CHAPTER II

SEMICONDUCTOR FILM PHOTOELECTROCHEMICAL SOLAR CELLS
2.1 PHYSICAL COMPARISON OF A p-n JUNCTION AND SEMICONDUCTOR/ELECTROLYTE INTERFACE

When a p-n junction is formed between two semiconductors, free carriers from one semiconductor diffuse to the other because of concentration gradient. The diffusing holes and electrons are annihilated due to recombination such that n- and p- regions near the junction become depleted of their respective majority carriers, electrons and holes. This depleted region near the junction is known as depletion layer which presents a barrier for further flow of majority carriers (however, minority carriers can flow). In Figure (2.1a) the positions of energy bands in n- and p- regions are shown before the formation of the junction. When a p-n junction is formed the band energies in different regions are shown in Figure (2.1b). The conduction and valence bands of a depleted n-region bend upward* while those in the depleted p-region bend downward*. The barrier height, $\Phi_b$, gives the electrostatic field in the junction. Under illumination, additional electron-hole pairs are generated in p- and n-regions. The photogenerated majority carriers are negligible in comparison with its equilibrium concentration. However, the minority carrier concentration drastically increases over its equilibrium value, since the minority carrier flow is permitted across the junction, a net photogenerated current results which is the sum of hole flow from

* Downward and upward band bending respectively mean decrease and increase in energy.
Fig 2.1 (a) Formation of a p-n junction.
(b) Position of energy bands near the junction. The left-hand side shows the two regions separately while the right-hand side is the situation after the formation of junction.
n- to p- region and electron flow from p- to n- region. This current has a direction opposite to the forward bias current. Figure (2.2) shows the i-V characteristics of an illuminated p-n junction. If we choose an operating point in the fourth quadrant (shown by a dot) it is clear that while the voltage has a positive value, the current flows in a negative direction. The diode thus acts like a battery from which power can be drawn. This is the principle of photovoltaic Solar Cells.

The situation in photoelectrochemical Solar Cell (PESC) is almost similar as in p-n junction photovoltaic Solar Cells discussed above with the only difference that either p- or n-region is replaced by an electrolyte. Hence the junction is between semiconductor/electrolyte instead of p-n. For a n-type semiconductor, electrons of n-region near the semiconductor/electrolyte interface would cross-over towards the electrolyte since the carrier concentration (electrons) in the semiconductor and electrolyte are different. Subsequently, a charge transfer reaction could be mediated via the ions present in the electrolyte (details of charge transfer reactions are dealt later in Section (2.3). The n-region near the interface would get depleted of electrons leading to an upward bending of energy bands as for p-n junction. As in illuminated p-n junction, the photogenerated excess minority carriers in the semiconductor cross-over the barrier towards the electrolyte and exchange charges with
Fig. 2.2. i-V characteristics of a illuminated p-n junction.
ionic species present in the electrolyte resulting in the generation of photovoltage. This is in brief, the principle of electrochemical photovoltaic Solar Cells. If, in some special case, the redox species mediating the charge transfer is water/O\textsubscript{2} couple, then it gets electrolysed as:

\[ \text{H}_2\text{O} + 2\text{h}^+ \rightleftharpoons \frac{1}{2}\text{O}_2 + 2\text{H}^+ \]

The above is in brief, the principle of "Photoelectrolysis Cells".

2.2 POTENTIAL DISTRIBUTION IN THE SEMICONDUCTOR/ELECTROLYTE INTERFACE

Figure (2.3) gives the potential and charge distribution at the semiconductor/electrolyte interface. We shall discuss the two regions in the following paragraphs.

