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## **CHAPTER – I**

**A BRIEF SURVEY ON THE “GROWTH OF  
SINGLE CRYSTALS”**

## CHAPTER 1

### A BRIEF SURVEY ON THE "GROWTH OF SINGLE CRYSTALS"

#### 1.1 Introduction

Good single crystals are essential for a variety of scientific and commercial purposes. They are needed for scientific appraisal of the crystallography, topography and tensor properties of all crystalline organic, inorganic and metallic materials. Silicon and germanium were listed as metals until pure crystals became available just before the Second World War. Modern Solid-State Electronics is based on the crystal growth revolution which has now made possible the commercial scale growth of large dislocation-free crystals of silicon and III-V compounds such as gallium arsenide, indium phosphide, gallium aluminium arsenide.

Single crystals have important applications in technology and industry. For example, much better frequency stability and lower acoustic losses can be achieved in single crystals than in polycrystalline aggregates. Thus single-crystal piezoelectrics such as quartz, are used for frequency control elements. Conductivity and mobility requirements need single crystal semiconductors for diodes, transistors and hence integrated circuits. Single crystal optical materials will have better optical properties (for example, transmittance) compared to polycrystalline materials. The existence of lasers and masers has created several new demands for single crystals for research and industrial applications. A few of the

applications that single crystals find in technology and in Solid State Device research include:

1. Transistors - Si, Ge, GaAs, GaAlAs
2. Tunnel diodes and signal diodes - GaAs, GaP, InP
3. Strain gauges - Si, GaAsP
4. Microwave limiters  
and tunable filters - Yttrium iron garnet
5. Optoacoustic devices - Lithium niobate ( $\text{LiNbO}_3$ )
6. Lasers -  $\text{CaWO}_4$ ,  $\text{CaF}_2$ , YIG, ruby, GaAs, InP, InSb, InAs, GaAsP
7. Electromechanical transducers - Quartz, Rochella salt, ADP, CdS, GaAs
8. Filters and oscillators - Quartz
9. Optical uses -  $\text{CaF}_2$ , quartz, LiF,  $\text{CaCO}_3$ ,  $\text{BaTiO}_3$
10. Radiation detectors - Anthracene, KCl, Sc, GaAs, TGS,  $\text{HgI}_2$ ,  $\text{HgCdTe}$
11. Industrial bearings - Sapphire
12. Cutting and abrasives - sapphire, diamond, SiC
13. Rectifiers - Si, Ge
14. Electroluminescent devices - GaP, GaAs, GaAsP
15. Bubble memory devices - YIG, GGG
16. Solar cells - Si, GaAs, GaAlAs, CdTe
17. Kidney stones - Calcium oxalate,  $\text{CaHPO}_4$ , Uric acid

The enormous flow of information related to the growth of single crystals can be broadly classified into the following groups:

- I Solution growth
- II Melt growth
- III Vapour growth
- IV Solid State growth

These four groups can be further classified into various sub-groups:

#### I. SOLUTION GROWTH

(a) Low temperature solution growth:

(1) Aqueous solution growth, (2) Growth from organic solvents, (3) Gel, (4) Electrocrystallization.

(b) High temperature solution growth:

(1) Flux growth, (2) Growth from metallic solvents, (3) LPE growth.

(c) High pressure solution growth:

(1) Hydrothermal growth, (2) High pressure and high temperature growth.

#### II. MELT GROWTH

(1) Zone refining, (2) Floating zone, (3) Bridgman-Stockbarger, (4) Kyropoulos, (5) Czochralski pulling, (6) Liquid encapsulation, (7) Vernenil flame fusion.

#### III. VAPOUR GROWTH

(1) Sublimation, (2) Chemical Vapour deposition (CVD), (3) Metal-organo CVD, (4) Vapour phase epitaxial growth, (5) Molecular

beam epitaxial growth, (6) Vacuum deposition, (7) Sputtering, (8) Flash evaporation.

#### IV. SOLID STATE GROWTH

(1) Strain annealing, (2) Strain hardening, (3) Grain growth, (4) Secondary grain growth.

Out of the above four main groups of crystal growth methods, Groups I to III are used for Solid State research and group IV is mostly used for metallurgical applications. Since it is not possible to discuss about all the crystal growth methods in one chapter, some of the most important and widely used techniques will be discussed.

##### 1.2 Growth of single crystals from solution:

###### General considerations:

If suitable solvent is found, crystals can be grown at temperatures below the melting point of the crystal. The low temperatures place much less demand on furnaces and power supplies. Growth from solution is often the only alternative if the substance decomposes below its melting point or undergoes a phase change.

