

CHAPTER-I

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1.1 An Overview of thin Film Technology and Solar Cells.

1.1.1 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 [1]. 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 a hybrid 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 μm 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^{cf} 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 example of a tailored solar selective surface . A suitable columnar structure of graded mixture (Cu, CuO , Cu₂O, thickness = 1 μ 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 undersirable 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.

1.1.2 Photo electrochemical (PEC)solar cells :

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^2 . The extraterrestrial solar spectrum referred to as Air Mass Zero (AMO) extends from 0.115 μm to about 1000 μm . The visible region carries about 51% 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 : solar thermal converters (uses the infra red region of the spectrum) and second, solar photoconverters (uses visible / UV region). In the first category, incident radiations are converted into thermal energy where as 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. 1.1.

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 [2-6]. The PEC cells have their origin in Becquerel effect [7] where in an AgCl electrode and a counter electrode placed in a suitable electrolyte shows current and voltage in an external circuit up on illumination. Much is now investigated on this subject and several reviews are now appeared in the literature [2,4,8-10]. 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. $G=0$), 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. $G \neq 0$). 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) [5]. The classification according to this energy change, G , is shown in fig. 1.2.

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 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

[11-18]. These electrochemical photovoltaic cells have the following overriding advantages over their solid state counter part [5,6] ;

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 characteristics 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 ~~the~~ 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 [19 - 22].

1.2 Basic Demands of a 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.

1.2.1 An active photoelectrode.

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

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^{15} to 10^{17} 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 lifetime.

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.

1.2.2. 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 $E_{F_{\text{semi}}}$ and $E_{F_{\text{redox}}}$ 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 ~~low~~ costing less.

1.2.3. The counterelectrode :

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..

1.3 Selection of the Materials

Owing to the fact discussed in section 1.2.1 we do feel bismuth trisulphide to be a promising material. It has an excellent bandgap match with the maximum span of the solar spectrum. The smaller band gap materials yield larger photocurrent and smaller photovoltage and vice versa for larger bandgap materials [23].

The number of electrolytes have been tested for Bi_2S_3 , however, none of these found suitable. A mixture of equimolar $\text{NaOH-S-Na}_2\text{S}$ is found suitable as it has many fold advantages

over others | 18,24,25,26,27 |.

Many counter electrode materials have been suggested and evaluated | 28 - 31 |. Platinum or graphite impregnated with electrocatalyst, CoS or NiS, seems quite suitable. Use of transparent counter electrode, if possible is also recommended. We have used impregnated, graphite as a counter - electrode in our studies.

1.4 Nature of the Work.

Considering the above observations, systematic studies have been proposed 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 photoelectrode material; the material, Bi_2S_3

is characterised in terms of its electrical and optical properties both for thin film and cell properties.

As a part of a continuing programme we have tried to develop & fabricate a chemical deposition process system . Some attempts have been diverted to avoid the complex and clumsy mechanical processes involved therein. Thin films of Bi_2S_3 have been prepared by a chemical growth process as it has multifarious advantages over the other conventional techniques. The different deposition conditions and preparative parameters are optimised in the few of the initial steps of the work. The deposition conditions and preparative parameters such as speed of rotation of the substrates,

temperature and time for the deposition, etc. are finalised at the beginning. The substrates used were amorphous glasses and stainless steel strips. The physical characterisation of the material is carried out prior to the formation of the PEC cell. Physically, the material is characterised for its electrical conductivity, thermopower and optical absorbance studies. The electrical conductivity and thermoelectric power units are developed in our laboratory. The material parameters such as conductivity, thermoelectric power, activation energy have been determined. The surface topography of the material and the structure of the material have been examined.

For the studies on PEC cell properties of the material, a glass cell of the configuration as described in chapter-III is fabricated and the cell configuration has been devised by using the thin films on stainless steel (photoelectrode), an electrolyte ($1\text{M Na}_2\text{S}$ - 1M NaOH - 1M S) and a counter electrode (sensitised graphite) . The electrical and optical characterisation of the cells have been carried out.

