CHAPTER 6

INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS
6.1 INTRODUCTION:

Today's energy crisis forces us to look around materials which can help to compensate for the tremendous energy consumption. It is well known to us that the resources of fossil fuels such as coal, oil, wood and other organic materials, with the exception of geothermal and tidal energy in the world are depleting fast, and by the turn of the century mankind will have to depend upon renewable sources of energy. Since the energy consumption level is almost reckoned as the measure of economic growth and the quality of life. It is obvious that the survival of mankind at present level of civilization will depend upon the availability of sufficient energy. The present situation demand a pollution-free and cheaper energy sources, which can be harnessed from sun, wind and oceans etc. Among these sources solar energy is the most attractive alternative. Since it is available in great quantity (approximately $7 \times 10^{17}$ KWh/ annum on the earth surface) which is nearly ten thousands times the world wide energy consumption per year. In addition it will not affect the thermal energy balance of our planet nor cause any additional pollution.

Among the several ways of collecting solar energy, the photovoltaic, the photochemical, the photoelectrochemical, the photothermal and the photosynthetic are some of the better known routes to achieve energy conversion. Out of all these ideas of converting solar energy directly into the chemical energy or electrical energy by use of photoelectrochemical systems has rapidly gained popularity in recent years. A number of review article [1-75] have been published in the field of photoelectrochemical conversion. Many efforts have been directed towards different solar energy conversion devices for almost two to three decades. Again the emergence of the field of photoelectrochemistry has created a link between photovoltaic devices and electrochemical devices and subsequent developments such as photoelectrochemical solar cells (PEC) and photodiodes have served to further strengthen the field.
A part from the solar energy conversion devices, there are various other devices which convert one form of energy into other electrical energy. The best examples of such devices are nuclear reactors, hydrothermal generators etc. The basic characteristic feature of this reactor is that a lot of thermal process is involved in the conversion of energy from one form to another. Besides solar cells are the devices which convert the solar energy into electrical energy without going through a thermal process which is very important as far as the technology and economy point of view is concerned.

In 1970s, an alternative strategy was suggested in which a solid-liquid junction was used. In 1972, Fujishima and Honda [9] used this junction to photoelectrolyte water and thus obtain hydrogen, which is a transportable form of energy. In 1975, Gerischer [7] used this junction for direct conversion of solar energy into electricity. In this dissertation, use of solid-liquid junction has been made to take up the strategy adopted by Gerischer i.e. direct conversion of solar energy into electricity.

Solar cells are generally maintenance free, portable and therefore, they are suitable in remote area. The important feature of such conversion process doesn't create any sound and pollution and they can be located at the place of use and hence, no additional, complicated and costly supporting network is required.

6.2 MODES OF SOLAR ENERGY UTILIZATION

Modes of utilization of solar energy can be classified into two categories.

I. The direct use of solar radiations incident on the surface of the earth known as Direct Methods.
II. The radiations incident on the earth leads to the water power, wind power, biomass etc. This is, in turn used by mankind known as the Indirect methods.

There are various processes involved in the solar energy conversions, it can be seen from figure 6.1. These processes depend on the region of the incident solar energy spectrum which is being used to accomplish the process.

![Modes of solar energy utilization diagram]

**Figure 6.1:** Modes of solar energy utilization

For example, if the infrared regions have been chosen for the applications then the solar energy can be converted into thermal energy, whereas if the visible regions have been chosen for the applications then the solar energy can be converted into electrical energy. The classification of direct use of solar energy has been

---

CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.
explicably shown in Fig. 6.2(a) & Fig.6.2 (b). This specifies the range of wavelength incident radiations used in photoconversion process.

The present work is based on the solar energy conversion devices using the concept of “Photo effect in Semiconductor” so these classes of devices have been discussed in more detail. The concepts developed here will be used later in the study on the photoresponse of PEC solar cells fabricated using germanium sulphoselenide as photoelectrodes.

**Figure 6.2 (a):** Classification of the solar energy conversion processes using directly the solar radiations

---

CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.
6.3 CLASSIFICATION OF SOLAR ENERGY CONVERSION DEVICES:

Generation of electromotive force on illumination of a rectifying junction is known as photovoltaic effect. It is well known fact that at a rectifying junction there excites an internal electric field. Solar cells depend upon the photovoltaic effect for their operation. This was first observed by Becquerel in 1839 for electrolyte cells and in 1876 for the solid state systems [1, 2].

