Optoelectronic Property Tailoring in CBD Grown Cupric Oxide (CuO) Thin Films

V Ramya, K Neyvasagam, R Chandramohan, Mohan, Valanarasu, Milton Franklin Benial

Abstract
In this study, CuO thin films were fabricated on glass substrates by using chemical bath method (CBD). The optical, electrical, structural, morphological and dielectric properties were investigated by changing the precursor concentrations (0.05, 0.075 and 0.1M). The XRD patterns confirmed the monoclinic structure of CuO thin film and the size of crystallite is in the range of 16 – 26 nm. Surface exploration using SEM images revealed that the surface is constituted by spherical shaped grains. The optical studies observed that the obtained thin films were remarkably absorbing in the visible range of electromagnetic radiation. Significant enhancement in the optical band gap is observed and value ranges from 2.29 to 1.96 eV with p-type behavior. The electrical parameters were analyzed with an effect of different concentration. The results of the analysis of physical properties of CuO films proved that these films might be considered as promising candidates for solar cells and optoelectronic applications.

Keywords
CuO nano thin films; CBD method; optoelectronic properties

1. Introduction
Cupric Oxide is a well known system due to its affinity and high adsorption of O₂ that can feed electrons during photon incidence to hold back the merging of electron and hole pairs [1]. that leads to act as a metal deficient p-type semiconductor and hence it is one of the essential constituent of pn junction devices [2]. CuO thin films create a center of attention in solar cell fabrication since it is having its potential in providing high solar absorbance and reasonable needed electrical properties [3]. A range of direct optical band gap energies has also been accounted for CuO [4]. Depending on the method of fabrication and stoichiometry, where it exhibits a value around 2.25eV that can efficiently make use of visible light [5], which induces it to act as an excellent material for the devices that functions as photovoltaic or photoelectron chemical solar cells [6, 7]. CuO offers band gap which is close to the energy gap suitable for solar cells and its applications. The value was good in the solar spectral absorption and is more attractive owing to its direct band gap. The understanding of the electronic conductivity mechanism in CuO is very difficult and hence the deposition of cupric oxide thin films prepared by techniques is of [8,9,10]. There are many reports on the prepared of cupric oxide thin films, using different techniques such

*Corresponding author: R Chandramohan, PG and Research Department of Physics, Sree Sevugan Annamalai College, Devakottai 630303, India. E-mail: rathinam.chandramohan@gmail.com

Received July 05, 2017; Accepted August 02, 2017; Published August 25, 2017

Citation: R Chandramohan (2017) Optoelectronic Property Tailoring in CBD Grown Cupric Oxide (CuO) Thin Films. SF J Metallurgical Science 1:1.

Copyright: © 2017 R Chandramohan. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
as spray pyrolysis [11]. SILAR [12], thermal oxidation technique [13], reactive magnetron sputtering [14]. Electrochemical [15], spin coating [16], chemical vapour deposition, electro-deposition and sputtering process [17, 18, 19], dc magnetron sputtering [20]. resistive evaporation method [21]. Ultrasonic spray pyrolysis [22]. sol-gel method [23]. Taguchi Method [24]. Aqueous chemical growth method [25]. Saravanakannan et al. [26]. reported the properties of CuO thin film prepared under varied molar concentration from 0.1 to 0.2 M in steps of 0.05 M and reported that all the obtained films showed high p-type behavior with enhanced conductivity. Fabrication of CuO thin films by chemical bath deposition has been carried out by changing pH [27]. In the present study, we emphasize towards the variation in concentration of molarities and it will bring remarkable tailoring of optoelectronic properties of the CuO thin films.

2. Experimental Details
2.1 Preparation of CuO Films
Cupric oxide thin films were synthesized via CBD method employing a solution bath consisting of 0.1 M copper (II) chloride dihydrate (CuCl₂·2H₂O) complexed with NH₃·H₂O. The solution concentration was incremented in steps of 0.025 M ranges between 0.05-0.1 M by employing different aqueous ammonia concentration. Before deposition of the metal precursor, the substrate was cleaned thoroughly with acetone and they were dipped in the deposition bath for a known standardized time. Copper (II) chloride dihydrate (CuCl₂·2H₂O) of 1.705 g was dissolved in 100 ml double distilled water to make 0.1M copper chloride solution. The bath was kept in a magnetic stirrer and stirred at room temperature for 1 hr. A transparent solution was obtained. After stirring, the concentration of the solution was varied with different proportions such as 0.05, 0.075 and 0.1M by adding ammonia (NH₃). The cleaned substrates were dipped into the solution bath. They were boiled at 90 °C. The substrates were withdrawn from the bath and rinsed in double distilled water for about 5 min in an ultrasonic bath to regularize and obtain tightly bonded particles after boiling for 15 minutes. The obtained thin films were subjected to some characterization studies to estimate its properties.

