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Structural, Optical and Magnetic Properties of Nanocrystalline Co-Doped ZnO Thin Films Grown by Sol–Gel

Abstract: Cobalt-doped ZnO thin films have been deposited using a sol–gel route by changing the number of coats on the substrate from 6 to 18. This project deals with various film thicknesses by increasing the number of deposited coats. The effect of thickness on structural, magnetic, surface morphology and optical properties of Co-doped ZnO thin film was studied. The crystal structure of the Co-doped ZnO films was investigated by X-ray diffraction. The films have polycrystalline wurtzite hexagonal structures. A Co\(^{2+}\) ion takes the place of a Zn\(^{2+}\) ion in the lattice without creating any distortion in its hexagonal wurtzite structure. An examination of the optical transmission spectra showed that the energy band gap of the Co-doped ZnO films increased from 3.87 to 3.97 eV with an increase in the number of coatings on the substrate. Ferromagnetic behaviour was confirmed by measurements using a vibrating sample magnetometer. The surface morphology of thin films was assessed by scanning electron microscope. The grain size on the surface of thin films increased with an increase in the number of coats.

Keywords: Co Doping; Growth from Solutions; Magnetic-Optic Materials; Solar Cells; ZnO.

1 Introduction

ZnO is an \(n\)-type semiconductor that is oxygen deficient. It has many important parameters, for example, it is highly transparent, it has large carrier mobility, direct band gap [1, 2], and room temperature luminosity. ZnO was doped with three-dimensional (3D) transition metal (TM) ions, especially Co [3], Fe, Ni [4], Cr, and Mn [5], to obtain diluted magnetic semiconductors (DMS). Various experimental analyses showed that TM-doped ZnO has ferromagnetic behaviour [3–5]. The difference in radii between divalent Co (0.58 Å) and divalent Zn (0.74 Å) allows Co\(^{2+}\) ion to easily replace Zn\(^{2+}\) ion in the ZnO lattice. ZnO is a compatible material for high-temperature, high-frequency electronic devices, and thus DMS Co-doped ZnO can be a good choice for all those applications in spintronic devices.

Cobalt-doped ZnO thin films can be found in numerous applications such as in memory devices, display devices, solar cells and sensors [6, 7]. Co-doped ZnO thin films are supposed to be a promising material because of its conductivity, transparency and low cost.

Many researchers have deposited Co-doped ZnO thin films by chemical vapour deposition, chemical solution deposition, and physical vapour deposition [8–11]. A famous method for thin film deposition is sol–gel, in which the hydrates of many materials are used as precursors; this route has been followed in this work to deposit thin films of Co-doped ZnO. Here, we mainly focus on producing Co-doped ZnO thin films. Ferromagnetism is inducted in DMS by the introduction of TM ions to substitute ions of semiconductors provided the concentration of the magnetic substituent is kept very low in the range of 1%–10%. We kept the percentage of Co doping at 5% in the ZnO lattice and changed the number of coats on the substrate from 6 to 18. The structural, optical, surface and magnetic properties of the synthesised films were studied.

2 Experimental Details

Cobalt-doped zinc oxide thin films were deposited; a total of 5% cobalt precursor was doped to 95% zinc oxide sol. The starting materials were zinc acetate dihydrate 0.5 M Zn(\(\text{CH}_3\text{COO}\))\(_2\)·H\(_2\)O and cobalt nitrate hexa-hydrate 0.5 M Co(NO\(_3\))\(_2\)·6H\(_2\)O. First, the calculated amount of zinc acetate dihydrate was added in 30 mL distilled water and zinc oxide sol was prepared. In a similar way, Co sol was prepared. Then, cobalt sol was added in the Zn sol and magnetically stirred for 0.5 h at 60°C. Then, 30 mL of ethanol and 5 mL of triethylamine were added to
the sol, which was magnetically stirred for 5 h; ethanol was used as a solvent and triethylamine acted as a stabiliser. After 24 h of aging, thin films were deposited on the glass substrate with the same withdrawal speed of 250 mm/s, but the number of coats varied between 6, 9, 12, 15 and 18. This deposition process was performed to obtain various thicknesses of the thin films and to study the effect of thickness on the characteristics of the films. After each coat, the film was dried at 200°C and, in this way, the required number of coats was obtained on films. Films were annealed in a furnace for 4 h at 500°C.

