

THEORIES AND TECHNIQUES OF CRYSTAL GROWTH

1.1 Introduction

Modern technologies based on optoelectronics, acousto-optics etc. have exploited the versatile properties of crystals. The rapid advances in these branches of technologies have been made possible due to the availability of a variety of crystalline materials. In other words the development of the crystalline materials is the backbone of the modern technologies. This led the investigators to concentrate on the development of new varieties of crystals with high purity. The need for good quality crystals also led to theoretical investigations and computer simulation studies on the growth process of different materials. Well-developed theories are now available to help the crystal growers to produce defect free pure crystals. In this modern scientific world the theory and technologies are developing hand in hand to grow specific crystals for specific utilities. This chapter gives an overview of the theories and techniques associated with the growth of different crystalline materials.



1.2 The thermodynamics of crystal growth

Crystal growth process occurs as a phase transformation phenomenon. Thermodynamic equilibrium between solid and liquid phases occurs when free energy of liquid phase (G_L) is equal to that of the solid (G_S).

$$G_L = G_S \quad 1.1$$

According to Gibbs equation¹ the free energy of the system relates to the internal energy and entropy of the system.

$$G = H - TS \quad 1.2$$

Where H is the enthalpy, S is the entropy and T is the temperature.

The driving force for crystallisation is therefore the free energy difference (ΔG), between the solid and supersaturated or super cooled liquid. During phase transformation there is thus a lowering of free energy of the system. The free energy change associated with this transition is

$$\Delta G = \Delta H - T\Delta S \quad 1.3$$

Where $\Delta H = H_L - H_S$

$$\Delta S = S_L - S_S$$

$$\Delta G = G_L - G_S$$

At equilibrium, $\Delta G = 0$

Therefore

$$\Delta H = T_e \cdot \Delta S$$

where T_e is the equilibrium temperature



Therefore

$$\Delta G \cong \Delta H \cdot \frac{\Delta T}{T_e} \quad 1.4$$

where, $\Delta T = T_e - T$

When $T_e > T$, ΔG is positive, and it depends on the latent heat of transition. The free energy change can also be represented as a product of the entropy change and supercooling ΔT .

$$\Delta G \cong \Delta S \cdot \Delta T$$

This representation is applicable for melt growth. But in solution growth or vapour growth one relies on concentration or supersaturation rather than supercooling. Thus the equation needs to be modified. They are

$$\Delta G \cong RT \ln \left[\frac{C}{C_0} \right]$$

$$\Delta G \cong RT \ln \left[\frac{P}{P_0} \right] \quad 1.5$$

In general

$$\Delta G \cong RT \ln S \quad 1.6$$

Where S is the supersaturation ratio. Equation (1.4) and (1.6) explain how the free energy changes depend on the parameters like supercooling and supersaturation, which are the driving forces of crystallisation process. The growth rate of a crystal is regarded as a monotonically increasing function of ΔG , if the other parameters remain the same.



1.3 Nucleation

Nucleation is the most important stage in crystal growth process. It is the conglomeration of atoms or molecules to form the first sub-microscopic speck or grain of the extended solid crystal. Two types of nucleation are possible: homogeneous and heterogeneous. Volmer and Weber² put forward a theory by considering the total free energy for a group of atoms.

Fluctuations in the supersaturated solution give rise to the formation of small clusters of molecules known as “embryos”. The change in free energy causes these embryos to grow into stable nuclei. If the free energy change between the solid and liquid is ΔG_v , the free energy of the system decreases by this amount for each unit volume of the solid created. But at the same time the free energy is increased by an amount equal to the interfacial energy σ , for each unit area of the solid-liquid interface formed.

Therefore the change in Gibbs free energy associated with the formation of a spherical embryo of radius ‘r’ is given by

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_v \quad 1.7$$

Fig.1.1 shows the graphical representation of the formula in which the contribution due to surface and volume to the free energy changes are represented. The surface energy term increases with ‘r²’ and the volume energy term decreases with ‘r³’. The net free energy change increases with the increase in size, attains a maximum and decreases for further increase in nuclear size. The size of the nucleus corresponding to the maximum free energy change is known as the “critical nucleus”. If the size of the nucleus formed is below the critical dimension, there is no further growth possible and it will re-dissociate into the mother system.

