CHAPTER 16

REVIEW OF THE PRESENT WORK

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16.1 Introduction

The studies of growth and perfection of TaS_2 single crystals have been described and discussed in this thesis. An attempt has been made here to review the conclusions drawn from the entire work and so also to suggest the scope for future work in TaS_2 crystals.

16.2 Crystal Growth

In the past single crystals of transition metal dichalcogenides ($MoSe_2$, WSe_2, TaS_2, NbS_2, MoS_2, WS_2, etc.) have been grown by chemical vapour transport method using bromine or iodine as the transporting agent. The size of the single crystals obtained depends upon a number of 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 the disadvantage that there is every possibility of the transporting agents being incorporated in the crystals. Hence in the present work, TaS_2 single crystals have been grown by direct vapour transport method without using transporting agent. Crystals as large as 15 x 10 x 0.05 mm^3 have been obtained by this method. They mainly possess 1T-polytype structure.

16.3 Microstructures

Microscopic examination of TaS_2 crystals revealed the presence of growth layers. The absence of spirals on one hand and the evidence of layer growth on the other hand clearly show that these crystals have been grown by two dimensional spreading of growth layers. Whiskers have also been observed to have been grown along with the crystals in the form of ribbons and platelets. Their study reveals that whiskers have also been grown by a layer growth mechanism.

16.4 Etching

An etchant capable of revealing the sites of non-basal dislocations in TaS_2 crystals has been developed. The effect of etching time, etchant concentration and temperature on the etching behaviour is investigated. It is observed that the etch rate is independent of time but however is influenced by etchant concentration and the temperature. The dependence of etch rate V_t, activation energy E_d and pre-exponential factor A_d on concentration of etchant has been worked out and a relation among them is established. The values of activation energy determined from the plots of etch rate versus temperature confirm that the process of etching in chromic acid is a diffusion controlled.

16.5 Polytypism

Almost all the layered crystals are well known for their different polytypic structures. Oscillation photographs taken from TaS_2 crystals suggest that these crystals are mainly 1T-type, and as a rare case 2H-type are also possible. An estimation of the density of dislocation from the streaking of the spots in oscillation photograph was in agreement with that obtained by etching technique.

16.6 Electrical Properties

The temperature dependence of electrical resistivity and Seebeck coefficient are studied. Both of these show a phase transformation at 350° K and the same is also found in agreement in phase transitions as studied by electron diffraction.

16.7 Electron Microscopic Studies

As TaS_2 single crystals grown were very thin it was not possible to obtain good prismatic cleavages, from them and hence etching technique could not be applied to study the basal dislocations in these crystals. As a consequense transmission electron microscopic technique was applied to study basal dislocations.

During the present investigation through TEM the author came across different types of dissociated and undissociated dislocations. Their dissociation is strikingly observed using weak beam technique. Improvements in the resolution of the defect structures as revealed by using the weak beam technique has been thoroughly described giving specific examples of dislocation structures, network patterns, node-patterns, etc. Estimation of stacking fault energy was carried out from the measurements of dislocation separation and radii of curvature of extended nodes. Since value of μ (shear modulus) being not known for these crystals, the ratio γ/μ which is proportional to stacking fault energy was estimated. Three-fold ribbons observed in WSe_2 single crystals were also used for estimating γ/μ in WSe_2 crystals.

TEM studies of TaS_2 crystals also revealed the presence of loops, hohlstellens, small crystallites and zone-axis patterns in some of the crystal samples. TEM studies of NbS_2 whiskers showed the presence of multiple loops in them. The loops observed in TaS_2 are characterised to be of interstitial type while the multiple loops observed in NbS_2 whiskers are characterised to be of vacancy type. The hohlstellens observed are simply circular voids or holes in the structure and are not the planar defects. A zone-axis pattern observed revealed a six-fold symmetry of the crystal structure.

Phase transitions of these crystals

reveal interesting physical properties. A crystal heated from 94.5° K showed the occurrence of δ-γ-β and α phases but at a temperature of 528° K all the superlattice spots disappeared and the crystal transformed completely to a 2H-phase. After heating the crystal upto 617° K and then allowing it to cool slowly, it was observed that at a temperature of 441° K superlattice spots reappeared, but this time all the superlattice spots were exactly at the centre of basic matrix spots $\{M\}$ and thereby giving the formation of $2a_o$ hexagonal superstructure. Upon reheating the crystal, the phase remained upto 540° K but then starts disappearing. Upon cooling the specimen again to room temperature the phase reappeared which leads to conclude that the phase is reversible in the temperature range 300° K to 540° K. The occurrence of this phase can be attributed to the auto interaction of TaS_2. Irreversible phase transitions similar to TaS_2 are also found to occur in W_3Se_4 single crystals grown by direct vapour transport method.

Variation of lattice parameter 'a' with temperature for 2H-TaS_2 crystals has been studied. The study enabled to determine the defect formation energy in the crystals, and the value so determined was found to be 0.7945 eV.

16.8 Scope for the Future Work

The properties of the layered crystals depend upon the stoichiometry of the materials and hence attempt should therefore be made to grow these crystals and to study their physical properties by using different techniques available in the department.

To carry out detail structure analysis and the phase transformation studies in TaS_3, it is desirable that one grows TaS_3 crystals by taking tantalum and sulphur powder in stoichiometric proportion and then follow the direct vapour transport method for their growth.

In order to modify the structural and electrical properties of the layered compounds their intercalation with alkali metal atoms a or molecules of organic complexes plays an important role. Both the a-axis and c-axis, but more particularly the c-axis is increased in length by intercalation. Some of the studies indicate that the crystallographic distortion apparent in metallic layer dichalcogenides at low temperatures is absent after intercalation.

Hence the study of the various properties of TaS_2 crystals after intercalation will be a little bit of more interest.

Except transmission electron microscopy the measurements of resistivity and Seebeck coefficient at lower temperature are not reported in this thesis because of the non-availability of this facility in the department during the course of the present work. Low temperature observations for such physical properties of these crystals are worth to study.