PART - A

CHAPTER - 1
GROWTH AND DISSOLUTION

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The word "Crystal" as used in every day life may have different meanings for a layman and for a scientist. The word "Crystal" comes from a Greek word meaning "clear ice". The existence of crystalline state of solids in nature was discovered by Rene Just Hauy (1743 – 1833) As we know today, the theories based on a single crystalline solid have helped us to understand the properties of both the crystalline and noncrystalline materials.

Single crystals were quite known in the nineteenth century. With increasing applicability and usage, the need of producing artificial crystals has increased.

To grow a good crystal is an art as well as a science (Gilman)[1]. During 1936 to 1949, Stockbarger grew about 1500 flourite crystals for military applications in high-quality optical lenses and Nacken successfully synthesized quartz crystals during the second world war. It was beginning of the systematic growth of synthetic quartz crystals. For the growth of synthetic crystals, there are many techniques developed. However, the success of the technique in obtaining good, pure and large crystals depends on various factors :

a) nature of material itself

b) its purity

c) thermal environment

d) the rate of growth

e) pressure

f) diffusion coefficients of the materials

g) impurity concentration and

h) homogeneity.

Crystals of a particular material can be grown by one or more of the various techniques and the choice of a particular technique for growing a crystal depends on the material properties and the purpose of its application. Hence a systematic classification of growth techniques to simplify this problem has been given by Laudise[2]. There are three basic categories of the crystal growth process :

(1) Solid growth : S → S Processes involving solid-solid phase transitions.

(2) Vapour growth : V → S Processes involving gas-solid phase transitions.

(3) Melt growth : L → S Processes involving liquid-solid phase transitions.

The present chapter gives a brief outline of various methods used for crystal growth.

CRYSTAL GROWTH FROM VAPOUR PHASE :

The method is useful when the size of the crystal is not important. Crystals with good perfection can be obtained from its vapour phase The method is of much theoretical importance and is used for production of thin films and also small good quality crystals[3]. The technique has been reviewed by several authors [4-8] This method is further divided into three categories :

(A) SUBLIMATION :

At a suitable high temperature, sublimation of the source material takes place. The sublimated material condenses into a crystalline solid if proper control over temperature and pressure conditions is maintained. For example, ZnSe and SiC crystals have been grown by this technique[9,10].

(B) VAPOUR TRANSPORT :

The transport of the source material takes place as a volatile specie by a suitable carrier gas to the crystallization region. For example SnSe single crystals with I_2 as a carrier, can be grown [3].

(C) GAS PHASE REACTION :

This technique involves the growth of crystals as a product from the vapour phase as a direct result of chemical reaction between the reactant vapour species The method of crystal growth from vapour phase is rarely applicable to grow large crystals due to the problem of multinucleation There are some exceptions such as CdS, ZnSe, GaP, GaAs and Cd_4GeS_6.

CRYSTAL GROWTH FROM SOLUTION :

This is the simplest and the oldest method of growing crystals in which the material to be crystallized is dissolved in water or an appropriate solvent to the desired degree of supersaturation. The solution is then slowly cooled or evaporated. Using a seed crystal and precise control over temperature, humidity and rate of evaporation, excellent quality large crystals can be grown. Well-known examples are ferroelectric and piezoelectric materials such as KDP, ADP, DGS and TGS[11,14].

CRYSTAL GROWTH BY GEL METHOD :

The growth of crystals from gel was recorded as early as 1913 by Leisegang, Bradford and Holmes. In the gel growth, crystals are formed usually at room temperature and hence are free from strain often present in crystals prepared from melt or from vapour The method has obvious limitations. However, for a certain class of substances which have a very slight solubility in water and which cannot be satisfactorily grown from melt or vapour, it offers reasonable prospects of success. The crystals like TGS, DGS and $KClO_4$ have been grown successfully in this laboratory [15], by this method. Obviously the method is more useful for organic and semiorganic compounds. The method has been discussed in detail by Henisch [16].

GROWTH BY HIGH TEMPERATURE SOLUTION METHOD :

This method is basically a solution method with the main difference of high melting point solvents being used. The melting point of the solvent is usually above 600°C. Though this method involves practical difficulties of proper choice of solvent, chemical and phase stability of the solute and solvent, obtaining high temperatures, contamination etc., many important materials like YIG, lithium Ferrite, gadolinium aluminate, barium titanate, ruby, emerald and $Ba_2MgGe_2O_7$ are grown by this method. The method is applicable to almost any material for which a suitable solvent can be found. Crystal perfection is much better than that obtained by any other method. In this method, optimum growth rate is quite small. The principles and techniques involved in this method have been discussed by Elwell et al [17].

