CHAPTER - I

CHAPTER-I

INTRODUCTION

1.1 General

Thin films of the noble metals have been used for decorating glasses and ceramics for over a thousand years. As early as the seventh century, it was known how to paint a suspension of a silver salt onto a glass medicine vial and then heat it to convert the salt to metallic silver. Another very old method of forming thin films is the beating of gold to form "gold leaf". The thinnest films made this way are about four or five millionths of an inch thick. Too much stress applied to this gold leaf leads to rupture, thus imposing a limitations on its thinness. Thickness of films is usually discussed in terms of angstrom units (A°). This dimension is equivalent to four billionths of an inch and is of the same order of magnitude as the dimension of a single atom.

Much more recently, thin films have been used in the study of relationship between the structure of solids and their physical properties. Practical applications include electrical and electronic circuits, optical instruments and magnetic information storage devices. These more modern films are formed by depositing the materials onto a clean supporting substrate to build up film thickness rather than by thinning down the bulk material. Thin films for electronic circuit applications range from a few hundred angstroms to tens of thousands of angstroms in thickness. A typical film might be 1000 A° thick while the glass substrate supporting it would be 10,000 times thick. Films vary in structure from amorphous films such as anodic oxide dielectrics to single crystal films such as epitaxially grown silicon. Most of the films fall between these extremes and are polycrystalline, composed of many small crystals called "crystallites" or "grains", fitted together with more or less random orientation. For very thin films, crystallite size is observed to be a function of thickness but for thicker films, it is usually indpendent of thickness. Sizes range from about 50 A° to 2000 A°. Crystallite size also depends on deposition parameters such as substrate temperature and deposition rate and after deposition, may be altered by annealing with the larger crystallites growing at the expense of the smaller ones /1/.

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 material, surface engineering and solar energy conversion devices is all too well known and is now recognised as the frontier area of microscience and microtechnology /2/. New and even more exciting fields are also emerging. The origin of such new frontiers lies in the exciting phenomena of microscience associated with low dimensional micro and nanomaterials and the industrial applications of microscience and microtechnology in VSLI/GSI communication, informatics, and solar energy conversion. With decreasing size of the active electronic devices; a higher packing density, higher speed performance and lower costs are obtained. Ultrathin films are 2-dimensional micromaterials which are obtained by one of the established techniques falling under the headings such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), Electrochemical Deposition (ECD) or a hybrid thereof. The films can be further cut into desired dimension and geometry by one or more microlithographic techniques. By tailored e-beam resists, material and devices of 0.1 to 0.2 μm or even less are easily obtained today.

The tailoring of materials properties arise basically from the numerous inherent characteristics of nucleation and growth of thin film and the occurrance of the new physical phenomena. The creation of a matter in a deposition process involves adsorption, desorption and migration and interaction of adatoms to reach a 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 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 microstructures into two or lesser dimensions and to study their structure sensitive properties. Among the properties being studied today for significant applications are: i] optical gap, ii]optical constants and thus reflectance, transmittance and emittance spectra, iii]spatial variation of optical thickness, iv] anisotrophy in structure and properties. v] stoichiometric deviations, vi] polymorphic and metastable structure with useful physical properties, vii] relaxed solubility, variable composition, multicomponent compounds and alloys, viii] spatial variation of electrical gap and electron transport parameters, ix] surface activation and passivation behaviour and x] surface mechanical and 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 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_2O, thickness ≈1 um) obtained during the chemical conversion process enhances the 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 a suitable dopant impurities, an approximately 90% transparent synthetic conductors are obtained which are being used extensively in several thin film solar cells and a number of optoelectronic devices.

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 these 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 a 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 structurally tailored, obliquely deposited amorphous (GeSe)S alloy films behave as an inorganic polymer. On irradiation with energatic particles, collapsing of voids occur and material exhibits radiation induced gaint contraction effect. This results into large changes in the refractive index, shift of absorption edge, and many of the chemical and electrochemical changes which allow generation of high resolution optical memories, reprographic images and lithographic patterns in submicron range. The artificial and quantum well structures obtained using nanometric structures provide perhaps the most exciting tailorability of electron transport phenomenon which has already opened a new era of synthetic semiconductors and exotic electronic devices.

