CHAPTER VII

PHOTOELECTROCHEMICAL SOLAR CELL STUDIES

7.1 Introduction

Harnessing solar energy has attracted the attention of scientists, economists and technologists of the world to counter the energy crisis. Much effort has recently been directed towards developing new and better solar energy conversion devices. A high degree of sophistication has already been achieved in the fabrication of p-n junction solar cells /206/. The main problem that posed challenge to solar energy research is solar energy storage. Ever since Fujishima and Honda /207/ used a semiconductor electrode dipped in a liquid electrolyte to photoelectrolyse water and obtained hydrogen (a transportable form of energy), the solar energy research has gained a large momentum. In 1975, Gerisher /208/ succeeded in direct conversion of solar energy into electricity using the photoelectrochemical (PEC ) solar cells that offered both energy conversion and energy storage. The promise of photoelectrochemical solar cells as an efficient source for clean power has remained unrealized because of non-availability of low band gap non-corrosive photo effective materials.

Effort is now being made to prepare a material by alloying two different materials, one exhibiting low band gap and other with a high band gap such that high efficiency and photoelectrochemical stability may be achieved simultaneously /209/. A photoelectrochemical effect is defined as one in which irradiation of electrode - electrolyte system produces a change in electrode
potential (open circuit) or a change in current flowing in the external circuit (short circuit). There are several advantages of using PEC solar cells over conventional solid state cells. They are (a) PEC devices can be easily fabricated unlike photovoltaic devices (b). The band bending can be varied conveniently by suitable choice of electrolyte and cell variables (c) the differential thermal expansion associated with a solid-solid junction are not exist (d) in-side storage facility and (e) possibility of fabricating hybrid systems (photovoltaic and photothermal). In this chapter, the principle and working of PEC cells are outlined. In addition, the behaviour of PEC cells fabricated using Cu$_2$O thin films (deposited under various techniques) are studied thoroughly and various semiconductor parameters evaluated are summarized. An attempt has been made to improve the performance of these PEC devices using surface modification of the electrodes.

7.2 Principle of PEC cells

When a semiconductor is brought in contact with the electrolyte, charge transfer takes place until equilibrium is reached. This gives rise to a depletion layer in the semiconductor, which is a consequence of the mismatch of the fermi level of the electrolyte, which is taken as the redox level. Bending of the energy bands at the surface of the semiconductor and electrolyte are not same. At equilibrium the band bending is energetically equal to the initial difference in fermi levels and the band bending may be favourable for observation of efficient photocurrents. The situation is similar to a semiconductor metal Schottky barrier /210/.

When a light of energy $h\nu > E_g$ falls onto the semiconductor surface, it is absorbed in the depletion region and electron hole pairs are created. The
two charge carriers move in opposite direction due to the electric field in the space charge layer. The generated holes and electrons migrate to surface and bulk respectively, if they do not recombine due to collisions or coulombic interactions. Hence n-type electrodes are photoanodes and dark cathodes, while p-type materials are photocathodes and dark anodes. In an ideal case the holes react at the interface exclusively with the electrolyte oxidizing the electron donors of the redox system. The various steps are described in the following equations. Here S.C.I refers to space charge layer.

Light absorption
\[ h^+ + \text{S.C.I.} \rightarrow h^+ \text{S.C.I.} + e^- \text{S.C.I.} \rightarrow \] (7.1)

Recombination
\[ h^+ + \text{S.C.I.} + e^- \text{S.C.I.} \rightarrow \text{heat} \rightarrow \] (7.2)

Charge separation
\[ e^- \text{S.C.I.} \rightarrow e^- \text{bulk} \rightarrow \] (7.3)
\[ h^+ \text{S.C.I.} \rightarrow h^+ \text{surf} \rightarrow \] (7.4)

Interfacial reactions
\[ h^+ \text{surf} + \text{Red} \rightarrow O x^+ \rightarrow \] (7.5)
\[ e^- \text{surf} + O x^+ \rightarrow \text{Red} \rightarrow \] (7.6)

To adjust equilibrium situation at the electrode, the accumulation of a positive charge on the semiconductor is important. Under illumination a photovoltage is obtained at open circuit which can be measured with respect to a reference electrode in contact with the electrolyte. The generation of a charge leads to a disturbance in the equilibrium charge distribution. An equal
reduction of the positive charge in the space charge layer and of the respective excess charge in the electrolyte occurs and hence, the band bending is diminished. The steady state is reached when the charge generation steps (7.1), (7.3) and (7.4) are balanced by the steps (7.4) and (7.6). Since the rates of reaction (7.2) and (7.6) increase with the decrease of band bending corresponding to an increase of the photovoltage, the open circuit photovoltage rises with illumination intensity. To exploit this photovoltage the semiconductor electrode has to be combined with a suitable counter electrode, which is a reversible redox electrode for the same redox potential, the fermi levels being equal in both electrodes and in the electrolyte.

7.3 Working of the PEC cell

If the semiconductor electrode is illuminated the band bending of the semiconductor is reduced and photovoltage is generated. This photovoltage acts as a driving force for electrons to move from the semiconductor to the counter electrode, while the holes react with the electrolyte. The result is that the oxidation of the reduced species of the electrode and reduction of the oxidized species at the counter electrode by reaction (7.6) takes place. In this ideal case, no net chemical change takes place. The effect of illumination is only to increase the electron energy in the voltage. In this way the electrons can do some work before they are captured again by oxidized species $O X^+$ of the electrolyte, which has previously been generated at the semiconductor by illumination.

The maximum open circuit photovoltage is equal to the amount of band bending and is controlled by the fermi level of the electrolyte for a given
semiconductor. The maximum theoretical efficiency is just open circuit photopotential divided by the band gap $E_g$, but the operational efficiency depend on the relative rates of electron-hole recombination and electron transfer reactions. There are number of ways of losses of energy responsible for the reduction of operational efficiency from the ideal one. Some of them are

a). $e_{e.c.i}$, Energy loss due to the loss of charge carriers in the s.c.i.

b). $e(l,R)$, Ohmic loss with $R = R_{int} + R_{ext}$

c). Efficiency redox = $E_v + e n_{s.c}$ = Energy loss connected with reaction (7.5) when $n_{s.c}$ is the over voltage at semiconductor.

d). $e n_{c,e}$ = Energy loss connected with eqn (7.6) at the counter electrode due to overvoltage at the counter electrode.

Here $R_{int}$ includes the inner resistance of semiconductor, the counter electrode and the electrolyte and $R_{ext}$ the resistance of any load of the cell and $n$, the all kinds of overvoltages, including the concentration polarization. In addition light losses by absorption outside the S.C.L and reflection losses in the electrolyte are some of the energy losses responsible for low efficiency of a PEC cell. Photo assisted decomposition of water, using metal oxide semiconductors, usually band gap of 3.0 eV uses only a small fraction of the light energy required to drive the reaction /211,212/. If PEC cells are to be used in solar energy conversion, visible light responsible systems are needed. To push up the efficiency of PEC cells using thin film electrodes, a lot of study are yet to be made.
7.4 Experimental details

The methodology of PEC cells is more or less standardized at the present time. Before the actual construction and performance evaluation of a liquid junction solar cell (LJSC), detailed studies are carried out with respect to the material preparation, evaluation, etching treatment, determination of the PEC parameters and the long term stability of the electrodes and electrolytes under continuous irradiation. Optimization of the properties and parameters are necessary for the proper functioning of the PEC cells. A standard three-electrode (photoelectrode, SCE and a platinum counter electrode) set up is employed for PEC studies on semiconductor thin film. A simple one with a quartz window and with the provision for the passage of gas and the electronic circuitry is shown in figure 7.1a. A schematic PEC cell is shown in figure 7.1b.

