OPTICAL DISPERSION CHARACTERIZATION OF SPRAYED CO$_2$O$_3$:Cu THIN FILMS

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Abstract: Uniform and adherent cobalt oxide Co$_2$O$_3$ and copper doped cobalt oxide Co$_2$O$_3$:Cu films have been deposited by using spray pyrolysis technique (SPT) on glass substrates. For investigating the structure and optical properties of thin films, X-ray diffraction (XRD) and UV-vis spectra were used. Increasing dopant caused an increase in the crystal size. The optical properties and dispersion parameters of cobalt oxide have been studied as a function of Cu dopant concentration. Changes in direct optical band gap of cobalt oxide films were confirmed after doping, the optical energy gap $E_g$ increased from 1.48 and 1.95 eV for the undoped Co$_2$O$_3$ to 1.55 and 2.05 eV with increasing the doping concentration of Cu to 5%. The changes in dispersion parameters and Urbach tails were investigated. An increase in the doping concentration causes a decrease in the average oscillator strength from 45.60 to 25.32. The single-oscillator parameter has been reported.

Keywords: TCOs, Dispersion parameters, Spray pyrolysis, Cobalt Oxide.

I. INTRODUCTION

The optical properties of thin films are very important for many applications, including interference devices, such as antireflection coatings, laser mirrors and monochromatic filters, as well as optoelectronics, integrated optics, solar power engineering, microelectronics and optical sensor technology depending on the reflectance and transmittance properties of the films during their preparation. Transparent conducting oxides (TCOs) are well known and have been widely used in optoelectronics and transparent electronics as well as in different research fields. Most of the existing TCOs are n-type, whereas it is very difficult to prepare binary metal oxides with p-type conductivity[1]. Among the transition metals, copper and cobalt are the most active for the decomposition of nitrous oxide and removal [2,3].

Cobalt oxide is an important functional material for a wide range of technological applications such as heterogeneous catalysts, anode materials in Li-ion rechargeable batteries, magnetism, and optical devices [4,7], gas and humidity sensors[8,9], solar selective absorber, pigment for glasses and ceramics [10], catalyst for oxygen evolution and oxygen reduction reaction [11,12]. It is widely used as an electrochromic material [13], electrochemical capacitors for high power devices in energy storage systems (supercapacitors) [14,15].

Owing to the influence of doping on the properties of materials, the controlled preparation of cobalt oxide of different doping materials and concentrations are always the researcher’s purpose. This paper reports the influence of Cu dopant on the preparation and properties of cobalt oxide (Co$_2$O$_3$) thin films by spray pyrolysis technique (SPT). The accurate determination of the optical properties of these materials is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications.
II. EXPERIMENTAL DETAILS

Cobalt (II) chloride hydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 0.1M as matrix material and copper chloride $(\text{CuCl}_2 \cdot 2\text{H}_2\text{O})$ 0.1M as a doping agent with different Cu/Co mole ratio = 1%, 3% and 5% have been dissolved in de-ionized water and ethanol to form the final spray solution, these two starting solutions were used for deposition of $\text{Co}_2\text{O}_3$ : Cu thin films on glass substrate. A few drops of HCl were added to make the solution clear, a total volume of 50 ml was used in each deposition. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle of 1 mm. The films were deposited on preheated glass substrates at a temperature of 450°C. With the optimized conditions that concern the following parameters, spray time was 10 sec. The period between spraying processes was about 3 min, this period is enough to avoid excessive cooling of glass substrate. The carrier gas (filtered compressed air) was maintained at a pressure of $10^5$ Nm$^{-2}$, distance between nozzle and substrate was about 29 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 300nm. A thermocouple was fixed to the substrate surface and the temperature was measured at the four corners of the glass substrate surface. Optical transmittance and absorbance were recorded in the wavelength range (300–900nm) using UV-visible spectrophotometer (Shimadzu Company Japan). Optical transmittance and absorbance were reported in order to find the effect of doping on the parameters under investigation.

III. RESULTS AND DISCUSSION

Structural analysis of cobalt oxide films was carried out on a Philips x-ray diffractometer system with CuK$_\alpha$ target by varying diffraction angle 2θ from (20–80) degree. XRD pattern of films reveal formation of $\text{Co}_2\text{O}_3$ cubic phase with (1 1 1) and (2 2 2) planes in all samples and $\text{CuCoO}_2$ in samples that contain Cu. Because of doping, major XRD peaks became sharper and improvement in the crystallinity can be observed. Also, by increasing dopant, another phase of hydrous Cobalt oxide $\text{Co}_3\text{O}_4$ was emerged. The average grain size of the $\text{Co}_2\text{O}_3$ thin films was calculated using the Debye–Scherrer’s equation [16–18]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$ ……… (1)

