CHAPTER-VIII

OXIDE FILMS OF COPPER PREPARED BY THE OXIDATION
OF COPPER SULPHIDE FILMS

Copper oxide (Cu$_2$O) is a well known semiconductor that is 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 and 1930s, this became 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 were made by Pfund /2/. More precise photoconductivity study began with the work of Schönhald /3/. He showed that p-type conduction in Cu$_2$O occurs through the presence of copper ion vacancies. Switching phenomena, similar to that observed in the case of many chalcogenide glasses was observed in Cu$_2$O crystals by Wang and Weichman /4/. Electrical /5-7/ and optical /8-11/ properties of Cu$_2$O has 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$_2$O 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/, electrodeposition /15/ and reactive sputtering /16/. A problem common to oxidation and electrodeposition methods is that the resulting Cu$_2$O 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 electrodeposited 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/.

In this chapter the preparation and optical properties of Cu$_2$O and CuO films prepared by the oxidation of copper sulphide films in air are discussed.

8.1 **EXPERIMENTAL**

Oxidation of the film was carried out by heating the films to a high temperature in air as in the case of tin disulphide. The heating set-up is as described in Chapter III. Both amorphous and crystalline films of CuS were used in these experiments. Since CuS films underwent a series of phase transformations before it reached the oxidized state, the activation energy for oxidation could not be determined by the method used for tin disulphide. The criterion used for the oxidation
8.2 RESULTS AND DISCUSSIONS

When CuS films are heated beyond 500K, after the series of phase transformations described in Chapter VII, the films get oxidized. This oxidation of the film is characterized by a sudden change in the colour of the film from yellow of chalcocite to the golden yellow of Cu$_2$O. The X-ray diffraction pattern of a film so oxidized is given in figure 1. The table given along with the figure lists the d-spacings given in JCPDS card and our results. It can be seen that after a 'd' value of 3.173Å, every lines in the JCPDS card and our results are
**Figure 1. X-ray diffraction pattern of Cu$_2$O**

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>Present results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.985</td>
<td>1/10</td>
</tr>
<tr>
<td>11.0</td>
<td>9/10</td>
</tr>
<tr>
<td>2.365</td>
<td>100</td>
</tr>
<tr>
<td>2.15</td>
<td>37/10</td>
</tr>
<tr>
<td>1.705</td>
<td>1/10</td>
</tr>
</tbody>
</table>

JCPDS card No.5-667
the same. The unidentified lines are not listed in the JCPDS card. It is not clear at present whether these lines are due to the presence of any other unknown phase or it was 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$_2$O film of thickness $\approx$100nm is shown in figure 2. It may be seen that this film shows a high absorption ($\alpha \sim 10^4$ 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 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
Figure 3. Plot of $(\alpha \nu)^2$ versus $\nu$ for a $\text{Cu}_2\text{O}$ film
the conduction band or just above the valence band which
merges to these bands. Weichman and Reyes /17/ 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. For the calculation of absorption coefficient,
refractive index data given in reference 16 was used. The
plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in figure 5. This
gives a band gap of $2.29 \pm 0.02$ eV and the transition
leading to this is a direct allowed one. The reported
band gap of Cu$_2$O polycrystalline specimens from photocon-
ductivity data lies between 1.94 eV and 2.14 eV. This
`band gap' corresponds to transitions from valence band
to exciton levels /18/ just below the conduction band.
Since the samples used in the present study show no
structure in the transmission curve due to exciton absorp-
tion and because of the large absorption coefficients
($\alpha \sim 10^5$ 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 conduc-
tion band and the band gap obtained as the true gap.
<table>
<thead>
<tr>
<th>JCPDS</th>
<th>Present results</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d(\AA) )</td>
<td>( I/I_0 )</td>
</tr>
<tr>
<td>2.751</td>
<td>12</td>
</tr>
<tr>
<td>2.623</td>
<td>12</td>
</tr>
<tr>
<td>2.530</td>
<td>49</td>
</tr>
<tr>
<td>2.523</td>
<td>100</td>
</tr>
<tr>
<td>2.323</td>
<td>96</td>
</tr>
<tr>
<td>2.312</td>
<td>30</td>
</tr>
<tr>
<td>1.959</td>
<td>3</td>
</tr>
<tr>
<td>1.866</td>
<td>25</td>
</tr>
</tbody>
</table>

JCPDS card No. 5-661

Figure 4. X-ray diffraction pattern of CuO.
Figure 5. Transmission spectra of CuO.
Figure 6. Plot of \((\alpha \nu)^2\) versus \(\nu\)
This is in agreement with the energy level diagram given in reference 19 for Cu$_2$O, where a band gap of 2.3 eV is taken.

