CHAPTER-I

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INTRODUCTION

1.1 General 2

1.2 The Thin Film Technology and Photoelectrochemical (PEC) Solar Cells : The State of Art 3

1.2.1 Thin film technology 3

1.2.2 Solar cells : Photoelectrochemical (PEC) cells 6

1.3 Essentials of The Photoelectrochemical (PEC) Cells 12

1.4 The V-VI chalcogens 14

1.5 The Proposed Work : Inbrief 16

1.1 General

THIN FILM can be interpreted mathematically as one which is bounded between two parallel planes extending infinitely in two directions but is restricted in its dimension along the third direction. This restricted third dimension is termed as "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 are of two types : (i) the continuous thin films and (ii) the discontinuous thin films.

The discontinuous film consists of large number of small islands of the materials separated by the small finite distances, the situation generally arise in ultra-thin films. The resistivity of such films is normally very high with a negative temperature coefficient of resistance. On the other hand, film becomes continuous when its thickness is increased and resistivity of such films decreases. As a result mean free path of the charge carriers decreases which 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 the solids are essential to understand the know how of the various types of devices. The basic transport properties are the electrical conductivity, thermoelectric power, Hall coefficient, optical studies etc.

1.2 The Thin Film Photoelectrochemical (PEC) Solar Cells : The State of Art

1.2.1 Thin Film Technology

Thin film technology plays a vital role in the development of diverse and challenging frontiers. These frontiers are 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 etc, and are now recognized as frontier areas of microscience and microtechnology |4|. 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 VLSI/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 hybrids thereof. The films can be further cut into desired dimensions and geometry by one or more microlithographic 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 materials properties arise basically from the numerous inherent characteristics of

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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, 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 in two or lesser dimensions and to study their structure sensitive properties. Among the properties being studied today for significant applications are : 1] optical gap, 2] optical constants and thus reflectance, transmitance, and emittance spectra, 3] spatial variation of optical thickness, 4] structural anisotrophy, 5] stoichiometric deviations, 6] polymorphic and metastable structures, 7] relaxed solubility, variable composition multicomponent compounds, and alloys, 8] spatial variation of electrical gap and electron transport properties, 9] surface activation and passivation behaviour, and 10] surface mechanical tribological properties. One can design micromaterials to give any desired reflectance /transmittance/emmittance 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 ≈1μm) 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 conductors are obtained which are 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 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 easily possible to dope such materials to obtain "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.

An alloyed combination of Ge with S or Se in thin film form behaves as an inorganic polymer, on irradiation with energatic

particles, collapsing of voids occur and material exhibits radiation induced giant contraction effect. This results into large changes in 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 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 optical energy into its electrical equivalent. Basically, the device produces source of 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 with energy, $E \geqslant h\nu$ is absorbed,an electron-hole pair is generated within the semiconductor and could be separated with the formation of a junction wherein 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 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 sun as the source of life and energy since time immemorial. The increasing energy crisis diverted the attention of the scientists, technologists, economists, sociologists and politicians towards the prime energy source, the

