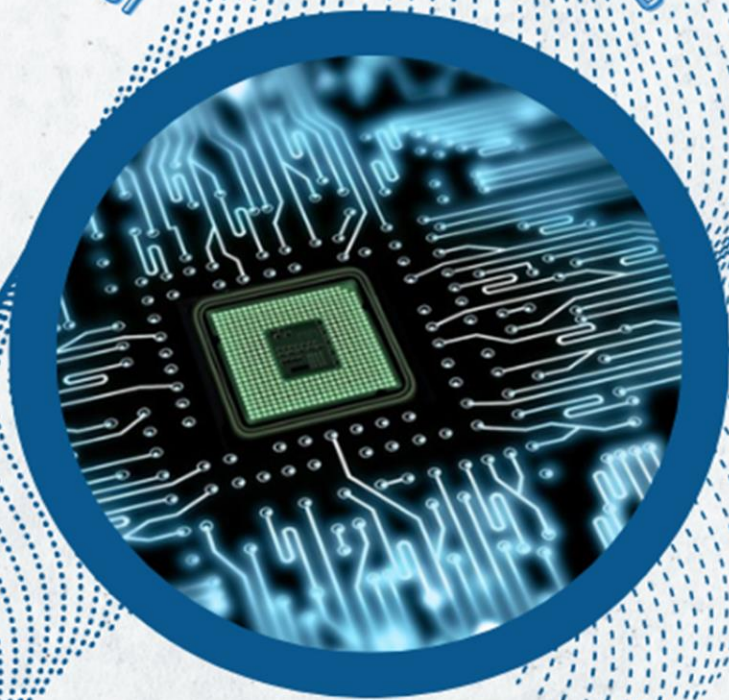




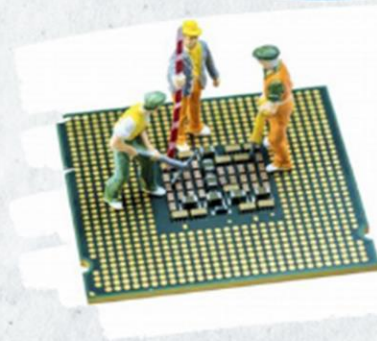
PHYSICS

CBSE

ELECTRONICS
SEMICONDUCTORS



UNIT:07
CH:01



CONDUCTORS, INSULATORS AND SEMICONDUCTORS

A solid is a form of matter which is characterised by definite shape and a definite volume.

CATEGORIES OF SOLIDS

In solids, the different types of forces acting between their ions or atoms or molecules account for their characteristic's properties, like hardness, electrical conductivity and thermal conductivity etc.

◆ On the basis of the characteristic properties, the solids have been classified into two categories:

.....(i) Crystalline solids and(ii) Amorphous solids.

(i) Crystalline Solids: *Those solids which have a definite external geometrical form are called crystalline solids.*

Or in other words, "The solids in which atoms are arranged in a regular and periodic manner are known as **Crystalline solids**".

☞ In a crystalline solid, the constituent ions or atoms or molecules are arranged in a definite, regular, repeated 3- D pattern within the solid.

Examples: Quartz, calcite, rock salt, sugar, mica, diamond etc.

☞ Crystalline solids have homogeneous composition.

☞ Their System enjoy stable equilibrium so they are in the minimum potential energy.

☞ Crystalline solids are bounded by flat surfaces.

➤ **Properties of the crystalline solids:**

1. The constituent ions or molecules in a crystalline solid are arranged in a definite, geometrical pattern, within the solid in all its three dimensions.
2. They have definite external geometrical shape.
3. They have a long-range order of ions or atoms or molecules in them.
4. All the bonds in ions or atoms or molecules of a crystalline solid are equally strong.
5. The crystalline solids have a sharp melting point, because on heating, all the bonds get ruptured at one and the same temperature. A latent heat for the change of the state is associated at this temperature.
6. They are anisotropic i.e., the physical properties (like mechanical strength, refractive index, electrical conductivity, thermal conductivity etc.) of a crystalline solid are different along different directions, i.e. the bonds of crystalline solids have directional properties.
7. They are considered as true and stable solids.

Fig. 1(a), shows the structural pattern of crystalline solid where the atoms A and B are represented by dots and circles respectively. In this structure, we note that each A atom is surrounded by three B atoms and each B atom is surrounded by two A atoms. There is a regular arrangement of group of atoms which is repeated in a regular fashion in three dimensions and thus the crystalline solid has a long-range order.

(ii) Amorphous or Glassy Solids: *Those solids which have no definite external geometrical form are called amorphous solids.*

Or, in other words, "The solids in which atoms are arranged in a completely irregular manner are known as **Amorphous solid**".

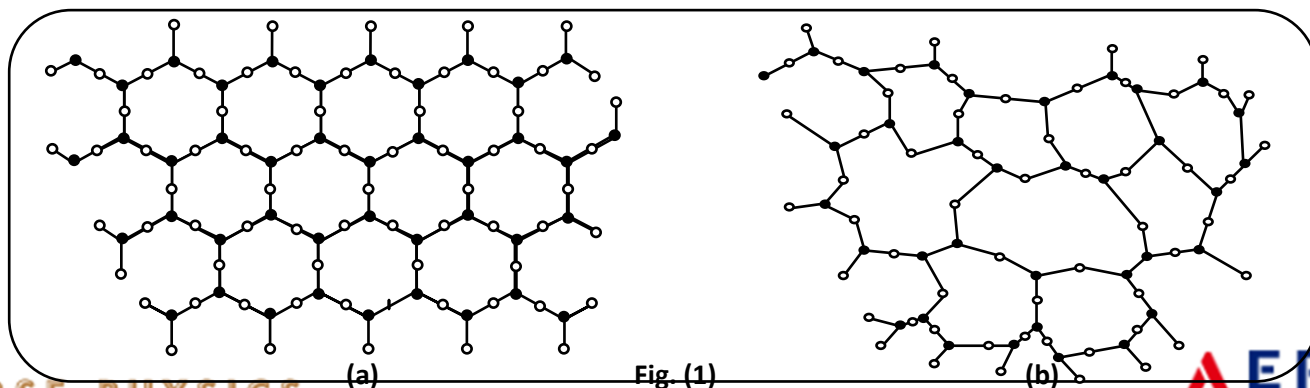
☞ In an amorphous solid, the constituent atoms or molecules are not arranged in a definite pattern repeating in three dimensions within the solid.

Examples: Rubber, glass, plastic, cement, paraffin wax etc.

➤ **Properties of the amorphous solids:**

1. The constituent atoms or molecules in an amorphous solid are not arranged in a regular, definite geometrical pattern, within the solid.
2. They do not have regularity in their external shape.
3. They do not have a long-range order of the ions or atoms or molecules in them.
4. All the bonds in ions or atoms or molecules of amorphous solids are not equally strong.
5. The amorphous solids do not have a sharp melting point, because on heating, the weakest bonds get ruptured first at lower temperatures and stronger bonds are ruptured at higher temperatures.
6. They are isotropic i.e., their physical properties are same in all directions.
7. They are not regarded as true and stable state of solids; but they are considered to be super cooled liquids of high viscosity.

Fig. 1(b), shows the structural pattern of **amorphous solid**. There is no regular arrangement of the group of atoms repeating in three dimensions within the amorphous solid and thus there is no long-range order in them.



CRYSTAL LATTICE

It is a geometrical arrangement of points in space where if atoms or molecules of a solid are placed, we obtain an actual crystal structure of the solid.

