

Oxide films of copper prepared by the oxidation of copper sulphide films

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Abstract. Copper sulphide films prepared by reactive evaporation, when heated in air at 500 K, oxidized to Cu_2O after a series of intermediate chemical transitions. Golden yellow coloured Cu_2O films showed a large absorption before the fundamental absorption edge. The optical band gap was found to be (2.29 ± 0.02) eV. When these Cu_2O films were further heated they got converted to CuO and the optical band gap was found to be (2.17 ± 0.02) eV.

Keywords. Thin films; optical properties; oxidation; high temperature treatment.

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1. Introduction

Copper oxide (Cu_2O) is a well-known semiconductor and that its finding renewed interest in the search for low cost materials for solar cell application [1]. It is a defect semiconductor with *p*-type conductivity and through the work carried out in the 1920s, it has become one of the first semiconducting materials to be investigated. Cuprous oxide layers on Cu have been known for many years to be photoconducting and to show photovoltaic effect. The first investigation on photoconductivity of these materials was made by Pfund [2]. More precise photoconductivity study began with the work of Schonwald [3]. He showed that *p*-type conduction in Cu_2O occurs through the presence of copper ion vacancies. Switching phenomenon, similar to that observed in the case of many chalcogenide glasses was observed in Cu_2O crystals by Wang and Weichman [4]. Electrical [5–7] and optical [8–11] properties of Cu_2O have been reported in the literature by various authors. But reports on the electrical and optical properties of CuO are rare.

For use in thin film solar cell technology it must be possible to prepare low resistivity films of Cu_2O with good optical properties in a reproducible manner on a variety of substrates. Preparation methods that are currently being investigated are thermal oxidation [12–14], electrode position [15] and reactive sputtering [16–18]. A problem common to oxidation and electrodeposition methods is that the resulting Cu_2O material tends to be of high resistivity, namely 10^2 – 10^4 ohm cm in the thermal case [14] and 10^4 – 10^6 ohm cm in the electro-deposited case [15]. Best films are formed by reactive sputtering of copper in an oxygen-argon mixture which gives films with controlled resistivity over the range 25 to 10^4 ohm cm [16].

Here we report the preparation and optical properties of Cu_2O and CuO films prepared by the oxidation of copper sulphide films in air.

2. Experimental

Copper sulphide films were deposited on glass substrates as described in reference [19, 20]. After deposition the films are taken out of the chamber and oxidized in air at a particular temperature. The set-up used for oxidation of the films in air is given in detail in [21]. The heating rate was approximately 0.5 K s^{-1} . Both amorphous and crystalline films of CuS were used in these experiments. The criterion used for the oxidation of the final phase of Cu-S (chalcocite, colour yellow) to Cu_2O was the sudden change in the colour of the film to golden yellow. And the criterion used for the further oxidation of Cu_2O into CuO was the change of golden yellow colour to a translucent foggy appearance. These oxidized films contained pin holes and non-uniformities. This was especially severe in the case of thicker films.

Optical measurements of these films were made by using a Hitachi 200-20 UV-Vis spectrophotometer. Films used in the optical study had a thickness around 100 nm. X-ray diffraction measurements were carried out in a Philips PW 1140/90 X-ray diffractometer. About 300 nm thick films were used in X-ray diffraction study.

3. Results and discussion

When CuS films are heated beyond 500 K, after a series of phase transformations [22], the films get oxidized. This oxidation of the film is characterized by a sudden change in the film from yellow of chalcocite to the golden yellow of Cu_2O . The X-ray diffraction pattern of a film so oxidized is given in figure 1. The table 1 lists the d -spacings given in JCPDS card and our results. The unidentified lines are not listed

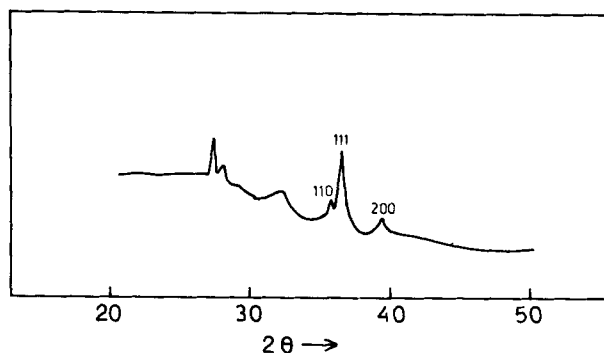


Figure 1. X-ray diffraction pattern of Cu_2O film.

