CHAPTER 11

CONCLUSIONS AND FUTURE SCOPE FOR FURTHER RESEARCH

There has been several reports on the growth of single crystals of transition metal dichalcogenides ($MoSe_2$, WSe_2, TaS_2, NbS_2, MoS_2, WS_2 etc.) by chemical vapour transport method using bromine or iodine as the transporting agent. In this technique the size of the grown crystals depends on many parameters, such as dimensions of the ampoule, temperature gradient, concentration of the transporting agent, etc. By trial and error one can get the optimum values of these parameters for obtaining large single crystals. The crystals grown by chemical vapour transport method suffer from a serious disadvantage that there is every possibility of the transporting agents being incorporated in the crystals. Hence, in the present work, W_xSe_{2-x} ($0 \leq x \leq 2$) single crystals were grown by direct vapour transport method without using transporting agent.

A critical examination of the work described in the previous chapters leads to the following major conclusions.

1. It is possible to grow contamination free stoichiometric single crystals of transition metal dichalcogenides by direct vapour transport method.

2. The presence of hexagonal spirals on the faces of the grown crystals suggest a screw dislocation mechanism of growth for these crystals.

3. The variation of the lattice parameters ('c' and 'a') as a function of composition (X) shows a slight deviation from the Vegard's Law.

4. The crystals of MB_xSe_{2-x} grown by direct vapour transport method have shown p-type semiconducting behaviour.

5. Weak-beam technique can be employed to study defects with greater resolution to determine the perfection of the crystals.

6. Information about lattice parameter (c), polytypic identification and point group can be well accounted by convergent beam diffraction patterns.

7. To understand the nature of semiconductor/ electrolyte junction in photoelectrochemical (PEC) cell, dark I-V characteristics are required which determines the junction ideality factor.

8. Photovoltaic I-V characteristics give the cell parameters such as efficiency and fill factors.

9. Potassium ferro-ferry cyanide electrolyte gives comparatively better efficiency for WS_2 crystals than any other compositions of the series WS_xSe_{2-x}. This may be due to the good junction (semiconductor/electrolyte) ideality factor (n).

10. The efficiency of the present PEC cells with WS_xSe_{2-x} crystals show decreasing trend while increasing excitation levels of light illumination.

11. An increase in temperature also decreases the efficiency of the cell.

12. Photoresponse of the PEC cell fabricated by WS_xSe_{2-x} crystals is in fairly good agreement with the Schottky barrier model.

13. Effect of concentration of the $K_3Fe(CN)_6$ electrolyte, also given the systematic variation in the results which is found to be similar to the reported data in the literature.

14. Spectral response of the photoelectrodes of

WS_xSe_{2-x} series gives uniform variation in band gap with composition.

15. A systematic variation in the flat band potential with composition is also observed.

16. Energy level diagram obtained from the Mott-Schottky plots gives a complete idea about the semiconducting behaviour of the WS_xSe_{2-x} single crystals in the PEC solar cells.

However, while noticing the above conclusions and entire text of the thesis following aspects for future scope of further research can be envisaged.

The author feels that surface microstructures can be studied in great detail and one can see carefully how the surface changes with composition. By employing the techniques like scanning electron microscopy, light profile, multiple beam interferometry, etc. a lot of information can be extracted about the surface features and more light can be thrown on the growth mechanism of these single crystals.

In the family of "Transition Metal

Dichalcogenides", most of the compounds belong to layer structure, where so many variations in stacking order of the sandwiches may exist and phenomenon of polytypism can be studied in these compounds. Although an attempt to study polytypism using CBED pattern has been made in the present work. For detailed study one can also use X-ray diffraction analysis.

Galvanomagnetic measurements as a function of magnetic field and temperature for each composition may be studied on single crystals to elucidate the conductivity mechanism and mobility of charge carriers. This will give good supplementation to the thermoelectric measurements like Seebeck effect.

There is no necessity of emphasizing the need for detailed optical studies. Through the use of standard reflection, one can obtain the reflectivity spectrum and a Kramers-Kroing inversion of the reflectivity spectrum can give the spectra of the imaginary part of the dielectric constant, joint density of states and the number of electrons taking part in the optical transitions along with the refractive indices and extinction coefficients.

