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Synthesis And Characterization of Co Doped ZnO Thin Film by Sol-Gel Dip Coating Method

Dr. S. Ashok Raj[1], N. Ajay[2], M. Abarna[3]
[1]Assistant Professor, PG and Research department of physics, Government Arts College (Autonomous) Kumbakonam, Tamil Nadu
[2, 3]M.Sc. Scholar, Department of physics, Government Arts College (Autonomous) Kumbakonam, Tamil Nadu

Abstract: ZnO have broad direct band gap and it can be applied for opto-electronics, photoluminescence, semiconductors and memory devices. When compared to pure ZnO thin films, Co doped ZnO thin films have higher electrical conductivity and enhanced magnetic properties. Sol-gel Technique employed to synthesize 0.1M of Co doped ZnO thin films on glass substrate by dip-coating process. The optical properties were determined using UV-VIS-NIR Spectrophotometer. Using GAUSSIAN the HOMO-LUMO value was estimated.The FTIR Spectrum certifies the functional group present. The X-ray diffractometer provides structural analysis of ZnO:Co thin films. The PL spectrum investigates the band gap in various regions. The Surface Morphology of coated thin films were characterized by SEM images. The thickness of the film was carried out using cross-sectional view of SEM. Surface Roughness parameters determined through Surface Profilometer. The obtained results were analyzed and discussed in detail.
Keywords: ZnO-Zinc Acetate Dihydrate, Co-Cobalt Chloride, SEM-Scanning Electron Microscope, PL-Photoluminescence, FTIR- Fourier Transform Infrared Spectroscopy.

I. INTRODUCTION

Zinc acetate dihydrate among (II-VI semiconductors) having broad direct band gap (3.2 eV) with greater exciton energy (60 meV) at room temperature twice that of Gallium Nitride (GaN)-(28 meV) [1,2]. Among TCO (Transparent Conductive Oxides) materials, Indium Tin Oxide (ITO) used for their various applications but ZnO supersedes ITO by their broad direct band gap, highly visible, near IR spectral transmission co-efficient (>80 percent), long life chemical permanence, non-toxicity and low cost [3,4]. Zinc acetate dihydrate absorb UV range of electromagnetic radiation [5]. ZnO has higher electron mobility than TiO_2 [6]. Zinc oxide contain natural n-type conduction with numerous native defects with oxygen vacancies and zinc interstitials. It crystallizes in Hexagonal Wurtzite structure with non-central symmetry, thus shows properties of piezoelectricity [7].

ZnO can be applied in different fields like Opto-electronics, Gas sensors, Solar cells, Laser diodes, Surface acoustic wave guides, Transparent Conductive Oxide electrodes, Photoluminescence, Piezoelectric nanogenerators, UV light emitters, Transparent transistors, Transistor transmitters, Memory devices, Optical coatings, Anti-bacterial activities, Flat-panel displays, Organic Light Emitting Diodes(OLED's), Quantum computing applications, Smartphone touch screen, Laser mirrors and Anti-reflex coatings [1-19]. Pure ZnO thin films exhibit poor properties with a low conductivity and the resistivity of 10^{-6} to 10^{6} ohm-m. Doping elements like Boron (B), Indium (In), Aluminium (Al), Silicon (Si), Gallium (Ga), Cadmium (Cd), Cobalt (Co) and Manganese (Mn) can certainly improve these properties [3,5,8]. Doping with transition metals effectively enhance the magnetic properties of spintronics [9].

Zinc oxide is effective when doped with cobalt as it has similar ionic radius enabling Co ions fuse into ZnO matrix, abundance of electronic states, provides great thermal stability with optical and magnetic behaviour [10,11]. Co doped ZnO thin films applied for studying Dilute Magnetic Semiconductors (DMS) [12]. ZnO:Co DMS exhibit ferromagnetism at room temperature vital for spintronic devices [9]. Different methods employed to obtain pure and doped ZnO thin films. The Sol-gel or Wet chemical process is a bottom-up synthesis method used to produce Thin films, Monoliths, Composites, Metal nano-oxides, Porous structures, Dense powder and Thin fibers at high purity with low temperature [13]. On using Sol-gel method, homogeneous solution can be produced with fine structures and desired thickness at low cost, simple for controlling chemical composition. The optical properties increases as sol concentration increases 1 mole/ml [1].

