CHAPTER 2

INDIUM PHOSPHIDE SINGLE CRYSTALS: THEIR IMPORTANCE AND GROWTH BY THE LIQUID ENCAPSULATED CZOCHRALSKI TECHNIQUE

2.1 IMPORTANCE OF INDIUM PHOSPHIDE

InP is a direct transition type compound semiconductor. InP crystals exhibit certain useful properties that are superior to those of GaAs single crystals for several optical and electrical applications. The advances in the bulk crystal growth of InP and epitaxial growth techniques have made InP-based materials very useful for ultra-high speed devices and for high-performance optoelectronic devices. The main use for InP and related compounds are in the field of semiconductor quantum devices using multiquantum wells and superlattices. Important applications of InP are given in Table 2.1.

Table 2.1

Various types of InP and their applications

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Source material or cover sheets for epitaxial growth</td>
</tr>
<tr>
<td>Sn</td>
<td>Laser diodes, LED’s</td>
</tr>
<tr>
<td>S</td>
<td>PIN-photodiodes, Avalanche photodiodes</td>
</tr>
<tr>
<td>Zn</td>
<td>High-power laser diodes, Solar cells</td>
</tr>
<tr>
<td>Fe</td>
<td>High frequency FET’s and OEIC’s</td>
</tr>
</tbody>
</table>
Some of the salient features of InP are given below:

1. The transmission loss of a quartz fiber used for electronic communication has a minimum at the wavelengths of 1.3 μm and 1.55 μm. InP can be used in lattice matching with InGaAsP mixed crystals, the band gap of which can be fitted to the optimum wavelength (Onabe 1982).

2. The electron drift velocity of InP is larger than GaAs at higher electric fields (=10^4 V/cm) (Nielsen 1972) and InP is very promising for high speed Field Effect Transistors (FET's) with a high cut-off frequency.

3. The thermal conductivity value (Jordan 1985) of InP is more advantageous for integrated circuits that need larger power dissipation.

4. The localized state density is smaller than that of GaAs and hence it is easy to form n-type inversion layers: InP has been found to be very promising for high speed MISFET's (Hasegawa et al 1981).

5. InP has been reported to give a high theoretical conversion efficiency for solar cells. InP is more radiation resistant than GaAs and Si and hence is better suited for space solar cells (Weinberg et al 1986; Okazaki et al 1988).

6. It is easier to obtain low dislocation density crystals with low level of impurity doping (Seki et al 1976,1978).

7. Semi-insulating crystals can be easily obtained by doping with iron, which forms a deep acceptor (Iseler 1979).
Low resistivity InP is now used industrially for the fabrication of Laser Diodes (LDs), Light Emitting Diodes (LEDs), Avalanche Photodiodes (APDs) and PIN Photodiodes. Fabrication of MISFET's and OEIC's is extensively carried out using semi-insulating InP substrate. The most promising application is the radiation-resistant solar cells for the space industry.

2.2 FUNDAMENTAL PROPERTIES OF INDIUM PHOSPHIDE

Indium Phosphide has the zinc blend crystal structure as shown in Figure 2.1. Its lattice may be considered as two interpenetrating face centered cubic sub-lattices, one made up of indium atoms and the other of phosphorous atoms. This structure is the same as those of the other III-V compound crystals but is different from the diamond lattice structure of silicon.

In shaping a single crystal, it is necessary to consider the orientation dependency according to the crystallographic structure, which is different from materials that are amorphous or polycrystal with no specific orientation. The zinc blend crystal structure possesses not only covalent bonding but also ionic bonding. As a result, its cleavage plane is not the (111) plane with the longest plane interval, but the (110) plane, which has electrical neutrality. The disagreement between the (111) slip plane and the (110) cleavage plane is a fracture of III-V compounds, which results in mechanical properties being different from those of silicon. In III-V compounds the mechanical properties show an orientation dependency. The hardness of a particular plane depends upon the angle difference against the cleavage plane.
Figure 2.1  Zinc blend structure
The other fundamental physical properties are presented in Table 2.2.

