Influence of substrate temperature on structure, morphology and optical properties of spray deposited ZnO thin films.

S. V. Jadhav[1] and L. S. Ravangave[2*]
[1,2] Physics Research Centre, Department of Physics Shri Sant Gadge Maharaj College Loha, Dist. Nanded, Maharashtra-431708 India.

Abstract:

Zinc Oxide (ZnO) thin films were deposited for five different substrate temperatures (150-350℃) using simple spray technique. The deposited films were characterized by X-ray diffractometer (XRD), Scanning Electron Microscope (SEM) and UV-Visible spectroscopy. XRD pattern revealed that deposited films represent wurtzite hexagonal crystal structure of ZnO material. Crystallite size was estimated using Lorentz Fit of XRD data was in the 20.02-26.32 nm range. The SEM image of (ZnO 300℃) film sample shows whole surface was uniformly coated with schematically arranged network of ZnO wires of average diameter 566 nm. Purity of the deposited sample was investigated by Energy Dispersive X-ray Analysis (EDX). All the ZnO films exhibit 70 to 80% transmittance. The optical band gap value calculated was in the 3.12 to 3.95 eV range.

Key Words: ZnO thin films, Spray pyrolysis, Microstructure, XRD, Optical band gap, Optical transmittance

*Corresponding author: lsravangave@gemail.com

Introduction:

Zinc oxide (ZnO) is a important n-type semiconductor (II–VI) material exhibit direct band gap of 3·2-3.37 eV and good transparency in visible region [1, 2], large exciton binding energy of 60 meV [3]. Due to these significant properties ZnO have potential applications in Optoelectronic devices such as in Optical wave guide [4] Light emitting diodes (LED) [5] Thin Film Transistors (TFT) [6], Metal oxide field Effect Transistor [7] etc. ZnO thin films exhibit high optical transmittance in the visible light region therefore it is used as a window materials in solar cell applications [8]. In recent years ZnO nano-materials have created much more interest for their application in laser diodes, piezoelectric transducers, and bulk acoustic wave devices and in biomedical materials such as in antiseptic creams, lotions and antibacterial creams. Various kinds of gas sensors, chemical and biological sensors were based on Zinc oxide thin films [9-11].

Zinc oxide generally represents the wurtzite crystal structure [12]. However, it is noteworthy that particle size, the quality of micro structure and the orientation of ZnO grains in particular directions were depend on the preparation methods and chemical and physical conditions of methods utilized in preparation. In this view, research community across the world has been continuously trying to modify and improve the structure and optical properties of the ZnO material by proper molding of structure and morphology.

ZnO films have been prepared by using various techniques, such as radio-frequency magnetron sputtering [13, 14], chemical vapor deposition [15], sol–gel method [16], atomic layer deposition [17], Laser ablation [18], thermal evaporation [19], pulsed laser deposition [20], and chemical spray pyrolysis (CSP) [21]. Spray pyrolysis is a promising method due to its low-cost nature and suitability for depositing large area thin-films [22].

In present study attempt has been made for synthesis of ZnO thin films at different substrate temperatures by simple spray technique using local available perfume atomizer. Structure, morphology and optical properties of deposited ZnO films have been estimated and discussed.

Martial and Method:

Experiment consists of pre-cleaned glass substrates were heated at different temperatures (150 to 350 ^oC) by simple digital hot plate on which clear precursor have been sprayed using locll available perfume atomizer. Precursor solution was prepared by dissolving reagent grade 0.1 M Zinc acetate hydrated (Zn $(CH3COO)_{2:}$ $2H_2O$) in distilled water. The solution was stirred by using magnetic stirrer for two hours till solution turn into clear homogeneous precursor. The clear precursor was sprayed on pre-heated glass substrates at different temperatures which were cleaned ultrasonically with organic solvents. The temperatures of the substrates were monitored by using automatic digital temperature controller. The distance of spraying nozzle form substrate 30 cm and spray rate of 5 ml per second were optimized previously.

