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STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF UNDOPED AND CZO THIN FILMS PREPARED BY SOL–GEL DIP COATING PROCESS

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ABSTRACT

Undoped and doped Zinc Oxide (ZnO) thin films that that of varying quantities of Cobalt (Co) have been formed onto the glass substrates by using sol-gel dip coating technique. As a precursor, doping source, solvent, and stabilizer, respectively, Zinc Acetate Dihydrate, Cobalt Acetate Tetrahydrate, Ethanol and mono ethanol amine (MEA) were all utilized. The concentration of metal ions is 0.5 mol L^{-1}, and the molar ratio of MEA to metal ions was kept constant at 0.5 M. The Co/(CZO) ratio, which ranged from 0 to 8 at. %, was used to establish the Co dopant level. The thin films produced in this way were examined using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis) and photoluminescence (PL) to determine their structural, morphological, and optical properties. According to the XRD data, all films exhibited a preferential orientation along the c-axis and crystallized under a hexagonal wurtzite structure. According to the SEM findings, the undoped ZnO thin film has a smooth, uniform surface with tiny ZnO grains, whereas the doped ZnO films exhibit uneven stripes that resemble fibers and a wrinkly network structure and the average transmittance of all films is between 72 and 99% in the visible region. The films PL revealed UV and defect-related visible emissions like violet, blue, and green and demonstrated that cobalt doping caused UV emission to shift to the red and reduced the intensity of the UV and visible emissions. All these results confirm that the prepared thin films can used as transparent conducting oxides (TCOs) in solar cells.

Keywords: *Chemical synthesis, Dilute magnetic semiconductor, Transmittance, Hexagonal wurtzite structure.*

1. INTRODUCTION

Vast band gap II-VI semiconductors have equipped the interest of numerous research groups recently, Zinc oxide (ZnO), a transparent semiconductor with a wide band gap of 3.37

eV and a significant exciton binding energy of 60 meV, has been extensively studied due to its broad range of applications. Its potential use in optoelectronics, photocatalysts, light emitting diodes, ultraviolet (UV) photoconductive materials, and gas sensors. For some optoelectronic applications, ZnO may replace another wideband gap semiconductor, GaN, which is frequently used for green, blue—ultraviolet (UV), and white light-emitting devices. For the creation of spintronic-based and optoelectronic devices, transition elements with exceptional physical properties and large magnetic moments, such as Fe, Co, and Ni, are necessary. Transition metals display magnetic characteristics necessary for spintronic-based quantum computers because of their partially filled d states. There aren't many studies that have examined the optical characteristics of Fe, Co, and Ni-doped ZnO. Band changing property is crucial for the manufacturing of quantum well devices for specific applications. Doping with Fe, Co, and Ni can also alter the band gap of ZnO. Furthermore, unpaired electrons responsible for magnetic activity are present in the 3d partially occupied d states of Fe, Co, and Ni. The insertion of *3d* transition metal ions such as Fe and Ni into ZnO matrix can shift the Fermi level that results in engineering the band gap. Due to their potential uses in spintronics, transition metal ions including Fe, Co, and Mn produce magnetic characteristics when doped into ZnO. Magnetic and optical characteristics of the ZnO system doped with transition metals. According to several studies, the concentration of intrinsic and extrinsic defects is connected to changes in the structural, electrical, and optical properties. Co is a crucial component for inclusion into the ZnO matrix because of its high solubility and ability to alter the structure, microstructure, magnetic, and optical properties of the ZnO system. Several experiments have detected impurity phases at lower concentrations of Co. Co-doped ZnO thin films manufactured using a variety of processes, including electrochemical deposition, spray pyrolysis, radio frequency magnetron sputtering, and sol-gel processing. Sol-gel is one of these methods that is gaining popularity for producing thin films due to many benefits, including its ease of use, low cost, broad substrate coating area, and simplicity in doping insertion [1-5].

This research examines how Co doping influences the structural, morphological, and optical properties of ZnO and CZO thin films, which have been deposited on glass substrates using the sol-gel spin coating technique. Many alternative deposition processes have been successfully used to create a variety of ZnO thin film nanostructures, including nanoparticles, nanorings, micro-rings, and micro-rods. Radio frequency magnetron sputtering, electron beam evaporation, spin coating, dip coating, and spray pyrolysis are among the most extensively studied deposition methods. Out of these, dip coating is of special interest because it is affordable, straightforward, doesn't require a high vacuum, safe, produces little waste, and can cover huge regions. It has many conveniences such as high mechanical, chemical and thermal stability, biological inertness, high transparency, photo stability, administrable porosity and discharge of embedded agents. Due to its inherent size and shape dependent applications, deliberate control of ZnO nano/micro-structure size and shape is becoming an important subject. Therefore, the creation of optoelectronic devices would benefit from the preparation and characterisation of such a material. As potential replacements for ITO films in optoelectronic applications, we describe the production and characterisation of ZnO thin films [6].

