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Preparation and study of Cu_2O thin films deposited by the dip technique

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Abstract : Copper oxide films are prepared using methanolic solution of cupric chloride ($CuCl_2$,$2H_2O$) by the dip-coating technique at different baking temperatures XRD study confirms that the films are of Cu_2O phase when prepared at baking temperature of 360°C and CuO phase when prepared at 400°C or more than 400°C baking temperature. The optical band gap of the Cu_2O films calculated from optical absorption measurements is 1.85 eV which is quite comparable with the reported value

Keywords : Dip-coating technique, XRD, optical bandgap

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1. Introduction

Copper oxide, which is a promising semiconductor material for fabrication of photovoltaic devices like solar cells [1], has been the subject of a number of studies in the past. The investigations carried out concern mainly its growth and optical properties [2-7]. Recently, with the discovery of high temperature superconductivity study of decomposition of CuO/CuO_x employing both metallic and oxide source has assumed special importance in the preparation of the thin film high temperature superconductors (HTSCS). Thin films of copper oxide have been prepared using various thin film deposition techniques such as chemical vapour deposition, electro-deposition, thermal oxidation and sputtering process [8-11]. Electron – beam evaporation technique also has been reported in the literature for the growth of Cu_2O thin films [2-6].

However, in comparison with other thin films of oxide semiconductors such as In_2O_3, ZnO and SnO_2, few data are available in the literature on the characterization of copper oxide films.

In the present work, preparation of copper oxide thin film by the dip technique and their structural and optical properties have been studied.

2. Experimental details

The setup used by us for the deposition of copper oxide thin films by the dip technique is shown in Figure 1. Here, the precleaned substrate in its holder moves freely at the end of a thread. The thread passes through a pulley, which is driven by a geared motor arrangement. The substrate is immersed into the solution in such a way that the holder remains just outside the liquid level. For smoothly drawing the substrate out of the liquid, air currents are avoided. The liquid is usually kept inside a long cylinder. Often it is found that abrupt exposure to air after withdrawal of the substrate leads to patchy films with cracks. To avoid this shock, the substrate with its liquid film is kept for a few minutes in an atmosphere of the solution vapour within the long cylinder before its transfer to the furnace for baking.

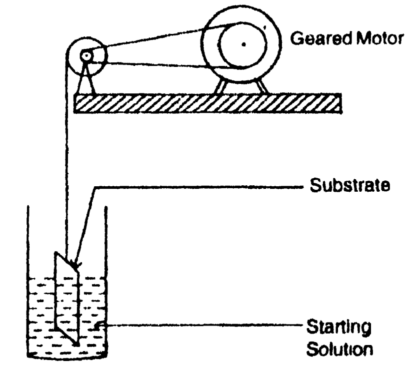

Figure 1. Experimental setup of dip technique for deposition of thin films.

Methanolic solution of cupric chloride ($CuCl_2.2H_2O$) is taken as a starting solution for the deposition of copper oxide thin films in this technique. The solution was prepared using 0.25 kg cupric chloride in one litre methanol. A clean substrate was then dipped into the starting solution and withdrawn vertically at a controlled speed (1.33 mm/sec), under atmospheric conditions using this setup. After withdrawal, the substrate with its liquid film adhering to it is baked at 360°C – 500°C for five minutes. Cupric chloride ($CuCl_2.2H_2O$) hydrolysed and reacted on the heated substrate inside the furnace at high temperature in open air and formed thin solid films according the following reaction

$$4CuCl_2 + 6H_2O = 2Cu_2O + 8HCl + 2H_2O + O_2 . \quad (1)$$

In this reaction, HCl and O_2 release whereas H_2O vaporise at higher temperature and thin solid layer of copper oxide deposited on the substrate. The characterization was mostly done on those deposited on glass substrate. The films were deposited at three baking temperature of 360° C, 400°C and 500°C. Films were uniform and black in colour. Films which were characterized had a thickness of the order of one micrometer and it is measured by the stylus method using α steep.

3. Results and discussion

3.1 X-ray diffractometric study :

X-ray diffractometric studies were carried out by PHILIPS diffractometer (model PW 1390) with CuK_α radiation (Ni-filter)

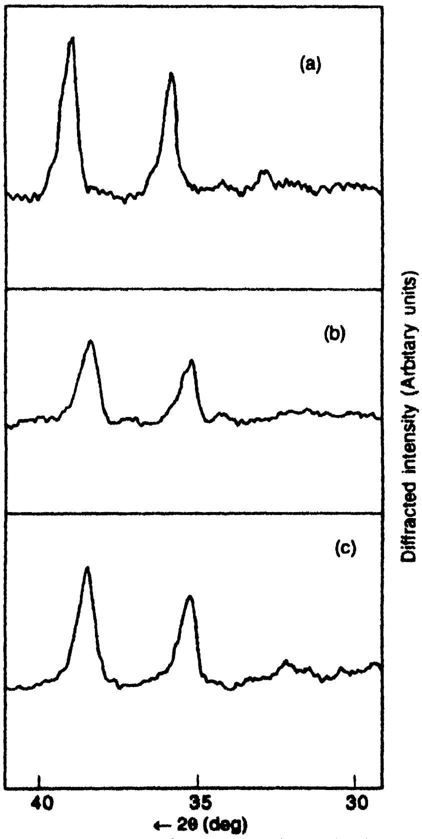

Figure 2. X-ray diffractogram of copper oxide thin films deposited on glass substrate at three different temperature [(a) Cu_2O, 360°C ; (b) CuO, 400°C and (c) CuO, 500°C].

at 1.54 Å. Analysis of diffraction spectra indicates that the peak positions correspond to Cu_2O phase when prepared at 360° C and shown (111) and (200) planes. It was also observed that when baking temperature is higher (400° C or more) the Cu_2O films converted into CuO phase. The X-ray diffraction spectrum of the copper oxide films prepared at different temperature is shown in Figure 2. The relevant diffraction planes are indicated in the spectra. Results of peak position observed for the films prepared at three different temperatures and their, comparison with the ASTM data values (file No. 5-661) are given below in the Table 1.

