

Physics of Electronic Materials and Devices

1. Fundamentals of Materials Science

Materials Science:

Materials Science is the study of properties of materials, that describes the relation between the synthesis, processing and structure of materials.

Materials Engineering focus on how to design transform materials into useful devices, and it also focus on designing and improving materials.

Classification of Materials :-

According to their nature, materials are classified into five groups, namely.

1. Metals and Alloys;
2. Ceramics, glasses and glass-ceramics;
3. Polymers (plastics);
4. Semiconductors and
5. Composite materials.

Metals and Alloys:

Metals include aluminium, magnesium, zinc, iron, titanium, copper and nickel. An alloy is a metal that contains additions of one or more metals or non-metals.

Metals have good electrical and thermal conductivities. Metals and alloys have relatively high strength, high stiffness, ductility or formability and shock resistance. Pure metals are rarely used, whereas alloys provide

improvement in a particular property or permit better combinations of properties.

Ceramics :

Ceramics are inorganic nonmetallic materials.

Beach sand and rocks are examples of naturally occurring ceramics. Advanced ceramics are materials made by refining naturally occurring ceramics and other special processes. These are used in computer chips, sensors and actuators, capacitors, wireless communications, spark plugs, inductors and electrical insulators. Also used in consumer products such as paints, plastics, tires and used as barrier coatings to protect metallic substrates in turbine engines.

Ceramics do not conduct heat well, they must be heated to very high temperatures before melting. Ceramics are strong and hard, but also very brittle. Normally, fine powders of ceramics are prepared and these are molded into different shapes.

Glasses and Glass-Ceramics :

Glass is an 'amorphous' material, in which 'amorphous' refers to materials that do not have a regular, periodic arrangement of atoms. Glasses can be thermally treated to make them stronger. Forming glasses and then nucleating small crystals within them by a special thermal process creates materials known as glass-ceramics. Zerodur is an example of glass-ceramic material, used to make mirror substrates for large telescopes. (Eg: Chandra & Hubble).

Polymers :

Polymers are organic materials produced by process of polymerization. Polymers are good electrical and thermal insulators, that have lower strengths than metals or ceramics. These are not suitable for use at high temperatures. Many polymers have very good resistance to corrosive chemicals. Polymers have thousands of applications ranging from bulletproof vests, compact discs, ropes and LCD's to clothes and coffee cups. Polymers also include rubber and thermoplastics.

Semiconductors :

Silicon, germanium and gallium-arsenide based semiconductors are used in computers and other electronic devices. The electrical conductivity of semiconducting materials is between ceramic insulators and metallic conductors. In some semiconductors, the level of conductivity can be controlled to produce electronic devices such as transistors and diodes, used to build integrated circuits. Large single crystals of semiconductors are grown from molten materials. Also, thin films of semiconducting materials are also made using specialized processes.

Composite Materials :

These are formed from two or more materials. concrete, plywood and fiberglass are examples of composite materials. With composites, we can produce light weight, strong ductile, temperature-resistant materials or we can produce hard, shock-resistant and cutting tools. Advanced aircraft, aerospace vehicles, & sports equipment heavily rely on composites.

Functional classification of Materials :

Materials further classified based on the important function they perform is mechanical, biological, electrical, magnetic or optical. The types of materials based on their function are-

1. Aerospace - Ex: C-C composites, SiO_2 , amorphous silicon, Al-alloys, super alloys, zerondur.
2. Biomedical Materials - Ex: Hydroxyapatite, titanium alloys, shape memory alloys, plastics.
3. Electronic Materials - Ex: BaTiO_3 , Tantalum oxide (Ta_2O_5), silicon, dielectric materials.
4. Energy Technology and Environmental Technology -
Ex: ZrO_2 , Ni-cd, LiCoO_2 , amorphous Si:H
5. Magnetic Materials - Ex: ceramic, metallic, polymeric materials, (Co-Pt-Ta-Cr) alloys, magnetic ferrites
6. Photonic or Optical Materials - Ex: Alumina, solar cells, photovoltaic modules, yttrium aluminium garnets (YAG), LCD's,
7. Smart Materials - Ex: Lead zirconium Titanate, photochromic glasses, magnetic paints.
8. Structural Materials - Ex: steel, concrete and composites used to construct buildings & bridges.

The structure of materials are classified as-

- Macrostructure
- Microstructure
- Substructure
- Crystal structure
- Electronic structure
- Nuclear structure.

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Based on the arrangement of atoms, the solids are classified into crystalline materials, polycrystalline materials and amorphous materials.

In crystalline materials, the atoms are arranged in a regular and periodic manner and the periodicity extends throughout the volume of the material forming three-dimensional array. This array is known as the crystal lattice and the smallest unit which can be repeated to make up the lattice is called 'unit cell.'

When the periodicity of array of atoms is interrupted at grain boundaries, the material is called 'polycrystalline material'. The size of the grains in which the structure is periodic vary from macroscopic to angstrom dimensions.

When there is no proper arrangement or irregular arrangement of atoms, then the material is called amorphous material. In such case the size of grains are comparable to the size of unit cell.

crystal structure :

A crystal is a three-dimensional body crystals made up of regular and periodic 3D patterns of atoms or molecules in space called the crystal structure.

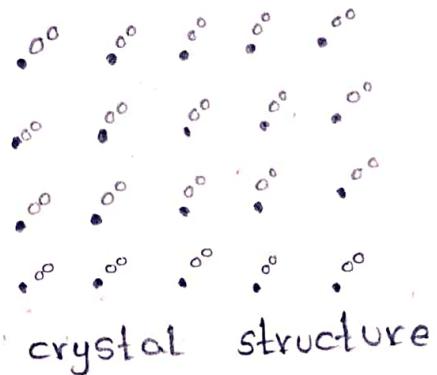
Lattice : The periodic arrangement of atoms in a crystal is called the lattice.

Space Lattice : The crystal structure described in terms of geometrical concept is called space lattice, i.e

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an array of points in space such that the environment about each point is same.

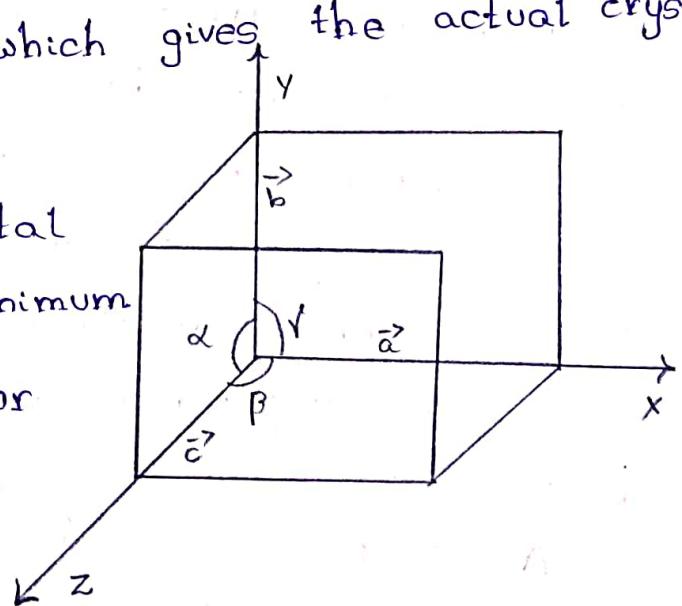
Basis : There exists a group of several atoms at each lattice point, this group is called as basis. A set of one or more atoms about a lattice point is called basis.



Crystal Lattice : The entire lattice structure of a crystal is found to consist of identical blocks. This lattice is known as crystal lattice.

Unit Cell : A unit cell is the smallest geometric figure, the repetition of which gives the actual crystal structure.

It is the fundamental elementary pattern of minimum no. of atoms, molecules or groups of molecules which represent fully all the characteristics of the crystal.



The unit cell is formed by the basis vectors \vec{a} , \vec{b} , \vec{c} as concurrent edges and including angles α , β , γ between \vec{b} and \vec{c} , \vec{c} and \vec{a} and \vec{a} and \vec{b} .

Phase Rule

Phase : The portion of a system which is physically distinct, mechanically separable and chemically homogeneous is called phase.

⇒ A system containing only one phase is called as homogeneous system.

⇒ A system containing two or more phases is called as heterogeneous system.

A substance can have different phases such as

- 1. Solid Phases 2. Liquid Phases 3. Gaseous phases
- 4. Solid- liquid phases and other.