In crystal lattice, the environment about each point is the same as that about each other point.

consider a two-dimensional crystal structure as shown in Fig. 2(a). Here, the group of two atoms (i.e., a molecule) is shown by circle with dot (O•). It is called **basis**. If we replace all the molecules by the points in space at their respective positions, we get an array of points as shown in Fig. 2(b). *The array of points so obtained is called a crystal lattice.*

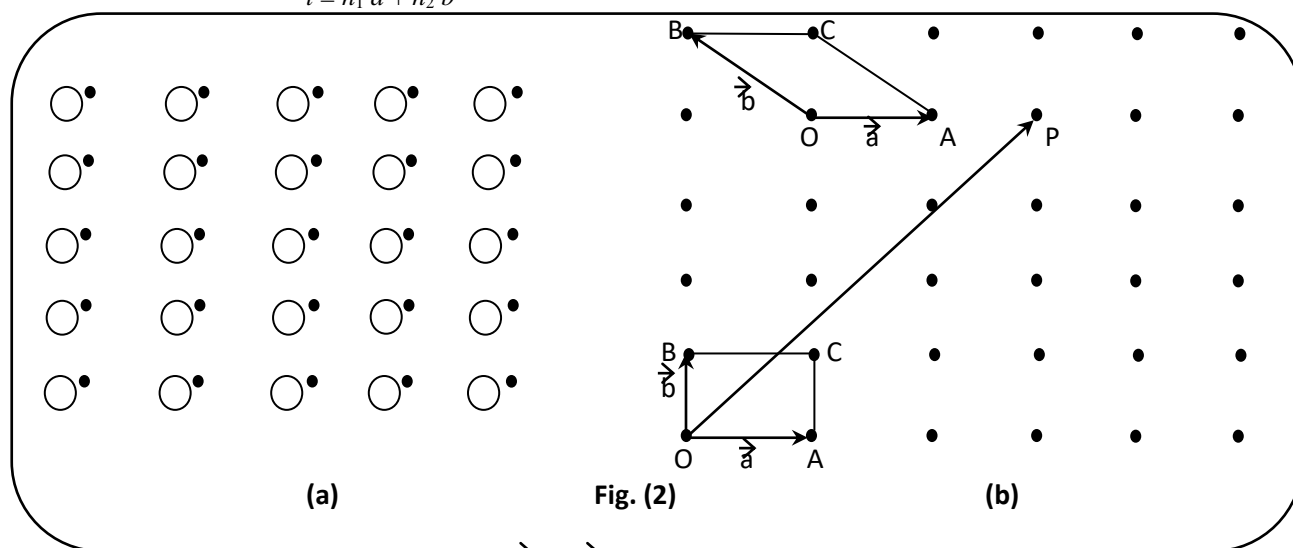
➤ For a given crystal; **Lattice + Basis = Crystal Structure.**

➤ Each point in the crystal lattice is called the *lattice point or lattice site.*

➤ In a given crystal lattice, there is regularity and orderliness regarding the arrangement of points around a given lattice point which is exactly similar to that around any other point.

Taking O as any arbitrary origin, we note that the lattice points along OA are at equal distances \vec{a} and those along OB are at equal distances \vec{b} , for a given pattern, Fig. 2(b). Thus, considering point O as any arbitrary origin, we can define any lattice point P, by the tip of vector \vec{l} , given by

$$\vec{l} = n_1 \vec{a} + n_2 \vec{b}$$

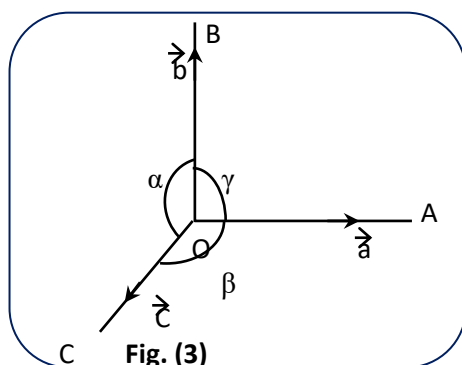


Where n_1 and n_2 are integers and a and b are called **translational vectors**.

➤ For lattice point P, (3, 4) the values are $n_1 = 3$ and $n_2 = 4$ in Fig. 2 (b).

➤ A lattice point P in a three-dimensional lattice is given by $\vec{l} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$

Where n_1, n_2, n_3 are integers and a, b and c are translational vectors along the axes OA, OB and OC respectively. **These a, b, c are called the lattice parameters** i.e., the length of the edges of a structural unit along the three axes. Fig (3).



UNIT CELL

Unit cell is the smallest portion of the crystal formed by minimum number of atoms or molecules which when repeated over and again in three dimensional spaces builds up to whole crystal structure.

➤ Thus, a unit cell is the **building block** of the crystal.

➤ In a three-dimensional lattice which is the actual case, the unit cell is in general, a parallelepiped. The unit cell can be selected in different ways.

➤ To describe a unit cell completely, six parameters are needed in all. These are

(i) The lengths a, b, c of the three sides of the unit cell, and

The angles α, β and γ between the vector a, b and c as shown in fig. (4)

■ The lines OX, OY and OZ drawn parallel to the lines of any three faces of the unit cell, which do not lie in the same plane are called *crystallographic axes*.

- ▶ All the parameters of unit cells of one crystal structure are identical whereas the parameters of unit cells of one crystal structure are identical whereas the parameters of the unit cell of different crystal structures are different.
- ▶ A simple unit cell with particles (ions/atoms/molecules) only at the corners is called *primitive unit cell* and other types of unit cells are called *non primitive unit cells*. The simple cubic cell is a primitive cell. The face centred cell and body centred cell are non-primitive cells.

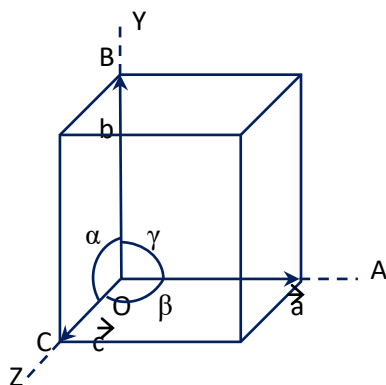


Fig (4)

To draw a crystal structure, we study first the six parameters of its unit cell i.e. a, b, c (length of the edges of the unit cell) and angles α, β and γ between a, b and c as shown in Fig. 5(a). Such unit cells are placed side by side, repeatedly in three dimensional spaces, and we get the actual crystal structure as shown in Fig. 5 (b).

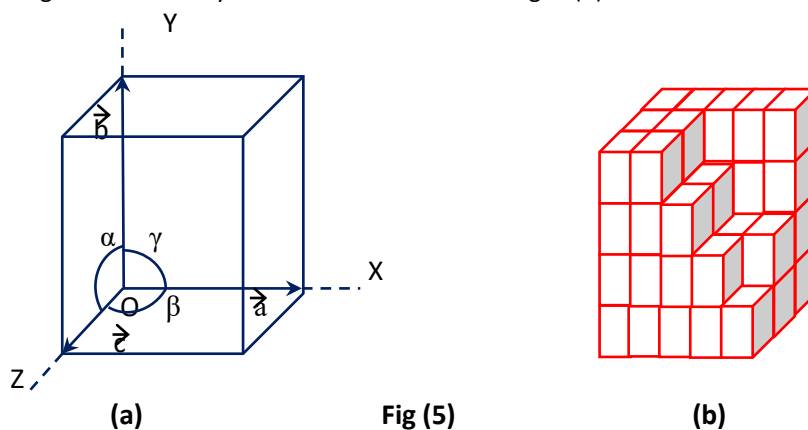


Fig (5)

CRYSTALLOGRAPHIC SYSTEMS

All the crystals can be grouped into seven crystallographic systems, depending upon the shapes of their unit cells. The description of these seven crystallographic systems is listed in a table given below.

S. No.	System	Lattice constants	Angles between lattice axes	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Li, Ni, Ag, NaCl, Po, Pb etc.
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	HgCl ₂
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	KClO ₃
5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇
6.	Rhombohedral	$a = b = c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Calcite, (CaCO ₃)

THREE KINDS OF CRYSTALS

[i] **Single crystals:** The crystals in which the periodicity of the pattern extends throughout the piece of crystal are known as single crystals.

- ▶ The size of a single crystal can vary from a fraction of a centimetre to a few centimetres. The small sized single crystals, whose features are not visible to the naked eye, are called **monocrystals**. The dimension of a typical unit cell of monocrystal is $\approx 5 \times 10^{-8}$ cm. Hence even if monocrystal has 10^4 -unit cells, its size will be $\approx 5 \times 10^{-4}$ cm, which cannot be visible to the naked eye.

✎ *Single crystals have anisotropic behaviour i.e.,* their physical properties (like mechanical strength, refractive index, thermal and electrical conductivity) are different along different directions.

[ii] **Polycrystals:** A polycrystal is the aggregate of the monocrystals whose well developed faces are joined together.

Metals are polycrystalline.

A polycrystal shows *isotropic properties*, though the monocrystals constituting them are anisotropic in behaviour. **Ceramics** are the important illustration of the polycrystalline solids. Ceramics are made of inorganic oxides silicates (for example, SiO_2) and are easy to melt. Ceramics are commonly used in making gas lighters and telephone receivers. Ceramics oxides are generally bad conductors of electricity. However, recently it has been found that ceramics made by the suitable combination of materials like Y_2O_3 , BaO and CuO_2 show *superconductivity*.

(iii) **Liquid crystals:** Some organic crystalline solids on heating are not converted directly into the liquid phase. In a certain temperature range between the solid and the liquid phases, they become fluids like liquids but their molecules remain oriented in particular directions, showing that they retain their anisotropic properties. *Such fluid like substances are said to have long range orientation order and are called the liquid crystals.*

Some materials (like cholesterol esters) in liquid crystal phase show a change in colour with change in temperature. This property is used to *measure temperature*. Some other liquid crystals (alkyl cyanobiphenyl) rotate the plane of polarisation of the incident light. They are used in liquid crystal displays (L.C.D.). These displays are now commonly used in electronic watches, clocks and micro calculators etc.

ENERGY BANDS OF SOLIDS (Band Theory of Solids)

According to Bohr's theory of atomic spectra and the concept of electronic configuration, the electrons in an isolated atom have certain definite discrete amounts of energy corresponding to different shells and subshells. It means *there are well defined energy levels of electrons in an isolated atom*.

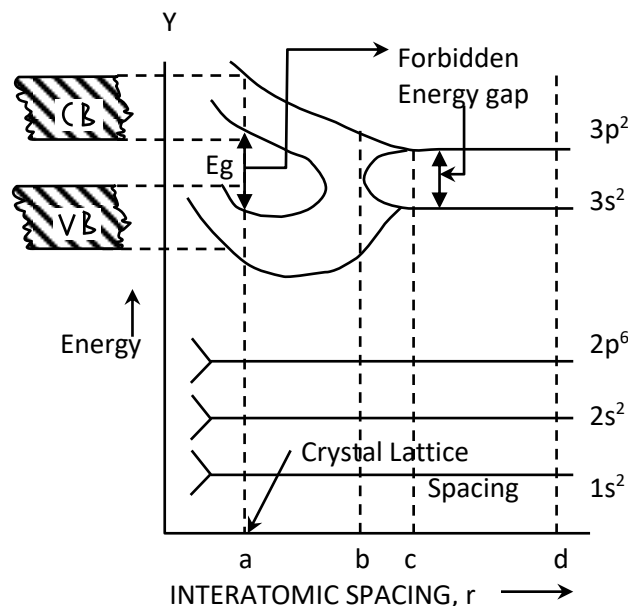
➤ If large numbers of atoms are brought close to one another to form a crystal, they begin to influence each other. **Due to this interatomic interaction**, there is no appreciable modification in the energy levels of electrons in the inner shells but there is a considerable modification in the case of energy levels of the electrons in the outer shells. This is due to the fact that the *valence electrons are shared by more than one atom in the crystal*.

consider a single silicon crystal having N atoms in all. Each atom is associated with a crystal lattice site. In Fig (6), the inter atomic spacing r is shown on X-axis and energy on Y-axis. The distance $r = a \approx 1 \text{ \AA}$ corresponds to equilibrium distance or actual crystal lattice spacing.

The process of splitting of energy levels can be understood by considering the different situations as discussed below:

(i) If the interatomic spacing of the atoms is very large (i.e., $r = d \gg a$), there is no interatomic interaction.

Each atom in the crystal behaves as a free atom. In this situation each of N atoms has its own identical energy levels, which are sharp, discrete and distinct. The electronic configuration of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$. This shows that the outer two subshells of silicon atom contain two electrons in **3s** subshell and two electrons in **3p** subshell, whereas six electrons are required to completely fill **3p** subshell. Thus, in the silicon crystal under study, there are **2N** electrons completely filling 2N possible 3s levels, all of which are of the same energy. There are 6N possible 3p levels, out of which only 2N levels are filled and all the filled 3p levels have the same energy. All these facts follow from Pauli's exclusion principle.



(Fig 6)

(ii) When the interatomic spacing r is less than d but greater than c (i.e., $c < r < d$), there is no visible splitting of energy levels.

(iii) When the interatomic spacing r is equal to c , the interaction between outermost shell electrons ($3s^2$ and $3p^2$) of neighbouring silicon atoms becomes appreciable. As a result, the energy of electrons corresponding to $3s$ and $3p$ levels of each atom starts changing i.e., the splitting of these energy levels commences, whereas there is no change in the energy levels of electrons in the inner shells.

(iv) When the interatomic spacing r lies in between b and c (i.e., $b < r < c$), the energy of electrons corresponding to $3s$ and $3p$ levels of each atom gets slightly changed. Instead of a single $3s$ or $3p$ level, we get a large number of closely packed levels ($2N$ levels corresponding to a single $3s$ level and $6N$ levels for a single $3p$ level of an isolated atom). This spreading of energy corresponding to $3s$ and $3p$ levels reduces the energy gap that existed between $3s$ and $3p$ levels of free atom. Since number N is very large ($\approx 10^{29}$ atom/ m^3) and the energy of $3s$ and $3p$ levels is of the order of few electrons' volt, the levels due to spreading of the energy of $3s$ or $3p$ levels are very closely spaced. **This collection of closely spaced levels is called an energy band.**

(v) When the interatomic spacing r becomes equal to b but greater than a (i.e., $r = b > a$), the energy gap between $3s$ and $3p$ levels completely disappears and the $8N$ energy levels are continuously distributed. In such a situation, it is not possible to distinguish between the electrons belonging to $3s$ and $3p$ subshell. We can only say that $4N$ levels are filled and $4N$ levels are empty.

