CHAPTER 3

BASIC CHARACTERISATION STUDIES ON INDIUM ANTIMONIDE CRYSTALS

3.1 INTRODUCTION

Characterisation forms an integral part of crystal growth research. It helps to assess the quality of the grown crystals and hence their suitability for a specific application. It also provides necessary feedback to determine the optimum growth parameters to obtain crystals with desired properties.

Crystal characterisation is very vast, covering almost every conceivable branch of physics and chemistry. In the present case, only the basic characterisation techniques have been chosen to analyse the quality of the crystals. Chemical etching and SEM-cathodoluminescence were employed to analyse the various defects present in the crystal and also to determine the dislocation density.

Determination of the electrical properties such as carrier concentration and mobility of semiconductor materials is very much essential. In the present investigation, the electrical characterisation was carried out using Hall measurements. Optical characterisation of InSb crystal is very much vital since it is dominantly used as infrared detectors and filters. It helps to ascertain the suitability of the grown crystals for infrared applications. A thorough investigation of the optical properties of the grown InSb crystals has been carried out and the growth parameters that affect the optical quality were determined. Studies on the mechanical properties of the grown InSb crystals have also been
carried out since knowledge of the mechanical properties is essential during device fabrication. Compositional analysis, X-ray diffraction studies and differential thermal analysis have also been carried out.

### 3.2 POWDER X-RAY DIFFRACTION STUDIES

In order to confirm the formation of InSb crystal and also to determine the lattice parameter, the powder of the grown crystals were subjected to X-ray diffraction studies. Rich-Seifert X-ray diffractometer was employed for the purpose. The XRD pattern is shown in Figure 3.1. The values of $2\theta$ and the corresponding intensities are given in Table 3.1. The grown crystals had (111) as the preferred orientation. The lattice parameter was found to be 6.478 Å, which is in accordance with the literature value (Wyckoff 1963).

<table>
<thead>
<tr>
<th>$2\theta$ (degree)</th>
<th>d (Å)</th>
<th>Intensity (%)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.8</td>
<td>3.739</td>
<td>100</td>
<td>111</td>
</tr>
<tr>
<td>39.3</td>
<td>2.298</td>
<td>80</td>
<td>220</td>
</tr>
<tr>
<td>46.5</td>
<td>1.957</td>
<td>55</td>
<td>311</td>
</tr>
<tr>
<td>56.8</td>
<td>1.623</td>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td>62.5</td>
<td>1.489</td>
<td>22</td>
<td>331</td>
</tr>
<tr>
<td>71.3</td>
<td>1.326</td>
<td>25</td>
<td>422</td>
</tr>
</tbody>
</table>

### 3.3 DIFFERENTIAL THERMAL ANALYSIS

In order to find the presence of subphases and also to determine the melting point of the grown crystal, differential thermal analysis (DTA) was employed. In differential thermal analysis (DTA) two samples of similar thermal capacity are heated and
Figure 3.1 X-ray diffraction pattern of InSb
cooled at the same uniform rate. Thermocouples measuring the temperature of the two samples are connected in opposition so that the temperature difference $\Delta T$ between the samples is measured. If neither of the samples undergoes a phase change, $\Delta T$ will be ideally zero throughout the entire heating range. However, if one sample is inert, while the other undergoes a phase change, say, solidification or melting, then the evolution or absorption of latent heat will result in a temperature difference between the samples. If $\Delta T$ is recorded as a function of temperature any thermal effect such as solidification or melting of the sample may be detected.

In the present investigation, Seiko SSC/520H differential thermal analyser was employed for the purpose. The experiment was performed in a reduced atmosphere with heating rate of 10°C/min. Figure 3.2 shows the DTA curve of InSb crystal grown by vertical Bridgman technique. The curve showed one sharp endothermic peak at 535°C indicating the melting point of the material and the presence of this single peak confirmed the absence of any phase other than InSb.

3.4 STRUCTURAL CHARACTERISATION

In the field of crystal growth, particularly of electronic materials, single crystals are grown either for research purposes or for technological exploitation. Therefore, it is essential that the material undergoes an evolution in terms of structural perfection upto a point where the material is acceptable for its proposed application. This requires a constant appraisal of the structural perfection and it is this appraisal which is called structural characterisation. Structural characterisation is not only the determination of crystal structure but also the structural quality. Thus, the objective of structural characterisation is to provide the crystal grower with the appropriate information to develop crystal of required quality.