Different solar energy conversion devices are broadly classified in two categories:
1. Solid-Solid junction cells
2. Solid-liquid junction cells

Figure 6.2(b) Classification of solar energy conversion devices
These cells are subdivided into some other devices which are shown in Fig 6.2(b). The solid-solid junction devices generally use, effectively by the photosensitive junction like as p-n junction, Schottky junction, MOS structure, MIS structure and SIS structure. Whereas the solid – liquid junction devices may be of photovoltaic type cells or photoelectrolysis cells in which solid –liquid interface may also be used. These devices have been briefly discussed below.

6.3.1 Solid-solid junction

(a) p-n junction devices

A p-n junction using semiconducting materials has been used as a photosensitive material on both sides of the interface in the photovoltaic cells. Here the light may be absorbed by both sides of semiconducting material across the junction. The effective transport of photo generated carriers takes place in either direction.

(b) Schottky junction devices

The semiconductor metal rectifying interface gives rise to the Schottky junction devices. Such devices also be used to harness the solar energy and hence these devices are known as Schottky junction solar cells. The Schottky junctions are fabricated using the rectifying contact between metal and semiconductor. Since, one side of the junction is metal, the absorption of incident radiation and consequent photogeneration of charge carriers essentially take place in the semiconductor regions.

(c) Metal-Oxide-Semiconductor (MOS) devices

Metal-Oxide-Semiconductor junctions can also be used in the solar energy conversion process. Here also, major absorption of light takes place in the semiconductor thereby generating the charge carriers. So, the efficient absorption of incident radiation by semiconductor primarily governs the photogeneration mechanisms of charge carriers.
(d) Metal-Insulator-Semiconductor (MIS) devices

Metal-Insulator-Semiconductor devices are more or less analogous to the MOS devices. Here also the effective photogeneration of the charge carriers takes place in semiconductor dominate the overall photoconversion process.

(e) Semiconductor-Insulator-Semiconductor (SIS) devices

The Semiconductor-Insulator-Semiconductor (SIS) structure is also used for the conversion of the solar energy into electricity. Here the insulator is being sandwiched between two semiconductor regions and the photogeneration of charge carriers mainly occurs in the semiconductor region.

6.3.2 Solid – liquid junction

(a) Photoelectrochemical (PEC) solar cells

Here Photoelectrochemical (PEC) solar cells belong to the category of photovoltaic cells. Photogenerated electron-hole pairs are separated by the internal inbuilt electric field within the cells anticipating the photovoltage or the photocurrent.

The existing technology is very much successful in reducing the high cost and simplifying the high degree of sophistication in the fabrication of p-n junction solar cell. However, a challenging problem in harnessing and usage of solar energy is solar energy storage. Recent activities reveal that instead of using p-n junction device, the solar energy conversion can be easily be achieved by using PEC solar cell, where the problem of solar energy storage can be overcome.

(b) Photoelectrolysis solar cells

The solid liquid interface used in the solid liquid structure devices can be used for the electrolysis of water which consequently generates the hydrogen and oxygen.
Here the photogeneration of carriers takes place in semiconductor region only. Whereas the electrolyte is supposed to be transparent to the incident solar radiations.

6.4 CLASSIFICATION OF PHOTOELECTROCHEMICAL SOLAR CELLS

Nozik has proposed the following classification for photoelectrochemical solar cells [3] as shown in figure 6.3. According to this classification, all cells are divided into:

1. Regenerative PEC solar cells, also known as “liquid junction solar cells” or “electrochemical photovoltaic cells”, in which the Gibbs free energy (G) of the electrolyte solution does not vary.

2. Photoelectrosynthetic solar cells, in which the Gibbs energy of the electrolyte solution changes when it is in operation.
Figure 6.3 Classification of photoelectrochemical cells.

- **Photoelectrochemical cells**
  - ΔG = 0
  - ΔG ≠ 0
  
  - **Regenerative cells**
    (Optical energy converted into electrical energy)
    - ΔG > 0
    - **Photoelectrolysis cells**
      (Optical energy stored as chemical energy in endoergic reactions,
      e.g. H₂O → H₂ + ½ O₂)
  
  - **Photoelectrosynthetic cells**
    (Optical energy used to affect electrochemical reactions)
    - ΔG < 0
    - **Photocatalysis cells**
      (Optical energy provides activation energy for exoergic reactions,
      e.g. N₂ + 3 H₂ → 2 NH₃)
### 6.5 COMPARISON OF PEC SOLAR CELL AND p-n JUNCTION SOLAR CELLS

