Effect Of Cobalt Doping On The Optical Properties Of Magnesium Cobalt Oxide Nanofilm Grown By Electrodeposition Method

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ABSTRACT: Cobalt doped Magnesium Oxide nanofilms were grown by electrodeposition method using heptahydrated Magnesium tetraoxosulphate (VI) salt as source of Magnesium ion, Citric acid as oxidizing agent. Hexahydrated Cobalt Chloride salt was used as source of Cobalt ion and Sodium hydroxide as pH adjuster. The percentage doping was varied from 3% to 23% in intervals of 5%. Results of the study show that the optical properties viz; absorbance, reflectance, refractive index, extinction coefficient, electrical conductivity, complex dielectric constant and optical conductivity are directly proportional to percentage doping with cobalt while transmittance is inversely proportional. The film exhibits low absorbance, reflectance, and high transmittance in all the regions of electromagnetic spectrum.

Keywords: Optical properties; Doping; nanofilm; electrodeposition

1. INTRODUCTION

This research is aimed at growing Magnesium cobalt oxide nanofilms by electrodeposition method and determining the effect of cobalt doping on the optical properties with a view to ascertaining the possible applications. MgO structure is similar to the well-known NaCl structure [1]. Many techniques have been used to deposit MgO thin film such as spray pyrolysis [2], pulsed laser deposition [3], RF sputtering [4], sol–gel spin casting [5], ion beam-assisted deposition [6], metallocrystic chemical vapor deposition (MOCVD) [7]. MgO has the advantages of a wide band gap, low optical loss, and refractive index (≈1.7) that permits confined optical modes in ferroelectric materials [8]. MgO thin films have been widely used as a chemically stable buffer layer for the deposition of high Tc superconducting films and perovskite-type ferroelectric films because of its good lattice matching with mentioned materials and low chemical reactivity [9]. Magnesium oxide is one of several materials used as thin insulating layers in electronic devices [10]. MgO thin films have been proposed for use as a protective coating on the phosphor screens [11], a passivation layer in high-electron-mobility transistors [12] and a substrate for carbon nanotubes growth [13]. Many ferroelectric and superconducting oxide films, such as PZT, LiNbO3, BaTiO3 and YBa2Cu3O7, etc, have been prepared on Si substrates using MgO as an intermediate layer [14]. Nanosized MgO could be used for improving the transesterification reaction at the supercritical/subcritical temperatures [15], decontamination of chemical warfare agents, reducing chlorofluorocarbons [16] and for reactive adsorbents [17]. MgO thin films have also been applied as protective layers of dielectrics to improve the discharge characteristics and the panel’s lifetime in an ac-plasma display panel (ac-PDP) [18]. Nano-MgO is desirable for a potent disinfectant against bacteria, spores and viruses after adsorption of halogen gases due to the existence of superoxide (\(O_2^-\)) anions at the corners, edges, or surfaces of cubic MgO particles [19].

2. MATERIALS AND METHODS

ITO used as deposition substrates were washed with detergent and rinsed three times with distilled water. They were soaked in acetone for fifteen minutes to degrease them. The substrates were rinsed again in distilled water three times without any body contact to avoid contamination, then immersed in a beaker almost half-full of distilled water and put inside Shanghai ultrasonics (SY-180) for ultrasonic bath for ten minutes. They were again brought out using clean forceps, put in another clean dry beaker, and put inside the oven for ten minutes for drying. The slides ready for use were handled with clean forceps to avoid contamination. The precursors for deposition of nanofilms of MgCo2O4 with various percentages of Cobalt dopant are Heptahydrated Magnesium tetraoxosulphate (vi) salt as source of Magnesium ion, Citric acid as oxidizing agent, Hexahydrated Cobalt Chloride salt as source of cobalt ion and sodium hydroxide as pH adjuster. The deposition was carried out at room temperature of 303K, pH of 8.6, deposition time of ten minutes, and deposition voltage of 10V. Constant concentrations and volumes of Citric acid and Sodium hydroxide were used while the concentrations of MgSO4.7H2O and CoCl2.6H2O were varied in accordance with the percentage doping as shown in the table 1. The deposited films were annealed at 200°C for thirty minutes. Characterization of absorbance and percentage transmittance of the films was done with UV/Visible spectrophotometer while other optical properties were calculated accordingly. Characterization of structural property was done by X-Ray diffraction(XRD) while compositional characterization was done with X-Ray
3.0: THEORY/CALCULATIONS

3.1: Analysis of optical properties

The following mathematical tools were applied in the analysis of the following optical properties

3.1.1: Reflectance

The Reflectance of the films was calculated using the relation according to Rubby et al (2011) [20]:

$$R = 1 - \left( A + T \right)$$

Where A = absorbance, T = transmittance. However the absorbance and transmittance were obtained by the spectrophotometer characterization.

