Structural and Optical Properties of CuO Doped (Li) Thin Films Prepared by Sol-Gel Technique

Raheem G. Kadhim\textsuperscript{a} and Ban Raheem Saleh Kzar\textsuperscript{b}

Department of Physics, College of Science, University of Babylon, Babylon, Iraq
\textsuperscript{a,b}E-mail address: Raheemnano2015@gmail.com, r.ban@yahoo.com

ABSTRACT

CuO and (Li–doped CuO) thin films have been prepared on glass substrates by sol-gel method using spin coating technique. X-ray diffraction (XRD) results reveal that the deposited CuO and (Li–doped CuO) thin films monoclinic crystal structure and the grain size increase with increasing concentration Li. The optical transition in the CuO and (Li–doped CuO) thin films are observed to be allowed direct transition. The value of the optical energy gap decreases with increasing of (Li) for all samples.

Keywords: CuO; Li; Sol-gel; spin coating; x-ray diffraction; UV-Visible

1. INTRODUCTION

Thin film is defined as thin layer built up on a solid support by controlled condensation of the individual, ionic species or atomic, molecular, either directly by a physical process, or via a chemical and / or electrochemical reaction [1]. Copper(II) oxide or cupric oxide (CuO) is the higheroxide of copper. As a mineral, it is known as tenorite. It is a black solid with anionic structure which melts above 1200 °C with some loss of oxygen. A monoclinic p-type semiconductor with band gap of 1.5-1.8 eV [2,3]. This is an attractive system for many researchers due to its photoconductive and photo-thermal applications and for studies of the transport mechanism in cuprates with high-TC superconductivity [4], Copper oxides have

...
found numerous applications in diverse fields such as solar cells and photovoltaic materials [5], electrochromic coatings [6], catalytic applications [7] and gas sensors [8]. Doped copper oxide thin films have found applications such as in the fabrication of p-type transparent conductors [9]. CuO have several advantages: (i) non-toxic nature (ii) availability and abundance of the starting materials, (iii) low production cost, (iv) p-type conductivity and (v) and band gaps lie in an acceptable range for solar energy conversion [10,11]. CuO thin films have been fabricated using different techniques such as electrodeposition [12] spray pyrolysis [13] and sol-gel techniques [14].

2. EXPERIMENTAL

CuO and (Li–doped CuO) thin films were deposited onto glass substrates by the sol–gel method using a spin–coating method. The CuO and (Li–doped CuO) precursor solutions were prepared starting from:

1. Copper (II) Chloride dehydrate (CCD) (2 g).
2. Methanol (20 mL).
4. Triethylamine (870 μL).
5. Hydrochloric acid (1 μ).

At first, the CuO precursor solution was prepared by the following procedure:

First solution: the Copper (II) Chloride dehydrate was dissolved in half of the methanol (10 mL) for each g of (CCD) at constant magnetic stirring until a transparent solution was obtained. The glycerol was added to the solution. Second solution: the trimethylamine previously dissolved in the other half of the methanol (10 mL) was also incorporated and the (HCl) was added in order easy dissolved process to the solution. Storing the mixture of the two solution for 24 hours at room temperature. The resulting solution is completely yellow-Green. The glass substrates were first cleaned by detergent, and then in methanol and acetone each for 10 min by using ultrasonic cleaner. At last, the substrates were rinsed with deionized water and dried with nitrogen. The dissolving of (0.1 g) of Lithium chloride monohydrate (LiCl, H₂O) nitrate in (25 ml) of methanol to prepare a Lithium and then doping the original solution with Lithium in three ratios of (1%, 2% and 4%) The coating solution was dropped into the glass substrate, which was rotated at 3000 rpm for (40 s) using LAURELL WS-400B-6NPP/LITE spin coater.

3. RESULT AND DISCUSSION

3. 1. X-ray diffraction results

X-ray diffraction patterns (XRD) of prepared for CuO and (Li–doped CuO) thin films are recorded at annealing temperatures 500 °C (1h) as shown in the Figures (1-3). The CuO (Li) doped CuO thin films are found to have a polycrystalline structure for all samples with a direction in the (111), (111) (020), (101)*, (211)* and (202)*, the intensity of (111) reflections increase with increase doped and grown in the monoclinic phase with strongly
preferred orientation, and it is noticed that the crystallite size increases with increasing of concentration of (Li). The crystallite size (D) was calculated using the Scherrer’s formula [15].