**Table 2.2**

**Physical properties of InP**

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Zinc blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>5.869</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.8</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1062</td>
</tr>
<tr>
<td>Dissociations pressure (atm) at M.Pt.</td>
<td>27</td>
</tr>
<tr>
<td>Linear expansion coefficient (10⁻⁶ /deg.)</td>
<td>4.5</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm.deg)</td>
<td>0.70</td>
</tr>
<tr>
<td>Band gap (eV) at room temperature</td>
<td>1.35</td>
</tr>
<tr>
<td>Optical transition</td>
<td>Direct</td>
</tr>
<tr>
<td>Specific dielectric constant</td>
<td>12.5</td>
</tr>
<tr>
<td>Intrinsic carrier concentration at R.T (cm⁻³)</td>
<td>2x10⁷</td>
</tr>
<tr>
<td>Electron mobility at R.T (cm²/V.s)</td>
<td>4500</td>
</tr>
<tr>
<td>Hole mobility (cm²/V.s)</td>
<td>150</td>
</tr>
<tr>
<td>Intrinsic resistivity (Ω.cm)</td>
<td>8x10⁷</td>
</tr>
</tbody>
</table>
In order to produce high-quality InP single crystals, it is essential to know the thermodynamic (Bachman and Buchler 1974), crystallographic and mechanical properties (Jordan 1985).

The complete phase diagram of InP system has not been obtained due to the high pressure of phosphorus equilibrated with melt, especially in the phosphorus rich region. The phase diagram (Boomgaard and Schol 1957) is shown in Figure 2.2. The dissociation pressure of phosphorus in InP is about 27.5 atm at the melting point of InP (1062°C), which is much higher than the 0.9 atm of arsenic in GaAs. Solid InP also exhibits high dissociation pressure of phosphorus, e.g., 0.6 atm at 1000°C. Therefore, it becomes necessary to prepare an optimum temperature profile and a suitable atmosphere during InP crystal growth in order to suppress the dissociation of phosphorus. These conditions make the growth of InP single crystals more difficult than that of GaAs.

2.3 CRYSTAL GROWTH USING LIQUID ENCAPSULATED CZOCHRALSKI TECHNIQUE

The important semiconducting compounds formed between the Group III (Gallium, Indium) and Group V elements (Arsenic, Phosphorus) dissociate at the melting point and it makes pulling difficult. Initial attempts to overcome this were based upon having the arsenic or phosphorus vapor in equilibrium with the melt by maintaining the whole enclosure at a temperature above the sublimation point of arsenic or phosphorus and by having a reservoir where temperature was adjusted to control the pressure problems associated with pulling. The above said conditions were entirely suppressed by the development of the liquid encapsulation technique. In this technique a layer of boric oxide which acts as the encapsulant covers the melt. B₂O₃ is used as an encapsulant due to its several advantages namely,
Figure 2.2  Phase diagrams of the In-P system
a. its relative low density enables it to float over the InP melt
b. chemically non-reactive with either the crucible or the InP melt
c. highly transparent
d. low melting temperature enabling it to melt before the charge melts
e. easily available in high pure form with specified quantities of water content

2.3.1 Improved methods of growth

The growth of InP was developed later than GaAs because of the difficulty in obtaining twin-free single crystals. Since InP has some superior physical properties compared with other III-V compounds, the demand and application are being extended year by year. In the growth of InP single crystals, there are two major processes, namely, the synthesis of polycrystals and the growth of single crystals. Polycrystals of InP can be synthesized by several methods, namely, horizontal Bridgman (HB) (Yamamoto et al. 1981), gradient freezing (GF) (Adamski 1983), Synthesis Solute Diffusion (SSD) (Kubota 1984; Kaneko et al. 1973) and injection of phosphorus into indium melt (Farges 1982).

Single crystals are grown using Liquid Encapsulated Czochralski technique (LEC) (Bonner 1981; Shinoyama et al. 1981; Arokiaraj et al. 1994). The Vertical Gradient Freeze method (VGF) (Gault et al. 1986) and modified LEC (Tada et al. 1987) have been developed to obtain single crystals with low dislocation densities. The HB and LEC methods are currently employed for the production of InP. The two major useful techniques in present technology for bulk growth are the Liquid Encapsulated Czochralski (LEC) and the Vertical Gradient Freeze (VGF). By using closed systems (like VGF or encapsulant free pressure controlled LEC, PC-LEC), one can change the melt stoichiometry as desired before and during the growth, through adjustment of the temperature of the group V reservoir.
One problem which arises in conventional LEC is that the crystal is exposed to high temperature for a long time with severe effects on the crystal quality (pronounced surface roughness, formation of indium or gallium droplets over the periphery). To overcome this problem either fully encapsulated Czochralski (FEC) (Kohda et al 1985) or a vapour-pressure controlled Czochralski (Hosokawa et al 1992) or Phosphorous Controlled Liquid encapsulated Czochralski (PC-LEC) (Kohiro et al 1996) have been investigated. This enables crystal growers to pull crystals under very low thermal gradients and thereby reduce the usual problems of surface decomposition and degradation. The addition of vapour control makes the Czochralski system very flexible and competitive with Bridgman technology, in relevance to stoichiometry control.

2.4 PROBLEMS ASSOCIATED WITH THE GROWTH OF InP

The growth of InP single crystals is more frequently impeded by the occurrence of twinning. Many investigators have reported on the twin-free growth conditions. Bonner (1981) and Bachmann et al (1975) have suggested that selection of the boric oxide encapsulant, polycrystalline InP and seed crystal, and control of the growing crystal diameter are effective for twin-free growth.

The magnitude of stacking fault energies for many III-V compounds has been reported by Gottschalk et al (1978). Table 2.3 shows the stacking fault energy and lower resolved yield stresses of III-V compounds. Iseler (1981) has shown that the probability of twinning is decreased by increasing the temperature gradient at the crystal-melt interface. However, Muller et al (1982) found that a distinct decrease of the twin formation and the EPD was obtained by decreasing the temperature gradient near the interface and shifting the maximum to crystal regions of lower temperature. Shun-ichi et al (1986) have studied the twin boundary structure by X-ray topography and have correlated between twinning and growth conditions,
the polycrystallisation process by twinning and the effect of twinning on dislocation behaviour. The application of magnetic field may also be effective in preventing the occurrence of twinning.

Table 2.3

Stacking fault energy and lower resolved yield stress of III-V compounds

<table>
<thead>
<tr>
<th></th>
<th>GaSb</th>
<th>GaAs</th>
<th>InSb</th>
<th>GaP</th>
<th>InAs</th>
<th>InP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stacking fault energy (meV/atom)(^a)</td>
<td>53</td>
<td>47</td>
<td>43</td>
<td>33</td>
<td>30</td>
<td>17</td>
</tr>
<tr>
<td>Lower resolved yield stress (N/mm(^2))(^a)</td>
<td>15.8</td>
<td>1.9</td>
<td>5.0</td>
<td>4.0</td>
<td>0.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\(^a\) At T= 0.65 T\(_m\), where T\(_m\) is the absolute temperature of the melting point.

There are many factors that could be responsible for twinning and these factors must be optimized before one can grow single crystals without any twinning.

Boric Oxide: The thickness of the B\(_2\)O\(_3\) layer and the water content in B\(_2\)O\(_3\) have all been attributed to play an important role in the quality of the grown crystals. However, no conclusive evidences could be made except the fact that the lower water content and optimum thickness control can be helpful to achieve the desired temperature gradient.

