Preparation of Copper Oxide thin Films by SILAR and their Characterization

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ABSTRACT

Polycrystalline copper oxide thin film was synthesized using Successive ionic layer adsorption and reaction (SILAR) technique. Fixed concentration of anionic precursor (1.0 M KOH) and varying concentration of cationic precursor (copper sulphate complex) was used. For lower concentrations of copper sulphate complex, mixed phase of CuO and Cu_2O was found. Phase pure Cu_2O was observed with enhanced concentration of copper sulphate complex. SEM micrograph shows formation of nanocrystalline grains on the surface. The bandgap energy was ~2.10 eV.

Keywords: Copper oxide, polycrystalline thin film, SILAR

1. Introduction

The synthesis and characterization of copper oxide (Cu_2O) thin films via different techniques have attracted considerable attention due to their potential application prospects in solar cells [1]. Cu_2O is p-type semiconductor with a band gap of approximately 2.0 eV [1-2] and a cubic structure. Cupric oxide (CuO) is also a *p*-type semiconductor having a band gap of 1.21–1.51 eV and monoclinic crystal structure. The different physical and chemical techniques that have been utilized to grow Cu_2O thin film on glass [2] include reactive sputtering, chemical vapor deposition, spraying, thermal oxidation, electrodeposition etc. Ristov et al. [3] and later on Nair et al [1] reported deposition of Cu_2O by SILAR. In SILAR, thin films are obtained by immersing the substrate into separately placed cationic and anionic precursors. Between every immersion it is rinsed in distilled water or ion exchanged water. For Cu_2O deposition, the method consists of alternate immersion of a glass substrate in a complex of copper ion and hot $NaOH$ solution. Fixed concentration of copper complex solution (0.5 M) and $NaOH$ solution (1.0 M) was used in these

works [2-3]. In the present work, the concentration of copper complex was varied to see the microstructural evolution of the deposited films. KOH solution was used instead of $NaOH$ in order to avoid the presence of highly mobile sodium ions in the film. Also the rinsing step between every immersion was avoided. The structural characterization of the synthesized film was carried out using x-ray powder diffractometer (Philips PW 1830) and scanning electron microscope (SEM). Optical characterization was made in a UV-VIS spectrophotometer (Shimadzu, Model: UV-1800).

2. Experimental

Cu_2O thin film was deposited on microscope glass slide substrates. The substrate was cleaned prior to deposition process. It was kept overnight in chromic acid. The chromic acid solution was prepared by adding 70 gm. $K_2Cr_2O_7$ in 320 cc distil water. Finally 120 cc sulphuric acid (99% H_2SO_4) was added to the mixture for complete dissolution of $K_2Cr_2O_7$. This was followed by rinsing the substrate in distilled water and ultrasonic cleaning in equivolume mixture of acetone and alcohol in an ultrasonic cleaner. The substrate was tightly held in a holder so that only a requisite area for film deposition was exposed. The film thickness was measured gravimetrically by taking the theoretical density of Cu_2O.

For preparation of Cu_2O thin film, 1.0 M KOH was prepared in deionized water. Solution of copper thiosulphate complex was prepared by adding sodium thiosulphate $(Na_2S_2O_3;$ Mol. wt. 248.18) to copper sulphate $(CuSO_4.5H_2O)$ solution until a colorless solution results.

X-ray diffraction (XRD) with CuK_α radiation ($\lambda = 1.5418$ Å) was used for structural characterization and phase identification of the deposited copper oxide films. Scanning electron microscopy (SEM) was used to illustrate the formation of crystallites on the film surface.

The cleaned solution was first dipped in hot KOH solution maintained at $70^o C$. A constant temperature bath was used for keeping the temperature of the hydroxide bath fixed at $70^o C$ during deposition. It was then withdrawn and was dipped in copper complex solution kept at room temperature. The dipping time in each bath was 5 seconds. 15 such dipping was performed. One complete set of dipping involves dipping in cationic and anionic precursors. The reaction between Cu^+ ion and OH^- ion takes place on the substrate surface leading to the formation of copper oxide. A thin blight brown adhesive film is formed on the glass substrate.

