
UNIT 14 CRYSTAL GROWTH AND ALLOYING

Structure

- 14.1 Introduction
 - Objectives
- 14.2 Crystal Growth
 - Nucleation and Growth
 - Methods of Growing Crystals
- 14.3 Defects in Crystals
- 14.4 Metal Alloys
- 14.5 Summary
- 14.6 Terminal Questions
- 14.7 Solutions and Answers

14.1 INTRODUCTION

In the preceding units of this course you have learnt about various properties of crystals. Now you may be curious to know: Do crystals exist in nature? How and why are crystals prepared artificially? Is there only one technique for growing crystals? If not, then what factors, physical and technological, govern the choice of a particular technique? From your school experimental science course work you may recall how crystals of copper sulphate or common salt grow. If you take a common salt solution and heat it, you will observe that crystals of salt are formed at the bottom of the container after evaporation of water.

Crystals of many elements and compounds grow in nature, but their growth rates are extremely slow. Due to industrial applications, we need crystals in large quantities and natural resources are not sufficient to meet these requirements. You may have heard of artificial pearl culture industries in Hyderabad. In some applications, we need materials (like compound semiconductors), which do not occur in nature at all. Their growth in the purest form has been a technological challenge for scientists in the past few decades. In Sec. 14.2 you will learn the principles governing crystal growth and various methods used to grow crystals artificially. The relative advantages/merits of different techniques are also discussed.

When a crystal is grown, it is quite possible that its lattice structure is not perfect, i.e. it possesses some *defects*. These defects can arise due to improper solution, fluctuations in temperature and/or pressure or due to presence of impurities. We expect the defects to affect the mechanical strength, heat capacity, electrical conductivity and magnetic behaviour of a material. Crystal defects and their influence on crystal properties are discussed in Sec. 14.3. For several technological applications, we need to modify properties of naturally existing materials. Scientists rightly took this as a challenge for development of society and have devised newer methods and techniques. The simplest of these consists of combining two or more elements, at least one of which is a metal. By this method, it is possible to form materials with desired electrical, mechanical, magnetic or thermal properties. Such materials are called *alloys*. You will learn about alloys, their formation, properties and applications in Sec. 14.4.

Objectives

After studying this unit, you will be able to:

- explain the process of crystal growth;
- list various methods used for growing crystals with their salient characteristics;
- describe how crystal defects affect material properties;

- explain the process of alloy formation; and
- list applications of metal alloys.

14.2 CRYSTAL GROWTH

From your school science curriculum and Block 1 of this course, you will recall the crystal structures of rock salt, quartz and diamond. The crystals of these materials occur in abundance in nature. In fact, crystals of some of these materials were discovered by human beings very early. These crystals were formed in nature over a period of hundreds and thousands of years. But now-a-days, crystals are produced artificially to meet the growing demands of industry, science and ornament manufacturing.

You may now like to know: How are crystals formed, what processes and methods are used and so on? The process of formation of crystals is known as **crystallisation**. This is a very important industrial process for the production of highly perfect crystals of silicon and germanium required in semiconductor industry. It is used, on a much larger scale, as an efficient method to purify materials like sugar and salt.

Crystals are developed by methods like growth from melt, solution or vapour phase. However, to achieve desired results, it is necessary to ensure suitable conditions with appropriate temperature, concentration of constituent elements, pressure etc.

As you know, in a crystal, atoms or molecules are arranged regularly in a 3-D space with specific geometrical symmetry. This arrangement, determined by the bonding pattern, is such that the solid is in the state of minimum potential energy. The process of crystal growth begins with the formation of a small cluster of atoms, called nucleus, around which additional atoms are attached. You will now learn about the nucleation and crystal growth process.

14.2.1 Nucleation and Growth

In artificial crystallisation, the material is first converted into a fluid phase. This brings all the atoms in a state of mobility with the result that they begin to move completely randomly. Moreover, they show no memory of past history. Such initial fluid stage is called **mother phase**. When cooled, growth of the crystal starts (in the mother phase) initially at the microscopic level, where few atoms or molecules join together to form a cluster. Such clusters of atoms are called **embryo**. The embryo formation brings these atoms into a state of low binding energy. An embryo may grow further or disintegrate. If it grows to a particular critical size, called **nucleus**, there is a high probability of growth of a crystal around it. Typically, the number of atoms in a nucleus can vary from 10 to a few thousand. In a nucleus, arrangement of atoms is similar to the lattice structure of the crystal. As the atoms approach the nucleus and attach themselves to it, they start to grow with an arrangement defined by the lattice structure of that crystal. This arrangement is quite likely as it corresponds to the minimum energy configuration of the structure. This microscopic arrangement of atoms, when allowed to grow for long time, leads to a big (few μm^3 to cm^3) single crystal. The actual shape of the crystal is largely determined by its lattice structure at the atomic scale. For example, a material with cubic lattice geometry will result into a cubic shaped crystal.

The nucleation process starts as the temperature of the mother phase is brought down by **supercooling**. Even **supersaturation** can result in the formation of nuclei. Quite often, in artificial crystallisation we wish to grow a large single crystal of the material. In such a situation it is necessary to avoid formation of many nuclei in the solution as that would lead to formation of many small crystallites. When these crystallites grow, neighbouring crystallites may touch each other and the boundaries between them will disrupt the periodicity of the crystal. This happens because all crystallites are randomly oriented. It means that supersaturation can give rise to a polycrystalline solid. To avoid this, it is necessary to control spontaneous formation of excess nuclei.

Every material always tries to go into the minimum energy state in order to have a stable structure.

Supercooling refers to cooling below the freezing point of a liquid without formation of solid crystal.

Supersaturation means that the dissolved substance is more than that required for saturation. This can be achieved by cooling a hot saturated solution.

This is done by putting a small piece of crystal in the mother phase. This is known as **seeding process**. The inserted crystal acts as a **seed** around which further crystal growth takes place. As nuclei formation is not necessary now, the mother phase need not be supercooled; the growth occurs at relatively higher temperatures.

The nucleation process within the mother phase can be induced by external influences like agitation, mechanical shock, friction, high pressures, electric and magnetic fields, spark discharge, ultraviolet radiation, X-rays, sonic and ultrasonic radiation, laser beam etc. In such cases, however, there is possibility of polycrystalline growth. Can you say why? This is because of the fact that the external influence is experienced by the entire solution and can simultaneously trigger more than one nucleations.

The growth of a nucleus, and hence the crystal, is governed by the laws of statistical thermodynamics. In the mother phase, the atoms are mobile and can stick to the nucleus or get detached from it. As the size of the nucleus grows, the probability of detachment reduces. This is because, in a small cluster, there are fewer nearest neighbours and less number of bonds per atom. This implies that smaller clusters are unstable compared to a bigger nucleus.

