CHAPTER 10

GROWTH OF HOLLOW CRYSTALS OF ANTIMONY
AND BISMUTH CHALCOHALIDES
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10.1 Introduction

Interest in ferroelectrics of V-VI-VII group compounds is mainly due to their semiconducting properties. SbSI is found to be superior to many known ferroelectrics by virtue of its characteristic properties; pyroelectric [1], piezoelectric [2], electro-optic [3] and photo-electric [4]. The combination of all these properties favours efficient fabrication of optical light modulators, low-pressure high-sensitivity pick up cartridges, piezo-electric elements, etc. When compared with other ferroelectric materials discovered so far, it has the maximum piezo-electric modulus. The compounds belonging to V-VI-VII group are high resistance semiconductors with a relatively narrow forbidden band approximately equal to 2 eV [5].

Most of the compounds of these group belong to orthorhombic system with the space group Pnam. [6]. Growth of hollow crystals has stimulated interest among the researchers for their practical applications. Paorici [7] and Mash and Firth [8] have reported the use of CdS hollow crystals as high energy detectors which constitute a suitable geometry for this purpose. SbSI has been used as a high sensitive gas pressure sensor in the pressure range $10^{-4}$ to $10^{-5}$ Pa [9,10]. SbSI is also used as an IR-radiation converter due to the combination of high photosensitivity with the anomalous dielectricity properties [11]. Piezoelectric elements manufactured from SbSI textures [12] were used in certain types of electromechanical transducers near the 293K and by doping with Sb$_2$S$_3$, the
transducers near the 293K and by doping with $\text{Sb}_2\text{S}_3$, the operating temperature can be increased up to 308 K.

10.2 Experimental

The preparation of the starting materials of $\text{SbSI}$, $\text{SbSeI}$, $\text{SbSeBr}$, [Chapter 4]. $\text{BiSI}$ and $\text{BiSeI}$ [Chapter 5] have been dealt in previous chapters. About 10 gm of $\text{SbSI}$ was placed in a glass ampoule of length 20 cm and diameter 1.2cm. The temperature in the source zone was kept at 420°C and 410°C while the grown zone temperature was varied from 340°C to 300°C. About 10gm of the prepared $\text{SbSeI}$ was taken in a glass tube of diameter 12mm and length 15cm and vacuum sealed. Experiments were carried out in a two zone horizontal furnace which were controlled independently. The source zone was kept at 460°C and the growth zone was kept at 410°C and 390°C.

The prepared $\text{SbSeBr}$ was taken in a glass tube of length 15cm and diameter 10mm and kept in a two zone horizontal furnace after vacuum sealing the ampoule at pressure of $10^{-4}$ torr. The source zone temperature was kept at 360°C and the growth zone varying from 320°C to 300°C respectively.

In the case of $\text{BiSI}$, 20 gm of $\text{BiSI}$ was taken in an ampoule of length 20 cm and diameter 1.5cm and sealed in a vacuum of $10^{-4}$ torr. Experiments were carried out in a two zone vertical furnace and the source zone was kept at 530°C, the grown zone being at 480°C.

10gms of the $\text{BiSeI}$ polycrystalline material was taken in ampoule of diameter 12mm and length 15cm. The temperature in the source zone of the horizontal two zone furnace was kept at 560°C. The growth zone was kept at 490° and 470°C.
10.3 Results and Discussion

10.3.1 Growth of SbSI hollow crystals

Hollow crystals of SbSI as shown in figure 1 (plate 10.1) were obtained after 4 to 5 hours for the growth zone temperature 340°C. It showed well developed (220) prism faces [13]. The tips of some of the hollow crystals were tapered. Whiskers were found to grow in between the open lateral surface of the crystal with the growth layers at the bottom surface of the crystal. Spiral like layers were also observed on one of the hollow edges. The external morphology of the SbSI hollow crystals was found to depend upon growth conditions. When the growth zone temperature was 330°C irregular shaped hollow needles were obtained as shown in figure 2 (plate 10.1). Figure 3 (plate 10.1) shows the hollow needle when the growth temperature was 320°C. One side of these crystals consisted of many hollow needles with a new type of morphology. When the growth zone temperature was kept at 300°C hollow crystals as shown in figure 4 (plate 10.1) were obtained with many needles branching from the main needle. Figure 5 (plate 10.2) shows the layer growth pattern with a gradual rising or elevation towards the hollow part. Figure 6 (plate 10.2) is a higher magnification of figure 5 (plate 10.2) showing growth layers gradually rising in height when they approach the hollow part. On some of the needle surface, layers with elevated mounds are seen just near the start of the hollow. In some needles growth hillocks arranged parallel to the opening are observed as depicted in figure 7 (plate 10.2). The surface of the cleaved hollow needle is as shown in figure 8 (plate 10.2).
10.3.2 Growth of SbSeI Hollow Crystals

