2.1. Introduction

The demand for large and perfect single crystals for devices, initiated a search for understanding the basic parameters involved in the process of crystal growth. This resulted in considerably improving the technology of producing highly perfect crystals. The present chapter deals with the technological aspects of the different growth methods currently employed.

2.2. Growth from Melt

For the growth of single crystals from melt, the transition from an equilibrium state in which the substance is completely molten to a state where the substance is completely solid, is to be controlled effectively. The portion of the grown crystal serves as a conducting path for the latent heat and the conductivities often coincide with the direction of easy growth. The growth from melt thus essentially involves the control of temperatures. The various methods described below achieves this by a variety of techniques.
a) Czochralski pulling

This technique proposed in 1918 still remains the most reliable method for the growth of large single crystals in a relatively short time. In this method the material to be grown as single crystal is melted in a crucible. A seed crystal is introduced into the melt and then withdrawn slowly. The seed crystal is often rotated while pulling to attain thermal symmetry and to stir the melt.

The various parameters that can be controlled are the rotation and pulling speeds, atmosphere of growth and temperature of growth. The efficiency of the method thus depends upon the smooth rotation and pull rates as well as the constancy of temperature of the melt.

The ideal materials suitable for pulling are those having a congruent melting point, a low vapour pressure and low viscosity. The absence of a phase change in the range of room temperature and growth temperature is desirable.

(1) Crucibles

The crucible material is to be so selected that it is insoluble or slightly soluble in the melt. Crucibles should be readily cleanable so that
impurities can be easily removed. Since crystal pulling often involves high temperatures, crucibles should have high strength and low porosity. If r.f. heating is used the resistance of the container is of importance. The non-uniformity of the crucibles will develop hot-spots and the temperature of the melt will vary laterally producing a non-circular cross section in the pulled crystal.

(ii) Methods of heating

The melt from which the crystal is being pulled should be heated up to an appropriate temperature and held constantly. A variety of techniques have been used to heat the charge. Resistance heating, in which the heating element is wires or tapes of nichrome, kanthal, tungsten or stainless steel [53], is widely used. Machined graphite or silicon carbide heaters which form self-supporting heaters are used in the high temperature region [54]. Radio frequency heating is the most commonly used method of heating which has the advantages of ease of control and operation [55]. R.f. heating only heats the outside layer of the susceptor. The depth of this layer $D$ called the skin depth is given by

$$D = \frac{2570}{V_f \mu} \text{ cms}$$  \hspace{1cm} (53)
where \( f \) is the frequency and \( \rho \) is the resistivity. As the frequency is reduced the skin depth is increased resulting in the uniform heating of the crucible. Frequencies of the order of 10KHz to 500KHz have been found to be the most useful.

(iii) Seeds

The chief advantage of Czochralski pulling method is that crystals of desired orientation can be grown by using a suitably oriented seed. Seeds of low dislocation density should be selected and etched to remove the work damaged outer layer. The seed is usually annealed to reduce the dislocation content. If a suitable seed crystal is not available polycrystalline material, single crystals of another material, a capillary tube or wires of non-reactive metals may be used. In order to grow better quality crystals the diameter of the crystal is reduced and then increased to the desired diameter. This necking operation, helps to eliminate the propagating dislocations from the seed and to select a single grain from the polycrystalline seed for further growth.

(iv) Pull and rotation rates

The rotation of seeds provide effective stirring of the melt decreasing the thermal gradient present in it. The quality of crystals is dependent
on the nature of the solid-liquid interface. A flat interface avoids both non-uniform impurity distribution and facet formation. The study of flow patterns [56] have shown that alternate stopping and/or reversing the rotation prevents the incorporation of impurities into the crystal.

The pulling rate controls the diameter of the crystal. The pull rate if increased will result in the reduction of the diameter of the growing crystal. The same effect can also be produced by increasing the temperature of the melt. Often control of both is required to perform the necking operation. An increase in diameter of the crystal increases the strain and result in the production of dislocations. Often a compromise is to be made between the ultimate crystal diameter, melt temperature and dislocation density.

(v) Modifications on the Czochralski system

The conventional apparatus have been modified by many workers to suit the different requirements for growing specific materials. Miyasawa et al [57] have effectively controlled the diameter of the growing crystals automatically by the use of an analogue control coupled with a crystal weighing system. Mateika et al [58] have described the details of a typical Czochralski
crystal puller with automatic diameter control. For InSe [59] a floating disc with a rectangular slit over the melt have been found to improve the crystal quality.