1. Solid Phase : Each solid form a separate phase. The no. of solid phase depends on the no. of solids present in it.

Solid may have one or more phases. Hence they are grouped as 1. single phase solid and 2. multi phase solid.

Ex: Many forms of sulphur can exist together, but these are all separate phases. [Monoclinic, Rhombic...]

2. Liquid Phase : The no. of liquid phase depends on the no. of liquids present & their miscibility.

i) If two liquids are immixable, they form two separate liquid phases.

Ex: Benzene and water.

ii) If two liquids are mixable, they form one liquid phase only.

Ex:- Alcohol and water.

3. gaseous phase : Since gaseous mixture are thoroughly mixable in all proportions, it will form 1 phase only.

Ex:- A mixture of N₂ and H₂ forms one phase only.

Phase Rule :

It states that, "If the equilibrium between any number of phases is not influenced by gravity or electrical or magnetic forces or surface action but are influenced by temperature, pressure and concentration, then the no. of degrees of freedom (F) of the system is related to the no. of components (c) and number of phases (P)."

Mathematically, it is expressed as,

$$F = c - P + 2$$

Derivation of Phase Rule :-

Consider a system of P Phases and C components. For each component, there are P concentration variables. So for C components, there are CP concentration variables. In addition to this, two external variables are pressure & temperature. Hence total no. of variables is CP+2.

Again for each phase there is one equation of state. So for P Phases there are P phase equations. Since for P Phases, we have (P-1) chemical Potential

equations. As there are C components, we have $C(P-1)$ chemical potential equations. Hence total no. of equations are $P + C(P-1)$.

$\therefore F = \text{Total no. of variables} - \text{Total no. of equations}$

$$= CP+2 - [P+C(P-1)] = CP+2 - P - CP + C$$

$$\boxed{F = C - P + 2.}$$

where, F = Degrees of freedom

C = Components & P = No. of Phases.

Components :

The minimum no. of independently variable constituents, by means of which the composition of each phase can be expressed directly or in the form of a chemical equation are called the components of the system.

Some common examples related to components are-

i. In the water system,



The chemical component of all three phases is H_2O and therefore it is one component system.

ii. Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is represented by 'S'. Thus, it is one component system.

iii) A system of saturated solution of NaCl consist of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H₂O. Therefore, it is two-component system.

iv) In the equilibrium, $\text{Fe(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{FeO(s)} + \text{H}_2\text{(g)}$, the minimum components required to express the composition of each phase is three. Thus, it is a three component system.

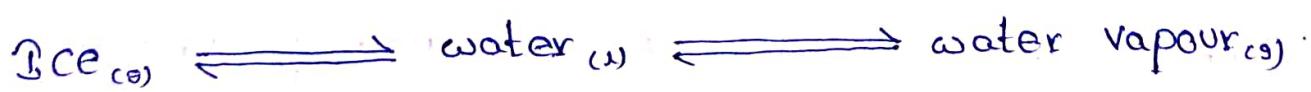
v) A mixture of gases, say O₂ and N₂ constituents one phase only. But its composition is expressed by two chemical substances O₂ and N₂. Hence it is two-component system.

Degrees of Freedom:

The minimum no. of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

A system having 0, 1, 2 or 3 degrees of freedom is called non variant (Invariant), univariant (monovariant), bivariant and trivariant respectively.

Ex:- i) In a water system,



The 3 phases can be in equilibrium, then no condition need to be specified. The system is therefore zero variant or has no degree of freedom.

2. For water \rightleftharpoons water vapour, $F=1$. The system water in equilibrium with water vapour, has two variables temperature and pressure. At definite temperature the vapour pressure of water can have only one fixed value. Thus if only one variable (T or P) is specified the other is fixed. Hence the system has one degree of freedom.

3. For a gaseous mixture of N_2 and H_2 , we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume becomes definite. Hence for a gaseous system, two factors must be stated in order to define it completely and thus it has two degrees of freedom or bivariant system.

Merits of Phase Rule:

1. It is applicable to both physical & chemical equilibria.
2. It requires no information regarding molecular/micro structure since it is applicable to macroscopic systems.
3. It is convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us predict the behaviour of a system under different sets of variables.
5. It indicates that different systems with some degree of freedom which behave similarly.
6. It helps in deciding whether a various substances would exist together in equilibrium or some of the substances

present would be interconverted or some of the substances present would be eliminated.

7. Very useful in metallurgical industries.

Limitations of Phase Rule:-

1. The phase rule is applicable to only one system in equilibrium, so it does not tell about other possible equilibrium present in that system.
2. The phase rule takes into account only the variables temperatures, pressure and composition.
3. It cannot be applied to system consisting two or more solutions separated by semi-permeable membrane.
4. It requires most care in deciding the no. of phases existing in an equilibrium state, since it considers only the no. of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total no. of phases.

Phase Diagrams

The graphical representation showing the relation between phases in equilibrium versus composition, pressure and temperature are called phase diagrams. It consists of areas, curves or lines and points.

Importance of Phase Diagrams:

- The important information obtained from a phase diagram is useful in materials development & selection.
- It shows phases present at different compositions and temperatures under slow cooling conditions.
- It indicates equilibrium solid solubility of one element/

compound in another.

- It suggests temperature at which an alloy starts to solidify and range of solidification.
- It signals the temperature at which an alloy different phases start to melt.
- Amount of each phase in a two-phase mixture can be obtained.

The phase diagrams are classified as follows:

1. Unary phase Diagram (single component system)
2. Binary phase Diagram (Two component system)
3. Ternary phase Diagram (Three component system)
4. Quaternary phase Diagram (Four component system).

One component System :

It is a system in which the composition of all phases can be expressed in terms of only 1 substance.

In one component system, $c=1$, then

$$F = 1 - P + 2 = 3 - P.$$

There exist atleast one phase, then $F = 3 - 1 = 2$.

Therefore, the maximum degrees of freedom is 2.

Ex: 'Water' is a three-phase, one component system. The three phases involved are liquid water, ice and water vapour. All these phases can be represented by 1 chemical entity H_2O and hence it is one component system. The number of phases which can exist in equilibrium any time depends on the conditions of temperature & pressure.

The features of the phase diagram are-

1. The curves OA, OB, OC and OA'
2. The triple point 'O'.

3. The areas AOC, AOB, BOC.

i. The curves OA, OB, OC :-

These three curves meet at the point 'o' and divide the diagram into three regions or areas. i) curve OA : This curve is called vapour pressure curve or vaporisation curve, as it gives the vapour pressure of liquid water in equilibrium with water vapour at different temperatures. The vapour pressure increases with the rise in temperature. This curve separates the liquid from vapour and explains how the two phases coexist in equilibrium. The OA curve starts from 'o' & ends at in equilibrium. The OA curve starts from 'o' & ends at

A. According to phase rule, $F = C - P + 2 = 1 - 2 + 2 = 1$.

Hence system is mono-variant.