Figure 1 (plate 10.3) shows the hollow SbSeI needle grown for the growth zone temperature of 410°C. The length of the hollow needles was about 8 to 10mm. It has two branching on either side of the main hollow needle and the branches also show hollow nature. The hollow starts just after some distance from the base of the needle. Figure 2 (plate 10.3) shows the hollow needle with the whiskers emerging from the tip of the needle obtained for the growth zone temperature of 390°C. Figure 3 (plate 10.3) shows the bottom part of the hollow needle. Figure 4 (plate 10.3) reveals clearly the hollow nature of the SbSeI needle. This hollow portion extends throughout the crystal but stops just after some distance from the bottom of the starting point (figure 5, plate 10.3). Brick like elevations were also observed. The cleaved hollow needles show that the hollow crystals consists of bundles of whiskers arranged parallel to the needle (C-axis). Small elevations and cavities as shown in figure 6 (plate 10.3) were also observed and were characteristic features of the hollow SbSeI needle [14].

10.3.3 Growth of SbSeBr Hollow Crystals

Hollow crystals of SbSeBr were obtained [15] (figure 1, plate 10.4) when the growth period is over 40 hrs. hollow needle of SbSeBr obtained for the growth zone temperature of 300°C. The length of the needles was 8 to 10mm and thickness 0.3 to 0.5 mm, found to start just after some distance from the base of the needle and also shows open layer surface. Figure 2 (plate 10.4) shows the hollow needle obtained for the growth temperature of 310°C. The needles were very thin and 1 to 1.5cm long. Figure 3 (plate 10.4) shows the needle depicting clearly the hollow nature. The top portion is not well developed and from one of the edges a whisker is found
to emerge out. Figure 4 (plate 10.4) shows the hollow needle with the hollow nature starting at the bottom of the needle and the needle is a hollow tube up to some distance and becomes open lateral surface. This may happen due to insufficient material supply or due to temperature fluctuation. For the same growth zone temperature of 300°C, whiskers were also found to grow. Figure 5 (plate 10.5) shows the needle with three way branching, occurring after some distance from the origin of the needle. The three needles emerging from the main needle are also found to show hollow nature. The bottom of the needle is as shown in figure 6 (plate 10.5). Almost all the hollow crystals obtained for three different growth temperatures showed the tapering end as shown in figure 7 (plate 10.5). Figure 8 (plate 10.5) shows the hollow needles consists of bundles of whiskers.

10.3.4 Growth of BiSI Hollow Crystals

Hollow crystals of BiSI were obtained after 16 hours [16]. The length of the crystal was 1.5 cm and thickness ranging from 0.5 to 1 mm were obtained (Figure 1, plate 10.6). For low temperature difference, there was practically no crystallization in the growth zone. The surface of the hollow crystal show that the crystals consists of bundles of whiskers arranged parallel to the needle axis (c-axis) (figure 2, plate 10.6). Figure 3 (plate 10.6) shows the needle with jagged end. Figures 4 and 5 (plate 10.6) show the hollow needle with a whisker emerging from the needle. Figure 6 (plate 10.6) show the tip of the needle depicting hollow.
10.3.5 Growth of BiSeI Hollow Crystals

Hollow needles of BiSeI were obtained after two days. The length of the hollow needle was 5 to 6mm (figure 1, plate 10.7). The hollow nature was found to continue all along the needle (c-axis). The surface of the cleaved hollow BiSeI needle is as shown in figure 2. Figure 3 shows the hollow needle obtained for the growth zone temperature of 470°C. Figure 4 (plate 10.7) shows the growth hillocks observed on the surface of the hollow BiSeI needle.

10.3.6 Growth Mechanism

The rate of growth of SbSI differ in various crystallographic directions. Growth can take place along the [001] direction, without the formation of two dimensional nuclei since there is a screw component in this (2\textsuperscript{1} screw axis) direction [17]. The (hko) faces can grow either by the formation of two dimensional nucleation or on dislocations and on other crystal surface defects. This different minimum supersaturations are required for growth to proceed along the [001] and perpendicular [001] directions. Small supersaturations will be sufficient for growth along the C-directions, since it is a K-face [18] and grows more rapidly, where as a critical supersaturation is necessary for the formation of the two dimensional nuclei in the other faces. The higher magnification (figure 7 plate 10.2) shows them as triangular hillocks.

the crystal consists of bundles of whiskers arranged parallel to C-axis. At some point due to dislocation or impurity, some of the whiskers are completely retarded form growing further and the other whiskers which are able to
continue, form the outer lateral surface. When the hindrance is at the centre, a complete hollow with well defined hollow prism is formed. If the hindrance is just near the edges, there is a chance of getting an open lateral surface. The surface of some of the hollow crystals show pits due to vapour etching. In some of the needles pits were lined up parallel to the cavity [19].