CRYSTAL GROWTH FROM MELT :

Here the crystal is obtained from its melt. The crystals almost free from impurity can be grown by this method. Moreover the crystal can be doped with a desired impurity and its exact proportion in ppm can be controlled. Metals, their alloys, semiconductors and alkali halides can be grown from melt Basically this method involves transfer of heat through the solid-liquid interface. The heat transfer can be given by the equation,

$$K_sG_s - K_LG_L = LV$$

where,

K_s = Thermal conductivity of solid

K_L = Thermal conductivity of liquid

G_s = Temperature gradient in solid

G_L = Temperature gradient in liquid

L = Latent heat of fusion / unit volume

V = Growth velocity

The melt is allowed to solidify in a controlled manner. Many parameters affect the growth process, such as the temperature gradient, the growth velocity and the composition of molten charge. In the case of alloys, if a gradient in concentration is established in the liquid during the growth, there results non-uniform composition of constituents in the alloy crystal and also the constitutional super-cooling. The composition of the frozen material in such a case is always different from that of the liquid or the molten charge The instability of interface occurs and cellular structure results. Tiller et al [18] and Delves [19] have shown that the constitutional super-cooling can be reduced to minimum,

(1) by using slow growth rate

(2) by stirring the melt to minimise solute concentration gradient and

(3) by using a steep temperature gradient

In the case of growth of the single crystal from a doped material or a noncongruently melting alloy, the solute transport plays an important role in addition to heat transport in the success of the growth process. During the crystal growth in such a case, solute segregation occurs at the solid-liquid interface due to :

(a) non-uniform solute distribution along the length of the crystal and

(b) constitutional supercooling

Rutter et al [20] had introduced the concept of constitutional super-cooling. The constitutional super-cooling results in the instability of the interface giving cellular structure, dendritic structure, stray nucleation, waviness of interface etc., spoiling the quality of the crystal obtained. Further, Delves [19] has defined a parameter "S" known as constitutional super-cooling parameter which is given by

$$S = \frac{mG_{LS}}{G_L}$$

where,

G_{LS} = Solute concentration gradient in liquid
= $-V(C_L - C_S) / D$
V = growth speed
D = diffusivity of solute in liquid
C_L = concentration in liquid
C_S = required concentration in solid
m = slope of the phase diagram liquids line at the given composition of alloy
G_L = temperature gradient in liquid

If $S>1$, constitutional super-cooling will occur. Thus the chances of constitutional super-cooling can be reduced by slow growth-rate, good stirring of the melt to minimize G_{LS} and steep temperature gradient.

The crystal growth from melt can be pictured as an atom-to-atom addition to the lattice similar to the growth from vapour and the experimental evidences rule out the necessity of a screw dislocation to promote the growth of metal crystal from melt. This has been concluded from a number of observations. Firstly Dash [21] has successfully grown large areas of single crystals of silicon free from dislocations. A few other metal crystals have also been grown without observable dislocations Secondly, if the dislocations were at all necessary to promote growth, the observed high symmetry of the dendritic growth cannot be accounted for. Hence the concept of nucleation at the re-entrant edge of a screw dislocation is not so important for the growth of metal crystals from melt. Chalmers et al [22] have proposed a step like interface which would provide permanent re-entrant steps not propagated by dislocations and evidences for the existence of such steps have been obtained.

Study of crystal growth from melt mainly involves

1. morphology of the interface and the effect of the various growth parameters on it.
2. the structures observed on the crystal grown from melt.
3. imperfections, their formation and distribution in the crystals and
4. preferred orientation and the influence of various parameters responsible for this property of crystals. Many crystals have been grown from melt by various workers [1,23-28].

There are three basic techniques of crystal growth from melt :

1. Bridgman method
2. Czochralski method
3. Zone-melting method.

BRIDGMAN METHOD :

In this technique, due to Bridgman [29], the melt in a suitable container is moved through a fixed temperature gradient so that the solidification starts from one end and proceeds gradually to the other. The tip of the container is made conical so that initially a small volume of the melt is cooled in a controlled way. This would favour only one nucleus to develop and therefore a single crystal results. To this method, a modification was introduced successfully by Stockbarger who used two furnaces at different temperatures and separated by a baffle, instead of using a single furnace. This method, called Bridgman-Stockbarger method, has been most frequently used for three types of material :

a. Metals
b. Semiconductors
c. Alkali and Alkaline Earth halides

Kumargawa et al [30] 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 $(Sb_xBi_{1-x})_2$-Te_3 single crystals with programmable temperature control by vertical Bridgman method has been reported by Fang-Lang Hsu [31]. CdTe crystals by horizontal two-zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 10^{-7} torr have also been grown [32]. 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 [33]. B.Cabric et al [34] developed a method for crystallization of several substances at different rates in a chamber furnace. Siddiqui [35] has grown eutectic intermetallic compound alloy crystals by the Bridgman Stockbarger method. Also two of the most important present day semiconductors, namely, CdTe and CdZnTe crystals are also usually grown by the Bridgman method [36-37].

CZOCHRALSKI METHOD :

Czochralski[38] developed this method for growing crystals from melt. Using this method the crystals with large size and relatively low dislocation density can be grown. In this method, the size and the diameter of the crystal can be controlled during the crystal growth process. The technique involves a rotating seed dipped in the melt surface and slowly pulled from the melt. Due to rotation, the melt is stirred and thermal symmetry is attained. The excess of heat is removed by conduction and the water circulation through the seed-holder which also helps in maintaining temperature gradient. The essential factors for obtaining good crystals are

a. Accurate control of temperature

b. Pulling rate

c. Rotation rate of seed

Large number of metallic as well as ionic crystals have been successfully grown by this method. The practical aspects of this method have been discussed in detail by Draper[39]. The method has reached hi-tech status due to its applicability for technologically important materials.

To quote examples, Laudise et al [40] have grown doped single crystals of Bi_2Te_3 by Czochralski method in H_2. Wenzle et al [41] have grown copper crystals by Czochralski method in inert atmospheres, at a pressure of 1bar. A modification known as liquid encapsulated Czochralski technique has also been used [42-43].

ZONE MELTING METHOD :

This is relatively a more efficient method of crystal growth from melt discovered by Pfann[44].The main function of the 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 The quality of the crystal depends on the relative zone length, growth velocity and the temperature gradient. Smaller the zone length better is the quality of the crystal.

The technique is capable of purifying a material to utmost sparse level of impurities by giving a large number of passes to the ingot in the same direction. This process is called zone refining process. 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 coefficiet K<1 are collected at the other end. The central portion of the inogt is much purer and purer after each successive zone pass. Also an ingot doped with a known impurity can be made homogenous by passing the "Zone" along the length of the ingot in alternate directions 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 homogenous distribution of impurity in the ingot. The technique can be applied for the preparation of semiconductors of very high purity. This technique is discussed and reviewed by Parr [45], Shah [46] and Harington [47]. It is widely used by different workers [48-53] to grow crystals and to refine various materials.

DISLOCATIONS AND ETCHING :

All real crystals contain defects. Various important properties of a crystals, from electrical conductivity to hardness, depend to more or less extent on these defects also. There are various types of defects in a crystal :

1. Point defect
2. Line defect
3. Planar defect and
4. Volume defect

The line defect is of two types, edge and screw dislocations [54]. It affects most of the physical properties of a crystal to a significant extent according to Orowan [55], Polanyi [56] and Taylor [57].

The dislocation in an as-grown crystal may originate due to

1. propagation from seed crystal
2. shear strain due to mechanical and thermal stresses
3. dendritic growth
4. collapse of vacancies [58]

The properties of dislocations with their various geometrical features have been well-worked out[59-61]. Crystal perfection can be judged in terms of its dislocation content, though many other lattice imperfections exist in a crystal. The dislocation density is defined as the dislocation line length per unit volume. The other practical definition used to measure dislocation density is, the number of dislocations intersecting a unit area of a surface of the crystal. Mott et al [62] and

Frank [63] proposed that dislocation lines can be curved and assume any orientation. Though dislocations may exist in the form of closed loops inside the crystal and hence don't intersect any surface of the crystal, this definition has been used as a fairly good measure of dislocation density. Various methods are employed to study line defects (dislocation), some of them being direct and other indirect. Electron microscopy and x-ray diffraction belong to the first class.

The simplest and easily accessible technique employed to observe dislocation is the "etch-pit" technique [64-66]. The etch pits at the sites of dislocations can be formed either by chemical reaction or by physical dissolution of a crystal in a suitable solution known as an etchant. Some times, etching is also done by other methods like ion bombardment and by thermal treatment. The etching process is in general almost opposite to that of growth.[67-69].

Three dimensional dislocation structures can be made visible by the method known as decoration. In this method, suitably chosen impurity is allowed to precipitate along dislocation lines, which makes the dislocations visible under the microscope in optically or infrared transparent crystals. Dislocations were observed in silicon crystals by Dash [21], in silver halides by Hedges et al [70] and in Alkali halides by Amelinckx [71].

