CHAPTER 14

CONCLUSIONS AND SCOPE FOR FUTURE WORK

Several layered materials possess favourable semiconducting properties and have attracted attention as a new class of solar cell materials. Significant optical-to-electrical/chemical energy conversion efficiencies have been obtained in solid state and photoelectrochemical solar cells. Research into the electronic interfacial device characteristics of this class of materials is rather recent and of growing interest. It opens up new opportunities for the application of layered materials. The potential of this class of materials has not been fully explored yet but appears to be limited mainly by the availability of suitable materials.

As a part of the programme to produce good quality crystals of layered semiconductors for photo-electronic device uses author had successfully undertaken the growth and characterization of tin monoselenide having an orthorhombic structure from the IV-VI family and tungsten disulphide having MoS_2 type structure from the VI-VI family of layered semiconductors.

Single crystals of tin monoselenide were successfully grown by a modified vapour transport technique without any transporting agent. The single crystalline nature of the grown samples was confirmed from the electron diffraction measurements. The stoichiometry of the crystals was confirmed from the EDAX analysis. DTA and TGA showed the stability of SnSe phase at higher temperature. The electrical and optical characterisation of the grown crystals was carried out with the help of transport property and optical absorption measurements. It was inferred from the optical absorption measurements that the grown samples showed an indirect transition across the energy gap. Thus it has been possible to grow well characterised crystals of tin monoselenide by a DVT technique.

Since the crystals grown by DVT method grew in the form of one large single crystal, thin flakes needed for the physical property measurements were always obtained from the large crystal by the method of cleaving. The process of cleaving might introduce a large number of defects. It was therefore decided to evolve a method by which crystals could be grown in the form of thin flakes so that they could be used as grown for the measurements. Author has successfully grown large size well characterized tin monoselenide single crystals in the form of thin flakes by a chemical vapour transport method using NH_4Cl to play a role as transporter.

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-dimensionally and therefore one might expect large anisotropies in their electrical properties. The values of resistivity and Hall parameters obtained along the basal plane of CVT and DVT grown crystals of SnSe in the present work clearly suggested that dc transport parallel to the layers is not affected by the presence of stacking disorder. However, the measurements carried out in a direction normal to the basal plane will certainly be affected by the presence of stacking faults. Author has attempted to explain satisfactorily the high c-axis electrical resistivity of the CVT grown samples in comparison to low c-axis resistivity of DVT grown samples due to the presence of stacking faults. The presence of stacking disorder in DVT grown samples has been confirmed from their electron microscopic studies.

Looking to the wide potential of tungsten disulphide, single crystals of WS_2 were grown both by DVT and CVT techniques. Well characterised crystals of very large size have been grown by the chemical vapour transport method. A thorough study of the microstructures on the as grown faces of the crystals has made it possible to classify them into three different types viz. crystals with absolutely plane faces, with growth layers and with spirals.

The importance of studying the effect of pressure on the physical properties of WS_2 has been thoroughly stressed in Chapter-10. Effect of pressure and temperature on the resistivity of WS_2 crystals having different microstructures has clearly indicated the effect of microstructures. For example crystals having plane faces are found to be more resistive as compared to those showing layered growth and spirals. Further the crystals showing layered growth are more resistive than those showing spirals. Simultaneous measurements of resistivity and Seebeck coefficient were carried out at different pressures.

These observations have indicated a phase transition at 42.5 Kbar which has never been reported in the literature so far.

Recent studies on the effect of temperature and pressure on the electronic transitions in SnS and SnSe semiconductors motivated the author to carry out such studies on single crystals of SnSe grown in the present work. The electrical resistivity in these crystals was found to be pressure dependent. A phase transition observed at 65 Kbar was explained on the basis of a transition from a predominantly two dimensional material to a more three dimensional one. Experiments on pressure dependence of thermoelectric power has also supported the observation of phase transition at 65 Kbar.

A number of investigators have shown the utility of WS_2 as an efficient electrode material in the photoelectrochemical devices whereas very little work has been reported in this direction on its isostructural compound WS_2.

A detailed investigation on the photoelectrochemical behaviour of DVT grown WS_2 crystals was therefore undertaken in the present thesis. Effect of electrode preparation and nature of electrolytes on the photoresponse of the cell has been thoroughly investigated.

The resistivity measurements along the basal plane of the grown single crystals of WS_2 and SnSe could only be carried out upto a temperature of 180°C. In order, that the energy gaps obtained from the resistivity variation with temperature be compared with the data obtained from the optical absorption studies. The experiments on basal plane resistivity should be taken in the higher temperature range i.e. from room temperature to about 800°C.

The author feels that a detailed work on Hall effect measurement can be carried out. The dependence of carrier concentration and mobility upon temperature requires still to be studied in a wider span of temperature and magnetic fields.

The resistivity and TEP measurements under various values of pressure have been measured along the basal plane in all the samples of WS_2 and SnSe single crystals. Looking to the highly anisotropic character of these crystals it is very much desirable that these measurements be carried out in a direction normal to the basal plane of the crystals. Such studies will help us better to understand the anisotropic behaviour of these layered materials under high pressure.

For optimum performance, WS_2 crystals with absolutely plane faces, should be selected as photoelectrodes in the photoelectrochemical solar cells. For obtaining better photoresponse the surfaces of the photoelectrodes should be given a pretreatment to reduce the surface states. It is expected that annealing of photoelectrodes and etching them in a suitable chemical etchant will improve the efficiency considerably. All this work can form a guideline for the future PEC investigations on these materials.

Thin films of layered materials are preferable for practical solar energy conversion devices, for lubrication and for electrochemical energy storage. The film characteristics required for each of these applications are different. Photoelectronic properties are strongly influenced by structural defects, impurities, size and orientation of the crystallites. Due to high levels of recombinations at the edge planes (parallel to c-axis) it is essential that these planes are not exposed to the junction. The polycrystalline thin films produced with large grains with their basal plane orientation parallel to the substrate and the crystalline edges should be passivated. However, the characteristics of the thin films of the layered compounds produced so far are far from satisfying the requirements for use in interfacial electronic devices. Hence there is enough scope to carry out the research investigations on thin films of the single crystals materials studied in the present thesis.

SnSe and WS_2 compounds investigated in this thesis possess a layered structure, where so many variations in stacking of tin, selenium, tungsten and sulphur sheets may exist. So a thorough study of polytypism can be made in them using the facilities of X-ray diffraction and electron microscopy. The conditions of growth can also be discriminated to produce desired polytypic structures.

It may be considered worthwhile to investigate photoconductive effects using incident monochromatic light on SnSe and WS_2 single crystals.

A lot of work has been reported in the fields of growth, physical and structural characterizations of layered semiconducting compounds, revealing their unique and distinguishing characteristics in comparison to those of normal semiconductors. However, comparatively very little work is reported in the direction of their applications utilizing their unique characteristics. The author feels that attention should now be focussed in this direction.