(vi) When the interatomic spacing r becomes equal to a (i.e., $r = a$, the actual spacing in the crystal), the band of $4N$ filled energy levels is separated from the band of $4N$ unfilled energy levels by an energy gap called forbidden gap, which is denoted by E_g . The lower completely filled band is called valence band and the upper unfilled band is called conduction band.

Quantum states in silicon crystal having N atoms are shown in the following table.

Energy level	Total states available	Total states occupied
1 s	2 N	2 N
2 s	2 N	2 N
2 p	6 N	6 N
3 s	2 N	2 N
3 p	6 N	2 N

Difference between Valence, Conduction and Forbidden Band`2q1

1. **In valence energy band**, there are valence electrons. This band may be partially or completely filled with electrons. This band may be partially or completely filled with electrons. This band is never empty. In this band electrons are not capable of gaining energy from external electric field, Therefore, the electrons in this band do not contribute to the electric current.

2. **In conduction energy band** electrons are rarely present. This band is either empty or partially filled with electrons. In this band, the electrons can gain energy from external electric field. Electrons in this band contribute to the electric current.

3. **In forbidden energy gap**, electrons are not found in this band. This band is completely empty.

The minimum energy required for shifting electrons from valence band to conduction band is called as band gap (E_g).

Distinction between Conductors (or Metals), Semiconductors and Insulators on the Basis of their Energy Bands:

Metals are good conductors of electricity; insulators are very poor conductors of electricity whereas the semiconductors have the conductivity in between that of conductors and insulators.

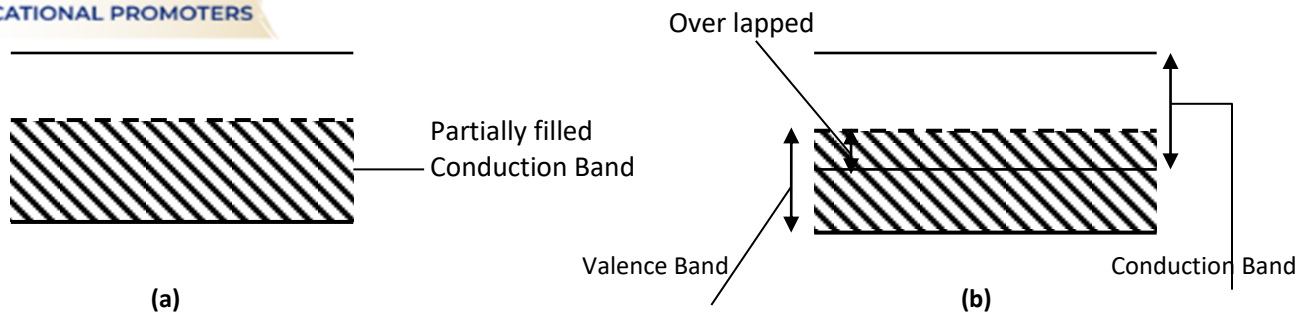
Fermi energy is the maximum possible energy possessed by free electrons of a metal at absolute zero temperature (i.e., 0K). The value of Fermi energy for different materials is different.

Fermi level in semiconductor: *It is that energy level in energy-band-diagram for which the probability of occupancy becomes half.*

➤ **For the present discussion the** Fermi level may be defined as that energy level in energy-band-diagram which corresponds to the centre of gravity of conduction electrons and holes weighted according to their energies.

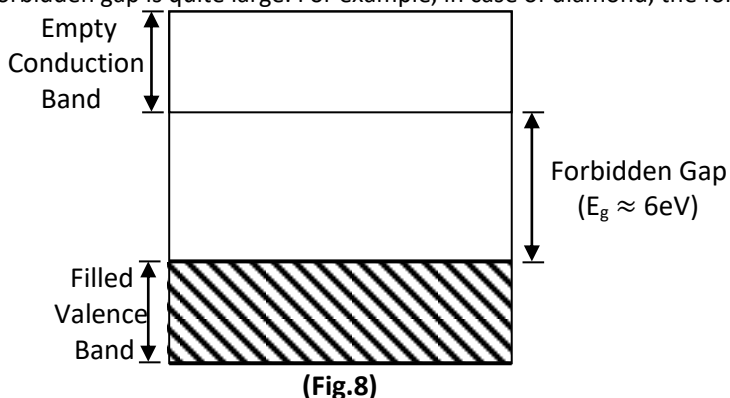
➤ Depending upon the relative positions of the valence band and the conduction band, the solids can be classified into metals (conductors), insulators and semiconductors.

◆ **Metals (conductors):** The energy band diagram for metals is such that the conduction band is partially filled with electrons, Fig. 7(a) or the conduction and valence band partly overlap each other and there is no forbidden energy gap in between. Fig. 7 (b). In both the situations, it can be considered that the metal has a single energy band which is partly filled and partly empty.



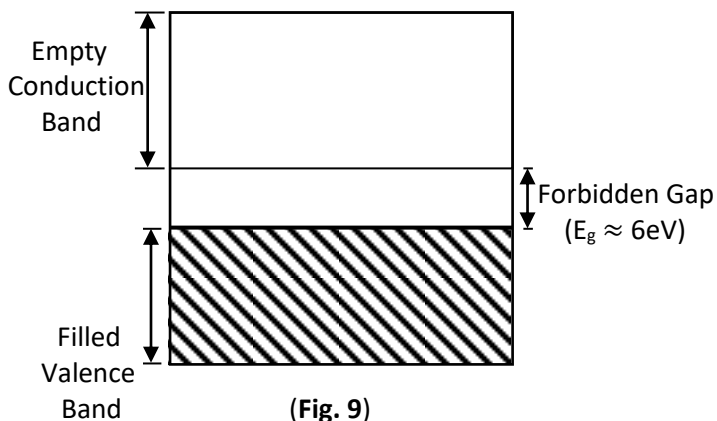
Many electrons from below the Fermi level, by acquiring a little more energy from any source, can shift to the higher energy levels above the Fermi level in the conduction band and behave as free electrons. In this situation, large numbers of electrons are available for electrical conduction, hence the resistance of such a material is low or the conductivity is high. Even if a small electric field is applied across the metal, these free electrons start moving in a direction opposite to the direction of electric field. Due to it, a current begins to flow through it and hence metal behaves as a conductor.

◆ **Insulators:** The energy band diagram is shown in Fig. 8. Here, the valence band is completely filled, the conduction band is empty and forbidden gap is quite large. For example, in case of diamond, the forbidden gap is of



6eV. Since the valence band is completely filled as per Pauli's exclusion principle, therefore the electrons are not free. Again, due to large forbidden gap, no electron is able to go from the valence band to the conduction band even if electric field is applied. Hence electrical conduction in this material is impossible and they behave as insulators.

◆ **Semiconductors:** The energy band diagram of semiconductors is shown in Fig. (9). Here also, the valence band is totally filled and the conduction band is empty but the forbidden gap between conduction band and valence band is quite small. It is about 1eV. For example, the forbidden gap for germanium is of 0.72 eV and for silicon it is of 1.1 eV.