The minimum size of a stable, critically sized nucleus is obtained by maximising equation (1.7) for r, which leads to



$$r^* = 2\sigma/\Delta G_v$$

It is worth noticing that, r^* decreases with increase of ΔG_v , i.e., with supersaturation or supercooling. The activation energy necessary for nucleation can be calculated by substituting r^* in equation (1.7)

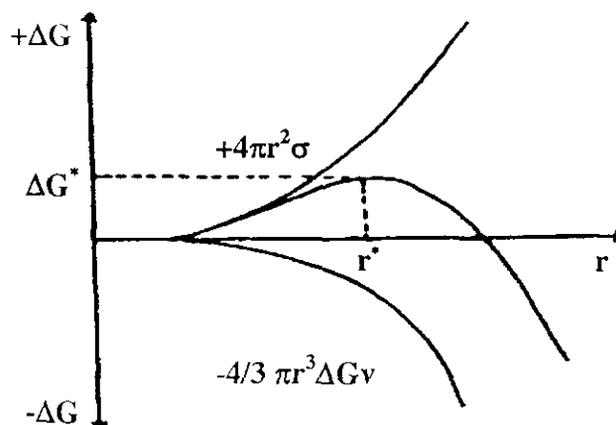


Fig. 1.1. Free energy change of a nucleus as a function of radius.

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} \quad 1.8$$

By rearranging (1.8) and using Gibbs-Thomson relation

$$\Delta G^* = \frac{16\pi\sigma^3\Omega^2}{3(kT \ln S)^2} \quad 1.9$$

Where Ω is the molar volume.

The number of nuclei formed per unit volume per unit time is called the rate of nucleation, and it can be expressed as

$$J = J_0 \exp\left[\frac{-\Delta G^*}{kT}\right] \quad 1.10$$

By substituting for ΔG^*

$$J = J_0 \exp\left[\frac{-16\pi\sigma^3\Omega^2}{3k^3T^3(\ln S)^2}\right] \quad 1.11$$

Where J_0 is a pre-exponential numerical factor. Equation (1.11) shows that the temperature, degree of supersaturation and the interfacial energy govern the nucleation rate. The critical supersaturation is obtained by rearranging equation (1.11) by choosing $J = 1$; this corresponds to the instant when the first nucleus is formed, so that $\ln J = 0$, and

$$S_{cri} = \exp\left[\frac{16\pi\sigma^3\Omega^2}{3k^3T^3 \ln J_0}\right]^{1/2} \quad 1.12$$

Critical supersaturation required for spontaneous nucleation can thus be estimated by using the value of various given parameters.

1.4 Theories of crystal growth

The formation of a good quality crystal is highly complex and usually takes place by phase change. The growth process occurs by the successive growth of critical nuclei of microscopic size. To explain the kinetics of crystal growth several theories have been proposed by investigators. The surface energy theory and the diffusion theory give a fair description of the growth process but all these theories are found to be unsatisfactory in explaining all features of crystal growth. Gibbs¹ proposed a theory by drawing the analogy between the growth of water droplet in mist and the growth of a crystal. The surface developing on the crystal in the area where surface energy is minimum. Curie³ calculated the shape and form of a crystal.



Later Kossel⁴ and others analysed the atomic inhomogeneity of a crystal and explained the role of step and kink sites on the growth process. This theory became popular, even though it is not capable to provide a complete explanation for the continuous growth of a crystal surface. Frank⁵ showed that crystal dislocations were capable of providing the sources of steps required for the continuous growth of a crystal. A great number of authors have described these theories thoroughly^{6,7,8,9}

1.4.1 Surface energy theory

Gibbs¹ put forward the surface energy theory on the basis of thermodynamical treatment of equilibrium states. By comparing the growth of crystals with the formation of water droplets in mist, he explained that the equilibrium form is one with minimum net surface energy for a given volume. Later a number of researchers extended this thermodynamical treatment. Curie³ calculated the shapes and end forms of the crystals in equilibrium with solution or vapour, consistent with Gibbs criterion. Wulff¹⁰ deduced a relation by connecting the growth rate of different faces and corresponding surface free energies. This has been further developed by Marc and Ritzel¹¹, on the basis that different faces have different solubility. They suggested that, when the difference in solubility is small, growth is mainly governed by surface energy and the change in surface of one form is by the expense of the other. Berthoud^{12,13} and Valetton¹⁴ assailed Curie's theory on the basis of supersaturation. They argued that greater supersaturation would cause rapid growth and the crystal habit ought to be spherical shape. This was in contradiction to the observed facts. Usually the fast growing crystals are predominantly in one simple form.

1.4.2 Diffusion theories

Diffusion theories proposed by Noyes and Whitney¹⁵ and Nernst¹⁶ are based on the following assumptions

- (a) There is a concentration gradient in the vicinity of the growing surface.
- (b) The growth process is a reverse process of dissolution.



