Chapter I : Generalities

I.1.Conductor - Insulator - Semiconductor

Matter exists in three states in nature – Solid, Liquid and Gas. In solids, the constituent particles have a fixed position because of the strong bonding intermolecular forces. Thus, the particles oscillate in their mean positions and are responsible for rigidity in the solid state of matter.

Solid materials can be divided into three categories - Conductors; Semiconductors and Insulators- according to their ability to conduct an electric current or their band structure.

I.1.1. Classification of solids according to their conductivity

- **Conductive materials** such as; Silver, Copper, and Aluminum are known for their ability to conduct electricity with ease. In general, substances that are good electrical conductors also tend to be efficient at conducting heat. Conductive materials contain a high density of free electrons—typically ranging from 10^{22} to 10^{23} per cubic centimeter. When an electric generator applies a voltage, these free electrons move uniformly toward the positive terminal, creating an electric current through their collective motion.
- **Insulating materials** such as; Glass, Silica (SiO_2), and Wood do not allow electric current to flow under normal conditions. This is because the valence electrons in these substances are tightly bound to their atoms, leaving very few free electrons available to move. As a result, electrical conduction is practically impossible. Insulators also tend to be poor conductors of heat.
- **Semiconductor materials** such as; Silicon and Germanium are materials whose properties place them between conductors and insulators. A semiconductor does not conduct electricity as well as a conductor, but it isn't as resistant as an insulator either. However, their electrical conductivity can be precisely adjusted through a process called doping, which involves adding small amounts of impurities to create an excess of charge carriers (electrons or holes).

By bringing together differently doped semiconductors, it's possible to form junctions that regulate both the direction and the amount of electric current flowing through a device. This principle underpins the operation of modern electronic components such as diodes and transistors. Silicon, in particular, is the most widely used semiconductor due to its favorable properties and natural abundance. Its conductivity lies between that of conductors and insulators.

➢ Orders of Magnitude

- **Conductors:** $\sigma \approx 10^4$ to 10^8 S/cm;
- **Insulators:** $\sigma \approx 10^{-18}$ to 10^{-8}S/cm;
- **Semiconductors:** $\sigma \approx 10^{-8}$ to 10^8 S/cm.