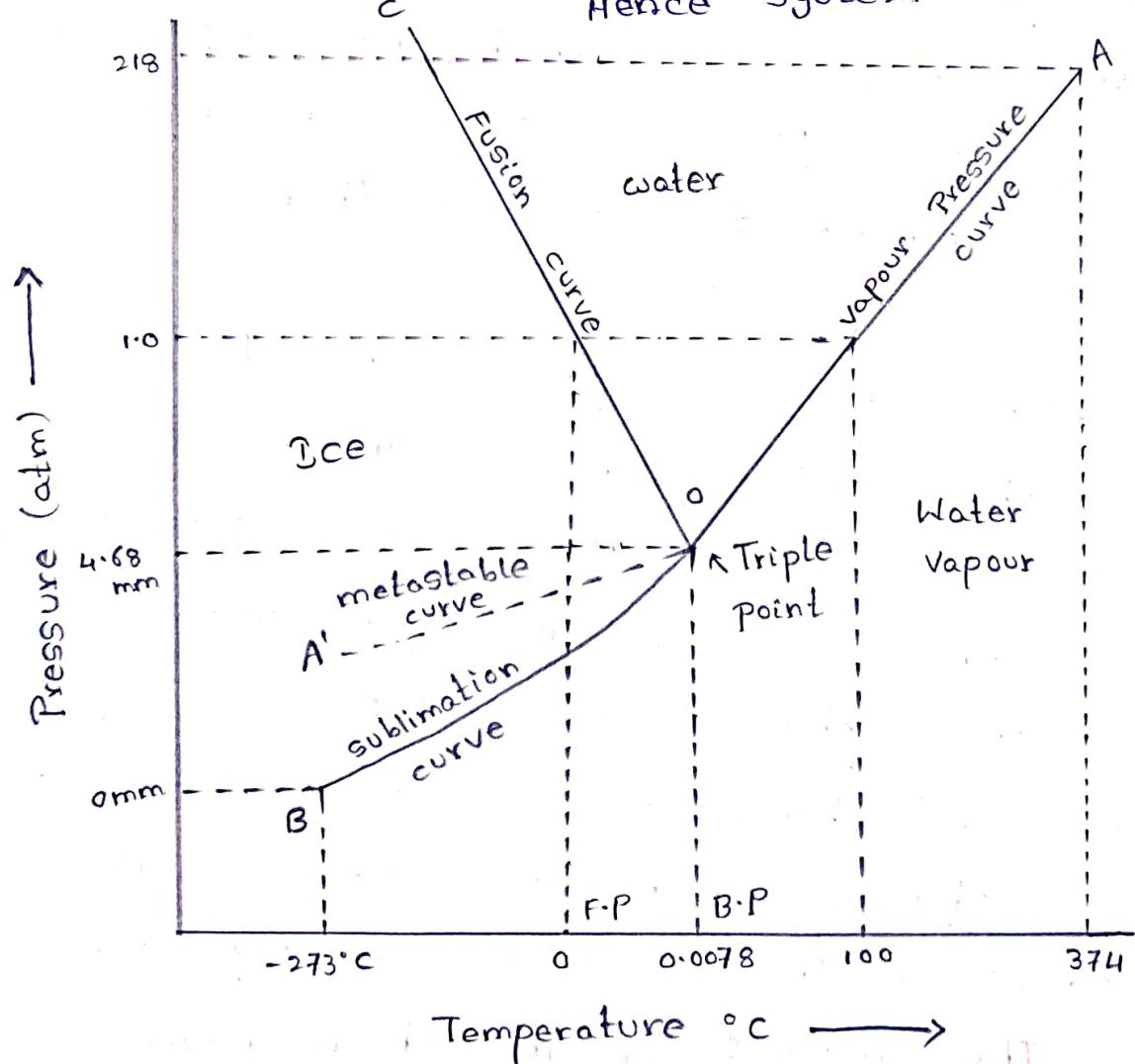


Fig: The phase diagram or PT graph of H_2O system.

ii) curve OB: This curve is called sublimation curve as it gives the vapour pressure of solid ice in equilibrium with water vapour at different temperatures. This curve separates the solid ice from water vapour and explains how the two phases coexist in equilibrium. The 'OB' curve starts from 'o' and terminates at B (absolute zero, -273°C), beyond of which no vapour exists. According to phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$

Hence system is mono variant.

iii) curve OC: This curve is called freezing point curve or fusion curve as it tells how the freezing temperature of water varies with pressure. This curve separates the solid ice from liquid water and explains how the two phases co-exist in equilibrium. The OC curve starts from 'o' and terminates at C. This indicates that melting point of ice is lowered with the increase in pressure. AS, $F=1$, the system is mono-variant.

Curve OA' :- Equilibrium which can be attended in only one direction is known as 'metastable equilibrium'. The dotted curve is a continuous extension of AO curve. It is obtained when liquid water is super cooled, i.e cooling of liquid water below the freezing point. Here water and vapour are in metastable equilibrium. As it is unstable, the super cooled liquid will be immediately converted into ice by slight disturbance in equilibrium. The degree of freedom is one. AS. $F = C - P + 2 = 1 - 2 + 2$.

Hence the system is mono-variant in nature.

2) study of areas :

The phase diagram is divided into three areas, namely BO_C, BO_A and AOC for the regions ice, vapour and water respectively. One phase is present in each area. According to phase rule,

$$F = C - P + 2 = 1 - 1 + 2 = 2. \text{ Hence the system is bi-variant.}$$

This means both temperature and pressure are required to define the system completely at any point within the area.

3. Triple Point :

The curves OA, OB, OC meet at this point where all the three phases are in equilibrium. The temperature and pressure corresponding to this equilibrium are 0.0078°C and 4.68 mm of Hg. According to phase rule,

$$F = C - P + 2 = 1 - 3 + 2 = 0. \text{ system is Invariant.}$$

The three phases can co-exist in equilibrium only under one set of conditions, i.e. if any of the two variables is slightly changed, the equilibrium do not exist and one of the phases would disappear.

Two-component system :

In a two component system, $c = 2$. According to phase rule ; $F = C - P + 2 = 2 - P + 2 = 4 - P$.

The minimum number of phases in a two-component system is one. so the maximum number of degree of freedom is, $F = 4 - P = 4 - 1$

$$F = 3$$

This means all the three variables must be specified in order to describe a two-component system completely. For the graphic representation of these variables, a 3D diagram is required in which 3 co-ordinate axes representing pressure, temperature and concentration at right angles to each other. But phase equilibria mainly deal with 2D diagram. So, one of the variables is kept constant. The possible equilibria in a two-component system are -

- solid \leftrightarrow liquid
- solid \leftrightarrow gas
- liquid \leftrightarrow liquid and
- liquid \leftrightarrow gas.

In a solid \leftrightarrow liquid equilibria, the gas phase is absent. So pressure variable is kept constant. Such system is called condensed system. The phase rule will be reduced by $F' = C - P + 1$. This is known as reduced phase rule equation. As the two variables are temperature and concentration, the phase diagram for two-component systems are represented by temperature-concentration (TC) graph.

Ex: Bismuth - cadmium (Bi-Cd) system.

It is a two-component system. The various phases are as follows :-

- solid bismuth
- solid cadmium
- solution of molten Bi & Cd
- vapour

The vapour phase is practically absent because the boiling point of Bi & Cd are very high. So, it is a condensed three phase system. Here pressure has no effect on the system. Hence two remaining variables are required to describe the system completely.

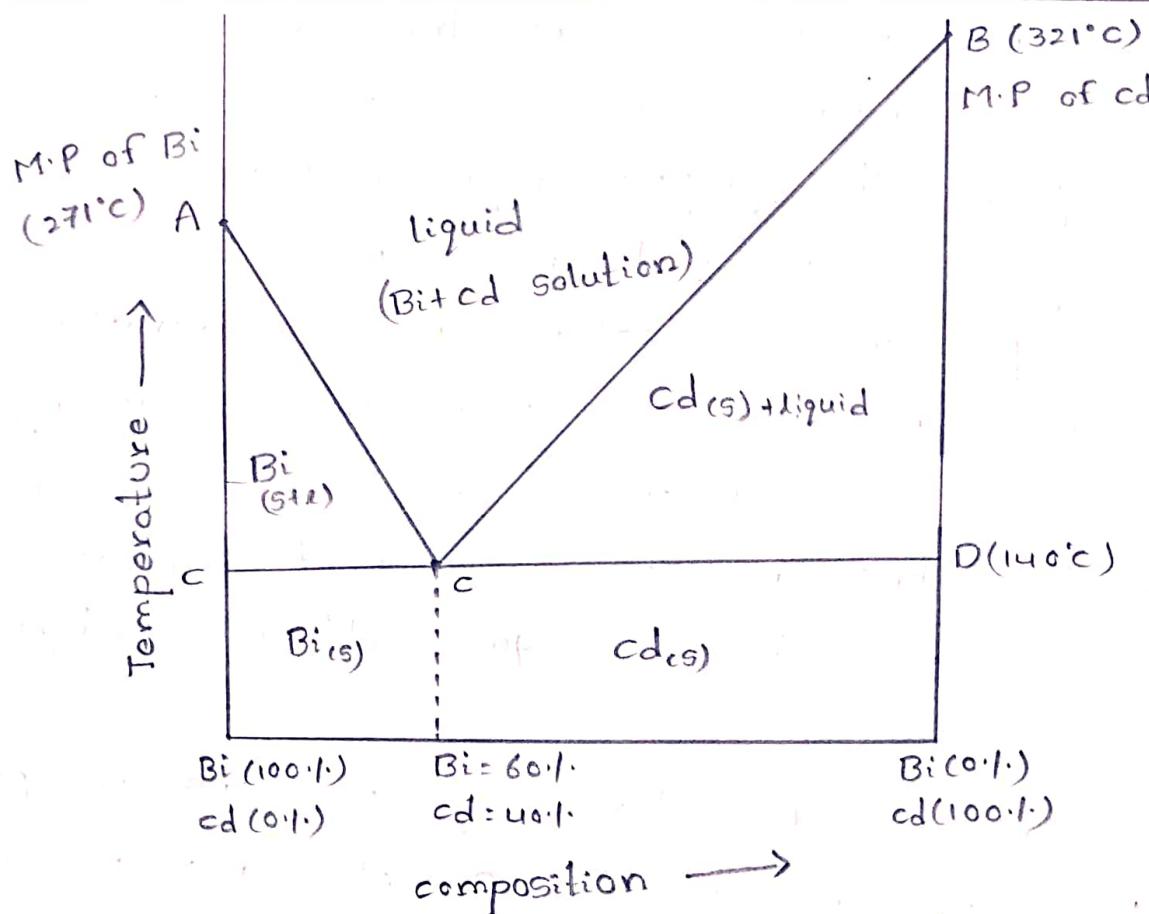


Fig: Phase diagram of Bi-cd system.