The characterisation of crystalline defects is invariably an essential part of semiconductor crystal growth studies. The first and foremost step to determine the
Figure 3.2  DTA curve of InSb crystal
fundamental physical properties of a crystalline semiconductor is the investigation of defects present in an as-grown crystal. In the electronics industry, defects often play a pivotal role in governing the performance, reliability and lifetime of solid state devices.

3.4.1 Chemical etching

The earliest and generally the cheapest and quickest method of assessing the structural perfection is etching. Examination of the bulk and the surface of a crystalline solid enables one to understand its evolution in relation to its interactions with the surrounding medium and also the effects of evolution on the physical and chemical properties of the solid (Sangwal and Rodriguez Clemente 1991). The features that happen during crystallisation are recorded in the bulk of the crystal because all parts of the solid have invariably been a part of the growing surface previously. Decrystallisation or etching is the erasing of matter. Therefore, decrystallisation of solid provides information about the remote periods of crystallisation, which are reflected in the remaining matter.

3.4.1.1 Defect analysis

All types of linear (dislocations), planar (stacking faults, twin boundaries, grain boundaries) and volume defects (clusters of point defects and impurities) emerging on the surface of a crystal results in the formation of etch features on it. Volume defects are localised at random positions in the crystal interior, planar defects extend to large areas, while linear defects do not terminate within a crystal. These geometrical properties of defects may be used to distinguish them by studying the etch patterns. Volume and linear defects produce etch figures at isolated positions. Planar defects such as stacking faults, twin boundaries and impurity striations produce grooves or ridges, while grain boundaries yield rows of etch figures. Etch figures resulting due to various defects may be recognised by examining the etch patterns on a surface after successive etching or after alternate etching and polishing. Etch figures due to volume defects disappear continuously on successive etching or on alternate etching and polishing.
Semiconductor etching can be classified as polishing and selective (preferential) etching. The ideal polishing etches have removal rates which are independent of crystallography, strain and chemical inhomogeneities and are inversely proportional to the local radius of curvature. Therefore, even a rough or damaged surface when etched for a sufficient length of time in a polishing etch will develop flat mirror-like surface with rounded edges. This will occur irrespective of the internal state of the material. In contrast, the ideal selective etches will act upon a highly defective but mirror-like surface only at strain or dislocation sites. Semiconductor etches of either type do not in practice achieve the ideal behaviour though many come close.

The action of both polishing and selective etches in removing material is actually the same, the process being known as oxidation-reduction mechanism. For this mechanism, the etchant was composed of an oxidiser, a complexer and a diluent. One component oxidised the surface while another complexed the oxidised species to make it soluble in the etching solution. A third agent, such as water or acetic acid, was normally added as diluent. Table 3.2 lists the most common of these chemicals for semiconductor materials. Etchants of many combinations of oxidiser-complexer-diluent on InSb crystals have been tried by several authors (Venables and Broudy 1958; Gatos and Lavine 1960a, 1960b; Runyan 1975).

In the present investigation, the cut and polished wafers of InSb crystals were subjected to chemical etching. The etchant used was 1 part 48% HF : 2 parts 30% H₂O₂ : 2 parts H₂O. Etching was carried out at room temperature for 30 s. The etched samples were observed by optical and scanning electron microscopes.

The formation of a visible etch pit will obviously depend on the ratio between the rate of nucleation of unit steps at a dislocation site and their velocity of lateral flow across the surface. In other words, the ratio between the solution rate along the dislocation (vₐ) and that parallel to the surface (vₚ), will determine the size and shape of the pit. The cross section through a hypothetical pit is shown in Figure 3.3, where vₑ represents the
<table>
<thead>
<tr>
<th>Oxidiser</th>
<th>HNO₃</th>
<th>H₂O₂</th>
<th>CrO₃</th>
<th>KmnO₄</th>
<th>Br₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complexer</td>
<td>HF</td>
<td>HCl</td>
<td>H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diluent</td>
<td>H₂O</td>
<td>CH₃COOH</td>
<td>CH₃OH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.3  Formation of an etch pit around a dislocation line
solution rate normal to the surface as a whole. If \( v_d << v_n \), very shallow pits will be formed. On the other hand, if \( v_d > v_n \), well-defined deep pits will be developed and the depth and diameter of the pits will increase with increasing etching time (Rhodes 1964). The geometry of a terraced etch pit is shown diagrammatically in Figure 3.4. Figure 3.5 shows the etch pits observed by scanning electron microscope. The pits revealed the characteristic terrace-like structure composed of closely spaced steps.