According to them, the amount of solute molecules that gets deposited over the surface of a growing crystal in the supersaturated solution can be written as

$$\frac{dm}{dt} = \frac{D}{\delta} A(C - C_0) \quad 1.13$$

Where dm is the mass of the solute deposited over a crystal surface of area A during time dt , D is the diffusion coefficient of the solute, C and C_0 are the actual and equilibrium concentration of the solute and δ the thickness of the stagnant layer adjacent to the crystal surface. But this theory also fails to be consistent with experimental observations.

1.4.3 Surface nucleation model

Since the growth takes place at the crystal surface, it is quite natural to imagine that the surface structure influences the growth. A pure perfect crystal of a single element has surfaces covered by steps with terraces in between. These steps possess kinks and hence there are three types of sites; terrace, ledge and kink sites. This model was developed by Kossel¹⁷, Volmer¹⁸ and Stranski¹⁹ presuming crystal growth is a discontinuous process taking place by the adsorption of matter layer by layer on the crystal surface. According to this theory the growth units approaching on a crystal surface do not incorporate immediately into the lattice, but becomes adsorbed and migrate over the surface. The migration distance X_s of the adsorbed molecule is given by

$$X_s^2 = D_s \tau_s \quad 1.14$$

Where D_s are the surface diffusion coefficient and τ_s is the mean lifetime of the adsorbed molecule on the surface. In this model

$$X_s \cong a \exp\left[\frac{3\phi}{2kT}\right] \quad 1.15$$

Where α is the nearest neighbour interaction parameter.



The possible lattice sites for the attachment of adsorbed atoms on crystal surface is illustrated in fig.1.2 in which adatoms are pictured as cubes. An atom reaching the growing surface has a maximum probability to attach to a kink since it leads to three bonds to be saturated. Atoms have minimum probability to attach on the terrace site since it can use up only one bond.

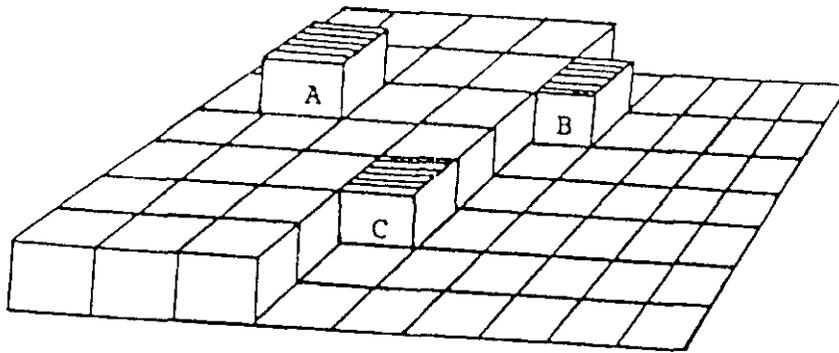


Fig. 1.2. The possible lattice sites for the attachment of adsorbed atom
A-Terrace site B- Ledge site C- Kink site

Due to this the maximum binding energy between the adatom and the existing crystal surface occurs for the incorporation at kink site. Hence the adatoms over the crystal surface migrate towards a step and move along it to a kink site and get incorporated. In an ideal case this step-wise stacking will continue until the whole layer is completed. The mode of advance of a step has been extensively analysed by Burton, Cabrera and Frank²⁰. The advances of steps incorporate more and more adatoms at kink sites. If we assume the diffusional flow of adatoms along the step, the rate of advance of a step can be expressed as

$$V = 2SX_s \nu \exp\left(-\frac{W}{kT}\right) \quad 1.16$$

Where ν is the frequency factor and W is the total evaporation energy. Then the rate of advance is proportional to supersaturation S and to the mean migration distance

X_s . Here it is assumed that the mean migration distance is much higher than the mean distance between two adjacent kink sites on a step.

If the advancing step covers the whole surface, further growth is possible only by the initiation of a two dimensional nucleus. According to Volmer¹⁸ this is possible on account of thermal fluctuations. Assuming a circular disc shaped nucleus of radius r and a height h , the free energy change associated with the formation of such a two dimensional nucleus may be written as

$$\Delta G_{id} = 2\pi r h \nu - \pi r^2 h \Delta G_v \quad 1.17$$

Where ν is the edge free energy. Employing the same technique adopted in section 1.3, the activation energy necessary for the two dimensional nucleation can be calculated as

$$\Delta G_{id}^* = \frac{\pi h \nu^2 \Omega}{kT \ln S} \quad 1.18$$

and the nucleation rate is given by

$$J_{id} = C_1 \exp\left[-\frac{\pi h \nu^2 \Omega}{k^2 T^2 \ln S}\right] \quad 1.19$$