2.2.1 In the Electrolyte Region

The chemical potentials (or charge concentrations) in the semiconductor and electrolyte are different which results in a charge transfer leading to an effective charge at the solid surface. This charged solid surface in turn, offers a preferential attractive force to the oppositely charged ions. These ions form a layer or sheath of ions at the interface, which is termed as Helmholtz layer (Figure 2.3a). The ion density in the first ion layer near the solid surface is high and gradually decreases as the distance from solid surface increases in the electrolyte. Thus, in general,
Fig. 2-3. (a) Semiconductor electrolyte interface. (b) Distribution of potential. (c) Charge distribution near the interface.
Helmholtz layer is diffused in nature rather than discrete. This diffused nature is due to the fact that the preferential electrostatic force responsible for the build up of Helmholtz layer would decrease with increasing distance in the electrolyte. The dense layer is formed as "Inner or first Helmholtz layer" while the ions in the diffuse part form the "Outer or Second Helmholtz layer (also known as Gouy layer)". The inner layer ions are almost immobile while the second layer ions are mobile, though somewhat restricted as compared to ions in the interior of the electrolyte. The thickness \( L_{H1} \) of the inner Helmholtz layer has a dimension of ionic radii \( \sim 2-3 \, \text{Å} \) while the thickness of the outer Helmholtz layer \( L_{H2} \) depends on the ionic concentration which is \( \sim 10000 \, \text{Å} \) for dilute solution. In concentrated solution \( L_{H2} \) is negligibly small.

2.2.2 In the Semiconductor Space Charge Region

The charge transfer occurring at the semiconductor/electrolyte interface would result in different potentials at the semiconductor surface \( \phi_s \) and deep inside the bulk \( \phi_o \) (see Figure 2.3b). A potential drop \( \phi_s - \phi_o = \phi_{sc} \), therefore, takes place across the space charge layer inside (but near) the semiconductor surface. The nature of space charge layer depends upon the manner in which charge transfer occurs as given below.

**Positive shift in potential corresponds to downward bending and is due to transfer of positive charge \( \text{h}^+ \) from semiconductor to electrolyte.**
(a) If the semiconductor surface acquires excess majority carriers (or gets enriched), the space charge layer is termed as "Enrichment layer". Such a layer leads to downward bending in n-type and upward bending in p-type semiconductors (Figure 2.4).

(b) If the semiconductor surface becomes depleted in majority carriers, this space charge is known as "Depletion layer". For n-type semiconductor the depletion layer leads to an upward band bending and for p-type, a downward bending (Figure 2.4).

(c) If the charge distribution occurs in such a way that the minority carrier concentration at the surface is greater than that within the bulk, space charge layer is called as "Inversion layer". It leads to a large upward bending for n-type and downward bending for p-type semiconductors (see Figure 2.4). For wide band gap semiconductors (as for most PESCs) the inversion layer often cannot be formed since the equilibrium between electrons and holes cannot be reached due to slow thermal generation of electron hole pairs (Gerischer, 1970).

The band bending $V_b$ can be completely removed by applying external bias to the semiconductor electrode. The corresponding electrode potential at zero band bending is called "Flat band potential" and is given by

$$ V_b = E_{F,\text{redox}} - V_{fb} \quad \cdots (2.1) $$
Fig. 2.4. The three types of space charge layers near the interface inside the semiconductor for: (a) n-type and (b) p-type. The extreme left is enrichment layer, the middle is depletion and the right side is inversion layer.
where $E_{F,\text{redox}}$ is the Fermi level of the redox species in the electrolyte (see Section 2.3). In practical electrochemistry, the electrode potentials are measured with respect to a reference electrode (such as calomel, normal hydrogen electrode etc.).

2.3 CHARGE TRANSFER REACTIONS

As discussed earlier, the charges are exchanged at the electrode/electrolyte interface. Depending upon the 'sign' of charge exchanged, the ionic species shall either be reduced (acquires a negative charge or loses a positive hole) or get oxidised (i.e. acquires a positive charge or loses an electron). A simultaneous occurrence of reducing and oxidising reaction is referred to as "Redox Reaction". A redox reaction is represented by

$$[\text{ox}] + e^- \rightleftharpoons [\text{red}]$$

where $[\text{ox}]$ and $[\text{red}]$ refer to the oxidised and reduced species.

Gerischer (1960, 1961, 1970) deriving an analogy with semiconductor physics has suggested that the oxidised and reduced species may be likened with the conduction band (i.e. an unoccupied electron state) and valence band (i.e. an occupied electron state) respectively. A term similar to the Fermi level $E_F$ of a semiconductor can be defined for a redox couple also, abbreviated as $E_{F,\text{redox}}$. 


The energy necessary to transfer electron from the reduced species to the oxidised species is analogous to the band gap of a semiconductor. The redox potential $E_{\text{redox}}$ is defined as the potential required to transfer an electron from a redox species to the vacuum level or vice versa.