Chemical etching also revealed certain other features such as subgrain boundaries and twins. Subgrain boundaries i.e. low angle boundaries which separate disoriented regions of crystal were revealed as rows of etch pits. Figures 3.6a and b show the optical and scanning electron micrographs of subgrain boundary as dislocation pile ups. Figure 3.7 shows a twin lamalla between two crystallites.

### 3.4.1.2 Dislocation density

The number of etch pits revealed by chemical etching is generally accepted as a reasonable estimate of the dislocation density of the crystal. The density of the etch pits was dependent on the amount of thermal strain suffered by the crystal during its growth from the melt. The dislocation density in InSb crystals varied widely from relatively few in the crystals grown under low-stress conditions to greater than \( 10^5 \) \( \text{cm}^{-2} \) in the more badly deformed specimens (Figures 3.8a and b).

### 3.4.2 Defect analysis by cathodoluminescence

Cathodoluminescence images were obtained in a Leica-Cambridge Stereoscan scanning electron microscope. Cathodoluminescence images helped to identify the defects, to observe their distribution and more importantly to determine the dislocation density with the advantage of viewing two kinds of dislocations, the ones coming out of the surface and the ones parallel to it.
Figure 3.4  Plan and elevation of an etch pit on a (111) surface
Figure 3.5  Scanning electron micrographs of InSb etch pits
Figure 3.6 Dislocation pile ups at subgrain boundary observed by (a) optical microscope and (b) scanning electron microscope
Figure 3.7  Optical micrograph of a twin lamella between two crystallites
Figure 3.8  Etched samples having (a) high and (b) low dislocation density
Cathodoluminescence images show contrasts which are interpreted as follows: defects, such as precipitates, grain boundaries and dislocations, play the role of traps for excess minority carriers and thus lead to a reduction of possible radiative transitions. In the case of dislocations, it is possible to distinguish the effects of both the core and the surroundings. The dislocation is considered, actually, as a non-radiative element and its effect appears on the image as a dark spot. On the other hand, the effect on the non-radiative element may be seen as a bright halo around the dark core. This effect can be explained by the fact that the precipitation of impurities on the dislocations improves the quality of the surrounding area (Guergouri et al 1994). Figure 3.9 shows the SEM-CL image taken on InSb crystal.

3.5 MECHANICAL PROPERTIES

The measurement of mechanical properties is necessary for the determination of cutting, lapping and polishing conditions while manufacturing crystal elements for various devices and for the prediction of reliability of these elements under mechanical and thermal loads during operation. Vicker’s pyramid indenters have been used widely to measure the hardness of the material. This test was designed by Smith and Sanland (1925).

3.5.1 Microhardness

Microhardness can be evaluated from the size of an impression left by the indenter after pressing it against the material to be tested and from the applied load. In the present investigation, Vicker’s microhardness studies were carried out on the cut and polished InSb wafers at room temperature using Leitz Wetzler microhardness tester type P1191 fitted with a Vicker’s Pyramidal diamond indenter with apical angle of 136° between the opposite pyramidal faces, which is attached to a Metallux-II metallurgical microscope (Figure 3.10). The indentation time was fixed at 10 s for all the loads varying from 5 to 200 g. The indentations were made at different sites such that the centre of an impression was never less than five times its diagonal length from the edge of the specimen.
Figure 3.9  SEM-Cathodoluminescence image taken on InSb sample
Figure 3.10  Metallurgical microscope fitted with a Vicker's pyramidal diamond indenter
or the edge of an adjacent impression in order to avoid mutual influence. The diagonal length of the indentation marks was measured with the aid of a calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made for every load and the average diagonal length of the indentation in each trial was calculated. The mean diagonal length \(d\) of the indentation marks for each load was used to calculate the microhardness \((H_v)\). The microhardness values were calculated using the relation

\[
H_v = 1.8544 \left( \frac{P}{d^2} \right)
\]

(3.1)

where \(H_v\) is the Vicker's microhardness number, \(P\) is the applied load in gram force and \(d\) is the diagonal length of impression in \(\mu m\). Figure 3.11 shows the variation of Vicker's microhardness of InSb crystal with applied load. It is to be noted that the hardness value decreases initially with increase in load and remains constant thereafter. The relation between load \(P\) and indentation diagonal length \(d\) is represented by Meyer's law

\[
P = Ad^n
\]