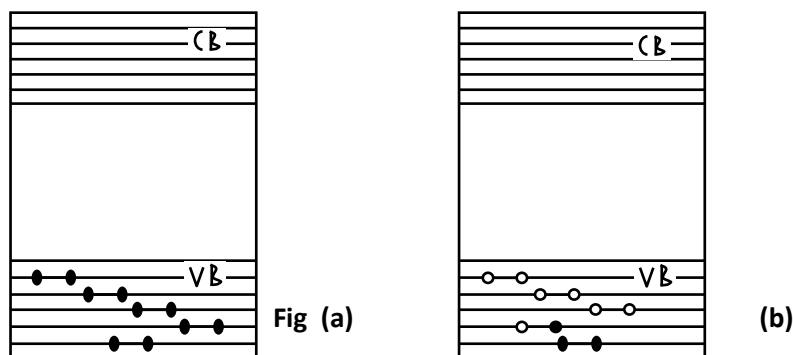


◆ At zero Kelvin, electrons are not able to cross even this small forbidden gap and hence the conduction band remains totally empty. Therefore, the semiconductor at zero Kelvin behaves as insulator. However at room temperature, some electrons in the valence band acquire thermal energy greater than energy gap of 1eV and jump over to the conduction band where they are free to move under the influence of even a small electric field. As a result of it, the semiconductor acquires small conductivity at room temperature. The resistance of semiconductor would not be as high as that of insulator.

FORMATION OF HOLES IN SEMI-CONDUCTORS

(i) *From the energy band diagram of the semiconductor:* In the energy band diagram of the semiconductor, there is an energy gap of about 1eV between the valence band and the conduction band. Fig (a).

- At zero Kelvin, the semiconductor behaves as an insulator, as no electron from the valence band can cross this energy gap and go to the conduction band. But at higher temperature, some of the electrons gain energy due to thermal agitation and move from the valence band to the conduction band. As a result of it, a vacancy is created in the valence band at a place



where the electrons was present before moving to the conduction band, Fig (b). **This vacancy is called a hole.** Since the absence of a negatively charged electron is equivalent to the presence of an equivalent amount of positive charge, therefore, *a hole is considered as a seat of positive charge, having charge equal to that of an electron. The hole is considered as an active particle in the valence band as an electron is in the conduction band. The motion of the electrons in the conduction band and also the motion of holes in the valence band are responsible for the electrical conduction in semiconductors.*

(ii) *From the valence bond study of the semiconductors:* Consider a semiconductor crystal of silicon or germanium under study. We know that the Si or Ge have four valence electrons. The crystal structure of Ge in two dimensions has been shown in Fig. c.

Every atom of Ge tends to share one of its four valence electrons with each of its four nearest neighbouring atoms, and also to take share of one electron from each such neighbour. This pair of shared electrons of two atoms of Ge is said to form a **covalent bond** or simply a **valence bond**. Thus, four valence electrons of a Ge atom form **four covalent bonds** by sharing the electrons of neighbouring four Ge atoms. Due to which the Ge atoms in the structure are strongly held by covalent bonds not in a plane as it may appear here but in space of tetrahedral angles.

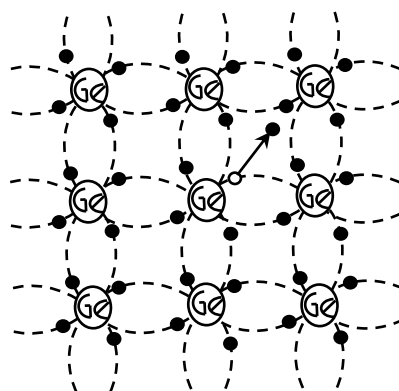


Fig. c

- At low temperature, in a Ge crystal structure, the two shared electrons in a covalent bond can be assumed to shuttle back-and-forth between the associated atoms, holding them together strongly.

- When the temperature of Ge is raised, the thermal energy ionises only a few atoms in the crystalline lattice. Due to which few valence electrons contributing to covalent bonds break and become free to move in whole of the crystal lattice. While coming out of a covalent bond, the electron leaves an empty space which is having positive charge equal to that of the electron which is shown in figure as an open circle. It is called a **hole**. An electron from a neighbouring atom can break away and can be attracted by the missing electron (or hole), thus completing the covalent bond and creating a hole at another place. In our two-dimensional example, we see that an electron from any of four neighbouring atoms can come to complete the bond and hole can move to any

of these atoms. It is to be noted that *breakage of each covalent bond produces one free electron and one hole in a crystalline lattice.*

In order to create the free electron and hole in a crystalline lattice a certain amount of ionisation energy E_g would be involved. This ionisation energy is least for Ge, more for Si and highest for C. Theoretically, it is found that the number of free electrons (n_e) produced as a result of an ionisation is given by

$$n_e = C e^{-E_g/2kT}$$

Where C is a constant, k is a **Boltzmann constant** and T is the absolute temperature. For a given E_g , as the temperature T increases, n_e increases.

ELECTRICAL CONDUCTION IN SEMI-CONDUCTORS

The electrical conduction in semiconductors is caused by the motion of the electrons in the conduction band and also by the motion of the holes in the valence band.

When an electric field is applied across a semiconductor, the electrons in the conduction band travel in opposite direction to that of the applied electric field and constitute a flow of **electronic current**. At the same time, the holes in the valence band travel in the direction of the applied electric field and constitute a **hole current**. It means there are two streams of current inside a semiconductor; namely the electronic current in the conduction band and the hole current in the valence band. The effective current in the semiconductor is the sum of these two streams of current. For a pure semiconductor at room temperature, the current strength is weak and of no use.

INTRINSIC SEMICONDUCTORS

A pure semiconductor which is free of every impurity is called intrinsic semiconductor. The electrical conductivity of a pure semiconductor is totally governed by the number of electrons excited from the valence band to the conduction band and is called **intrinsic conductivity**.

Germanium and silicon are the important examples of intrinsic semiconductors which are widely used in electronic and transistor manufacturing. The electronic configuration of silicon and germanium are:

Silicon (14), $1s^2, 2s^2 2p^6 3s^2 3p^2$

Germanium (32), $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^2$

Both the atoms have thus four valence electrons.

The crystal structure of germanium in two dimensions is shown in Fig. 12 (a). The four valence electrons of a germanium atom form four covalent bonds by sharing the electrons of neighbouring four germanium atoms. **Each covalent bond shares two electrons one from each atom.** By forming such covalent bonds, each Ge atom in the crystal behaves as if the outermost orbit of each atom is complete with eight electrons, having no free electrons in the Ge-structure.

At temperature 0K, for Ge-structure, the valence band is all full. The energy gap is 0.72 eV and the conduction band is totally empty, Fig. 12 (b). Since no electron is available for conduction therefore, the Ge-crystal at 0K *acts as electrical insulator. The conduction is possible if some of the electrons break away from their covalent bonds and become free.* The minimum energy required to break a covalent bond is 0.72 eV for Ge and 1.1 eV for Si.