Here, ZnO doped with Co using Sol-gel coupled with dip-coating technique. The morphological, structural and optoelectronic properties were investigated by SEM images, XRD, FTIR, Thickness, UV-VIS-NIR spectrum and Photoluminescence in this paper.

II. EXPERIMENTAL PROCEDURE

The sol-gel dip coating method employed to obtain ZnO thin film on the glass substrates. The precursors used Zinc Acetate dihydrate [$(CH_3COO)_2Zn.2H_2O$] as starting material, 2-Methoxy ethanol (2-MEA) as solvent, Cobalt Chloride as dopant and Diethanolamine (DEA) as stabilizer. The Zinc Acetate dihydrate dissolved and stirred with 2–Methoxy ethanol at 40^0C for 2 hours to obtain base solution (A). The chelating agent Diethanolamine (DEA) added in drop wise until clear solution obtained.

The Cobalt Chloride dissolved and stirred with 2-Methoxy ethanol at room temperature for 30 minutes to obtain clear dopant solution (B). The dopant solution (B) added dropwise to base solution (A) in order to obtain 0.1M of ZnO:Co solution stirred at room temperature for 2 hours to obtain homogeneous mixture and aging process carried out for 72 hours at room temperature. The concentration of the solution remains 0.1M and molar ratio of ZnO to DEA maintained at 1:1 before deposition.

The Processed Glass plates were used as substrate, the process was taken with soap solution, normal water, Chromic acid at 50^0 C and Acetone. 0.1M ZnO:Co solution coated on well cleaned glass substrates by dip coating method with timing of 10 seconds dip and 30 seconds dry at room temperature. This process repeated for 10 times. The coated substrates annealed at 130^0 C for 4 hours and cooled to room temperature.

III. RESULT AND ANALYSIS

A. *Optical Analysis*

1) *UV-VIS-NIR Spectrum Analysis:* UV–VIS-NIR spectroscopy is a characterization method to evaluate the absorbance of samples at a certain wavelength. This technique is based on the principle of electronic transition in molecules or atoms, which is caused by absorption of light in the visible area of the electromagnetic spectrum (400–800 nm) under excitation of an electron from the ground state into a higher orbital. Generally, the transmittance spectra of ZnO thin film have the transmission higher than 80% in the visible region 400-600 nm, compared with the ZnO film, the doped films have higher transmission [20]. In this way fig (3.1), shows the transmittance spectra of Co doped ZnO thin film. It can be observed that the film has the 90% transmission in the UV region.

