PREFACE

Recent investigations in the field of energy sources have been aiming at harnessing the solar energy to meet the challanges of diminishing fossil fuels. Photo-electrochemical reaction have been found to be of great importance for this purpose and attempts are on way to find out new potential materials for such energy conversion and for improving the conversion efficiency. Semiconductor-electrolyte interface in PEC solar cells is of prime importance in deciding the conversion efficiency. It is essential that semiconductor surface should be non-corroding and stable under conditions of illumination and environment of electrolyte. It is also important that chosen semiconducting materials should have band gap in the range of 1.1 eV to 2.1 eV to provide good optical matching for better solar energy conversion. Since transition metal dichalocogenides occupy very favourable position in this regard, author has concentrated on these materials for PEC solar cell investigations.

Preliminary investigations were carried out on natural MoS_2 crystals and after encouraging results, facilities for synthesis and growth of such crystals were developed. The crystal growth facilities by way of

direct vapour transport and chemical vapour transport techniques have been completely developed and have been utilised for the present work. PEC solar cells using grown crystals as photoanodes and platinum as counter electrodes have been fabricated and their behaviour have been investigated, after suitable electrolyte identification by energy band location and E_F redox analysis through Mott-Schottky plots. Prior to the use of grown crystals as photoanodes of PEC solar cells, its compositional characterization by ESCA, its structural characterization by X-ray diffraction, electrical transport properties by Hall effect and Seebeck coefficient measurement and optical characterization by absorption measurement have also been done. Apart from natural MoS_2 crystals, single crystals of mixed series crystals of MoS_xSe_{2-x} have been grown and investigated. The latter series has an advantage that its band gap can be varied between 1.4 eV and 1.75 eV by controlling the sulphur content.

The result of all these investigations have been complied in the form of a thesis.

A brief survey of the existing information on $MoSe_2$ and MoS_2 single crystals and the scope of the present work is described in Chapter 1.

Chapter 2 provides a description of the vapour transport techniques. The salient features of chemical vapour transport method are pointed out in the earlier part of this chapter whereas the details of the direct vapour transport method is given in the latter part. Details of experimental set up, temperature controlling system, construction of the furnace etc. have also been thoroughly described.

Chapter 3 deals with the brief review on the characterization of single crystals of molybdenum sulphoselenides. Lattice parameters, cell volumes, X-ray densities and absorption coefficients have been determined. The compositions of the as grown crystals have been examined by electron spectroscopy for Chemical Analysis (ESCA). A study of the microstructure of the grown faces of the crystals reveals the presence of hexagonal as well as circular spirals upon them.

In the chapter 4 a descri ption of the resistivity measurements and effect of temperature on Seebeck coefficient have been incorporated. The Hall constants have been determined from Hall mobility measurements. The results obtained have been compared with those reported by earlier workers.

A necessary introduction to PEC solar cells has been

presented in chapter 5. Different types of solar cells have been described and discussed by giving their classification. The advantages and disadvantages of PEC solar cells over the solid state photovoltaic cells have also been discussed. The basis electrode processes and mechanism of charge transfer processes in to the electrolyte has also been presented.

The fabrication of PEC solar cells with natural crystals of MoS_2 has been described in chapter 6. Semiconductor-electrolyte interface has been characterized by locating valence and conduction bandedges, for which flat band potential measurement has been carried out and incorporated in this chapter. The effect of illumination intensity on the performance of cells has also been studied and has been given in the latter part of this chapter.

Chapter 7, deals with the study of PEC solar cells with molybdenum sulphoselenides single crystals. The spectral responses of the grown crystals have been recorded at different wavelengths and direct band gaps have been estimated. Semiconductor-electrolyte interface characterization,

in terms of location of valence and conduction bandedges and fermi levels has also been carried out and is described in the latter part of this chapter.

Chapter 8, describes the effect of iodine concentrations on the performance of photoelectro-chemical solar cells formed from molybdenum sulphoselenides. Effect of temperature on solar cell parameters such as open circuit voltage, short circuit current, fill factor and efficiency etc. have been studied and their description has been given in the latter half of this chapter.

A study of the effect of light intensity on the current-voltage characteristics of the PEC cells has been carried out. The sunlight to electrical and monochromatic light conversion efficiencies have also been estimated. A description of these observations has been given in chapter 9.

In order to compare the effect of steps on the electrode surfaces PEC cells fabricated from rough as well as smooth surfaces have been compared. It has been seen that the output power is drastically affected by the presence of steps on the surfaces of the electrodes. The effect of removal of steps by etching the crystals on the

output power has been studied. Chapter 10 describes the observations thus made. In the latter part of this chapter photocorrosion studies on electrodes of molybdenum sulphoselenides have been incorporated. The photoelectrochemical corrosion, studied by Rotating Ring Disc Electrode technique, provides a qualitative identification of the corrosion of the samples.

Chapter 11 deals with author's attempts on the photoelectrolysis of water using molybdenum dusulphide crystals which are representative of molybdenum sulphoselenide series.

Conclusions of the entire present work and scope for further developement are given at the end of the thesis in chapter 12.