Annealing temperature effect on the Structure, Morphology and Optical properties of Copper Oxide CuO thin Films

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Abstract
Copper oxide (CuO) thin films were deposited on glass substrates by (sol-gel) method using a spin-Coating technique and the speed of the spin coater was fixed at 3000 rpm for 30 sec and the samples were annealed at temperatures (250, 350, 450, and 550 °C) for 1 hrs. The structural, Morphology, and optical properties of the film are determined by using X-ray diffraction (XRD), Atomic force microscopy (AFM) and UV-visible spectroscopy respectively. The XRD patterns showed that copper oxide (CuO) thin films prepared has polycrystalline structure and when increase the annealing temperature of the thin film over than 300° C the thin film turns from phase Cu2O to CuO phase and through examination (AFM) showed that the average grain size increases with the annealing temperature either Optical examinations showed decrease in transmission and increase in absorption coefficient with increase annealing temperature. The prepared thin films have direct energy gap and the value of the optical energy gap decreased with increasing annealing temperature from 3.99 eV to 3.94 eV.

Keywords: CuO thin film, Structure properties, Morphology analysis, optical properties, Annealing temperature, Spin-Coating method

1. Introduction
Study material as thin film is one of the important topics of solid-state physics contributed significantly in thin-film technology and the study of semiconductor and many of the physical and chemical properties and it have identification in order to determine the use in different applications [1]. Therefore, thin films raised in preparation a revolution in the field of applications, they have become a successful alternative to rigid materials (materials Bulk) in achieving their characteristics as well as the possibility of changing the physical and chemical properties of these materials [1, 2]. Copper oxide, is one of the semiconducting material and is not soluble in water and is not in the rule, can be obtained from oxidized of copper [3]. It is monoclinic crystal structure. The two main semiconductor phases of copper oxide are cuprous oxide (Cu2O) and cupric oxide (CuO) with narrow band gap [4, 5]. Their optical band gaps are (1.3 - 2.1) eV for Cu2O and (2.1 - 2.6) eV for CuO [6, 7]. Both CuO and Cu2O thin films are well known p-type semiconductors [5, 8]. The annealing of Cu2O in air at temperature up to 300 °C could turned from phase Cu2O to phase CuO [9, 10]. Thin films of Cu2O and CuO are widely used in a variety fields as applications of solar application. It is used in thermal photovoltaic complexes that require high efficiency and good range of stability and high absorbency in visible wave length range [11, 12], and in devices that convert solar energy [13], used in magnetic devices [14], in the magnetic storage media [15], and in Optoelectronic Device, where his various applications in photovoltaic devices as used in various devices such as smart windows [16], IR detector [17], light emitted diode (LED) [18], and fields emission [19], and Gas Sensors[20]. Thin films of copper oxide have been prepared by various deposition techniques such as chemical deposition [21], electrochemical deposition [22], thermal vacuum evaporation [23], sol gel techniques [24], chemical spray pyrolysis [25], pulsed laser deposition [26], plasma based ion implantation deposition [27] and Magnetron sputtering [28]. The current research used sol gel technique due to that enjoyed by the technology's many features, the substances prepared as less than pure form undesired impurities when preparing that way, it is also easy and inexpensive, it does not require high temperatures, co-synthesize two or more materials simultaneously, precisely control the microstructure of the final products, and precisely control the physical, mechanical, and chemical properties of the final products, etc [29].

