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Synthesis and Functional Group Analysis of Solution Processed Zinc Oxide Thin Film Grown on Polyethylene Terephthalate

Mahima Asthana[1,*], Shri Kant[2]

Abstract

Flexible electronics field is growing every day. Existing technology is facing issues like brittleness, toxicity, inadequacy. Fabrication cost increases in processing of such materials. In this work, zinc oxide nanoparticles synthesized by solution processing technique were used to grow 120nm thick thin film (TF) on Polyethylene terephthalate (PET). This method reduces the processing cost and Zinc Oxide (ZnO) is cheaper and abundant in comparison to other semiconductors option. Material was synthesized by dissolving Zinc acetate, using ethanol as solvent. Sol gel was obtained using dissolution of colloidal solution followed by gelation. Spin coater technique was used for film deposition, followed by annealing at 300°C. Chemical composition, Structure and optical properties of PET substrate were analyzed by Energy Dispersive X-ray (EDX) Analysis, Fourier Transform-Infrared (FT-IR) spectroscopy, X-Ray Diffraction (XRD) and Ultra-violet (UV) Spectroscopy. Impact of substrate was also observed by characterization of substrate before deposition of thin film layer. Hexagonal wurtzite structure was obtained after annealing at 300°C, confirmed by XRD graphs. The FT-IR spectra confirmed the presence of strong covalent bonds confirming chemical presence of all the compounds of film and substrate. EDX images confirmed the elemental presence of Zinc and oxygen. UV visible absorption spectra confirmed the absorption in desired band. Band gap calculated was around 3.00eV, which makes it wide band gap TF. This work appears to be suitable for optoelectronics and piezoelectric applications like sensors, photo-detectors, actuators.

Keywords: PET, ZnO, Thin films, FT-IR Spectra, Band gap

INTRODUCTION

Wearable electronic devices like watches, rings, foldable mobile phones etc are emerging as popular choice among people. This enhances the need of advancement in field of flexible and transparent electronics materials and substrates is there. Devices suitable for flexible electronics need to be light in weight and have better performance characteristics. Material of substrate is crucial parameter in electronic devices. Films are grown on substrates, so it plays important role in device structure and could be responsible for variations in properties. Researchers were using wide range of substrate materials like Silicon wafer, clean bare glass, PET plastic, semi-transparent polyamide foil, Cr glass bearing, alkali free glass, quartz and elastomeric substrates [1][19][20][21]. Brittleness of glass and silicon makes it poor choice for flexible electronics. Polymer substrates are gaining popularity as a material for substrates. Polymers do not absorb light in visible range, thus causes negligible effect on optical properties of prepared devices. PET is produced in large quantity across the world for various application like fibres, textiles etc. PET

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consists of (C10H8O4) units in repetition. Its Chemical structure is shown in Figure 1 [2]. Various researchers experimented with semiconductor materials like Cadmium Telluride (CdTe), Indium Gallium (IG) etc [3]. Such materials offer better efficiency but are toxic in nature and processing cost is high. These things encouraged researchers to find alternatives in Transparent Conductive Oxides (TCOs).

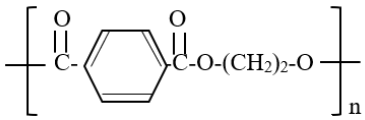

Figure 1. Chemical structure of unit cell of PET.

Various TCO are popular for touch screens, sensors, displays all over the world. Zinc oxide (ZnO) is wide band TCO, which is popular among researchers for its unique structural and optical properties. Hexagonal wurtzite crystal structure is most stable and desirable structure for optoelectronics devices [4]. Such structure consists of two connected interpenetrating hexagonal sublattices, for both Zinc cations and Oxygen anions. Hexagonal wurtzite structure of ZnO is shown in Figure 2.