The structural analysis of the films was performed using Model D/MAX-II, RIGAKU, Germany X-ray diffractometer. The diffraction angle was adjusted from 30° to 80° with a step width of 0.02°. The surfaces of the thin films were evaluated using a scanning electron microscope (SEM; Hitachi S-3400, UK). Magnetic study was carried out using a vibrating sample magnetometer (Lake Shore 7407; Westerville, USA). Optical transmittance was recorded using a Hitachi U-2800 UV–VIS–NIR (Hitachi U-2800 UV–VIS, USA) double beam spectrophotometer. Chemical bonding was evaluated by Fourier transform infrared (FTIR) spectroscopy (Model M 2000; Midac, USA).

3 Results and Discussion

3.1 FTIR

As shown in Figure 1, FTIR was performed to observe the chemical bonds in Co-doped ZnO and thus to infer the types of bonds located in the material. The absorbance bands at wave numbers 1552 and 1650 cm⁻¹ are caused by the organic group carbon (carbonyl carbon –C=O). The symmetric stretching occurs between 1430 and 1379 cm⁻¹ because of C–O. Bands in the wave number region 600–1200 cm⁻¹ were due to ZnO and Co–O bonding [3]. The absorption bands at wave numbers 456 and 485 cm⁻¹ were caused by the bond between zinc and oxygen [1, 2].

3.2 Structural Properties

The X-ray diffraction (XRD) spectra of Co-doped ZnO thin films are presented in Figure 2, with recorded peaks that belong to the polycrystalline wurtzite ZnO (JCPDS card no. 89-0510). The preferred orientation remains at (101) for films having 6, 9, 12 and 15 coats of Co-doped ZnO. For 18 coats, the preferred orientation shifted to (100). The (100) and (101) peaks became less intense with an increase in the number of coats whereas the intensity of the (002) peak was almost the same with the number of coats except for the (100) planes, whose intensity increased with 18 coats. Due to the lower atomic structure factor for Co compared with Zn [12], in which the atomic structure factor relies on the material scattering of incident radiation and correlates the observed diffracted intensity per atom to that formed by a single scattering unit, it is presumed that the intensity of the peaks becomes smaller with an increase in the number of coats. Peaks belonging to (102), (110), (103) and (112) of ZnO can also be seen in the diffraction patterns but their intensities are very small and decrease further with an increase in the number of coats.

The average crystallite size, $D$, was evaluated using Scherrer’s formula [13]

$$D = \frac{0.94\lambda}{\beta_{2\theta} \cos \theta}$$

where $\lambda$ is the wavelength of CuKα radiation, $\theta$ is the Bragg angle of the highest intensity diffraction peak, and $\beta_{2\theta}$ is

![Figure 1: FTIR spectroscopy was used to identify the chemical bonds in Co-doped ZnO.](image)

![Figure 2: XRD pattern of Co-doped ZnO thin films with a different number of coats: (a) 6, (b) 9, (c) 12, (d) 15 and (e) 18.](image)
the full-width at half-maximum of the same peak. The crystallite size increased from 39.38 to 48.13 nm with an increase in the number of coats from 6 to 18. The presence of Co dopant and number of coatings are an obstacle for the growth of oxide, but reduce the crystal growth, causing an increase in crystallite size with an increase in the number of coatings.

The dislocation density ($\delta$) measures defects and imperfections created during film formation and is calculated using the equation:

$$\delta = \frac{1}{D^2}$$

Table 1 shows that dislocation density decreases with an increase in crystallite size leading to a decrease in defects in films.

The strain ($\varepsilon$) of the thin films was evaluated using the relation:

$$\varepsilon = \beta \cos \theta / 4$$

The strain was interpreted as a structural deformation, which is caused by an increase of the complex defect density in the material. The Co atoms produce imperfections in the ZnO lattice. The reason for the strain decrease is to capture more substitution sites by Co due to the increased number of coatings, which partially relaxes the compressive strain.

### 3.3 Optical Analysis

The optical properties of dip-coated thin films were studied using UV–VIS measurements in the 300–900 nm wavelength region. Figure 3 shows the transmission spectra recorded for all films. The transmission behaviour is as presumed, i.e. when the number of coats increases, the thickness of the films and the Co content increases, and the transmission decreases consequently. The dopant ions produce imperfections in the host lattice that confines the excitons, helps capture electron-hole pairs, and leads to decreased transmission in the IR region. Although transmission increased with an increase in the number of coats in the visible region. This increase was due to a decrease in the surface roughness of the films as confirmed by SEM images. Actually, these grains build up in an orderly manner by increasing the number of coats, decreasing the scattering of light, and increasing the optical transmission of the films. The decrease of the refractive index is also an indication of the increase of optical transmission. The absorption edge displayed a blue shift with enhancement in the number of coats. The recorded blue shift points to a modification of the band gap energy ($E_g$) of the thin films. The band gap of the thin films is evaluated from the Tauc equation [14]. The Tauc equation for a direct band gap material is narrated by the equation