In electron microscopy, author feels that by using convergent beam and simple diffraction one can find out cell volume of single crystals. High temperature study in this field will give an idea about the dependence of cell volume on temperature and anharmonicity.

The study of changes in the zone axis patterns gives information about the strength of the crystal potential, thickness of the samples, symmetry of the structure and other related intrinsic characteristics of the material. So this study can also be carried out for the series WS_xSe_{2-x} single crystals.

Photocorrosion of the photoactive material is still a problem which is to be tackled and one should think in this direction also. Photo-corrosion is nothing but the decomposition of semi-conductors which may be brought about by either (i) electrons or (ii) holes or (iii) chemical reaction with ionic species in the electrolyte.

The problem of corrosion prevention in PEC cell should be approached from three different aspects.

(i) In the first approach, a fast redox couple

should be added to the electrolyte which can provide an alternative path to minority carrier capture. A number of II-VI and III-V compound semiconductors could thus be stabilized in aqueous solution. Another similar strategy adopted to prevent corrosion is the use of non-aqueous solutions containing appropriate redox couples.

(ii) The use of such semiconductor electrodes should be made in which the phototransitions do not involve bonding orbitals.

(iii) Attempts to prevent corrosion by applying a thin metallic coating on electrode surface could also be tried.

Second aspect has already been taken into consideration in the present work by selecting TMTC crystals which do not involve the breaking of bonding orbitals. The other aspects still remain to be considered in the future work.

Finally, it is pointed out that looking to the current developments in the field of solid state electronics, the semiconductor compounds such as studied in the present work, may be employed in some solid state devices. This might accomplish the applied aspects of the present investigations.

List of Research Papers

1. Growth and characterization of layer compounds in series WS_xSe_{2-x}
   J. Cryst. Growth (1985) (In press).

2. Some transport measurements of WSe_{2-x} single crystals
   Kristall und Technik. Vol.19, 12 (1984), 1575.

3. Some photoelectrochemical (PEC) measurements of WS_xSe_{2-x} single crystals
   Published in proceedings of symposium on photovoltaic Materials and Devices, held at National Physical Laboratory, New Delhi during May 10-11, 1984.

4. Photoelectrochemical solar cells with n-type natural MoS_2 single crystals
   Solar Cells (communicated).

5. Photoelectrochemical properties of tungsten sulfo-selenide single crystals.
   Solar Energy Materials (communicated).

6. Weak beam microscopy of WS_xSe_{2-x} single crystals
   (Ready for publication)

7. Study of convergent beam electron diffraction patterns of tungsten sulfoselenide single crystals.
   (Ready for publication)

Research papers presented in Conferences/symposia

1. Growth of Re-doped intercalated WSe_2 single crystals.
XIV National Seminar on crystallography held at I.I.T. Kharagpur, during December 20-23, 1982.

2. Growth and characterization of layer compounds in the series WS_xSe_{2-x} single crystals.
XV National seminar on crystallography and special symposium in Honour of Prof. S. Ramaseshan held in I.I.Sc. Bangalore during April 17-19, 1984.

3. On the semiconducting nature of WSe_{2-x} single crystals
XV National seminar on crystallography and special symposium in Honour of Prof. S. Ramaseshan held in I.I.Sc., Bangalore during April 17-19, 1984.

4. Some photoelectrochemical (PEC) measurements of WS_xSe_{2-x} single crystals.
Symposium on photovoltaic materials and Devices held at National Physical Laboratory, New Delhi during May 10-11, 1984.

5. Spectral sensitivity of photoelectrochemical solar cells with synthetic MoS_2, $MoSe_2$ and natural MoS_2 single crystals as photoanodes.
National seminar on physics of semiconductors and devices held at the Indian Institute of Science, Bangalore during 3-7, January 1984.

6. I-V characteristics of photoelectrochemical solar cells using p-type WS_xSe_{2-x} single crystals.
Second International Workshop on the Physics of semiconductor devices held during 5-10, December 1983, at Solid State Physics Laboratory, Delhi.