Let us consider a cluster of n atoms. We denote the capture rate of atoms by γ_n and detachment rate of atoms by δ_n . As n increases, δ_n decreases; that is decay rate reduces implying that once attached, the atom is less likely to leave the crystal. γ_n is determined by the concentration of solute atoms. Once the critical nucleus size is attained, γ_n determines crystal growth. If the material to be crystallised is dissolved as a solute in the mother phase, its concentration reduces as the crystal grows. This gradually reduces the value of γ_n hampering the growth rate.

When the crystal starts growing, an atom can attach itself at one of the various sites. Refer to Fig. 14.1 which shows an atomic arrangement in a simple cubic structure. The newly arriving atom prefers to attach itself where it can have maximum nearest neighbours and maximum bonding possibility, in order to go into minimum energy configuration. Hence the sites near corners (A), where possibility of satisfying 3 bonds, and steps (B), where possibility of satisfying 2 bonds exists, are preferred over the sites on the flat face (C), where only single bond is satisfied.

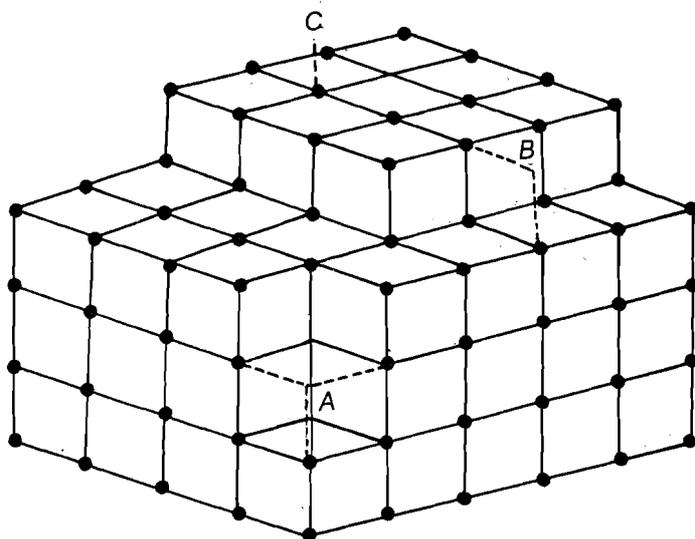


Fig. 14.1: Schematic depiction of crystal growth sites

We hope, you now appreciate the physics of crystal growth process. You will now learn about various commercial methods of crystal growth.

14.2.2 Methods of Growing Crystals

Different methods are used to manufacture crystals artificially. The choice of a particular method is determined by the type of material to be grown, purity

requirements and cost factors. The process of crystal growth is classified into four major categories:

- a. Melt growth
- b. Solution growth
- c. Vapour phase growth
- d. Solid state growth

We now discuss these in some detail.

a. Melt Growth

Melt growth is the most commonly used method for growing semiconductor, metal or organic crystals of large size. In this method, it is possible to ensure perfect structural and compositional control. For this reason it is useful for growing crystals with stringent specifications required by microelectronics industries. The material to be crystallised is first brought to a molten state and then cooled slowly. The growth rate is very fast and large crystals can be produced quickly. The materials for which this method can be used must:

- melt without dissociating or decomposing;
- not sublime before melting; and
- exhibit low chemical reactivity.

Do you know why these conditions are necessary? These are essential because if a material decomposes in the melt state, the crystal of homogeneous composition cannot be formed. If the material is prone to sublimation, it will never attain the melt state. The chemical reactivity aspect is very crucial. When the material is brought in the melt state, its atoms have high energy and they can readily react with the surrounding gases to form oxides, nitrides etc. To avoid this contamination, the melt is kept in vacuum or inert surroundings. Various techniques used in melt growth method are:

The melt of the material includes the dopants required for tailoring the crystal properties like electrical conductivity.

- i) **Directional freezing (Bridgman-Stockbarger method):** In directional freezing technique, the melt is kept in a crucible placed in a vertical furnace having temperature gradient. (The temperature in the furnace is maintained such that it is more at the top of the crucible and decreases vertically downwards.) The crystal is grown by directional solidification in the furnace whose average temperature is reduced gradually with time. The solidification occurs in the direction of the temperature gradient and for this reason, the process is termed directional freezing. Refer to Fig. 14.2. Note that the crucible has molten material on top and solidified crystal at the bottom. The temperature profile required for this growth is also shown on the right hand side. T_m denotes the melting temperature of the material. The region in which temperature changes from higher than T_m to lower than T_m defines the solidification boundary. With reduction in the average temperature of the furnace, the solidification boundary keeps on shifting higher and higher resulting in the crucible being completely filled with the solidified crystal.

The capillary shaped end of the crucible at the bottom is used to initiate nucleation. The growth thereafter takes place in the capillary and a single seed grows into the bulk of the melt. This is the simplest and the cheapest method of crystal growth from melt. However, the crystal takes the shape of the crucible. Also the interface of crystal with crucible wall can be a major source of contamination of the crystal. And at the crystal-crucible boundary, the crystal growth is strained as the atoms here are in different surroundings from the bulk crystal atoms and undergo changes in bonding pattern.

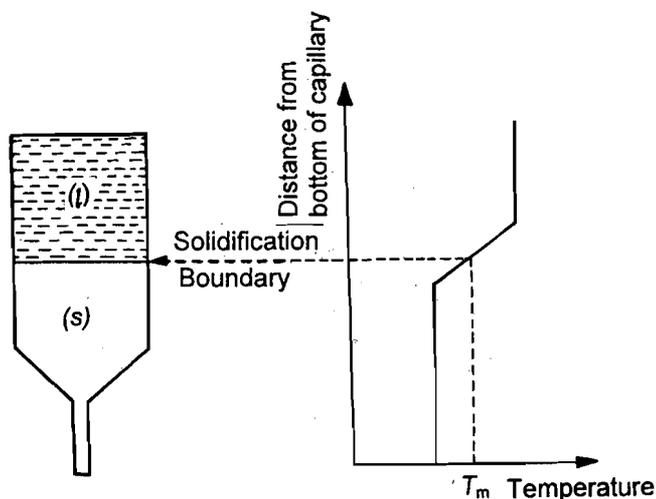


Fig. 14.2: Crystal growth using directional freezing technique

The problems arising because of contact of crystal with crucible are avoided in the crystal pulling method. You will learn about it now.

- ii) **Crystal pulling or Czochralski method:** This is one of the most common techniques used for semiconductor crystal growth and is schematically illustrated in Fig. 14.3a.