The liquid encapsulated Czochralski (LEC) method [60] uses a thick blanket of molten boric oxide and a sufficiently high pressure over the melt to prevent the decomposition and escape of vapours. The need for high pressures to prevent the loss of vapours of volatile compounds have resulted in the design of chambers which can withstand such pressures [61].

b) Bridgman method

In this method the control of the transition from melt to solid is effected by controlling the temperature at the melt-solid interface. The furnace often has two halves separated by an insulating disc. The upper half is maintained at a temperature higher than the melting point of the material while the lower at a temperature below it. The material in a tubular container is held in the upper zone so as to melt completely. The container, suspended from a wire is then lowered to the second zone with the help of a reduction motor. Spontaneous nucleation occurs at the tip of the container as it traverses the gradient. For specific materials the tip shape [62], temperature
gradient [63] and the lowering rate are found to be of importance. To select a single grain out of the many formed during the spurious nucleation a constriction in between the main body of the container and tip, is found to be effective.

(1) Containers

The containers vary from glass, silica and quartz to refractory materials [64]. For low melting point materials glass containers can be conveniently used. This may be evacuated and then sealed. For high melting point materials graphite, carbon, platinum and some refractory oxides have been used. The bulk of the heat of fusion liberated on solidification is to be removed by conduction along the container and through the grown crystal. For materials having low temperature conductivities silica tubes coated with graphite have been found successful.

(ii) Furnaces

Depending upon the temperature required, the furnaces can be made from tubes of glass or graphite wound with kanthal wire. R.f. heated furnaces can also be used. The temperature profile is to be carefully shaped by proper winding or through the reduction
of tube diameters. The general profile of temperature depends upon whether both ends of the furnace tubes are closed or opened.

(iii) Traverse mechanism

Many variants of this method exists in which either the crucible is lowered or the heater is raised, slowly. In the former case rotation of the crucible while lowering have been found to increase the probability of strain-free single crystal growth. The movement of either crucible or furnace can be made by a simple clockwork mechanism or other complex rotation lowering systems [65].

The method has several disadvantages. The crystal, being confined to the crucible, will be highly strained. Solids which expands on solidification cannot be grown by this method. The orientation of the crystal cannot be controlled.

For materials having low melting points and low decomposition pressures externally supported crucibles have been used to prevent the thermoelastic expansion and subsequent explosion [65]. Other variants of this method have been discussed in detail by Fischer [66].

c) Zone melting

In zone melting, a small portion of the relatively large ingot is melted and the molten zone is
made to travel along the length of the charge. This method, suggested by Pfann [67] is mainly intended for the purification of materials. The technique can be used to grow single crystals as well.

(1) Zoning in a container

For successful zoning, the container for the charge should have a good lateral heat transfer and a poor longitudinal heat transfer. To achieve this, the container walls are made as thin as possible and in special cases, tubes made up of alternate rings of good and poor conductors pressed together have been designed. For horizontal zone melting the cross-sections of the container vary from semi-circular to trapezoidal. The longitudinal shape should be selected so as to minimise the strain due to solidification. Radial, helical and spiral models have been described by Pfann [68].

The molten zone should preferably have a constant length, a stable solid-liquid interface and a well defined thermal gradient. For materials having low thermal conductivities, the zone width tends to vary. This has been overcome by slowly rotating the container about its axis. Intermittent rotation has been found to be more effective [69].
(ii) Zone refining without containers

Materials which are reactive at their melting point cannot be purified or grown as single crystals by zoning in a container due to the container contamination. The need for a container in such cases have been avoided by using a compacted rod of the material held vertically. A small heater produces a molten zone, which holds the two vertical colinear rods by the surface tension. The molten zone is made to traverse the rod slowly in one direction and fast in the other direction. This method called the Floating Zone Method (FZM) has been successfully used for the growth of LaB$_6$ [70] and other materials [71,72].

2.3. Growth from Vapour

Growth from vapour phase is the most versatile growth process, for the production of pure crystals. Vapour growth of epitaxial films on similar or foreign substrates has immense application potentialities in the semiconductor, opto-electronic and acousto-electric devices.

Any substance, which has appreciable vapour pressure, may be grown as single crystals by condensation on a comparatively cold surface. During growth, molecules
or atoms get incorporated into the kinks on a step after the adsorption and diffusion. A fraction get reevaporated after diffusion.

a) Physical transport techniques

In this technique the polycrystalline source material is heated to appropriate temperatures and the vapour is made to condense on an externally cooled substrate. The problem of crucible material contamination can be avoided in this method by using an electron-beam, focussed on the charge. High power lasers may also be used [73]. Flash evaporation of stoichiometric powders [74] and molecular beam techniques [75] can also be considered as physical transport methods.

Single crystals can be grown by sublimation where the substance is converted directly from the solid to vapour and back again to solid. This may be assisted by vacuum. To obtain flawless crystals the growth rate is to be controlled by working under low supersaturations. The temperature difference between the source and substrate may be conveniently controlled to produce optimum supersaturations. The rate of transfer of molecules, may be further restricted by the use of an inert gas, which then becomes diffusion controlled.
Travelling containers or heaters have also been used satisfactorily for the growth of crystals from vapour. In this technique a quartz ampoule filled at one end with the source material is passed through a furnace whose temperature profile has a single peak. The ampoule can either be closed or plugged with a loose fitting plug. The presence of a tapered end at the growth end has been found to often promote the growth of single crystals. Both horizontal and vertical pulling of heater or container have been found effective for specific materials.

