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Optical Analysis of ZnO Thin Films by SILAR Method

M. Nirmala[1*], B. Kavitha[2], K. Iswarya[3], A. Firose Banu[4]

[*1,2,3,4]*Department of Physics, Sri GVG Visalakshi College for Women, S.V Mills post, Udumalpet, TN, India.*

Abstract

Zinc oxide (ZnO) thin films were grown on glass substrate by the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The structural, morphological surface and optical properties of the films have been studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-VIS-spectrophotometer. Effects of experimental parameters on the structural and optical properties were discussed. The X ray diffraction analysis shows that the films are polycrystalline with zincite hexagonal structure. The study of surface morphology reveals that deposited ZnO films the film contains the grains in the form of flakes and further magnification the flakes can be viewed as flower like morphology. Obtained ZnO films exhibit a moderately high transmittance in visible band, and optical band gap of 3.2 eV which can be applicable for photovoltaic applications.

Keywords: *Band gap; Polycrystalline; SEM; XRD; Zinc Oxide.*

1. INTRODUCTION

Thin film technology is stretching its hands in all its directions and thin film devices coming out of it play a dominant role in all walks of life. The need for new and improved optical and electronic devices have stimulated a new branch of solid state physics called thin film physics and technology which comprises the study and application of thin films of elements as well as binary and ternary systems with controlled compositions and specific properties. ZnO thin film is an interesting wide band gap (3.37 eV) II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. In recent years for developing highly oriented and transparent ZnO thin films has attractive potential application in transparent electrode in display, window layer in solar cells, field emitters, ultraviolet laser emission, photo detector and bio sensors (Yoon *et al.* 1997). ZnO thin film considerable attention because of their size dependent properties and wide range of applications.

Various chemical and physical processes have been employed for thin film deposition, such as conventional sputter deposition technique (Chiou *et al.* 2003), chemical vapor deposition (CVD) (Lyu *et al.* 2002; Wu *et al.* 2002) thermal evaporation (Wang *et al.* 2003; Hu *et al.* 2001) spray pyrolysis (Dela *et al.* 2002; Van *et al.* 1997) and electrodeposition (Fahoume *et al.* 2006). Like chemical bath deposition technique, the Successive Ionic Layer Adsorption and Reaction (SILAR) technique for the preparation of thin films from aqueous solution is a promising technique because of its simplicity and economics. The facts affecting the process are the quality of the precursor solutions, their concentrations, pH values, complexing agents and individual rinsing and immersion time periods (Pathan *et al.* 2004). In this paper, thin films of ZnO have been deposited on silica glass substrate using SILAR method.

2. EXPERIMENTAL METHODS

2.1 Cleaning of the substrates

Substrates must be cleaned for durable and adherent coating with reproducible properties. Cleaning involves removal of contaminants without damage to the substrates. While cleaning the bond between the contaminants and the substrate molecules are broken and contaminants are set free from substrates. The energy required to break these absorption bond could be supported by chemical, salvation and ion bombardment, thermal or mechanical process. The substrate cleaning procedure adopted in the present work involves five steps.

1. The substrates kept in the zig are cleaned in soap solution for 25-30 minutes.
2. The substrates are then cleaned in distilled water for 25-30 minutes.
3. The substrates are then dried in hot air oven for about 30 minutes.

M. Nirmala** **Tel:+919842247125
email: saicharan.kumar16@gmail.com

Table 1. Details of chemicals used for the deposition of ZnO thin film

$ZnSo_4$ (mol)	$Cs(NH_2)_2$ (mol)	NH_3 (ml)	Distilled Water (ml)	Stirring Time (hr)	Deposition Time (hr)
0.1	1	2	100	1	2

Table 2. Optimised deposition parameters

Parameter	Variation range	Optimized value
pH	10 -11	11
Temperature	Room Temperature -40 ^{0}C	Room Temperature
Time	1hr	20 min
cycle	50-200	150