When the Cu$_2$O films are maintained at 500K for some length of time, the characteristic golden yellow of Cu$_2$O disappears and a film with a transparent foggy appearance is obtained. X-ray diffraction pattern of such a film is shown in figure 4. The diffraction data 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 of ~100nm thickness is shown in figure 5. It may be seen that as in the case of Cu$_2$O films, these films also show high absorption 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 reference 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 $2.17 \pm 0.02$ 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$_2$O films. A film of a 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 transparent appearance. The apparent transparency suggests a band gap more than 3 eV. The apparent 'fundamental absorption' show 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 upto a temperature in excess of 500K is a series of chemical changes taking place in the structure and composition of the film:

CuS(hexagonal) → djurleite (orthorhombic) + S(rhombohedral)
→ djurleite (orthorhombic) → chalcocite (orthorhombic)
→ Cu$_2$O (Cubic) → CuO (monoclinic)

It may have been clear from now that films of Cu$_2$O and CuO prepared by oxidation in air of the corresponding sulphide films are not of good quality; i.e. they showed too much optical absorption. But when tin dioxide was prepared by the oxidation in air of tin disulphide, highly transparent and good optical quality
films were obtained (see chapter V). Let us compare the oxidation of tin disulphide with that of copper sulphide in some detail. An important factor is the grain size of the films. It was found in the case of tin disulphide that the as prepared films were amorphous in nature and when the films were heated they crystallized at 410K. It was also found that if the oxidation of tin disulphide films were carried out at low temperatures, the conductivity of the films decreased considerably and optical transmission became poor and was explained as due to the incomplete oxidation of the large grains of tin disulphide formed due to prolonged heating at low temperatures.

In the case of CuS and Cu$_2$S films used in this study, the grain size was greater than 1 micron (see figure 3 of Chapter VI). In the case of amorphous films of CuS also when they underwent all the chemical transformations and finally reached Cu$_2$S, their grain size was at least one micron. It is highly probable that these large grains will not get completely oxidized when heated in air. When these large grains are oxidized, the surface of the grains will get oxidized first. This oxide layer may inhibit further diffusion of oxygen in and sulphur and sulphur dioxide out resulting in incomplete oxidation. The incomplete oxidation of grains can certainly make the films too defective causing poor
optical and electrical properties.

Another important point is that tin being a low melting point element (in that case all the respective metal elements of all known transparent conducting oxides) will get good mobility on the high temperature substrate (relative to the melting point of the element). This high mobility may be essential because a structural rearrangement of lattice is to take place. But in the case of copper, its melting point is 1356K and its mobility will be very low on the relatively cold substrate (temperature ≈ 500K).

It is quite clear that either of these factors or both contribute to the quality of the films. More work is needed to determine the following:

1) Whether during the conversion from metal sulphide to metal oxide a complete decomposition of the sulphide take place followed by oxidation. In this case low melting point metals have a definite advantage as they will get good mobility on the substrate surface.

2) Whether only a chemical displacement of atoms take place with a minor structural rearrangement. In this case small grained films will be in an advantageous position, because oxygen will be able to diffuse
into the interior of the crystallite
thus producing complete oxidation of the crystallite.

Data from the present work regarding the oxidation of the films is given in Table I

<table>
<thead>
<tr>
<th>Material oxidized</th>
<th>Melting point of the respective metallic component</th>
<th>Grain size of Film</th>
<th>Initial quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>tin disulphide</td>
<td>505K</td>
<td>very small</td>
<td>good</td>
</tr>
<tr>
<td>copper sulphide</td>
<td>1356K</td>
<td>large</td>
<td>poor (≈ micron)</td>
</tr>
</tbody>
</table>

Further work is to be done on other compounds with low melting point metallic components to further clarify these points.

CONCLUSION

Films of CuS when heated in air at 500K, after a series of intermediate chemical transitions, get oxidised to Cu$_2$O. These Cu$_2$O films have a golden yellow colour and show large absorption before the fundamental absorption
edge. The band gap obtained \((2.29 \pm 0.02 \text{ eV})\) from optical studies agrees with that reported in the literature for \(\text{Cu}_2\text{O}\) layers. When these \(\text{Cu}_2\text{O}\) films are further heated they get converted to \(\text{CuO}\) films. These films also show large optical absorption before the absorption edge. The band gap obtained for \(\text{CuO}\) films is \(2.17 \pm 0.02 \text{ eV}\). The quality of the films obtained by this method are rather poor.
References:


