CHAPTER 1

REVIEW ON MELT GROWTH, CZOCHRALSKI PULLING AND RECENT ADVANCES IN SEMICONDUCTOR CRYSTAL GROWTH

1.1 INTRODUCTION

In recent years, the field of semiconductors has witnessed a giant leap from the point of view of both science and technology. This has brought about a greater understanding of the underlying physical processes which give semiconductors their unique properties. The advances in growth technology has created better materials which have resulted in faster devices like high electron mobility transistors. The requirements of starting materials has become more severe as device dimensions have shrunk and packing densities have increased. The requirements of industrial production of very-large-scale-integrated (VLSI) circuits necessitate large diameter crystals, virtually free of dislocations and variations in radial and axial resistivity. These needs are largely met with the development of newer crystal growth techniques and sophisticated instrumentation.

Crystal growth plays a vital role in the field of semiconductor electronics. Ability to grow good quality crystals is essential not only for fabricating devices, from the technological point of view, but also for the detailed study of the properties of the crystals, from the fundamental point of view.
The rapid progresses made in the past two decades in the field of semiconductors owe largely to the parallel development in the area of materials. Whether it is for device structuring, or for the study of the material from a fundamental point of view, crystal growth is the starting point. Apart from providing samples for characterisation or device structuring, the growth activity can yield valuable information about the material if a careful study is made to correlate the growth conditions with the electrical and other properties. The growth conditions can also be modified and/or improved to obtain the desired electrical and other characteristics of the crystal. Thus, there is a large inter-play between crystal growth and the study of the various properties of the material. Hence, the interest in crystal growth has always been an integral part of research on materials. The work described in this thesis reflects this spirit and deals with the investigations on both the crystal growth and characterisation studies on Indium Phosphides (InP).

Though there are many crystal growth techniques, the following section will only lay emphasis on the basic aspects of melt growth method.

1.2 IMPORTANCE OF MELT GROWTH

Melt growth is undoubtedly the best method for growing large single crystals at a relatively faster rate and with high perfection. It has been used for many metals, semiconductors, ionic crystals and a few organic compounds. Often, as in the case of semiconductors and laser host crystals, impurities can be deliberately added and homogeneously dispersed in a large percentage of the grown crystals. Melt growth techniques have been widely developed for the growth of crystals used in electronics, optics and synthetic gemstone industries.

However, melt growth normally requires that the material melt congruently and has a manageable vapour pressure at its melting point.
Materials which do not satisfy these requirements are grown from modified melt growth techniques. As good ideas and techniques developed in one growth technique are often carried over and applied to other methods, it is not possible to classify melt growth in an unambiguous way. However, the various melt growth processes can be classified under four major techniques:

1) Normal freezing : ingot gradually frozen from one end to another
2) Crystal pulling : the crystal grows on a seed which is slowly withdrawn from the melt
3) Zone melting : a molten zone is passed through the ingot
4) Flame fusion or pedestal growth : crystal grows below a melt which is fed from the top

1.2.1 Advantages of Melt growth

For bulk growth of high quality single crystal materials seeded melt growth (e.g. crystal pulling or float zone melting) is undoubtedly the best method available today as the method is fast, efficient and can be automated. Particularly, in the bulk growth of compound semiconductors like Gallium Arsenide, Indium Phosphide and elemental semiconductors like Silicon etc., the method produces the most perfect crystals. The use of microgravity conditions for space processing of crystal growth are exciting for the future, since the elimination of gravity-induced problems could compensate for the increased expense, especially if the products are to be used in space.

1.2.2 Concept of Melt growth

There is a latent heat associated with a first order phase change and consequently the removal of that liberated heat is an important aspect
of the process. It is necessary to control this process by allowing heat flow to occur only from the liquid to the solid i.e. by maintaining the temperature in the melt everywhere greater or equal to the solidification temperature. Failure to achieve this will cause the growth front to be dendritic and also lead to nucleation in supercooled melts ahead of the advancing interface. Hence planar solidification fronts are usually desired. The three primary modes of heat transfer are radiation, convection and conduction.