2.2 Preparation of ZnO thin films by SILAR technique

In the first step of a SILAR cycle solvated cationic precursor is adsorbing on the surface forming an electrical double layer. This layer is composed of two layers the inner (positively charged) and outer (negatively charged) layers. Positive layer consists of the cations and negative from the counter ions of the cations. Excess unabsorbed precursor is rinsed away from the diffusion layer. This results in a saturated electrical double layer. In the reaction phase the anion precursor is introduced to the system. Due to the low solubility of the material K_mA_n a solid surface is formed on the interface. The last step rinses the counter ions of both types of precursors as well as the reaction by product out of the system. By repeating these cycles thin layer of a material K_mA_n can be grown. If the measured growth rate exceeds the lattice constants of the material a homogenous precipitation in the solution could have taken place.

In the present study very accurate electronic balance (SHIMADZU-AY220 digital electronic balance) is used for thickness measurements. Mass difference of the substrate before and after deposition gives the mass of the film 'm'. Knowing the length (1) and breadth (b) of the deposited film, area of deposition can be determined. If ρ is the density of the material of the film, then thickness (t) of the film is determined using the formula.

t = mass of the deposited film/area of the film x density of the film

$$t = \frac{m}{lb\rho} \quad (1)$$

[The density of 5.606 kg/m^3].

3. RESULTS AND DISCUSSION

3.1 XRD analysis

Fig. 1 shows the x-ray diffractogram of ZnO thin film prepared at room temperature. From the diffraction profile it has been found that the film is polycrystralline in nature with hexagonal structure. The XRD patterns has shows peaks at $2\theta=31.9^0$ with high intensity, weak intense at $2\theta=34.4^0$ and $2\theta=36.4^0$ are corresponding to (100), (002) and (101) planes respectively. From the XRD profiles (Fig 4.3) the lattice spacing 'd' has been determined and it has been found that it is in very good agreement with those of ASTM card, earlier researchers (Kathalingan *et al.* 2010; Chewki *et al.* 2014) and is presented in Table 3.

Table 3. XRD data of ZnO thin films

Plane (hkl)	2θ degrees		*d* (Å)	
(100)	31.9024	31.777	2.8029	2.813
(002)	34.4407	34.432	2.6019	2.601
(101)	36.36533	36.264	2.4685	2.475
(100)	31.9024	31.777	2.8029	2.813

3.2 SEM analysis

Surface morphology of thin film is very important tool to investigate microstructure of thin films. Fig.2 shows the surface morphology of the prepared ZnO thin film of different magnification. It reveals that film has a good crystalline quality and the

film surface has a generally smooth and dense morphology. In smaller magnification Fig. 2 the film shows a uniform and smooth morphology of the grown film containing an accumulation of small grains and here the deposit distribution is less porous and this the ZnO thin film is polysrystalline crystalline in nature (Van *et al.* 1997; Fahoume *et al.* 2006). Fig.2 shows that the film contains the grains in the form of flakes and further magnification the flakes can be viewed as flower like morphology which can be applicable for photovoltaic devices (Raidoua *et al.*2010; Suman *et al.* 2013).

The individual crystalline size (D_c) of prepared film of thickness 510nm have been estimated and are in very good agreement with the reported values (Chewki *et al.* 2014). Using the size of the crystallites, the dislocation density, the number of crystallites per units surface area and strain have been determined and presented in Table 4.