$$\alpha h\nu = A(\nu - E_g)^n$$

where $\alpha$ is the absorption coefficient, and $A$ is the absorbance. As ZnO is a direct band gap material, the power $n$ is equal to 0.5. $(\alpha h\nu)^2$ is plotted versus $h\nu$. In the graph, a linear line is incorporated in the linear region. The envision of the linear line to the x-axis provides the band gap. Figure 4 and Table 2 show calculated band gap $E_g$ values of the Co-doped ZnO thin films.

The evaluated $E_g$ values for Co-doped ZnO thin films are 3.87, 3.94, 3.95, 3.96 and 3.97 eV for 6, 9, 12, 15 and 18 coats, respectively. As the number of coats increased, the thicknesses of the thin films increased, leading to an increase in the band gap. The energy band gap is enhanced because of active transitions between 3D levels in Co$^{2+}$ ions and great sp–d exchange interactions between the peripatetic ‘sp’ electrons and the ‘d’ electrons of Co [15].

<table>
<thead>
<tr>
<th>No. of coats</th>
<th>Crystallite size $D$ (nm)</th>
<th>Dislocation density $\delta \times 10^{2}$ (nm$^{-2}$)</th>
<th>Strain $\varepsilon \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>39.4</td>
<td>6.45</td>
<td>8.7</td>
</tr>
<tr>
<td>9</td>
<td>41.3</td>
<td>5.85</td>
<td>8.29</td>
</tr>
<tr>
<td>12</td>
<td>41.9</td>
<td>5.69</td>
<td>8.27</td>
</tr>
<tr>
<td>15</td>
<td>45.9</td>
<td>4.74</td>
<td>7.47</td>
</tr>
<tr>
<td>18</td>
<td>48.1</td>
<td>4.34</td>
<td>7.14</td>
</tr>
</tbody>
</table>

Table 1: Structural properties of Co-doped ZnO thin films with a different number of coats.
Figure 4: Variations in $(\alpha h \nu)^2$ as a function $h \nu$ of Co-doped ZnO thin films.

Table 2: Thickness and optical properties of Co-doped ZnO thin films.

<table>
<thead>
<tr>
<th>No. of coats</th>
<th>Thickness ($\mu$m)</th>
<th>Band gap $E_g$ (eV)</th>
<th>Extinction coefficient $k$</th>
<th>Optical conductivity ($\sigma$)</th>
<th>Refractive index ($n$)</th>
<th>Urbach’s energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.1</td>
<td>3.87</td>
<td>0.0055</td>
<td>0.021</td>
<td>1.62</td>
<td>0.24</td>
</tr>
<tr>
<td>9</td>
<td>4.0</td>
<td>3.94</td>
<td>0.0024</td>
<td>0.036</td>
<td>1.57</td>
<td>0.4</td>
</tr>
<tr>
<td>12</td>
<td>5.8</td>
<td>3.95</td>
<td>0.0014</td>
<td>0.071</td>
<td>1.55</td>
<td>0.26</td>
</tr>
<tr>
<td>15</td>
<td>6.3</td>
<td>3.96</td>
<td>0.0066</td>
<td>0.024</td>
<td>1.54</td>
<td>0.15</td>
</tr>
<tr>
<td>18</td>
<td>6.4</td>
<td>3.97</td>
<td>0.0048</td>
<td>0.016</td>
<td>1.56</td>
<td>0.14</td>
</tr>
</tbody>
</table>
The variation in the optical band gap energy with an increase in the number of coats is also attributed to an improvement in the crystalline quality of the films. Table 1 shows that as crystallite size increases with an increase in the number of coats, so does the band gap (Tab. 2). This increase in the band gap could be explained by the Burstein-Moss effect \[16, 17\]. When the number of coats is increased for Co-doped ZnO thin films, the excessive carriers are supplied to fill the conduction band edges, hindering the low energy transitions and widening the band gap of Co-doped ZnO thin films (Fig. 4); hence, a larger $h\nu$ transition clearly results in the blue shift.