The critical supersaturation can be expressed as

$$S_{cri} = \exp\left[\frac{\pi h \nu^2 \Omega}{k^2 T^2 \ln C_1}\right] \quad 1.20$$

The rate of growth of a singular face is in principle controlled by the rate of nucleation and the rate of advance of a step and can be expressed as

$$R = h J_{id}^{1/3} V^{2/3} \quad 1.21$$

The rate of growth is calculated by using the above equation. But this does not match with observed results in many cases. According to Kossel, Volmer and



Schulze²¹ the growth of the crystals is controlled by the probability of two-dimensional nucleation, which is not appreciable, until the supersaturation reaches a considerable percentage in order. But in real cases it is observed that crystal grows at supersaturation down to a value 1% or lower.

1.4.4 Screw dislocation theory

The lack of agreement between the growth rate of crystals by theoretical calculation and the experimentally observed values leads to the conclusion that prediction based on two dimensional nucleation theory may not be the correct mechanism and there is some other mechanism responsible for the continuous growth of a crystal surface.

Frank proposed that if a crystal contained a dislocation, which was self-perpetuating, the need for surface nucleation would be layerly²² but not entirely circumvented²³ and the crystal would grow continuously even at very low supersaturations. The screw dislocation and various modifications meet these specifications and the simplest form is shown as a block model in fig.1.3

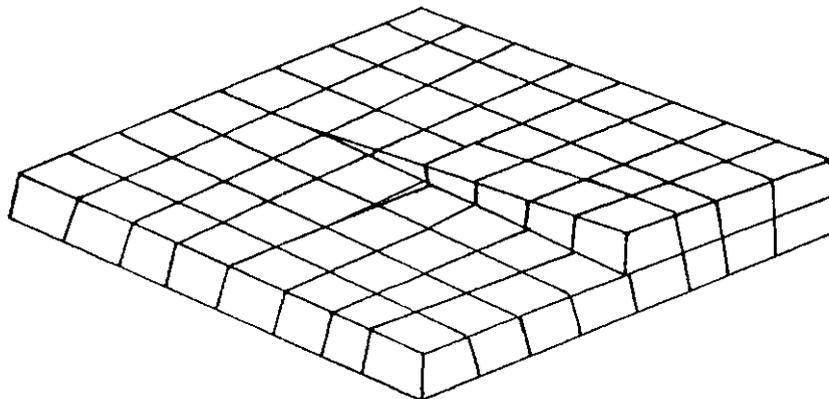


Fig. 1.3. The end of a screw dislocation

When an atom diffuses over the surface of a crystal as shown in fig.1.3 it will be attached at the top step formed by the two planes. The crystal surface becomes essentially a helical ramp arranged in the direction of a right or a left-handed screw. After completing one entire layer the dislocation will still be present, but one layer

higher. The atoms will attach themselves all along the step at about the same rate but the angular velocity near the centre will be much greater. This can be seen in fig.1.4. which represents the top view of a spiral dislocation. Line 1 is the flaw as shown in fig 1.4 (a) . As this line grows by the addition of atoms, it assumes portion 2, 3, 4, 5 etc. This process is continuous until the form in fig1.4 (b) is generated. The actual shape of the spiral will depend upon the rate of growth and the crystal itself. Since a step is always present in the crystal, the need for two-dimensional nucleation is absent and the crystal continues to grow at supersaturations below those otherwise required.

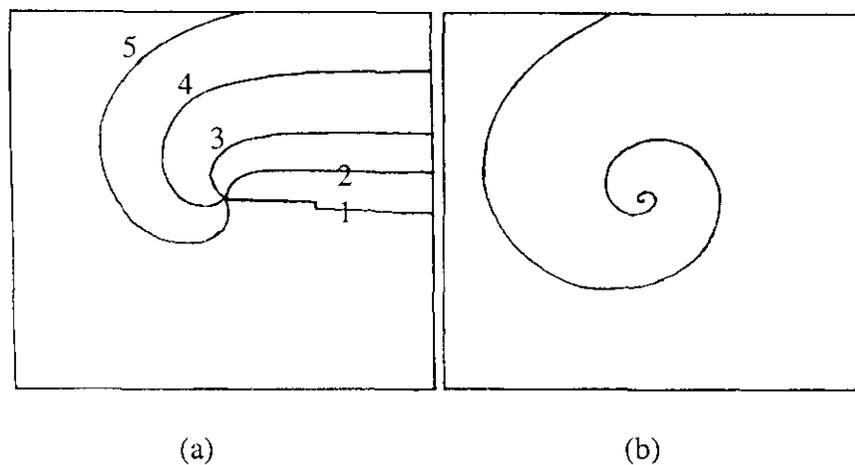


Fig. 1. 4. Growth spiral resulting from growth on the wall due to screw dislocation