2. Experimental
Procedures for sample preparation are described by figure (1), water copper chlorides (CuCl2.2H2O) used when preparing the solution used for the deposition of thin films of CuO, which is a fast greenish blue crystals soluble in water, the equivalent weighing (170.48g/mol), since the solution was attended temperature (60 °C) and concentration (0.1 M) by the concentration (1: 1) and then dissolving (0.68 g) of the material in (40ml) of ethanol and adding Diethanolamine (C2H11NO2) (DEA) (0.42 g) as stabilizer material, Using a magnetic mixer and after the completion of the process of solvent leaves the solution for (24 hrs.) to ensure homogeneity before and after the deposition, then filter the solution to get rid of plankton, then deposited using deposition system Spin-Coating (model VTC -100 Vacuum Spin Coater) processed Inc. (MTI Corporation) German origin on glass bases prepared in advance. The speed of the spin coater was fixed at 3000 rpm for 30 sec and samples are dried at a temperature (100 °C) for (10 min) and then at a temperature (150 ° C) for (10 min) and after the completion of the deposition layers and the drying process the
The annealing process was performed in this study to thin films prepared at temperatures (250, 350, 450, 550)°C for (1 hrs.) in an electric furnace heat (Model Thermconcept KLS 45/12) to get (CuO) and (Cu₂O) thin films. Crystal structure were investigated by X-ray diffraction (XRD) model PHILIPS PW 1840 using CuKα, (λ=1.540598Å, 30mA, 40 kV) in 2Θ range from 10° to 90°.

Fig (1): Procedures for the preparation of thin films

The Morphology of the surface has been studied by device: AA 3000 SPM Scanning probe Microscope. Optical measurements have been studied for prepared thin films for a range of wavelengths (300-1100) nm using a spectrometer, known as (UV-1800 (UV_Visible Spectrophotometer) processor from a company (Shimadzu) Japanese. Optical measurements included measuring the absorbance and transmittance within the wavelengths range the above-mentioned.

3- results and discussion
3-1 X-ray diffraction (XRD)
Figure (2) shows the results of XRD of the thin films of (CuO) prepared from water copper chlorides deposited on glass substrate and annealing at temperatures (250, 350, 450, 550)°C for 1 hrs. The results showed that all films were polycrystalline structure, at temperature (250°C) two peaks has been appeared one of the peaks toward (110) at the corner (2Θ = 29.3°) belonging to the (Cu₂O) phase and second peaks toward (110) at the angle (2Θ = 32.8 °) belonging to the (CuO) phase according to JCPDS card No. (05.0667 and 45.0937) respectively. But at a temperature (350 °C), the film turns into (CuO) phase, and at temperatures (350, 450 and 550) °C two peaks appear toward (110) and (002) at the angle (2Θ = 32.2° and 35.6°) respectively. These results showed match with researches [21,30,31].

Grain Size (D) was calculated using Debye-Scherrer [32]
\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] …… (1)

Where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half maximum (FWHM) in radians of the XRD peak and \( \theta \) is the Bragg's angle (deg).

Results of XRD examination are shown in table (1).
Fig (2): XRD patterns of the thin films prepared are annealed at temperatures (250,350,450 and 550 ° C) for 1 hrs.

Table (1) : The results of X-ray examination of the thin films prepared and are annealed at temperatures (250,350,450 and 550 ° C) for 1 hrs.

<table>
<thead>
<tr>
<th>Annealing temperature °C</th>
<th>2θ (deg)</th>
<th>Grain Size D (nm)</th>
<th>d(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>29.3</td>
<td>47.4</td>
<td>3.04</td>
</tr>
<tr>
<td>350</td>
<td>32.1</td>
<td>59.6</td>
<td>2.77</td>
</tr>
<tr>
<td>450</td>
<td>32.2</td>
<td>50.8</td>
<td>2.77</td>
</tr>
<tr>
<td>550</td>
<td>32.5</td>
<td>44.3</td>
<td>2.75</td>
</tr>
</tbody>
</table>

3-2 Atomic force microscopy (AFM)

Atomic force microscopy AFM used to study the Morphology of the surface and crystal structure of the surface thin films precipitated, and which was calculated average grains size, average surface roughness and average square root. Figure (3- 5) describe the two-dimensional images, three-dimensional pictures and distribution of the grains respectively for surfaces of prepared thin film. Table (2) shows that the value of each average grains size, surface roughness and average square root are increased with increase annealing temperature due to transmission, so spread of atoms increases with increasing temperature, and these results matches with [30,33], and values less when temperatures (450 and 550) °C is due to an increase in the surface energy at high temperatures, and this explains why low surface roughness and other values[30].

