Study the Structural, Optical and Electrical Conductivity Properties of Copper Oxide Thin Films Prepared by Chemical Bath Deposition

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Abstract

Copper oxide thin films were prepared on glass substrate by using chemical bath deposition (CBD) method, with thickness of 0.23µm. In this study, aqueous solutions of copper oxide at low temperature were used. The structural (nano structure) of the film was studied by using X-ray diffraction (XRD), optical examination microscopic and Scanning electron micrographs (SEM). Also electrical conductivity and optical properties by were studied. The band gap energy was ~2.6eV.

Key Words: Chemical Bath Deposition, Copper Oxide Thin Film, Optical Properties Nanostructure and Electrical Conductivity.

دراسة الخواص التركيبية والبصرية والتوصيلية الكهربائية لأغشية اوكسيد النحاس المحضر بتقنية الترسيب الكيميائي

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الخلاصة

في هذا البحث حضر اوكسيد النحاس بسمك 0.23 µm بتقنية الترسيب الكيميائي (CBD) على قواعد زجاجية. كما وحددت في هذه الدراسة المحاليل المائية لأوكسيد النحاس بدرجة حرارة منخفضة ، ودرست الخصائص التركيبية (التركيب النانوية) باستخدام فحوصات حيود الاشعة السينية (XRD) ومجهر الفحص البصري و الماسح الضوئي (SEM)، وكذلك درست التوصيلية الكهربائية والخصائص البصرية للأغشية المحضرة. وجد ان فجوة الطاقة كانت (~2.6 eV).

الكلمات المفتاحية: ترسيب كيميائي، اغشية اوكسيد النحاس ،خصائص بصرية ، تركيب نانوي والتوصيلية الكهربائية.

Introduction

The deposition of thin films using chemical bath deposition (CBD) techniques has been previously studied by a many researchers. They have reported that electrodeposited Cu_2O films in slightly acidic aqueous baths behave as n-type conductivity (*Siripala and Jayakody, 1986).* Cu_2O and CuO have two different colours. Both oxides are being studied as photovoltaic applications because of their electrical reasonable and optical properties. A part from their semiconductor applications, these materials have been employed as heterogeneous catalysts for several environmental processes (*Ortiz, et al., (2001) and Kharas, (1993*). Copper oxides are semiconductors that have been studied for their available in nature and non-toxic(Papadimitropoulos, *et al*., 2006). Copper forms two well-known oxides: tenorite (CuO) and cuprite (Cu_2O), both of them are p-type semiconductors having energy band gap of (1.21 to 1.51 eV) and (2.10 to 2.60 eV) respectively (*Sekhar, (2001) and Pierson, et al., (2003*), which lies in the acceptable range of window material. As a n-type semiconductor, conduction arises from the presence of holes in the valence band (VB) (*Richardson and Rubin, 2001*). CuO is attractive selective solar absorber which has high absorbance and low thermal emittance of solar energy (*Richardson, 2003*). Copper oxides generally have been many applications such as optoelectronic devices (*Aslani and Oroojpour, 2011*), sensors (Ezenwa I.A,2012), solar cells and use in multijunction cells for photo-electrolysis of water (*Minami and Tadatsugu, 2006*). Polycrystalline thin or thick films of copper oxides have been prepared by various techniques such as thermal oxidation, electro deposition, chemical conversion, chemical brightening, spraying(*Parhizkar, et al., 2005*), chemical vapor deposition, sol-gel method (*Lidia, et al., 2003*),plasma evaporation, reactive sputtering, molecular beam epitaxy *(Hari, et al.,2010),* SILAR method (Mitra , 2010), and chemical deposition method for Cu_2O thin films on glass substrates (*Valtierra and Ruiz, 2004*). CBD is an aqueous analogue of CVD. The technology is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. It is briefly described and discussed in the next article. The condition for compound to be deposited from a solution bearing its ions is that its ionic product (I.P) should be greater than the solubility product (Ksp). The complexing agent of a metal in solution forms a fairly stable complex ions of the metal and provides a controlled release of free ions according to an equilibrium reaction of the form: Applying the law of mass action,$K = [CA^{+} \times CB^{-}] / CAB$, where CA^{+}, CB^{-} and CAB are concentrations of A^{+}, B^{-} and AB in the solution, respectively.. The deposition technique can be improved by controlling the addition of another complexing agent with pH opposed to that of bath constituents. The chemical bath technique has frequently been used for the deposition of metal oxide thin films (Ezema, and Okeke. 2003). The technique has also been used widely to deposit other materials*(Nair, and Nair, (1991) and Tanusevski, (2003).*

