CHAPTER 2

ALLOY CRYSTAL GROWTH

Crystal growth concepts have been fundamental to many areas of science for quite sometime. Disciplines as diverse as mineralogy, meteorology, biology, medical science, astrophysics and chemical engineering have contributed to and benefitted from the crystal growth concepts. It was, however, not before the onset of the materials science era and the mushrooming development of the electronic and optical materials industries that crystal growth began to develop into a discipline in its own right. In concerted efforts, solid-state physics and crystal growth research has led to many new materials and devices. Their applications have had a great impact on modern life. Today crystal growth forms one of the main pillars of modern technology.

To grow a good crystal is an art as well as a science. At present time it is probably best described as a craft. The growth techniques involve an immense arsenal of laboratory methods ranging from ultra-high vacuum to ultra-high pressures and from cryogenics to plasma temperatures. The success of a technique in obtaining good large crystals depends on various factors:

(a) nature of material itself
(b) its purity
(c) thermal environment
(d) growth rate
(e) pressure
(f) diffusion coefficients of the materials
(g) impurity concentration
(h) homogeneity

The classification scheme for growth techniques can best be an abbreviated version of that of Laudise[1] and is summarized in Table 1.

TABLE 1
Crystal Growth Methods

Monocomponent		Polycomponent	
A	Solid-solid (solid growth) 1. Strain annealing 2. Devitrification 3. Polymorphic-phase change	A	Solid-solid (solid growth) 1. Precipitation from solid solution
B	Liquid-solid (melt growth) 1. Conservative (a) Directional solidification (Bridgman-Stockbarger) (b) Cooled seed (Kyropoulos) (c) Pulling (Czochralski) 2. Non conservative (a) Zoning (horizontal, vertical, float zone, growth on a pedestal) (b) Verneuil (Flame fusion, plasma, arc image)	B	Liquid-solid 1. Growth from solution (evaporation, slow cooling, and temperature differential) (a) aqueous solvents (b) organic solvents (c) molten-salt solvents (d) solvents under hydrothermal conditions (e) other organic solvents 2. Growth by reaction (media as above- temperature change, concentration change) (a) chemical reaction (b) electrochemical reaction
C	Gas-solid (vapor growth) 1. Sublimation-condensation 2. Sputtering	C	Gas-solid (vapor growth) 1. Growth by reversible reaction (temperature change, concentration change) (a) Van Arkel (hot wire processes) 2. Growth by irreversible reaction (a) Epitaxial processes

Thus, as shown in the table, crystals can be grown from the solid, liquid or vapour phases. Since the author has grown single crystals from the melt, only this technique will be described in this chapter.

MELT GROWTH

Growth from melt is the most widely used method for the preparation of large single crystals of metals, alloys and compound semiconductors. The basic principle underlying the melt growth is controlled solidification of the melt so as to promote the extension of a single nucleus without introduction of new nuclei and with minimum of chemical and structural disorders in the crystal. Basically this method involves transfer of heat through the solid-liquid interface. If the temperature gradients in the solid and liquid phases at the growth interface are G_S and G_L, the continuity of heat flux requires

$$K_S G_S - K_L G_L = Lv$$

where K_S and K_L are thermal conductivities of the solid and the liquid, L is the latent heat of solidification per unit volume and v is the growth velocity.

If we require $G_L > 0$, clearly for $v \geqslant 0$, we must have $G_S > 0$ i.e. we must extract heat from the growing crystal. This can occur by conduction down the crystal and radiation from its surface. Also convection will be important.

In the case of alloys, if a gradient in concentration is established in the liquid during growth, there results non-uniform composition of constituents in the alloy crystal and also constitutional super-cooling. The composition of frozen material in such a case is always different from that of the liquid or the molten charge. Also, the probability of stray nucleation is given by

$$P = A^2 v / 2G$$

where A is the constant, v is the rate of growth and G is the temperature gradient. The effective value of G is decreased as a result of constitutional super-cooling and hence P increases. Rutter et al.[2] had introduced the concept of constitutional super-cooling. Constitutional super-cooling results in the instablility of the interface giving cellular structure, dendritic structure, stray nucleation, waviness of interface etc., spoiling the quality of the crystal obtained.