3.1.2: Refractive index (n)

Employing the mathematical relation as given by Rubby et al (2011) [20], the refractive index of the films was calculated using the relation:

$$n = \frac{1 + \sqrt{1 - R^2}}{1 - \sqrt{R^2}}$$

Where R = reflectance

3.1.3: Absorption coefficient (α)

The absorption coefficient of the films was calculated using the relation as given by:

$$\alpha = \frac{A}{\lambda}$$

Where A = Absorbance and λ = wavelength

3.1.4: Extinction coefficient (k)

Extinction coefficient of the films was determined using the relation as expressed by Nabeel (2011) [21], thus:

$$k = \frac{\alpha \lambda}{4\pi}$$

Where α = absorption coefficient and λ = wavelength

3.1.5: Optical conductivity (σo)

By the mathematical relation according to Sharma et al (2007) [22], the optical conductivity of the films was calculated thus:

$$\sigma_o = \frac{\alpha n c}{4\pi}$$

Where α = absorption coefficient, n = refractive index and c = velocity of light

3.1.6: Electrical conductivity (σe)

Electrical conductivity of the films was calculated using the relation;

$$\sigma_e = \frac{2\pi \sigma_o}{\alpha}$$

Where σo = optical conductivity and α = absorption coefficient.

3.1.7: Complex dielectric constant (εc)

This parameter was calculated by the relation according to Chopra (1969)[23], thus:

$$\varepsilon_c = \varepsilon_r + \varepsilon_i$$

Where $$\varepsilon_r = n^2 - k^2$$ = real dielectric constant and $$\varepsilon_i = 2nk$$ = imaginary dielectric constant., Nabeel (2011) [21],

3.2: Structural analysis

3.2.1: Average crystallite size (D)

The average crystallite size of the films was calculated using the Debye-Scherrer formular thus:

$$D = \frac{k \lambda}{\beta \cos \theta}$$

Where shape factor k ≈ 0.9 , λ = wavelength of the X-ray radiation, 

$$\beta = \text{full width at half maximum(FWHM)of the diffraction path}$$ , \( \theta = \text{diffraction angle} \)

3.2.2: Dislocation density (δ)

This can be evaluated from Williamson and Smallman’s formular thus:

$$\delta = \frac{1}{D^2} \text{ (lines/m}^2 \text{)}$$

3.2.3: Microstrain (ε)

This is calculated using the relation,

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

4.0 : RESULTS

4.1.: Absorbance
From fig. 1, Magnesium Cobalt oxide and magnesium oxide nanofilms generally exhibit low absorbance, maximum value (0.08=8%) for 23% doped, the undoped has maximum value of 0.035=3.5%. However, absorbance of the films is maximum in the ultraviolet region and decreases to zero in the near infrared region of the electromagnetic spectrum. From the result, it is observed that the absorbance increases with increasing percentage doping.

4.2: Transmittance

From fig. 2, the transmittance of the films is generally high, with minimum value (84%) in the UV region and increases to 100% in the NIR of electromagnetic spectrum. The transmittance decreases with increasing percentage doping with cobalt.

4.3: Reflectance

From fig. 3, the reflectance of the film is generally low, with maximum value in the UV region (0.0781 ≈ 7.8%) and decreases to zero in the NIR region of electromagnetic spectrum. The reflectance increases with increasing percentage doping with cobalt.

4.4: Refractive index

From fig. 4, the doped films exhibit high refractive index (< 1.59) in the UV region and decrease to minimum in the VIS-NIR regions of electromagnetic spectrum. Undoped film has maximum refractive index of 1.4 in UV region. The refractive index increases with increasing percentage doping with cobalt.
4.5: Extinction coefficient

From fig. 5, extinction coefficient of the film is maximum in the UV region and decreases to zero in the NIR region of electromagnetic spectrum. The extinction coefficient increases with increasing percentage doping with cobalt.

4.7: Complex dielectric constant

Fig. 7 shows that the complex dielectric constant of the film is maximum in the UV region and decreases to minimum in the VIS-NIR regions of electromagnetic spectrum. The complex dielectric constant increases with increasing percentage doping with cobalt.