In this study n-type Cu_2O thin films were deposited on glass substrate using chemical bath deposition (CBD) method and study nanostructure, optical and electrical properties of copper oxide thin films.

Materials and Methods

Preparation of Copper Oxide Thin Films

Using chemical bath deposition (CBD) method, copper oxide thin films were prepared onto glass substrates. The glass substrates were washed with soap solution rinsed in acetone and finally cleaned by ultrasonic with double distilled water before the deposition with Cu_2O thin film. For the preparation of copper oxide thin films the analytical grade (Merck chemicals) copper sulphate pentahydrate thiourea, sodium hydroxide were used in an aqueous medium and dimethylamine works to form a compound with copper in order to slow down the interaction for the nanostructure. The interaction can be explained by the following chemical reaction:

$$CuSO_4, H_2O^{-} + (NH_2CH_3)_2 \rightarrow \mathbf{[Cu\ (NH_4)_2]^{-}.}\ H_2O + \mathbf{[S_4O_5]^{2-}}$$

$$\mathbf{[Cu\ (NH_4)_2]^{-}.}\ H_2O + (NH_2)_2CS \rightarrow \mathbf{CuS}^{+} + \mathbf{S_2O_3^{2}}$$

Adhere to the substrate and react with $(OH)^{-}$ ions present on the surface to form Cu_2O by the reaction:

$$\mathbf{2CuS}^{+} + Na\mathbf{O}H^{-} \rightarrow \mathbf{Cu_2O} + NaS + H_2O$$

Results and Discussions

Structural Properties

Optical microscopic was used to study the surface topography of the copper oxide thin films as shown in Figure (1). The disappearance of most of the surface defect, holes and the emergence of the border beloved in a clear, this refers to the crystal structure improvement of the thin film.

SEM images of the sample to illustrated the formation of crystallites on the film surfaces as shown in Figure (2). The surface of Cu_2O film showd high density of grains. These grains implies that the nucleation was occurred on all sites. It showd uniformity in the distribution of the grains(the grains were small and regular).

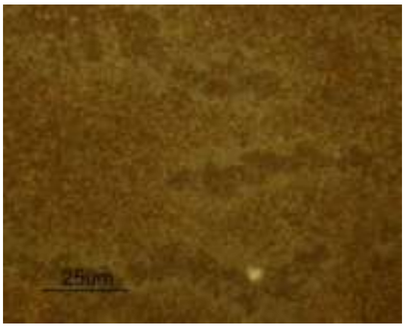


Fig. (1) Optical Micrograph of Copper Oxide Thin Film Image in 1000X

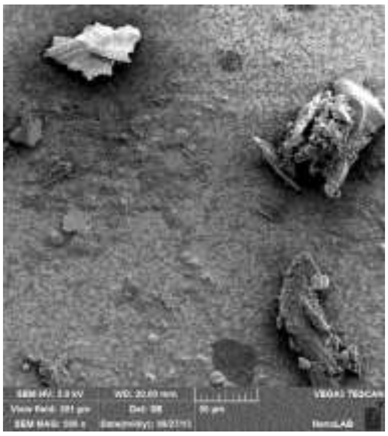


Fig.(2)Scanning Electron Micrographs of Typical Cu_2O Thin Film

XRD diffraction patterns of the deposited copper oxide films was shown in Figure(3) with thickness of 0.23 µm.

