PREFACE

The increasing demand for energy has greatly stimulated research into new sources of energy during the last two decades or so. Solar energy is of great interest here because it is independent of energy resources. As we know,nature makes extensive use of this energy source in photosynthesis, a process in which solar energy is converted into chemical energy. Conversion into electrical energy was first achieved in p-n junction and in Schottky photovoltaic cells. These devices are used in many optoelectronic applications. However, systems of high conversion efficient have only been made with single crystals. The p-n junctions also have to be made by a complicated diffusion technology to ensure that the depth of the junction below the surface is about the same as the penetration depth of the light.

During the last few years there has been an ever increasing interest in the photoelectrochemical devices for solar energy converters. These consists mainly of semiconductor/electrolytic junctions which can easily be made. They canbe used for conversion of solar energy either into electrical energy or into chemical energy. The primary problem of these systems is the susceptibility of the semiconductor to photodecomposition. In order to develop durable photoelectrodes for such solar cells stabilizing redon systems or protection by surface coatings has largely been tried by several investigators. Another idea which has been followed by some of the scientists is to use semiconductors which are characterised by optical transitions which do not influence the chemical reactivity of the surface to a large extent. Such materials with appropriate band gaps are found among transition metal dichalcogenides with layer structures like MoS_2, $MoSe_2$, etc. They are characterized by energy gaps between 1 eV and 2 eV, separating two d-bands which are derived from the transition metal atoms and have very little interaction with the chalcogen atoms. As a result of light absorption in the visible and near infrared spectral regions there are consequently d-d electron transition which do not very much affect the bonding situation in the semiconductor surface in contrast to p-s transition in other compound semiconductors which break chemical bonds at the surface and lead to photocorrosion. Further these transition metal dichalcogenides are compound of readily available non-precious materials like W, Mo, S, Se and Te.

It was therefore thought worthwhile to carry out PEC solar cell investigations using these materials. The crystal growth facilities by way of direct vapour transport and chemical vapour transport have been completely developed and have been utilized for the present work.

A survey of the literature revealed that WSe_2 crystals would yield maximum conversion efficiencies, as a result of which we grew $W_{1.02}Se_2$ and $W_{1.04}Se_2$ crystals by direct vapour transport technique and carried out electrical and optical measurements on them. But when photoelectrochemical solar cells using the above crystals were fabricated and the measurements were carried on them, we did not get any encouraging results, so we thoughtof diverting our efforts in search of a better material for PEC solar cells. In the course of time it was realised that n-type semiconducting materials would serve as better photoelectrodes for PEC solar cells, bearing this in mind mixed crystals of $MoSe_xTe_{2-x}$ $(0 \leqslant x \leqslant 2)$ were grown by chemical vapour transport technique. Apart from the n-type semiconducting nature, the above series has the advantage that its band gap can be varied between 1.1 eV and 1.4 eV.PEC Solar cells using grown crystals as photo-anodes and platinum as converter electrodes have been fabricated and their behaviour has been investigated after suitable electrolyte identification by energy band location and E_F redon analysis through Mott-Schottky plots. Prior to the use of grown crystals as photoanodes of PEC solar cells their compositional characterisation by EDAX, structural characterisation by X-ray diffraction, electrical transport properties by Hall effect and Seeback coefficient measurements have been done.

The results of allthe these investigations have been compiled in the form of a thesis.

A brief survey of the existing information on $MoSe_2$ and $MoTe_2$ single crystals and scope of the present work is described in Chapter 1.

Chapter 2 provides a description of the direct vapour and chemical vapour transport techniques.

Details of experimental set up, tempereture controlling system, construction of the furnace etc. have also been thoroughly described.

Chapter 3 deals with the growth and characterisation of single crystals of $W_{1.02}Se_2$ and $W_{1.04}Se_2$. Lattice parameters, cell volumes and X-ray densities have been determined. The composition of the as-grown crystals has been examined by EDAX. A study of the microstructures of the grown faces of the crystals reveals the presence of hexagonal spirals upon them. The band gaps of the above crystals have been determined using the reflectivity measurements.

Chapter 4 deals with a brief review on the characterization of single crystals of $MoSe_xTe_{2-x}$. Lattice parameters, cell volumes and X-ray densities have been determined.Here also the compositions of the as grown crystals have been examined by EDAX.

Inchapter 5, a description of the resistivity measurements and effect of temperature on Seeback coefficients have been provided.The Hall mobility for the series has been determined fromthe the Hall effect measurements.

A necessary introduction to PEC solar cells has been given in Chapter 6. Different types of solar cells have been described and discussed by giving their classifications. The advantages and disadvantages of PEC solar cells over the solid state photovoltaic cells have been discussed. The basic electrode processes in the electrolyte have also been presented.

Chapter 7 deals with the study of PEC solar cells with $MoSe_2Te_{2-x}$ single crystals. The band gaps of the crystals have been determined from the spectral responses of the photoelectrodes prepared with these crystals. Semiconductor-electrolyte interface characterisation in terms of location of valence and conduction band edges and fermi-levels has also been carried out.

Chapter 8 describes the effect of iodine concentrations on the performance of PEC solar cells prepared out of $MoSe_xTe_{2-x}$ single crystals. Effect of temperature on solar cells parameters has been studied and its description is given. A study of light intensity on the current voltage characteristics of the PEC cells has also been carried out and described in the later part of this chapter.

In chapter 9, the life-time of minority carriers has been measured by using the open-circuit voltage decay technique. The effect of temperature and composition of MoS_xTe_{2-x} photoanodes has been studied and described in this chapter.

Conclusions of the entire present work and scope for further developments are given at the end of the thesis in chapter 10.