6.1 Introduction

In recent years, considerable attention has been devoted to the development of low cost solar energy converting devices. In this regard, polycrystalline photoelectrodes of different semiconducting materials have been investigated and tested. Particularly metal oxides were studied for photoelectrochemical solar cells. Different experimental techniques have been used to prepare the polycrystalline electrodes. Apart from the applications in PEC solar cells these techniques are important in solid state devices and integrated circuit applications.

However, the quality and the cost of production is important in practical applications. The studies on the transport properties have attracted much attention due to their higher potential in photoelectrochemical solar cell applications. The electrical properties of Cu$_2$O films are found to depend on the various deposition parameters and annealing conditions of the films. Hence, a detailed study about the electrical conduction of Cu$_2$O film is important. The available literature regarding the studies of electrical properties of Cu$_2$O thin films are only limited. The present study deals mainly with the electrical conduction through these films and their related parameters.
6.2 Review on electrical properties of Cu$_2$O thin films

Resistivity of Cu$_2$O thin films were measured by Bardeen et al /41/ and he predict that the decrease in resistivity of the film can be achieved by the production of more copper ion vacancies. Fitzgibbons et al /58/ reported the importance of various deposition techniques in the construction of solid state devices and in the applications of integrated circuits. Assimos et al /61/ carried out annealing studies and reported that annealing at 500°C is an optimum value for producing higher conductivity in large crystals. Mitra et al /64/ considered the errors in the series expansion of a logarithmic function of T and showed that a plot between ln T vs 1/d$^2$ should be non-linear.

Deposition at low temperature had been carried out and the results on electrical properties of p-type Cu$_2$O thin films were reported by Rai et al /68/. Reports on capacitance – voltage characteristics of Cu$_2$O/Cu diodes were given by Datta et al /73/. Resistivity value of Cu$_2$O thin films deposited by chemical deposition technique was reported by Ristov et al /87/. Rai /65/ gave reports on electrical properties of Cu$_2$O thin films which were fabricated at low temperatures. Electrical characteristics of Cu–Cu$_2$O diodes fabricated by anodic oxidation technique have been reported by Ikata et al /93/. Thermostimulated impurity conduction in characterization of electrodeposited Cu$_2$O thin films was reported by Rakshani et al /102/. Reports on electrical properties of Cu$_2$O thin films deposited by galvanostatic deposition technique have been given by Mukhopadhyay et al /103/. Brown et al /106/ reported that the Cu$_2$O / Cu contact
behaves as tunnel diode and such diode depends on quantum mechanical tunneling. Electrical properties of Cu$_2$O thin film had been studied and the results on electrical properties were reported by Golden et al. /108/.

Snoke et al. /110/ reported that the Bose–Einstein condensation of excitons occur in Cu$_2$O at relatively high temperature. Photovoltaic properties and barrier heights of single–crystal polycrystalline Cu$_2$O–Cu contact have been reported by Assimos et al. /75/. Variation of the composition of semiconductor leading to changes in electrical conductivity or in electrochemical behaviour and it can be accomplished more easily during the preparation of polycrystalline films through various deposition techniques. Such ideas have been suggested by Siu et al. /192/ and Mollers et al. /193/. Electrical properties of thermally grown p-Cu$_2$O polycrystalline film electrodes have been reported by Hardee et al. /194/ and Tennakone et al. /195/. Schewehun et al. /196/ assured tunneling probability as unity and gave reports on electrical properties of Cu-Cu$_2$O diode. Kaufman et al. /197/ reported that annealing at 500°C can produce higher conductivity. Fortin et al. /198, 199/ and Berezin et al. /200/ conducted studies about electrical properties of Cu$_2$O thin films by constructing Cu-Cu$_2$O contact. Sze et al. /201/ analysed and reported about current-voltage characteristics of Cu$_2$O diodes. Hanselaer et al. /202/ and Hattori et al. /203/ gave reports on MIS Cu$_2$O diode. Grondahl /204/ gave reports on Cu-Cu$_2$O rectifier.
6.3 Electrical conductivity

The electrical conductivity of intrinsic semiconductors at low temperatures is due to intrinsic charge carriers (i.e., electrons and holes). Such conductivity is sometimes termed as intrinsic conductivity.

Since there are two types of carriers in the intrinsic semiconductor, electrons and holes, its specific conductance is the sum of the conductivity \( \sigma_e = |e| n \mu_e \) due to free electrons, with the concentration \( n \) and mobility \( \mu_e \) and of conductivity \( \sigma_h = |e| p \mu_h \) due to the presence of holes, with the concentration \( p \) and mobility \( \mu_h \). The mobility is the magnitude of the drift velocity per unit electrical field,

\[
\mu = |v| E \quad \Rightarrow \quad (6.1)
\]

The mobility is defined to be positive for both electrons and holes, although their drift velocities are opposite. In an ideal intrinsic semiconductor the mobility is determined by collisions between electrons and photons, the electrical conductivity of an intrinsic semiconductor is

\[
\sigma = |e| (n \mu_e + p \mu_h) \quad \Rightarrow \quad (6.2)
\]

and since for an intrinsic semiconductor \( n = p \), we have \( \sigma_i = |e| n (\mu_e + \mu_h) \)

where \( \sigma_i \) denotes the intrinsic conductivity. Substituting the value of \( n \) from

\[
n_e = n_h = (2\pi K_B T / \hbar^2)^{3/2} (m_e^* m_h^*)^{1/2} e^{-E_g / 2K_B T} \quad \Rightarrow \quad (6.3)
\]

\[
\sigma_i = 2|e| (2\pi K_B T / \hbar^2)^{3/2} (m_e^* m_h^*)^{1/2} e^{-E_g / 2K_B T} (\mu_e + \mu_h) \quad \Rightarrow \quad (6.4)
\]
The exponential term $\exp[-E_g/2K_BT]$ dominates all other temperature dependence, as is seen by writing the above equation as

$$\log \sigma_i = -E_g/2K_BT + \log [2|e|(2\pi K_B T/h^2)^{3/2} (m_e^* m_h^*)^{3/4} (\mu_e + \mu_h)] \rightarrow (6.5)$$

(or)

$$\log \rho = -\log \sigma_i = E_g/2K_BT - \log [2|e|(2\pi K_B T/h^2)^{3/2} (m_e^* m_h^*)^{3/4} (\mu_e + \mu_h)] \rightarrow (6.6)$$

where $\rho$ is the resistivity. If we plot $1/T$ along the X-axis and $\log \rho$ along the Y-axis, we will obtain a straight line. The slope determines $E_g$.

### 6.4 Type of conductivity

The type of conductivity in electrodeposited Cu$_2$O films was determined by a modified hot-probe technique. This is a simple method which indicates the direction of electron flow and hence makes us possible to determine the nature of semiconductor. The arrangement is as shown in figure 3.35.

The semiconductor is placed on a plate and metal heater is connected to the conducting substrate base through a multimeter. While the hot probe is momentarily touched over the semiconductor, current flows from cold junction to the hot junction for n-type and the reverse for p-type. The electrodeposited Cu$_2$O thin films were found to have p-type conductivity and it may be due to higher mobility of Cu ion vacancies.
6.5 Electrical characteristics of SnO$_2$--Cu$_2$O diode

The current-voltage characteristics of the as-deposited Cu$_2$O/SnO$_2$ diodes were studied and the resultant plot of In J against V is shown in figure 6.1. The value of the Richardson constant at room temperature was calculated using the equation

$$A^* = 1.2 \frac{m_h^*}{m_0} \text{A cm}^{-2} \text{K}^{-2}$$

where $m_0$ is the electronic mass and $m_h^*$ is the valence band hole effective mass. The value of $m_h^*$ was taken as $0.84m_0$ using the earlier reports /46/. The value of Richardson constant at room temperature was calculated to be $100 \text{ A cm}^{-2} \text{K}^{-2}$ for cuprous oxide. Using the Richardson constant, the values of barrier height ($\Phi_B$) and ideality factor ($n$) determined from the forward characteristics were found to be 0.75 eV and 1.50 respectively.

The forward and reverse characteristics are found to be similar. However, the reverse currents are slightly less than the forward currents at certain voltages, which indicates little rectification during reverse bias. The capacitance-voltage characteristics of the diodes are given in figure 6.2. From these the intercept on the voltage axis is found to be 1.75 V.

The device characteristics such as low forward current and the large difference of barrier potential values determined from the voltage-current characteristics and the voltage intercept on the capacitance-voltage characteristics reveal that the prepared diodes are metal-insulator-semiconductor diodes. Similarly very little rectification produced by the prepared Cu$_2$O-SnO$_2$
Fig 6.1  Current – Voltage characteristic of a Cu$_2$O / SnO$_2$ diode
(Current density : 1.4 mA cm$^{-2}$, Dep. time : 60 min.,
Dep. temp. : 70°C, pH : 9.0 ± 0.1)
Potential, V vs SCE

Fig 6.2 Capacitance – Voltage characteristics of Cu$_2$O/SnO$_2$ diode. (Current density : 1.4 mA cm$^2$, Dep. time : 60 min., Dep. temp. : 70°C, Solution pH : 9.0 ± 0.1)
diodes indicate the tunnel assisted transport process that only have significant minority carrier contribution, whereas space-charge-limited transport process caused the device to exhibit marked rectification. Thus the preparation of Cu$_2$O-SnO$_2$ diode results in the fabrication of MIS diode.

6.6 Electrical properties of galvanostatically deposited Cu$_2$O thin films

6.6.1 Preheating resistivity

Crack and pin-hole free Cu$_2$O films deposited at a bath temperature of 70°C at a current density of 1.4 mA cm$^{-2}$ using solution with pH 9.0 ± 0.1 for a deposition time of 60 min. were taken for electrical studies. The room-temperature resistivity of Cu$_2$O films deposited on SnO$_2$ substrates was measured using a two-probe technique. The resistivities measured were in the range of 10$^6$ ohm.cm, which is within the range of resistivity value reported for Cu$_2$O films prepared by thermal oxidation and chemical deposition techniques /103/. The higher resistivity of the as-deposited film is due to lower concentration of Cu ion vacancies.

6.6.2 Effect of temperature

The resistivity of the film was measured as a function of temperature in the range between 27°C and 330°C. The thin film showed a strong dependence of resistivity on temperature as shown in figure 6.3. The plot of resistivity versus reciprocal of absolute temperature shows linearity between 130°C to 330°C. From the slope of the line and using the resistivity relation $\rho = \rho_0 \exp (E_g/KT)$,
Fig 6.3  Variation of resistivity with reciprocal absolute temperature of as-deposited galvanostatic Cu₂O film  
(Current density : 1.4 mA cm⁻², Dep. time : 60 min., Dep. temp. : 70°C, Solution pH : 9.0 ± 0.1)
thermal activation energy is estimated to be 0.80 eV, which is higher than the value of 0.3 eV reported by Kuzel and Weichman /205/. The activation energy measured in the present work appears to be due to intrinsic conduction of holes because the corresponding band gap \( E_g = 2E_B \) of 1.60 eV is in reasonable agreement with the reported value of 1.90 eV.

### 6.6.3 Effect of film thickness

Seto formulated a model to interpret electrical conduction in polycrystalline thin films exhibiting grain boundary limited conduction. According to Seto's theory, the electrical conduction of semiconductors at higher temperature (>300K) is given by,

\[
\sigma = \frac{e^2 n}{(2 - mK)^{1/2}} \exp \left( \frac{E_B}{K T} \right) \to (6.8)
\]

Where 'l' is the grain size, 'n' is the average carrier concentration, 'm' is the effective mass of the carriers at the fermi surface and 'E_B' is the activation energy for grain boundary limited conduction.

According to Seto's model, the film conductivity \( \sigma \) is directly proportional to the grain size 'l' of the film. The above method assumes a grain boundary limited conduction in which electrical conduction is brought about by thermionic emission of charge carriers across the grain boundaries. Hence an increase in grain size is expected to reduce the grain boundary width. It has been reported earlier that grain size depends on film thickness. Hence an increase in film thickness is expected to enhance the conductivity of films.
In the present work, the influence of film thickness on film resistance is studied. The dependence of resistivity on temperature for films with various thickness is shown in figure 6.4. The figure 6.4 reveals a steady decrease in film resistance with increase in film thickness. Also it reveals a decrease in film resistance with increase in temperature. The decrease in film resistance with increase in film thickness for Cu$_2$O film is attributed to the improvement in the grain size of the films with increase in film thickness. The improvement in crystallinity observed in films with increase in film thickness result in the reduction of grain boundary width. The effect of improved crystallinity on film resistivity is shown as a reduction in the resistivity of the films with increase in film thickness. Since the predominant scattering mechanism at higher temperatures (300K to 600K) is mainly grain boundary scattering, the grain boundary width may considerably affect the electron transport in these films. Hence the decrease in film resistance with increase in temperature and thickness observed at this present work is due to the reduction of grain boundary width with increased temperature and thickness. Thus the results observed in our present work agree with the Seto's model.

6.6.4 Effect of Cu concentration

Conductivity measurements show p-type conductivity for Cu$_2$O film which reveals that the conduction in Cu$_2$O film is due to the production of Cu ion vacancies during the film formation. Resistivity measurements at room temperature shows higher resistivity of the order of $5 \times 10^6$ ohm.cm. The higher
Fig 6.4 Variation of resistivity with reciprocal absolute temperature of galvanostatically deposited Cu\textsubscript{2}O films with various thickness.

(a) 1.0 \mu m  (b) 2.0 \mu m  (c) 3.0 \mu m

(Current density : 1.4 mA cm\textsuperscript{-2}, Dep. temp. : 70°C, Solution pH : 9.0 ± 0.1)
resistivity of the film indicates the lower concentration of Cu ion vacancies within the film. Hence Cu concentration reduction in the electrolyte can enhance the conductivity of the films. Cu concentration reduction is achieved by the reduction of concentration of CuSO4 in the solution. The decrease in film resistivity with decrease in CuSO4 concentration is shown in figure 6.5 and the grain size variation is shown in Table 6.1. The increase in rate of deposition increases the grain size of the film and higher rate of deposition causes decrease in grain size at 0.6 M. The effect of temperature on the electrical resistivity of Cu2O films deposited at various CuSO4 compositions are studied and the resultant pattern observed is shown in figure 6.6. A decrease in resistivity with increase in temperature is observed from figure 6.6, which is due to the production and increased mobility of Cu ion vacancies within the film. The creation of Cu ion vacancies with the increase in temperature and decrease in CuSO4 concentration results in the enhancement of conductivity of Cu2O films.

6.6.5 Effect of annealing

As the electrical properties of semiconducting compounds depend upon the crystalline size, further improvement in conductivity can be achieved by the improvement of crystallinity of the films. Crystallinity improvement can be achieved by means of annealing treatment. Annealing at higher temperatures (>350°C) shows CuO peaks in addition to Cu2O peaks. Also annealing above 550°C causes peeling off the film from the substrate. Hence annealing at temperatures below 350°C was carried out for a duration of 30 minutes, which
Fig 6.5 Variation of resistivity with CuSO₄ concentration of the electrolyte during galvanostatic deposition of Cu₂O films
(a) 0.6 M  (b) 0.45 M  (c) 0.3 M  (d) 0.2 M  (e) 0.1 M
(Current density : 1.4 mA cm⁻²,  Dep. temp. : 70°C,
  pH : 9.0 ± 0.1,  Dep. time : 60 min.,)
Table 6.1

Effect of CuSO₄ concentration on resistivity and grain size in galvanostatic deposition of Cu₂O thin films

<table>
<thead>
<tr>
<th>S.No</th>
<th>CuSO₄ concentration (M)</th>
<th>Grain size (µm)</th>
<th>Resistivity (ohm.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0045</td>
<td>0.02</td>
<td>45</td>
</tr>
<tr>
<td>2.</td>
<td>0.10</td>
<td>0.19</td>
<td>9 x 10⁴</td>
</tr>
<tr>
<td>3.</td>
<td>0.20</td>
<td>0.25</td>
<td>4 x 10⁵</td>
</tr>
<tr>
<td>4.</td>
<td>0.30</td>
<td>0.30</td>
<td>1.1 x 10⁶</td>
</tr>
<tr>
<td>5.</td>
<td>0.45</td>
<td>0.40</td>
<td>5 x 10⁶</td>
</tr>
<tr>
<td>6.</td>
<td>0.60</td>
<td>0.27</td>
<td>1 x 10⁷</td>
</tr>
</tbody>
</table>
Fig 6.6 Variation of resistivity with reciprocal absolute temperature of Cu$_2$O films deposited under various CuSO$_4$ concentrations

(a) 0.6 M  (b) 0.45 M  (c) 0.3 M  (d) 0.2 M  (e) 0.1M

(Current density : 1.4 mA cm$^2$, Dep.temp. : 70°C,

pH : 9.0 ± 0.1, Dep. time : 60 min.,)
causes an increase in crystalline size as given in Table 6.2. This improvement in crystallinity results in the reduction of grain boundary width. It causes more thermionic emission of charge carriers across the grain boundary width and hence decreases the film resistivity from the order of $10^8 - 10^3$ ohm.cm as given in Table 6.2. Thus annealing enhances the film conductivity. The conductivity of film annealed at 350°C shows an increase of three orders of magnitude of unannealed films. The increase in conductivity is due to the emission of excess holes within the valence band.

6.6.6 Effect of temperature on annealed films

The temperature dependence on resistivity of annealed films are studied in detail and the results observed are shown in figure 6.7. From the slope of the linear portion of the curves the activation energies and hence the band widths for films annealed at various temperatures are estimated and shown in Table 6.2. The slight decrease in band width and improvement in conductivity is also related to the production of excess holes within the lattice at higher annealing temperatures. The number of Cu ion vacancies emitted into the valence band begins to increase at a faster rate from the hole emission peak point ($T_p$).

The position of hole emission peak observed at 130°C for as-deposited film is due to the emission of trapped holes within the valence band. The position of the hole emission peak was found to be dependent on annealing temperature. In the presence of annealing temperature, the ionization energy of the films can be reduced. This inturn enhances the rate of emission of trapped charges and
Fig 6.7  Temperature dependence of resistivity of annealed Cu2O films
(Dep. current density: 1.4 mA cm$^{-2}$, Solution pH: 9.0 ± 0.1, Dep. time: 60 min., Dep. temp.: 70°C. Annealing time: 30 min., Annealing temp: (a) 150°C (b) 250°C (c) 350°C
Table 6.2

Variation of electrical parameters with annealing temperature for galvanostatically deposited Cu_2O films
(Deposition current density : 1.4 mA cm\(^{-2}\), Dep. time : 60 min., Solution pH : 9.0 ± 0.1, Bath temperature : 70°C)

<table>
<thead>
<tr>
<th>S.No</th>
<th>Annealing temperature (°C)</th>
<th>Crystal size (μm)</th>
<th>Resistivity 'ρ' (ohm.cm)</th>
<th>Activation energy (eV)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As-deposited</td>
<td>0.20</td>
<td>5x10^6</td>
<td>0.80</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>0.31</td>
<td>9x10^5</td>
<td>0.78</td>
<td>1.56</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>0.40</td>
<td>3x10^4</td>
<td>0.75</td>
<td>1.50</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>0.53</td>
<td>8x10^3</td>
<td>0.72</td>
<td>1.44</td>
</tr>
</tbody>
</table>
therefore the peak position shifts towards a lower temperature as shown in figure 6.7. The peak position decreases with increasing annealing temperature.

6.6.7 Effect of doping

The annealed Cu$_2$O semiconductors have their resistivities in the order of $10^3$ ohm.cm. Such intrinsic Cu$_2$O semiconductors are of little importance in various fields due to its higher resistivity. These limitations are overcome by adding a small and measured amount of chemical impurity to the intrinsic semiconductor. These added impurity is very small of the order of 1 atom per million atoms of the pure semiconductor. When impurity atoms are incorporated in a pure semiconductor, the resistivity of the film get reduced due to the production of more charge carriers. The electrical properties are altered and most of the charge carriers originate from impurity atoms.

Since Cu$_2$O is p-type semiconductor, the addition of impurities must enhance the concentration of Cu ion vacancies in the film. Cu ion vacancies can be enhanced by means of doping. The useful doping agent may be S, P, K, Mg, Cl, Al, Ar, Ca, Na. In the present work materials such as KCl, MgCl$_2$, Na$_2$S are used as doping agents. Addition of such doping agents with the electrolyte (0.1 M CuSO$_4$ + 3.25 M lactic acid + NaOH) reduce the resistivity of the film to the order of $10^2$ ohm.cm. (figure 6.8). The ratio between the concentration of doping agent and CuSO$_4$ are maintained interms of 2:100, 4:100, 6:100, 8:100 and 10:100. Increasing the concentration of doping agent more than 10% increase the resistivity of the film due to the conversion of Cu$_2$O into CuO.
Fig 6.8  Variation of resistivity with concentration of various doping materials (a) Na$_2$S  (b) KCl  (c) MgCl$_2$

(Current density : 1.4 mA cm$^{-2}$, Solution pH : 9.0 ± 0.1,  
Dep. time : 60 min., Dep. temp. : 70°C)
Hence the optimum doping level is found to be in the ratio of 10:100 (i.e) 0.01 M : 0.1 M.

6.7 Potentiostatically deposited Cu₂O thin films

6.7.1 Preheating resistivity

Crack and pinhole free Cu₂O films deposited at a temperature of 70°C using solution with pH = 9.0 ± 0.1 under the deposition potential of - 0.55V vs SCE for a deposition time of 30 min were taken for electrical studies. The room temperature resistivity of Cu₂O films deposited on SnO₂ substrates was measured using two probe technique. The resistivities measured were in the range of 2 x 10⁷ ohm.cm, which agrees with the previous report /102/. Such higher resistivity of the film is due to the lower concentration of Cu ion vacancies within the lattice.

6.7.2 Effect of temperature

The resistivity of as-deposited film was measured as function of temperature in the range between 27°C and 330°C and the dependence of resistivity on temperature was studied. The film showed a strong dependence of resistivity on temperature as shown in figure 6.9. The plot of resistivity versus the reciprocal of absolute temperature shows linearity between 150°C to 330°C. The slope of the linear portion of the curve gives an activation energy of 0.85 eV which is much better than the previous results /102/. The corresponding band gap of 1.70 eV is in reasonable agreement with the reported value of 1.95 eV.
Fig 6.9  Resistivity dependence on temperature for potentiostatically deposited Cu₂O film
(Dep. potential : -0.55 V vs SCE, Dep. time : 30 min., Dep. temp. : 70°C, Solution pH : 9.0 ± 0.1)
6.7.3 Effect of film thickness

According to Seto's model, the film resistivity is inversely proportional to the grain size of the film which in turn depends on film thickness. This method assumes a grain boundary limited conduction in which electrical conduction is brought about by thermionic emission of charge carriers across the grain boundaries. Hence an increase in grain size is expected to reduce the grain boundary width which in turn decreases the film resistance.

In the present work, the influence of film thickness on film resistance of potentiostatically deposited Cu$_2$O films was studied. The resultant plot shown in figure 6.10 reveals decrease in film resistance with increase in film thickness. The dependence of resistivity on temperature for films with various thickness is shown in figure 6.10, which also shows a decrease in film resistivity with increase in temperature. The decrease in film resistivity with increase in film thickness is due to the improvement in the grain size of the films with increase in film thickness. The predominant scattering mechanism at higher temperatures (>300K) is grain boundary scattering which increases with increase in temperature due to reduction in grain boundary width with temperature. Hence a decrease in film resistivity with increase in temperature is observed which agrees with the previous Seto's model.
Fig 6.10 Variation of resistivity with reciprocal absolute temperature for potentiostatically deposited Cu$_2$O films with various thickness (a) 1.0 \( \mu \)m (b) 2.0 \( \mu \)m (c) 3.2 \( \mu \)m
(Dep. pot. : -0.55 V vs SCE, Dep. temp. : 70°C, pH : 9.0 ± 0.1)
6.7.4 Effect of Cu concentration

The higher resistivity observed at room temperature indicates the lower concentration of Cu ion vacancies within the film. Hence Cu concentration reduction by means of reduction of CuSO$_4$ in the electrolyte decreases the film resistivity. The decrease in film resistivity observed with decrease in CuSO$_4$ concentration is shown in figure 6.11 which is due to the enhancement of Cu ion vacancies within the film. The effect of temperature on the electrical resistivity of Cu$_2$O films deposited at various CuSO$_4$ concentrations is shown in figure 6.12. A decrease in resistivity with increase in temperature observed from figure 6.12 is due to the increased mobility of Cu ion vacancies with increase in temperature. This results in the enhancement of conduction of potentiostatically deposited Cu$_2$O films. The increased grain size with increase in CuSO$_4$ concentration shown in Table 6.3 is due to the increase in rate of deposition. The higher rate of deposition causes decrease in grain size at 0.6 M.

6.7.5 Effect of annealing

As the electrical properties of semiconducting compounds depend upon the crystalline size, further improvement in conductivity can be achieved by the improvement of crystallinity of films. The improvement of crystallinity can be achieved by means of annealing treatment. Annealing at higher temperatures (>350 °C) shows CuO peaks in addition to Cu$_2$O peaks. Hence annealing at temperatures below 350°C for 30 minutes duration was carried out. The resultant increase in crystalline size observed was shown in Table 6.4. The improvement
Fig 6.11 Resistivity of Cu$_2$O films deposited under various CuSO$_4$ concentrations (a) 0.6 M (b) 0.45 M (c) 0.3 M (d) 0.2 M (e) 0.1 M
(Dep.pot : - 0.55 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time : 30 min.)
Fig 6.12 Temperature dependence of resistivity of potentiostatically deposited Cu$_2$O films under various CuSO$_4$ concentrations.

(a) 0.6 M  (b) 0.45 M  (c) 0.3 M  (d) 0.2 M  (e) 0.1 M

(Dep.pot : - 0.55 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time : 30 min.)
Table 6.3

Effect of CuSO₄ concentration on resistivity and grain size in potentiostatic deposition of Cu₂O thin films

<table>
<thead>
<tr>
<th>S.No</th>
<th>CuSO₄ concentration (M)</th>
<th>Grain size (µm)</th>
<th>Resistivity (ohm.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0045</td>
<td>0.005</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.021</td>
<td>$2 \times 10^5$</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.034</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>4</td>
<td>0.30</td>
<td>0.042</td>
<td>$5 \times 10^6$</td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>0.055</td>
<td>$2 \times 10^7$</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.030</td>
<td>$6 \times 10^7$</td>
</tr>
</tbody>
</table>
in crystallinity results in the reduction of grain boundary width, which causes thermionic emission of charge carriers across the grain boundary width which in turn decreases the film resistivity from the order of $10^7 - 10^3$ ohm.cm as shown in Table 6.4. The conductivity of film annealed at 350°C shows an increase of four orders of magnitude of unannealed films. This increase in conductivity is due to the emission of excess holes within the valence band.

6.7.6 Effect of temperature on annealed films

The temperature dependence of resistivity of annealed films are studied and the resultant curve is shown in figure 6.13. The slope of the linear portion of the curves yields activation energy and band width of the films annealed at various temperatures (Table 6.4). The decrease in bandwidth and improvement in conductivity is also related to the production of excess holes within the lattice at higher annealing temperatures.

The position of the hole emission peak observed at 150°C for as-deposited film is due to the beginning of emission of trapped holes within the valence band, which depends on annealing temperature. In the presence of annealing temperature, the ionization energy of the films can be reduced. This in turn enhances the rate of emission of trapped charges and therefore the peak position shifts towards a lower temperature as shown in figure 6.13. The decrease in peak position with increase in annealing temperature is noted from the figure 6.13.
Fig 6.13 Temperature dependence of resistivity of Cu$_2$O films annealed at various annealing temperatures
(a) 150$^\circ$C   (b) 250$^\circ$C   (c) 350$^\circ$C
(Dep. potential: -0.55 V vs SCE, Dep. time: 30 min., Dep. temp.: 70$^\circ$C, Annealing time: 30 min..)
Table 6.4

Variation of electrical parameters with annealing temperature for potentiostatically deposited Cu$_2$O films

(Deposition potential : - 0.55V vs SCE, Solution pH : 9.0 ± 0.1,
Bath temperature : 70°C, Dep. time : 30 min.)

<table>
<thead>
<tr>
<th>S.No</th>
<th>Annealing temperature (°C)</th>
<th>Crystal size (μm)</th>
<th>Resistivity 'ρ' (ohm.cm)</th>
<th>Activation energy (eV)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As-deposited</td>
<td>0.055</td>
<td>2x10$^8$</td>
<td>0.85</td>
<td>1.70</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>0.15</td>
<td>6x10$^6$</td>
<td>0.83</td>
<td>1.62</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>0.29</td>
<td>8x10$^5$</td>
<td>0.78</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>0.57</td>
<td>6x10$^3$</td>
<td>0.74</td>
<td>1.48</td>
</tr>
</tbody>
</table>
6.7.7 Effect of doping

Enhancement of Cu ion vacancies within the lattice can be achieved by means of doping. Hence effort is taken to reduce the resistivity of the film through doping. Reduction of CuSO₄ concentration in the electrolyte reduces the resistivity of the film from the order of \(10^7\) to \(10^5\) ohm.cm. Further reduction in resistivity was achieved by doping the electrolyte with either KCl (or) MgCl₂ (or) Na₂S. Doping with these chemicals decreases the resistivity of the film to the order of \(10^2\) ohm.cm. Resistivity variation with doping agent for potentiostatically deposited Cu₂O film is shown in figure 6.14. Addition of MgCl₂ shows higher decrease in resistivity. The optimum doping level is found to be in the ratio of 11:100.

6.8 Electrical properties of pulse plated Cu₂O films

In recent years, considerable attention has been devoted to the development of low cost solar energy converting devices. Hence deposition of Cu₂O thin films by pulse deposition technique has been carried out and the studies on the transport properties have attracted much attention due to their high potential in photoelectrochemical solar cell applications.

6.8.1 Preheating resistivity

Crack and pin-hole free pulse plated Cu₂O films deposited at a temperature of 70°C using solution with pH 9.0 ± 0.1 under the deposition
Fig 6.14  Variation of resistivity with concentration of various doping materials (a) Na₂S  (b) KCl  (c) MgCl₂

(Dep. potential : - 0.55 V vs SCE, Dep. time : 30 min.,
Dep. temp. : 70°C, Solution pH : 9.0 ± 0.1)
potential of 0.4 V vs SCE for the deposition time of 20 min. were used in electrical studies.

Hot-probe technique was used in the determination of type of conductivity of pulse plated films. The conductivity is found to be p-type for Cu$_2$O films. Two-probe technique used in the determination of resistivity of the films shows a resistivity of the order of 6x10$^7$ ohm-cm at room temperature, which is within the range of resistivity value reported for Cu$_2$O films prepared by thermal oxidation and chemical deposition techniques /103/. Such higher resistivity also reveals the presence of lesser number of Cu ion vacancies within the lattice.

6.8.2 Effect of temperature

The effect of temperature on the resistivity of as-deposited pulse plated film was studied for various temperatures in the range between 27 and 330°C. The resultant variation in resistivity with temperature is shown in figure 6.15. The plot shows a strong dependence of resistivity on temperature and shows linearity between 180 to 330°C. The slope of the linear portion of the curve yields an activation energy of 0.88 eV, which agrees with the results predicted by Mukhopadhyay /103/ and shows better results than the value predicted by Kuzel and Weichman /205/. The activation energy measured in the present study appears to be due to intrinsic conduction of holes because the corresponding band gap of 1.76 eV agrees with the previous reported value of 1.99 eV.
Fig 6.15  Temperature dependence of resistivity of Cu₂O films deposited under pulse deposition technique
(Dep.pot. : 0.4 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time : 20 min.)
6.8.3 Effect of film thickness

According to Seto’s model, the film conductivity increases with grain size of the film. It has been reported earlier that grain size depends on film thickness. Hence, an increase in film thickness is expected to enhance the conductivity of the films. In this work, the influence of film thickness on film resistivity was studied and the resultant variation is shown in figure 6.16. The figure shows a decrease in film resistivity with increase in film thickness. Further decrease in resistivity with increase in temperature is observed due to heating. The dependence of resistivity on temperature for films with various thickness is shown in figure 6.16. A decrease in film resistivity with increase in temperature is noted from the figure 6.16.

The decrease in film resistivity with increase in film thickness is attributed to the improvement in grain size of the films with increase in film thickness. The improvement in grain size with film thickness results in the reduction of grain boundary width. The effect of improved crystallinity on film resistivity is shown as a reduction in the resistivity of the films with increase in film thickness.

The predominant scattering mechanism at higher temperature is mainly grain boundary scattering. The decrease in film resistivity with increase in temperature observed in this present work is due to the enhancement of grain boundary scattering due to the reduction of grain boundary width with temperature. The results observed in our present work agreed with the Seto’s model.
Fig 6.16  Resistivity variation with temperature for pulse plated Cu$_2$O films with various thickness.
(a) 1.0 μm  (b) 2.0 μm  (c) 3.0 μm
(Dep.pot. : 0.4 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1)
6.8.4 Effect of Cu concentration

Resistivity measurement at room temperature shows higher resistivity of the order of $10^7$ ohm-cm. The higher resistivity of the film indicates the lower concentration of Cu ion vacancies within the film. Hence Cu concentration reduction in the electrolyte can enhance the conductivity of the films. Cu concentration reduction is achieved by the reduction of CuSO$_4$ concentration (figure 6.17). The effect of temperature on the electrical resistivity of Cu$_2$O films deposited at various CuSO$_4$ composition are studied and the result obtained is shown in figure 6.18. A decrease in resistivity with increase in temperature is observed from figure 6.18, which is due to the production and increased mobility of Cu ion vacancies within the film. The creation of Cu ion vacancies within the lattice due to the decrease in CuSO$_4$ concentration and increase in temperature results in the enhancement of conductivity of Cu$_2$O films. The increase in grain size with increase in CuSO$_4$ concentration shown in Table 6.5 is due to increase in rate of deposition and higher rate of deposition causes decrease in grain size at 0.6 M.

6.8.5 Effect of annealing

As-deposited pulse plated films were annealed at higher temperatures between $150^\circ$C and $350^\circ$C for a duration of 30 minutes. Annealing causes increase in crystalline size of the film as shown in Table 6.6. This improvement in crystallinity results in the reduction of grain boundary width, which causes more
Fig 6.17 Resistivity of pulse plated Cu$_2$O films deposited under various CuSO$_4$ concentrations

(a) 0.6 M    (b) 0.45 M    (c) 0.3 M    (d) 0.2 M    (e) 0.1 M

(Dep.pot.: 0.4 V vs SCE, Dep.temp.: 70°C, pH: 9.0 ± 0.1, Dep.time: 20 min.)
Fig 6.18 Temperature dependence of resistivity of pulse plated Cu$_2$O films deposited under various CuSO$_4$ concentrations

(a) 0.6 M  (b) 0.45 M  (c) 0.3 M  (d) 0.2 M  (e) 0.1 M

(Dep.pot. : 0.4 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time : 20 min.)
Table 6.5

Effect of CuSO₄ concentration on resistivity and grain size in pulse deposition of Cu₂O thin films