The crystal structure of Cu_2O was the cubic cuprite structure with lattice parameter 4.2696 Å as shown in figure (4) (Nair. and Nair , (1991) and Tanusevski, , (2003). Furthermore, Figure (3) shows the presence of peaks at 29.53° and 48.65° can be assigned to (110) and (202) planes of Cu_2O, while the peak at 32.46° be at least one of CuO. The calculated texture coefficient values of copper oxide thin film for different (*hkl*) planes as presented in Table 1.

As seen from table (1) the preferential orientation of the deposited film was (110) plane. This denotes that the number of grains along this plane was more than the other planes. Assigned to (110) plane of Cu_2O as compared with standard (X-ray diffraction data file [N 1997 JCPDS prevalent).Thus it is seen from the present investigation, that Enhancement concentration of copper complex solution leads to a mixed phase of CuO and Cu_2O.

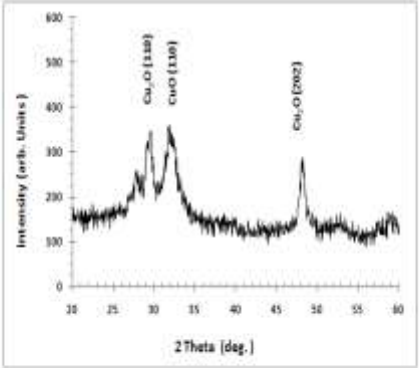


Fig. (3)XRD Pattern of Copper Oxide Thin Films

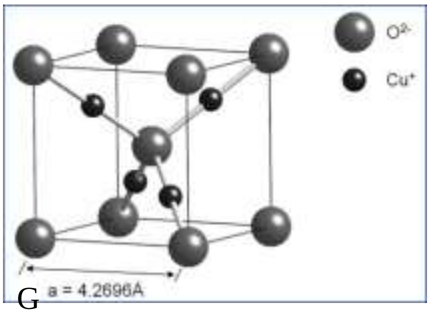


Fig.(4) Cubic Cuprite Crystal Structure of Cu_2O

Grain size was calculated by compensation values that were obtained from the X-ray diffraction results of the previous figures in the Shearer's equation (Kissinger *et al*., 2003) as shown in the Tables 1.

$$D = \mathbf{k\,\lambda / \beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Where D is the grain size, k = a constant (0.94),λ is the wavelength of the Cu-Kα radiation used (λ=1.5405 Å), β was experimentally observed diffraction peak width at half maximum intensity (FWHM), θ was the Bragg angle.

For the fabrication of good quality thin film to use in optical devices, it is necessary to reduce the surface roughness and dislocation density of the copper oxide film. So the value of the dislocation density (δ) which gives the number of defects in the film was calculated from the average values of the crystallite size D by the relationship (Williamson and Smallman, 1956):

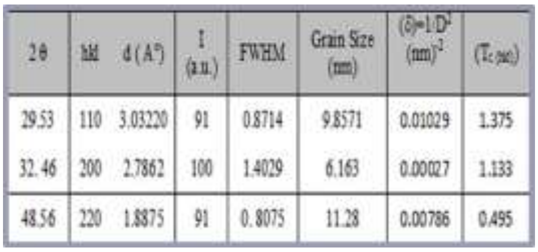
$\delta = 1/D^2$ …………….. (2)

The (hkl) plane, FWHM value, grain size (D) and dislocation density (δ) values of copper oxide thin film are listed in Table 2. In order to characterize a material exactly, its crystal structure, lattice parameters, size, shape and preference orientation of its grains must be known; therefore, the texture coefficient was determined in order to find preferential orientation of crystals in deposited polycrystalline material. The texture coefficient is one of the basic structure parameters in all polycrystalline materials. So texture coefficient was calculated from the x-ray diffraction result by using the equation :

$Tc_{(hkl)} = I_{(hkl)} / Io_{(hkl)}\, N^{-1} / \Sigma n I_{(hkl)}) / Io_{(hkl}$ ….(3)

Where $Tc_{(hkl)}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity measured for (hkl) plane, $Io_{(hkl)}$ is the intensity of (hkl) plane taken from standard data in PDF card fitting in the x-ray diffraction pattern of material, n is the diffraction peak number and N is the total reflection number. For a film to have a preferential orientation at any (hkl) plane, the texture coefficient must be at least one. The calculated texture coefficient values of copper oxide thin film for different (*hkl*) planes as shown in Table 1. As seen from Table 1 the preferential orientation of the deposited film was (110) plane. This denotes that the number of grains along this plane was more than the other planes.

