

## UNIT- IV

## SOLID STATE CHEMISTRY

Types of solids – Crystal defects- Frenkel and Schottky defects – Spinel and Inverse spinel.

Hall Effect and Applications.

Semiconductors: Preparation of pure semiconductors by Zone refining, Distillation and Czochralski crystal pulling technique, Doping- Epitaxy, Diffusion and Ion-implantation technique- Intrinsic and Extrinsic semiconductors - Applications.

Insulators: Electrical Insulators and their Applications.

### INTRODUCTION

Solid-state in Chemistry is the study of the structure, properties and the synthesis of solid materials. It basically helps us understand the compound from a molecular level to the crystal structure level.

### SOLID

Solids are substances that have a definite shape and volume.

They are highly incompressible and rigid and have high mechanical strength.

The atoms and ions constituting the solid are closed packed and held together by strong intermolecular forces.

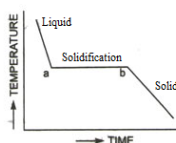
The constituent particles occupy fixed positions in the solid and cannot move about freely.

A true solid is characterized by a sharp melting point, a characteristic heat of fusion, incompressibility and a definite three-dimensional arrangement.

**TYPES OF SOLIDS:** Solids are two types: 1. Crystalline solids 2. Amorphous solids

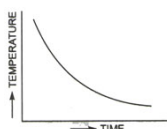
### CRYSTALLINE SOLIDS

1. In crystalline solids, the atoms, molecules or ions constituting the solid are arranged in a regular manner to form a three-dimensional pattern.
2. Crystalline solids have long range order and the arrangement of particles is so regular.
3. They have sharp melting point.
4. They are anisotropic, i.e., their physical properties are different in different directions.
5. They can be cleaved along curved planes.
6. They have definite heat of fusion (amount of energy needed to melt a given mass of solid at its melting point)
7. They are regarded as True solids.
8. Examples: NaCl, KCl, CsCl, etc
9. Cooling curve:



### AMORPHOUS SOLIDS

1. In amorphous solids, the atoms, molecules or ions constituting the solid are arranged in a random manner to form a three-dimensional pattern.
2. Amorphous solids have short range order and the arrangement of particles is not regular.
3. They don't have sharp melting point. They melt in a range of temperature.
4. They are isotropic, i.e., their physical properties are same in all directions.
5. They can be cleaved along curved planes. They give irregular cut.
6. Amorphous solids do not have definite heat of fusion due to its irregular arrangement of the particles.
7. They are regarded as pseudo solids or supercooled liquids.
8. Examples: Glass, Rubber, Plastics and Polymers
9. Cooling curve:



## DEFECTS IN SOLIDS

A defect in crystal is deviation from perfectly ordered arrangement of the constituent ions, atoms or molecules of the crystal thereby resulting in change in the properties. These defects may be a lattice point along a line or over a surface.

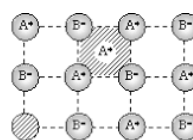
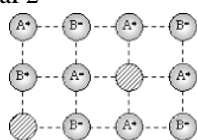
- **Types of Defects:** Defects can be classified into point defects, linear defects and planar defects.
- **Linear defects:** Linear defects are groups of atoms in irregular positions. Linear defects are commonly called dislocations.
- **Planar defects:** Planar defects are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.
- **Point defects:** Point defects are placed where an atom is missing or irregularly placed in the crystal lattice structure. Point defects include stoichiometric, non-stoichiometric and impurity defects.
- **Non-stoichiometric defect:** Non-stoichiometric compounds are those where the number of different type of atoms or ions are not present exactly in the same ratios as indicated by their formulae. These defects arise due to either metal excesses or metal deficiency.
- **Stoichiometric defect:** Stoichiometric compounds are those where the number of different type of atoms or ions present are exactly in the same ratios indicated by their formulae. Two types of defects are normally observed in such compounds, namely Schottky and Frenkel defect.