Result and Discussion

XRD Patterns of spray deposited ZnO thin films are shown in figure 1. XRD spectra represent wurtzite hexagonal polycrystalline crystal structure confirmed by standard JCPDS card no. 75-1526. As the substrate temperature increased the intensity of (002) peak was found increased. At 250 ℃ substrate temperature the height of (002) peak was significantly increased. The film deposited at substrate temperature 300 ℃ exhibit dominant peak along (002) orientation. Similar results have been reported in pervious literature [12]. The XRD pattern revealed that monitoring the substrate temperature ZnO thin films can grow along particular direction (002). The martial growing along (002) direction was widely useful in solar cell device applications. Because (002) peak provides the lattice matching to the chalcogenide semiconductors used in solar cell devices [23]. The full width at half maximum (FWHM) was estimated using Lorentzian fitting of XRD data and presented in Table 1.

The crystallite size was estimated from full width at half maximum (FWHM) of (002) peak by using equation (1) [24].

$$\boldsymbol{D = \frac{0.94\lambda}{\beta COS\theta}} \qquad \text{--------------- (1)}$$

Where λ is wavelength of X-ray, 1.504 A^o, β is full width at half maximum (FWHM) of the peak and θ is the position of (002) peak. The crystallite size was presented in **Table.1.** All the films composed of ZnO nano crystals. The crystallite size for all film samples excluding ZnO (300 ℃) sample were exhibit approximately $\approx$20 nm crystallite size.

However the ZnO sample deposited at 300 °C show 26.32 nm larger crystallites as compared to other samples.

Table. 1. Showing thickness of the films, XRD data, Grain size of ZnO Thin films

Film Sample	2*θ* (degree	Inter planer spacing d (degree)	FWHM (Radians)	*hkl*	Crystallite Size D (nm)
ZnO (150 °C)	34.649	2.590	0.2309	(002)	20.19
ZnO (200 °C)	34.7589	2.579	0.2354	(002)	19
ZnO (250 °C)	34.7645	2.579	0.2546	(002)	19.80
ZnO (300 C)	34.9443	2.568	0.1762	(002)	26.32
ZnO (350 °C)	34.7717	2.582	0.232	(002)	20.02

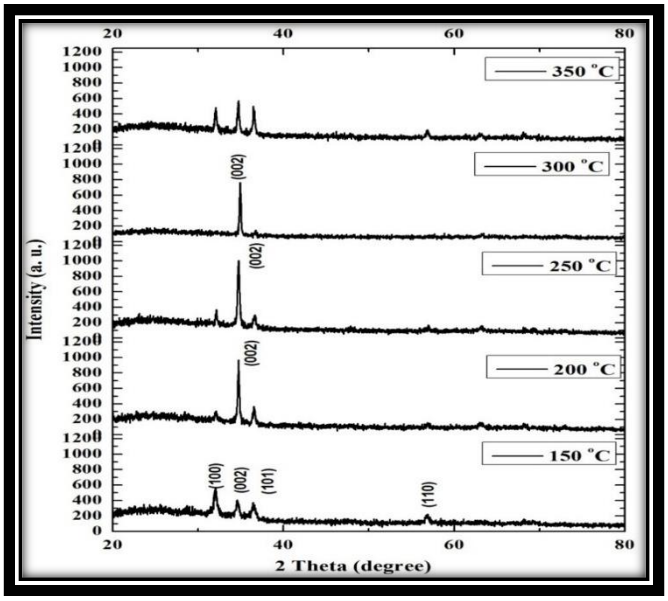


Figure 1.XRD Spectra of ZnO thin films

Surface Morphology of (ZnO 300 oC) Film Sample

The SEM micrograph of ZnO thin film deposited at 300°C was shown in Figure 2. The SEM image shows whole surface was uniformly coated with schematically arranged network of ZnO wires. The average diameter of ZnO wires was found to be 566 nm. The average size of ZnO grains is larger than crystallite size calculated from XRD data. This is due to agglomeration effect. The surface morphology support the growth of ZnO crystals along (002) direction which was explained in the XRD pattern.

