2' , and L_3') and bond angles (α_1 and β_1) are shown in Table-2, which are affirmative with the computed values for prepared films.²⁹

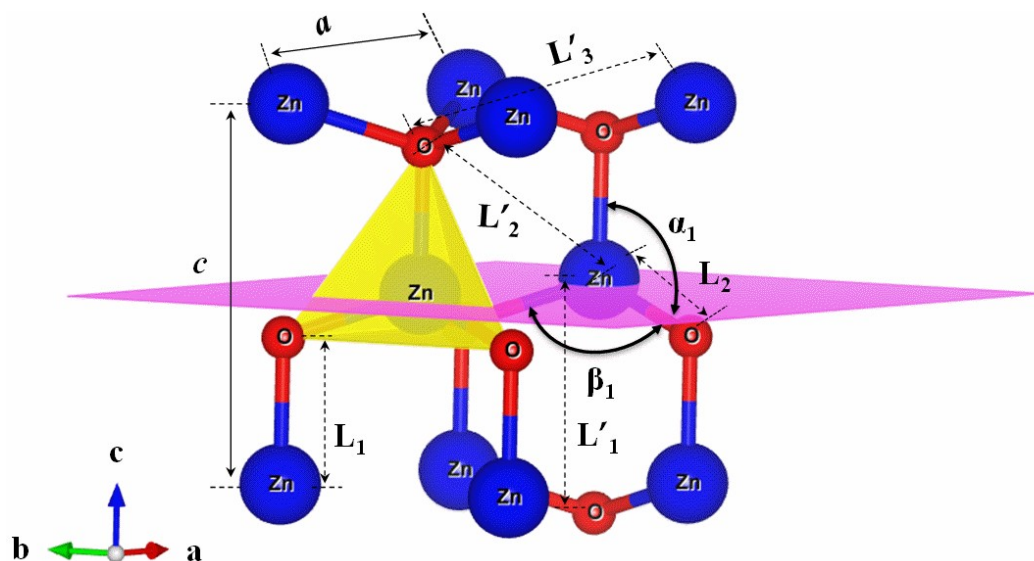


Fig.-5: Schematic representation of a wurtzite structure with lattice parameter “ a ” along the (002) plane, and “ c ” perpendicular to (002) plane, two type nearest-neighbor distance (L_1 and L_2) and three type next nearest neighbor distance (L'_1 , L'_2 , and L'_3) and bond angles (α_1 and β_1) for ZnO film.

Table-2: Various Parameters were obtained from the Packing Diagram of ZnO film.

$a = b$ (nm)	c (nm)	c/a (nm)	u	uc/a (nm)	L_1 (nm)	L_2 (nm)	L'_1 (nm)	L'_2 (nm)	L'_3 (nm)	α_1 ($^\circ$)	β_1 ($^\circ$)
0.3221	0.5154	0.1600	0.385	0.617	0.1986	0.1951	0.3168	0.3784	0.3766	107.62	111.26

UV-Visible Spectroscopy of ZnO Film

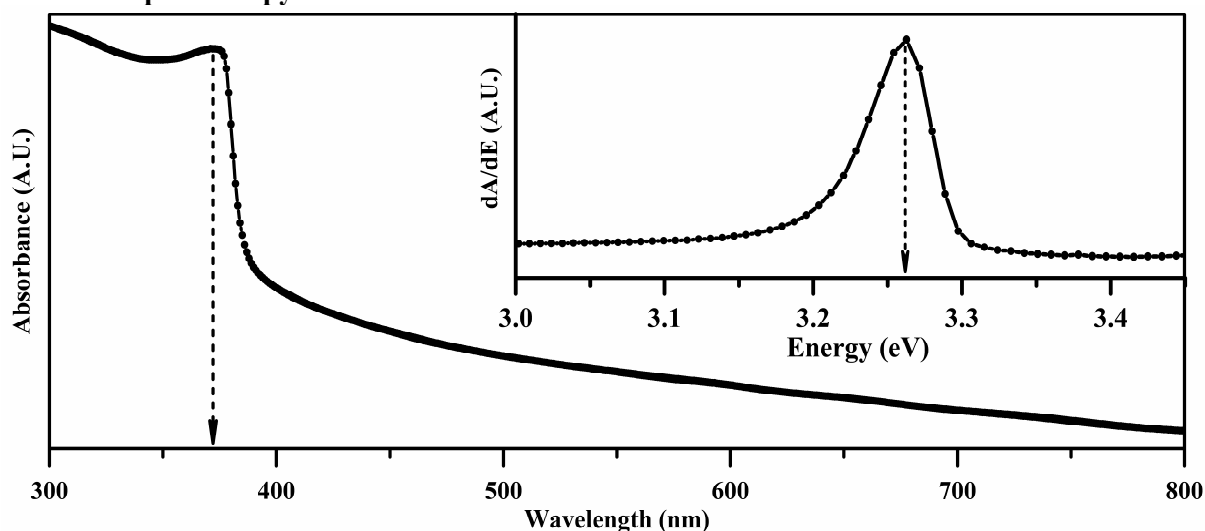


Fig.-6: UV-Vis. absorption spectra and the inset of the Fig. shows variation dA/dE with E_g for ZnO film.

