Synthesis and characterisation of copper oxide thin films by double dip method

Shifa Salam¹, Ben Jose¹,², Rakhy Raphael¹ and E I Anila¹,³,⁴
¹Optoelectronic and Nanomaterials’ Research Laboratory, Department of Physics, Union Christian College, Aluva, Kerala, India-683102
²Sree Sankara College, Kalady, Kerala, India-683574
³Christ (Deemed to be University), Bengaluru, Karnataka, India-560029
⁴Corresponding author, Email: anilaei@gmail.com

Abstract. Cupric Oxide thin films were prepared and deposited on glass plate by double-dip method. The study was conducted on samples annealed at different temperatures. The deposited films showed poly crystalline nature with a preferred orientation of monoclinic structure along (111) plane. The thicknesses, as well as the refractive indices of all the films, were determined by using Near Normal Spectroscopic Reflectometry. Optical studies revealed a decrease in band gap with annealing temperature. The V-I graphs were found to be linear for a short-range when measured by two probe method. The thin films showed a resistivity of the order of kΩ-cm. An increase in electrical conductivity with temperature reveals the semiconducting nature of the thin films.

Keywords: Copper Oxide; Double dip method; Electrical properties; Bandgap; Activation energy

1. Introduction
Copper forms two well-known oxides namely CuO (Teronite) and Cu₂O (Cuprite). A transitional stage compound, Cu₄O₃, has also been reported. CuO is reported to be a p-type transition metal oxide with a bandgap ranging between 1.8 to 2.1 eV [1,2]. This behavior of electrical conductivity is explained based on copper vacancies present in the crystal lattice [3,4]. CuO belongs to monoclinic crystal structure with lattice parameters a = 4.684Å, b = 3.425 Å, c = 5.129Å and β = 99.28Å. CuO has earned the interest of researchers due to its ease of fabrication, the abundance of precursors, high surface area and non-toxicity [5]. It has a wide range of applications in the fields such as solar cell photovoltaics [6,7], in the fabrication of electrochromic devices [8], glucose sensors [9], as gas sensors [10,11], as anodes in Li-ion batteries [12], dilute magnetic semiconductors [13] for antibacterial activity [14,15] etc.

Different coating techniques like dip coating, sputtering, spray pyrolysis, electro-deposition, thermal oxidation, chemical vapor deposition etc. can be used for CuO thin film preparation [12,16,17,18]. In this work, the deposition method adopted is double-dip coating, which is a sol-gel deposition method consisting of the successive dipping of substrates in precursor as well as the hot bath solution (distilled water at 70°C). We adopted this technique since it is cost effective and requires no sophisticated equipment. The dip coating method has several advantages over other physical methods. This offers large area of deposition, lower preparation costs, wide flexibility in the choice of chemicals and compositions etc. [1]. In this paper we report the impact of annealing temperature on the structural, optical, and electrical properties of dip coated thin films of CuO.
2. Experimental
The dipping solution was prepared by mixing 100ml each of aqueous solution of 0.1 molar sodium hydroxide and 0.5 molar copper acetate using double distilled water. The resultant clear blue colored solution was stirred until a colloidal blue-color solution was obtained. Thoroughly cleaned glass substrates were mounted on a programmable dip coating unit (HOLMARC-HO-TH-01). The dip duration as well as the dry duration was set to be 2 minutes and 20 s respectively. The glass slides were first dipped in the precursor solution and then dipped in the hot water maintained at 70˚ C, at a speed of 6mm/s and then dried. This procedure was repeated for 60 dips. After this procedure, the samples were annealed for 30 minutes. Different samples were synthesised by setting annealing temperatures as 100˚ C, 200˚ C, 300˚ C and 400˚ C. These samples were labeled as C1, C2, C3 and C4 respectively and the unannealed sample was referred as C. All the samples were characterized by XRD (Bruker, D8 advance), UV-Vis absorption spectroscopy (Shimadzu, UV-2600), two-probe measurement (Keithley 2450) and SEM analysis (Jeol, JSM-6390LA) for studying the structural, optical, electrical, and surface morphological properties of the thin films deposited.

3. Results and Discussion
X-ray Diffraction analysis was carried out with Cu-Kα (k = 0.154 nm) as source radiation over the 2θ scan range of 20–80˚. XRD pattern of the samples (Figure 1) match with that of CuO in monoclinic structure as per JCPDS file no.44-0706 The plot also reveals that the material has a preferred orientation along (111) plane. The increase in intensity of diffraction peaks from C to C4 samples confirms that the crystallinity of CuO thin films increases with annealing temperature. The crystallite size of each sample was calculated with the help of Scherrer formula and found to be varying from 14 nm to 23 nm as the annealing temperature vary from 100 to 400˚ C. The thickness and refractive index of the samples were also determined by near normal spectroscopic reflectometer and is given in table1.