Where D is the grain size, $\lambda$ is the x-ray wavelength, $\theta$ is the Bragg angle and $\beta$ is the full width at half-maximum of diffraction peak. Table (1) shows average grain size which are varied between 21-38 nm for different samples. They were increased by increasing dopant. It is noteworthy that we could achieve the oriented growth of $\text{Co}_2\text{O}_3$ onto amorphous glass substrate using the spray pyrolysis technique. The oriented growth might be due to the heating of substrates during deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mole ratio Cu/Co</th>
<th>2θ</th>
<th>$\beta$</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>19.31</td>
<td>0.375</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>1 %</td>
<td>18.85</td>
<td>0.335</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>3 %</td>
<td>18.75</td>
<td>0.255</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>5 %</td>
<td>18.65</td>
<td>0.231</td>
<td>38</td>
</tr>
</tbody>
</table>

The optical properties of films by means of optical absorption in the UV to Vis region of (500–900) nm have been investigated. The absorption coefficient ($\alpha$) could be calculated by using the following relation [19]:

$$\alpha = \frac{2.303A}{t}$$ ………………….(2)
Where \( A \) is the absorption and \( t \) is the film thickness.

Fig. (1) Shows the dependence of the absorption coefficient \( (\alpha) \) on the wavelength. The absorption coefficient decreases with increasing the doping concentration of Cu. It can be seen from the figure that the absorption coefficient decreases up to wavelength 620 nm and then increases up to 750 nm and again decreases from 780 nm, depicting two regions of optical transitions. Similar type of results were reported by Shinde et al. [20]. Also it can be observed from the figure that the absorption coefficient decreased with increasing the doping concentration of Cu to 5%.

From the transmittance data and according to Tauc [21] relation, \((\alpha h\nu)^{\frac{1}{2}}\) versus incident photon energy \((h\nu)\), plots were obtained. The graphs are represented in Figure 2. As cobalt oxide is a direct transition semiconductor, the estimated band gap energy values are found to be 1.48 and 1.95 eV for the un-doped films, which is in consistent with the band gap energy of cobalt oxide films reported earlier for spray pyrolysis method [22,23]. After doping and increasing the doping concentration to 5% of Cu, the band gap energy values were increased to 1.55 and 2.05 eV. Many reports exist for cobalt oxides, such as CoO and Co\(_2\)O\(_3\), but the literature is deficient of the information on Co\(_3\)O\(_4\) thin films, particularly on its energy band gap. Drasovean et al. [24] reported 2.09-2.10 eV and 1.25-1.30 eV for direct and indirect band gaps respectively for Co\(_3\)O\(_4\) thin films. However, bandgap values of 2.2-2.8 and 1.4-1.8 eV have also been reported for CoO and Co\(_2\)O\(_3\), respectively [25]. The values obtained in this work are close to others previously reported for the direct transition in CoO, Co\(_2\)O\(_3\), and Co\(_3\)O\(_4\) thin films [24-27].

It can be seen from fig. (2) that all films have two different regions was put in evidence, corresponding to different phases. It was proved that \( E_g \) values, corresponding to these phases. The activation energy calculated from the slopes of graphs represents the location of trap levels below the conduction band.
The incorporation of impurity into the semiconductor often reveals the formation of band tailing in the band gap. The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [28]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [21, 29]:

$$ \alpha = \alpha^0 \exp \left( \frac{h\nu}{E_U} \right) $$

(3)

Where $\alpha^0$ is a constant, $E_U$ is the Urbach energy, which characterizes the slope of the exponential edge. Fig. (3) shows Urbach plots of the films. The value of $E_U$ was obtained from the inverse of the slope of $\ln(\alpha)$ vs. $h\nu$ and is given in Table (2). The dopants change the width of the localized states in the optical band. $E_U$ values change inversely with the optical band gap. The Urbach energy values of $Co_2O_3$, $Co_2O_3:Cu 1\%$, $Co_2O_3:Cu 3\%$, and $Co_2O_3:Cu 5\%$ films were calculated to be 152, 110, 102 and $81$ meV respectively. The decrease of $E_U$ suggests that the atomic structural disorder of $Co_2O_3$ films increases by copper doping. This behavior can result from increasing the concentration of point defects induced by the dissolution of Cu atoms in $Co_2O_3$ crystals and formation of solid solution. So, this decrease leads to a redistribution of states, from band to tail. As a result, both an increase in the optical gap and a narrowing of the Urbach tail are taken place.
The refractive index dispersion plays an important role in optical communication and designing of the optical devices. Therefore, it is important to determine dispersion parameters of the films. The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation [30,31]:

\[ n^2 - 1 = \left[ \frac{E_o E_o}{E_o^2 - E_d^2} \right] \quad \text{……… (4)} \]