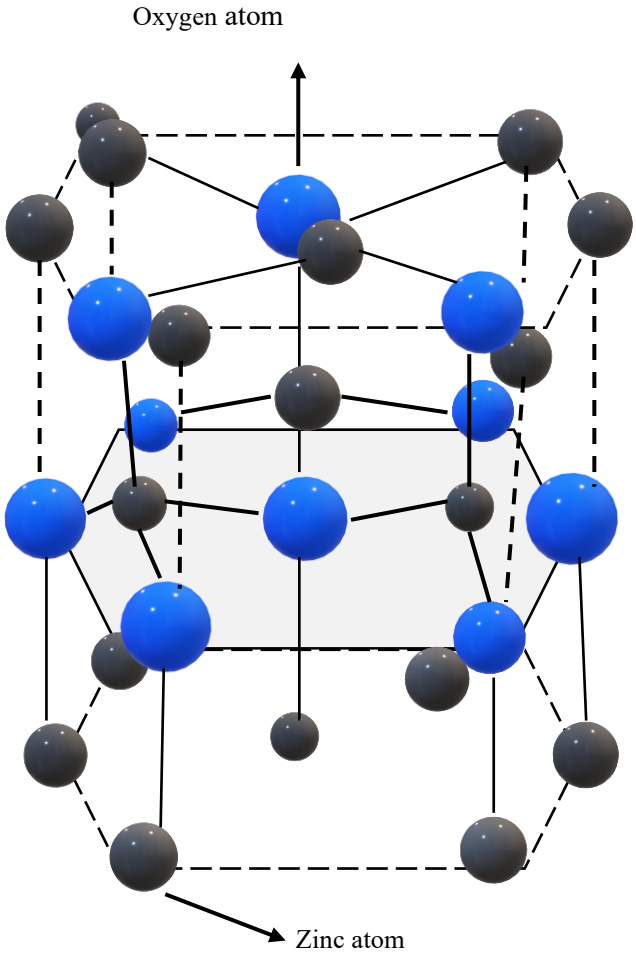

Figure 2. Hexagonal Wurtzite Structure of crystal of ZnO.

This structure results in robust and stable ZnO material with strong interatomic bonds exhibiting good mechanical strength. Non-centrosymmetric structure of material exhibits piezoelectricity when subjected to mechanical stress. Due to this structure ZnO has wide band gap of around 3.37 eV [5]. This

work is using Indium Tin Oxide coated Polyethylene terephthalate (ITO-PET) as substrate for deposition of ZnO Thin film (TF). ITO layer provides conducting path and ITO ZnO layer has ohmic contact between them, that minimizes energy barrier and promotes efficient charge injection/extraction in devices. Optical transparency is additional benefits of such substrates. Physical vapour deposition techniques are popular but those methods are complex and expensive. In this work, cost efficient solution processing technique with spin coating is used in deposition of thin film of ZnO on ITO-PET substrates. Next section will give overview about materials used, synthesis process and deposition technique. This will be followed by characterization techniques, result discussion and conclusion.

MATERIALS

ITO-PET, Polyethylene terephthalate film, Indium Tin Oxide (ITO) coated, surface resistivity 60Ω/square, L x W x thickness 1feet x 1 feet x 5mil by Sigma-Aldrich was used as substrate. Transmittance of sheet was reported at 550 nm, Coating is of In_2O_3/SnO_2 (This information is provided by seller). Absolute Ethanol (C_2H_5OH) (99.9% pure) was solvent for this process. Zinc acetate dihydrate ($Zn\ (CH_3COO)_2.2H_2O$) by CDH Fine Chemicals (99% purity) was precursor material, Ethanolamine (mono) (C_2H_7NO) (MEA), by Loba Chemie Pvt. Ltd (99% pure) was stabilizer for process.

Synthesis of Material

Sol-gel technique is used for synthesis of materials. This is based on principle of colloidal chemistry, based on dissolution of raw materials (mainly powder) in solvent, and further transformed into homogeneous solutions. Dispersed phase obtained is transferred into gel. The solution was prepared by dissolving 0.37 mole of Zinc acetate dihydrate with 50ml of Ethanol to undergo hydrolysis. This solution was stirred on magnetic stirrer at speed of 250 rpm for 15 minutes at room temperature and then heated at 50°C on stirrer for another 15 minutes. MEA was added to solution drop by drop to maintain molar ratio of MEA to Zinc acetate as 1. Solution was stirred after obtaining transparency for 2 hours. This solution undergoes polycondensation reaction to form colloid of ZnO dispersed in ethanol. This solution evolves through Gelation process after resting at room temperature for 24 hours.