2. Experiment specifications

ZnO thin films, both undoped and co-doped, have been deposited onto glass substrates using the sol-gel spin coating method. Figure 1 depicts the process flow for creating ZnO thin films. Cobalt acetate tetrahydrate [Co (CH3COO)24H2O] and zinc acetate dihydrate [Zn $(CH_3COO)_2 2H_2O$] were utilised as the starting material and dopant sources. The solvent and stabiliser used were ethanol and mono ethanol amine (MEA). The concentration of metal ions is 0.5 mol L^{-1}, and the molar ratio of MEA to metal ions was kept constant at 1.0. The Co/(CZO) ratio, which ranged from 0 to 2% mol, defined the Co dopant level. After being agitated for two hours at 65 degrees Celsius to produce clear, homogeneous solutions, the solutions were aged for 24 hours at room temperature. Using an ultrasonic cleaner, the glass substrates were cleaned in acetone for 40 minutes each, followed by a rinse in deionized water and drying. Using dip coating method, the solution was deposited onto a glass substrate. The film was warmed at 200 °C for 10 min in a hot air oven to evaporate the solvent and eliminate organic residues after the dip coating deposition. After multiple iterations of the dip coating and pre-heating processes, the films were annealed at 450 °C for 4 hours in an atmosphere of air.