Even at room temperature, the thermal vibrations of the atoms provide energy to the electrons in valence band to enable some electrons cross the forbidden gap and enter into the conduction band as free electrons, accounting for some electrical conductivity of the semiconductor. Higher is the temperature, larger will be the number of electrons crossing over to the conduction band, leaving behind equal number of holes in the valence band. *In intrinsic semiconductor at room temperature, Fermi level is about half way in the forbidden gap.*

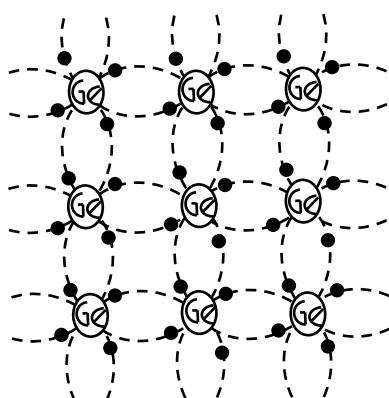
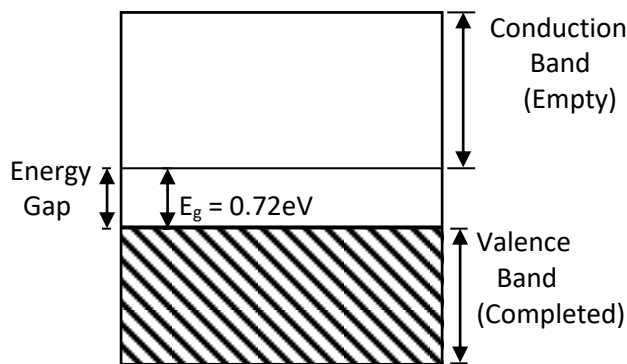


Fig. 12 (a)



(b)

When an electron breaks away from a covalent bond, the empty place or vacancy left in the bond is called a hole, shown by a hollow circle in the Fig. 12 (a). When an external electric field is applied, these free electrons and holes move in opposite directions and constitute a current flow through the germanium crystal. The number of free electrons (in conduction band) and holes (in valence band) is exactly equal in an intrinsic semiconductor.

Thus, in intrinsic semiconductor,

$$n_e = n_h = n_i$$

Where n_e , n_h are number density of electrons in conduction band and number density of holes in valence band. n_i is the number density of intrinsic carries (electrons or holes) in a pure semiconductor.

The number of electrons or holes in a pure semiconductor at a temperature T K is given by

$$n_e = n_h = AT^{3/2} e^{-E_g/2kT}$$

Where k is a Boltzmann constant and E_g is the energy gap between conduction band and valence band. It means on increasing temperature; the number of current carriers increases.

It is very difficult to make an intrinsic semiconductor because of the difficulty in preparing extremely pure material. **Limitations of developing pure semiconductor based devices.**

1. In a pure semiconductor, at room temperature, the number of intrinsic charges carries (electrons and holes) is very small ($\approx 10^{16} \text{ m}^{-3}$). That is why the pure semiconductor is a low conductivity material.
2. In a pure semiconductor, the intrinsic charge carries are always produced due to breakage of covalent bonds by virtue of **thermal motion**. Hence enough flexibility is not available to control their number in a pure semiconductor.
3. In pure semiconductor, the number of electrons (n_e) is always equal to number of holes (n_h). It is never possible in a pure semiconductor to have either large number of conduction electrons only or large numbers of conduction holes only. That is why pure semiconductor is not of much use.

POINT DEFECT IN CRYSTALS

A crystal is a structure of periodic ordered arrangement of ions or atoms or molecules in three dimensional spaces. There are several kinds of defects in crystals and it is impossible to have a crystal without any defects. The properties of the crystals are greatly affected by these defects. **It is very difficult to get a 100 % chemically pure material.** Therefore, the crystals formed may have the various defects as shown in Fig. 13 (a), (b) & (c).

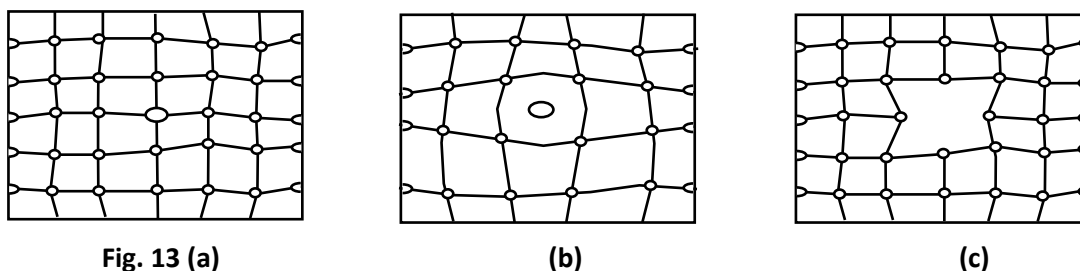


Fig. 13 (a)

(b)

(c)

In Fig. 13 (a), some undesirable impurity atoms are present at the lattice site. In Fig. 13 (b), the impurity atoms are present between the lattice sites. In Fig. 13 (c), the atom of the crystal itself may be missing from the lattice site. These are called **point defects**. The undesirable impurity atoms can be removed by purifying the material chemically.

DOPING

Doping is a process of deliberate addition of a desirable impurity atom to a pure semiconductor to modify its properties in a controlled manner. The impurity atoms added are called dopants.

◆ The impurity added may be ≈ 1 part per million (ppm).

➤ In a doping process, it is required that

- ☞ (i) The dopant atom should take the position of semiconductor atom in the lattice.
- ☞ (ii) The presence of the dopant atom should not distort the crystal lattice.
- ☞ (iii) The size of the dopant atom should be almost the same as that of the crystal atom.
- ☞ (iv) The concentration of dopant atoms should not be large (not more than 1% of the crystal atoms).

➤ the **doping of a semiconductor increases its electrical conductivity to a great extent.**

Methods of doping: Doping is achieved in many ways; for this, we can

1. Add the impurity atoms in the melt of the semiconductor, or
2. Heat the crystalline semiconductor in an atmosphere containing dopant atoms or molecules so that the latter diffuse into the semiconductor, or
3. Implant dopant atoms by bombarding the semiconductor with their ions.

EXTRINSIC SEMICONDUCTOR

A doped semiconductor or a semiconductor with suitable impurity atoms added to it is called extrinsic semiconductor. Extrinsic semiconductors are of two types:

- (i) **N-type semiconductors**
- (ii) **P-type semiconductors**

(i) **N-type semiconductor:** When a pure semiconductor of silicon (Si) in which each Si atom has four valence electrons, is doped with a controlled number of pentavalent atoms, say **arsenic or phosphorus** or antimony or **bismuth**, which have five valence electrons, the impurity atoms will replace the silicon atoms as shown in Fig. 14(a). The four of the five valence electrons of the impurity atoms will form covalent bonds by sharing the electrons with the adjoining four atoms of silicon, while the fifth electron is very loosely bound with the parent impurity atom and is comparatively free to move.

➤ Thus, each impurity atom added donates one free electron to the crystal structure. These impurity atoms which donate free electrons for conduction are called **donor atoms**.

➤ Since the conduction of electricity is due to the motion of electrons i.e., negative charges or n-type carriers, therefore, the resulting semiconductor is called **donor-type** or **n-type semiconductor**. On giving up their fifth electron, the donor atoms become positively charged. However, the matter remains electrically neutral a whole. The extra electron of the donor atom orbits around the donor nucleus, in a hydrogen like manner.

➤ It has been found that 0.05 eV energy in Si and 0.01 eV energy in Ge is required to remove this electron from the impurity atom and makes it a free electron.

