Low annealing temperature effect on Structural, and optical properties of CuO nanostructure thin films

Adel H. Omran Alkhayatt¹  Shawki Khalaf Muhammad²  Azher A. Habieb¹
Asala H. Ali³  Suhad H. Mohsen¹  Ruua Radhi Munem¹

¹University of Kufa - Faculty of Science, Iraq
² University of Kufa Faculty of Education for Girls
³Jabir Ibn Hayyan Medical University, Iraq
E-mail: adilh.alkhayat@uokufa.edu.iq

Abstract: In present work, the modified chemical bath deposition method (CBD) called successive ionic layer adsorption and reaction effective coast method was used for deposited copper oxide CuO nanostructured thin films. Structural, surface texture and optical characteristics of the deposited films were studied as a function of low annealing temperature (150, 200 and 250) °C. X-ray diffraction studies showed that the as-deposited and annealed films exhibited low crystallinity of polycrystalline nature in the monoclinic phase. It is observed a fixed or very little increment of peaks intensity and the crystallinity of the deposited films with the increase of annealing temperature to 250 °C. The lattice constants were calculated and show good agreement with the standard values. The crystallite size was decreased, whereas the dislocation density and the number of crystallites were increased with the increment of annealing temperature. The average grain diameter was increased and the average surface roughness decreased with the increment of annealing temperature. The optical energy gap for the as-deposited film is 1.87eV and increased to (2.03, 2.06 and 2.09) eV with the increment of annealing temperatures. The Urbach tails energy width decreased from 0.91 eV to (0.73, 0.54 and 0.46) eV for as-deposited and annealed films at low temperatures (150, 200 and 250) °C respectively. The low annealing temperatures was used because the deposition process was performs at low temperatures below 100 °C, therefore, it can be concluded that the low annealing temperatures used in this work are not suitable temperatures for the growth of CuO films and it can be above 300 °C to enhance the film crystallinity and formation of CuO phase.

1. Introduction
Thin films of semiconductor metal oxides such as CdO, CuO, ZnO, SnO₂, In₂O₃ and etc. was attractive very large scientific attention due to its wide range of applications. One of the most important of metal oxide is copper oxide (CuO) which exhibits distinguishable properties, direct forbidden energy band gap (~1.2-2.1) eV, p-type conductivity nontoxicity nature, physical and chemical stability, low cost material, superfluity in nature and receptivity good optical and electrical properties [1–4]. Therefore CuO has got considerable attention in photovoltaic and optoelectronic applications [5], such as solar energy transformations and solar cells [6] gas sensors [7], batteries [8] magnetic storage media [6] catalysts [9], diodes, transistors and superconductors high-Tc [10]. The
semiconductor pn junction devices such as diodes, transistors, light emitting diodes, photodiodes and solar cells depend on junction technology. So the p-type semiconductors were very important for developing these devices and its applications [11]. CuO nanostructure thin films have been deposited using various physical and chemical methods such as electro deposition [4], pulsed laser deposition [12], spray pyrolysis [13], sputtering [14], thermal oxidation [15], chemical vapor deposition (CVD) [16], sol–gel [17] and (m-CBD) SILAR [3, 18]. Within these methods, modified chemical bath (SILAR) is an unrivaled method where the thin films of semiconductors compound can be prepared by frequently submersion the desired substrate into the solutions containing the components ions. The deposition of thin films by m-CBD (SILAR) method has many advantages such as the low cost, low deposition temperature, and large film area. The features and quality of the film could be modified and controlled by variation of the adsorption and reaction time which leads to control the growth rate [19, 20]. The influence of annealing temperature on CuO films characteristics have been previously studied using different annealing temperature (500, 700 and 900) °C and (400, 500, 600 and 700) °C by Zahra et al. [21] and Navale et al. [22]. Whereas low annealing temperature were used in few studies, Figueiredo et al. [23] were post-annealing copper oxide thin films at temperatures (100-400) °C and Oudah et al. [24] were annealed CuO films by drop casting method at (80, 200, 300, and 400) °C. In present work, the impact of low annealing treatment on the structural, surface texture and optical characteristics of CuO thin films were investigated.

