Journal of New Materials for Electrochemical Systems 15, 49-55 (2012)
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Electroplated CuO Thin Films from High Alkaline Solutions

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Received: July 29, 2011, Accepted: October 26, 2011, Available online: December 06, 2011

Abstract: *CuO thin films were coated on ITO substrates by an electrodeposition route through potentiostatic mode. The electrodeposited CuO thin films were characterized and the role of copper sulphate concentration on the structural, morphological and optical properties of the CuO films was studied. Film thickness was measured by a stylus profilometer and found to be in the range between 800 and 1400 nm. The structural characteristics studies were carried out using X-ray diffraction and found that the films are polycrystalline in nature with a cubic structure. The preferential orientation of CuO thin films is found to be along (111) plane. The estimated microstructural parameters revealed that the crystallite size increases whereas the number of crystallites per unit area decreases with increasing film thickness. SEM studies show that the grain sizes of CuO thin films vary between 100 and 150 nm and also morphologies revealed that the electrodeposited CuO exhibits uniformity in size and shape. The surface roughness is estimated to be 15 nm by atomic force microscopy. Optical properties of the films were analyzed from absorption and transmittance studies. The optical band gap energy was determined to be 1.5 eV from absorption coefficient. The variation of refractive index (n), extinction coefficient (k), with wavelength was studied and the results are discussed.*

Keywords: CuO thin films, Structural properties, Optical constants, Surface roughness

1. INTRODUCTION

Thin films of CuO find some potential applications in solar energy converting devices, electro-chromic devices, transparent conducting devices, gas sensors [1-4] and superconducting devices [5]. Samarasekara [6,7] deposited thin films of zinc oxide and copper oxide for photo-voltaic applications. Cupric oxide (CuO) is of great interest due to its properties such as catalytic and as well as its close connection to high temperature superconductors [8,9]. CuO is a p-type semiconductor with a band gap of 1.2 eV, and since this gap is smaller than 1.85 eV, this compound has started to be studied for its field emission properties [10]. Moreover, CuO has interesting photovoltaic, electrochemical and catalytic properties [11–14]. On the other hand, the large fraction of surface area, excellent stability, low production cost, and good electric properties of nanostructured CuO have fueled new studies to determine its applicability as material for solar cells, in particular due to its photoconductivity and photochemical properties. CuO thin films were prepared using various deposition techniques such as reactive magnetron sputtering [15], spray pyrolysis [16], reactive evaporation [17], RF sputtering [18], Ion beam sputtering [19], plasma evaporation [20], sol-gel [21], molecular beam epitaxy [22], spin coating [23] and electrodeposition [24]. Brijiani et al [25] have prepared Cu_2O thin films by electrodeposition for lithium batteries and studied their characteristics. Kose et al [26] have studied the structural and optical properties of CuO thin films synthesised by spray pyrolysis. Poizot et al [27] reported the electrochemical deposition of CuO from different solution and studied the effects of solution composition and pH on the preparation of the films. Eventhough several reports on the growth and studies of CuO thin films are available, very little work is reported on the influence of deposition parameters such as deposition potential on the properties of electrodeposited CuO thin films.

In the present study, we report the preparation of cupric oxide thin films by electrodeposition on indium tin oxide (ITO) coated glass substrates. The thickness, structural, morphological and optical properties of the prepared thin films were obtained using sur-

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face profilometer, X-ray diffraction pattern, scanning electron microscopy, atomic force microscopy and optical absorption techniques. Various microstructural parameters are evaluated and the results are discussed.