The charge transfer $\text{Semiconductor} \rightleftharpoons \text{Electrolyte}$ shall continue till the Fermi level positions in semiconductor equals $E_{F,\text{redox}}$. Therefore, at equilibrium

$$E_F (\text{semiconductor}) = E_{F,\text{redox}} \quad \cdots (2.2)$$

Gerischer (1970) has postulated that non-radiative charge transfer occurs when the participating states have energy within $\pm kT$ (a principle similar to Franck-Condon Principle). An obvious corollary to this statement is that redox species having energy near valence or conduction band edges would only participate in charge transfer. However, it has been found (Memming, 1978) that redox species with $E_{F,\text{redox}}$ substantially different from conduction or valence band edges also give charge transfer reactions due to involvement of surface states or broadening of redox energy levels.

** A possible confusion in nomenclature used in Electrochemistry and Semiconductor Physics may be noted. In Semiconductor Physics, energy levels are with respect to vacuum level ($E_{\text{vac}}$) while in Electrochemistry these are with respect to Normal Hydrogen Potential ($E_{\text{NHE}}$). The two are related as (Lohmann, 1967):

$$E_{\text{vac}} = E_{\text{NHE}} + 4.5 \text{ eV}.$$
due to (a) thermal fluctuations, (b) interaction with solvent, (c) interaction with directly bonded ligands (Gerischer, 1970; Memming et al., 1972; van den Berghe et al., 1973). These distribution of states are respectively denoted by distribution functions \( W_{\text{red}} \) and \( W_{\text{ox}} \) for the reduced and the oxidised species. The corresponding density of occupied (\( D_{\text{red}} \)) and unoccupied (\( D_{\text{ox}} \)) states are given by

\[
D_{\text{red}} = C_{\text{red}} \cdot W_{\text{red}} \quad \ldots \quad (2.3a)
\]

\[
D_{\text{ox}} = C_{\text{ox}} \cdot W_{\text{ox}} \quad \ldots \quad (2.3b)
\]

where \( C_{\text{red}} \) and \( C_{\text{ox}} \) are the concentrations of reduced and oxidised species respectively.

The occurrence of charge transfer reaction would depend on the relative overlap of energy distribution function of the redox species with the conduction or valence band. Thus we can have two types of reactions, viz. (i) in which only the conduction band participates and (ii) in which only the valence band participates. Further, the charge transfer can take place either from electrode to the solution or vice versa. Thus, in general, the charge transfer current will be given by

\[
j_c = j_c^+ - j_c^-
\]

\[
j_v = j_v^+ - j_v^-
\]

where \( j_c \) and \( j_v \) respectively give the electron transfer
reactions involving conduction and valence bands respectively. The positive superscript denotes a transfer of electron from the electrolyte to the electrode.

The charge transfer reactions in a particular system can be modified by altering the degree of overlap by changing either:

(i) the position of $E_g$ and $E_v$ band edges by applying a bias, or

(ii) the position of $E_g$ and $E_v$ by light induced carriers generation, or

(iii) the energy distribution function of the redox species by light excitation.

We shall address ourselves to only those charge transfer reactions which are induced by illumination with photons.

2.4 PHOTOINDUCED CHARGE TRANSFER REACTIONS

As the charge transfer reactions occur because of difference in concentrations of charge carrier in the semiconductor and electrolyte region, they can be modified by changing the carrier concentration within the semiconductor. One of the ways in which this can be accomplished is to illuminate the semiconductor surface with light of intensity greater than or equal to its band gap. Such an illumination will generate excess-electron-hole pairs. Since in an extrinsic semiconductor it is only the minority carrier
concentration which changes appreciably, a change in minority carrier controlled charge transfer reaction will be observed.

As discussed earlier, a potential exists in the space charge layer which is of such a nature that excess majority carriers move towards the bulk while the excess minority carriers accumulate near the surface (or in other words, photogenerated electron-hole pairs are separated in space charge layer). For n-semiconductor, the electrons move towards the semiconductor bulk while the holes accumulate near the surface (see Figure 2.5). Thus, they can oxidise the reduced species in the electrolyte.

\[ [\text{red}]_{\text{solv}} + h^+ \rightleftharpoons [\text{ox}]_{\text{solv}} \]

For a p-type illuminated semiconductor the reduction reactions due to photogenerated electrons (minority) occur at the conduction band edge.

