In recent years there has been much interest in copper sulphide films because of its use as absorber material in CdS:Cu$_2$S thin film solar cells which still hold promise for large scale terrestrial power generation. The photovoltaic conversion efficiency in these cells depends markedly on the composition of the Cu$_{2-x}$S layer /1/. It is reported that chalcocite phase gives the maximum short circuit current and efficiency followed by djurleite phase. Other than this particular interest, copper sulphide in itself is an important material from the point of view of basic research, because this material is known to exist in several crystallographic phases. The number of independent chemical phases which exist at room temperature is still a matter under discussion. There are at least five known phases in the Cu$_x$S system at room temperature when $x$ varies from 1 to 2. These are, in the copper rich region, orthorhombic chalcocite ($\gamma$-Cu$_2$S), djurleite (orthorhombic, $x = 1.96 - 1.94$), low temperature dignite (pseudocubic, $x = 1.79 - 1.765$), anilite (orthorhombic, $x = 1.75$) and in the sulphur rich region, covellite (CuS, hexagonal). When the temperature increases, the new phases which exist are mid temperature form of chalcocite ($\beta$-Cu$_2$S)
Figure 1: Phase diagram of Cu-S system.
between 103.5°C and 435°C, and the high temperature form (\( \gamma \)-Cu\(_2\)S). Another phase, the tetragonal, exists from \( x = 1.8 \) to \( x = 2 \). This phase was supposed to be metastable until Cook /2/ showed that it forms a solid solution between Cu\(_2\)S and Cu\(_{1.95}\)S at temperatures from 94°C to 140°C. This is also the domain of high temperature form of dignite. Figure 1 shows the phase diagram of the Cu-S system; the upper figure showing all compositions between 0 and 600°C and the lower figure showing compositions involved in CdS:Cu\(_x\)S solar cells. The present view is that a stoichiometric Cu\(_2\)S crystal consist of a highly ordered S-sublattice and a disordered Cu-sublattice. The S-sublattice being the rigid armature of the crystal. The Cu ions are mobile and can occupy a large number of equivalent sites thus giving rise to different phases at least in the vicinity of the region where \( x \approx 2 \).

Optical and electrical properties of the different phases in the Cu-S system has not been investigated thoroughly. Only properties of the composition relevant to application in CdS:Cu\(_2\)S solar cells has been studied in some detail. Here too, the results obtained by different groups of workers vary to a considerable extent. For example the value of the forbidden energy gap reported by various authors for \( \gamma \)-Cu\(_2\)S vary from
1.05 to 2.50 eV/3-7/. Electrical properties also show large scattering. It is reported that the carrier concentration varies from $\sim 10^{15}$ to $\sim 10^{21}$ cm$^{-3}$ and hole mobility varies from 1 to 15 cm$^2$/volt sec. These scattering are primarily due to the existence of different phases in the same stoichiometric interval and also due to the non-stoichiometries of the phases themselves. In the sulphur rich region of the Cu-S phase diagram, electrical properties of pressed samples of CuS (Covellite) has been reported /8/ and it is also reported here that CuS exhibits metallic conductivity.

Copper sulphide (Cu$_2$S) films had in the past been prepared in a number of ways. Carlson prepared copper sulphide films by vacuum evaporation /9/, Ellis used flash evaporation /10/, Jonath et al used reactive sputtering /11/ and Islam and Haque used coevaporation /12/. A number of chemical methods are also available to deposit Cu$_2$S on CdS for solar cell applications /13-15/.

It was thought that reactive evaporation of copper in a sulphur atmosphere which was not yet reported, is a promising technique for the preparation of copper sulphide films and this method was used for preparing films reported in this chapter.

6.1 PREPARATION OF THE FILM.

Films were prepared in a conventional vacuum
system as described in Chapter III. The system was first pumped to $2 \times 10^{-5}$ Torr and the optically flat substrate heated to the required temperature. Doubly electrolyzed copper and three times recrystallized sulphur were used as evaporants. A glass crucible placed in a conical basket made of molybdenum wire was used as the sulphur source. A molybdenum boat was used to evaporate copper. The boat was covered with stainless steel heat shields so that the substrate temperature could be kept within 4K of the required temperature.

