

SEMICONDUCTORS

Semiconductors are classified basing on their conductivities and resistivity's.

Electrical resistivity of semi conductors lies in between those of conductors and insulators.

In semiconductors, there are two types of carriers namely electrons and holes.

Hence semiconductors are bipolar materials.

The current in semiconductors is due to two types of carriers namely electros and holes.

Pure semi conductors are known as intrinsic semiconductors.

Example : Silicon and Germanium.

The electrical conductivity can be enhanced by a process called doping. i.e. the number of carriers can be increased by a process called doping. Doping is the process of adding an impurity to a pure semi conductor. By adding a suitable impurity to an intrinsic semi conductor, it will become an extrinsic semi conductor. The transportation of charge carriers (movement) takes place due to drift and diffusion.

The extrinsic semi conductors are widely used in solid state electronic devices and semi conductor electronic devices.

To study electronic devices, it is important to study the fundamental electronic transportation properties in semi conductors.

Intrinsic semiconductors

Usually pure semiconductors are known as intrinsic semiconductors. Examples are Silicon (Si) and Germanium (Ge) .Silicon (Si) and Germanium belongs to **IV group** of periodic table.

Atomic Number of Silicon is 14.

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^2$

Atomic number of Germanium is 32.

.Electronic configuration is

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

In Silicon and Germanium, there are four valence electrons. Bonding in these semiconductors is covalent bonding.

Each silicon Atom forms four covalent bonds with the surrounding electrons from neighboring Silicon atoms in the silicon Semiconductor crystal.

Here no electrons are available freely for conduction and the semi conductor acts like an insulator.

The conduction process can be understood with the help of energy band diagram.

In the energy band diagram, we have conduction band and valence band.

The conduction band and valence band are separated by a forbidden energy gap Eg., known as energy band gap. The covalent bond representation and the energy band structure is shown in figure (1) at 0°K .

At 0°K , all valence electrons are tightly bound to their atoms and are taking part in covalent bond formation.

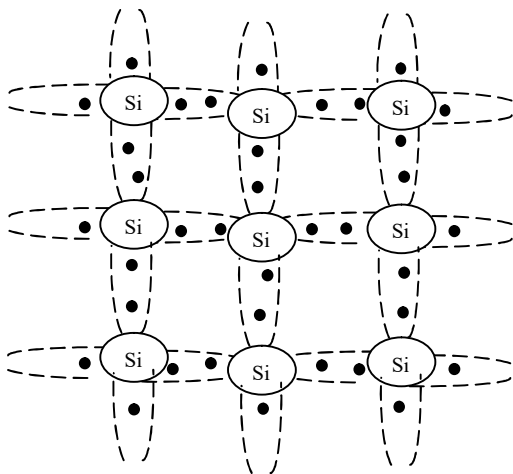


Fig. (1)a: Intrinsic silicon at 0°K
– Two dimensional Representation.

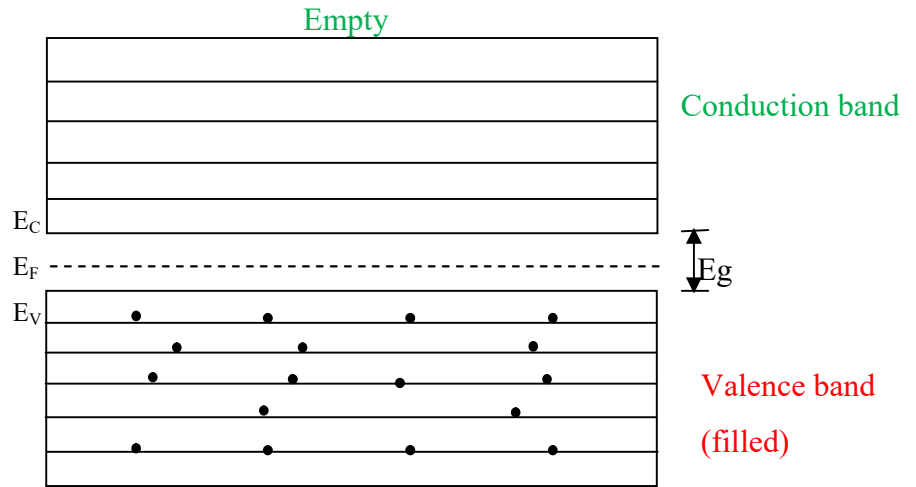


Fig (1)b: Energy band structure of Intrinsic Semiconductor Silicon at 0°K .

For Silicon $E_g = 1.12 \text{ eV}$.
Germanium $E_g = 0.69 \text{ eV}$.

In the figure (1) b E_c = Energy level corresponding to Bottom of the conduction band.

E_v = Energy of the energy level corresponding to the top of the Valence band.

E_f = Fermi energy level.

At 0°K , the semiconductors behave like insulators.

At 0°K , the valence band is completely filled and the conduction band is empty.

Above 0°K (i.e. At Room temperature), the valence electrons acquire sufficient amount of thermal energy. Due to this they break the covalent bonds and make themselves available as free electrons. Against to creation one free electron, a vacancy is created in its initial position in the crystal structure. This vacancy is known as a hole.

The hole is a virtual positive charge, having the magnitude of charge of the electron.

The free electrons after acquiring sufficient thermal energy, and crosses the energy gap.

These electrons will enter into the conduction band from valence band and occupy energy levels in the conduction band.

The electrons leaving the valence band create holes in its original place.

Now the valence band will have holes and the conduction band contains electrons.

The crystal structure and energy band structure above 0°K is shown in figure (2).

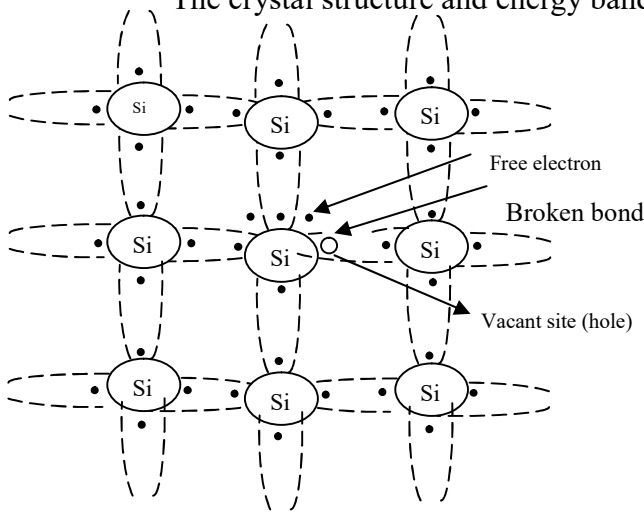


Figure (2) a: Two dimensional crystal structure of intrinsic semiconductor silicon above 0°K

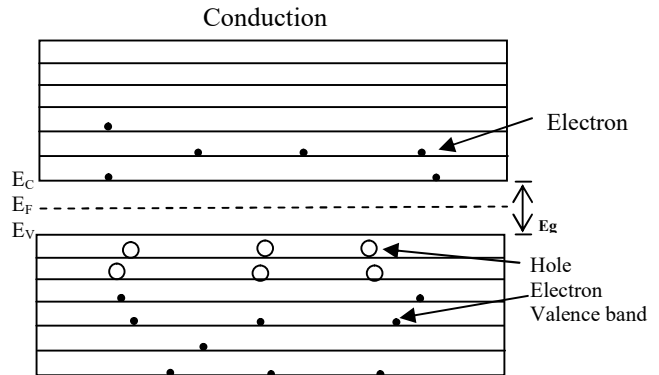


Figure (2) b: Intrinsic Silicon – Energy band structure above 0°K .

In an intrinsic semiconductor,

$$\text{Number of holes} = \text{No. of electrons} = n_i; \quad n=p=n_i$$

n = Number of electrons per unit volume (or) electron concentration (or) electron density.

p = Number of holes per unit volume (or) hole concentration (or) hole density.

n_i = Intrinsic concentration.

Now $np = n_i^2$ (Law of mass action)

Intrinsic carrier concentration

Above 0°K , in an intrinsic semiconductor, each broken bond leads to generation of two carriers. They are electron and hole.

At any temperature T , the number of electrons generated will be therefore equal to the number of generated Holes.

Let n = Number of electrons per unit volume or electron concentration in the Conduction band.

P = Number of holes per unit volume or Hole concentration in the valence band.

For an intrinsic semiconductor;

$$n = p = n_i \quad \text{--- (1)}$$

Where n_i = intrinsic carrier concentration.

Now the electron concentration in the conduction band is given by

$$n = N_c e^{-(E_c - E_F)/K_B T}$$

$$n = N_c e^{(E_F - E_c)/K_B T} \quad \text{--- (2)}$$

The Hole concentration in the valence band is given by

$$P = N_v e^{-(E_F - E_v)/K_B T}$$

$$p = N_v e^{(E_v - E_F)/K_B T} \quad \text{--- (3)}$$

Here N_c, N_v are known as **pseudo constants**, depends on temperature.

K_B = Boltzmann constant

T = Temperature in $^{\circ}\text{K}$ of the intrinsic semiconductor.

Now $n_i^2 = np$

$$n_i^2 = N_c e^{(E_F - E_c)/K_B T} N_v e^{(E_v - E_F)/K_B T}$$

$$n_i^2 = N_c N_v e^{\frac{(E_F - E_c + E_v - E_F)}{K_B T}}$$

$$n_i^2 = N_c N_v e^{\frac{(-E_c + E_v)}{K_B T}}$$

$$n_i^2 = N_c N_v e^{\frac{-(E_c - E_v)}{K_B T}}$$

$$n_i^2 = N_c N_v e^{\frac{-E_g}{K_B T}}$$

Where $E_c - E_v = E_g$, Energy Gap.

$$n_i = (N_c N_v)^{1/2} e^{\frac{-[E_g]}{2K_B T}} \quad \text{----- (4)}$$

From equation (4), It is clear that

- i) Intrinsic carrier concentration is independent of Fermi level.**
- ii) Intrinsic carrier concentration n_i is a function of temperature T.**
- iii) Intrinsic carrier concentration n_i is a function of Energy gap E_g .**

Fermi level expression

The **Fermi level is the top most occupied energy level**. The Fermi level indicates the probability of occupation of energy levels of the electrons in conduction and valence bands.

In intrinsic semiconductors, electron and hole concentrations are equal.

i.e. it indicates that the probability of occupation of energy levels in conduction band and valence band are equal.

Usually in an intrinsic semiconductor, the Fermi level lies in the middle of the energy gap Eg.

For an intrinsic semiconductors, $n=p$.

$$n = N_c e^{-(E_c - E_f)/K_B T}$$

Now $n = N_c e^{(E_f - E_c)/K_B T}$ ----- (1)

$$\text{Hole concentration, } p = N_v e^{-(E_f - E_v)/K_B T}$$

$$p = N_v e^{(E_v - E_f)/K_B T}$$
 ----- (2)

Equations (1) and (2) represent electron and hole concentrations for intrinsic semiconductors.

Since $n=p$.

$$N_c e^{(E_f - E_c)/K_B T} = N_v e^{(E_v - E_f)/K_B T}$$

$$\Rightarrow \frac{N_v}{N_c} = \frac{e^{\frac{(E_f - E_c)}{K_B T}}}{e^{\frac{(E_v - E_f)}{K_B T}}}$$

$$\Rightarrow \frac{N_v}{N_c} = e^{\frac{(E_f - E_c)}{K_B T} - \frac{(E_v - E_f)}{K_B T}}$$

$$\Rightarrow \frac{N_v}{N_c} = e^{\frac{(E_f - E_c - E_v + E_f)}{K_B T}}$$

$$\Rightarrow \frac{N_v}{N_c} = e^{\frac{[2E_f - (E_c + E_v)]}{K_B T}}$$
 ----- (3)

Taking Naparian Logarithm on both sides.

$$\log_e \left(\frac{N_V}{N_C} \right) = \text{Log}_e e^{[2E_F - (E_C + E_V)]/K_B T}$$

$$\log_e \left(\frac{N_V}{N_C} \right) = \frac{2E_F - (E_C + E_V)}{K_B T}$$

$$\Rightarrow 2E_F - (E_C + E_V) = K_B T \log_e \left(\frac{N_V}{N_C} \right)$$

$$\Rightarrow 2E_F = E_C + E_V + K_B T \log_e \left(\frac{N_V}{N_C} \right)$$

$$\Rightarrow E_F = \left(\frac{E_C + E_V}{2} \right) + \frac{K_B T}{2} \log_e \left(\frac{N_V}{N_C} \right)$$

For an intrinsic semiconductor $m_e^* = m_h^*$

Hence $N_v = N_c$

$$\therefore E_F = \left(\frac{E_C + E_V}{2} \right) + \frac{K_B T}{2} \log_e (1)$$

$$\therefore E_F = \frac{E_c + E_v}{2}$$

Therefore Fermi level lies exactly midway between conduction band and valence band.

Expression for intrinsic conductivity

Let us consider intrinsic semiconductors. This is applied with a potential difference of V volts.

Due to the applied voltage an electric field E will be established as shown in the figure.

Now the charge carriers drift as indicated in figure (3). This constitutes an electric current I.

The drift velocity acquired by the charge carriers is given by.

$$V_d = \mu E \quad \text{----- (1)}$$

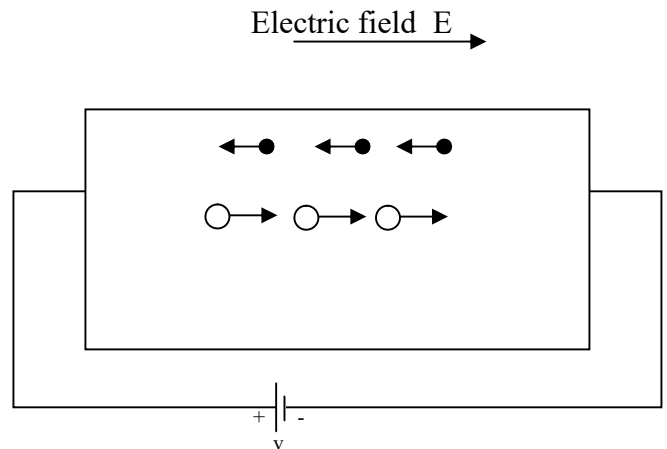


Fig. 3 Conduction in an intrinsic semiconductor

Where μ = Mobility of charge carriers. E= Electric field

Also the current density due to drift of electrons is given by

$$J_n = nev_d \quad \text{----- (2)}$$

Where n= electron concentration

e = charge on the electron.

v_d = drift velocity of the electrons.

From Equations (1) &(2), we get,

$$J_n = ne\mu_n E \quad \text{----- (3)}$$

Where μ_n = Mobility of electrons.

$$\text{Current density } J = \frac{\text{Current}}{\text{Area}} = \frac{I}{A}$$

Also the holes will drift in a direction opposite to electrons, the hole current density is given by

$$J_p = pe\mu_p E \quad \text{----- (4)}$$

Where p = Hole concentration.

e = charge on the hole.

μ_p = Mobility of holes.

Now the total current density is given by

$$J = J_n + J_p$$

$$J = ne\mu_n E + Pe\mu_p E \quad \text{----- (5)}$$

$$J = (n\mu_n + P\mu_p) eE$$

But according the classical theory, ohms law is given by

$$J = \sigma E \quad \text{----- (6)}$$

Where σ = Electrical conductivity

\therefore From equations (5) and (6), we have

$$\sigma E = (n\mu_n + P\mu_p) eE$$

$$\sigma = (n\mu_n + P\mu_p) e$$

But according to law of mass Action, for an intrinsic semiconductors $n = p = n_i$

$$\therefore \sigma = (n_i\mu_n + n_i\mu_p) e$$

$$\sigma = n_i e (\mu_n + \mu_p) \quad \text{----- (7)}$$

Where n_i = Intrinsic concentration.

$$\text{But } n_i = (N_C N_V)^{1/2} e^{-E_g/2K_B T} \quad \text{----- (8)}$$

Substituting (8) in (7), we get

$$\sigma = (N_C N_V)^{1/2} e (\mu_n + \mu_p) e^{-E_g/2K_B T}$$

Electrical conductivity for intrinsic semi conductors is given by

$$\sigma = Ae^{-E_g/2K_B T} \text{ ----- (9)}$$

Where $A = (N_C N_V)^{1/2} e^{(\mu_n + \mu_p)}$

A = a constant

In pure Semiconductors electrical conductivity is due to both electrons and holes.