Rotation conditions (crystal rotation and crucible rotation): The melt convection phenomenon is theoretically explained by Donaghey (1980) as a function of crystal rotation and crucible rotation. By controlling the crystal rotation and crucible rotation, the solid/liquid interface shape can be
Convex shape towards the bottom of the crucible has been found to be preferable to prevent twin formation (Oda et al. 1990).

**Temperature distributions:** For growing twin-free single crystals, a larger axial temperature gradient is desired. The temperature gradient can be controlled in various ways: by changing the crucible heater structure (Shimada et al. 1984), by changing the inert gas pressure (Shinoymama and Uemura 1985) or by changing the axial gradient by using suitable thermal baffles (Katagiri et al. 1986).

The radial temperature distribution on the surface of the InP melt affects the solid-liquid interface. When it is small, the interface shape becomes flatter, and when it becomes larger, the interface shape becomes convex towards the bottom of the crucible. The radial temperature distribution can also be controlled by factors such as rotation conditions, inert gas pressure, boric oxide amount and the application of a magnetic field.

Localized temperature variations also influence the occurrence of twinning and in some cases the segregation of dopants and impurities. Temperature variations are influenced by various parameters such as the atmospheric gas pressure, the structure of the hot zone and the boric oxide thickness. Application of an appropriate magnetic field has been found to be effective in decreasing the temperature variations. It is very difficult to minimize localized temperature variations while meeting the other requirements, but this must be achieved to eliminate twin formation and effectively reduce the precipitation of impurities and dopants.

**Crystal shape:** The crystal shape, especially the development of the cone angle or the shoulder shape, is a factor that contributes to twin formation. Normally when twin occurs, it begins from the shoulder part as shown in Figure 2.3. Since the normal twin planes have <111> orientation,
twin planes are of two different kinds, the indium plane (A plane) or the phosphorus plane (B plane) towards the growth direction. Angle relationships between twin planes and pulling directions are shown in Figure 2.4. Bonner (1981) has recommended enlarging the shoulder with an angle less than 19° towards the growth direction. However, Muller et al (1985) has discussed that the cone angle does not have any effect on the twin formation. It was observed that the enlargement of the cone angle does not influence twin formation in the present investigation.

Melt composition stoichiometry: The melt composition is important to prevent twin formation and also in reducing the defect densities. If the initial melt composition itself deviates from stoichiometry then the deviation becomes larger and larger as growth proceeds. In the case of InP, normally the starting material stoichiometry is towards the indium-rich side. Hence, twinning and/or polycrystallization takes place easily and therefore, indium inclusions in InP polycrystals should be avoided.

Growth Rate: Decreasing the growth rate is also considered to be one of the ways to prevent twin formation, but this has not been recommended due to several practical reasons, such as the exposure of the crystal surface to a high temperature for longer time resulting in the loss of phosphorous.

Optimization of the above said parameters is necessary for establishing dependable technology to grow twin free and low dislocation InP. Hence, in the present study, efforts have been made to obtain a better understanding of the twinning mechanisms in LEC grown InP crystals and to find out the parameters of twin-free growth.
Figure 2.3  Twinning planes relative to the crystal pulling direction

Figure 2.4  Angle relationship with twinning
2.5 SYNTHESIS

Due to the high pressure of phosphorous (Bachman et al 1974; Fornari et al 1994), it is difficult to perform "in situ" synthesis before pulling (Farges 1982; Prasad et al 1994) and hence the LEC method requires InP polycrystals to be synthesised as starting materials outside the pulling machine, by another method.

\[ \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \]

2.5.1 Different types of synthesis of polycrystalline InP

There are a number of methods used for synthesizing polycrystalline InP, but the most commonly used methods are horizontal Bridgman technique, gradient freeze technique synthesis in a high-pressure puller. The best polycrystal synthesis technique should produce high purity polycrystals, less indium inclusions and high synthesis rate.

The horizontal Bridgman technique is more widely accepted since the synthesis rate is reasonably fast and it is possible to realize InP polycrystals with reasonable purity and few indium inclusions.