7.4.1 Electrode preparation

Electrode of Cu$_2$O thin film was used as photocathodes. Ohmic contacts were made on thin films with In-Ga eutectic alloy (purity 99.9% Nuclear fuel complex, Hyderabad, India) and silver-epoxy (Epo-tek H.31, USA) was used to attach a Cu-lead wire. The samples were mounted onto a glass holder. Ordinary epoxy resin (Araldite) was used to insulate all the other surfaces of the electrode except the front surface to be exposed to light. A glass cell with a quartz window was used to perform the experiments.
Fig 7.1  Standard 3-electrode set up for current–voltage (I–V) and capacitance measurements. (b) Schematic representation of a PEC cell.
7.4.2 Surface etching

Polishing and etching of the electrode surface is an important step in the PEC studies. An etched surface gives a reticulate surface (‘matte’ surface) which is clean and helps in the absorption of light (by multiple reflections) by the semiconductor. Etching can also remove surface states. Etching involves preferential dissolution of the material at the grain boundaries. Optimum etchant composition (acid, alkali, etc) varies from one semiconductor to another and is usually arrived at by trial and error. The process of ‘Photoetching’ involving etching of the surface of a semiconductor under irradiation ($h\nu \geq E_g$) has also been reported by many investigators /213,214/.

7.4.3 Counter electrode

Platinum is the material of choice in most applications involving PEC cells although cheaper substitutes (e.g. brass, carbon) may function equally well for selected redox systems in PEC cells. The counter electrodes should have very good electronic conductivity (for current pick-up) and should be chemically inert to the electrolyte. Usually, a large area counter electrode is employed to avoid kinetic factors influencing the PEC cell performance.

A photoresponsive n-type semiconductor can be employed as a counter electrode in LJSC by irradiation of both the anode and the cathode with $h\nu \geq E_g$ to increase the efficiency of conversion. High efficiency was not obtained for these double photoelectrodes because of the low absorption of one of the high band gap electrodes and also due to poor matching of the energetics of these two electrodes.
7.4.4 Electrolyte

A wide choice is available in the selection of suitable electrolytes with varying $E_0$ values. To avoid $O_2$ reduction (at the cathode), it is advisable to purge the electrode with $N_2$ or $Ar$. The electrolyte should have good ionic conductivity to avoid large internal resistances of the PEC cell. It is highly advantageous if electrolyte does not absorb in the region of wavelength ($h\nu \geq E_g$) of interest to semiconductor absorption.

The electrolyte comprised 1M sodium sulphide ($Na_2S$), 1M sulphur (S) and 1M potassium hydroxide (KOH) in water. The aqueous electrolyte preparation is done by adding sulphur, sodium sulphide and sodium hydroxide in succession. Great care has been taken to confirm the dissolution of sulphur before adding the other species. The electrolyte was stored in a light protected container before use. Licht and Davis [215] have recently reported an excellent work on the stability of polysulphide electrolytes.

7.5 PEC solar cell parameters

7.5.1 Open circuit voltage ($V_{oc}$)

In PEC cells, the photoeffect is exhibited as the photovoltage and photocurrent on illumination of the semiconductor electrode with light of $h\nu \geq E_g$. The photoeffect varies significantly from one material to another in the magnitude of PEC parameters such as photovoltage, photocurrent, flat band potential and photocurrent saturation behaviour. The basic feature of the photocathode is the shift in the potential of the electrode (w.r.t. SCE or counter electrode) on illumination. For example, in the case of n-type
semiconductors, the shift will be towards negative direction (w.r.t SCE). The opposite will be the case for p-type semiconductors.

For thin film electrodes, which also do not possess good electronic conductivity ($\sigma$) considerable dark potentials are usually noted. The difference between the photo and dark potential is the open circuit voltage, $V_{OC}$. The maximum $V_{OC}$ obtainable is given by the equation,

$$V_{OC} = |E_X - E_0|$$

$$= E_B \rightarrow (7.7)$$

for a given semiconductor.

Similarly, a sharp onset of photocurrent (at zero or non-zero applied bias w.r.t counter electrode) on irradiation and sharp drop (in the light `off` position) after irradiation is a good PEC behaviour in a semiconductor electrode.

### 7.5.2 Current - voltage characteristics

The potentiostatic current-voltage curve of the semiconductor electrode, usually obtained by impressing varying voltage on the semiconductor (w.r.t SCE) and measuring the current both in dark ($i_d$) and under illumination ($i_{\text{photo}}$) provides important information. Negligibly small dark currents (for both positive and negative voltage bias) and a sharp rise of photocurrent at a given applied bias which saturates at higher positive bias potential is obtained for a good photoresponse p-type semiconductor. The saturation of $i_{\text{photo}}$ is due to the rare limiting process of carrier charge transfer to the electrolyte. Since, due to high applied bias, large band bending is
ensured which will suppress the electron-pair recombination. The magnitude of $i_{\text{photo}}$ depends on the light intensity 'I' and as a first approximation /216/.

$$I = i_{\text{photo}} - i_0 \exp \left( \frac{q I_{\text{sc}} R_s}{A k T} \right) \quad \rightarrow \quad (7.8)$$

where 'Rs' is the series resistance of the cell, 'q' is the charge on the electron, 'I_{sc}' is the short circuit current, 'k' is the Boltzmann constant, 'T' is the absolute temperature, 'I_0' is the reverse saturation current and 'A' is a constant.

Similarly, the open circuit potential ($V_{\text{OC}}$) is also dependent on the light intensity as the equation /217, 218/.

$$V_{\text{OC}} = \frac{kT}{q} \ln \left( 1 + \frac{P}{P_0} \right) \approx \frac{kT}{q} \times \frac{P}{P_0} = \frac{kT}{q} \tau \quad \rightarrow \quad (7.9)$$

where 'P_0' is the density of holes in the bulk of the semiconductor, 'P' is the increase in hole density on illumination, 'τ' is the proportionally factor and 'I' is the light intensity.

For a given wavelength (monochromatic) and intensity (photo flux, F_0), the $i_{\text{photo}}$ is related to the flat band potential, ($V_{\text{fb}}$) as per the Gartner's equation reported by Butler /219/.

$$i_{\text{photo}} = q F_0 \times \left( \frac{\exp [-\alpha W_0 (V - V_{\text{fb}}) \frac{1}{2}]}{1 + \alpha L_n} \right) \quad \rightarrow \quad (7.10)$$

where 'α' is the optical absorption coefficient of the semiconductor. 'W_0' is the depletion layer thickness for a potential of one volt across the semiconductor and can be expressed as
where 'α' is the dielectric constant, 'ε₀' is the permittivity of free space and 'Nₐ' is the hole carrier concentration. 'V' in equation (7.10) is the applied potential (relative to SCE) and 'Lₐ' is the electron (minority carriers in the case of p-type semiconductor) diffusion length.

7.5.3 Spectral response of the photoelectrode

Spectral response (photocurrent vs wavelength curve) of the semiconductor under applied conditions will be useful for (a) Quantum efficiency (ηₑ) calculation (b) band gap, Eₕ measurements (c) observation of sub-band gap response, if any and (d) information about electrolyte absorption, if any.

7.5.4 Flat band potential (Vₕᵦ)

As mentioned earlier, the flat bed potential is an important parameter of the semiconductor in a PEC cell. In an LJSC, Vₕᵦ enables to estimate the maximum Vₜₒₙₖ obtainable. Vₕᵦ can be estimated either from potentiostatic i-v curves or the electrode capacitance measurements or both. These are described below.

i) Vₕᵦ determination from i-v curves

Rough estimate of Vₕᵦ is obtained from the voltage at which iₕₒₜₐₒₜₒₜₖ onset occurs in the potentiostatic i-v curve. More accurate value of Vₕᵦ can be
obtained by plotting $i_{\text{photo}}$ vs V and extrapolating to zero photocurrent, provided $i_{\text{photo}}$ measurements are done at monochromatic radiation and $\h \nu = \frac{hc}{\lambda^2} \geq E_g$. This follows by a consideration of equation (7.10) as follows.

When $\alpha W_0 (V - V_{fb})^2 << 1$, equation (7.10) can be reduced to

$$ \frac{i_{\text{photo}}}{\alpha W_0 q F_0} \propto (V - V_{fb})^{1/2} $$

and hence

$$ n \propto (V - V_{fb}) $$  \rightarrow (7.12)

However, it should be noted that the accuracy of the linear extrapolation relation between $i_{\text{photo}}^2$ and V increases for increasing wavelength and hence decreasing $\alpha$. This implies that measurements taken at nearer to $E_g$ and the data points retained in a region with a small band bending should be used for extrapolation to give $V_{fb}$ /220/.

ii) Determination of $V_{fb}$ from Mott – Schottky plots

(Capacitance – Voltage measurements)

The capacitance of the electrode (C) is related to the applied potential (V) through the flat band potential ($V_{fb}$) by the Mott – Schottky equation /221/.

$$ \frac{1}{C^2} = 2 \varepsilon \varepsilon_0 q N_D [(V - V_{fb}) - (kT/q)] $$  \rightarrow (7.13)

and hence $1/C^2 \propto (V - V_{fb})$. Thus the inverse square of the surface capacitance of the electrode is directly proportional to the applied potential and $V_{fb}$ can be obtained by extrapolation of the linear plot to zero on the x-axis. Assuming the acceptor levels to be completely ionised, the majority charge carrier concentration, $N_A$ can also be calculated from the slope of this $C^{-2}$ vs V plot as per the equation (6.7) /220, 221/.
Power characteristics (I vs V plots)

Power characteristics of an LJSC cell can also be measured by imposing variable external resistance (in the range 1 – 10,000 ohms) in series and measuring the voltage drop with a voltmeter. Then, from the I vs V plots, the efficiency of LJSC’s and fill factor (FF) can be calculated by using the equations,

$$\eta(\%) = \left( \frac{(I \times V)_{max} / P_{input}}{x \times 100} \right)$$  \rightarrow (7.14)

$$FF = \left[ \frac{(I \times V)_{max}}{(I_{sc} \times V_{oc})} \right]$$  \rightarrow (7.15)

where $(I \times V)_{max}$ is the maximum output power of the solar cell, $P_{input}$ is the light (optical power) input. $I_{sc}$ is the short circuit photocurrent and $V_{oc}$ is the open circuit photovoltage.

Estimation of $E_g$, $N_A$ and $L_n$ from PEC studies

As discussed above, $E_g$ the band gap, $N_A$, the effective carrier concentration and $L_n$, the electron diffusion length (minority carriers) are the important parameters required for the construction of high efficiency PEC cells. They can be estimated from the quantum efficiency curves and are described below.

(i) $E_g$ determination

In order to study the nature of the primary optical transition in a semiconductor, the nature of the variation of the absorption coefficient ($\alpha$) near the band edge should be known. The exact nature of this behaviour is complicated and depends on selection rules and the band structure of the semiconductor in detail. If we assume, for simplicity, spin–allowed transitions,
then it can be shown that near the band edge the optical absorption has the following behaviour /220/.

\[(\alpha h\nu) = A(h\nu - E_g)^{n/2}\] \rightarrow (7.16)

where A is a constant. The value of n depends on whether the transition is direct \((n = 1)\) or indirect \((n = 4)\). The photocurrent characteristics in a Schottky junction can be explained by the equation (7.10) and (7.16).

The spectral response of the photocurrent of the semiconductor electrode is governed by the behaviour of its optical absorption coefficient, \(\alpha\), containing equations (7.10) and (7.16) and for \(\alpha w_0 \ll 1\) and using the definition of the quantum efficiency,

\[\varphi_e = \frac{I_{\text{photo}}}{qF_0}\] \rightarrow (7.17)

where \(F_0\) is the photon flux, we obtain:

\[\varphi_e h\nu = [L_n + w_0 (V - V_{fb})^{1/2}] A (h\nu - E_g)^{n/2}\] \rightarrow (7.18)

\[(\varphi_e h\nu) \alpha (h\nu - E_g)^{n/2}\] \rightarrow (7.19)

where \(n = 1\) for direct band gap; \(n = 4\) for indirect band gap. Thus the band gap of the semiconductor and its nature (direct or indirect) can be evaluated by an extrapolation of the linear portions of the plots of \((\alpha h\nu)^{2/n}\) versus \(h\nu\).

ii) \(N_A\) and \(L_n\) determination

Gartner’s equation (7.10) can be used to determine the parameters of \(N_A\) (acceptor density) and \(L_n\) (minority carrier diffusion length). Rewriting equation (7.10) as:
\[
\ln(1 - \eta_e) = -\alpha \left( \frac{2\varepsilon\varepsilon_0}{q_f\varepsilon_0} \right) (V - V_{fb})^{1/2} - \ln (1 + \alpha L_n) \quad \rightarrow \quad (7.20)
\]

where \(\eta_e\) represents the quantum efficiency. A plot of \(\ln(1 - \eta_e)\) versus \((V - V_{fb})^{1/2}\) should be linear with a slope of \(-\alpha (2\varepsilon\varepsilon_0/q_f)^{1/2}\) and an intercept of \(-\ln(1 + \alpha L_n)\), from which \(N_A\) and \(L_n\) can be obtained if \(\varepsilon\) and \(\alpha\) are known. However equation (7.17) holds only for negligible recombination of electrons and holes in the depletion region, a condition which is not fulfilled for low over voltages if recombination centres are present /214/. \(N_A\) can also be calculated from the slope of \(C^{-2}\) vs \(V\) plot if \(\varepsilon\) is known.

The cell was illuminated with a 250 W tungsten halogen lamp and the intensity of radiation at various wavelengths are measured using a thermopile detector (Eppley, USA).

7.6 Review of Literature

Economou et al /69/ fabricated Cu2O thin film by electrodeposition method and used it for the fabrication of photovoltaic devices. Using Cu2O as active layer Roos et al /68/ gave reports on the characteristics of solar cells. Olsen et al /71/ made effort on fabrication of low cost material and constructed the solar energy conversion devices based on these materials. Photovoltaic properties of Cu2O–Cu contact have been reported by Assimios et al /75/. Extensive studies on Cu2O Schottky barrier solar cells have been carried out by Berrezin et al /78/.
Sears et al /80/ developed Cu$_2$O photovoltaic junction by the anodic oxidation of copper and gave report on the photovoltaic properties of Cu$_2$O thin film. Reports on photovoltaic properties of photovoltaic cell based on indium tin oxide/Cu$_2$O contact have been given by Sears et al /81/. Iwanowsaki et al /83/ predicted the use of Cu$_2$O as active layer in various types of solar cells. Conversion of solar energy into chemical energy through photoelectrolysis cell was reported by Rakhshani et al /95/. Wijesundara et al /100/ studied about the characteristics of PEC cell based on Cu$_2$O and reported that the output of PEC cell can be improved by sulphiding the films. Extensive studies on Cu$_2$O Schottky barrier solar cells have been conducted and the results on efficiencies of front wall and back wall cells and the effect of sulphidation have been reported by Fernando et al /107/. n-type PEC cell with energy conversion efficiency of 0.01% have been reported by Jayewardena et al /114/. Photovoltaic properties of annealed films have been reported by Siripala et al /112/. Briskman et al/222/ and Siripala et al /223/ gave reports on the effect of sulphidation in PEC cell.

7.7 PEC solar cell studies on Cu$_2$O thin films

7.7.1 Introduction

During the last two decades much work has been done on photoelectrochemical (PEC) systems, in search of suitable liquid junction solar cells (LJSC). A lot of research has been also inspired by the unique opportunities that PEC cells offer in the study of energetics and the chemistry of semiconductor - electrolyte is immersed in the electrolyte. The second advantage is that with a proper choice of redox couples in the electrolyte, the
fermi level in the electrolyte can be controlled and thus the barrier height adjusted to the desired level. The good contact formed at the electrode/electrolyte interface materials. The results of studies conducted the photoelectrochemical behaviour dealt in this chapter.

7.7.2 Experimental details

The photoelectrochemical (PEC) solar cell is constructed in a cylindrical pyrex glass vessel. The cell consists of a standard three-electrode configuration with the Cu$_2$O film as a photocathode, a platinum cathode and a saturated calomel electrode as reference electrode. The electrolyte is a solution containing 1M sodium sulphide (Na$_2$S), 1M sulphur (S) and 1M sodium hydroxide (NaOH) in water.

7.8 Results and discussions

7.8.1 Galvanostatically deposited Cu$_2$O thin films

7.8.1.a Spectral response studies

The electrodeposition of copper oxide film was carried out at a current density of 1.4 mA/cm$^2$ with Cu and SnO$_2$ as substrates using electrolyte (0.45M CuSO$_4$ + 3.25 M lactic acid + NaOH) with pH 9.0 ± 0.1 for a deposition time of 30 min. The SnO$_2$/Cu$_2$O contact was illuminated from the front side by using 250 W projector lamp. The SnO$_2$/Cu$_2$O contact showed a photovoltaic effect. Figure 7.2 shows the spectral response of the as-deposited Cu$_2$O film electrode in a photoelectrochemical cell (PEC) containing 0.1M sodium acetate as electrolyte. The observation of figure 7.2 shows p-type photocurrent for entire spectral range of 500 to 1200 nm. The shape of the
Fig 7.2 Spectral response of as-deposited Cu$_2$O film by galvanostatic deposition technique.
Fig 7.3  Current-potential characteristics of galvanostatically deposited Cu$_2$O films (a) Cu substrate  (b) SnO$_2$ substrate
spectral response was same for all the substrates. The gross features of the spectral response agree with the previous results on thermally grown Cu$_2$O film electrodes /224/. To find evidence for the photocurrent produced by the electrodeposited Cu$_2$O thin films, the variation of the current with the applied potential for Cu$_2$O thin film photoelectrodes was studied.

Figure 7.3 shows the photocurrent vs potential behaviour of Cu$_2$O thin films on Cu and SnO$_2$ substrates. It is observed that the photocurrent increases with increasing positive potential, which assures p-type conductivity and may be due to the barrier formed at the Cu$_2$O /electrolyte interface. The observed p-type conductivity may be due to the presence of Cu ion vacancies. The solar cell parameters of as-deposited Cu$_2$O film electrodes are estimated and shown in Table 7.1.

7.8.1.b Annealing effects on PEC parameters

Polycrystalline semiconducting materials have shown great promise of solar energy into electricity through PEC cells. However, because of the internal defects present in polycrystalline materials as compared to single crystals, a considerable amount of photogenerated charge carriers is lost due to recombination particularly in the intergrain regions of the bulk. The overall performance of the cells will be poor due to the above reason. To minimize recombination losses, the semiconductor electrodes are to be given a heat treatment in air or in an inert atmosphere like argon and nitrogen. This causes incipient fusion of the crystallites and thereby increase the crystallite size and reduces grain boundaries.
### Table 7.1

Solar cell parameters of as-deposited and annealed galvanostatically deposited Cu$_2$O films

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Annealing conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As – deposited</td>
<td>100</td>
<td>0.60</td>
<td>0.13</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>150°C</td>
<td>130</td>
<td>0.75</td>
<td>0.20</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>250°C</td>
<td>180</td>
<td>1.12</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>350°C</td>
<td>250</td>
<td>1.50</td>
<td>0.30</td>
<td>0.11</td>
</tr>
</tbody>
</table>
During the annealing process the point defects exist at the grain boundaries which act as trap centres for the charge carriers will also get reduced to a considerable amount. Consequently the effective carrier concentration and life time of charge carriers would be increased. A strong adhesion between the substrate and the thin film is one of the most important requirements for the fabrication of a thin film photoelectrode. Annealing of the films improves adhesion and crystallinity which are important criteria for application in a PEC solar cell.

The electrodeposited Cu$_2$O films were annealed at different temperatures between 150 to 350°C. Figure 7.4 shows the effect of annealing at 150°, 250° and 350° C for 30 minutes. As shown in figure 7.4, the photocurrent for front wall illumination is p-type and the spectral response has been enhanced by annealing. The photocurrent potential behaviour for annealed films shown in figure 7.5 illustrates that the photocurrent increases with increasing annealing temperature.

The effect of annealing temperature on open circuit voltage (V$_{oc}$) was studied. Figure 7.6 shows the variation of open circuit voltage of Cu$_2$O photocathode PEC solar cell with the heat treatment duration time for various annealing temperatures in air. It is observed from the figure 7.6 that as the annealing time is increased, V$_{oc}$ increases and attained saturation. As a result of the heat treatment, the photovoltage is increased from about 100 mV for unheated samples to 250 mV for heat treated samples. During heat treatment, a recrystallization process takes place in the Cu$_2$O thin films which increases
Fig 7.4 Spectral response of galvanostatically deposited Cu$_2$O films annealed at various annealing temperatures (a) 150°C (b) 250°C (c) 350°C
Fig 7.5 Current-potential characteristics of galvanostatically deposited Cu$_2$O films annealed at various annealing temperatures (a) 150°C (b) 250°C (c) 350°C
Fig 7.6 Variation of open circuit voltage ($V_{oc}$) with annealing time for galvanostatically deposited Cu$_2$O films annealed in air at various annealing temperatures (a) 150°C (b) 250°C (c) 350°C
the average crystal size, which in turn decreases the resistivity of the film and hence enhances the open circuit voltage ($V_{oc}$) of the Cu$_2$O films.

Photoelectrochemical solar cell studies on annealed Cu$_2$O samples exhibited best results for Cu$_2$O films annealed in air at $350^0$ C. Table 7.1 represents solar cell parameters for annealed and un-annealed Cu$_2$O films. Figure 7.7 shows the variation of short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) on the annealing temperature. The Cu$_2$O films are annealed in the temperature range of $150^0$C to $350^0$C in air. As shown in the figure, $J_{sc}$ and $V_{oc}$ increases with annealing temperature.

Annealing increases the minority carrier diffusion length ($L_p$). $L_p$ depends upon mobility and lifetime which, in turn, are estimated by scattering and recombination centres at the grain boundaries. Annealing increases the photovoltaic conversion efficiency by increasing the crystalline size and reducing grain boundaries. In addition, in the case of Cu$_2$O thin films it has been observed that annealing also causes removal of excess Cu. Hence, the improvement in cell performance is attributed to the enhancement of Cu ion vacancies

### 7.8.1.c Etching effects on PEC parameters

The photoelectrochemical (PEC) solar cell studies are carried out in a cell consisted of the galvanostatically deposited photoelectrode (Cu$_2$O), a platinum counter electrode and a saturated calomel reference electrode. The electrolyte is an aqueous solution mixture of KI (1M) and I$_2$ (0.01 M). For photovoltaic and PEC applications, chemical etching is usually beneficial to
Fig 7.7 Variation of open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$) with annealing temperatures.
remove damaged surfaces. The as-deposited and annealed Cu2O photoelectrodes were etched chemically at 60°C for 15 seconds in a dilute acid mixture containing HCl, HNO3, H2SO4 and CH3COOH in the ratio 4 : 1 : 0.2 : 0.1 (by volume) and then rinsed in distilled water. The photoelectrodes were dipped into a polyelectrolyte bath to remove oxidation products of the chemical etching. In order to inhibit photocorrosion, the photoelectrodes were photoetched by illumination with a polychromatic light in 0.5M Na2SO4 electrolyte at 0.1 V versus SCE for 5 seconds.

The current – voltage characteristics of annealed Cu2O photoelectrode under various etching conditions is shown in figure 7.8. It is observed from figure 7.8 that the current is maximum for photoetched samples than for other electrodes. These result suggest that surface damages, surface states and traps are effectively removed from photoelectrodes subjected to photoetching followed by chemical etching. Table 7.2 represents various solar cell parameters for galvanostatically deposited Cu2O photoelectrodes subjected to various surface treatments.

7.8.1.d Effect of film thickness on PEC parameters

The effect of film thickness on Jsc and Voc is shown in figure 7.9. Both Jsc and Voc increase rapidly with increasing film thickness and attains saturation after 3.0 μm. The variation of efficiency of a Cu2O PEC cell with the thickness of a galvanostatically deposited Cu2O film is shown in figure 7.10. It is found that the cell efficiency increases rapidly with increasing Cu2O thin film thickness upto 3.0 μm and later levelled off slowly. From these
Fig 7.8  Current-voltage characteristics of annealed Cu$_2$O films etched under various etching conditions (a) Unetched  (b) Chemical etched (c) Photoetching followed by chemical etching.
Table 7.2

Variation of solar cell parameters for various etching conditions in galvanostatic technique

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Etching conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unetched</td>
<td>250</td>
<td>1.5</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>Chemically etched</td>
<td>300</td>
<td>1.8</td>
<td>0.35</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>Photoetch followed by chemical etching</td>
<td>335</td>
<td>2.4</td>
<td>0.39</td>
<td>0.34</td>
</tr>
</tbody>
</table>
Fig 7.9 Effect of film thickness on open circuit voltage ($V_{oc}$) and short circuit density ($J_{sc}$) for galvanostatically deposited Cu$_2$O film.
Fig 7.10 Variation of efficiency with thickness of galvanostatically deposited Cu$_2$O film.
studies the optimum thickness to yield high efficiency PEC cells is identified as 3.0 \( \mu \text{m} \).

7.8.1.e Flat band potential measurements

The flat band potential, \( V_{fb} \), is the electrode potential at which there is no band bending in the semiconductor electrolyte and is a property of the electrode/electrolyte interface. \( V_{fb} \) can be estimated by two independent methods.
1. Capacitance - Voltage measurements (Mott-Schottky plot).
2. From the measured \( j_{\text{photo}}^2 \) Versus potential and extrapolating to zero photocurrent.

1. Capacitance - Voltage measurements (Mott-Schottky plot)

The flat band potential \( V_{fb} \) can be calculated by using Mott-Schottky \( (1/c^2 \text{ vs V}) \) plots for the electrodes. Figure 7.11 shows a representative \( 1/C^2 \) Versus \( V \) plot for a typical Cu\(_2\)O semiconductor thin film electrode. The intercept on the voltage axis yield the value of flat band potential \( V_{fb} \) as 1.75 V vs SCE. Using Mott-Schottky plot, the important semiconductor parameters such as acceptor concentration (\( N_A \)) and depletion layer width (\( W \)) are estimated and presented in Table 7.3. The values of acceptor density and flat band potential are comparable to the reported values of Cu\(_2\)O thin films /102/.

2) \( j_{\text{photo}}^2 \text{ versus potential (v) plot} \)

The flat band potential, \( V_{fb} \), was evaluated for a typical Cu\(_2\)O photoelectrode by illuminating the semiconductor-electrolyte interface with a monochromatic light of wavelength 580 nm. The wavelength of 580 nm was
Fig 7.11  Mott-Schottky plot for galvanostatically deposited Cu$_2$O film
Table 7.3
Semiconductor parameters of galvanostatically deposited Cu2O film

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Semiconductor parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flat band potential ($V_{fb}$)</td>
<td>1.75 V</td>
</tr>
<tr>
<td>2</td>
<td>Doping density ($N_A$)</td>
<td>$2.5 \times 10^{14} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>Depletion layer width ($W$)</td>
<td>$3.0 \times 10^{6} \text{ cm}$</td>
</tr>
<tr>
<td>4</td>
<td>Barrier height ($\phi_B$)</td>
<td>0.77 eV</td>
</tr>
<tr>
<td>5</td>
<td>Band bending ($V_b$)</td>
<td>0.39 V</td>
</tr>
</tbody>
</table>
chosen in order to keep $\alpha$ small, so that the condition $\alpha L_p << 1$ holds good. The linear plot of $i^2_{\text{photo}}$ versus potential 'V' Versus SCE (figure 7.12) is extrapolated to a $V_{fb}$ of 1.738 V versus SCE. This value is in good agreement with the value obtained from C-V studies.

7.8.1.f Quantum efficiency

Quantum efficiency measurements are necessary for the understanding of photoelectrochemical behaviour. Gartner's model /141/ of the metal-electrolyte junction provides a successful description of the semiconductor-electrolyte interface for both single crystal and polycrystalline photoelectrodes. According to this model (i) each photon absorbed by the semiconductor produces an electron-hole pair (ii) the contribution to the photocurrent of the majority carriers crossing the interface with the electrolyte is negligible (iii) absence of recombination in the electric field region and at the semiconductor interface and (iv) the transfer of charge through the semiconductor-electrolyte interface is not a limiting step of the photoelectrochemical reaction.

The variation of quantum efficiency ($\phi$) with the applied potential for Cu$_2$O electrodes annealed at different temperatures in air is shown in figure 7.13. It is observed from the figure that the quantum efficiency increases with annealing temperature.

7.8.1.g Effect of doping

The electrolyte (0.45M CuSO$_4$ + 3.25M lactic acid + NaOH) for the deposition of Cu$_2$O thin film was doped with 0.045M MgCl$_2$ and then the films
Fig 7.12 Variation of $i_{\text{photo}}^2$ vs voltage for galvanostatically deposited Cu$_2$O film.
Fig 7.13 Variation of quantum efficiency with wavelength for Cu$_2$O films annealed at (a) 150°C (b) 250°C (c) 350°C
Fig 7.14 Spectral response of MgCl₂ doped Cu₂O film
Fig 7.15  Current–Voltage characteristics of MgCl$_2$ doped galvanostatic Cu$_2$O film
Table 7.4

Solar cell parameters of doped Cu₂O film in galvanostatic deposition technique

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Solar cell parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Open circuit voltage (V&lt;sub&gt;oc&lt;/sub&gt;)</td>
<td>400 mV</td>
</tr>
<tr>
<td>2</td>
<td>Short circuit current density (J&lt;sub&gt;sc&lt;/sub&gt;)</td>
<td>2.8 mA cm⁻²</td>
</tr>
<tr>
<td>3</td>
<td>Fill factor (FF)</td>
<td>0.39</td>
</tr>
<tr>
<td>4</td>
<td>Efficiency (η)</td>
<td>0.44%</td>
</tr>
</tbody>
</table>
were deposited under galvanostatic deposition conditions. The resultant doped Cu₂O film shows lower resistivity. The doped Cu₂O film was used as photocathode in PEC cell and the resultant spectral response of the film was studied. The observation shows enhanced positive photovoltage and photocurrent as shown in figure (7.14). Figure (7.15) shows the I-V characteristics of the doped film. Doped Cu₂O film shows \( V_{oc} \) of 400 mV and \( J_{sc} \) of 2.8 mA. The solar cell parameters due to the doped Cu₂O film is shown in Table 7.4.

7.8.2 Potentiostatically deposited Cu₂O thin films

7.8.2.a Spectral response studies

The potentiostatic deposition on Cu and SnO₂ substrates at a deposition potential of -0.55 V Vs SCE were carried out for the deposition time of 10 minutes. A well deposited Cu₂O thin film was used as photocathode in PEC solar cell. The SnO₂/Cu₂O contact was illuminated from the front side by using 250W projector lamp and the spectral response of the film was studied for the wavelength range of 500 to 1200nm. Figure 7.16 shows the spectral response of the potentiostatically deposited Cu₂O film electrode in a photoelectrochemical cell (PEC). The figure 7.16 shows p-type photocurrent for the entire spectral response and found to be the same for all the substrates. The features of spectral response agree with the previous results /224/. However the magnitude of the photocurrent is less than that produced by galvanostatically deposited Cu₂O films due to its higher resistivity.