Deposition and Annealing

Thin film of prepared ZnO gel was deposited using spin coating technique. Substrate was thoroughly cleaned by placing it in ultrasonic bath filled with Acetone and sonicated for 15 minutes at 50°C, to dislodge particles stuck on surface. Substrate was rinsed assiduously with De-ionized (DI) water for 10 minutes and later on it was dried at clean place in air [17]. For spin coating, cleaned substrate was rotated at speed of 2000rpm, at room temperature for 30 seconds and dried at around 50°C for 10 minutes.

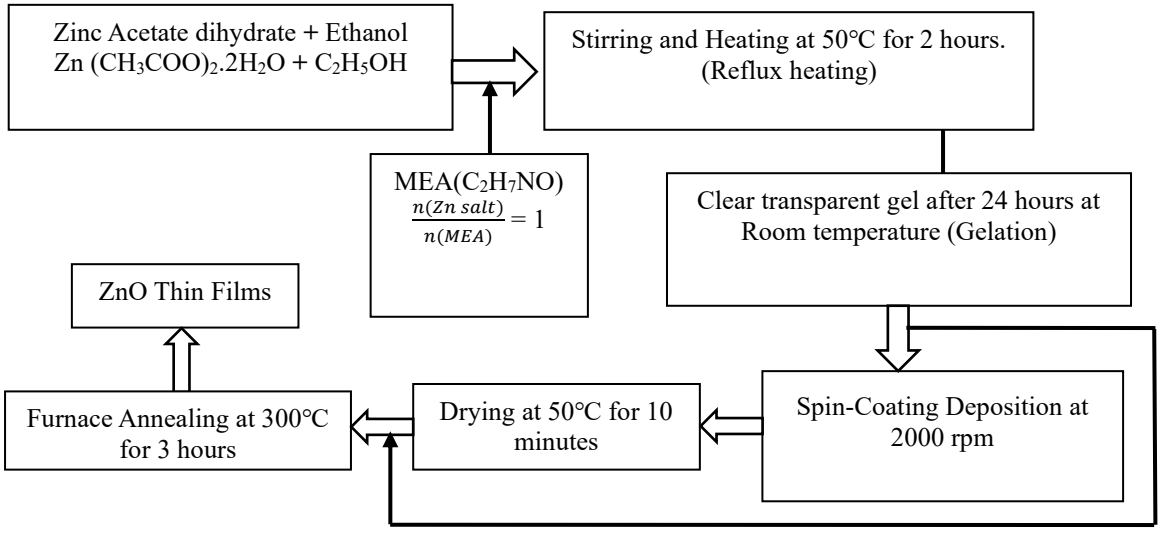

Figure 3. Process Flow of Sol gel Spin coating method of deposition of ZnO thin film.

This process could be repeated at desired number of times for getting thin films of desired thickness, here it was repeated 5 times to get approximately 120nm thickness. Film was annealed at 300°C for 3 hours in air. Figure 3 is showing process of thin film deposition through Sol gel spin coating technique.

RESULTS AND DISSCUSSION

This section will be providing information about chemical composition and bonding of thin film using Fourier-Transform Infrared Spectroscopy (FT-IR) and Energy-Dispersive X-ray Spectroscopy (EDX). Structural analysis is done using X-Ray Diffraction (XRD). Ultra-Violet Visible spectroscopy (UV) is done to measure absorption spectra of thin film.

FT-IR Spectroscopy

FTIR spectra were recorded using Perkin Elmer's FTIR spectrometer. This gives insight into bonding environment and chemical composition of TFs. Intensity and sharpness of peaks provides information about the film's quality. Measurements are done in range 400 cm-1 to 4000 cm-1 in ATR mode. Figure 4 shows the FTIR of ITO-PET substrate. Characteristic peaks required are clear and sharp in spectra [8]. Wavenumber (υ) and corresponding functional groups are discussed in table 1 [6].