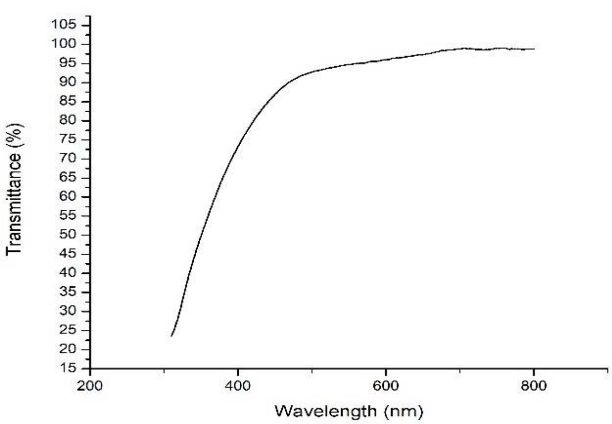


Fig (3.1) UV Transmittance spectrum for ZnO:Co film

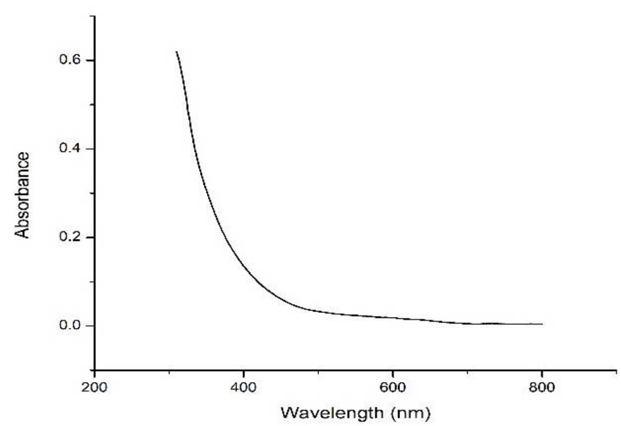


Fig (3.2) UV Absorbance spectrum for ZnO:Co film

The Absorbance spectra of coated film fig (3.2), shows a strong absorption in visible region, which is attributed to the intrinsic absorption originated from the direct transition of electrons [21]. The optical band gap of Co doped ZnO thin film was determined using Tauc relation. The Tauc method is based on the assumption that the energy-dependent absorption coefficient α can be expressed by the following equation [22]

$$(\alpha h\vartheta)^2 = A\left(h\vartheta - E_g\right)$$

Where A is constant and E_g is the optical band gap. The absorption coefficient (α) is estimated using the following relation:

$$\alpha = \frac{\left[ln\left(\frac{1}{T}\right)\right]}{d}$$

Where T is the transmittance and d is the thickness of the film. The Tauc plot is shown in fig (3.3). From this, the estimated band gap value of Co doped ZnO thin film is E_g **= 1.67eV,** which corresponds to a wavelength of 743 nm. Red light is emitted [23].

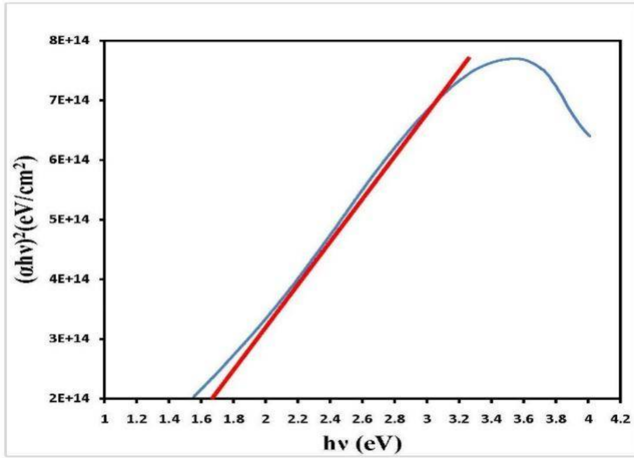


Fig (3.3) Tauc plot for ZnO:Co film

2) *HOMO-LUMO Energy Gap Calculation:* The HOMO-LUMO analysis of the coated film was performed by combining the experimental and theoretical information using pulay's DFT, Hartree-Fock (HF) based on quantum mechanical approach. The HOMO is the orbital that primarily acts as the electron donor and the LUMO is the orbital that largely acts as the electron acceptor [24]. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO energy gap of Co doped ZnO thin film was calculated at the B3LYP/6-311++G (d, p) level is,

LUMO = –0.18394 eV

HOMO = –0.23810 eV
HOMO - LUMO energy gap = 0.05416 eV
The lower energy gap explains the eventual charge transfer interactions taking place within the molecule. The pictorial illustration of HOMO- LUMO distribution is shown in fig (3.4)

