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Properties of Zno Thin Film Deposited on Flexible Substrate Using Rf Sputtering

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Abstract

Semiconductor materials demand is increased in recent years, due to new emerging technologies. There is need to find the alternate for silicon in electronics industry, as silicon is brittle in nature and has low efficiency, which makes it unsuitable for transparent and flexible device. Zinc oxide (ZnO) is emerging as popular choice of researchers due to its wide range of properties, abundancy and non-toxicity. This work explores the properties of ZnO thin film deposited on Polyethylene terephthalate (PET) substrate using RF Sputtering Technique. This technique deposited film in controlled environment with better precision and uniformity. Fourier Transform-IR (FT-IR) Spectroscopy confirms the presence of desired covalent bonds of zinc and oxygen. Energy Dispersive X-Ray (EDX) mapping was done to confirm the presence of functional groups in film. Optical properties of substrates were determined by ultraviolet-visible spectrophotometer (UV) absorption spectra and band gap calculated was around 3.1eV. Surface morphology was studied via atomic force microscopy (AFM) and surface roughness measured was around 3.5nm. Structural properties were studied by X-ray Diffraction (XRD). High-quality crystal structure was obtained in this work. Scanning electron microscopy (SEM) results confirmed crack free surface with proper adhesion of ZnO layer on ITO. Surface topology and morphology results confirmed uniform deposition and grain formation. This film shows promising results for optoelectronics devices like sensors, organic LED's, photovoltaics, solar cells.

Keywords: ZnO, Thin film, PET, XRD, FE-SEM, FTIR

INTRODUCTION

Semiconducting materials are popular for wide range of applications like solar cells, sensors, transistors, conductors etc. New age technology of flat panels, LED displays, wearable devices, foldable mobile phones etc. are creating demand of research in thin films. Thin film's advantageous qualities for the electronics industry are making them popular choice of researchers. These properties are quite different from bulk materials. Materials choice plays an important role in film structure, as film is grown on material. 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]. Indium Tin Coated (ITO) coated PET is emerging as good choice for flexible films. PET is cheaper than glass substrates, 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 [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). Various TCO are popular for touch screens, sensors, displays all over the world.

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Zinc Oxide is emerging as popular choice, due to its unique properties like wide band gap (~3.4 eV), high breakdown voltage, saturation velocity and exciton binding energy. This is common substance as well as non-toxic in nature. ZnO is reactive with both acids and alkalis, making it fabrication easier.

Deposition techniques plays an important role in fabrication, as this can impact uniformity and crystal size of film grown. Sputtering is widely used for obtaining high density, fast deposition rate, precise stoichiometry, uniform deposition [4]. This paper presents overview about structure of Zinc oxides thin film prepared by RF sputtering and characterization done by various methods. Experiment details are discussed in next section followed by characterization and results.

Experimental Details

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-Sigma Aldrich). ZnO thin film of 90 nm thickness was deposited using 3 mm thick and 2 inches diameter target size, target to substrate distance as 8 cm, using target down process. Deposition rate was kept as 0.3A/s, base pressure was $9.54x10^{-6}$ mbar, process pressure was $9x10^{-3}$ mbar, surface rotation was 8 rpm. Process was done at room temperature with RF power as 100 watts. Coolant used was Nitrogen. Argon gas flow was kept 15 SCCM.

RESULTS AND DISCUSSIONS

Characterization of thin film was done using various techniques. Chemical bonds are analyzed using FT-IR spectroscopy. EDX mapping confirms the presence of elements. Structure is observed by XRD. Surface study was done using AFM and SEM. Optical properties were studied using UV-VIS Spectrometer.

FT-IR Spectroscopy

FTIR spectra were recorded using Perkin Elmer's FTIR spectrometer. This gives insight into bonding environment and chemical composition of TFs. Graph obtained is shown in Figure 1. ZnO desired spectrum range varies from 400-700 cm-1 [5].