Based on spiral growth mechanism Burton, Cabrera and Frank (BCF)²⁰ could establish a relation between the rate of growth R and the relative supersaturation, which is expressed as

$$R = C \left(\frac{S^2}{S_1} \right) \tanh \left(\frac{S_1}{S} \right) \quad 1. 22$$

Where ' S_1 ' is defined as

$$S_1 = \frac{19v\Omega}{2kTX_s} \quad 1. 23$$

and $C = D_s c_{sc} \beta \Omega / X_s^2$
 where S = relative supersaturation
 S_1 = a constant for BCF model
 c_{sc} = equilibrium concentration of growth units on surface
 β = retardation factor
 Ω = volume of the growth unit.

This growth rate variation with supersaturation depends on two parameters; C which determines the absolute value of growth rate and S_1 which determines actual growth rate.

If $S \ll S_1$
 $R \propto S^2$

If $S \gg S_1$
 $R \propto S$

Therefore the BCF theory predicts that the growth rate is proportional to the square of the supersaturation for low supersaturation, changing to a linear dependence at higher supersaturation. It is found that Frank model provides excellent agreement between theory and observation on growth rate as well as the direct observation of spiral pattern, characteristic of this mechanism^{24,25,26,27}. However Keller²⁸ and Bauser²⁹ observed that edge dislocations can also act as persistent source of steps for crystal growth. Frank⁵ proposed a general explanation of nucleation at edge dislocation based on the fact that the surface stresses provide the extra energy for formation of the growth nuclei when the dislocation component perpendicular to the surface is absent.

1.5 Crystal growth techniques

Crystal growth is a highly complex phase change phenomenon. The phase change may occur from the solid, liquid or vapour state. With regards to the phase transitions, the crystal growth methods are broadly classified into four main categories^{30,31,32,33}



1. Solid state growth (Solid \rightarrow Solid)
2. Solution growth (liquid \rightarrow Solid)
3. Melt growth (Liquid \rightarrow Solid)
4. Vapour growth (Vapour \rightarrow Solid)

1.5.1 Solid state growth techniques

In this technique the growth of single crystal takes place from the polycrystalline mass of that particular material which we intend to grow. Usually the straining of the material with subsequent annealing is utilised for crystallisation. Metallic crystals of large size have been grown by this method³⁴. The growth will take place at low temperature without the presence of additional component, which is the advantageous feature of this technique. But the control of growth rate and quality is very difficult because of the lack of control on nucleation rate.

1.5.2 Growth from solution

Another method of growth of crystals is by the precipitation technique from solution. In this method the crystals are prepared from a solution at temperature well below its melting point. This may help to grow crystals even at room temperature, and it will turn out to be more advantageous³⁵. Here the crystallisation takes place from the critically supersaturated solution. The supersaturation may be achieved by the lowering of temperature of the solution or by slow evaporation or by giving continuous supply of materials to compensate for the material that precipitates out. The present work utilises this method. The solution growth methods are classified according to the temperature range and to the nature of the solvents used.

The main methods commonly used in this process are

- i. High temperature solution growth.
- ii. Hydrothermal growth
- iii. Slow cooling or slow evaporation method
- iv. Gel growth



1.5.2 (i) High temperature solution growth

High temperature solution growth includes a number of related techniques³⁶. The flux method and liquid phase epitaxy^{37,38} are the two widely used methods. A high temperature solvent, which reduces the melting temperature of the solute, is referred as flux³⁹. The main advantage of the flux growth is the reduction of high temperature. The materials to be crystallised are dissolved in proper solvent at temperature slightly above the saturation temperature, slow cooling of the container allows the growth of crystals. Slow cooling of the flux is also effective in obtaining slightly bigger crystals.

1.5.2 (ii) Hydrothermal Growth

This is a well known and widely used technique to grow crystals of certain class or species of materials, which are insoluble in water at standard temperature and pressure. This is more imitative to the natural growth of certain important minerals. Almost all metals and oxides show an appreciable increase in solubility due to the increase in temperature and pressure. It can be treated as aqueous solution growth at elevated temperature and pressure. Autoclaves with gold or silver linings are usually utilised for the growth purpose. A charge of crystal is dissolved in the lower part of the autoclave. The hot saturated solution is directed towards the upper (colder) part, where it become cold and supersaturated and hence the growth takes place. The spent solution returns to the other part and this process continues until the whole charge is re-crystallised. The solution simply acts as a transporting agent for the solid phase. Synthetic quartz crystals are grown by this technique⁴⁰. The natural process of crystallisation beneath the earth resembles this growth technique.