Excellent crystals of hexamethylene tetrarnine and urotropine have been grown by Honingman [77] and Heyer [78]. The heating was achieved by a metal block thermostat and nucleation was promoted by a cold spot. The latter incorporated provision for the measurement of growth rates of individual crystal faces.

b) Chemical transport techniques

In chemical transport technique, the material to be grown as single crystals is made to react with a transporting agent to convert the same into a volatile material and deposition is made by inducing the reverse chemical reaction. The process is mainly used in
systems which has low vapour pressures by themselves and can undergo a reversible chemical reaction.

For the growth of ZnSe, the material is enclosed in a tube with a small amount of iodine gas. At a temperature $T_1$, the material kept at one end of the tube reacts with iodine to form ZnI$_2$

$$\text{ZnSe} \,(s) + \text{I}_2(v) \rightarrow \text{ZnI}_2(v) + \frac{1}{2}\text{Se}_2(v) \quad (54)$$

The vapours travel by convection to the other end kept at a temperature $T_2$ favourable for the reverse reaction,

$$\text{ZnI}_2(v) + \frac{1}{2}\text{Se}_2(v) \rightarrow \text{ZnSe} \,(s) + \text{I}_2(v) \quad (55)$$

(Single crystals)

The ZnSe is deposited in the solid form in this region. Under controlled conditions single crystals have been found to form.

In general the overall reaction for the transport of an element $A$ by an agent $Y$ may be written as

$$A + Y \rightleftharpoons AY \quad (56)$$

The equilibrium constant $K$ is given by

$$K = \frac{P(AY)}{(PY)^Y} = \frac{1}{\alpha_A} \quad (57)$$

where $\alpha_A$ is the equilibrium activity of $A$. If the
value of $\alpha_A$ is below unity, volatalisation will result and if above unity, deposition. This can either be brought out by changing the pressure or the temperature of the system. Due to the convenience the latter is always preferred wherever possible.

c) Chemical vapour deposition (CVD)

CVD is one of the many techniques used, by which a solid material can be deposited on a support. In this method a chemical reaction is used to produce a solid deposit from the gaseous reactants. Currently three different types of reactions are used for the production of single crystal films, viz- 1) the pyrolysis of hydrides, 2) halide reduction and 3) the direct chemical reaction between volatile species to form the desired compound.

For the growth of silicon the reduction of $\text{SiH}_4$ or the reduction of $\text{SiCl}_4$ [79] in presence of hydrogen gas can be used. GaAs, GaP or $\text{GaAs}_{(1-x)}\text{P}_x$ can be grown by the direct reaction of the type

$$ \text{GaCl} + \frac{1}{2} \text{H}_2 \rightarrow \text{GaM} + \text{HCl} $$

where M is either As or P.

Tietjen et al [80] have grown $\text{GaAs}_{(1-x)}\text{P}_x$ by passing HCl over a gallium source kept at 775°C. The volatile gallium chloride which is carried to the
reaction zone at 850°C, reacts with phosphine and arsine. The deposition is made on a suitable substrate kept at 750°C. Bloem et al [81] have reviewed the CVD techniques for silicon. The CVD technique have been used to deposit scandium hydride [82], A-15 superconductors [83] and similar compounds.

2.4. Growth from Solution

Single crystals of materials which have a structural phase transition near their melting points can be conveniently grown from solutions. In this method a saturated solution is prepared in a suitable solvent and crystallisation is initiated by the slow cooling of the solution or by the slow evaporation of the solvent. In the former case the solutions are prepared at a higher temperature and cooled slowly to a lower temperature to produce the supersaturation necessary for growth. This requires a positive coefficient of solubility. A compact arrangement for the growth from solution by slow cooling has been described by James et al [84]. The saturated solution is kept in a tank, heated by an infrared lamp. The seeds are fixed on a seed holder attached to a rotating shaft which enters to the tank through the lid of the container. The temperature of the solution is reduced
at a rate of 0.1°C/day or lower with a Beckman type thermometer and a suitable programmer. Large α-sulfur crystals have been grown by this method [85]. Large and perfect crystals of industrially important crystals like ethylene diamine tartrate (EDT), ammonium di-hydrogen phosphate (ADP) and potassium di-hydrogen phosphate (KDP) crystals are grown by this method. The designs of solution growth apparatus vary from the simple laboratory model described above to complex industrial models.