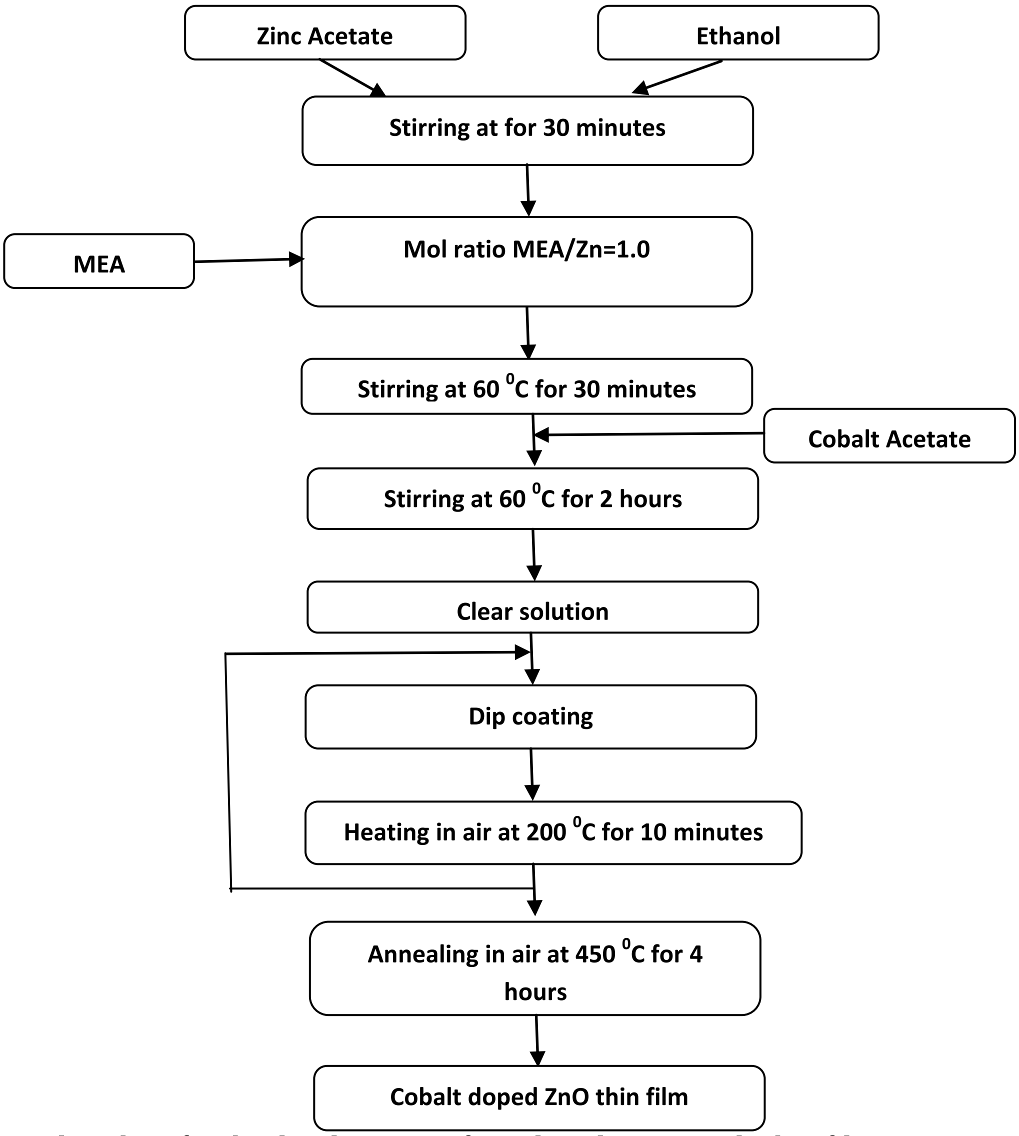

Figure 1. Flowchart for the development of Co-doped Zinc Oxide thin films preparation.

2.1 Thin films characterizations

X-ray diffraction (XRD) was employed to determine the crystal structure of the thin films using a Bruker D8 Advance diffractometer. The chemical composition and surface morphology of the films were analyzed with an energy dispersive X-ray spectrometer (EDX) attached to a JEOL JSM-5800 LV scanning electron microscope (SEM). Optical transmission spectra were measured in the 200–800 nm wavelength range using a UV-Vis spectrophotometer (UV-3101 PC-Shimadzu). Photoluminescence (PL) was assessed at room temperature with an excitation wavelength of 250 nm using a Perkin Elmer LS 50B spectrofluorometer. Raman spectroscopy was performed using a 514 nm laser for spectral analysis of the films.

3. Results and discussions

3.1 Structural studies

Figure 2 displays the XRD patterns of both Co-doped and undoped ZnO thin films. The results reveal that all samples possess a wurtzite structure with a polycrystalline hexagonal phase (JCPDS36-1451). The texture coefficient (TC) was used to determine the preferred orientation of the films. A TC (hkl) value of 1 indicates randomly oriented crystallites, while values above 1 suggest a higher abundance of crystallites in a specific (hkl) direction. The calculated texture coefficients show that all films exhibit their highest TC values (TC = 1.5) in the (002) plane, demonstrating preferential growth along the c-axis, as illustrated in Figure 2.