Figure 2. SEM Micrograph of ZNO thin film deposited at 300 °C substrate temperature

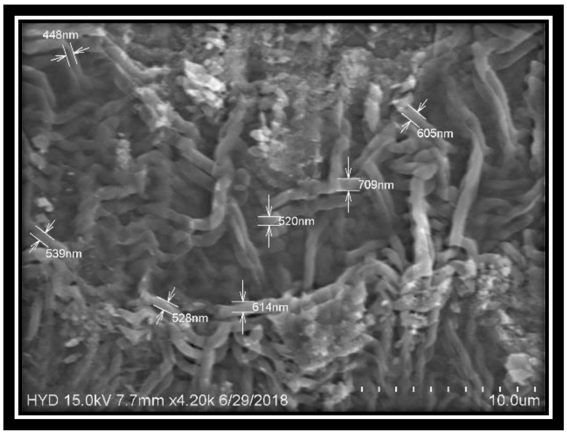
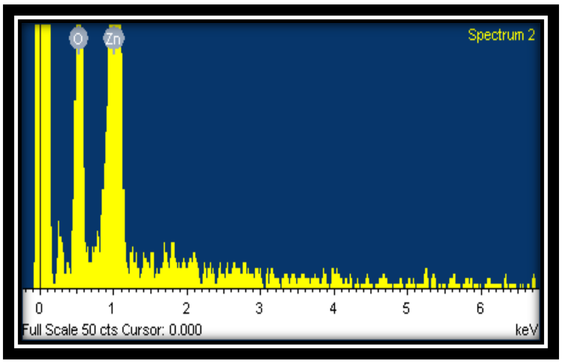


Figure 3. EDX spectra of ZNO thin film deposited at 300 °C substrate temperature



Elemental Analysis of (ZNO 300°C) Film Sample

Elemental analysis of ZnO thin film deposited for 300°C substrate temperature was carried out using EDX. Figure 3 shows the EDX spectra of ZnO thin film. The elemental analysis confirms that prepared sample composed by Zinc and Oxygen elements. There were no impurities present in the sample. The weight % and atomic % was shown in Table 2. The weight % and atomic % shows that deposited film sample is Oxygen reach.

Table. 2. Weight and Atomic % of composition of ZnO(300°C) film sample

Film Sample	Element	Weight%	Atomic%
ZnO (300 °C)	O K	22.32	54.00
	Zn L	77.68	46.00
	Totals	100.00	100.00

Effects of substrate temperature on Optical properties of ZnO thin films:

The optical absorption and transmittance spectra are recorded by using Systronics (2201) double beam spectrophotometer in the 300 to 1000 nm range and presented in figures 4 and 5 respectively. Figure 4 represents all ZnO films exhibit low absorption in the wide range from 360 to 1000 nm of the electromagnetic spectra. The absorption edge was found shifted slightly towards the blue side of the electromagnetic spectrum with increase in substrate temperature.

Figure 5 show all ZnO films exhibit higher transmittance up to 70 to 80% in the 360 to 1000 nm range. The low absorption and higher transmission is most important characteristics of the window layer used in solar cell device application [23].

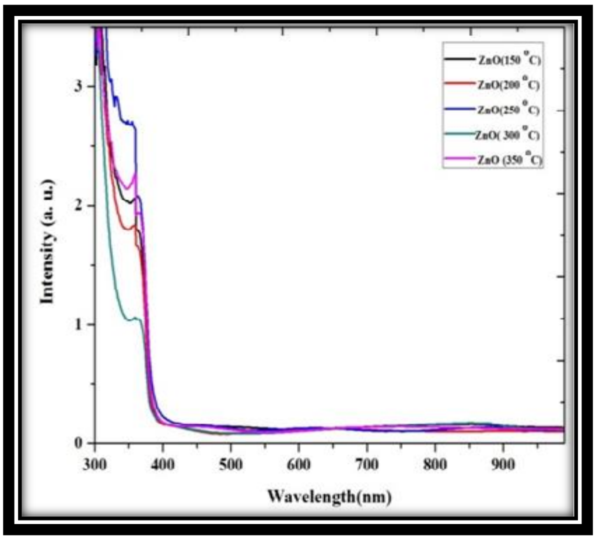


Figure 4. The Absorption Spectra of ZnO thin Films

The optical band gap can be obtained from the Tauc relationship. Tauc relation explains variation of the absorption coefficient α is linked to the band gap E_g of the material by the following expression [25]:

$$(\boldsymbol{\alpha h\nu}) = \boldsymbol{A}(\boldsymbol{h\nu} - \boldsymbol{Eg})^{\boldsymbol{n}} \qquad \textbf{(2)}$$

Where, E_g (eV) is the band gap energy and A is an energy-independent constant. The index n is theoretically equal to 1/2and 3/2 for direct allowed and forbidden transitions respectively. ZnO is direct band gap material therefore, n is set equal to 1/2. The band gap energy values E_g are calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus $h\nu$ plot, and shown in Figure 6. The shift of the absorption edge to shorter wavelengths indicates that the optical band gap increases with the substrate temperature in the growing process. The band gap obtained for ZnO films deposited at substrate temperatures 150, 200,250, 300, and 350 $°C$ were 3.12, 3.75, 3.76, 3.95, and 3.91 eV respectively. The variation of band gap with substrate temperature was presented in figure 7.

The observations confirm that the optical band gap increases with the substrate temperature during the growth. The similar finding has been

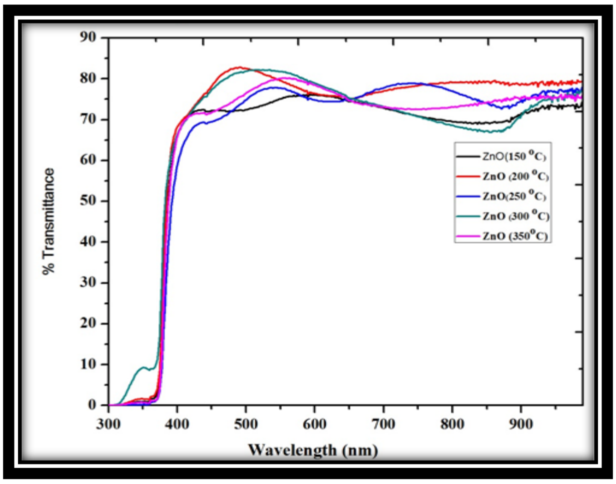


Figure 5. Plot of % transmittance verses wavelength (nm) of ZnO thin films

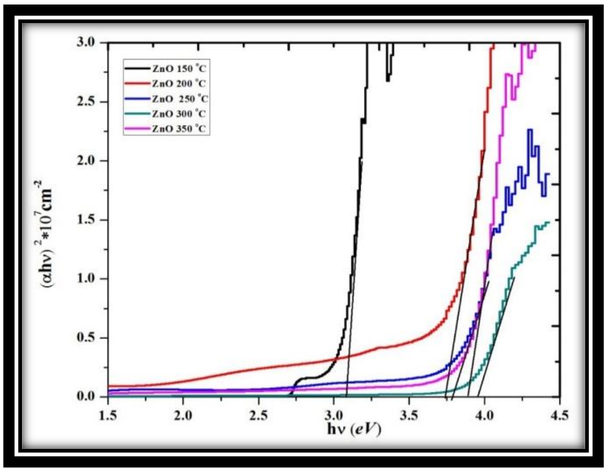


Figure 6. Tauc Plot of ZnO thin films

reported in earlier study [13]. The film deposited at 300 ℃ substrate temperature exhibit higher band gap (3.95eV).

