CHAPTER VI

STUDIES ON PHOTOELECTROCHEMICAL SOLAR CELLS

6.1 Introduction
6.2 Principle of photoelectrochemical cells
6.3 Working principles of the PEC cell
6.4 Experimental requirements of PEC cell
6.5 Application of PEC cell
6.6 Estimation of various PEC parameters
6.7 Studies on (molybdenum, tungsten dichalcogenide) PEC solar cells
6.8 Summary and Conclusion

References
CHAPTER - VI
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 photoelectrolyte water and obtained hydrogen (a transportable form of energy) the solar energy research has gained a large momentum. In 1975, Gerischer [3] succeeded indirect conversion of solar energy into electricity, using the photoelectrochemical solar cells. The photoelectrochemical solar cells are inexpensive and then 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 band gap 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-CuInSe₂ / 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 proved to show efficient optical energy conversion [26,27]. Layered MoSe₂ is considered a promising material for PEC cells because of its resistance against photocorrosion [28-30]. The aqueous electrolyte used is 0.5 M K₂SO₄ + 0.1 M KI + 0.025 M I₂ + 0.5 M H₂SO₄. For MoSe₂ single crystal after heat treatment the maximum efficiency reported is 7.62% [31] and for thin film of 10 micron thickness the efficiency reported is 0.632% only [32]. A 17.1% of photoconversion efficiency of n-WSe₂ single crystals grown via a vapour transport technique, employing SeCl₄ as transporter has been reported [33]. The PEC effect of electrodeposited tungsten diselenide has been investigated [34]. The PEC behaviour of MoₓW₁₋ₓSe₂ solid solution has also been reported [35].

In this chapter, the principle and working of the PEC cells fabricated using pulse plated MoSe₂, WSe₂ and Mo₀.₅W₀.₅Se₂ thin film 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 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 the Schottky between a semiconductor and a metal [36], the redox electrolyte is playing the role of metal in this case. In principle all semiconducting materials of n or p-type 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 shows band diagram under illuminated conditions for a p-type semiconductor

\[ E_c \] - conduction band edge,
\[ E_F \] - Fermi level
\[ h\nu \] - incident light photon
Fig. 6.1 Band diagram under illumination condition for a p-type semiconductor. 
Ec - conduction band edge, Ef - Fermi level 
hv - Incident light Photon 
Ev - valence band edge E^*_{redox} - Redox potential
If light photon with energy $h \nu > E_g$ (band gap) falls onto the semiconductor and is absorbed in space charge region, hole electron pairs are generated. These two charge carriers move in opposite direction due to the electric field in the space charge region. If they do not recombine, either by direct cumbic interaction or by collisions with the charge 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 photo anodes 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./ = space charge layer):

**Light absorption**

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

**Recombination**

$$h^+ + e^- \rightarrow \text{heat} \quad (6.1b)$$

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

**Charge separation**

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

**Interfacial reactions**

$$h^+_{\text{surf}} + \text{Red} \rightarrow O^+_x \quad (6.1e)$$
Reactions (6.1f) 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 in open circuit condition, 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 an 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 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 potential divided by the band gap \(E_g\), but the operational efficiency depends on the relative rate of the hole-electron 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) \(e_{\text{inc}}\), Energy loss due to the loss of charge carriers in the s.c.

(b) \(e(I,R)\), Ohmic loss with \(R = R_{\text{int}} + R_{\text{ext}}\)
(c) $E_{\text{redox}} = E_v + n_{sc}$ = Energy loss connected with reaction where $n_{sc}$ is the over voltage at semiconductor.

(d) $e_n c e$ = Energy loss connected with eqn 6.1f at the counter electrode due to over voltage.

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./. 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 band gap 3.0 eV uses only a small fraction of the light energy required to drive the reaction [37,38]. 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 (photo electrode, 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 Fig.6.2 (b)
Fig. 6.2. (a) Standard three electrode set up for current-voltage (I-V) and capacitance measurements
1. Semiconductor electrode
2. Saturated Calomol Electrode (SCE)
3. Platinum (counter) electrode
4. Quartz window for illumination of the photoelectrode
5. Electrolyte
6. Glass cell
7. Galvanostat
8. Null detector
9. Oscillator and
10. D C Power supply
(b) Schematic representation of a PEC Cell
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 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.

Fig 6.2 (a) Three standard electrode set up for current-voltage (I-V) and capacitance 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) Galvanostat (8) Null detector (9) Oscillator and (10) D.C. Power supply.

(b) Schematic representation of a PEC Cell.

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 ($10^3$ - $10^4$ cm$^{-1}$)
- Smaller reflection and transmission coefficient
- Optimum value of band gap (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 ('malte' 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 \( h \nu > E_g \) has also been reported by many investigators [3, 8, 39, 40].

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.

6.4.3. Counter Electrode

Plantinum is the material of choice in most applications involving PEC assisted electrode (PAE) cells although cheaper substitutes (e.g. brass, graphite) 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 carries from photoelectrode to counter electrode. As the difference between $E_r$ of semiconductor and $E_r$ 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 [40, 41].

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 mega watts), generated at one end 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 so many 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; that there are many other applications of the PEC cells, such as photo catalytic degradation of carcinogenic organic compounds, synthesis of value-added organic compounds, etc.

6.6 ESTIMATION OF VARIOUS PEC PARAMETERS

6.6.1 $V_{\text{oc}}$ – The Open Circuit Voltage

In PEC cells, the photo effect 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 towards negative direction in the case of n-type semiconductors. For a 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, $V_{\text{oc}}$. The maximum $V_{\text{oc}}$ obtainable is given by equation (6.2) for a given semiconductor.

$$V_{\text{oc}} \ (\text{max}) = V_{\text{B}} = |E_F - E^0|$$  \hspace{1cm} (6.2)
Where $E^0$ 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 good PEC behaviour in a semiconductor electrode.

6.6.2 Current – Voltage Characteristics

The potentiostatic current-voltage curve of a semiconductor electrode, usually obtained by impressing different voltage on a semiconductor (with respect to 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 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 hole-electron 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 [41].

$$I = I_{\text{ph}} - I_0 \exp\left(\frac{qE_{\text{sc}}R_s}{AKT}\right)$$  \hspace{1cm} (6.3)

where

$R_s$ is the series (internal) resistance of the cell

$q$ is the charge of an electron
Isc is the short circuit current

k is the Boltzmann constant

T is the absolute temperature

Io is the reverse saturation current or the dark current, and

A is a constant

Similarly, the open circuit potential (Voc) is also dependent on the light intensity [42, 43] as in equation (6.4).

\[
I_{in} = \left(\frac{kT}{q}\right)\ln \left[1 + \left(\frac{P}{P_o}\right)\right] \approx \left(\frac{kT}{q}\right) \times \frac{P}{P_o} = \left(\frac{kT}{q}\right)I
\]  

(6.4)

Where Po is the density of holes in the bulk of the semiconductor, P is the increase in hole density on illumination, i is the proportionality factor and I is the light intensity.

For a given wavelength (monochromatic) and intensity (photon flux \( \eta_\omega \)), the \( I_{ph} \) is related to the flat band potential (\( V_{fb} \)), as per the Gartners’ equation [44].

\[
I_{ph} = q\phi (1 - \frac{1}{1 + \alpha l_e}) \exp(-\alpha W_o (V - V_{fb})^{1/2})
\]  

(6.5)

Where \( \alpha \) is the optical absorption coefficient of a semiconductor, \( W_o \) is the width of the depletion layer for a potential of one volt across the semiconductor and can be expressed as
\[ W_0 = \left[ \frac{2\varepsilon \varepsilon_0}{q^2 N_d} \right]^{1/3} \]  

(6.6)

where \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity of free space and \( N_d \) is the donor concentration. \( V \) in equation (6.5) is the applied potential (relative to SCE) and \( L_p \) is the hole (majority 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 a 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 \( I_{ph} \) versus \( V \) and extrapolating to zero photocurrent, provided \( I_{ph} \) measurements are done at monochromatic radiation and \( h\nu = hc / \lambda \geq Eg \). 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

\[ (I_{ph} / \alpha W_0 q F_0) \propto (V-V_{fb})^{1/2} \]  

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 $V_{fb}$ [45].

**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 Mott-Schottky equation [46, 47].

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 q N_D [(V - V_{fb}) - \left(\frac{kT}{q}\right)]}$$  \hspace{1cm} (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 ionized, the majority charge carrier concentration, $N_D$ can also be calculated from the slope of this $C^2$ versus $V$ plot.

**6.6.4. Other Parameters Derived from M.S-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 $1/C^2_{sc}$ versus $V$ plots would be different for n and p-type semiconductors. Hence, type of conductivity may be deduced from M.S-plot.