It should be mentioned here that, in these films, we kept the Co doping percentage to 5% and increased the number of coats on the substrate. In these films, both transmission and optical band gaps increased with an increase in the number of coats whereas both had a decreasing trend when Co percentage was increasing \[18\] and the number of coats remain fixed.

The refractive index can be calculated from the following relation:

$$n = \left[ N + \left( N^2 - n_0^2 n_1^2 \right)^{1/2} \right]^{1/2}$$

where,

$$N = \left( n_0^2 + n_1^2 \right) / 2 + 2 n_0 n_1 (T_{\text{max}} - T_{\text{min}}) / (T_{\text{max}} * T_{\text{min}})$$

$n_0 = 1.0$ and $n_1 = 1.532$

Table 2 shows that the refractive index decreases with an increase in the number of coats on the substrate. The decrease in the refractive index with an increase in the number of coatings is due to the decreased polarisability \[19\] of the smaller Co$^{2+}$ ionic radius 0.54 Å compared with the Zn$^{2+}$ ionic radius 0.74 Å. At the same time, an increase in the number of coats decreased $n$ due to the improvement of crystallinity, which modified the structure and bonding arrangement.

The extinction coefficient (attenuation coefficient $k$) measures the energy loss of electromagnetic waves through the thin film. It depends on the thin film and the wavelength. This is the imaginary part of the complex relation index. Figure 5 shows a decrease of the extinction coefficient of Co-doped ZnO thin films with an
increase in the number of coats. This is explained by the very modest absorption of Co-doped ZnO thin films after an increase in the number of coats. The absorption coefficient $\alpha$ and the extinction coefficient $k$ are related by the formula \[ K = \alpha \lambda / 4\pi \]

Optical conductivity is related to absorption coefficient by the relation \[ \sigma = \alpha n c / 4\pi \]

$\sigma$ is the optical conductivity that decreases with the number of coats due to the addition of charge carriers. This was because the absorption coefficient of the Co-doped ZnO thin films decreases with an increase in the number of coats as shown in Figure 5 and Table 2.

The skin depth is defined as the distance at which the value of the photon energy has decreased to approximately $1/e$ of its initial value at the surface of the thin film. It is represented by $\chi$

\[ \chi = 1 / \alpha \]

Skin depth increased with an increase in the number of coats of thin films (Fig. 5 and Tab. 2).

The Urbach energy measures disarray in the film network, which is narrated as the following:

\[ A = A_0 \exp \left( \frac{hv}{E_u} \right) \]

where $A_0$ is a constant and $E_u$ is the Urbach energy. The decrease in the Urbach energy is attributed to the decrease of the defects, which is also confirmed by XRD, as the crystallinity of the films increases with an increase in the number of coats. The width of the Urbach tail $E_u$ was concluded from the linear fit (Tab. 2).

The high transmittance of the nanoparticles makes it suitable for solar energy collection because if it is attached to the surface of the collector, it will cut down on the reflection of solar light and transmit more light to the collector.

Table 3: Magnetic properties of Co-doped ZnO thin films.

<table>
<thead>
<tr>
<th>No. of coats</th>
<th>Saturation magnetisation, $M_s$ (emu/cm$^3$)</th>
<th>Coercivity $H_c$ (Oe)</th>
<th>Remanent magnetisation, $M_r$ (emu/cm$^3$)</th>
<th>Squareness, $S = M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In field</td>
<td>Out of field</td>
<td>In field</td>
<td>Out of field</td>
</tr>
<tr>
<td>6</td>
<td>7.26</td>
<td>6.73</td>
<td>207.2</td>
<td>279.3</td>
</tr>
<tr>
<td>9</td>
<td>4.58</td>
<td>3.72</td>
<td>243.3</td>
<td>315.4</td>
</tr>
<tr>
<td>12</td>
<td>2.85</td>
<td>2.47</td>
<td>285.3</td>
<td>321.4</td>
</tr>
<tr>
<td>15</td>
<td>2.53</td>
<td>2.18</td>
<td>357.4</td>
<td>393.5</td>
</tr>
<tr>
<td>18</td>
<td>2.36</td>
<td>2.13</td>
<td>429.5</td>
<td>471.6</td>
</tr>
</tbody>
</table>

Figure 6: Hysteresis of Co-doped ZnO thin film when magnetic field is applied (a) in field and (b) out of field.