4.6: Electrical conductivity

Result as shown in fig. 6, shows that electrical conductivity of the film is maximum in the UV region and decreases to minimum in the visible-NIR region of electromagnetic spectrum. The electrical conductivity increases with increasing percentage doping with cobalt.

4.8: Optical conductivity

Fig. 8 shows that the optical conductivity of the film is maximum in the UV region and decreases to zero in the NIR region of electromagnetic spectrum. The optical conductivity increases with increasing percentage doping with cobalt.
4.9: MORPHOLOGICAL ANALYSIS

![Fig. 9: Optical micrograph of MgCo2O4 nanofilm.](image)

The micrograph as shown in fig. 9 reveals the film as being uniformly deposited and polycrystalline.

4.10: COMPOSITIONAL ANALYSIS

**Table 2: Compositional analysis for Magnesium cobalt oxide nanofilm**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage doping</th>
<th>Mg</th>
<th>O</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>N23</td>
<td>3</td>
<td>58.4863</td>
<td>39.7022</td>
<td>1.8089</td>
</tr>
<tr>
<td>N14</td>
<td>8</td>
<td>55.4744</td>
<td>39.7018</td>
<td>4.8238</td>
</tr>
<tr>
<td>N24</td>
<td>13</td>
<td>52.4590</td>
<td>39.7023</td>
<td>7.8387</td>
</tr>
<tr>
<td>N25</td>
<td>18</td>
<td>49.4438</td>
<td>39.7026</td>
<td>10.8536</td>
</tr>
<tr>
<td>N26</td>
<td>23</td>
<td>46.4306</td>
<td>39.7009</td>
<td>13.8685</td>
</tr>
</tbody>
</table>

4.11: Structural analysis for Magnesium cobalt oxide nanofilm

![Fig. 10: XRD Pattern of MgCo2O4 nanofilm](image)

5.0 : DISCUSSIONS

The films generally have low absorbance due to their ultrathin nature. From fig. 1, the absorbance is maximum in the UV region (23% : 0.08→8%) and decreases to zero in the NIR region. Absorbance is directly proportional to the percentage doping with cobalt. As shown in fig. 2, the transmittance of the films is generally high in all the regions (UV-VIS-NIR), with minimum in the UV region (23% doped: 84%) and increases to maximum in NIR (≈100%). This property makes the films good material for phosphors, solar cell and photothermal application.

Fig. 3 shows that the reflectance of the films is generally low with maximum value of 0.0781→7.8% for 23% doped and decreases to zero in the NIR. This property makes it a good material for antireflection coating. By virtue of its low absorbance and low reflectance in UV, VIS, NIR regions of electromagnetic spectrum, the film could be used for Photo thermal application, Photovoltaic cells and Phosphors. Reflectance is directly proportional to the percentage doping with cobalt. Result as shown in fig. 4, shows that the refractive index of the doped films is generally high in the UV region with 23% doped having maximum (1.78) while 3% doped has minimum (1.6). The undoped film has refractive index of 1.4. However, refractive index decreases to minimum in the VIS-NIR region. This makes the film a good material for antireflection film stack. The refractive index is directly proportional to the percentage doping with cobalt. From fig. 5,6,7, and 8, the films exhibit maximum extinction coefficient, electrical conductivity, complex dielectric constant, and optical conductivity respectively, in the UV region. Optical conductivity and extinction coefficient decrease to zero in the NIR while electrical conductivity and complex dielectric constant decrease to their minimum in the NIR. The optical properties viz: absorbance, reflectance, refractive index, extinction coefficient, electrical conductivity, complex dielectric constant and optical conductivity of the films are directly proportional to the percentage doping with cobalt while the transmittance is in inverse proportion. As a dilute magnetic semiconductor, MgCo2O4 finds good application in Spintronics, hard disks, magnetic discs, micro drive. Result of XRD analysis shows that the film has cubic structure with mean crystallite size of 1.907nm, dislocation density of 0.275lines/nm² and microstrain of 0.2160.

6.0: CONCLUSION

Cobalt doped Magnesium oxide nanofilm could be grown by electrodeposition method.

The Optical properties of the film viz: absorbance, reflectance, refractive index, extinction coefficient, electrical conductivity, complex dielectric constant and optical conductivity are directly proportional to percentage doping with cobalt while transmittance is inversely proportional.

7.0: REFERENCES