(3.2)

where \(A\) (standard hardness) and \(n\) are constants (Mott 1956). The value of \(n\) represents the capacity of work hardening. Kick postulated a constant value of \(n = 2\) for all the indenters and for all geometrically similar impressions. However, according to Onitsch (1950), \(n\) will be lesser than 2 if \(H_v\) decreases with increase in load. In order to determine the work hardening coefficient \((n)\), the graph between \(\log d\) and \(\log P\) was plotted (Figure 3.12). The work hardening coefficient using the least square fit method was found to be 0.57. This is in accordance with Onitsch's concept.

### 3.5.2 Fracture toughness

The indentation method can also be used to determine the fracture toughness of the material (Zlatkin and Lube 1992). The mechanical stresses arising due to the action of
Figure 3.11  Variation of microhardness ($H_v$) with applied load ($P$)
Figure 3.12  Log d vs log P plot for InSb crystal
the load interact with the residual stress field in the crystal. When the load exceeds certain critical value, the cracks begin to propagate starting from the corners of the impression. The fracture toughness can be calculated from the measured crack lengths and the applied load.

Figure 3.13 shows the variation of crack length with applied load for InSb crystal. The crack length was found to increase with increase in load. From the crack length, the fracture toughness ($K_c$) of the material was calculated using the relation

$$K_c = \frac{P}{\beta l^{\frac{1}{2}}} \quad (3.3)$$

where $P$ is the indenter load, $l$ is the crack length and $\beta$ is the indenter constant which is 7 for a Vicker's indenter. The value of $K_c$ was found to be 0.125 MPa$\text{m}^{\frac{1}{2}}$.

3.6 COMPOSITIONAL ANALYSIS

Crystals intended for use as substrates for devices must satisfy two basic requirements. The crystals must be highly homogeneous and the dislocation density must be as low as possible. Otherwise, the command of the implanted devices will hardly be possible. Also the dislocations play the role of non-radiative recombination centres, thus reducing the optical efficiency of the material (Garandet et al 1990). The chemical homogeneity of the crystals has been analysed using inductively coupled plasma analysis, energy dispersive X-ray analysis and electron probe microanalysis.

3.6.1 Inductively coupled plasma analysis

The crystals grown under optimised thermal conditions were subjected to inductively coupled plasma analysis. Samples were taken from the resultant crystal at various distances from the tip along the entire transverse cross-section. Each sample was
Figure 3.13  Variation of crack length with applied load
dissolved in a solution of distilled water and HNO₃. Samples were also checked for any compositional nonuniformity along the radial direction. Figures 3.14a and b show the indium composition in the axial and radial direction. The figures show that the composition of the grown crystals lie within 0.5 wt % of the stoichiometric composition. InSb alloys with less than 0.5 wt % of the stoichiometric composition form single phase α-InSb material and only outside this narrow composition a second phase will be realised (Hulme and Mullin 1962). Thus, it is evident that the InSb crystals grown under optimised growth conditions were stoichiometric and highly homogeneous.

The ICP analysis was also carried out on the crystal grown by two-ampoule process under optimised growth conditions. The result indicated that the crystal was also stoichiometric and highly homogeneous. Thus, it is evident that the quality of the crystals depends only on the growth parameters and not on the process viz. one-ampoule or two-ampoule.

3.6.2 Energy dispersive X-ray analysis

The composition of the material was also determined using energy dispersive X-ray (EDX) analysis. In order to study the homogeneity and stoichiometry of the grown crystals, energy dispersive X-ray analysis was performed at various positions of each wafer. The analysis was done using Horiba EMAX 5770 spectrometer coupled to a Hitachi S-5000 scanning electron microscope. Figure 3.15 shows one such typical EDX spectrum of InSb crystal. The results obtained confirmed the stoichiometry of the grown crystal and identical results obtained all along the length of the crystal indicated the high homogeneity of the grown crystal.

