CHAPTER-6
STUDIES ON PHOTOELECTROCHEMICAL SOLAR CELLS

6.1. INTRODUCTION

During the last two decades, interest in solar energy has considerably increased. This is because of the increasing demands of commercial energies due to increasing population, the depletion of the present sources of commercial energies – the fossil fuels and the current concern about pollution leading to environmental degradation, acid rains and global warming. Solar energy is unique as it is inexhaustible, nonpolluting and does not contribute to global warming. Harnessing solar energy has attracted the attention of scientists, economists and technologists of the world to counter the energy crisis. Much effort has been directed towards developing new and better solar energy conversion devices.

The solar photon conversion devices called solar cells can be classified into

(i) Solid-state photovoltaic (p/n junction) solar cells.
(ii) Metal-Semiconductor based Schottky barrier (M-S) solar cells, and
(iii) Semiconductor-liquid junction based photoelectrochemical (PEC) solar cells.

A high degree of sophistication has already been achieved in the fabrication of p-n junction solar cells [1]. The main problem that posed challenge to solar energy research is solar energy storage. Ever since Fujishima and Honda [2] 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, Gerischer [3] succeeded in direct conversion of solar energy into electricity, using the photoelectrochemical solar cells. The photoelectrochemical solar cells are inexpensive and they can be easily fabricated and a possibility exists of in-situ storage [4-17]. The promise of photoelectrochemical solar cells as an efficient source for clean power has remained unrealized because of non-availability of low bandgap non-corrosive photoeffective materials.

The PEC cells have some potential advantages over conventional solid state devices, e.g. in minimizing problems arising from lattice mismatch, in controlling the barrier height, easy method of fabrication, direct penetration of solar radiation to the active semiconductor surface and no requirement of antireflective coating. Therefore, PEC cells have received considerable attention as an alternative to solid state cells for the solar energy conversion purpose.

The necessity of testing new materials as photoelectrode for their possible applications in PEC based devices has been pointed out [18]. Various designs of PEC cells have been demonstrated [19-24]. The efficiency and suitability of PEC cells are strongly dependent on the preparation of the photoelectrode and electrolyte used. By systematic modification of the potassium cyanide electrolyte, Chandra Babu et.al. [25] have described in detail the feasible efficiency enhancement processes such as electrode surface modification, electrolyte modification etc. The conversion efficiency of n-CulnSe2/polysulphide cell has been found to be enhanced by 12% due to suitable modification of electrolyte [25].

p-type semiconductors such as p-InP have been proven to show efficient optical energy conversion [26,27]. The dark and photocorrosion behaviours of electrodeposited SnS films are discussed with the help of Pourbaix diagram [28]. The electrodeposition and photoconductance of SnSe from the aqueous and non-aqueous bath has been reported [29]. A 0.16% of photo-conversion
efficiency of p-SnSe in pellet form has been reported. The PEC effect of tin di
sulphide has been investigated [30]. The PEC behaviour of SnS0.5Se0.5 solid solution
has also been reported [31,32].

In this chapter, the principle and working of the PEC cells are outlined. In
addition, the behaviour of PEC cells fabricated using electrodeposited and brush
plated SnSe, SnS and SnS0.5Se0.5 thin films is studied and various
semiconductor parameters are evaluated and summarized. An attempt has been
made to improve the performance of these PEC devices using surface
modifications of the electrodes.

6.2. PRINCIPLE OF PHOTOELECTROCHEMICAL 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 semiconductor and the Fermi level of the electrolyte, which is taken
as the redox level. Bending of the bands at the surface of the semiconductor
takes place when the Fermi levels of the semiconductor and electrolytes are not
the same. At equilibrium the band bending is energetically equal to the initial
difference in Fermi levels and band bending may be favourable for observation of
efficient photocurrents.

Favourable band bending scheme is shown in Fig. 6.1 for p-type
semiconductors. The situation is equivalent to a Schottky between a
semiconductor and a metal [33], the redox electrolyte having the function of
metal in this case. In principle all semiconducting materials of n- or p-type
character can be used for a photo cell electrode when a suitable redox system is
found which induces, in contact with the particular semiconductor, the formation
of a depletion (or inversion) space charge layer. The stability of the electrodes or
other implications for practical use is decisive for the technical applicability.
Fig. 6.1. Band diagram under illuminated conditions for a p-type Semiconductor.

$E_c$ – conduction band edge, $E_f$ – Fermi level

$E_v$ – valence band edge $E^*_{\text{redox}}$ – Redox potential
If light with $h\nu \geq E_g$ falls onto the semiconductor and is absorbed in space charge region, electron hole pairs are generated. The two charge carriers move in opposite direction due to the electric field in the space charge layer. If they do not disappear by recombination, either by direct coulombic interaction or by collisions with other carriers on their path through the space charge layer, the electrons migrate to the bulk, the holes to the surface. Thus, n-type semiconductors are photoanodes and dark cathodes whereas p-type materials are photocathodes and dark anodes. In an ideal case the holes react at the interface exclusively with the electrolyte to oxidizing the electron donors reduction (Red) of the redox system. The various steps are described in the following equations (s.c.l = space charge layer):

Light absorption

$$h\nu + \text{s.c.l} \rightarrow h^+_{\text{s.c.l}} + e^-_{\text{s.c.l}} \quad (6.1a)$$

Recombination

$$h^+_{\text{s.c.l}} + e^-_{\text{s.c.l}} \rightarrow \text{heat} \quad (6.1b)$$

$$e^-_{\text{s.c.l}} \rightarrow e^+_{\text{bulk}} \quad (6.1c)$$

Charge separation

$$h^+_{\text{s.c.l}} \rightarrow h^+_{\text{surf}} \quad (6.1d)$$

Interfacial reactions

$$h^+_{\text{surf}} + \text{Red} \rightarrow \text{Ox}^+ \quad (6.1e)$$

$$e^-_{\text{surf}} + \text{Ox}^+ \rightarrow \text{Red} \quad (6.1f)$$

Reactions (6.1 f) of this series which occur only to such an extent as electron can reach the surface against the force of the electric field in the space charge layer, are important for the adjustment of the equilibrium situation at the electrode which needs the accumulation of a positive charge on the semiconductor.

A photovoltage is obtained under illumination at open circuit which can be measured while any reference electrode is brought in contact with the electrolyte. The generation of electric charge leads to a deviation from 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 6.1a, 6.1c and 6.1d are balanced by the steps 6.1b and 6.1f. Since the rates of reactions 6.1b and 6.1f increase with the decrease of band bending corresponding to an increase of the photovoltage, the open circuit photovoltage rises with illumination intensity. To exploit photovoltage, the semiconductor electrode has to be combined with a suitable counter electrode, which is a reversible redox electrode for the same redox system. The equilibrium is then controlled at both electrodes by the same redox potential, the Fermi levels being equal in both electrodes and in the electrolyte.

6.3. WORKING PRINCIPLES 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 at the electrode and reduction of the oxidized species at the counter electrode by the above reaction take place. In this ideal case, no net chemical charge 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 OX⁺ 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 bandgap $E_g$, but the operational efficiency depends on the relative rate of the 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) $e_{s.c.l}$, Energy loss due to the loss of charge carriers in the s.c.l.
(b) $e(l,R)$, Ohmic loss with $R = R_{int} + R_{ext}$
(c) $E_{r, redox} = Ev + e_{n_{s.c}} = Energy loss connected with reaction where n_{s.c} is the over voltage at semiconductor.
(d) $e.n_{c, e} = Energy loss connected with eqn (6.1 f) at the counter electrode due to overvoltage.

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 over voltages, including the concentration polarization. In addition, light losses by absorption outside the s.c.l and reflection losses in the electrolyte. These are some of the energy losses responsible for low efficiency of a PEC cell.

Photo assisted decomposition of water, using metal oxide semiconductors, usually of bandgap 3.0 eV uses only a small fraction of the light energy required to drive the reaction [34,35]. If PEC cells are to be used in solar energy conversion, visible light responsive systems are needed. To push up the efficiency of PEC cells using thin film electrodes, lot of studies are yet to be made.

6.4. EXPERIMENTAL REQUIREMENTS OF PEC CELLS

A standard three electrode (photoelectrode, SCE and a Pt counter electrode) set up is employed for PEC studies on semiconductor thin films. A simple one with a quartz window and with the position for the passage of gas and the electronic circuitry is shown in Fig. 6.2.a. A schematic PEC cell is shown in Fig. 6.2.b.

The methodology of PEC cells is more or less standardized at the present time. Before the actual construction and performance evaluation of the cell, detailed studies are carried out with respect to the materials preparation, evaluation, etching treatment, determination of the PEC parameters and the long
Fig. 6.2. (a) Standard three electrode set up for current-voltage (I-V) and capacitance (c) measurements (1) Semiconductor electrode (2) Saturated Calomel Electrode (SCE) (3) Platinum (counter) electrode (4) Quartz window for illumination of the photoelectrode (5) Electrolyte (6) Glass cell (7) Potentiostat (8) Null detector (9) Oscillator and (10) D.C. Power supply.  
(b) Schematic representation of a PEC Cell
term stability of the electrode as well as electrolytes under continuous irradiation. Proper choice of the constituent parts is necessary for the desirable functioning of the PEC cells. These aspects are presented below.

6.4.1. Electrode Materials

The electrode should have a thickness of the order of light absorption depth (~ 1-5 μm).

The photoelectrode should possess the following properties:

- Large absorption coefficient ($10^3$ to $10^4$ cm$^{-1}$)
- Smaller reflection and transmission coefficient
- Optimum value of bandgap (1.3 to 1.7 eV)
- Stable in electrolyte
- Large diffusion length for minority carriers
- Minimum recombination states
- Ohmic contact with metal surface

In addition to the above requirements, the film thickness, grain size and grain boundaries are to be controlled.

6.4.2. Surface Etching and Removal of Surface States

Polishing and etching of the electrode surface is an important step in the PEC studies. An etched surface gives a reticulate structure (‘matte’ surface) which is clean and helps in the absorption of light (by multiple reflections) by the semiconductor. Etching can also remove surface (electronic) states. It involves preferential (chemical) 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 semiconductor under irradiation 
(hv\geq E_{g}) has also been reported by many investigators [3,8,36,37].