The diagram consists of -

- Two curves (AC and BC)
- Eutectic point (c) - the point at which liquid line and solid line meet.
- Three areas (above ACB; below AC, below BC).

curve AC: It is the freezing point curve of Bi and shows how the melting point lowered by the addition of cd. Point A represents the freezing point or melting point of solid Bi. Here the two phases solid Bi and solution (Bi & cd) are in equilibrium. According to reduced phase rule equation -

$$F' = c - p + 1 = 2 - 2 + 1 = 1. \text{ System is mono. variant.}$$

curve BC: It is the freezing point curve of cd and shows how the melting point is lowered by addition of Bi.

Point B represents the freezing point or melting point of solid cd. Here the two phases solid cd and solution (Bi & cd) are in equilibrium. As $F' = 1$, the system is mono variant.

Eutectic Point (C):

Eutectic point c is the intersect of Ac and Bc. Here the three phases solid Bi, solid cd and solution (Bi & cd) are in equilibrium.

According to reduced phase rule equation -

$$F' = C - P + 1 = 2 - 3 + 1 = 0 \text{ Invariant}$$

The eutectic temperature is 140°C and the eutectic composition is 60.1% (Bi) and 40.1% (cd).

Area above ACB :-

It represents a single phase system of solution Bi & cd. According to reduced phase rule equation -

$$F' = C - P + 1 = 2 - 1 + 1 = 2 \text{ (bivariant)}$$

Area below Ac:

It represents a two phase system (i.e. solid Bi & solution) are in equilibrium. According to reduced phase rule equation.

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ (monovariant)}$$

Area below BC :

It represents two phase system (i.e. solid cd & solution). As $F' = 1$, the system is monovariant.

The area below 140°C :

It represents a two phase system (solid Bi & solid cd). According to reduced phase rule equation,

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ (monovariant)}.$$

Nucleation and crystal growth

Nucleation: The initial stage in a phase transformation or the formation of tiny stable particles is called nucleation.

It is evidenced by the formation of small particles called nuclei of the new phase which are capable of growing. Once this nucleation has occurred, the crystal starts growing.

Crystal growth: When the nuclei attain macroscopic dimensions, it is called crystal growth.

Nucleation can occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include :

- i) in gas : creation of liquid droplets in saturated vapour.
- ii) in liquid : formation of gaseous bubbles, crystals or glassy regions.
- iii) in solid : nucleation of crystalline, amorphous and even vacancy clusters in solid materials.

Such solid state nucleation is important for semiconductor industry.

Ex: of Nucleation :

- i) Dust and pollutants provide nucleation sites for H_2O vapour in atmosphere to form clouds.
- ii) In the diet coke & mentos eruption, the mentos candies offer nucleation sites for the formation of CO_2 bubbles.
- iii) If you place your finger in a glass of soda, CO_2 bubbles will nucleate around it.
- iv) Ice formation from liquid water.
- v) Formation of curd from milk.

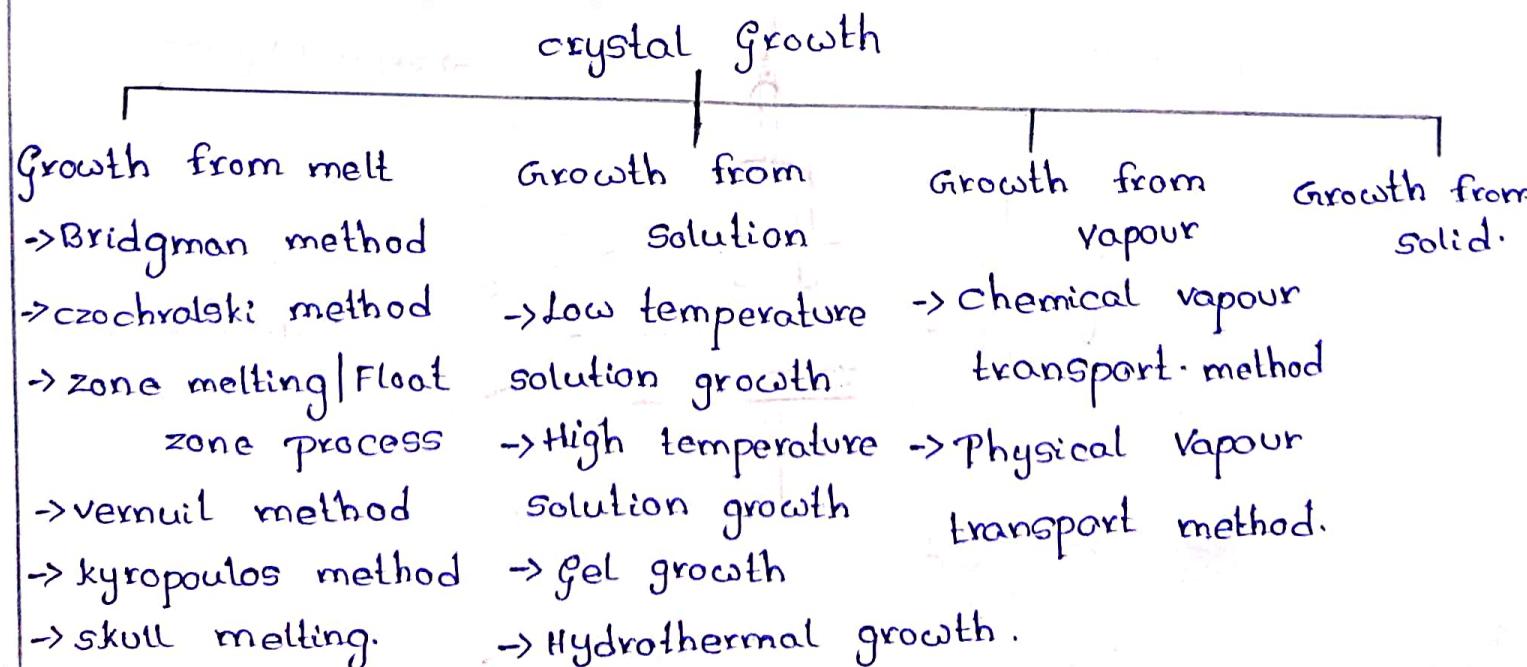
The initial and most important study of nucleation is done by Tammann in 1925. He studied the rate of nucleation in complex organic materials.

There are two types of nucleation. They are.

i) Homogeneous nucleation and ii) Heterogeneous nucleation.

Homogeneous Nucleation	Heterogeneous Nucleation
→ It is also known as self nucleation.	→ It is a type of nucleation which starts at the surfaces, imperfections and severely damaged regions.
→ In this the formation of nuclei starts in the interior of a uniform substance such as pure liquid metal.	→ In this process, the liquid metal requires ability to absorb the foreign particles.
→ In this we need to provide super cooling or super heating to occur nucleation.	→ In this nucleation we don't need the supercooling or we need in very less amount.
→ It is a slower process.	→ It is a faster process and takes place very easily.
→ It occurs with much more difficulty.	

Methods of crystal growth:



Growth from melt:

Melt growth is the process of crystallization by fusion and re-solidification of the starting materials from the melt. The important growth from melt techniques are -

1. Czochralski method.
2. Bridgman method.
3. Float zone process.

1. Czochralski Method :

Principle : crystals are grown by a gradual layer by layer condensation of melt. It is based on liquid - solid phase transition initiated by a seed crystal.

Description :

1. The pure material which is to be grown in the form of single crystal is taken in the crucible.
2. The material is heated above the melting point using induction heater.

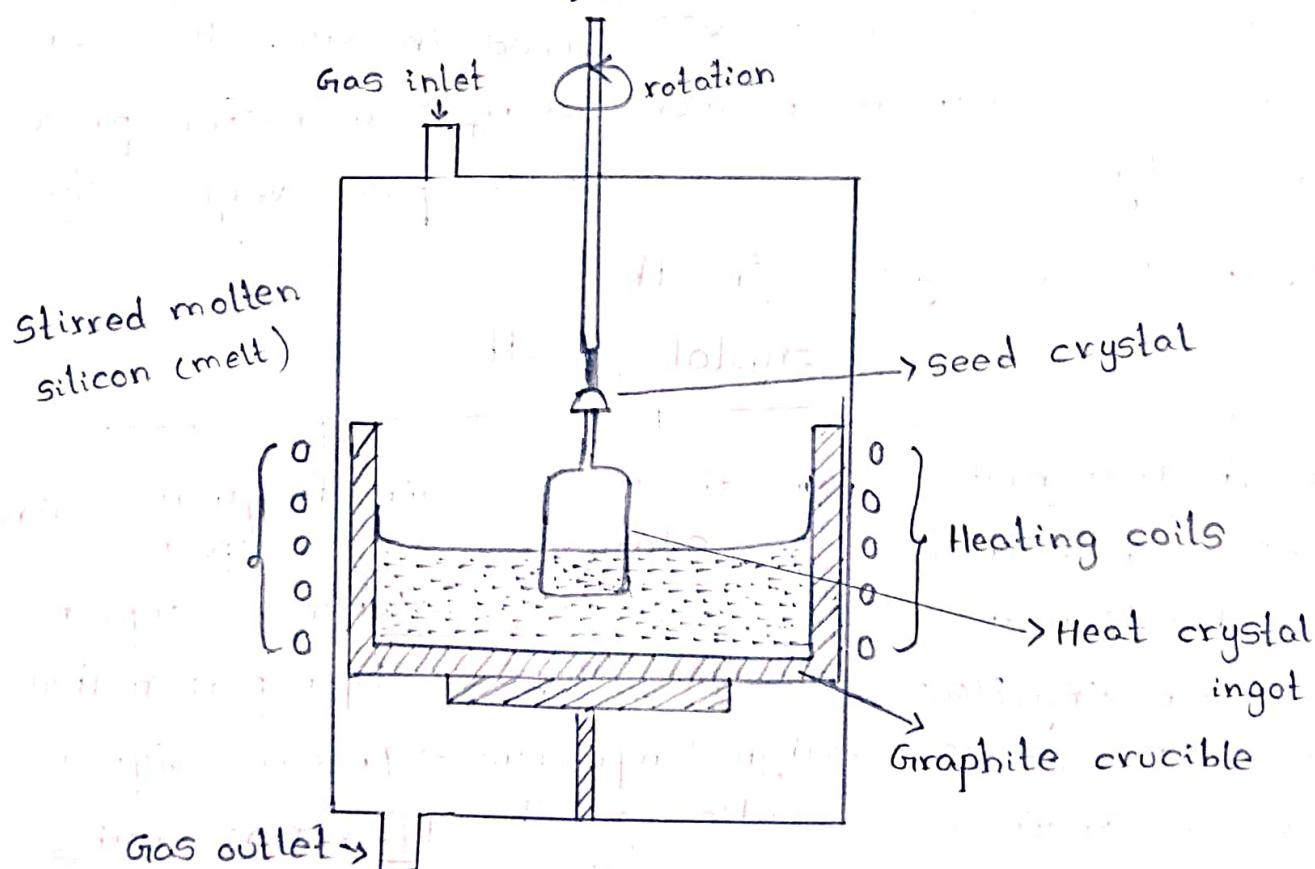


Fig : Czochralski Technique.

3. Thus melt is obtained in the crucible. A small defect free single crystal called seed crystal is introduced into the melt.
4. The seed crystal is attached to a rod, which is rotated slowly.
5. The seed crystal is rotated and gradually pulled out of the melt.
6. A single crystal grows on the seed crystal.
7. The seed crystal acts as
 - i) a nucleation centre
 - ii) heat sink through which the latent heat of solidification escapes.
8. The temperature difference between the melt and the seed crystal establishes the desired growth condition.
9. The seed is slowly withdrawn from the melt by pulling and rotating such that the crystal diameter is gradually increased to the desired value.
10. The seed crystal is dipped into the melt held at a temperature slightly above the melting point.
11. The shape of the crystal is initially in the form of thin neck and then the diameter of the crystal is increased to the required size. This is known as necking procedure.
12. By using necking procedure and pulling mechanism, bulk single crystals can be obtained by this method.

Advantages :

- It produces defect free crystal.
- It produces large single crystals.

- It allows convenient chemical composition of crystals.
- The dopant distribution in the crystal will be uniform.

Disadvantages:

- High vapour pressure of the materials can be used.
- Possibility of liquid phase encapsulation occurs during solidification.
- It may produce contamination of melt by crucible.

2. Bridgman Technique:-

Principle:

The selective cooling of the molten material is used to form single crystal by solidification along a particular direction. It is classified into two types.

They are :

1. Vertical bridgman technique 2. Horizontal bridgman.

In both techniques, the melt in a sealed crucible is increasingly frozen from one end to other.

Description :

1. The material to be grown in the form of a single crystal is taken in a cylindrical crucible.
2. Crucible is made of platinum and tapered conically with pointed tip at the bottom.
3. The crucible is suspended in the upper furnace until the material in the crucible is completely melted into molten liquid.
4. Crucible is then slowly lowered from upper furnace into lower furnace with help of an electric motor.

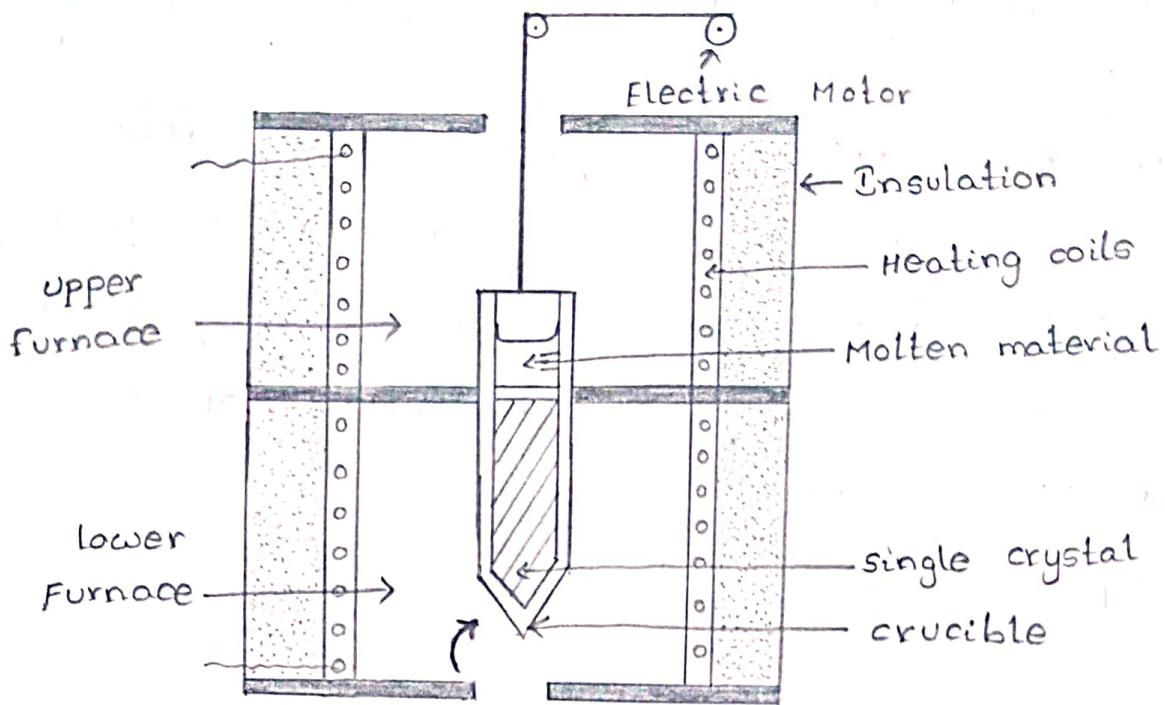


Fig: Bridgman Technique

5. Temperature of the lower furnace is maintained below the melting point of the material inside the crucible.
6. Thus, a bulk single pure crystal can be grown in the crucible by lowering the crucible at a steady rate of (1-3 mm/hr).