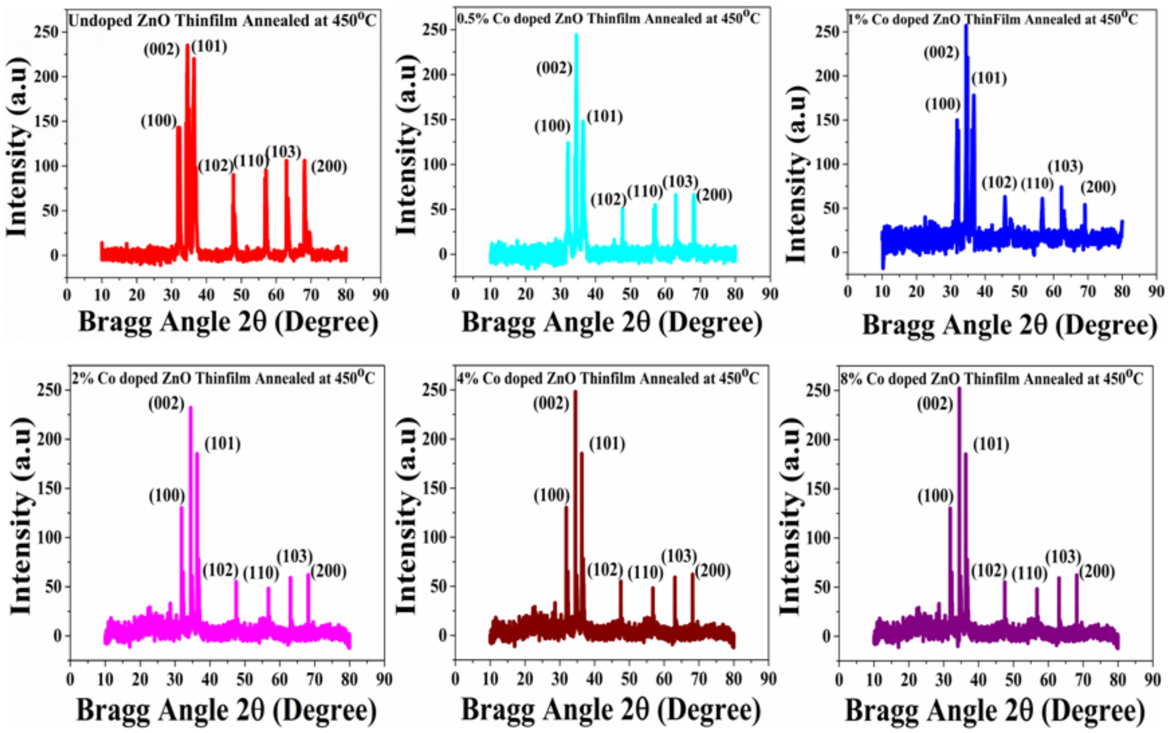

Figure 2: XRD pattern of immaculate and various at .% Co doped ZnO thin films.

Co-doping did not affect the hexagonal wurtzite structure of the ZnO films, and no secondary phases or Co element impurities were detected, suggesting that the doped Co ions were successfully incorporated into the ZnO lattice. The crystallite size of the films was estimated using Scherrer's formula [7].

$$d = \frac{k\lambda}{\beta Cos\theta} \quad (1)$$

were,
d- Average crystalline size
λ- Wave length
k- Constant=0.9
β- Angular width of diffraction peak at FWHM on the 2θ scale
θ- Bragg's angle
The (002) peaks were used to estimate the crystallite size. The calculated average crystallite sizes of ZnO thin films are given in the TABLE 1.

Table I: Average crystalline size of ZnO and Co doped ZnO thin films.

Sl No.	Doping Concentration(at%)	θ (Degree)	Cos θ (Degree)	FWHM (β) (Rad)	Average Crystalline size (nm)
1	0	17.2612	0.954961	0.0055	27.561
2	0.5	17.4737	0.953854	0.00612	24.797
3	1	17.2357	0.9550939	0.00693	21.871
4	2	17.2102	0.9552257	0.00480	31.571
5	4	17.1998	0.9552794	0.00705	21.494
6	8	17.5522	0.9534425	0.00738	20.573

3.2 Surface Morphology

Figure 3. clearly depicts the typical EDAX spectrum of undoped and Co doped nanostructured ZnO thin film. It exhibits the peaks associated with Zinc (Zn) and Oxygen (O) molecules. Figure 3 clearly shows the compositional investigation of $ZnOCo_5$ samples, which shows the existence of Zn, O then Co elements alone, which designates that the nanostructured thin film contains Zinc, Oxygen and Cobalt ions.

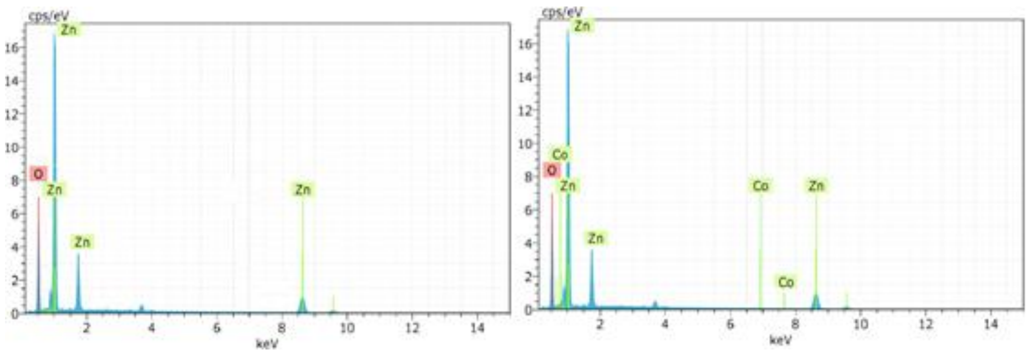

Figure 3: (a) EDAX image of undoped ZnO thin film, (b) EDAX image of Co undoped ZnO thin film

To confirm the presence of Co and assess the cleanliness of the films, an EDX measurement was performed. Figure 3 displays the EDX spectrum for both undoped and 8% Co-doped ZnO films, confirming the presence of cobalt in the ZnO matrix. The EDX results indicate successful doping of Co into the films.