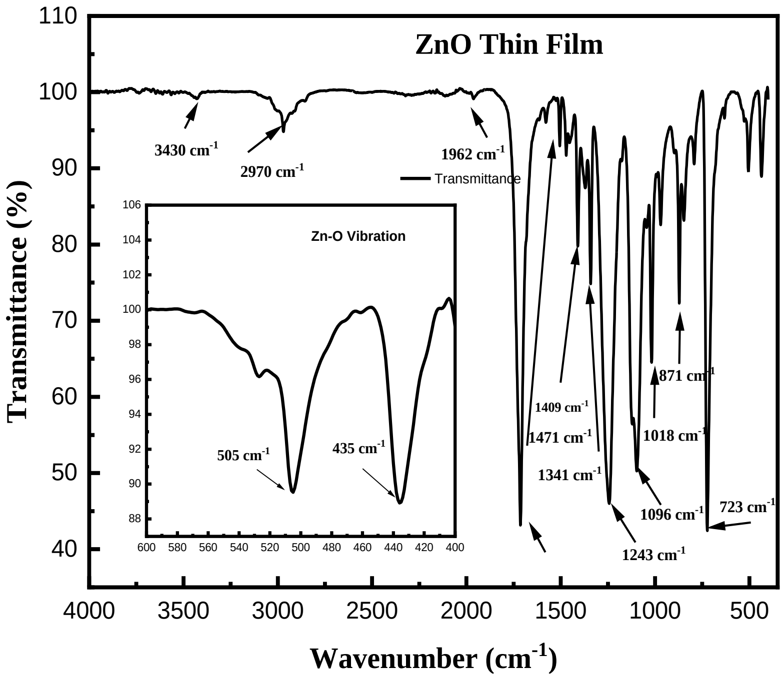

Figure 1. FTIR Spectra of ZnO TF, inset figure: peak corresponding to Zn-O vibration.

Table 1. FT-IR Inference of ZnO TF.

S. No	υ (cm$^{-1)}$	Functional Group
1.	435	Zn-O stretching
2.	505	In-O Vibration
3.	723	Zn-O Bond
4.	871	Carbonate Vibrations
5.	1018	C-O stretch (Ethers)
6.	1096	C-O (Esters)
7.	1243	C-O stretch (Ethers)
8.	1341	N=O stretch
9.	1409	N=O Bend (Nitro Groups)
10.	1471	N-H Bend (Amines)
11.	1713	C=O stretch (Carboxyl)
12.	1962	C-H bond
13.	2970	H-C-H (Alkanes)
14.	3430	≡ C-H stretch (Alkynes)

The observed spectrum confirmed the presence of ZnO. Vibrations at 435 cm-1, and 505 cm-1 confirms the desired bonds [9]. However, a sharp peak across 723 cm-1 is observed. This could be combining effect of In-O bond from ITO layer of substrate [6]. Carbon bond peaks intensity and sharpness is observed 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 1 is giving details of peaks of spectra and functional group corresponding to it [5]. Here υ denotes wavenumber. Presence of Carbon groups are due to substrate [6].

X-ray diffraction

X-ray diffraction data of ZnO thin film was obtained using the Cu-Kα radiation and range for 2θ was kept from 4° to 80°. Figure 2 shows the diffraction patterns of ZnO thin film by RF Sputtering.

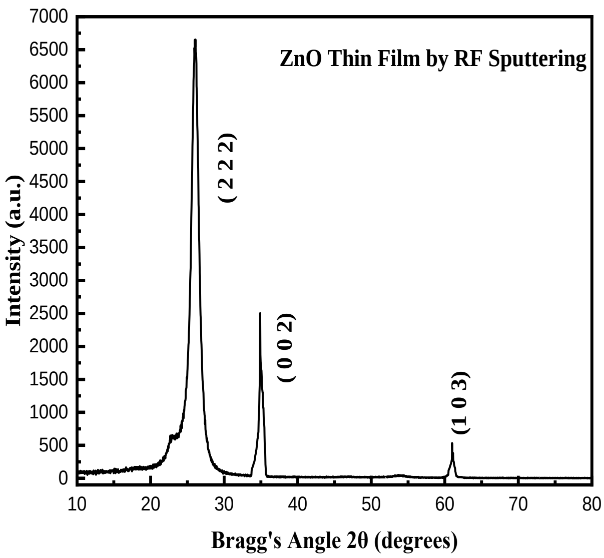

Figure 2. XRD spectra of ZnO TF by RF sputtering.