Determination of Energy Gap (Eg) for intrinsic semiconductors

The energy gap between the conduction Band and the valence band is represented as band gap Eg. For intrinsic semi conductors, the energy gap is given by

$$\sigma = Ae^{-E_g/2K_B T}, \sigma = \text{Electrical conductivity. ----- (1)}$$

Where A = a constant

Eg= Energy band Gap.

K_B= Boltzmann constant.

T = Absolute scale of temperature.

Let ρ = Electrical Resistivity.

$$\rho = \frac{1}{\sigma}$$

$$\therefore \rho = \frac{1}{Ae^{-E_g/2K_B T}}$$

$$\rho = \frac{1}{A} e^{E_g/2K_B T}$$

$$\rho = Be^{E_g/2K_B T} \text{ ----- (2), Where } B = \frac{1}{A}, \text{ a new constant.}$$

Taking Neparian logarithm on both sides,

$$\log_e \rho = \log_e (Be^{E_g/2K_B T})$$

$$\log_e \rho = \log_e B + \log_e e^{\left(\frac{E_g}{2K_B T}\right)}$$

$$\ln \rho = \ln B + \frac{E_g}{2K_B T}$$

$$\ln \rho = \frac{E_g}{2K_B T} + \ln B \text{ --- (3)}$$

(3) is slope intercept form equation.

Where m = slope of the straight line

From figure (1), $m = \frac{E_g}{2K_B} = \frac{\Delta y}{\Delta x}$

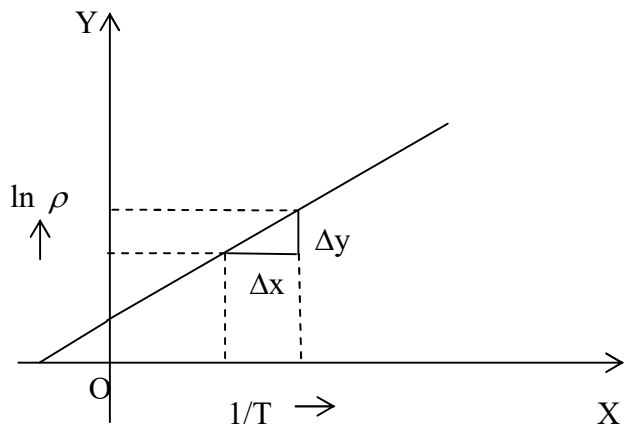


Fig 4: Plot of 1/T and ln ρ

$$\therefore E_g = \left(\frac{\Delta y}{\Delta x} \right) 2K_B \quad \text{---- (4)}$$

If a graph is plotted between $\frac{1}{T}$ on X-axis and $\ln \rho$ on y-axis, a straight line graph is obtained. The straight line graph is shown in figure (4).

Extrinsic Semiconductors

Extrinsic semi conductors are impure semiconductors. With the addition of impurities, a pure semi conductors becomes an extrinsic semiconductors.

An extrinsic semi conductor shows good conducting properties due to the presence of impurities.

Depending on the type of impurity present in the intrinsic semi conductors, extrinsic semi conductors are classified into two types.

- 1) N – type extrinsic semi conductors.
- 2) P - type extrinsic semi conductors.

N-Type semi conductors

For silicon if a small amount of pentavalent impurity such as phosphorous, arsenic or antimony or Bismuth is added, we get N-type semiconductors.

Four valence electrons of phosphorous form covalent bonds with the adjacent four silicon atoms. The fifth electron is left free. It cannot form bond with any other electron in the lattice structure. This is shown in figure (1).a.

At 0°K , this fifth electron is bound to phosphorous with 0.045 eV.

The corresponding energy Band diagram and lattice structure are shown in figure (1) at 0°K . At 0°K , the valence Band and the conduction band are separated by an Energy Gap E_g .

Pure Silicon+ Pentavalent impurity =N-type Semiconductor.

Pentavalent Impurities EX: Arsenic ,Antimony,Bismuth, Phosphorous.

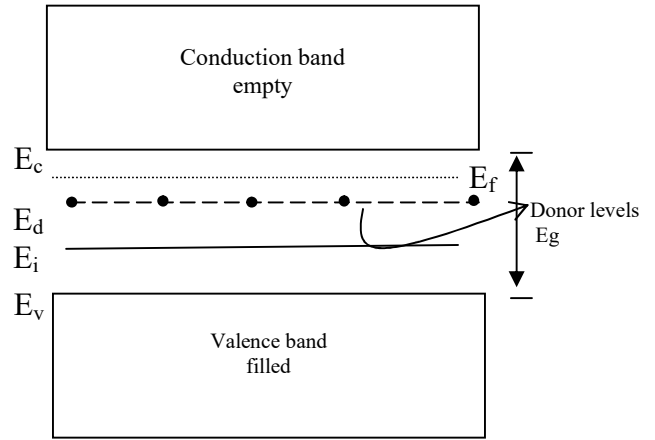
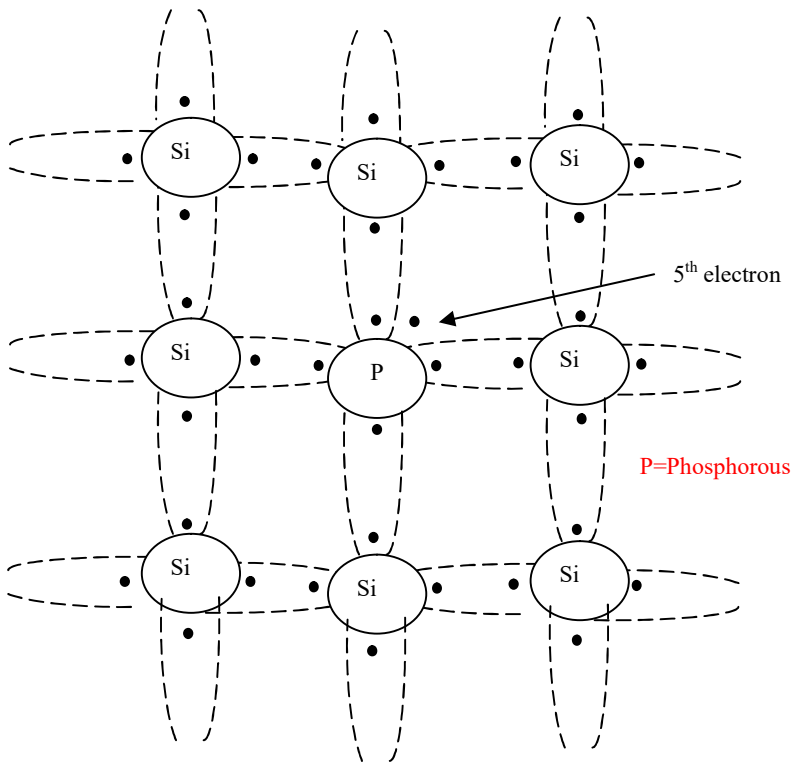


Figure (1) b: Energy band diagram of N-type semiconductor at 0^0k

Figure (1)a: N-type silicon at 0^0k

The donor energy level E_d lies below the bottom of conduction band. This donor energy level contains phosphorous atoms. Which denotes electrons at $T > 0^0k$ The donor energy level in shown in the figure (1) b. Above 0^0k , when temperature is increased. The 5th bond electron becomes a free electron. This free electron enters into the conduction band. Due to this the Donor Atoms will get ionized, by denoting an electron to the conduction band. When temperature is further increased, the covalent bonds will break down. Here electron hole pairs will be generated.

Electrons will move from valence bond to conduction bond, leaving holes in the valence bond. At higher temperatures, the energy band diagram of N-type silicon is shown in figure (2)

The Fermi level varies as shown in fig (2) b at 300^0k .

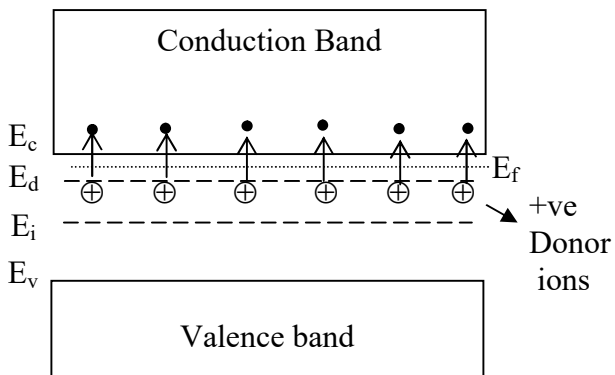


Figure (2)a: Energy band diagram of N-type semiconductor at $T > 0^0k$

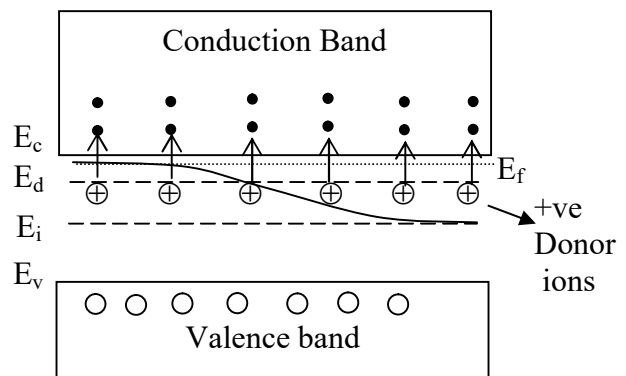


Figure (2)b: Energy band diagram of N-type silicon at $T = 300^0K$ and above

Now the concentration of electrons increases in the conduction band when compared to holes. Hence the electrons become the majority charge carriers and holes the minority charge carriers.

The variation of Fermi level is also shown in figure 2(b).

P-type semi conductors

For silicon if a small amount of trivalent impurity such as indium, Gallium, Thallium or Aluminum or Boron is added, we get a P- Type semi conductors. Three valence electrons of Boron form covalent bonds with the adjacent three silicon Atoms. There is not fourth electron to form a covalent bond with the neighboring silicon atom. This is like a missing bond. This is represented as a missing electron or vacant site. This is shown in figure (1)

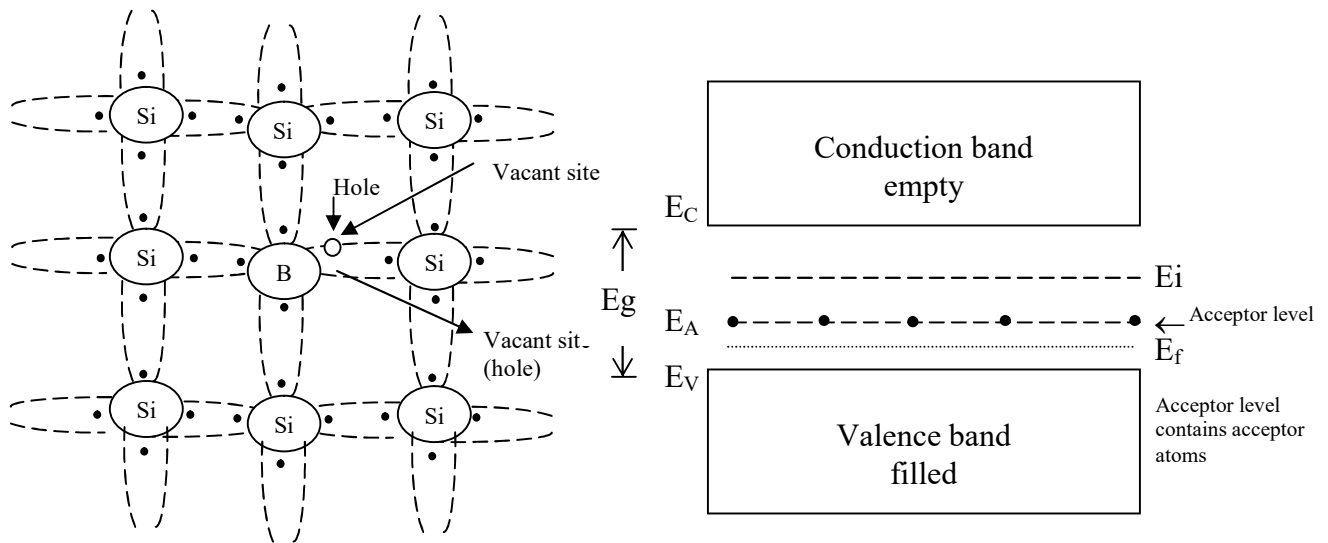


Fig. (1)a: P-type silicon at 0^0K

fig.(1)b: Energy band structure of P-type silicon at 0^0k

This missing electron is called Hole. The energy Band structure of P-type semi conductors is shown in figure (1) b.

At 0^0k , the conduction Band is empty and the valence B and contains electrons.

The acceptor energy level E_A is just above the top of the valence Band.

Acceptor energy level E_A contains the acceptor atoms.

Here E_c = Bottom of the conduction band.

E_v = Top of the valence band.

E_i = Intrinsic energy level.

The Energy band structure of P-type silicon is shown in figure (2) a above 0^0k .

When the temperature is above 0^0k , the covalent bonds with the silicon are broken down.

E_A level contains acceptor negative ions.

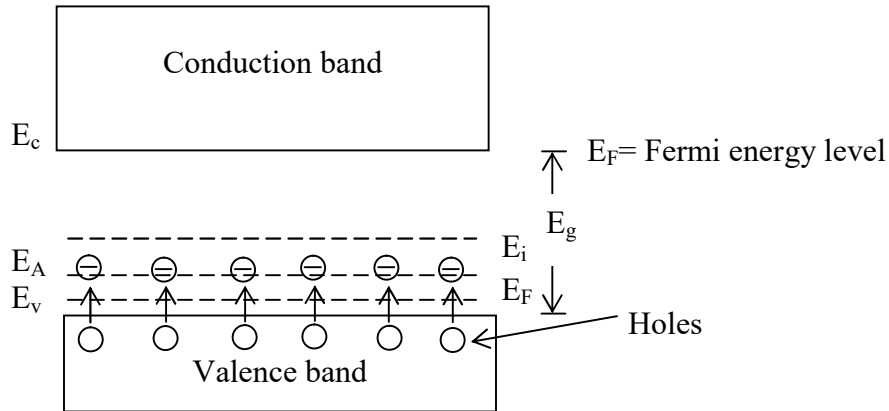


Fig.(2)a: Energy band structure of P-type silicon above 0^0k

Here some electrons are released and the acceptor atoms accept three electrons and there by they become negatively charged ions. There are called negative acceptor ions. Here the Fermi energy level lies just above the top of the valence band and below the acceptor level.

The energy band diagram of P-type semi conductors is shown in the figure (2) b. at $T = 300^0k$. At and above 300^0k , the bonds in silicon with further breakdown and the electrons will move from valence band to conduction band. Therefore electrons are available in the conduction band. At 300^0k the Fermi level varies as shown in the figure.