The reaction occurring on the substrate surface can be represented as:

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O$$
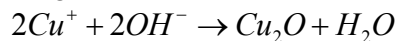
The concentration of copper complex solution was 0.25M and 0.5 M respectively for two sets of film deposition. The concentration of *KOH* solution was kept fixed at 1.0 M in both the cases. The film thickness, measured gravimetrically [4], was found to be approximately 0.3 μm for 0.5M copper complex solution. It was on the lower side (~02 μm) for 0.25 M copper complex solution.

3. Results and Discussions
3.1 Structural characterization

Figure 1 shows the XRD patterns of the films. Figure 1(a) shows the XRD pattern of a film deposited from 0.25 M copper complex and figure 1(b) shows that for film deposited from 0.5 M copper complex solution. The material was scanned in the range 20-50°. Figure 1(b) shows the presence of peaks at 35.7^o, 36.3^o , 38.65^o and 42.25^o. The peaks at 35.7^o and 38.65^o can be assigned to (111) and (200) planes of CuO, while the peak at 36.3^o can be assigned to (111) plane of Cu_2O. These are in good agreement with the Joint committee on powder diffraction standard (JCPDS) data [5-6].

Figure 1(a) on the other hand shows the presence of two peaks at 36.3^o and 42.25^o respectively. They can be assigned to (111) and (200) planes of Cu_2O. Thus it is seen from the present investigation, that lower concentration of copper complex solution leads to a mixed phase of CuO and Cu_2O. Enhancement of concentration leads to the formation of single phase Cu_2O.
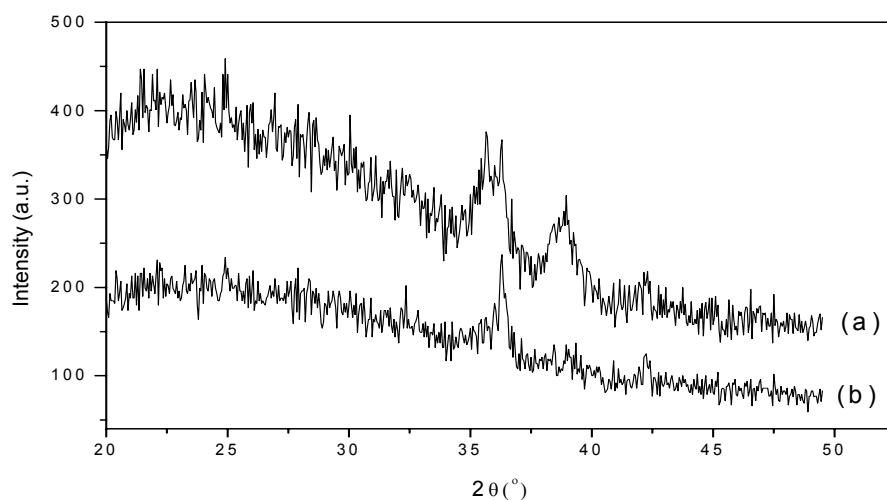

Figure 1: XRD pattern of (a) film deposited from 0.25 M copper complex and (b) 0.5 M copper complex.

The lattice parameter for Cu_2O was calculated from the relation

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

d – value (Inter planar spacing) was calculated from Bragg's law. Its value for 36.3°
is 4.282 $\overset{\circ}{A}$ and 4.27 $\overset{\circ}{A}$ for 42.25°. This is in good agreement with JCPDS value of
4.2696 $\overset{\circ}{A}$ [6].