The observed peaks are matched with standard data of ZnO (JCPDS card no. 01-089-0510). XRD pattern was observed to study crystal structure of the prepared film. The peak observed at 2θ (Bragg's angle) value 26.073 degrees is corresponding to cubic bixbyite phase of In2O3. Peak observed at 34.895 degrees have miller indices as (0 0 2), confirmed hexagonal wurtzite crystal structure and peak at 60.995 degrees (1 0 3) indicates presence of atomic plane within a ZnO thin film with wurtzite structure [7]. The mean crystallite size (D) and lattice micro strain (ε) was calculated using Debye-Scherrer Equation [8], formula for D is given below:

$$D = \frac{K\lambda}{\beta \ \mathrm{Cos}\theta}$$

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. Obtained crystal size is 29nm corresponding to miller indices (0 0 2). Size obtained at (1 0 3) is around 37nm. This variation in size was responsible for peak variation in FT-IT spectra.

Energy Dispersive X-ray (EDX Mapping)

EDX is done to verify the film composition, relative number of materials present and presence of impurities as well. Figure 3 shows the EDX composition of prepared film. Elemental analysis of EDX confirmed the presence of Zn- 72%, O-11%. Sn, In, C all elements were found due to ITO-PET. Red colour in graph is indicating presence of gold atom, as gold coating is done for prepared film before SEM and EDX. EDX error % is found to be around 2.25%. Figure 3(a)(b).

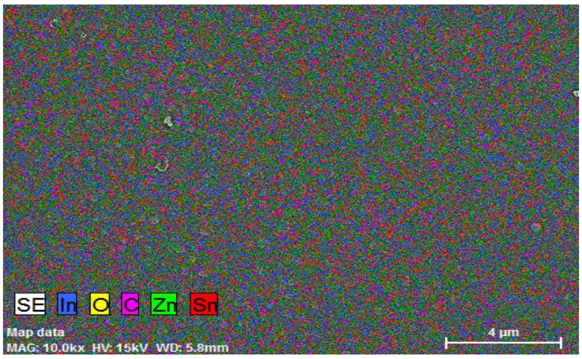

Figure 3. (a): EDX mapping of ZnO TF surface

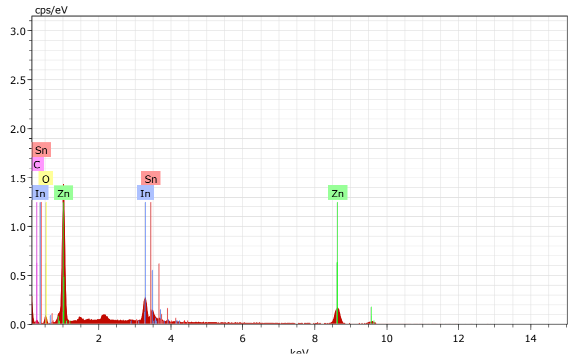

Figure 3. (b): EDX mapping spectra of ZnO TF

Atomic force microscopy* (*AFM)

Surface roughness is analyzed by this technique, thus important in determining the quality of film. Figure 4 shows 3D AFM images of ZnO thin film. Surface appears is smooth, granular, dense and uniform spread is there. Each film includes columnar grains growing along the c-axis, perpendicular to the substrate surface, which is in agreement with the XRD results. Average surface roughness was calculated as 3.5nm.