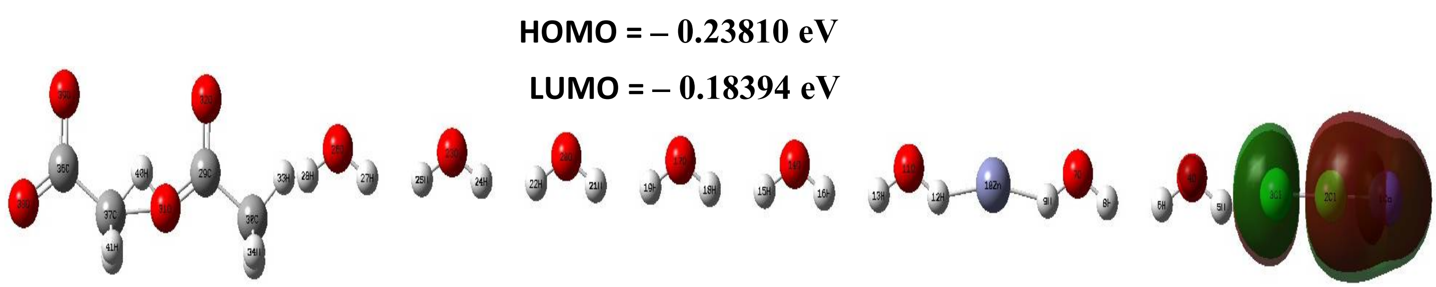
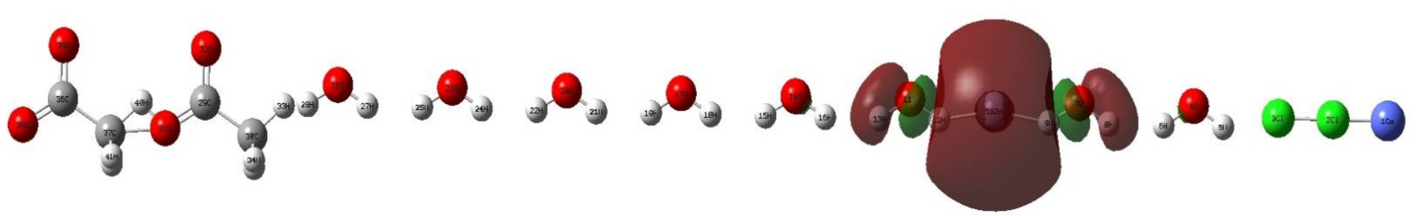


Fig (3.4) Plots of the frontier molecular orbitals of zinc acetate dihydrate doped with cobalt chloride hexahydrate



3) *Refractive Index:* The refractive index can be calculated from UV Transmittance spectrum using the Swanepoel method.

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2}$$

For medium and weak absorption regions, $N = 2S \frac{[T_M - T_m]}{T_M T_m} + \frac{[S^2+1]}{2}$

Where S – Refractive index of glass substrate (1.655).
T_M, T_m – Transmittance envelope functions for maxima and minima.

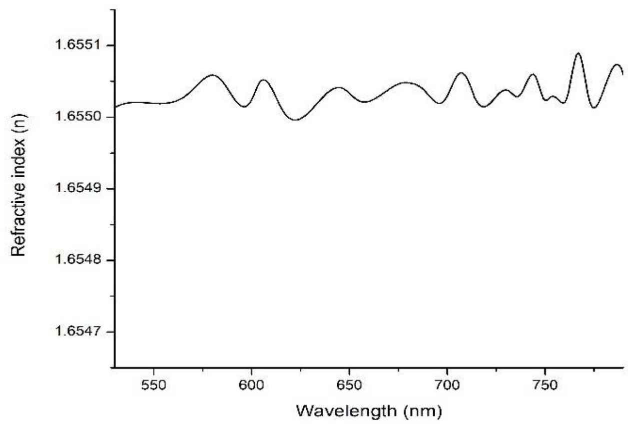


Fig (3.5) Refractive index for ZnO:Co film

As the refractive index of Co doped ZnO film approximately close to the refractive index of substrate material in medium and weak absorption regions, the transmittance is very much higher in 500 nm – 800 nm as suggested by UV Transmittance spectrum. when compared to undoped ZnO film, doping Co in ZnO film effectively decreases the refractive index, which in turn increases the transmittance value [25].

4) *PL Spectrum Analysis:* Fig (3.6) Shows the PL spectrum of Co doped ZnO thin film. Which, portrays strong UV emission at 360 nm and another strong green emissions were occurred at 500 nm – 550 nm, beyond 650 nm red emission started. These results were merely coincided with UV spectrum. The reason for UV emission is related to near band-edge emission, whereas the green is resulted from the recombination of electrons with holes trapped in singly ionized oxygen vacancies [26,27].