<table>
<thead>
<tr>
<th>p - n junction solar cells</th>
<th>Photoelectrochemical solar cells</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Junction type</strong></td>
<td></td>
</tr>
<tr>
<td>(a) p-n</td>
<td>(a) p-electrolyte, n-electrolyte</td>
</tr>
<tr>
<td>(b) Solid-Solid</td>
<td>(b) Solid-Liquid</td>
</tr>
<tr>
<td><strong>Potential barrier at the junction</strong></td>
<td></td>
</tr>
<tr>
<td>(a) Yes</td>
<td>(a) Yes</td>
</tr>
<tr>
<td>(b) The barrier is formed due to inter-diffusion of majority charge carriers between p- and n-region</td>
<td>(b) The barrier is formed because of the transfer of majority carriers from semiconductor to electrolyte</td>
</tr>
<tr>
<td>(c) The potential drop or band bending in the two regions of semiconductor is almost equal</td>
<td>(c) Major potential drop in semiconductor space charge layer, only a small fraction of the drop is in the electrolyte region</td>
</tr>
<tr>
<td>(d) Facilitates flow of majority carrier and inhibits majority carrier flow</td>
<td>(d) Same as in p-n junction</td>
</tr>
<tr>
<td><strong>Photo effect</strong></td>
<td></td>
</tr>
<tr>
<td>(a) Excess carriers are generated</td>
<td>(a) Excess carriers are generated</td>
</tr>
<tr>
<td>(b) Mutual diffusion of excess photogenerated minority carriers in the two regions give photovoltage</td>
<td>(b) The excess photogenerated minority carriers transfer charge with ions of the electrolyte to give photovoltage or lead to electrolysis</td>
</tr>
</tbody>
</table>

---

**CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.**
The research articles [3 -75] have been written in the field of photoelectrochemical conversion of solar energy. In the last decade two monograms one on PEC solar cells [76] and the other on photoelectrochemistry and photovoltaics of layered semiconductors [77] have also been published. A review article by Pandey et al. [78] focuses on the prospective and perspectives of high conversion efficiency photoelectrochemical solar cells.

In order to develop the concepts needed for studying the behavior of PEC solar cells, description of a p-n junction vis-a-vis a semiconductor electrolyte interface is given below. The concepts developed here will be used later in the study of effect of growing germanium sulphoselenide by transporting agent I₂ on the photoresponse of PEC solar cells fabricated with them as photoelectrodes.

6.6 SEMICONDUCTOR - ELECTROLYTE INTERFACE

The charge transfer across the semiconductor- electrolyte interface in dark or under illumination results in the flow of current through the junction of the electronically conducting solids and ionically conducting liquids. This is the main concept in the working of PEC solar cell. The detailed analysis of semiconductor-electrolyte interface can be obtained from the review by Brattien and Garrett [79, 80]. The equilibrium concentration of carriers and hence the chemical potential of lets take for example n-type semiconductor and the electrolyte are originally different when they are brought in contact with each other. As a result transfer of electrons takes place from the conduction band of the semiconductor to the ionic species in the electrolyte. Accepting these electrons, the ionic species near the interface get reduced. The reaction can be given as

\[ [X] + e^- \rightarrow [X]^\text{-}\]

This process continues till the equilibrium is set up when the chemical potentials of the semiconductor and the electrolyte become
same and no further flow of electrons from the semiconductor to the electrolyte takes place. As a result of this charge transfer, the semiconductor region near the interface gets depleted of electrons, giving rise to a positively charged space charge layer. Corresponding to this layer at the interface, there is a sheath of negatively charged ions in the electrolyte, which is known as the Helmholtz layer. The ion density in the Helmholtz layer is high and gradually decreases as the distance in the electrolyte from the interface increases. Thus this layer, in general, is diffused rather than discrete in nature. The diffused nature of this layer is due to the fact that the preferential electrostatic force responsible for building up of the Helmholtz layer which decreases with increasing distance towards the electrolyte from the interface. The denser layer within the sheath of ions in the electrolyte is known as the first Helmholtz layer or simply the Helmholtz layer whereas the ions in the diffused part form an outer or second Helmholtz layer normally termed as Gouy layer. The ions in this layer are somewhat mobile though restricted compared to the ions in the interior of the electrolyte. At equilibrium, the energy bands in the semiconductor are bent upward and Fermi levels of the semiconductor and redox level of the electrolyte align. The general structure of the n-type semiconductor electrolyte interface and the corresponding energy band diagram are shown in figure 6.4.
Thus the complete picture of the semiconductor electrolyte interface can be summarized as