The choice of solvent is of great importance. It is easier to grow large perfect single crystals if the solute has solubility exceeding 5 mole per cent. Low viscosity is desirable. The volatility of the solvent must be controllable over a wide range. The solvent should not react with the container or the atmosphere.

The growth rates by this method are much smaller than the growth rates from the melt. It is extremely difficult to produce spontaneous nucleation in a solution in such a manner that only a single or even a very few nuclei are formed. Because of the difficulty of controlling the nucleation, seeding is almost essential if large crystals are to be grown from solution.

#### Crystal growth from aqueous solution:

Solutions are mixtures either in the solid or in the liquid state. A saturated solution contains the maximum amount of material which can be dissolved and its concentration is the saturation concentration. The solubility of a material depends upon the temperature at constant pressure. The solubility may be influenced by impurity in the starting materials and pH value of the solvent. Figure 1 shows the solubility of KBr and NaCl as a function of temperature. Solubility curve of KBr type is more suitable for growing single crystals from aqueous solution.

Any crystal growth process involves three steps: (i) Attainment of supersaturation, (ii) Formation of critical nucleus and (iii) Growth of a crystal.

The state of supersaturation is the most important factor for crystal growth. The degree of supersaturation can be expressed as  $S = \frac{C}{C^*}$  where 'C' is the concentration of solution and  $C^*$  is the equilibrium saturation concentration at the same temperature.

Thus, for a saturated solution  $S = 1$ ,  $S < 1$  denotes undersaturation and  $S > 1$  indicates supersaturation. (Figure 2). Other common expressions of supersaturation are the concentration driving force,  $\Delta C$ , and the relative supersaturation  $\sigma$ , defined by

$$\sigma = \frac{\Delta C}{C^*} = S - 1 \text{ where } \Delta C = C - C^*$$

Of these three expressions, only  $\Delta C$  is dimensional.  $\sigma$  is also called as the percentage of supersaturation. Solution compositions are generally expressed as gm/kg or gm/litre. In order to grow good quality single crystals, different supersaturated solutions must be prepared.

The formation of nucleus in the absence of any defect requires a supersaturation of about 25 to 50 per cent. Supersaturation may be obtained by cooling, evaporation or rarely by addition of other materials. For most of the solution techniques a two-stage growth process is used: (i) First by allowing slow evaporation or cooling a saturated or supersaturated solution which will give small crystals, (ii) Some of these crystals are selected and used as seeds to grow larger ones.

Two basic methods are used to grow large crystals by using the seed crystals as shown schematically in Figs. 3 and 4. In both the cases a saturated or slightly supersaturated solution is prepared and the seed crystal is inserted. In one technique the temperature is lowered slowly so as to reduce the solubility

and produce crystallization; in the other technique the temperature is held constant but the solvent is permitted to evaporate with the same result. The seed crystal may be rotated if necessary during the growth. By these methods large crystals (several inches) of inorganic salts such as alkali halides, rochelle salt (potassium sodium tartrate), ethelene diamine tartrate (EDT), ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), sodium nitrate, tryglycenesulfate (TGS) etc. crystals have been grown.

If the solubility of materials in pure water is too low, then organic solvents can be employed. In some cases, the presence of some metal ions in very small quantities (a few ppm) favourably influences the growth of certain compounds from aqueous solutions. Additives of Pb and Fe materials helped in growing good quality crystals of  $\text{KNO}_3$  and ADP respectively, probably by changing the viscosity and surface tension of the solution.

### 1.3 Growth of single crystals from melt:

#### General Considerations:

For growing crystals from melt the material to be grown in the form of a single crystal is placed in a suitable container and heated in a furnace above the melting point. To initiate the growth the melt is cooled from above the equilibrium melting point and if the seed crystal is present, crystal growth will normally begin when the temperature is slightly below the equilibrium melting



**point.** If no seed is present the melt will generally super-cool until a stable nucleus is formed. There is a rapid transition from an equilibrium state in which the substance is completely molten above the melting point to a state such that the system is completely solid below the melting point. The crystal grower's problem is to control this transition so that single crystal may grow. This is achieved by permitting at a time, a small volume of the melt to pass through the transition temperature to crystallize. A temperature gradient is also necessary with one portion of the system above and the other portion below the melting point having a uniform temperature gradient. Usually the crystal growth from pure melt is successfully controlled by controlling the thermal gradient.