2.2 Film Characterization
Thickness of the deposited films was measured using a stylus profilometer at room temperature and the thickness values are proportional to the crystallite sizes. X-ray diffraction pattern of the films was recorded using (PANalytical) X’pert PRO diffractometer employing CuKα radiation (λ = 0.15405 nm) in steps of 0.1° over the 2θ range of 15–70°. Scanning electron microscopy technique was employed to examine the morphology of the thin films which was carried out employing Hitachi S-3000H. The band gap was estimated from the absorption studies recorded using Lambda 35 Perkin Elmer spectrophotometer. The Hall studies were carried out by applying magnetic field perpendicular to film’s surface using the Vander Pauw configuration EcopiaHMS-3000 model, was employed.

3. Results and Discussions
3.1 Structural Studies
The precursor concentration in molarity can change the structural properties of the CuO thin films. When the precursor concentration in molarity values was varied and changes in the characteristic features in the films observed. The x-ray diffraction (XRD) patterns shown in (fig.1) consist of peaks of different intensities and FWHM. The occurrence of multiple peaks in the XRD pattern obtained specifies that all the CuO thin films have polycrystalline nature. From the figure, it was observed that the all the film exhibits monoclinic structure and highly intense (002) orientation which corresponding to CuO phase. The mean crystallite size of the thin films was estimated from FWHM using Debye-Scherrer’s formula

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

where \( \theta \) is the Bragg’s angle, \( \beta \) is full-width at half maximum (FWHM) in radians, \( \lambda \) the X-ray wavelength \((CuKα = 0.15405nm)\) and the average particle size ranges from 16-26 nm. The line profile analysis of XRD pattern revealed the convolution of many factors like RMS micro strain, an occurrence of stacking faults and crystallite size. Using the line profiles of XRD the values of RMS micro strain, crystallite size were estimated [28]. Group of crystallite could affect the variance as a measure of crystallite size and strain [29]. The strain has a restoring force that developed on the surface of the thin film. The length of dislocation lines per unit volume is the dislocation density (\( \delta \)) of the crystal was evaluated from the microstrain (\( \varepsilon \)) and crystallite size \( D \) by the relation,
where \( D \) the crystallite size, \( F \) is an interaction parameter, \((e^2)^{1/2}\) is \( \text{rms} \) microstrain, \( K \) the constant depends on strain distribution, ‘\( n \)’ is the number of dislocations on each face of the particle and ‘\( b \)’ the Burgers vector. The \((\alpha)\) stacking fault probability is the fraction of layers undergoing stacking sequence faults in a given crystal and hence one fault is expected to be found in \( 1/\alpha \) layers. The presence of stacking faults gives rise to a shift in the peak positions of different reflections with respect to ideal positions of a fault-free, sample. Typical experimental profile with peak shift for most prominent reflection of CuO thin films prepared in different concentration solution values was used to estimate the value of ‘\( \alpha \)’ of the synthesized CuO thin films. The relation connecting stacking fault probability with peak shift \( \Delta(2\theta) \) is given by,

\[
\delta = \left[ \frac{3nk}{F} \right]^{1/2} \left( \frac{\epsilon^2}{\sqrt{hD}} \right) \tag{2}
\]

\[
\alpha = \frac{2\pi^2}{45\sqrt{3}} \left( \frac{\tan \theta_{511}}{\delta(2\theta)} \right) \tag{3}
\]

From the obtained CuO thin films the values were determined and mentioned in the (table 1), where the studies on functional dependency of micro structural parameters on molarity solution shows that strain values decrease with increase in molarity concentration and due to the release of stress built-up in the layers, the variation of interplanar spacing decreases, which finally leads to a decrease in stacking fault probability and dislocation density of the films. Similar results also have been obtained for the FeSe thin films reported by Kyungsik Kim et al [30]. (Fig. 2) remarked the functional dependence of stacking fault probability, microstrain and dislocation density with different molarity concentration. Hence, the increase of crystallite size infers that alteration of the concentration of precursor is a key factor for creating structures of various sizes with limited strain and dislocations needed.