The substances which have less marked variation of solubility with temperature can be grown by the constant temperature method. The saturated solution is allowed to evaporate at a constant temperature to produce the supersaturation by solvent depletion. A solution prepared in a beaker covered by a filter paper or placed in a desiccator is enough for the growth of crystals. Better control of the evaporation rate have been achieved by Robinson [86]. Forno [87] have designed an apparatus for the growth of hexamine crystals, which involves a vapour recycling principle with suitable stirring mechanism.

Various models of the apparatus used for solution growth have been reported [88]. Delfino [89] have modified the apparatus to grow crystals of ionic
salts not by the temperature change but by the electrolytic solvent-decomposition.

2.5. Hydrothermal Growth

The hydrothermal growth mainly used to grow crystals of quartz [90], utilises the increased solubility of materials in water at very high temperatures above the boiling point of $\text{H}_2\text{O}$. The apparatus required for the method is a thick walled autoclave which can withstand the pressure of the superheated water. A temperature gradient is produced along the length of the autoclave so that the upper portion is at a temperature lower than the bottom. The autoclave is filled with the nutrient and water and closed by self-sealing seals [91]. The seeds crystals, introduced into the upper portion, begins to grow as the nutrient dissolves and moves up the gradient.

Usually, to increase the solubility, a mineraliser like $\text{NaOH}$ is to be added in different proportions. Thus for quartz an addition of 0.5M $\text{NaOH}$ solution has been found to increase the solubility considerably [92]. Zircon single crystals have been grown by Uhrin et al [93]. They have reported that $\text{KF}$-$\text{LiF}$ is a suitable mineraliser for zircon. Addition of $\text{KOH}$ and $\text{K}_2\text{CO}_3$ solutions have been reported to increase the solubility
of tri-octahedral mica in water [94]. Single crystals of a large number of materials like VO₂, Y₃Fe₅O₁₂ and Al₂O₃ have been grown by this method [95,96,97].

2.6. Flux Growth

Flux growth technique is one of the most versatile of the current techniques used to grow crystals. Flux growth is mainly used to grow crystals of materials, whose melting point is too high. The method utilises the lowering of the melting point of materials in molten salts. In the actual growth, the material is melted with a suitable salt, preferably having the material itself as one of the constituents. If the material has a positive coefficient of solubility in the flux, the solution prepared at a high temperature is slowly cooled. In other materials a slow evaporation akin to the solution growth is commonly used.

Platinum crucibles are used wherever possible due to the low reactivity. The crucibles are either closed by a lid and welded together or partially covered. The crucibles are embedded in the hollows made in a refractory brick, and packed with alumina powder. The whole assembly is then placed in a muffle furnace. The growth run is usually performed with the help of a temperature programmer which can be programmed for different cooling rates ranging from 1°C per hour to 40°C per minute.
After the growth, the grown crystals can be removed by washing in a suitable acid which dissolves the flux and not the crystals. The different fluxes suitable for particular materials have been listed in the various reviews [98,99,100]. New fluxes for new materials can be selected from the known phase diagrams [101] or in the absence of a phase diagram by trial and error.

A large number of important crystals have been satisfactorily grown by this method. Beryllia [102], garnet crystals [103] and corundum [104] have been grown, to quote a few. The advantages of flux growth are

1) the low growth temperature compared to the melting point of the pure material
2) the easy doping facility
3) control of stoichiometry, and
4) simple apparatus and control.

The main disadvantages of this method are that

1) the nucleation is spontaneous
2) the exact measurement of the growth temperature is not possible.
2.7. Growth from Gels

The gel method offers reasonable prospects of success in the growth of single crystals of materials which cannot be grown from melt, vapour and solution, due to the decomposition before melting, low vapour pressure or low solubility. Other materials [105,106,107] can also be grown by this method to avoid the thermal strain often introduced during growth from melt and vapour. In the gel method the growth takes place at low temperatures. The gel can be prepared in different ways. In one method a solution of sodium silicate of suitable specific gravity [106] is mixed with a component of the final compound to be grown. On the top of this the other reactant is placed in the form of a solution. This supplies the other component of the material to be crystallised and also keeps the gel from drying out. The components slowly diffuse and react to form the compound. Crystals start to nucleate at the micro-flaws in the gel or at the dust particles, inherently present in them. Another variant of the method uses a U-tube. The gel is kept at the centre of the vertically kept U-tube. The reactants, in the form of solutions, are kept above the gel in the two limbs of the U-tube.
The nucleation and growth of crystals in the gel matrix is controlled by several parameters. The concentration of the feed solution and the pH of the gel have been found to affect the nucleation. The ageing of the gel and gel density also influences the growth and perfection of crystals [108,109]. The optimum values of the various parameters for a particular material is to be found out by trial and error.

The disadvantages of this method are the slow growth rate, which is essentially diffusion limited, the inability to control the nucleation and the relatively small sizes of the crystals obtained.