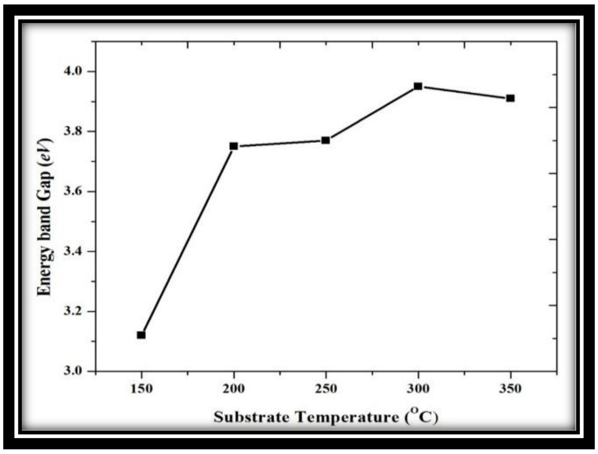


Figure 7. Variation of band gap energy verses substrate temperature

Conclusion:

ZnO thin films were deposited by using chemical spray pyrolysis using locally available perfume atomizer. XRD pattern confirm that peak intensity of (002) peak dependence on the substrate temperature. The film deposited for 300 ℃ temperature exhibit singe dominant peak at (002) lattice plane. This concluded that monitoring the substrate temperature ZnO thin films can grow along particular direction. The growth of ZnO crystals along (002) direction was confirmed by surface morphology of (ZnO 300℃)sample. The ZnO thin film was deposited for substrate temperature 300 ℃ exhibit higher band gap, larger crystallite size (26.32 nm) and excellent network morphology of ZnO wires can be used in solar cell device application as window layer material. Therefore it is concluded that optimum value of substrate temperature is 300 ℃ for deposition of ZnO thin films using presently reported spray pyrolysis technique,

Acknowledgement:

The authors are grateful to Director Physics Research Centre, Shri Sant Gadge Magharj College, Loha (M. S.) India for providing research facilities.

References:

[1]. J. B. Baxter and E. S. Aydil, "Dye-Sensitized Solar Cells Based on Semiconductor Morphologies with ZnO Nano- wires," Solar Energy Materials and Solar Cells: 90 (5) (2006) 607-622

[2]. N.R More, U.B Chanshetti, "Review Article on ZnO thin films by Spray Pyrolysis," International Journal of Chemical and Physical Sciences: 7, Special Issue, RACBS (Feb 2018) 51-54

[3]. S. T. Shishiyanu, T. S. Shishiyanu and O. I. Lupan, "Sensing Characteristics of Tin-Doped ZnO Thin Films as NO2 Gas Sensor," Sensors and Actuators B Chemical.: 107 (1) (2005) 379-386

[4]. J. M. Szarko, J. K. Song, B C. W. Lackledge, I. Swart, S. R. Leone, S. Li, *et al*., "Optical Injection Probing of Sin-gle ZnO Tetrapod Lasers," Chemical Physics Letters: 404 (1-3) (2005) 171-176

[5]. T. Ootsuka, Z. Liu, M. Osamura, Y. Fukuzawa, R. Kuroda, Y. Suzuki, *et al*., "Studies on Aluminum-Doped ZnO Films for Transparent Electrode and Antireflection Coating of *β*-FeSi2 Optoelectronic Devices," Thin Solid Films: 476 (1) (2005) 30-34

[6]. Keis, C. Bauer, G. Boschloo, A. Hagfeldt, K. Westermark, H. Rensmo, H. Siegbahn, J. Photochem. Photobiol. A: 148 (2002) 57

[7]. Junhee Cho, Seongkwon Hwang , Doo-Hyun Ko and Seungjun Chung,"Transparent ZnO Thin-Film Deposition by SprayPyrolysis for High-Performance Metal-OxideField-Effect Transistors," Materials: 12 (**2019)** 1-14 doi:10.3390/ma12203423

[8]. X. Yu, J. Ma, F. Ji, Y. Wang, X. Zhang and H. Ma, "In- fluence of Annealing on the Properties of ZnO: Ga Films Prepared by Radio Frequency Magnetron Sputtering," Thin Solid Films: 483 (1-2) (2005) 296-300

[9]. S.J. Lim, S. Kwon, H. Kim, "ZnO thin films prepared by atomic layer deposition and rf sputtering as an active layer for thin film transistor", Thin Solid Films: 516 (2008) 1523–1528.