### SCHOTTKY DEFECT

1. A Schottky defect consists of a pair of holes in the crystal lattice formed due to removal of cation and an anion.
2. This defect mainly occurs in ionic compounds where ions are of similar size and the coordination number is high (usually 6 or 8)
3. This defect results in an overall decrease in density of crystal.
4. Ex: NaCl, KCl and CsCl

### FRENKEL DEFECT

1. A Frenkel defect consists of vacant lattice site, i.e., a hole and a ions which should have occupied the site now remains in the alternate interstitial position.
2. Mostly cations are relatively smaller in size and therefore it is easier to place cations in interstitial positions.
3. This effect is found in ionic compounds where ions differ widely in their sized and the coordination number is low (usually 4 or 6)
4. There is no change in the overall density of crystal.
5. Ex: ZnS, AgCl, AgBr and CaF<sub>2</sub>



### SPINEL AND INVERSE SPINEL

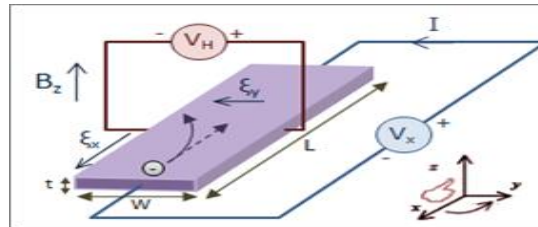
1. Spinel is compounds with the general formula  $AB_2O_4$  Where A and B are two different cations  $A^{+2}$  and  $B^{+3}$  and Oxygen is the anion. Eg:  $MgAl_2O_4$  and Ferrites such as  $ZnFe_2O_4$
2. In a spinel structure the oxygen ions are arranged in FCC arrangement. For every four anions, there are four octahedral voids and eight tetrahedral voids (total 12 voids/sites).
3. According to the above formula  $AB_2O_4$ , the cations (A and B) will occupy only 3 voids out of these 12 voids.
4. In normal spinel structure, the cation A occupies the tetrahedral void and cation B occupies the octahedral voids.
5. In an inverse spinel structure, the cation A occupies the octahedral void and cation B is distributed equally between octahedral and tetrahedral voids i.e., one half of cation B occupies tetrahedral voids and other half occupies octahedral voids.  
Eg: Ferrites  $Fe_3O_4$  and  $MgFe_2O_4$  have inverse spinel structure and are important magnetic materials.
6. It is important to note that in both normal and inverse spinel structures only one half of the octahedral sites and one-eighth of the tetrahedral sites are filled.

## HALL EFFECT

Electricity is nothing but the flow of charged particles (either electrons or holes) through a solid material. If a conducting material is connected to a battery the electrons will flow in a straight line. These moving charges generate electric field perpendicular to their motion.

Now if this current carrying material is placed between the poles of a permanent magnet, the electrons will be deflected along a curved path (because the magnetic field of the conductor will interact with the external magnetic field of the permanent magnet). As a result of this deflection, there will be more electrons on one side of the material than the other and hence a potential difference will appear perpendicular to both the magnetic field from the permanent magnet and the flow of current. This is termed as the Hall effect. The Hall potential is proportional to both the magnitude of electric current and magnetic field.

Consider a conducting slab of length ( $L$ ) in  $x$  direction, width ( $w$ ) in  $y$  direction and thickness ( $t$ ) in  $z$  direction. If the current flows along the length of the slab ( $x$  direction) and the slab is placed in a magnetic field perpendicular to the plane of the slab (in  $z$  direction) then the charge carriers will experience a Lorentz force and will be deflected towards one side of the slab. Due to this deflection an electric field is created in the  $y$  direction which counteracts the magnetic field. This field generated in the  $y$  direction is the hall effect which is perpendicular to both the electric field in  $x$  direction and magnetic field  $B$  in the  $z$  direction.