Table 1. X-ray diffraction data for Cu_2O film.

hkl	JCPDS (Card No. 5-667)		Present results	
	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0
110	3.020	9	3.173	8
111	2.465	100	2.456	30
200	2.135	37	2.296	7
211	1.743	1		

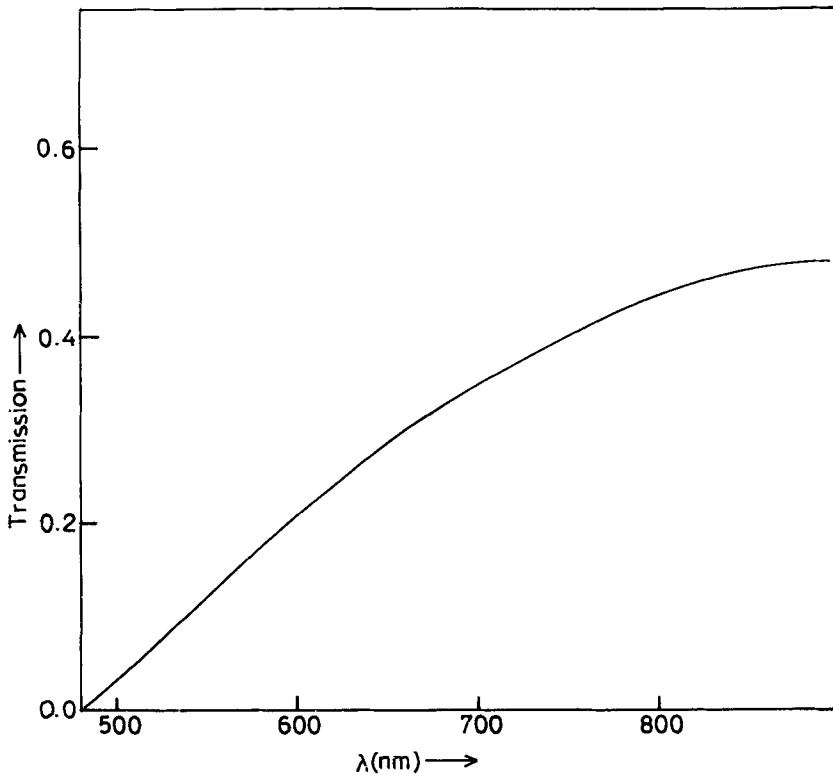


Figure 2. Transmission spectra of a typical Cu_2O film.

in the JCPDS card. It is not clear at present whether these lines are due to the presence of any other unknown phase or was it simply left unlisted in the JCPDS card because of the low inherent accuracy of these lines (low angle diffractions). The uniform colour of the film and the failure to detect two or more phases under crossed polaroids in an optical microscope and also the fact that the unlisted lines are not due to CuO almost rule out the first possibility.

From X-ray diffraction study no preferred orientation of the grains in the films could be found.

The samples obtained show *p*-type conductivity and were of high electrical resistivity. This is in general agreement with earlier reported data in the literature.

