

CHAPTER-I

CHAPTER - I

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INTRODUCTION

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## 1.1 General

Mathematically thin film can be interpreted as one which is bounded between two parallel planes extending infinitely in two directions but is restricted in its dimension along the third direction. The restricted third dimension is termed as the "thickness" of the film and it may vary from two to several times the wavelength of light but always remains much smaller than the other two dimensions. Thin films can be grouped into two :

- i) the continuous films and
- ii) the discontinuous films.

The discontinuous film consists of large number of small islands of the materials separated by the small finite distances, the situation generally arises in ultra-thin films. Due to such discontinuities in thin films, the resistivity is normally very high and the film shows negative temperature coefficient of resistance. On the other hand film becomes continuous when thickness of the film is increased and resistivity of such film decreases. This causes the mean free path of the charge carriers to decrease which in turn originates from the imperfections and scattering of the carriers at the surface. The surface scattering invariably influences the properties of the continuous film upto the thickness comparable to the mean free path of the carriers [1-3].

The studies on electrical transport properties of solids are highly essential to understand various types of devices. The basic transport properties are the electrical conductivity, thermoelectric power, hall coefficient, optical studies etc.

## 1.2 An Overview of Thin Film Technology and Solar Cells.

### 1.2.1 Thin Film Technology :

The pivotal role of THIN FILM TECHNOLOGY in the development of diverse and challenging frontiers as microelectronics, optical coatings and integrated optics, thin film superconductivity and quantum engineering, micromagnetism, metallurgical coatings, and amorphous materials, surface engineering and solar energy conversion devices is all too well known and is now recognised as a frontier area of microscience and microtechnology [4]. New and even more exciting fields are also emerging. The driving forces behind the exploration of the new frontiers are the exciting phenomena of microscience associated with low dimensional micro and nanomaterials and the industrial applications of microscience and microtechnology for the development of synthetic materials of tailored properties for VLSI/GSI communication, informatics, and solar energy conversion. With decreasing size of active electronic devices, a higher packing density, higher speed performance, and lower costs are obtained. At the same time with the decrease in active size of

the materials, geometrical and quantum size effects begin to dominate the physical phenomena. These low dimensional materials exhibit quantization, non equilibrium electron, phonon, and photon transport processes, metastable and unstable structures and surface dominated diffusion and chemical processes.

Ultrathin films are 2-dimensional micromaterials which are obtained by one of the established techniques falling under the headings such as PVD (Physical Vapour Deposition), CVD (Chemical Vapour Deposition), ECD (Electrochemical Deposition), or hybrids thereof. The films can be further cut into desired dimensions and geometry by one or more microlithographic techniques. By depositing a radiation sensitive thin film of an organic/inorganic resist material, the resist is exposed through a patterned mask. The chemical changes occurred as a result of irradiation of the resist is utilised to micromachine the film by wet or dry etching techniques. By using tailored e-beam resists, materials and devices of 0.1 to 0.2  $\mu\text{m}$  or even less are easily obtained today.

The tailoring of properties of the materials arises basically, from the numerous inherent characteristics of nucleation and growth of thin film and the occurrence of new physical phenomena. The creation of a matter in a deposition process involves adsorption, desorption and migration of adatoms,

interaction of adatoms to reach critical nucleation stage, lateral and perpendicular growth of nuclei, sintering and recrystallisation. These processes take place under high supersaturation, rapid thermalisation and nonequilibrium thermodynamic conditions. By varying deposition parameters, one can manipulate one or more of these processes to obtain a whole range of structural disorder, microstructure, topographic, and geometrical features, growth anisotropies, frozen-in point, and line defects and compositional profiles.

The enormous flexibility provided by the thin film growth processes allows the fabrication of desired geometrical, topographical, physical, crystallographic, and metallurgical "structures" in two or lesser dimensions. The features are increasingly being exploited to study the structure sensitive physical, mechanical, chemical, and electrochemical properties of micromaterials.