1.2.2 Photoelectrochemical (PEC) solar cells

Solar cell is a semiconductor device that converts the optical energy into its electrical equivalent. Basically device produces source of the electrons and holes at the consumption of the photons. This can be achieved by using a suitable semiconductor material as the active device element. When a photon of energy, $h\nu \geq E_g$ is absorbed, an electron hole pair is generated within the semiconductor and are separated at the junction where in transport of charge carriers across the junction give rise to a local field so called "built in potential". Schematic showing the separation of an e-h pair at the junction is depicted in figure 1.1; one side of the junction acts as a source of electrons while other the sink of electrons.

Mankind has regarded the sun as the source of energy since time immemorial. With increasing energy demands, man is again looking towards a prime energy source, "the sun". All the solar energy converters convert the solar radiations into another usable form and hence understanding of these radiations is imperative. The energy from the sun received down to the earth is a function of number of parameters such as atmospheric absorption, scattering, reflection from the earths surface, sun´s position relative to earth etc.The solar energy that is input on the earth surface, therefore exhibits a wide variation. On the other hand, the energy received just outside the earth´s atmosphere is practically constant, and is expressed interms 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 a solar constant according to the recent estimate is between 1368 to 1377 W/m^2. The extraterrestrial solar spectrum, referred as Air Mass Zero (AM0), extends from 0.115 μm to about 1000 μm. The visible region carries about 51% of the energy useful for photovoltaic applications, where as rest of the 49% infra red

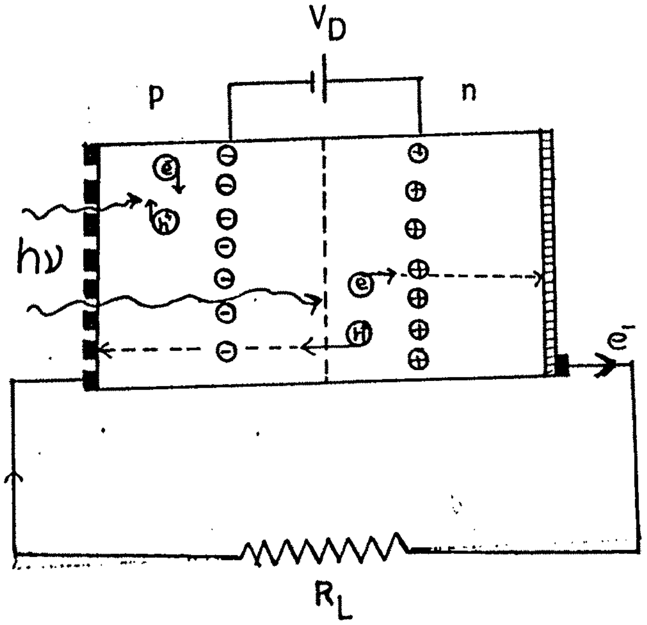
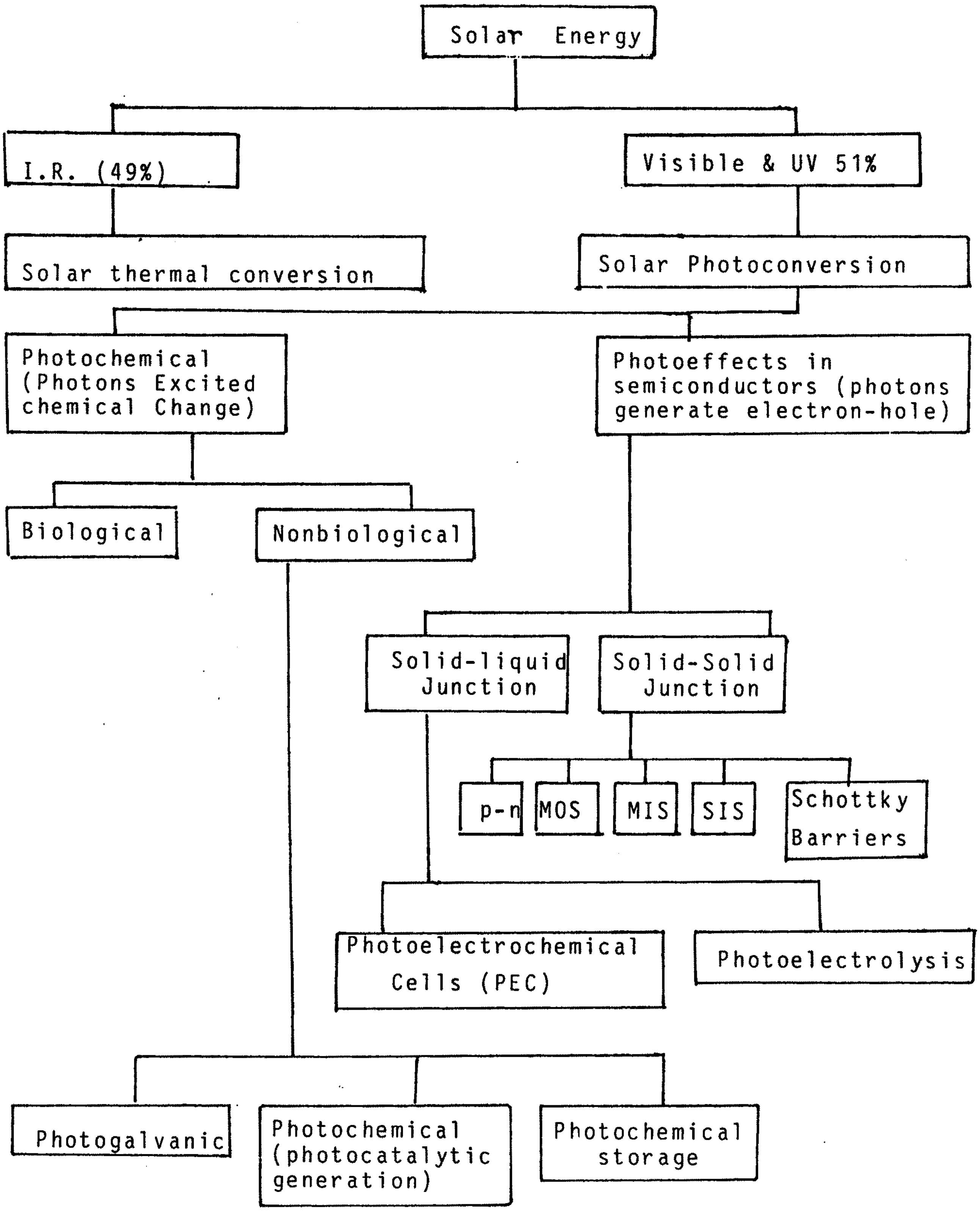