6.4.3. Counter Electrodes

Platinum is the material of choice in most applications involving PEC and 
photo assisted electrode (PAE) cells although cheaper substitutes (e.g. brass, 
carbon) may function equally well for selected redox systems in PEC cells.

The counter electrode must possess the following properties:

a) Counter electrode should have very good electronic conductivity.
b) Low over potential of the reduction reaction.
c) Large area to avoid concentration polarization.
d) Chemically inert to the electrolyte.

6.4.4. Electrolyte

An electrolyte consists of oxidized and reduced species which help for the 
transfer of photogenerated carriers from photoelectrode to counter electrode. As 
the difference between E_{f} of semiconductor and E_{f} redox of an electrolyte defines 
the upper limit to photovoltage, the choice lies both for semiconductors and 
electrolytes. The aqueous electrolytes cause surface modifications and therefore 
molecular organic or inorganic solvents with supporting electrolytes and mixtures 
of totally ionic salt are the substituted electrolytes [37,38].

In order to select suitable electrolyte following aspects must be taken into 
consideration:

a) Oxidation-reduction potential
b) Electron transfer states of oxidized and reduced species.
c) Photo and thermal stability
d) Non-corrosive to electrode

e) Optical transparency

f) Fluidity, solubility and conductance

g) Non-reactivity to environment and cost.

6.5. APPLICATIONS OF PEC CELL

The trend in energy requirements of the world suggests that one would need two types of power sources (I) high power (in terms of megawatts), generated at one point and then distributed to different areas, and (ii) a portable low power (few watts) for running portable electronic instruments and portable light sources such as a torch. The photovoltaic solar cell perhaps could meet the need of a localized power generation system. The photovoltaic cell could, in principle, also meet the second requirement, but its production system will always be sophisticated and expensive. Whereas it is possible to develop a solar chargeable battery or a solar charger based on the principle of a PEC solar cell which can be cheap and its process of fabrication may be simple enough to be produced by small scale industry [17].

A PEC based solar cell, in principle, can be used: (i) for the generation of high power electrical energy, (ii) a low-powered solar chargeable battery, and (iii) a solar charger. But due to variety of reasons, it is almost certain that a PEC based solar cell can not be cheap enough to be used for the generation of high power electricity of the order of a few kW or so. But the PEC based solar cells can show their potentiality for two other purposes, i.e., a solar chargeable battery or a solar charger.

It is true, however, that there are many other applications of the PEC cells, such as photocatalytic degradation of carcinogenic organic compounds, synthesis of value-added organic compounds, etc.
6.6. ESTIMATION OF VARIOUS PEC PARAMETERS

6.6.1. $V_{oc}$ – The Open Circuit Voltage

In PEC cells, the photoeffect is exhibited as the photovoltage and photocurrent on illumination of the semiconductor 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 a photoelectrode is the shift in the potential of the electrode (with respect to SCE or counter electrode) on illumination. In the case of p-type semiconductors, the shift will be towards positive direction (with respect to SCE). The shift will be negative in the case of n-type semiconductors. For a good single crystal electrode exhibiting near ideal PEC behaviour, dark potential will be zero. For polycrystalline discs or thin film electrodes, which also do not possess good electronic conductivity ($\rho > 10^3$ ohm cm), 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 eqn. (6.2) for a given semiconductor

$$V_{oc} (\text{max}) = E_B = \left| E_F - E^o \right|$$

(6.2)

where $E^o$ is the redox potential of the electrolyte and $E_B$ is the magnitude of the height of the potential barrier (extent of band bending). Similarly, a sharp onset of photocurrent (at zero or non-zero applied bias with respect to counter electrode) on irradiation and sharp drop (in the light ‘off’ position) after irradiation is a good PEC behaviour in a semiconductor electrode.

6.6.2. Current-Voltage Characteristics

The potentiostatic current-voltage curve of the semiconductor electrode, usually obtained by impressing different voltage on the semiconductor (w.r.t.
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 photoresponsive n-type semiconductor. The saturation of \(I_{\text{ph}}\) is due to the rate 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-hole pair recombination. The magnitude of \(I_{\text{ph}}\) depends on the light intensity \(I\) as given in equation (6.13) and as a first approximation \([39]\).

\[
I = I_{\text{ph}} - I_o \exp \left( \frac{q I_{\text{sc}} R_s}{A k T} \right) \quad (6.3)
\]

where
- \(R_s\) is the series (internal) resistance of the cell
- \(q\) is the charge on the electron
- \(I_{\text{sc}}\) is the short circuit current
- \(k\) is the Boltzmann constant
- \(T\) is the absolute temperature
- \(I_o\) 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 \([40,41]\).

\[
V_{\text{oc}} = \frac{kT}{q} \ln \left( 1 + \frac{P}{P_0} \right) \approx \frac{kT}{q} \frac{P}{P_0} = \frac{kT}{q} \tau \quad (6.4)
\]

where \(P_0\) is the density of holes in the bulk of the semiconductor, \(P\) is the increase in hole density on illumination, \(\tau\) is the proportionality factor and \(I\) is the light intensity.

For a given wavelength (monochromatic) and intensity (photon flux, \(\phi_o\)), the \(I_{\text{ph}}\) is related to the flat band potential, \((V_{\text{fb}})\) as per the Gartners' equation \([42]\).
\[ I_{ph} = q\phi_0 \left[ \frac{\exp[-\alpha W_o(V-V_{fb})^{1/2}]}{1 + \alpha L_p} \right] \]  

(6.5)

where \( \alpha \) is the optical absorption coefficient of the semiconductor; \( W_o \) is the depletion layer width for a potential of one volt across the semiconductor and can be expressed as

\[ W_o = \left[ \frac{2\varepsilon \varepsilon_0}{qN_A} \right]^{1/2} \]  

(6.6)

where \( \alpha \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of free space and \( N_A \) is the electron carrier concentration. \( V \) in equation (6.5) is the applied potential (relative to SCE) and \( L_p \) is the hole (minority carriers in the case of p-type semiconductor) diffusion length.

### 6.6.3. Flat Band Potential \( V_{fb} \)

The flat band potential is an important parameter of the semiconductor in a PEC cell. In an liquid junction solar cell (LJSC) \( V_{fb} \) enables to estimate the maximum \( V_{oc} \) obtainable. \( V_{fb} \) can be estimated either from potentiostatic I-V curves or the electrode capacitance measurements or both. These are described below.

(i) \( V_{fb} \) determination from i-v curves

Rough estimate of \( V_{fb} \) is obtained from the voltage at which \( I_{ph} \) onset occurs in the potentiostatic I-V curve. More accurate value of \( V_{fb} \) can be obtained by plotting \( I_{ph} \) vs \( V \) and extrapolating to zero photocurrent, provided \( I_{ph} \) measurements are done at monochromatic radiation and \( h\nu = h\nu_0 \geq E_g \). This follows by a consideration of equation (6.5) as follows.
when $\alpha W_0 (V-V_{fb})^{1/2} \ll 1$, equation (6.5) can be reduced to

$$(I_{ph} / \alpha W_0 qF_0) \propto (V-V_{fb})^{1/2}$$

and hence $i^2 \propto (V-V_{fb})$

However, it should be noted that the accuracy of the linear extrapolation relation between $I_{ph}^2$ and $V$ increases for increasing wavelength and hence decreasing $\alpha$. This implies that measurements are done nearer to $E_g$ and the data points retained in a region with a small band bending should be used for extrapolation to give $V_{fb}$ [43].

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

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 [44,45].

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

(6.7)

And hence $1/C^2$ is proportional to $(V-V_{fb})$. 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, $N_D$ can also be calculated from the slope of this $C^{-2}$ vs $V$ plot.

**6.6.4. Other Parameters Derived from MS-Plots**

Though the measurement of capacitance as a function of applied bias is simple, many useful parameters are deduced from these measurements.
(a) Type of conductor

The signs of the slope of \(1/C_{sc}^2\) versus \(V\) plots would be different for \(n\)-and \(p\)-type semiconductors. Hence, type of conductivity may be deduced from MS-plot.

(b) Acceptor density

Using the intercept and slope, the values of acceptor density are deduced.

(c) Band bending

The maximum open-circuit voltage \((V_{oc})\) obtainable from a PEC solar cell is obtained from an important parameter known as band bending \(V_b\) as

\[
V_b = (E_{f\text{\,redox}}/e) - V_f \tag{6.8}
\]

where \(E_{f\text{\,redox}}\) is the Fermi level associated to a particular redox species, given by

\[
E_{f\text{\,redox}} = -(4.5\ eV_{NHE} + eV_{\text{redox}}) \tag{6.9}
\]

(d) Depletion layer width

If \(V_f\) and \(N_A\) are known, then the width of the majority carrier depletion layer \(W\) can be calculated using the relation

\[
W = \sqrt{\frac{(2\epsilon_o\epsilon_a / eN_A) (V-V_f - kT/q)}} \tag{6.10}
\]

(e) Position of band edges

The electron and hole density in the conduction and valence bands are given by

\[
\begin{align*}
    n_o &= N_c \exp\left[-\frac{(E_c - E_f)}{kT}\right]; \\
    p_o &= N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right]
\end{align*} \tag{6.11}
\]
where \( N_c \) and \( N_v \) are the density of states for conduction and valence band and \( E_c \) and \( E_v \) are the conduction and valence band edges respectively. The band edges are given by

\[
E_c = E_F - kT \ln (n_0 / N_c); \\
E_v = E_F + kT \ln (p_0 / N_v)
\] (6.12)

For a semiconductor electrode in contact with an electrolyte in equilibrium, \( E_F = E_{f,\text{redox}} \) and hence we can determine \( E_c \) and \( E_v \) using equation (6.12).

