

CHAPTER 7

INTRODUCTION TO PHOTOELECTROCHEMICAL (PEC)
SOLAR CELLS

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7.1. INTRODUCTION

New venture in the field of energy sources have been aiming at harnessing the solar energy to supplement and eventually replace diminishing fossil fuels. Solar photovoltaic technology for conversion of solar energy into electrical energy is receiving increasing attention as a prospective source of bulk, electric utility power within the next 15 to 20 years.

Recently research into photoelectrochemical (i.e. solar-liquid junction) solar cells has also gained momentum because of interest in their potential for practical application and because of the advantages they present with respect to cells with a solid-solid junction. Their two basic advantages are (1) the easy attainment of the junction that allows for the separation of the photogenerated charges (by simply immersing the semiconductor into the electrolyte) and (2) the relatively small sacrifice in conversion efficiency when single crystals are replaced by polycrystals or polycrystalline films.

A photoelectrochemical (PEC) cell is a device in which a semiconductor electrode is illuminated in a suitable liquid or electrolyte, causing electrochemical reaction at

both electrodes. Second electrode is used as a reference electrode. There are two types of PEC cells; one which converts solar energy directly into electrical energy, called as wet photovoltaic or photoelectrochemical cell and other which converts incident solar energy into chemical energy. For a PEC cell to be effective in the conversion of solar energy to useful electrical or chemical energy, the net cell reaction occurring during illumination must be endoenergetic. In this thesis, use of solid-liquid junction has been made in accordance with strategy adopted by Gerischer et al. [1] for direct conversion of incident solar energy into electricity.

7.2. DEFINITION OF PEC CELL

The photoelectrochemical (PEC) cell is stated as a cell by simply immersing a semiconductor into a liquid electrolyte. Junction is formed of semiconductor/electrolyte interface. A PEC effect is defined as one in which the irradiation of a semiconductor electrode/electrolyte system produces a change in the electrode potential (on open circuit) or in the current flowing in the external circuit (under short circuit condition) [2].

7.3. SOLAR ENERGY CONVERSION

Solar energy or photons are the wave packet or

quanta of electromagnetic radiation. Generally, solar energy conversion is taken as a process through which the visible electromagnetic radiation of energy is converted into electrical energy. In general, the solar radiation conversion process involves interaction of these electromagnetic photon with materials, which give rise to,

- (1) Photoemission from metallic surfaces and
- (2) Photoeffects in semiconductors.

On incidence of solar radiation or photoirradiation of semiconducting material and subsequent absorption of this radiation in the semiconductor, following processes may result

1. Excitation of electron from valence band to the conduction band.
2. Excitation of electron from and to the impurity levels.
3. Excitation of electrons to higher energy states in the same band.
4. Excitation of phonons.
5. Excitation of excitonic states.

With one or more of the above kind of processes occurring, two kinds of photoeffects; namely photoconductive and photovoltaic have generally been recognised. It may be pointed out that it is the photovoltaic effect which is at the

root of the liquid junction solar cells.

7.4. SEMICONDUCTOR-ELECTROLYTE INTERFACE

When a solid-solid 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 prevents further flow of majority carriers. Under the illumination condition, additional electron-hole pairs are generated in the p and n regions. Since the minority carrier flow is permitted across the junction, a net photogenerated current results which is the sum of hole flow from n- to p- region and electron flow from p- to n-region. This current has a direction opposite to forward bias currents. This is the principle of photovoltaic solar cell.

Distribution of potential at the semiconductor-electrolyte interface is almost similar to that of p-n junction and direct conversion of solar energy into electrical

energy is possible. The difference is that either the p- or n-region gets replaced by an electrolyte. Here the junction is between semiconductor and electrolyte instead of p-n.

For an n-type semiconductor and electrolyte, the equilibrium concentration of carriers and the chemical potentials are initially different when they are brought in contact with each other. Transfer of electrons, from the conduction band of the semiconductor to the ionic species in the electrolyte takes place. Accepting these electrons, the ionic species near the interface get reduced. This reaction can be given as,



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 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 1st Helmholtz layer or simply the Helmholtz layer whereas the ions in the diffused part form an outer or 2nd Helmholtz layer normally termed as Gouy layer. Ions in these layers 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 upwards and the Fermi level 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 Fig. 7.1.