Since the grown portion of the crystal can serve as a conducting path, the thermal conductivity of the crystal is of interest. Crystals will usually grow most rapidly in certain crystallographic direction in which the thermal conductivities are larger.

#### **Crystal growth by Czochralski crystal pulling method:**

"Crystal pulling" or the Czochralski technique (1917) is a popular method of crystal growth from the melt because it can produce large (upto several inches), dislocation-free crystals in a relatively short period of time. It received much study and development in 1950's when it was applied to grow single crystals of

silicon and germanium for their use in transistors. Even at present much of the silicon, germanium, III-V compound semiconductors (GaAs, GaP etc.), oxides are being grown by this method.

The general criteria that must be fulfilled for crystal growth by this method are:

- (1) The crystal should melt congruently without decomposition.
- (2) The crystal should not be reactive with the crucible or the atmosphere present during pulling.
- (3) The melting temperature should be attainable with the heaters available and should be below the melting temperature of the crucible.

For Czochralski growth the following equipment is required:

- (1) A means of heating the melt and controlling melt temperature and gradients (RF heating, resistance heating, temperature controllers etc.),
- (2) A means of containing the melt (i.e., crucible made of silica, graphite, tungsten, platinum etc.),
- (3) A means of holding, rotating and withdrawing the seed (i.e., motor),
- (4) A means of controlling the atmosphere (i.e., inert), if air is not a compatible atmosphere.

Basic principle of the pulling method is schematically shown in Fig. 5.

The material to be grown [for example, Si (melting point 1412°C) or  $\text{CaWO}_4$  (melting point 1535°C) or Ge (melting point 937°C) or any other material] is melted in a crucible. To begin growth the melt temperature is brought slightly above the melting point as the seed crystal is touched with the melt. Thus, a small amount of the seed is melted to ensure that growth begins on a clean surface. Growth is begun when the temperature of the melt is lowered by decreasing the power. At exactly right conditions, as judged by the experience of the grower, pulling is commenced. That is, a seed crystal is dipped into the melt and slowly withdrawn. The seed is rotated at the same time in order to attain thermal symmetry and also to stir the melt. By arranging the system such that the seed is slightly cooler than the melt, the material solidifies on the seed as it is slowly withdrawn. If suitable precautions are taken, the material withdrawn from the melt solidifies as a large single crystal.

The main requirements for growing good crystals by this method are that the pull and rotation rates should be smooth and the temperature of the melt should be accurately controlled. The diameter of the crystal is dependent on both the temperature of the melt and the pull rate. To increase the diameter of the crystal

being grown, either the power is reduced or the pull rate decreased, the opposite applies for reducing the diameter. The maximum size of the crystal that can be produced by this technique is governed by the volume of the melt, the diameter of the crucible, the distance that the pull rod can move and the strength of the crystal at its maximum diameter.

**Liquid encapsulation Czochralski method:**

Volatility of the melt causes considerable difficulties in crystal pulling. For materials containing volatile constituent (i.e., GaAs, PbSe, GaP, PbTe etc.), it is sometimes necessary to prevent excessive evaporation causing decomposition. An effective method to do this is to make use of the liquid encapsulation method as shown in Fig. 6.

In this method, an immiscible non-volatile material floats on the melt to inhibit the volatilization. To grow single crystals of PbSe, GaAs, GaP, InP and other volatile materials,  $B_2O_3$  powder has been used extensively where an inert gas at substantial pressures has been used over the  $B_2O_3$  melt. The inert gas keeps the liquid encapsulate in contact with the melt. The encapsulate thus acts as a "piston" and an equilibrium pressure of the volatile constituents from the melt can be thought of as existing between the melt and its piston. Using this method, II-IV, IV-VI and III-V compound semiconductors can be grown.

Even though several important crystals can be grown using aqueous solution, Czochralski pulling, liquid encapsulation and chemical vapour deposition methods, there are still several scientifically and technologically useful crystals such as  $\text{PbI}_2$ ,  $\text{CaCO}_3$ ,  $\text{Ag}_2\text{H}_3\text{IO}_6$ , silver halides, cuprous halides etc. cannot be grown by the above three types of methods. Therefore, gel method has been found to be the most suitable technique to grow a variety of useful single crystals which cannot be conveniently grown either by solution or melt or vapour methods. Many of the advantages of gel method over the other crystal growth methods will be discussed in Chapter 3.