The I-V output can be represented by a single diode model with \( R_s \) and \( R_{\text{sh}} \) factors. This gives the five parameters of a solar cell. The photocurrent \( I_{\text{ph}} \) is delivered by the solar cell under illumination which flows in the diode impedance, the series resistance \( R_s \) and the shunt resistance \( R_{\text{sh}} \). For a given intensity of illumination, the voltage (\( V \)) produced and the current (\( I \)) delivered are given by the equation

\[
I = I_o \left[ \exp \left( \frac{V - IR_s}{A} \right) - 1 \right] + \frac{V - IR_s}{R_{\text{sh}}} - I_{\text{ph}}
\] (6.13)

where \( I_o \) is the reverse dark saturation constant.

\( A \) is the diode quality factor
\( B = q / kT \) where \( q \) is the electronic charge
\( k \) is the Boltzmann constant = 1.38 x 10\(^{-14}\) eng k\(^{-1}\)
\( T \) is the absolute temperature = 300 K

The open circuit voltage \( V_{\text{oc}} \) is obtained from the intercept with current axis. The series resistance \( R_s \) and the shunt resistance \( R_{\text{sh}} \) are given by the slope of the curve at \( I = 0 \) where \( V = V_{\text{oc}} \) and at \( V = 0 \) where \( I = I_{\text{sc}} \) respectively. \( V_m \) and \( I_m \) are the experimental values of the voltage and current at the maximum power point. \( I_{\text{ph}} \) is the current produced under illumination which is flowing against the diode current.
6.6.5. Power Characteristics (I vs V plots)

Power characteristics of an LJSC 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. In this section, a review on SnSe film is given first followed by the experimental results relating to PEC solar cells such as flat band potential, photoresponse, I-V studies etc. Then, from the I vs V plots, the efficiency of LJSC’s and fill factor (FF) can be calculated by using the equations.

\[
\eta(\%) = \left(\frac{I_{\text{max}} \times V_{\text{max}}}{P_{\text{input}}}\right) \times 100 \tag{6.14}
\]

\[
\text{FF} = \left(\frac{I_{\text{max}} \times V_{\text{max}}}{I_{\text{sc}} \times V_{\text{oc}}}\right) \tag{6.15}
\]

\[
\frac{dI}{dV}|_{V=0} \approx \frac{1}{R_{\text{sh}}} \tag{6.16a}
\]

\[
\frac{dI}{dV}|_{V=0} \approx \frac{1}{R_{\text{sh}}} \tag{6.16b}
\]

where \((I_{\text{max}} \times V_{\text{max}})\) is the maximum output power of the solar cell, \(P_{\text{input}}\) is the light (optical power) input.

A computer simulation programme has been developed using VISUAL BASIC to extract the PEC parameters for all the films deposited by electrodeposited and brush plated techniques.

6.7. STUDIES ON TIN CHALCOGENIDE PEC SOLAR CELLS

During the past two decades much work has been done on photoelectrochemical (PEC) systems in search of suitable Liquid Junction Solar Cells (LJSC). A lot of research interest has been also inspired by the unique opportunities that PEC cells offer in the study of energetics and the chemistry of semiconductor-electrolyte interfaces. The characterization of tin chalcogenide thin films photoelectrodes used in PEC cells is essential for their optimization.
The spectral response in the wavelength range 400 to 1100 nm has been studied using narrow band width interference filters (Oriel, USA). The incident light intensity on the sample surface for different wavelengths is measured with an Oriel thermopile, USA in milli watts (mW/cm²); the photon flux is then calculated. The results of studies conducted to characterize the photoelectrochemical behaviour of the electrodes are dealt in this chapter.

6.7.1. Experimental Details

A conventional single compartment photoelectrochemical cell was formed by using SnSₓSe₁₋ₓ photoelectrodes (1.5 cm²) with x = 0, 0.5 and 1.0 prepared by both electrodeposition and brush plating technique. They were used as photocathodes. Ohmic contacts were made on thin films with 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 surface 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. Platinum counter electrode (2.5 cm²) and saturated calomel electrode (SCE) as a reference electrode are used in the PEC cell as shown in Fig. 6.2. The electrodes were immersed in different electrolytes as follows.

0.1M (Na₂S-S-NaOH); 0.1M [K₃Fe(CN)₆ - K₄Fe(CN)₆]; 0.1M (KI-I₂) and 0.1M (FeCl₂ - FeCl₃), 0.05M H₂SO₄. Preliminary PEC studies are carried out for these electrolytes to choose the most suitable electrolyte for best conversion efficiency and stability. It is found that 0.1M (FeCl₂ - FeCl₃), 0.05M H₂SO₄ is the most suitable electrolyte which shows photoactivity and the layers are very stable in this electrolyte. Based on this observation, all the PEC related studies have been carried out using the electrolyte 0.1M (FeCl₂ - FeCl₃), 0.05M H₂SO₄ unless otherwise stated.
6.7.2. Tin Selenide Thin Films

6.7.2.1. Review of earlier work on SnSe

p-SnSe was prepared from its elements by a vapour transport method. SnSe was found to be chemically and photochemically stable in acidic solutions [46]. It was observed that Fe$^{3+}$, Fe$^{2+}$ (0.5M H$_2$SO$_4$) redox electrolyte and a platinum counter electrode are the most suitable for constructing a PEC cell with p-SnSe [26]. Nevertheless, the efficiency of the reduction process of Fe$^{3+}$ ions at the illuminated SnSe was studied to improve the overall charge-transfer reaction occurring at the interface of the semiconductor and electrolyte. A PEC cell of the type p-SnSe/Fe$^{2+}$, Fe$^{3+}$ (0.5M H$_2$SO$_4$) / Pt was designed to measure the photocurrent and the photovoltage outputs for the efficiency studies. A 250W tungsten halogen lamp with a water filter was used as the power input ($I_{input}$, 12 mW cm$^{-2}$). The cyclic voltammetric curves as well as photocurrent vs time plots of p-SnSe electrodes indicated the slow photoresponse of the system. A similar behaviour of the electrode was observed with low mobility n-SnS based PEC cells by Sharon and Basavaswam [46]. The maximum power efficiency and the fill factor were calculated from the I-V characteristics of the cell and were found to be 0.16% and 0.19 respectively. The low efficiency of the cell was attributed to the low carrier concentration.

The cyclic voltammetric curves in a 0.1M Fe$^{3+}$, Fe$^{2+}$ redox system with platinum, as well as in dark and illuminated conditions of p-SnSe electrodes showed that the cathodic current was found to be light intensity dependent, as expected for a p-type semiconductor. However, an anodic current was observed in the dark as well as under illuminated conditions (beyond the potential of +0.5V). The small anodic current could be due to either the photooxidation of anion impurities present in the redox couple or a strong absorption of ions on the electrode surface [47,48]. The photocurrent method was used to determine the bandgap of the semiconductor. The photocurrent was measured from 200 nm to 950 nm [49]. The value of 1.04 eV recorded was close to the values obtained
from reflectance (0.9 eV) and conductivity (0.85 eV) methods [46]. The flat-band potential, using the Mott-Schottky relation [44,45], was determined for the system p-SnSe/Fe$^{3+}$,Fe$^{2+}$ / Pt, and found to be 0.66 V (SCE). The acceptor concentration $N_A$, was calculated as $1.55 \times 10^{18} \text{cm}^{-3}$. This value differed from the value of $5.55 \times 10^{16} \text{cm}^{-3}$ obtained from Hall effect studies. The width of the space charge layer was calculated to be $2.425 \times 10^{-5} \text{cm}$.

SnSe films were electrodeposited onto stainless steel substrates and the photoconductivity was studied by constructing a PEC cell using Fe$^{3+}$/Fe$^{2+}$ electrolyte [50]. The films showed p-type semiconducting nature. Flat band potential of the constructed PEC cell was 0.7 V (SCE). The current-voltage (I-V) characteristics were obtained in dark and under illumination (80 mW/cm$^2$). The estimated energy conversion efficiency and the fill factor were 0.0104 % and 0.54 % respectively. The low efficiency was attributed to the presence of surface states and grain boundaries which can act as recombination centres for the photogenerated carriers [51,52]. The value of the junction ideality factor ($A$) calculated from the graph of log($I$) vs $V$ was found to be 4.0.

A new technique to measure surface conductivity of pellets or thin films was developed [53] which can also provide (i) flat-band potential at a desired pH, (ii) barrier height developed at the interface of semiconductor-electrolyte at any desired pH and (iii) flat-band potential at a desired surface change present at the semiconductor. A model has been developed to explain the mechanism of surface conductivity of a semiconductor, such as n-$\alpha$-Fe$_2$O$_3$ or n-SnS or p-SnSe.

6.7.2.2. 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. Flat band potential is estimated for SnSe
photoelectrodes by using the capacitance – voltage measurements and also from
the $I_{ph}^2$ versus $V$ curve.

In Fig. 6.3 Mott-Schottky (M-S) plots obtained for the SnSe films are shown. The negative slope nature of the M-S plots shows that both the electrodeposited and brush plated SnSe films are of p-type. The intercept on the voltage axis yields the value of flat band potential $V_{fb}$ as 0.67 V(SCE) for electrodeposited and 0.7 V(SCE) for brush plated SnSe film which are in good agreement with the reported values of $V_{fb} = 0.7$ V(SCE) for SnSe film [46]. Using M-S plot, the important semiconductor parameters such as acceptor concentration ($N_A$) and depletion layer width ($W$) are estimated and presented in Table 6.1.

6.7.2.3. Current-voltage characteristics of SnSe

To investigate the nature of the junction formed with SnSe and the electrolyte, dynamic current-voltage ($I$-$V$) characteristics of the PEC cell are studied. The potentiostatic current-voltage ($I$-$V$) curve of the semiconductor electrode, usually obtained by impressing varying voltages on the semiconductor and measuring the current both in dark ($I_d$) and under illumination ($I_{ph}$) provides important informations. It is observed from the Fig.6.4 that the curves obtained for the film under illumination are shifted to higher current region. It indicates that the films prepared by the electrodeposition and brush plating technique have high photosensitivity. The log $I$ versus $V$(SCE) plot is shown in Fig. 6.5.

The junction ideality factor, $A$, estimated from this plot is found to be equal to 1.9 for electrodeposited film and 1.7 for brush plated film. The nature of the curve implies that the junction formed is a rectifying one.
Fig.6.3. Mott-Schottky plot for the electrodeposited (A) and brush plated (B) p-SnSe/Fe^{3+},Fe^{2+}/Pt systems at a frequency of 1 kHz
Table-6.1

Summary of results obtained from Mott-Schottky plots of p-SnSe films

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Physical Parameter</th>
<th>Electrodeposited SnSe</th>
<th>Brush plated SnSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Electrolyte used</td>
<td>Fe^{3+} / Fe^{2+}</td>
<td>Fe^{3+} / Fe^{2+}</td>
</tr>
<tr>
<td>2.</td>
<td>Redox Fermi level of the electrolyte E_F redox V(SCE)</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td>3.</td>
<td>Flat band potential, (V_f) V(SCE)</td>
<td>0.67</td>
<td>0.70</td>
</tr>
<tr>
<td>4.</td>
<td>Acceptor concentration (N_A) (cm^{-3})</td>
<td>6.9 \times 10^{16}</td>
<td>7.7 \times 10^{16}</td>
</tr>
<tr>
<td>5.</td>
<td>Density of states in the valance band, (N_V) (cm^{-3})</td>
<td>4.05 \times 10^{19}</td>
<td>4.1 \times 10^{19}</td>
</tr>
<tr>
<td>6.</td>
<td>Built in Voltage (band bending) (V_b) (Volt)</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>7.</td>
<td>Depletion width (W) (cm)</td>
<td>5.6 \times 10^{-5}</td>
<td>5.3 \times 10^{-5}</td>
</tr>
<tr>
<td>8.</td>
<td>Carrier type</td>
<td>p</td>
<td>p</td>
</tr>
</tbody>
</table>
Fig. 6.4. Current-voltage (I-V) characteristics for the electrodeposited (A) and brush plated (B) p-SnSe/Fe^3+,Fe^2+/Pt.

Fig. 6.5. The plot of log I versus V for the PEC cell formed using electrodeposited (A) and brush plated SnSe films.
6.7.2.4. Photoresponse

$I_{sc}$ and $V_{oc}$ are noted as a function of light intensity and plotted to study the photoresponse of the PEC cell as shown in Fig.6.6. The equivalent circuit diagram of the cell implies that the short circuit current ($I_{sc}$) varies linearly with light intensity. From Fig. 6.6. it is seen that $V_{oc}$ increases linearly with increasing intensity of light and $I_{sc}$ saturates at higher intensity. This clearly shows the dependence of $V_{oc}$ on the extent of band bending and change in photo Fermi level of photoelectrode when exposed to light.

6.7.2.5. $I_{ph}^2$ versus potential (V) plot

The flat band potential $V_{fb}$ was evaluated for the electrodeposited and brush plated SnSe photoelectrodes (Fig.6.7) by illuminating the semiconductor/electrolyte interface with a monochromatic light of wavelength 580 nm in 1M 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 $I_{ph}^2$ versus potential $V$(SCE) is extrapolated to intercept the x-axis. The flat band potential value of $V_{fb}$ of 0.66 V(SCE) for electrodeposited and 0.69 V (SCE) for the brush plated film has been obtained. These values are in good agreement with the values of 0.67 for electrodeposited and 0.70 for brush plated films obtained from C-V studies.

6.7.2.6. Spectral response

Spectral response study is important in the sense that it enables to identify the recombination centres and consequently in diagnosing the problems that have influence on the conversion efficiency [54]. Ideally, the normalized spectral response is flat at wavelengths below the edge limit and is independent of the irradiance.
Fig. 6.6. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with intensity of illumination for the PEC cell formed using p-SnSe electrode.

- $O$: electrodeposited SnSe film
- $\triangle$: brush plated SnSe film
Fig. 6.7. Variation of $I_{\text{photo}}^2$ versus potential for the electrodeposited (A) and brush plated (B) SnSe films.

Fig. 6.8. Variation of photocurrent (I) with wavelength ($\lambda$) for the PEC cell formed using electrodeposited (A) and brush plated (B) SnSe films.
The spectral response of the cell was studied by recording short circuit photocurrent as a function of wavelength (\(\lambda\)) of the source and is illustrated in Fig.6.8. The \(I_{sc}\) values are found to increase up to the region of 1150 - 1200 nm and then decreased.

The estimated bandgap of SnSe corresponding to the peak photocurrent is 1.01 eV for electrodeposited SnSe film and 1.03 eV for brush plated films which is in good agreement with the value reported from the optical absorption studies in chapter 5.

The decay of the photocurrent towards the shorter wavelength side may be due to the absorption of the incident light by the electrolyte or due to large amount of the surface recombination of the photo generated minority carriers. Similarly, the sharp decay of photocurrent towards the longer wavelength side is attributed to the poor absorption of light of short wavelength by the photoelectrode [54].

6.7.2.7. Annealing effects on PEC parameters – SnSe films

The as-prepared SnSe films show very poor performance in PEC conversion of solar energy due to the internal defects present in polycrystalline materials as compared to single crystals. A considerable amount of carriers generated is lost due to recombination in the intergrain regions of the bulk. This loss can be minimized by the heat treatment in air or in an inert atmosphere or in vacuum. This will cause an increase in size of the crystallites, reduction in grain boundaries, incipient fusion of the crystallites and removal of point defects at the grain boundaries. Consequently the generation and life time of the carriers would be increased. Besides, annealing increases the adhesion of the films to substrate which is essential for the PEC electrode. In the present work, annealing of the films has been carried out in air and vacuum and their influence on the PEC parameters.
Annealing was carried out at 150, 200 and 250°C for different heating durations varying from 5 to 30 min. The $V_{oc}$ values increase exponentially up to an annealing time of 15 min and then show a low variation. Saturation is observed at 30 min for both air and vacuum annealing. This is in conformity with the observation that the stoichiometric SnSe films are obtained after annealing for 30 min as given in chapter 4.

The effect of annealing on $V_{oc}$ for the electrodeposited and brush plated SnSe films are shown in Fig. 6.9 and 6.10. It is observed that vacuum annealing produces better output compared to that of air annealed films. It is evident that the $V_{oc}$ for air annealed factor is 0.13 V and that for the vacuum annealed film is 0.21 V for the electrodeposited films. The same behaviour is observed for the brush plated films annealed in air and vacuum. The $V_{oc}$ of air annealed film is 0.27 V whereas for the vacuum annealed film is 0.25 V. This shows that vacuum annealing provides more advantageous results compared to air annealing. Further the brush plating technique yields SnSe films of better quality than the films produced by the electrodeposited techniques.

Fig. 6.11 and 6.12 show the $I_{sc}$ values observed for the electrodeposited and brush plated films. Annealing was carried out in air and vacuum at temperatures 150, 200 and 250°C for different durations. The $I_{sc}$ value is higher for the vacuum annealed films and shows the same trend as that for $V_{oc}$. The discussion given earlier holds good for this also.

The variation of $V_{oc}$ and $I_{sc}$ with temperature for the electrodeposited SnSe films annealed in vacuum for 30 min is shown in Fig. 6.13. The maxima for both occur for annealing temperature of 200°C. The same result is observed for the brush plated SnSe films also as shown in Fig. 6.14.
Fig. 6.9. Variation of open circuit voltage ($V_{oc}$) with annealing time for the electrodeposited SnSe film.

Fig. 6.10. Variation of open circuit voltage ($V_{oc}$) with annealing time for the brush plated SnSe film.
Fig. 6.11. Variation of short circuit current ($I_{sc}$) with annealing time for the electrodeposited SnSe film.

Fig. 6.12. Variation of short circuit current ($I_{sc}$) with annealing time for the brush plated SnSe film.
Fig. 6.13. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the electrodeposited SnSe film.

Fig. 6.14. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the brush plated SnSe film.
These observations reveal that annealing in vacuum produces better results compared to air annealing. Based on these results, the optimized annealing temperature in vacuum is found to be 200°C and the duration is 20 min for both the electrodeposited and brush plated SnSe films.

6.7.2.8. Effect of film thickness on PEC parameters

The PEC output has been recorded for the electrodeposited and brush plated SnSe films with varying thickness. The $V_{oc}$ and $I_{sc}$ variation of electrodeposited SnSe films are shown in Figure 6.15. Both values increase continuously up to a thickness of about 1.0 $\mu$m and then show nearly no variation up to a thickness of 1.5 $\mu$m. It shows that SnSe films of thickness 1.0 to 1.2 $\mu$m, prepared by electrodeposition technique, are capable of giving good PEC output. The maximum values of $V_{oc}$ and $I_{sc}$ are 0.17 V and 1.0 mA respectively.

Figure 6.16 shows the $V_{oc}$ and $I_{sc}$ variations with thickness for the brush plated SnSe films. The variation is linear and steep up to about 1.7 $\mu$m and then saturation has been observed up to about 2.5 $\mu$m. This reveals the fact that SnSe films of thickness in the range 1.7 to 2.0 $\mu$m may be the optimum for getting maximum $V_{oc}$ and $I_{sc}$ values through the brush plating route. The observed values of $V_{oc} = 0.25$ V and $I_{sc} = 1.1$ mA are higher than the values obtained for the electrodeposited SnSe films.

6.7.2.9. Effect of etching on PEC parameters

Etching of semiconductors is carried out to remove damaged surface layers and study the defect structure of the semiconductor. In particular for the PEC solar cell applications, etching plays an important role in removing the damaged surface layers.
Fig. 6.15. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the electrodeposited SnSe film.

Fig. 6.16. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the brush plated SnSe film.
The vacuum annealed films are etched chemically at 50°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 rinsed in triple distilled water. The photoelectrodes are dipped into a 0.1M FeCl₃-FeCl₂, 0.05M H₂SO₄ bath to remove oxidation products of the chemical etching. Finally the electrodes are rinsed in triple distilled water.

A few of these chemically etched electrodes are additionally subjected to photoetching in 0.1M FeCl₃-FeCl₂, 0.05M H₂SO₄ bath under white light illumination. The current-voltage measurement was carried out on annealed SnSe photocathodes under the following conditions.

(i) Without etching
(ii) Chemical etching, and
(iii) Photoetching

The current-voltage characteristics of the electrodes under the above conditions are shown in Fig. 6.17. The I-V output for unetched film shows an open circuit voltage of 0.26 V and short circuit current of 1.23 mA as seen from the curve (a). The PEC output for chemically etched SnSe films is improved as shown in (b). The improvement on the surface due to chemical etching enhances the output characteristics. The possible explanation can be given as: The dissolution of Sn²⁺ is effected due to the oxidation of surface layer by the photogenerated holes. In turn, Se layer is formed on the film surface and blocks the current flow in a PEC cell. Chemical etching removes the surface damages and results in the formation of a very thin Se layer on the electrode surface which is removed by the dissolution process taking place in aqueous electrolyte bath.

The output for the photoetched SnSe films is further enhanced. This is attributed to the fact that the photoetching further removes the surface damage,
Fig. 6.17. Power output characteristics of PEC cells using electrodeposited SnSe films
Fig. 6.18. Power output characteristics of PEC cells using brush plated SnSe films.
surface states and traps thereby enhances the PEC output. Further the photoetching of the annealed film improves its mobility and minority carrier diffusion length which in turn increases the I-V output slightly more as shown in Fig. 6.17 (c). The I-V output of the PEC cells fabricated using the brush plated SnSe films and etched are given in Fig. 6.18. A comparison of the curves shows the same trend as that for the electrodeposited films. However, the PEC output are higher than that for the electrodeposited SnSe films under all etching conditions. This observation confirms the better film quality of the brush plated films and supports the previous results on various parameters.

6.7.2.10. PEC parameters of SnSe photocathodes

The power characteristics of SnSe photoelectrodes are studied by carrying out I-V characteristics at various intensities. The current and voltage through the PEC solar cells were measured at various loads and the efficiency of PEC cells was estimated through the relation given in section 6.6.5. The I-V analysis of the best PEC cells, using electrodeposited and brush plated SnSe films, surface modified by photoetching has been done. The experimental PEC values are presented in Table 6.2 and 6.3 for electrodeposited and brush plated films respectively. It is observed from the tables that efficiency is improved much for the photoetched films. The overall low efficiency may be attributed to the low carrier concentration and low mobility of the carriers, high densities of the surface state and grain boundaries which can act as recombination centres for photogenerated carriers. The higher series and considerably lower shunt resistance values of the PEC cell also put the limitation on the efficiency of the cell [1].

Simulation programme has been used to simulate the PEC parameter for the PEC cells fabricated using photoetched SnSe films which show the best output performance of all the PEC cells. The simulated parameters are given in
### Table-6.2
PEC parameters obtained from power output plots of electrodeposited SnSe film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.2</td>
<td>0.26</td>
<td>0.34</td>
<td>0.11</td>
<td>81</td>
<td>315</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>1.3</td>
<td>0.24</td>
<td>0.41</td>
<td>0.13</td>
<td>113</td>
<td>486</td>
</tr>
<tr>
<td>Photoetching</td>
<td>1.6</td>
<td>0.29</td>
<td>0.43</td>
<td>0.19</td>
<td>42</td>
<td>437</td>
</tr>
</tbody>
</table>

### Table-6.3
PEC parameters obtained from power output plots of brush plated SnSe film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.3</td>
<td>0.28</td>
<td>0.38</td>
<td>0.14</td>
<td>55</td>
<td>500</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>1.45</td>
<td>0.27</td>
<td>0.40</td>
<td>0.16</td>
<td>8</td>
<td>416</td>
</tr>
<tr>
<td>Photoetching</td>
<td>1.8</td>
<td>0.32</td>
<td>0.43</td>
<td>0.25</td>
<td>31</td>
<td>625</td>
</tr>
</tbody>
</table>
Table 6.10. A good agreement is observed between the experimental and simulated PEC parameters for the photoetched SnSe photoelectrode films.

6.7.3. Tin Sulphide Thin Films

In the following sections, a review of the properties of SnS films prepared by different techniques are presented. Then the results obtained from the I-V and M-S studies of the SnS films deposited in the present work by electrodeposited and brush plated techniques are presented.

6.7.3.1. Review of earlier work on SnS

The photoactivity of SnS thin films was prepared by room-temperature electrodeposition technique on indium tin oxide coated substrates [28]. A well-behaved semiconductor electrode is expected to show rectifying behaviour in the polarization region corresponding to minority carrier current flow [55]. Polarisation curves for the SnS thin film samples in a Fe(CN)$_6^{3/4-}$ redox electrolyte revealed partial rectification for cathodic current flow through the sample in the dark. This incomplete rectification is attributable to defects (e.g., grain boundaries) in the (polycrystalline) thin film. Dark measurements quickly established the SnS samples as p-type. PEC measurements were done on SnS in contact with a S$_2$O$_3^{2-}$ redox electrolyte. The photocurrent onset was observed at ~0.35 V. The shape of the photocurrent spike was discussed [56].

Photoaction spectrum of SnS electrode showed a gradual rise in the photocurrent near the band edge is indicative of an indirect bandgap material. A value for the indirect bandgap of 1.10 eV is obtained. SnSe is also characterised by an indirect bandgap in the same energy range.

Dark and photocorrosion behaviour of SnS films was discussed with the aid of Pourbaix diagrams [28]. The stability regions of the various species in the Sn-S-H$_2$O system were analysed using Pourbaix diagrams. Thermodynamic data
were collected from the literature [57-60]. Thermodynamic analyses suggest the following reactions for the cathodic (reaction (a)) and anodic (reactions (b to e)) corrosion process associated with the dissolution of SnS films.

\[
\begin{align*}
\text{SnS} + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{Sn} + \text{H}_2\text{S} \quad \text{(6.17.a)} \\
\text{SnS} + 2\text{h}^+ & \rightarrow \text{Sn}^{2+} + \text{S}^0 \quad \text{(6.17.b)} \\
\text{SnS} + \text{H}_2\text{O} + 2\text{h}^+ & \rightarrow \text{SnO} + 2\text{H}^+ + \text{S}^0 \quad \text{(6.17.c)} \\
\text{SnS} + 2\text{H}_2\text{O} + 4\text{h}^+ & \rightarrow \text{SnO}_2 + \text{S}^0 + 4\text{H}^+ \quad \text{(6.17.d)} \\
\text{SnS} + 6\text{H}_2\text{O} + 12\text{h}^+ & \rightarrow \text{SnO}_2 + \text{SO}_4^{2-} + 12\text{H}^+ \quad \text{(6.17.e)}
\end{align*}
\]

The surface energy levels of SnS, estimated from the flat band potential, and the \( E_g \) information, have been superimposed on the Pourbaix diagram. This sort of correlation was employed by [61] for corrosion analyses of other semiconductor electrodes. The conduction and valence band levels in SnS are seen to encompass all the corrosion reactions represented in Eqn. (6.17.a-e). Since these decomposition potentials lie within the bandgap region, both electrons and holes can corrode SnS [61,62].

SnS films on glass substrates at room temperature prepared by chemical method were found to be photoconducting; hence the spectral response of the photocurrent was ascertained for the determination of bandgap of films. The spectrum had a maximum at 830 nm corresponding to 1.49 eV [63].

The photoactivity measurement of the electrodeposited SnS films on ITO substrate was carried out in contact with \( \text{Fe}^{3+} \) and thiosulphate solution. The light was manually chopped to better delineate the dark and the photocurrent. The latter which was again apparent on the cathodic directions thus confirmed the \( p \)-type nature of the deposit [64].

The Sn\(_{1-x}\)S films prepared by low temperature chemical precipitation and vapour deposition exhibited moderate photoconductance with apparent
recombination times ~ 1 ms [65]. Supporting electrolytes (Li⁺, Na⁺, K⁺ and Cs⁺) are found to suppress the photocorrosion and enhance the fill factor of a PEC cell formed with n-SnS and p-SnSe electrodes [66]. An increase of fill factor has been observed in the order of Li⁺ < Na⁺ < K⁺ < Cs⁺. It is concluded that the addition of suitable supporting electrolytes, like Cs⁺ ions can help in improving the overall photoconversion efficiency of a semiconductor electrode in a PEC cell.

6.7.3.2. Flat band potential measurements

The flat band potential measurements were performed for SnS photocathodes synthesized by electrodeposition and brush plating techniques by using C-V measurements and i²_ph versus potential curve.

The M-S plots obtained for these films are shown in Fig. 6.19. The nature of conductivity of all the films was found to be 'p' type as evident from negative slope of the M.S. plots. The value of flat band potential Vfb is found to be 0.46 V(SCE) for electrodeposited and 0.49 V(SCE) for brush plated films which are in good agreement with the reported values of Vfb = 0.46 V(SCE) for SnS films [46]. The important semiconductor parameters obtained using M-S plots are represented in Table 6.4.

6.7.3.3. Current-voltage characteristics of SnS

The nature of the junction between the photoelectrode, SnS synthesized by electrodeposition and brush plating method and the redox electrolyte Fe³⁺/Fe²⁺ was investigated by the studies of the dynamic current voltage characteristics in dark and under 100 mW/cm² illumination intensity. From the Fig. 6.20. it is observed that the curves obtained under illumination are shifted from that in dark, which show the photosensitivity of SnS films prepared by both techniques.
Fig. 6.19. Mott-Schottky plot for the electrodeposited (A) and brush plated (B) p-SnS/Fe³⁺,Fe²⁺/Pt systems at a frequency of 1 kHz.
Table 6.4
Summary of results obtained from Mott-Schottky plots of p-SnS films

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Physical Parameter</th>
<th>Results obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electrodeposited SnS</td>
</tr>
<tr>
<td>1.</td>
<td>Electrolyte used</td>
<td>Fe$^{3+}$/Fe$^{2+}$</td>
</tr>
<tr>
<td>2.</td>
<td>Redox Fermi level of the electrolyte $E_{F,\text{redox}}$ V(SCE)</td>
<td>0.53</td>
</tr>
<tr>
<td>3.</td>
<td>Flat band potential, $(V_{FB})$ V(SCE)</td>
<td>0.46</td>
</tr>
<tr>
<td>4.</td>
<td>Acceptor concentration, $(N_A)$ (cm$^{-3}$)</td>
<td>$7.36 \times 10^{16}$</td>
</tr>
<tr>
<td>5.</td>
<td>Density of states in the valance band, $(N_V)$ (cm$^{-3}$)</td>
<td>$4.13 \times 10^{19}$</td>
</tr>
<tr>
<td>6.</td>
<td>Built in voltage (band bending), $(V_b)$ (volt)</td>
<td>0.07</td>
</tr>
<tr>
<td>7.</td>
<td>Depletion width (W) (cm)</td>
<td>$4.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>8.</td>
<td>Carrier type</td>
<td>p</td>
</tr>
</tbody>
</table>
Fig. 6.20. Current-voltage (I-V) characteristics for the electrodeposited (A) and brush plated (B) p-SnS/Fe$^{3+}$/Fe$^{2+}$/Pt.

Fig. 6.21. The plot of log I versus V for the PEC cell formed using electrodeposited (A) and brush plated SnS films.
Log I vs V plot is shown in Fig. 6.21. The nature of the curve indicates that the junction formed is a rectifying one. The junction ideality factor, A, estimated from this plot was found to be equal to 1.6 for electrodeposited SnS films and 1.4 for brush plated SnS films.

6.7.3.4. Photo response

The photo response of the PEC cell formed with SnS films prepared by both electrodeposition and brush plating techniques as photo cathode was studied by noting the short circuit current, I_{sc} and the open circuit voltage, V_{oc} as a function of intensity of the incident light, shown in Fig. 6.22. It is seen that in both cases, the I_{sc} and V_{oc} vary linearly with the light intensity. The I_{sc} seems to approach a saturation state around 100 mW/cm^2 light intensity.

6.7.3.5. I^2_ph versus potential (V) plot

The flat band potential V_{fb} was evaluated for the electrodeposited and brush plated SnS photocathodes (Fig.6.23) by illuminating the semiconductor/electrolyte interface with a monochromatic light of wavelength 580 nm in 1M KOH. The linear plot of I^2_ph versus potential V(SCE) is extrapolated to intercept the x-axis. The flat band potential value of 0.46 V(SCE) for electrodeposited SnS film and 0.52 V(SCE) for brush plated SnS film have been obtained. This is in good agreement with the values of 0.46 V(SCE) and 0.49 V(SCE) obtained from M-S plots for electrodeposited and brush plated SnS films respectively.

The linear plot of I^2_ph versus potential V(SCE) is extrapolated to intercept the x-axis. The flat band potential value of 0.52 V(SCE) for electrodeposited SnS film and 0.46 V(SCE) for brush plated SnS film have been obtained. This is good agreement with the values of 0.48 V(SCE) and 0.42 V(SCE) obtained for electrodeposited and brush plated SnS films respectively.
Fig. 6.22. Variation of short circuit current density ($I_{sc}$) and open circuit voltage ($V_{oc}$) with intensity of illumination for the PEC cell formed using p-SnS electrode.

- O electrodeposited SnS film
- Δ brush plated SnS film
Fig. 6.23. Variation of $I_{ph}^2$ versus potential for the electrodeposited (A) and brush plated (B) SnS films.

Fig. 6.24. Variation of photocurrent ($I_{sc}$) with wavelength ($\lambda$) for the PEC cell formed using electrodeposited (A) and brush plated (B) SnS films.
6.7.3.6. Spectral response

The spectral response of the PEC cell formed with SnS photoelectrode synthesized by electrodeposition and brush plating techniques was studied by recording the short circuit photocurrent as a function of wavelength (\(\lambda\)) of the illumination light and is illustrated in Fig. 6.24. The \(I_{sc}\) values are found to increase up to the region of 1030-1070 nm and then decrease. It is observed that a peak photocurrent at the wavelength of about 1000 nm which corresponds to the bandgap of the SnS semiconductor equal to 1.16 eV for electrodeposited SnS films and 1.18 eV for brush plated films. The results obtained are in agreement with the results from optical absorption studies in chapter 5.

The rapid fall of photocurrent towards the shorter wavelength side can be attributed to the absorption of incident light by the electrolyte and the sharp fall in the photocurrent towards longer wavelength side may be due to the poor photoresponse of the electrode.

6.7.3.7. Annealing effects on PEC parameters

Polycrystalline SnS films can be a promising photoelectrodes for the conversion of solar energy. The performance of photovoltaic energy conversion system has been shown to depend strongly on the treatment of the semiconductor electrode prior to use in the solar cells. SnS films prepared by both electrodeposition and brush plating methods, subjected to a heat treatment exhibited a remarkable increase in conversion efficiency and improved the stability of the solar cells. The films were subjected to annealing at 250, 275 and 300°C in vacuum and 250°C in air.

Annealing was carried out at 250, 275 and 300°C for different durations. The effect of annealing on \(V_{oc}\) for the electrodeposited and brush plated SnS
photoelectrodes is shown in Fig. 6.25 and 6.26. It is observed that vacuum annealing gives better results than air annealed films. The $V_{oc}$ for air annealed film is 0.13 V and that for the vacuum annealed at 275°C is 0.18 V for the electrodeposited SnS film. A similar trend is obtained for the brush plated films annealed in air and vacuum. The $V_{oc}$ for air annealed film is 0.18 V and for the vacuum annealed at 275°C is 0.24 V. This shows that the vacuum annealed brush plated films yields a better result than the electrodeposited vacuum annealed film.

The $V_{oc}$ values increase linearly upto an annealing time of 15 min and then show nearly constant values. Saturation is observed at 30 min for both air and vacuum annealing. This is in conformity with the observation that the stoichiometric SnS films are obtained after annealing for 30 min as given in chapter 4. Fig. 6.27 and 6.28 show the $I_{sc}$ values observed for the electrodeposited and brush plated films. Annealing was carried out in air at 250°C and in vacuum at 250, 275 and 300°C for different durations. The $I_{sc}$ value is higher for the vacuum annealed films and shows the same trend as that of $V_{oc}$. The discussion given in the previous paragraph holds good for this also.

The variation of $V_{oc}$ and $I_{sc}$ with annealing temperature for the films prepared by both techniques and annealed in vacuum is shown in Fig. 6.29 and Fig. 6.30. In both the cases, the maxima occur for annealing temperature of 275°C.

The above results show that the optimum annealing temperature is 250 and 275°C for the electrodeposited and brush plated films respectively for the duration of 30 min.
Fig. 6.25. Variation of open circuit voltage ($V_{oc}$) with annealing time for the electrodeposited SnS film.

Fig. 6.26. Variation of open circuit voltage ($V_{oc}$) with annealing time for the brush plated SnS film.
Fig. 6.27. Variation of short circuit current ($I_{sc}$) with annealing time for the electrodeposited SnS film

Fig. 6.28. Variation of short circuit current ($I_{sc}$) with annealing time for the brush plated SnS film
Fig. 6.29. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the electrodeposited SnS film.

Fig. 6.30. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the brush plated SnS film.
6.7.3.8. Effect of film thickness on PEC parameters

The PEC parameters were studied for the electrodeposited and brush plated SnS films with varying thickness. The $V_{oc}$ and $I_{sc}$ variation of electrodeposited SnS films are shown in Fig. 6.31. Both values increase continuously up to a thickness of about 1.0 $\mu$m and then only a slight variation up to a thickness of 1.6 $\mu$m. It is observed that SnS films of thickness 1.0 to 1.2 $\mu$m prepared by electrodeposition technique are capable of yielding good PEC output. The maximum values of $V_{oc}$ and $I_{sc}$ are 0.22 V and 1.37 mA respectively.

Fig. 6.32 shows the $V_{oc}$ and $I_{sc}$ variations with thickness for the brush plated SnS films. The variation is linear and steep up to 1.6 $\mu$m and then saturation has been observed up to about 2.5 $\mu$m. SnS films of thickness in the range 1.6 to 2.0 $\mu$m may be optimum for getting maximum $V_{oc}$ and $I_{sc}$ values through the brush plating technique. The observed value of $V_{oc} = 0.285$ and $I_{sc} = 1.6$ mA is higher than the values obtained for the electrodeposited SnS films.

6.7.3.9. Effect of etching on PEC parameters

On account of the poor efficiency of the SnS photoelectrodes, the etching experiments are carried out on 1.2 $\mu$m thick SnS films prepared by electrodeposition and 1.8 $\mu$m thick brush plated films. They have been annealed in vacuum under optimised conditions.

The vacuum annealed SnS films are etched as described in section 6.7.2.8. The current and voltage measurements are carried out on the annealed SnS thin films under (i) without etching, (ii) chemical etching and (iii) photoetching. The current-voltage characteristics of the electrodes under the above conditions are shown in Fig. 6.33.
**Fig. 6.31.** Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the electrodeposited SnS film

**Fig. 6.32.** Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the brush plated SnS film
Fig. 6.33. Power output characteristics of PEC cells using electrodeposited SnS films.
The I-V output for unetched films shows an open circuit voltage of 0.28 V and short circuit current of 1.51 mA as seen from the curve (a). The PEC output for chemically etched SnS films is improved as evidenced from the curve (b). The improvement in the surface due to chemical etching enhances the output characteristics. The output for the photoetched SnS films is further enhanced. This is attributed to the fact that the photoetching further removes the surface damage, surface states and traps thereby enhances the PEC output. The photoetching of the annealed film improves its mobility and minority carrier diffusion length which in turn increases the I-V output slightly more as shown from the curve (c). The I-V output of the PEC cells fabricated using brush plated SnS films and etched is given in Fig. 6.34. A comparison of the curves show the same trend as that for electrodeposited films. However, the higher PEC output for brush plated SnS films confirms that SnS films of better quality can be prepared by the brush plating technique.

6.7.3.10. PEC parameters of SnS photocathodes

The I-V analysis of the best PEC cells, using electrodeposited and brush plated SnS films, surface modified by chemical etching and photoetching has been carried out. A computer simulation programme has been developed as in the case of SnSe films to extract the PEC parameters and compared with the experimentally observed data.

The PEC parameters of SnS films are presented in Table 6.5 and 6.6. The fill factor and efficiency of the vacuum annealed films of electrodeposited and brush plated SnS are found to be 0.51 and 0.31% and 0.44 and 0.33% respectively for photoetched films. The low efficiency of the cell may be due to the presence of surface states and grain boundaries acting as recombination centres for the photogenerated carriers [1,50]. Higher resistivity of the samples may also be attributed for the limitation of the efficiency. The simulated values are given in Table 6.10 which agree well with the experimental values.
Fig. 6.34. Power output characteristics of PEC cells using brush plated SnS films
Table-6.5
PEC parameters obtained from power output plots of electrodeposited SnS film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.43</td>
<td>0.27</td>
<td>0.39</td>
<td>0.15</td>
<td>109</td>
<td>350</td>
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<td>Chemical etching</td>
<td>1.68</td>
<td>0.29</td>
<td>0.40</td>
<td>0.19</td>
<td>90</td>
<td>454</td>
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<tr>
<td>Photoetching</td>
<td>2.0</td>
<td>0.3</td>
<td>0.51</td>
<td>0.31</td>
<td>52</td>
<td>770</td>
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</table>

Table-6.6
PEC parameters obtained from power output plots of Brush plated SnS film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.6</td>
<td>0.24</td>
<td>0.36</td>
<td>0.14</td>
<td>71</td>
<td>325</td>
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<tr>
<td>Chemical etching</td>
<td>1.75</td>
<td>0.27</td>
<td>0.36</td>
<td>0.17</td>
<td>40</td>
<td>333</td>
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<tr>
<td>Photoetching</td>
<td>2.30</td>
<td>0.32</td>
<td>0.44</td>
<td>0.33</td>
<td>43</td>
<td>461</td>
</tr>
</tbody>
</table>
6.7.4. Tin Sulphoselenide Thin Films

PEC properties of solid solutions of SnS-SnSe are reviewed first. The studies on SnS_{0.5}Se_{0.5} films prepared by both techniques have been carried out to characterize their PEC properties.

6.7.4.1. Review of earlier work on SnSSe

As there are no reports available in the literature for the PEC properties of SnS_xSe_{1-x} thin films, PEC and corrosion study made on n-type SnSSe is presented. Single crystals of n-type SnS_xSe_{2-x} (x = 1.04) obtained both by Transport and Bridgman methods exhibit an energy gap of 1.53 eV [32]. SnSSe has a diode-like blocking behaviour in acidic solutions (the dark current being equal to $4 \times 10^{-7}$ A cm$^{-2}$ at anodic potentials); however, the dark current increased with increasing pH, and at pH = 14 a substantial increase in anodic current was observed. A sharp increase in current was observed at pH values greater than 7. The anodic current was accompanied by the corrosion of the sample. The corrosion in alkaline solution was enhanced upon addition of the oxidized state of a redox reagent such as Fe(CN)$_6^{3-}$. The dark current and the corrosion intensity increased with increasing concentration of Fe(CN)$_6^{3-}$. The corrosion rate as well as the magnitude of the anodic current depends on pH and the concentration of the oxidizing state of the couple. Light-driven reactions in both acidic and alkaline media are corrosion reactions.

The PEC behaviour of SnS_{0.5}Se_{0.5} films prepared by electrodeposition and brush plating techniques is reported for the first time.

6.7.4.2. Flat band potential measurements

Fig.6.35 shows the plots of $1/C^2$ versus V (Mott-Schottky plots) for the typical SnS_{0.5}Se_{0.5} films prepared by electrodeposition and brush plating.
Fig. 6.35. Mott-Schottky plot for the electrodeposited (A) and brush plated (B) p-SnS$_{0.5}$ Se$_{0.5}$/Fe$^{3+}$, Fe$^{2+}$/Pt systems at a frequency of 1 kHz.
techniques in the Fe$^{3+}$/Fe$^{2+}$ redox electrolyte solution. The nature of the Mott-Schottky plots shows that all the films are of p-type. The intercept on the voltage axis yields the value of flat band potential, $V_{fB}$ as 0.57 $V_{SCE}$ for electrodeposited film and 0.6 $V_{SCE}$ for brush plated film. Using Mott-Schottky plots, the important semiconductor parameters such as acceptor concentration, density of states in the valence band and depletion layer width ($W$) are estimated and presented in Table 6.7.

6.7.4.3. Current-voltage characteristics of SnS$_{0.5}$Se$_{0.5}$

To understand the nature of the junction between the photoelectrode, SnS$_{0.5}$Se$_{0.5}$ synthesized by electrodeposition and brush plating techniques, and the electrolyte, Fe$^{3+}$/Fe$^{2+}$, the dynamic current-voltage characteristics in dark and under 100 mW/cm$^2$ illumination intensity were studied. From Fig. 6.36, it is seen that the curves obtained under light are shifted from that in dark, which implies the photosensitizing ability of SnS$_{0.5}$Se$_{0.5}$ thin films.

The plot of log $I$ versus $V$ is illustrated in Fig. 6.37. The junction ideality factor, $A$, estimated from this plot was found to be equal to 1.5 for electrodeposited SnS$_{0.5}$Se$_{0.5}$ film and 1.4 for brush plated film. The nature of curve implies that the junction formed is a rectifying one.

6.7.4.4. Photoresponse

The photoresponse of the SnS$_{0.5}$Se$_{0.5}$ photoelectrodes was carried out by measuring the values of the $I_{sc}$ and $V_{oc}$ as a function of intensity of illuminating light. The results are shown in Fig.6.38 It can be seen that the $I_{sc}$ and $V_{oc}$ vary linearly with the light intensity for both the films prepared by electrodeposition and brush plating methods.
Table-6.7
Summary of results obtained from Mott-Schottky plots of p-SnS_{0.5}Se_{0.5} films

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Physical Parameter</th>
<th>Results obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Electrolyte used</td>
<td>Electro-deposited SnS_{0.5}Se_{0.5}</td>
</tr>
<tr>
<td>2.</td>
<td>Redox Fermi level of the electrolyte</td>
<td>Fe^{3+}/Fe^{2+}</td>
</tr>
<tr>
<td></td>
<td>EF redox V(SCE)</td>
<td>0.53</td>
</tr>
<tr>
<td>3.</td>
<td>Flat band potential, (V_{FB}) V(SCE)</td>
<td>0.57</td>
</tr>
<tr>
<td>4.</td>
<td>Acceptor concentration, (N_A) (cm^{-3})</td>
<td>4.5 x 10^{16}</td>
</tr>
<tr>
<td>5.</td>
<td>Density of states in the valance band,</td>
<td>4.02 x 10^{19}</td>
</tr>
<tr>
<td></td>
<td>(N_V) (cm^{-3})</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Built in voltage (band bending), (V_b)</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>(volt)</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Depletion width (W) (cm)</td>
<td>4.4 x 10^{-5}</td>
</tr>
<tr>
<td>8.</td>
<td>Carrier type</td>
<td>p</td>
</tr>
</tbody>
</table>
Fig. 6.36. Current-voltage (I-V) characteristics for the electrodeposited (A) and brush plated (B) p-SnS_{0.5}Se_{0.5}/Fe^{3+},Fe^{2+}/Pt cell.

Fig. 6.37. The plot of log I versus V for the PEC cell formed using electrodeposited (A) and brush plated SnS_{0.5}Se_{0.5} films.
Fig. 6.38. Variation of short circuit current density ($I_{sc}$) and open circuit voltage ($V_{oc}$) with intensity of illumination for the PEC cell formed using p-SnS$_{0.5}$Se$_{0.5}$ electrode
O electrodeposited p-SnS$_{0.5}$Se$_{0.5}$ film
△ brush plated p-SnS$_{0.5}$Se$_{0.5}$ film
6.7.4.5. $I_{ph}^2$ versus potential (V) plot

The flat band potential, $V_{fb}$, was evaluated for a typical SnS$_{0.5}$Se$_{0.5}$ photoelectrode by illuminating the semiconductor-electrolyte interface with a monochromatic light of wavelength 580 nm in 1M KOH. The wavelength of 580 nm was chosen in order to keep absorption ($\alpha$) small, so that the condition $\alpha L_p << 1$ holds good. The linear $I_{ph}^2$ versus potential $V$(SCE) is extrapolated to intercept the x-axis as shown in Fig. 6.39. The flat band potential of 0.61 V(SCE) for electrodeposited and 0.67 V(SCE) for brush plated SnS$_{0.5}$Se$_{0.5}$ film is obtained. This value is in agreement with the value obtained from C-V studies.

6.7.4.6. Spectral response

The spectral response of the PEC cell formed with SnS$_{0.5}$Se$_{0.5}$ photoelectrodes was studied by recording the short circuit photocurrent as a function of wavelength ($\lambda$) of the illumination light and is illustrated in Fig.6.40. The $I_{sc}$ values are found to increase with increase in wavelength upto 1100-1150 nm and then decreased. It is seen that the PEC cell with electrodeposited SnS$_{0.5}$Se$_{0.5}$ photoelectrode exhibits a peak photocurrent corresponds to the bandgap of 1.09 eV and the bandgap of 1.12 eV for brush plated SnS$_{0.5}$Se$_{0.5}$ photoelectrode is obtained. The results obtained are in good agreement with the results from optical absorption studies in chapter 5.

The steepfall of photocurrent towards the higher energy (shorter wavelength) side may be due to absorption of incident light by the electrolyte and the sharp fall in the photocurrent towards the longer wavelength can be attributed to the poor photoresponse of the electrode.
Fig. 6.39. Variation of $I_{\text{photo}}^2$ versus potential for the Electrodeposited (A) and brush plated (B) Sn$_{0.5}$Se$_{0.5}$ films.

Fig. 6.40. Variation of photocurrent (I) with wavelength ($\lambda$) for the PEC cell formed using electrodeposited (A) and brush plated (B) Sn$_{0.5}$Se$_{0.5}$ films.
6.7.4.7. Annealing effects on PEC parameters

The SnS$_{0.5}$Se$_{0.5}$ films are used as photoelectrodes for the conversion of solar energy. A heat treatment of the SnS$_{0.5}$Se$_{0.5}$ electrodes is found to be highly beneficial to obtain better conversion efficiencies. Films prepared by both electrodeposition and brush plating techniques were annealed at different temperatures between 200 and 300°C in air and vacuum.

The annealing was carried out at 250, 275 and 300°C in vacuum and 250°C in air for different durations between 5.0 and 30 min. Fig. 6.41 and 6.42 show the effect of open circuit voltage (V$_{oc}$) for the electrodeposited and brush plated SnS$_{0.5}$Se$_{0.5}$ films respectively. The maximum V$_{oc}$ value of electrodeposited film air annealed at 250°C is 0.14 V and vacuum annealed film is 0.19 V. Whereas an improved V$_{oc}$ value of 0.17 V for air annealed and 0.22 V for vacuum annealed brush plated film is observed. This shows that vacuum annealing provides more advantageous results compared to air annealing. Further it is observed that the films prepared by brush plating technique yield SnS$_{0.5}$Se$_{0.5}$ films of better quality than the films produced by the electrodeposition route. An exponential variation in the V$_{oc}$ is observed upto an annealing time of 15 min and then a low variation is observed upto 30 min for both air and vacuum annealing.

Fig. 6.43 and 6.44 show the I$_{sc}$ values observed for the electrodeposited and brush plated films. A similar observation as in the case of V$_{oc}$ is observed for I$_{sc}$. The discussion given earlier holds good for this also. The variation of V$_{oc}$ and I$_{sc}$ with temperature for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ films annealed in vacuum for 30 min shown in Fig. 6.45. A maximum value of I$_{sc}$ and V$_{oc}$ is observed at annealing temperature of 275°C and further increase in temperature reduces V$_{oc}$ and I$_{sc}$. The same result is observed for the brush plated SnS$_{0.5}$Se$_{0.5}$ film as shown in Fig. 6.46.
Fig. 6.41. Variation of open circuit voltage ($V_{oc}$) with annealing time for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film.

Fig. 6.42. Variation of open circuit voltage ($V_{oc}$) with annealing time for the brush plated SnS$_{0.5}$Se$_{0.5}$ film.
Fig. 6.43. Variation of short circuit current ($I_{sc}$) with annealing time for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film

Fig. 6.44. Variation of short circuit current ($I_{sc}$) with annealing time for the brush plated SnS$_{0.5}$Se$_{0.5}$ film
Fig. 6.45. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the electrodeposited $\text{SnS}_{0.5}\text{Se}_{0.5}$ film.

Fig. 6.46. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with annealing temperature in vacuum for the brush plated $\text{SnS}_{0.5}\text{Se}_{0.5}$ film.
6.7.4.8. Effect of film thickness on PEC parameters

The thickness of tin chalcogenide influences the solar cell parameters. The effect of film thickness on $V_{oc}$ and $I_{sc}$ is shown in Fig. 6.47 for electrodeposited SnS$_{0.5}$Se$_{0.5}$ film and figure 6.48 for brush plated SnS$_{0.5}$Se$_{0.5}$ film. It is observed from the figures that $V_{oc}$ and $I_{sc}$ increases with thickness and attains a saturation at 1.2 $\mu$m for electrodeposited film and at 1.5 $\mu$m for brush plated film. The maximum value of $V_{oc}$ and $I_{sc}$ are 0.28 V and 1.40 mA respectively for electrodeposited SnS$_{0.5}$Se$_{0.5}$ film whereas a higher value of $V_{oc} = 0.33$ V and $I_{sc} = 1.63$ mA is observed for brush plated films.

6.7.4.9. Effects of etching on PEC parameters

For photoelectrochemical solar cell applications, a chemical etching is usually beneficial to remove damaged surface layers. The vacuum annealed SnS$_{0.5}$Se$_{0.5}$ films are etched as described in section 6.7.2.8.

The performance of the photoelectrodes depends strongly on the etching treatment used. Fig. 6.49 curve (a) shows the I-V behaviour of unetched photocathode which exhibit poor performance due to irregular morphology and damage. $V_{oc}$ value of 0.24V and $I_{sc}$ value of 1.55 mA is found. Chemical etching yields an open circuit voltage ($V_{oc}$) of 0.23 V and short circuit current ($I_{sc}$) of 1.63 mA as shown in curve (b). An appreciable increase in efficiency is observed by a subsequent photoetch as observed from curve (c). Etching (chemical and photo) removes the surface layer in selenium and sulphur vacancies. A similar trend is observed for the brush plated SnS$_{0.5}$Se$_{0.5}$ films as illustrated in Fig. 6.50. This observation confirms the better film quality nature of brush plated films.

6.7.4.10. PEC parameters of SnS$_{0.5}$Se$_{0.5}$ photocathode

The power characteristics of SnS$_{0.5}$Se$_{0.5}$ photoelectrodes prepared by electrodeposition and brush plating are performed by carrying out I-V studies at
Fig. 6.47. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the electrodeposited SnS$_{0.5}$Se$_{0.5}$ film.

Fig. 6.48. Variation of short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) with thickness for the brush plated SnS$_{0.5}$Se$_{0.5}$ film.
Fig. 6.49. Power output characteristics of PEC cells using electrodeposited SnS$_{0.5}$Se$_{0.5}$ films
Fig. 6.50. Power output characteristics of PEC cells using brush plated Sn\textsubscript{0.5}Se\textsubscript{0.5} films
Table-6.8  
PEC parameters obtained from power output plots of electrodeposited SnS$_{0.5}$Se$_{0.5}$ film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.56</td>
<td>0.24</td>
<td>0.32</td>
<td>0.12</td>
<td>56</td>
<td>372</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>1.63</td>
<td>0.23</td>
<td>0.42</td>
<td>0.16</td>
<td>80</td>
<td>400</td>
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<tr>
<td>Photoetching</td>
<td>2.15</td>
<td>0.28</td>
<td>0.46</td>
<td>0.34</td>
<td>18</td>
<td>276</td>
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Table-6.9  
PEC parameters obtained from power output plots of electrodeposited SnS$_{0.5}$Se$_{0.5}$ film

<table>
<thead>
<tr>
<th>Condition of the thin film</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (without etching)</td>
<td>1.63</td>
<td>0.26</td>
<td>0.37</td>
<td>0.16</td>
<td>64</td>
<td>318</td>
</tr>
<tr>
<td>Chemical etching</td>
<td>1.75</td>
<td>0.23</td>
<td>0.52</td>
<td>0.21</td>
<td>72</td>
<td>587</td>
</tr>
<tr>
<td>Photoetching</td>
<td>2.25</td>
<td>0.28</td>
<td>0.49</td>
<td>0.39</td>
<td>30</td>
<td>555</td>
</tr>
</tbody>
</table>
Table-6.10
PEC parameters obtained from computer simulations for the photoetched SnS$_x$Se$_{1-x}$ films

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodeposited SnSe</td>
<td>1.64</td>
<td>0.30</td>
<td>0.39</td>
<td>0.19</td>
<td>32</td>
<td>458</td>
</tr>
<tr>
<td>Brush plated SnSe</td>
<td>1.83</td>
<td>0.35</td>
<td>0.39</td>
<td>0.25</td>
<td>30</td>
<td>583</td>
</tr>
<tr>
<td>Electrodeposited SnS</td>
<td>1.92</td>
<td>0.34</td>
<td>0.42</td>
<td>0.32</td>
<td>46</td>
<td>781</td>
</tr>
<tr>
<td>Brush plated SnS</td>
<td>2.39</td>
<td>0.33</td>
<td>0.42</td>
<td>0.32</td>
<td>41</td>
<td>431</td>
</tr>
<tr>
<td>Electrodeposited SnS$<em>{0.5}$Se$</em>{0.5}$</td>
<td>2.20</td>
<td>0.30</td>
<td>0.45</td>
<td>0.33</td>
<td>15</td>
<td>300</td>
</tr>
<tr>
<td>Brush plated SnS$<em>{0.5}$Se$</em>{0.5}$</td>
<td>2.30</td>
<td>0.31</td>
<td>0.45</td>
<td>0.38</td>
<td>32</td>
<td>540</td>
</tr>
</tbody>
</table>
various solar fluxes. The efficiency ($\eta$) and fill factor (FF) of the PEC solar cells based on $\text{SnS}_{0.5}\text{Se}_{0.5}$ are estimated.

The I-V analysis of the optimized $\text{SnS}_{0.5}\text{Se}_{0.5}$ photocathodes prepared by electrodeposition and brush plated techniques and surface modified by etching has been done. The PEC parameters are presented in Table 6.8 & 6.9. These experimentally observed PEC parameters are in good agreement with the parameters obtained from computer simulation for the photoetched films (Table 6.10). The solid solution prepared by both techniques is found to show good stability against photocorrosion.

6.8. SUMMARY AND CONCLUSION

Photoelectrochemical solar cells based on $\text{Sn(S,Se)}$ semiconductor films are fabricated and studied. Electrodeposition and brush plating routes are employed to fabricate these films. Using Mott-Schottky plots, the important semiconductor parameters are estimated and presented. The effect of film thickness on solar cell parameters is studied and optimum thickness required to obtain maximum efficiency is estimated to be 1.2 $\mu$m for electrodeposited tin chalcogenide films and 1.8 $\mu$m for the brush plated films. Annealing studies in air and vacuum are carried out. An improvement in open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and efficiency ($\eta\%$) is observed for the films annealed in vacuum. The effect of chemical and photoetching on vacuum annealed photoelectrodes is studied. A computer simulation programme has been developed and the extracted PEC parameters are compared with the experimentally observed data.
REFERENCES