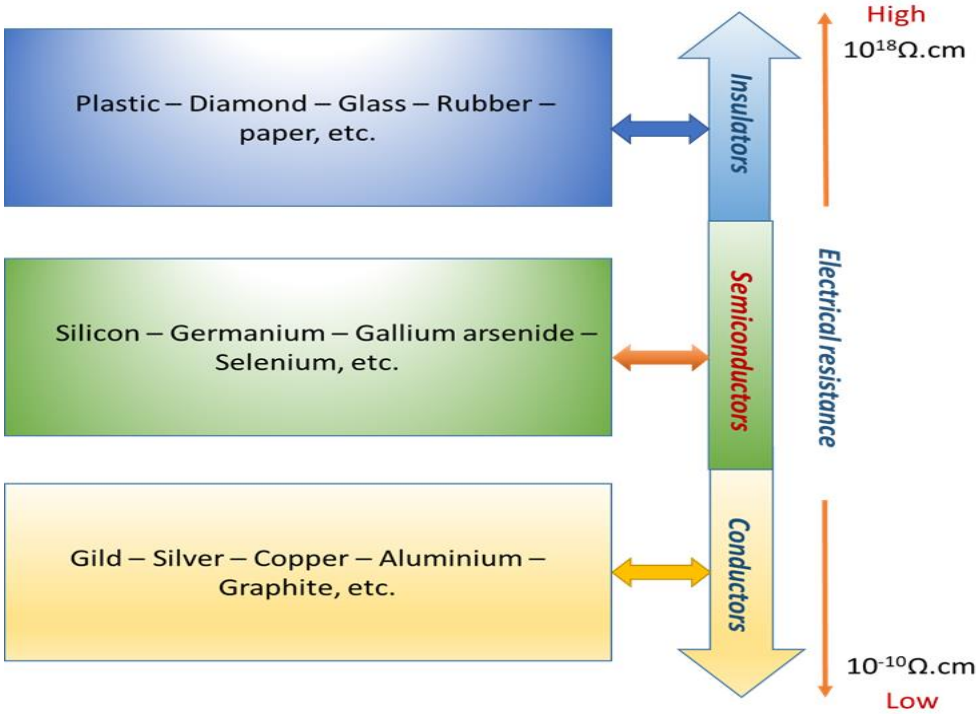

Figure I.1: Categories of materials according to their electrical resistivity (inverse of conductivity).

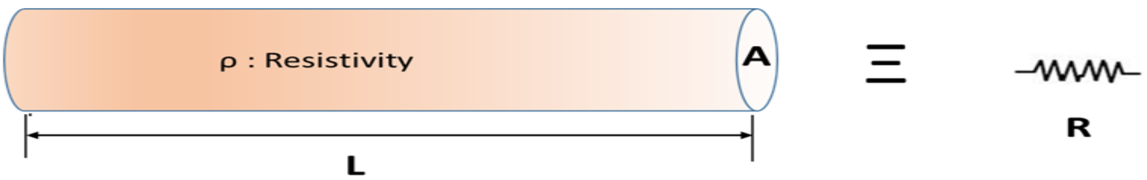

Figure I.2: Electrical resistivity

$$R = \rho \frac{L}{A} \tag{I.1}$$

L: Length;

A: Area.

I.1.2. Classification of solids according to their band structure

In solid-state physics, band theory is a model that describes the range of energy values that electrons in a solid can have. Generally, these electrons can only occupy certain energy intervals, which are separated by energy gaps (or forbidden bands). This model leads to the concept of *energy bands* or *band structure*. Depending on how these bands are arranged, it is possible—at least schematically—to explain the differences in electrical behavior between an insulator, a semiconductor, and a conductor. Materials are thus classified into three types based on band occupancy and the value of the energy gap (*band gap*).

The band structure of these three types of materials is shown in the following figure:

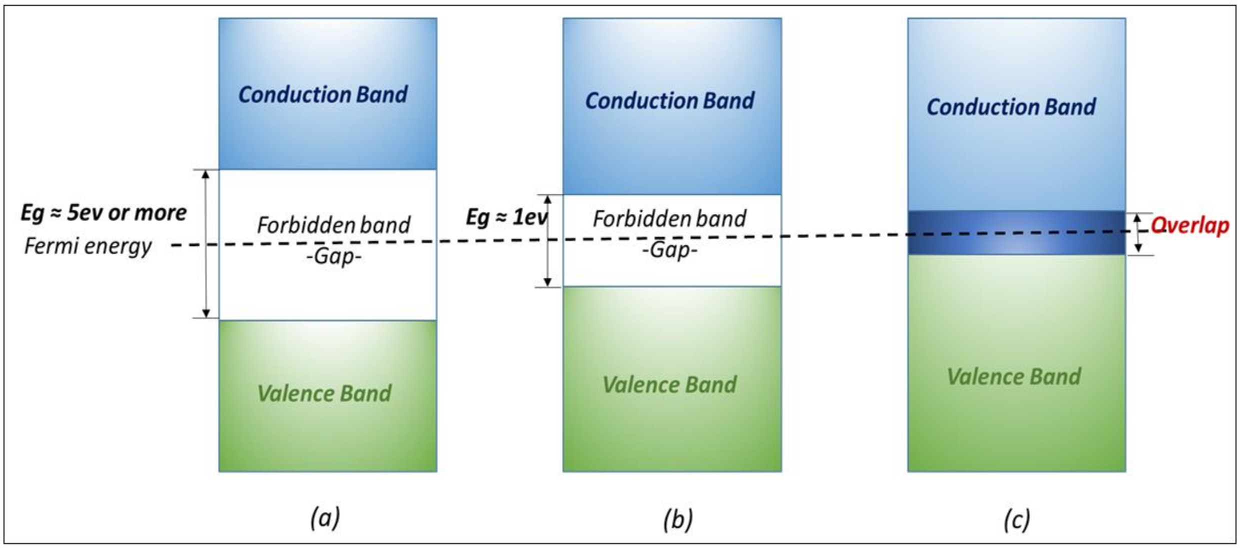

Figure I.3: Energy bands diagrams in: (a) Insulators, (b) Semiconductors, (c) Conductors