The horizontal gradient freezing technique offers a very high growth rate. Since this method requires a temperature higher than the melting point, the purity normally degrades due to the introduction of silicon from the quartz ampoule.

Synthesis by the solute diffusion (SSD) is a technique by which it is possible to obtain ultra-pure InP polycrystal because growth can be performed at lower temperatures and the contamination of silicon from the quartz ampoule is less.
The direct synthesis technique offers the possibility of producing more pure InP crystals with a very rapid synthesis rate. For direct synthesis, three methods have been investigated:

1) phosphorus vapor injection technique (Sasaki et al. 1985)
2) the liquid phosphorus encapsulation method (Inada et al. 1987)
3) the direct synthesis of indium and phosphorus in a very high pressure chamber (Tongnian et al. 1991; Prasad et al. 1994)

2.6 InP LEC SINGLE CRYSTAL GROWTH

2.6.1 Starting Material

The starting polycrystalline InP ingots used for the growth experiments were procured from Hebei Semiconductor Research Institute, China. The synthesis have been carried out in-situ in a high pressure puller to obtain starting materials as pure as possible for single crystal growth. The starting material used for synthesis were of 6N phosphorus and 6N indium. The starting polycrystalline yielded a background donor density $N_d-N_a = (1-5) \times 10^{15}$ cm$^{-3}$ and mobility $\mu = (2-4) \times 10^3$ cm$^2$/V-s at 300K. Higher quality InP has only been reported using low pressure low temperature solution synthesis techniques. Antypas et al. (1977) have synthesised InP with $N_d-N_a = 6.8 \times 10^{14}$ cm$^{-3}$ and $\mu = 9.1 \times 10^4$ cm$^2$/V-s (at 77K) by horizontal Bridgman (HB) at 940°C and 2.5 atm of phosphorus. In contrast to this Allred et al. (1981) obtained ingots weighing 1-2 Kg within few hours by rapid synthesis of nearly stoichiometric melts followed by controlled directional freezing in an autoclave. However, the average net carrier concentration and mobility at 77K for approximately 20 ingots were $1.5 \times 10^{16}$ cm$^{-3}$ and 15,000 cm$^2$/V-s respectively. Wardill et al. (1981) have obtained ingots weighing 1600g with carrier concentration and mobilities in the range $2.7-8.0 \times 10^{15}$ cm$^{-3}$ and 4000-5300 cm$^2$/V-s at room temperature. The highest mobility measured at 77k was 41,000 cm$^2$/V-s. Nearly equivalent electrical
characteristics have been reported for bulk InP prepared using the synthesis solute diffusion (SSD) technique (Kubota and Suggii 1981).

2.6.2 LEC crystal growth

LEC pulling was first described and applied to InP by Mullin et al (1968) and has been developed to a high degree of perfection (Kohiro et al 1996). The apparatus employed for the present investigations is a CI 351 high pressure puller (Figure 2.5) which consist of a graphite resistance heating system and stainless steel pressure chamber. The cross-sectional view of the puller is shown in Figure 2.6. The whole system is placed on a vibration free platform and housed in a well guarded room with proper ventilation and exhaust systems. The growth chamber is cooled through a continuous water circulation chilling plant. The entire system is supported by uninterruptible power supply (UPS) in turn backed up with a diesel generator (DG).

Before any crystal growth process, the inner walls of the high pressure chamber is properly cleaned and the system is baked under vacuum for few hours at the operating temperature and all controls are checked to ensure that there is no problem in the system. The system is baked twice or thrice and cleaned properly before commencing the actual crystal growth experiment. Once when the system is made ready, the polycrystalline InP ingots are etched in HCl:HN0₃ solution for a few minutes. After etching, the polycrystal is properly washed using deionised water to completely remove the acid content and is kept under methanol. If necessary the quartz crucible of 4 inch diameter, (either flat or round bottom) is also etched in acqua regia and cleaned well. An oriented seed of either <100> or <111> of 4mm x 4mm cross-section and 5 cm length is fixed to the seed holder. The seed is etched in HCl:H₂O for few minutes and washed in deionised water and rinsed in methanol. <111> oriented seed is
Figure 2.5 High pressure LEC puller used for the growth of InP
Figure 2.6  Cross-section view of the high pressure puller
mounted always with <111>B face towards the melt since with <111>A face indium drains cause instability problems at the interface.

The polycrystalline material and the crucible are dried and the polycrystalline material is closely packed inside the crucible. The charge with the crucible is transferred into the chamber and is placed inside the crucible holder in the growth chamber and the boric oxide pellets of known water content and weight is put on top of the polycrystalline material; the growth chamber is immediately evacuated; then, high pure Argon gas is passed into the system.

The melting process of InP is carried out as quickly as possible under the boric oxide encapsulant with an over pressure of argon (40 to 45 atm.). Seed rotation rate of 5-8 rpm, crucible rotation rate of 5-10 rpm and the pulling rate of 4-10 mm/h are usually used for the growth of InP crystals. When the temperature of the InP melt is stabilized, the seed crystal is made to touch the melt surface. The diameter of the growing crystal is estimated using the differential weight, recorded through a load cell housed on the top of the pull rod. The shape of the crystal can be controlled by adjusting the temperature at the growth interface and the pulling rate of the crystal. After growth the furnace is slowly cooled to room temperature, since rapid cooling increases the dislocation density in the crystal and also breakage of wafers during slicing. The grown InP single crystal is removed from the chamber and the subsequent evaluation of the crystal is carried out after oriented cutting and polishing.

Investigations have been made to understand the influence of the growth parameters on the probability of twinning.

Initial growth runs resulted in twinned crystals. The temperature gradient at the crystal melt interface was observed to be very high and was inferred that this enhanced the occurrence of twinning. In order to reduce
the temperature gradient at the interface to an optimal minimum, suitable modifications were made in the heater assembly. Round bottom quartz crucibles were used to increase the melt level with respect to the graphite resistance heater, so that the temperature gradient at the solid / melt interface was optimum. The thermal field was made to be more concentrated by introducing a graphite blanket in between the thermal shields.

The encapsulant thickness greatly alters the thermal gradient at the seed/melt interface. Relatively thick layers of boric oxide were used during the initial growth runs and this always resulted in a high degree of twinning. The temperature gradient was altered by decreasing the thickness of the boric oxide and this reduced the probability of twinning.

The crucible position inside the heater assembly greatly contributed to the temperature gradient present at the interface. A high thermal gradient between the growth interface and the encapsulant resulted in thermally etched outer surface of the grown crystals (Figure 2.7). By locating the suitable crucible position within the heater, the optimal thermal field was attained which reduced thermal etching and improved upon the yield of untwinned boules.

The crucible configuration was further modified by reducing the height of the crucible. 3 to 3.5 cm of the top portion of the 100 mm crucible was cut away and growth runs were performed. InP crystals grown with reduced crucible height were of good quality.

Any attempt to remelt partly or fully a growing crystal which showed indications of twinning resulted in poor visibility of the growth interface. Table 2.4 shows the important growth parameters that were varied and optimised to grow good quality InP single crystals.
Table 2.4
Varied and Optimised Growth conditions for InP