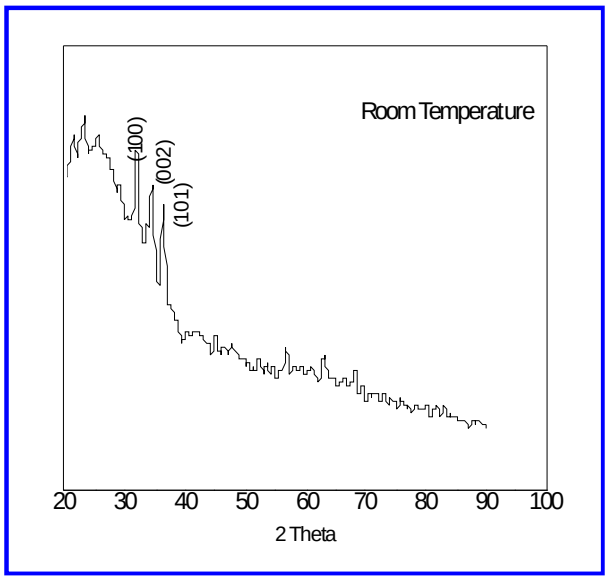

Fig. 1: X-ray diffractogram of ZnO thin film

3.3 Optical analysis

The optical transmittance spectra of ZnO thin film is shown in Fig .3, Transmittance of the films increases and absorbance decreases with wavelength. The moderately high transmittances of the films throughout the visible region make it a good material for photovoltaic applications. The typical behaviour was observed by earlier researchers (Sara et al 2015). In the visible region of solar spectrum transmission spectra of ZnO thin show sinusoidal behaviour, this may be due to the layered structure of thin film(Ghodsi *et al.* 2010; Zial *et al.* 2011). The optical parameters such as absorption coefficient, extinction coefficie nt and band gap are estimated and are presented in Table 5.

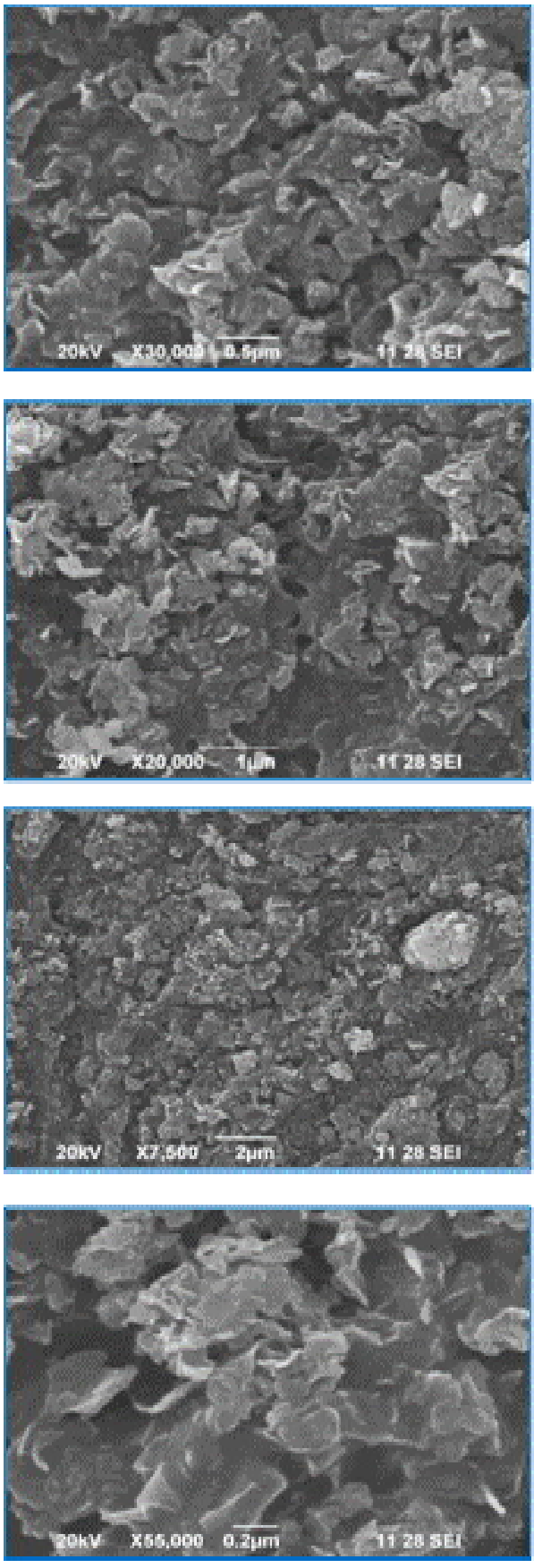

Fig. 2 : SEM micrographs of ZnO thin film of different magnification.