1. Diffused space charge layer in the semiconductor
2. Helmholtz layer.
3. Diffused ionic layer (Gouy layer)

The total charge in the semiconductor side of the interface is

\[ q_s = q_{sc} + q_{ss} + q_{ads} \]

where \( q_s \) = total charge
\( q_{sc} \) = charge in the space-charge region
\( q_{ss} \) = charge due to surface states
\( q_{ads} \) = adsorbed charge
The electroneutrality condition demands that
\[ q_{s} = q_{el} \]
where \( q_{el} \) is charge in the electrolyte.

The total interface potential, \( \phi_{Ga} \) (Galvanic potential) can be written as
\[ \phi_{Ga} = \phi_{sc} + \phi_{G} + \phi_{H} + \phi_{ss} \]
where \( \phi_{sc} \) is potential across the space charge layer
\( \phi_{G} \) is potential across the Gouy layer
\( \phi_{H} \) is potential across the Helmholtz layer, and
\( \phi_{ss} \) is potential across the surface states.

But we know that, for continuity of electric vectors
\[ \varepsilon_{s} E_{s} = \varepsilon_{H} E_{H} = \varepsilon_{G} E_{G} \]
Also as \( L_{D}, L_{H} \) and \( L_{G} \) are Debye lengths in the semiconductor, Helmholtz and Gouy regions respectively, then

\[ E_{sc} = \frac{\phi_{sc}}{L_{D}}, \quad E_{H} = \frac{\phi_{H}}{L_{H}} \quad \text{and} \quad E_{G} = \frac{\phi_{G}}{L_{G}} \]

The differential capacitance is defined as
\[ C_{sc} = \frac{\varepsilon_{s}\varepsilon_{0}}{L_{D}}, \quad C_{H} = \frac{\varepsilon_{H}\varepsilon_{0}}{L_{H}} \quad \text{and} \quad C_{G} = \frac{\varepsilon_{G}\varepsilon_{0}}{L_{G}} \]

The simplest electrical equivalent of a semiconductor - electrolyte junction can be regarded as a series combination of these capacitors. The total capacitance is given by
\[ \frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_{H}} + \frac{1}{C_{G}} \]
6.7 PRINCIPLE OF PHOTOELECTROCHEMICAL SOLAR CELL

The various steps involved in a PEC cell fabricated with a n-type semiconductor can be summarized as follows:

1. Light absorption (in space charge and bulk)
   \[e^- + h^+\]

2. Electron-hole separation in space charge layer
   \[e^-_{sc} \rightarrow e^-_{bulk}\]
   \[h^+_{sc} \rightarrow h^+_{surface}\]

3. Electron-hole recombination in bulk
   \[e^- + h^+ \rightarrow \text{heat (in semiconductor)}\]

4. Semiconductor surface holes react with redox species.
   \[h^+ + (\text{red})_{solv} \rightarrow (\text{ox})_{solv}\]

5. Semiconductor surface holes may react with the semiconductor bands itself
   \[h^+ + \text{semiconductor} \rightarrow \text{semiconductor photodecomposition}\]

   This has to be avoided.

6. Reduction of relevant redox species at the counter electrode
   \[e^- + (\text{ox})_{solv} \rightarrow (\text{red})_{solv}\]

The presence of reactions (3), (5), (6) limits the utility of photogenerated carriers. Minimization of the surface states and space charge layer recombination, are additional desirable features for improved PEC solar cell behavior. The photoconversion of practical
PEC solar cell affected due to the absorption of radiant energy in the electrolyte and its reflection from the semiconductor surface.

6.8 REQUIREMENTS OF SEMICONDUCTING MATERIALS USED AS PHOTOELECTRODES

The semiconductor photoelectrode is the heart of a PEC solar cell. Overall performances of PEC solar cell mainly depend on the type of material chosen for the fabrication of semiconducting electrode and its parameters. For the achievement of good performance it should satisfy the following requirements:

- The optical absorption coefficient of semiconductor photoelectrode material should be high.
- The band gap ($E_g$) of the photoelectrode material should be optimum so as to match with maximum span of solar spectrum ($E_g=1.2$ to $1.8$ eV).
- It should be of direct band gap type with high optical absorption coefficient.
- The diffusion length for minority carriers should be as long as possible.
- The width of the space charge layer must be large.
- Photoelectrode should be stable in the electrolyte and should not get corroded during illumination.
- Thickness and area of the photoelectrode should be large enough to absorb all the incident radiation.
- Series resistance $R_s$ should be as small as possible and shunt resistance $R_{sh}$ should be large enough. Ideally $R_s=0$ and $R_{sh}=\infty$.
- Cost of the material manufacturing process and efficiency should be acceptable.

