

UNIT-II LESSON I

Objectives

At the end of this lesson we shall understand that valence electrons in metal are treated as molecules of gas. The free electrons in metal move from atom to atom among positive ion cores. The flow of current in metal is the consequence of drift velocity.

Introduction

In this lesson, we will study about free electron theory proposed by Drude to explain some of the outstanding properties of metals and drift velocity and its significance.

ELECTRICAL CONDUCTIVITY

3.1 Drude – Lorentz's Free Electron Theory of metals: [Classical Free Electron Theory]

In order to explain some of the outstanding properties of metals like very high electrical, thermal conductivities in the year 1900; Drude proposed free electron theory of metals. According to this theory valence electrons in metals are free to move inside the metal among positive ionic cores, these electrons are called conduction electrons and they are responsible for most of the properties of metals.

It is assumed that the metal consists of large number of atoms, which are held together, thus valence electrons move from atom to atom throughout the metal. When an electron leaves the parent atom, the atom loses its electrical neutrality, thus it is ionized. These ions are localized in the metal and the structural formation of these ions in three dimensional arrays is known as lattice. The positive ions are fixed in the lattice frame but constantly vibrating about their mean positions due to thermal agitations. The thermal agitation is responsible for random motion of electrons in the metal, hence free electrons in metal is treated as molecules of gas called electron gas.

When an electric field is applied, the negatively charged electrons move along the direction of positive field and hence produce current in the metal. In order to prevent the electrons accelerating indefinitely it is assumed that they collide elastically with metal ions, this leads to steady current, which is directly proportional to applied voltage and this explains ohm's law.

In the year 1909 Lorentz applied Maxwell – Boltzmann distribution law to electron gas to explain free electron theory of metals & hence it is known as Drude – Lorentz theory.

The assumptions of free electron theory of metals:

1. The free electrons in metal is treated as molecules of gas, hence it is assumed that they obey laws of kinetic theory of gases and in the absence of applied electric field energy associated with each electron. At temperature T is $\frac{3}{2} k_B T$, which is equal to kinetic energy of electron $\frac{3}{2} k_B T = \frac{1}{2} m v_{th}^2$,
 v_{th} = thermal velocity or r.m.s velocity
2. The field due to positive ion is constant and force of repulsion between electrons is very small hence it is neglected.

3. The flow of current in metal is due to applied field is consequence of drift velocity.

Drift velocity

The free electrons in metal are random in motion in the absence of electric field. However when electric field is applied, even though randomness persist but overall there is a shift in its position opposite to applied field. The electrons acquire kinetic energy and collide with ions, loses energy and this process continues until electrons acquire constant average velocity opposite to applied field. This velocity is called drift velocity.

When electric field E is applied, electrons acquires constant average velocity V_d
If 'm' is mass of electron and 'e' is charge carried by electron then the resistive force F_r

Acting on electron is equal to $m a = \frac{mV_d}{\tau}$

The driving force = $- eE$

Therefore $\frac{mV_d}{\tau} = - e E$ τ = mean collision time

$$V_d = \frac{eE\tau}{m}$$

Summary:

The free electrons in metal are responsible for most of the properties exhibited by metals

In metal the absence of electric field electrons are random in motion

The flow of current in metal is due to drift velocity

LESSON-II

Objectives

At the end of this lesson we shall understand that:

- The current flowing through it is directly proportional to drift velocity
- The current density is directly proportional to electric field

Introduction:

In this lesson we will study some important definitions like relaxation time, mean free path and mean collision time and expression for current in a conductor.

Relaxation time:

“The time required for the average vector velocity to decrease to 1/e times its initial value when the field is just turned off is called the relaxation time”.

Explanation:

In a metal due to the randomness in the direction of motion of the conduction electrons, the probability of finding an electron moving in any given direction is equal to finding some other electron moving in exactly the opposite direction in the absence of an electric field. As a result the average velocity of the electrons in any given direction becomes zero.

i.e. $\mathbf{v}_{av} = \mathbf{v}'_{av}$, in the absence of the field

However, when the metal is subjected to an external electric field, there will be a net positive value \mathbf{v}'_{av} for the average velocity of the conduction of the electrons in the direction of the applied field due to the drift velocity.

i.e. $\mathbf{v}_{av} = \mathbf{v}'_{av}$, in the presence of the field

If the field is turned off suddenly, the average velocity \mathbf{v}_{av} reduces exponentially to zero from the value \mathbf{v}'_{av} which is also the value of \mathbf{v}_{av} just when the field is just turned off.

The decay process is represented by the equation (figure 2)

$$\mathbf{v}_{av} = \mathbf{v}'_{av} e^{-t/\tau_r} \text{-----(1)}$$

Where t: time counted from the instant the field is turned off.

