

CHAPTER I

INTRODUCTION

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1.1 Introduction

Photovoltaic conversion of solar energy appears to be one of the most promising ways of meeting the increasing energy demands of the future in a time when conventional sources of energy are being depleted. In terms of human history, the life of the sun is effectively infinite, its energy is being radiated to the earth whether it is directly used or not, and the use of photovoltaics for direct conversion of solar energy introduces no direct contamination of the environment. Furthermore, it appears that major advances in the understanding and fabrication of semiconductor devices over the past 40 years have shown the way for the kind of massive efforts required if the photovoltaices are to make a significant contribution to the energy requirements of the future. Needless to mention, remarkable progress has been made in the past four decades. Megawatt solar power generating plants have been built, solar cells are being combined with building materials and very recently the first solar-cell-powered plane demonstrated a transcontinental flight across the United States. Applications of solar cells are now an important and integral part of our daily lives, ranging from calculators and wrist watches to solar powered irrigation systems. Over 95 % of the solar cells in production are silicon based. The conversion of radiant energy in to an electrical energy is, in general, the photovoltaic effect. The most important photovoltaic device is the solar cell. The primary requirements for a material to be applicable to solar cells is its bandgap matching with the solar spectrum and high mobility and life times of the charge carriers.

1.1.1 Sources of energy

The growing interest in photovoltaic conversion is a consequence of the concern to identify future sources of energy that will be inexpensive as well as

consistent with the maintenance and safety of the environment. Traditional sources of energy - fossil fuels; such as coal, petroleum and natural gas are running out as presently foreseeable rates of use are projected in to the near future. Just a century ago, the principal source of energy was wood. Subsequent industrial development was built on the large scale exploitation of our coal resources. About the time of World War - I, oil began to become a major contributor to our energy consumption. Finally, about 1950, natural gas took over a significant role in our economy. The large scale utilisation of these fossil fuels is therefore a rather recent development against the history of the planet itself. The advent of heat engines and fossil fuel made energy portable and introduced much more flexibility in the motion. This flexibility was further enhanced with the aid of electricity and development of the central power generating stations. A relatively new source of energy - the nuclear energy - came on the scene after the Second World War, however, posed the serious problems as radioactive leakage and disposal of the nuclear ash. Thus today, every nation draws its energy needs from a variety of sources. As it has become a part of our way of life, the world's appetite for energy is growing at an unusual rate.

The conventional energy sources are in limited reservoir and may probably be exhausted by the end of coming century. Solar energy with its endless origin and large abundance can be one of the solutions for this problem as it is; i) free of pollution, ii) non exhaustive, iii) safe to handle and iv) available without cost /1-2/.

1.1.2. The solar energy

The solar energy has its relevance and significance in the needs of a country like India which represents approximately 15 % of the world's population and a consumption of about 1.5 percent. The high intensity solar irradiance for a longer

duration of the year opened a new era for launching a programme for its efficient conversion and effective use in almost all the possible fields. The major advantage of the solar energy is that it is a perennial source of energy and is non exhaustive. The solar radiations occupy the electromagnetic spectral range from 2000 \AA to 20000 \AA . At mid day with normal sunshine, the surface of the earth receives about 1 KW/m^2 energy. Forty five percent of this energy is distributed in the visible region, 52 % in the near IR and the rest in the UV and far IR regions. There are various ways of trapping this energy for useful applications (Fig.1.1). The direct means include thermal and photovoltaic conversions, while the indirect means include the use of water power, the wind, biomass and temperature difference in the ocean. Direct conversion of solar energy in to an equivalent electrical energy by means of a photovoltaic effect is well known. These devices essentially use a p-n junction between the similar and/or dissimilar semiconductors termed "homo" or "hetero" junction. Recently semiconductor electrolyte junctions are gaining much popularity in the field of solar energy conversion as they have many more advantages over the conventional p-n junctions or Schottky barrier cells [1-2].

1.2 Solar Cells : History and Status

The origin of photovoltaic cells can be traced back 160 years to the discovery by Becquerel (1839) that a photovoltage resulted from the action of light on an electrolyte solution. Some 40 years later, Adams and Day (1877) observed the similar effect in the solid selenium shortly after Smith (1873) had demonstrated the phenomenon of photoconductivity in selenium. Subsequent work on the photovoltaic effects in selenium and cuprous oxide led to the development of the selenium photovoltaic cells widely used for many years exposure meters. By 1914, solar