(b) **Acceptor density**

Using the intercept and slope, the values of acceptor density is 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

$$V_b = (E_{f\text{ redox}} / e) - V_{fb}$$  \hspace{1cm} (6.8)

Where $E_{f\text{ redox}}$ is the Fermi level associated to a particular redox species, given by

$$E_{f\text{ redox}} = - (4.5 \text{ eV}_{\text{NHE}} + eV_{\text{redox}})$$  \hspace{1cm} (6.9)

(d) **Depletion layer width**

If $V_{fb}$ and $N_A$ are known, then the width of the majority carrier depletion layer $W$ can be calculated using the relation

$$W = \sqrt{(2e_0e_N/cN_A) \left(1 - I_{ph} \right) - \left(\frac{kT}{q} \right)}$$  \hspace{1cm} (6.10)
(e) Position of band edges

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

\[ n_o = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right] \]
\[ p_o = N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right] \]  \hspace{1cm} (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

\[ E_c = E_F - kT \ln(n_o / N_c) \]
\[ E_v = E_F + kT \ln(p_o / N_v) \] \hspace{1cm} (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 equations (6.12).

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

\[ I = I_o \left[ \exp\left( \frac{V - I R_s}{I_o B} \right) - 1 \right] + \frac{V - I R_s}{R_{sh}} - I_{ph} \] \hspace{1cm} (6.13)
where $I_o$ is the reverse saturation or dark current

$A$ is the diode quality factor

$B = \frac{q}{kT}$ where $q$ is the electronic charge

$k$ is the Boltzmann constant $= 1.38 \times 10^{-14}$ erg K$^{-1}$

$T$ is the absolute temperature $= 300K$

The $I$-$V$ analysis of the best PEC cells, using pulse electrodeposited MoSe$_2$ films has been carried out. A computer simulation programme has been developed to extract the PEC parameters and compared with the experimentally observed data.

The PEC parameters of MoSe$_2$, WSe$_2$ and Mo$_{0.5}$W$_{0.5}$Se$_2$ films are presented in Table 6.1, 6.2 and 6.3 respectively. The fill factor and efficiency of the vacuum annealed films of pulse electrodeposited MoSe$_2$ films are 0.51 and 0.189% Wse$_2$ films are found to be 0.346 and 0.123% Mo$_{0.5}$W$_{0.5}$Se$_2$ films are 0.250 and 0.490% respectively. The low efficiency of the cell may be due to the presence of surface states and grain boundaries acting as recombination centers for the photo generated carriers [139, 166]. Higher resistivity of the samples may also be attributed for the limitation of the efficiency.

The open circuit voltage $V_{oc}$ is obtained from the intercept with current axis. The series resistance $R_s$ and the shunt resistance $R_{sh}$ are given by the slope of the curve at $I = 0$ where $V = V_{oc}$ and at $V = 0$ where $I = I_{sc}$ respectively.
Table – 6.1
Summary of results obtained from Mott-Schottky Plots of p- MoSe₂ films

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Physical Parameter</th>
<th>Pulse Electrodeposited MoSe₂ film</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Electrolyte used</td>
<td>KI / I₂</td>
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<tr>
<td>2.</td>
<td>Redox fermi level of the electrolyte E_{F, redox} V_{(SCE)}</td>
<td>0.54</td>
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<td>3.</td>
<td>Flat band potential, V_{fb, V_{(SCE)}} (V)</td>
<td>0.82</td>
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<td>4.</td>
<td>Acceptor concentration Nₐ (cm⁻³)</td>
<td>1.01 x 10¹⁸</td>
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<td>5.</td>
<td>Density of states in the valence band, N_V (cm⁻³)</td>
<td>8.98 x 10⁸</td>
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<td>6.</td>
<td>Built in voltage (band bending) V_{b} (V)</td>
<td>0.34</td>
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<tr>
<td>7.</td>
<td>Depletion width, W (µm)</td>
<td>0.44</td>
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<td>8.</td>
<td>Carrier type</td>
<td>P</td>
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Table – 6.2
Summary of results obtained from Mott-Schottky Plots of p-WSe₂ films

<table>
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<th>Sl. No.</th>
<th>Physical Parameter</th>
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<td>Electrolyte used</td>
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<tr>
<td>2.</td>
<td>Redox fermi level of the electrolyte $E_{F_{redox}}$ $V_{(SCE)}$</td>
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<td>3.</td>
<td>Flat band potential, $V_{fb} V_{(SCE)}$ (V)</td>
<td>0.81</td>
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<td>Acceptor concentration $N_A$ (cm⁻³)</td>
<td>$1.099 \times 10^{18}$</td>
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<td>5.</td>
<td>Density of states in the valence band, $N_V$ (cm⁻³)</td>
<td>$9.72 \times 10^{8}$</td>
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<td>6.</td>
<td>Built in voltage (band bending) $V_b$ (V)</td>
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<td>7.</td>
<td>Depletion width, $W$ (µm)</td>
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<td>8.</td>
<td>Carrier type</td>
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</tbody>
</table>
### Table – 6.3

**Summary of results obtained from Mott-Schottky Plots of p- Mo$_{0.5}$ W$_{0.5}$Se$_2$ films**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Physical Parameter</th>
<th>Pulse Electrodeposited Mo$<em>{0.5}$W$</em>{0.5}$Se$_2$ film</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Electrolyte used</td>
<td>KI / I$_2$</td>
</tr>
<tr>
<td>2.</td>
<td>Redox fermi level of the electrolyte $E_{F, \text{redox}}$</td>
<td>0.54</td>
</tr>
<tr>
<td>3.</td>
<td>Flat band potential, $V_{fb}$ $V_{(SCE)}$ (V)</td>
<td>0.92</td>
</tr>
<tr>
<td>4.</td>
<td>Acceptor concentration $N_A$ (cm$^{-3}$)</td>
<td>0.5992 x $10^{18}$</td>
</tr>
<tr>
<td>5.</td>
<td>Density of states in the valence band, $N_V$ (cm$^{-3}$)</td>
<td>3.742 x $10^8$</td>
</tr>
<tr>
<td>6.</td>
<td>Built in voltage (band bending) $V_b$ (V)</td>
<td>0.237</td>
</tr>
<tr>
<td>7.</td>
<td>Depletion width, $W$ (µm)</td>
<td>0.4318</td>
</tr>
<tr>
<td>8.</td>
<td>Carrier type</td>
<td>P</td>
</tr>
</tbody>
</table>
\[ V_m = I_m \] are the experimental values of the voltage and current at the maximum power point. \( I_{ph} \) is the current produced under illumination, which is flowing against the diode current.

### 6.6.5. Power Characteristics (I versus 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 MoSe\(_2\), WSe\(_2\) 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 versus V plots, the efficiency of LJSC’s and fill factor (FF) can be calculated by using the equations.

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

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

\[
\frac{dl}{dv} = 1/R_s \tag{6.16a}
\]

\[
\frac{dl}{dv} = \approx 1/R_{sh} \tag{6.16b}
\]

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

### 6.7 STUDIES ON MOLYBDENUM, TUNGSTEN DICHALCOGENIDE PEC SOLAR CELLS

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 interest has also been inspired by the unique
opportunities that PEC cells offer in the study of energetics and the chemistry of semiconductor - electrolyte interfaces. The characterization of molybdenum, tungsten dichalcogenide 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 bandwidth interference filters (Oriel, USA). The incident light intensity on the sample surface for different wavelengths is measured with an Oriel thermopile, USA in milliwatts (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 section.

6.7.1. Experimental Details

A conventional single compartment cell was formed by using MoₓW₁₋ₓSe₂ photoelectrodes (1.0 cm²) with x = 0.0, 0.5 and 1.0 prepared by pulse electrodeposition technique. (MoSe₂, WSe₂ and Mo₀.₅W₀.₅Se₂). 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) are used in the PEC cell as shown in Fig.6.2. The electrodes were immersed in different electrolytes as follows.
0.5 M H₂SO₄ + 0.5 M K₂SO₄ + 0.1 M KI + 0.025 M I₂; 2 M KI + 0.05 M I₂; and 0.5 M Na₂SO₄ + 0.5 M H₂SO₄ + 1.0 M NaI + 0.025 M I₂. 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 2M KI + 0.05 M I₂ 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 2.0 M KI + 0.05 M I₂.

6.7.2. Molybdenum diselenide thin films

6.7.2.1. Review of earlier work on MoSe₂

Interest in the use of photoelectrochemical (PEC) solar cells for low-cost energy conversion has lead to an extensive research in the search for novel and suitable thin film semiconductor materials [48, 49]. Recent investigations have shown that the layered type semiconducting group VI transition metal dichalcogenides (MoSe₂, WSe₂ and MoS₂), which absorb visible and near-IR light are particularly interesting materials for photoelectrochemical solar energy conversion. The solar cell is considered a major candidate for obtaining energy from the sun, since it can convert directly light energy to electrical energy with high conversion efficiency, can provide nearly permanent power at low operating cost, and is virtually free of pollution. Solar cells at present furnish the most important long-duration power supply for satellites and space vehicles. Recently, research and development of low-cost, flat panel solar cells, thin film devices, concentrator systems and many innovative concepts have increased. The main objective concepts have increased. The main objectives of all technological
developments are to develop energy sources, which may be long lasting, pollution free, easily available and cost effective [48, 56]. For application in photovoltaic and PEC solar cells, semiconductor thin films like CdSe, CdS, CdHgTe, GaAs, CuInSe₂, CuInS₂, CdTe, SrTiO₃, SnO₂, In₂O₃, TiO₂, SnS, SnSe, MoSe₂ and WSe₂ have been elaborately studied [53, 57 and 58]. The most efficient system till date turned out to be MoSe₂ [59]. Recent applications include intercalation compounds and long-life PEC solar cells. Some studies on PEC with MoSe₂ have been carried out on single crystals. However, polycrystalline electrodes are economically desirable for solar cell applications, where large area semiconductor substrates are necessary. Hence, this study has been directed towards obtaining molybdenum diselenide in thin film form. Many workers have succeeded in co-depositing Mo together with iron group metals [60-70]. Molybdenum diselenide thin films have been deposited under potentiostatic route and soft selenization technique by Sanjeeviraja et.al [71]. Using electrodeposition technique Chandra et.al [70] have been electrodeposited cathodically on titanium substrates from an ammoniacal solution of H₂MoO₄ and SeO₂ under galvanostatic conditions. The I-V characteristics of the MoSe₂ film in contact with 2I⁻/I₂ electrolyte indicate that the charge transfer at the interfaces is via the valence band and it also involves the surface states. Results from photoelectrochemical solar cells fabricated using various electrodeposited films are also discussed. n-type MoSe₂ single crystal, grown by the vapour transport technique by Martinez Chaparro et.al [72] have studied the photocurrent and electrolyte electro reflectance (EER) measurements are done. Again n-type MoSe₂ single crystal grown by the SeCl₄ transport method was used digital
images of photocurrent, photovoltage and electrolyte electro reflectance at the electrolyte interface, with micrometric lateral resolution are presented under different experimental conditions [66]. Using direct vapour transport technique, n-type MoSe\textsubscript{2} crystals, grown from a stoichiometric mixture of molybdenum 99.95\% pure, and selenium 99.999\% are used as photoanodes in n-MoSe\textsubscript{2} / (0.025 N I\textsubscript{2}, 1 N KI, 2 N Na\textsubscript{2}SO\textsubscript{4}, 0.5 N H\textsubscript{2}SO\textsubscript{4}) / Pt electrode PECs [61]. n-type MoSe\textsubscript{2} crystals were grown by bromine transport from the gas phase [73] by Wolfgang Kautek et.al, and the pH dependence of photocurrent was discussed. Helmut Tributsch [74] obtained layered crystals of MoSe\textsubscript{2} grown by iodine-transport reactions from the "Kristallographisches Institute" of the Universai Freciburg and used it successfully as photoelectrodes in electrochemical solar cells. MoSe\textsubscript{2}: I/I\textsubscript{2} solar cells stable within 15\% with conversion efficiency between 0.5 and 5\% was reported. Ohuchi et.al [75] used the molecular beam epitaxy (MBE) and grown MoSe\textsubscript{2} single crystals and the characterization studies were done. Pathak et.al grown single crystals of n-type MoSe\textsubscript{2} by the direct transport method. The electrolyte having concentration (0.025 M I\textsubscript{2} + 1 M NaI + 2 M Na\textsubscript{2}SO\textsubscript{4} + 0.50 M H\textsubscript{2}SO\textsubscript{4}) was identified as the most suitable one and the photo conversion behaviour was studied [62].

The general survey for this review article has been made from the literature available upto 2003. The present article will help research workers in selecting preparative and crystal growth methods and stimulate further research work on the properties of molybdenum / tungsten dichalcogenides.
The layer-type transition metal dichalcogenides like MoS$_2$, WS$_2$ and their homologous selenides and tellurides, can be considered a new class of semiconducting electrodes for photoelectrochemical (PEC) solar cells. Since the original work of Tributsch [86] a number of papers have demonstrated that these semiconductors have energy band gaps well suited to the solar energy conversion, a high absorption coefficient in the visible range, and an extremely good stability when in contact with various aqueous and non-aqueous electrolytes. In particular, it has been shown since then the PEC solar cells using halogen / halogenides redox couples can have the same time long time durability and about 10% solar conversion efficiency, and are stable in time, if good dichalcogenide crystal with an appropriate surface morphology are chosen.

Such binary compounds have been known for several years not only for their properties of solid lubricants [87], but also for their unusual physical properties as materials with two dimensional layered crystal structures [88, 89]. Molybdenum and tungsten dichalcogenides, which are compounds with a trigonal prismatic crystal symmetry (Fig. 4.1). Their upper energy band, derived from the transition metal d-states, is split into two bands, a lower $d_z^2$ occupied energy band and a higher unoccupied d-band derived by $d_{xy}$ and $d_z^2 - y^2$ states, separated by an hybridization indirect band gap ranging from 1 to 2 eV [90 - 92]. This gives to these compounds the characteristics of a semiconductor not only appropriate for the absorption of the solar spectrum, but also with favourable optical transitions between nonbonding electronic orbitals which would not affect the original bonds of the semiconductor, thus enhancing its stability against
photodecomposition. In fact, in all the semiconducting electrodes, where the absorption of a photon with energy larger than the band gap corresponds to breaking an electronic bond, the missing electron at the electrode surface can catalyze the anodic dissolution reaction of the semiconductor or the anodic formation of an insulating area, unless a fast charge-transfer reaction to restore this band.

MoSe₂ was prepared from elements having purities Mo and Se 99.99% each. Stoichiometric amounts of the powder elements were introduced into a silica ampoule, which was evacuated to a pressure less than 10⁻⁶ torr before sealing. The powder mixture was distributed along the length of the horizontally held ampoule which was then slowly heated, over a period of 5 h, to a temperature of 700°C and maintained at this temperature for 24 h. At this stage the reaction product was in the form of a free-flowing fine black powder. Then the ampoule and the contents were vibrated for a period of 30 min and the powder distributed along the length of the ampoule. After heating the ampoule in the appropriate temperature gradient [92] for two weeks large single crystals are found growing from the polycrystalline mass. Layer crystals of MoSe₂ were grown by iodine-transport reactions obtained from the "Kristallographichs Institute" of the Universitat Freiburg. The photochemical and electrochemical properties of which has hitherto not been investigated either. Layer crystals of MoSe₂ was grown by iodine – transport reactions and successfully used as photoelectrodes in electrochemical solar cells and their photovoltaic behaviour was studied. With MoSe₂: I/ I₂ solar cells photocurrent densities of 22 mA / cm², photovoltages of
0.55 V and energy conversion between 4 and 5% were obtained in the red and near infra red spectral region [93]. Molybdenum diselenide can be prepared by the interaction of H₂Se and Se with metallic molybdenum [94] or by heating MoO₃ / (NH₄)₆ Mo₇O₂₄ at 900-1300°C in a stream of H₂Se [95]. Powder synthesis method has also been used by several workers [96 - 99]. Single crystals of MoSe₂ were obtained by Br₂ vapour transport, as in the case of MoS₂ [100]. Silverman [102] synthesized a new crystalline rhombohedral form of MoSe₂ by heating a mixture of Mo and Se at 600 – 2000°C under 20-80 kbar pressure. The usual form of MoSe₂ obtained was hexagonal. This paper describes the chemistry of molybdenum dichalcogenides, the aspects being covered are their properties, structural and their important application [103]. n-type MoSe₂ crystals were grown from a stoichiometric mixture of molybdenum 99.95% pure, Koch Lift Laboratories, (London) and selenium (99.999% pure) Johnson - Matthey Chemicals London) by the direct vapour transport technique were used in the present investigations. This material - possessing sandwiched layers of Se-Mo-Se held together Van der Waals forces between them is known to exhibit highly anisotropic properties [103]. The electrical resistivity exhibits an anisotropy ratio of 10³ to 10⁵ between its values parallel and perpendicular to the c axis. The general observation over PEC cells made from as-grown semiconducting crystals belonging to the TMC group show low efficiency values [104 - 106]. These values of efficiency varied among different electrodes, which are a normal observation arising from variations in exposed surface morphology within the exposed area, stoichiometry and doping levels [107 - 109]. Heat treatment improves the PEC behaviour of thicker crystals quite significantly; it degrades the PEC behaviour for
thinner crystals [110]. Electrochemical experiments give clear evidence that water is involved in the anodic dissolution process under illumination with a reaction order of unity. The water is involved in the anodic dissolution process under illumination with a reaction order of unity. The water reacts in two different initial steps depending upon the pH of the solution [111]. The major advantage of the layered semiconductors is in their optical transitions, which do not involve bonding orbitals. This should in principle assure good stability against photocorrosion. The values of the energy gap of the most common of them, i.e., MoSe$_2$, MoS$_2$ ranges between 1.4 and 1.8 eV, this offering promises good energy conversion efficiencies. Again crystals with a macroscopically defect-free, smooth surface exhibit high values of fill factor and efficiency. When average crystals were used instead, the output performance drastically decays [112, 113].

The results reported in this work tend to indicate that dark electrodeposition processes may be effectively used to stabilize the layered semiconductor photoanodes with respect to surface imperfections, in view of their use in electrochemical solar cells, as originally proposed by Bard et.al [115, 116].

The Molecular Beam Epitaxy (MBE) is described where a material with primarily two-dimensional bonding is grown on a substrate, which also has a 2D structure. The films were characterized in situ with reflection high-energy electron diffraction, Auger electron spectroscopy, and low energy electron loss spectroscopy, low energy electron diffraction; transmission electron microscopy confirmed the highly ordered nature of the films. Scanning tunneling microscopy provided real space images of the morphology of the epitaxial layer [117]. Electronic structures of MoS$_2$ and MoSe$_2$ surfaces are investigated by first-
principles electronic structure calculations. The ultras of pseudopotential by Vanderbilt are used to perform band calculations with a plane-wave basis [118].

A linear combination of atomic orbitals (LCAO) method has been used in the calculation. The indirect band gap value of 1.23 eV and lattice parameters a = b = 3.288 and c = 12.90 Å was reported. The shape of the valence and the conduction bands are a circle and a triangle respectively, difference of the shapes reflects the difference of the components of the wave functions [119]. n-MoSe₂ crystals were grown by a direct vapour transport technique and characterized using Electron Dispersive Analysis by X-rays (EDAX). The structural characterization was carried out through X-ray diffraction. The semiconducting nature of these crystals was also investigated, and it was found that the electrical resistivity is highly anisotropic [120]. Semiconductor electrodes for PEC solar cells were fabricated using these crystals as in [121] and the photoconversion characteristics, both for fixed and varying illumination intensities, were investigated by studying the photocurrent characteristics under illumination for a neon incandescent lamp [122]. Single crystals of n-MoSe₂ were grown by direct vapour transport process. The electrolyte having composition (0.025 M I₂ + 1 M NaI + 2 M Na₂SO₄ + 0.50 M H₂SO₄) was identified the most suitable after investigations on a number of electrolytes [123].

The energy gap value reported was around 1.4 eV. The photoconversion behaviour was studied after illuminating the photoelectrode with a polychromatic arc xenon lamp. Kratos Instruments Ltd. (USA) at an intensity of around 10
mW/cm² secured using suriyamapi CEL (India) and investigating it V-I characteristics. Considerable improvement in the photoconversion behaviour was obtained after controlled processing technique such as etching, heating etc. [124]. The effect of photo etching on the photoelectrochemical behaviour of n-MoSe₂ and n-WSe₂ layered compound in contact with iodide electrolytes has been studied by scanning microscope from semiconductor characterization (SMSC) [125]. n-MoSe₂ single crystals were grown by the vapour transport technique. Photocurrent and electrolyte electro reflectance (EER) measurements have been carried out, on a microscopic scale, in order to characterize the photoelectrochemical behaviour of an n-MoSe₂ single crystal as a function of its surface morphology [126]. Digital images of photocurrent, photovoltage and electrolyte electro reflectance at the n-MoSe₂ electrolyte interface, with micrometric lateral resolution, are presented under different experimental conditions [127]. Molybdenum diselenides were synthesized at 1273 K for 24 h. The X-ray diffraction (XRD) analysis showed the compound as non-stoichiometric in the approximate range of 1.85 ≤ Se/Mo ≤ 2.0. The density of the stoichiometric MoSe₂ was determined to be 6.95 ± 0.02 gcm⁻¹, which is in agreement with the theoretical value (6.97 gcm⁻³). Electrical and optical properties are reported. The thermal activation energies of Ea were estimated through the least squares fitting on these plots, resulting of 0.31 – 0.35 eV for 1.9 ≤ Se/Mo ≤ 2.0 and 0.08 – 0.11 eV for 1.85 ≤ Se/Mo ≤ 1.9 [128]. Sputtered MoSe₂ layers are obtained by solid-state reaction, induced by annealing under Se pressure, layers of Mo and Se are sequentially deposited. These layers are
investigated by optical absorption and electrical resistivity measurements. The optical properties are enhanced and the electrical resistivity is governed by hopping conduction in the low temperature range (80 to 200 K) and by grain boundary scattering mechanisms at higher temperatures. The films are p-type semiconductors as shown by the hot probe technique. The dc conductance of the films has been measured with an electrometer between 80 and 500 K. In the ohmic region, the currents generated during measurement are between 1 nA (2 MΩ < R < 2 GΩ) and 100 µA (2 kΩ < R < 20 kΩ). Electrical measurements have been carried out in the dark. The synthesized and sputtered MoSe₂ layers crystallize in the hexagonal structure and the preferential orientation is along (0 0 1) direction. The full width at half maximum (FWHM) method gives a grain size of about 80 nm for sputtered MoSe₂ layers and 100 nm for the synthesized MoSe₂ layers [129]. Goldberg et al. [130] have shown that the absorption coefficient begins to increase at 1.15 eV, but it appears there are absorption regions with different slopes, so that these two regions originate from distinct processes. The low absorption is due to the roughness of the film and the larger value of Eg may be explained as follows: the stronger absorption region can be assigned to the onset of the indirect p-d transition as discussed by Goldberg et al. [130]. MoSe₂ thin films were synthesized by annealing a molybdenum foil under selenium pressure, have been investigated by scanning electron microscopy, X-ray analysis, electron spectroscopy (XPS) and electrical resistance measurements [131]. Thin films of MoSe₂ were prepared by soft-selenization of r.f. sputtered molybdenum films in a closed - tube system.
Stoichiometry and single phase of the MoSe$_2$ films were detected by X-ray energy spectrometry and X-ray diffraction respectively. The average grain size calculated from the X-ray diffraction spectra was between 20 and 80 nm. Scanning electron microscopy pictures revealed crystallite sizes up to 20 $\mu$m x 14 $\mu$m x 6 $\mu$m. The colour of the film obtained was grayish black [132]. Molybdenum selenide films have been electrodeposited cathodically on titanium substrates from an ammoniacal solution of H$_2$MoO$_4$ and SeO$_2$ under galvanostatic conditions. Structural characterization of the electrodeposited films using EDAX, EM and SEM studies have been carried out [133]. Electrodeposited MoSe$_2$ films have been characterized by optical, electrical and electrochemical studies. The I-V characteristics of the MoSe$_2$ film in contact with 2I$^-$/I$_2$ electrolyte indicate that the energy transfer at the interface is via the valence band and it also involves the surface states [134]. The influence of sputtering and annealing on the properties of MoSe$_2$ film was investigated by scanning electron microscopy, electron microprobe analysis, X-ray photoelectron spectroscopy (XPS), X-ray analysis, optical absorption and electrical resistivity measurements. It was found that stoichiometric thin films are obtained after appropriate annealing. The crystallite size varies between 10 and 20 nm. Annealing treatment improved the crystallization, and the crystallites exhibit a (0 0 1) orientation. The optical band gap was determined to be 1.15 eV and 1.26 eV. The quantitative analysis shows that almost stoichiometric films can be obtained after annealing whatever the substrate (glass, mica, molybdenum foil) and the substrate temperature are. The room temperature resistivity of the films varied from $0.1 \times 10^3$ to $15 \times 10^3 \Omega$-cm.
The temperature dependence of the electrical resistivity between 80 and 550 K was studied and is in the temperature range 500 – 550 K the activation energy is 0.57 eV. The molybdenum crystallizes in the b.c.c. system with lattice parameter $a = 3.14 \, \text{Å}$ and for hexagonal system $a = b = 3.28 \, \text{Å}$ and $c = 12.93 \, \text{Å}$ [134 - 136].

The efficiency and the stability of layer-type transition metal dichalcogenides such as MoSe$_2$ and WSe$_2$, depend on the chemistry of redox couple involved in the formation of the semiconductor / electrolyte interface. Generally, in a semiconductor / electrolyte junction, illuminated with radiation whose energy is equal or greater than the band gap energy of the semiconductor, the absorption of photons allows the electrons to be transformed from the valence band into the conduction band, and electron-hole pairs are created and separated by the electric field in the space charge region. Under open circuit this process leads to a decrease of the band bending, i.e., the energy bands are shifted towards the flat condition and thus a corresponding maximum photovoltage $V_{ph}$ is developed. The value of this photovoltage depends on the degree of band bending and it is related to the equilibrium between the Fermi level of the semiconductor and that of the electrolyte in dark.

The photovoltage obtained with a semiconductor in contact with the redox couple situated within the forbidden gap is easily calculated from simple energetic considerations. Under high illumination $V_{ph}$ is given by the equation:

$$V_{ph} = U_{\text{redox}} - U_{fb} - U_{sc}$$

(6.17)
where \( U_{\text{redox}} \) is the redox electrode potential in dark, \( U_{fb} \) is the flat band potential and \( U_{sc} \) is the potential drop in the space charge region \( \text{Versus}_{c} \). \( U_{sc} \) depends on the illumination intensity.

From this relationship the photovoltage is expected to be proportional to the redox potential of the electrolyte and theoretically to linearly increase with increasing positive values of redox potentials.

MoSe\(_2\) layer crystals were successfully used as photoelectrodes in electrochemical solar cells. Their mechanism is based on d→d transitions in the electrode in combination with anodic electron transfer from suitable redox couples in the adjoining electrolyte. (I\(_1\)/I\(_2\)) Redox agents with potentials more negative than that of water can be oxidized by holes from the low lying Mo 4d\(_z^2\) energy is before the anodic onset of the photoreaction with water molecules which would lead to the formation of selenic acid and to the photodissolution of the electrode. In this way it is possible to operate regenerative electrochemical solar cells by passing corrosive reactions. With MoSe\(_2\): I\(_1\)/I\(_2\) solar cell photocurrent density of 22 mA/cm\(^2\), photovoltage of 0.55 V and energy conversion efficiency between 4 and 5% were obtained over a period of more than 1200 hours (50 days) [137].

Single crystals of MoSe\(_2\) were grown by the direct vapour transport technique and it was found that the grown crystals posses n-type character [138]. The electrolyte having composition (0.025 M I\(_2\) + 1 M NaI + 2 M Na\(_2\)SO\(_4\) + 0.50 M H\(_2\)SO\(_4\)) was identified as the most suitable after investigations on a
number of electrolytes [139]. The photoconversion behaviour was studied after illuminating the photoelectrode with a polychromatic (neon lamp Kratos Instruments Ltd., USA) at an intensity of around 10 mW/cm² (measured using Suryamapi Cell, India) and investigating its V-I characteristics. For different open circuit voltage, short circuit current and efficiency was analyzed for MoSe₂ crystals as grown used as electrodes and the same thing after heat treatment and chemically treated successfully. This clearly shows that the controlled processing improves the forward dark current characteristics considerably by reducing the resistance and other losses. In addition, it also seems to improve the quality of the diode by increasing the shunting resistance - may be by reducing the trapping energy of the surface and recombination centres within the bulk [140]. By the direct vapour transport technique n-type MoSe₂ crystals, grown from a stoichiometric mixture of molybdenum (99.95% pure Koch Laboratories, London) and selenium (99.9999% pure Johnson - Matthey Chemicals, London). The semiconductor electrodes so prepared were used as photoanodes in n-MoSe₂ / (0.025 N I₂, 1 N or 2 N Na₂SO₄, 0.5 N H₂SO₄) / Pt electrode PECs. Photovoltage – Photocurrent characteristics of n-MoSe₂ / I / I₂ / Pt electrode PEC cell before and after heat treatment was studied [141]. Photoconversion at a constant polychromatic illumination intensity of around 20 mW/cm² from a number of photoelectrodes fabricated using grown and cleaved crystals was investigated. The conversion efficiency and fill factor were found to be changing randomly. This observation is expected from the randomness of the interfacial morphological structure and the series resistance of the photoelectrode [32].
This is the only report available for MoSe$_2$ thin film used as PEC. The photoelectrode consists of MoSe$_2$ film electrodeposited on a titanium substrate. Films prepared with different deposition parameters were used as photoelectrodes is an attempt to optimize the cell performance. The counter electrode was platinum. The light source was a tungsten filament lamp adjusted to give 65 mW/cm$^2$ intensity of illumination measured by a solar flux meter (Suryamapi, manufactured by Central Electronic Ltd.). The aqueous electrolyte is 0.50 M K$_2$SO$_4$ + 0.10 M KI + 0.025 M I$_2$ + 0.50 M H$_2$SO$_4$. A detailed I-V characteristic of each cell was studied to determine the maximum possible power output of each cell. From the film stability and cell performance characteristics, we have found that the film prepared using electrolyte with 10:100 of H$_2$MoO$_4$ and SeO$_2$ mother solutions at 40°C and 2.4 mA/cm$^2$ electrolysis current density gave the best PESC. MoSe$_2$ film is an indirect band gap semiconductor and hence, its absorption coefficient, $\alpha$, is generally small. The number of photogenerated carriers depends exponentially on the absorption coefficient as

$$g(x) = \alpha I_0 e^{-\alpha x}$$  \hspace{1cm} (6.18)$$

where $g(x)$ is the carrier generation rate, for a higher generation rate $\alpha$ and $x$ should be large. We have seen that $\alpha$ is small, so a greater thickness is necessary for the generation of reasonable number of photocarriers. For 1.1 $\mu$m thickness of the MoSe$_2$ film the efficiency $\eta$ reported was 0.125 and the Fill Factor FF was 0.27. The film structure is full of defects, voids and non-uniformity, having a trap density $\approx 10^{14}$ cm$^{-3}$ which is found to cause a loss of efficiency. From the Mott-Schottky plots the following points of difference are of interest.
(i) \( V_b \) is high for low thickness film

(ii) The value of depletion layer width \( W \) is small for low thickness film

The value of \( N_0 \) is large for low thickness film. The maximum electrochemical solar cell voltage obtainable for any electrolyte is equal to band bending voltage \( V_b \) \[142\].

6.7.2.3. Review of earlier work on Mo\(_{x}\)W\(_{1-x}\)Se\(_2\)

As there are no reports available in the literature for the PEC properties of Mo\(_{x}\)W\(_{1-x}\)Se\(_2\) thin films, photoactivity was investigated by electrochemical methods \[164\]. The behaviour in various redox electrolytes used to determine the contact formation behaviour. The dark and photocurrent voltage characteristics of p-Mo\(_{0.5}\)W\(_{0.5}\)Se\(_2\) prepared from different flux and by chemical vapour transport are discussed with an electrolyte 0.50 M K\(_2\)SO\(_4\), illuminated with W-I lamp. In the further characterization of the mixed cation layered crystals, only the CVT material is investigated since it appears to exhibit better physical and electrochemical properties. Dark and photocurrent - voltage characteristics of CVT grown p-Mo\(_{0.5}\)W\(_{0.5}\)Se\(_2\) electrodes with various redox electrolytes 0.10 M K\(_3\)Fe(CN)\(_6\), 0.50 M KI, 50 mM I\(_2\), 0.35 M VCl\(_2\) – VCl\(_3\), 4 M HCl was also reported. The poor photovoltage and the comparable high dark currents are believed to originate from a shift in flat band potential due to I\(_3\) adsorption on Van der Waals surfaces or J“ adsorption at steps and defects \[165\].

Single crystals of p-type Mo\(_{x}\)W\(_{1-x}\)Se\(_2\) (\(x = 0.25, 0.50\) and \(0.75\)) prepared by chemical vapour transport (CVT) exhibit an energy gap \( E_g \approx 1.3 \) to 1.4 eV
The electrochemical measurements were performed in a standard three-electrode potentiostatic arrangement using a graphite counter electrode and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte was 1 M K₂SO₄ and the light source of 150 W tungsten iodine lamp. Measurements using different redox electrolytes such as K₃[Fe(CN)₆] + K₄[Fe(CN)₆]; V²⁺ / V³⁺ in HCl and KI/I₂ / H₂O or KI/I₂/HI were also done. The potentials are referred to that of the employed redox electrolyte. All electrolyte solutions were prepared with bidistilled water and analytical grade chemicals and stored under argon or nitrogen.

Capacitance and Voltage measurements were employed to investigate the electrochemical and photoelectrochemical (PEC) behaviour of n-WSe₂, p-WSe₂ and n-MoSe₂ single crystal electrodes in aqueous solutions containing various redox couples Br⁻ / Br₂, I⁻ / I₃⁻, Fe(CN)₆⁴⁻/ Fe(CN)₆³⁻, Fe²⁺ / Fe³⁺, HV⁺ / HV²⁺ and MV⁺ / MV²⁺. In supporting electrolyte (0.5M Na₂SO₄) the conduction band edges of MoSe₂ and WSe₂ determined from the capacitance measurement, are at −0.14 and −0.44 V versus. SCE [166]. A rough surface that exhibit high photoactivity with high reproducibility. Conversion efficiency upto 12.4% was reported [167]. The optical and photoelectrochemical properties of the polyiodide electrolyte / WSe₂ interface were studied. The conversion efficiency for various electrodes were analyzed and found the stepped electrodes has a weak efficiency compared to cleaved electrodes [168]. n-type WSe₂ was grown by chlorine or bromine transport method. A solar to electrical conversion efficiency of 3.7% is reached on a smooth photoanode in the n-WSe₂ / 2 M KI –
0.05 I₂ / C cell and in the case of p-WSe₂ the conversion efficiency is only 2% [169].

Au / n-WSe₂ Schottky junctions usually exhibit linear dark current – voltage characteristics, apparently dominated by structural defects and low open circuit voltages. After treatment of the WSe₂ with polyiodide in a liquid junction configuration and subsequent deposition of Au, good diode characteristics and high V_{oc} are obtained which are similar to those exhibited by WSe₂ / polyiodide liquid junctions [170]. WSe₂ crystals have been grown via vapour transport technique, employing SeCl₄ as transporter. Photoelectrochemical solar cells with n-WSe₂ / I⁻, I₂ / Pt have been fabricated. In order to improve upon, the efficiency, the effective WSe₂ crystal surfaces have been etched in aqua-regia. A high conversion efficiency upto 17.1% was obtained. This corresponds to the most efficient WSe₂ – based PEC solar cell reported so far [171]. The dark electrochemical behaviour of polycrystalline p-WSe₂ electrodes is investigated. The dominant role of tungsten bonds for both the equilibrium behaviour of the electrode and the reactions that take place at different electrode potentials (hydrogen tungsten bronze formation and oxidation, hydrogen evolution reaction etc) is analyzed [172]. The effect of polyiodide solution treatment on WSe₂ both n and p type prior to Schottky junction formation, has been studied. Single crystals of n-WSe₂ have shown reasonable conversion efficiencies in LJ cells – 14% for red light [173] and greater than 13% for solar illumination [174]. The most efficient of these cells use a polyiodide electrolyte (KI + I₂ → KI₃) [175]. The p-type WSe₂ semiconductor electrode was introduced in an aqueous solution of
ferric / ferro cyanide electrolyte with concentrations 0.05 M $K_3[Fe(CN)_6] + 0.05$ M $K_4[Fe(CN)_6] + 0.50$ M KCl along with the platinum electrode acting as a counter electrode. The maximum conversion efficiency is 9.05% for p-type WSe$_2$ [176].

The PEC cell consisted of the n-WSe$_2$ electrode and a platinum foil counter electrode immersed in a solution of 0.50 M H$_2$SO$_4$, 0.50 M Na$_2$SO$_4$, 1.0 M NaI and 0.025 M I$_2$. The maximum power conversion efficiency without corrections is about 14% [177]. The voltage distribution at the n-WSe$_2$ and n-MoSe$_2$ / electrolyte interface is obtained from electroreflection and capacitance measurements [178]. An energetically favourable energy band position makes it possible to operate p-type material as photocathodes energy conversion. Photocell outputs in the order of 15 mA/cm$^2$ and 0.5 V were obtained in 100 mW/cm$^2$ illumination shown that the produced photovoltage is not systematically dependent on the redox potential of the redox agent but influenced by their chemical reactivity due to a specific interaction with the electrode surface [179]. Careful photoetching of n-WSe$_2$ leads to a large improvement in its photoresponse. Conversion efficiencies in excess of 14% were obtained in polyiodide solution under simulated solar light [174]. Polycrystalline thin films of p-WSe$_2$ can be prepared and that they can be made, through the appropriate choice of reagents, to show respectable energy conversion efficiencies [180]. The photoelectrochemical behaviour of p-type WSe$_2$ single crystal electrodes in acetonitrile solutions containing a number of redox couples was investigated [181]. The PEC behaviour of n and p-type WSe$_2$ single crystal electrodes in aqueous solutions containing a number of redox couples was investigated. The
n-WSe$_2$ / I$^-$ (0.025 M), I$^-$ (1.0 M) / Pt cell showed a 0.71 V open circuit voltage, 65 mA/cm$^2$ short circuit current, 0.46 fill factor and ~14% power efficiency under 150 mW/cm$^2$ red light irradiation. A rechargeable PEC cell based on the p-WSe$_2$ / MV$^{2+}$, I$^-$/ n- WSe$_2$ system was constructed [182]. A photoelectrochemical storage cell for water decomposition with p-WSe$_2$ was described. It was shown that a considerable energy was reached by the catalytic action of platinum deposits on the surface of the electrode [183]. Electrodeposited tungsten selenide films are characterized optically, electrically and electrochemically. Mott-Schottky plots are drawn for the WSe$_2$ film 2I$^-$/ I$_2$ system from which various semiconductor parameters and energy band position at the interface are determined. The characteristics of PEC solar cells with the configuration of the WSe$_2$ film 2I$^-$/ I$_2$/ Pt system are also reported [184].

6.7.3.1. Methods of preparations

There are several methods for preparing thin films. Some of them are vacuum evaporation, sputtering hot wall epitaxy, spray pyrolysis, chemical vapour solution growth, electrodeposition, electroless deposition, deposition, brush plating, screen printing, pulse electrodeposition etc. Discussion about the various methods of film preparation was given by Chopra [66], Maissel and Glang [76] and Behrndt [77]. Chemical deposition techniques like electrodeposition, chemical vapour deposition, brush plating are particularly used for preparing large area semiconducting devices and are low in cost. A simple and brief discussion about the various methods of film preparation was discussed in [78]. Crystals with isoelectric group VI mixed cations of composition
Mo<sub>1-x</sub>W<sub>x</sub>Se<sub>2</sub> were grown by the reaction of the constituent elements. Single crystals were prepared by chemical vapour transport (CVT) [79], direct vapour transport [80, 81] molybdenum / tungsten dichalcogenides constitute structurally and chemically a well defined family of compounds having a general formula MX<sub>2</sub> (M = Mo, W; X = S, Te, Se). The methods of preparation of molybdenum / tungsten dichalcogenides are discussed below.

Among molybdenum chalcogenides MoSe<sub>2</sub> has led to the best solid state cells with efficiencies exceeding 6%, in particular due to surprisingly large short circuit currents of 33 mAcm<sup>-2</sup> [82, 83]. Unfortunately the low open circuit voltage still keeps the efficiency low, but Molecular Beam Epitaxy (MBE) is a new field, where automatically smooth and abrupt interfaces can be fabricated. But this heteroepitaxial systems is limited by surface dangling bonds, surface states, surface symmetry, ability to smooth the surface, the lattice mismatch between the two materials. In addition, the difference in the thermal expansion coefficients between epilayer and substrate result in appreciable thermal stresses at the interface. Van der Waals epitaxy (VDWE), a method recently developed by Koma [84, 85] gives a new route to hetero epitaxy about most of the constraints mentioned above. VDWE is growth of several 2D metal chalcognide material one upon the other, where the layers are bound together by weak Van der Waals forces. Many metal dichalcognide materials with structures characterized by chalcogen - metal - chalcogen layers held together by Van der Waals forces. Fig.4.1(a) shows the conceptional difference between a conventional heterointerface and an interface fabricated via the Van der Waals
epitaxy growth. Fig. 4.1(b) shows the crystal lattice structure of MoSe₂ showing the (h k l) planes and the location of Mo, Se atoms. Fig.4.1. (c) shows the layer structure of WSe₂ with different orientations (i) WSe₂ crystal layers perpendicular to the substrate and (ii) WSe₂ crystal layers parallel to the substrate are shown in Fig.4.1. (d) and 4.1. (e) respectively.

6.7.3.2. Flat band potentials measurements

The flat band potential measurements were performed for MoSe₂ photocathodes synthesized by pulse electrodeposition technique using C-V measurements potential curve.

The M.S-plots obtained for this film are shown in Fig.6.3. 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 Vₚ is found as 0.82 V (SCE) for pulse electrodeposited thin films which is in good agreement with the reported values of Vₚ = 0.81 V (SCE) for MoSe₂ film [75]. The important semiconductor parameters obtained using M-S plots are represented in Table.6.1.

6.7.2.6. Current – Voltage characteristics of MoSe₂

The nature of the junction between the photoelectrode, MoSe₂ synthesized by pulse electrodeposition technique and the redox electrolyte KI / I₂ was investigated by the studies of the dynamic current voltage characteristics in dark and under different illumination intensities. From Fig.6.6 it is observed that
Fig. 6.3. Mott-Schottky plot of (MoSe₂)
the curves obtained under illumination are shifted from that in dark, which show the photosensitivity of MoSe$_2$ films prepared.

6.7.2.7. Photoresponse

The photoresponse of the PEC cell formed with MoSe$_2$ films prepared by pulse electrodoposition technique as photocathode was studied by noting the short circuit current, $I_{sc}$ and the open circuit voltage, $V_{oc}$ as a function of deposition time and annealing time for a 40 mW/cm$^2$ intensity of the incident light, shown in Fig.6.4 and Fig. 6.5. It is seen that, the $I_{sc}$ and $V_{oc}$ vary with the time of deposition and annealing time respectively light intensity. The out power approaches a saturation state around 40 mW/cm$^2$ light intensity taken from Fig 6.6.

6.7.2.8 Annealing effects on PEC parameters - MoSe$_2$ films

The asprepared MoSe$_2$ 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,
Fig. 6.4. Time of deposition versus short-circuited current $I_{sc}$ (MoSe$_2$)
Fig. 6.5 Annealing time versus short circuited current $I_{sc}$ ($\text{MoSe}_2$)
Fig. 6.6. I-V characteristic under dark and illumination (MoSe$_2$)
annealing of the films has been carried out in vacuum and their influence on the PEC parameters.

Annealing was carried out at 100, 150, 200 and 250°C for different heating durations 30 to 60 min. The $V_{oc}$ values decreases linearly upto an annealing time of 60 min.

The effect of annealing on $V_{oc}$ and $I_{sc}$ for the pulse electrodeposited MoSe$_2$ film was shown in Fig.6.7 and 6.8 for annealing temperatures 100°C and 200°C. It is observed that vacuum annealing produces better output than the asdeposited films. It is evident that the $V_{oc}$ for asdeposited film is 0.19 V and that for the vacuum annealed film is annealed at 150°C to 0.29 V (Fig.6.5).

These observations reveal that annealing in vacuum produces better results. Based on these results, the optimized annealing temperature in vacuum is found to be 150°C and the duration is 45 min for pulse electrodeposited MoSe$_2$ films.

6.7.2.9. Effect of film thickness on PEC parameters

The PEC output has been recorded for the pulse electrodeposited, MoSe$_2$ films with varying thickness. The $V_{oc}$ and $I_{sc}$ variation of pulse electrodeposited MoSe$_2$ films is shown in Fig.6.4. Both values $I_{sc}$ and $V_{oc}$ for the deposition time of 45 minutes for the film thickness of about 6.8 μm are reasonable to give maximum output power. It shows that the film prepared by pulse
Fig. 6.7. Annealing time versus short circuit current $I_{sc}$ (MoSe$_2$)
Fig. 6.8. Annealing time versus short circuited current $I_{sc}$ (MoSe$_2$)
electrodeposition technique, is capable of giving good PEC output. The corresponding values of $V_{oc}$ and $I_{sc}$ are 205 mV and 1.0 mA cm$^{-2}$ respectively.

Fig. 6.4 shows the $V_{oc}$ and $I_{sc}$ variations with thickness for the pulse electrodeposited MoSe$_2$ films. The variation is a linear and steep up to about 45 min of deposition having thickness of about 7.0 $\mu$m. This reveals the fact that MoSe$_2$ film of thickness in the range 6.5 to 7.3 $\mu$m may be the optimum for getting maximum $V_{oc}$ and $I_{sc}$ values through pulse electrodeposition route.

Based on this observation, all the PEC related studies have been carried out using the electrolyte 2 M KI + 0.05 M I$_2$ unless otherwise stated.

6.7.3 TUNGSTEN DIESELENIDE THIN FILMS

In the following sections, a review of the properties of WSe$_2$ films prepared by different techniques are presented. Then the results obtained from the I-V and M-S studies of the WSe$_2$ films deposited in the present work by pulse electrodeposition technique is presented.

6.7.3.1. Review of earlier work on WSe$_2$

The polycrystalline WSe$_2$ was prepared by direct synthesis at 1253 K from the constituent elements in evacuated quartz ampoules. The dark electrochemical behaviour of polycrystalline p-WSe$_2$ electrodes is investigated. The dominant role of tungsten bonds for both the equilibrium behaviour of the electrode and the reactions that take place at different electrode potentials (hydrogen tungsten bronze formation and oxidation, hydrogen evolution
reactions, etc) is analyzed [143]. Single crystals of WSe₂ have earlier been used for photoelectrochemical solar cells attain high efficiency up to 14% [144]. The PESC consists of the WSe₂ film electrodeposited on titanium. Platinum is used as a counter electrode and the aqueous electrolyte consists of 0.50 M K₂SO₄ + 0.50 M H₂SO₄ + 0.10 M KI + 0.025 M I₂. I-V characteristics and power characteristics across the load for photoelectrodes prepared at different electrolysis time was analyzed. The open circuit voltage does not change much (it changes only from 160 to 240 mV). However, the short-circuit current density drastically decreases by an order of magnitude as we go to higher thickness films. This is attributed to high recombination encountered by the defective bulk nature of the electrodeposits. The efficiency and fill factor of few samples were also reported [34].

The energy scheme of a regenerative photoelectrochemical cell is discussed. The reduction process at the metal counter electrode compensates the oxidation process by holes. Energy gain = energy of the excited electrons in the semiconductor relative to their energy in the redox system. The performance of a material in photoelectrolysis can best be judged from a photocurrent voltage curves obtained in a potentiostatic arrangement [145]. This report present after thorough characterization of large-area polycrystalline thin films of p-WSe₂ and demonstrate that recombination losses can be suppressed through electropolymerization of O-phenylenediamine. In addition, the kinetics of hydrogen evolution can be greatly accelerated via surface modification with a viologen polymer and colloidal platinum. Efficiencies for photoassisted hydrogen
evolution in excess of 1% were obtained for these modified electrodes. From Mott-Schottky plot we can estimate the flat band potential to be about +0.86 V versus SCE < in good agreement with our previous results [146] as well as with results on single-crystal materials [147] and the doping density of about 5.2 \times 10^{17} [148]. The current-voltage characteristics of the samples in 2 M KI + 0.05 M I_2 solution exposed to air are discussed. A correlation exists between the short circuit current, the open circuit voltage, and the fill factor on one side and surface perfection, determined by SEM, on the other. We propose that, an electric field component, which parallels the layers is introduced by the steps. Because of the highly anisotropic conductivity of layered compounds the holes, on their way to the interface, are deflected and move to recombination sites at the edges of the steps. Thus it raises the conversion efficiency from 3.7% to 5.2% [149]. The effect of polyiodide solution treatment on WSe_2 both n and p type prior to Schottky junction formation has been studied. The junctions have been mainly characterized by (photo) current / voltage and spectral response measurements. The most efficient of these cells use a polyiodide electrolyte (KI + I_2 → KI_3) [150]. It is generally believed that there is a specific interaction between the I_3^- ion and the WSe_2 surface, which is a beneficial for the photovoltaic activity. This interaction has been variously described as intercalation of iodine [151], blocking of recombination sites by elemental iodine [152 - 154] or a donor-acceptor interaction [155].

Au/n-WSe_2 Schottky junctions usually exhibit dark current-voltage characteristics apparently dominated by structural defects, and low open circuit
photovoltages. After treatment of the WSe₂ with polyiodide in a liquid junction configuration and subsequent deposition of Au, good diode characteristics and high $V_{oc}$ are obtained which are similar to those exhibited by WSe₂/polyiodide liquid junctions [156]. Tenne et al. have reported that careful photoetching of n-WSe₂ leads to a large improvement in its photoresponse. Conversion efficiencies in excess of 14% were obtained in polyiodide solution under simulated solar light. A significant red shift in the photocurrent spectrum is observed after photoetching as well as hexagonal etch pits which reduce the reflectivity of the surface [157]. High solar energy conversion efficiencies in such cells require a semiconductor band gap energy ($E_g$) which matches well with the solar spectrum, a semiconductor flat-band potential ($V_{fb}$) and solution redox couple potential ($V_{redox}$) which maximizes the output voltage, and condition which minimize recombination process in the semiconductor and solution and at the interface [158]. The solution redox couple and the solvent are selected to stabilize the semiconductor from photoinduced corrosion processes [159, 160]. A single crystal of WSe₂ grown by a chemical vapour transport has been used in the fabrication of photoelectrochemical solar cells. The semiconductor electrode prepared was then introduced in an aqueous solution of ferri / ferro cyanide electrolyte with concentrations 0.05 M $K_3[Fe(CN)_6]$ + 0.05 M $K_4[Fe(CN)_6]$ + 0.50 M KCl along with the platinum electrode acting as a counter electrode. This cell was illuminated with a xenon lamp (Kratos, LPS 251 HR). The intensity of illumination was measured with the help of Suryamapi (Central Electronics, India). The photocurrent – photovoltage of this cell was evaluated at different intensities of illumination. The maximum efficiency reported in this case 9.05%
The current voltage characteristics of all investigated samples showed strongly asymmetrical behaviour with large cathodic photocurrents arising in the negative potential region. Typically for p-conducting material hydrogen evolution depend on photoexcitation of electrons into the conduction band of the electrode, while the anodic reaction of hole which lead to selenic acid and traces of selenium is a dark reaction [162]. WSe$_2$ crystals (photo-electrodes) have been grown via vapour transport technique, employing SeCl$_4$ as transporter. Many attempts have been made to improve the conversion efficiencies. These include surface cleaving, surface modification, photoetching etc. The I-V characteristics of the WSe$_2$ crystal before and after photoetching were analyzed. The PEC conversion efficiency before photo etching is -8.3% and this changes to 17.1% after photoetching. It should be mentioned that the said efficiency (~ 17.1%) is one of the highest reported value for WSe$_2$ based PEC solar cells. The electrolyte used for electrochemical studies corresponded to 1 M KI + 0.05 M I$_2$ (pH ~ 9). Illumination was provided with a tungsten lamp with an intensity of 60 mW/cm$^2$ [33]. The photoelectrochemical (PEC) behaviour of n and p-type WSe$_2$ single crystal electrodes in aqueous solutions containing a number of redox couples (Br$_2$ / Br$^-$, Fe$^{3+}$ / Fe$^{2+}$, I$_2$ / I$^-$, Fe(CN)$_6$$^{3-}$ / Fe(CN)$_6$$^{4-}$ and MV$^2+$ / MV$^+$, where MV is methylviologen) was investigated. The results are consistent with a model of the interface where ideal behaviour is approached with some couples, but recombination effects are important with others. The n-WSe$_2$ / I$_3$(0.025 M), I(1.0 M) Pt cell showed a 0.710 V open circuit voltage, 65 mA/cm$^2$ short circuit
current, 0.46 fill factor and -14% power efficiency under 150 mW/cm² red light irradiation [163].

6.7.3.2. Flat band potential measurements

The flat band potential measurements were performed for WSe₂ photocathodes synthesized by pulse electrodeposition technique using C-V measurements versus potential curve.

The M-S plot obtained for these film is shown in Fig.6.9. The nature of conductivity of all the films was found to be ‘p’ type as evident from negative slope of the M.S-plot. The value of flat band potential $V_{fb}$ is found to be 0.81 V (SCE) which is in good agreement with the earlier result of $V_{fb} = 0.86 V_{(SCE)}$ for WSe₂ thin films [185]. The important semiconductor parameters obtained using M.S- plots are represented in Table 6.2.

6.7.3.3. Current – Voltage characteristics of WSe₂

The nature of the junction between the photoelectrode, WSe₂ synthesized by pulse electrodeposition technique and the redox electrolyte KI / I₂ was investigated by the studies of the dynamic current voltage characteristics in dark and under different illumination intensities. From Fig.6.10 it is observed that the curves obtained under illumination are shifted from that in dark, which show the photosensitivity of WSe₂ films.
Fig. 6.9. Mott-Schottky plot of (WSe₂)
Fig. 6.10. I-V characteristic under dark and illumination (WSe₂)
6.7.3.4. Photoresponse

The photoresponse of the PEC cell formed with WSe$_2$ films prepared by pulse electrodeposition technique as photocathode was studied by noting the short circuit current, $I_{SC}$ and open circuit voltage, $V_{OC}$ as a function of deposition time and annealing time for a 60 mWcm$^{-2}$ intensity of the incident light, shown in Fig. 6.11 and 6.12 respectively. For the time of deposition 45 min and for annealing temperature 150$^\circ$C $I_{SC} = 1.4$ mAcm$^{-2}$ and $V_{OC} = 190$ V yielding maximum output power. Fig. 6.12 shows the variation of $I_{SC}$ and $V_{OC}$ for different annealing times. For WSe$_2$ films annealed in vacuum for 1 h for 150$^\circ$C $I_{SC} = 0.40$ mAcm$^{-2}$ and $V_{OC} = 194$ mV.

6.7.3.5. Annealing effects on PEC parameters

Polycrystalline WSe$_2$ films can be a promising photoelectrode 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. WSe$_2$ films prepared by pulse electrodeposition method, subjected to a heat treatment exhibited a remarkable increase in conversion efficiency and improved the stability of the solar cell. The films were subjected to annealing at 100, 150 and 200$^\circ$C in vacuum.

Annealing was carried out at 100,150, 200 $^\circ$C for different durations. The effect of annealing on $V_{OC}$ for the pulse electrodeposited WSe$_2$ photoelectrodes is shown in Fig.6.13 and 6.14 for annealing temperature 100 and 200$^\circ$C. The $V_{OC}$
Fig. 6.11. Time of deposition versus short-circuited current $I_{sc}$ (WSe$_2$)
Fig. 6.12. Annealing time versus short circuited current $I_{sc}(\text{WSe}_2)$
Fig. 6.13. Annealing time versus short circuited current $I_{sc}$ ($\text{WSe}_2$)
Fig. 6.14. Annealing time versus short circuited current $I_{sc}$ ($\text{WSe}_2$)
for vacuum annealed pulse electrodeposited WSe₂ film annealed at 150°C is 190 mV for the time of deposition 60 min (Fig. 6.11).

The V_oc values vary with annealing time as shown in Fig. 6.11. Maximum current is observed at 60 min for vacuum annealing at 150 °C. This is in conformity with the observation that the stoichiometric WSe₂ films are obtained after annealing for 60 min as given in chapter IV. Annealing was carried out in vacuum at 100, 150, 200°C for different durations. The I_sc value is higher for vacuum annealed films annealed at 150°C and shows the small variations in V_oc.

6.7.3.6. PEC parameters of MoSe₂ photocathodes

The photoresponse of the PEC cell formed with MoSe₂ thin film prepared under optimized pulse electrodeposition condition annealed at 150°C for 1 h was analyzed by observing the short circuit current I_sc and open circuit voltage V_oc with different incident light intensities as shown in Fig. 6.6. From the I - V curve for the incident light intensity 40 mW/cm² the solar conversion efficiency η = 0.189 and fill factor F.F = 0.51 are determined.

6.7.3.7 PEC Parameters of WSe₂ photocathodes

The photoresponse of the PEC cell formed with WSe₂ prepared by pulse electrodeposition technique under optimized condition vacuum annealed at 150°C for 60 minutes duration was studied by noting the short circuit current I_sc and the open circuit voltage V_oc vary with the incident light photon intensities. The power seems to approach a saturation
state around 60 mW/cm$^2$ light intensity and is shown in Fig. 6.10. The PEC output has been recorded for the pulse electrodeposited WSe$_2$ film since the product of $I_{sc}$ and $V_{oc}$ values are maximum for the deposition time of 60 minutes during this time the film thickness is about 8.3 $\mu$m. The values of $V_{oc}$ and $I_{sc}$ are 166 mV and 0.75 mA/cm$^2$ respectively. From the I.V plot with the incident light intensity of 60 mW/cm$^2$ the solar conversion efficiency $\eta$ and the fill factor F.F. are calculated and the values are 0.129% and 0.346 respectively.

6.7.3.8 Flat band potential measurements

Fig. 6.15 shows the plot of $1/C^2$ versus $V$ (Mott-Schottky plot) for the typical Mo$_{0.5}$W$_{0.5}$Se$_2$ films prepared by pulse electrodeposition technique in the KI/I$_2$ redox electrolyte solution. The nature of the Mott-Schottky plot 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 0.92 V$_{SCE}$ for pulse electrodeposited film. Using Mott-Schottky plot, the important semiconductor parameters such as acceptor concentration, density of states in the valence band and depletion layer width are estimated and given in Table 6.3

6.7.3.9 Current - Voltage characteristics of Mo$_{0.5}$W$_{0.5}$ Se$_2$

To understand the nature of the junction between the photoelectrode, Mo$_{0.5}$W$_{0.5}$Se$_2$ prepared by pulse electrodeposition technique, and the electrolyte KI/I$_2$, the dynamic current – voltage characteristics in dark and under different illumination intensities were studied from Fig. 6.16.
Fig 6.15. Mott-Schottky plot of (Mo_{0.50}W_{0.50}Se_{2})
Fig. 6.16. I-V characteristic under dark and illumination ($Mo_{0.50}W_{0.50}Se_2$)
It is seen that the curves obtained under light are shifted from that in dark, which implies the photosensitizing ability of Mo$_{0.5}$W$_{0.5}$Se$_2$ thin films.

6.7.3.10 (Mo$_x$W$_{1-x}$Se$_2$) Dichalcogenides of molybdenum and Tungsten thin films

PEC properties of solid solutions of MoSe$_2$, WSe$_2$ are reviewed first. The studies on Mo$_{0.5}$W$_{0.5}$Se$_2$ films prepared by pulse electrodeposition technique have been carried out to characterize their PEC properties as in the case of MoSe$_2$ and WSe$_2$ thin films. The fill factor and efficiency of the vacuum annealed films of pulse electrodeposited Mo$_{0.5}$W$_{0.5}$Se$_2$ films are found to be 0.251 and 0.490%.

6.8. SUMMARY AND CONCLUSION

Photoelectrochemical solar cells based on Mo$_x$W$_{1-x}$Se$_2$ (0 ≤ x ≤ 1) semiconductor thin films are prepared using pulse electrodeposition technique and characterized. Using Mott-Schottky plots, the important semiconductor parameters are estimated and tabulated. The effect of film thickness, annealing in vacuum and illumination intensity on solar cell parameters are studied. An improvement in open circuit voltage $V_{oc}$, short circuit current $I_{sc}$ fill factor F.F, efficiency $\eta$ are observed for the films annealed in vacuum at 150°C.
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