Table (1) Some Structural Properties Copper Oxide.



2θ	hkl	d (A°)	I (a.u.)	FWHM	Grain Size (nm)	(δ)=1/D² (nm)⁻²	(Tc (hkl))
29.53	110	3.03220	91	0.8714	9.8571	0.01029	1.375
32. 46	200	2.7862	100	1.4029	6.163	0.00027	1.133
48.56	220	1.8875	91	0. 8075	11.28	0.00786	0.495

Warren had assumed that the mathematical representation of curves resulting from the X-ray diffraction (XRD) depends primarily on the similarity amount among these curves and functions of each of Cauchy and Gauss. When we consider the XRD curve is similar to the Cauchy's function, which take the form $(1 + k^2x^2)^{-1}$, the broadening correction is given by the following relationship, which called Scherer's correction

1- $\beta cs = \beta m - \beta i$ ..……. (4)

βm: Show X-ray diffraction curve in the middle of the great intensity measured in practice.

βi: Show X-ray diffraction curve in the middle of the great distress caused by the device used

By compensation (4) in (1) we get

$D = K\lambda / [(\beta m - \beta i)\cos\theta]$………. (5)

In consideration XRD curve is similar to the Gauss's function which takes the form $e\,(-k^2x^2)$, the accuracy to be higher because of the great similarity between this function and the diffraction curves, Warren suggested the correction in the form: -2- $\beta cs^2 = \beta m^2 - \beta i^2$ ………. (6)

In consideration XRD curve is similar to the Gauss's function, which takes the form e $(-k^2x^2)$, the accuracy to be higher because of the great similarity between this function and the diffraction curves, Warren suggested the correction in the form: -

Which called Warren's Correction by compensation (6) in (1) we get

$D = K\lambda / [(\beta m^2 - \beta i^2)^{1/2} \cos(\theta)]$ …. (7)

Warren suggested a relationship takes into account the geometric meaning, which is: -

3-$\beta cs = [(\beta m - \beta i)(\beta m^2 - \beta i^2)^{1/2}]^{1/2}$… (8)

By compensation (8) in (1) we get

$D = K\lambda / [[(\beta m \beta i)(\beta m^2 \beta i^2)^{1/2}]^{1/2} \cos\theta]$..(9)

As show in table (2)

Table (2) The Crystalline Size by Using Scherrer's and Warren's Correction and Their Comparison

Sample	D(nm) Scherrer's eq. (1)	D (nm) Scherrer'scorrection eq.(3)	D (nm) Warren's correction eq. (5)	D (nm) Warren's geometrical correction eq. (7)
Copper Oxide	9.8571	11.275	11.489	10.58
	6.163	6.688	4.4	6.43
	11.28	13.056	14.23	12.19

The Optical Properties of Copper Oxide Thin Films.

The optical characterizations of Cu_2O thin films gave us something about the physical properties such as the absorption, transmittance, absorption coefficient and band gap energy and band structure were determined by UV-VIS spectrophotometer (Optima Sp – 300 Plus). The high absorbance value in the UV indicates that these films can be used as photoactive materials and photo electrochemical cell and transmittance spectra recorded for copper oxide films as a function of wavelength range 200-1100 nm as was shown in Figure (5: a and b).