2. EXPERIMENTAL DETAILS

CuO thin films were grown by electrodeposition technique using potentiostatic method. The deposition process depends on various parameters such as deposition potential, bath temperature, solution pH and electrolyte concentration. A standard three electrode cell was used for the electrodeposition CuO. Indium doped tin oxide (ITO) was used as working electrode, graphite rod as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. ITO coated glass substrates were first cleaned in acetone, and thoroughly rinsed with distilled water. The electrodeposition of CuO was carried out cathodically from an aqueous bath composed of $CuSO_4$ and L (+) tartaric acid. The deposition of CuO thin films was carried out from an aqueous electrolyte containing equimolar (0.02 to 0.04 M) concentrations of $CuSO_4$ and 0.03 M L(+) tartaric acid at a deposition potentials of -650mV vs SCE. The solution pH was adjusted to 13 by the addition of NaOH solution. The deposition bath temperature was varied from 75^0C and CuO thin films were deposited.

Electrodeposition was carried out using an electrochemical system consisting of PAR (EG&G Princeton Applied Research, USA Model 362A) potentiostat/galvanostat unit. Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer system [X'PERT PRO PANalytical, Netherlands] with Cuk$_\alpha$ radiation (λ = 0.1540) nm was used to identify the crystal structure of the films. Surface morphological was carried out using a scanning electron microscopy (Philips Model XL 30, USA). Model DSR-XE-100^{TM} atomic force microscopy has been used for the surface analysis of CuO thin films. Optical properties of the samples were analyzed using a UV- Vis- NIR double beam spectrophotometer (HR - 2000, M/S ocean optics, USA).

3. RESULTS AND DISCUSSION

The electrochemical deposition of cupric oxide thin films is carried out potentiostatically from an aqueous acidic bath containing CuSO4 and L(+) tartaric acid. The equation [28] is attributed to the formation of Cu^{2+},

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \; (E^0 = 0.34V) \tag{1}$$

Cu^{2+} ions and OH^- ions are generated on the surface of anode and cathode at the same time when direct current passes through the electrochemical cell, and then Cu^{2+} ions react with OH^- ions to produce $CuSO_4$ followed by hydration of $Cu(OH)_2$ to give CuO.

$$SO_4^{2-} + H_2O + 2e \rightarrow 2OH^- + SO_3^{2-} \; (E^0 = -0.94V) \tag{2}$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \tag{3}$$

$$Cu(OH)_2 \rightarrow Cu^{2+} + 2OH^- \tag{4}$$

Equation (4) leads to the formation CuO thin films by electrodeposition technique. In this reaction the tartarate ions induce the separation of $CuSO_4$ molecules from meta-stable state to yield cupric oxide at pH 13.0. Finally, cupric oxide film is obtained by the reaction,

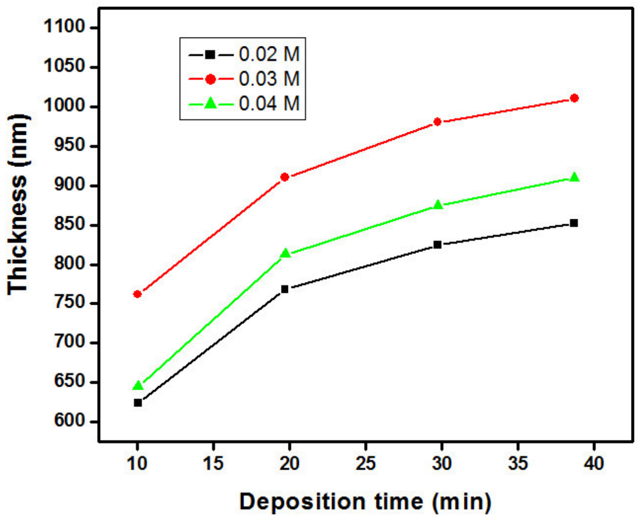

Figure 1. Variation of film thickness with deposition time for CuO thin films obtained at various copper sulphate concentrations (a) 0.02 M (b)0.03 M and (c) 0.04 M.