Advantages :

- It is relatively cheaper than other pulling techniques.
- simpler technology.
- Melt composition can be controlled during the growth.
- It enables easy stabilization of temperature gradient.

Disadvantages :

- Growth rate is very low.
- sometimes instead of single crystals, polycrystals may grow.
- Since the material is in contact with the walls of the container for long period, it leads to dislocations of the nucleus.
- This technique can't be used for materials which decompose before melting.

3. Zone - Melting Technique or Float - zone process:

Principle :

In this technique a liquid zone is created by melting a small amount of materials in a relatively large or long solid charge. zone melting techniques basically enable one to manipulate distribution of soluble impurities or phases through a solid.

Description :

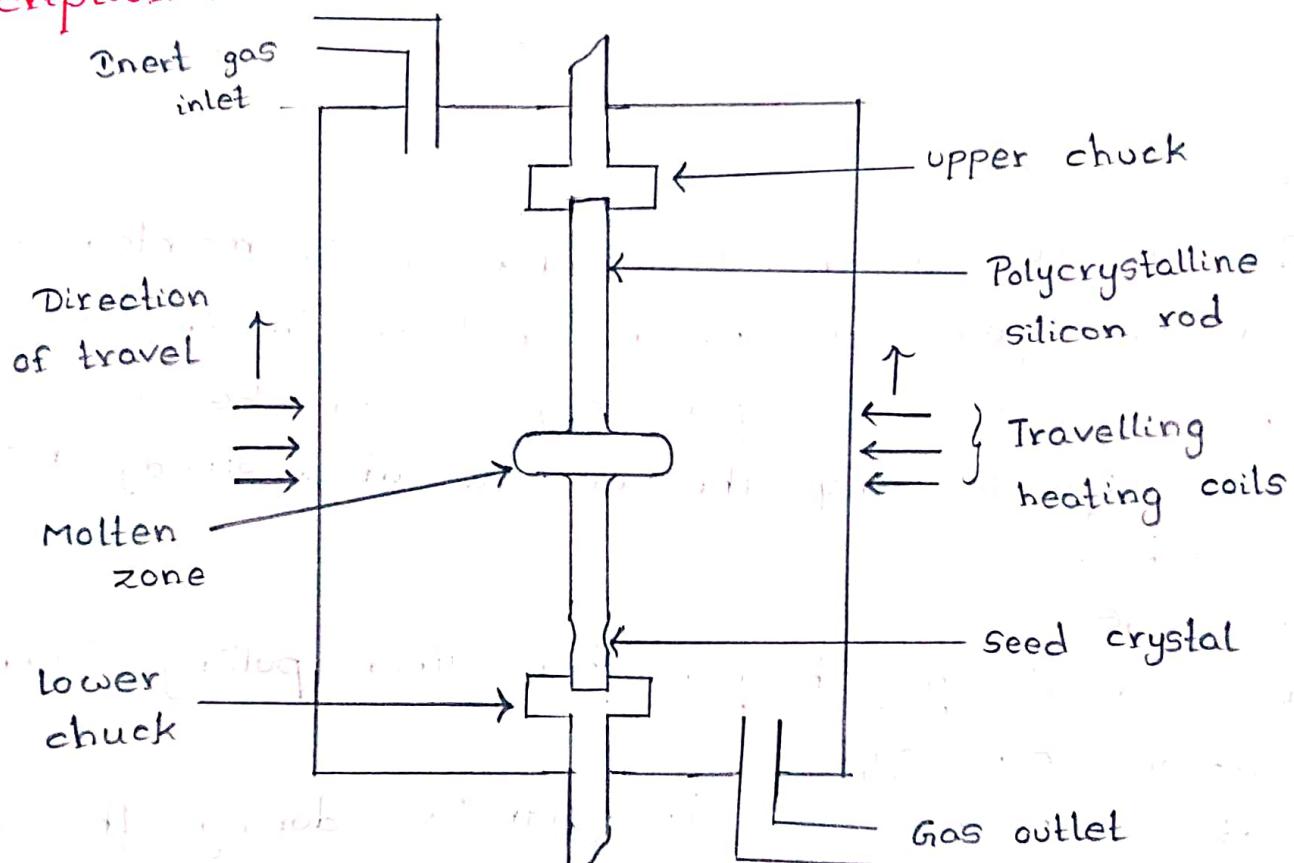


Fig: Float zone process

1. The float zone process uses a rod of ultrapure polycrystalline silicon rod.
2. The rod is maintained in a vertical position by means of two chucks and is enclosed in a chamber in which an argon gas is passed.
3. A heating coil is placed around the chamber.
4. A single crystal seed is clamped at the lower end of the rod, which is rotated around its axis.

5. The molten zone is then slowly moved upward along the length of the rod by moving the heating coil.
6. As the coil is moved upward, recrystallization of the molten zone at the bottom occurs while the new material begins to melt at the top.
7. The diameter of the growing crystal is controlled by the motion of the heating coil.
8. The desired impurity level is obtained by starting with an appropriately doped polycrystalline material.

Advantages:

1. This method is used to purify semiconductor crystals.
2. In this process the impurities tend to be concentrated in the melted portion of the sample.
3. This process sweeps impurities out of the sample and concentrates them at the end of the crystal bowl, which is then cut off and discarded.
4. The oxygen and carbon concentration are much lower as compared to other process, since the melt does not come into contact with a quartz crucible, and no hot graphite container is used.
5. No need to control the shape of the crystal.

Disadvantages:

1. Materials of high vapour pressure can not be grown.
2. High cost & difficult in operating, due to the use of poly rods.
3. Less production due to small size of material.
4. The repair is technically challenging.
5. It requires uniform, crack-free cylindrical feed rod.

Defects / Imperfections

Definition: The deviation from the perfect periodicity of atomic arrays in crystals is known as crystal defects.

- A perfect crystal, with every atom of the same type in correct position, does not exist.
- Thus, all crystals have some defects.

Why defects are important?

There are lot of properties that are controlled or affected by defects. For example -

- * Electrical & thermal conductivities in metals - strongly reduced by point defects.
- * Electronic conductivity in semiconductors - controlled by substitution defects.
- * Diffusion - controlled by vacancies.
- * Ionic conductivity - controlled by vacancies.
- * Plastic deformation in crystalline materials - controlled by dislocation.
- * Colors of materials are affected by defects.
- * Mechanical strength - strongly depend on defects.

Imperfections in crystalline solids are normally classified according to their dimension as follows:

1. Point Imperfections / defects [zero dimensional defects]
2. Line imperfections / Dislocations [one dimensional defects]
3. Planar or surface defects [2D defects]
4. Volume or Bulk defects [3D defects]

These defects are further classified into many defects such as -

crystal defects

Point defects

- > Vacancy
- > Interstitial
- > Substitutional
- > Schottky
- > Frenkel.

Line defects /

- dislocations
- > Edge dislocation
- > Screw dislocation

Surface defects

- > Grain boundaries
- > Tilt boundaries
- > Twin boundaries
- > Stacking faults.

- volume or
bulk defects
- > Inclusions
- > Voids

Point Defects:

When an atom is missing or an atom is in an irregular place in the lattice structure, the corresponding defects are known as point defects.

* A point defect produces strain in a small volume of the crystal surrounding the crystal, but does not affect the perfect distant parts of the crystal.

* In general, point defects occur in metallic & ionic crystals.

1. Vacancies :

The defects due to the missing atoms at their lattice sites are called vacancies.

* Vacancy defects are mainly due to the imperfect packing during the formation of crystal or due to thermal vibrations of atoms at high temperature.

* At high temperature atoms are frequently with vacancy defect and regularly change their positions leaving empty lattice sites behind their positions.

0 0 0 0 0 0
0 0 0 0 0 0
0 0 0 0 0 0
0 0 0 0 □ 0
0 0 0 0 0 0

Fig: A crystal lattice

2. Interstitial defects :

When an impurity atom tries to settle in the interstitial space between the parent atoms of the crystal without displacing, then such a

0 0 0 0
0 0 0 0
0 0 0 0

Fig showing formation of interstitial impurity defect

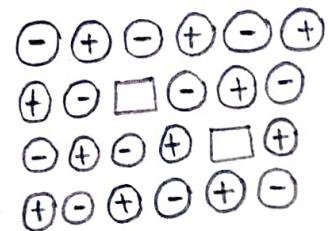
defect is known as interstitial defect.

Ex: Carbon atoms are interstitial impurity atoms that are added to iron to make steel. In steel, carbon atoms with radius of 0.071 nm are well fitted in the interstitial spaces between the larger iron atoms of radius 0.124 nm .