Transmission spectra of a Cu_2O film of thickness ≈ 100 nm is shown in figure 2. It may be seen that this film shows a high absorption ($\alpha \sim 10^4 \text{ cm}^{-1}$) before the onset of band to band transitions. A visual inspection of the film shows that the film is not clear, i.e. they scattered light too much. The absence of interference fringes also shows that the films are not optically perfect. It may also be noted that transmission decreases continuously from 900 nm. This may be due to the existence of large number of levels in the forbidden gap just below the conduction band or just above the valence bands. Weichman and Reyes [23] report that copper inclusions are responsible for absorption peaks in the 1.1 eV to 2.0 eV range. In the present case these absorption peaks may have merged into a single one due to the large number of defects present causing high absorption before the onset of band to band transitions.

Because of the large absorption before the absorption edge, interference fringes were absent and consequently refractive index of the film could not be determined.

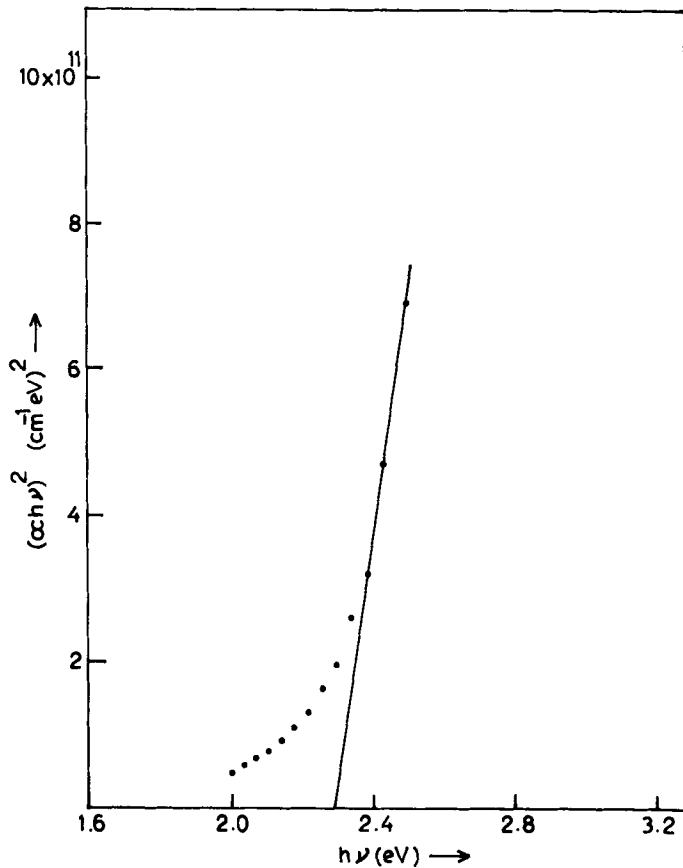


Figure 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for a Cu_2O film.

For calculation of absorption coefficient, refractive index data given in [16] was used. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in figure 3. This gives a band gap of 2.29 ± 0.02 eV and the transition leading to this is a direct allowed one. The reported band gap of Cu_2O polycrystalline specimens from photoconductivity data lies between 1.94 eV and 2.14 eV. This band gap corresponds to transitions from valence band to exciton levels [24] just below the conduction band. Since the samples used in the present study show no structure in the transmission curve due to exciton absorption and because of the large absorption coefficients ($\alpha \sim 10^5 \text{ cm}^{-1}$) characteristic of direct transitions, the band gap obtained in the present case may be taken as due to transitions taking place from valence band to conduction band and the band gap obtained as the true gap. This is in agreement with the energy level diagram given in [25] for Cu_2O , where a band gap of 2.3 eV is taken.

When the Cu_2O films are maintained at 500 K for some time, the characteristic golden yellow of Cu_2O disappears and a film with a translucent foggy appearance is obtained. X-ray diffraction pattern of such a film is shown in figure 4. The diffraction data (table 2) shows lines due to monoclinic CuO together with three other lines which are unidentified. It is not clear at present whether this is due to the presence of any other phase.

The transmission spectra of a CuO film at ≈ 100 nm thickness is shown in figure 5. It may be seen that as in the case of Cu_2O films, these films also show high absorption

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Table 2. X-ray diffraction data for CuO film.