1.5.2 (iii) Low temperature solution growth

This is the easiest and most effective way for growing a variety of crystals at ambient condition or even at room temperature⁴¹. In this method, saturated solution of the material is prepared in a suitable solvent and crystallisation is initiated by slow cooling of the solution or by the slow evaporation of the solvent. The crystals grown



by this technique are larger in size and relatively free of defects. Several industrially⁴² and technologically⁴³ important materials are grown by this method^{44,45,46}

1.5.2 (iv) The gel method

For the growth of crystals of materials having poor water solubility and unstable thermal behaviour the above techniques are unsuitable. For such materials, the gel method is found suitable. In gel technique the supersaturation is achieved either by the slow inter diffusion of solution of two reacting species, which on mixing react to form the solute, or by the inter-diffusion of a solution with a solvent in which the solute is insoluble or less soluble. Crystals of smaller size and free of defects are grown using the well known rather ease gel technique⁴¹. The author has utilised this technique to grow the rare earth mixed hydrogen selenite crystals and therefore further elaboration for this specific technique is appropriate here. The following chapter covers the matter in detail.

1.5.3 Growth from vapour

The vapour growth technique is usually employed to grow crystals of the materials for which suitable solvents are not readily available and have satisfactorily high vapour pressure at ambient condition. This method is utilised to grow bulk crystals and for preparing thin layers on crystals with a high degree of purity. Generally the growth from vapour phase is subdivided into two.

- i. Physical vapour transport (PVT)
- ii. Chemical vapour transport (CVT)

1.5.3 (i) Physical vapour transport (PVT)

The technique of growing crystals from its vapours does not involve any extraneous compound formation or reaction. The PVT methods are utilised to grow materials having satisfactorily high vapour pressure at attainable temperature. Generally two types of techniques are employed in PVT process: sublimation-condensation and



sputtering. The first method involves the sublimation of the charge at high temperature region of the furnace followed by the condensation at colder end^{47,48}. Sputtering techniques are preferred for low vapour pressure materials and are used to prepare crystalline films rather than discrete perfect crystals. The main advantage of the method is that growth of films takes place at low temperature. A variety of the crystals have been grown by the PVT method^{49,50,51}. The method has also been used extensively for fabricating epitaxial films^{52,53}.

1.5.3 (ii) Chemical vapour transport (CVT)

The chemical vapour transport method is employed for relatively non-volatile materials. This involves a chemical reaction between the source materials to be crystallised and transporting agent. The materials to be crystallised is converted into one or more gaseous product which either diffuse to the colder end or get transported by a carrier (transporting) gas. At the cold end the reaction is reversed so that the gaseous product decomposes to deposit the parent material, liberating the transporting agent, which diffuses into the hotter end and again reacts with the charge. Production of thin layers of crystals achieved by this method assumes enormous commercial advantages.^{54,55,56,57,58}

1.5.4 Melt growth techniques

This is the fastest of all crystal growth methods and is widely used for the preparation of bigger and larger quantity of crystals. It is the process of crystallisation by fusion and resolidification of the pure material. Melt growth technique is commonly used in the case of materials which melt congruently and having an experimentally viable vapour pressure at its melting point. One of the foremost advantages of this technique is the requirement of simple systems. Primarily the material to be grown is melted and afterwards progressively cooled to yield crystalline form. This method has been utilised to produce commercially important semiconductors, metals and laser host crystals. The availability of pure and perfect crystals is the main advantage of this technique.

Generally the melt growth methods are grouped into two main categories:



1. Normal freezing technique
 - a. Bridgmann technique
 - b. Czochralski technique
2. Zone- growth methods

1.5.4.1 (a) Bridgmann method

There are two variations in Bridgmann's method: horizontal Bridgmann method (Chalmers technique) and vertical Bridgmann technique (Bridgmann - Stockbarger technique). In these the withdrawing of boat or capsule containing molten materials through a temperature gradient results in the growth^{59,60}. This method is often utilised for growing the crystals of metals, semiconductors and alkaline earth halides.^{61,62,63} This method is not very suitable for materials having high melting point and expansion coefficient.

1.5.4.1(b) Czochralski method

The Czochralski method is used in the case of materials having high melting and high volume expansion coefficients associated with the solidification. Czochralski method has gained wide recognition particularly in growing single crystals of semiconductors like silicon⁶⁴ and other materials.^{65,66}

1.5.4.2 Zone growth methods

Zone melting is mainly considered as a refining or purification technique. This technique is exploited for the growth of single crystals. In this technique a part called 'zone' of the solid material is melted and this molten zone is allowed to pass along the length of the charge together with heating elements. Zone melting method of growing single crystals has usually been confined to materials of moderate to low melting temperatures.