Among the properties being studied today for significant applications are : 1) Optical gap, 2) Optical constants and thus reflectance, transmittance and emittance spectra, 3) Spatial variation of optical thickness, 4) Anisotropy in structure and properties, 5) Stoichiometric deviations, 6) polymorphic and metastable structures with useful physical properties, 7) relaxed solubility, variable composition, multicomponent compounds, and alloys, 8) Spatial

variation of electrical gap and electron transport parameters, 9) Surface activation and passivation behaviour, and 10) Surface mechanical tribological properties. One can design micromaterials to give any desired reflectance/ transmittance/emittance spectrum by using graded composition of two or more materials. The conversion of surface of a number of metals ( so called "metals" ) having high absorptance in the visible region of the solar spectrum and a high reflectivity in infrared region represents one of the best examples of a tailored solar selective surface . A suitable columnar structure of graded mixture ( Cu, CuO , Cu<sub>2</sub> O, thickness = 1  $\mu$ m ) obtained during the chemical conversion process enhances optical selectivity for very efficient solar energy conversion.

By controlling the stoichiometric deviations of oxygen in oxides of Cd , Zn, Sn etc. and alloys , and with suitable dopant impurities , an approximately 90% transparent synthetic , transparent conductors are obtained , which are being used extensively in several thin film solar cells and a number of optoelectronic devices. Rapid condensation of atoms of many materials results in the formation of non crystalline structures.

Due to the tetrahedral structure (geometrical constraints) rapid deposition of such materials ( Ge, Si) results in the formation of defects such as voids and dangling bonds. The defects give rise to

undesirable localised states in the band gap of the material. Incorporation of an impurity such as hydrogen helps to tie up the dangling bonds in amorphous silicon and thus effectively cleans up its dirty band gap which can be controlled to increase almost by a double value of the crystalline silicon. It now becomes possible to dope such a material to yield "n" or "p" type conductivity. This hydrogenated amorphous silicon micromaterial has given birth to a whole new technology of junction device microelectronics including amorphous silicon solar cells.

A combination of Ge with S or Se chalcogen, structurally tailored, obliquely deposited amorphous Ge-Se(s) alloy films behaves as an inorganic polymer. On irradiation with energetic particles, collapsing of voids occur and material exhibits radiation induced giant contraction effect. The physical densification is accompanied by large changes in refractive index, shift of absorption edge and variety of chemical and electrochemical changes. These changes allow generation of high resolution optical memories, reprographic images and lithographic patterns in submicron range.

The artificial superlattices and quantum well structures created by depositing nanometric thin films of one or more materials in periodically arranged multilayers provides perhaps the most exciting tailorability of electron transport phenomena which has



already opened a new era of synthetic semiconductors and exotic electronic devices.

### 1.2.2 Solar cells: Photoelectrochemical (PEC) cells :

In principle solar cell is a semiconductor device that converts the radiant energy into its electrical counterpart. Basically the device includes an arrangement for both sinking and sourcing of an electron. When these arrangements are connected together current flows through the external circuitry. Therefore, it is our prime intention to produce source of electrons and holes at the consumption of the radiant energy which can be achieved by using the suitable semiconductor material as one of the device elements. When a photon with energy,  $E \geq h\nu$ , is absorbed an electron-hole pair is generated within the semiconductor. There is every possibility of these electrons and holes to attract and annihilate, however this situation demands immediate separation of an electron and hole. This can be made possible with formation of a junction wherein transport of charge carriers across the junction give rise to a local field so called "built in potential". Under such circumstances, when a light of energy  $h\nu \gg E_g$ , the band-gap of a semiconductor, is allowed to incident on this interfacial layer the generated electron-hole pairs are separated by this driving interfacial potential. The schematic showing the separation of e-h pair is depicted

in figure 1.1 One side of the junction acts as a source of electrons while the other sink of electrons.