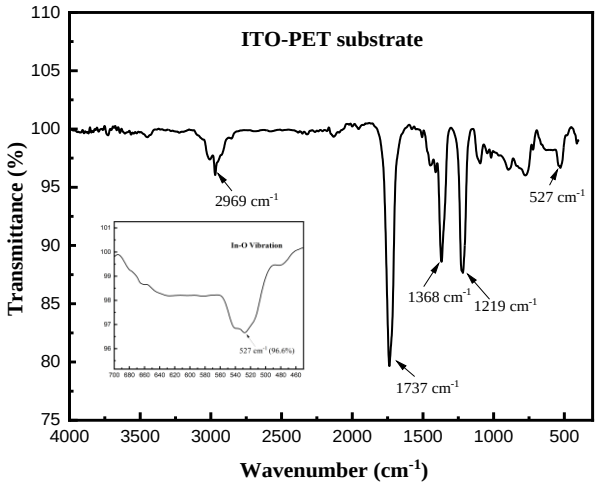

Figure 4. FTIR Spectra of PET Substrate, inset fig: Peak corresponding to In-O vibration.

Table 1. FT-IR Inference of ITO-PET.

S.N.	υ (cm^{-1})	Functional Group
1.	527	In-O Vibration
2.	1219	C-O stretch (Ethers)
3.	1368	N=O Bend (Nitro Groups)
4.	1737	C=O stretch (Aldehydes)
5.	2969	H-C-H (Alkanes)

This spectrum confirmed the presence of Indium, Oxygen. Vibrations at 527 cm-1, corresponding to that confirms it. All other vibration peaks are due to PET [6]. Figure 5 Shows the FT-IR Spectra of ZnO Thin film.

Table 2 shows the functional group corresponding to peak values [7].

This spectrum confirmed the presence of ZnO. Vibrations at 417 cm-1, and 671 cm-1 confirms the desired bonds [9]. Carbon bond peaks intensity and sharpness is reduced in TF's spectra. Presence of

additional groups is due to synthesis method. However, ZnO having two vibration indicates variation in crystal size in thin film. This will be further analyzed by XRD.

Table 2. FT-IR Inference of ZnO TF.

S.N.	υ (cm^{-1})	Functional Group
1.	417	Zn-O stretching
2.	515	In-O Vibration
3.	671	Zn-O Bond
4.	1020	C-O stretch (Ethers)
5.	1403	N=O Bend (Nitro Groups)
6.	1550	N=O Stretch (Nitro Groups)
7.	1730	C=O stretch (Aldehydes)
8.	2964	H-C-H (Alkanes)
9.	3278	≡ C-H stretch (Alkynes)

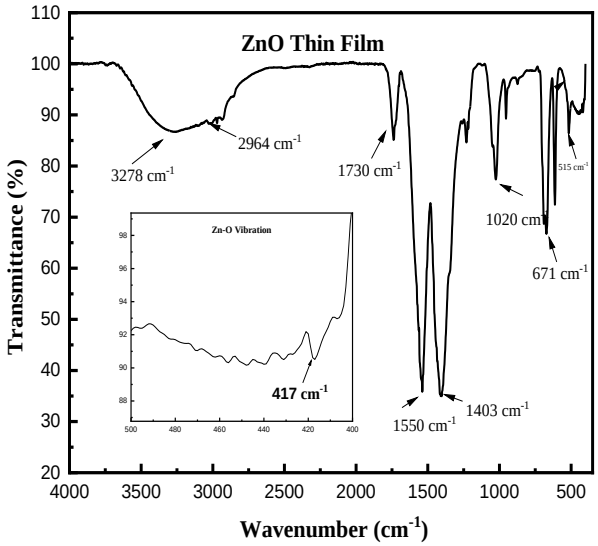

Figure 5. FTIR Spectra of ZnO TF, inset fig: Peak corresponding to Zn-O vibration.