Table 4. Structural parameters of ZnO thin films

Film thickness (nm)	Lattice constant				Crystalline size (nm)	Volume (V)	Dislocation density (10^{14}/lines/m^2) δ	Number of crystallite per unit area (10^{15} m^2)	Strain $\varepsilon \times 10^{-3}$
	a (Å)		c (Å)						
	Observed	ASTM	Observed	ASTM					
510	3.23	3.2648	5.2059	5.2194	10.1158	33.6982	9.72	0.4926	3.425
					10.007		9.986	0.5089	3.4625
					11.8508		7.12	0.306427	2.9238

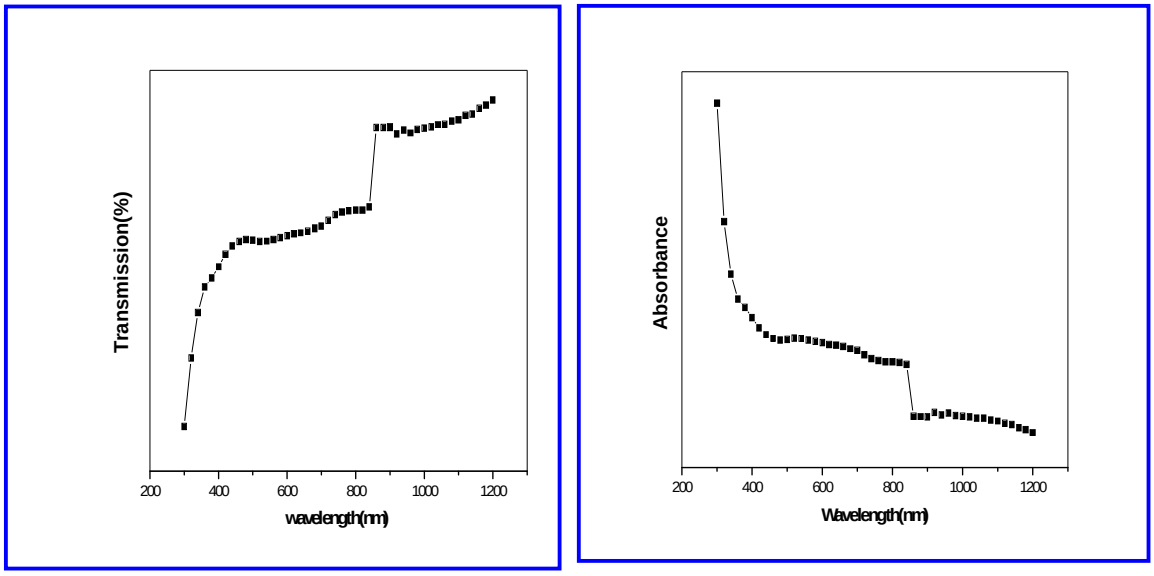

Fig. 3: Transmittance and Absorbance spectra of ZnO thin film

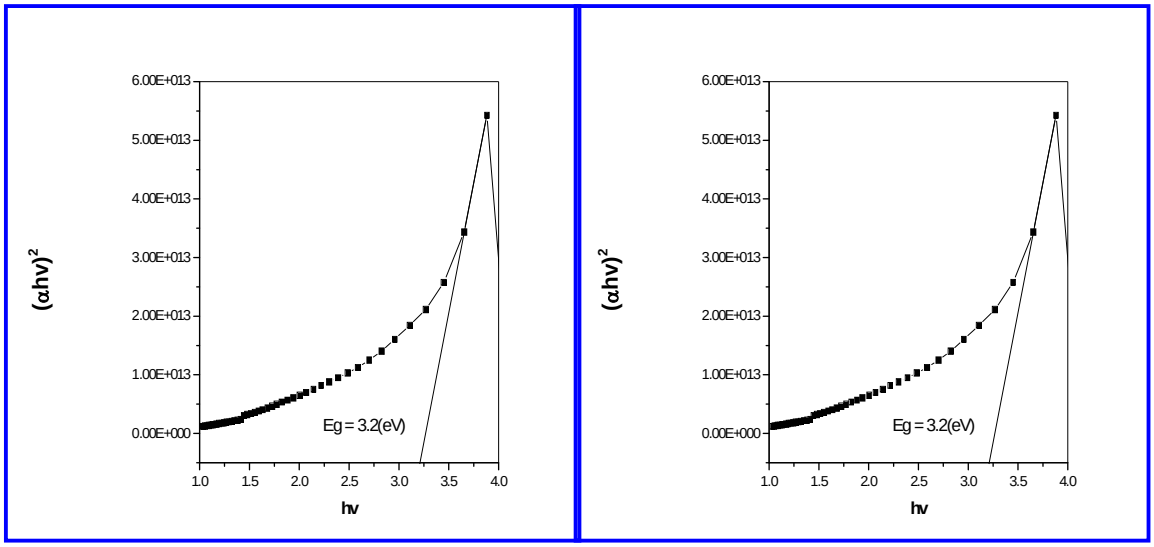

Fig. 4: Plot of $(\alpha h\nu)^2$ vs.$(h\nu)$ of ZnO thin film

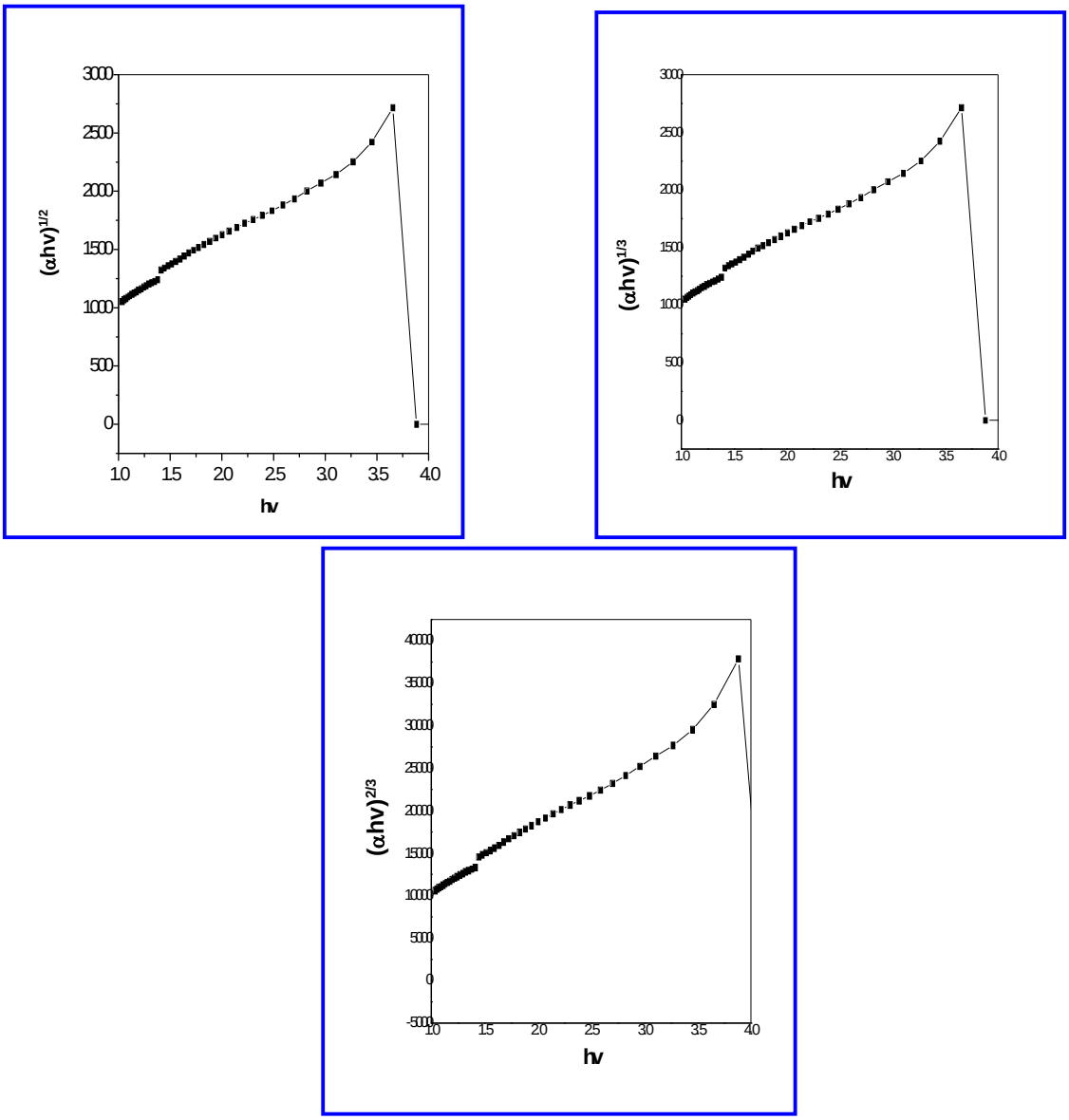

Fig. 5 : Plot of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$ and $(\alpha h\nu)^{2/3}$ vs. (hν) of ZnO thin film

Important optical parameters such as type of transition, band gap etc. can be satisfactory analyzed on the basis of formulae derived for 3D and 2D models. By 3D crystal model, nature of transition in film composition can be obtained by plotting $(\alpha h\nu)^{1/2}$ versus (hν) for various values of r [α is the absorption coefficient, hν is the photon energy and exponent r determines the type of transition and dimensionality