**Fig. 1** X-ray diffraction (XRD) pattern of different concentration of 0.05, 0.075 and 0.1M CuO thin film

**Fig. 2** Structural parameters of CuO thin films with different molarity

<table>
<thead>
<tr>
<th>Molarity (M)</th>
<th>Thickness (µm)</th>
<th>Crystallite size (nm)</th>
<th>Microstrain ( (\epsilon) ) x ( 10^3 ) lines (^2).m(^{-4})</th>
<th>Dislocation density ( (\delta) ) x ( 10^9 ) lines. m(^{-2})</th>
<th>Stacking fault Probability ( (\alpha) ) x ( 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.42</td>
<td>16</td>
<td>1.02</td>
<td>0.831</td>
<td>0.64</td>
</tr>
<tr>
<td>0.075</td>
<td>0.47</td>
<td>18</td>
<td>0.08</td>
<td>0.602</td>
<td>0.50</td>
</tr>
<tr>
<td>0.1</td>
<td>0.54</td>
<td>26</td>
<td>0.04</td>
<td>0.201</td>
<td>0.22</td>
</tr>
</tbody>
</table>

**Table. 1** Thickness and Structural Parameters of CuO thin films
3.2 Surface Morphology Studies

In Fig. 3 (a-c) the morphology of CuO thin films deposited using different concentration in a variation of molarity (0.05M, 0.075 and 0.1M). It is evident from Fig. 3(a-c) that the surface is to be non-uniform and the near round shaped grains were observed. This resulted in the nucleation overgrowth forming a compact structure. The Depiction of the morphology of the CuO films, in this case, leads to the demonstration that nucleation was an extremely non-linear and fast process resulting from the effective collision among single-nuclei, molecule clusters and primary particles under the influence of random motion as depicted by Brownian and fluid shear motion. The main growth mode being an aggregation of spherical polycrystalline nature for all samples [31]. A pores surface and holes were seen in some areas in the SEM picture which was trusted to provide a large specific surface area for electron-hole pair productions might find a good platform for the solar cell applications. An increase in crystallite size with a concentration of molarity is also proved in the SEM micrograph. The average sizes of the grains are found to be in the range of 20-60 nm. (Fig. 3)d shows the EDAX spectra of the CuO films confirmed the presence of the anticipated elements Cu and O in the film.

Fig. 3 SEM and EDAX images of variation in molarity of CuO thin films
3.3 Optical Studies

(Fig. 4) shows the CuO films prepared by chemical bath deposition technique using different molarity concentration. In the visible region, CuO films were found to have a very high absorption. It was observed that all films behaved as absorber materials at near 400-800 nm for the films prepared at different molarity concentration. The shift in the absorption edge from 390 to 450 nm with the increase of molarity concentration from 0.05 to 0.1 M clearly reflects the incorporation of Cu atoms in the lattice. The absorbance values of the films decreased sharply after wavelengths greater than 800 nm because of their improved transmittance properties. The absorption coefficient and band gap are evaluated from absorption studies. The absorption coefficient value in the strong absorption region is estimated using the following Eq. (4),

\[ \alpha = \frac{1}{t} \ln \left( \frac{A}{T} \right) \]  

where \( t \) is the thickness of the films, ‘\( \alpha \)’ is the absorption coefficient in cm\(^{-1}\), \( T \) is transmittance and \( A \) is absorbance. The nature of transition is determined using the following Eq. (5),

\[ \alpha h\nu = A(h\nu - E_g) \]  

\( h\nu \) is the photon energy in eV, \( \alpha \) is the absorption coefficient in cm\(^{-1}\), \( A \) is a constant which is related to effective masses associated with the valence and conduction band and \( E_g \) is an energy gap in eV. The value of ‘\( n \)’ determines the type of transition present in the material. In this case, \( n = 1/2 \) denotes that the transition involved in the material is direct allowed. A graph of \( h\nu \) versus \( (\alpha h\nu)^2 \) for CuO thin films obtained at molarity ranges from 0.05-0.1M is shown in (Fig 5). The extrapolation of the linear portion gives the band gap value. The band gap value of the material obtained in the present study was found to be 2.29, 2.13 and 1.96eV for concentration 0.05, 0.075 and 0.1M respectively.