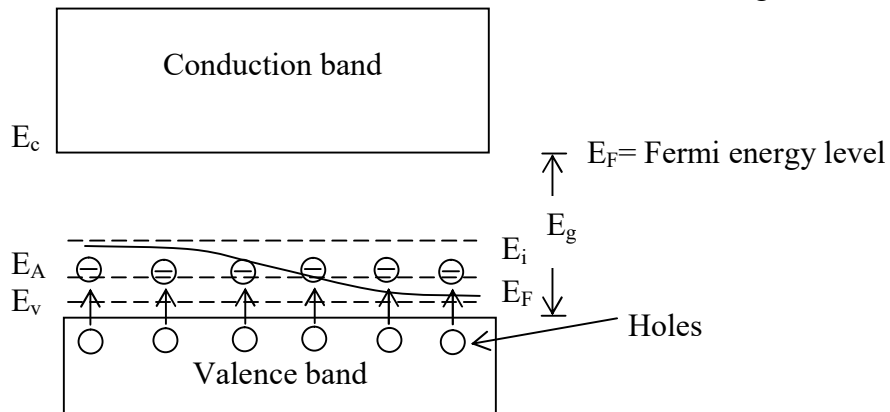


Fig.(2)b: Energy band diagram of P-type silicon at 300^0K & above

Pure Silicon+ Trivalent impurity =P-type Semiconductor.

Trivalent impurities EX: Indium, Gallium,Thallium, Aluminium,Boron.

Doping: It is the process of adding an impurity to a pure Semiconductor.

Law of Mass Action

The electron concentration in intrinsic semi conductors is given by

$$\begin{aligned}n &= N_c e^{-(E_c - E_f) / K_B T} \\n &= N_c e^{(E_f - E_c) / K_B T}\end{aligned}\quad \text{---- (1)}$$

Similarly in an intrinsic semiconductors, the hole concentration is given by

$$\begin{aligned}P &= N_v e^{(E_f - E_c) / K_B T} \\P &= N_v e^{(E_v - E_f) / K_B T}\end{aligned}\quad \text{---- (2)}$$

Where N_c and N_v are pseudo constants.

K_B is the Boltzmann constant.

T is temperature in $^{\circ}\text{K}$.

E_F is the energy of Fermi level.

E_C is the bottom of the conduction band.

E_V is the top of the valence band.

In an intrinsic semiconductors $n=p=n_i$

$$\begin{aligned}\therefore np &= N_c e^{(E_f - E_c) / K_B T} \cdot N_v e^{(E_v - E_f) / K_B T} \\np &= n_i^2 = N_c e^{(E_f - E_c) / K_B T} \cdot N_v e^{(E_v - E_f) / K_B T} \\np &= n_i^2 = N_c N_v e^{-(E_f - E_c) / K_B T} \\np &= n_i^2 = N_c N_v e^{-E_g / K_B T} \quad \text{Where } E_c - E_v = E_g \\ \Rightarrow n_i &= (N_c N_v)^{1/2} e^{-E_g / 2 K_B T}\end{aligned}\quad \text{--- (3)}$$

The above relation shows that for any arbitrary value of E_g the product of n and p is a constant.

This is known as Law of Mass Action

For an extrinsic semiconductors, the electrons and hole concentrations are given by expressions similar to Equations (1) and (2)

For an N-type semiconductor

$$N_n = N_c e^{(E_f - E_c) / K_B T} \quad \text{----- (4)}$$

$$P_n = N_v e^{(E_v - E_f) / K_B T} \quad \text{----- (5)}$$

Where n_n = Electron concentration. And P_n = Hole concentration.

Now $N_n P_n = N_c N_v e^{(E_f - E_c) / K_B T} \cdot N_v e^{(E_v - E_f) / K_B T}$

$$n_n P_n = N_c N_v e^{-(E_f - E_c) / K_B T}$$

$$n_n P_n = N_C N_V e^{-E_g / K_B T} \quad \text{----- (6)}$$

Where $E_c - E_v = E_g$

$$n_n P_n = n_i^2 \quad \text{---- (7)}$$

The above expression (7) is known as Law of Mass action for N-type semi conductors. For P-type semi conductors, the law of mass action is given by

$$p_p n_p = n_i^2 \quad \text{----- (8)}$$

Equations (7) and (8) imply that the product of majority and minority carrier concentrations in extrinsic semi conductors at a given temperature is equal to the square of Intrinsic carrier concentration at that temperature.

The law of mass action is very important in conjunction with charge neutrality condition.. This enables us to calculate minority carrier concentration. This law states that the addition of impurities to intrinsic semi conductors increases the concentration of one type of carrier, which consequently becomes majority carrier and simultaneously decreases the concentration of the other carriers, which is known as the minority carrier.

The minority carriers decrease in number below the intrinsic value.

This is because there is an increase of majority charge carriers Recombination rate.

According to the law of Mass action, the product of majority and minority carriers remains constant in an extrinsic semi conductors and it is independent of the amount of donor and acceptor impurity concentrations. When the doping concentration levels are high, the minority carrier concentration will be low and the majority carrier concentration will be high when the doping concentration levels are low, the majority carrier concentration is low and the minority carrier concentration is high.

Charge neutrality

Let us consider extrinsic semi conductors with both donor and Acceptor impurities.

At usual ambient temperatures, we may assume that impurity atoms are ionized and no charge carriers are created due to breaking of covalent bonds.

Now concentration of electrons n = concentration of positively ionized donor impurity atoms, N_d .

Concentrations of holes P = concentration of negatively ionized acceptor impurity atoms N_a .

Now the total charge neutrality of the material can be written as

$$P + N_d = n + N_a \quad \text{--- (1)}$$

According to law of Mass action, in any semiconductor, under thermal equilibrium condition, the product of the number of electrons and number of holes is a constant.

$$np = n_i^2 \quad \text{----- (2)}$$

Where n_i = intrinsic carrier concentration.

$$\text{Also } n = \frac{n_i^2}{p} \text{ and } p = \frac{n_i^2}{n}$$

Now from equation (1), we have

$$p = n + N_a - N_d$$

But $n = \frac{ni^2}{p}$

$$p = \frac{ni^2}{p} + (N_a - N_d)$$

$$\Rightarrow p^2 = ni^2 + P(N_a - N_d)$$

$$\Rightarrow p^2 - P(N_a - N_d) - ni^2 = 0$$

This is a quadratic equation of the type

$$ax^2 + bx + c = 0$$

$$\therefore P = \frac{N_a - N_d}{2} \pm \sqrt{\frac{(N_a - N_d)^2 + 4ni^2}{2}}$$

$$P = \frac{N_a - N_d}{2} \pm \left[\frac{(N_a - N_d)^2}{4} + ni^2 \right]^{1/2} \quad \text{---- (3)}$$

Similarly we can show that

$$n = \frac{N_d - N_a}{2} \pm \left[\frac{(N_d - N_a)^2}{4} + ni^2 \right]^{1/2} \quad \text{----- (4)}$$

Equations (3) and (4) represent the equations for charge densities.

Case I: For intrinsic semi conductors.

$$N_a = 0$$

Hence we get $n = p = ni$ ---- (5)

Case II: N – type semiconductors

Now
$$p = \frac{-Nd}{2} \pm \left[\frac{(-Nd)^2}{4} + ni^2 \right]^{1/2}$$

$$p = -\frac{Nd}{2} \pm \frac{(-Nd^2 + 4ni^2)^{1/2}}{2}$$

$$p = \frac{-Nd \pm (-Nd^2 + 4ni^2)^{1/2}}{2}$$

$$p = \frac{-Nd \pm Nd^2 \left[1 + \frac{4ni^2}{Nd^2} \right]^{1/2}}{2}$$

Since p cannot be negative

$$p = -\frac{-Nd + Nd \left(1 + \frac{4ni^2}{Nd^2} \right)^{1/2}}{2}$$

Expanding using power series and neglecting higher power terms

$$P = -\frac{Nd}{2} + \frac{Nd}{2} \left[1 + \frac{1}{2} \left(\frac{4ni^2}{Nd^2} \right) + \dots \right]$$

$$P = -\frac{Nd}{2} + \frac{Nd}{2} \left(1 + \frac{2ni^2}{Nd^2} \right)$$

$$P = -\frac{Nd}{2} + \frac{Nd}{2} + \frac{Nd^2}{2} \frac{2ni^2}{Nd^2}$$

$$P = \frac{ni^2}{Nd} \quad \text{---- (6)}$$

Similarly electron concentration

$$n = \frac{Nd}{2} + \left(\frac{Nd^2 + 4ni^2}{4} \right)^{1/2}$$

$$n = \frac{Nd}{2} + \frac{Nd}{2} \left(1 + \frac{4ni^2}{Nd^2} \right)^{1/2}$$

Expanding using power series and neglecting higher power terms

$$n = \frac{Nd}{2} + \frac{Nd}{2} \left[1 + \frac{1}{2} \left(\frac{4ni^2}{Nd^2} \right) + \dots \right]$$

$$n = \frac{Nd}{2} + \frac{Nd}{2} \left(1 + \frac{2ni^2}{Nd^2} \right)$$

$$n = N_d + \frac{ni^2}{N_d}$$

At low temperatures $ni \ll 0$

Hence $n \approx N_d$ ----- (7)

Case III : P-type semi conductor

In this case $N_d = 0$

$$\text{Now } n = -\frac{Na}{2} \pm \left[\frac{(-Na)^2}{4} + ni^2 \right]^{1/2}$$

$$n = -\frac{Na}{2} \pm \left[\frac{4a^2}{4} + ni^2 \right]^{1/2}$$

$$n = -\frac{Na}{2} \pm \left(\frac{Na^2 + 4ni^2}{4} \right)^{1/2}$$

$$n = -\frac{Na}{2} \pm \frac{(Na^2 + 4ni^2)^{1/2}}{2}$$

$$n = -\frac{Na \pm (Na^2 + 4ni^2)^{1/2}}{2}$$

$$n = \frac{-Na \pm Na \left(1 + \frac{4ni^2}{Na}\right)^{1/2}}{2}$$

Since n cannot be negative

$$n = \frac{-Na \pm Na \left(1 + \frac{4ni^2}{Na}\right)^{1/2}}{2}$$

Expanding using power series and neglecting higher power terms

$$n = -\frac{Na}{2} + \frac{Na}{2} \left[1 + \frac{1}{2} \left(\frac{4ni^2}{Na}\right) + \dots\right]$$

$$n = -\frac{Na}{2} + \frac{Na}{2} \left(1 + \frac{2ni^2}{Na}\right)$$

$$n = -\frac{Na}{2} + \frac{Na}{2} + \frac{Na}{2} \frac{2ni^2}{Na}$$

$$\therefore n = \frac{ni^2}{Na} \quad \text{--- (8)}$$

Similarly Hole concentration

$$P = \frac{Na}{2} \pm \left[\frac{Na^2}{4} + ni^2\right]^{1/2}$$

$$P = \frac{Na}{2} \pm \left(\frac{Na^2 + 4ni^2}{4}\right)^{1/2}$$

$$P = \frac{Na \pm (Na^2 + 4ni^2)^{1/2}}{2}$$

$$P = \frac{Na \pm Na \left(1 + \frac{4ni^2}{Na}\right)^{1/2}}{2}$$

$$P = \frac{Na}{2} + \frac{Na}{2} \left(1 + \frac{4ni^2}{Na}\right)^{1/2}$$

Expanding using power series and neglecting higher power terms.

$$P = \frac{Na}{2} + \frac{Na}{2} \left[1 + \frac{1}{2} \left(\frac{4ni^2}{Na}\right) + \dots\right]$$

$$P = \frac{Na}{2} + \frac{Na}{2} \left(1 + \frac{4ni^2}{Na}\right)$$

$$P = \frac{Na}{2} + \frac{Na}{2} + \frac{Na}{2} \frac{2ni^2}{Na^2}$$

$$P = Na + \frac{ni^2}{Na}$$

At low temperature $ni \ll 0$

Hence $p \approx Na$

---- (9)

Equation of Continuity

This equation governs the behavior of charge carriers in a semi conductor.

This equation gives a condition of dynamic equilibrium for the density of charge carriers in any elementary volume of semiconductors.

This is based on the fact that charge can neither be created nor be destroyed.

When an N-type semiconductor is exposed to light, excess carriers are generated at the exposed surface.

The generated carriers are in the form of electron – hole pairs. Since the given semiconductors are N-type, here the excess carriers are holes.

These charge carriers diffuse throughout the material. Hence the carrier concentration in the semiconductor is a function of both time and distance.

Consider the infinitesimal volume element of are A and length dx as shown in figure (1).

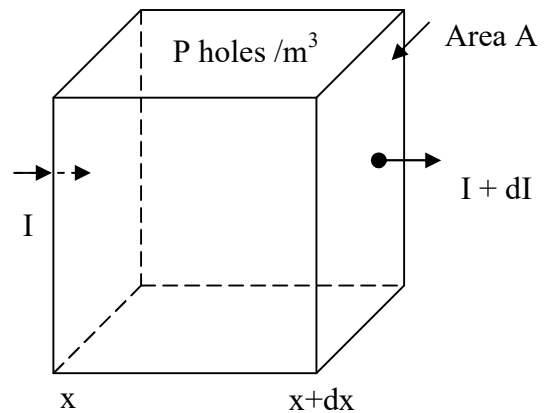


Figure (1) Conservation of charge carriers

Let P be the average hole concentration within this volume.

Let τ_p = Mean life of holes.

Now the holes lost per unit volume by recombination is $\frac{P}{\tau_p}$.

The rate of loss of charge within the volume under consideration = $eAdx \frac{P}{\tau_p}$ -----(1)

Recombination : Electrons combining with holes is called recombination

Let g = Thermal rate of generation of electron hole pairs per unit volume.

Now rate of increase of charge within the volume under consideration = $eAdxg$ ---- (2)

Let I = The current entering the volume at x .

$I + dI$ = The current leaving the volume at $x+dx$.

It is found that the current leaving the sample has increased by an amount dI .

This means that there is a decrease of hole concentration. Now the decrease of holes (in coulombs) per second from the volume under consideration = dI .

Due to above stated three effects, the hole density changes with time.

Now increase in the number of holes per second

Within the given volume = $eA \frac{dp}{dt} dx$ ----- (3)

According to conservation of charges, charge can neither be created nor be destroyed.
 \therefore Increase of Holes = generation of Holes – loss of Holes.

$$eA dx \frac{dp}{dt} = eA dx g - eA dx \frac{p}{\tau_p} - dI \quad \text{----- (4)}$$

Now total current due to excess carries (holes) in given by
 Total current = Diffusion current + drift current

$$I = -AeD_p \frac{dp}{dx} + Ape\mu pE \quad \text{----- (5)}$$

Where E = Intensity of the electric field with in the given volume when there is no external field applied, then E = 0 under thermal equilibrium conditions the hole density attains a constant value P_0

Under these conditions $dI=0$ and $\frac{dp}{dt} = 0$

Now equation (4) becomes

$$0 = eA dx g - eA dx \frac{P_0}{\tau_p}$$

$$\Rightarrow g = \frac{P_0}{\tau_p} \quad \text{----- (6)}$$

Here g = generation rate.

This equation (6) indicated that, the rate of generation of holes is equal to the rate of loss due to recombination under equilibrium conditions.

Also (5) $\Rightarrow I = -AeD_p \frac{dp}{dx} + Ape\mu pE$

Now $\frac{dI}{dx} = -AeD_p \frac{d^2 p}{dx^2} + Ae\mu p \left(\frac{dp}{dx} \right) E$ ----- (7)

From equations (4), (6) and (7), we get

$$eADx \frac{dp}{dt} = eA dx \frac{P_0}{\tau_p} - eA dx \frac{p}{\tau_p}$$

$$- \left[-AeDp \frac{d^2 p}{dx^2} dx + Ae\mu p \left(\frac{dp}{dx} \right) E dx \right]$$

$$\cancel{eA} \cancel{dx} \frac{dp}{dt} = - \cancel{eA} \cancel{dx} \left(\frac{P - P_0}{\tau_p} \right) + \cancel{A} \cancel{e} D_p \frac{d^2 p}{dx^2} \cancel{dx} - \cancel{A} \cancel{e} \mu p \frac{dp}{dx} E \cancel{dx}$$

$$\Rightarrow \frac{dp}{dt} = - \left(\frac{P - P_0}{\tau_p} \right) + D_p \frac{d^2 p}{dx^2} - \mu p \left(\frac{dp}{dx} \right) E \quad \text{----- (8)}$$

This equation (8), is called equation of continuity, since hole concentration P is a function of tome t and distance x, we have to use only partial derivatives.

$$\Rightarrow \frac{\partial p}{\partial t} = -\left(\frac{P - P_0}{\tau_p}\right) + D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \left(\frac{\partial p}{\partial x}\right) E \quad \text{----- (9)}$$

For holes in an n-type semiconductor

$$\therefore \frac{\partial p_n}{\partial t} = -\left(\frac{P_n - P_{on}}{\tau_p}\right) + D_p \frac{\partial^2 p_n}{\partial x^2} - \mu_p E \frac{\partial p_n}{\partial x} \quad \text{----- (10)}$$

For electrons in a p-type semiconductor

$$\frac{\partial n_p}{\partial t} = -\left(\frac{n_p - n_{op}}{\tau_n}\right) - D_n \frac{\partial^2 n_p}{\partial x^2} + \mu_n E \left(\frac{\partial n_p}{\partial x}\right) \quad \text{----- (11)}$$

This sign difference between the above two equations is due to the different directions of drift of holes and electrons in an applied electric field.