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

(1.1)

where \( \lambda \) (1.54056 Å) is the X-ray wavelength, \( \theta \) is the Bragg’s angle and \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak in radians. From the Table (1) it has been shown that the values of FWHM of peaks increases with the increasing concentration of (Li) but the crystalline quality become healthy compared to low doped and The standard interplanar distances (d-values) of CuO thin films are (1.70, 2.34, and 2.52) Å for diffraction peaks (111), (111) and (020) respectively, and the d-values are shown in Table (1).

Table 1. The calculated crystalline size (D), lattice spacing (d), full width at half maximum (FWHM) and angle for undoped CuO and different concentrations (Li) doped films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (Deg.)</th>
<th>( d_{hkl} ) Exp. (Å)</th>
<th>FWHM (Deg.)</th>
<th>D (nm)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>35.5</td>
<td>2.52</td>
<td>0.2272</td>
<td>38.38</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>38.3</td>
<td>2.34</td>
<td>0.3409</td>
<td>25.79</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>53.7</td>
<td>1.70</td>
<td>0.4545</td>
<td>20.46</td>
<td>(202)</td>
</tr>
<tr>
<td>Li 2%</td>
<td>35.5</td>
<td>1.32</td>
<td>0.2272</td>
<td>47.70</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>36.25</td>
<td>2.475</td>
<td>0.1703</td>
<td>51.20</td>
<td>(101)*</td>
</tr>
<tr>
<td></td>
<td>38.75</td>
<td>2.32</td>
<td>0.2272</td>
<td>38.70</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>1.72</td>
<td>0.1704</td>
<td>54.37</td>
<td>(020)</td>
</tr>
<tr>
<td></td>
<td>66.25</td>
<td>1.402</td>
<td>0.2275</td>
<td>43.46</td>
<td>(211)*</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>1.223</td>
<td>0.2272</td>
<td>46.97</td>
<td>(202)*</td>
</tr>
<tr>
<td>Li 4%</td>
<td>35.5</td>
<td>2.525</td>
<td>0.2840</td>
<td>30.66</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>36.5</td>
<td>2.458</td>
<td>0.2272</td>
<td>38.44</td>
<td>(111)*</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>2.306</td>
<td>0.3409</td>
<td>25.81</td>
<td>(111)</td>
</tr>
<tr>
<td></td>
<td>51.25</td>
<td>1.780</td>
<td>0.1704</td>
<td>53.81</td>
<td>(020)</td>
</tr>
<tr>
<td></td>
<td>69</td>
<td>1.359</td>
<td>0.2840</td>
<td>35.43</td>
<td>(211)*</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>1.223</td>
<td>0.2272</td>
<td>46.96</td>
<td>(202)*</td>
</tr>
</tbody>
</table>
Figure 1. XRD spectra of undoped (CuO) thin film.

Figure 2. XRD spectra of Li 2% doped CuO thin film.
3.2. The Optical Properties of undoped CuO and Li-doped CuO Thin films

The optical properties of deposited CuO and (Li) doped CuO thin films on glass, substrates have been determined by using visible transmittance spectrum in the region of (300-1100) nm, also calculate the optical energy gap for direct transition, absorption coefficient and optical constants like refractive index and extinction coefficient.

3.2.1. Absorbance

![Absorbance Graph](image)

**Figure 4.** The optical absorbance as a function of wavelength for undoped CuO and Li-doped CuO Film
The optical absorbance dependence on the wavelength (\(\lambda\)) in the spectra range 300-1100 nm for undoped CuO and (Li) doped CuO thin films measured at thicknesses of 120 nm respectively are shown in Figure (4). Films higher absorption on the shorter wavelength side (ultraviolet region), and low absorption on the higher wavelength side (visible region). The spectra reveal that the absorbance was decreased by the increase in doping.

3. 2. 2. Transmittance

The optical transmittance dependence on the wavelength (\(\lambda\)) in the spectra range 300-1100 nm for undoped CuO and (Li) doped CuO thin films measured at thicknesses of 120 nm respectively. are shown in Figure (5). It is clear from this Figure that the transmittance spectrum of all deposited thin films increases with the increasing of wavelength (\(\lambda\)). On the other hand, the transmittance spectrum increases with the increasing concentration of (Li) and this is due to the increase of the surface roughness promoting the decrease of the surface scattering of the light.