3.4 Magnetic Studies

The magnetic properties of Co-doped ZnO thin films were studied by using a vibrating sample magnetometer. Co doping into ZnO induces ferromagnetism. The ferromagnetic behaviour of Co-doped ZnO thin films was further
investigated by measuring M–H curves at room temperature as shown in Figure 6. The magnetic field was applied vertically and parallel to the surface of the thin films. In Table 3, a summary of the ferromagnetic properties for Co-doped ZnO films with a different number of coats measured at room temperature is provided. Oxygen vacancies [21] produced due to an increase in the number of coats could markedly alter the band structure of ZnO and contribute to the ferromagnetism. The observed ferromagnetism is possibly due to the diffusion of Co into the ZnO lattice, which does not show any Co-related impurity phases or Co clusters as confirmed by XRD. This proposes that the ferromagnetic behaviour is not due to Co-related secondary phases, but likely due to

![SEM micrographs of Co-doped ZnO thin films with a different number of coats: (a) 6, (b) 9, (c) 12, (d) 15 and (e) 18.](image)

**Figure 7:** SEM micrographs of Co-doped ZnO thin films with a different number of coats: (a) 6, (b) 9, (c) 12, (d) 15 and (e) 18.
defects such as zinc vacancies and zinc interstitials [19]. Table 3 shows that coercive force increased and saturation magnetisation decreased with an increase in the number of coats. This means that the imperfections in the films are enhanced with a decrease in the number of coats on the substrates. Hence, it is inferred that room temperature ferromagnetism is only slightly linked to the imperfections [22]. The remanent magnetisation \( (M_r) \) for thin films lies between 0.8 and 0.19 emu/cm\(^2\) for the parallel, and 1 and 0.15 emu/cm\(^2\) for the vertically applied magnetic fields. The remanent magnetisation decreases with an increase in the number of coats on the substrate. The view of somewhat good magnetic moments at room temperature provides accurate proof of ferromagnetism in thin films. According to the Ruderman-Kittel-Kasuya-Yosida theory, the ferromagnetism is produced from the exchange coupling between ferromagnetic layer, host materials, and oscillatory damp with distance between magnetic cations. The decrement in magnetisation with the piling of the number of coats is generally assumed to be the consequence of aggregation of the Co ions, which produces a decrease in the Co–Co distance, and results in the decrease of ferromagnetism [23]. Therefore, the number of coats is crucial for Co-doped ZnO thin films to obtain ferromagnetism. Furthermore, saturation magnetisation has a reverse relation to the thickness of films [10]. Therefore, saturation magnetisation decreases whereas the thickness of the films increases with the number of coats (Tabs. 2 and 3).

3.5 Surface Morphology

Figure 7 shows the SEM of Co-doped ZnO films deposited at room temperature using a sol–gel dip-coating technique that increases the number of dips to 6, 9, 12, 15 and 18 to deposit five films. After six dips (Fig. 7a), the Co-doped ZnO thin films show porous anisotropic surface morphologies with a wedge shape. The wedge shape originates from an \( a \)-axis preferred orientation similar to the XRD results. Figure 7b shows a porous surface with cracks. The structure shows that the cracks were created after hydrolysis and carbonate formation during synthesis. It was observed that films with 12 coats (Fig. 7c) were composed of clustered grains with fewer unfilled sites on the surface of the film with average grains of 200 nm. This result assured that Co perfectly settled into the ZnO lattice and these results are in accordance with the XRD results. Figure 7d of the Co-doped ZnO thin film shows the polycrystalline surface of the film with hexagonal grains in accordance with the XRD results with an average grain size of 300 nm. Figure 7e shows that a further increase in the number of coating to 18 results in an increase in grain size within the films, with the appearance of cracks and large agglomerates on the surface. The Co-doped ZnO thin film’s surface shows the presence of grain boundaries and pores due to evaporation and decomposition of organic materials. This means that changes in the film’s thickness also affect the grain size of the Co-doped ZnO, where the average grain size was noticed to increase with an increase in the thickness of the thin films.

4 Conclusions

Co-doped ZnO thin films were prepared using a low-cost sol–gel dip-coating technique. It can be seen that the change in the number of coats of sol on the glass substrate played a vital role regarding the changes in the structural, optical, surface and magnetic properties of the thin films. XRD results assured doping of Co in the ZnO wurtzite lattice. The band gap values of the dip-coated film were in the range of 3.87 to 3.97 eV. The other optical constants such as extinction coefficient, skin depth, Urbach energy and the optical conductivity were also calculated and it showed a change by varying the number of coats on the substrate. The coercivity and remanence of the films were found to increase with an increase in the number of coats.

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References