2.5 ELECTROCHEMICAL PHOTOVOLTAIC SOLAR CELLS

The principle of charge transfer reaction at semiconductor/electrolyte interface has been used for the first time by Gerischer (1975) to construct an electrochemical photovoltaic cell for direct conversion of solar energy into electricity. His PESC consisted of a n-Cds single crystal photoanode alongwith a SnO₂ counter electrode dipped in an electrolyte containing redox couples Fe(CN)₃⁻_/Fe(CN)₆⁴⁻. A typical electrochemical photovoltaic cell is
Charge transfer across an illuminated n-semiconductor/electrolyte interface.
shown in Figure (2.6a). It can be understood as a split Schottky type contact (a metal-semiconductor contact) with electrolyte filled in between the metal and semiconductor. For a n-type semiconductor electrode the energy level diagram is shown in Figure (2.6b). Illumination reduces the depletion layer barrier increasing the capture probability of semiconductor holes by the reduced ionic species of electrolyte. Further, the charge transfer is facilitated if the energy levels of the two states overlap substantially as shown in Figure (2.6b). On short circuiting, the electron is driven via the external circuit towards the metal counter electrode where it participates in the reduction reaction of the oxidised species. The whole redox reaction can be described as:

(1) At the semiconductor electrode:

\[
\text{[red]}_{\text{solv}} + h^+ \rightleftharpoons \text{[ox]}_{\text{solv}}
\]

(ii) At the metal counter electrode:

\[
\text{[ox]}_{\text{solv}} + e^- \rightleftharpoons \text{[red]}_{\text{solv}}
\]

The electrodes do not participate in chemical reaction, they only serve as 'shuttle' for the charge transfer mechanism. The net free energy change of the system is therefore zero.

* Similar discussions shall apply for p-type electrodes.
Fig.2.6.  (a) A typical electrochemical photovoltaic Solar Cell
1-semiconductor, 2-metal counter electrode, 3-glass vessel, 4-electrolyte.
(b) Current flow and energy level diagram.
The open circuit voltage that can be obtained from such a cell is given by Equation (2.1). If $E_{F,\text{redox}}$ is in eV, Equation (2.1) can be written as

$$V_{\text{cell}} = -V_{fb} + \frac{E_{F,\text{redox}}}{e}$$

This reaction is crucial to the choice of the redox species. $E_{F,\text{redox}}$ should conform to the following two conditions:

(i) $E_{F,\text{redox}} \approx E_v$ at the valence band edge to permit energy overlap for charge transfer to take place. In most cases, however, if $E_{F,\text{redox}}$ is very near to $E_v$ it leads to decomposition.

(ii) Nearer is $E_{F,\text{redox}}$ to $E_v$, higher would be the cell voltage, $V_{\text{cell}}$. However, if $E_{F,\text{redox}}$ is more positive than the decomposition potential, then the hole instead of participating in charge transfer reactions "decomposes or corrodes" the electrode.

Thus, we see that two contradictory criteria exist - one for stability of semiconductor electrode and the other for better cell voltage. A compromise has to be struck.

Table (2.1) summarises the various electrochemical photovoltaic cells studied to-date. Table (2.2) summarises the various photoelectrolysis cells studied so far.
### Table 2.1: A summary of electrochemical photovoltaic cells

<table>
<thead>
<tr>
<th>References</th>
<th>Semiconductor</th>
<th>Form</th>
<th>Gap</th>
<th>Redox Stability</th>
<th>Band</th>
<th>Stability</th>
<th>couple</th>
<th>polarity</th>
<th>needed</th>
<th>achieved</th>
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<td></td>
<td>n-CdS Single Cryst.</td>
<td>-</td>
<td>1.0</td>
<td>Stable 5.0</td>
<td>Pe-CN 6.0</td>
<td>Stable 1.0</td>
<td>couple 1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>n-CdS+CdSe Poly Cryst.</td>
<td>-</td>
<td>0.9</td>
<td>Stable 2.4</td>
<td>Pe-CN 7.0</td>
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<td>-</td>
<td>-</td>
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<td>couple 0.4</td>
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<td>-</td>
<td>-</td>
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<td></td>
<td>p-CdTe/CdS Film</td>
<td>-</td>
<td>0.4</td>
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<td>couple 3.0</td>
<td>-</td>
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<td></td>
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<td>couple 0.4</td>
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<tr>
<td></td>
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<td>Stable 0.4</td>
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**Notes:**
- Gap: Energy gap of the semiconductor.
- Redox Stability: Stability of the redox couple.
- Band Stability: Stability of the band structure.
- couple: Type of couple used in the cell.
- polarity: Polarity of the cell.
- needed: Additional materials or conditions needed to achieve the cell.