Mankind has regarded sun as the source of life and energy since time immemorial . With the increasing energy crisis, man is again looking towards the prime energy giver the sun. Harnessing solar energy has therefore attracted the attention of the scientists, technologists, economists, sociologists and politicians. All the solar energy converters utilize the radiations received from the sun. Hence understanding of these radiations is imperative . The energy from the sun received on the earth is a function of number of parameters such as atmospheric absorption, scattering, reflection from the earth surface, sun's position relative to earth etc. The solar energy input on the earth's surface, therefore, exhibits wide variation. On the other hand, the energy received just outside the earth's atmosphere is practically constant expressed in terms of a " Solar Constant " which is defined as the energy received from the sun per unit area perpendicular to the incident solar radiation, in the absence of earth's atmosphere per unit time at the earth's mean distance from the sun. The typical value of solar constant according to the recent estimate is between 1368 to 1377 W/m<sup>2</sup>. The extraterrestrial solar spectrum referred to as Air Mass Zero (AM0) extends from 0.115  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . The visible region carries about 51%

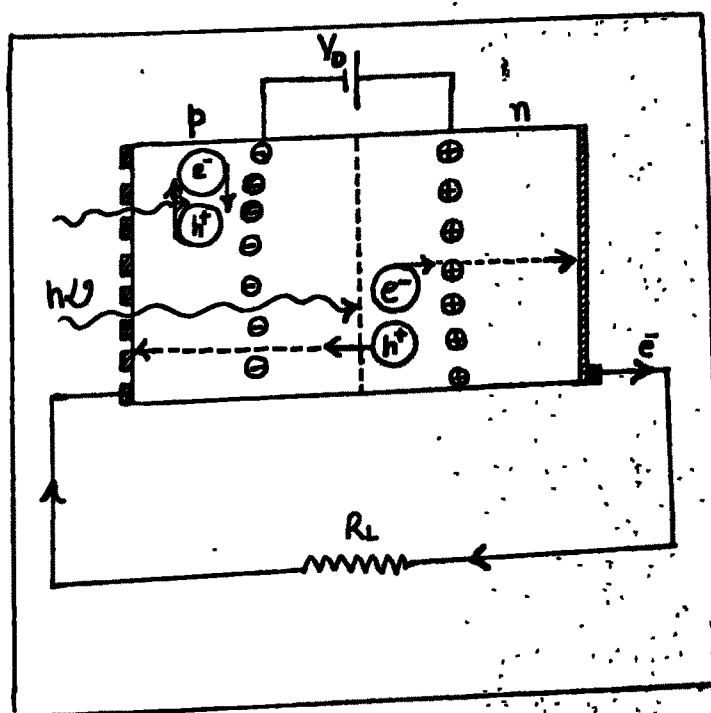


Fig.1.1 p-n junction under the influence of local electric field.

of the energy useful for photovoltaic converters & rest of the 49% infra red energy is useful for solar thermal conversion. The air mass is defined as the ratio of the actual length traversed with the sun at the Zenith angle. Because of the curvature of the earth, zenith angle becomes large and under such circumstances  $AM_1$ ,  $AM_2$  and  $AM_3$  are defined.

Thus an efficient and less expensive system for utilizing solar radiations is the need. Two distinct types are: the solar thermal converters (uses the infra red region of the spectrum) and second, the solar photoconverters (uses visible / UV region). In the first category, incident radiations are converted into thermal energy whereas second process is the age-old photosynthesis. The photosynthesis includes photochemical conversion in non-biological systems and photovoltaic effect or photoexcitation of semiconductors. The various photoconverters are listed in fig. 1.2.