$$Cu^{2+} + 2OH^- \rightarrow CuO + H_2O \tag{5}$$

The variation of film thickness with deposition time for CuO thin films prepared at various copper sulphate concentrations ranging from 0.02 M to 0.04 M is shown in figure1 (a,b,c). Figure 1 represents that the film thickness increases linearly with deposition time and tends to attain saturation after 40 min of deposition. The copper concentration of the electrolytic bath plays an important key role to control the rate of deposition and film thickness by: (i) increase of precursor solubility and (ii) increasing the diffusion coefficient of the species and decrease of viscosity [29]. The increase in value of film thickness is described by the following two mechanisms: first one is the deposition of CuO which leads to the film growth, and the second one is the reaction of formation of CuO with acid in time being prolonged, the thickness of the film increases, at the same time the resistance of the film increases. So, the density of electrons decreases relatively and the CuO thin films were eroded by acid in the solution. Therefore, after a particular time of deposition, the dissolution process predominates over the deposition thereby results to be indicating decrease in film thickness. Film thickness is found to influence the microstructural [25] and optical properties [26] of CuO thin films. In microelectronic applications, the film thickness is to be scaled down proportional to the device size. In this context, it is valuable to examine the effect of film thickness on the physical properties of CuO thin films.

The structural properties of electrodeposited CuO thin films was investigated by X-ray diffraction using Cuk$_\alpha$ radiation with λ = 0.154 nm. Figure 2 shows typical X-ray diffractogram of CuO films deposited at various copper sulphate concentrations such as

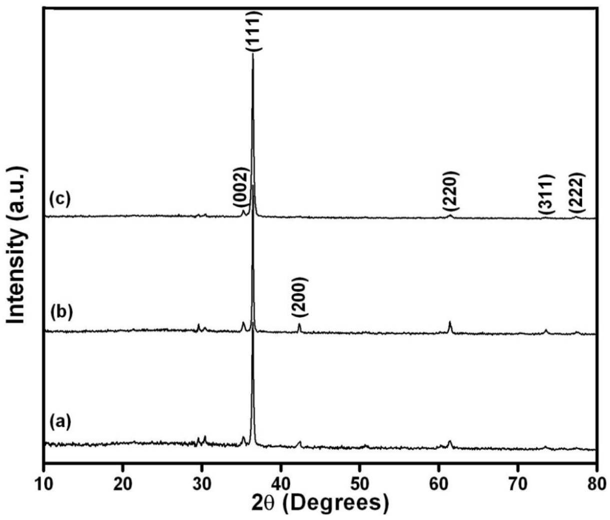

Figure 2. X-ray diffraction patterns of typical CuO thin films deposited at various copper sulphate concentrations (a) 0.02 M (b)0.03 M and (c) 0.04 M.

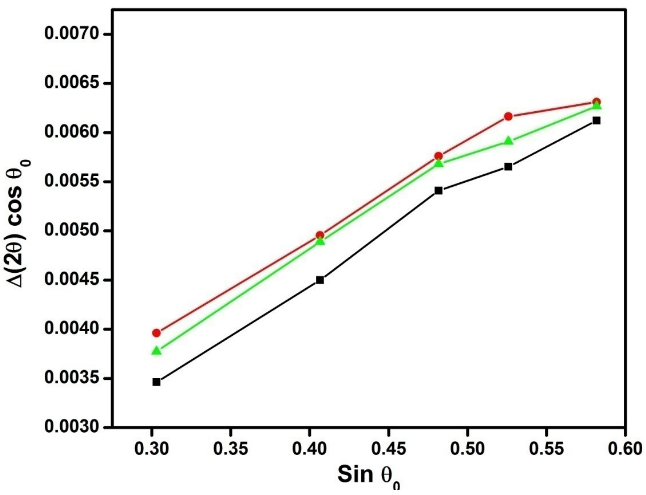

Figure 3. Crystallite size/ strain separation calculated using β2θ breadth according to ''Williamson–Hall'' method.