When a crystal freezes from the melt, it tends to reject impurities. If zone refining is applied to such crystals, the resulting single crystal can be purer than the original. If



more than one pass is made, a high degree of purity of the crystal can be achieved. Such a procedure is called 'zone refining'. This process is suitable for the preparation of high purity silicon and germanium. The main advantage of the zone melting is that it offers a relatively simple way of producing doped crystals containing deliberate additives in given concentration and uniform distribution⁶⁷. Keck⁶⁸ proposed floating zone technique and Golay used a variant of the zone melting technique in which no crucible is used.

References

- ¹ Gibbs, J.W. (1878), '*Collected works*', Longmans, Green and Co., New York, 1928.
- ² Volmer, M. and Weber, A., *Z. Phys. Chem.*, **119** (1925) 127.
- ³ Curie P., *Bull Soc. France; Miner* **8** (1885) 145
- ⁴ Kossel, W., '*Zur theorie des Kristallwachstums*', *Nachr. Ges. Wiss. Gottingen* 1927
- ⁵ Frank, F.C., *J. Crystal growth*, **51** (1981) 367.
- ⁶ Vere, A.W., '*Crystal growth; Principles and Progress*', Plenum Press, New York, 1987.
- ⁷ Hartman, P. (Ed.), '*Crystal Growth; An introduction*', North Holland Publishing Company, Amsterdam, 1973.
- ⁸ Sangwal, K., '*Etching of crystals*', North Holland Publishing Company, Amsterdam, 1987.
- ⁹ Goodman, C.H.L.(Ed.) '*Crystal Growth; Theory and Techniques*', Plenum Press, New York, Vol. 1, 1980.
- ¹⁰ Wulff, G., *Z. Krist.*, **343** (1911) 449.
- ¹¹ Marc, R. and Ritzel, A., *Z. Physik Chem.*, **76** (1911) 584.
- ¹² Berthound, A., *J. Chem. Phys.*, **10** (1912) 624.
- ¹³ H.E. Buckley, '*Crystal growth*' John Wiley & Sons NY.1951.
- ¹⁴ J.Valeton, J. P.K Sche. *Ges. Wiss Math. Physik.*, **67** (1951) 1.



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- ¹⁵ Noyes, A.A. and Whitrey, W.R., *Z. Physik. Chem.*, **23** (1891) 689.
- ¹⁶ Nernst, W., *Z. Physik. Chem.*, **67** (1909) 470.
- ¹⁷ Kossel, W., *Nachr. Ges. Wirs. Goettingen Math. Phys.* KL **11 A** (1927) 135.
- ¹⁸ Volmer, M., '*Die Kinetik der phasenbildung*', Steinkopff Dresden 1939.
- ¹⁹ Stranski, I.N., *Z. Phys. Chem.* **136** (1928) 259.
- ²⁰ Burton, W.K. Cabrera, N., Frank, F.C. *Phil. Trans. Roy. Soc.*, A **243** (1951) 299.
- ²¹ M.Volmer and Schultze, *Phys. Chem. A* **156** (1931) L.
- ²² Perry, J.H., '*Chemical Engineer's handbook*', New York, John Wiley and sons, 1951.
- ²³ Chalmers, B., '*Progress in metal Physics*', 6 Vols., New York, Interscience publishing Co. 1953.
- ²⁴ Griffin, L., *J. Phil. Mag.*, **41** (1950) 196.
- ²⁵ Verma, A.R., *Phil. Mag.* **42** (1951) 1005.
- ²⁶ Amelincka, S., *Nature*, London, **167** (1951) 939.
- ²⁷ Forty, A.J., *Adv. Phys.*, **3** (1954) 1.
- ²⁸ Keller, K.W., '*Crystal Growth and characterization*' (Vede.R. and Mullin, J.B., Eds, North Holland, Amsterdam, 1975).
- ²⁹ Bauser, E. and Strink, H., *J. Crystal growth*, **51** (1981) 362.
- ³⁰ Buckley, H.E., '*Crystal Growth*', John Wiley and sons, Inc. NY, 1951.
- ³¹ Laudice, R.A., '*The growth of single crystals*', Prentice Hall, Inc. NJ, 1970.
- ³² Pamplin, B.R. (Ed.) '*Crystal growth*', Pergamon Press, Oxford. 1975.
- ³³ Brice, J.C., '*Crystal growth Process*', John Wiley and Sons, New York, 1986.
- ³⁴ Basrat, C.S and Massalski, T.B, '*Structure of Metals*', 3rd ed Mc Graw-Hills, New York, 1966.
- ³⁵ Czochralski, J., *Z.Phy Chem.* **92** (1971) 219.