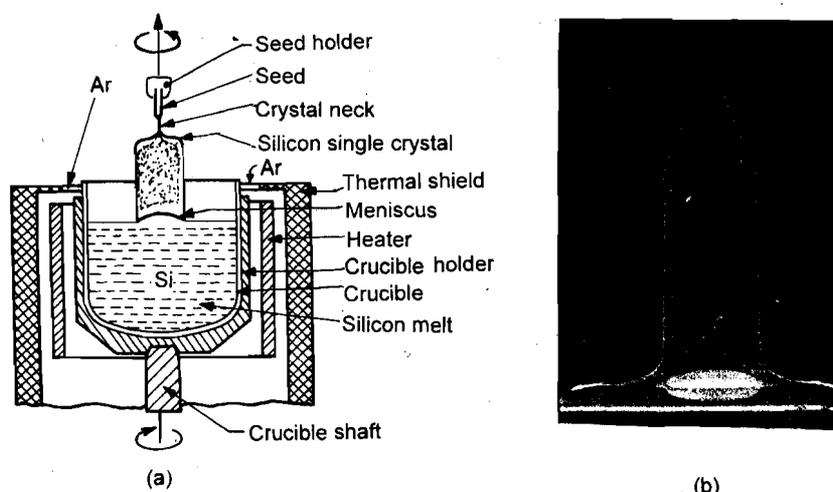


Fig. 14.3: Crystal pulling technique: a) schematic diagram of crystal pulling techniques; and b) Si crystal is being pulled

In this technique, the seed of the crystal is attached to a holder and the melt is kept under controlled temperature conditions in a crucible. To start with, the holder rod is brought down such that the seed crystal touches the meniscus formed on the melt. The atoms near the surface (forming meniscus) get attached to the 'seed' and begin to grow. The holder rod is then slowly pulled up at a predetermined speed of a few millimeters per minute (Fig. 14.3b). This allows the growth of the crystal at its interface with meniscus. In this case cooling is achieved by pulling the crystal away from the hot melt. The heat is lost to the surrounding environment (of inert gas). To achieve uniform growth, crystal holder and melt crucible are rotated slowly in opposite directions.

You must have realised that in this technique, the crystal is at no stage in contact with the crucible and the growth is strainless. However, since the melt is held in

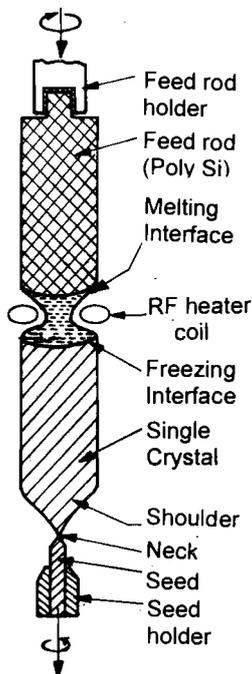


Fig 14.4: Schematic diagram of float zone crystal growth

Table 14.1: Equilibrium segregation coefficient for dopants in Si

Dopant	Type	k_0
As	<i>n</i>	0.3
P	<i>n</i>	0.35
Te	<i>n</i>	2×10^{-4}
Al	<i>p</i>	2.8×10^{-4}
Ga	<i>p</i>	8×10^{-3}
B	<i>p</i>	0.8

Spend
5 min.

- iii) **Float zone technique:** Fig. 14.4 shows the schematic diagram of the float zone crystal growth technique. The rod of polycrystalline material, whose crystal is to be grown, is held in vacuum or an inert gas atmosphere. A seed crystal is held at the bottom in contact with the polycrystalline sample. By using RF heating, the polycrystalline rod is melted near the bottom. The heating is then gradually carried out vertically upward. In the region where rod is heated, the material melts locally. While solidifying, this material grows into a single crystal. The hot zone between the original sample rod and the solidified single crystal is gradually shifted from bottom to top. As the floating zone moves upwards, a single crystal freezes at the zone's retreating end and grows as an extension of the seed crystal. The molten part of the material is held together between the polycrystalline rod and the grown crystal due to surface tension.

This method is most useful for obtaining single crystals characterized by high resistivity. This is because the RF heating is most effective in case of low electrical conductivity samples. The float zone grown crystals are used mainly for high power, high voltage devices, where such high resistivity materials are required.

In unit 11 of this course you have learnt that when a semiconducting material of required resistivity is needed, doping is carried out. The dopant material is added in the molten semiconductor in the required proportion. When the semiconductor material crystallises, the dopant gets incorporated in the crystal. However, the dopant concentration in the melt state differs from that getting incorporated in the solid phase i.e. as the crystal is pulled out from the melt, the dopant concentration in the crystal (C_s) is different from the dopant concentration in the melt (C_l). While calculating the amount of dopant to be added in the melt, this factor is also considered. The ratio of these two concentrations signifies the equilibrium segregation coefficient k_0 :

$$k_0 = \frac{C_s}{C_l} \quad (14.1)$$

The values of k_0 for commonly used dopants in silicon are listed in the Table 14.1.

You may now like to answer an SAQ.

SAQ 1

A silicon crystal with doping of 10^{16} boron atoms per cm^3 is required. For initial silicon melt load of 60 kg, calculate the mass of boron to be added. Assume that the value of k_0 remains constant throughout the growth process. Take the density of silicon in melt as 2.53 g cm^{-3} and atomic weight of boron as 10.8u.

b. Solution Growth

This method is mainly used for growing crystals of compounds/materials that dissociate in the melt state. In this method, the material to be crystallised is first dissolved in an aqueous or organic solvent below the dissociation temperature. Next the solution is brought to supersaturation state by lowering its temperature.

The growth is induced by slow cooling of the solution or slow evaporation of the solvent. Another method known as liquid phase epitaxy (LPE), about which you will learn later in the section, allows growth of a thin layer of material on the parent crystal.

You must remember that the solution growth differs from the melt growth technique in that, in melt growth the solvent (major component) freezes whereas in solution growth the solute crystallises. The solution growth is usually carried out well below the melting temperature of the crystal.

Let us take an overview of the solution growth techniques now.

- i) **Slow cooling technique:** In slow cooling technique of crystal growth, the material to be crystallised is dissolved in a solvent and a saturated solution is obtained at a high temperature. When such a solution is cooled slowly, we obtain supersaturated solution. The material in undissolved state tends to grow into an ordered structure to form a crystal. This method is commonly used to purify crystals from a solution containing impurities.

One of the best examples of this method is separation of salicylic acid from an impurity like acetanilide. These two compounds have different solubilities in water. Salicylic acid dissolves in water upto 0.20 g per 100 ml at 20°C and 7.5 g per 100 ml at 100°C, while acetanilide has solubility in water of 0.50 g per 100 ml at 20°C.

Suppose 5.0 g sample of salicylic acid contaminated by 0.25 g of acetanilide is dissolved in water at 100°C. To completely dissolve 5.0 g salicylic acid at 100°C, we need 67 ml water. In this solution, the acetanilide impurity will be completely dissolved. When this solution is cooled down to 20°C, only 0.13 g of salicylic acid remains dissolved and 4.87 g salicylic acid will get crystallised in pure form. However, the acetanilide remains dissolved in the solution as 67 ml water at 20°C can have upto 0.35 g dissolved acetanilide. This process allows us nearly 97% recovery (4.87 g of pure salicylic acid from 5.0 g sample).

- ii) **Evaporation of solvent:** You now know that if a saturated solution prepared at a high temperature is cooled, it becomes supersaturated and the undissolved part tends to grow as a crystal. We can also prepare a supersaturated solution from a saturated solution by reducing the amount of solvent in the solution. This method is commercially used for production of salt, sugar etc where water is allowed to evaporate. However, the rate of evaporation is kept slow to obtain larger crystals. If evaporation is rapid, a large number of nuclei are formed, and each one grows on its own resulting in as many small crystallites.

- iii) **Liquid phase epitaxy:** This method is useful for production of thin layered crystals of different dopings which are required for fabrication of micro-electronics devices like planar transistors and integrated circuits. In this technique, the seed is a piece of thin crystal (commonly known as substrate). This substrate is held by a holder above the solution of the material to be grown. This is shown in Fig. 14.5. The solution is put in a graphite or alumina crucible at the lower end of the furnace. The seed wafer, i.e. substrate fixed on a movable holder, is initially positioned just above the solution. At a particular temperature, growth is initiated by immersing the substrate in the solution and terminated by pulling the substrate out of the solution. The growth occurring here is epitaxial.

You must note that the purity of crystals obtained from the solution growth techniques is less than that obtained using melt growth techniques. This is essentially because the solvent in solution growth techniques can dissolve impurities together with the solute (to be crystallised). During crystal growth, these impurities also get incorporated. Also, the growth rates in solution method are lower as compared to melt growth. In spite of these drawbacks, the solution growth techniques are preferred as they are cheaper and commercially viable, since sophisticated instrumentation is not needed. The industry has preference for this technique for large-scale production of salt, sugar, fertilizers etc.

$$\frac{5.0\text{g}}{7.5\text{g}} \times 100\text{ml} = 67\text{ ml water}$$

$$0.2\text{g} \times \frac{67\text{ml}}{100\text{ml}} = 0.13\text{g of Salicylic acid}$$

$$0.5\text{g} \times \frac{67\text{ml}}{100\text{ml}} = 0.35\text{g of acetanilide}$$

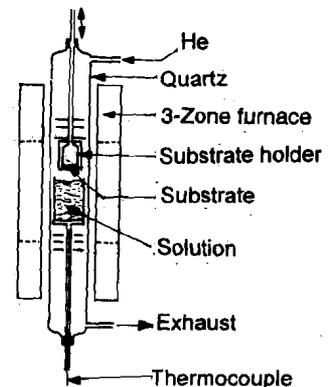


Fig. 14.5: Schematic diagram of liquid phase epitaxy set up

Epitaxy means growing a crystal structure on top of a substrate with the same periodicity and atomic arrangement as that of the substrate. On the top of a substrate, the bonds of substrate atoms in vertically upward direction are broken and external atoms can get attached to these bonds. If each broken bond captures an external atom, the added atoms automatically acquire the periodicity of the substrate surface.

In MBE process, since every element is individually vapourised, the temperature of each evaporator has to be controlled very precisely. Rarely an impurity element can have the same evaporation temperature. Hence the vapours in MBE process are very pure.

For materials that pass from solid to vapour phase, it is not possible to use the melt or solution growth techniques. In such cases, we use the method of **vapour phase growth**. You will learn about this method now.

c. Vapour Phase Growth

From your school science curriculum you know that elements like sulphur and iodine sublime, i.e. when heated, they pass from solid to vapour phase. When allowed to settle down on a cool surface, they recondense in solid phase. This principle is used to grow crystals of compound semiconductors. In compound semiconductors, more than one element constituting the semiconductor are present e.g. GaAs, AlGaAs, InP etc. In such cases, the molecular beam epitaxy (MBE) technique is employed. The constituent elements are individually vapourised under ultra high vacuum condition (pressure $\sim 10^{-9}$ Pa or less). The individual elemental beams are directed at the substrate surface on which the crystal in thin layer form is to be grown. The temperature of the substrate is maintained so as to facilitate the growth. Though the growth rates are very small (a single atomic layer per second), the purity of crystal is assured. Being in vapour phase, atoms possess high energies and are prone to react. Hence extra efforts are needed to avoid contamination in the chamber atmosphere. For this purpose, apart from ultra high vacuum, procedures like flushing of the system by an inert gas need to be performed. Fig. 14.6 shows a typical molecular beam epitaxy chamber used for growth of a compound semiconductor. The elements and dopants are evaporated from the evaporators (1-4) in a controlled fashion, to achieve proper proportion of constituents in the crystal. Each evaporator has a separate shutter, and it enables us to control flow of each element individually and achieve varying elemental concentrations during the growth. That is, we can grow tailored layered semiconductor structures.

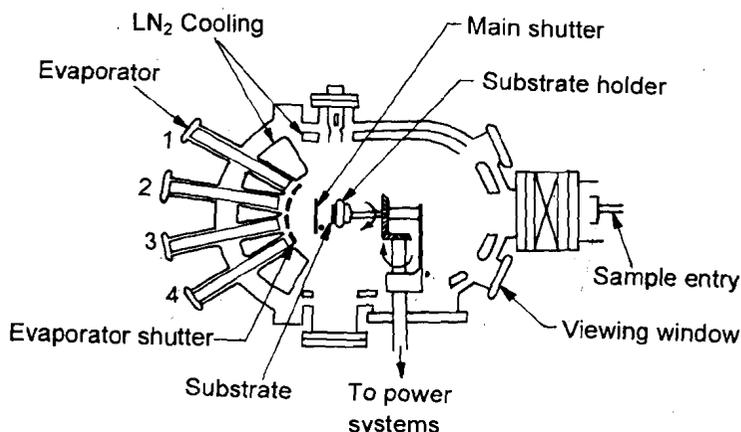


Fig. 14.6: Molecular beam epitaxy setup for compound semiconductor crystal growth

Note that the substrate in this method is held at constant temperature (by a cooling-heating combination) for homogeneous growth throughout the crystal. To ensure uniformity over the entire substrate surface, the substrate is rotated during crystal growth. Vapour phase growth using molecular beam epitaxy is one of the most advanced methods of material growth and is employed widely in semiconductor industry.

Another method of crystal growth is the so-called **solid phase growth**. You will learn about it now.

d. Solid Phase Growth

In solid phase growth technique, a single crystal is grown from a polycrystalline sample without melting. The sample is kept in a furnace in which temperature variation can be controlled. The interior of the furnace is either vacuum or an inert gas, depending on the material. When the polycrystalline sample is heated, the atoms in the solid acquire energy, vibrate more vigorously and tend to leave their sites giving

Sintering is heating of pre-pressed powder.

rise to *atomic diffusion*. Once this process sets in, atoms can cross the boundary and move into the neighbouring crystallite. Then they rearrange themselves in an orientation similar to the neighbouring crystallite and effectively merge to grow in a bigger crystal. The point to note here is that in this process *we are not heating the sample to reach its melt state*; only diffusion of atoms within the solid is initiated. When the sample is held at such temperatures for a long time, it can change into an ordered single crystal. This method is particularly useful for forming metallic crystals such as tungsten, nickel etc. The single crystals of high temperature superconductors like $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ etc are grown by a similar method. Here the constituent chemicals (oxides of all metals) are mixed together in appropriate proportion and this powder is pressed together to form a pellet. This pellet is then *sintered* in the furnace in oxygen environment. The pellet is converted into a crystalline superconducting material. The oxygen environment here is necessary for forming the desired material.

There are many other methods of crystal growth but a discussion of all these may carry us too far.

Now that you have learnt various processes of crystal growth, you must have noted that

- the purity of crystals can vary,
- no unique method is applicable in all situations, and
- faults can appear in the structure of a crystal.

You will now learn about *crystal defects* and their consequences as manifested in the properties of materials.

14.3 DEFECTS IN CRYSTALS

Once a crystal is formed, it is important to know whether or not it is perfect. Most of the crystals do possess some faults. These defects essentially signify departure of periodic arrangement of atoms from what exists in an ideal lattice structure.

In a pure crystal, all atoms should be arranged exactly as determined by the lattice structure. However, many a times one or more atoms may be missing/displaced/substituted or an additional atom may be sitting in-between the regularly arranged atoms. There can be even a row of atoms displaced or missing. The crystal surface is also a sort of defect because surface atoms experience a break in periodicity. All these defects are broadly classified as:

- point defects,
- edge defects, and
- surface defects.

Now you will learn about these defects in detail.

a. Point Defects

Refer to Fig. 14.7. It shows various types of point defects. In Fig. 14.7a, an atom in regular crystal is replaced by another type of atom that acts as an impurity. Such a defect is called *substitutional impurity*. The number of valence electrons in impurity atom may be different from those of regular crystal atoms. This results in an excess or deficiency of free electrons at substitutional sites and influences electrical conductivity of the sample. In Fig. 14.7b, the impurity atom enters the inter-atomic space of a regular crystal. This type of defect is called an *interstitial impurity*. The interstitial

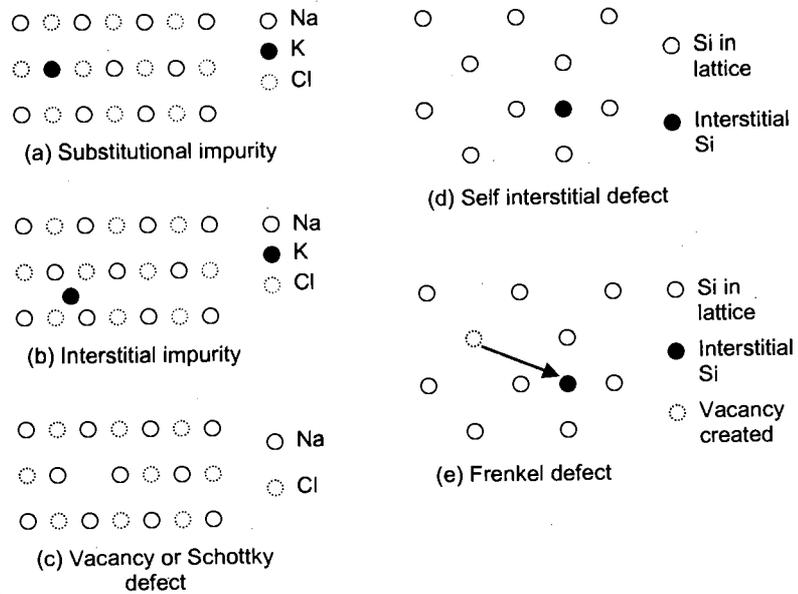


Fig. 14.7 Point defects

atoms cause local strains in the bonds with surrounding atoms leading to local mechanical weakness in the structure. Sometimes, an atom is missing from the regular lattice structure (Fig. 14.7c). This is known as *vacancy defect* or *Schottky defect*. This vacancy leaves the bonds of neighbouring atoms broken and cause local rearrangement of remaining atoms. Another kind of defect shown in Fig. 14.7d, arises when an atom of the same material occupies an interstitial site. This is known as *self-interstitial defect*. When an atom leaves its regular position in the lattice and occupies an interstitial site, as shown in Fig. 14.7e, the defect is called *Frenkel defect*. Note that in this case, the total number of atoms is not altered with respect to original lattice structure.

You must have noted that all the defects discussed here essentially create a local disturbance in the bonding pattern of atoms in a crystal. In some defects, bonds are broken resulting in unsaturated (or dangling) bonds, while in some cases, the length of a bond changes depending on the altered position of atom with respect to its neighbours. This disturbs the energy equilibrium of the atoms in the vicinity of the defect.

You will agree that point defects are zero-dimensional, and are confined to a few points in the crystal, but crystal defects could span a complete row of atoms. These are known as *edge defects*. In the following section you will learn about these defects. However you may like to answer an SAQ before that.

Spend 3 min.

SAQ 2

Identify the point defects in the crystal shown in Fig. 14.8.

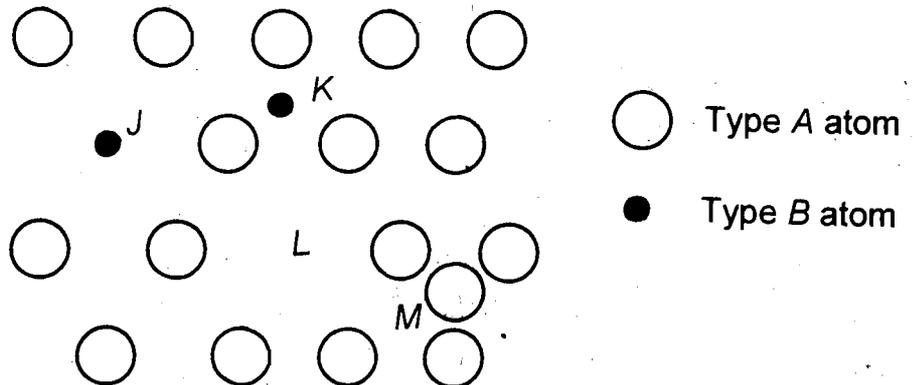


Fig. 14.8: Point defects in solid crystals

b. Edge Defect

Edge defect spans a row of atoms in a crystal and is one-dimensional. It is also called *dislocation defect*. Fig. 14.9 shows a typical dislocation defect where a column of atoms terminates abruptly in the middle of the crystal. This discontinuity in the (regular periodic) arrangement of atoms in the crystal disturbs their bonding pattern. As can be seen from Fig. 14.9, at *A* one column of atoms terminates. The bonds between atoms *B-C*, *D-E*, *F-G*, *H-I* show a large distortion in periodic arrangement. Atoms in column *A* have no neighbour below them to bind. In two-dimensional representation (Fig. 14.10a), this point is further clarified. Since some atoms have no bonds in one direction, the energy of the system increases. These atoms tend to break the bonds in the neighbouring column to

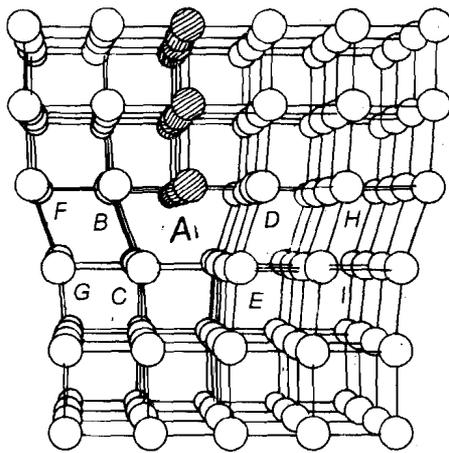


Fig. 14.9: Linear dislocation

attain stable configuration. As a result, the dislocation shifts towards the crystal surface by changing the bonding atoms, one at a time (Fig. 14.10b).