Fig. 1.1 p - n junction under the influence of a local electric field.

energy is utilised for the solar thermal applications. 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 inexpensive system for utilizing the solar radiations is the need. Two distinct types are: Solar thermal converters (use the infrared region of the spectrum) and solar photoconverters (use visible/ UV region). In the first, incident radiations are converted into the thermal energy where as later is an age-old photosynthesis process that includes photochemical conversion in the nonbiological and photovoltaic systems. The various photoconverters are listed in figure 1.2. In the electrochemical literature, these cells are known by a 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 /3-9/. The PEC cells have their origin in the Becquerel effect /7/ where in an AgCl elctrode and a counter electrode placed in a suitable electrolyte shows current and voltage in an external circuit up on illumination. Much data are now available on this issue and several reviews are now appeared in the literature /3,5,8-10/. These cells consist of an effective redox couple and the oxidation reaction at the anode is reversed at the cathode. Although there is no net chemical change in the process (i.e. $G=0$), the light quanta gets converted into an equivalent electrical energy. The photoelectrolysis cells are characterised



Photochemical and Electrochemical photovoltaic (ECPV) area.

Conventional photovoltaic cell area.

Fig. 1.2. Block diagram of various photoconversion devices.

by a difference in oxidation and reduction reactions at the photoelectrode and the counter electrode thus causing a net chemical change (i.e.$\Delta G \neq 0$). If free energy change, ΔG, is positive, the optical energy gets converted into chemical energy (photoelectrolysis) and for ΔG to be negative, the optical energy activates the reaction (photocatalysis) /9-11/. The classification according to these energy changes (ΔG) is shown in figure 1.3.