of the bands]. ν has values ½ (direct allowed), 3/2 (indirect allowed), 2 (direct forbidden). Extrapolation of straight-line portion of $(\alpha h\nu)^{1/2}$ versus (hν) plot at ($h\nu > E_g$; E_g = direct band gap) to zero absorption (hν-axis) gave the value of energy gap.

Plot of $(\propto h\nu)^2$ versus (hν) (Fig. 4.a & b) for ZnO thin film was plotted and the straight line portion is extrapolated to cut the x axis which gives the band gap. The estimated band gaps for found to be 3.2eV (Table 5) and in agreement with the earlier researchers (Zial et al 2011; Wasan *et al.*2012). Plot of (hν) versus $(\propto h\nu)^{1/2}$, $(\propto h\nu)^{1/3}$ and $(\propto h\nu)^{2/3}$ shown in Figures 5.a,b & c reveal that ZnO films did not have line above hν> Eg. Since extrapolation of it did not touch the zero absorption axis which confirms the fact that ZnO phase do not have indirect allowed direct forbidden and indirect forbidden transitions. The optical parameters such as absorption coefficient, extinction coefficient, reflectance, refractive index and band gap are estimated and are presented in Table 5.

4. CONCLUSION

The ZnO thin films are prepared by Successive Ionic Layer Adsorption and Reaction method. Thickness of the prepared films are calculated by

Gravimetric method. The structure of the prepared films has been analyzed by XRD.It revealed that the prepared films are polycrystalline in nature with hexagonal structure. The characteristics peaks are identified and the structural parameters are calculated and presented. SEM micrograph showed the morphology of the prepared film as flower like morphology in higher magnification which can be applicable for photovoltaic cell. The type of transition and bandgap has been estimated from optical analysis. The bandgap is found to be 3.2eV.Then the optical parameters such as absorption coefficient, extinction co efficient, are calculated and presented.

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REFERENCES

Chewki Zegadi, Khalil Abdelkebir, Denis Chaumont, Mohamed Adnane and Saad Hamzaoui, Influence of Sn Low Doping on the Morphological, Structural and Optical Properties of ZnO Films Deposited by Sol Gel Dip-Coating, Advances in Materials Physics and Chemistry, 4(5), 93-104(2014). doi:10.4236/ampc.2014.45012

Chiou W. T., Wu, W. Y. and Ting, J. M., Growth of single crystal ZnO nanowires using sputter deposition, Diam. Relat. Mater., 12(10-11), 1841-1844(2003). doi:10.1016/s0925-9635(03)00274-7