![FIGURE 1. XRD pattern of dip coated CuO thin films](image)

The optical characterisation of the CuO thin films were carried out in the wavelength range 300- 1000 nm and they are depicted in figure 2. From the graph, it can be observed that all the samples show a maximum transmission at 900 nm and the transmission percentage decreases with annealing temperature. This may be due to factors such surface smoothness, defect density and structural properties.
TABLE 1. Average grain size, thickness and refractive index of CuO thin films

| Sample         | C   | C1  | C2   | C3   | C4   |
|----------------|-----|-----|------|------|------|
| Average Grain Size (nm) | 14.99 | 15.00 | 15.47 | 18.27 | 22.75 |
| Thickness (nm)  | 194  | 199  | 189  | 182  | 186  |
| Refractive Index| 1.674 | 1.624 | 1.66  | 1.675 | 1.686 |

The bandgap of each film was determined using the Tauc plot (figure 3) and is given in table 2. It is evident from the graph that the dip coated CuO thin films possess direct bandgap transitions. The bandgap values vary from 1.8eV to 2.0 eV when annealing temperature changes from 100-400˚ C. This decrease in bandgap is due to the increase in grain size.

FIGURE 2. Transmission spectra of CuO thin films
Electrical studies of the coated films were conducted using Keithley source meter unit (SMU 2450) with two probe arrangement. The V-I graphs are found to be linear for a short-range (figure 4). Mechanisms like scattering from phonons, grain boundaries, impurities and point defects may contribute to the film resistivity. It was noted that resistivity of the CuO thin films decreased with annealing temperature. This can be attributed to the increase in crystallinity and reduction in scattering of carriers at the grain boundaries and crystal defects.

TABLE 2. The bandgap of CuO films determined from the Tauc plot

| Sample | C   | C1  | C2  | C3  | C4  |
|--------|-----|-----|-----|-----|-----|
| Bandgap(eV) | 2.00 | 1.85 | 1.84 | 1.83 | 1.82 |
FIGURE 4. V-I graphs of the CuO thin films

The surface morphology of all the samples analyzed by SEM is depicted in figure 5(a) to 5(e). For the as synthesized film (sample C), the particles do not have any definite shape. On annealing at 100 °C (sample C1), we can clearly observe an agglomeration of particles forming clusters with large space between them. Some rod-like structures were also observed among the large clusters. The clusters grow in size as the annealing temperature was increased and a homogeneous smooth film was obtained on annealing the film at 400 °C.

FIGURE 5. Scanning electron micrograph of dip-coated CuO thin films
The dependence of resistivity of the CuO thin films on temperature was also analyzed. For this Arrhenius plots were drawn by taking \( \ln(\sigma) \) along y-axis and \( 1000/T \) along x-axis. Arrhenius plots obtained for different samples are shown in figure 6. The variation of conductivity with temperature confirms the semiconducting nature of the thin films. The activation energy was determined by applying the relation:

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{K T} \right)
\]

\[
\ln(\sigma) = \ln(\sigma_0) - \frac{E_a}{K T}
\]

Where, \( \sigma \) is the conductivity, \( \sigma_0 \) is a constant, \( E_a \) represents the activation energy, \( K \) is the Boltzmann constant and \( T \) is the temperature. The slope of the Arrhenius curve when multiplied by Boltzmann constant will give activation energy. A careful examination of figure 6 (a), 6 (b) and 6(c) reveals that there are two linear segments with different slopes indicating two activation energies and figure 6(d) and 6(e) have only one slope. The activation energies determined from the slopes of the linear portion of the graph is given in table 3. This leads us to the conclusion that the thin films C, C1 and C2 have two activation energies which imply the presence of two defect levels whereas, the films C3 and C4 has one activation energy, which suggests the presence of single defect level. The room temperature resistivity of all the samples was analyzed and is given in the table 3. Annealing temperature influences the electrical characteristics of the CuO thin film. Resistivity shows an increasing trend with increase in annealing temperature except for sample annealed at 300 \(^\circ\)C.

**FIGURE 6.** Arrhenius plots of the CuO thin films
TABLE 3. The resistivity and activation energy of CuO films

| Sample | C | C1 | C2 | C3 | C4 |
|--------|---|----|----|----|----|
| Resistivity (kΩ-cm) | 1.18 | 1.28 | 1.45 | 1.18 | 1.74 |
| Activation Energy (eV) | 0.116 | 0.164 | 0.144 | 0.138 | 0.153 |
| | 0.054 | 0.056 | 0.074 | - | - |

4. Conclusion
Thin film coating of CuO synthesized by sol-gel was dip coated on glass substrates and the influence of annealing temperature on their structural, optical and electrical properties were studied. Crystallinity of the films increases with annealing temperature. The sample annealed at 300 °C and 400 °C have homogeneous and smooth surface morphology. But, sample annealed at 300 °C offers minimum resistivity. So we consider the sample C3 as a candidate for our further studies. The variation of conductivity with temperature suggests the semiconducting nature of the thin films. The activation energies determined from the Arrhenius plots reveals the presence of defect levels in the CuO thin films.

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