I.1.2.1 Types of energy bands in solids

- **Valence Band (VB):** It is the range of energies occupied by valence electrons at 0 Kelvin (-273.15°C). Valence band has the electrons of highest energy in the atom.

- **Conduction Band (CB):** It constitutes the range of energies possessed by conduction electrons. Conduction electrons are the valence electrons which get detached the atom and become free electrons. These free electrons are responsible for the conduction of current in a conductor. Conduction band is the first allowed energy band that empty of electrons at 0 Kelvin.
- **Forbidden Band (Band gap):** Conduction band is separated from valence band by a gap called forbidden energy gap. This gap represents the energies which can not be possessed by electrons of either band. When an electron from valence band absorbs energy equal to forbidden gap energy, it jumps the forbidden energy gap and enters the conduction band. Forbidden Band width, Eg, is a characteristic property of the material.

Notations and Acronyms

- **E_V :** Highest energy level of the valence band;
- **E_C:** Lowest energy level of the conduction band;
- **E_g:** Energy difference between the bottom of the conduction band and the top of the valence band. Thus: $E_g = E_C - E_V$;
- **E_F (Fermi Level):** Highest occupied energy level at absolute zero. In the case of conductor, the Fermi level lies within the conduction band. In the case of an insulator or a semiconductor, the Fermi level lies within the band gap.

I.1.2.2 Conductive, Insulating and Semiconducting materials

- **Conductive materials**

The overlapping of the valence and conduction bands implies that there is no energy gap. The conduction band is therefore partially filled (even at low temperatures), which allows the material to conduct electricity efficiently. In conductors, the valence band and conduction band overlap, so electrons can directly move into the conduction band and flow throughout the solid. The conductivity is high.

- **Insulating materials**

In insulators, the valence band and conduction band are separated by a band gap of approximately 6 eV. This value is too high for electrons to gain enough energy to jump into the conduction band.

- **Semiconducting materials**

In semiconductors, the valence band and the conduction band are separated by a smaller band gap, typically between 0.5 and 4 eV, most commonly around 1 eV. If electrons are supplied with this energy, some can transition into the conduction band and move through the material. This energy input can come from heating, applying an electromagnetic field, or illumination. At room temperature, conductivity is low but increases rapidly with temperature.

Table I.1: Examples of band gap values for selected materials.

Element	Eg (eV)	Type de material
C (Carbon)	5,5	Insulator
Si (Silicon)	1,1	Semiconductor
Ge (Germanium)	0,7	Semiconductor
Sn (Tin)	0	conductor

I.2. Classification of solids according to their structure of solid-state

Solid materials can be broadly classified into three main categories:

- **Crystalline materials**, in which atoms are arranged in a highly ordered, periodic lattice. The basic unit cell (or repeating pattern) is regularly repeated throughout the structure.
- **Amorphous materials**, where atomic arrangement lacks long-range order. In these materials, order exists only at a local scale and does not extend throughout the material.

- **Polycrystalline materials,** have a high degree of order over many atomic or molecular dimensions.