Table (2): Values obtained from AFM analysis.

<table>
<thead>
<tr>
<th>Annealing temperature °C</th>
<th>Average grains size (nm)</th>
<th>Average roughness (nm)</th>
<th>Average square root (nm)</th>
<th>Height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>87.66</td>
<td>0.414</td>
<td>0.481</td>
<td>2.51</td>
</tr>
<tr>
<td>350</td>
<td>98.19</td>
<td>0.564</td>
<td>0.658</td>
<td>2.85</td>
</tr>
<tr>
<td>450</td>
<td>92.60</td>
<td>0.411</td>
<td>0.476</td>
<td>2.60</td>
</tr>
<tr>
<td>550</td>
<td>87.32</td>
<td>0.349</td>
<td>0.4</td>
<td>2.28</td>
</tr>
</tbody>
</table>
Fig(3): Photos of AFM of the prepared thin films of copper oxide (CuO) are annealed at temperatures (250, 350, 450, and 550) °C for 1 hrs. in 2D.
Fig (4): Photos of AFM of the prepared thin films of copper oxide (CuO) are annealed at temperatures (250, 350, 450, and 550) °C for 1 hrs. in 3D.
Figure (5): The distribution of the grains on the surfaces of the prepared thin films of copper oxide (CuO) are annealed at temperatures (250, 350, 450 and 550) ° C for 1 hrs.

3-3 Optical measurements

Optical properties of materials important characteristics that can be relied upon to determine the spectral range in which they operate electro-optical devices and solar cells in particular optical detectors, and for optical identification must study the transmission and the absorbance spectrum of the thin films prepared.

Figure (6) shows transmittance spectrum of the prepared thin films (CuO) and are annealed at temperatures (250, 350, 450 and 550) ° C as a function of wavelength falling within the range (300-1100) nm, transmittance of thin films depends on the crystal structure of the material and annealing temperature. From Figure, we find that the transmittance values of the prepared thin films (CuO) increased with increasing wavelength, transmittance values are as little as possible in the wavelength region corresponding to the gap of the optical energy of thin films (CuO), i.e., in the ultraviolet region of the spectrum within the range (300-350) nm. Transmittance values begin increase gradually with increasing values of the wavelength in the visible region of any within the range (350-800) nm and almost start Stability (constant) from wavelength (380 nm) and continue regularity until a wavelength (1100 nm) and recorded the lowest transmittance when temperature (350°C). Also we noted the transmittance values decrease with increasing degree of annealing temperature, due to the appearance of new crystallographic defect or reason for this may be due to increased scattering and the increase of surface roughness due to annealing [34, 35].

Figure (6) transmittance spectrums of the prepared thin films of copper oxide (CuO) are annealed at temperatures (250, 350, 450 and 550) ° C for 1 hrs.
Absorption coefficient depends on the energy of incident photons, and the properties of the semiconductor, which includes the optical energy gap and the type of electronic transition, absorption coefficient ($\alpha$) was calculated using equation (2)[36]:

$$\alpha = \frac{2.303 A}{t} \ldots (2)$$

Where: $A$: absorbance, $t$: the thickness of the thin film.

Figure 7 shows the change of absorption coefficient as function of photon energy of the prepared thin films and are are annealed at temperatures (250,350,450 and 550) °C for 1 hrs. The figure notes that the absorption coefficient increase slightly with increasing the photon energy and the extent energies (1.1-3.8) eV, then followed by a sharp increase and suddenly when increasing photon energy for (3.8 eV), also notes that increasing the annealing temperature decreases the value of absorption coefficient. We note also absorption coefficient possess values higher than ($\alpha > 10^4$cm$^{-1}$) within the same range of energies, and this helps to expect transitions occur directly to this range of energies, it is possible to conclude the nature of the electron transition through the study of absorption coefficient values and the extent of change these values with the incident photon energy. As the high values of the absorption coefficient indicates that the possibility of electron transition be large and leads to a direct transitions and the energies that calculated in these values are the energy gap directly [37].