0.02, 0.03 and 0.04 M grown on ITO substrates. X-ray diffraction studies reveal that as-deposited films are polycrystalline in nature and belong to the cubic phase with a preferential orientation along (111) direction. The (111) peak position is located at 2θ = 36.43 corresponding to the lattice parameter value 0.2464 nm, for films grown at various copper sulphate concentrations. The copper content increased considerably for samples deposited at potential and bath temperature -550 mV vs SCE and 75^{0}C, respectively, deposited at various copper sulphate concentrations. It is found that when the copper sulphate is increased the intensity of cubic peak is also increased. In higher concentration (0.04 M) of copper sulphate the high intensity peaks for the CuO cubic phase were observed in the X-ray diffraction patterns. The observed peaks in the diffraction patterns were indexed and the corresponding values of lattice spacing "d" were calculated and compared with JCPDS standards [30].

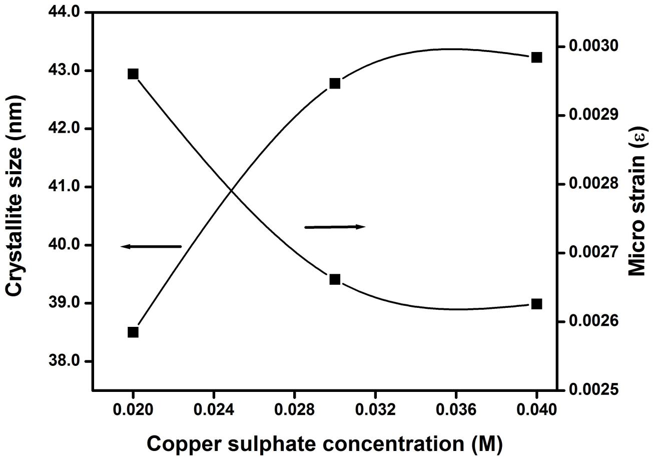

Figure 4. Crystallite size and micro strain of the electrodeposited CuO thin films versus copper sulphate concentrations.

Figure 3 illustrates the plot of Δ(2θ) cos θ_0 vs. sin θ_0 and the values of e and D can be calculated from the slope and the ordinate inter section, respectively .Eq.(6) was first proposed by Williamson and Hall [31] and is customarily referred to as the ''Williamson–Hall method'' [31–33].

$$\Delta(2\theta)\cos\theta_0 = \frac{\lambda}{D} + 4\varepsilon\sin\theta_0 \tag{6}$$

Figure 4 shows a comparative look of microstructure parameters of both crystallite size (D) and microstrain (ε) of the CuO thin films of different concentration of copper sulphate deposited on conducting glass substrates. The crystallite size D of the films was calculated from the above equation (6). The crystallite sizes are estimated at 38.5, 42.5 and 43 nm for films deposited at copper sulphate concentrations 0.02, 0.03 and 0.04 M, respectively. It is observed from figure 4 that as the copper concentration increases 0.02 M to 0.04 M the peak intensities and crystallite size along the preferential orientation direction (111) increases which indicates an improvement in the crystallinity of the samples. This improvement may be caused by the effective mass transfer and increased rate of deposition at optimized concentration. The above results reveal that CuO thin films with a higher crystallite size may be prepared at 0.03 M of copper sulphate concentration. On the other hand the microstrain exhibited an opposite behavior, i.e., it decreases with increasing film copper sulphate concentration. Such a decrease in microstrain may be due to the decrease in lattice defects among the grain boundaries with the crystallite size increasing.

Figure 5 shows dislocation density and number of crystallites per unit area of the cupric oxide thin film deposited at various copper sulphate concentrations. The dislocation density δ defined as the length of dislocation lines per unit volume of the crystal and can be evaluated from the particle size D by the relation:

$$\delta = \frac{n}{D^2} \tag{7}$$

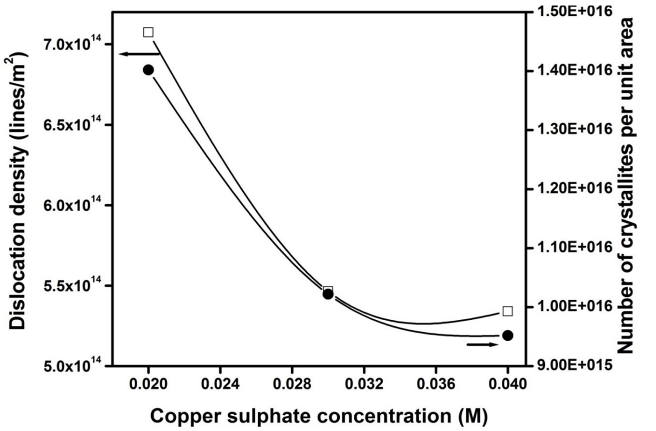

Figure 5. Dislocation density and number of crystallites per unit area of the electrodeposited CuO thin films versus copper sulphate concentrations.

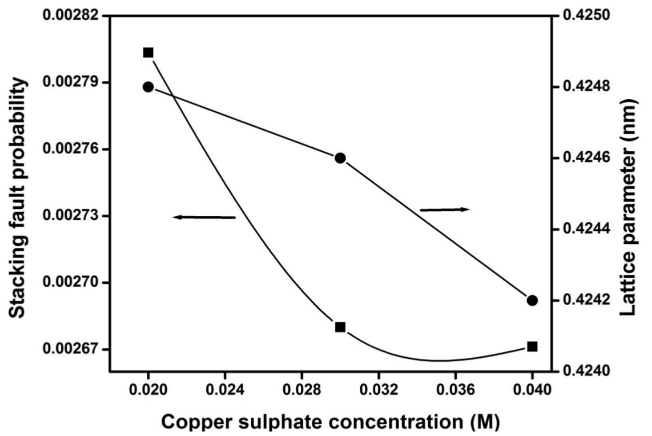

Figure 6. Stacking fault probability and Lattice parameter of the electrodeposited CuO thin films versus copper sulphate concentrations.

where n is a factor, when equal unity giving minimum dislocation density. The number of crystallites per unit area (N) of the films was determined with the use of the following formula:

$$N = \frac{t}{D^3} \tag{8}$$

where t is thickness of the film and D is the crystallite size. It is observed that the number of crystallites per unit area is found to decrease with the copper sulphate concentration 0.02 to 0.04 M. The maximum value of dislocation density and number of crystallites per unit area are found to be 7.4 × 10^{14} lines/m^2 and 1.6 × 10^{16} m, respectively, for the film deposited at 0.04 M of copper sulphate concentration. As the copper sulphate concentration is increased, it is evident that the crystallite size increases and in turn the number of crystallites per unit area is decreased.

The stacking fault probability (α) is estimated using the expression given in (9).