![Figure 5](image)

**Figure 5.** The optical transmittance as a function of wavelength for undoped CuO and Li-doped CuO Film

3. 2. 3. The Absorption Coefficient (\(\alpha\))

The absorption coefficient (\(\alpha\)) of the CuO and (Li) doped CuO thin films deposited on glass substrate at annealing 500 ºC. are shown in Figure (6). The absorption coefficient dependence on the wavelength in the spectral range 300-1100 nm, and then (\(\alpha\)) decreases with the increasing of wavelength. It is observed that the absorption coefficient (\(\alpha\)) decrease with increasing the concentration of Li. the absorption coefficient (\(\alpha\)) for the prepared thin film which calculated from eq. (1.2).

\[
\alpha = 2.303 \frac{A}{t} \quad (1.2)
\]
4.3.4. Refractive Index

The refractive index of the CuO and (Li) doped CuO thin films deposited on glass substrate at annealing 500 °C are shown in Figure (7). It can be noticed that the refractive index decreases with the increasing of doped ration and the refractive index decreasing with increasing of wavelength. The refractive index (n) was calculated from relation (1.3).

\[
n = \left[ \frac{4R}{(R-1)^2 - k^2} \right]^{1/2} - \frac{(R+1)}{(R-1)} \tag{1.3}
\]

where R represents the reflectance which can be calculated from the following equation (1.4)
\[ R + T + A = 1 \]  \hspace{1cm} (1.4)

4.3.5. Extinction Coefficient

The extinction coefficient CuO and (Li) doped CuO thin films deposited on glass substrate at annealing 500 °C. are shown in Figure (8). In general, it is clear that the extinction coefficient (k) decreases with the increasing of wavelength (λ) for all prepared samples and the extinction coefficient (k) decreases with the increasing concentration of (Li), the extinction coefficient of the films has an inverse relation with the transmittance spectra. The high (low) transmittance means low (high) extinction coefficient. The values of extinction coefficient (K) are calculated using the relation (1.5).

\[ K = \frac{\alpha \lambda}{4 \pi} \]  \hspace{1cm} (1.5)

where
\[ \lambda : \text{is the wavelength of incident photon rays} \]
\[ \alpha : \text{is the absorption coefficient} \]

![Figure 8](image_url)

**Figure 8.** The extinction coefficient (k) as a function of wavelength for CuO and (Li-doped CuO) thin films.

3.2.6. Optical Energy Gap

The values of optical energy gap (E_{g opt}) for CuO and (Li) doped CuO thin films deposited on glass substrate at annealing 500 °C. have been determined using Tauc equation. E_{g opt} is determined by the extrapolation of the portion at (\alpha h\nu)^2 from the relations between (\alpha h\nu)^2 versus the photon energy (h\nu), as shown in Figure (9) and Table (2). The direct optical energy gap (E_g) was calculated by using the relation (1.6)

\[ \alpha h\nu = A \sqrt{h\nu - E_g} \]  \hspace{1cm} (1.6)
In general, the values of direct optical energy gap decreasing with increasing concentration of Li for all samples. The direct $E_g^{\text{opt}}$ decrease from (1.6 to 1.49) eV.

Figure 9. The variation of $(a\hbar\nu)^2$ as a function of photon energy ($\hbar\nu$) for CuO and (Li-doped CuO) thin film.

Table 2. Show the values of $E_g^{\text{opt}}$ for CuO and (Li-doped CuO) thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO pure</td>
<td>1.6</td>
</tr>
<tr>
<td>Li 1%</td>
<td>1.59</td>
</tr>
<tr>
<td>Li 2%</td>
<td>1.5</td>
</tr>
<tr>
<td>Li 4%</td>
<td>1.49</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Monoclinic structure is the CuO phase for CuO and (Li-doped CuO) thin films and orientated along (111). The optical transition in the CuO and (Li-doped CuO) thin films is observed to be allowed direct transition. The value of the optical energy gap decreases with increasing concentration of (Li) for all samples.

References


(Received 19 September 2016; accepted 06 October 2016)