To find evidence for the photocurrent produced by the potentiostatically deposited Cu₂O thin films the variation of the current with the applied potential
Fig 7.16  Spectral response of as-deposited potentiostatic Cu$_2$O film
Fig 7.17  Current–potential characteristics of potentiostatically deposited Cu$_2$O film
was studied. Figure 7.17 shows the photocurrent Vs potential behaviour of 
$\text{Cu}_2\text{O}$ thin films on $\text{SnO}_2$ substrates. Figure 7.17 shows that the photocurrent 
increases with increasing positive potential, which assures p-type 
photocurrent due to $\text{Cu}_2\text{O}$ thin films in PEC cell.

7.8.2.b Annealing effects on PEC parameters

Polycrystalline $\text{Cu}_2\text{O}$ thin films have shown promise as photoelectrodes for 
the conversion of solar energy into electricity through photoelectrochemical 
(PEC) solar cells. However, the performance of photovoltaic energy conversion systems has been shown to depend strongly on the treatment of the semiconductor electrode prior to use in the solar cells. Polycrystalline thin films subjected to a heat treatment exhibited a remarkable increase in conversion efficiency and stability of the solar cells. Hence, potentiostatically deposited $\text{Cu}_2\text{O}$ thin films were subjected to annealing at different temperatures in air. The films were annealed at $150^\circ\text{C}$, $250^\circ\text{C}$ and $350^\circ\text{C}$.

Figure 7.18 shows the effect of annealing on the spectral response for samples annealed at 150, 250 and $350^\circ\text{C}$ for 30 minutes. As shown in figure 7.18, the photocurrent for front illumination is p-type and the spectral response has been enhanced by annealing. The photocurrent-potential behaviour for annealed films shown in figure 7.19 illustrates that the p-type current increases with annealing temperature.

The monochromatic I-V behaviour of $\text{Cu}_2\text{O}$ photocathodes annealed in air was investigated. The dependance of open circuit photo potential upon annealing temperature was also studied. The variation of open circuit voltage
Fig 7.18 Spectral response of potentiostatically deposited Cu$_2$O films annealed at (a) 150°C  (b) 250°C  (c) 350°C
Fig 7.19  Current-Voltage characteristics of potentiostatically deposited Cu$_2$O films annealed at (a) 150°C  (b) 250°C  (c) 350°C
Table 7.5

Solar cell parameters of as-deposited and annealed potentialstatically deposited Cu$_2$O film

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Annealing conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As-deposited</td>
<td>90</td>
<td>0.50</td>
<td>0.11</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>150°C</td>
<td>160</td>
<td>1.15</td>
<td>0.24</td>
<td>0.044</td>
</tr>
<tr>
<td>3</td>
<td>250°C</td>
<td>225</td>
<td>1.60</td>
<td>0.26</td>
<td>0.094</td>
</tr>
<tr>
<td>4</td>
<td>350°C</td>
<td>290</td>
<td>2.00</td>
<td>0.34</td>
<td>0.196</td>
</tr>
</tbody>
</table>
of a typical potentiostatically deposited Cu₂O PEC cell for various annealing temperatures in air is shown in Figure 7.20. It is observed from the Figure 7.20 that as the annealing time is increased Vₐₑₙ increases and attained saturation value. As a result of the heat treatment the open circuit photovoltage is increased from 90 mV for unheated samples to 290 mV for heated samples. It is seen from the Figure 7.20 that as the annealing temperature is increased, the time required to obtain maximum photovoltage got reduced. The photovoltage is increased to 290 mV for a film annealed at 350°C.

Photoelectrochemical solar cell studies on annealed Cu₂O samples exhibited best results for Cu₂O films annealed in air at 350°C. Table 7.5 represents the solar cell parameters for annealed films. The variation of open circuit voltage (Vₐₑₙ) and short circuit current density (Jₛₖₙ) on the annealing temperature is shown in Figure 7.21. As shown in Figure 7.21, Jₛₖₙ and Vₐₑₙ increases with annealing temperature by increasing the crystalline size and reducing grain boundaries. In analogy with galvanostatically deposited Cu₂O thin film, improvement in cell performance of potentiostatically deposited PEC solar cell is attributed to the production of more copper ion vacancies and increase in grain size.

7.8.2.c Etching effects on PEC parameters

The photoelectrochemical (PEC) solar cell studies are carried out in a cell consisted of the potentiostatically deposited photoelectrode (Cu₂O), a platinum counter electrode and a saturated calomel reference electrode. The electrolyte is an aqueous solution mixture of KI (1M) and I₂(0.01 M). The
Fig 7.20 Variation of open circuit voltage with annealing time for potentiostatically deposited Cu$_2$O films annealed in air at various annealing temperatures (a) 150°C (b) 250°C (c) 350°C
Fig 7.21 Variation of open circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) with various annealing temperatures.
photoelectrodes are etched under chemical etching techniques and photoetching technique.

The current – voltage characteristics of annealed Cu$_2$O photoelectrode under various etching conditions is shown in figure 7.22. The current is found to be maximum for photoetched samples. Since annealing shows higher crystallinity in potentiostatically deposited film, it shows much better results than galvanostatically deposited film. Table 7.6 represents various solar cell parameters for potentiostatically deposited Cu$_2$O photoelectrode subjected to various surface treatments.

7.8.2 d Effect of film thickness

The effect of film thickness on $J_{sc}$ and $V_{oc}$ is shown in figure 7.23. Both $J_{sc}$ and $V_{oc}$ increase with film thickness and attain saturation after 3.0 $\mu$m. The variation of efficiency of a typical potentiostatically deposited Cu$_2$O photocathode with film thickness is shown in figure 7.24. It is observed from the studies that the efficiency of potentiostatically deposited Cu$_2$O PEC solar cell increases rapidly with film thickness upto 3.0 $\mu$m and attain saturation slowly. These studies reveal that the optimum thickness to yield high efficiency is 3.0 $\mu$m.

7.8.2.e Flat band potential measurements

Figure 7.25 shows a representative $1/c_{sc}^2$ versus V plot (Mott-Schottky) for a typical potentiostatically deposited Cu$_2$O semiconductor thin film. The intercept on the voltage axis yields the value of flat band potential, $V_{fb}$ as 1.78 V vs SCE. Using Mott-Schottky plot, the important semiconductor
Fig 7.22 Current–Voltage characteristics of annealed Cu$_2$O films under various etching conditions (a) Unetching (b) Chemically etching (c) Photoetching followed by chemical etching
Table 7.6

Variation of solar cell parameters for various etching conditions in potentiostatic method

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Etching conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unetched</td>
<td>300</td>
<td>1.8</td>
<td>0.35</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>Chemically etched</td>
<td>365</td>
<td>2.2</td>
<td>0.40</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>Photoetch followed by chemical etching</td>
<td>380</td>
<td>3.0</td>
<td>0.55</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Fig 7.23 Effect of film thickness on open circuit voltage ($V_{OC}$) and short circuit current density ($J_{SC}$) for potentiostatically deposited Cu$_2$O film.
Fig 7.24 Variation of efficiency with thickness of potentiostatically deposited Cu$_2$O film.
Fig 7.25 Mott-Schottky plot for potentiostatically deposited Cu$_2$O film
parameters such as acceptor concentration \( N_A \) and depletion layer width \( W \) are estimated and presented in Table 7.7.

The flat band potential, \( V_{fb} \), was evaluated for a potentiostatically deposited \( \text{Cu}_2\text{O} \) photocathode by illuminating the semiconductor-electrolyte interface with a monochromatic light of wavelength 580nm in 1M KOH. The wavelength of 580nm was chosen in order to keep \( \alpha \) small, so that the condition \( \alpha L_p < 1 \) holds good. The linear plot of \( i_{\text{photo}}^2 \) versus potential \( V \) (figure 7.26) is extrapolated to a \( V_{fb} \) of 1.79 V vs SCE. This value is in good agreement with the value obtained from C-V studies.