Although conversion of the optical energy into electrical energy by means of a photovoltaic effect is well known phenomena, the reduction in cost has been a great hindrance in order to provide an economically competitive source of electricity. One of the ways predicted to achieve this low cost goal is the development of thin film technology for photovoltaics. Thin film direct bandgap semiconductors with a high absorption coefficient found suitable in this respect. The II - VI and III-V compounds meet these requirements and could be obtained radially in thin film form with a low fabrication cost and easy and expensive processing steps /12 - 15/. These cells have the following overriding advantages over the conventional solid state cells /6,9,11/:

1) The PEC cells are easy to fabricate. Just immersion of the semiconductor in the electrolyte forms a junction.

2) They provide the means for direct storage of optical energy.

3) The problem of differential thermal expansion and interdiffusion does not arise.

4) The band bending characteristic of a semiconductor can easily

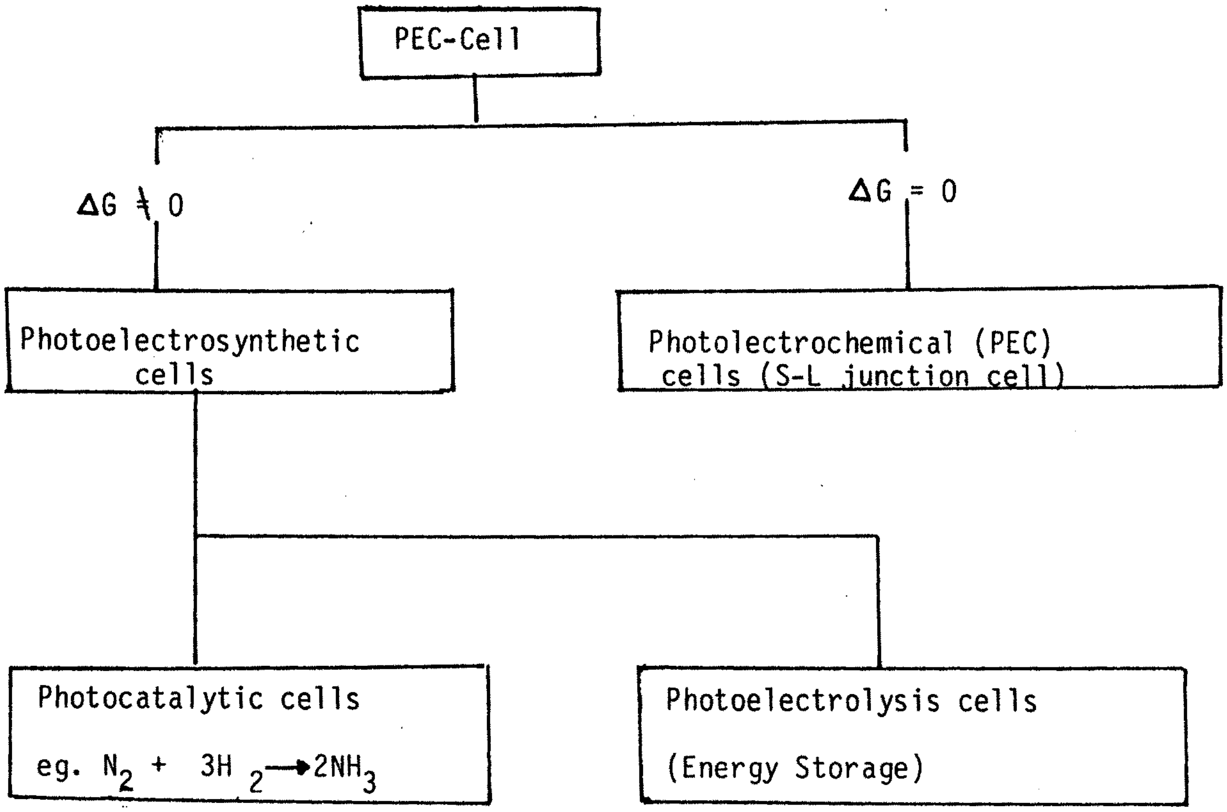


Fig. 1.3 Classification scheme for Photoelectrochemical cells.

be achieved by a suitable choice of a redox electrolyte system.

5) No antireflective coatings are required.

6) The photosensitive junction is abrupt (transparent from one side) and more photons are adsorbed in the interface region where charge carries are separated and collected more effectively.