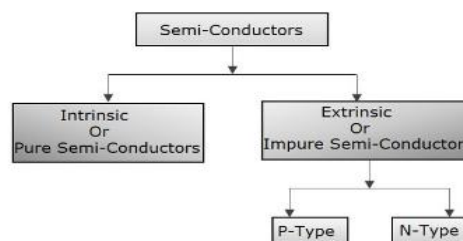


### **Applications**

1. Hall probe helps to measure the strength of magnetic field with great precision
2. Hall effect sensors are used in wide variety of gadgets. A hall sensor placed on a door frame with a magnet helps to sense whether the door is open or close.
3. Hall effect magnetic sensor are helps to locate the exact position of the motor. These magnetic sensors not only help in location the position but also help in sensing the distance and speed.
4. Magnetic sensors are used in anti-lock braking system (ABS) in automobiles for speed detection and control of air bags.
5. Poyanting Vector wattmeter uses Hall effect. This watt meter is used for measuring the power loss density at the surface of a magnetic material.

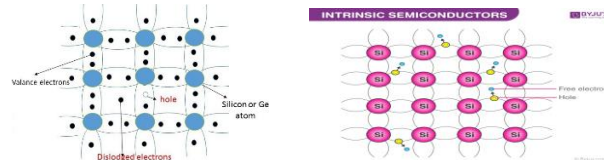
## SEMI-CONDUCTOR

Semi-conductors are the materials and their properties lie between those of conductors and insulators. In semi-conductors the forbidden energy band gap is very small. The valence band is completely filled at 0K and conduction band has no electrons. If some energy is supplied to them, the electrons from valence band jump to the conduction band. As the temperature increases more and more electrons cross over to the conduction band and the conductivity increases.



## INTRINSIC SEMI-CONDUCTORS

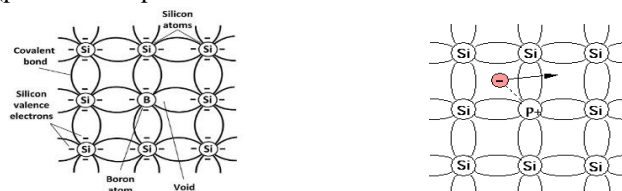
1. They are extremely pure semi-conductors (above 99.999% pure). For example, silicon Si and Germanium Ge. They have four valence electrons.
2. Their forbidden energy gap is about 1 eV. In such semiconductors, the energy gap is so small that even at ordinary temperatures the electrons possess sufficient energy to jump across the forbidden gap and go to the conduction band.
3. On the removal of an electron from the valence band, a vacancy termed as hole is created.
4. The neighboring electrons in the valence band fill this hole and in turn leave behind a hole in their place.
5. Thus, when an electric field is applied to an intrinsic semiconductor, the electrons in the conduction band move toward the anode and the holes in the valence band move in the opposite direction, i.e., toward the cathode. Hence, in an intrinsic semiconductor the charge is carried by electrons and holes in equal numbers.



## EXTRINSIC SEMI-CONDUCTORS

These are also called as impure semiconductors. In this type of semiconductors (Si or Ge) an impurity has been added to improve their conductivity. The added impurity is called dopant and the process is called doping. Extrinsic semiconductors can be of two types:

1. **N-Type semiconductor:** They are obtained by adding a pentavalent impurity (such as Phosphorous, Arsenic or Antimony) to pure intrinsic semiconductor (such as Si or Ge). The four electrons of the dopant form bond with Si or Ge and the fifth electron is the 'excess electron', that is loosely bound and can easily be excited from the valence band to the conduction band. Hence, conduction in n-type semiconductor is because of excess electrons and the name n-type (n is used for negatively charged electrons)
2. **P-Type semiconductor:** These are obtained by doping the parent Si or Ge with a trivalent impurity such as boron or aluminium (both of them have three valence electrons). The three valence electrons of boron or aluminium form three bonds with three Si or Ge atoms and the fourth Si or Ge atom is linked to boron atom by an incomplete bond containing only one electron. Thus, the crystal lattice has an electron deficiency called a hole. In the electric field, the electron from an adjacent atom moves into a hole, which is in-turn replaced by an electron from another atom. Thus, the condition is brought because of the migration of holes and hence the name p-type (p is used for positive holes).