### 7.8.2.f Quantum efficiency

Quantum efficiency measurements are necessary for the understanding of photoelectrochemical behaviour. Gartner's model of metal-electrolyte junction has been applied to the semiconductor-electrolyte interface to evaluate the important semiconductor parameters. The variation of quantum efficiency with the applied potential for \( \text{Cu}_2\text{O} \) electrodes annealed at different temperatures in air is shown in figure 7.27. It is observed from the figure 7.27 that the quantum efficiency increases with annealing temperature.

### 7.8.2.g Effect of doping

The electrolyte (0.45M \( \text{CuSO}_4 \)+3.25M lactic acid + NaOH) for the deposition of \( \text{Cu}_2\text{O} \) thin film was doped with 0.49 M \( \text{MgCl}_2 \) and then the films were deposited under optimum potentiostatic deposition conditions. The resultant doped \( \text{Cu}_2\text{O} \) film was used as photocathode in PEC cell and the
Table 7.7

Semiconductor parameters of potentiostatically deposited Cu₂O film

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Semiconductor parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flat band potential ((V_{fb}))</td>
<td>1.78V</td>
</tr>
<tr>
<td>2</td>
<td>Doping density ((N_A))</td>
<td>(4.0 \times 10^{14}) cm(^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>Depletion layer width ((W))</td>
<td>(5 \times 10^7) cm</td>
</tr>
<tr>
<td>4</td>
<td>Barrier height ((\phi_B))</td>
<td>0.78 eV</td>
</tr>
<tr>
<td>5</td>
<td>Band bending ((V_B))</td>
<td>0.40 V</td>
</tr>
</tbody>
</table>
Fig 7.26 Variation of $i_{\text{photo}}^2$ vs voltage for potentiostatically deposited Cu$_2$O film.
Fig 7.27 Variation of quantum efficiency with wavelength for potentiostatically deposited Cu2O films annealed at (a) 150°C (b) 250°C (c) 350°C
Fig 7.28 Spectral response of MgCl₂ doped Cu₂O films deposited by potentiostatic deposition technique
Fig 7.29   I-V characteristics of MgCl$_2$ doped potentiostatic Cu$_2$O film
Table 7.8

Solar cell parameters of doped Cu$_2$O film in potentiostatic deposition technique

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Solar cell parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Open circuit voltage ($V_{oc}$)</td>
<td>370 mV</td>
</tr>
<tr>
<td>2.</td>
<td>Short circuit current density ($J_{sc}$)</td>
<td>2.4 mA.cm$^{-2}$</td>
</tr>
<tr>
<td>3.</td>
<td>Fill factor (FF)</td>
<td>0.38</td>
</tr>
<tr>
<td>4.</td>
<td>Efficiency ($\eta$)</td>
<td>0.34%</td>
</tr>
</tbody>
</table>
spectral response of the film was studied. The observation of figure 7.28 shows enhanced spectral response for the doped film. The I-V characteristics of the doped film is shown in figure 7.29, which shows enhanced p-type photocurrent for the increasing applied potential. Doped film shows $V_{oc}$ of 370 mV and $J_{sc}$ of 2.4 mA. The improvement in cell parameters are due to the enhanced Cu ion vacancies within the film. The solar cell parameters due to the doped potentiostatically deposited Cu$_2$O thin film is shown in Table 7.8.

7.8.3 Pulse plated Cu$_2$O thin films

7.8.3.a Spectral response studies

Pulse plated thin films are found to be suitable for photovoltaic and photoelectrochemical solar cells. The important advantages of these materials are their high optical absorption, stability and suitable band gap for solar energy conversion. The fabrication and characterization of PEC solar cells based on pulse plated Cu$_2$O films are dealt in this chapter.

Deposition of Cu$_2$O thin films on Cu and SnO$_2$ substrates was carried out at a deposition potential of +0.4 V vs SCE for a deposition time of 5 minutes using pulsed technique. Due to higher rate of deposition films with lower grain sizes are yielded. Then resultant pulse plated film was used as photocathode in PEC cell and was illuminated from the front side by using 250W projector lamp and the spectral response of the film was studied. Figure 7.30 shows the spectral response of as-deposited pulse plated Cu$_2$O film electrode in a photoelectrochemical cell. Figure 7.30 shows p-type photocurrent for the entire spectral range of 500 to 1200nm, which agrees with the previous results on thermally grown Cu$_2$O film electrodes and
Fig 7.30  Spectral response of pulse plated Cu$_2$O film
Fig 7.31  Current-voltage characteristics of pulse plated Cu$_2$O film
galvanostatically and potentiostatically deposited Cu$_2$O electrodes. To find evidence for the photocurrent provided by the pulse plated films, the variation of current with the applied potential for pulse plated Cu$_2$O thin film photoelectrodes was studied.

Figure 7.31 shows the photocurrent vs potential behaviour of pulse plated Cu$_2$O thin films on Cu and SnO$_2$ substrates. The photocurrent increases with increasing positive potential which assures the p-type photocurrent produced by the Cu$_2$O thin films. The solar cell parameters for as-deposited Cu$_2$O film is shown in Table 7.9.

7.8.3.b Annealing effects on PEC parameters

Pulse plated Cu$_2$O films have shown promise as photoelectrodes for the conversion of solar energy into electricity through PEC cells. However, the performance of photovoltaic energy conversion systems has been shown to depend strongly on the treatment of the semiconductor electrode prior to use in the solar cells. Hence, pulse plated Cu$_2$O films were subjected to annealing in air at different temperatures between 150°C to 350°C. Due to annealing recrystallization process takes place, which causes incipient fusion of the crystallites and thereby yields film with larger grain size and hence reduces grain boundaries. Hence, annealing causes the production of Cu$_2$O films with lower resistivity in the case of pulse plated film than the Cu$_2$O films produced by other techniques such as galvanostatic and potentiostatic techniques.

Figure 7.32 shows the effect of annealing on the spectral response for samples annealed at 150°C, 250°C and 350°C for 30 minutes. As shown in
Fig 7.32  Spectral response of pulse plated Cu2O films annealed at
(a) 150°C  (b) 250°C  (c) 350°C
Fig 7.33  Current – Voltage characteristics of pulse plated Cu$_2$O films annealed at (a) $150^\circ$C (b) $250^\circ$C (c) $350^\circ$C
Table 7.9

Solar cell parameters of pulse deposited Cu$_2$O film

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Annealing conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As – deposited</td>
<td>80</td>
<td>0.4</td>
<td>0.10</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td>150°C</td>
<td>180</td>
<td>1.3</td>
<td>0.25</td>
<td>0.050</td>
</tr>
<tr>
<td>3</td>
<td>250°C</td>
<td>250</td>
<td>1.8</td>
<td>0.27</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>350°C</td>
<td>320</td>
<td>2.3</td>
<td>0.36</td>
<td>0.26</td>
</tr>
</tbody>
</table>
figure 7.32 the photocurrent for front illumination is p-type and the spectral response has been enhanced by annealing. The I-V characteristics of annealed films shown in figure 7.33 illustrates that the p-type photocurrent increases with increasing annealing temperature.

The effect of annealing temperature on the open circuit voltage ($V_{oc}$) was studied and shown in figure 7.34. The variation of open circuit voltage of Cu$_2$O photocathode PEC solar cell with heat treatment duration time for various annealing temperatures in air is shown in figure 7.34. It is observed from the figure that as the annealing time is increased, $V_{oc}$ increases and attain saturation. As a result of the heat treatment the photovoltage is increased from about 80 mV for unheated samples to 320 mV for heat treated samples.

Photoelectrochemical solar cell studies on annealed Cu$_2$O films exhibited best results for pulse plated Cu$_2$O films annealed in air at 350°C. Table 7.9 represents the solar cell parameters for annealed films. Figure 7.35 shows the variation of short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) on the annealing temperature. As shown in figure 7.35, $J_{sc}$ and $V_{oc}$ increases with annealing temperature.

7.8.3.c Etching effects on PEC parameters

The PEC cell consisted of the pulse plated photoelectrode (Cu$_2$O), a platinum counter electrode and a saturated calomel reference electrode. The electrolyte is an aqueous solution mixture of KI (1M) and I$_2$(0.01M). The as deposited and annealed Cu$_2$O photoelectrodes were etched chemically at 60°C for 15 seconds in a dilute acid mixture containing HCl, HNO$_3$, H$_2$SO$_4$
Fig 7.34 Variation of open circuit voltage ($V_{oc}$) with annealing time for pulse Cu$_2$O films annealed in air at various annealing temperatures (a) 150°C (b) 250°C (c) 350°C
Fig 7.35  Variation of open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$) with annealing temperatures for pulse-plated Cu$_2$O film
and CH$_3$COOH in the ratio 4:1:0.2:0.1 (by volume) and then rinsed in distilled water. The photoelectrodes were photoetched by illumination with polychromatic light in 0.5M Na$_2$SO$_4$ electrolyte at 0.1 V versus SCE for 5 seconds.

The current-voltage characteristics of annealed Cu$_2$O photoelectrode under various etching conditions is shown in figure 7.36. The photoelectrodes subjected to photoetching followed by chemical etching show higher current-voltage response. Also it exhibits much better results than galvanostatically and potentiostatically deposited film. Table 7.10 shows various solar cell parameters for pulse plated Cu$_2$O photoelectrode subjected to various surface treatments.

7.8.3.d Effect of film thickness on PEC parameters

The thickness of Cu$_2$O thin film influences the solar cell parameters. The effect of film thickness on $V_{oc}$ and $J_{sc}$ increases with thickness and attains saturation slowly after 3.0 $\mu$m (figure 7.37). The effect of film thickness on the efficiency of PEC solar cell based on pulse plated Cu$_2$O thin film is shown in figure 7.38. The efficiency of the cell increases rapidly with film thickness and attain saturation after 3.0 $\mu$m.

7.8.3.e Flat band potential measurements

Figure 7.39 shows a representative $1/C^2_{sc}$ versus V plot for a typical pulse plated Cu$_2$O thin film. The intercept on the voltage axis yields the value of flat band potential $V_{fb}$ as 1.8 V vs SCE. Using Mott-Schottky plot, the
Fig 7.36  I–V characteristic of annealed Cu$_2$O film etched under various etching conditions (a) Unetching  (b) Chemical etching  
(c) Photoetching followed by chemical etching
Table 7.10

Variation of solar cell parameters for various etching conditions in pulse method

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Etching conditions</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unetched</td>
<td>330</td>
<td>2.2</td>
<td>0.36</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>Chemically etched</td>
<td>400</td>
<td>2.7</td>
<td>0.43</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>Photoetch followed by chemical etching</td>
<td>430</td>
<td>3.5</td>
<td>0.58</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Fig 7.37  Effect of film thickness on open circuit voltage ($V_{oc}$) and short current density ($J_{sc}$) for pulse plated Cu$_2$O film
Fig 7.38  Variation of efficiency with thickness of pulse plated Cu₂O film
Fig 7.39  Mott-Schottky plot for pulse plated Cu$_2$O film
Fig 7.40 Variation of $i_{\text{photo}}^2$ with voltage for pulse plated Cu$_2$O film
important semiconductor parameters such as acceptor concentration ($N_A$) and depletion layer width ($w$) are estimated and presented in Table 7.11.

The flat band potential, $V_{fb}$, was evaluated for a typical pulse plated Cu$_2$O thin film photoelectrode by illuminating the semiconductor-electrolyte interface with a monochromatic light of wavelength 580 nm in KOH. The wavelength of 580 nm was chosen in order to keep $\alpha$ small, so that the condition $\alpha L_p << 1$ holds good. The linear plot of $i_{photo}^2$ vs potential $V$ shown in figure 7.40 is extrapolated to a $V_{fb}$ of 1.8 V vs SCE. This value is in good agreement with the value obtained from C-V studies.

7.8.3.f Quantum efficiency

Quantum efficiency measurements under monochromatic radiation ($\lambda$=580 nm) are performed in an aqueous solution of composition of 1M Na$_2$S, 1M KOH and 0.5M S. Quantum efficiency measurements are necessary for the understanding of photoelectrochemical behaviour. Gartner's model /141/ of the metal-electrolyte junction provides a successful description of the semiconductor-electrolyte interface for both single crystal and polycrystalline photoelectrodes.

The variation of quantum efficiency with the applied potential for pulse plated Cu$_2$O electrodes annealed at different temperatures in air is shown in figure 7.41. It is observed from the figure 7.41 that the quantum efficiency increases with annealing temperature.
Table 7.11
Semiconductor parameters of pulse plated Cu$_2$O film

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Semiconductor parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flat band potential ($V_{fb}$)</td>
<td>1.8 V</td>
</tr>
<tr>
<td>2</td>
<td>Doping density ($N_A$)</td>
<td>$6.1 \times 10^{14}$ cm$^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>Depletion layer width ($W$)</td>
<td>$8 \times 10^7$ cm</td>
</tr>
<tr>
<td>4</td>
<td>Barrier height ($\phi_B$)</td>
<td>0.81 eV</td>
</tr>
<tr>
<td>5</td>
<td>Band bending ($V_b$)</td>
<td>0.42 V</td>
</tr>
</tbody>
</table>
Fig 7.41 Variation of quantum efficiency with wavelength for pulse plated films annealed at (a) 150°C  (b) 250°C  (c) 350°C
Fig 7.42  Spectral response of MgCl₂ doped pulse plated Cu₂O films
Fig 7.43  \( I-V \) characteristics of \( \text{MgCl}_2 \) doped pulse plated \( \text{Cu}_2\text{O} \) films
Table 7.12

Solar cell parameters of doped Cu$_2$O film in pulse deposition technique

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Solar cell parameters</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Open circuit voltage ($V_{OC}$)</td>
<td>350 mV</td>
</tr>
<tr>
<td>2</td>
<td>Short circuit current density ($J_{SC}$)</td>
<td>2.00 mA.cm$^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>Fill factor (FF)</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>Efficiency ($\eta$)</td>
<td>0.26%</td>
</tr>
</tbody>
</table>
7.8.3.g Effect of doping

The electrolyte consisting of 0.45M CuSO₄, 3.25M lactic acid and NaOH was doped with 0.054M MgCl₂ and then the films were pulse plated under optimum conditions. The resultant doped film with lower resistivity was used as photocathode in PEC cell and the spectral response of the doped film is shown in figure 7.42, which shows enhanced photocurrent than annealed and sulphided films. The I-V characteristics of the doped film is shown in figure 7.43, which shows enhanced p-type photocurrent. Doped film shows \( V_{oc} \) of 350 mV and \( J_{sc} \) of 2 mA. The improvement in solar cell parameters are due to the enhanced Cu ion vacancies within the lattice. The solar cell parameters for doped pulse plated Cu₂O film is shown in Table 7.12.

7.9 Conclusions

The photoelectrochemical solar cells based on Cu₂O semiconducting thin films deposited under various techniques are fabricated and studied. The effect of annealing on solar cell parameters are studied and annealing in air resulted in an improvement in open circuit voltage, short circuit current density and efficiency. The lowering of sheet resistance by etching and doping resulted in the improvement of PEC parameters. The capacitance-voltage studies are performed and the Mott-Schottky plots are drawn for electrosynthesised Cu₂O thin films. Various semiconducting parameters are evaluated and the results are discussed.