Energy-Dispersive X-ray Spectroscopy (EDX)

This was done to confirm the elemental analysis of area within the thin film. The elemental composition of ZnO TF is shown in figure 6. This composition clearly exhibits that thin film of ZnO is grown properly as Carbon (from PET) is not having major presence in film. Uniformity in deposition is analyzed by Map data of the film. This data gives clear insight of the presence of elements. Mapa data is shown in figure 7.

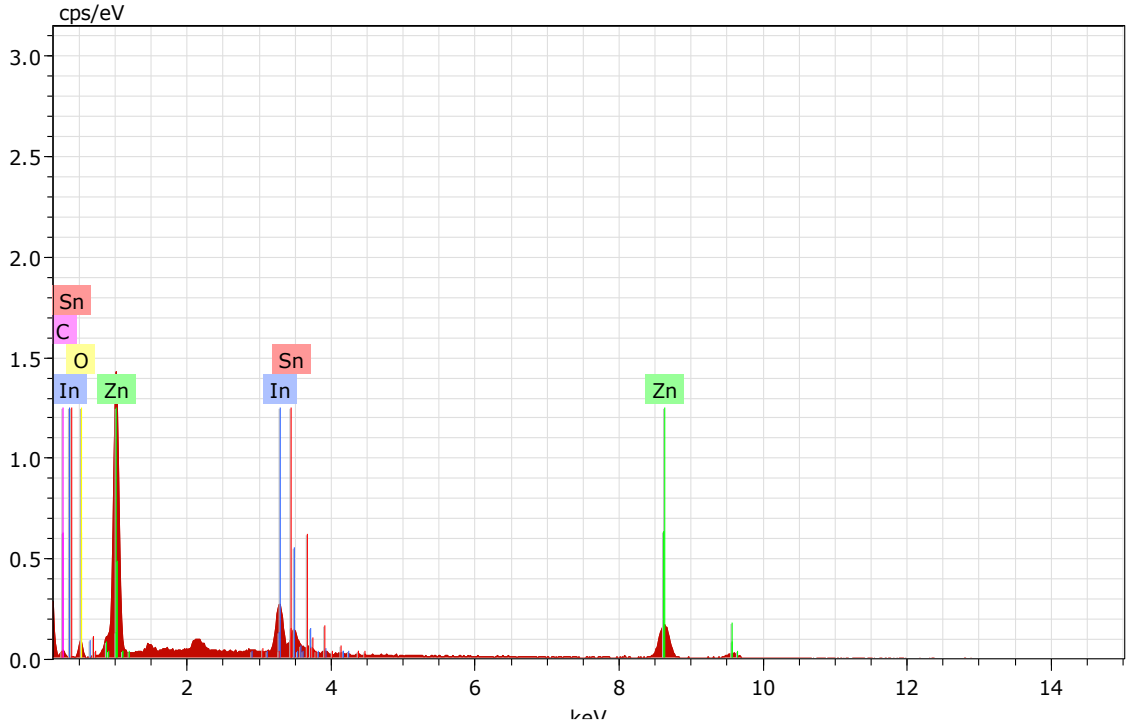

Fig 6. Elemental composition of TF by EDX.

This EDX mapping clearly indicates that sample is having Zinc, Oxygen. Presence of Indium, Tin, Carbon is due to substrate. Table 3 shows the elemental composition of TF.