3. Schottky defects :

When a pair of vacancies is produced at one +ve ion site and one -ve ion site due to absence of +ve and -ve ions, then this type of defect is called the schottky defect.

* In ionic crystals, there are two types of possible vacancies, namely cation vacancies and anion vacancies.



* When a +ve ion from the interior of the lattice moves out of the crystal to its surface, then a +ve vacancy is formed at its site.

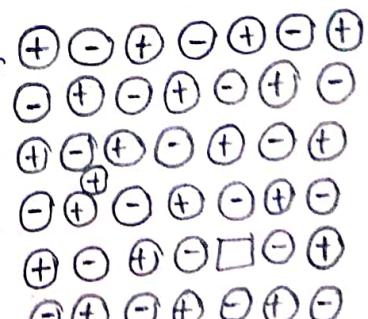
* The formation of +ve ion vacancy results in excess -ve charges inside the crystal.

* To maintain charge neutrality, a -ve ion moves to the crystal surface creating a -ve ion vacancy at its site.

* NaCl, CsCl etc... exhibits schottky defects.

4. Frenkel Defects :

When an ion displaced from a regular location in the crystal lattice to an interstitial location in the crystal lattice, then this type of defect is called the frenkel defect.



* Consider the periodic distribution of +ve and -ve ions in an ionic crystal.

* When a +ve ion leave its site and settles in the interstitial position then it creates a vacancy in its position.

* Thus, a vacancy and interstitial defects are created. This pair of defect is known as frankel defect.

* In case of frankel defect also charge neutrality is maintained.

* AgBr, AgCl, ZnS etc... exhibits frankel defects.

5. Substitutional defects :

When an impurity atom occupies the one of the positions of the parent atoms of the crystal, then such a defect is known as substitutional defect.



* A substitutional impurity atom is an atom of a different type than the bulk atoms.

* Usually, substitutional atoms are close in size to the bulk atom.

Ex: zinc atoms are substitutional impurity atoms that are added to copper to make brass. In brass zinc atoms with radius of 0.133 nm have replaced some of the copper sites of radius of 0.128 nm.

Line Defects :

* These are also called as linear defects or dislocations

* These are one-dimensional defects.

Definition: Dislocations are areas where the atoms are out of position in the crystal structure. or

A dislocation is a one-dimensional defect around which some of the atoms are misaligned.

* Thus, dislocations refer to a linear disturbance of the atomic arrangement in a crystal.

* Dislocations are generated in crystals due to growth accidents, thermal stress, phase transformation etc...

* They can be observed in crystalline materials with the help of electron microscope.

* There are two basic types of dislocations:

* Edge dislocations and screw dislocations.

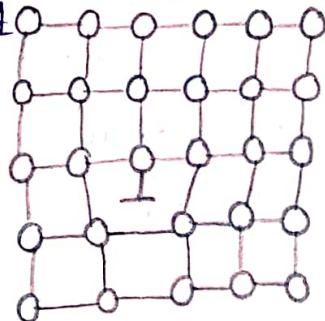
• Edge dislocations and

• screw dislocations.

* Most of the dislocations found in crystals are neither pure edge nor pure screw dislocations, but contain components of both these types. They are called mixed dislocations.

1. Edge dislocations:

If one of the vertical planes does not extend to the full length, but ends in between within the crystal, then such a defect is known as edge dislocation.



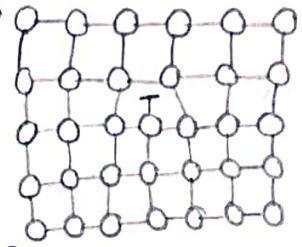
* Because of dislocation, i) just above the discontinuity, the atoms are squeezed and are in state of compression and ii) just below the discontinuity; the atoms are pulled apart and are in state of tension.

* The maximum distortion is centered around the edge of the incomplete plane.

* This distortion represents a line imperfection and is called an edge dislocation.

* Edge dislocations are symbolically represented by L or T.

* When the incomplete plane starts from the top of the crystal, then it is called +ve edge dislocation and is represented by "I".

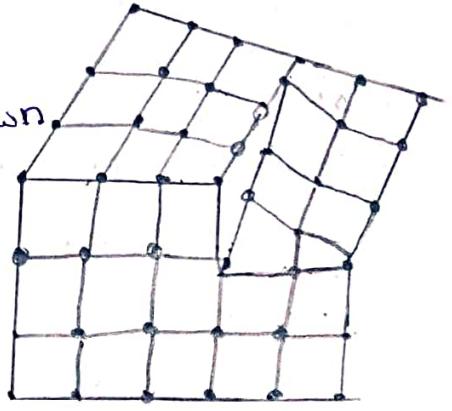


* When the incomplete plane starts from the bottom of the crystal, then it is called -ve edge dislocation and is represented by "T".

2. Screw dislocations :

* The screw dislocations are also known as Burger dislocations.

* These dislocations arise due to the displacement of atoms in one part of a crystal relative to the other part.



Burger vector: The magnitude and direction of the lattice distortion associated with a dislocation is called Burger vector.

* The Burger vector is perpendicular to the edge dislocation, and parallel to screw dislocation.

Planar Defects or Surface Defects :-

* These are two-dimensional defects.

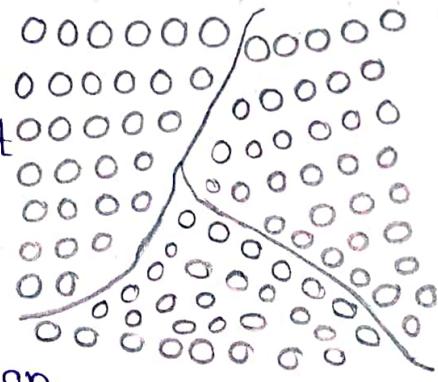
* The regions of distortions that lie about a surface having a thickness of few atomic diameters are known as surface defects.

* Surface defects are two-dimensional defects that separate two regions of the crystal.

* If the crystal is heated close to its melting point, many of the surface imperfections would disappear.

1. Grain Boundaries :

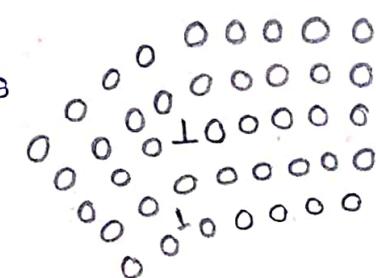
* During solidification of liquid metals, when growing crystals having different orientations meet other, the atomic packing between two adjacent grains get distorted and region of imperfection is generated.



* This transition zone not aligned with either of the grains is known as grain boundary.

2. Tilt boundaries :

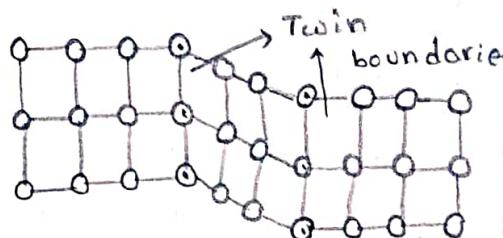
* Known as low (small) angle boundaries as orientation difference between neighbouring crystals is less than 10° .



* These are formed when arrays of parallel edge dislocations of same sign get arranged one above the other.

3. Twin boundaries :

* These are the boundaries in the grains at which the atomic arrangement on one side of the boundary is the mirror image of the atoms on the other side.



* The region between the pair of boundaries is called the twinned region.

4. Stacking Faults :

* A stacking fault represents interruption of one or two layers in the stacking sequence of atom planes.

* In a Face centered cubic (FCC) structure, the normal stacking sequence is ABCABCABCABC.

Due to plastic deformation, this arrangement may be disrupted and a stacking sequence is ABCABCACABC.

Concept of Thin Films

Thin - less than about one micron

Film - layer of material on surface

- Thin films are (low dimensional materials) thin material layers ranging from fractions of a nm to several μm in thickness.
- created by condensing species of matter, either by one by one atomic/molecular/ionic deposition.
- Thin film deposition is performed at very low pressure high vacuum.

The number of thin film materials, their deposition processing and fabrication techniques are used to produce many no. of devices.

