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Structural and Optical Characterization of Chemically Synthesized Nanostructured Zinc Oxide Thin Film

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Abstract
Zinc Oxide (ZnO) thin film has been synthesized using the chemical spray pyrolysis technique and ethylene glycol has been used as solvent during the synthesis. X-ray diffraction (XRD) results show cubic and tetragonal phases of ZnO and the grain size was calculated to be 2.57nm. Optical characterization reveals very high transmittance within the visible-ultraviolet region and a bandgap of 3.49 eV was obtained for ZnO thin film. Scanning Electron Microscopic (SEM) analysis showed a void-free non-homogenous surface.
Keywords: *ZnO; Spray pyrolysis; Ethylene glycol; Grain size.*

INTRODUCTION

Zinc oxide (ZnO) has distinguished itself as an excellent, novel material in the fields of water engineering where it is applied as biomolecule in water purification (Deak *et al.,* 2019) and more importantly optoelectronics where it finds applications as semiconductor in thin film transistors (Goyal and Kachhwaha, 2012), light emitting diodes , ultraviolet spectra detector, gas detectors (Foo *et al.*, 2014) and solar cells (Kolodziejczak – Radzimska *et al.*, 2014; Hussein *et al.*, 2015; Muchuweni *et al.,* 2017). ZnO has a wide direct energy bandgap of about 3.37 eV, high thermodynamic stability, high optical transparency and environmentally benign properties, making it a good candidate for thin film solar cell fabrication (Muchuweni *et al.*, 2017). Due to the scarcity of indium, ZnO can be considered as a potential replacement of the popular indium titanium oxide (ITO) as transparent conducting oxides in solar cell (Werner *et al.*, 2015; Diwater *et al.,* 2016). It can also serve as replacement for cadmium sulphide (CdS) as n-layer in thin film heterojunction device since cadmium has been reported to cause health related issues in humans (Rahimzadeh *et al.*, 2017; Offor *et al.,* 2015). Several techniques, both physical and chemical, has been employed in the deposition of ZnO thin films. The techniques include, radio frequency (RF) sputtering (Vyas *et al.*, 2015; Stamate, 2019), thermal evaporation (Stamate, 2019; Faraj and Ibrahim, 2011), chemical vapour deposition (Hassan and Kashim, 2013), sol-gel (Konan *et al.*, 2019), electrodeposition (Kumar and Sasikumar, 2014), chemical bath deposition (Huang *et al.*, 2012; Thool *et al.*, 2014) and chemical spray pyrolysis (Tecaru *et al.*, 2010; Cho *et al.*, 2019). Spray pyrolysis stands out as a simple and low cost deposition technique which does not require a high vacuum environment. Spray pyrolysis promotes spherical morphology of films and narrow particle size distribution. The spray pyrolysis technique can be increased to industrial scale and is applicable over a large area. Stoichiometry can also easily be controlled in spray pyrolysis. Several parameters which includes drying temperature, spray rate, nozzle to target distance, precursor and solvent govern the properties of spray-deposited ZnO thin films (Rajeshmon, 2013; Jeyadheepan *et al.*, 2019). The influence of solvent on spray-deposited thin films is very crucial because, the residence time of microsized droplets in drying chamber is heavily dependent on vapor pressure of the solvent. Water, which has been the most popular solvent in preparing chemical solutions has a high vapour pressure. For most researchers, the need to add drops of acid into precursor solution usually arises due to formation of precipitates. In recent times, the influence of solvents on structural, optical and electrical properties of chemically synthesized ZnO thin films and nanoparticles has been reported though, a deeper explanation of how the solvents affect these properties has not been provided. In this work, ZnO thin film has been synthesized by spray pyrolysis technique using ethylene glycol as solvent for precursor preparation.

MATERIALS AND METHODS

Experimental details

Zinc precursor solution (0.025 M) was prepared by dissolving zinc acetate dihydrate ($(Zn(CH_3CO_2)_2.2H_2O)$ in ethylene glycol ($(CH_2OH)_2$). The mixture was stirred for 60 minutes using magnetic stirrer. 30 ml of the solution was sprayed in open air on glass substrates that has been cleaned ultrasonically in acetone heated to 60^{o}C centigrade. The spraying was done at a pressure of 60 psi, spray rate of 2ml per minute and spray to target distance was maintained at 28 cm. The substrate temperature was maintained at 300^{o}C during the spraying. The spray pyrolysis experimental setup is home-assembled and is shown in Figure 1. The sample was allowed to cool to room temperature and later annealed in a muffled furnace at 300^{o}C for 120 minutes All reagents used in preparation of the mixture are analytical grade and were purchased from Sigma Aldrich.