**Fig. 4** Absorption spectra of CuO thin films

**Fig. 5** The \( h\nu \) vs.\((\alpha h\nu)^2 \) Tauc’s plots of CuO thin films

The value of the refractive index (\( n \)) and (\( k \)) the extinction coefficient was a measure of the rate of attenuation of transmitted light through absorption and scattering for a medium determined using the following Eqs. (6) and (7). The value of real and imaginary dielectric constants (\( \varepsilon_r \) and \( \varepsilon_i \)) is evaluated using the following Eqs. (8) and (9):

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

where \( R \) is the reflectance.
where \( k \) is the extinction coefficient, \( n \) is the refractive index of the material, \( \varepsilon_r \) and \( \varepsilon_i \) are real and imaginary dielectric constants, \( \lambda \) is the wavelength of nm and \( R \) is reflectance (%). The optical constant values for various molarity concentrations are shown in (fig 6). The maximum value of real part of the refractive index is observed as 2.48 at 0.05M. Also, the refractive index of CuO thin films prepared with different molarity values was estimated to be 2.38 and 2.36 respectively. The variation of the refractive index as a function of wavelength may be due to damping of CuO thin films. It is noted that the refractive index value varies at higher wavelength region, implying that the refractive index of a material can be tuned by varying the precursor concentration.

3.4 Electrical Studies

Fig.8 demonstrates the change of optical conductivity of CuO films prepared under different molarity concentrations. The increase of optical conductivity at high photon energies is due to the re-crystallization and also may be due to the high absorbance of cupric oxide thin films to the oxidation and diffusion of copper atoms from the deposited films into glass matrix. Resistivity, Hall mobility and carrier concentration as a function of variation different molarity are shown in (fig.8). The resistivity of

\[
\sigma = \alpha n c
\]
the cupric oxide thin film fabricated with the variation of molarity concentration by the chemical bath deposition method. By using this method the resistivity values in the present work between the ultrasonic spray pyrolysis method and Electro deposition method [32]. The p-type of conduction was defined by the sign of Hall effect at room temperature. Polycrystalline CuO film prepared onto a glass substrate showed a resistivity decrease from 8.46 x 10^6 Ω cm with an increase in the molarity concentration and the minimum value was obtained for 0.1M, which can be attributed to the deficiency found in CuO films due to copper vacancies, which is associated with the native defects of oxygen vacancies and copper interstitials. The carrier concentration was increased from 1.07 x 10^13 cm^-3 with an increase in molarity concentration and the minimum value was obtained at 0.1 M. The mobility increased with an increase in molarity concentration and the maximum value of 17.02 cm^2/V.s was obtained at 0.1M. It is determined that the decrease in lattice defects to the increase in mobility is attributed due to the growth of highly oriented columnar CuO grains [33]. The mobility is generally limited by scattering defects including lattice defects, grain boundaries, and ionized impurities. The CuO thin films composed of aggregated grains and contain both the copper vacancies and impurities. They act as ionized impurities and also at a very low level as demonstrated by the lower hole density.

4. Conclusions
CuO thin films have been successfully deposited on glass substrates employing CBD method by varying the concentration of the solution as 0.05, 0.075 and 0.1M respectively. X-ray diffraction indicated that the films were polycrystalline nature with monoclinic structure along with preferential orientation (002) plane. Also, the microstructural parameters such as stacking fault probability, crystallite size, dislocation density, strain, and microstrain were estimated. Surface morphology showed that the thin films are with spherical shaped grains. EDX analysis revealed that films are near stoichiometric with Cu and O elements are obtained. Optical studies revealed that the deposited film has a direct band gap value of 2.29, 2.13 and 1.96eV for 0.05, 0.075 and 0.1M respectively. Hence, CuO system with pores may be a smart choice for fabricating CuO films of good quality. The thin films are suitable for photovoltaic and optoelectronic applications and good device quality films may be synthesized using CBD by altering the molarity conditions.

Acknowledgments
The authors gratefully acknowledge the UGC New Delhi, India for providing financial support to carry out this work by way of MRP -No. F.41-913/2012.

References