[10]. T. Maruyama, J. Shionoya, "Zinc oxide thin films prepared by chemical vapour deposition from zinc acetate", Journal of Material Science Letter: 11, (1992)170–172

[11]. J. Ma, F. Ji, D. Zhang, H. Ma and S. Li, "Optical and Electronic Properties of Transparent Conducting ZnO and ZnO: Al Films Prepared by Evaporating Method," Thin Solid Films: 357(2) (1999) 98-101

[12]. J. Srinivasan, Kumar, "Optical and structural characterization of zinc oxide thin films prepared by sol-gel process", Cryst. Res. Technol.: **41** (2006) 893–896

[13]. A. Goktas, F. Aslan, I. H. Mutlu, "Effect of preparation technique on the selected characteristics of $Zn_{1-x}Co_xO$ nanocrystalline thin films deposited by sol–gel and magnetron sputtering" Journal of Alloys Compounds, 615 (2014) 765–778

[14]. M. Bouderbala, S. Hamzaoui, B. Amrani, A. H. Reshak, M. Adnane, T. Sahraoui and M. Zerdali, "Thickness dependence of structural, electrical and optical behavior of undoped ZnO thin films", Physica B: 403 (2008) 3326–3330.

[15]. M.G. Faraj, K. Ibrahim, "Optical and structural properties of

thermallyevaporated zinc oxide thin films on polyethylene terephthalate substrates", International J. Polymer Science: 12 (2011) 302843

[16]. L. Zhao, J. Lian, Y. Liu, Q. Jiang, "Structural and optical properties of ZnO thin film deposited on quartz glass by pulsed laser deposition", Appllied Surface Science: 252 (2006) 8451–8455

[17]. J. Zou, S. Zhou, C. Xia, Y. Hang, J. Xu, S. Gu, "Structural Optical and Electrical roperties of ZnO Films Grown on c-Plane Sapphire and (1 0 0) γ-LiAlO2 by Pulse Laser Deposition," Journal Crystal Growth: 280 (1-2) (2005) 185-190

[18]. R. Ayouchi, D. Leinen, F. Martín, M. Gabas, E. Dalchiele, J.R. Ramos-Barrado, "Preparation and characterization of transparent ZnO thin films obtained by spray pyrolysis", Thin Solid Films 426 (2003) 68–77

[19]. A. Serdar, T. Guven, Y. Mehmet, E. Mehmet, " Fabrication of Nanorods by Simplified Spray pyrolysis", Journal of Science and technology: 1(2004) 1-3

[20]. K. Ravichandran, P. philominathan, "Investigations on microstructural and optical properties of CdS films fabricated by a lo-cost simplified spray technique using perfume atomizer for solar cell applications", Solar Energy. 82 (2008) 1062-106

[21]. Nadia Chahmat, Ammar Haddad, Azzedine Ain-Souya, Rachid Ganfoudi, Nadir Attaf, Mouhamed Salah Aida, Mokhtar Ghers," Effect of Sn Doping on the Properties of ZnO Thin Films Prepared by Spray Pyrolysis", Journal of Modern Physics: 3 (2012) 1781-1785

[22]. D. A. Lamb and S. J. C. Irvine, "Growth Properties of Thin Film ZnO Deposited by MOCVD with n-Butyl Alcohol as the Oxygen Precursor," Journal Crystal Growth: 273 (1-2) (2004) 111-117

[23]. S. Rajathi, N. Shankarasubramaniam, K. Ramanathan, M. Senthamizhselvi, "Structural and Optica electronic Properties of Pyralyticall Spraed CdZnS Thin Films", Chalcogenide Letters: 9 (12) (2012) 495-500,

[24]. Cullity B.D. & Stock, S.R. (2001*)*. Elements of X-Ray diffraction (3rd ed.), Prentice Hall

[25]. J. Tauc, (1974) Amorphous and Liquid Semiconductors, Plenum, London