Radiation is emitted or reabsorbed within the solid itself directly or after internal reflection from the boundary surfaces. Heat losses occur by radiation from the surfaces of the growing crystal or from the free melt surface itself. For most of the melt growth activities the materials are usually heated by radiation. The most commonly used geometry is a cylindrical furnace. This allows heat losses to occur along the furnace axis where the crystal is located. Heat flow through the melt is usually by natural (density gradient driven) and/or forced convection (rotation of crystal and/or melt) and through the solid by conduction. Gaseous thermal convection has also been considered in high pressure CZ system. Convective flows provide very important sources of enhancing mass transfer and thus growth rates in crystal growth processes. Figure 1.1 shows a simplified sketch of the heat transfer mechanisms that are dominant in a LEC puller.

In natural convection, the fluid motions are caused entirely by the action of gravity field on density gradients in the fluid. The important local heat flow balance at the interface is

\[ K_s G_s = V d_s L + K_l G_l \]  \hspace{1cm} (1.1)

where \( K \) is thermal conductivity, \( G \) is temperature gradient, subscripts \( s \) and \( l \) respectively represent the solid and liquid, \( V \) is the growth rate, \( d_s \) is the density and \( L \) is the latent heat of fusion. From the above equation, the growth rate can be determined.
Figure 1.1 Heat-transfer mechanisms in a LEC puller
The controlling parameter in growth from the melt is the heat flow associated with the dissipation of the latent heat liberated at the growing face. The direction of heat flow depends on whether the heat is removed through the melt, or the growing crystal or both. The heat flow provides "forced growth" conditions in which the supersaturation at the interface is again self-regulating to provide the externally imposed growth rate.

1.3 CRYSTAL PULLING TECHNIQUE

Among the crystal growth methods used today, one method which can produce crystals weighing from several grams to many kilograms is the crystal pulling technique. This technique and its various modifications have become the dominant process used in industry today for the production of semiconductor and oxide single crystals.

Growth of crystals by pulling from their melts has become a popular method, largely because of the rapidity with which the method can produce large good quality crystals.

Crystal pulling was first employed by Czochralski to determine the solidification rate of metallic materials. Its real importance was realised in early 1950's when it was developed for the production of pure and doped crystals of Germanium and Silicon. Subsequently, it has been used for some III-V semiconductors using the Liquid Encapsulation Czochralski (LEC) when there is high vapour pressure of arsenic or phosphorous (Mullin et al 1968; Metz et al 1962).

The schematic of the crystal pulling process is shown in Figure 1.2. The material to be grown is placed in a suitable crucible. The crucible is then heated either by resistance or induction heating until the charge is melted. The temperature of the molten charge is then adjusted so that the center of the melt is at its freezing point. A seed crystal is dipped into the
Figure 1.2  Schematic process of pulling technique
melt, and the crystal growth or "pulling" process is begun by slowly withdrawing the seed. With proper temperature control of the melt, crystallization on the seed crystal can be started as the seed is withdrawn from the melt. Further adjustments of the melt temperature during the pulling process provide control of the crystal diameter. When the desired length has been reached, the crystal is quickly raised from the melt surface or the melt temperature is slowly increased to reduce the diameter. When the crystal is free from the melt, the temperature is lowered to room temperature and the crystal withdrawn from the growth apparatus.

Dislocation free crystals have been grown by necking technique originally introduced to produce a single crystal from a polycrystalline seed. Dash (1959) grew dislocation free Si crystals and since then crystals of Ge, GaAs, InP and GaP have been grown. All these materials find their use in the electronic industry, primarily as substrates for electronic devices. Because this technique is a relatively fast crystal growth process, it also finds wide application in the laboratory for the synthesis of single crystals of many new materials. The general advantages of the pulling method are shown in Table 1.1. These are desirable when versatility and ease of adaptability are of prime concern.

Table 1.1

Advantages of Pulling Method

<table>
<thead>
<tr>
<th>Technique</th>
<th>Metals</th>
<th>Semiconductors</th>
<th>Oxides/ceramics</th>
<th>Other ionic materials</th>
<th>Organic materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal Bridgman</td>
<td>***</td>
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<td>*</td>
<td>**</td>
</tr>
<tr>
<td>Vertical Bridgman</td>
<td>*</td>
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<td>**</td>
<td>***</td>
<td>*</td>
</tr>
<tr>
<td>Czochralski</td>
<td>*</td>
<td>***</td>
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<td>**</td>
<td>*</td>
</tr>
<tr>
<td>Zone melting</td>
<td>***</td>
<td>***</td>
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</tr>
</tbody>
</table>

* - More number of stars indicate stability and extent of application
1.3.1 Material Considerations for Crystal Pulling

The material which is to be grown by the crystal pulling technique has several requirements and restrictions. For a material to be considered as a possible candidate for crystal growth by the crystal pulling technique, it has to satisfy several conditions. The material should have a congruent melting point and the material should not decompose upon or before melting. It should not have a first order phase transitions or reconstructive phase transitions and there must be a crucible material which is non reactive with the material above its melting point. Once the material has been chosen to be grown by the crystal pulling technique, the first important selection which must be made is the choice of a crucible and its size.