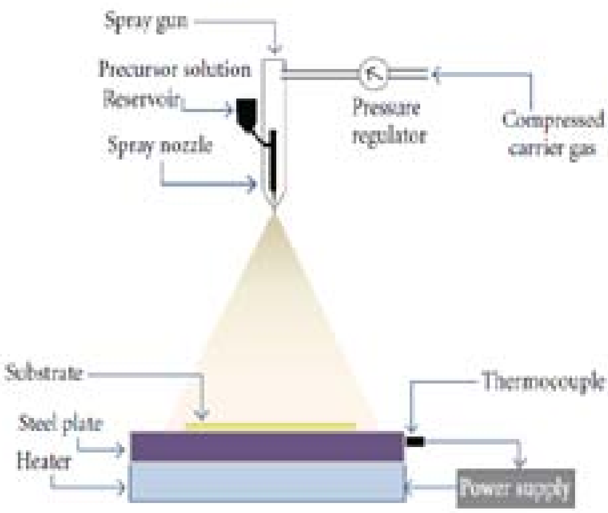

Figure 1. Schematic diagram of spray pyrolysis setup (Patil *et al*, 2012).

Characterization of ZnO thin films

The structural properties of synthesized ZnO thin film samples were studied using a Rigaku D/Max-IIIC X-ray diffractometer with a lynx eye detector using a copper target (Cuα,1.5418 Å). All X-ray diffraction (XRD) data for the specimens were recorded at current and acceleration voltages of 25mA and 40 kV respectively. Surface morphology of the samples were studied by using Hitachi scanning electron microscope (SEM) and optical characterization was done using UV-vis spectrophotometer of CyberLab (model no. UV-100).

RESULTS AND DISCUSSION

Structural properties

The XRD pattern of ZnO is shown in figure 2. Peaks can be observed at 2θ equals 32.2^o, 34.2^o, 36.0^o, 47.8^o, and 56.0^o which can be indexed to (100), (002), (101), (102), and (102) reflection planes of hexagonal wurzite ZnO. The peaks matched well with standard JCPDS pattern for ZnO (file number: 043-0002). Broadening of the peaks is an evidence of nanosized grains present in synthesized ZnO. The grain size was calculated from the (002) preferred orientation to be 2.57 nm. The Scherrer formula is written as

$$G = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where G is the grain size, λ is the CuKα, β is the full width at half maximum and θ is the angle of diffraction. The results are in agreement with previous works that have reported cubic and hexagonal phases of ZnO (Chandappa and Venkatesha, 2012; Kumar *et al.*, 2014; Munoz-Aguirre *et al.*, 2019). The vapour pressure and polarity of the solvent may have been responsible for the nano-sized grains of the synthesized ZnO thin film. Ethylene glycol has very low vapour pressure and high dipole moment [34]. The low vapour pressure will increase the residence time of the microsized droplets during spraying which will prevent the droplets from drying too quickly, or blown away before it reaches the substrate. Relatively high grain sizes have been reported for ZnO thin films prepared by alcohol, deionized water or a mixture of both (Boukaous *et al.*, 2014; Benramache *et al.*, 2014; Bekkari *et al.*, 2019). We propose that a higher aggregate formation can be as a result of loose coiling of chemical bonds which causes a reduction in solvent polarity, and consequently, smaller aggregates are formed during thermal decomposition of solution, in which the solvent has higher dipole moment. The relationship between grain size and vapour pressure has been reported by Chin *et al.* (2019). The vapour pressure and dipole moment of some liquids that has been reported in literature on preparation of ZnO is shown in Table 1.