Table 3: Elemental composition of ZnO TF on ITO-PET

Elements	C norm (wt.%)	C Atom (at%)	C Error (%)
Zn	70.21	58.67	2.31
O	3.10	10.56	0.72
In	16.79	8.86	0.53
Sn	1.17	0.58	0.08
C	8.73	21.33	1.04

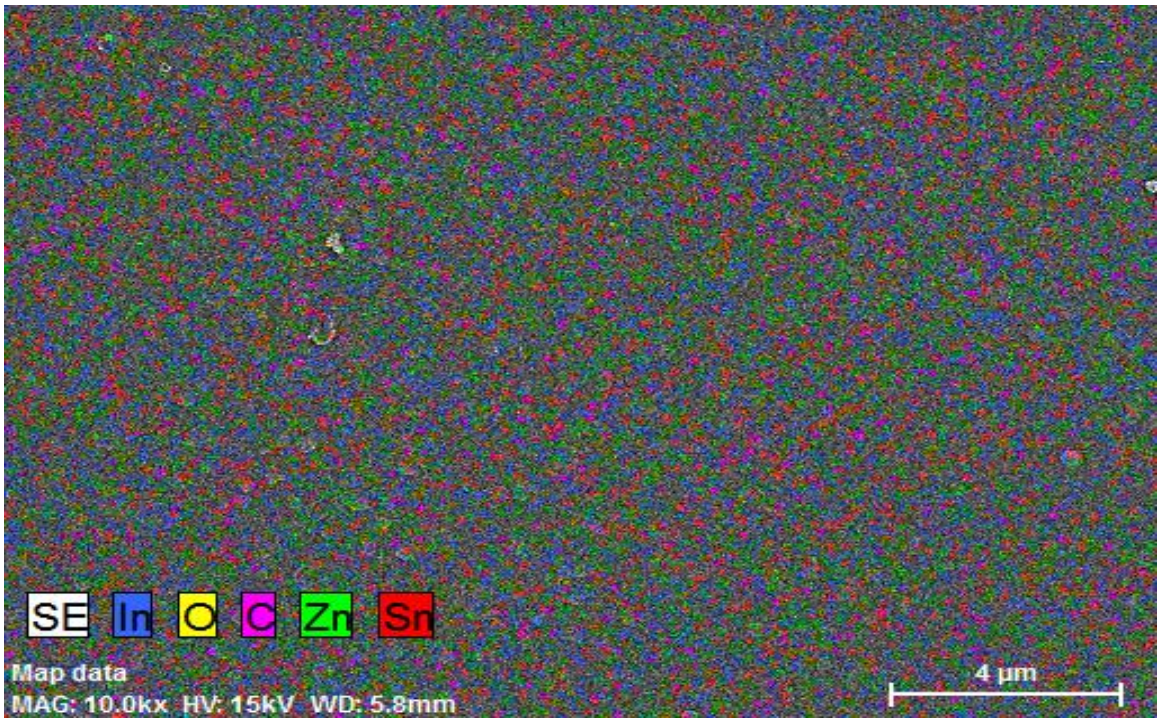

Fig 7. Map Data by EDX of ZnO Thin Film.

Elements	C norm (wt.%)	C Atom (at%)	C Error (%)
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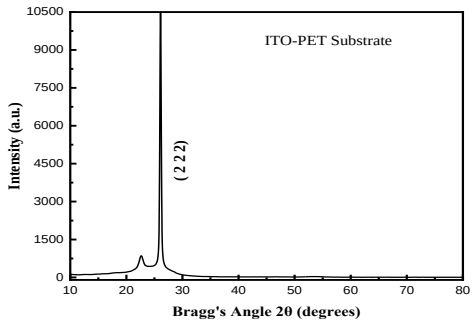
Table 3. Elemental composition of ZnO TF on ITO-PET.

X-ray Diffraction (XRD)

P-Analytical X Pert Pro system was used for X-Ray Diffraction. This was done to determine crystal structure, size of particle formed and defects [16]. XRD spectra of substrate is given in figure 8(a) and spectra of ZnO TF is in figure 8 (b).