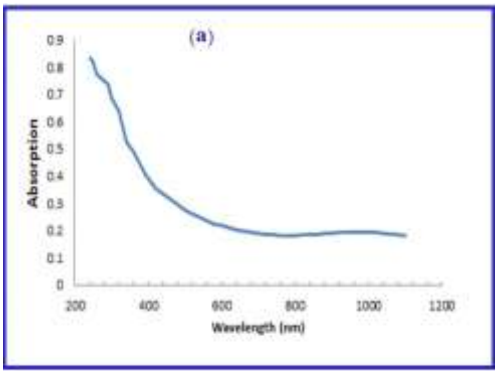


Fig.(5) (a) Absorption of Copper Oxide Films

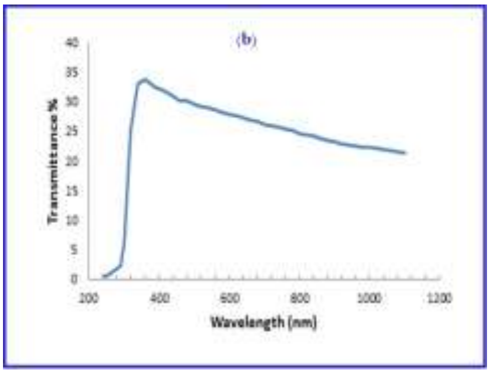


Fig.(5) ((b) Transmittance of Copper Oxide Films

Figure **6.** Showed the absorption coefficient as a function of wavelength of copper oxide films. In order to estimate the optical band gap, the equation connecting the photon energy with optic absorption value was used (Stern, 1963).

$(\alpha h\upsilon)=B\,(h\upsilon - E_g)^{n}$…………. (10)

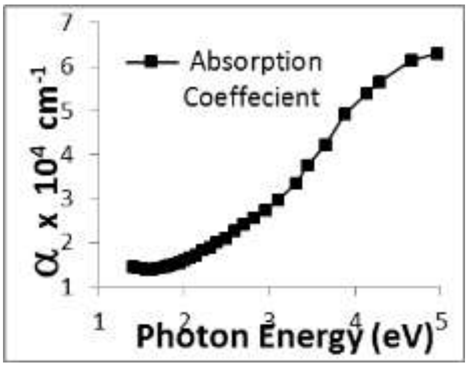


Fig.(6) Absorption Coefficient of Copper Oxide Films

Where B is a constant, Eg is the energy band gap, α is the absorption coefficient, *n* is a coefficient having the value 1/2 or 2 depending on the nature of electronic transitions and *h* is Planck constant. *n* has the value direct transition ,obtained from the extrapolation of the linear portion of these curves to $(\alpha hv)^2=0$ are shown in figure 7. Dependence of photon energy on absorption coefficient is an important transition type of electrons and energy band structure The direct gap of the optical transitions at a crystal or polycrystalline depend on material structure. In terms of this, while some scientists have classified optic transition of copper oxide thin films as direct band gap. The direct value of energy band gap of copper oxide film was investigated during the study. The point where the linear part of $(\alpha hv)^2 = f(hv)$ graphic intersects the *hv axis* gives us the forbidden band value for allowed direct transitions. From figure5, it was determined that absorption of copper oxide thin film began at wavelength of 200 nm. As a result of the fits done on $(\alpha hv)^2$-(hv) graphics we can estimate the (a) allowed direct energy band values as 2.6eV and (b) indirect 1.38 eV as shown figure (7) .

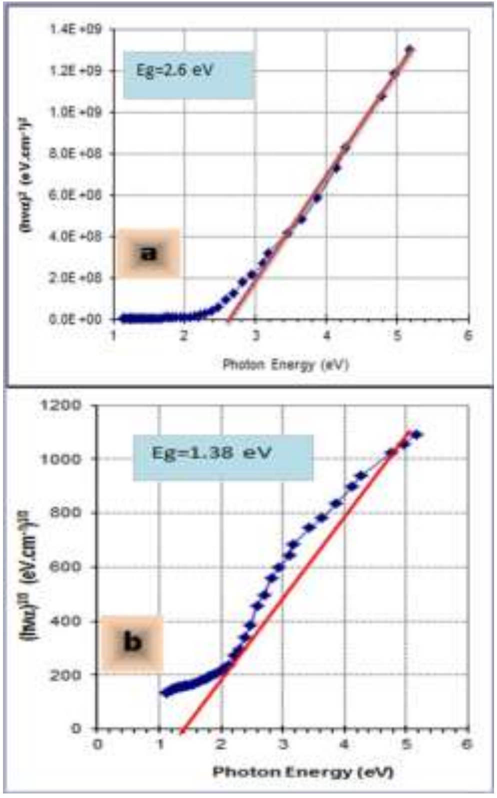


Fig.(7) (a) Allowed and (b)Forbidden Direct Electronic Transitions of Copper Oxide