7) Both amorphous and polycrystalline semiconductor electroldes are useful.

8) All the preparative processing steps are simplified. Although PEC cells have some inherent advantages, they are less stable owing to the photocorrosion of the photoelectrodes and problems encountered in cell sealing because of the liquid electrolyte. The stability of the various photoelectrodes has been successfully tackled by different groups around the world working in this area /16-19/.

1.3 Essentials of The Photoelectrochemical (PEC) Cell

The essential constituents of a PEC cell are: a semiconductor photoelectrode, an electrolyte consisting of redox species and a counter electrode. The following key precautions should be noted while devicing an efficient cell.

1.3.1 The semiconductor photoelectrode

The photoelectrode should satisfy the following requirements:

a) The bandgap of the material should be such that the maximum part of the solar spectrum can be utilised (1.2 to 1.7 eV).

b) It should have a high optical absorbance (10^4 to 10^5 cm^{-1}) and direct mode of transition.

c) The minority carrier diffusion length (L_D) and depletion layer width (W) should be large.

d) The donor concentration (N_D) should be optimum (10^{16} to 10^{18} atoms/cm^3).

e) It should be stable against photocorrosion and electrochemical corrosion when dipped in a specific redox couple.

f) Photoelectrode thickness should be large enough to absorb all the incident radiations.

g) The carrier mobility and life time should be high.

h) Cost of the basic materials, manufacturing processes and quantum efficiency should be acceptable.

1.3.2 An electrolyte

An electrolyte helps to drag the photogenerated holes from photoelectrode to the counter electrode and the difference between E_F, and E_F, defines the upper limit to photovoltage. Therefore the redox electrolyte should be:

a) Transparent.

b) The ionic species should be diffusion limited.

c) The conductivity of the supporting electrolyte should be high.

d) It should be stable under illumination for longer duration.

e) It should be non toxic and cheap.

1.3.3 The counter electrode

The choice of a counter electrode is also important. It should have:

a) Low over potential for redox reactions.

b) Large area for reducing concentration polarisation.

c) Chemical inertness with an electrolyte.

1.4 The Selection and Problem Inbrief

As discussed in section 1.3.1 we have selected mixed copper-lead sulphide as the photoelectrode material as its effective band gap can be made to match with the maximum span of the solar spectrum. Impurity addition not only extends the photoresponse but improves efficiency also /20 - 24/. A mixture of equimolar NaOH - S - Na_2S is used as an electrolyte. Many counter electrode materials have been suggested and evaluated /25 - 28/ for PEC cells. Platinum or CoS or NiS impregnated graphite seems to be quite suitable. Use of transparent counter electrode, if possible, is also recommended. In our studies CoS impregnated graphite is used as counter electrode.

Systematic studies have been carried out to understand the photoelectrochemical behaviour of copper mixed PbS thin films. As the performance of a PEC cell is found to depend on the properties of the photoelectrode material, it is worth to know the prehistory of the active electrode material. Studies have been therefore, planned to prepare the copper mixed thin films of lead sulphide.

Solution growth method was used for this purpose. The source materials used were lead acetate, copper sulphate and thiourea. The deposition was carried out at room temperature. The copper concentration incorporated in PbS is from 0 to 0.8 M. The substrates used were nonconducting glasses and well polished stainless steel strips. The physical characterisation of the samples was carried out prior to the formation of photoelectrochemical cells. The electrical conductivity, thermoelectric power, activation energy, carrrier concentration and carrier mobility have been studied as a function of temperature. The effects of addition of Cu-concentration on these properties have been revealed and an optimum composition is searched out.

The second aspect of our studies is the formation of photoelectrochemical cells and their electrochemical characterisation. Different PEC cell configurations have been deviced with a varying Cu-concentration lead sulphide electrode. The cell properties namely I-V and C-V in dark, power output curves, photo, speed and spectral responses have been examined. The performance of the cells has been deduced in terms of several parameters such as short circuit current (I_{sc}), open circuit voltage (V_{oc}), junction ideality factor (n_d), flat band potential(V_{fb}), efficiency (η), form factor (ff), lighted quality factor (n_L), series and shunt (Rs and Rsh) resistances, barrier height (ØB) etc.

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