CHAPTER - I

Introduction

INTRODUCTION

1.1 General Introduction :

It is found that there is ever increasing need and world demand for electrical energy. New energy resources need to be generated to fulfill the demands of electricity for use in future. The development of new energy resources constitutes a very active and challenging area of modern day research. The goal of the research in this field is to convert the radient energy into the form of electrical energy. Semiconductor devices are used as solar energy converters. Thin film science is a relatively young and ever growing field. Studies on thin film formation are being pursued with increasing interest. Recent progress in thin film formation by employing various deposition techniques has brought us to understand the microscopic basis of the surface science through electrochemical route The microscopic view point of solid state physics has been injected into electrochemistry and surface chemistry. The development of thin film technology for the fabrication of large area using physical and chemical deposition technique. The fundamental interest is created in field of electrochemistry. Some gradual or sharp changes in chemical and physical properties of thin films are observed in passing through the deposition techniques by routine measurements. A better understanding of either constituents of the thin film can be obtained by studying their structural optical and electrical properties.

There is considerable interest in the development of the system for the deposition of thin films which are capable of collecting and storing the solar energy.

Thin chalcogenide films are now seriously considered as potential applications in Science and Technology for fabrication of various types solar energy converters. It has been pointed out by many research workers (1-3) that conventional thin film deposition techniques suffers from affecting the stability, homogeneity, reproducibility and final structure of the resulting films. Much of the recent research in this area has been invested in the development of thin films deposition techniques. One of them is the solution growth Technique which is presently attracting considerable attention (~~4~~, 1-7, ~~5-7~~). There are different methods in solution growth technique and these are :

1) Electroplating
2) Electrophoresis
3) Spray pyrolysis
4) Controlled precipitation technique (chemical bath deposition)
5) Electrodeposition
6) Dip and dry (wetting) etc.

1·2 Electrodeposition :

In recent years, electrodeposited thin film semiconductors are becoming popular in the fields of solar cells; optoelectronic devices, solar selective coatings. For the requirements of a photovoltaic cell for large scale terrestrial use namely, high efficiency, stability and low cost are met with electrodeposited thin film, n-CdS/p-$CuInSe_2$ and P-HgCdTe n-CdS cells, greater than 9% solar conversion efficiencies have been reported (8,9). These cells are quite reproducible. The solar selective coatings based on oxides of Ni, Cr, Pb etc. have been widely used (10,11). The Electrodeposition of elemental semiconductor or one of the components in the cases of binary or ternary thin film semiconductors could be very useful in the process of device formation.

In view of the present state, the preparation of thin film semiconductors with electrodeposition technique has many advantages over physical and chemical deposition techniques, it is easy and economic as semiconductor with no or small wastage of materials could be prepared.

Because of the purification which often result from electrodeposition methods, it is not required to have very pure starting materials as is the case for other methods. Semiconductor properties like conductivity, band gap variation, control over stoichiometry, doping etc. could be controlled with electrodeposition with a great accuracy, as the parameters like current and deposition time can be controlled to the levels of micro-colombs and milliseconds respectively (12-14).

Electrodeposition technique has been successfully employed for elemental semiconductors, binary semiconductors intermetallic compounds and ternary compounds. The problem of electrodeposition of alloys is of considerable interest. This problem has been solved by electrodeposition technique. The co-deposition of binary or ternary alloy or compound semiconductor is easily possible under critical condition.

In the present study attempt has been made to prepare thin chalcogenide films of CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S etc. which are important for solar energy conversion. In solar selective coating, mostly metal oxides or sulphides have been used due to their optimum bandgap and optical properties like absorption coefficient. Above sulphides are prepared by electrodeposition method and studied for their preparative parameters, optical absorption coefficients, variation of band gaps, and m microstructure; XRD etc. The attempt has been made to use these binary and ternary semiconductors in ECPV cells and storage cells.

1-3 Energy conversion through electrochemical photovoltaic(ECPV) cells.

Sun is the biggest source of energy. Solar energy comming down to the earth's surface per year is approximately ten thousand times the world wide energy consumption per year. Solar energy is converted into electrical energy with the help of electrochemical photovoltaic device. Sun light in the near infrared visible and near ultraviolet regions has considerable energy of about 0.9 eV to 3.2 eV per photon. Photoelectrochemical cells are used for conversion of solar energy into electrical energy. Solar cell is the semiconductor device. A variety of elemental, binary, and ternary semiconductors are important for solar energy conversion. The formation of solid state solar cells and photoelectrochemical (PEC) cells with such electrodeposited semiconductors have been described. Solar cells can be made by both solid state and semiconductor liquid junctions. An ECPV cell consists of (i) a semiconductor photoelectrode (ii) an electrolyte (iii) a counter electrode. All these parts play an important role for the better performance of the ECPV cells (15).