It is found that a stoichiometric interval exists for the reactive evaporation of copper in a sulphur atmosphere with the following parameters:

- Metal atom flux = $1-2 \times 10^{14}$ atoms/cm$^2$/sec
- Chalcogen flux = $1-2 \times 10^{16}$ molecules/cm$^2$/sec
- Substrate temperature = 295-440K

It is also found that films prepared with substrate temperatures from 295K to 315K have a golden yellow colour and films prepared from 325K to 440K have a deep green colour. The deposition rate of the films were 0.2 - 0.5 nm/sec.

Composition of the films were determined by taking the X-ray diffraction pattern of the films prepared at various temperatures. For these measurements films were not detached from the substrate. A Philips PW 1140/90 X-ray unit fitted with PW 1050/70 goniometer was
used for X-ray diffraction studies. Filtered Cu Kα radiation (\( \lambda = 1.5405\text{Å} \)) was employed. Thickness of the films used for X-ray diffraction studies were between 300 and 500 nm.

Optical measurements were made using a Carry 17D double beam spectrophotometer which can cover the wavelength region from 2500 nm to 200 nm. Refractive index and absorption coefficient of the films were determined as described in Chapter III.

Electrical conductivity and Hall effect measurements were made after depositing gold electrodes to the film. It was found that copper and aluminium electrodes do not give an ohmic contact to these films; only gold electrodes give an ohmic contact. Electrical conductivity and Hall effect of the films were measured in the set-up described in Chapter III.

6.2 STRUCTURAL STUDIES

The X-ray diffraction pattern of the film-substrate system prepared at various substrate temperatures are shown in figure 2. It can be seen that films prepared at the higher substrate temperatures are crystalline in nature. From the colour of the films crystalline and amorphous films can be easily distinguished. Crystalline films have a deep green colour and amorphous ones a golden yellow colour. From the colour of the films it was inferred that films prepared above a substrate temperature of 320K are crystalline in nature.
Figure 2: X-ray diffractograms of films prepared at various substrate temperature $T_s$: (a) 400K, (b) 345K, (c) 305K. The amorphous nature of the film prepared at 305K is evident. The background is due to the glass substrate.
<table>
<thead>
<tr>
<th>hkl</th>
<th>JCPDS d A.U.</th>
<th>FILM-A $I/I_1$</th>
<th>FILM-B $I/I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>002</td>
<td>8.190</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>3.287</td>
<td>11</td>
<td>3.269</td>
</tr>
<tr>
<td>101</td>
<td>3.223</td>
<td>16</td>
<td>3.207</td>
</tr>
<tr>
<td>102</td>
<td>3.050</td>
<td>47</td>
<td>3.034</td>
</tr>
<tr>
<td>103</td>
<td>2.815</td>
<td>100</td>
<td>2.803</td>
</tr>
<tr>
<td>006</td>
<td>2.726</td>
<td></td>
<td>2.795</td>
</tr>
<tr>
<td>105</td>
<td>2.319</td>
<td></td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>2.099</td>
<td></td>
<td></td>
</tr>
<tr>
<td>008</td>
<td>2.045</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>1.898</td>
<td>53</td>
<td>1.891</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.888</td>
</tr>
</tbody>
</table>
and films prepared below 315K are amorphous in nature. The d-spacings calculated for films with well-defined diffraction peaks (a and b) agrees with that given for covellite (CuS) in JCPDS cards [16]. The d-spacings and relative intensities given in JCPDS card for covellite along with our results are given in Table I. This table is obtained after normalizing the intensities obtained from the films to the 100 line of the JCPDS card and also taking into consideration the fact that in the diffractometer with Bragg-Brentano geometry, at any incident angle θ, the films gives an effective thickness of t/sin θ and consequently the reflected intensity will be angle dependent. Films prepared at room temperature (305K) does not show any sharp peaks (film c). It can be concluded that these films are amorphous in nature. The diffused background exhibited by all films is due to the glass substrate.