In addition to the above requirements the parameters such as e.g. film thickness, grain size and grain boundaries should be controlled for polycrystalline thin films.

CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.
6.9 PROPERTIES OF THE ELECTROLYTE

Another important parameter in PEC solar cell is the electrolyte. An electrolyte is a liquid substance which acts as a medium to conduct electricity. Electrolyte consists of the oxidized and reduced species. These species are ionic species, which help in transferring the photogenerated holes from photoelectrode to counter electrode.

Requirements of properties of the electrolyte, which PEC solar cell should satisfy, are listed below:

- The charge transfer rates due to redox system at both semiconductor and counter electrode should be high or effective.
- The electrolyte should have minimal optical absorption.
- Oxidized species, reduced species and solvent components should have photo and thermal stability throughout usable solar spectrum and operational temperature range.
- Oxidized species, reduced species and supporting electrolyte concentration in solvent should be adequate to reach required current densities.
- Ionic conductance of electrolyte should permit negligible ohmic losses.
- Electrolyte should not react with the semiconductor electrode and should be non-corrosive to the electrode and container material.
- Cost, toxicity and environmental aspect should be preferably low.

6.10 REQUIREMENTS OF THE COUNTER ELECTRODE

A counter electrode is the third part of the PEC solar cell. The requirements of counter electrode for better performance in PEC solar cell are as follows:
The counter electrode should not react with electrolyte i.e. it should be chemically inert.

The counter electrode must be electrically active i.e. the charge transfer between the counter electrode and redox species in the electrode must be fast.

The area of the counter electrode must be larger than that of the semiconductor electrode. This improves the collection efficiency and avoids the concentration polarization.

When a counter electrode is immersed into the electrolyte, the half cell potential of the semiconductor electrode should match with the half cell potential of the semiconductor electrode.

Counter electrode should have low over potential for the reduction reaction.

Counter electrode must be cheaper, platinum and graphite are more widely used. Many counter electrode materials have been evaluated electrochemically by Allen and Hickling [81].

6.11 SPACE CHARGE CAPACITANCE AND MOTT SCHOTTKY PLOT

The relation between the space charge capacitance and the space charge potential is represented by well known Mott-Schottky equation as

\[
\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{\varepsilon_0 \varepsilon_s e N_D} \left(\phi_s - \frac{kT}{e}\right)
\]

where $C_{sc}$ is space charge capacitance

$\varepsilon_0$ is permeability

$\varepsilon_s$ is dielectric constant of semiconductor

$e$ is charge of electron

CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.
$N_D$ is donor density

$\phi_{sc}$ is space charge potential

$k$ is Boltzmann constant

$T$ is absolute temperature

According to this equation $(1/C_{sc})^2$ versus $\phi_{sc}$ plot is a straight line. However, $\phi_{sc}$ cannot be measured directly, generally, in electrochemistry electrode potentials are measured against a reference electrode (usually a Normal Hydrogen Electrode (NHE)).

The measured potential difference $V$ corresponds to

$$V = \phi_{sc} - \phi_{NHE}$$

for $\phi_{sc} = 0$, there is no band bending corresponding to a flat band situation. Suppose the flat band potential is $V_{fb}$ and the electrode potential is $V$ then the Mott-Schottky equation can be written as

$$\left( \frac{1}{C_{sc}} \right)^2 = \frac{2}{\varepsilon_0 \varepsilon_r \varepsilon N_D} \left( V - V_{fb} - \frac{kT}{e} \right)$$

Therefore, a plot of $(1/C_{sc})^2$ versus electrode potential ($V$) will be a straight line.

Some important application of Mott-schottky plots like from Mott-schottky plots one can find out type of semiconductor, flat band potential and donor density, band banding, depletion layer width and position of bend edges etc. The detail explanation of all these parameters is given in chapter 7.
REFERENCES


CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.

CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.


CH.6. INTRODUCTION TO PHOTOELECTROCHEMICAL SOLAR CELLS.