<table>
<thead>
<tr>
<th></th>
<th>Varied parameters</th>
<th>Optimised parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of polycrystalline InP</td>
<td>1200 - 600 gms</td>
<td>1000 gms</td>
</tr>
<tr>
<td>Seed Orientation</td>
<td>&lt;111&gt;, &lt;100&gt;</td>
<td>(111&gt;, &lt;100&gt;</td>
</tr>
<tr>
<td>Seed Rotation rate</td>
<td>5 - 8 rpm</td>
<td>6 rpm</td>
</tr>
<tr>
<td>Crucible rotation rate</td>
<td>5 - 10 rpm</td>
<td>8 rpm</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$ water content</td>
<td>100 - 350 ppm</td>
<td>310 ppm</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$ thickness</td>
<td>10 - 15 mm</td>
<td>13 mm</td>
</tr>
<tr>
<td>Argon counter pressure</td>
<td>35 - 55 atm</td>
<td>40 atm</td>
</tr>
<tr>
<td>Pulling rate</td>
<td>4 - 10 mm/hr</td>
<td>9 mm/hr</td>
</tr>
</tbody>
</table>

2.7 OBSERVATION OF TWINS IN LEC InP

InP single crystal growth by the LEC technique sometimes failed due to twinning (Hurle 1995), since InP crystals have a strong tendency to twin due to their lower stacking fault energy. Twin boundaries have been observed with simple vision, by chemical etching technique and by X-ray topographic studies (Shun-ichi and Akinori 1986). Twin morphologies were classified as random twins, oblique twins and laminar twins.

2.7.1 Random Twins

The occurrence of random twins and indium drains have been observed when crystals were grown in a high thermal field. Figure 2.8 shows indium drain along the axial length of the grown crystal. Indium drain hinders the growth interface which in turn gives rise to twinning.
Figure 2.7  Crystals showing the outer etched surface

Figure 2.8  Indium drain along the axis of the grown crystal
2.7.2 Oblique Twins

The oblique twins occurred about once out of every ten growth runs. The generation process of the twin boundary is expected to be as follows: if the interface near the boundary is assumed to be slightly concave, the growth process along the radial direction propagates from the crystal periphery to the interior. In this case, the twin boundary, propagates from one point of the periphery and the matrix growth continues from the opposite side of the periphery into the crystal interior. Polycrystallization caused by the oblique twinning is shown in Figure 2.9. From the shoulder part of the growing crystal, one oblique twin boundary nucleated and propagated into the crystal interior. If, new oblique twin boundaries nucleate in the twinned crystal region, then it results in polycrystallinity. The oblique twinning also changes the growth direction as suggested by Steinemann and Zimmerli (1963).

2.7.3 Laminar Twins

Laminar twins are usually observed at the surface of the growing crystal as shown in Figure 2.10. They do not penetrate into the interior of the growing crystal. These kinds of laminar twins have been observed by Bonner et al (1981). Crystals of this habitus occasionally are free of twins once the (111) laminar twins intersect the crystal surface. Twin-free crystals have been grown by maintaining a planar to slightly convex crystal-melt interface in conjunction with the rate of diameter increase.

The surface finish of the crystals were greatly improved by reducing the post heating effects from the crucible walls. Figure 2.11 shows the single crystals of InP grown using the optimised growth conditions.
Figure 2.9  Crystal with Oblique twins.

Figure 2.10  Crystal with Laminar twins
Figure 2.11 Single crystals of InP
2.8 DOPING TECHNIQUES

Specific dopants are added to the melt to realize InP single crystals with desired electrical characteristics and reduce the dislocation densities. The nature and the quantity of dopants is dictated by the specific device structure and its applications. Tin or sulphur are the commonly used dopants to obtain n-type substrate while zinc is added to p-type substrate. Semi-insulating crystals are normally obtained by doping with iron, which can compensate for the excess shallow donors by forming a deep acceptor level. The segregation co-efficient of each dopant varies and hence the crystal property along the growth direction also varies. It is therefore desirable to select dopants that have a very low evaporation rate and an effective segregation coefficient very close to unity. When the dopant has a high dissociation pressure it should be added in the form of indium compounds (In$_2$S$_3$) or phosphorus compounds (Fe$_2$P, Zn$_2$P$_3$) which are having relatively low dissociation pressure.

2.9 WAFER PROCESSING

InP wafer processing steps are shown in Figure 2.12 and is presented below in detail.