De la Olvera, M. L., Maldonado, A., Asomoza, Meléndez-Lira, R. M., Effect of the substrate temperature and acidity of the spray solution on the physical properties of F-doped ZnO thin films deposited by chemical spray, Sol. Energy Mater. Sol. Cells, 71(1),61-71(2002). doi:10.1016/s0927-0248(01)00044-7

Fahoume, M., Maghfoul, O., Aggour, M., Hartiti, B., Chrabi, F., and Ennaoui, A., Growth and characterization of ZnO thin films prepared by electrodeposition technique, Sol. Energy Mater. Sol. Cells, 90(10), 1437-144(2006). doi:10.1016/j.solmat.2005.10.010

Ghodsi, F. E. and Absalan, H., Comparative Study of ZnO Thin Films Prepared by Different Sol-Gel Route, Acta physica polonica A, 118(4), 659-664(2010).

Hu, J. Q., Ma, X. L., Xie, Z. Y., Wong, N. B., Lee, C. S. and Lee, S. T., Characterization of zinc oxide crystal whiskers grown by thermal evaporation, Chem. Phys. Lett. 344(1-2), 97-100(2001). doi:10.1016/s0009-2614(01)00720-5

Lyu, S. C., Zhang, Y., Ruh, H., Lee, H. J., Shim, H. W., Suh, E.K. and Lee, C. J., Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires, Chem. Phys. Lett. 363(1-2), 134-138(2002). doi:10.1016/s0009-2614(02)01145-4

Kathalingam, A., Ambika, N., Kim, M. R., Elanchezhiyan, J., Chae, Y. S. and Rhee, J. K., Chemical bath deposition and characterization of nanocrystalline ZnO thin films, Materials Science-Poland, 28(2), 513-522(2010).

Khan, Z. R., Khan, M. S., Zulfequar, M., and Khan, M. S., Optical and Structural Properties of ZnO Thin Films Fabricated by Sol-Gel Method, Materials science and applications, 2, 340-345(2011). doi:10.4236/msa.2011.25044

Kushwaha, S. and Bahadur, L., Studies of structural and morphological characteristics of flower-like ZnO thin filmand its application As photovoltaic material, Optik- IJLEO- 124(22),5696-5701(2013). doi:10.1016/j.ijleo.2013.04.019

Pathan, H. M. and Lokhande, C. D., Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method, Bull. Mater. Sci. 27, 85-111(2004). doi:10.1007/BF02708491

Raidou, A., Aggour, M., Qachaou, A., Laanab, L. and Fahoume, M., Preparation and Characterisation of ZnO Thin Films Deposited by SILAR Method, M. J. Condensed Matter,12(2) , 25-130(2010).

Saleh, W. R., Saeed, N. M., Twej, W. A. and Alwan, M., Synthesis Sol-Gel Derived Highly Transparent ZnO Thin Films for Optoelectronic Applications, Advances in Materials Physics and Chemistry, 2(1), 11-16(2012). doi:10.4236/ampc.2012.21002

Sara Moradi and Haleh Kangarlou, Production and investigation about structural Properties of Al doped ZnO thin films by chemical Bath deposition, Indian Journal of Fundamental and Applied Life Sciences 5(S1), 2819-2821(2015).

Van Heerden, J. L., and Swanepoel, R., XRD analysis of ZnO thin films prepared by spray pyrolysis, Thin Solid Films 299(1-2), 72- (1997). doi:10.1016/s0040-6090(96)09281-4

Wang, Y. G., Yuen, C ., Lau, S. P., Yu, S. F., Wu, J. J. and Liu, S. C., Catalyst-free growth and characterization of ZnO nanorods, J. Phys. Chem. B 106(37), 9546-9551(2002). doi: 10.1021/jp025969j

Yoon, D. H. and Choi, G. M., Electrical and CO gas sensing properties of ZnO–SnO_2 composites, Sens. Actuators B: Chemical, 52(3), 251-256(1998). doi:10.1016/s0925-4005(98)00275-5