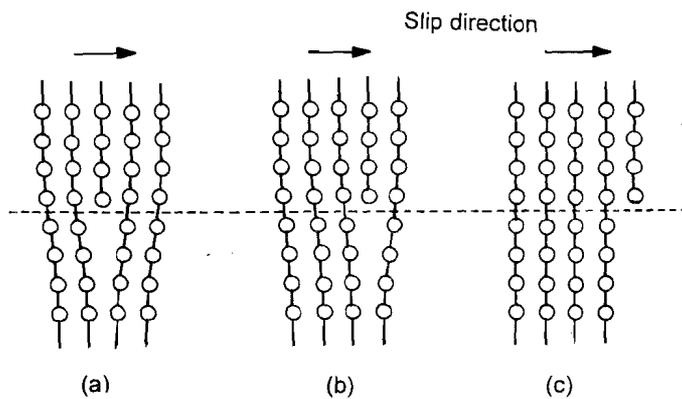


Fig. 14.10: Movement of dislocation

In the process of regaining periodicity, the faulty column is thrown out at the crystal boundary (Fig. 14.10c). Strictly speaking, the crystal has slipped at the defect boundary and the two halves of the crystal are displaced with respect to one another. So when viewed in 3-D, the dislocation causes a step on the surface as seen in Fig. 14.11a-c.

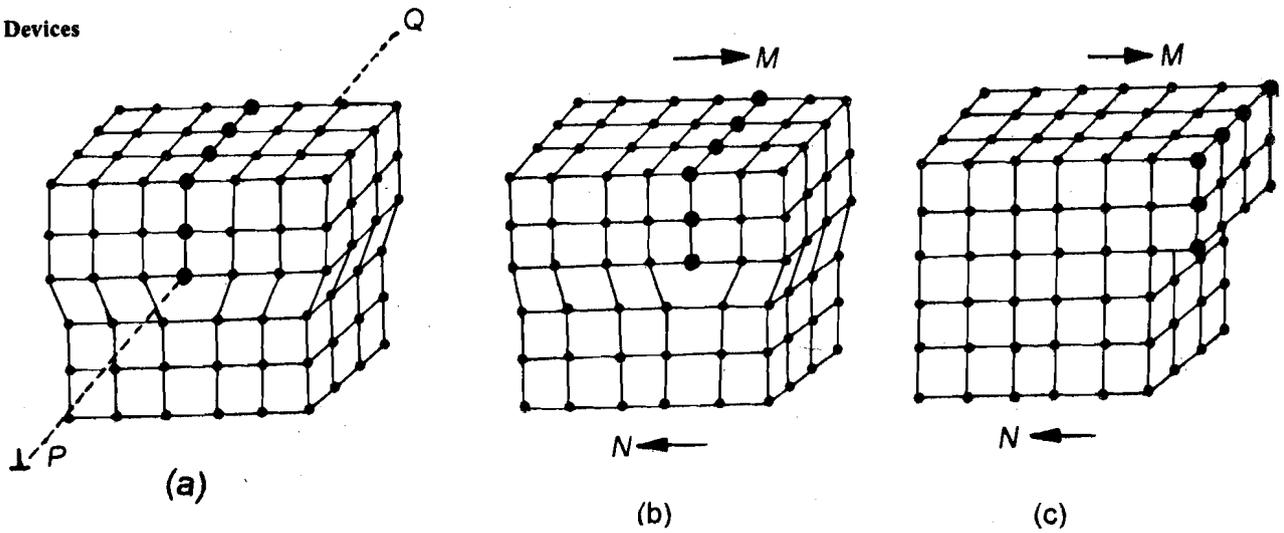


Fig. 14.11: Slipping in a crystal due to linear dislocation

Note that in this case

- upper part of the crystal has displaced or slipped towards right with respect to the lower part;
- the dislocation fault (indicated by PQ) is normal to the slip directions M and N ;
- small energy is involved in creating the slip since the distance by which each atom is displaced at a time is equal to the lattice constant of the crystal along MN ; and
- the slip leads to permanent dislocation in the crystal.

When a force is applied on a body, it undergoes deformation. The property by virtue of which a body regains its original state is known as *elasticity*. If the force is large, it can induce permanent deformation. This state is known as *plasticity*.

We all know that while engineering the materials (like metals) for various mechanical applications, the strength of material plays a very important role. The permanent deformation is characteristic of *plasticity*.

In another kind of dislocation, called *screw dislocation*, there is a wedge shaped dislocation, as shown in Fig. 14.12. The slip starts at point A and results into

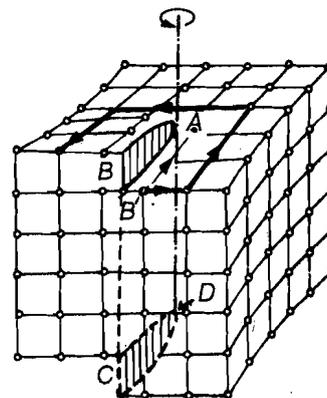


Fig. 14.12: Screw dislocation

dislocation from B to B' following the shaded portion. This fault can be thought of as created by cutting the crystal at $ABCD$ plane and then slipping the left side up with respect to right side through a distance BB' . Line AD defines the centre of dislocation. If we now move in an atomic plane around the dislocation (AD), as shown by arrows, we start in the lower plane and reach the upper plane effectively spiraling around the dislocation. That is why we call it a *screw dislocation*. The screw dislocation plays a vital role in crystal growth. You have learnt in Sec. 14.2, that the growth takes place around the steps in the crystal preferably as these sites offer more neighbouring atoms (and hence bonding possibility) and help in attaining a stable, minimum energy structure. In screw dislocation, the wedge on the crystal surface gives a ready site for

crystal growth. The crystal with screw dislocation grows in beautiful spiral patterns (Fig. 14.13).



Fig. 14.13: SiC crystal growth along two screw dislocations (printed with the permission of Prof. A.R. Verma)

c. Surface Defects

Whenever a crystal terminates (either at the crystal-air interface or at crystal-crystal boundary), there is discontinuity in the periodicity of the crystal. This is called the *surface defect*. A polycrystalline specimen has such defects at every boundary between crystallites. On either side of the grain boundary, the crystal lattice exhibits periodicity, but these grains are randomly arranged and hence the periodicity breaks at the boundary. This fact sometimes helps us in improving the material strength against plastic deformations. This is because the slip occurs only along the periodically arranged atoms in the crystallite. The slip cannot propagate beyond the crystallite boundary and the dislocation movement is arrested improving the strength.