The physical meaning of the single-oscillator energy \( E_o \) is that it simulates all the electronic excitation involved and \( E_d \) is the dispersion energy related to the average strength of the optical transitions [32], which is a measure of the intensity of the inter band optical. This model describes the dielectric response for transitions below the optical gap. The \((n^2 - 1)^{-1}\) vs. \((h\nu)^2\) plots for the films was plotted as shown in Fig. (4). \( E_o \) and \( E_d \) values were determined from the slope, \((E_o/E_d)^{-1}\) and intercept \((E_o/E_d)\), on the vertical axis and are given in Table (2). \( E_o \) values increased with the dopants as the optical band gap increase. According to the single-oscillator model, the single oscillator parameters \( E_o \) and \( E_d \)are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum \( M_{-1} \) and \( M_{-3} \) moments can be derived from the following relations [33]:

\[ E_o^2 = M_{-1} / M_{-3} \quad \text{……… (5)} \]
\[ E_d^2 = M_{-3} / M_{-3} \quad \text{……… (6)} \]

The values obtained for the dispersion parameters \( E_o \), \( E_d \), \( M_{-1} \) and \( M_{-3} \) are listed in Table (2). The obtained \( M_{-1} \) and \( M_{-3} \) moments changes with the dopants.

For the definition of the dependence of the refractive index \( n \) on the light wavelength \( (\lambda) \), the single-term Sellmeier relation can be used [30]:

\[ n^2(\lambda) - 1 = S_o \lambda_o^2 / \left[ 1 - (\lambda_o / \lambda)^2 \right] \quad \text{……… (7)} \]

Where \( \lambda_o \) is the average oscillator position and \( S_o \) is the average oscillator strength. The parameters \( S_o \) and \( \lambda_o \) in Eq. (7) can be obtained experimentally by plotting \((n^2 - 1)^{-1}\) against \( \lambda^{-2} \) as shown in Fig. (5), the slope of the resulting straight line gives \( 1 / S_o \), and the infinite-wavelength intercept gives \( 1 / S_o \lambda_o^2 \). The results shows an increase in the band gap which may be attributed to the presence of unstructured defects, that decrease the density of localized states and cause a narrowing in the Urbach tail and consequently increase the energy gap.
Table (2): The optical parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole ratio Cu/Co</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_{ume}$ (eV)</th>
<th>$E_{\infty}$</th>
<th>$n(0)$</th>
<th>$M_1$ eV$^{-2}$</th>
<th>$M_3$ eV$^{-2}$</th>
<th>$S_o\times 10^3$ m$^{-3}$</th>
<th>$\lambda_o$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>2.96</td>
<td>45.60</td>
<td>1.48</td>
<td>152</td>
<td>16.38</td>
<td>4.05</td>
<td>15.38</td>
<td>1.75</td>
<td>13.1</td>
</tr>
<tr>
<td>2</td>
<td>1 %</td>
<td>3.02</td>
<td>30.15</td>
<td>1.50</td>
<td>110</td>
<td>11.00</td>
<td>3.32</td>
<td>10.00</td>
<td>1.10</td>
<td>5.93</td>
</tr>
<tr>
<td>3</td>
<td>3 %</td>
<td>3.03</td>
<td>27.52</td>
<td>1.51</td>
<td>102</td>
<td>10.00</td>
<td>3.18</td>
<td>9.10</td>
<td>0.99</td>
<td>5.71</td>
</tr>
<tr>
<td>4</td>
<td>5 %</td>
<td>3.04</td>
<td>25.32</td>
<td>1.52</td>
<td>81</td>
<td>9.30</td>
<td>3.06</td>
<td>8.30</td>
<td>0.90</td>
<td>5.56</td>
</tr>
</tbody>
</table>
The optical conductivity was calculated using the relation [34]:

\[ \sigma = \alpha \frac{n c}{4\pi} \ldots (8) \]

Where \( c \) is the velocity of light. Fig. (6) shows the variation of optical conductivity with the wavelength. It can be seen that the optical conductivity decreases as the percentage of Cu in the Co\(_2\)O\(_3\) films increases to 5%. Also, it can be noticed that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region.

The skin depth could be calculated using the following relation [35]:

\[ \chi = \frac{\lambda}{2\pi k} \ldots (9) \]

Where \( \lambda \) is the wavelength of the incident photon, \( k \) is the extinction coefficient. Fig. (7) shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen for all samples, but the skin depth increases as the doping concentration increases, so the skin depth is a transmittance related.
IV. CONCLUSION

The oriented cobalt oxide thin films were prepared onto glass substrate by spray pyrolysis technique. Both doped and undoped samples were characterized. XRD pattern of films reveal formation of cubic phase with (1 1 1) and (2 2 2) planes in all samples and CuCoO₂ in samples that contain Cu. Optical band gap increased due to doping. Similarly, optical transmittance was affected for moderate doping. The small value of the absorbance in the visible region offered the most promise for realizing visible laser diodes (LD) and efficient light-emitting–diode (LED) displays, by using CoO₂:Cuxthin films in these devices. The single–oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value increased from 2.96 for CoO₂ filmsto 3.04 for CoO₂:Cuxfilms with increasing the doping concentration to 5%.

REFERENCES