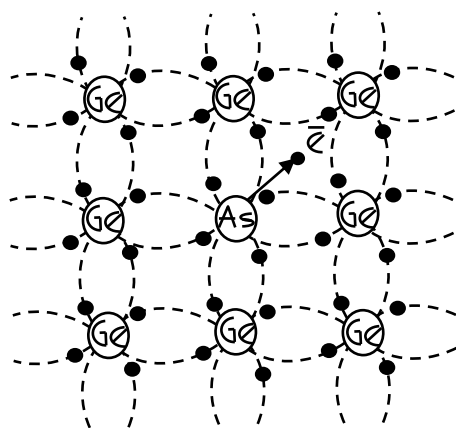
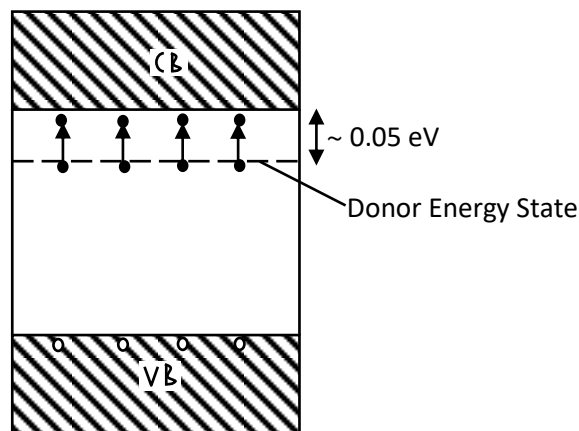


Fig 14 (a)



(b)

At room temperature, some of the covalent bonds may get ruptured, producing thereby free electrons and an equal number of holes in the n-type semiconductor. But overall, the total number of holes in n-type semiconductor is relatively low, **hence in n-type semiconductor, electrons are majority carriers and holes are minority carriers.**

Energy band diagram of a n-type semiconductor is shown in Fig. 14 (b). For a silicon semiconductor with impurity atoms of **arsenic or phosphorus**, the energies of the free electrons are slightly less than the energies of the free electrons in the lowest energy level of conduction band. As a result of it, these electrons occupy discrete energy levels (called donor energy levels) between the valence and conduction band and the lowest donor electron energy level lies at 0.05 eV below the bottom of the conduction band.

☞ When we add pentavalent impurity in a pure semiconductor of Ge or Si, the Fermi level in forbidden gap shifts very close to conduction band. If doping is very large, **the Fermi level may move into the conduction band.**

This energy is comparable to the thermal energy of electron at room temperature (= 0.03 eV). Thus, a very small energy supplied can excite the electrons from donor levels to conduction band. Due to it, the semiconductor shows the conductivity remarkably improved.

◆ (ii) **P-type semiconductor:** When a pure semiconductor of Germanium (Ge) in which each atom has four valence electrons is doped with a controlled number of trivalent atoms say gallium, or Indium (In) or Boron (B) or Aluminium (Al) which have three valence electrons, the impurity atoms will replace the Ge atoms as shown in

Fig. 15 (a). The three valence electrons of the impurity atom will form covalent bonds by sharing the electrons of the adjoining three atoms of Ge, while there will be one incomplete covalent bond with a neighbouring Ge-atom, due to the deficiency of an electron. This deficiency is completed by taking an electron from one of the Ge – Ge bonds, thus completing the In – Ge bond.

☞ This makes Indium ionised (negatively charged) and creates a 'hole'. An electron-moving from a Ge-Ge bond to fill a hole, leaves a hole behind. That is how, holes move in the semi-conductor structure. The trivalent atoms are called *acceptor atoms* and the conduction of electricity occurs due to motion of holes i.e., positive charges of *p-type* carriers. That is why the resulting semiconductor is called *acceptor type or p-type semiconductor*.

☞ At ordinary temperature, some of the covalent bonds may get ruptured, releasing equal number of holes and electrons. Therefore, the total number of electrons is relatively small as compared to the number of the holes in the p-type semiconductor, *electrons are minority carriers and holes are majority carriers*.

Energy band diagram of p-type semiconductor is shown in Fig. 15(b). For a Ge or Si semiconductor, the doping of impurity atoms of Indium or boron produce some allowed energy levels which are situated in the forbidden gap slightly above the valence band. These levels are called *acceptor energy levels*.

☞ *When we add a trivalent impurity in a pure semiconductor of Ge or Si, the Fermi level in forbidden gap shifts very close to valence band.* If doping is very large, the Fermi level may move into the valence band. If doping is very large, the Fermi level may move into the valence band.

▶▶ ☞ At room temperature, due to thermal energy, the electrons from the valence band are easily transferred to the acceptor level until these levels are filled. This produces a large number of holes in the valence band and thereby the valence band becomes a hole conducting band. When an external electric field is applied to a p-type semiconductor, these holes will act as carriers of current. Due to it, the p-type semiconductor shows its electrical conductivity much improved than what it was for pure semiconductor.

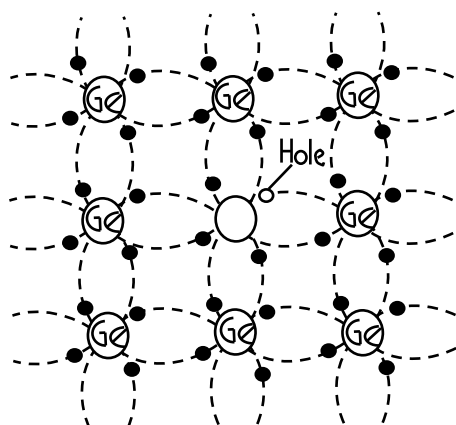
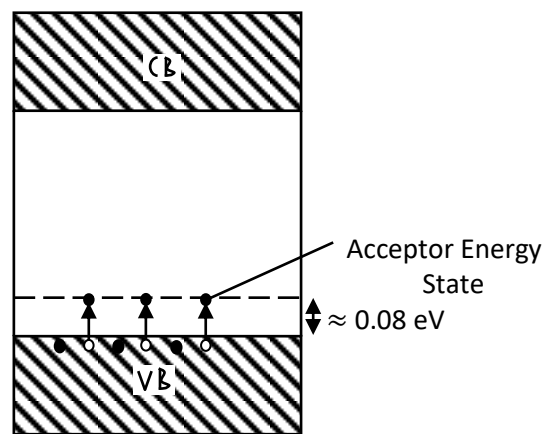


Fig 15 (a)



(b)

▶1. In a doped semiconductor, the number density of electrons and holes is not equal. But it can be established that

$$n_e n_h = n_i^2$$

Where n_e , n_h are the number density of electrons and holes respectively and n_i is number density of intrinsic carriers (i.e., electrons or holes) in a pure semiconductor.

- ▶2. In **n-type** semiconductor, the number density of electrons is nearly equal to the number density of donor atoms N_d and is very large as compared to number density of holes. Hence $n_e \approx N_d \gg n_h$
- ▶3. In **p-type** semiconductor, the number density of holes is nearly equal to the number density of acceptor atoms N_a and is very large as compared to number density of electrons. Hence $n_h \approx N_a \gg n_e$

Distinction between Intrinsic and Extrinsic Semiconductors

INTRINSIC SEMICONDUCTOR	EXTRINSIC SEMICONDUCTOR
<ol style="list-style-type: none"> 1. It is pure semiconducting material and no impurity atoms are added to it. 2. Examples are crystalline forms of pure silicon and germanium. 3. The number of free electrons in conduction band and the number of holes in valence band is exactly equal and very small indeed. 4. Its electrical conductivity is low. 5. Its electrical conductivity is a function of temperature alone. 	<ol style="list-style-type: none"> 1. It is prepared by doping a small quantity of impurity atoms to the pure semiconducting material. 2. Examples are silicon and germanium crystals with impurity atoms of arsenic, antimony, phosphorous etc. or indium, boron, aluminium etc. 3. The number of free electrons and holes is never equal. There is excess of electrons in n-type semiconductors and excess of holes in p-type semiconductors. 4. Its electrical conductivity is high. 5. Its electrical conductivity depends upon the temperature as well as on the quantity of impurity atoms doped in the structure.