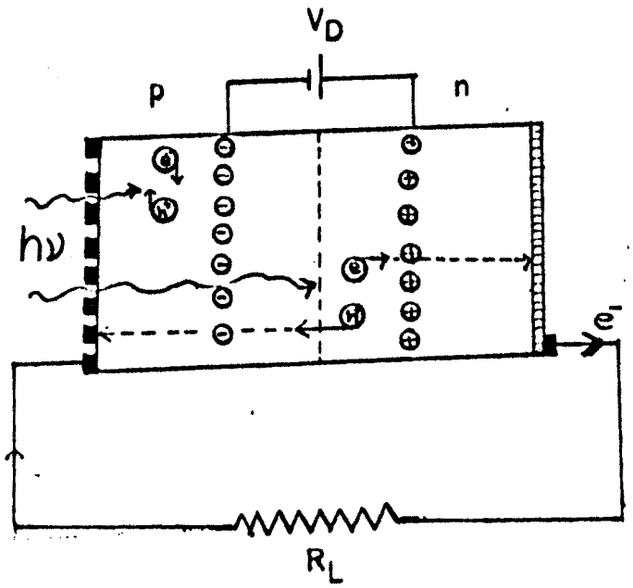
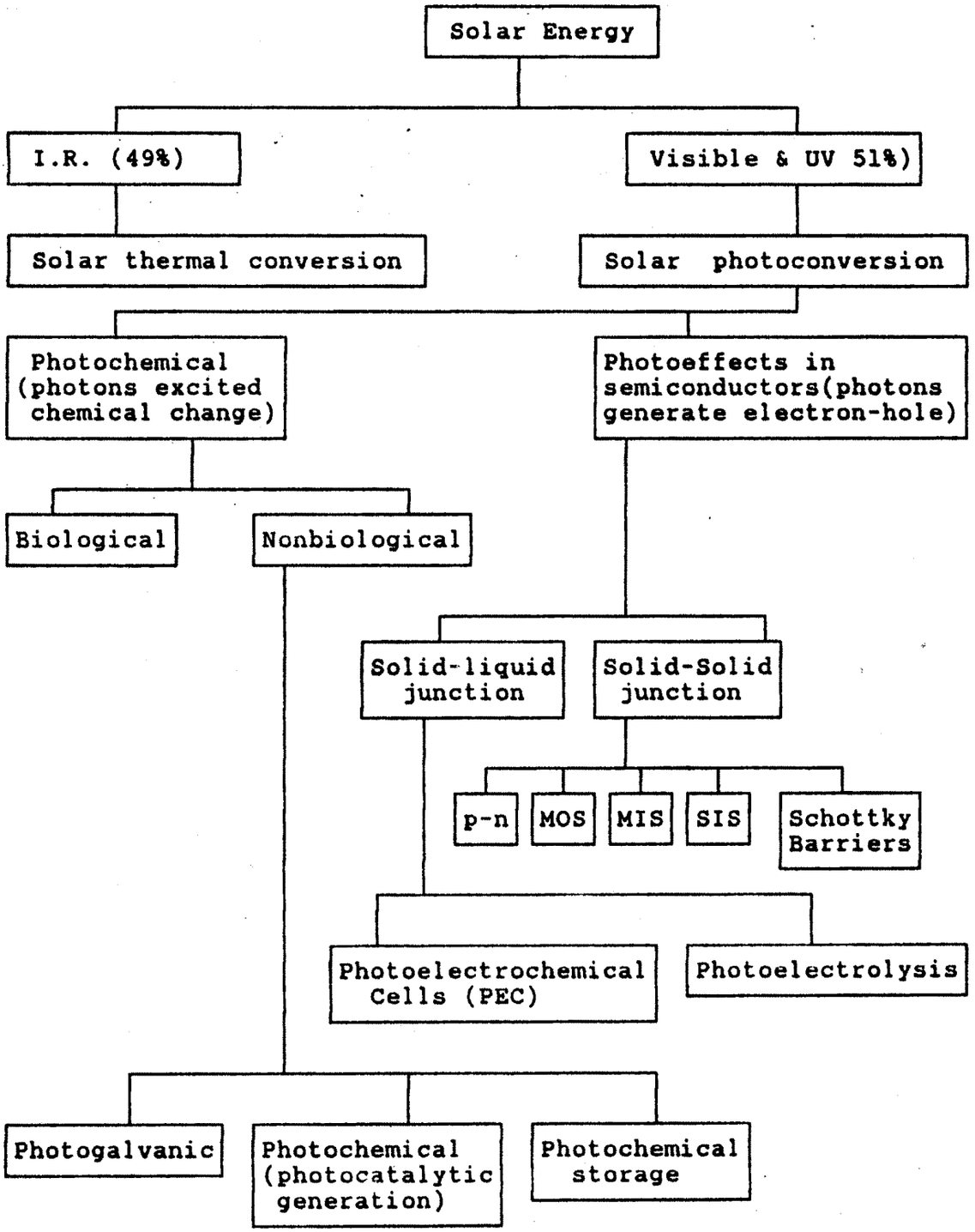


Fig-1.1 p-n junction under the influence of a local electric field.

sun. All the solar energy converters utilize the radiations received from the sun and therefore, understanding of these radiations is imperative. The Solar energy coming down the earth's surface depends on the various factors such as atmospheric absorption, scattering, reflection, suns position relative to earth etc and therefore, it exihibits wide variation.