1.3.2 Crucible Selection

Selection of the crucible material is based upon (1) compatibility with the melt (2) melting point of the crucible material (3) type of heating to be used (4) chemical stability and (5) mechanical properties. For the growth of semiconductor materials like Silicon, Germanium, Gallium Arsenide, Indium Phosphide, Gallium Phosphide etc, the most commonly used crucible material is fused silica. It provides the most suitable compromise between chemical stability, cost, ease of fabrication and several other factors. Usually, these crucibles are used only once and discarded because, upon cooling, expansion of the freezing liquid causes the crucible to fracture. With the advent of Pyrolitic Boron Nitride (PBN) crucible better quality crystals are grown and can be used for several times with proper cleaning and preservation of the crucible.

The second factor which must be considered is the size and the shape of the crucible, which can strongly influence the results of any crystal growth experiment. In any heated system the primary source for the fluid
motion within the crucible is due to liquid density changes resulting from temperature gradients. This effect is always present except in space.

The final factor which must be considered is the crystal size which can be grown from a crucible of given dimensions. A general rule is that the final crystal diameter should be approximately half of the crucible diameter. When this value is exceeded, growth becomes more difficult for several reasons:

1. Small irregularities in the crucible diameter can produce large changes in the growth rate.
2. The rotating crystal has a much stronger influence on the fluid flow thereby giving rise to abrupt flow transitions and large temperature fluctuations.

### 1.3.3 Furnaces

In all crystal pulling techniques, the material from which the crystal is to be grown must be kept in the molten state. The commonly used heating systems are either of resistance heating or of induction heating. Resistance heated furnaces are usually used for lower temperature ranges (less than 1500°C). They are mainly used in the growth of semiconductor materials and for a few low melting oxides. A general advantage of the resistance heated furnaces over others is the greater electrical efficiency and reduced operational costs.

The other source of heating is r.f. or inductive heating which is generally used for higher melting oxides. However, it can also be used for the growth of semiconductor materials. The use of r.f. heating system depends on the physical conditions of the crucible and proper load matching. Improper load matching will cause enormous loss of efficiency. Thus in
choosing a r.f. heating unit, care must be taken to select a unit which provides the best compromise between uniformity and versatility.

1.3.4 **Requirements of a good puller**

The main requirements of a good puller are:

* a rigid, vibration-free main frame
* vibration-free lifting and lowering mechanism for both seed and crucible with seed pulling rate as low as 0.1mm per hour and as high as 10 cm per hour
* a limiting switch for the axial movement of both seed and the crucible; vibration-free rotating mechanism for the seed and the crucible
* a stable and controllable power supply to heat the charge to a temperature in excess of its melting point and water cooled vessel for high pressure growth
* gas inlet and outlet facility with the outlet passing through a suitable solvent system
* dependable gas metering and safe exhaust facilities
* a good viewing system with a video monitor to continuously assess the growth process

Other requirements for a better pulling are:

* high purity chemicals and clean environment
* suitable range of crucibles designed to give an appropriate thermal distribution and those which do not contaminate the melt
* good vacuum pump to evacuate the system initially
* good ventilation system
1.3.5 Operations of high pressure puller

A typical procedure for operating such a puller are:

* all the system functions are checked thoroughly
* the growth chamber is cleaned well and the viewing ports are also cleaned well
* the crucible is cleaned properly as required for the given crucible material
* the charge is prepared in the purest environment and may be etched to remove oxides as well as unwanted impurities on the surface
* the seed is fastened to a seed holder ensuring that there is no axial disalignment
* the crucible is loaded with the charge and the seed crystal is fitted into the chuck and the axial alignment of the seed is secured
* the chamber is assembled, evacuated and then flushed with ambient gas
* the crucible and seed rotation are started
* the charge is molten with the use of preset power control programme and the temperature of the melt is held a little above its melting point
* the seed initially held well above the melt is slowly lowered to a position a little above the melt surface and is allowed to attain thermal equilibrium
* the seed is lowered into the melt very slowly and fine adjustments to the melt power is made until the seed supports a meniscus (a fine halo is always seen around a growing crystal and it is normal practice to loose the first contact)
* after ensuring the seed crystal diameter has started to enlarge, pulling is started in such a way that a thin neck has been
made and then it is pulled at the desired speed normally ranging from 5-20 mm/hr