Figure (7): The change of absorption coefficient with photon energy of prepared thin films are annealed at temperatures (250,350,450 and 550) °C for 1 hrs.

Direct energy gap for samples can be calculated using Tauc relation [38]

$$\alpha h v = B (h v - E_g)^{1/2} \ldots (3)$$

Where B is a constant depends on the nature of the material, $h$ is Planck’s constant and $v$ is the photon frequency.

The relationship between $(\alpha h v)^2$ and photon energy $(hv)$ and extended straight portion of the curve to cut the photon energy axis at the point $(\alpha h v)^2 = 0$ we get the value of the energy gap.

Figures (8-10) show the optical energy gap for direct transmission of the copper oxide films are annealed at temperatures (250,350,450 and 550) °C respectively for 1 hrs. The results showed a decrease in the energy gap values with increase the annealing temperature, from 3.99 eV to 3.94eV. This result is consistent with [23, 24, 39, 40]. Since higher annealing temperatures lead to the formation of new localized levels down conduction band and this ready to receive the electrons and generate tails levels of optical energy gap and the tails are working towards reducing the energy gap due to increased nanoparticles the size of the thin films (CuO) as a result of increasing the annealing temperature [39, 41]. The CuO thin films show higher direct energy gap as compared to bulk value (1.3 - 2.1), the blue shift in the direct band edges as seen in present case is due to the quantum confinement effect [23,39].

Figure (8): Variation of $(\alpha h v)^2$ with Photon Energy of CuO thin film are annealed at temperatures 250 °C for 1hrs.

Figure (9): Variation of $(\alpha h v)^2$ with Photon Energy of CuO thin film are annealed at temperatures 350 °C for 1hrs.

Figure (10): Variation of $(\alpha h v)^2$ with Photon Energy of CuO thin film are annealed at temperatures 450 °C for 1hrs.
Copper oxide (CuO) thin films on glass substrates were prepared by the (sol-gel) method using a spin coating technique and are annealed at temperatures 350-550 °C for 1 hr.

4. Conclusion

The copper oxide (CuO) prepared has polycrystalline structure. The increase in the annealing temperature more than 300°C leads to transformation of the material phase from Cu2O to CuO. Particles size of the prepared films increases with the degree of annealing temperature, as well as increases surface roughness and the average square root.

5. References


تأثير درجة حرارة التمدين على الخصائص التركيبية والطبوغرافية والبصرية للأغشية الرقيقة (CuO)

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المتخص

في هذه الدراسة تم ترسيب الأغشية الرقيقة لأوكسيد النحاس (CuO) على قواعد زجاجية بطريقة (sol-gel) باستخدام تقنية الطلاء الدوراني (spin-Coating) وسرعة دوران ثابتة (3000 rpm) وبمدة ثانية واحدة (30 sec) وثمن ترسيب (250,350,450,550 °C) ولدنت العينات تحت درجات حرارة C. وتم تحديد الخصائص التركيبية والطبوغرافية والبصرية بواسطة حيود الأشعة السينية (XRD) وموجر القوة الذرية (AFM) ومطياف الأشعة فوق البنفسجية العميق (AFM) ومطياف الأشعة الفوق البنفسجية والمريمية على التوالي. أظهرت أنماط حيود الأشعة السينية أن الأغشية الرقيقة المحترقة لأخير أوكسيد CuO ذات تركيب متعدد البلورات عند زيادة درجة حرارة الغشاء إلى درجة حرارة أكثر من °C يتحول الغشاء من الطور Cu2O إلى الطور CuO، وتبين من خلال فحص CuO أن معدل الحجم الجيبي يزداد مع زيادة درجة حرارة التلدين. وأظهرت اختلافات في النافاذية وزيادة في معدل الاختصاص مع زيادة درجة حرارة التلدين. وأن الأغشية المحترقة تمتلك فجوة طاقة مباشرة 3.99 eV إلى 3.94 eV من الطاقة الحرة المتناقشة مع زيادة درجة حرارة التلدين من °C.