

## **S.P.24. VALSALAKUMARI, C.K.—Growth and Characterisation of Tin Dichalcogenide Crystals—1985—Dr. Joy George**

During the past few decades, a wide spread interest in the structural, optical, electrical and other physical properties of the transition metal dichalcogenide layer compounds has evolved. The members of this family of compounds can be regarded as strongly bonded two dimensional chalcogen-metal-chalcogen layers which are loosely coupled to one another by the weak van der Waal's

forces. Because of this type of bonding, the crystals are easily cleavable along the basal plane and show highly anisotropic properties.

This thesis contains the growth and the study of the physical properties of certain tin dichalcogenide crystals ( $\text{SnS}_2$  and  $\text{SnSe}_2$ ). Tin disulphide and tin diselenide crystallise in the hexagonal  $\text{CdI}_2$  type crystal structure. This structure consists of layers of tin atoms sandwiched between two layers of chalcogen atoms. A tin atom is surrounded by six chalcogen atoms octahedrally. In the layers the atoms are held together by covalent bonding and in between the layers there is van der Waal's bonding.

These crystals are normally grown by chemical transport method with iodine as the transporting agent, the growth time being about 8 to 24 hours. But crystals grown using transporting agent are usually contaminated by the transporting agent and this has a pronounced effect on the physical properties. Therefore physical vapour transport method was used for the growth of crystals in the present investigations. Even though a relatively larger period of growth time is necessary for the physical vapour transport method (40-150 hrs), the crystals obtained from this method have a much less impurity concentration than that obtained from chemical vapour transport method.

Since the growth temperatures of tin disulphide and tin diselenide are comparatively high, fused quartz tubes were used for the growth. Stoichiometric proportion of the starting materials were filled in pre-cleaned quartz ampoules and evacuated to a pressure of  $10^{-5}$  Torr and sealed. For the growth process a horizontal two zone linear gradient furnace and temperature controllers with accuracy better than  $\pm 1^\circ\text{C}$  were used. A source temperature of  $700^\circ\text{C}$  and a growth temperature of  $630^\circ\text{C}$  was used for the growth of tin disulphide crystals. After a growth period of 40-150 hours, golden yellow platelet like crystals of approximately  $1.5\text{ cm}^2$  in area and  $10-60\ \mu$  thickness were obtained. For the growth of tin diselenide crystals, a source temperature of  $640^\circ\text{C}$  and a growth temperature of  $475^\circ\text{C}$  was used. Usually thin platelets of metallic coloured crystals having a thickness of  $\leq 100\ \mu$  were obtained.

Crystals with good plane surfaces were selected for morphological studies. Beautiful circular and hexagonal spirals were observed on the as grown faces of tin disulphide and tin diselenide crystals. These observations reveal that these crystals grow from the vapour phase by the screw dislocation mechanism. Spirals with hollow core and change of curvature were observed on tin disulphide crystals. The change of curvature of the spiral step depends on the stress field around the dislocation. Eccentric spirals originating from single screw dislocation were also observed. The eccentricity of the spirals depends on the supersaturation gradient of the growth crystal. Eccentric spirals and spirals showing change of curvature were observed on tin diselenide crystals also. One of the most striking features observed on  $\text{SnSe}_2$  crystals was the interlaced spirals. Interlaced spirals result from the dependence of growth rates on crystallographic direction.

Optical studies provide a wealth of information on the band structure of the semiconductor and also about the impurity levels in the band gap. Optical properties of the crystals were studied by transmission measurements. Refractive index of the crystals was determined from the interference fringes obtained in the transmission spectra of thin crystals. Absorption coefficient was also calculated from the transmission spectra of the crystals.

In tin disulphide crystals, it was found that there is a shoulder in the absorption just before the onset of band to band transitions. This shoulder is caused by

transitions from valence band to donor levels (due to doubly ionizable sulphur vacancy) situated 0.17 eV below the conduction band. From absorption edge measurements it was also found that, in tin disulphide the valence band is split into three due to spin-orbit interaction and crystal field splitting.

The fundamental absorption data was analyzed in terms of the theory of Bardeen et al and from this analysis, an indirect forbidden band gap of 2.07 eV and a direct forbidden band gap of 2.40 eV have been detected in tin disulphide crystals. In the case of tin diselenide crystals, the indirect band gap obtained is 1.03 eV. From the functional dependence of absorption coefficient on photon energy it was found that the transition is forbidden.

Conductivity type of the crystals was determined by the hot probe method. All the tin disulphide and tin diselenide crystals grown were n-type.

From the electrical measurements, activation energy required for conduction, mobility, carrier concentration etc. were determined. Resistivity of tin diselenide crystals was measured at different temperatures and from the temperature dependence of resistivity, activation energy for conduction parallel to c-axis was obtained (0.072 eV). Resistivity and Hall effect perpendicular to c-axis were measured by van der Pauw's technique. From these values, mobility and carrier concentration of tin diselenide crystals were calculated. From the results it was found that crystals grown by physical vapour transport (carrier concentration  $\sim 10^{16}$ ) are less contaminated than that grown from chemical transport (carrier concentration  $\sim 10^{18}$ ) method.

Electrical conduction mechanism in tin disulphide crystals was studied using A1-SnS<sub>2</sub>-A1 (MIM) structures. The current voltage characteristics obtained show four discrete regions. At low voltages, the current is proportional to the voltage (ohmic law region) followed by a square law region at high fields. This region is the shallow trap square law region. The square law region is followed by another region where current increases sharply with voltage ( $I \propto V^n$ ;  $n \geq 3$ ) and this is due to the filling up of the traps. This region is followed by the trap free square law region. These observations indicate a charge injection into the semiconductor. The log I versus log d plot in the shallow trap square law region shows a  $d^3$  dependence establishing that the conduction mechanism is space charge limited. From the threshold voltage, where the ohmic current cross over to space charge limited current in the absence of traps, the density of thermally generated free carriers was determined ( $2.3 \times 10^{11} \text{ cm}^{-3}$ ). Mobility of the charge carriers was calculated using the equation for SCL conduction ( $6 \text{ cm}^2/\text{V}\cdot\text{Sec}$ ). From this mobility, conductivity of the specimen was calculated ( $2.2 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ ) and the calculated value agrees very well with the experimental value obtained from the ohmic law region. Due to the filling of the traps in the semiconductor, current increases sharply after the shallow trap square law region. The trap filled limit voltage measures the fraction of the total concentration of traps that is empty in thermal equilibrium and from the trap filled limit voltage, the trap concentration was calculated ( $2.3 \times 10^{13} \text{ cm}^{-3}$ ). Trap depth, Fermi level, effective density of states in the conduction band etc. have also been determined from the measurements. Dependence of the current on temperature in the ohmic law region gave an activation energy of 0.40 eV.