* the growth is continuously monitored and once the growth is over the furnace is cooled in such a way that there is no great thermal shock to the grown crystal

* the grown crystal is weighed and then characterised to understand the influence of the growth parameters.

1.4 RECENT DEVELOPMENTS IN THE GROWTH OF LARGE SIZE CRYSTALS OF III-V COMPOUNDS

1.4.1 Current Growth Techniques

The choice of growth methods [(i.e., Czochralski (CZ), Float-Zone, (FZ), Vertical and Horizontal Bridgman (VB and HB), Vertical Gradient Freeze (VGF), and their modifications, Magnetic Czochralski (MCZ), Horizontal Magnetic Czochralski (HMCZ), Liquid Encapsulated Czochralski (LEC), Magnetic Liquid Encapsulated Kyropoulos (MLEK)] is often discussed in terms of the dislocation density and maximum diameter attainable. Growth of low dislocation III-V crystals using the Vertical Gradient Technique (VGF) (Figure 1.3) has other major advantages in which low-thermal gradient can be easily achieved (Hofmann et al 1993). However, CZ or its modifications have been used most frequently because of their high yield rates and easy handling.

Recent developments in the growth technology for single crystals of InP and GaAs are by modified CZ techniques. A larger diameter is always an industrial target and there is a close relationship between the dislocation density and the temperature gradient across the growth interface (Masatomo et al 1993; David et al 1993). For example, with increase in the diameter size of InP crystal from 2 to 3 inches, temperature gradient near the interface should be decreased from 140 to 35°C/cm in order to keep a low dislocation density (EPD<10⁴ cm⁻²). However, a lower temperature gradient
Figure 1.3  Schematic process of VGF technique
leads to a higher surface temperature of the grown InP crystal where InP easily dissociates. The phosphorous vapour controlled LEC (PC-LEC) method has been developed and used to successfully suppress the dissociation of InP as shown in Figure 1.4. In the growth of GaAs crystal, the arsenic precipitates in undoped GaAs material can be reduced by Multiple-Wafer-Annealing (MWA) method. This technique is employed at a high temperature, up to 1100°C, under an arsenic atmosphere of the stoichiometric composition, which converts an initial arsenic-rich composition to nearly stoichiometric composition.

Advances in silicon bulk crystal growth has so far achieved a crystal diameter of 8 inches. However, manufacturers are now intensively developing giga bit DRAM chips, which hopefully will motivate them to achieve further large diameter growth of silicon single crystals by the year 2000. Currently special attention is focussed on the problems associated with micro defect formation resulting from the crystal size enhancement. This problem must be solved in order to grow still large diameter crystals. A possible solution envisaged is growth by HMCZ method, controlling the thermal gradient and thermal history during crystal growth (AACG, Newsletter 1995).

1.4.2 Recent Advances in InP devices

Multimedia applications need very fast electronics and InP material systems based on band gap engineering and other techniques have already demonstrated

* High electron mobility transistors (HEMTs) with cut-off frequencies as high as 340 Ghz
* AT & T and Hughes with hybrid transistors (HBTs) in the 160 Ghz range
* 213 GHz oscillators
* wide band (0.1 to 70 GHz) MIMICs with 17dB gain.
Figure 1.4 Modified LEC technique
1.5 SUMMARY

In summary, InP materials may be unchallenged over a range of commercially significant operating frequencies in the optoelectronics device arena. This group of devices would include detectors, photodiodes, lasers and opto-electronic integrated circuits (OEICs). In the field of HBT, HEMT, FET discrete devices and for small scale integrated circuits, indium phosphide materials have already demonstrated a very wide operating bandwidth. In spite of competition from silicon and gallium arsenide based systems, InP circuits appear to be creating important new commercial markets. The reliability and performance of some InP based HBT devices already exceed those of gallium arsenide devices, thereby opening up further potential markets for InP based devices.