Table 1. Comparison of observed value and ASTM data value of Cu_2O and CuO thin films deposited by dip technique.

Observed value			ASTM data value			h k l
2θ	d(Å)	(I/I_0)	2θ	d(Å)	(I/I_0)	
T_B = 360° C (Cu_2O)						
35.7	2.51	78	35.6	2.52	100	111
38 9	2.31	100	38.9	2.31	30	200
T_B = 400°C and T_B = 500°C (CuO)						
35 3	2 56	78	35 4	2 53	49	002
38.3	2 35	100	38 7	2 32	96	111

3.2 Optical properties :

The optical absorption of the cuprous oxide thin films was measured using SHIMADZU UV - 240 double beam spectrophotometer in the range 200–800 nm. A typical recording for the optical absorption of copper oxide film is shown in Figure 3. To analyse these results, $(\alpha h\nu)^2$ is plotted against $h\nu$ [Figure 4] and from the intercept of the straight line on the $h\nu$ axis the

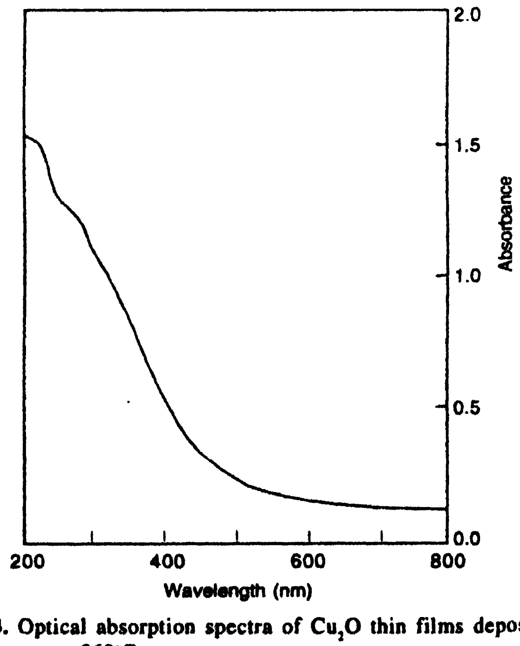

Figure 3. Optical absorption spectra of Cu_2O thin films deposited on glass substrate at 360°C.

band gap is estimated. The band gap value thus obtained is about 1.85 eV, which is in good agreement with the value 1.80 eV obtained by Miller *et al* [8].

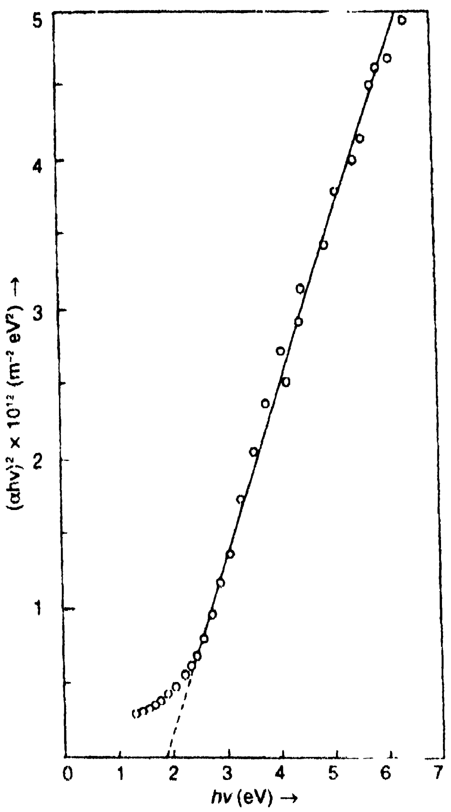

Figure 4. Plots of $(\alpha h\nu)^2$ against $h\nu$ curves for Cu_2O films deposited on glass substrate at 360°C

4. Conclusion

It has been demonstrated that the dip-coating technique can be used to deposit copper oxide films in a simple manner using metallic chlorides ($CuCl_2.2H_2O$) as a starting material.

Dip technique is a very simple and low-cost method, which requires no sophisticated specialized setup. Coating of the substrate of a large surface area can be easily obtained by this technique compared to that in sputtering, vacuum vapour deposition and spray pyrolysis. Another advantage of the dip technique is that it is very easy to coat both sides of the substrate instead of only one and to deposit otherwise inaccessible surfaces. This method is well suited for applying coating on the inner and outer surfaces of tubes of various diameters and shapes. The main advantage of the dip coating method lies in fact that it is possible to deposit a variety of layers having good homogeneity and mechanical and chemical stability with a very simple setup Multi-layer thin films of different metal oxide layers one after another can be deposited easily by this technique.

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