Crystallographic properties and electrical properties of the ingots grown by the LEC method are investigated from the seed and tail ends. The outside of the crystal ingots, are ground by a cylindrical grinding machine to define the diameter of the material. A rotating cutting tool makes multiple passes down a rotating ingot until the chosen diameter is attained. Following diameter grinding, two flats are ground along the length of the ingot. The orientation flats serve several purposes for the III-V compound substrate. They serve as identifiers on both sides of the wafers and also as mechanical locations in automated processing equipment. Prior to generating the identifying flats, the ground single crystal ingots are etched
Figure 2.12 InP wafer processing steps
and inspected for the etched surface characteristics. Normally, on the (0\(\overline{\text{1}}\)) face primary flat is identified, and the secondary flat is identified on the (0\(\overline{\text{1}}\)) face.

Slicing is an important process because it determines four wafer parameters: surface orientation, thickness, taper and bow. Orientation can be determined by cutting test wafers and then resetting the ingot axis until the correct orientation is achieved.

The conversion of ground ingots into slices is typically accomplished by inner diameter (ID) diamond sawing. The ingot is prepared for slicing by mounting it in a suitable epoxy, and then positioning the support on the saw. The standard wafers are cut as either 650 or 800 micron in thickness.

Sliced wafers have a vertical flat periphery which tends to be laden with microcracks and is easy to break. Hence the wafers are edge bevelled.

Edge-rounded wafers have the following advantages:
* less damages are developed during device fabrication
* the wafer is more fracture resistant
* the epicrown growth is reduced and
* the buildup of photoresist at the wafer edge is controlled

The previously described shaping operations leave the surface and edges of the wafer damaged and contaminated. The application of etching media to as-cut wafers or as-lapped wafers is effective in removing the surface layers that have residual damage and contamination. The damaged region of InP as-cut wafers is about 10 micron deep and can be removed by chemical etching by using mixed bromine and methanol (or) nitric acid, hydrochloric acid and deionized water. Etching must be carefully done because it is prone to cause nonuniform and nonplanar wafer surface due
to the variation of the etching conditions and the condition of the surface before etching.

Lapping has the following operating functions:

* the regulation and reduction of wafer thickness
* the improvement of the dimensional uniformity and surface flatness.

Lapping can be conducted as a single side or double side process. Alumina abrasive powders typically of 5 to 10 micron size, have been used. This process is carried on until the wafer surface is without any scratch or cutting saw damages.

Polishing is the final step in wafer processing. Sub-surface damage, which is the most important characteristic for InP substrate, is controlled in this process. The required characteristics in this step are

* wafer thickness and its variation
* wafer planarity
* surface smoothness of polished face
* residual damage layer on the polished surface and
* cleanliness of the polished surface.

InP wafer polishing is typically accomplished by a bromine-methanol solution and a rotating pad. Typical processes remove 25-35 µm stock of InP. In the polishing process, the following parameters must be controlled to maintain the polished wafer characteristics such as flatness, taper, and quality of surface finish:

1) composition, flow rate, radial distribution of the polishing material, and temperature of the polishing solution
2) surface speed, relative diameters, rigidity and geometrical contours of the plate on which the wafers are mounted
3) wafer mounting procedures
4) compressibility and polishing solution retention of pads
5) life of polishing pads

The purpose of the wafer cleaning process are as follows:

1) the removal of residual material such as wax and contamination on the wafer backside and
2) the removal of residues such as particles and stains on the wafer front side.

Following very closely all the above said parameters, InP wafers were polished with very good mirror finish. The control of bromine to methanol concentration ratio and the rpm of the rotating pad has been found to play the most important role in obtaining very good polished surface. The pads which are used conventionally for GaAs were not of much use and hence special pads procured from M/s Logitech, UK were only used for InP polishing.

InP polished wafers are cleaned in organic solvents such as trichloroethylene, acetone and methanol and the polished wafers are investigated for their characteristics and further device processing.