The crystallite size was calculated by the X-ray line broadening method using
the Scherrer formula [7]:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where λ is the wave length of radiation used (CuK_α in this case), k is the Scherrer
constant, β is the full width at half maximum (FWHM) intensity of the diffraction
peak for which the particle size is to be calculated, θ is the diffraction angle of the
concerned diffraction peak and D is the Crystallite dimension (or particle size).
Assuming $k = 0.89$, which corresponds to spherical crystallites, the particle size
calculated using Scherrer formula for the peak at 36.3° for Cu_2O is ~5.0 µm.
However, while calculating the particle size, the instrumental broadening and
strain broadening was not taken into account. The actual particle size will be
little higher than the measured value of ~5.0 µm if instrumental and strain
broadening are taken into account.

Figure 2 shows the SEM micrograph of Cu_2O film. The formation of sub-
micrometer crystallites distributed more or less uniformly over the surface is evident
from the figure. Some holes indicating porosity and agglomeration of small
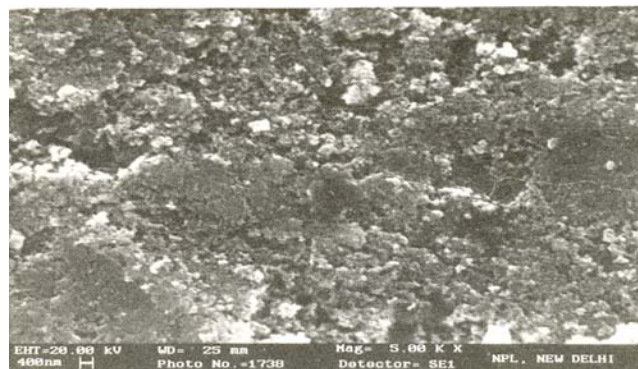crystallites also seem to be present in certain regions on the film surface.

Figure2: Scanning electron micrograph of Cu_2O film deposited on glass substrate

3.3 Optical studies

Figure 3 shows the absorption spectrum of Cu_2O thin film recorded in UV-VIS spectrophotometer (Shimadzu, Model UV-1800).
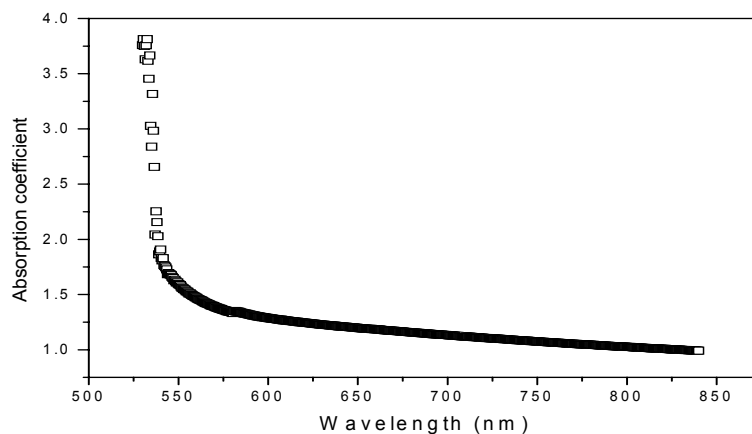

Figure 3: Absorption spectrum of Cu_2O

Figure 3 shows the spectrum in the wavelength range 500-850 nm. The Band gap energy $\left(E_g \right)$ was ~2.10 eV. This was calculated from the relation $E_g = h\nu = \dfrac{hc}{\lambda}$. Here ν is the frequency, h is the Planck's constant and λ is the cut-off wavelength. Extrapolation of the line to the base line, where the value of absorption coefficient is zero, gives the cut-off wavelength of ~545 nm.

4. Conclusions

Polycrystalline thin film of copper oxide was prepared by SILAR technique. It is seen from the present work that lowering of concentration of copper complex solution leads to a mixed phase of CuO and Cu_2O and also a low growth rate of the film. Enhancement of concentration leads to the formation of single phase Cu_2O. The films so prepared are adhesive and contains extremely fine particles. A detailed structural investigation of the materials is underway.

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