Hall Effect:

Some times it is necessary to determine whether a material is n-type or p-type. Measured conductivity of a specimen will not give this information since it cannot distinguish between positive hole and electron conduction.

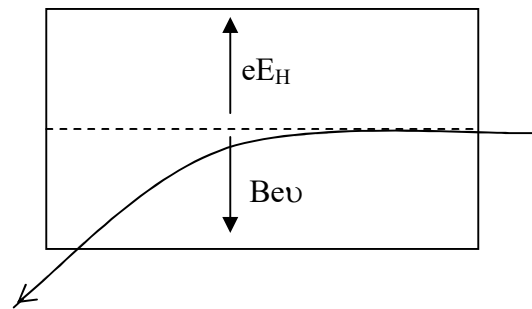
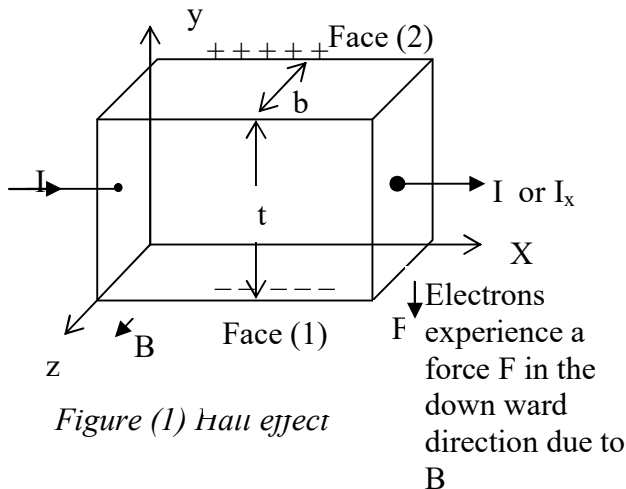
The Hall Effect can be utilized to distinguish between the two types of carriers, and it is also useful in the determination of density of charge carriers.

Hall Effect definition

“If a piece of conductor or Specimen (metal or semiconductor) carrying current is subjected to a transverse magnetic field, an electric field is generated inside the specimen in a direction normal to both the current and the magnetic field”

This phenomenon is known as Hall Effect. The generated voltage is known as Hall voltage. The corresponding electric field is known as Hall Electric field.

Let us consider a sample having thickness t and width b. the sample is a rectangle sample, as shown in the figure(1).



Assuming that the material is an n-type semiconductor, the current flow consists of almost due to electrons, moving from right to left.

This corresponds to the direction of conventional current from left to right as shown in figure (1).

Current I is in the positive X-direction and the magnetic field B is applied in the positive Z direction. According to Flemings, left hand Rule, The electrons experience a force, called Lorentz force. This Lorentz force acts in the negative Y-direction.

Now Lorentz force $F_L = B \times ev$ (cross product)

$$F_L = Bev \sin \theta \text{ -----(1)}$$

Where v = velocity of electrons.

Since the velocity of electrons and B are perpendicular . $\theta=90^0$

$$F_L = Bev \text{ -----(1)a}$$

Electrons experience a force downwards in the negative Y-direction and the positive charges drift upwards in the positive Y-direction. As a consequence, the lower surface collects negative charge and upper surface becomes positively charged. Due to this an electric field called Hall electric field will be established between upper and lower surface of the specimen.

This hall electric field E_H establishes a potential called the Hall Voltage V_H .

The hall field E_H exerts an upward force F_H on the electrons as shown in figure (2).

$$\therefore F_H = eE_H \text{ ----- (2)}$$

But total force on the electrons, is given by

$$Bev + eE_H = 0 \text{ ----- (3)}$$

The above equation is called Lorentz equation. Under equilibrium conditions.

$$\therefore E_H = -Bv \text{ ----- (4)}$$

Now the current density in the X-direction is given by

$$J_x = nev \text{ ----- (5)}$$

$$\text{Now (5)} \Rightarrow v = \frac{J_x}{ne} \text{ ----- (6)}$$

Here n = electron density (electron concentration)

e = charge on the electrons.

Now from (4) and (6),

$$E_H = -\frac{BJ_x}{ne} \text{ ----- (7)}$$

Now the Hall coefficient R_H can be described as follows.

For a given semiconductor electron concentration n is constant and charge on the electron e is constant.

$$\therefore E_H \propto BJ_x$$

$$E_H = R_H BJ_x \text{ ----- (8)}$$

Where R_H is a constant of proportionality.

$$\therefore R_H = -\frac{1}{ne} \text{ ----- (9)}$$

Here E_H, B and J_x are measurable. Hence Hall coefficient R_H and carrier density 'n' can be found.

Determination of Hall coefficient

Let t be the thickness of the rectangular slab.

b be the width of the sample.

Now the Relation between E_H and V_H is given by

$$V_H = E_H t \text{ ----- (10)}$$

$$\text{Also (8)} \Rightarrow E_H = R_H B J_x \text{ ----- (8)}$$

Now from (8) and (10), we get

$$V_H = R_H B J_x t \text{ ----- (9)}$$

But J_x = current density

$$J_x = \frac{I_x}{A} = \frac{\text{current}}{\text{area}}$$

$$J_x = \frac{I_x}{bt} \quad (\text{Since } A = \text{Area of cross section})$$

$$A = b t)$$

∴ Equation (9) becomes

$$V_H = R_H B X \frac{I_x}{b t}$$

$$V_H = R_H \frac{I_x B}{b}$$

$$\Rightarrow R_H = \frac{V_H b}{I_x B} \text{ ----- (10)}$$

V_H, b, I_x and B all are measurable and substituting them in equation (10), we can obtain the value of Hall coefficient R_H .

Note that the polarity of V_H will be opposite for n and p type semiconductors.

Carrier concentration and mobility

$$\text{Hall coefficient } R_H = -\frac{1}{ne}$$

$$R_H = \frac{1}{ne} \text{ (Magnitude)}$$

Electron concentration $n = \frac{1}{R_H e}$ can be determined.

Now electrical conductivity $\sigma = ne\mu$.

Where μ = mobility

$$\text{Mobility } \mu = \frac{\sigma}{ne}, \mu = R_H \sigma$$

For a P-type material Hall coefficient is positive.

$$R_H = \frac{1}{pe}, \text{ Where } p = \text{hole concentration. } e = \text{Charge on hole Which is +ve.}$$

Application of the Hall Effect:

1. Useful in determining whether the given semiconductor is n-type or p-type.
2. Hall Effect can be used to find the carrier concentration and mobility of carriers.
3. Hall Effect is used to measure the magnetic field.
4. Hall Effect semi conducting devices are used as sensors to sense the magnetic fields.
5. The Hall Effect is used in magnetically activated electronic switches. They are used as non contacting key boards and panel switches.

PN Junction

When a P type material is suitably joined with an N type material, a PN junction is formed. When an intrinsic semi conductors is simultaneously doped with P-type and n-type impurities, a PN junction is formed.

The PN junction may be formed by crystal growth or alloying or diffusion method.

The plane dividing the two zones is called PN Junction.

The PN junction is shown in figure (1) a

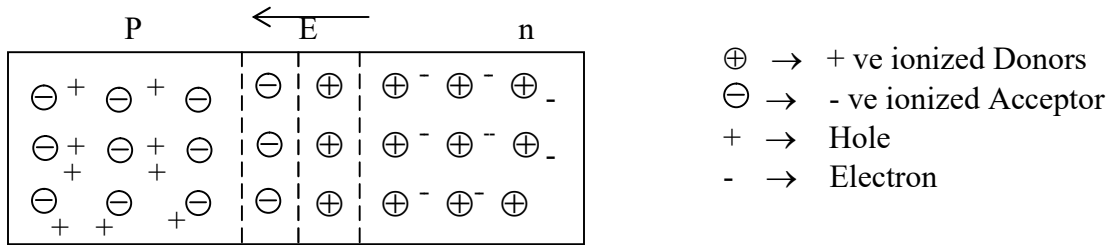


Fig (1) a: a Pn junction

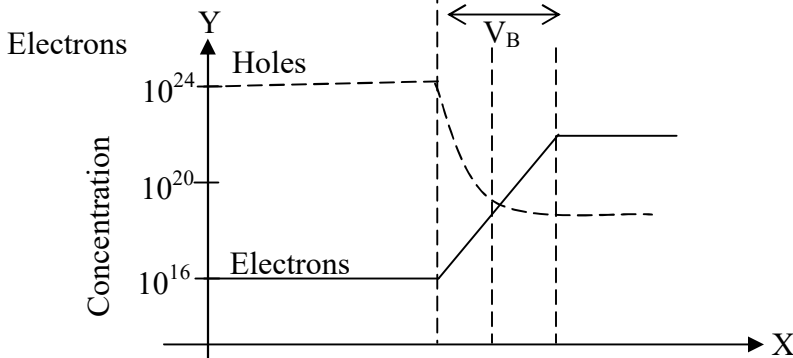


Fig (1) b: Diffraction of electrons and holes

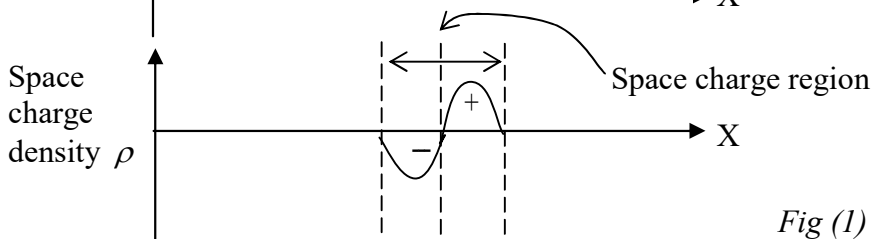


Fig (1) c: Space charge region for an alloy or abrupt junction

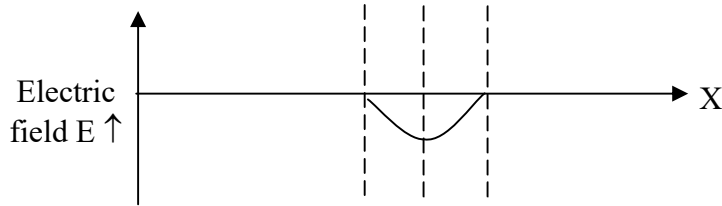


Fig (1) d: Electric field due to space charge region

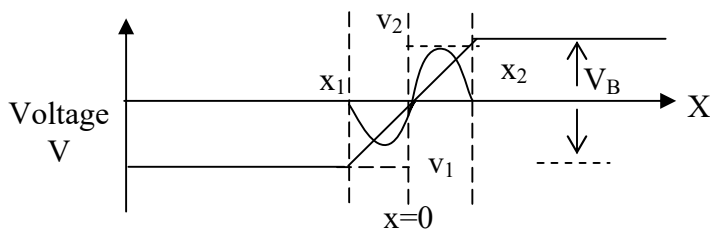


Fig (1) e: Barrier potential (or) contact potential

In the p side '+' represents holes. In the n side '-' represents electrons.

In the n-side there is a high concentration of electrons.

In the P- region there is a high concentration of holes.

Therefore, at the junction there is a tendency for the electrons to diffuse from n-region to p-region and holes from p-region to n-region. This process is called diffusion. When the free electrons move across the junction from n-side to p-side. The demotions become positively charged. Hence a not positive charge is built on the n-side of the junction.

The free electrons that cross the junction uncover the negative acceptor ions by combining with the holes.

Therefore a not negative charge is established on the p-side of the junction.

This not negative charge n the p-side prevents further diffusion of electrons from n-side to p-side.

Similarly the net positive charge on the n side prevents further diffusion of holes from p side to n side.

Due to this a barrier is set up near the junction.

This barrier prevents further movement of charge carriers i.e. electrons and holes. This barrier is called potential barrier.

It should be noted that outside this barrier an each side of the junction. The material is still neutral.

Only inside the barrier, there is positive charge on n side and negative charge on p-side.

This region is called depletion layer. This is so because mobile charge carriers are depleted in this region.

It is clear that a potential barrier V_O or V_B is set up.

As a consequence of this an electric field is established across the depletion layer.

The Barrier potential is about 0.3v for Germanium and 0.72V for silicon.

The depletion layer and the Barrier potential are shown in the fig (1)a and Fig (1)e.

The width of the depletion region is less than $1 \mu m$ ($\sim 0.5 \mu m$). Since the depletion region has immobile ions which are electrically charged it is known as space charge region. The space charge region is shown in figure (1) c. the established electric field is shown in figure (1) d.

Hence across the junction no current flows and the system is in equilibrium.

To the left of this depletion layer (in the P side), the carrier concentration is $P \sim N_A$.

To the right of the depletion layer (in the n side), the carrier concentration is $n \sim N_D$.

Width of depletion layer

For a PN junction, the potential barrier is shown in the figure below.

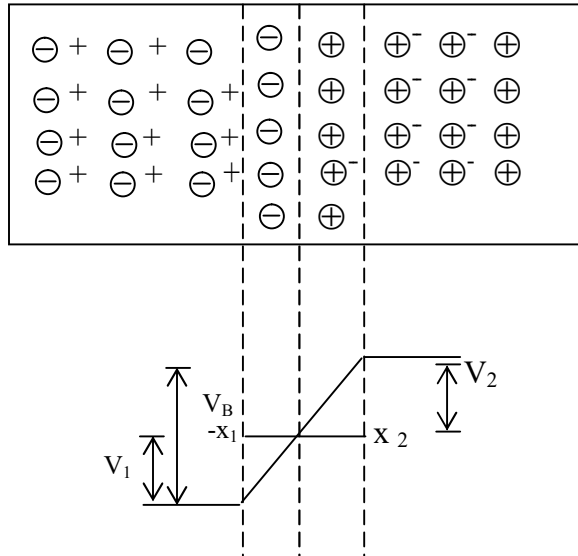


Figure (1) Potential Barrier in a Pn junction

This figure shows the space charge region in the two sides of the junction and the consequent potential variation.

Let X_1 = width of the space charge region in the P side.

X_2 = Width of the space charge region in the N side.

The area of the depletion layer in each region depends on the concentration of the impurities in the regions.

The effective areas of the depletion layer can be calculated using Poisson's equation.

According to Poisson's equation, the second derivative of the potential with respect to distance is proportional to the charge density.

In one dimension, the voltage varies only in the X-direction only. The length of the crystal.

Now the Poisson's equation may be written as

$$\frac{d^2V}{dx^2} \propto -p$$

$$\frac{d^2V}{dx^2} = \frac{-p}{\epsilon} \quad \text{---- (1)}$$

Here V = voltage

P = volume charge density

E = Permittivity of the medium.

In the position of the depletion layers situated in the P-region near the junction the charge density may be given by

$$P = -eN_a \quad \text{---- (2)}$$

Where N_a = Density of Acceptors Atoms.

e = charge on the electron.

Negative sign is used, since acceptors atoms are negatively ionized.