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- ³⁶ R.Udea and J B Mullin (eds) '*Crystal Growth and characterization*'. Proc. ISSCG-2 spring school North Holland, Amsterdam 1975.
- ³⁷ Brice, J C., '*The growth of crystals from Liquids*', North Holland Amsterdam 1973.
- ³⁸ Hastmann, P., (ed) '*Crystal growth: An introduction*', North Holland, Amsterdam 1973.
- ³⁹ Ellwell, D. and Scheel, H.J., '*Crystal growth from high temperature solutions*', Academic Press, London, 1975.
- ⁴⁰ Laudise, R.A , *J.Am. Chem. Soc.* **81** (1959) 562.
- ⁴¹ Heinisch, H.K., '*Crystals in Gels and Liesegang rings*'; Cambridge University Press, Cambridge, 1988.
- ⁴² Sasaki,T., *J.Cryst. Growth*, **99** (1990) 820.
- ⁴³ Skrtic, D., Vincekovic, N.F., Milhofertt, *J.Cryst. Growth*, **114** (1991) 118.
- ⁴⁴ Bahadur, S.A., Ramakrishnan, V. and Rajaram, R.K., *Bull. Mater. Sc.*, **13** (1990) 161.
- ⁴⁵ Chaoyang, T.U., Zundu, L., Chem. G. and Wang, G., *Cryst. Res. Tech.*, **29** (1994) K 47.
- ⁴⁶ Yokotani, A.Sasaki,T. Fujioka, K., Nakai,S. and Chiyoe, Y. *J. Cryst. Growth*, **99** (1990) 815.
- ⁴⁷ Faktor, M.M. and Garnett, I., '*Growth of Crystals from the vapour*', Cahapman and Hall, London, 1974.
- ⁴⁸ Piper, W.W. and Polich, S.J., *J.Appl. Phys.* **32** (1961) 1278.
- ⁴⁹ Brenner, S. S., '*The Art and Science of Growing Crystals*' (Gilman, J.J., Ed.), Wiley, New York, 1963.
- ⁵⁰ Bradley, '*The Art and Science of Growing Crystals*' (Gilman, J.J.Ed.), Wiley, New York, 1963.
- ⁵¹ Reynolds, '*The Art and Science of Growing Crystals*' (Gilman, J.J.Ed.) Wiley, New York, 1963.
- ⁵² Holland, L., '*Vacuum Deposition of thin films*', Chapman and Hall, London 1956.
- ⁵³ Archilbald, P. and Parent, E., *Solid State Technology*, **19** (1976) 32.



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- ⁵⁴ Schaefer, H., '*Chemical Transport Reactions*', Academic Press, New York, 1964.
- ⁵⁵ Kaldis, E., *J. Cryst. Growth*, **17** (1972) 3.
- ⁵⁶ Kulkarni, A.K., *Bull. Mater. Sci.*, **17** (1994) 1379.
- ⁵⁷ Char, K., Antognazza, L. and Geballe, T.H., *Appl. Phys. Lett.*, **63** (1993) 2420.
- ⁵⁸ Arivuoli, D., Gnanam, D. and Ramasamy, P., *J Mater. Sci. Lett.*, **5** (1986) 959.
- ⁵⁹ Bridgmann, P.W., *Proc. Am. Accd. Arts. Sci.* **60** (1925) 305
- ⁶⁰ Stock barger, C., *Rev. Sci. Instr.*, **7** (1938) 133.
- ⁶¹ Shah, P.C., *Ind. J. Phys.*, **67A** (1993) 467.
- ⁶² Bhatt, V.P., Gireesan, K. and Pandya, G.R., *J. Cryst. Growth*, **96** (1989) 649.
- ⁶³ Berry, C., West, W. and Moser, F., '*The Art and Science of growing Crystals*' (Gilman, J.J.Ed.) Wiley, New York, 1963.
- ⁶⁴ Howe, S. and Elbaum, C., *Phil. Mag.* **6** (1961) 1227.
- ⁶⁵ Dash, W. C., *J. Appl. Phys.*, **30** (1959)459.
- ⁶⁶ Furukawa, Y., Sato, M., Nitanda, F. and Ito, K., *J. Cryst. Growth*, **99** (1990)832.
- ⁶⁷ Pfann, W.G., '*Zone Melting*', 2nd ed., John Wiley, New York 1966.
- ⁶⁸ Keck, P.H and Golay, M. J. E., *phys. Rev.*, **89** (1953)1297.