1-4 Storage Cell :

In view of present state, the use of ECPV cell for storage of energy has been also attempted. Electrolyte in ECPV cell can react reversibly and electrochemically. Then it can visualise the possibility of storing the solar energy in the form of a chargable solar battăry. The characteristics of such a battery would depend on the electrolytes and photoanodes selected [~~16~~,~~17~~,16-23] ECPV cells can be converted into an electrochemical storage cell when the counter electrode is replaced by a storage electrode capable of undergoing a reversible chemical change, which can be indicated as (23)

$$Ax + ne^- \rightleftharpoons A + X^{n-}$$

where A is storage electrode and X is a solute present in the electrolyte.

ECPV storage cell consisting of two compartment having separated by a membrane or a salt bridge. When photoanodes are used in a cell, oxidation can take place in the anodic compartment and reduction in the cathodic compartment. In discharging mode the photo-anode acts as the counter electrode and oxidised species are reduced at its surface. This reaction should be minimised at the photoanode to obtain maximum efficiency during illumination. The photoanode limits the back current in the dark, The storage electrode have large are if it is to be used efficiently, then it will also act as the counter electrode and reduce the species from the electrolyte during illumination; resulting in the loss of storage capacity. This is the disadvantage. These disadvantages are overcome by using two and three compartment cells.

Most recent development based on photochemical conversion and photovoltaic effect of photoexcitation of semiconductor. Photochemical conversion implies light induced chemical changes in a system yielding products capable of supplying energy. The charge transfer across a semiconductor-electrolyte interface in a photoelectrochemical solar cell results in some sort of a redox reaction. Storage of solar energy offers a challenge even today and desired end product is electricity.

1-5 Purpose of Dissertation :

In view of the above literature survey it is found that, there are some reports on optical and electrical properties chalcogenide compounds. ECPV cells formed with CdS, ZnS, $Cd_{1-x}Zn_xS$, Bi_2S_3 and Bi_2CdS_4 films prepared by electrodeposition techniques are well studied. But very few reports are available on the ECPV cells and storage cells formed with films prepared by the electrodeposition technique. A systematic study has been planned to understand the behaviour and suitability of electrodeposited alloyed sulphide. The performance of the ECPV cells and storage cells mainly depends on the properties of the photoelectrode semiconductor material.

Among the low cost devices, thin film structures prepared by electrodeposition have advantage of consuming the least raw material and simple fabrication. The films prepared by electrodeposition method are found polycrystalline. The polycrystalline films are used to obtain the photovoltaic effect. The electrodeposition techniques does not require high temperature, the films can be prepared at room temperature and preparative parameters are controllable and optimised in order to get reproducible, thick and good quality films. Solution concentration, composition, current density, voltage versus SCE, time of deposition etc. were optimised. Zinc composition in $Cd_{1-x}Zn_xS$ films and Bismuth composition in Bi_2CdS_4 films was varied from 0 to 100%. The electrodeposition technique is the unique from the stand point, that the necessary elements are contained in solution deposit on substrate under controlled condition of current density and deposition potential.

In the present investigation, thin films of CdS, ZnS, Bi_2S_3, CdZnS , Bi_2CdS_4 have been prepared on conducting and amorphous glass substrates and also on stainless steel substrate by electrodeposition technique. The films have been characterised by various techniques such as X-ray diffraction, optical absorption, microstructure photographs, band gap variation with composition, etc. The above properties have been studied in detail and reported.

The ECPV cells have been formed with CdS, ZnS, Bi_2S_3, CdZnS, $Bi_2 CdS_4$ by using polysulphide electrolyte and carbon as a counter electrode.

The cell properties such as photovoltaic output, photoresponse spectral response, I-V characteristics have been studied. Further, attempt has been made by giving heat treatment to the film. The storage cells have been formed with Cd-Zn-S, Cd-Bi-S and CoS, by using polysulphide electrolyte and Ag_2S film as a storage electrode in place of counter electrode in place of counter electrode. The performance of ECPV cells and the storage cells have been studied.

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