On the other hand, the energy received just outside the earth's atmosphere is practically constant and is expressed in terms of a "Solar Constant". The typical value of solar constant according to the recent estimate is 1368 - 1377 W/m^2. The extraterrestrial solar spectrum referred to as Air Mass Zero (AM_0) 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, AM_3 are defined.

Thus an efficient and less expensive system for the conversion of solar radiations into electricity 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). The various photoconvereters are listed in Fig.1.2. In the 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



Photochemical and Electrochemical photovoltaic (ECPV) area.

Conventional photovoltaic cell area.

Fig.1.2 Block diagram of various photoconversion devices.

cells or photoelectrochemical (PEC) solar cells are frequently used names |5-8|. The PEC cells have their origin in Becquerel effect |9| 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 available on this issue and several reviews are now appeared in the literature |5,7,10-12|. These 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. Photoelectrolysis cells are characterised by the different oxidation and reduction reactions at the photoelectrode and counter electrode and therefore causing a net chemical change, (i.e.$\Delta G \neq 0$). If the free energy G is +ve, the optical energy gets converted into chemical energy (photoelectrolysis) and for ΔG to be -ve,optical energy activate the reaction (photocatalysis). Fig.1.3 shows the classification of these cells according to the change in G.

Although photovoltaic effect is a well known phenomena, the reduction in cost has been a great problem 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. Thin film direct bandgap semiconductors with high absorption coefficient and high quantum yield find suitable in this respect. The II-VI and III-V compounds meet these requirements and could be managed to obtain in thin film form with ease, low cost, and