Hence for the single crystals grown from melt, we must avoid having

a) extensive zones of super-cooling in the melt and
b) the segregation of components (either solutes or components of the compound) at the growth interface.

In order to avoid constitutional supercooling, we must remove the latent heat generated by the solidification process by conduction into the solid rather than into the liquid. To achieve this, we must have directional solidification in which growth occurs onto part of the crystal whilst a heat sink is attached to the remainder. Also, segregation products are removed from the vicinity of the solid-liquid interface by diffusion and convection. Mass diffusion occurs much more slowly than thermal diffusion and so the rate at which we perform the solidification is limited so as to allow time for mass diffusion in the vicinity of the interface.

Thus to grow alloy crystals from the melt, it is necessary to use:

(a) a much steeper temperature gradient than may be necessary for the growth of crystals of pure metals,
(b) stirring of the melt to minimise solute concentration gradient and
(c) also much smaller growth rate, as shown by Delves[3] and Tiller et al.[4].

The latter, (b) and (c), also help to reduce the solute segregation within the crystal by allowing more time for diffusion.

Assuming that the solid and liquid phases are of approximately the same composition (at least in terms of their major components), the principal methods of growth from the melt have been split into three groups as given by Brice and are summarized in Table 2.

The classification scheme for melt growth as given by Hurle[5] is summarized in Table 3.

TABLE 2.

Brice's Scheme

Melt Growth		
Growth in Crucibles a) Bridgman method b) Stober method c) Zone method	Crystal Pulling	Growth without Crucibles a) Verneuil method b) Floating Zone

TABLE 3.

Hurle's Scheme

Melt Growth	
Normal Freezing (Molten charge is directionally solidified)	Zone Melting (Zone is melted in a solid ingot and then caused to pass along the ingot)
(a) Crystal Pulling or Czochralski (b) Pedestal growth (c) Vertical Bridgman/Stockbarger (d) Kyropoulos (e) Verneuil (flame fusion) (f) Horizontal normal-freeze or Chalmers technique	(a) Horizontal zone melting (b) Float-zone melting

The various techniques of melt growth are described below.

1) VERNEUIL TECHNIQUE

The method with the longest history is that due to Verneuil[6]. This technique eliminates the usage of crucible. In this technique the powdered charge material falls from the canister into the hopper at a controlled rate by a tapper. Hydrogen and oxygen are fed down the outer annular tubes and burnt. The flame melts the powder which rains down into a shallow pool of liquid on top of the seed crystal. As the crystal grows it is lowered down into the subsidiary furnace in the growth chamber at a rate commensurate with the feed rate. If no seed is used it is usual to build up a sintered mass of material on an alumina pedestal before melting. The initial growth of a narrow rod usually tends to produce a single crystal which can then be caused to grow wider by increasing the feed rate or decreasing the rate at which the pedestal is lowered. Rotation of the pedestal averages out any lack of symmetry in the flame, but it is necessary that the axes of rotation and the burner be collinear.

Advantages:

a) Materials with high melting point can be grown by this technique.

b) As this method eliminates the use of crucible, there is no liquid-crucible interface to cause spurious nucleation nor is there the possibility of crucible contamination or of strains due to differential expansion of the crystal and the crucible.

Disadvantages:

a) Poor control of the thermal environment and limited freedom in the choice of gas ambient.

b) The total volume of liquid is small and thus minute variations in growth rate have large effects on the impurity concentration, giving rise to striations.

The Verneuil technique is a well established method for the growth of refractory oxide crystals of very high melting point like $SrTiO_3$ (M.P.= 2050°C)[7], Si (M.P. = 1430°C)[8], $3BeO.Al_2O_3.6SiO_2$ known as Emerald (M.P. = 1410°C)[9] and ZrO_2 (M.P. = 2700°C)[10].

Jack and Stephenson[11] have described a technique in which the material to be grown and any necessary doping agents are added as volatile components to the gases producing the flame.