In electrochemical literature, these cells are known by host of names such as semiconductor liquid junction solar cells, semiconductor-liquid junction photovoltaic cells, wet photocells and electrochemical solar cells or photoelectrochemical (PEC) solar cells are frequently used names; 5-8!. The PEC cells have their origin in Becquerel effect 19! where in an AgCl electrode and a counter electrode placed in a suitable electrolyte shows current and voltage in an external

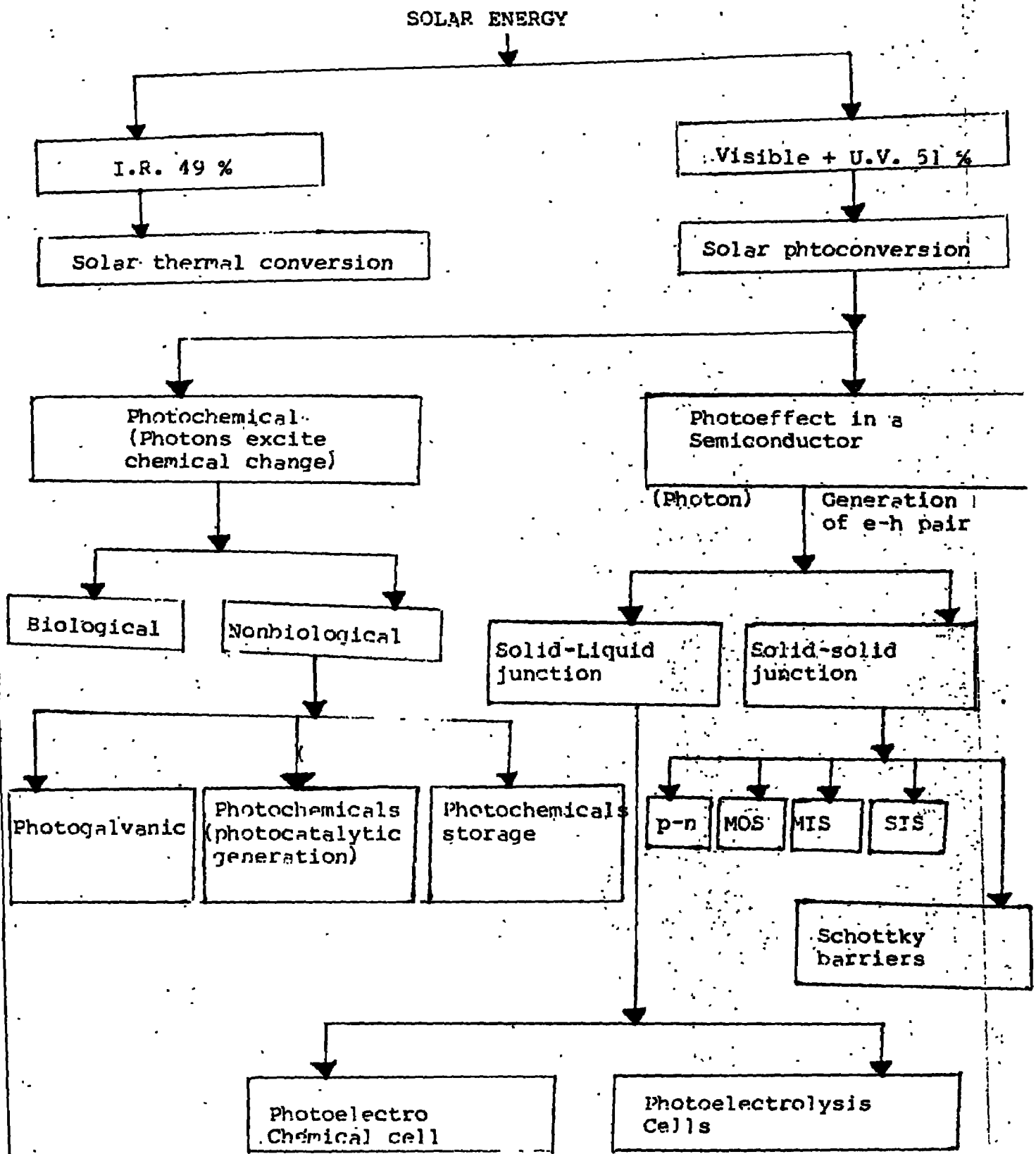


Fig 1.2 Summary of various photoconversion devices.