Thus the complete picture of the semiconductor electrolyte interface can be summarised as,

1. Diffused space charge layer in the semiconductor (plus surface states, adsorbed ionic species).

2. Helmholtz layer
3. Diffused ionic layer (Gouy layer)

The distribution of charge and potential are shown in Fig. 7.2.

The total charge in the semiconductor side of the interface is,

$$q_s = q_{sc} + q_{ss} + q_{ads}$$

where q_s is total charge
 q_{sc} is charge in the space charge region
 q_{ss} is charge due to surface states
 q_{ads} is adsorbed charge.

The electroneutrality condition demands that

$$q_s = q_{el}$$

where, q_{el} is charge in the electrolyte.

The distribution of potential across the interface is given in Fig. 7.2. The total interface potential, ϕ_G (Galvanic potential) can be written as

$$\phi_{Ga} = \phi_{sc} + \phi_G + \phi_H + \phi_{SS}$$

But we know that, for continuity of electric vectors

$$\epsilon_S E_S = \epsilon_H E_H = \epsilon_G E_G$$

Suppose L_D , L_H and L_G are respectively the Debye lengths in the semiconductor, Helmholtz and Gouy regions.

Then,

$$E_S = \frac{\phi_{sc}}{L_D}; \quad E_H = \frac{\phi_H}{L_H}; \quad E_G = \frac{\phi_G}{L_G}$$

The differential capacitance is defined as $C = \frac{dq}{d\phi}$

so that,

$$C_{sc} = \frac{\epsilon_s \epsilon_o}{L_D}; \quad C_H = \frac{\epsilon_H \epsilon_o}{L_H}; \quad C_G = \frac{\epsilon_G \epsilon_o}{L_G}$$

The simplest electrical equivalent of a semiconductor-electrolyte can be regarded as a series

combination of these capacitors. The total capacitance is given by

$$\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_H} + \frac{1}{C_G}$$

7.5. SPACE CHARGE CAPACITANCE AND THE MOTT-SCHOTTKY PLOT

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

$$\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{\epsilon_0 \epsilon_s e n_D} \left(\phi_{sc} - \frac{kT}{e}\right)$$

where C_{sc} is space charge capacitance

ϵ_0 is permittivity

ϵ_s is dielectric constant of semiconductor

e is charge of electron

N_D is donor density

ϕ_{sc} is space charge potential

k is Boltzmann constant

T is absolute temperature

According to this equation $(1/C_{sc})^2$ versus ϕ_{sc} plot is a straight line. However, ϕ_{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

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

Then the Mott-Schottky equation can be written as

$$\left(\frac{1}{C_{Sc}} \right)^2 = \frac{2}{\epsilon_o \epsilon_s e N_D} \left(V - V_{fb} - \frac{kT}{e} \right)$$

where, V_{fb} is the flat band potential. Therefore a plot of $(1/C_{sc})^2$ versus electrode potential will be a straight line.

7.6. SOME APPLICATIONS OF MOTT-SCHOTTKY PLOTS

1. Type of Semiconductor

The sign of the slope of $(1/C_{sc})^2$ versus V plots, would be different for n- and p-type semiconductors. A

positive slope indicates n-type semiconductor and a negative slope indicates p-type semiconductor.

2. Flat band potential and donor density

The intercept of the $(1/C_{sc})^2$ versus V curve on the voltage V axis gives flat band potential V_{fb} and the slope of the curve gives donor density N_D .

3. Band bending

Band bending V_b can be obtained as

$$V_b = \frac{E_{f,redox}}{e} - V_{fb}$$

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

$$E_{f,redox} = -(4.5 \text{ eV}_{NHE} + eV_{redox})$$

4. Depletion layer width

The majority carrier depletion layer width W , can be calculated from the following relation, knowing the values

of V_{fb} and N_D .

$$W = \left[\frac{2 \epsilon_o \epsilon_s (V - V_{fb} - kT/e)}{eN_D} \right]^{1/2}$$