The use of flame fusion apparatus is limited in that the atmosphere in which the crystal grows is not readily controlled, so that reactive materials cannot be grown. The other alternative heating methods are arc image furnaces[12] and radio frequency heating[13]. Arc image furnaces have the advantage that if a transparent jacket surrounds the system, it is possible to control the growth atmosphere. With this heating method the feed material strikes the liquid film on the growing surface as solid particles. Haldane and Sedlacek[10] found it necessary to use large particles (10 – 74 μm diameter) because small particles tend to float on the liquid without melting. This will also be necessary if radio frequency heating is used. R. F. heating with direct coupling to the melt has the advantage over the arc image method that non transparent deposits on the chamber walls are unimportant.

2) CRYSTAL PULLING TECHNIQUE

Czochralski[14] developed a melt crystal growth method in 1918. It is known as crystal pulling/ Czochralski technique. The characteristic of this technique is that, although a crucible is used, the solid-liquid interface is not in contact with it. By this method crystals with large size and relatively low dislocation density can be grown.

In this method, the material to be grown is first melted by induction or resistance heating under a controlled atmosphere in a suitable nonreacting container. The melt temperature is then adjusted to be slightly above the melting point and a seed crystal is lowered to the melt surface. After thermal equilibration, the seed is contacted with the melt and the melt temperature raised to establish the desired growth interface configuration. By activating a pulling mechanism, the seed is withdrawn from the melt (with simultaneous temperature adjustment) at such a rate that the crystal diameter is gradually increased to its desired value (frequently a "necking" process is used initially to reduce the dislocation density in the grown material).

The various parameters affecting the growth are

1) the rate of pulling
2) accurate control of melt temperature
3) the rate of liquid level drop (determined by the relative diameters of crystal and crucible)
4) the heat fluxes into and out of the system
5) the seed and/or crucible rotation

Full dimensional control is frequently achieved by automatic control techniques employing both analogue and digital systems.

The crystal growth rate under the above described conditions cannot be expected to be equal to the imposed pulling rate. The macroscopic growth rate is always greater than the pulling rate since the melt level drops during growth. The instantaneous microscopic growth rate can deviate substantially from the macroscopic growth rate. Large number of metallic as well as ionic crystals have been successfully grown by this method. The method has reached Hi-Tech status due to its applicability for technologically important materials.

To quote examples, Laudise et al.[15] have grown doped single crystals of Bi_2Te_3 by Czochralski method in H_2. Wenzle et al.[16] have grown copper crystals by this technique in inert atmospheres at a pressure of 1 bar.

The chief advantages of this technique are :

1) the growing crystal is not in contact with a mould
2) by using oriented seed crystals, crystals of a variety of orientations can be prepared
3) suitable dopants can be added to the melt during growth
4) the crystal is viewed as it is growing.

The disadvantages of this technique which may be significant in heavily doped semiconductors depending on the application of the materials are:

1) obtaining a crucible of material which does not contaminate the growth material in its molten state
2) the shape of the resultant crystal is not exactly reproducible
3) the formation of growth striations or variations in concentration of the dopant in the crystal
4) development of growth facets on surfaces of the crystal.

There also exist other important variants of this technique which were basically devised to meet problems/requirements specific to the material to be grown like Liquid Encapsulation Technique[17,18] and Pressure Balancing technique[19].

Liquid Encapsulation:

The unique advantage of Liquid Encapsulation over other techniques is the ease with which very highly dissociable compounds can be handled. The technique provides a complete liquid environment for the crystal and melt which would isolate them from the crucible and gaseous environment. The encapsulant must be less dense than the melt of the compound, transparent (although crystals can be grown through opaque media) and chemically inert to the melt and the crucible. The most important property of an encapsulant in crystal pulling is its ability to wet the crystal melt and crucible. A sharp temperature dependence in the viscosity of the encapsulant below the melt temperature is also desirable. These properties ensure that the crystal remains coated with encapsulant as it is withdrawn from the crucible. This technique has been used in the growth of a variety of materials including PbTe[20], InP[21], GaP[22], InAs[18], GaAs[18], MnTe[23] etc.