The bottom part of the SbSeI needle as shown in figure 11 reveals that initially a thin needle is formed and many whiskers (orienting along c-axis) grow on its lateral surface due to two-dimensional nucleation. The whiskers grown on the lateral surface of the initial needle grow as needles and again whiskers grow on the side surface of these whisker-like needle. So the whiskers which were grown on the initial needle form a cavity at the centre as shown in figure 6 (plate 10.3). This leads to hollow nature and this mechanism of growth mechanism is similar to that suggested by Iwanaga et al [20].

The bottom of the hollow SbSeBr crystal shown in figure 21 clearly shows that after some distance from bottom the needles some more whiskers join with the original needle on its lateral surface by two-dimensional nucleation. These whiskers or needle grow along the C-axis which is the characteristic property of its structure. These whiskers develop as needles. When the needles, growing around the initial needle are united, a cavity of formed, finally developing into a hollow crystal. If the needles growing around the original needle are not united, open lateral surface as shown in figure 4, (plate 10.4) is formed. Figure 5 (plate 10.4) shows clearly that the hollow needle consists of bundles of whiskers. If
whiskers growing around the original needle are retarded due to some hindrances, the whiskers which are able to grow overcoming this hindrances, develop as needles leading to branchings.

In this case of BiSeI dislocations or impurities are responsible for the formation of hollow nature. They create crevice and this extends further during the growth of the needle. The growth steps usually begin from the emerging point of dislocations with screw components. The dislocations come out to the surface most frequently in the centres of the faces where convexities (vicinal hillocks) are formed. It is interesting to note that the cleaved hollow crystals of SbSI, SbSeBr, SbSeI and BiSI consist of array of bundles of whiskers arranged parallel to the C-axis. But in the case of hollow BiSeI crystal, the surface is found to be smooth, entirely different from the other crystals. From the observed surface features, it is found that the growth mechanism of SbSI, SbSeI, SbSeBr and BiSI are almost similar but the hollow crystal growth mechanism of BiSeI is entirely different.

According to Dziuba [21], with excess SbI$_3$ only condensation of melt takes place and nucleation of SbSI is not possible. Crystals grown from a source material rich in few percent of SbI$_3$ grow in the form of hollow rectangular tubes for the growth zone temperature of 350°C and source zone temperature of 400°C. The dimension and position of the tube determine the convection of the gas atmosphere inside the tube. According to him vapour growth appears when the gas atmosphere has a low concentration of the high volatile components which corresponds to a source material rich in few percent of Sb$_2$S$_3$. Crystallization from melt occurs in an atmosphere having a higher concentration of high volatile molecules which
corresponds to a source material a few percent rich in $T_2$ and SbI$_3$. As mentioned earlier, in the case of source material with excess SbI$_3$ crystallization occurs from melt resulting in vapour liquid-solid growth mechanism i.e after the formation of liquid SbI$_3$, SbSI vapour condenses in the liquid and so the liquid is supersaturated. A prerequisite for VLS mechanism is the mechanism of a liquid alloy composed by the needle material (S) and an impurity substance (I); the binary system S-I is characterised by miscibility in the liquid phase and immiscibility in the solid phase. i.e. eutectic phase diagram. So due to precipitation of supersaturated liquid at the liquid-solid interface, SbSI grows as needles due to the chain type structure, perpendicular to the solid-liquid interface.

A sudden fluctuation in temperature may cause unstable contact angle configuration and so the droplets meet the side surface of the crystal to increase the interfacial area. So a new droplet configurations results and so unidirectional growth takes place resulting in whiskers. This might lead to the hollow crystals, because the initially formed needle is retarded from growing further due to the insufficient material supply.

10.4 Conclusion

Hollow crystals of SbSI, SbSeI, SbSeBr, BiSI and BiSeI were grown from vapour for the first time. The morphology of the crystals was found to be dependent upon the temperature difference between the two zones. A possible mechanism of growth by VLS mechanism was also given as there is no quantitative theory which explains the observed morphologies.
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