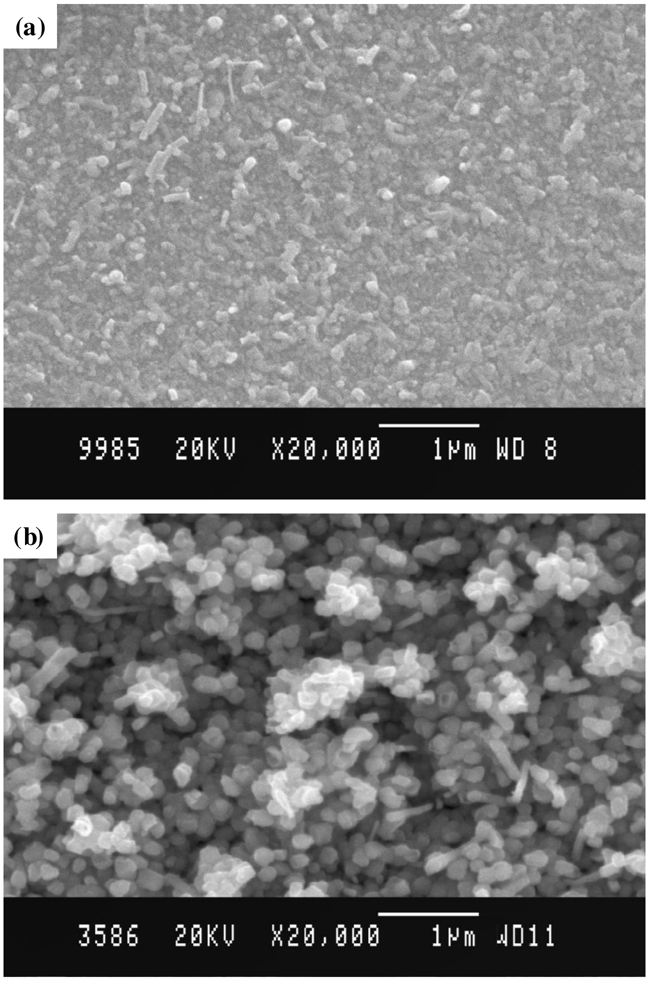

Figure 7. SEM pictures of electrodeposited CuO thin films deposited at (a) 0.02 M and 0.03 M of copper sulphate concentrations.

$$\alpha = \left[{2\pi^2}/{45\sqrt{3}} \right] \left[{\Delta(2\theta)}/{\tan\theta_{111}} \right] \tag{9}$$

From (hkl) planes, the lattice constants were evaluated using the relation,

$$d = \left[\frac{a}{\sqrt{\left(h^2 + k^2 + l^2\right)}} \right] \tag{10}$$

where d is the inter planar spacing of the atomic plane. Initially, the lattice constant is decreases slowly with copper sulphate concentration shown in figure 6. This suggests that crystallinity and preferential orientation increases with increasing copper sulphate concentration 0.02 M to 0.04 M and then it is eventually decreasing with increase copper sulphate concentration. CuO film prepared at optimized molar concentration with lower micro strain, dislocation density and stacking fault probability improves the stoichiometry of the films which in turn causes the volumetric expansion of thin

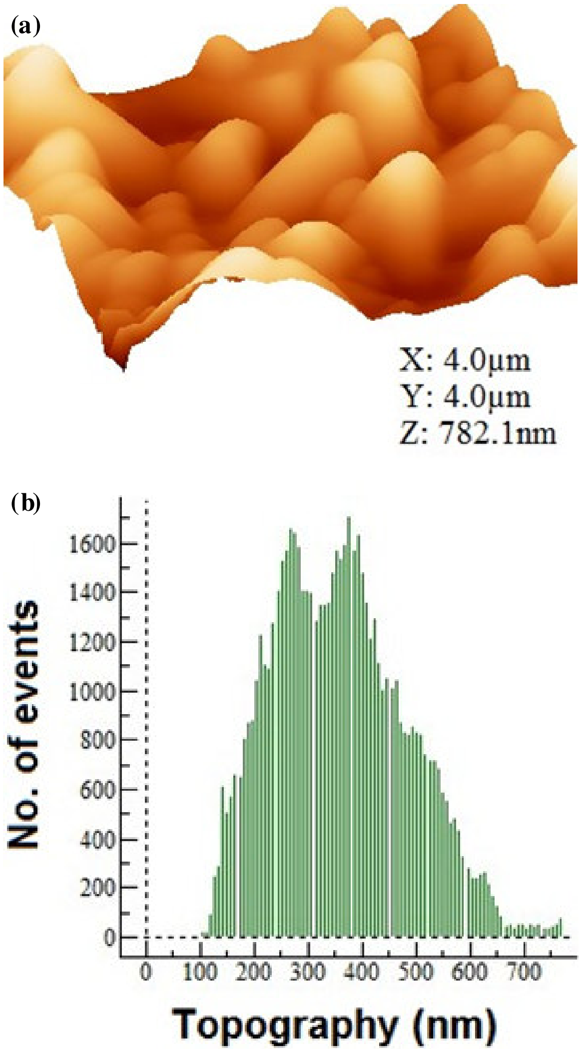

Figure 8. (a) 3D spectra of atomic force microscopy image (b) average roughness of the AFM image prepared at 0.03 M of copper sulphate concentration.