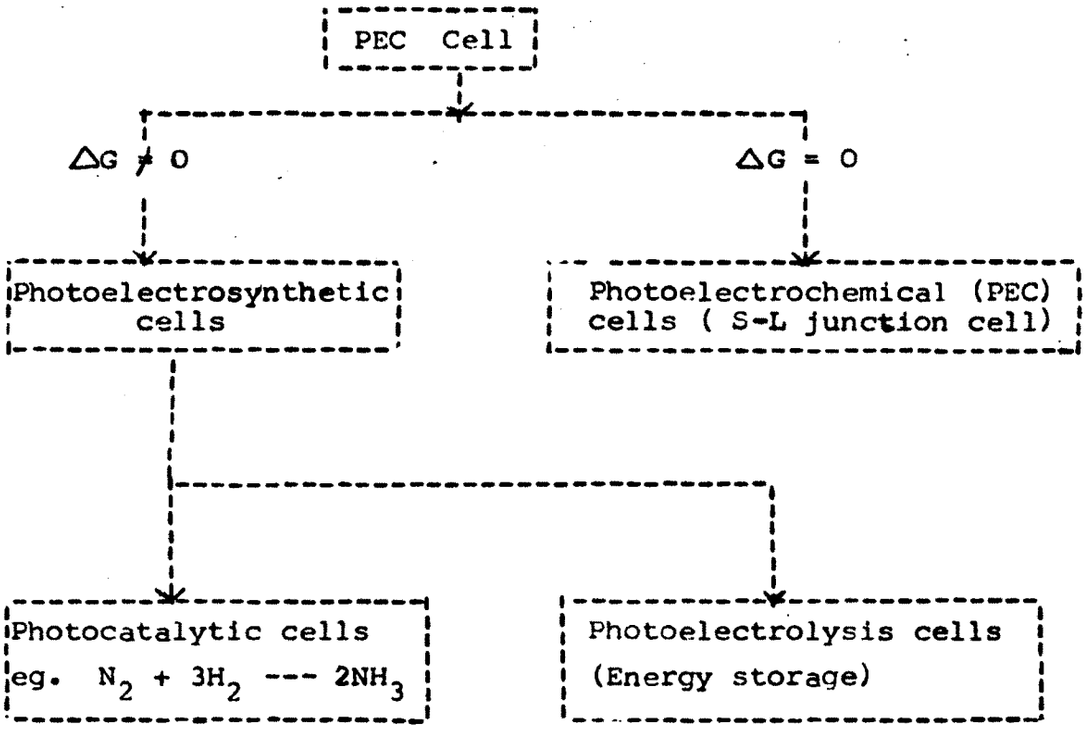


Fig. 1.3 Classification scheme for photoelectrochemical cells.

inexpensive processing steps |13-16|.

The PEC cells have following overriding advantages over the conventional solid - solid junctions |5,8| :

1. Cells are easier to fabricate. Just immersion of the semiconductor in the electrolyte forms a junction. The junction formation in the solid state solar cells involve complicated processing steps, highly costed equipments, and process further is time consuming.
2. The PEC cell provides a means for direct storage of an optical energy and thermal expansion and interdiffusion problems are eliminated.
3. A suitable choice of redox species can accomplish the desired band bending. The photosensitive junction is abrupt and carriers are separated effectively and collected.
4. No antireflective coatings are required.
5. Both amorphous and polycrystalline semiconducting electrodes are useful due to increased surface area and all the preparative processing steps are simple in PEC cells.

Even though PEC cells have some inherent advantages, they suffer from the photoelectrode unstability and cell sealing problems owing to the presence of a liquid electrolyte. The stability of the photoelectrodes against photo corrosion have been successfully tackled by different groups around the world working in this area |18-20|.

1.3 Eessentials of The Photoelectrochemical (PEC) Cells

The minimum requirements of a PEC cell are : a semiconductor photoelectrode, an electrolyte redox species and a

counterelectrode. Care should be taken of the following points while selecting the proper constituents of a cell for an efficient conversion. The choice of a semiconductor photoelectrode is a very complex problem. However, it should satisfy the following requirements :

a] The bandgap of the material should be such that the maximum span of the solar spectrum is utilised (1.2 to 1.8 eV).

b] A high optical absorbance (10^4 to 10^5 cm^{-1}) and direct mode of transition is desirable.

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

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

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

f] Photoelectrode thickness should be large enough to absorb all the incident radiations and carrier mobility and life time should be high.

g] Cost of the materials, manufacturing processes, and quantum efficiency should be acceptable.

An electrolyte plays an equally important role in deciding the efficiency and hence the desirable performance of a PEC cell. It should be competant enough to drag the photogenerated holes from photoelectrode to counterelectrode. As the difference between $E_{F,semi}$, and $E_{F,redox}$ defines the upper limit to photovoltage, the choice lies both for a photoelectrode

and an electrolyte. Following are a few points to be considered while selecting a proper electrolyte.

a] An electrolyte should be transparent with high conductivity of the supporting electrolyte.

b] Ionic species participating the redox reaction should be diffusion limited and should be stable under illumination for a longer duration.

c] Should be cheap and non toxic.

The proper choice of a counter electrode is important. It should have : 1] Low over potential for redox reaction to take place. 2] Large area for reducing the concentration polarisation. 3] Chemical inertness with an electrolyte.

1.4 The V-VI Chalcogenides

The chalcogenides of bismuth, antimony, and arsenic can be obtained radially from their elements and stable compounds by fusing the mixtures, a direct reaction with a hydrogen sulphide gas or any other sulphur containing source etc. They have rather complex layer lattic structures and have been extensively studied because of their proven useful semiconducting properties. The compounds are highly colored and colors are often dependent on nature (amorphous/ crystalline), purity, deposition technique, and preparative conditions |21|. Among these, ANTIMONY (III) sulphide is a technically important material in view of its high photosensitivity, photoconductivity, and thermoelectric power and that it has important applications as : i] in polymer and paint industries as dark pigment in camouflage |22|, ii] in television, as pick up tube target material |23|, iii] as dielectric material

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at microwave frequencies, iv] as a switching material, and v] many of its electrical, magnetic, and photoelectric properties |23,24|.

