CHAPTER 10

GROWTH AND MORPHOLOGY OF VAPOUR-GROWN 
Bi$_2$Se$_3$ CRYSTALS

10.1 INTRODUCTION

The narrow band gap semiconductor Bi$_2$Se$_3$, which possesses the layer structure is of interest for its desirable thermoelectric and Hall-effect applications. As stated in chapters 6 & 9, extensive investigations [1-12] have been made to study the optical, electrophysical, and galvanomagnetic properties of this compound. For all these studies Bi$_2$Se$_3$ crystals grown from its melt have been used. Crystals of V$_2$-VI$_3$ group compounds (Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Se$_3$, Sb$_2$Te$_3$ etc.) have been rather easier to grow from the melt than from their vapour. Due to the high vapour pressure of chalcogens, it is more difficult to obtain the stoichiometric crystals of these compounds. Arivuoli et al. [13] have studied the microhardness of the vapour-grown crystals of V$_2$-VI$_3$ family compounds. The morphological studies of the vapour-grown crystals of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ have been conducted by Kunjomana [14] and Ivan Sommer [15], respectively. But the study of the growth morphology of Bi$_2$Se$_3$, a prominent member among this group has not been reported.
In this chapter, the growth of $\text{Bi}_2\text{Se}_3$ crystals by physical vapour deposition technique and their morphology is presented. According to Ghosh et al [16], in sublimation method, platelets do grow only in a gas ambient and it is also reported [17] that the growth of well defined crystals at high temperature is favoured by the ambient gas (argon, hydrogen, air etc.), by lowering the evaporation rate. But in the present investigation well defined platelets of $\text{Bi}_2\text{Se}_3$ have been grown by vacuum sublimation. One of the most striking features of crystals with layered structures is the existence of screw dislocations with Burgers vector perpendicular to the plane of the layers giving rise to growth spirals. Such growth spirals have been observed on the as-grown faces of $\text{Bi}_2\text{Se}_3$ crystals for the first time.

10.2 EXPERIMENTAL

Bismuth selenide was synthesized from high purity (99.999%) elements; Bi and Se. Appropriate amount of the elements with little excess selenium were sealed at low pressure ($\sim 10^{-5}$ torr) into a quartz ampoule with length 10 cm and diameter 12 mm. The ampoule was then slowly heated to 800°C in a muffle furnace and maintained at this temperature for 24 hours, to complete the reaction. The ampoule was rotated and rocked mechanically to ensure the proper mixing of the constituents.

Pre-cleaned quartz ampoules with typical dimensions of 190 mm in length and 10 to 18 mm in diameter were loaded with about 10 gm, of the synthesized charge to grow $\text{Bi}_2\text{Se}_3$ crystals by PVD method. The whole system was evacuated and sealed off at about $10^{-5}$ torr. The reaction ampoule was then heated in a temperature gradient by means of a two-zone horizontal
furnace, the temperatures of which were kept at constant with in ±1°C, using temperature controllers. In order to remove any trace of the starting material at the growth zone of the ampoule, a reverse temperature gradient was applied before starting the growth. For this, the source region was kept at a lower temperature than the condensation for more than three hours.

In closed-tube-vapour-transport technique, it is observed that the transport rate mainly depends on the cross-section of the reaction ampoule [18], and to obtain best results the length-to-diameter ratio of the ampoule should be greater than 7 [19]. In the present case, best results were obtained with the 15 mm diameter reaction ampoules.

The effect of the temperatures of the two zones for the successful growth of the crystals was also studied. When the temperatures of the source zone and growth zone were 760°C and 655°C respectively, metallic coloured thin platelets with maximum surface area 0.5 cm² were obtained after a growth period of 72 hours. Identification of the grown crystals was made by X-ray diffraction studies with CuKα radiation. The as-grown surfaces of the crystals were observed under reflection mode of the metallographic microscope. Chemical etching characteristics of these crystals were also studied.

10.3 X-RAY DIFFRACTION STUDIES

A typical, X-ray diffraction pattern using CuKα radiation, obtained for vapour-grown crystals is shown in Fig. 10.1. The d-values and the relative intensities of the peaks are given in Table 10.1. All the values obtained in the present case are well matched with the standard pattern for Bi₂Se₃ [20].
Fig. 10.1
X-ray diffraction profile of Bi₂Se₃ crystal
TABLE 10.1
X-ray diffraction data of vapour-grown Bi$_2$Se$_3$ crystals

<table>
<thead>
<tr>
<th>hkl</th>
<th>Standard Pattern</th>
<th>Grown Crystal</th>
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<tr>
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<tr>
<td>208</td>
<td>1.600</td>
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</table>
10.4 MORPHOLOGY AND GROWTH MECHANISM

The predominant shape of the crystals grown in closed system by physical vapour deposition technique was plate-like. Very few ribbon-like crystals were also found. A good few of these vapour-grown Bi$_2$Se$_3$ crystals have been examined under the reflection mode of the microscope. Well developed areas of the crystals have been found as ideally smooth. However, a variety of interesting growth patterns were observed on the as-grown surfaces of the crystals.

Fig 10.2a shows the typical growth steps observed on the as-grown faces of the crystals, which is characteristic to the layer structure of Bi$_2$Se$_3$. Such growth steps have been observed on the surfaces of vapour-grown crystals of Bi$_2$Te$_3$ [21], and Sb$_2$Te$_3$ [15], which also have a similar layer-type structure as that of Bi$_2$Se$_3$. Fig. 10.2b, shows the magnified "feather pattern" observed at the tip of the plate having smoothed surface (upper part of Fig. 10.2a).