2. Experimental details

CuO thin films were synthesized on glass slide substrates by using the m-CBD (SILAR) method as previously reported [25 , 26, 27]. The glass substrates were cleaned in an ultrasonic bath using dilute sulfuric acid solution (H2SO4:H2O, 1:5, v/v), acetone, and de-ionized water for 10 minutes for each one. The growth bath solution was prepared as follow: 0.1 M (Molarity) of copper chloride solution was prepared by dissolve 1.7048 g of copper (II) chloride dehydrate (CuCl2.2H2O) in 100 ml of deionized water (DI water). The solution was well mixed using a magnetic stirrer for 10 minutes to obtain a transparent and clear solution at room temperature. The solution pH value was adjusted to 10.0 by adding ammonia solution (NH3) (25-30) % concentration, then heated to (80-90)°C and kept constant during the deposition time. In order to reach enough thickness for the deposited thin films, 10 cycles of SILAR were applied. The SILAR cycle can be described as follows: (i) the cleaned glass substrates were submerged into the solution for 20 sec, (ii) then it was swilled with DI water for another 20 sec. to remove weakly bonded/unconnected ions, (iii) finally the substrates have been dried in an air atmosphere (one can use a simple hair dryer) for 20 sec. These three steps were reduplicated for 10 times. Finally, the samples were ultrasonically cleaned for 10 min. to separate larger and tightly bonded particles. Then the prepared samples were annealed at different temperatures (150, 200 and 250) °C for 90 minute. The equation of the chemical reaction for deposition CuO thin films is as follow:

\[
\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{NH}_3 \xrightarrow{90^\circ \text{C}} \text{[[Cu(NH}_3\text{)]Cl}_2 + 2\text{H}_2\text{O}]}_{4} \xrightarrow{90^\circ \text{C}} \text{[[Cu(NH}_3\text{)]}_4} \xrightarrow{90^\circ \text{C}} \text{2(H}_2\text{O)}_{4} \xrightarrow{90^\circ \text{C}} \text{Cu(OH)}_{2} (\text{s}) + 4\text{NH}_3 \xrightarrow{90^\circ \text{C}} \text{Cu(OH)}_{2} (\text{s}) + \text{4H}_2\text{O}_{4} \xrightarrow{90^\circ \text{C}} \text{CuO + H}_2\text{O}_{4} (\text{s}) + \text{CuO + H}_2\text{O}_{4} (\text{s}) + \text{(1)}
\]

The structural, surface morphology and optical properties of the prepared films were studied using XRD-6000 Shimadzu diffractometer, CuKα radiations (λ=1.5406Å) during the range of 2θ(20°-70°) at an operating voltage and current of 40 keV and 20mA respectively, CSPM model AA3000 AFM and Mega 2100 UV/Vis spectrophotometer in wavelength range (200-1100nm) , respectively.

3. Results and Discussion

3.1 Structural properties

The crystal structure and the orientation of the films have been investigated by XRD and the x-ray diffraction patterns were depicted in Fig.1. The diffraction pattern of CuO thin film deposited by (m-CBD) SILAR method and annealed at (150, 200, 250)°C, reveals that the films have low crystallinity with polycrystalline structure in nature and grown in monoclinic phase (JCPDS card 41-0254). It is observed that the diffraction peaks have appeared at 2θ= 32.9°,35.2°,38.5° and 46.8° which belonging to (110), (002), (111) and (202) planes, respectively. The preferred orientation was along
(002) and (111) planes, and its intensity was fixed or very little increment with increase of annealing temperature to 250 °C, where at (150 and 200) °C the diffraction becomes slightly low intense and the annealing process does not enhance the crystallinity of the deposited films. Therefore it can be concluded that the low annealing temperatures 150 and 200 °C is not suitable for improve the crystallinity of the films where the suitable preparation temperature of CuO films was higher than 250 or 300 °C [21, 22, 28, 29]. These results were similar behavior with the literatures [28, 30]. The values of the full width at half maximum FWHM decrease then increase with increase annealing temperatures, as shown in Table (1). The interplaner spacing dhkl was calculated using Bragg’s law [31]:

\[ n\lambda = 2d_{hkl} \sin \theta \]  