To find X_1 in the P-region, we use Poisson's equation.

i.e. from equations (1) and (2), we have

$$\frac{d^2v}{dx^2} = \frac{-p}{\epsilon} = \frac{\epsilon Na}{\epsilon} \quad \text{----- (3)}$$

On integrating the above equation, we get

$$\begin{aligned} \frac{d}{dx} \left(\frac{dv}{dx} \right) &= \frac{eNa}{\epsilon} \\ \Rightarrow d \left(\frac{dv}{dx} \right) &= \frac{eNa}{\epsilon} dx \\ \Rightarrow \int d \left(\frac{dv}{dx} \right) &= \int \frac{eNa}{\epsilon} dx + A \\ \Rightarrow \frac{dv}{dx} &= \left[\frac{eNa}{\epsilon} \right] x + A \end{aligned} \quad \text{----- (4)}$$

Again (4) $\Rightarrow dv = \frac{eNa}{\epsilon} x dx + A dx$

Integrating the above equation, again

$$\begin{aligned} \int dv &= \int \frac{eNa}{\epsilon} x dx + \int A dx + B \\ V &= \frac{eNa}{\epsilon} \frac{x^2}{2} + Ax + B \end{aligned} \quad \text{---- (5)}$$

Where A and B are the arbitrary constants. A and B can be determined by applying boundary conditions.

We assume that $V = 0$ Where $X=0$, so that all voltages are measured with respect to the potential at the boundary between P-type and N-type materials.

Using this boundary condition, we get

$$0 = 0 + 0 + B \Rightarrow B = 0$$

In the p-type semi conducting material, the potential is constant at the end of the depletion layer or depletion region.

Thus the depletion region may be assumed to end at a point $x = -X_1$ where $\frac{dv}{dx} = 0$

At this point the field strength is zero.

Using the condition in equation (4), we get

$$\begin{aligned} 0 &= \left(\frac{eNa}{\epsilon} \right) (-x_1) + A \\ \therefore A &= \frac{eNa}{\epsilon} x_1 \end{aligned} \quad \text{----- (6)}$$

Now substituting the values of the constants A and B in equation (5), we get

$$V = \frac{1}{2} \left(\frac{eNa x^2}{\epsilon} \right) + \frac{eNa}{\epsilon} x_1 x \quad \text{----- (7)}$$

At $V = x_1$, we have $V = V_1$

∴ from (7), we have $V = V_1$

$$-V_1 = \frac{1}{2} \left(e \frac{Na \times l^2}{\epsilon} \right) - \left(e \frac{Na \times l^2}{\epsilon} \right)$$

$$\therefore -V_1 = -\frac{eNa \times l^2}{\epsilon}$$

$$V_1 = -\frac{eNa \times l^2}{2\epsilon} \quad \text{----- (8)}$$

In the same manner the Poisson's equation may be applied for the position of the depletion layer situated in the n-region near the junction. Now the charge density in the n-region, of depletion layer is due to positively ionized donor atoms,

The charge density is given by

$$p = eN_d \quad \text{----- (9)}$$

Now the Poisson's equation is given by

$$\frac{d^2}{dx^2} = \frac{-p}{\epsilon_0} \quad \text{----- (10)}$$

In equation (9), N_d = Density of Donor Atoms.
e = Charge on the electron.

From equations (9) and (10), we get

$$\begin{aligned} \frac{d^2v}{dx^2} &= -\frac{eN_d}{\epsilon} \quad \text{----- (11)} \\ (11) \Rightarrow \frac{d}{dx} \left(\frac{dv}{dx} \right) &= -\frac{eNd}{\epsilon} \\ \Rightarrow d \left(\frac{dv}{dx} \right) &= -\frac{eNd}{\epsilon} dx \end{aligned}$$

On integrating the above equation

$$\begin{aligned} \int d \left(\frac{dv}{dx} \right) &= -\int \frac{eNd}{\epsilon} dx + c \\ \frac{dv}{dx} &= -\frac{eN_d}{\epsilon} x + c \quad \text{---- (12)} \end{aligned}$$

By integrating the equation (12), we get

$$\begin{aligned} dv &= -\frac{eN_d}{\epsilon} x dx + c dx \\ \int dv &= -\int \frac{eN_d}{\epsilon} x dx + \int c dx + D \\ V &= -\frac{1}{2} \frac{eN_d x^2}{\epsilon} + cx + D \quad \text{---- (13)} \end{aligned}$$

Where C and D are arbitrary constants. C and D are determined by applying the boundary conditions.

Where $x = 0, v = 0$

∴ from (13), We get D=0.

In the n-region, the potential is constant at $X = X_2$.

$$\therefore \text{ At } X = X_2, \frac{dv}{dx} = 0$$

$$\therefore \text{ from equation (12), we get } c = \frac{eN_d X_2}{\epsilon} \quad \text{----- (14)}$$

$$\text{Thus } V = -\frac{1}{2} \frac{eN_d x^2}{\epsilon} + \frac{eNd}{\epsilon} x X_2 \quad \text{----- (15)}$$

At $x = X_2, V = V_2$, now we get

$$V_2 = -\frac{1}{2} \left(\frac{eNd \times x_2^2}{\epsilon} \right) + \left(\frac{eNd}{\epsilon} \right) X_2^2$$

$$V_2 = \frac{eNd \times x_2^2}{\epsilon} \quad \text{----- (16)}$$

This V_2 is the potential at $x = X_2$. At $x = X_2$ the depletion layer in the n-region will ends.

Now the potential barrier at the junction is given by

$$V_B = V_2 - (V_1)$$

$$V_B = V_2 + V_1$$

$$V_B = \left(\frac{eN_d X_2^2}{\epsilon} \right) \frac{1}{2} + \left(\frac{eN_d X_2^2}{\epsilon} \right) \frac{1}{2}$$

$$V_B = \frac{e}{2\epsilon} (N_a X_1^2 + N_d X_2^2) \quad \text{---- (17)}$$

The equation of charge neutrality is given by

$$eN_a X_1 = eN_d X_2$$

$$X_2 = \frac{N_a X_1}{N_d} \quad \text{---- (18)}$$

Now substituting the value of X_2 in equation (17)

$$V_B = \frac{e}{2\epsilon} \left[\frac{N_d N_a^2 X_1^2}{N_d^2} + N_a X_1^2 \right]$$

$$V_B = \frac{e}{2\epsilon} \left[\frac{N_a^2 X_1^2}{N_d^2} + N_a X_1^2 \right]$$

$$X_1^2 = \frac{2\epsilon V_B}{eN_a \left(1 + \frac{N_a}{N_d} \right)}$$

$$X_1 = \left[\frac{2\epsilon V_B}{eN_a \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} \quad \text{---- (19)}$$

From equation (18) and (19), we get

$$\begin{aligned}
 X_2 &= \frac{N_a}{N_d} \left[\frac{2 \in V_B}{eN_a \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} \\
 X_2 &= \left[\frac{2 \in V_B}{e \frac{N_d^2}{N_a^2} N_a \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} \\
 X_2 &= \left[\frac{2 \in V_B}{e \frac{N_d^2}{N_a} \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} \\
 X_2 &= \left[\frac{2 \in V_B}{eN_d \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} \quad \text{---- (20)}
 \end{aligned}$$

Now the total width of the depletion layer is given by

$$X = X_1 + X_2$$

$$\begin{aligned}
 \therefore X &= \left[\frac{2 \in V_B}{eN_a \left(1 + \frac{N_a}{N_d} \right)} \right]^{1/2} + \left[\frac{2 \in V_B}{eN_d \left(1 + \frac{N_d}{N_a} \right)} \right]^{1/2} \\
 X &= \left[\frac{2 \in V_B}{e \frac{N_a}{N_d} (N_a + N_d)} \right]^{1/2} + \left[\left(\frac{N_d}{N_a} \right)^{1/2} + \left(\frac{N_a}{N_d} \right) \right]^{1/2} \\
 X &= \left[\frac{2 \in V_B}{e(N_a + N_d)} \right]^{1/2} + \left[\frac{N_d + N_a}{(N_a N_d)^{1/2}} \right] \\
 X &= \left[\frac{2 \in V_B (N_a + N_d)}{eN_a N_d} \right]^{1/2} \quad \text{---- (21)}
 \end{aligned}$$

Diode Current Equations

The diode current pertaining to VI characteristics is given by

$$I = I_0 \left[e^{\left(\frac{V}{\eta V_T}\right)} - 1 \right]$$

Where I = Diode current

I_0 = Diode reverse saturation current at room temperature.

V = External voltage applied to the diode.

η = A constant

$\eta=1$ for Germanium

$\eta=2$ for Silicon

V_T = Volt equivalent temperature or thermal voltage.

$$V_T = \frac{K_B T}{q}$$

K_B = Boltzmann constant

$K_B = 1.3806 \times 10^{-23} JK^{-1}$

q = Charge on the electron

q = 1.602×10^{-19} coulomb

T = Temperature of the junction in $^{\circ}K$.

When the diode is reverse biased, the current equation is given by

$$I = I_0 \left[e^{-\left(\frac{v}{\eta V_T}\right)} - 1 \right]$$

Light Emitting Diode (LED)

Light Emitting diode (LED) is a PNjunction diode that emits light when forward biased. The light is emitted by the forward biased junction by a phenomenon called Electroluminescence.

The materials that are used for fabricating LED are Galliumphosphide (GaP), Gallium Arsenide Phosphide (GaAsP) and Gallum Arsenide.

Usually direct B and Gap semiconductors are used for the fabrication of LEDs.

When an LED is forward biased, carrier recombination takes place i.e. electrons from the n-side cross the junction and recombine with the holes on the p-side.

In silicon and Germanium semiconducting P_n junctions greater percentage of energy is given out in the form of heat and the emitted light is not visible.

A forward biased LED and its symbol are shown in the figure (1)

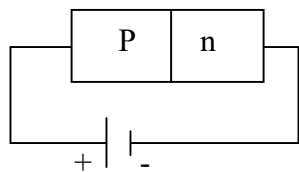


Fig (1) a: Forward biased LED

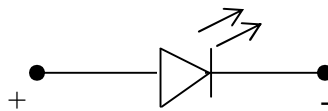
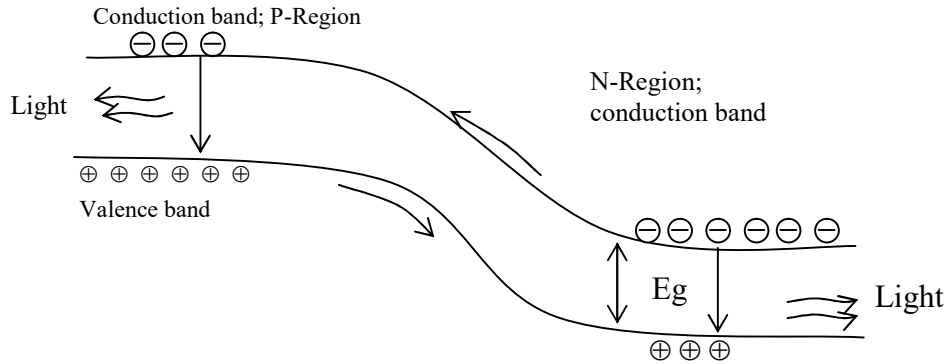


Fig (1) b: Symbol of LED

When an LED is forward biased, the electrons and holes move towards the junction and recombination takes place. As a result of recombination, the electrons present in the conduction band side of n-region fall into the holes present in the valence band side of P-region. When recombination takes place, energy emitted out in the form of light. The emitted light will have energy equal to the energy difference between conduction band and the valence band. For every recombination light energy is emitted. The excess energy in the process of recombination is given to the emitted photons. The light emitted is directly proportional to the forward bias current in the LED. The energy band diagram for the LED is shown in the figure (2)



Figure(2) Energy Band diagram of an LED

The basic structure of a LED is shown in the figure (3). Here an n-type layer is grown on a substrate and a p-type is deposited on it by diffusion.

Since carrier recombination takes place in the p-region, it is kept uppermost.

Metal contacts are made on the p-layer act like anodes.

Current is allowed through these anodes. A thin metal (gold) film at the bottom will act as a cathode. This also provides the reflection of light by the thin metal layer back into the medium.

LEDs are usually encased to protect their delicate metal contact wire.

The emission of light and its efficiency can be increased by increasing the junction current (injected current) LEDs are used to radiate different colors of light. The wavelength of light emitted depends on the energy gap of material.

The following table shows the colors emitted by different materials.

Material	Colors	Wavelength
GaAS	IR	9000
Gap	Green	5600
GaAsp	Yellow	5900

Usually a protective resistor of 1 k a or 1.5 ka is connected in series with the LED in a circuit. LEDs operate as a forward bias voltage of 1.5 volt to 3.3 V. Usually the current is in mill amperes.

The power requirement is 10 mw – 150 mw.

The switching time is around 1ms.

The wavelength of emmited light is given by

$$\lambda = \frac{hc}{E_g}$$

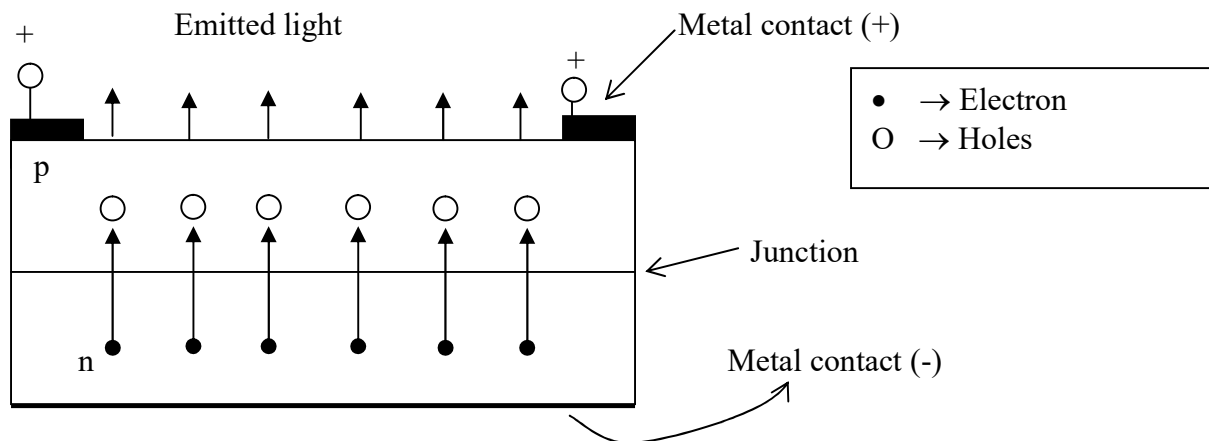


Figure (3) Structure and Recombination of electrons and holes in a LED.

Applications of LED

LEDs are used in

1. Intercoms
2. Digital clocks
3. Digital display systems
4. Instrument display systems

5. Power on/off indicating
6. Optical switching applications
7. Optical communication for energy coupling circuits
8. Opto isolation circuits
9. Solid state video-display system
10. used in computers
11. Calculators
12. Electronic panels

Photo diode

A Silicon photodiode is a light Sensitive Device. A photo diode is also known as photo detectors.

A photo diode converts light signals (optical signals) into electrical signals.

A photo diode must be always reverse biased. The reversed biased photodiode and its symbol are shown in figure (1)

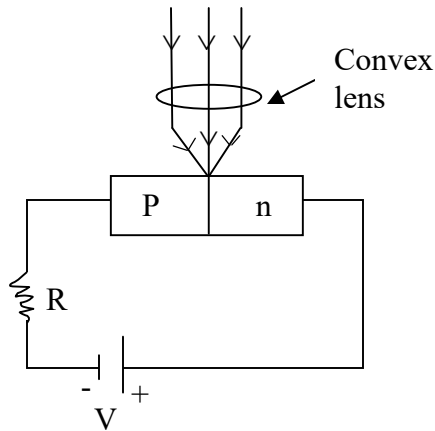


Figure (1) a: Photo diode and reverse bias

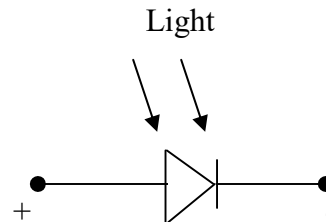


Figure (1)b: photo diode symbol

The photodiode is made of semiconductor PN junction kept in a sealed plastic or glass casing.