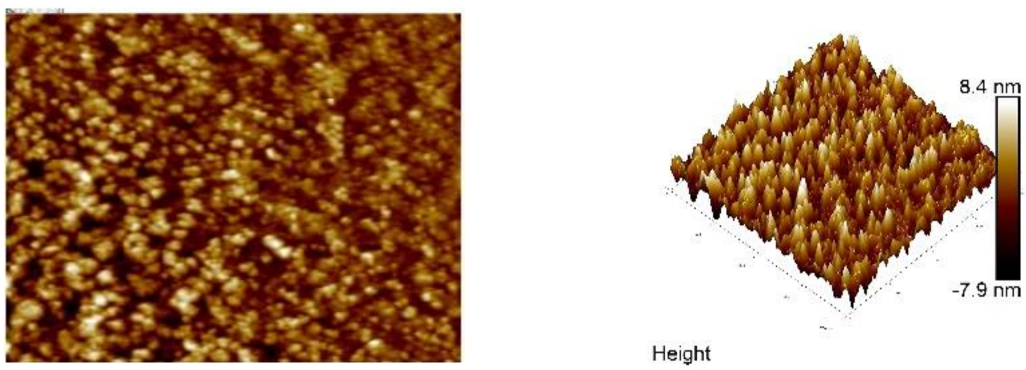

Figure 4. (a)2D AFM image of ZnO TF **Figure 4.** (b) 3D AFM image of ZnO TF

Scanning Electron Microscopy (SEM)

SEM micrographs reveals information about grain size, shape and distribution of ZnO crystals. The film of thickness 90 nm showed individual grains clearly. Images showed proper adhesion. No cracks were observed. Average surface thickness was found around 90 nm. Figure 5 shows the SEM images of the ZnO thin film.

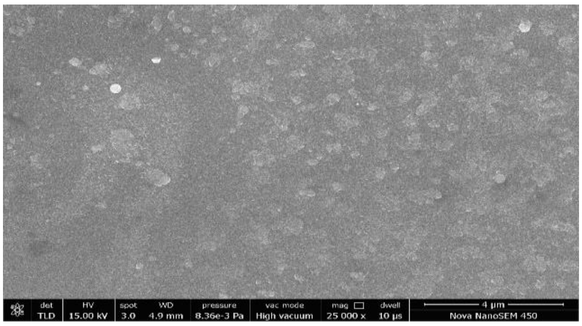

Figure 5. (a): ZnO TF SEM micrograph at 4μm Resolution

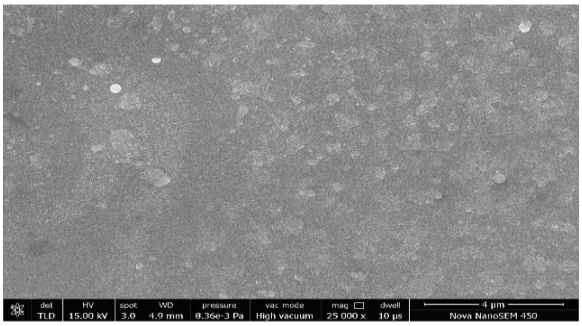

Figure 5. (b): ZnO TF SEM micrograph at 500nm Resolution

UV- visible spectral analysis

Absorption Spectra of thin film is observed for optical properties. Band gap is calculated for further analysis. Substrate used is ITO_PET, it does not absorb in visible range, thus neglected [8]. In this film absorption peak is at 352nm, which is in range with ideal spectra of ZnO TFs [9]. Figure 6 shows the observed spectra.