The crystal phases available for CuO is monoclinic structure where characterized by determining the lattice constants a, b, c from X-ray diffraction spectrum by using the following formula [32]:

\[ \frac{1}{d_{hkl}^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2\sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hkl \cos \beta}{ac} \right) \]  

The calculated values of interplaner spacing and lattice constants a and c were in good agreement with the standard values in the (JCPDS card no. 41-0254) as shown in Table (1).

The crystallite size (D) of CuO nanostructure thin films was calculated from the full width at the half maximum (FWHM) using the Scherrer’s formula [32]:

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

Where k is the shape factor (0.94), λ is the X-ray radiation wave length, θ is the peak diffraction angle and β is FWHM in radiant. The crystallite size (D) of the CuO films for the preferred orientation (002) plane was slightly decreased from (18.4 to 13.8) nm with increase of annealing temperature from as-deposited to 250 °C, which can be attributed to the low crystallinity of the prepared films. The values of crystallite size of the CuO films different annealing temperatures is tabulated in Table (2). The dislocation density (δ) is defined as the number of dislocation lines per unit volume and determined from the equation [33]:

\[ \delta = \frac{1}{D^2} \]  

The value of the dislocation density increase with increasing annealing temperature where it represents the density of crystal defect. It increase with the annealing temperature by increasing the grain boundaries as a dislocations defect centers by decrease the crystallite size as shown in Table (2). The crystallite numbers per unit of surface area (N) was determined according to [34]:

\[ N = \frac{t}{D^2} \]  

Where (t) is the thickness of the film, as illustrate in Table (2) the number crystallites (N) increment with increase annealing temperature depending on the crystallite size. The lattice micro-strain (ε) was calculated from the following relation [35]:

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

It can be noticed that the lattice micro-strain (ε) increase with the increasing of annealing temperature where the type of the micro- strain changes can be attributed to the crystallization process in polycrystalline thin films. The strain directly proportional to the lattice constant c_{XRD} and its value is related to the shift from the JCPDS standard value, it can be determined using the equation [36, 37]:

\[ \text{Strain} = \left| \frac{c_{XRD} - c_{JCPDS}}{c_{JCPDS}} \right| \times 100 \% \]
Where $c_{\text{JCPDS}}$ is the lattice constant according to the JCPDS card and $c_{\text{XRD}}$ is that calculated from XRD pattern data. When the $c_{\text{XRD}}$ value varies from its $c_{\text{JCPDS}}$ value, it gives an indicates that there is a positive or negative micro-strain which means a tensile strain or a compressive strain respectively depending on the deposition conditions. The variation in the strain values at different annealing temperature attributed to the grain boundaries due to the variation of the crystallite size as shown in Table (2).

Figure 1: XRD patterns of the CuO thin films at different low annealing temperatures.