<table>
<thead>
<tr>
<th>S.No</th>
<th>CuSO₄ concentration (M)</th>
<th>Grain size (μm)</th>
<th>Resistivity (ohm.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0045</td>
<td>0.001</td>
<td>30</td>
</tr>
<tr>
<td>2.</td>
<td>0.10</td>
<td>0.015</td>
<td>6 x 10⁵</td>
</tr>
<tr>
<td>3.</td>
<td>0.20</td>
<td>0.020</td>
<td>7 x 10⁶</td>
</tr>
<tr>
<td>4.</td>
<td>0.30</td>
<td>0.029</td>
<td>9.5 x 10⁶</td>
</tr>
<tr>
<td>5.</td>
<td>0.45</td>
<td>0.041</td>
<td>6 x 10⁷</td>
</tr>
<tr>
<td>6.</td>
<td>0.60</td>
<td>0.023</td>
<td>3 x 10⁸</td>
</tr>
</tbody>
</table>
thermionic emission of charge carriers across the grain boundary width. This
inturn decreases the film resistivity from $10^7$ to $10^3$ ohm.cm as shown in Table
6.6. The conductivity of films annealed at $350^\circ$C shows an increase of four
orders of magnitude of unannealed films, which is due to the emission of excess
holes within the valence band.

6.8.6 Effect of temperature on annealed films

The temperature dependence of resistivity of annealed films are studied
and shown in figure 6.19. The slope of the linear portion of the curve yields
activation energy and bandwidth of the films annealed at various temperature
and shown in Table 6.6. The decrease in bandwidth and improvement in
conductivity is also related to the production of excess holes within the lattice at
higher annealing temperatures.

The position of the hole emission peak observed at $180^\circ$ C for as-
deposited film is due to the beginning of emission more of trapped holes within
the valence band. Due to annealing the ionization energy of the film can be
reduced, which inturn enhances the rate of emission of trapped charges and
therefore the peak position shifts towards a lower temperature as shown in figure
6.19. The decrease in peak position with increase in annealing temperature is
noted from figure 6.19.
Fig 6.19 Temperature dependence of resistivity of pulse plated Cu$_2$O films annealed at various annealing temperatures
(a) 150°C  (b) 250°C  (c) 350°C

(Dep.pot. : 0.4 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time : 20 min., Annealing time : 30 min.)
Table 6.6

Variation of electrical parameters with annealing temperature for pulse plated Cu$_2$O films

<table>
<thead>
<tr>
<th>S.No</th>
<th>Annealing temperature ($^\circ$C)</th>
<th>Crystal size ($\mu$m)</th>
<th>Resistivity $\rho$ (ohm.cm)</th>
<th>Activation energy (eV)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As-deposited</td>
<td>0.041</td>
<td>$6 \times 10^7$</td>
<td>0.88</td>
<td>1.76</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>0.22</td>
<td>$4.5 \times 10^7$</td>
<td>0.80</td>
<td>1.61</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>0.49</td>
<td>$4 \times 10^5$</td>
<td>0.73</td>
<td>1.46</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>0.68</td>
<td>$1.5 \times 10^3$</td>
<td>0.70</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Fig 6.20  Resistivity variation with concentration of various doping materials (a) Na₂S  (b) KCl  (c) MgCl₂
(Dep.pot. : 0.4 V vs SCE, Dep.temp. : 70°C, pH : 9.0 ± 0.1, Dep.time. : 20 min.)
6.8.7 Effect of doping

Reduction in resistivity can be achieved by means of doping. Hence, doping the electrolyte with chemicals was carried out in the present work. Reduction of CuSO₄ concentration in the electrolyte decreases the resistivity of the film from the order of $10^7$ to $10^5$ ohm.cm. Further reduction in resistivity was achieved by doping the electrolyte with KCl or MgCl₂ or Na₂S. Addition of these agents to the electrolyte decreases the resistivity to the order of $10^2$ ohm.cm. Resistivity variation with doping agent for pulse plated Cu₂O film is shown in figure 6.20. Figure reveals that the resistivity of the film decreases with the increase of doping material. Films doped with MgCl₂ shows lower resistivity than other doped films. The optimum doping level is found to be in the ratio of 12:100 (i.e) 0.012 M : 0.1 M.

6.9 Conclusion

Electrical properties of Cu₂O thin films deposited under various deposition techniques are studied in air in the temperature range of 303 to 603 K. As-deposited Cu₂O thin films exhibit electrical resistivity in the range of $10^6$ to $10^7$ ohm.cm. Annealing at higher temperatures causes decrease in resistivity of the film to the lower value of $10^3$ ohm.cm due to the production of excess Cu ion vacancies within the lattice. Thermal activation energies and band gaps of as-deposited and annealed films are estimated and the results are discussed. It is observed that the resistivity decreases with increase in Cu ion vacancies. Cu₂O film with lower resistivity can be produced by the processes such as annealing,
CuSO₄ concentration reduction, and doping. Among these processes doping shows higher reduction in resistivity and hence doped films exhibit much lower resistivity of the order of $10^2$ ohm.cm. The reduction in resistivity with increase of annealing temperatures suggests that the Seto's polycrystalline model could produce a good approximation to these films.