The chemical dislocation etching technique is discussed below in detail but restricted to metals and semiconductors and whenever it is necessary, some references to non-metals are given. The chemical etching gives rise to various types of geometrical features on a crystal surface. Due to anisotropy of a crystal, the dissolution rates are different in different directions giving rise to production of depressions, with regular geometrical out lines at the preferential sites of attack on the crystal surface, known as etch pits. Etch pits were used by minerologists to determine crystal planes and their orientations Dissolution of a crystal surface is effected by the re-treat of monomolecular steps, the process being reverse to that of growth which takes place due to the addition of steps on the surface. It is believed that when a crystal face is exposed to a solvent, dissolution begins by nucleation of unit pits of one molecule depth and these unit pits grow as steps retreat across the crystal surface through the action of kinks. The chemical etching of a crystal surface involves the following sequences :

Reactants :

1. Approach the surface
2. Interact with the surface and
3. React chemically

Products

1. Disengage themselves from the surface

2. Move away from the surface.

The overall etching process may be electrochemically controlled or diffusion controlled or controlled by the combination of both as suggested by Gatos [72] and Gatos et al [73]. The factors affecting the process of dissolution of a crystal surface are as follows :

a. Crystallographic orientation of the surface
b. Impurity concentration on the surface
c. Crystal defects present in the surface
d. Surface damage and cleanliness

The above said factors affecting the etching process are discussed in detail by Irving [74]. Regarding the formation of etch pits at dislocation sites, explanations have been given by various workers. For the initiation of etch pits, the presence of impurities preferentially segregated at dislocations was considered essential for long time. Impurity segregation has been reported to be responsible for the formation dislocation pits in zinc and copper crystals.[75-76].

Cabrera [77] and Gilman et al [78] have reported the etch pit formation as nucleation process analogous to crystal growth and attributed the nucleation of etch pits at dislocations to the elastic energy associated with dislocation.

A new approach to the problem was given by Frank [67] proposing a kinetic theory of growth and dissloution. The theory was later applied to etching process [79] According to this, the visibility of an etch pit depends on

a) The dissolution velocity V_d, along dislocation line,

b) The ledge dissolution velocity V_l and

c) The average vertical dissolution velocity V_s, at a dislocation free region of the crystal surface.

For the formation of visible etch pits,

$$V_d/V_l \geq 0.1 \text{ and } V_d > V_s$$

An excellent review of etching as used on LiF crystals has been given in detail by Gilman[80]. The technique has also been used to study dislocations in some present day important crystals like $Cd_xZn_{1-x}Te$ and CdTe[81-82]. The formation of slip pattern in copper crystals and its dilute alloy crystals has been very fruitfully studied with the use of etching technique[83].

In order to study the etching mechanism with various parameters, systematic investigation has been carried out by many workers[84-89]. Lin et al[90] have reported anisotropic etching on different crystallographic surfaces of AlSb single crystals To study dislocations, in some cases, the chemical etching is done in magnetic field[91-92] or electric field[87]. Also a crystal can be etched electrolytically [93-94].

The reliability of an etchant as a dislocation etchant can be judged by one or more of the following tests :

1) Etch pits associated with individual dislocations reappear after each successive polishing and etching, since a dislocation line cannot terminate inside a crystal.
2) The etch pattern produced by the etchant on two oppositely matched cleaved surfaces should appear as mirror images of each other, if cleavage of a grown crystal is possible. Sagar et al[95] and Bhatt et al[96] have shown branching and bending of dislocations at the cleavage which may result in deviations from one to one correspondence of etch pits on the oppositely matched cleavage surfaces.
3) The etch pit density should show a reasonable agreement with the theoretically estimated dislocation density.
4) Plastic deformation always involves the creation and motion of dislocations which result in increase of etch pit density at least in the vicinity of the region of deformation.

For the development of a dislocation etchant for a given material, a trial and error method has usually to be used. Etching can be effeciently used to characterize the crystal and

1) To decide whether a given solid is a single crystal or not.

2) To distinguish between different faces of a crystal.

3) To reveal the growth history of a crystal.

4) To determine dislocation density of a crystal.

5) To assess the impurity distribution.

6) To study stress-velocity relation for individual dislocation motion.

7) To study deformation patterns like pile-up and polygonization.

8) To study dislocation multiplication.

9) To study plastic flow around indentation

10) To study fracture mechanism.

11) To study slip and twin systems and interaction of dislocations under stress.

12) To study kink configuration and inclination of dislocation.

13) To study origin of dislocations in as-grown crystals.

14) To distinguish between fresh and as-grown dislocations.

15) To delineate grain boundary and

16) To study polarity of crystal lattice [97-104].

Chemical etching, though an old technique is quite useful even in modern days in a variety of crystals [105-109]. The results on crystal growth of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ and dislocation etching on their cleavage faces carried out by the author are reported in chapter VI.

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