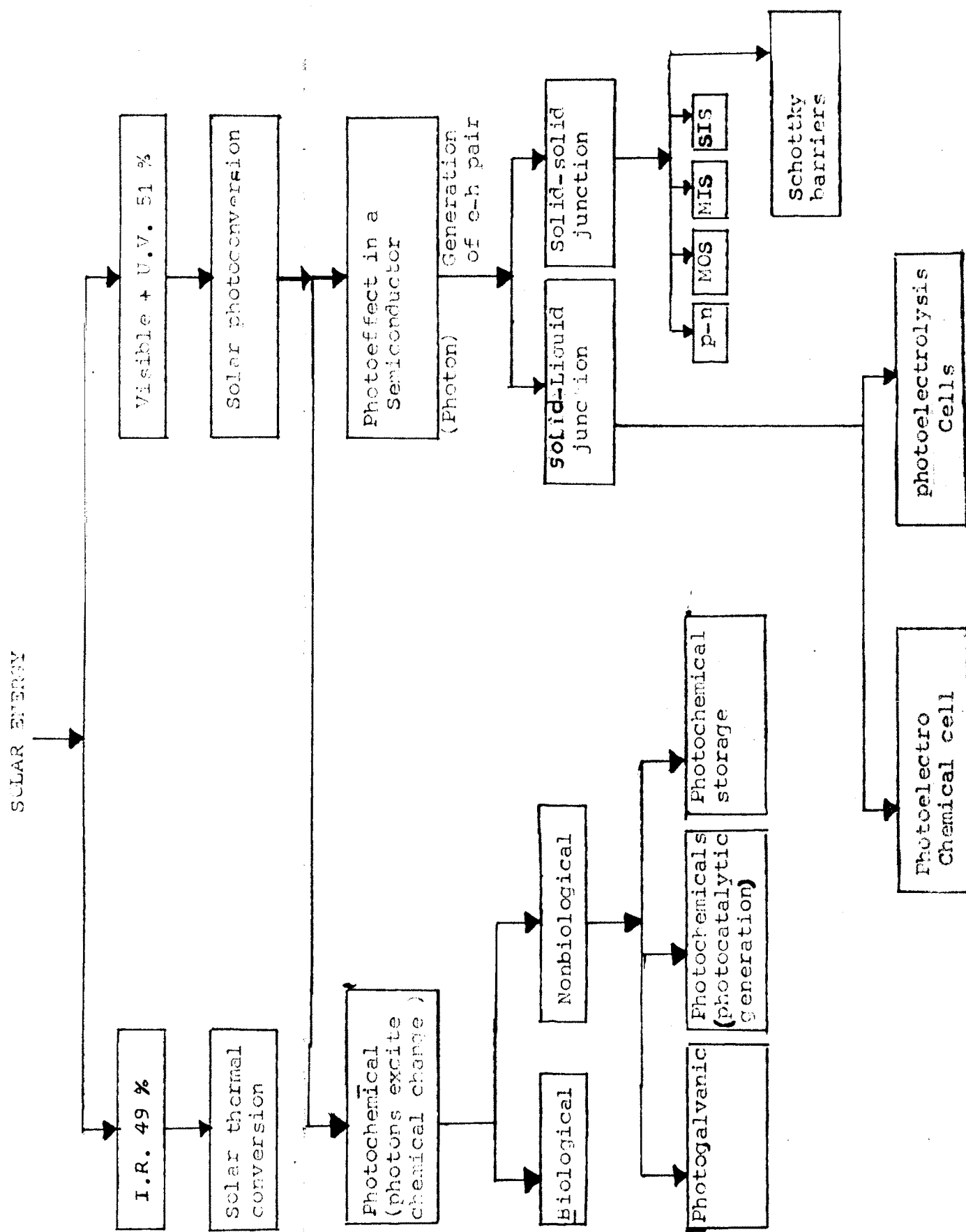


FIG 1.1 Summary of various photoconversion devices

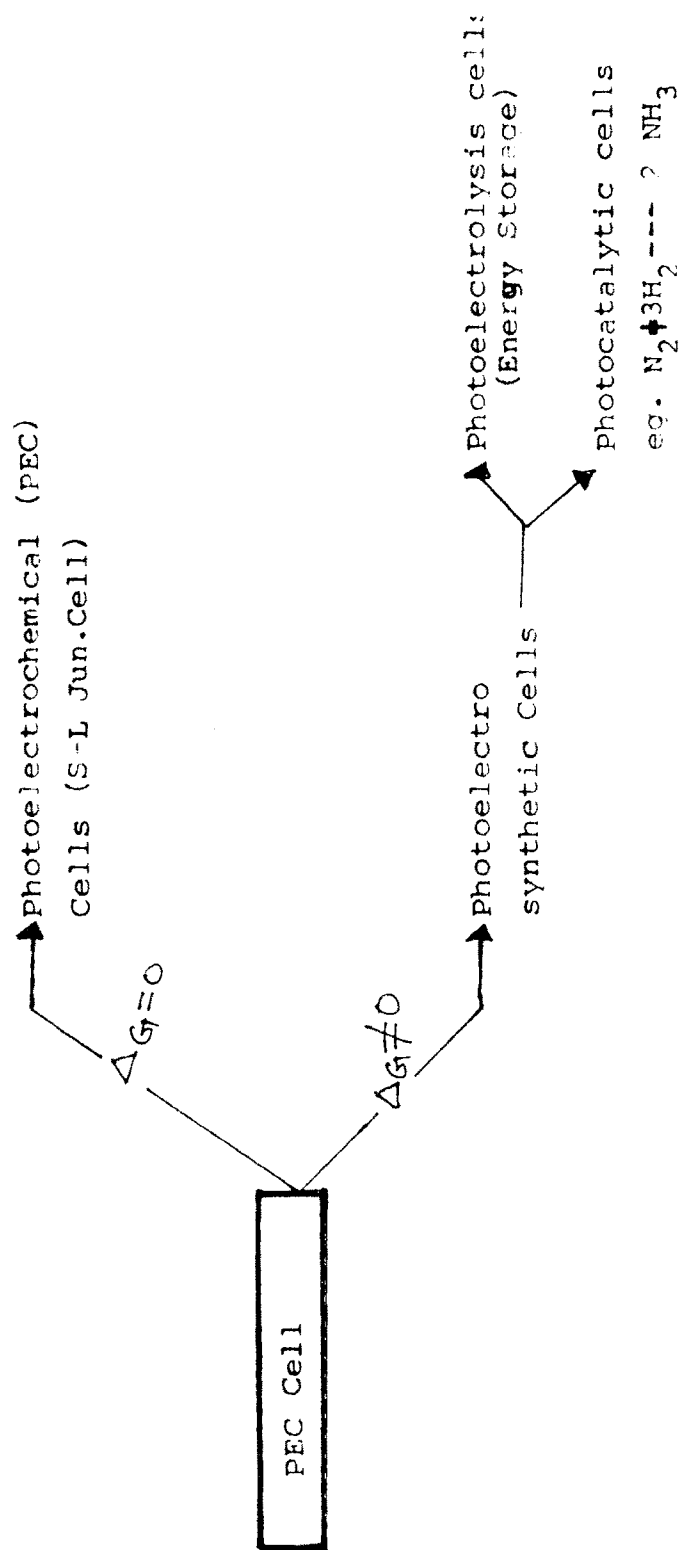


Fig.1.2 Classification scheme for photoelectro-chemical cells.