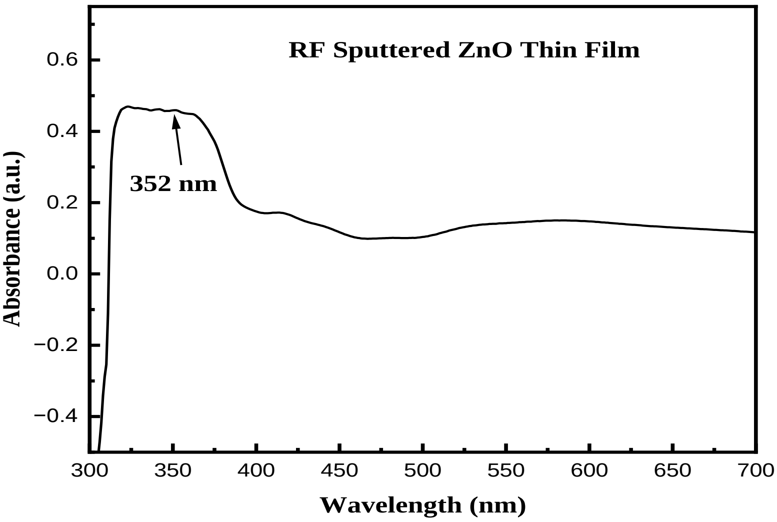

Figure 6. UV spectra of ZnO thin film.

Band gap is crucial for optical properties. ZnO is wide band gap semiconductor. Band gap of prepared film was measured by UV-VIS absorption spectroscopy. Tauc and Davis-Mott relation is used for calculation of Band Gap. Equation for same is given below:

$$(\alpha h\upsilon)^2 = K\,(h\upsilon - Eg)$$

Here, α is absorption coefficient, calculated by Beer Lambert Law [10], 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).

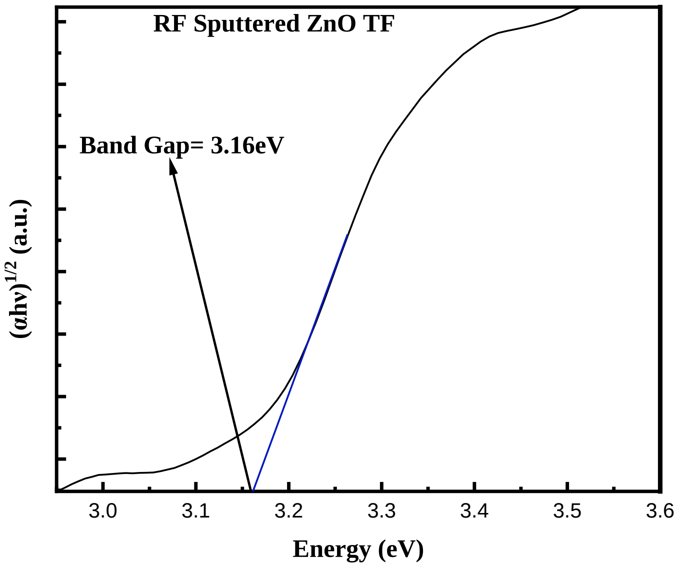

Figure 7. Tauc plot of ZnO thin film.

To calculate the optical band gap (Eg), Tauc plots are plotted. Graphs are shown in Figure 7. The band gap measured is 3.16eV. This is less than ZnO particles band gap, which is around (3.37 eV), but properties change slightly in thin films compared to particles [10].

CONCLUSION

The structural, optical and morphological properties of ZnO thin film deposited on ITO coated PET by RF Sputtering process were investigated. XRD measurements confirmed presence of wurtzite hexagonal structure and polycrystalline nature. Proper adhesion between the layers is observed via study of surface morphology. No cracks were observed in deposited thin films. Surface observed was having uniform deposition and even thickness of 90nm. FTIR spectra confirmed presence of Zn-O vibrations, and due to substrate presence of In-O vibrations, carbon vibrations were observed. All elements were found in desired proportion through EDX mapping. Atomic force microscopy showed smooth surface topology with desired columnar growth and average surface roughness as 3.5nm. UV absorption spectra confirms absorption spectra in desired range. Band gap was measured as 3.16ev which is good for 29nm nanoparticle of ZnO. Overall high-quality crystal structure with good optical characteristics was observed in grown films. This film shows promising results for optoelectronics devices, UV sensors, solar cells etc. After proper analysis of mechanical properties like tensile strength, bending radius it could be used in wearable devices.

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