circuit up on illumination. Much is now investigated on this subject and several reviews are now appeared in the literature [5,7,10-12]. The absorption of light in the PEC cells can be used for the production of just electrical energy without resulting in photoelectrolysis. Such cells consist of one effective redox couple and the oxidation reaction at the anode is reversed at the cathode. Thus, there is no net chemical change in the process, (i.e.  $\Delta G=0$ ), however, the light quanta gets converted into equivalent electrical energy. In the case of photoelectrolysis cell there are two effective redox couples and the oxidation and reduction reactions at the photoelectrode and counter electrode are different causing a net chemical change, (i.e.  $\Delta G \neq 0$ ). If the free energy change  $G$  is +ve, the optical energy gets converted into chemical energy (photoelectrolysis) and for  $G$  to be -ve optical energy activate the reaction (photocatalysis). The classification according to this energy change,  $\Delta G$ , is shown in fig. 1.3.

Although conversion of optical energy into an electrical by the use of photovoltaic effect is a well known phenomena, the reduction in cost has been a great hindrance in recent years in order to provide an economically competitive source of electricity. One of the ways predicted to achieve this low cost solar cell goal is the development of thin film technologies for photovoltaics. Direct band gap semiconductor materials having high absorption coefficient and high quantum

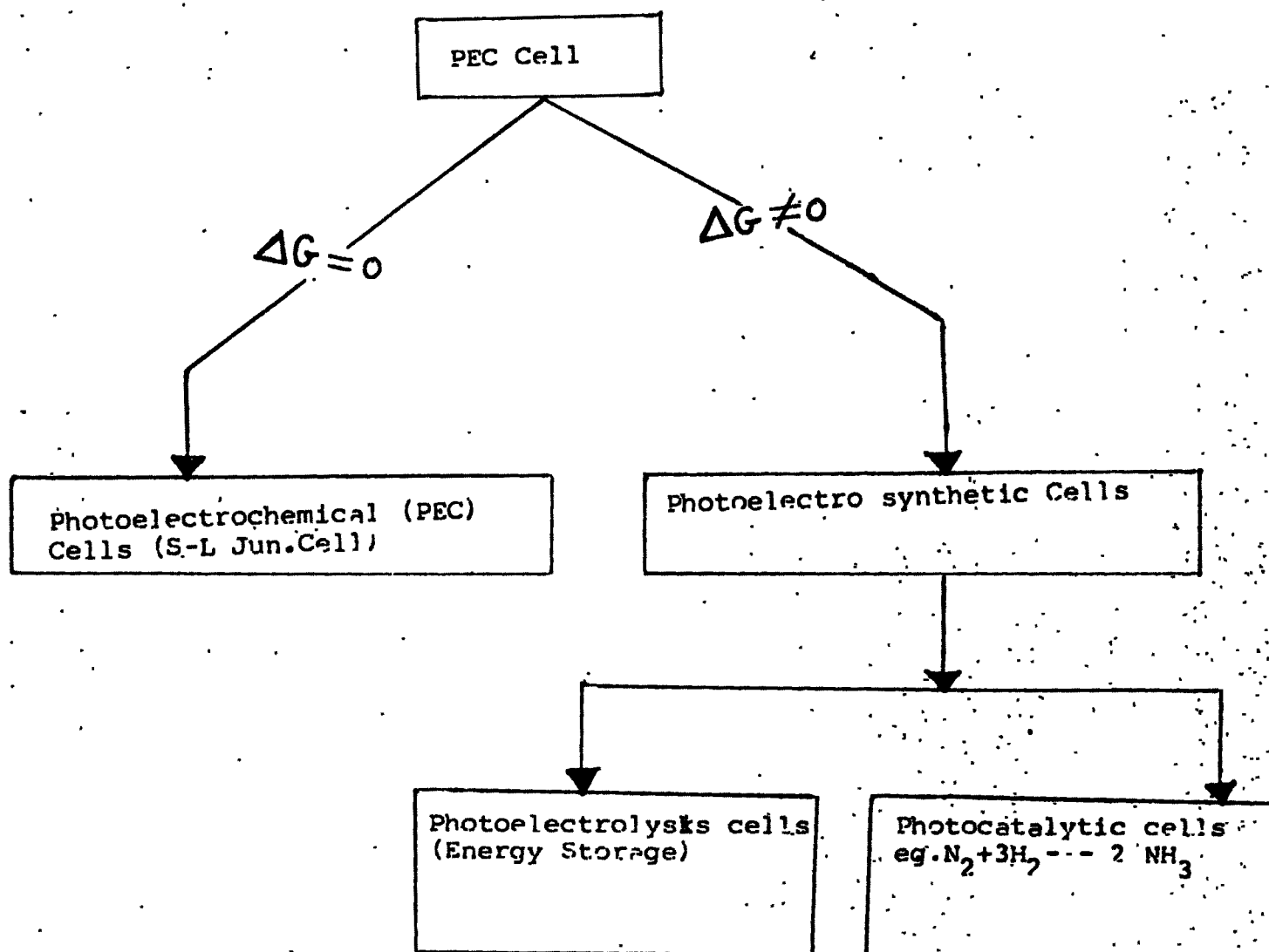


Fig.1.3 Classification scheme for photoelectro-chemical cells.

yield find suitable in this respect. The II-IV and V-VI compounds meet these requirements and can be made available in thin film form with a low cost and inexpensive techniques [13-20]. These electrochemical photovoltaic cells have the following overriding advantages over their solid state counterpart [5,8] :

1. The PEC cells are easier to fabricate . Just immersion of the semiconductor in the electrolyte forms a junction. The process of junction formation in the case of solid state solar cells involve complicated processing steps and highly costed equipments. The process further is time consuming.
2. The PEC cells provide the means for direct storage of an optical energy.
3. The problem of differential thermal expansion and interdiffusion does not arise in case of PEC cells.
4. The band bending characteristic of the semiconductor can easily be achieved by a suitable choice of redox electrolyte system.
5. No antireflective coatings are required in PEC cells unlike the solid state solar cells.