The electrical conductivity of the copper oxide film was study at different temperatures. Cu_2O showed spontaneous n-type semiconductor characteristics and it was shown that this n-type conductivity comes from cation deficiency, which was mainly due to the copper vacancies rather than oxygen interstitials or other defects. That electrical conductivity depend on two factors: the density of charge carriers and the mobility of these carriers in the material under the influence of an electric field that the amount of mobility determined by the interaction between the electrons and the lattice waves or photons were dependent on temperature, which found that mobility in general depend on the $[T^3 / 2]$ (Su, *et al.*, 1984). The electrical resistivity was increased as shown in Fig. (8).

Conductivity of the Cu_2O materials was calculated from the resistivity measurements. The conductivity initially decreases with increase in temperature. This reduction in resistivity could arise due to the removal of defects after annealing. It is also observed that resistivity initially increases slowly with the increase of temperature .

Lastly it is possible to change the description of conductivity with temperature equation (11)(Dakhel, A.A. and Henari,F.Z. 2003)

$\sigma = \sigma_{\circ} \exp [Ea/K_BT]$……(11)

Where, $\sigma_{\circ}$: constant represent to conductivity at high temperature

Ea: electrical conductivity for activation energy, K_B: Boltasmans constant and

T: Temperature

$$\rho = \frac{R*A}{L} \text{...where } A = (w.t), \sigma = \frac{1}{\rho} \ldots(12)$$

w is Pole width , t is membrane thickness, L is distance between electrodes as shown in figure (8).

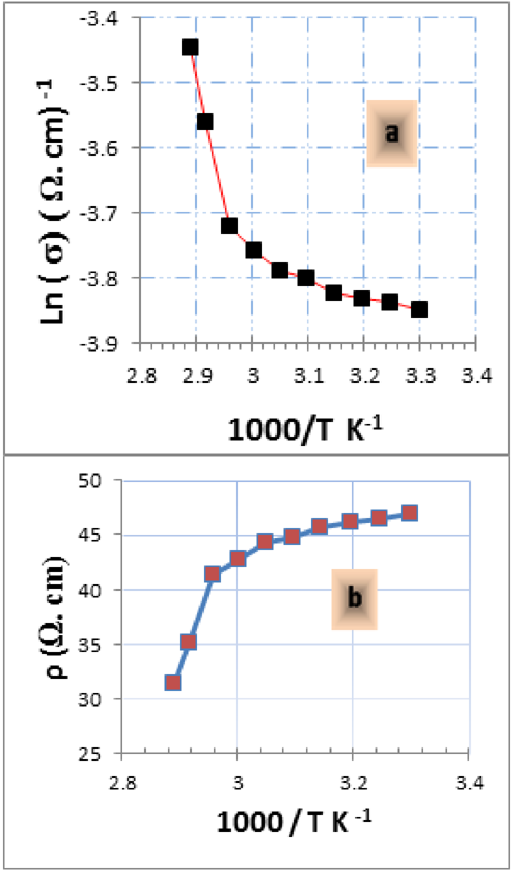


Fig. (8) a. Electrical Conductivity and b. Change of Resistivity of Copper Oxide Thin Film as a Function of Temperature

Conclusions

Copper oxide thin film was successfully deposited onto glass substrates by chemical bath deposition at room temperature. The x-ray diffraction spectrum shows that copper oxide film is polycrystalline with an orthorhombic structure. According to SEM, the thin film had good adherence with substrate and were free of pinholes. The direct and indirect energy band gaps of the film was determined as 2.6 eV and indirect energy gap1.38eV. Due to the suitable direct band gap value for an absorber layer for efficient light absorption, copper oxide thin films can be used as absorber layer in solar cells.

Conductivity shows two types of activation process within the measured temperature range. In the low temperature region Cu_2O shows metallic nature.

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