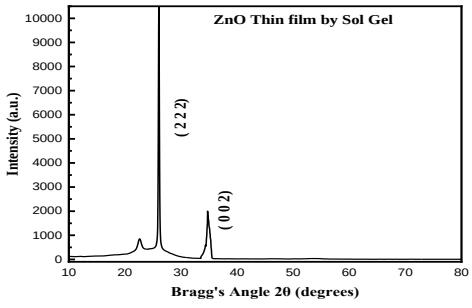


Fig 8 (a). XRD Spectra of Substrate ITO-PET. **Fig 8 (b)**. *XRD Spectra of ZnO TF*

The mean crystallite size (D) and lattice micro strain (ε) was calculated using Debye-Scherrer Equation [11], formula for D is given below:

$$D = K\lambda/(\beta \cos\theta)$$

Here D represents the mean crystallite size. K (shape factor) is generally taken as 0.9, λ indicates wavelength of X-Ray source (1.54056 Å), β is Full Width Half Maxima (FWHM) of the peaks in degrees and θ is Bragg's angle in degree. Lattice micro strain is calculated using formula given below:

$\varepsilon=\beta/(4\tan\theta)$

Here ε, represents the lattice micro strain, β is FWHM and θ is Bragg's angle. Dislocation density is important factor for microstructure analysis, as it shows number of imperfections in crystal lattice. The dislocation density is calculated using formula given below:

$\delta=1/(D^2)$

Table 4. displays values of peaks of the Bragg's angle (2θ), FWHM, crystallite size, dislocation density and lattice micro strain of ZnO TF

Sample	**Peak (2θ)**	**FWHM**	**(D) (nm)**	**(ε)**	**(δ) (nm^{-2})**
PET	22.6315	0.166	Broad amorphous halo structure.		
	26.0731	0.2657			
Sol Gel ZnO TF	34.735	0.2213	39.1066	3.24×10^{-3}	6.538×10^{-3}

Table 4. XRD data inference for ZnO TF

Sample Peak (2θ) FWHM (D) (nm) (ε) (δ) (nm-2)

PET 22.63150.166 Broad amorphous halo structure.
26.07310.2657

Sol Gel ZnO TF 34.735 0.2213 39.10663.24 x 10-3 6.538 x 10-3

The Bragg's angle (2θ) peak observed between 26-27 degrees is corresponding to substrate. This is prominent peak of ITO [12]. This confirms cubic bixbyite phase of indium oxide, with miller indices (2 2 2), indicating lattice parameters as confirming body center cubic structure [13]. The value of 2θ in range 33-35 degrees are corresponding to diffraction peak (0 0 2) confirms hexagonal wurtzite crystal structure. The results obtained for dislocation density and lattice micro strain were within required parameters [14].

Ultra-Violet Visible Spectroscopy (UV-VIS)

LAMBDA 750 (Perkin Elmer) UV-Vis NIR Spectrophotometer is used to observe the absorption spectra of the thin film. Substrate (ITO-PET) does not absorb in visible range, thus does not cause much impact on optical properties of devices. Absorption Spectra of substrate and ZnO thin film is shown in figure 9. Band gap is crucial for optical properties [10]. ZnO is wide band gap semiconductor. Band gap of prepared film was measured by UV-VIS absorption spectroscopy.

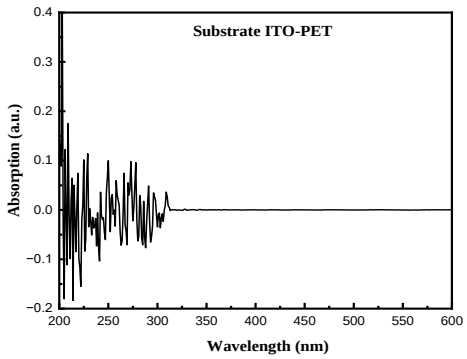


Fig 9 (a): UV absorption spectra of ITO-PET

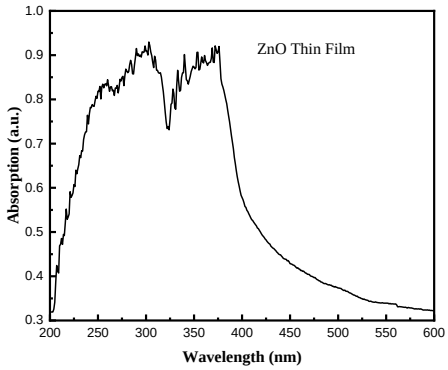


Fig 9 (b): UV absorption spectra of ZnO TF

Tauc and Davis-Mott relation is used for calculation of Band Gap. Equation for same is given below:

〖(αhυ)〗^2=K (hυ-E_g)

Here, α is absorption coefficient, calculated by Beer Lambert Law [15], α= 2.303 A/l, A is observed absorbance and l is film thickness here; h is Planck's Constant (6.6260 x 10-34 Joules per second), 1ev=1.602x10-19J, υ is frequency in hertz, K is energy independent coefficient, Eg is optical bandgap, n is nature of transmission (2 for direct band gap and ½ for indirect band gap). As per Planck- Einstein relation E is photon energy and E= hυ, here υ = C/λ, C is speed of light (3x108 m/s) and λ is wavelength (nm). To calculate the optical band gap (Eg), Tauc plots are plotted [18]. Graphs are shown in figure 10.

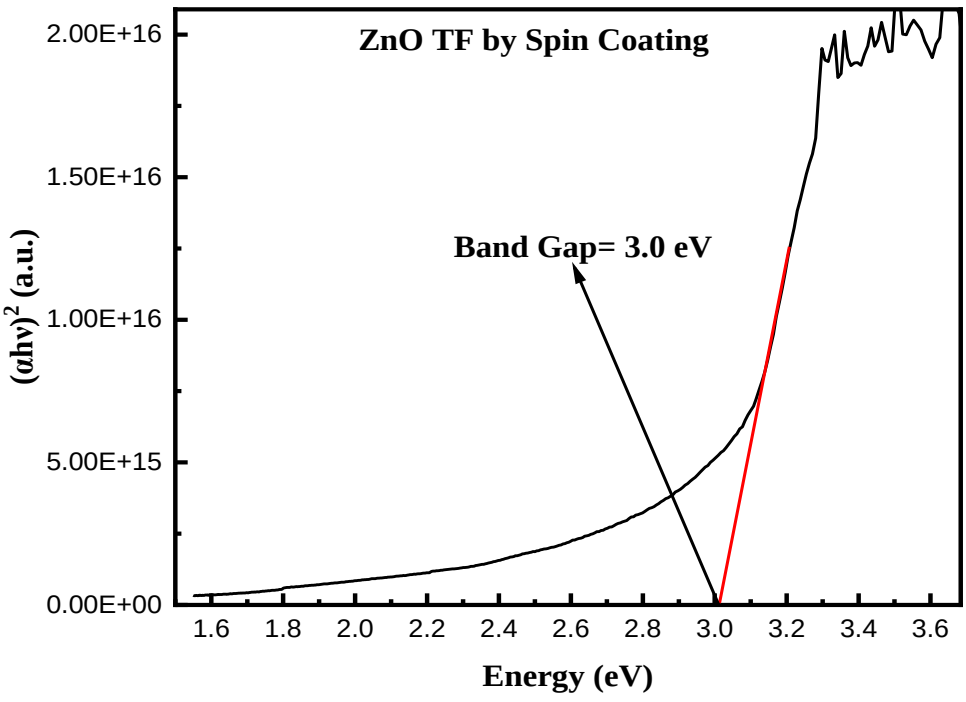


Fig 10. Tauc Plot of ZnO Thin film for band gap.

The band gap for thin film prepared by sol gel spin coating is 3.0eV. The determined Eg values are less than band gap of ZnO (~3.34 eV), this could be due to effect of substrate material or can be quantum confinement effect (nano-particle size impact) [15].

CONCLUSION

A low-cost solution processed thin film of Zinc oxide was successfully deposited on ITO-PET substrate. The particle size measured was around 40nm. Functional and elemental group testing confirmed the uniform thin film formation. Structural analysis confirmed the presence of hexagonal wurtzite structure in the grown film. This makes it suitable for piezoelectric applications. This work provides an alternate to high cost and complex processing techniques for thin films. This work can be incorporated in flexible electronic application after mechanical properties analysis. This work reported band gap of 3.0 eV which is suitable for optoelectronics applications like sensors, photo voltaic cells, actuators.

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