**References:**
1. Gerischer (1975)
2. Gerischer et al. (1976)
3. Anderson and Ch (1976)
4. Heller et al. (1978)
5. Heller et al. (1977)
6. Heller et al. (1978)
7. Hodes et al. (1976b)
8. Hodes et al. (1976a)
9. Heller et al. (1977)
10. Miller et al. (1977)
11. Miller et al. (1976)
12. Miller et al. (1978)
13. C-band et al. (1976a, 1976b)
14. C-band et al. (1977a, 1977b)
15. C-band et al. (1978)
16. C-band et al. (1979)
17. C-band et al. (1980)
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<th>Stability</th>
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<th>Band Structure</th>
<th>Spin Polarization</th>
<th>Form</th>
<th>Band Gap</th>
<th>Efficiency</th>
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<tr>
<td>Miller and Heller (1979)</td>
<td>n-1i-3 Film</td>
<td>Stable</td>
<td>2.8 eV</td>
<td>Se/Se_2</td>
<td>Single Crystals</td>
<td>(1977)</td>
<td>26±2°</td>
<td>n-60°</td>
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<td>Miller and Heller (1976)</td>
<td>n-Bi_2 S_3 Film</td>
<td>Stable</td>
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<td>s~-s_2-</td>
<td>Single Crystals</td>
<td>(1976)</td>
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<td>(1977)</td>
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The starred (*) values are for single crystals.
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<td>n-BaTiO3 / Pt</td>
<td>3.3</td>
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**Table 2.2: Photoelectrolysis Cells**
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(Table 2.2)
2.6 EFFICIENCY OF PESC

The solar cell efficiency is defined as:

\[ \text{efficiency} = \frac{\text{output power}}{\text{input power}} \times 100\% \]

Another term used is quantum efficiency:

\[ q = \frac{\text{No. of photoelectrons/unit area}}{\text{No. of photons/unit area}} = \frac{1/C(j_{\text{light}} - j_{\text{dark}})}{\text{No. of photons/unit area}} \]

Both these definitions are connected with the efficacy of photo-conversion.

The efficiencies of some PESCs are given in Table 2.1.

2.7 PESC FOR SOLAR ENERGY STORAGE

Photoelectrochemical cells offer a possibility for solar energy storage which is a big problem in commercial exploitation of solar energy. One possibility in PESCs is to store hydrogen produced in photoelectrolysis cells which can later be used in any type of fuel cell (Takahasi, 1972) to generate power. This is, however, not yet economically viable (Nozik, 1977).

A unique possibility of electrochemical storage through charge transfer reaction has been recently demonstrated by Hodes et al (1976) and Manassen et al (1977). Their storage photoelectrochemical cell is schematically shown in
Fig. 2.7. A photoelectrochemical Solar Cell with a storage facility. A - semiconductor photoelectrode; B - counter electrode, and C - storage electrode.
Figure (2.7). In addition to two electrodes of PESC, a third electrode, called the storage electrode, like $\text{Ag}_2\text{S}$, Fe$_2$S$_3$, Tin etc., is introduced. The storage electrode is reversible with respect to one of the ionic species present in the electrolyte. The load $R_L$ is adjusted in such a way that a part of the photocurrent flows to the storage electrode $\beta$. For $\text{Ag}_2\text{S}$ storage electrode, the following reaction occurs:

$$\text{Ag}_2\text{S} + 2e^- \xrightarrow{\text{dark}} 2\text{Ag} + \text{S}^{2-}$$

In dark, sulfur is reduced to sulfide on the surface of semiconductor electrode $\alpha$. Not much work has been reported in this direction so far. The feasibility of incorporating such a storage mode is yet uncertain but certainly deserves more attention.

This thesis primarily concerns with the Electrochemical Photovoltaic Solar Cells using semiconductor films and the results are described in Chapters III, IV and V.