Referring to Table I it can be seen that reflections from planes having Miller indices 001 are missing in crystalline films. From this it can be concluded that the grains are oriented with 001 planes perpendicular to the substrate surface. Scanning electron microscopic observations also confirmed this. An SEM micrograph of a film prepared at 440K is shown in figure 3. This is rather surprising, because when materials with hexagonal structure grow with
Figure 3. SEM micrograph of a c-CuS film
preferred orientation on amorphous surfaces, they usually have a columnar growth with 001 planes along the substrate surface; a well known example being the columnar growth of CdS.

From the X-ray diffraction pattern, no other phases in the Cu-S system is detected. Taking into consideration the deposition condition (chalcogen flux to metal flux ratio greater than hundred) it can be seen that if there are enough sulphur molecules present for reaction, only covellite phase is formed. There has not yet been any report of covellite formation in evaporation of bulk Cu₂S. The formation of covellite phase in this case is highly probable because in the initial stages of evaporation when the bulk Cu₂S melts, a large proportion of Cu₂S molecules may dissociate causing preferential evaporation of sulphur. This excess partial pressure at the initial stages of evaporation will assist in the formation of covellite.

6.3 ELECTRICAL PROPERTIES OF CRYSTALLINE CuS films.

Hot probe measurement showed that the film is p-type. Electrical conductivity of the films were measured after depositing gold electrodes on either end of the film. Electrical measurements showed that films were highly conducting with a resistivity of 10⁻⁴ ohm cm. The variation of resistivity of the film with temperature was positive and very small down to liquid nitrogen
temperature. No significant information could be obtained from these measurements. The positive temperature coefficient of resistance and the very low film resistivity shows that the films are degenerate. Electrical resistivity measurements reported by Okamoto et al /8/ on pressed samples of CuS are very similar to this.

Hall effect measurements showed that the carrier concentration in these films was $10^{22}\text{cm}^{-3}$ and the mobility $2.5\text{cm}^2/\text{volt sec}$. Because of the high carrier concentration and the low mobility of the carriers, the Hall voltage developed was only a few microvolts, typically 6 to 8 microvolts for a current of 10mA and a magnetic field of 7K gauss. The temperature variation of this small Hall voltage, if any, could not be determined because of the lack of resolution of the measuring instrument used (maximum resolution of the digital meter was only one microvolt).

6.4 OPTICAL PROPERTIES OF CRYSTALLINE CU$_2$S FILMS.

The transmission spectra of crystalline CuS films are shown in figure 4. It can be seen that the spectra is characteristic of a semiconductor. Absorption at wavelengths less than 500 nm is due to the onset of band to band transitions in the semiconductor. Increasing absorption beyond 550 nm to the long wavelength side is due to free carrier absorption or due to transitions taking place from a filled acceptor level situated
Figure 1: Transmission spectra of cyto-
tactic CuS film. Film thickness is indicated.
Figure 1: $(a^2 v)^{1/3}$ versus $h\nu$. 
just above the valence band to the conduction band.
The large absorption ($A \sim 10^5 \text{ cm}^{-1}$) shown by the films before the onset of fundamental absorption is due to the degenerate nature of the films.

Absorption data in the fundamental absorption region was analyzed in terms of the theory of Bardeen et al /17/. This theory gives for a direct transition

$$A = \frac{A(h\nu - E_g)^r}{h\nu}$$

(6.4.1)