5. Position of band edges

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

$$n_o = N_C e^{-(E_C - E_F) / kT}$$

$$p_o = N_V e^{-(E_F - E_V) / kT}$$

where N_C , N_V are density of states respectively for conduction and valence band; E_C , E_V are respectively conduction and valence band edges. Then the above equation gives,

$$E_C = E_F - kT \ln \left(\frac{n_o}{N_C} \right) \text{ and}$$

$$E_V = E_F + kT \ln \left(\frac{p_c}{N_V} \right)$$

For a semiconductor electrode in contact with an electrolyte at equilibrium.

$$E_F = E_{F, \text{redox}}$$

$E_{F, \text{redox}}$ is known, and hence E_C and E_V can be obtained. With the help of all these values obtained from Mott-Schottky equation, complete location of various energy levels for the semiconductor photoelectrode of n-CuInS₂ PEC solar cell will be described in the next chapter.

7.7 PRINCIPLE OF DIFFERENT PHOTOELECTROCHEMICAL SOLAR CELLS

Nozik [3] has proposed the following classification for photoelectrochemical cells (Fig. 7.3). According to this classification, all cells are divided into :

1. regenerative photoelectrochemical cells, also known as "liquid junction solar cells" or "electrochemical photovoltaic cells", in which the Gibb's free energy G of the electrolyte solution does not vary, and
2. Photoelectrosynthetic cells in which the Gibb's

energy of the electrolyte solution changes when in operation.

In the present work attention has been mainly focused on the regenerative photoelectrochemical solar cells.

7.8. ATTRACTIVE FEATURES OF PEC SOLAR CELLS TO SOLID STATE SOLAR CELLS

The important advantages of a PEC compared to solid state cells in general can be summarized as follows :

1. The great ease with which the semiconductor/ liquid junction can be formed.
2. Since the photosensitive junction in a PEC is extremely abrupt compared to the solid-state counterpart and one side of the junction is practically transparent to the incident solar spectrum, more of the incident light is absorbed within the region of high electric field at the interface where charge carriers are more efficiently separated and collected.
3. The simple formation and the abruptness of the photosensitive semiconductor /liquid junction make the use of polycrystalline material in PEC feasible [4-13].

4. Processing steps of p-n cells are simplified or eliminated in the PEC i.e. growing of large single crystals, crystallites size and orientation, and epitaxial layers can be replaced with simple chemical treatment to reduce surface recombination [14].
5. In an electrochemical photovoltaic cell the band bending may be increased by adjusting the redox potential (V_{redox}) of the electrolyte, thus increasing the attainable open circuit voltage. In comparison, the open circuit voltage (barrier height) in Schottky type cell is generally independent of the metal work function because of the Fermi level pinning [15].

7.9. PARAMETERS NECESSARY FOR CHARACTERISATION OF PEC SOLAR CELLS

The performance of a photovoltaic or PEC device can be described by the following measurements :

- (a) The short circuit current
- (b) The open circuit voltage
- (c) The maximum power
- (d) The fill factor
- (e) The efficiency

Short Circuit Current (I_{sc})

The current measured directly across the electrodes in the absence of any load in the circuit is referred to as the short circuit current (I_{sc}).

Open circuit voltage (V_{oc})

The voltage measured across the electrodes when there is no load in the circuit is termed as the open circuit voltage (V_{oc}).

Maximum Power (P_m)

The product of current and voltage gives the output power i.e. $P_{out} = V \times I$. For a particular load resistance value, this output power will be maximum. This point is referred as the maximum power point and the value is called the maximum power (P_m).

Fill Factor (FF)

Ideally a solar cell should have $V_{mp} = V_{oc}$ and $J_{mp} = J_{sc}$. However, various loss mechanisms operating within the cell make it deviate from the ideal behaviour. The term used to express this departure is known as the "fill factor" (FF) defined by

$$FF = \frac{J_{mp} V_{mp}}{J_{sc} V_{oc}}$$

where J_{mp} is current density at maximum power point and

V_{mp} is voltage at maximum power point.

J_{sc} is the short circuit current density and V_{oc} is the open circuit voltage.