You may now logically ask: Can we improve strength of metals? This is achieved by mixing in it small quantities of other metals or non-metals, forming an *alloy*. In the following section you will learn about formation of alloys and their properties.

14.4 METAL ALLOYS

In modern industrial age, search of materials with tailored properties has been a challenging task for the technologists. Extensive experimentation has shown that by mixing small proportion of another element (metal/non-metal), the properties of parent metal can be significantly modified. This process of mixing two or more elements is known as **alloying**. The main component of an alloy is a metal; though carbon, a non-metal, is an essential constituent of the most widely used industrial alloy, *steel*.

An alloy is produced by melting the mixture of its ingredients. In the Foundation Course on Science and Technology, you have learnt that importance of alloys had been recognised since very ancient times; *brass* (copper and zinc) and *bronze* (copper and tin) were used in the early growth of human civilization. Today, the most important alloy is steel. The principal alloying elements for steel are iron, carbon, chromium, nickel, manganese, molybdenum, silicon, tungsten, vanadium, and boron. Alloy steels have a wide range of special properties, such as hardness, toughness, corrosion resistance, magnetisability and ductility. Nonferrous alloys, mainly copper-nickel, bronze and aluminium alloys, are used mostly to make coins. The distinction between an alloying metal and an impurity is sometimes subtle. In aluminium, for example, silicon may be considered an impurity or a valuable component, depending on the application, because silicon adds strength but reduces corrosion resistance of aluminium.

The term fusible metal, or fusible alloys, denotes a group of alloys that have melting point below that of tin (505 K). Most of these substances are mixtures of metals that

by themselves have low melting points, such as tin, bismuth and lead. Fusible alloys are used as solder, in safety sprinklers that automatically spray out water when heat of a fire melts the alloy, and in fuses for interrupting an electrical circuit when the current becomes excessive.

The alloy exists in what is called a **solid solution**. This has similar meaning as in conventional solution used for a mixture in liquid state. In alloys, the elements in solid form are mixed together. The atomic arrangement in an alloy may be ordered or disordered. The essential difference between an alloy and a chemical compound is that while in a chemical compound, concentration of the constituent elements is fixed e.g. CuSO_4 will always have fixed proportions of copper, sulphur and oxygen with appropriate bonding patterns, in alloys the concentrations of solutes (added elements) are of varying proportion in the solvent (parent metal) and there is no ordered bonding between them.

The structure of solid solution can be in the form of *substitutional solid solution* or *interstitial solid solution*. Let us learn about these now.

a. Substitutional Solid Solution

The elements added to a metal can form a solid solution to result in an alloy, if the atomic sizes of the solute and solvent are similar and have similar electronic structure. In such a case, the additive atoms can easily replace the parent atoms in its crystal structure and get homogeneously dispersed throughout the crystal. For example, Cu and Zn have comparable atomic diameters; 2.56 Å and 2.78 Å respectively. They both form crystals with coordination number 12 each. Hence when Zn is added to Cu, it can easily replace the Cu atoms; upto 35% of Zn can be incorporated in Cu to form brass (Fig. 14.14). The Zn atoms are randomly arranged in the Cu lattice but the fcc pattern of Cu crystal is not altered.

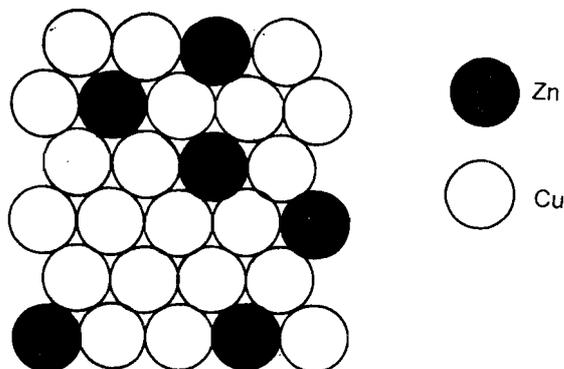


Fig. 14.14: Substitutional solid solution

b. Interstitial Solid Solution

Look at Fig. 14.15. It shows that an additive atom takes the interstitial position in the lattice. This can happen when the size of the atom of the added element is extremely small compared with the parent metallic atom. The most familiar example of interstitial solid solution is steel where carbon atoms take up interstitial sites in the iron lattice. As the carbon atoms occupy interstitial sites, they resist 'slip' that can occur due to dislocation defect. This effectively reduces the possibility of permanent deformation when the magnitude of applied force is small. That is, the possibility of plastic deformation of crystal decreases. In other words, we can say that the strength of the metal has increased. That is why steel is used in load bearing structures, automobiles and other machinery.

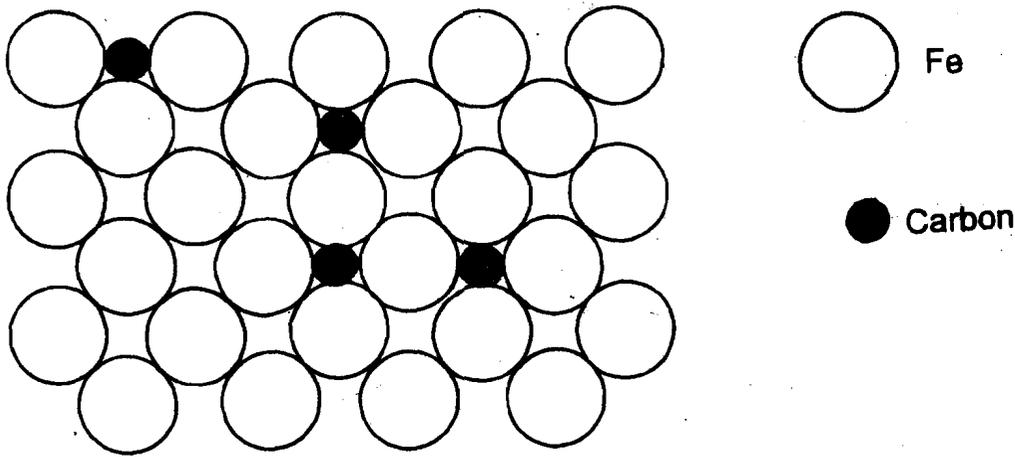


Fig. 14.15: Interstitial solid solution

Fig. 14.16 shows the phase diagram of lead-tin (Pb-Sn) alloy, which is used for soldering the electronic components on PCB. The phase diagram shows the phases of different Pb-Sn alloy concentrations at various temperatures. The origin of the coordinate system corresponds to 100% Pb. If we start from the left hand side of the diagram, the alloy is in liquid form above the melting point of lead (600K). As temperature is lowered, Pb starts solidifying in fcc structure, called α -phase. The solubility of Sn in α -Pb increases as temperature decreases and reaches the maximum of 61.9 weight percentage at 456K. Below this temperature, the solubility of Pb in Sn β -phase (body centre tetragonal structure) governs the phase diagram. It means that even if the individual melting points of Pb and Sn are 600K and 505K respectively, 61.9: 38.1 weight percentage of Sn-Pb results into an alloy composition with melting point as low as 456K. This property of Pb-Sn alloy is made use of while employing it as a solder material where the composition of Sn : Pb is in 60 : 40 proportion and its melting point is considerably lower. The solder can be melted by a low wattage soldering iron easily. In this way, it is possible to tailor mechanical strength and thermal behaviour also.