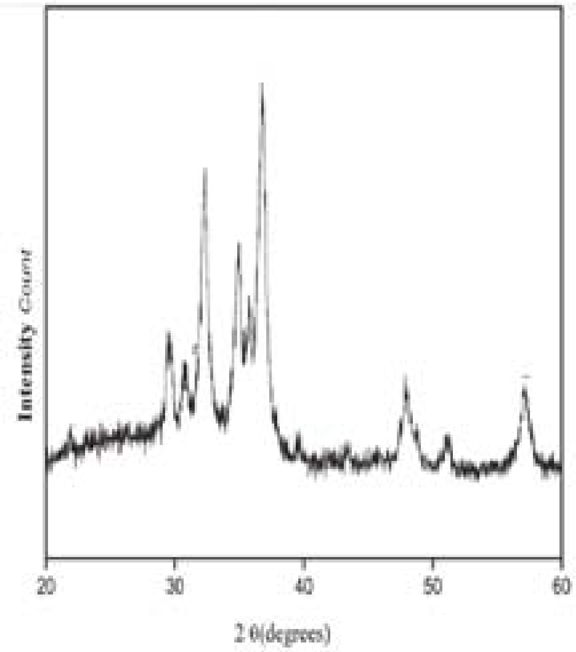

Figure 2: XRD patterns for ZnO thin film.

Table 1. Dipole moments and vapour pressures of solvents

Solvent	Dipole Moment (Debye)	Vapour Pressure (kPa)
Alcohol	1.660	5.950
Water	1.850	2.400
Ethylene Glycol	2.747	0.007

(Stamate, 2019; Patil *et al,* 2012).

Optical properties

The plot of transmittance and absorbance versus wavelength for ZnO thin film are shown in Figures 3 and 4. It can be observed that more than 80% transmittance was recorded within the ultraviolet – visible region. The smoothness of the curve and absence of interference pattern is an indication of homogeneity and low surface roughness of the film. A spike in the ultraviolet absorption edge from blueshift to redshift can be observed around 375 nm. The bend of the plot of absorbance versus wavelength can be observed at 350 nm. This observation is consistent with previous reports on the optical properties of ZnO (Tang *et al.*, 2013; Foo *et al.*, 2014; Marouf *et al.*, 2017). The optical bandgap of ZnO thin film was calculated from the Tauc's plot to be 3.49 eV and the plot is shown in figure 5. The plot is derived from equation 2.