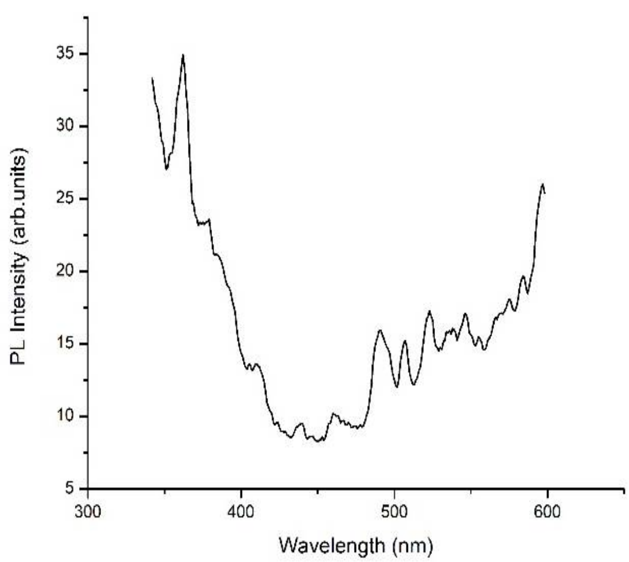


Fig (3.6) PL spectrum for ZnO:Co film

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B. FTIR Analysis

FTIR spectroscopy is a key tool for investigating a vibrational property of new synthesized material, The band position, the absorption of the peak and morphology of the thin film depends upon the chemical composition and structure of the thin film [28]. Here, the fig (3.7) Shows the FTIR spectrum of Cobalt doped ZnO thin film, the bands between 2450 cm^{-1} and 3050 cm^{-1} were caused by the O-C-O bond [29]. The broad peak in the range of 3500 to 4000 cm^{-1} is attributed to water molecule present in thin film. The weak peaks around 400-500 Cm^{-1} were indicating the formation of stretching mode of ZnO, its COOH and OH group [30]. The spectra shows that the Zn-O bond appear at around 450–490 cm^{-1} [31]. The band at around 490 cm^{-1} may be related with oxygen vacancy or oxygen deficiency in ZnO. The usual approach with FT-IR spectrum is identifying the functional groups with their individual vibrational frequency appeared between 400 cm^{-1} to 4000 cm^{-1}, here the characteristic ester carbonyl C=O stretching frequency between 1650 – 1800 cm^{-1} was not marked, it is evident that due to reaction temperature, the acetate group dissociated in to carbon dioxide and eliminated.

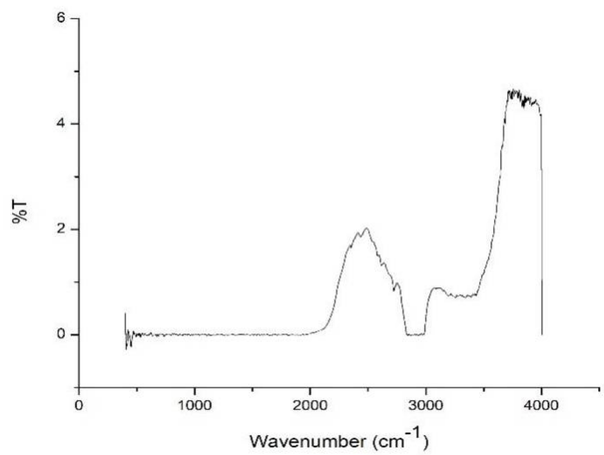

Fig (3.7) FTIR spectrum for ZnO:Co film

C. Morphological Studies

1) *XRD Analysis:* The Crystal structure of Co doped ZnO film investigated using X-ray diffraction (XRD) technique. The diffraction peaks identified and indexed according to the standard diffraction data (JCPDS card no: 36-1451). From fig (4.1) XRD pattern reveals that the peaks along (111), (311), (222) confirms the presence of cobalt oxide. There is no existence of ZnO phase, due to the high processing temperature. The inter-planar spacing (d) indicates that the coated film has hexagonal wurtzite structure.