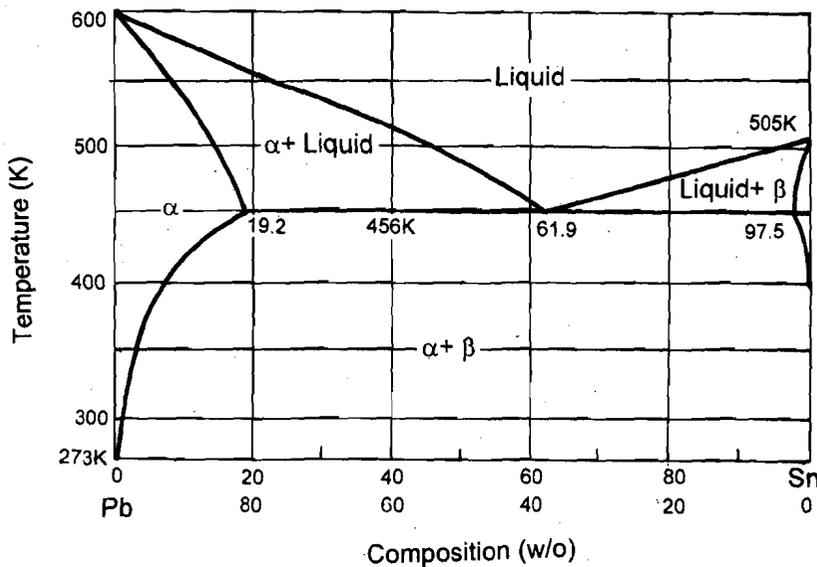


Fig. 14.16: Phase diagram of Pb-Sn alloy

You may now like to answer an SAQ now.

*Spend
3 min.*

SAQ 3

Relook at the phase diagram of Fig. 14.16 and determine the alloy composition that will facilitate a soldering material with melting point of 525K.

Let us now summarize what you have learnt in this unit.

14.5 SUMMARY

- The crystal growth starts with **nucleation**.
- The crystals can be grown from the **melt, solution, vapour or solid phase**.
- **Melt growth** is a faster process and is most widely used for growing semiconductor crystals.
- **Solution growth** is a cheaper process and is used for industrial production of salt, sugar etc. It is useful for purifying materials.
- **Vapour phase growth** is useful for the materials that sublime. Though slow, it allows growth of high purity thin crystals.
- **In solid phase**, single crystals are grown from polycrystalline samples by heating it to initiate atomic diffusion without melting.
- The imperfections in the structure of crystals are called **crystal defects**. These can be point defects, edge defects (dislocations) or surface defects. The most common deformation is caused by the dislocation defect.
- **An alloy has greater strength than its constituents**. Steel is much stronger than iron. Carbon atoms take up the interstitial sites in the iron lattice and arrest occurrence of slip. Alloy formation allows us to tailor the properties of a solid.

14.6 TERMINAL QUESTIONS

Spend 15 min.

1. The solution growth methods are cheaper as compared with melt growth method. Yet melt growth techniques are preferred for semiconductor crystal growth. Explain.
2. The nucleation process becomes more stable as the size of nucleus increases. Discuss.
3. Amongst the melt growth processes, which method is the cleanest? Give reasons.
4. 'Introduction of defects in semiconductor crystals is very normal'. Comment.
5. Mechanical deformation is caused by crystal defects and can be cured by crystal defects. Discuss.

14.7 SOLUTIONS AND ANSWERS**Self-Assessment Questions**

1. Segregation coefficient for boron $k_0 = 0.8$. Assuming $C_s = k_0 C_l$ throughout the growth, the initial concentration in melt should be

$$C_l = \frac{C_s}{k_0} = \frac{10^{16}}{0.8} = 1.25 \times 10^{16} \text{ boron atoms per cm}^3.$$

We are told that density of molten silicon is 2.53 g cm^{-3} . Therefore volume of 60 kg silicon,

$$V_s = \frac{60 \times 10^3 \text{ g}}{2.53 \text{ g cm}^{-3}}$$

$$= 2.37 \times 10^4 \text{ cm}^3.$$

The total number of boron atoms in the melt

$$N_b = 1.25 \times 10^{16} \times 2.37 \times 10^4$$

$$= 2.96 \times 10^{20}.$$

Atomic weight of boron is 10.8 u. This means that 10.8 g of boron contains 6.02×10^{23} atoms. Hence 2.96×10^{20} atoms correspond to $5.31 \times 10^{-3} \text{ g}$; i.e. 5.31 mg boron has to be added in 60 kg silicon melt. Note that very minute quantity of dopant is needed to tailor the conductivity of the semiconductor.

2. The point defects in Fig. 14.8 are as

J: Substitutional impurity

K: Interstitial impurity

L: Vacancy or Schottky defect

M: Self-interstitial defect.

L and *M* together form Frenkel defect.

3. For attaining an alloy with 525K melting temperature, the Sn:Pb composition should be 37.5 : 62.5.

Terminal Questions

- For semiconductor devices, the crystals should have very high purity. As the impurity concentration determines the resistivity of the semiconductor, it needs to be controlled very precisely. This is possible in melt state. In solution growth, incorporation of impurities from solvent is possible. Further, the growth rates in melt growth are much higher (few mm per minute) as compared to solution growth (few atomic layers per minute). Hence melt growth results into larger pure crystal in lesser time and is preferred.
- As size of nucleus increases, more and more atoms provide the bonding sites to the new approaching atoms. Hence there is a possibility of such atoms establishing bonds with more than one atom of the nucleus and getting attached strongly to the nucleus. This reduces the possibility of that atom to disintegrate back into the mother solution and gives stability to the nucleus.
- In float zone method, there is no contact of crucible with the crystal material. This reduces the possibility of impurity incorporation at the crystal/crucible interface. This makes the process cleaner.

Materials and Devices

4. The doping in semiconductor crystals to tailor the conductivity of the sample consists of adding small amount of dopant material in the semiconductor melt. This is effectively impurity incorporation in the pure semiconductor sample. These are mostly point defects in form of substitutional impurities.
5. The mechanical slip (dislocation) occurs due to an edge defect in the crystal. This can be arrested by alloying, where impurities are added at interstitial sites.