The main disadvantages of this technique are the need to use a synthesised material and the difficulty of finding encapsulants which do not react with the melt and impair the encapsulant's transparency. Higher melting point II-IV compounds such as ZnSe and ZnTe have not been grown successfully by this method.

Pressure Balancing:

Pressure Balancing is being developed in an attempt to overcome the difficulties observed in the case of Liquid Encapsulation technique.

The basic principle of this technique is that the dissociation pressure of the compound is dynamically balanced by a pressure of inert gas. This balance can be achieved by using a liquid seal to sense and control the means for eliminating the development of a pressure differential across the walls of the growth chamber. Another method of pressure balancing is by partition balance[24].

3) KYROPOULOS TECHNIQUE

Kyropoulos worked on this technique in 1926[25]. The apparatus is basically that used for crystal-pulling, usually with forced cooling of the seed crystal except that here the growth is achieved by slowly lowering the melt temperature rather than by pulling out a crystal.

4) PEDESTAL GROWTH

This method avoids the crucible contamination problem by pulling from a melt formed by melting the end of a large charge rod. (It could be argued that it is in fact a zone-melting technique). It has been found useful for the growth of Si for which no completely inert crucible material has been discovered. (The commonly used SiO_2 crucible contaminates the melt with oxygen).

5) ZONE MELTING TECHNIQUE

Zone melting was first employed for crystal growth by Andrade and Roscoe[26] in 1937. They used a travelling zone to produce single crystals. The purpose of the zone was to produce a temperature gradient near the growing interface. However, its potential for the ultrapurification of materials was not recognized until W. G. Pfann[27] at the Bell Laboratories applied it in 1952 to Ge.

The main function of this technique is the manipulation and redistribution of soluble impurities (or phases) in the ingot.

In this method a small molten zone is created in a large solid ingot of the material to be crystallized and passed from one end of the ingot to the other. As the zone travels, it redistributes impurities along the charge. The advantage is that the control of impurities can usually be obtained at the same time. The final distribution depends on the impurity distribution in the starting charge, on the segregation coefficient K of an impurity in the liquid and solid phases of the charge material, and on the size, number and travel direction of the zones. It is often observed that, as a material is purified by subsequent passes, the grain size tends to increase so that single crystals result as a happy 'accident' of ultra purification. Particularly for the growth of homogeneous alloy crystals, steep temperature gradient and slow growth rates are the essential factors. Smaller the zone length better is the quality of the crystal.

Zone refining is the most important zone melting method. In zone refining a number of molten zones are passed along the charge in one direction. Each zone carries a fraction of the impurities to the end of the charge, thereby purifying the remainder. Due to this, various impurities are collected at two ends of the ingot (depending on their segregation coefficients) leaving the central part of the ingot almost free from impurities. In this process, the impurities with segregation coefficients K>1 are collected at one end whereas the impurities with segregation coefficient K<1 are collected at the other end. The central portion of the ingot is much purer and purer after each successive zone pass. If K is close to unity the ratio of ingot length to zone length must be made larger.

A single crystal with a uniform concentration of a desired impurity can be grown by passing the "zone" along the length of the ingot in alternate directions for several times. The process is called "zone levelling". After several alternate repeated passes, the segregation of the dopant can be virtually eliminated which results in homogeneous distribution of impurity in the ingot. This technique can be applied for the preparation of semiconductors of very high purity. Among many crystals that have been grown by this method, mention may be made of Ag_2Te, CdSb, CdTe, SnS and SnSe and many other alloys.

Harman et al.[28] have grown single crystals of Bi_2Te_3 under Te (vapour) atmosphere by using horizontal zone melting method. Richard[29] has reported the growth of GaAs crystals with low dislocation density. He used carbon coated silica boat and the growth rate was adjusted between 1.25 to 5.0 cm/h. The polycrystalline ingots were given 20 passes at 5 cm/h prior to the final pass. Heumann[30] and Lorentz et al.[31] have grown single crystals of Bi_2Te_3 and CdTe alloys, respectively, by using vertical zone melting technique.

6) FLOAT ZONE MELTING

The float zone melting is a relatively recent variant of the zone melting method and it eliminates the usage of crucible by using surface tension as the principal force for supporting a molten zone. In this technique, the material to be purified or grown as a single crystal is arranged in a vertical compacted rod[32]. In this technique surface tension holds a molten zone of liquid in a sample whose axis is vertical. As the technique does away with the container – it is 'crucibleless' – so reactivity with the container is no longer a problem : the melt is in contact only with its own solid. The technique is of considerable industrial importance for the preparation of oxygen-free Si. Materials with high surface tension and low liquid density are required.

Tamura et al.[33] have reported the refining conditions for obtaining high purity Fe by using the float zone technique. Lawley and Maddin[34] have grown Ta based alloys containing upto 39 at.% Re by this method, keeping growth rate 2 mm/min.

7) BRIDGMAN-STOCKBARGER TECHNIQUE:

A particularly useful method of controlling supercooling so as to yield a single crystal, is that first used by Bridgman[35] in 1925 and especially exploited by

Stockbarger in 1939. In this technique, the melt in a container is moved relative to a fixed temperature gradient in the vertical furnace, so that solidification starts at one end and moves progressively along the sample. The tip of the crucible is kept conical so that initially only a small volume of the melt is supercooled in a controlled way. As a result, only one nucleus will be formed or if at all more than one nuclei are formed, only one nucleus with favourable orientation is given the chance to grow by the tapering end. If the nucleus is suitably oriented it may dominate the growing interface and therefore a single crystal results.

To this method, a modification was introduced successfully by Stockbarger who used two furnaces having different temperature gradients and separated by a baffle, instead of using a single furnace. This method is called Bridgman-Stockbarger method and provides for desired variation of the temperature gradients.

The three classes of materials to which Bridgman-Stockbarger growth has been most frequently applied are metals[36-38], semiconductors[39-40] and alkali and alkaline earth halides[41-42].

Stockbarger[43] showed that LiF and CaF could be grown and the methods that pioneered have provided a basis for an extensive commercial growth of halide crystals for optical applications. This method is seldom used for the growth of semiconductor like Germanium and silicon as they expand on freezing which leads to large stresses. Bridgman technique has been applied to grow single crystals of Cu-Be, Cu-Al, Mg-Mn, Fe-Ni and other binary systems. With the help of this technique, Lawson[44] grew PbS, PbTe and PbSe crystals. Price and Kelley[45] have grown single crystals of Cu-1.8wt% Be by using vertical soft mould of Aluminium. Kumagawa et al[46] have grown ternary mixed crystals on InSb and GaSb seed crystals successfully by the Bridgman method with high speed rotation of about 80 to 120 rpm. The growth of $(Sb_xBi_{1-x})_2Te_3$ single crystals with programmable temperature control by the vertical Bridgman method has been reported by Fang-Lang Hsu[47]. B. Cabric et al.[48] developed a method for crystallization of several substances at different rates in a chamber furnace. Siddiqui[49] has grown eutectic intermetallic compound alloy crystals of SnSe-$SnSe_2$ by the Bridgman Stockbarger method. One of the most important present day semiconductor crystals, namely, CdTe is also usually grown by the Bridgman method[50].

8) HORIZONTAL BRIDGMAN / CHALMERS TECHNIQUE

In this technique the charge is contained in a boat which is placed within a horizontal furnace tube which can be filled with the required ambient gas (or evacuated). A muffle furnace is placed around the tube and serves to melt the charge. Directional solidification is obtained by slowly withdrawing the boat from within the furnace (or moving the furnace away from the boat).

Hence the limitation of the Bridgman technique that it can be used only for low melting point metals is overcome by the horizontal moving furnace technique given by Chalmers[51].

CdTe crystals by horizontal two-zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 10^{-7} torr. have been grown[52]. To grow pure and doped CdF_2 single crystals by the Bridgman method, unwanted vapour reactions were avoided by using an argon atmosphere and glassy carbon crucibles[53].

For growing Sb_2Te_3 and Sb_2Te_3 based single crystals, different techniques have been employed by different authors. The present author reports the crystal growth of these materials by Zone-melting and the Bridgman technique. These are described in Chapter 7.

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