JCPDS (Card No. 5-661)			Present results	
<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀
110	2.751	12	2.802	9
			2.623	12
002	2.530	49		
$\bar{1}11$	2.523	100	2.520	22
111	2.323	96	2.320	18
200	2.312	30		
$\bar{1}12$	1.959	3		
$\bar{2}02$	1.866	25		

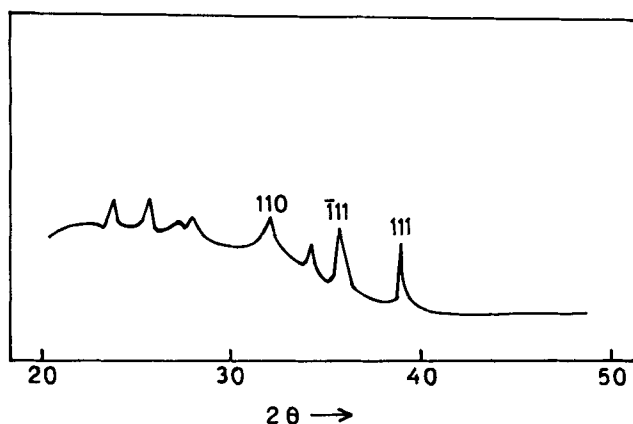


Figure 4. X-ray diffraction pattern of a CuO film.

before the absorption edge. Because of the absence of interference fringes, refractive index in this case also could not be obtained. For the calculation of absorption coefficient, refractive index data given in [16] was used. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for a typical CuO film is shown in figure 6. This gives a direct band gap value of 2.17 ± 0.02 eV and the transition leading to this is an allowed one. Band gap value of CuO films has apparently not been reported in the literature and hence a comparison is not possible. The band gap value obtained in the present case for CuO film is less than that obtained for Cu_2O films. A film of material with a band gap of 2.17 eV should have appeared yellow in transmission as it cuts off wavelengths lesser than yellow. But CuO films obtained in the present case, it seems, does not do this; as mentioned earlier they have a foggy translucent appearance. The apparent transparency suggests a band gap of more than 3 eV. The apparent fundamental absorption shown by these films may be due to a large number of structural and stoichiometric defects which causes band tailing, i.e. impurity bands merging with conduction or valence bands. Evidently more work is needed to clarify these points.

So it can be seen that the effect of heating CuS films in air up to a temperature in excess of 500 K is a series of chemical changes taking place in the structure and composition of the film:

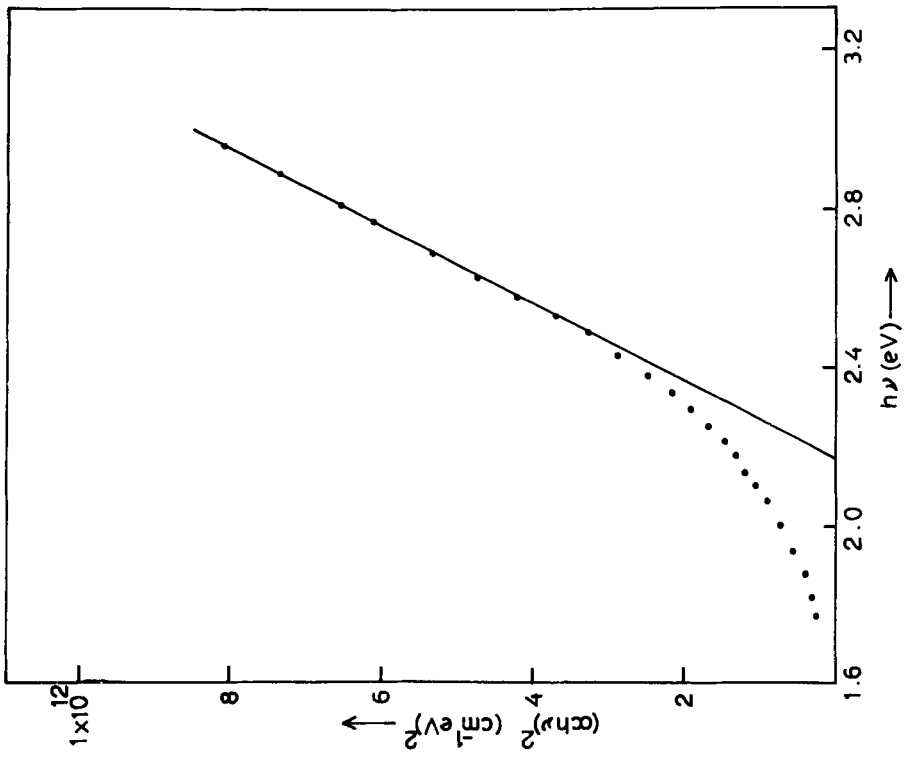


Figure 6. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for a CuO film.

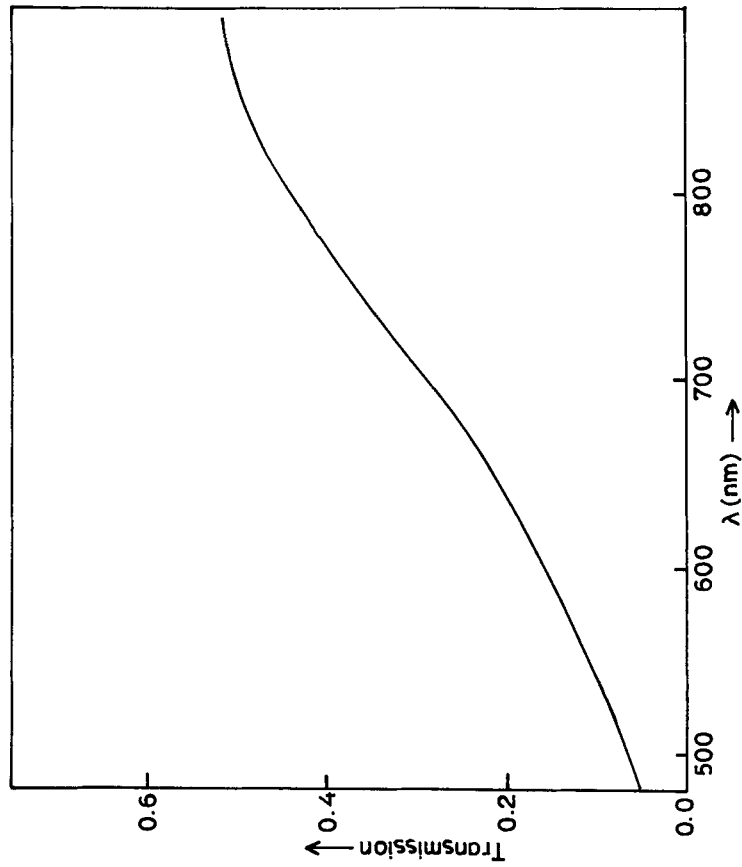


Figure 5. Transmission spectra of a typical CuO film.

CuS(hexagonal)→djurleite (orthorhombic + S(rhombohedral))→djurleite (orthorhombic)→chalcosite(orthorhombic)→Cu₂O(Cubic)→CuO(monoclinic).

4. Conclusion

Films of CuS when heated in air at 500 K, after a series of intermediate chemical transitions, get oxidized to Cu₂O. These Cu₂O films are golden yellow and show large absorption edge. The band gap obtained (2.29 ± 0.02 eV) from optical studies agrees with that reported in the literature for Cu₂O layers. When these Cu₂O films are further heated they get converted to CuO films. These films also show large optical absorption before the absorption edge. The band gap obtained for CuO films is 2.17 ± 0.02 eV. The quality of the films obtained by this method are rather poor.

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