The casing is designed in such a manner that the light rays are allowed to fall on one surface across the junction.

The remaining sides of the casing are painted to restrict the penetration of light rays.

A convex lens permits the light rays to fall on the junction. When light falls on the reverse biased PN junction photodiode, electron – hole pairs are generated.

The movement of these electron hole pairs in a properly reverse biased circuit results in a current.

The energy band diagram of a photodiode is shown in figure (2)

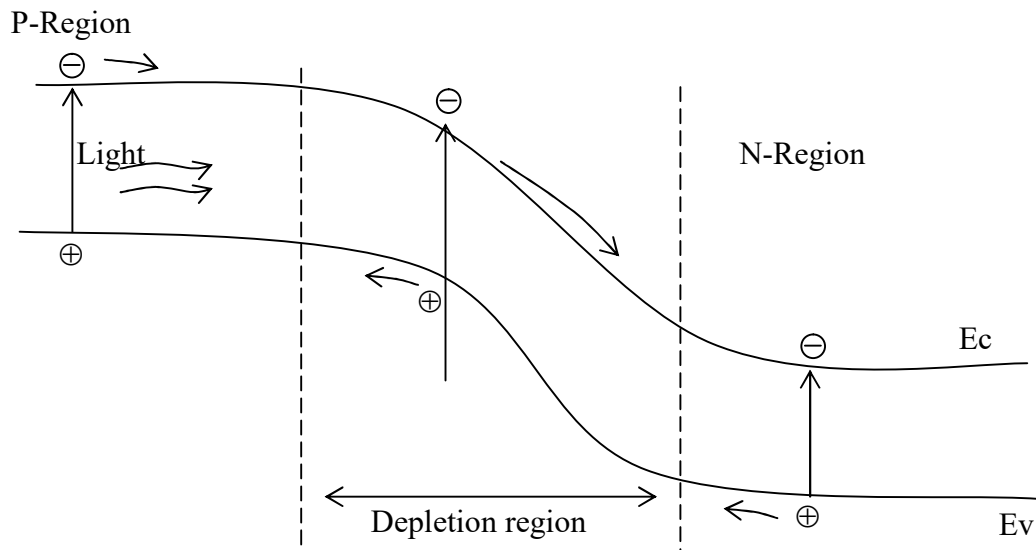


Figure (2) Energy band diagram of a photodiode

When reverse bias is applied, the depletion layer is widened, the junction capacitance reduced. Here in this situation the junction will not conduct current. However the reverse biased junction can conduct current when free carriers are generated in the junction by radiation of sufficient energy.

The magnitude of the photo current depends on the number of charge carriers generated and also on the illumination and the diode.

The photocurrent also depends upon the frequency of light falling on the photodiode.

The magnitude of the current with large reverse bias is given by

$$I = I_s + I_0 \left(1 - e^{-\frac{v}{\eta V_T}} \right)$$

Where I_0 = Reverse saturation current

I_s = Short circuit current which is proportional to the intensity of light.

V = Voltage across the diode.

V_T = volt equivalent of temperature.

η = A constant

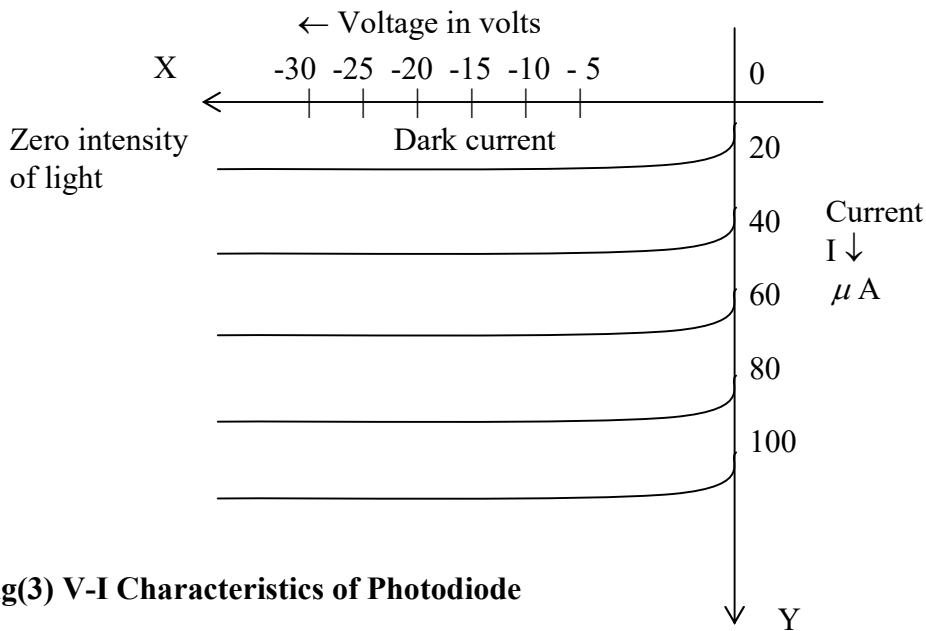
For Ge, $\eta=1$

Si, $\eta=2$

The volt ampere characteristics of a photodiode are shown in the figure (3).

The reverse current increases with increase in illumination. Even if there is no light is falling on the photodiode, there is a minimum leakage current called dark current, flowing through the device.

Germanium has a higher dark current than silicon, but it also has a higher level of reverse current.



Fig(3) V-I Characteristics of Photodiode

Applications of photodiode

1. Photodiodes are used as light detectors, demodulators and encoders.
2. They are used in optical Communication systems.
3. They are used in high speed counting circuits.
4. They are used in high speed switching circuits.
5. They are used in high operated switches.
6. They are used in computer card punching and tapes.
7. They are used in electronic control circuits.
8. They are used in retrieving of sound from sound track film.

Liquid Crystal Display (LCD)

Liquid crystal displays came under passive types of display since no light generation is required.

There are two types of LCD's namely.

- i) Reflective type, requiring illumination on the front side.
- ii) Transmittive type requires illumination on the rear side.

The liquid crystal state is a phase of matter exhibited by a large number of organic molecules of organic material over a restricted temperature range.

The material becomes a crystalline solid at the lower temperature range while it changes into a liquid at the upper temperature range.

In the liquid state, molecules will have the shape of rod. In any small volume of liquid crystal state the orientation of the molecules is described in terms of a unit vector called Directors.

They are basically two liquid crystal materials commonly used as LCD's.

They are Nematic and Cholestric

The arrangement of molecules is shown in the figure (1) and figure (2) for Nematic and Cholestric type of LCD's.

The properly used liquid crystal structure (NLC). In Nematic type the molecules are aligned parallel to each other as shown in figure (1). But these molecules are free to move relative to each other. Hence they represent a liquid phase. Here the molecules will have complete translational motion.

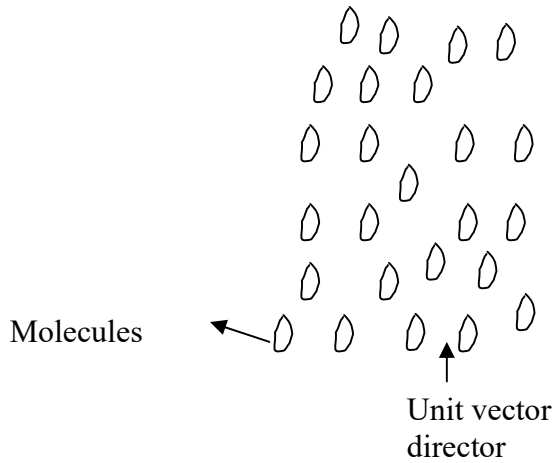


Figure (1) : Arrangement of Molecules in a Nematic liquid crystal

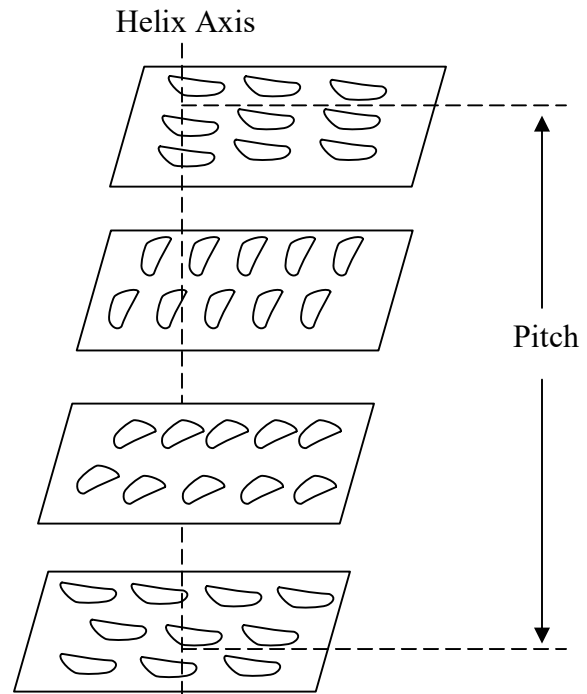


Figure (2) Arrangement of molecules in a cholesteric liquid crystal

The liquid is completely transparent. When the liquid is subjected to a strong electric field, the well ordered liquid crystal structure is disturbed.

This makes the liquid to polarize and turns opaque. When the electric field is removed, the liquid crystal regains its original structure and form.

Here the material becomes transparent.

In the cholesteric phrase the molecules are arranged in a large number of planes.

In each plane all the molecules are arranged in the direction of director as shown in figure (2).

The director directions thus display a helical twist through the material.

The distance between planes having the same director's direction is called the Pitch P.

Depending on the construction LCDs are classified into two types.

Dynamic scattering type

The dynamic scattering type liquid crystal cell is shown in the figure (3).

This consists of two thin glass plates, each coated with tin oxide on the inner side. This is transparent and act as electrodes.

These two glass plates are separated by a liquid crystal layer of 5-50 μm thick.

The front glass sheet is etched to produce a single or multi segment pattern of characters.

When a weak electric field is applied to a liquid crystal, the molecules align in the direction of the field.

When the voltage exceeds a certain threshold value, the liquid crystal structure entirely distributed and the appearance changes.

As the voltage further increases, the flow becomes turbulent and the material turns optically inhomogeneous.

In this disordered state, the liquid crystal scatters light.

Thus when there is not external electric field applied, the liquid crystal is transparent.

When electric field is applied, the disturbance causes scattering of incident light in all directions. Here the cell appears bright.

Field effect type

The field effect type of liquid crystal is similar to Dynamic type. This is also known as twisted nematic field effect display.

Its construction is same as dynamic type. But it is sandwiched between two pieces of polarized.

The polarized directions of the two polaroids are perpendicular to each other.

1st polarized is called polarizer and the 2nd one is called Analyser.

The 1st polarizer is in front of the LCD cell and the 2nd one is at its back. Both of these are arranged perpendicular to each other. Beyond Polaroid 2 a reflector is placed in reflective mode.

When a beam of polarized light passes through the polarizer, plane polarized light rotates through 90° as it transverses the cell.

When no electric field is applied, it passes through the analyser and then reflects back at the mirrors and light retraces the path.

Thus when no field is applied the device reflects light and appears bright.

When a field is applied, the direction of polarization of light traversing the cell is not rotated. Hence it is stopped by the second polarizer (Analyser).

No, light is reflected from the device and hence it appears dark. This means that in the absence of the field the incident light is reflected while it is blocked when the field is applied.

Advantages

1. Liquid crystals consume small amount of energy.
2. Hence the voltages required are less.
3. Because of low power consumption, a Seven segment display requires about 140w (20w per segment), whereas LEDs require 40mw per numerical.
4. They are economical and cheap.
5. In a seven segment display, the current drawn is $25\mu\text{A}$ for dynamic scattering cells and $300\mu\text{A}$ for field effect type cells.
6. LCDs require AC voltage supply.
7. They are economical and cheap.
8. They are used as temperature, measuring sensor.
9. Since thin layers are used, they are most suitable for display devices.

Disadvantages

1. Angle of viewing is limited.
2. External light must be used.

3. LCDs are slow devices. The ON and OFF times are quite large. ON time is a few ms. and off time is 10 ms.
4. When used with DC, there life time is less. Hence they are used with AC supply only.

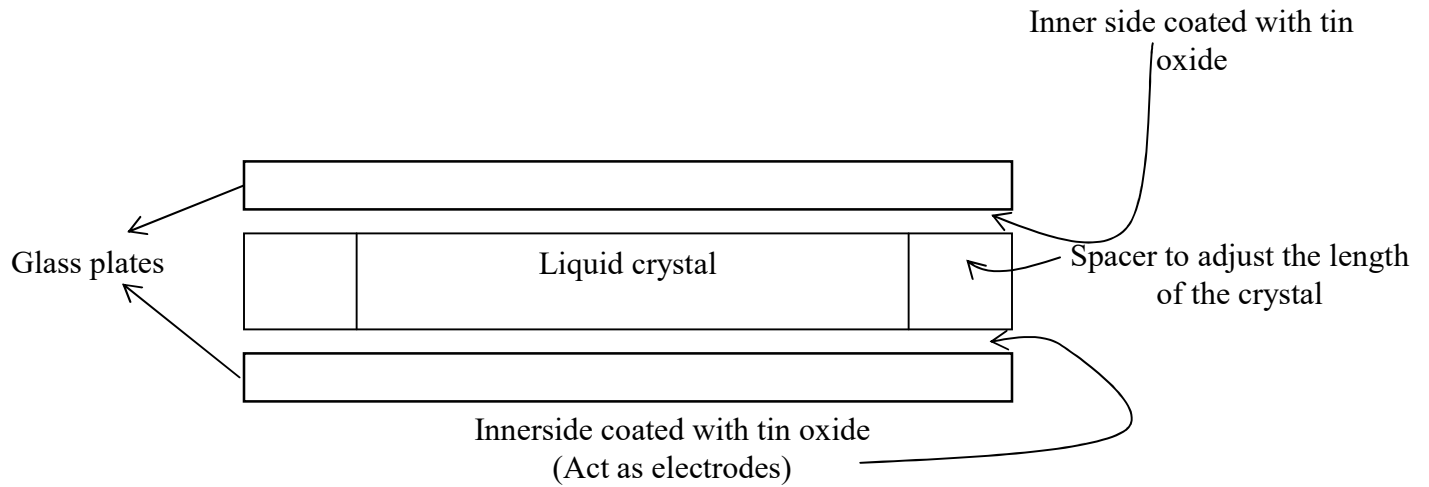


Figure (3) Construction of dynamic scattering LCD.

Drift current:

In a perfect crystal the periodic electric field enables electrons and holes to move freely as if in vacuum.

When there is no electric field, there is no net current. This is because charge movement in any direction is balanced by charge movement in the other direction. **In the presence of the electric field, the carriers experience directed movement. This is called drift.**

Definition Of drift: Forcible movement of Charge carriers under the influence of an Electric field is called drift.

With the field carriers drift and this results in current flow through the semiconductor.

Movement of charge carries under the influence of an applied electric field is called drift.

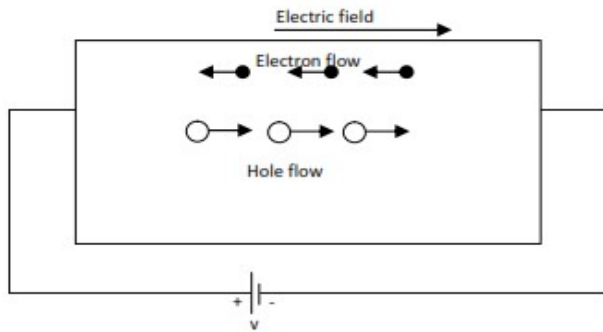


Fig. 1. Drift in semiconductor

The current density is given by

$$J = neV_d \text{ ----- (1)}$$

Here V_d = drift velocity.

$$\text{Also } V_d \propto E \Rightarrow V_d = \mu E \text{ ----- (2)}$$

Where μ is called the mobility of the carriers. E= Electric field.