Fig. 10.3 shows an interesting "fountain view" of layers appearing at the tip of another platelet. A ribbon shaped crystal pattern is shown in Fig.10.4(a,b). Unlike on the platelets, holes and longitudinal cavities, as seen, are present on the ribbon-like crystals. This may be due to the difference in growth mechanisms responsible for the growth of platelets and ribbon-like crystals. Fig. 10.5 shows a kinked net work with well smoothed surfaces.

There are different growth mechanisms responsible for the growth of crystals. The theory of crystal growth in presence of screw dislocation
mechanism have been developed by Burton, Cabrera and Frank [22]. According to them, when a single screw dislocation emerges on the face of the crystal, a molecular ledge will run from the point of emergence on the crystal surface, to the boundary of the face. If the supersaturation of the vapour in contact with the crystal is higher than that of a critical value, the crystal will start to grow and the ledge will wind itself into a helicoid. Such a spiral originating from an isolating single dislocation will have a regular shape, if it is not perturbed by spiral layers from other sources and the growth conditions are steady [22-24]. Ideal spirals originating from isolated screw dislocations are not commonly observed on crystal faces.

Fig. 10.6(a,b) shows a circular spiral pattern observed on the as-grown face of the Bi$_2$Se$_3$ crystal. The two spiral having the same sign are originating from the single screw dislocation with a change of curvature as they escape from the central core. On the basis of the theoretical predictions of Frank [25], and Cabrera & Levine [23], and from the experimental evidence obtained from haematite crystals, Sunagawa et al. [26] reported that if the step height of the spiral is very high, the spiral steps escapes with a change of curvature from the central core depending on the stress field. The eccentricity of the growth spirals may be due to supersaturation gradient over the surface of the crystals during the growth process. At the higher supersaturation side, the spiral step advance more rapidly and form wider step separation, while at the lower supersaturation side the step separation becomes narrower and the spiral as a whole take the eccentric shape.

The intersection and further development of growth spirals originating from screw dislocation at separate points is shown in Fig. 10.7.
Fig. 10.2a  \( \times 62.5 \)

Fig. 10.2b  \( \times 200 \)

Fig. 10.3  \( \times 100 \)
The presence of growth spirals on the surfaces of Bi$_2$Se$_3$ crystals grown by physical vapour transport method establishes that these crystals are grown from the vapour phase by the screw dislocation mechanism. As mentioned earlier, during the growth process in closed-tube-vapour-transport a supersaturation gradient exists over the surfaces of the growing crystal and this can account for the distinct features observed in vapour-grown crystals [27]. At high supersaturation, the growth mechanism by screw dislocations becomes less important and causes the growth of ribbon-shaped crystals. Cardetta et al. [18] have observed the growth of the ribbon and needle shaped crystals of GaSe from vapour with its platelets, which have also been accounted for the supersaturation gradient exist in the closed-tube sublimation.

10.5 CHEMICAL ETCHING STUDIES

Chemical etching on the as-grown faces of the crystals were carried out to study the etching characteristics of the vapour-grown Bi$_2$Se$_3$ crystals. A solution of iodine, bromine and methanol, which is found to be a reliable etchant for revealing the dislocations in Bi$_2$Se$_3$ crystals (described in chapter 9) have been used to etch the vapour grown crystals.

Fig. 10.8 shows the etched pattern of the surface of a platelet in a solution of 200 mg I$_2$ + 10 ml CH$_3$OH + 0.2 ml Br$_2$ for 30 sec. As seen, very few shallow triangular pits were found to develop on the as-grown faces of Bi$_2$Se$_3$ crystals. Repeated etching suggests that these triangular pits are at the sites of emergence of the dislocations on the surface. A close observation on the circular patterns developed on the crystals surface revealed that these patterns are constituted
by tiny circles. These closed circular features are at the sites of the vacancy condensation. Similar features have been observed on the surfaces of vapour-grown Bi$_2$Te$_3$ crystals also [21]. An interesting pit shape that is occasionally observed on the surface of a platelet is shown in Fig. 10.9.

Comparing to melt-grown crystals described in chapter 9, it can be seen that the dislocation density in this case is much less and is as expected in vapour-grown crystals.

10.6 CONCLUSION

The presence of circular growth spirals observed on the basal plane of Bi$_2$Se$_3$ crystals revealed that they grew from the vapour phase by the screw dislocation mechanism. The change of the curvature of the spiral step as it escapes from the centre core is due to the increase in strain at the dislocation centre. The distinctive growth features are due to the supersaturation gradient over the growing crystals. Dislocation density in vapour-grown crystals is much less as expected.
FIGURE CAPTIONS

Fig. 10.2a. Step-like growth features on the as-grown faces of Bi$_2$Se$_3$ crystals

Fig. 10.2b. A ‘feather pattern’ appeared at the upper part of the plate-let in Fig. 10.2a with higher magnification

Fig. 10.3. A ‘fountain view’ of layers formed at the tip of a plate-let

Fig. 10.4a. A ribbon-like vapour grown crystal of Bi$_2$Se$_3$

Fig. 10.4b. A group of ribbon-like crystals

Fig. 10.5. A kinked Bi$_2$Se$_3$ crystal

Fig. 10.6a. Circular spirals on the as-grown faces of Bi$_2$Se$_3$ crystals

Fig. 10.6b. The spiral pattern in Fig. 10.a with higher magnification

Fig. 10.7. The intersection of growth spirals originated from separate screw dislocations

Fig. 10.8. Etch patterns formed on the as-grown face of Bi$_2$Se$_3$ crystal after etching in 200 mg I$_2$ + 10 ml CH$_3$OH + 0.2 ml Br$_2$ for 30 sec.

Fig. 10.9. Triangular etch pits formed on the surface of the vapour-grown Bi$_2$Se$_3$ crystal
REFERENCES


20. JCPDS Card No. 12 - 732.