Figure-6 depicts the absorption spectra for ZnO film at room temperature. The characteristic peak for ZnO was found at 371 nm, having a strong and sharp nature indicating the crystallinity of the prepared sample. The highly crystalline nature of the sample was also confirmed from the XRD data that might be due to the intrinsic bandgap of ZnO.³⁰ This intrinsic bandgap exists due to the electronic transition mainly from valence (O_{2p}) to the conduction band (Zn_{3d}).³¹ The peak position of the absorption band was shifted towards the higher wavelength, indicating a red shift relative to the bulk hexagonal wurtzite ZnO.³² The red shift of the absorption peak indicates the decrease of the optical bandgap for the prepared sample.³³ The inset of Fig.-6 depicts the 1st order numerical derivative of absorbance with respect to photon energy, i.e., (dA/dE), indicating a bandgap of 3.26 eV for the film. The bandgap energy can also be computed using the Tauc plot method¹⁶, where absorption spectra data were fitted using the following expression;

$$(\alpha h\nu)^{\frac{1}{n}} = S(h\nu - E_g) \quad (4)$$

where α , h , ν , E_g represents the absorption coefficient, Planck constant, photon frequency, and bandgap, respectively. Here S is the slope of the Tauc plot in a linear region (1.8-3.2 eV), and n denotes the nature of the transition.

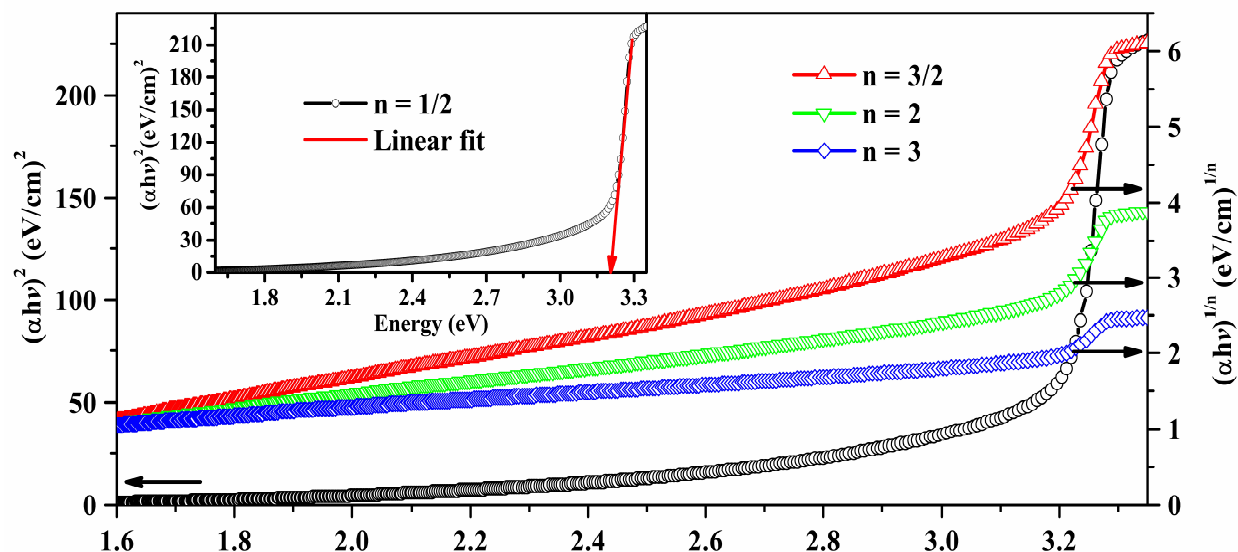


Fig.-7: Tauc plot of ZnO films for different transition values and the inset of Fig. shows the linear fit for $n = 1/2$ (direct allowed transitions).

Figure-7 shows the Tauc plot of the prepared ZnO film with different values of n regarding equation 4. It can be inferred from the inset of Fig.-7 that the Tauc plot has two regions, i.e., linear and non-linear/curved. The linear region indicates a fundamental absorption between (3.2 - 3.3 eV) of the Tauc plot, whereas the non-linear region depicts the residual absorption between (0 - 3.2 eV) due to defect states.³⁴ The inset of Fig.-7 represents the best fit for given data because of the Urbach tail's presence compared to other plots for $n = 3/2$, $n = 2$, and $n = 3$, indicating a direct bandgap.¹⁶ In Fig.-7, except for $n = 1/2$, the value of $(\alpha h\nu)^2$ is not zero for lower energy sides (below 1.8 eV). However, according to the literature, there is a certain amount of cutoff value prior to that the value of $(\alpha h\nu)^2$ should be zero.¹⁵ In addition, if the linear region in all the cases were extrapolated, then the bandgap energy for $n = 1/2$ is 3.2 eV. However, for others cases, the values of the bandgap deviate from the standard value of (3.24 eV for bulk ZnO sample).³⁵ This indicates that the Tauc plot is being best fitted with $n = 1/2$ (direct bandgap with allowed transitions). Among these two methods, as discussed, the numerical derivative method is more accurate and feasible than the Tauc plot method for calculating the bandgap energy. The energy bandgap value computed for the sample may be due to the effect of optical confinement, which corresponds to the difference in the diameter of ZnO film comparative to the bulk sample.³⁶

CONCLUSION

ZnO film has been synthesized successfully by a wet chemical route on the ITO substrate. The SEM images of the synthesized sample confirmed one-dimensional growth of ZnO film with a hexagonal structure having an average diameter of 102.5 ± 4.4 nm (cross-sectional view). The Rietveld analysis on XRD data confirms the formation of a single-phase polycrystalline wurtzite hexagonal structure with $TC(hkl) = 3.84$ preferential growth along the (002) plane. The UV-Vis. analysis indicates an absorption band at the wavelength of 371 nm with a bandgap energy of 3.2 eV. The Tauc plot method indicates a direct bandgap in the prepared ZnO film with the allowed transition for $n = 1/2$.

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