$$(\alpha hf)^{1/n} = A(hf - E_g) \qquad (2)$$

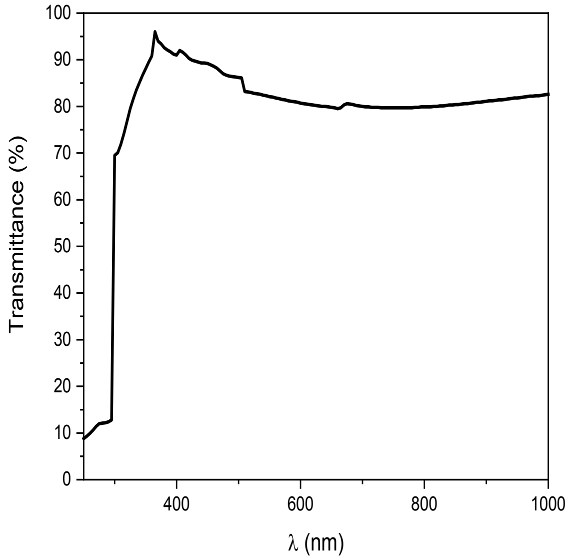

Figure 3: Transmission spectra of ZnO thin film

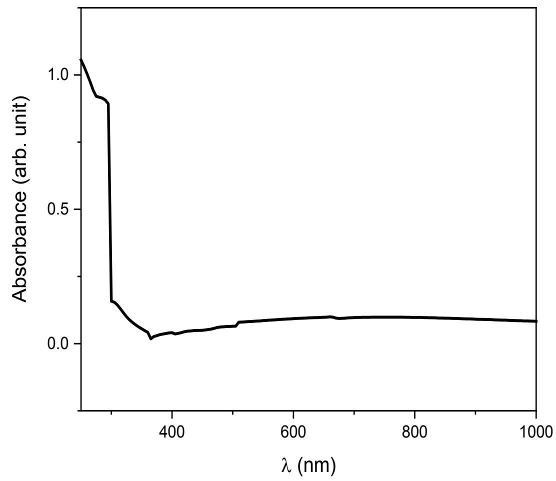

Figure 4: Absorption spectra of ZnO thin film

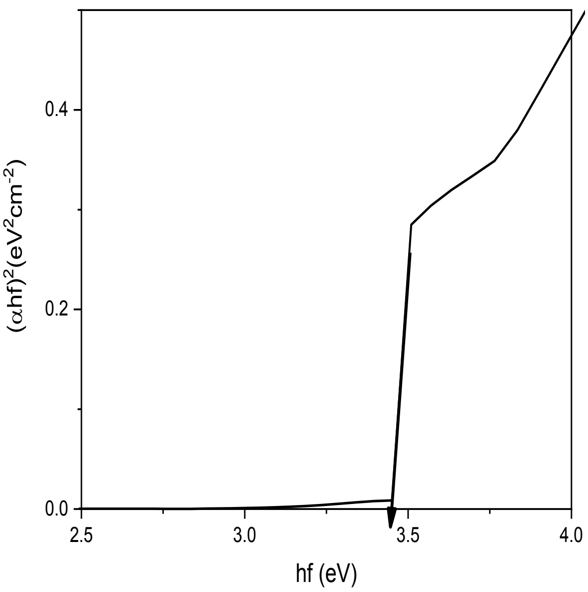

Figure 5: Optical bandgap of ZnO thin film.

Morphological Properties

Flower like morphology can be observed in ZnO thin film shown in Figure 6. The SEM image shows a rough non-homogenous grains surface with voids absent. Flower shape morphologies have been reported in previous works on synthesis of ZnO that have shown the best optical response for solar cell applications (Stamate, 2019; Qiu *et al.*, 2014).

Compositional Analysis

The composition of the sprayed ZnO thin film layer was carried out by energy dispersive X-ray spectrophotometer and the EDX spectra is shown in Figure 7. The analysis showed the presence of zinc and oxygen in the ZnO thin film sample.

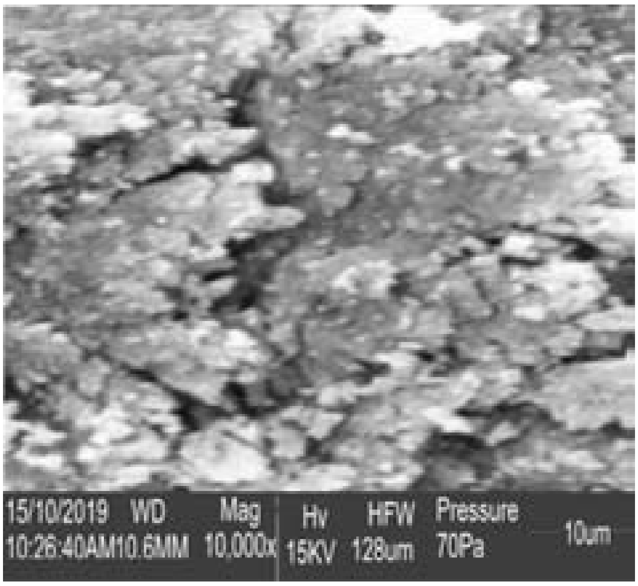

Figure 6: SEM micrograph of ZnO thin film.

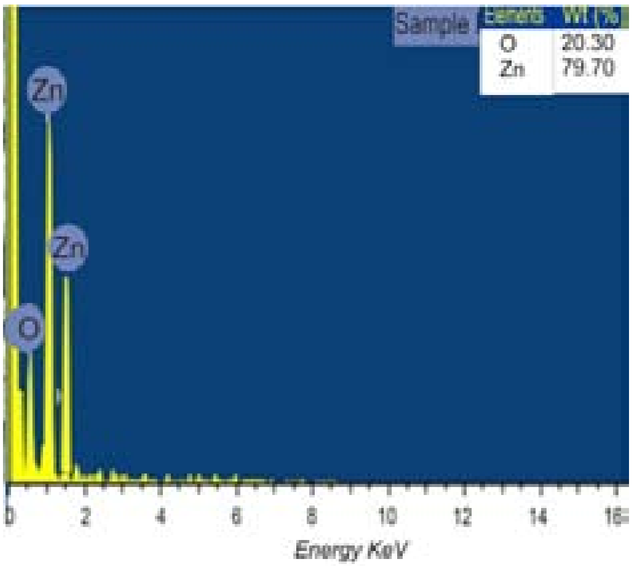

Figure 7: EDX spectra of ZnO thin film.

Conclusion

ZnO thin film have been deposited using chemical spray pyrolysis technique using ethylene glycol as solvent. Cubic and tetragonal phases of ZnO were revealed by XRD study with the film having high orientation along the (002) direction. The small grain size is evidence that the synthesized ZnO thin film is nanostructured. The film exhibited very high transmittance and low absorbance within the visible-ultraviolet region of electromagnetic spectrum with a bandgap of 3.49 eV. SEM image revealed a surface free of voids.

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