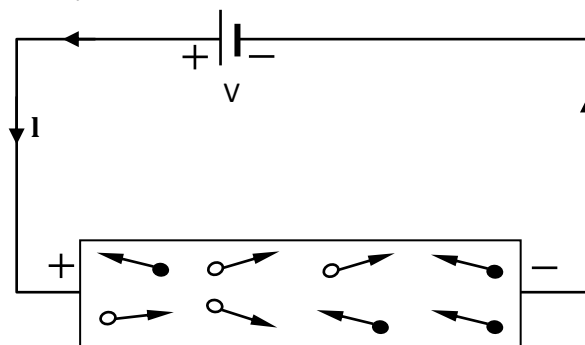
Distinction between N-type Semiconductors and P-type Semiconductors

n-TYPE SEMICONDUCTOR	p-TYPE SEMICONDUCTOR
<ol style="list-style-type: none"> 1. It is an extrinsic semiconductor which is obtained by doping the impurity atoms of Vth group of periodic tables to the pure germanium or silicon semiconductor. 2. The impurity atoms added, provide extra electrons in the structure, and are called donor atoms. 3. The electrons are majority carriers and holes are minority carriers. 4. The electron density (n_e) is much greater than the hole density (n_h) i.e. $n_e \gg n_h$. 5. The donor energy level is close to the conduction band and far away from valence band. 6. The Fermi energy level lies in between the donor energy level and conduction band. 	<ol style="list-style-type: none"> 1. It is an extrinsic semiconductor which is obtained by doping the impurity atoms of III group of periodic table to the pure germanium or silicon semiconductor. 2. The impurity atoms added, create vacancies of electrons (i.e. holes) in the structure and are called acceptor atoms. 3. The holes are majority carriers and electrons are minority carriers. 4. The hole density (n_h) is much greater than the electron density (n_e) i.e. $n_h \gg n_e$. 5. The acceptor energy level is close to valence band and is far away from conduction band. 6. The Fermi energy level lies in between the acceptor energy level and valence band.

Electrical Conductivity of Extrinsic Semiconductors

Consider a block of semiconductor of length l and area of cross-section A , having electron density n_e and hole density n_h . Let V be the potential difference applied across the ends of the conductor. The magnitude of the electric field applied is

$$E = \frac{V}{l} \quad \dots (1)$$



Due to the electrical field, both electrons and holes in this semiconductor move in mutually opposite directions with drift velocities v_e and v_h and contribute current I_e and I_h in the same direction in the semiconductor.

$$\therefore \text{Total current, } I = I_e + I_h \quad \dots (2)$$

Since electrons in the conduction band and holes in the valence band are moving randomly like electrons in metals, therefore,

$$I_e = n_e A e v_e$$

And $I_h = n_h A e v_h$

∴ From (2), $I = n_e A e v_e + n_h A e v_h$
 $= e A (n_e v_e + n_h v_h)$... (3)

Or $\frac{I}{A} = e (n_e v_e + n_h v_h)$... (4)

Let R be the resistance of the semiconductor and ρ be its resistivity, then

$$\rho = RA / l \quad \dots (5)$$

Dividing (1) and (5) we get

$$\frac{E}{\rho} = \frac{V/l}{RA/l} = \frac{V}{RA} = \frac{I}{RA} \quad \dots (6)$$

From (4) and (6) we have

$$\frac{E}{\rho} = e (n_e v_e + n_h v_h)$$

We know that mobility of electron is defined as the drift velocity per unit electric field. If there is no electric field applied; drift velocity is zero.

∴ mobility of electrons, $\mu_e = \frac{v_e}{E}$

Or $v_e = \mu_e E$

And mobility of holes, $\mu_h = \frac{v_h}{E}$

Or $v_h = \mu_h E$

∴ $\frac{E}{\rho} = e [n_e \mu_e + n_h \mu_h] E$

Or $\frac{1}{\rho} = e (n_e \mu_e + n_h \mu_h)$... (7)

But electrical conductivity (σ) is the reciprocal of resistivity (ρ), therefore,

Electrical conductivity,

$$\sigma = \frac{1}{\rho} = e (n_e \mu_e + n_h \mu_h) \quad \dots (8)$$

The relations (7) and (8) show that the conductivity and resistivity of a semiconductor depend upon the electron and hole number densities and their mobilities.

☞ As n_e and n_h increase with rise in temperature, therefore, conductivity of semiconductor increases with rise in temperature and resistivity decrease with rise in temperature. At room temperature σ for Ge is greater than that for Si because number density of charge carriers is more in Ge than in Si.

➤ The current density in a semiconductor is given by $J = \frac{I}{A} = e (n_e v_e + n_h v_h)$

$$= e (n_e \mu_e E + n_h \mu_h E)$$

➤ **Conductivity of intrinsic semiconductor:** In case of intrinsic semiconductor (silicon or germanium),

$$n_e = n_h = n_i$$

Where n_i is the number density of intrinsic carriers (i.e., electrons or holes). Thus, the conductivity of intrinsic semiconductor is

$$\sigma_i = e (n_i \mu_e + n_i \mu_h) = e n_i (\mu_e + \mu_h)$$

➤ **Conductivity of n-type semiconductor:** In this case $n_e \gg n_h$ and $n_e \approx N_d$, where N_d is the number density of donor atoms. Therefore, conductivity of **n-type** semiconductor is

$$\sigma_n = e N_d \mu_e$$

➤ **Conductivity of p-type semiconductor:** In this case $n_h \gg n_e$ and $n_h = N_a$, where N_a is the number density of acceptor atoms. Therefore, conductivity of **p-type** semiconductor is

$$\sigma_p = e N_a \mu_h$$

► **Intrinsic concentration:** The number density of intrinsic current carriers (n_i) of a semiconductor varies with temperature T . According to relation

$$n_i = A_0 T^{3/2} e^{-E_g/kT}$$

Where, A_0 = constant, independent of temperature

k = Boltzmann constant

E_g = energy gap at 0 K

► **The energy gap:** The forbidden energy gap E_g in a semiconductor is a function of temperature. It has been found that For germanium,

$$E_g(T) = 0.785 - 2.23 \times 10^{-4} T$$

For silicon, $E_g(T) = 1.21 - 3.60 \times 10^{-4} T$

At room temp. (300 K),

For Ge, $E_g = 0.72$ eV

And for Si, $E_g = 1.1$ eV

► **The mobility** of charge carriers varies as T^{-m} over a temperature range of 100 to 400 K.

i.e. $\mu \propto T^{-m}$

In case of germanium, $m = 1.66$ for electron and 2.33 for hole.

Effect of Temperature on a Mobility and Conductivity of Electrons and Holes

With the increase in temperature, the mobility of electrons and holes in a semiconductor actually decreases, like the decrease in mobility of electrons in metals. But, there is a large increase in the charge carrier concentration due to more breakage of covalent bonds with the increasing temperature. It is so large that conductivity increases with increasing temperature and the decreases in mobility has no influence.

According to the equation of the drift velocity

$$\left(v = \frac{eE}{m} \tau \right), v \propto E \quad \dots (A)$$

But v cannot be increased indefinitely by increasing E and the relation (A) does not hold good at high values of E . It is so because, at high temperature, the increase in drift velocity of free electrons will bring more collisions and hence average time between collisions (i.e. τ) starts decreasing. As a result of it, the drift velocity saturates at thermal velocity and becomes almost independent of electric field at higher values of E .

► The exact value of E where drift velocity saturates depends on the nature of semiconductor, doping and other defects in the semiconductor crystal.