Efficiency (η)

The theoretical conversion efficiency of a solar cell at the maximum power point is given by

$$\begin{aligned} \eta &= \frac{V_{mp} \times I_{mp}}{P_{in}} \\ &= FF \times \frac{V_{oc} \times I_{sc}}{P_{in}} \end{aligned}$$

where P_{in} is the solar power input

$$\eta = \frac{V_{mp} \times J_{mp}}{P_{in}} \text{ or}$$

where J_{mp} is current density at maximum power point

$$= \frac{I_{mp}}{\text{area}}$$

7.10. REQUIREMENTS FOR FABRICATION OF EFFICIENT PEC SOLAR CELLS

Essentially a PEC solar cell consists of,

1. a semiconductor photoelectrode
2. an electrolyte and
3. a counter electrode

All these parts play an important role for the better performance of PEC cells. The requirements which these parts should meet for the efficient PEC cells are detailed below.

Semiconductor Photoelectrodes

Semiconductor photoelectrode is the heart of the PEC cell. For the achievement of good performance it should satisfy the following requirements.

1. The optical absorption coefficient of semiconductor photoelectrode material should be large.

2. The band gap (E_g) of the photoelectrode material should be large so as to match with maximum span of the solar spectrum i.e. $E_g = 1.2$ to 1.8 eV.
3. It should be of the direct bandgap type with high optical absorption coefficient.
4. The diffusion length for minority carriers should be as large as possible.
5. The width of the space charge layer must be large.
6. Photoelectrode should be stable in the electrolyte and should not get corroded during illumination.
7. Thickness of the material and area of photoelectrode should be large enough to absorb all the incident radiation.
8. The lattice mismatch and thermal mismatch between two materials should be small.
9. Cost of the material and manufacturing process and efficiency should be acceptable.

In addition to the above requirements the parameters as film thickness, grain size, grain boundaries are to be controlled for polycrystalline thin films.

Electrolyte

Another important parameter in PEC cell is

electrolyte. Electrolyte consists of the oxidised species and reduced species. These species are ionic species which help to transfer the photogenerated holes from photoelectrode to counter electrode.

Requirements of properties which the electrolytes for PEC cells should possess are listed below,

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

[16].

7.11. CONCLUSION

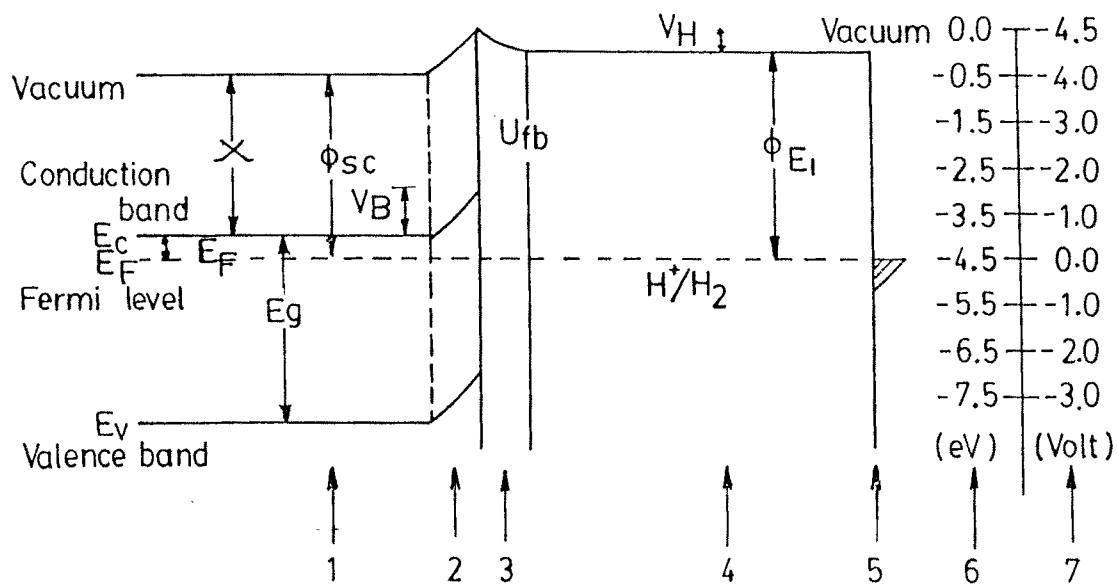
The basic principles of photoelectrochemical cells (PEC) detailed in general in this chapter will be applied to characterise the PEC solar cells fabricated using n-CuInS₂ single crystals as semiconductor electrode and polysulfide electrolyte in the next chapter.