## **Difference Between Intrinsic and Extrinsic Semiconductors**

Intrinsic Semiconductor	Extrinsic Semiconductor
Pure semiconductor	Impure semiconductor
Density of electrons is equal to the density of holes	Density of electrons is not equal to the density of holes
Electrical conductivity is low	Electrical conductivity is high
Dependence on temperature only	Dependence on temperature as well as on the amount of impurity
No impurities	Trivalent impurity, pentavalent impurity

## PREPARATION METHODS OF SEMI-CONDUCTORS

The most commonly used semiconductors for electronic devices are Si and Ge. However, because of its obvious advantages silicon continues to be the most widely used material in electronic industry. The silicon to be used for semiconducting devices must be at least 99.9999% pure. The common methods for preparation of semiconductors are 1. Distillation 2. Zone Refining 3. Czochralski Process

### I. DISTILLATION

1. It is a process where separation is carried out by taking the difference in boiling points.
2. Germanium is taken in a series of stills with a layer of HCl over it and heated it, while passing chlorine through it.
3. The vapours produced were collected and passed into a fractionating column.
4. The distilled vapours are collected into a receiver placed in ice bath.
5. Pure  $\text{GeCl}_4$  thus obtained is treated with water to get  $\text{GeO}$  which is reduced in an atmosphere of  $\text{N}_2$  to get elemental Germanium, which is further subjected to purification by Zone refining.

### II. ZONE REFINING

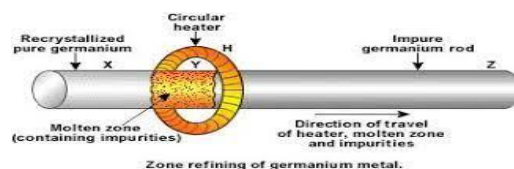
#### **Principle**

Zone refining refers to the method of purifying a crystal wherein a thin region of the crystal undergoes melting. This 'molten zone' is now moved across the crystal. The principle of zone refining is that the impurities in an ore of metal are more soluble in the melt state when compared to the corresponding solid state of the impurities. The impurities in the metal are melted at the forward edge by the molten zone and move through the block of metal, leaving the solidified pure element behind.

**Process:** In the zone refining process, a circular mobile heater is fixed at one end of the impure metal rod. Now, the circular mobile heater is moved slowly across the metal rod.

The metallic impurities melt at the temporary position of this heater. The melt containing the impurities moves forward along with the heater through the entirety of the metal rod. The pure metal is left to solidify as the heater moves along the rod.

As the heater moves forward, the concentration of the impurities in the melt increases. This is because the impurities are more soluble in their corresponding melt state. Finally, the impurities are accumulated at one end of the metal rod.

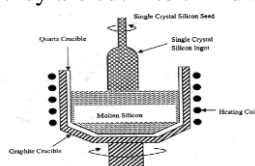


### III. CZOCHRALSKI PROCESS (SINGLE CRYSTAL FORMATION)

Czochralski process is commonly used for the single crystal formation.

A CZ apparatus consists of a crucible, heating element, seed shaft, rotating mechanisms and vacuum systems. All of which are controlled by microprocessors and sensors. A CZ apparatus weight about 20 tonnes, 7 to 8 m tall and can hold a charge of 100 kg of silicon.