From equations (1) and (2),

$$\text{Now current density } J = nev_d \text{ ----- (3)}$$

$$J = ne\mu E \text{ -----(4)}$$

In semi conductors, the current flow is due to electrons and holes.

Electron current density is given by

$$J_n(\text{drift}) = ne\mu_n E \text{ ----- (5)}$$

Hole current density is given by

$$J_p(\text{drift}) = pe\mu_p E \text{ ----- (6)}$$

The two charge carriers move in the opposite direction.

Now the total drift current density is given by

$$J(\text{drift}) = J_n(\text{drift}) + J_p(\text{drift})$$

$$J(\text{drift}) = ne\mu_n E + pe\mu_p E$$

$$J(\text{drift}) = E(ne\mu_n + pe\mu_p) \quad \text{----- (7)}$$

For intrinsic semiconductors $n = p = n_i$

$$J(\text{drift}) = En_i(e\mu_n + e\mu_p) \quad \text{----- (8)}$$

$$J(\text{drift}) = n_i E e(\mu_n + \mu_p)$$

Equation(8) gives current density equation.

Diffusion current :

Usually directed movement of charge carriers will give rise to electric current.

The movement of charge carriers may be due to either drift or diffusion.

Usually non-uniform concentration of carriers gives rise to diffusion.

Definition: Movement of charge carriers from high concentration region to low Concentration region in a semiconductor is known as diffusion.

Let us suppose that the concentration of electrons varies with distance x in the semi conductors. Here the concentration gradient is given by $\frac{\partial n}{\partial x}$.

Ficks law states that the rate at which carriers diffuse is proportional to the density gradient and the movement is in the direction of negative gradient.

Mathematically, the rate of flow of electrons can be written as

$$f_n \propto -\frac{\partial n}{\partial x} \quad \text{-----(1) Here } f_n = \text{rate of flow of electrons}$$

across unit area.

The rate of flow of electrons is given by

$$f_n = -D_n \frac{\partial n}{\partial x} \quad \text{----- (2)}$$

Here D_n = Diffusion coefficient for electrons.

Partial derivatives are used because n is a function of temperature and distance.

This flow of electrons constitutes an electron diffusion current density. Since conventional current is the rate of negative charge, we have

$$J_n(\text{diffusion}) = -(e)(\text{Rate of flow of electrons across unit area})$$

$$J_n(\text{diffusion}) = (-e)(-D_n \frac{\partial n}{\partial x})$$

$$J_n(\text{diffusion}) = eD_n \frac{\partial n}{\partial x} \quad \text{----- (3)}$$

If an excess hole concentration is created in the same region, hole diffusion takes place in the same direction at a rate per unit area.

The rate of flow of holes per unit area is given by

$$f_p = -D_p \frac{\partial p}{\partial x} \quad \text{----- (4)}$$

This results in a hole diffusion current density .

Now $J_p(\text{diffusion}) = +e(\text{rate of flow of holes across unit area})$

$$J_p(\text{diffusion}) = -eD_p \frac{\partial p}{\partial x} \quad \text{----- (5)}$$

Here D_p = Hole diffusion coefficient for holes.

Einstein Relations or Einstein Equations

At equilibrium with no field, the free electron distribution is uniform and there is no net current flow. Any tendency to disturb the state of equilibrium which would lead to diffusion current creates an internal electric field.

This internal electric field creates a drift current balancing the diffusion current component.

Under equilibrium conditions, we have therefore the drift and diffusion currents.

These currents are due to an excess density of electrons.

$$\text{Now } J_n(\text{drift}) = n\mu_e E \quad \text{----- (1)}$$

$$J_n(\text{diff}) = eD_n \frac{\partial n}{\partial x} \quad \text{----- (2)}$$

Under equilibrium conditions, $J_n(\text{drift}) = J_n(\text{diff})$

$$\therefore n\mu_n eE = eD_n \frac{\partial n}{\partial x} \text{----- (3)}$$

The force F on excess carriers restoring equilibrium is given by the product of excess charge and Electric field.

$$F = (ne)E \text{----- (4)}$$

$$(3) \Rightarrow n = \frac{D_n \frac{\partial n}{\partial x}}{\mu_n E} \text{----- (5)}$$

Now from (4) and (5), we get

$$\therefore F = e \frac{D_n E \frac{\partial n}{\partial x}}{\mu_n E}$$

$$F = \frac{e D_n \frac{\partial n}{\partial x}}{\mu_n} \text{----- (6)}$$

This force F depends on the thermal energy of the excess carriers.

By making an analogy between the excess carriers in a semiconductors and gas molecules in a low pressure gas, the force F corresponds to pressure gradient.

$$\text{Pressure gradient} = K_B T \frac{\partial n}{\partial x}$$

$$\therefore K_B T \frac{\partial n}{\partial x} = \frac{eD_n \frac{\partial n}{\partial x}}{\mu_n} \Rightarrow K_B T = \frac{eD_n}{\mu_n}$$

$$D_n = \frac{\mu_n}{e} K_B T$$

$$D_n = \frac{K_B T}{e} \mu_n \text{----- (7)}$$

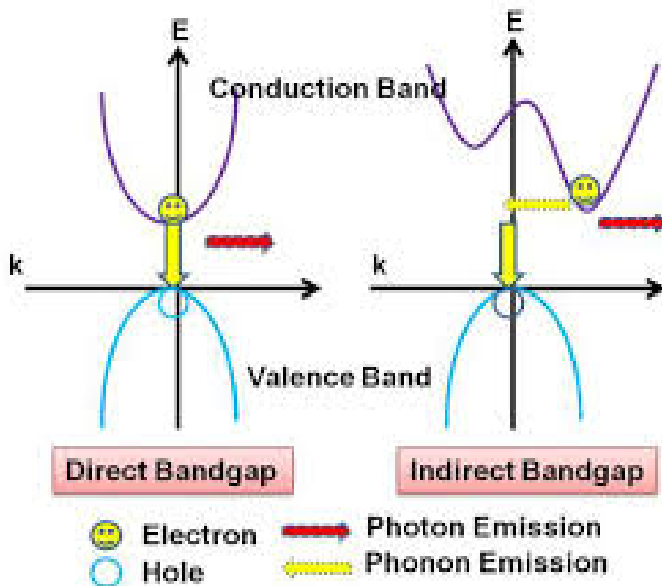
$$\text{Similarly for holes } D_p = \frac{K_B T}{e} \mu_p \text{----- (8)}$$

$$\frac{7}{8} \Rightarrow \frac{D_n}{D_p} = \frac{\mu_n}{\mu_p} \text{----- (9)}$$

Equations (7), (8) and (9) are called Einstein's Relations.

Direct Bad Gap and Indirect Band Gap Semiconductor.

Direct Band Gap Semiconductors	Indirect Band Gap Semiconductors
<p>1. Empirical formula $GaAs_{1-x}P_x$ Where x is molar concentration. If $x \leq 0.45$, then semiconductor is called Direct Band Gap Semiconductor.</p> <p>2. Transition of electrons from conduction band to valence band takes place directly.</p> <p>3. Intra band Transition occurs with high probability.</p> <p>4. Radiative recombination mechanism is dominant.</p> <p>5. Momentum of Charge carries is conserved.</p> <p>6. Life time of emitted photons is large.</p> <p>7. Life time Charge carriers is less.</p> <p>8. Natural or Artificially occurring materials. Like InP, Ga, GaAs, CdS.</p> <p>9. Used in LEDs and Semiconductor Laser diodes.</p>	<p>1. Empirical formula $GaAs_{1-x}P_x$ Where x is molar concentration.. If $x > 0.45$, then semiconductor is called Indirect Band Gap Semiconductor.</p> <p>2. Transition of electrons from conduction band to valence band takes place indirectly.</p> <p>3. Intra band Transition occurs with low probability.</p> <p>4. Recombination centers are present in the form of impurities to enhance radiative process.</p> <p>5. Momentum of Charge carries is not conserved.</p> <p>6. Life time of emitted photons is less.</p> <p>7. Life time Charge carriers is large.</p> <p>8. Artificially or naturally occurring materials. Like Gap, PbS, PbTe, Si, Ge.</p> <p>9. Used in LEDs</p>



Zener Diode:

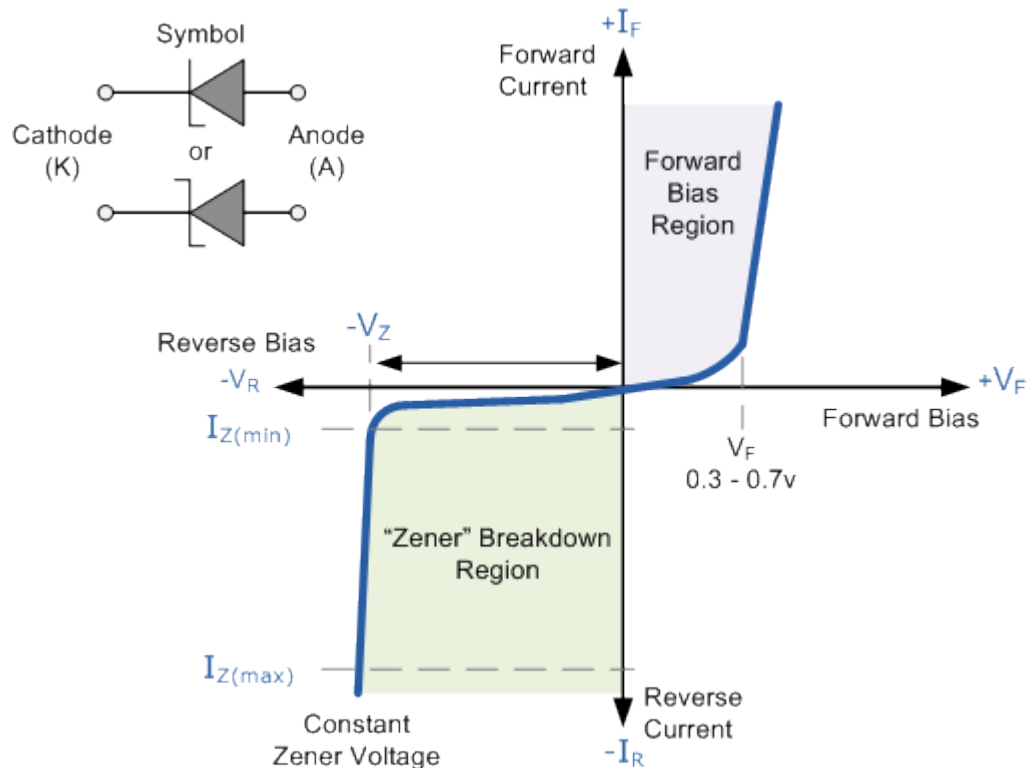


Fig (1) Zener Diode symbol and V-I Characteristics

Zener diode is similar to ordinary PN junction Diode.

The PN junction is moderately doped.

Zener diode is having a sharp breakdown voltage.

A Zener diode must be always connected in reverse bias.

Zener Diode Symbol and V-I Characteristics are shown in figure (1).

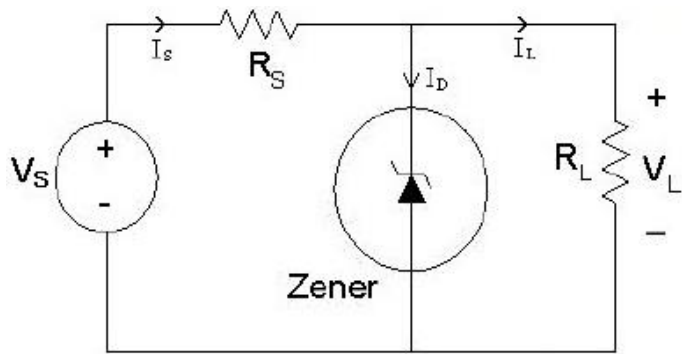
In forward bias, current increases slowly. At voltage called forward voltage (V_f) or Knee voltage (V_{knee}) current increase sharply.

In reverse bias originally current is very less. But with increase in reverse voltage, at a voltage called zener breakage voltage (V_Z) current increases abnormally. This breakdown voltage is negative.

Zener Diode Voltage Regulator:

A voltage regulator circuit with Zener diode is shown in figure(2).

Figure (2) Zener diode -voltage Regulator.



In fig (2), V_S = Variable voltage source.

I_S =Source current.

R_S = source Resistance.

R_L = Load resistance.

V_L =Load voltage.

With increase in source voltage, at a voltage called Zener breakdown voltage, voltage across the Zener diode remains constant.

This constant voltage appears across the diode and hence the same appears across the load.

NANOMATERIALS

Introduction:-

Nano meaning that 10^{-9} .

A nanometer is one thousand millionth of a meter. i.e. a nanometer equal to 10^{-9} m. In elements of atoms are very small. The diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example carbon atom is approximately 0.15 nm in diameter.

Also diameter of Red Blood Cell (RBC) is approximately 7000 nm.

Diameter of water molecule is around 0.3 nm. Thickness of human hair is around 80,000 nm. Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.

Nanoscience:-

Nano science can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macro molecular scales, where properties differ significantly from those at a larger scale.

Nano technology:-

Nano technology can be defined as the design, characterization, production and application structures, devices and systems by controlling shape and size at the nano scale.

Nanomaterials:-

If we take any material it will be composed of grains, which in turn comprise of many atoms. depending on the size, the grains may be visible or invisible to the naked eye.

Conventional materials have grains of size varying from hundred of microns to centimeters. Nano materials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.

Examples:-

One dimensional Nanomaterial:-

Materials that are on nanoscale in one dimension are layers such as thin films or surface coatings. In these materials, the particles are layered on layers or multilayers.

Two dimensional nano materials:-

materials that are on nano scale in two dimensions are nanowires and nano tubes.

This consists of ultrafine grains laid over layers.

Three dimensional nano materials:-

Materials that are on nanoscale in three dimensions are particles or grains.

Examples are precipitates, colloids and quantum dots.

Basic principles of nanomaterials:

The properties of nano materials are different from those of bulk materials.

Two important factors that make the nanomaterials to differ significantly from other materials are increased surface area and quantum effects.

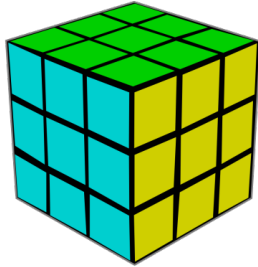
1. Increase in surface area to volume ratio:

Nano materials have a relatively larger surface area when compared to the same volume (or mass) of the material produced in a larger form

Let us consider a sphere of radius 'r'

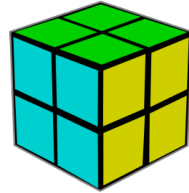
$$\text{Surface area} = 4\pi r^2 \text{ and Volume} = \frac{4}{3}\pi r^3$$

$$\text{Surface area to volume ratio} = \frac{\text{surface area}}{\text{Volume}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$



sides = 3
 surface = $3^2 \times 6 = 54$
 volume = $3^3 = 27$

surface/volume = 2



sides = 2
 surface = $2^2 \times 6 = 24$
 volume = $2^3 = 8$

surface/volume = 3



sides = 1
 surface = $1^2 \times 6 = 6$
 volume = $1^3 = 1$

surface/volume = 6

Thus when the radius of the sphere decreases its surface area to volume ratio increases. Let us consider another example.

For a cube of 1 unit volume shown in figure (1) the surface area is 6m^2

When it is divided into eight pieces its surface area becomes 12m^2 .

When the same volume is divided into 27 pieces its surface area becomes 18m^2

When a given volume is divided into smaller pieces the surface area increases.