The SEM images in Figure 4 reveal that the undoped ZnO thin film has a smooth, uniform surface with small ZnO grains. In contrast, the Co-doped ZnO films exhibit irregular, fiber-like stripes and a wrinkled network structure, with this morphology being more pronounced and denser in the 4% and 8% Co-doped ZnO films. Generally, sol-gel ZnO thin films display a network-like structure with wrinkles and fiber-like stripes on their surface. The incorporation of Co ions into the ZnO thin films altered the surface morphology from a granular texture to a wrinkled network, likely due to the introduction of impurities and subsequent structural imperfections in the ZnO crystal. This study suggests that the Co dopant influences nucleation growth in various directions, affecting the overall surface morphology of the Co-doped ZnO film.

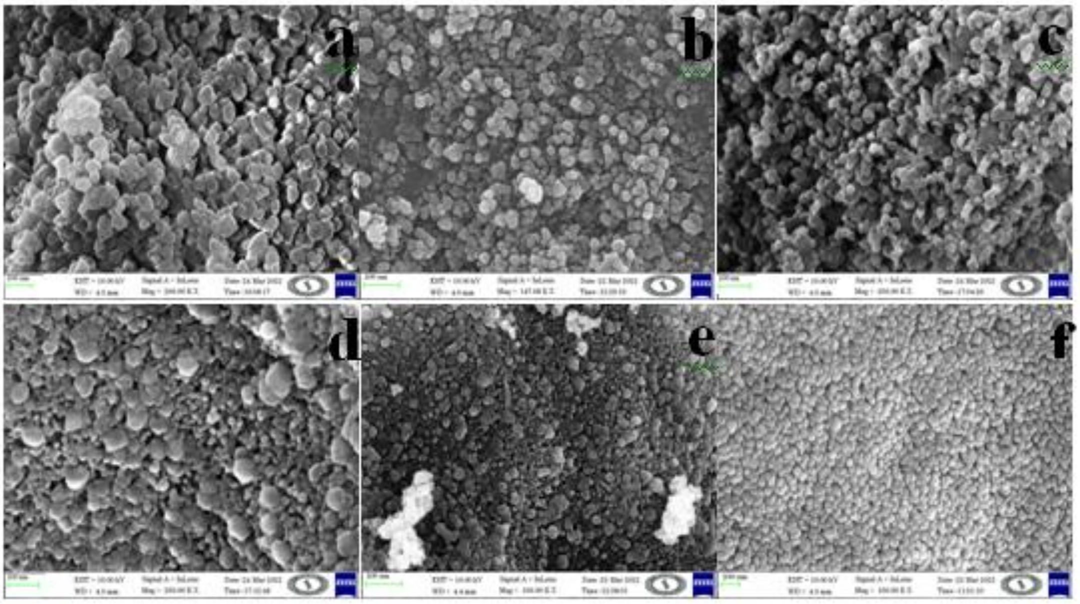

Figure 4: SEM images of (a) undoped ZnO thin film, (b) 0.5 at.% CZO thin film, (c) 1 at.% CZO thin film, (d) 2 at.% CZO thin film, (e) 4 at.% CZO thin film and (f) 8 at.% CZO thin film.

High doping concentrations and annealing temperatures can lead to grain agglomeration, resulting in larger grains. However, as the concentration of Co ions increases, the extent of agglomeration tends to decrease. The agglomeration is attributed to magnetic interactions between the particles. At the nanoscale, particles have a high surface-to-volume ratio, which increases interfacial surface tension and contributes to agglomeration. Additionally, the accumulation of Co^{2+} ions at grain boundaries applies tensile stress and pressure on the grains, which reduces their size. The results confirm successful Co doping in the films, which clearly exhibit a hexagonal shape. In contrast, undoped films show a spongy microstructure. Furthermore, as the annealing temperature rises, the intermolecular spacing decreases, leading to an increase in conductivity [8].

4. CONCLUSION

Bulk samples of CZO thin films with uniform thickness were produced using Sol-Gel dip coating techniques, with varying Co concentrations and annealed at different temperatures. The study explored the effects of cobalt on the structural, optical, and electrical properties of CZO thin films. Analysis of the diffraction patterns confirmed that the nanoparticles maintain a hexagonal wurtzite structure and that Co is well-integrated into the ZnO crystal lattice. The lattice strain increases with higher doping concentrations and annealing temperatures, aligning with the crystalline size measurements obtained from XRD peaks, which range from 28 to 22 nm. Optical properties were assessed through absorption spectra, revealing that the band gap decreases with increasing annealing temperature and doping concentration. The film with 1 at% Co-doped ZnO annealed at 450°C exhibits the smallest bandgap energy. The conduction mechanism of the film varies with temperature. The produced films demonstrate low resistivity, high conductivity, a strong optical bandgap, and good transparency in the visible range, making them well-suited as transparent conductive oxides (TCOs) for solar cells.

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