The techniques are classified into two ways:

- Physical vapour Deposition (PVD)
- chemical Vapour Deposition (CVD)

Thin-film Deposition Techniques

Physical vapour Deposition (PVD)

Evaporation

sputtering

Thermal

Electron-beam

Pulsed laser

Molecular-beam epitaxy

Reactive sputtering

DC sputtering

Radio-frequency

Magnetron sputtering

Reactive sputtering

Spin-coating

Electroplating

sol-gel techniques

Screen printing

Dip coating

Laser-induced CVD

LPCVD

MOCVD

PECVD

CVD

Low-pressure CVD

Atmospheric pressure CVD

Low-pressure CVD

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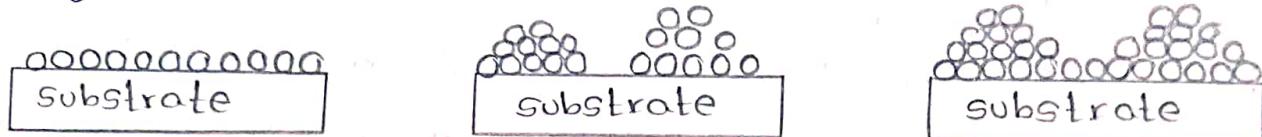
Low-pressure CVD

Atmospheric pressure CVD

Low-pressure CVD

Thin Film Deposition :

Thin film deposition is the process of creating and depositing thin film coatings onto a substrate material.



- Movement of vaporized target atoms or molecules to the substrate.
- Formation of layers by atoms or molecules.
- Growth of the layered atoms or molecules.

Physical Vapour Deposition (PVD) :

- A vaporization coating process.
- Material is removed from a target and deposited onto a substrate.
- Basic mechanism: An atom-by-atom transfer of material from the solid phase to the vapour phase and back to solid phase, gradually building a film on the surface to be coated.
- Materials to be deposited are heated to the point of vaporization, and then evaporate to form a thin film covering the surface of the substrate.
- All film deposition takes place under vacuum or very careful controlled atmosphere.

Chemical Vapour Deposition (CVD) :-

- Chemically reacted materials at the substrate surface form thin film of product material.
- Chemical reactions may depend on thermal effects as in vapour phase deposition and thermal growth.
- A definite chemical reaction is required to obtain final film.

Deposition of thin films by sputtering methods:

sputtering :

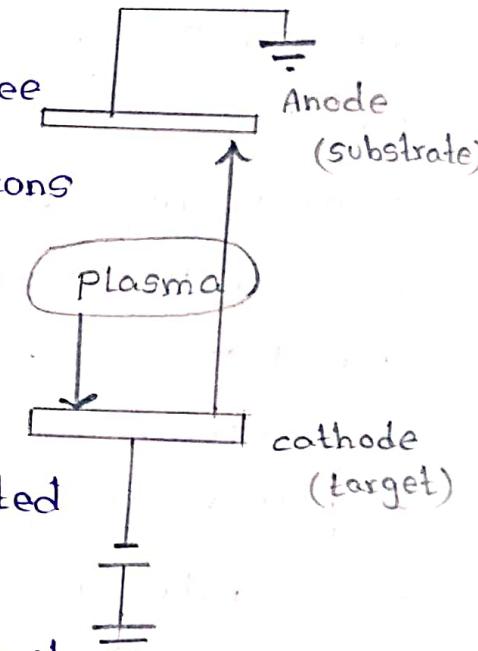
sputtering is a technique used to deposit thin films in which the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms.

Fundamental steps in sputtering process :

- A negative electrical potential is applied to the target material to be sputtered which act as cathode and the tve anode or ground is 'chamber body'.
- This electrical potential will cause free electrons to accelerate. When these electrons collide with a process gas atom, they strip an electron from the gas atom & creates a positively charged gas ion.
- The tvely charged ion is then accelerated towards the target.
- This ion carries enough energy with it to "knock off" or 'sputter' some of the target material.

Target material will then collect on the substrate.

- Additionally, a plasma^{glow} is created when the ions recombine with free electrons into a lower energy state. When a free electron recombines with an ion it has a voltage but the ion needs relatively less voltage. so this voltage is let off as light or plasma. This is also called as plasma glow.
- The energies required for sputtering are much higher than lattice bonding or vibrational energies.



Direct Current (DC) sputtering :

→ It is the simplest and most frequently used with electrically conductive target materials like metals because it is, easy to control and relatively low cost in power consumption.

→ In a DC sputtering system, Argon is ionized by a strong potential difference and are accelerated to a target.

→ After impact, target atoms are released and travel to the substrate, where they form layers of atoms in the thin film.

Parameters for DC sputtering :

→ Sputter voltage typically -2 to -5 KV.

→ Substrate Bias Voltage-

- Substrate is being bombarded by electrons and ions from target.

- Neutral atoms deposit independently.

- Put negative bias on the substrate to control this.

- Able to change properties of the film significantly.

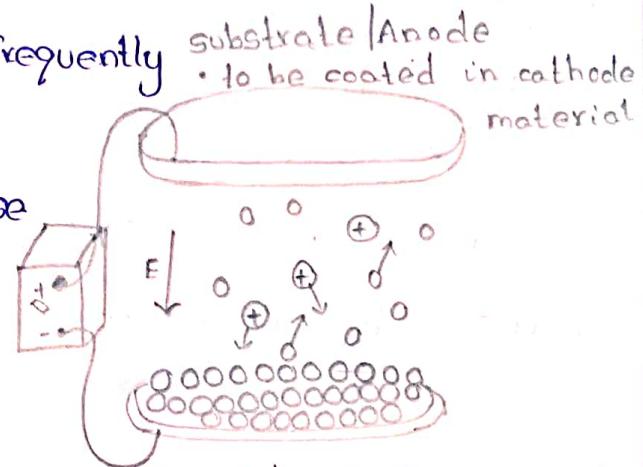
→ Deposition rate-

- changes with Argon pressure.

- Increases with no. of emitted particles / incident particles.

Advantages :

→ It can be relatively inexpensive, cost effective solution



for coating a wide range of decorative metal coatings.

→ It is easy to adjust film thickness because current is directly proportional to film thickness.

→ Adhesion strength is high.

Disadvantages :

→ It has limitations when it comes to dielectric target materials.

→ The high pressures required to achieve a plasma can degrade film quality.

→ Only a small fraction of the gas is converted to ions.

RF Sputtering :

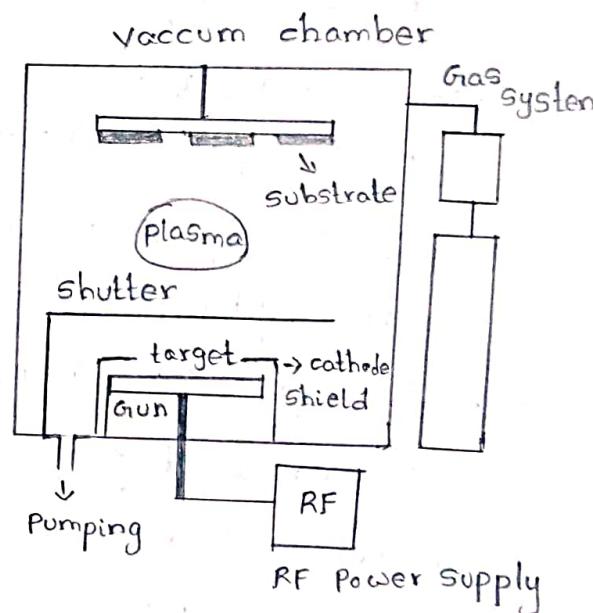
→ This technique involves running an energetic wave through an inert gas to create the ions.

→ The target material, which will ultimately become the thin film coating, is struck by these ions & broken up into a fine spray that covers the substrate.

→ Power supply is a high voltage RF source often fixed at 13.56 MHz.

→ The RF power source is then turned on, sending radio waves through the plasma to ionize the gas atoms.

→ Once the ions begin to contact the target material, it is broken into small pieces that travel to the substrate and begin to form a coating.



Advantages :

- It works well with insulating targets.
- High efficiency, i.e. can operate at lower Ar pressure.

Disadvantages :

- High cost of the power supplies.
- Deposition rates are very low for some materials.
- Requires additional impedance matching circuit to reduce reflected power.

Applications of Thin Films:-

1. Solar cells.
2. Light emitting diodes
3. Photoconductors.
4. Light crystal displays
5. Magneto-optic memories
6. Electro-optic coatings
7. Multilayer capacitors
8. Flat-panel displays
9. Smart windows
10. Computer chips
11. Magneto-optic discs
12. Microelectromechanical systems
13. Decorative coatings.
14. High purity semiconductors
15. Thermal insulation
16. Biological sensors.
17. Protective coatings.
18. Thin-film batteries.