CHAPTER - VIII

GROWTH AND MORPHOLOGY OF TIN DISELENIDE CRYSTALS

Tin diselenide is a layered semiconductor isostructural to tin disulphide and these crystals have been grown by chemical vapour transport method /1-5/. Garg et al /6/ have reported the growth of these crystals from vapour using synthesised charge. The most prominent features of crystals with layered structures is the existence of screw dislocation, giving rise to growth spirals. None of the earlier reported workers have studied the growth morphology of tin diselenide crystals. But Acharya and Srivastava /5/ reported that they were not able to observe any evidence of growth spirals on the as grown faces of these crystals.

In this chapter is described the growth of tin diselenide crystals by physical vapour transport method and their morphology. Growth spirals have been observed on the as grown faces of tin diselenide crystals for the first time.

3.1 EXPERIMENTAL

Tin diselenide crystals were grown by the physical vapour transport method. Quartz ampoules
Fig. 1. Temperature profile of the furnace used for the growth of CaSe₂ crystals.
of 15 cm length and 1.6 cm inner diameter were used for the crystal growth. Ampoules were cleaned as described in Chapter IV. Stoichiometric composition of tin (99.999%) and selenium (99.999%) were filled in the ampoule and was sealed at a final pressure of $10^{-5}$ Torr. The sealed ampoules were then placed in the horizontal two zone furnace. The temperatures of the zones were controlled with an accuracy of $\pm 1^\circ$C using temperature controllers as described in Chapter IV. Figure 1 shows the temperature profile of the furnace used for the growth of tin diselenide crystals. The source temperature was maintained at $640^\circ$C ($T_1$) and the growth temperature at $475^\circ$C ($T_2$). The transport time was around 100 hours. Crystals obtained were metallic coloured platelets having a thickness of 150 $\mu$m and surface areas up to 1.5 cm$^2$. As grown surfaces of the crystals were observed using metallurgical microscope.

8.2 RESULTS AND DISCUSSION

According to Burton, Cabrera and Frank /7/, Cabrera and Levine /8/, Muller-Krumhhar et al /9/, when a spiral originating from an isolated single screw dislocation is formed under a steady growth condition and is not perturbed by spiral layers from other
sources, the spiral will take regular shape. Ideal spirals originating from isolated screw dislocations are not commonly observed on crystal faces. If the growth conditions are so controlled and perturbations are not present, the whole surface will be covered by a single spiral. Figure 2 shows a single growth spiral observed on as grown face of the tin diselenide crystal. Several hexagonal spirals were also observed on the as grown faces and these growth spirals confirms that the growth of SnSe$_2$ crystals is due to the screw dislocation mechanism.

Based on the theoretical predictions by Frank /10/, Cabrera and Levine /8/, if the Burgers vector of a dislocation becomes relatively high, a cylindrical hollow core will develop around the dislocation. Hollow cores at the centre of growth spirals were first observed by Verma on SiC /11/ and Forty /12/ on CdI$_2$ crystals. From the experimental evidence obtained from faces of haematite crystals, Sunagawa and Bennema /13/ reported that if the step height of the spiral is very high, the spiral step escapes with a change of curvature from the hollow core depending on the stress field. Figure 3 shows such a spiral pattern. Both spirals having the same sign are originating from the single screw dislocation with a clear change of curvature as they escape from the central core.
Fig. 2. A circular spiral originating from a single screw dislocation. (x 300)
Fig. 3. Two spirals of same sign with central core and change of curvature. (x1000)
When two screw dislocations of the same sign are closer together than $2\pi f_c$ where $f_c$ is the radius of curvature of the two dimensional nucleus, they will generate a pair of non-intersecting growth spirals. Such an example is shown in figure 4. Here the spiral is doubled and will behave like one dislocation of double strength. A group of spirals observed on the basal plane of the tin diselenide crystal is shown in figure 5. All the spirals are originating from the central core of the same dislocation and have same sign and strength of dislocation. Eccentric spirals originating from a single screw dislocation were also observed on the as grown faces of these crystals (Figure 6). During the growth process a supersaturation gradient is over the surface of the growing crystal. Hence at the higher supersaturation side, the spiral step advance more rapidly and form wider step separation. At the lower supersaturation side, step separation becomes narrower and the spiral as a whole take the eccentric shape.

Another interesting feature observed was the interlaced spirals. A typical example is shown in figure 7. In this spiral pattern, interlacing appears along the six corners of the hexagon and the dissociation of the
Fig. 4. Two screw dislocations of the same sign at a distance of separation less than \( f_c \), cooperating with one another. (x 300)
Fig. 5. A group of spirals originating from the centre of the same screw dislocation. (x 1000)
Fig. 5. A group of spirals originating from the centre of the same screw dislocation. (x 1000)
Fig. 6. Eccentric spiral. (x 300)
Fig. 7. Interlaced spiral. (x 300)
spiral step into its components can be seen. The splitting have occurred in orientations parallel to the three alternate edges of the hexagonal spiral. Tin diselenide is a polytypic crystal which exhibit 2H, 4H and other higher order structures. In the crystal, for each successive monolayer in the repetition sequence, the force field is slightly different. In a given orientation of the step, one of these monolayers will have the slowest rate of growth. The other faster moving monolayer will overtake it and pile up behind it /14,15/. Therefore on alternate edges of the hexagon, the growth layers form alternate groupings. Thus the interlacing pattern results from the dependence of the growth rates on crystallographic directions and the change of the growth rate of the monolayers in different orientations of the crystal.

CONCLUSION

Circular and hexagonal growth spirals observed on the basal plane of tin diselenide single crystals revealed that they grew from the vapour phase by the screw dislocation mechanism. The change of curvature of the spiral step as it escape from the centre core is due to the increase in strain at the dislocation centre. Interlaced spirals are the result of the change in growth rate of the monolayers in different orientations
of the crystal. Almost all growth spirals observed on the as grown face of SnSe₂ crystals are similar to that observed on SnS₂ crystals.
References


14. F.C. Frank, Phil. Mag. 42 (1951) 1014.