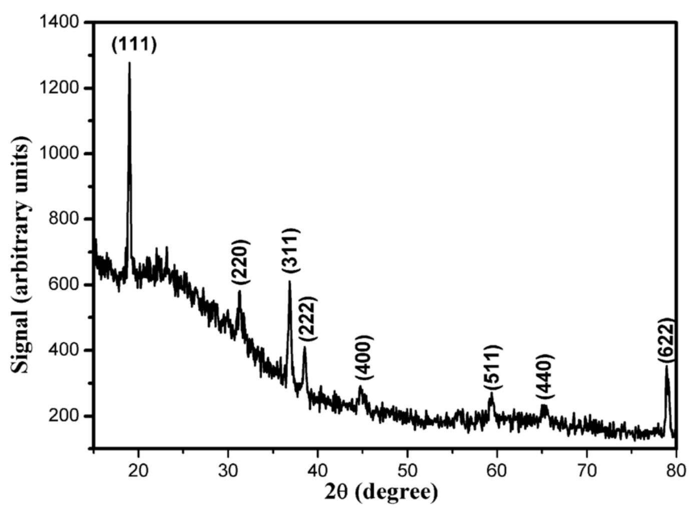

Fig (3.8) XRD pattern for ZnO:Co film

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Crystallite size (nm)	Average crystallite size D (nm)
10.4139	3010.06	0.1476	8.49485	100	56.44817308	41.96719183
13.522	93.07	0.2952	6.54844	3.09	28.30444969	
14.7905	56.65	0.492	5.98955	1.88	17.0060291	
16.1956	177.27	0.1476	5.47296	5.89	56.7813974	
18.9377	97.63	0.1476	4.68622	3.24	56.99173563	
21.0687	537.39	0.1476	4.2168	17.85	57.17895797	
22.1782	34.84	0.5904	4.0083	1.16	14.32119563	
30.564	84.99	0.1476	2.92498	2.82	58.27585237	
36.6202	20.66	0.5904	2.45397	0.69	14.80329777	
38.5903	170.33	0.1476	2.3331	5.66	59.56082969	

The average crystallite size determined through full width half maximum (FWHM) of the diffraction peaks using Scherrer's formula. The average crystallite size was found out to be 41.96 nm.

$$D = \frac{0.94\,\lambda}{\beta \cos\theta}$$

Where D stands for the size of the crystallites in nm.

λ refers to the wavelength value of Cu K_α line (λ = 0.15406 nm).

β is the FWHM of the diffraction peak in radians.

θ is the Bragg's diffraction angle.

2) *SEM Analysis:* The Morphology of the Co doped ZnO thin film was analysed by SEM image fig (4.2). The fig shows the crack free surface having the ZnO crystals. The homogeneous average grain sizes are distributed over the surface.

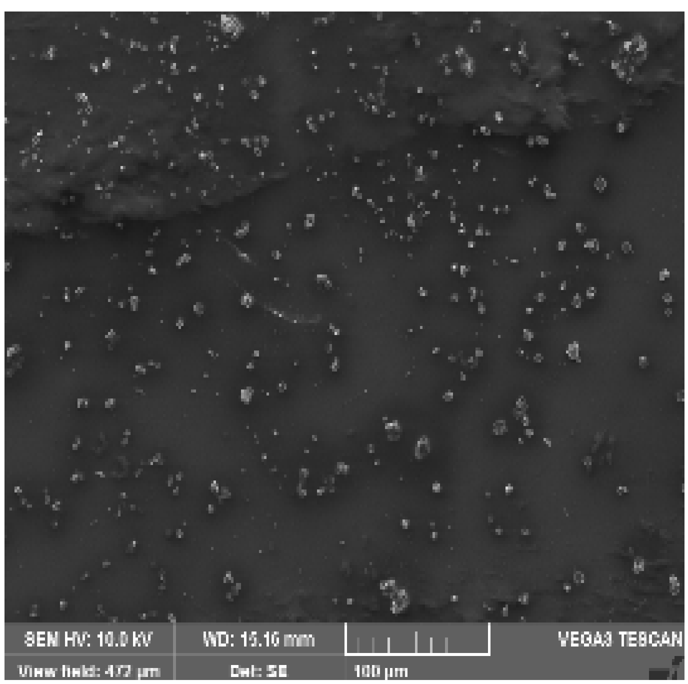

Fig (3.9) SEM image for ZnO:Co film

3) *Cross-sectional view of SEM:* Thickness plays a vital role in the physical and opto-electronic properties. The cross-sectional view of SEM reveals the thickness of thin film. In order to be conductive, additional gold layer sputtered to make SEM measurement possible with high accuracy. In this way, the thickness of film is determined to be 2.2 µm from the cross-sectional view of SEM fig (4.3).