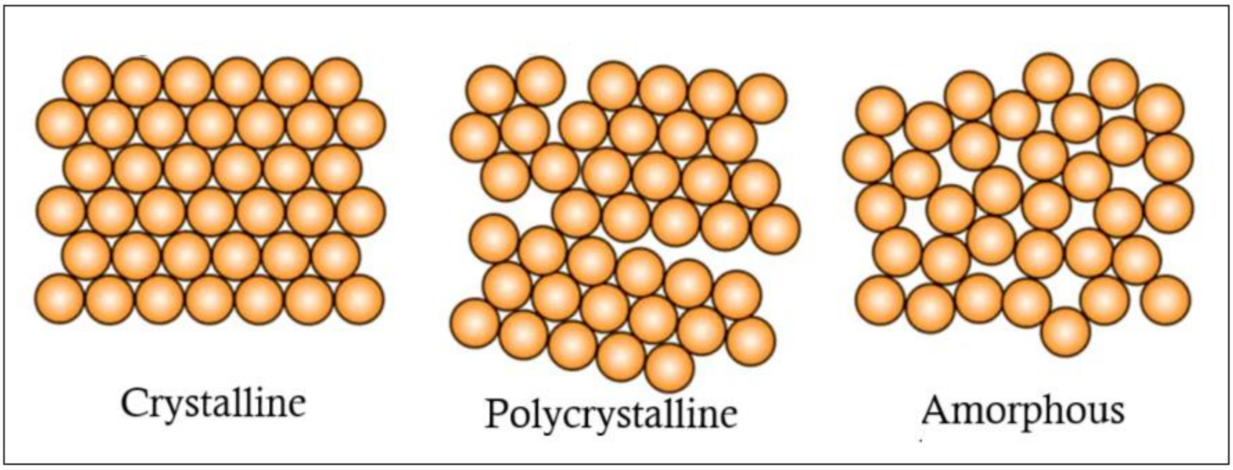

Figure I.4: Two-dimensional illustration of crystalline, polycrystalline and Amorphous material

Crystalline Solids are further Classified into Four types based on the binding forces between the constituent particles:

- **Ionic Crystals** (e.g., $Na^{+}Cl^{-}$): These are composed of ions held together by strong Coulomb forces. Since there are no free electrons, these materials are electrical insulators and are generally very hard due to the strength of the ionic bonds.
- **Covalent Crystals** (Group IV elements: C, Si, Ge, Sn): Each atom shares its four valence electrons with four neighboring atoms, forming covalent bonds. These bonds are generally weaker than ionic bonds, and the physical properties of the crystal depend on the bond strength. For instance, diamond (carbon) is an excellent insulator, while tin (Sn) behaves as a conductor.
- **Metallic Crystals** (e.g., Li, Na, K, Cu, Ag, Au): These are good electrical conductors, with each atom contributing a free electron to a "sea of electrons." Their melting points are usually lower than those of covalent crystals due to the nature of metallic bonding.

- **Molecular Crystals**, such as ice: These are formed by neutral molecules held together by relatively weak intermolecular forces (like hydrogen bonds), and their physical properties differ significantly from the other families.

I.3.Crystal systems and crystal lattices

A crystal can be described as a periodic repetition of a fundamental building block called the unit cell. There are seven distinct crystal systems: triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, and cubic. Most semiconductor materials tend to crystallize in the cubic system.

The Seven Crystal Systems		Example
Cubic (Isometric)	$a = b = c$, $\alpha=\beta=\gamma= 90°$	Silicon (Si), NaCl
Rhombohedral	$a = b = c$, $\alpha=\beta=\gamma\neq 90°$	Calcite ($CaCO_3$)
Hexagonal	$d = a = b \neq c$, $\alpha=\beta=90°$ $\gamma=120°$	Graphite, ZnO
Tetragonal	$a = b \neq c$, $\alpha=\beta=\gamma= 90°$	Tin (Sn, white form)
Orthorhombic	$a \neq b \neq c$, $\alpha=\beta=\gamma= 90°$	Sulfur (S_8)
Monoclinic	$a \neq b \neq c$, $\alpha=\gamma= 90°$ $\beta\neq120°$	Gypsum ($CaSO_4 \cdot 2H_2O$)
Triclinic	$a \neq b \neq c$, $\alpha\neq\beta\neq\gamma\neq 90°$	potassium dichromate ($K_2Cr_2C_7$)

Figure I.5. Classification and Geometries of Crystal Systems.