CAPTIONS TO THE FIGURES

Fig. 7.1 Energy level diagram and energy scales for semiconductor-electrolyte junction.

Fig. 7.2 Charge and potential distribution at the semiconductor-electrolyte interface, ϕ_{sc} , ϕ_H , ϕ_G , ϕ_{Ga} are respectively potentials across the space charge layer, Helmholtz layer, Gouy layer and Galvanic potential.

Fig. 7.3 Classification of photoelectrochemical cells.



- | | |
|--------------------------------------|----------------------------------------|
| 1 n-Type semi conductor electrode | H^+/H_2 Electrolyte redox couple |
| 2 Depletion layer | V Helmholtz layer potential drop |
| 3 Helmholtz layer | Eg Band gap |
| 4 Electrolyte | X Electron affinity |
| 5 Metal electrode | ϕ_{sc} Work function |
| 6 Solid state scale (eV) | U_{fb} Flat band potential |
| 7 Electrochemical scale (NHE)(volts) | ϕ_{E_i} Electrolyte work function |
| | V_B Band bending |

Fig. 7.1

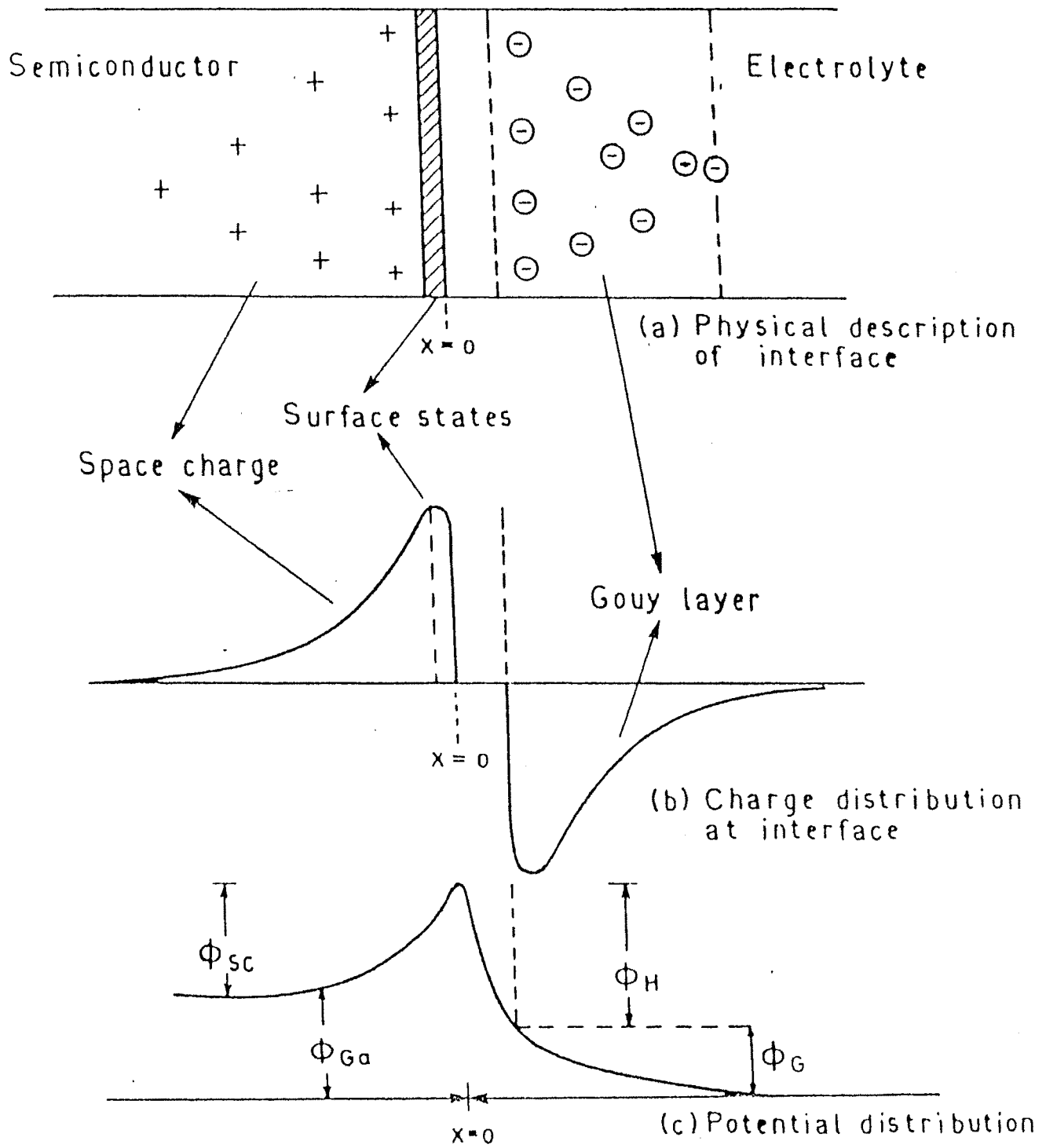


Fig. 7.2

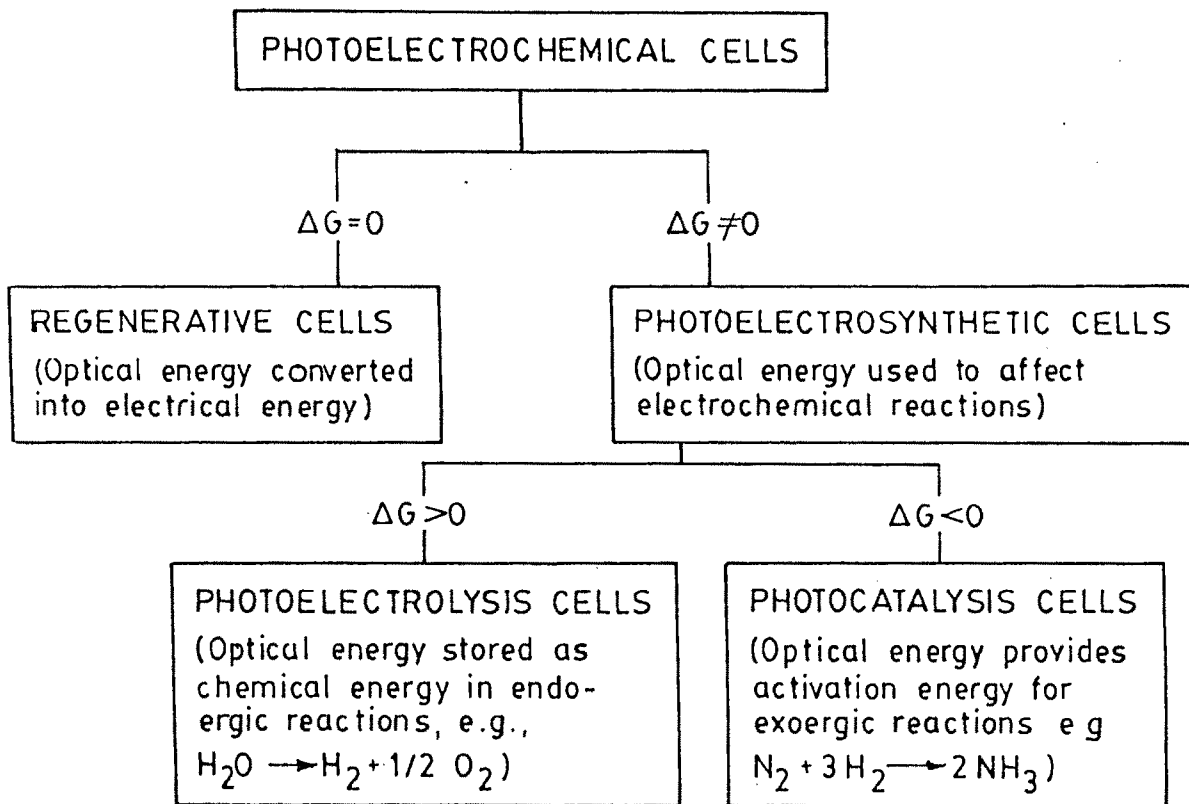


Fig. 7.3

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