6. Photosensitive junction is abrupt ( transparent from one side) more photons are absorbed in the interface region where charge carriers are more effectively separated and collected.



7. Both amorphous and polycrystalline semiconducting , electrodes are useful due to increased surface area.
8. All the preparative processing steps are simplified in PEC cells.

Even though PEC cells has some inherent advantages, they are less stable owing to the photocorrosion of the photoelectrode and problems encountered in cell sealing because of the liquid electrolyte . The stability of the photoelectrodes have been successfully tackled by different groups around the world working in this area : 21 - 24 .

### 1.3 Requirements of Photoelectrochemical (PEC) Cells.

The essential constituents of a PEC cell are : Semiconductor photoelectrode , an electrolyte consisting of redox species and a counter - electrode. The following points should be noted while devising an efficient photoelectrochemical cell.

#### 1.3.1 An active photoelectrode.

The choice of a semiconductor material as a photoelectrode is a very complex problem for a PEC cell. It should satisfy the following requirements.

- a) The bandgap of the material should be such that the maximum span of solar spectrum is utilised . Most of the visible part of solar energy reaching the earth's surface is centred in the range 1.0 to 3.0

eV. Therefore very wide bandgap semiconductors are not used. }

- b) Material should be of direct bandgap type with high optical absorption coefficient ( $10^4 - 10^5 \text{ cm}^{-1}$ ).
- c) The minority carrier diffusion length ( $L_p$ ) and depletion layer width ( $W$ ) should be large.
- d) The magnitude of donor atom concentration,  $N_D$ , should be optimum. Actually when  $W$  is large Debye length must be large indicating the smaller value of  $N_D$ . However,  $N_D$  cannot be made very small since it would lead to increased ohmic losses within the material itself. The optimum value of  $N_D$  is of the order  $10^{19}$  to  $10^{20} \text{ cm}^{-3}$ .
- e) For a practical longlife photoelectrochemical cell the photoelectrode must be stable against dissolution, photocorrosion, and electrochemical corrosion when placed in the specific redox couple. Low bandgap materials are easily corrosive. Thus from (a) and (e) the material selected should have an intermediate bandgap.
- f) Charge carriers should have high mobility and life time.
- g) Thickness of the material should be large enough to absorb all the incident radiations.

h) Cost of the material, manufacturing process, and quantum efficiency should be acceptable.

