

PREFACE

Single crystals of IV-VI and VI-VI family of layered structures always grow in the plane direction, and their surfaces invariably consist of a chalcogen-layer which is only Van der Waals bound to the next one. A perfect surface therefore does not have dangling bonds and is expected to be self passivated. This is true also for cleaved crystals because cleaving occurs always between chalcogen layers. This fact represents a unique situation among semiconductors, exhibiting intrinsically a chemically inert surface with no dangling bonds, no surface density of states and therefore no Fermi-level pinning at the surface. Electrochemical cells built from such layered materials should exhibit considerably higher chemical stability without passivation than other semiconductors such as Si, GaAs, InP, CdSe, etc. which need special passivation procedures in order to avoid photocorrosion.

It is therefore obvious that truly layered semiconductors are attractive as base materials for photovoltaic applications, since one does not have to worry about the lattice mismatch problem here.

An important point concerning with transition metal semiconductors of VI-VI family having MoS_2 type structure is

that band gap in this type of compound arises mainly from crystal field splitting. An electron promoted from the filled band into the next higher empty band represents a transition from one d-subband to a higher d-subband, without generating a hole among the valence electrons as is the case in "normal" semiconductors, e.g. Ge, Si, GaAs, etc. leading to an enhanced reactivity at the surface (surface photocorrosion). This fact, makes the crystals of this family highly attractive in PEC solar cell fabrication for reasons of their expected enhanced electrochemical stability.

A further important property concerning layered semiconductors is the strong anisotropy of most properties, in particular the transport properties. A thorough study of anisotropy should therefore be carried out in them and while analysing photovoltaic devices this anisotropic behaviour of transport properties must always be kept in mind. Finally layered crystals are mechanically extremely delicate and improper handling of as grown crystals leads to plastic deformation and plane slippage between Van der Waals bound layers, which can strongly impair device properties. This aspect should always be taken in consideration while carrying out investigations upon these crystals. Studies made on single crystals of these compounds will allow a comparison with polycrystalline devices which are

mechanically far less problematic than single crystals.

As a part of the programme of studying layered semiconductors the author has selected an example of **Tin monoselenide** having an orthorhombic structure from the IV-VI family and an example of **Tungsten disulphide** having MoS_2 type structure from the VI-VI family of layered semiconductors.

The selection of SnSe from orthorhombic IV-VI compounds is because of its electronic and optical properties. While the selection of WS_2 a compound from VI-VI family is because of its similarity with MoS_2 . High pressure studies on this compound synthesised by different techniques will throw an important light on its utility as a self lubricating solid. Moreover its use in the fabrication of liquid junction solar cells is also worth investigating. Since this material exhibits favourable optical transitions between non-bonding orbitals so that the original bonding situation in the semiconductor electrode surface in the PEC cell is not affected.

The entire work presented in this **Thesis** has been divided into four parts.

Part-I deals with Growth, characterization and electrical property measurements of Tin monoselenides.

Part-II describes the High Pressure work on Tin monoselenide and Tungsten disulphide single crystals.

The photoelectrochemical studies on Tungsten disulphide is described in **Part III**.

Conclusions drawn from the entire work and the future scope of the work is presented in **Part IV**.

Brief abstracts of various Chapters placed under different parts are as follows :

Chapter 1 of the **Thesis** deals with the survey of the literature and the existing information on Tin monoselenide.

The experimental techniques employed in the present investigation are briefly described in **Chapter 2**.

Chapter 3 describes the essential features of Direct Vapour Transport and Chemical Vapour Transport methods of crystal growth.

Tin monoselenide single crystals have been grown by a modified Direct Vapour Transport technique in which no transporting agent has been used. The grown crystals have been characterised by X-ray and Electron diffraction techniques. The stoichiometry of the single crystals has been tested by EDAX measurements. The p-type semiconducting

nature of the grown samples has been confirmed from the Thermoelectric power measurements. The DTA and TGA analysis of SnSe samples has been carried out in detail. Optical band gaps of the materials have been determined by UV and IR measurements. All these results have been described in **Chapter 4.**

In the DVT method described in Chapter 4 the crystals always grow in the form of one large size single crystal. Thin flakes needed for the physical property measurements are therefore obtained from the large size crystal by the method of cleaving. The process of cleaving may introduce a large number of defects. It is therefore desirable to evolve a method by which these crystals can be grown in the form of thin flakes so that they can be used as such for the measurements. The crystal growth by Chemical Vapour Transport technique using NH_4Cl as the transporting agent yielded Tin monoselenide single crystals in the form of thin flakes. The entire growth process and the characterization of the samples has been presented in **Chapter 5.**

An interesting question particularly relevant to the layered structure family is the anisotropy of the transport properties. Mechanically single crystals of layered materials behave extremely two-dimensional. They are very

difficult to handle because planes slide easily along the Se-Se layers held together by the very weak Van der Waals bond. Intuitively one might expect also similar anisotropy in the electrical properties i.e. conductivities or mobilities. Anisotropic studies carried out in Tin monoselenide crystals grown in the present work are described in **chapter 6**.

Chapter 7 describes in brief the existing information on Tungsten disulphide.

The Growth and Characterization of WS_2 crystals by DVT and CVT techniques have been presented in **Chapter 8**.

Chapter 9 reviews the technique of High Pressure research and describes in detail the production and measurement of high pressure upto 100 Kbar.

Chapter 10 describes the effect of pressure on electrical resistivity and thermoelectric power of WS_2 single crystals. The samples for different measurements have been selected from the crystals grown both by DVT and CVT techniques.

The influence of pressure on the electrical resistivity and thermoelectric power of the grown crystals of SnSe has been studied and results have been explained on

the basis of a transition from a predominantly two dimensional material to a more three dimensional one. All these studies form the subject matter for **Chapter 11**.

Chapter 12 outlines the general characteristics and requirements of photoelectrochemical solar cells.

A photoelectrochemical study of Tungsten disulphide crystals with and without spirals has been presented in **Chapter 13**.

Finally the far reaching conclusion of the entire work described in the **Thesis** and the scope of the future work are precisely narrated in **Chapter 14**.