$r = 1/2$ for an allowed transition

$r = 3/2$ for a forbidden transition

The plot of $(A h\nu)^{2/3}$ versus $h\nu$ is shown in figure 5. This gives a band gap of $2.37 \pm 0.01 \text{ eV}$ and the transition leading to this is a direct forbidden one. This value of band gap is only a representative one, since in degenerate materials, the value of band gap obtained can vary somewhat depending on the carrier concentration. The exact band gap of the material can only be obtained when high quality defect free films of CuS are available. This also holds true for the determination whether CuS is a direct or indirect band gap semiconductor. In the films used in the present study any indirect transition occurring before the direct transition will be masked by the high absorption coefficient of the film before the onset of band to band transitions.
Mooser and Pearson /18/ have introduced the concept of semiconducting bond, which has proved valuable in analyzing and predicting semiconducting properties of compounds and in particular in differentiating between metallic alloys and semiconductors. According to the concept of the semiconducting bond, the solid is a semiconductor if all the possible valence structures lead to filled sub-shells, whereas the metallic state is characterized by partially filled valence orbitals of the component atoms. This valence bond rule was successfully applied to many intermetallic compounds which are formed by s or p electrons of each atom. But this rule was not applicable to compounds which contain transition elements or rare earths. Hullinger and Mooser /19/ extended the bond treatments of intermetallic compounds to the criterion where d-orbitals as well as s- or p-orbitals concern to the valencies of the compounds. They established that semiconductivity occurs if cation d-electrons are assumed to be localized, while if sub-shells are less than half filled, metallic conduction results.

Mooser and Pearson's expression for the condition of occurrence of semiconductivity in solids is

$$\frac{n_e}{n_a} + \frac{a}{b} - b = 8$$  \hspace{1cm} (6.4.2)

where $n_e$ is the number of valence electrons (not counting any unshared electrons on the cations) per unit formula, $n_a$ is the number of anions per unit formula,
\( b_a \) is the average number of anion-anion bonds and \( b_e \) is the average number of cation-cation bonds. If the above condition is not satisfied, the solid is a metallic conductor.

Application of the above rule to CuS predict that it is a semiconductor. From the results of their electrical measurements, Okomoto et al concluded that CuS is metallic in nature and as such Mooser and Pearsons rule does not hold in this case. But results reported in this chapter confirms that CuS is a semiconductor and that Mooser and Pearsons rule hold in this case also. Magnetic susceptibility data given by Okomoto et al indicates the presence of partially localized 3d electrons in CuS which is a necessary condition for the occurrence of semiconductivity in compounds where d-orbitals as well as s- or p- orbitals concern to the valencies of the compound according to Hullinger and Mooser. From what is given above it can be safely concluded that CuS is a semiconductor with a band gap of 2.37 eV.

6.5 Amorphous Films of CuS

It was found that when copper is reactively evaporated in an atmosphere of sulphur, and when the substrate temperature is lower than 315K, the films are amorphous in nature (see figure 2). These films have a golden yellow colour and highly transparent before the onset of fundamental absorption. Since crystalline CuS films have a deep green
colour, amorphous CuS films with their golden yellow colour can be easily distinguished. Films prepared with substrate temperature between 315K and 320K has a colour in between golden yellow and green and with a slight increase in temperature the films turned to the crystalline deep green colour. Obviously films prepared at these temperatures contain amorphous and crystalline regions.

6.6 ELECTRICAL PROPERTIES OF AMORPHOUS CuS FILMS

Hot probe measurements show that amorphous CuS films exhibit n-type conductivity. It is interesting to note that all the other compounds in the copper-sulphur system are p-type semiconductors, including crystalline CuS. Electrical measurements show that films are fairly resistive (room temperature resistivity ~ 10^5 ohm cm). The variation of resistance of the films with temperature is shown in figure 6. The activation energy for conduction calculated on the basis of the equation

\[ J = J_0 \exp\left(\frac{E_a}{k_B T}\right) \]

is 0.26 eV. This indicates a thermally activated process and is exhibited by many amorphous semiconductors in this temperature range.

When these films are heated to above 220K, these films crystallize and their resistivity falls by about nine orders of magnitude (from 10^5 ohm cm to 10^{-4} ohm cm). The variation in resistivity of these crystallized films
Figure 6: Current versus temperature (V = 1V) $E_a = 0.26$ eV.
with temperature, is very low as in the case of crystalline CuS films. Both exhibit positive temperature coefficient of resistance. The overall behaviour exhibited by CuS films are similar to that for tin disulphide films as discussed in Chapter IV. The only difference being, amorphous films of tin disulphide are more stable, as they crystallize only when heated to 410K, whereas amorphous films of CuS crystallize when heated to 320K.