#### **1.4 Growth of Single Crystals from Vapour:**

##### General Considerations:

In case the materials being grown decompose or sublime before melting at atmospheric pressure and a suitable solvent is not available, crystals can often be grown conveniently from the vapour phase.

It is generally more difficult to grow large crystals from the vapour than from the melt or from solution. However, the process does offer advantages. The degree of supersaturation is more easily controlled than during growth from the melt. In addition, vacuum or a truly inert gas such as helium can be used as the diluent without introducing the complications of a chemically active solvent.

The growth process involves three stages: (1) transport

of material, (ii) surface reaction, and (iii) dissipation of heat. The temperature of the vapour source and the temperature of the substrate on which the crystals grow are among the most important of the growth variables. The former controls the vapour supply while the difference between the two temperatures determines the supersaturation at the growing crystal. The magnitude of the supersaturation required for a given growth rate will depend strongly on the particular system being studied.

If a precursor is used which will be converted to the desired substance during growth, the process may be considerably complicated. Usually there will be a minimum temperature for the growing crystal or substrate below which the desired reaction will not take place. If the necessary reaction is a reduction, it is usually necessary to supply a reducing agent such as hydrogen which will affect both the thermal and particle transport process. In addition there will invariably be reaction products which can affect growth and must be removed.

Three types of vapour growth methods will be briefly discussed in the following:

**(1) Sublimation - Condensation technique:**

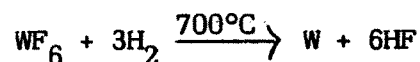
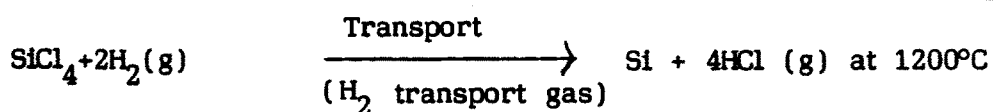
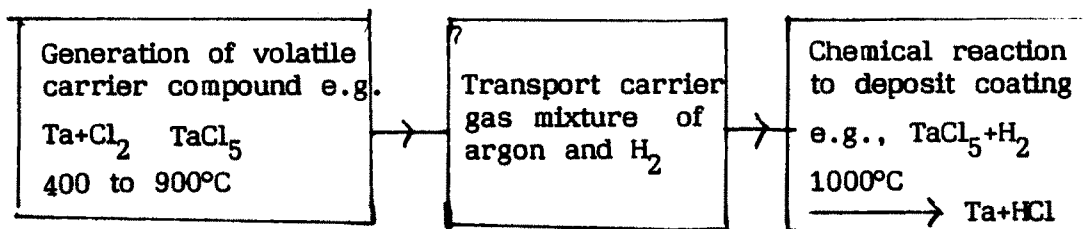
In this method, a substance is directly converted from the solid into the gas, and back again to the solid without the intermediate liquid step. High vacuum assists this process and heating

or cooling the said crystal or area where growth initiation is desired is often required.

In a typical version of the closed tube technique, the material to be transported is placed within a tube (usually silica) and the tube is evacuated. Sometimes the tube is back-filled to a desired pressure with a gas that represses decomposition or with an inert gas. The inert gas may act to improve transport, because its convection may act to improve transport, because its connection may help to move the subliming pieces toward the growth region. In this way, "source material evaporated at hot region and condenses in the form of crystals at the cool region of the silica tube". Using this method, single crystals of Cd, Zn, Au, Ag, Fe, ZnS, CdS etc. can be grown.

**(ii) Chemical Vapour Deposition:**

The chemical vapour deposition (CVD) describes a very broad group of processes all of which use a chemical reaction between gaseous reagents at or near a heated surface to deposit material on the surface. In CVD volatile chemical compounds are used to transport materials which are much less volatile. The actual deposition is achieved by a chemical reaction such as reduction or thermal decomposition.



Generally CVD process involves three steps:

- (a) the generation of the volatile carrier compound,
- (b) the transport of volatile compound to the deposition zone, and
- (c) the chemical reaction to form a solid product

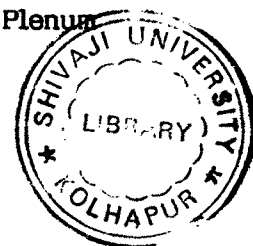
The chemicals used in the CVD processes must have properties which match the requirements of the above three steps. The carrier compound must have sufficient volatility to be transported from the source to the deposition zone without being so unstable that it decomposes on the way. However, once the carrier compound has reached the deposition zone it must react readily and heterogeneously to form a smooth coherent deposit.

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