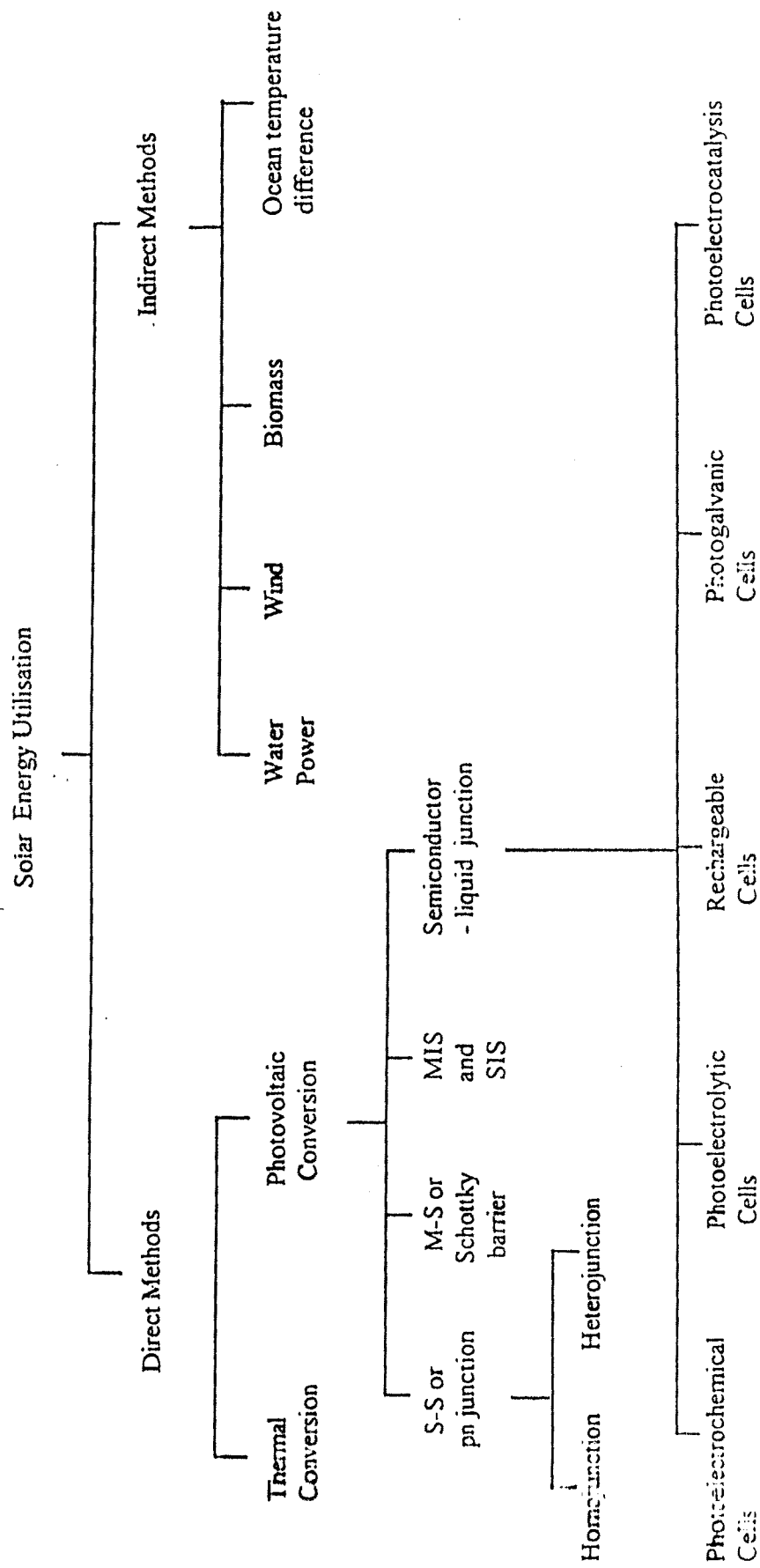


Fig. 1.1 Methods for Solar Energy Utilisation

conversion efficiencies of about 1 % were achieved with the selenium cell. Later, it was finally realised that an energy barrier was involved both in this cell and in the copper/copper oxide cell /1,2/.

The modern era for photovoltaics began in 1954. Chapin et al (1954) reported a solar conversion efficiency of 6 % for a silicon single crystal cell. With improved technology, silicon solar cell efficiency under terrestrial sunlight has reached 14 % by 1958. It was also in 1954 that a paper by Reynolds et al reported 6 % efficiency in what latter come to be understood as the cuprous sulphide/cadmium sulphide heterojunction. The silicon single crystal photovoltaic cell has become the prototype of all homojunction cells and has been the prime focus of research and development for many years. The cuprous sulphide / cadmium sulphide heterojunction was the first all thin film photovoltaic system to receive a significant attention; after more than 20 years of intermittent research and development, its conversion efficiency has been increased to about 10 %. By taking advantage of new technology, research have rapidly raised the efficiency of the gallium arsenide based cell reported by Jenny et al (1956) with 4 % efficiency to present efficiencies approaching 24 %.

The present high cost of Si solar cells diverted the research efforts towards semiconductor electrolyte interface (PEC cells). By forming the interface between semiconductor and electrolyte high efficiency has been achieved. CdS, CdSe, CuInS₂, CuInSe₂ are the prominent semiconductor materials in this field. The applicability, in PEC systems, of chemically deposited CdS and CdSe have been explored by several research groups. PEC systems using chemically deposited CdSe films with excellent prospectus were reported by the group of Rauh et. al. /3,4/ with efficiency 6.8 % and by the group of Mandal et al with efficiency 11.7 % /5-6/.