6.7 OPTICAL PROPERTIES OF AMORPHOUS CuS FILMS

Figure 7 shows the transmission spectra of an amorphous CuS film of thickness 390 nm. It can be seen that films are fairly transparent before the onset of band to band transitions except for a slight decrease in transmission around 1200 nm. Electrical data given above (negative temperature coefficient of resistance) and the transmission spectra conclusively establish that amorphous CuS is a semiconductor.

The variation of refractive index of the films with wavelength is shown in figure 8. The refractive index of crystalline CuS films and also of amorphous films recrystallized could not be determined as they exhibited no interference fringes.

In many amorphous materials in the photon energy region where $\omega \approx 10^5$ cm$^{-1}$, the absorption coefficient is found to obey a law of the form /20/

$$\alpha \propto (h\nu - E_g)^F$$  

(6.7.2)
Figure 7: Transmission spectra of amorphous CuS film. Thickness 390 nm.
Figure 8: Refractive index as a function of wavelength for amorphous CuS film.
Figure 9: $\xi$ versus $h\nu$ in the fundamental absorption region. The intercept gives an optical band gap of $1.60 \pm 0.02$ eV.
values of $r$ between 1 and 3 have been observed. The constant $E_g$ can be used to define an optical gap although it may represent an extrapolated rather than a real zero in the density of states.

The plot of $\alpha$ versus $h\nu$ is shown in figure 9. The value of $E_g$ obtained 1.60 eV is in agreement with the transmission data. The plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, which is the more commonly observed relationship ($r=2$), gives an energy gap of 1 eV which obviously is not in agreement with the transmission data. The unity value obtained for $r$ indicates a sharp rise in the density of states at the band edges. This type of behaviour ($\alpha \propto (h\nu - E_g)$) was earlier reported in the case of amorphous selenium /21/.

In amorphous materials when a law of the form given by equation (6.7.2) holds, transitions are believed to take place between the extended states of the valence band and the extended states of the conduction band and hence the band gap in the crystalline and amorphous phases must be approximately equal /22/. But it can be seen that in the case of covellite, the value of the band gap for the crystalline material is 0.77 eV higher than that for amorphous material. This high value may be due to the top of the valence band being empty of electrons and transitions taking place from deeper lying levels in the valence band to the conduction band. This emptying
of the valence band is highly probable because of the high p-type conductivity ($\rho \sim 10^{-4}$ ohm cm) exhibited by the crystalline samples.

CONCLUSIONS

When copper is evaporated in an atmosphere of sulphur vapour, films of covellite (CuS) are formed. Films prepared below a substrate temperature of 315K are amorphous in nature, whereas films prepared above 320K are crystalline in nature. Films prepared in the transition region (i.e. substrate temperature between 315 and 320K) exhibit both crystalline and amorphous areas. Crystalline films have their grains oriented with 001 planes perpendicular to the substrate surface. Crystalline films show p-type conductivity with a room temperature resistivity of $\sim 10^{-4}$ ohm cm and positive temperature coefficient of resistance down to liquid nitrogen temperature. Amorphous films of CuS exhibit n-type conductivity with a room temperature resistivity of $\sim 10^5$ ohm cm. Activation energy for electronic conduction in amorphous CuS films is 0.29 ± 0.05 eV. The amorphous films crystallize when heated to 320K and their resistivity changes by nine orders of magnitude (i.e. from $\sim 10^5$ ohm cm to $\sim 10^{-4}$ ohm cm). Crystalline films have a deep green colour and amorphous films, a golden yellow colour. Crystalline films exhibit large
absorption \( (\alpha \sim 10^5 \text{ cm}^{-1}) \) before the onset of band to band transitions. This together with the positive temperature coefficient of resistance indicate that the crystalline films are degenerate. The forbidden band gap obtained for crystalline films from optical studies is 2.37 eV. This establishes that CuS is a semiconductor contrary to what was believed earlier. Amorphous films of CuS are fairly transparent before the onset of band to band transitions and are of good optical quality. The band gap obtained for amorphous CuS is 1.60 eV. The absorption coefficient in the fundamental absorption region in these films obey a law of the form \( \alpha \sim (h\nu - E_g) \) which indicates a sharp rise in density of states at the band edges.
References:


