# CHAPTER 6

A TEST   CASE STUDY OF PHOTOELECTROCHEMICAL
SOLAR CELLS USING n-TYPE NATURAL $MoS_2$ SINGLE
CRYSTALS

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## 6.1    Introduction

One of the most important criterion for fabricating a PEC solar cell is the selection of a suitable semiconducting material which would serve as a stable electrode against photodecomposition. While making a search for such type of materials one should go for a material which is capable of undergoing phototransitions in the visible spectral region but which however should not break chemical bonds, because only phototransitions of electrons which would leave the bonding situation in a semiconductor electrode surface unchanged, will spare the electrode entirely from photodecomposition.

So there started a search for an appropriate type of material. The basic idea for the search was, that visible light phototransition should not be an electron transition from an anion valence band to cation conduction band, as is characteristic for polar semiconductors such as CdS, GaAs or GaP which results in the breaking of polar bond, but the transition should occur between energy bands resulting from the orbitals of metal component of the semiconductor.

The investigation consequently concentrated

upon transition metal dichalcogenides with the problem of finding those compounds with a maximum of d-d splitting which would be necessary for the absorption of photons of energy approximately 2 eV. Such materials were found to be tungsten disulphide and molybdenum disulphide. Since there is no problem of obtaining good natural $MoS_2$ crystals, initial experimental research was concentrated upon molybdenum disulphide. The energy band structure of $MoS_2$ has been shown in Fig. 1.7 (Chapter 1). It can be very clearly seen that the phototransition of electron corresponds to a transition between d-orbitals of Molybdenum component of $MoS_2$.

Tributsch[1] has studied the PEC behaviour of natural $MoS_2$ single crystals in $Fe^{2+}/Fe^{3+}$ solution. He has reported exhaustive results for natural $p-MoS_2$ crystals. Influence of crystal surface orientation on redox reactions at semiconducting $n-MoS_2$ has also been examined by Ahmed and Gerischer[2] and better conversion efficiencies are found in iodine/iodide solution by Kline et al[3] for $MoS_2$ photoelectrodes. These results have shown that PEC behaviour of n-type natural $MoS_2$ is interesting.

The potential distribution of semiconductor-electrolyte interface is a key parameter in order to understand the kinetics of redox reactions at electrode and in determining the utility of electrode in PEC cell. The flat

band potential $V_{fb}$ is an important parameter in PEC cell which determines the relative Fermi levels of electrolyte and semiconductor (conduction and valence band) and the amount of band bending at the interface. The knowledge of these energy level positions are useful to estimate the exchange current and to get an idea about which band will be involved in the charge transfer reaction at the interface. There are several methods available to determine the flat band position ($V_{fb}$). The most common method, which has proved very successful and which has been used in the present work in determining the flat band position and the doping level is the measurement of the space charge capacitance as a function of the electrode potential.

Another widely used possibility is to observe photovoltages or the onset of photocurrents in dependence of the potential. The disappearance of photocurrents and photovoltages at $V_{fb}$ is the basis of these methods. A third method of locating energy levels of semiconductors relative to the potentials of various redox couples by cyclic voltammetry has also proved successful.

The cardinal interest of the present work was to characterize the interface between natural $n-MoS_2$ and iodine/iodide electrolyte, using flat band potential

obtained from Mott-Schottky plot, to provide a guide line
for future work and to study the effect of incident light
intensity on the performance of PEC cells.

6.2    Experimental

        Naturally available n-type single crystals
of molybdenite, $MoS_2$ were used in the present work.  The
semiconducting nature of the crystals was confirmed by
hot-probe method and from Mott-Schottky plot. EDAX analysis
of crystals showed the presence of impurities as Al, P, Ni,
Pi, Si.  The concentration of these impurities was found to
vary from sample to sample.

Fabrication of photoelectrochemical solar cells

        A glass tube with a bore and flattened end
was used for mounting the single crystals. A copper wire
was introduced through the bore and connected to the crystals
using silver paste. The electrode surface was insulated at
the edges using a good epoxy. The semiconductor electrode
was then immersed in an aqueous iodine/iodide electrolyte
prepared by mixing 2M NaI, 0.025 M $I_2$, 0.5 M $Na_2SO_4$, 0.5 M
$H_2SO_4$ in doubly distilled water and platinum grid as
counter electrode.

        Capacitance measurements were made by using

the LCR meter ( VLCR-27, Vasavi Electronics, India). During

the capacitance measurements photoelectrochemical cell was

well protected from light. A saturated calomel electrode

(SCE) was employed as reference electrode to measure the

potential applied to semiconductor electrode. A schematic

diagram representing the experimental set up of PEC cell

for capacitance measurements is shown in Fig. 6.1. For

studying the effect of incident light intensity the cell

was illuminated by light from an incandescent lamp. The

schematic diagram of experimental set up of cell is displayed

in Fig. 6.2. The intensity of illumination was varied by

changing the distance  between light source and photoanode.

The incident intensity of illumination was measured using

"Suryamapi" (light intensity measuring instrument by Central

Electronics Ltd., India). Photovoltage and photocurrent were

recorded using digital multimeters.

## 6.3    Results and Discussion

### Capacitance measurements

The semiconductor-electrolyte interface can

be treated as two capacitances in series, one in the electro-

lyte near the surface (Helmholtz layer) $C_H$ , and the other

capacitor formed in the semiconductor by the depletion

region $C_{SC}$[4] . Since these two capacitors are in series

Fig. 6.1    Schematic diagram of experimental
            set up of PEC cell for capacitance
            measurement.

Fig. 6.2    PEC solar cell using natural n-$MoS_2$
            crystal as photoelectrode and
            platinum grid as counter electrode.

            (1) semiconductor  (2) Incident light
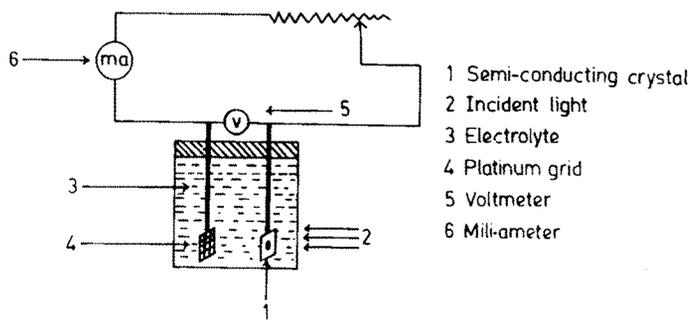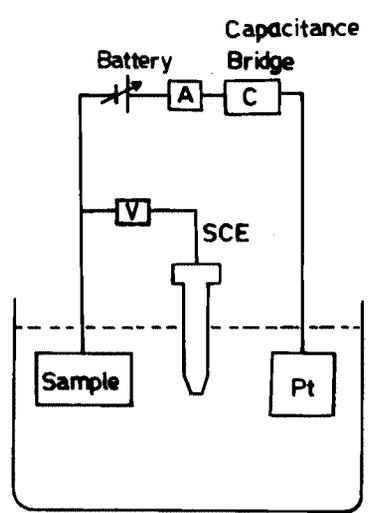            (3) Electrolyte    (4) Platinum grid.

1 Semi-conducting crystal
2 Incident light
3 Electrolyte
4 Platinum grid
5 Voltmeter
6 Milli-ameter

Fig. 6.2



Fig. 6.3 1

and $C_{SC} \ll C_H$, the net capacitance is very close to $C_{SC}$. According to the depletion layer approximation the capacitance of space charge layer varies with the bias applied to the semiconductor by the Mott-Schottky relation[5,6],

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon \epsilon_o e N_D} ( |V_{sce}| - \frac{kT}{e} )$$  (6.1)

where $\epsilon$ is the dielectric constant, $\epsilon_o$ the permittivity of free space, e the charge of electron, $N_D$ donor concentration, $V_{sce}$ applied potential across the space charge layer which can be expressed as $V_{sce} = V - V_{fb}$, $V_{fb}$ is the flat band potential. From equation (6.1) it is seen that the straight line would be obtained if $1/C_{SC}^2$ versus V is plotted. This is termed as Mott-Schottky plot. The intercept on the V axis gives the flat band potential $V_{fb}$ and from the slope of the curve the value of donor concentration $N_D$ can be calculated.

Mott-Schottky plot for natural $MoS_2$ single crystal at 1 KHz frequency in 0.025 M $I_2$, 2 M NaI, 0.5 M $Na_2SO_4$ and 0.5 M $H_2SO_4$ is shown in Fig. 6.3. The flat band potential $V_{fb}$ evaluated from the plot is 0.18 V Vs SCE. This agrees with the value found by Gobrecht et al[7] in

aqueous $I^-/I_2$ electrolyte. The donor concentration $N_D$ was

determined from the slope of Mott-Schottky relation

$$N_D = 2 \left[ e \; \epsilon\epsilon_o \; (\text{slope}) \right]^{-1} \qquad (6.2)$$

where $\epsilon$ is the dielectric constant of crystal which is
equal to 7.35 for $MoS_2$ (Evans et al[8] ). The evaluated donor
concentration for natural n-$MoS_2$ is found to be $N_D = 4.158$
x $10^{17}$ cm$^{-3}$. Tributsch[1] has reported the direct band gap
for n-$MoS_2$ as 1.75 eV. Further it has been found by Ahmed[9]
that a difference of 0.2 eV exists between the Fermi level
and the edge of conduction band ($E_c$) for n-$MoS_2$ crystals.
This enables us to locate the position of conduction band
($E_c$) at -0.02 V Vs SCE and valence band edge is located
at + 1.73 V Vs SCE. Thus a complete energy level diagram
for a system of semiconductor - electrolyte-metal at
equilibrium in the dark is obtained. The corresponding
positions of valence band, conduction band and Fermi level
so obtained are shown in Fig. 6.4. This suggests that the
redox couple with potential $V_{redox}$ within the gap -0.02 V
and 1.73 V Vs SCE should be appropriate for PEC cells with
natural n-$MoS_2$. In the present case the redox couple
potential is 0.3 V vs SCE.

Fig. 6.3     Mott-Schottky plot for PEC cell
             based on natural, n-type $MoS_2$
             crystal in aqueous iodine/iodide
             electrolyte.

Fig. 6.4     Energy level diagram  of system
             on natural n-$MoS_2$-electrolyte-
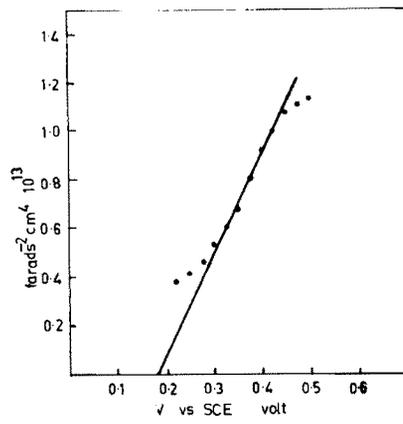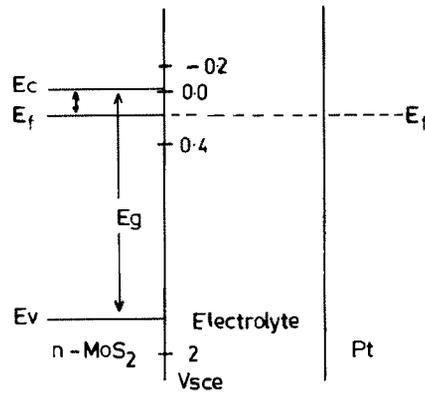             platinum electrode at equilibrium
             in dark.

Fig. 6.3



Fig. 6.4

## Effect of light intensity on the performance of the cell

The quality of the natural n-MoS$_2$/ electrolyte junction for the electrochemical photovoltaic applications has been assessed by examining the effect of varying light intensity on photocurrent behaviour. The effect of light intensity on photovoltage current characteristics of natural n-MoS$_2$ based PEC cell is illustrated in Fig. 6.5. According to Rajeshwar et al[10], the current-voltage characteristics of a semiconductor/electrolyte junction may be represented in terms of Schottky barrier theory by equation[11],

$$J = J_{ph} - J_d = J_{ph} - J_o [ \exp(eV/nkT) - 1 ] \qquad (6.3)$$

Here J is the net current density, $J_{ph}$ and $J_d$ are photocurrent and dark current densities respectively. $J_o$ is the reverse saturation current density, V is the voltage, n is "Junction-ideality" factor and other terms have their usual significance. At equilibrium (open circuit condition), $J_{ph} = J_d$ and $V = V_{oc}$ so that rearrangement of equation (6.3) yields,

$$V_{oc} \cong \frac{nkT}{e} \ln (J_{sc}/J_o) \qquad (6.4)$$

where last term in the bracket in equation (6.3) is neglected due to $V_{oc}$ exceeding $3kT/e$, here $V_{oc}$ is the open circuit voltage and $J_{sc}$ is the short circuit current density. If we further assume that $J_{sc}\ \alpha\ I_L$ ( = incident light intensity) and $J_{sc} \gg J_o$, equation (6.4) reduces to the following expression,

$$V_{oc}\ \alpha\ \frac{nkT}{e}\ \ln\ I_L$$

A plot of $V_{oc}$ against $\ln I_L$ should yield a straight line from which n, junction ideality factor can be determined for a particular device. An ideal device should have an n value of unity so that the slope of straight line plot of $V_{oc}$ Vs $\log I_L$ should be 60 mV. Fig. 6.6 illustrates such a plot for natural $n$-$MoS_2$. The magnitude of slope and ideality factor are 87.5 mV and 1.5197 respectively, which correspond to nearly ideal diode behaviour. Higher values of n are characteristics of the propensity of recombination processes involving photogenerated electron-hole pairs either at semiconductor surface or in depletion region[12]. The tunneling currents and interfacial layers can result in considerable higher values of n equal to or greater than 2[11]. These recombination processes cause a deviation
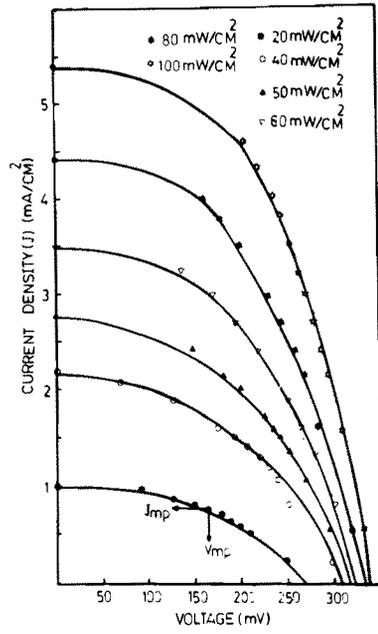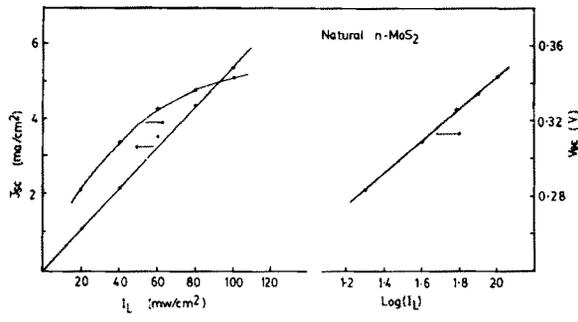
Fig. 6.5



Fig. 6.6

from the ideal current-voltage characteristics. According to author a significant factor in the non-ideal behaviour may be an ultrathin tunnelable layer of iodine formed at electrode surface[13] which affects the properties of electrode surface. The surface morphology can also lead to non-ideal behaviour has been shown by Razzini et al[14]. They found that "irregular" surfaces show relatively high diode quality factor $n \geq 2$, which are of "bad" photodiodes with low fill factors and "smooth" semiconductor surfaces give values of $n \cong 1$ to 1.5, which correspond to nearly ideal behaviour.

The assumption that $J_{sc}$ is directly proportional to the light intensity is borne out by data shown in Fig. 6.6. The linear dependence demonstrates that the transport of electroactive $I^-$ species to the natural $n$-$MoS_2$/ electrolyte is not limiting the overall charge transfer reaction over the range of light intensity employed in present study.

The functional dependence of $J_{sc}$ and $V_{oc}$ on light intensity has been noted by author for synthetic $MoS_2$ and $MoS_xSe_{2-x}$ based PEC cells and by previous workers, which is discussed in detail in chapter 9. The effect of light intensity on the conversion efficiency ( $\eta$ %) is

illustrated in Fig. 6.7. It has been observed that conversion
efficiency is found to increase with light intensity. It is
also noted that fill factor (Table 6.1) also increases with
intensity. The data corresponding to open circuit voltage,
short circuit current, fill factor and efficiency for the
different levels of illuminations are summarized in Table
6.1. The similar trend of increasing efficiencies and fill
factors were also reported by Audas and Irwin[15] for
natural n-MoS$_2$ crystals. The increase in fill factors with
the increasing light intensity indicate that the charge
transfer kinetics are sufficiently rapid to accommodate
the higher photon fluxes[16].

The time dependence of the photocurrent
was recorded for natural n-MoS$_2$ electrode. Fig. 6.8 shows
the result of a stability test. A slight decrease in a
photocurrent has been observed after 40 hours. This decrease
in photocurrent can be attributed to photocorrosion[17].

6.4    Conclusion

In the present preliminary work on natural
n-MoS$_2$ low energy conversion efficiencies have been found.
It was noticed that conversion efficiencies varied from
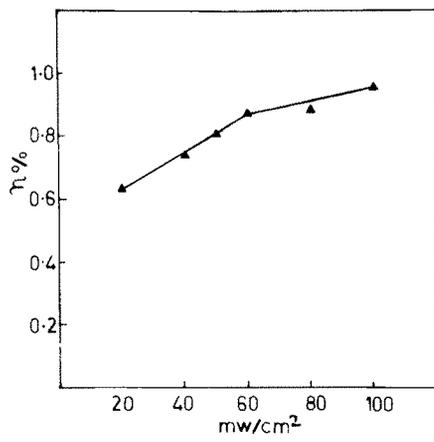0.15 to 0.95 % and from sample to sample. This may be due
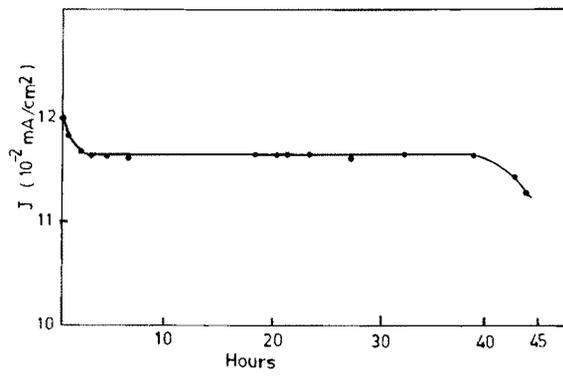
Fig. 6.7



Fig. 6.8

Table 6.1

Performance parameters of PEC cells based on natural n-MoS$_2$ crystals

| Light intensity $I_L$ (mw/cm$^2$) | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | Fill factor | Conversion efficiency $\eta$ (%) |
|---|---|---|---|---|
| 20 | 0.284 | 1.1364 | 0.392 | 0.626 |
| 40 | 0.309 | 2.218 | 0.428 | 0.734 |
| 60 | 0.328 | 3.517 | 0.459 | 0.873 |
| 80 | 0.336 | 4.437 | 0.472 | 0.880 |
| 100 | 0.343 | 5.41 | 0.513 | 0.952 |

to a non-uniform distribution   of impurities in the natural crystals. In the present studies the surfaces were not given any pretreatment or etching to reduce the surface states. It was hence realised that through the synthesis of $MoS_2$ crystal material with fewer electron-hole recombination traps and better p- and n-character it can be possible to increase not only the photocurrent output but also the photopotential considerably.

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