1.3 A Photoelectrochemical (PEC) Cell : Requirements

A photoelectrochemical (PEC) cell consists of a semiconductor / electrode, an electrolyte consisting of redox species and a counter electrode. The important considerations those should be taken into account while fabricating a PEC cell are as follows / 7 /;

a) A photoelectrode

The active photoelectrode material should satisfy the following conditions.

1. It should be of the direct bandgap type with a high optical absorption coefficient (10^4 - 10^5 cm^{-1}).
2. The band gap should be such that the maximum span of the solar spectrum should be utilised.
3. The effective donor concentration should be of the order of 10^{16} to 10^{18} cm^{-3} .
4. The minority carrier diffusion length (L_D) and the depletion layer width (W) should be large.
5. The material should be stable against photo dissolution and electrochemical corrosion when placed in a redox couple and its quantum efficiency should be acceptable.
6. Charge carriers should have high mobility and life time.
7. It should be thick enough to absorb all the incident radiations.
8. The contacts to the semiconductor material should be ohmic.
9. The cost of the basic materials and the manufacturing process should be acceptable.

b) An Electrolyte

As the electrochemical performance and hence the conversion efficiency of a PEC cell depends on the electrolyte, proper choice of an electrolyte is very important. An electrolyte should possess the following properties.

1. It should be transparent.
2. The redox reactions should be diffusion limited and stable for a longer duration under illumination.
3. It should be cheap and non toxic.

c) The counter electrode

The choice of a counter electrode is also equally important. It should have the following characteristics;

1. Low over potential for redox reactions to occur.
2. Large surface area to reduce the concentration polarisation.
3. Chemical inertness with an electrolyte.

1.4 Advantages of PEC cells

An electrochemical photovoltaic cell has the following overriding advantages over a conventional p-n junction or Schottky barrier solar cell / 7 /.

1. A PEC cell is easy and simple to fabricate.
2. Many complicated processing steps in the fabrication of a p-n junction are simplified or eliminated.
3. Growth of large area single crystal is not required. Polycrystalline materials can serve the purpose.
4. Since the junction formation is a spontaneous process, randomly oriented crystallites can be used.

5. A transparent epitaxial layer to reduce electron-hole recombination losses at the surface is not needed.
6. The need for A. R. coatings can be avoided by building a non reflective structure into the surface of a semiconductor by simple etching process.
7. The most important advantage of a PEC cell is that it has a facility for chemical storage / 7- 10 /.

1.5 Selection / Scope of the Problem

There are three main areas in which a commercially viable solar cell must excel; 1) cost, 2) efficiency, and 3) operating lifetime. Clearly, these are not independent, but are mutually related. Though the performance of a solid-solid junction solar cell is up to an acceptable limit, the fabrication and other process costs put certain limits on its large scale utilisation. Photovoltaic energy conversion through semiconductor / liquid junction route is growing exponentially and becoming one of the popular alternatives. II-VI, III-V, and IV-VI group compounds, especially chalcogenides and oxides of cadmium and lead, are of great importance in this respect. These materials provide; i) optical band gaps which respond to the visible and IR regions of the solar spectrum, ii) a high coefficient of an absorption (10^4 - 10^5 cm⁻¹), iii) direct mode of optical transitions and iv) an easy control over the structural, optical and electrical properties through the solid solution formation that make them suitable for electrochemical solar cell and other optoelectronic device applications. For detailed study cadmium selenide material is selected because; i) the optical bandgap of CdSe ($E_g = 1.70$ eV) lies in the visible region of the solar spectrum, ii) it is highly stable in the electrolyte and iii) could be prepared by a very inexpensive chemical deposition process.

The work was carried out through the two successive linked stages; i) preparation and characterisation of the thin films and ii) photoelectro chemical cell fabrication and its characterisation. A chemical deposition process was employed for this purpose. The technique works on the principle of ion-by-ion condensation and is capable to produce excellent thin films of uniform, homogeneous and controlled composition [11-13]. The preparation parameters such as bath temperature, pH, deposition time, speed of the substrate rotation, etc were finalised and the kinetics of growth mechanism was examined. The CdSe films were then doped with an indium doping concentration ranging between 0.005 mole % to 0.5 mole % to reduce the electrical resistivity. The films were then characterised through the structural, optical and electrical properties and various film parameters, viz. grain size, lattice parameters, optical absorbance, optical gap, mode of optical transitions, electrical conductivity, activation energies, carrier concentration, mobility, barrier height etc were determined. The samples were also obtained on the stainless steel substrates and the photoelectrochemical cells were constructed using CdSe / CdSe : In films as an active photoelectrode, sulphide / polysulphide as an electrolyte and graphite rod as a counter electrode. The various cell characteristics, namely I - V and C - V characteristics in dark, power output curves under constant illumination, photo and spectral responses etc were then examined and evaluated to yield the various cell parameters viz. junction quality factors (n_d and n_i), flat band potential (V_{fb}), barrier height (ϕ_b), efficiency (η %), form factor (ff %), series and shunt resistances (R_s & R_{sh}), etc to understand the effect of In - doping concentration.

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