| Variable          | 2Θ degree | d(A) | d(A) | (hkl)  | a (Å) | b (Å) | c (Å) | FWHM degree |
|-------------------|-----------|------|------|--------|-------|-------|-------|-------------|
| As deposited      |           |      |      |        |       |       |       |             |
| 35.199            | 2.5496    | 2.5310 | (002)| 4.687 | 3.42  | 5.170 | 0.47  |
| 38.215            | 2.3551    | 2.3230 | (111)| 2.68  |
| 61.593            | 1.5045    | 1.5055 | (I13)|       |
| 66.235            | 1.4134    | 1.4091 | (311)| 0.14  |
| 150°C             |           |      |      |        |       |       |       |             |
| 32.926            | 2.7203    | 2.7520 | (110)| 4.567 | 3.42  | 5.156 | 0.39  |
| 35.295            | 2.5429    | 2.5310 | (002)| 0.55  |
| 38.590            | 2.3331    | 2.3230 | (111)|       |
| 61.751            | 1.5022    | 1.5055 | (I13)| 0.62  |
| 200°C             |           |      |      |        |       |       |       |             |
| 35.204            | 2.5493    | 2.5310 | (002)| 4.414 | 3.42  | 5.169 | 0.62  |
| 38.316            | 2.3491    | 2.3230 | (111)| 0.94  |
| 35.194            | 2.5501    | 2.5310 | (002)| 0.62  |
| 250°C             |           |      |      |        |       |       |       |             |
| 38.561            | 2.3348    | 2.3230 | (111)| 4.687 | 3.42  | 5.171 | 0.47  |
| 46.898            | 1.9373    | 1.9608 | (112)| 0.13  |
Table 2. Structural parameters of the CuO thin films prepared in different low annealing temperatures for (002) plane.

| Annealing Tem. °C | Crystallite size (nm) | $\delta \times 10^{14}$ (line $m^{-2}$) | $N \times 10^{15}$ $m^{-2}$ | $\epsilon \times 10^{-3}$ | Strain% |
|-------------------|-----------------------|----------------|----------------|----------------|---------|
| As deposited      | 18.44                 | 2.94           | 4.32           | 1.96           | 0.741   |
| 150               | 15.81                 | 4.00           | 7.24           | 2.29           | 0.467   |
| 200               | 13.82                 | 5.23           | 7.19           | 2.60           | 0.721   |
| 250               | 13.80                 | 5.25           | 8.94           | 2.61           | 0.759   |

3.2 Surface Morphology

Atomic force microscope (AFM) is the well-proper approach for, conceive the surface texture of the prepared CuO thin films, especially when the surface feature sizes are far lower one micron. Figs. 2 (a, b, c, d) illustrate the AFM images of CuO thin films on the glass substrate at the different annealing temperature. The investigated results showed that deposited CuO thin films on the glass substrate exhibit different surface texture and retrieved from the possibilities on tailoring the surface texture of the CuO thin films by varying annealing temperature as shown in figs.2 (a-d). These figures show that the surface of all samples is regular and homogenous without any cracks. At different annealing temperature, the average roughness and root mean square (RMS) in general it decreases with increasing of annealing temperature as shown in the Table (3). The variation of average roughness, RMS roughness, and the average grain diameter values clearly indicate that the annealing temperature affects the surface texture of the prepared films and the quality of the film surface could be controlled by the modification of these parameters according to the AFM results. These results were similar behavior with the literature's [38, 39].

Figure 2: AFM images of CuO thin films (a) as deposited and at different low annealing temperatures (b) at 150°C, (c) at 200°C, (d) at 250°C.
Table 3. The average roughness and root mean square of CuO thin films at different low annealing temperatures.

| Annealing Tem. °C | Average Roughness (nm) | Root Mean Square (nm) | Avg. Diameter (nm) |
|-------------------|------------------------|-----------------------|--------------------|
| As deposited      | 47.1                   | 54.2                  | 84.10              |
| 150               | 29.8                   | 35.5                  | 100.05             |
| 200               | 23.2                   | 27.8                  | 87.10              |
| 250               | 21.1                   | 24.8                  | 113.26             |

3.3. Optical properties

A plot of optical transmittance spectra of the deposited films as a with the variation of annealing temperature in the visible and near infrared regions of the electromagnetic radiation are shown in Fig. (3). At different annealing temperature, the transmittance has the lower value for as deposited CuO thin film which about 10% in the visible region, whereas its higher value is about 80% in the NIR region. Then it increased with the increment of annealing temperature in the both regions. It is clear from the figure that the absorption region of the prepared films was shifted to the short wavelengths and high energies (blue shift) with increase of an annealing temperature. Where this can be attributed to the reduced of localized states near the ban gap edges. These results are inconsistent with this literature's [23,24, 40].