Studies were done on the antimony tripsulphide layers as early as 1951 |25| and the electrical and photoelectric properties of these films have been investigated by several workers in order to study the charge carrier transport mechanism, spectral distribution of photoconductivity etc |24,26|.

The literature data shows that these films are generally prepared by a vacuum evaporation technique and show considerable deviation from the stoichiometry |27|. Some studies are available to account for this deviation |23| at about 0 to 100°C preparation temperature. Reports are also available on electrical, magnetic, and electromagnetic properties of the Sb_2S_3 thin films prepared by the different techniques to discuss the nature of the electrical conduction and therefore, the mechanism of charge carrier transport in them |26,28-36|. An electrical conductivity of the order of 10^{-8} to 10^{-9} Ω^{-1} cm^{-1} at room temperature with an activation energy of electrical conduction in the range 0.70 eV to 1.5 eV has been reported. It is further observed from these studies that the thermal energy gaps determined from the conductivity measurements do not match with the optical energy gaps. Various types of electrical contact systems to Sb_2S_3 films have been studied by Mitchael and Denure |33|, Pawar and Bhosale |32|, and Deshmukh et al |31,34|.

Antimony trisulphide exists in two colors : orange red and dark grey. The orange red variety when heated approximately to 180°C changes to dark grey. Both the varieties have orthorhombic

type of lattice however, dark grey variety is more coarser than the orange red |31,32,34|. The changes in optical properties of these films have been observed during their transition from amorphous to crystalline state |36|.

It is a direct bandgap material with high coefficient of absorption (10^4 - 10^5 cm^{-1}) having bandgap energy in the range 1.65 eV to 2.0 eV and therefore, seems to be a promissing candidate for utilising in the photoelectrochemical (PEC) cells for the conversion of solar energy into electricity. No studies are available on the photoelectrochemistry of this material.

1.5 The Proposed Work : Inbrief

Examining the literature data and considering the above observations, a thorough investigation of Sb_2S_3 in thin film form and Sb_2S_3 based photoelectrochemical solar cell have been planned within our experimental limits. The studies have been broadly divided into : 1] thin film properties and 2] photoelectrochemical cell properties.

It is now clearly understood that the photoelectrode material plays a very significant role in deciding the electrochemical behavior of a photoelectrochemical solar cell. This demands systematic preparation and characterisation of the photoelectrode material. As a starting step, we have developed a modified chemical deposition process system and efforts have been put to eliminate the difficult, complex, and clumsy mechanical processes therein. Antimony (III) sulphide thin films of approximately 0.5 µm thick have been deposited using the above deposition process onto the glass and stainless steel substrates. The

preparative parameters and deposition conditions necessary for obtaining the desired quality samples have been finalised at the initial stages of the work. The physical characterisation of the Sb_2S_3 thin films is carried out prior to the fabrication of a PEC cell. The samples have been characterised through their electrical, optical, and structural properties. The different material properties such as electrical conductivity, thermoelectric power, and activation energy, optical and thermal energy gaps, optical absorbance, mode of transition, determination of crystal structure, grain growth and hence the grain diameter etc have been examined. In order to study the photoelectrochemical behavior, a corning glass cell of the suitable design and dimensions was fabricated in our laboratory and a photolectrochemical (PEC) cell has been constructed by using Sb_2S_3 on stainless steel as an active photoelectrode, Ferrocence redox couple in dimethyl sulphooxide (DMSO), and graphite as a counter electrode. The performance of a cell has been studied in terms of its current-voltage and capacitance-voltage characteristics in dark, photovoltaic output characteristic under 100 mW/cm^2, photo, spectral, and speed responses. The different cell parameters have been determined from these studies.