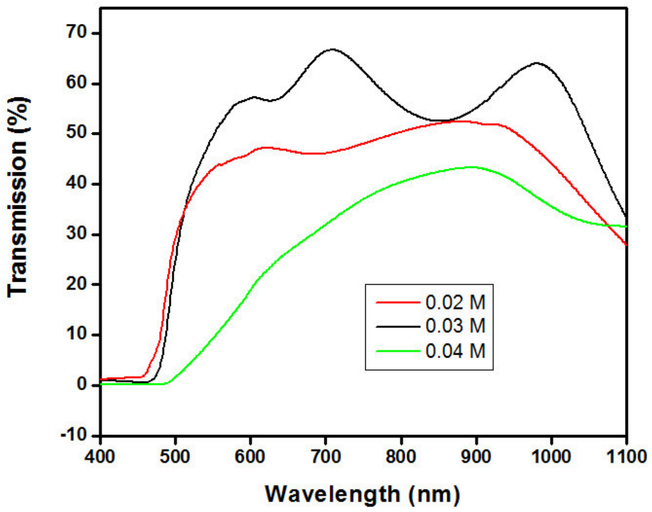

Figure 9. Optical transmission spectra of CuO thin films for various copper sulphate concentrations.

films. The p-type conductivity of CuO film is due to the presence of Cu ion vacancies within the lattice. Crystallinity improvements in optimized concentration and mobility of Cu ion vacancies within the lattice and hence reduce the resistivity of the films. The studies on functional dependency of microstructural parameters on molar concentration indicate that the micro strain, dislocation density, stacking fault probability decreases with less that 0.04 M of copper sulphate concentration whereas the crystallite size increases. Similar functional dependency of microstructural parameters with bath temperature for ZnTe thin films have been reported earlier [34].

Scanning electron microscopy is proved to be a unique, convenient and versatile method to analyze surface morphology of a film and to determine the grain size. Figure 7a and 7b shows a typical scanning electron micrograph of CuO thin film deposited at 0.02 and 0.03 M copper sulphate concentrations. Ii is observed from figure 7a that the surface morphology is for the film deposited at 0.03 M copper sulphate is uniform. It is also observed that small grains agglomerate to further bunches of larger grains. The crystallite sizes of CuO thin film covered the entire surface of the film are estimated to be in the range between the range of 80 and 120 nm. The surface is well covered with CuO grains with uneven spherical grains. However, the films deposited at copper sulphate concentration 0.02 M revealed grains with different sizes and grain boundaries are not observed shown in figure 7b. Atomic force microscope studies reveal smaller grains on the surface of the CuO film grown at 0.03 M copper sulphate concentration is as shown in figure 8a. However, larger grains were observed on the surface of the films deposited at optimized molar concentration. Atomic force microscope studies exhibit the formation of uniform CuO thin films with average size of 150 nm. AFM reveals the granular nature of particles and agglomeration of particles is seen from the 3D micrographs. The surface roughness profile was drawn by using the reported software [35]. The average surface roughness spectra of CuO thin film is as shown in figure 8(b).

Optical transmission spectra were recorded at room temperature in air to obtain information on the optical properties of cupric oxide thin films shown in figure 9. Transmission spectrum is used to calculate the refractive index using the envelope method proposed by Swanepoel [36].

$$n = \left[N_1 + \left(N_1^2 + s^2 \right)^{1/2} \right]^{1/2}$$

$$N_1 = 2s\frac{T_M - T_m}{T_M T_m} + \frac{\left(s^2 + 1\right)}{2} \qquad (11)$$

T_M and T_m are the values of maximum and minimum transmission values at a particular wavelength, '*s*' is the refractive index of the substrate. Refractive index can be estimated by extrapolating envelops corresponding to T_M and T_m. Extinction coefficient (k) of