![Optical transmittance spectra of CuO films at different low annealing temperatures.](image)

**Figure 3:** Optical transmittance spectra of CuO films at different low annealing temperatures.

For the direct gap semiconductor materials, the optical energy gap can be calculated from the absorbance spectrum by using Tauc relation [41]:

\[(\alpha h\nu) = C(h\nu - E_g)^{1/2}\]  \[(9)\]

Where C is constant [28]. Hence, in order to investigate the effect of annealing temperature on the optical energy gap. The optical energy gap (Eg) of the deposited films for the direct electronic transition could be determined from the graph of \((\alpha h\nu)^2\) versus \((h\nu)\) extrapolate the straight-line part of this curve to the energy as in the fig. 4 (a, b,c,d) . It can be noticed that the band gap values of the prepared films linearly dependence on annealing temperature which clearly indicates that the
The increment of annealing temperature leads to broadening of the optical energy gap of as-deposited CuO films as illustrated in Table (4). The widening in the optical band gap could be attributed to the a: quantum confinement effect and b: fundamental quantum size effect in nanostructure semiconductor materials with a nanosize lower than 20 or 25 nm [42, 43]. The crystallite size of the annealed films is getting smaller according to the XRD results, which is produced the widening in their optical energy gap which also due to the reduced in band bending [44]. These results are in similar behavior with the literature [1, 24, 45].

**Figure 4:** Variation of \((\alpha h\nu)^2\) vs. \(h\nu\) of CuO thin film as deposited and annealed at different low annealing temperatures.

In the energies lower than optical energy gap there is absorption in the tails states called Urbach energy, such tails are formed at most from the exchange in bond angles and length. In the exponential edge region, Urbach rule is expressed as [46, 47]:

\[
\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right)
\]  

(9)

Where \((\alpha)\) is the absorption coefficient and \((\alpha_0)\) is constant and \((E_u)\) is the Urbach energy. The Urbach energy values were estimated from the slopes of the plots inset of Fig. (5). The figure showed and confirmed that the prepared CuO thin films with different annealing temperature were verified Urbach rule and obey his empirical equation (9). This equation depicts the optical transition from the occupied states in the valence band tail to the unoccupied states in the conduction band edge. The results show that \((E_u)\) decreases from 0.91 eV for as deposited films to 0.46 eV for annealed film at 250 °C as shown in Table (4). Also it can be related crystallinity of the films as confirmed in the structure properties where the annealing process release some of the localized states within the band gap above and below valance and conduction bands edges.
Figure 5: Variation of ln (α) with photon energy of CuO thin films as deposited and at different low annealing temperatures.

Table 4. The optical properties of the CuO thin films at different low annealing temperatures.

| Annealing Tem. °C | $E_g$ (eV) | $E_u$ (eV) |
|-------------------|------------|------------|
| As deposited      | 1.87       | 0.91       |
| 150               | 2.03       | 0.73       |
| 200               | 2.06       | 0.54       |
| 250               | 2.09       | 0.46       |

4. Conclusion:
CuO thin films were deposited by successive ionic layer adsorption and reaction SILAR method. The effect of low annealing temperatures on the structural, surface texture, optical energy gap ($E_g$), and Urbach tails energy was investigated. From the analysis of results, it can be concluded the following: The deposited CuO films have polycrystalline nature and grown in the monoclinic phase, the crystallite size (D) of the films decreases with the increase of annealing temperature. The average roughness and the measured root means square (RMS) decreased with the increase of annealing temperature. The films have high transmittance and high absorbance in the NIR and Vis regions respectively. The optical energy gap ($E_g$) increased with increasing annealing temperature due to quantum confinement and quantum size effects, and the Urbach energy ($E_u$) decreased with increasing annealing temperature. It can be concluded that (m-CBD) SILAR method was suitable for preparation of CuO films and the low annealing temperature doesn't affect the low crystallinity of deposited films which can be useful for photovoltaic, optoelectronic and solar cell applications.

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