### 1.3.2. A redox electrolyte :

An electrolyte plays equally an important role in deciding the efficiency and hence the acceptable performance of a PEC cell. It helps to drag the photogenerated holes from photoelectrode to counterelectrode. As the difference between  $E_{F,semi}$  and  $E_{F,redox}$  define the upper limit to photovoltage, the choice lies both for a photoelectrode and an electrolyte. Following are a few points while selecting a proper electrolyte.

- i) An electrolyte should be transparent.
- ii) Ionic species participating in the redox reaction should be diffusion limited.
- iii) Conductivity of the supporting electrolyte should be high.
- iv) It should be stable under illumination for longer duration.
- v) Should be non toxic and costing less.

### 1.3.3. The counter electrode :

The proper choice of a counter electrode is important. It should have,

- a) Low over potential for redox reaction to take place.



b) Large area for reducing concentration polarisation.

c) Chemical inertness with electrolyte.

#### 1.4 Selection of the Materials.

Considering the above observations cadmium sulphide is an important material for use in solar cells and also finds use in some other numerous devices. It has intermediate bandgap which can be made optimum in respect of photovoltage and photocurrent. (As smaller bandgap materials yield larger photocurrent and smaller photovoltage and vice versa for larger bandgap materials [25]). Hence the preparation and characterization of CdS films have drawn much attention. The poorly lapping absorption spectra of CdS can be improved as it has got considerable scope for doping. The impurity doping not only extends photoresponse but improves efficiency [26-30]. The dopant material is trivalent antimony.

The number of electrolytes have been tested for CdS however, none of these found suitable. A mixture of equimolar NaOH-S-Na<sub>2</sub>S is found suitable as it has many advantages over the others [20, 28-32].

Many counter electrode materials have been suggested and evaluated [33-35]. Platinum or graphite impregnated with electrocatalyst, like COS or NiS, seems quite suitable. Use of transparent counter electrode, is also recommended. We have used impregnated graphite as a counter electrode in our studies.

### 1.5 Aim Of The Present Investigation :

Accounting the above observations systematic studies have been planned in two aspects.

- i) thin film properties and
- ii) photoelectrochemical cell properties.

As most of the photoelectrochemical cell properties are found to depend on the properties of the active photoelectrode material, the photoelectrode is characterised in terms of its electrical and optical properties. As a starting step we have tried to develop a chemical deposition process system. Efforts have also been put to avoid the difficult, complex and clumsy mechanical processes involved therein.

Thin films of cadmium sulphide have been prepared by a chemical deposition process as it has certain advantages over the other conventional techniques. The optimisation in the process has also been done in respect of the different deposition conditions and preparative parameters. These deposition conditions and preparative parameters such as; speed of rotation of the substrates, rate of addition of thiourea, and molar concentration of the reactants, deposition temperature, and time for the deposition etc are finalised in the initial stages of the work. The substrates used were amorphous glass and stainless steel plates. The physical characterisation of the material is carried out prior to the formation of a PEC cell. Physically, the

material is characterised for its electrical conductivity, thermoelectric power and optical absorption studies. The electrical conductivity and thermoelectrical power units are developed in our laboratory. Various material parameters such as conductivity, thermoelectric power, carrier concentration, barrier height, mobility, and activation energy have been examined. The trivalent antimony is used as a dopant material and its effects on various film properties are studied.

For the studies on photoelectrochemical cell, a glass cell, of the structure as discussed in chapter V, is fabricated and the cell is constructed by employing the samples on conducting substrates (photoelectrode), an electrolyte (1M  $\text{Na}_2\text{S}$ -1M  $\text{NaOH}$ -1M S) and a counter electrode (graphite). The electrical and optical behaviours of the cells have been carried out and an optimum cell composition is searched out including the effects of doping material.