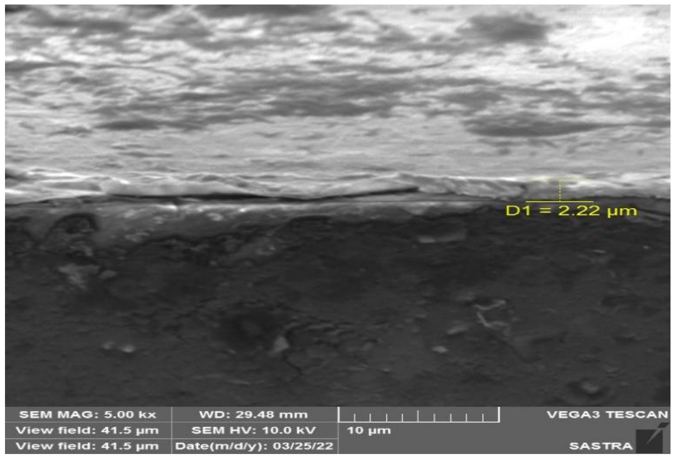

Fig (3.10) Cross-sectional view of SEM for ZnO:Co film

4) *Surface Profilometer:* The surface roughness of the coated Co doped ZnO thin film was estimated with SJ-301 Mitutoyo surface profilometer - contact profilometry method. Profilometer characterizes line profile of surfaces.

Surface Roughness parameters: R_a = 0.40 µm, R_y = 3.56 µm, R_t = 7.20 µm

Where R_a – Roughness average or center line average is the arithmetic mean of peaks and valleys or departures from center-line.

R_y – Largest value of the maximum peak to valley height within sampling length.

R_t - Total Roughness height is the maximum peak to valley height of surface profile within evaluation length.

R_a 0.4 µm indicates that the surface is smooth having high quality. They can be applied for applications that are under high tension or stress. They have less adhesion with low friction co-efficient. Smooth surfaces possesses less wear and tear and corrosion resistive.

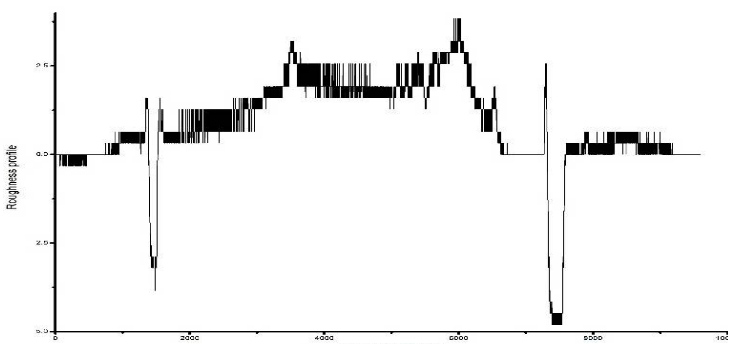

Fig (3.11) Roughness profile for ZnO:Co film

IV. CONCLUSION

Co doped ZnO thin films were synthesized by sol-gel dip coating method. Optical analysis using UV-VIS-NIR spectrophotometer reveals that the transmission reaches 90% in UV region, the optical band gap was found out to be 1.67 eV by Tauc relation, which can be applied for opto-electronic devices like LED. The HUMO-LUMO energy gap of coated film were determined based on quantum mechanical approach.

The refractive index value shows the film has highest transmission. PL spectrum analysis shows strong UV emission at 360 nm related to near band-edge emission. FTIR analysis confirms the presence of Co and ZnO. Structural studies through X-ray diffraction analysis confirms the presence of Cobalt Oxide along (111), (311), (222) peaks. SEM analysis portrays that the ZnO crystals distributed over crack free surface. Thickness of film determined to be 2.2 µm from cross-sectional view of SEM. Smooth surface with high quality corrosion resistive film validated by surface profilometer.

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