3.6.3 Electron probe microanalysis

Energy dispersive X-ray analysis and inductively coupled plasma analysis are not so sensitive to minor deviations in the homogeneity of the crystal. These trace
Figure 3.14a Composition of indium along axial direction in InSb crystal as observed by ICP analysis.
Figure 3.14b Composition of indium along radial direction in InSb crystal
Figure 3.15  Typical EDX spectrum of InSb crystal
variations may greatly affect the quality of the crystal. Microstructures observed in the crystals were analysed by electron probe microanalysis using Shimadzu EPMA C1 microanalyser. The analysis revealed these microstructures as indium inclusions. Further, the analysis also substantiated that the InSb crystals grown under optimised thermal conditions were free from microscale inhomogeneity.

3.7 ELECTRICAL CHARACTERISATION

Measurement of the electrical properties of semiconductors is fundamentally important since they provide information regarding the purity and perfection of the crystals in terms of utility. The electrical characterisation of the grown InSb crystals was carried out using Hall measurement technique. Hall measurement technique is applied widely to characterise semiconductors in order to estimate the resistivity, carrier concentration and mobility of the semiconductor. The Hall effect can be explained as follows: when electric and magnetic fields are applied in a mutually perpendicular direction to a semiconductor, a voltage is developed across the semiconductor. The direction of the potential gradient is perpendicular to both the applied electric and magnetic fields. This effect is called Hall effect and the voltage developed is the Hall voltage. By measuring the amount and direction of Hall voltage, the number and type of charge carriers can be obtained.

The Hall measurements were carried out on cut and polished InSb samples by Van der Pauw technique. Contacts were made using indium at 200°C for 5 min in argon flow. The crystals exhibited n-type conductivity with a carrier concentration of $2.71 \times 10^{17} \text{cm}^{-3}$ and high carrier mobility of about 60,000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature (Premila Mohan et al 1999).

3.8 OPTICAL CHARACTERISATION

In order to evaluate the suitability of the grown crystals for infrared devices, the grown crystals were subjected to optical characterisation studies. As mentioned earlier, InSb crystals are predominantly used as infrared detectors and also as infrared filters. Three
characteristics which are important in the evaluation of such filters are (i) the sharpness of
the cut-off wavelength (ii) the transparency of the nonabsorbing window and
(iii) sufficient thickness for mechanical strength. A material to be used as a filter must
essentially satisfy all these conditions.

Infrared transmission studies were carried out on the vertical Bridgman grown InSb
crystals using Perkin Elmer 2000 FTIR spectrophotometer. Wafers of 1.5 cm diameter and
300 µm thickness were used for this purpose. The infrared transmission spectrum of the
inclusion-free InSb crystal grown under optimised thermal conditions is shown in
Figure 3.16. It is evident that the crystal had a very sharp cutoff and a good percentage
transmittance (31%) enabling the crystals suitable for infrared filters. The IR spectrum of
the crystal obtained by two-ampoule process also showed a high percentage transmittance.

The IR transmission studies were also carried out on crystals which had inclusions.
Wafers of the same thickness (300 µm) were used in this case. Figure 3.17 shows the IR
transmission spectrum of one such crystal. Eventhough the cut-off occurred at the same
wavenumber (1350 cm⁻¹), the percentage transmittance was found to be very low (2%).
Thus, it is evident that the presence of inclusions is detrimental for device applications and
should be avoided at all costs.

The energy bandgap of the grown InSb crystal can be determined from the plot
of χhv² vs hv (Figure 3.18). The bandgap of InSb crystal was found to be 0.18 eV which
is in accordance with the literature value (Mooradian and Fan 1966).

3.9 CONCLUSIONS

Powder X-ray diffraction studies confirmed the formation of InSb crystals. The
melting point of InSb determined by differential thermal analysis was found to be 535°C.
Etching studies carried out on the cut and polished wafers showed the presence of various
defects such as low-angle grain boundaries, dislocation etch pits and twins. The crystals
Figure 3.16  IR transmission spectrum of inclusion-free InSb crystal
Figure 3.17  IR transmission spectrum of InSb crystal with inclusions
Figure 3.18  Plot of $(\alpha h \nu)^2$ vs $h \nu$
grown under optimised thermal conditions were free from twins and the dislocation density was quite low. Microhardness of InSb crystals was found to be 230 kgmm$^{-2}$. The compositional analysis carried out on the grown crystals showed that the crystals were highly homogeneous and also free from inclusions. The crystals showed a high percentage transmittance and absorption edge was found to be very steep indicating the suitability of the grown crystals for infrared applications. Thus, the vertical Bridgman grown InSb crystals grown under optimised thermal conditions were highly homogeneous with low dislocation density, satisfying both the conditions which are stringent for device fabrication.