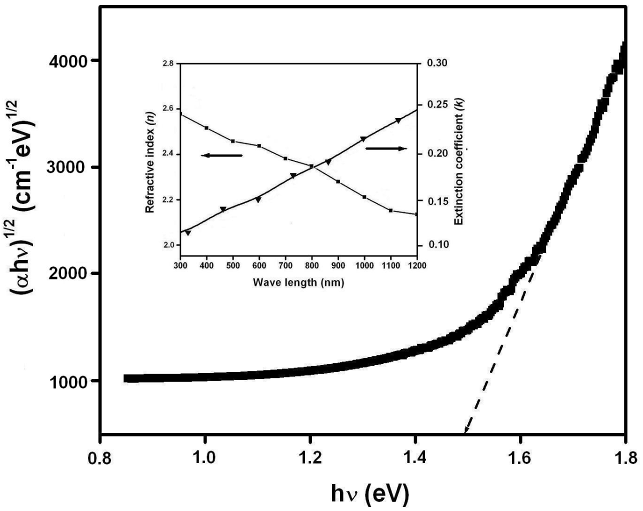

Figure 10. Indirect band gap of the CuO thin film deposited at 0.03 M of copper sulphate concentration (Inset figure shows refractive index and extinction coefficient of the CuO thin film).

cupric oxide films are estimate using the expressions.

$$k = \frac{\alpha\lambda}{4\pi} \tag{12}$$

where α is absorption coefficient, λ is wave length and R is reflectance of the CuO thin films. The refractive index and extinction coefficient of the thin films are estimated from following equations (11) and (12).The optical parameters such as absorption coefficient and band gap are determined from optical absorption measurements. The value of absorption coefficient for strong absorption region of thin film is calculated using the following Eq. (14) [37].

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \tag{13}$$

where α is the absorption coefficient in cm^{-1}, t is the thickness of the films, A is absorbance and T is transmittance. The nature of transition is determined using the following Eq. (13) [37].

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{14}$$

where α is absorption coefficient in cm^{-1} , hν is photon energy, Eg is an energy gap, A is energy dependent constant and n is an integer. The value of n determines the type of transition present in the material. Optical absorption study of CuO thin films was carried out in the wave length range between 400 and 1100 nm at room temperature. The optical absorption data is used to plot a graph of $(\alpha h\nu)^{1/2}$ versus $h\nu$, where α is the optical absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of the plots to the x-axis gives the band gap energy of the CuO film deposited at 0.03 M of copper sulphate concentration (Figure 10). The band gap energy of CuO thin film deposited at optimized deposited conditions is 1.51 eV and this value is in good agreement with the value reported earlier [37]. The variation of refractive index and extinction coefficient with wavelength (λ) is shown in the inset in figure 10. It was observed from inset figure 8 that the refractive index decreases with wavelength, while the extinction coefficient increases for electrodeposited CuO thin films.

4. CONCLUSIONS

Electrochemical synthesis was carried out potentiostatically to prepare polycrystalline CuO films by single step electrodeposition process from an aqueous solution mixture of $CuSO_4$ and L(+) tartaric acid. The effect of Cu^{2+} concentration on the film stoichiometry was studied and it was found that a maximum concentration of Cu^{2+} in the bath yielded nearly stoichiometric CuO thin films. The structure was found to be cubic and the degree of crystallinity increased with increasing Cu^{2+} concentrations. The surface morphology reveals uniform grain size, grain growth occur, thereby the average grain size is increased due to agglomeration of smaller grains together for films deposited at 0.03 M of $CuSO_4$ concentration. The grains tend to agglomerate and the tension may be comparatively less is the surface of the films with the number of needle like ellipsoidal grains are less. The band gap value of CuO films obtained in this work is varied from 1.51 eV for varying the $CuSO_4$ concentrations from 0.02 to 0.04 M and it is quite closer to the value reported earlier.

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