As particle size decreases, a greater proportion of atoms are found at the surface compared to those inside. For example a particle of size 30nm has 5% of its atoms on its surface at 10nm 20% of its atoms, and at 3nm 50% of its atoms on its surface.

Due to this, nano materials are more chemically reactive. Some materials in bulk form are inert; when they are in nano form they are reactive.

This affects their properties.

Quantum confinement: When atoms are isolated the energy levels are discrete. When a very large number of atoms are closely packed to form a solid the energy levels split and form bands. Nano materials represent an intermediate stage when the material is of nano size and nano scale, the energies of the electrons change.

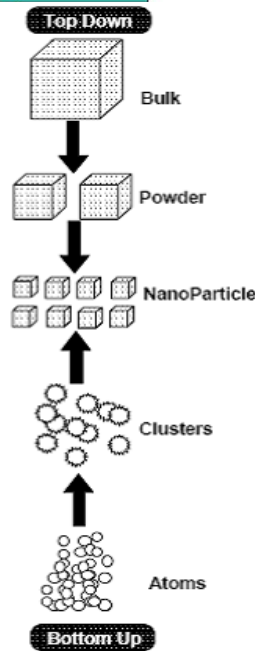
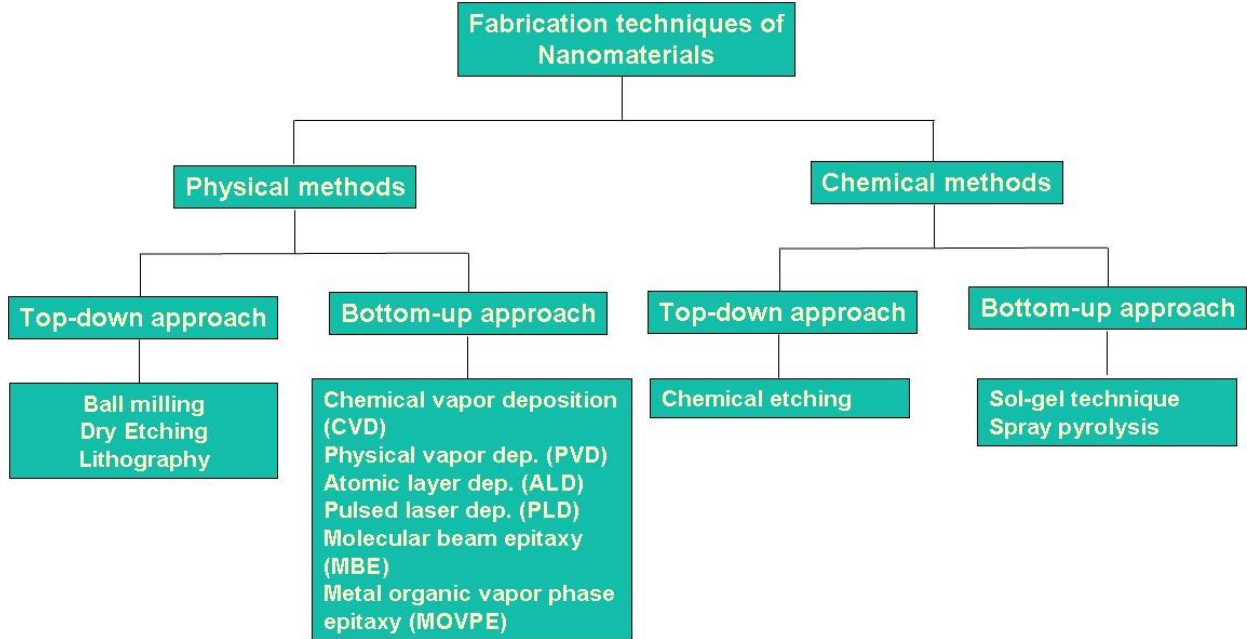
This effect is called quantum confinement

Due to this the electrical, optical and magnetic properties of the nanomaterials change.

Fabrication of nanomaterials:-

The nanomaterials can be synthesized by two techniques namely top-down and bottom up techniques

In the bottom-up approach, the nanomaterials are synthesized by assembling the atoms or molecules together to form the nanomaterials



In the top-down approach the bulk solids are disassembled (broken down to pieces) into finer pieces until the particles are in the order of nanoscale. The schematic representation of the synthesis and fabrication of nanomaterials are shown in figure above.

In top down method there are different techniques to fabricate nonmaterial's

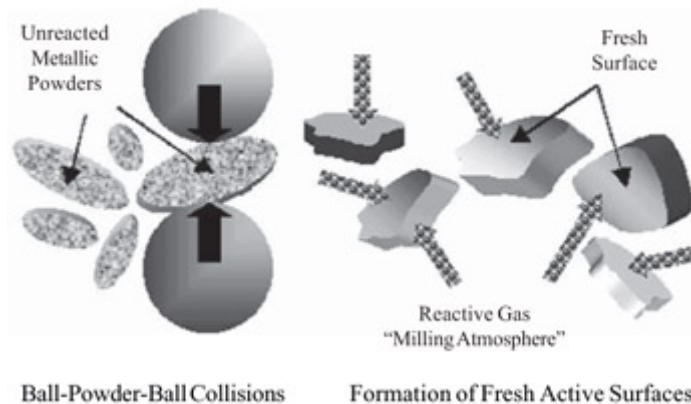
For example Ball milling and sol-gas are the methods used for fabricating nonmaterials in top-down approach

The chemical vapour deposition method, and plasma arching method are the methods employed in the fabrication of nanomaterials in bottom up approach

Fabrication of nanomaterials:-

Ball milling method

Ball milling method is a top down method. It is also known as mechanical crushing. This is a simple method to synthesize all classes of nanomaterials. This method is used to produce nano crystalline or amorphous materials.



The mechanical attrition mechanism or mechanical crushing mechanism is used to obtain nanocrystalline structures. The nano materials are prepared from single phase powders or dissimilar powders or amorphous materials. The ball milling method is shown in figure above.

Depending on the material to be synthesised refractory balls or steel balls or plastic balls are used.

When the balls are rotating with certain RPM, the energy is transferred to the powders.

This reduces the size of the powder particles to the nanoscaled particles. Here the nano particles are produced due to shear action between the balls and the metal pieces. The energy transferred to the powder from the balls depends on the factors such as rotational speed of the balls, size of the balls, number of balls, milling time, the ratio of the ball to the powder mass and milling atmosphere.

By using a cryogenic liquid the brittleness of the particles can be increased.

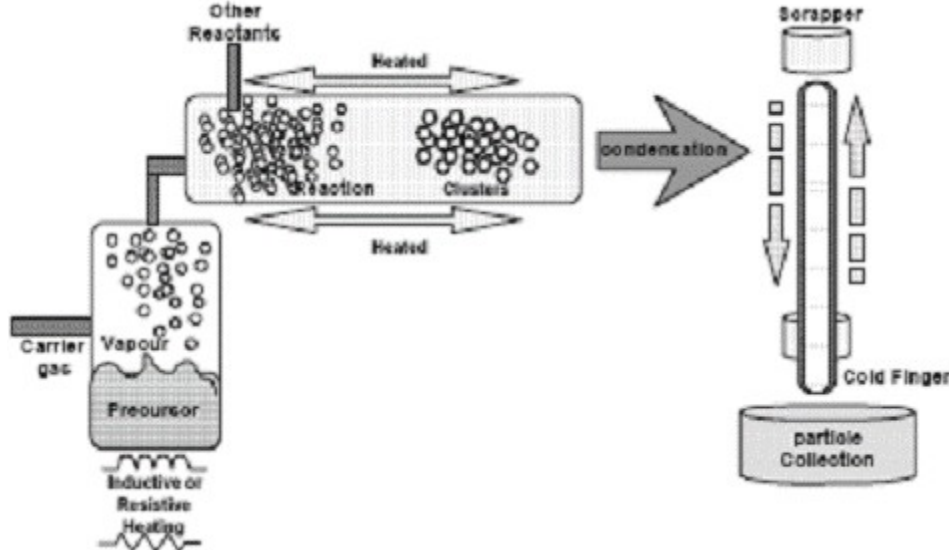
Care should be taken to prevent oxidation during the process of milling. For fabricating softer materials, usually harder balls will be chosen. Usually alumina and zirconium are used widely as balls synthesizing the nanomaterial. This is because they have high grinding resistance values.

In this method scaling can be achieved up to tonnage quantity of materials. In this technique non metal oxides cannot be fabricated due to contamination of milling media.

Chemical Vapor Deposition Method:

In a chemical vapor deposition (CVD) the atoms or molecules which are in gaseous state are allowed to react homogeneously or heterogeneously.

In a homogeneous CVD, the particles or atoms or molecules in the gas phase are diffused towards the cold surface. This occurs only due to thermophoretic forces.



The diffused particles can be scrapped from the cold surface to get nano powder. Also, the diffused particles are deposited into a substrate to form a film known as a particulate film.

In a heterogeneous CVD, a dense film of nano particles is obtained on the surface of a substrate. In the CVD method, particle size, crystal structure, and chemical composition can be controlled.

The schematic representation of CVD is shown in the figure above. The metal-organic precursor is introduced into the hot zone of the reactor with a flow controller.

The precursor is vaporized by using inductive heating or resistive heating. An inert gas like argon or neon is used as a carrier gas. The evaporated matter consists of hot atoms which undergo condensation into small clusters through homogeneous nucleation.

Other reactants are added to the clusters to control the chemical reactions. The cluster size is controlled by controlling the rate of evaporation, rate of condensation, and rate of gas flow. The condensed clusters are allowed to pass through the cold finger.

The nano particles are collected by using a scraper, as shown in the figure above.

The CVD method is used to produce defect-free nano particles.

Properties of Nano materials.

Physical properties:

Usually, for nano particles, the surface-to-volume ratio increases. Due to this, there is a variation in material properties. The following are the physical properties.

1. The inter-atomic spacing decreases with the nano scale. This is because of short-range core-core repulsion.
2. Melting point decreases due to the decrease in size of the particle.
3. Due to the increase in surface area, surface pressure decreases.

CHEMICAL PROPERTIES:-

1. When particle size is reduced to nano scale, the electronic bands in the metals

becomes narrow. This leads to the transformation of the delocalized electronic states into more localized molecular bands. This results in the increase of ionization potential.

2. The large surface to volume ratio, the variations in geometry and electronic structures takes place. This will have a strong effect on catalytic properties
3. The chemical potential increases
4. When particles size decreases the hydrogen absorbing capacity increases.
5. **Mechanical properties:-**

Most metals are made up of small crystalline grains. If these grains are nanoscale in size the interface area within the material greatly increases, which enhances its strength.

For example nano crystalline nickel is as strong as hardened steel.

At low temperatures a reduction in grain size lowers the transition temperature in steel from ductile to brittle the average grain size and yield strength are given by Hall Petch relation

$$\sigma = \sigma_0 + \frac{K}{\sqrt{d}}$$

σ = yield strength.

σ_0 = Friction Stress.

K = Constant of Proportionality.

d = Average grain size.

The relation between Hardness and average grain is given by

$$H = H_i + \frac{K}{\sqrt{d}}$$

H = Hardness.

H_i = Vickers hardness

K = Constant of Proportionality.

d = Average grain size.

At high temperatures, the nonmetals behave like superplastic materials. Superplastic materials will have extensive tensile deformation without fracture. In nonmetal's the occurrence of superplastic temperature decreases due to the decrease in grain size.

MAGNETIC PROPERTIES:-

In nano magnetic particles the magnetic properties are different from the bulk material.

When the material is at nanoscale, the particle will have only single domain

The coercivity and saturated value of magnetization values increases with a decrease in grain size. Nano particles are more magnetic than bulk material. The magnetic moment of nano cobalt particles of size 2nm is found to have 20% higher value than that of bulk cobalt.

Nano particles of non magnetic solids are found to be magnetic.

At small size the cluster become spontaneously magnetic.

The following table illustrates the behaviour of nano particles.

Metal	Bulk	Cluster
Na,K	Paramagnetic	Ferromagnetic
Fe,W,Ni	Ferromagnetic	Super paramagnetic
Rh	Paramagnetic	Ferromagnetic

Electrical properties:--

The ionization potential at small sizes is higher than that for the bulk materials.

This is because of quantum confinement effect the electronic bands in metals become narrower

In nanoceramics and magnetic composites the electrical conductivity increases with reduction in particle size. Bulk silicon is an insulator which becomes a conductor in nanophase.

Usually the electrical conductivity increases with reduction in particle size.

OPTICAL PROPERTIES:-

Nano crystalline systems have novel optical properties. If semi conductor particles are made small enough quantum effects come into play. This limits the energies of particles at which electrons and holes can exist.

Golden nano spheres of 100nm size appears orange in color.

Gold nano spheres of 50nm size appear green in color.

Therefore the optical properties can be changes by controlling the particle size.

Nano matericles can be used as large electro chrome devices.

APPLICATIONS OF NANO MATERIALS:-

Materials technology:-

1. Magnets made of nano crystalline yttrium- samarium-cobalt grains possess unusual magnetic properties. This is because they are having large interface area. Nano magnetic crystals will have high coactivity .they are used in motors and analytical instruments like magnetic resonance imaging (MRI)
2. Nano sized titanium dioxide and zincoxide are currently used in sunscreens. They absorb and reflect ultra violet rays (UV). They are transparent to visible light.
3. Nano engineered membrane could potentially lead to more energy- efficient water purification processes. They are used in desalination water plants by reverse osmosis.
4. Nano sized iron oxide is used in lipsticks as a pigment
5. Ceramics are hard, brittle and difficult to machine. However with a reduction in a grain size to thenano scale ductility in ceramics can be increased. Zirconia, normally a hard, brittle ceramic, and can be rendered super plastic. It can be deformed up to 300%
6. An important use of nano particles and nano tubes in composites carbon fibres and bundles of multiwall CNTs are used in composites having potential long term applications.
7. Carbon nano particle act as fillers in a matrix. They are used as a filter to reinforce car tires.
8. Clay particles based composites containing plastics and nano-sized flakes of clay also used in the fabrication of car bumpers.

9. Improved control porosity at the nanoscale has applications in textiles. Breathable water proof and stain resistant fabrics can be fabricated using nano materials.
10. Nano particles are having high surface area. They can be used as catalytically active agents.
11. Nano magnetic fluids can be prepared by using nano magnetic materials. Smart magnetic fluids are used as Vacuum seals. Viscous dampers cooling fluids magnetic separators.
12. Unusual color paints can be prepared by using nano particles; this is because nano particles exhibit different optical properties.

INFORMATION TECHNOLOGY:-

1. Nano scale fabricated magnetic materials are used in storage of data.
2. Nano crystalline zinc selenide, zinc sulphide, cds and telluride fabricated by sol-gel technique are the materials for high emitting phosphors and are used in flat panel displays.
3. Nano particles are used for information storage.
4. Nano dimensional photonic crystals are used in chemical/optical computer.
5. Coatings with thickness controlled at the nano scale are used in optoelectronic devices.

BIOMEDICALS:-

1. nano crystalline silicon carbide is used for artificial valves of heart because of low weight high strength and inertness
2. Biosensitive nano particles are used for tagging of DNA and DNA chips.
3. Nano structured ceramics readily interact with bone cells and hence are used as implant material
4. Controlled during delivery and controlling the decrease are possible with nano technology.
5. Nano materials are used as agents in cancer therapy

ENERGY STORAGE:-

1. Addition of nano particles (Cerium oxide) to diesel fuel improves fuel economy by reducing the degradation of fuel consumption over time
2. Nano particles are having high absorbing capacity nano particles of nickel, platinum are used in hydrogen storage devices
3. Nano particles are used in magnetic refrigeration
4. Metal nano particles are very useful in the fabrication of Ionic batteries.

Prepared By

P.V.Ramana Moorthy
Associate Professor,
SITAMS, Chittoor