- A semiconductor grade poly crystalline silicon is melted in a quartz lined graphite crucible. The melt is maintained at a temperature of 1690K which is slightly greater than the melting point of Silicon (1685K).
- The single crystal silicon of desired orientation is attached on the rod to acts as the seed crystal.
- The seed crystal is dipped in the surface of the melt. The rod is rotated in the molten silicon and the crystal is pulled out of the melt. The molten semiconductor solidifies on the seed crystal with an identical structure and orientation.
- Wafer manufacture: the diameter of obtained crystal is nearly 20 to 30 cm. These crystals are removed and ground to be perfectly round and then they are cut into thin discs called wafers



## **DOPING TECHNIQUES**

Calculated quantity of dopant (B, P, As or Sb) is added to the melt before the crystal pulling stage. The commonly employed doping techniques are as follows:

### **DIFFUSION**

1. Diffusion technique involves in conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atoms into the crystalline lattice of the semiconductor material without any melting.
2. The process consists of heating a p- type dopant (Sb or P). This causes some of the impurity atoms to condense on the surface of wafer and diffuse, thereby resulting in a p-type semiconductor material. By this technique, the extent of impurity atoms penetration can be controlled, even less than a few millionths of a centimeter by controlling the concentration of dopant atoms and temperature. This technique is employed for preparing n or p-type semiconductor, used in high frequency devices and to prepare n-p-n type transistor with a base width of even  $5\mu$ .
3. In this process the dopants are introduced into the wafers by solid state diffusion.
4. In the first step the vapors of the dopant atoms are deposited at the silicon surface at a high temperature of  $1000^{\circ}\text{C}$ . At this temperature the silicon atoms move out of their lattice sites creating high density of vacancies. The dopant atoms on the surface move into the vacant locations of the silicon atom.

### **ION IMPLANTATION**

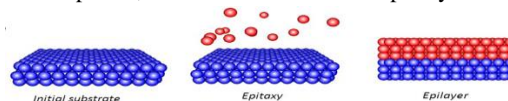
1. This process is employed for doping at lower temperature.
2. In this, the dopant can be introduced into selected areas of the wafer.
3. The semiconductor material is bombarded with an electrically controlled beam of high energy ions of B or P with energy of the order of  $10,000\text{eV}$ . This causes the implantation of the dopant into the crystal lattice of the semiconductor.
4. In the ion implantation charged dopants of B or P are accelerated in an electric field and irradiated onto the wafer. The penetration depth can be set very precisely by reducing or increasing the voltage needed to accelerate the ions. Since the process takes place at room temperature, previously added dopants cannot diffuse out. Regions that should not be doped, can be covered with a masking photoresist layer.
5. The wafers obtained by above methods are then cut into chips by using chemical etching, ultrasonic vibrations, laser beams etc

### **EPITAXY**

The word 'epitaxy comes from the Greek, epi means 'above' and taxis means 'ordered manner'. Epitaxy refers to a type of crystal growth or material deposition in which new crystalline layers are formed with a well-defined orientation with respect to the crystalline substrate. The new layers formed are called the epitaxial film or epitaxial layer.

**Homoepitaxy:** Extension of the substrate lattice by the overgrowth of a layer of identical material (e.g. Si on Si, GaAs on GaAs). In the simplest case, the epitaxial layer can be a continuation of the same exact semiconductor compound as the substrate; this is referred to as homoepitaxy. This technology is used to fabricate layers having different doping levels.

**Heteroepitaxy:** any two materials of different crystalline structure and orientation (e.g. GaAs on Si or Si on sapphire). If the epitaxial layer is composed of a different compound; it is referred to as heteroepitaxy. Examples include Si on Ge or Ge on Si.



One of the main commercial applications of epitaxial growth is in the semiconductor industry, where semiconductor films are grown epitaxially on semiconductor substrate wafers. Epitaxial films may be grown from gaseous or liquid precursors.

The Si or Ge wafer is placed in a long cylindrical quartz tube reactor, which is then heated. Then, gases containing compounds of Ge or Si mixed with calculated quantities of dopants are introduced into the reactor. The process of heating is continued, till a thin film of dopant over the wafer results. The doped wafer is ready for the fabrication of semiconductor devices. For getting Si epitaxial film,  $\text{SiCl}_4$ ,  $\text{H}_2$  and  $\text{N}_2$  mixture is used. For carrying out n-type doping, this mixture is mixed with a calculated amount of phosphine and for p-type doping diborane is employed.

#### **Applications of Epitaxial growth:**

1. Nanotechnology
2. Semiconductor fabrication.
3. High quality crystal growth
4. To grow layers of pre-doped silicon (in pacemakers, computers, automobiles, etc)

## **APPLICATIONS OF SEMICONDUCTORS**

1. Semiconductors are used in almost all electronic devices. Without them, our life would be much different.
2. Their reliability, compactness, low cost and controlled conduction of electricity make them ideal to be used for various purposes in a wide range of components and devices. transistors, diodes, photosensors, microcontrollers, integrated chips and much more are made up of semiconductors.
3. Temperature sensors are made with semiconductor devices.
4. They are used in 3D printing machines
5. Used in microchips and self-driving cars
6. Used in calculators, solar plates, computers and other electronic devices.
7. Transistor used as a switch in Electrical Circuits are manufactured using the semiconductors.
8. Flat panel displays: computers, television, mobile handheld devices
9. High brightness LEDs: OLED state lighting, large display panel, automotive applications, LCD backlighting.
10. Diode lasers.
11. Imaging array sensors: Digital cameras.
12. Optical storage
13. Robotics.
14. Medical Electronics.
15. Industrial Electronics.
16. Telecommunications.
17. Wireless communication.
18. Global positioning by satellite (GPS)
19. Smart cards.
20. Memories.

## **INSULATORS**

The substances which are capable of retarding or prohibiting the flow of heat or electricity or sound through them are known as Insulators or Insulating materials. In insulators the electrons are tightly bound to the parent atom and the forbidden energy gap is large. Even if there is high electric field, the electrons cannot jump from valence band to conduction band.

Insulators are two types: Thermal Insulators and Electrical Insulators.

Some of the common insulator examples are Plastic, Wood, Glass

### **Electrical Insulators**

Electrical insulators are those materials through which electrical charges cannot pass through.

In insulators, no free electrons are available for conduction.

They are non metallic materials.

Important characteristics of electrical insulators are:

1. The electrical charges cannot pass through the insulator.
2. They possess low conductivity i.e., high resistivity ( $10^9 - 10^{20}$  ohm-cm at room temp.)
3. They should be resistant to chemicals, solvents, acids, alkalis, oils and organic solvents.
4. They should have low thermal contraction and expansion.
5. They should have low dielectric constant.
6. The electrical properties of insulators should not be altered by change in chemical composition.

### **Solid Insulators**

Synthetic resins, glass, polyester resins, paper and press boards are the common examples of solid insulators.

Generally solid insulators are thermally and chemically stable and possess excellent dielectric properties.

Some of commonly used solid insulators and their applications are

Silicone rubber-Used in aircraft cables and motor winding insulations.

Butadiene rubber- Used in low voltage domestic cables, insulating wires.

Teflon- Used as insulator for all kinds of windings.

PVC-For insulation of flexible wire covering and insulating electric wires.

Polyethylene- High frequency insulator in radio, TV, communication circuit cables and power submarine cables

**Liquid Insulators**

Mineral oils and synthetic hydrocarbons are most commonly used liquid insulators. They possess low dielectric count, good thermal, chemical and electrical stability.

Some of commonly used liquid insulators and their applications are

Mineral oils- Used in oil filled high-voltage cables. In transformers to allow cooling by convection. Chlorinated hydrocarbons- Used in transformer fluids.

**Gaseous Insulators**

Air, Nitrogen, Hydrogen and SF<sub>6</sub> etc. are used as gaseous insulators. They are non-inflammable and chemically inert.

Some of commonly used gaseous insulators and their applications are

Air- Provides insulation between overhead transmission lines.

Nitrogen- Used in transformers to replace harmful oxidizing atmosphere. Also used under high pressure as dielectric in electrical capacitors.

SF<sub>6</sub>- Used in electrical devices such as capacitors and cables.

Hydrogen- Used as coolant in electrical machines such as turbo generators