τ_r : constant called relaxation time

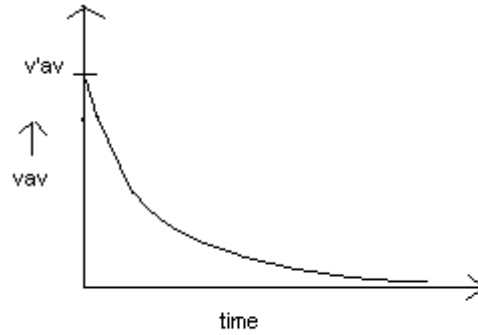


Figure: Decay of average velocity

In equation (1) if $t = \tau_r$, then

$$v_{av} = v'_{av} e^{-1}$$

$$v_{av} = \frac{1}{e} v'_{av}$$

Therefore the relaxation time can be defined as:

“Consequent to the sudden disappearance of an electric field, across a metal, the average velocity of its conduction electrons decays exponentially to zero & the time required in this process for the average velocity to reduce to 1/e times its value just when the field is turned off is known as relaxation time”.

Mean free path (λ)

According to kinetic theory of gases, the mean free path is the distance traveled by a gas molecule in between two successive collisions. In the classical theory of free electron model, it is taken as **the average distance traveled by the conduction electrons between successive collisions, with the lattice ions.**

Mean collision time (τ)

“The average time that elapses between two consecutive collisions of an electron with the lattice points is called mean collision time”. The averaging is taken over a large number of collisions.

If ' v ' is the velocity of the electrons which is the velocity due to the combined effect of thermal & drift velocities, then the mean collision time is given by,

$$\tau = \frac{\lambda}{v}$$

where λ is mean free path.

If v_d is the drift velocity, then $v_d = v_{th}$

$$\rightarrow v \approx v_{th}$$

In the case of metals, it can be shown that the relaxation time ' τ ' always refer to a single total velocity called Fermi velocity.

Mean free path

It is the average distance travelled by conduction electron between successive collisions.

Mean free path is about 10^{-7} m.

Electric Field (E)

The electric field is defined as potential per unit length of homogeneous

conductor of uniform cross-section. i.e $E = \frac{V}{L}$ volts/m

If 'L' is the length of a conductor of uniform cross – section & of uniform material composition & 'V' is the potential difference between its two ends, then the electric field 'E' at any point it is given by

$$E = \frac{V}{L} \text{ ----- (2)}$$

Conductivity (σ):

It is the physical property that characterizes the conducting ability of a material.

If 'R' is the uniform resistance of uniform material of length 'L' & area of cross – section 'A' then the electrical conductivity is given by

$$\sigma = \frac{1}{R} \times \frac{L}{A} \text{ ----- (3)}$$

If we consider the product σE , then from (2)

$$\sigma E = \frac{1}{R} \times \frac{L}{A} \times \frac{V}{L}$$

$$\sigma E = \frac{V}{RA}$$

Since $I = V/R$, we have

$$\sigma E = \frac{I}{A} \text{----- (4)}$$

Comparing (1) & (4) we get

$$J = \sigma E \text{----- (5)}$$

This represents the Ohm's law.

Resistivity (ρ):

Resistivity signifies the resistance property of the material & is given by the inverse of conductivity.

i.e $\rho = \frac{1}{\sigma} \text{----- (6)}$

Expression for current in a conductor:

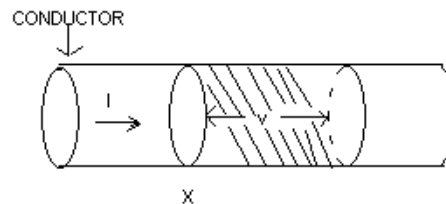


Figure: Current carrying conductor

Consider a conductor of uniform area of cross-section 'A', carrying a current 'I' as shown in figure (5). If 'v' is the velocity of the electrons, then the length traversed by the electron in unit time is 'v'.

Consider in the conductor, an imaginary plane at 'X' normal to the current's direction. If we consider the motion of electrons as a group starting from 'X', then they sweep a volume 'vA' of the conductor in unit time as indicated in the figure.

Let 'n' be the number of electrons/unit volume. Therefore

the number of electrons in a volume $vA = n(vA)$

In other words, the number of electrons crossing any cross-section in unit time
 $= n(vA)$

If 'e' is the charge on each electron crossing any section per second is the same as rate of flow of charge. Therefore

$$\text{the rate of flow of charge} = nevA \text{-----(1)}$$

Since the velocity acquired by the electron is due to an applied electric field, it is same as drift velocity v_d i.e $v = v_d$

$$\therefore I = nev_d A \text{----- (2)}$$

Expression for electrical conductivity:

Consider the motion of an electron, in a conductor subjected to the influence of an electric field. If 'e' is the charge on the electron and 'E' is the strength of the applied field, then the force 'F' on the electron is

$$F = -eE \text{----- (1)}$$

If 'm' is the mass of an electron then as per Newton's second law of motion force on the electron can be written as

$$F = -m \frac{dv}{dt} \text{-----(2)}$$

Equating (1) & (2)

$$eE = m \frac{dv}{dt}$$

$$\therefore dv = \frac{eE}{m} dt$$

Integrating both sides,

$$\int dv = \int_0^t \frac{eE}{m} dt$$

$$\therefore v = \frac{eE}{m} t \text{-----(3)}$$

where t: time of traverse

Let the time of traverse 't' be taken equal to the collision time 'τ'. Since by definition the collision time applies to an average value, the corresponding velocity in (3) also becomes the average velocity v.

$$v = -\tau \frac{eE}{m}$$

We have the expression for electrical conductivity 'σ' as

$$\sigma = \frac{J}{E} \text{-----} (5)$$

Where 'J' is the current density & $J = I / A$, where 'I' is the in the conductor & 'A' is the area of cross-section of the conductor.

$$\therefore \sigma = \frac{I}{AE} \text{-----} (6)$$

Now the distance covered by electrons in a unit time is v. They sweep a volume equal to vA (figure) in a unit time. If 'e' is the charge on the electron, 'n' is the number of electrons per unit volume, then the quantity of charge crossing a given point in the conductor per unit area per unit time i.e the current 'I' is

$$I = nevA \text{-----} (7)$$

Substituting for 'I' from (7) in (6) we get

$$\sigma = \frac{nevA}{AE}$$

$$\sigma = \frac{nev}{E} \text{-----} (8)$$

Substituting for 'v' from (4) in (8) we get

$$\sigma = \frac{ne}{E} \times \left(\frac{eE}{m} \right) \tau$$

$$\sigma = \frac{ne^2 \tau}{m} \text{-----} (9)$$

Equation (9) is the expression for electrical conductivity of a conductor.

Mobility of Electrons

The mobility of electrons is defined as the magnitude of the drift velocity acquired by the electrons in unit field. Thus if 'E' is the applied electric field, in which the electrons acquire a drift velocity v_d , then the mobility of electrons

$$\mu = \frac{v_d}{E} \text{-----(1)}$$

We have for Ohm's law,

$$J = \sigma E$$

Hence,

$$\sigma = \frac{J}{E}$$

$$\sigma = \frac{ne v_d}{A E} = ne \mu$$

$$\therefore \mu = \frac{\sigma}{ne} \text{----- (2)}$$

We know that,

$$\sigma = \frac{ne^2 \tau}{m}$$

Therefore (2) becomes,

$$\mu = \frac{ne^2 \tau}{m} \times \frac{1}{ne}$$

$$\text{Hence, } \mu = \frac{e \tau}{m} \text{----- (3)}$$

Mobility represents the ease with which the electrons could drift in the material, under the influence of an electric field. Different materials have different values for mobility.

Failure of classical free electron theory

Though the classical free electron theory has been successful in accounting for certain important experimental facts such as electrical and thermal

conductivities in metals: it failed to account for many other experimental facts among which the notable ones are specific heat, temperature dependence of σ and the temperature dependence of electrical conductivity on electron concentration.

(1) Specific Heat:

The molar specific heat of a gas at constant volume is

$$C_v = \frac{3}{2}R$$

As per the classical free electron theory, free electrons in a metal are expected to behave just as gas molecules. Thus the above equation holds good equally well for the free electrons also. But experimentally it was found that, the contribution to the specific heat of a metal by its conducting electrons was smaller than the classical value $(3/2)R$ by a factor of about 10^{-2} .

(2) Temperature dependence of electrical conductivity:

It has been observed that for metals the electrical conductivity ' σ ' is inversely proportional to the temperature 'T'.

$$\text{i.e. } \sigma_{\text{exp}} \propto \frac{1}{T} \text{-----(1)}$$

But according to the main assumptions of classical free electron theory

$$\frac{3}{2}KT = \frac{1}{2}mv_{\text{th}}^2$$

$$v_{\text{th}}^2 = \sqrt{\frac{3KT}{m}}$$

$$v_{\text{th}} \propto \sqrt{T}$$

Since the mean collision time τ is inversely proportional to the thermal velocity, we can write,

$$\tau \propto \frac{1}{v_{\text{th}}}$$

or

$$\tau \propto \frac{1}{\sqrt{T}} \text{----- (2)}$$

But σ is given by,

$$\sigma = \frac{ne^2\tau}{m}$$

Therefore the proportionality constant between σ and τ can be represented as
 $\sigma \propto \tau$

or

$$\sigma \propto \frac{1}{\sqrt{T}} \text{----- (3) [From proportionality (2)]}$$

Now from the proportionality representations (1) & (3), it is clear that the prediction of classical free electron theory is not agreeing with the experimental observations.

3. Dependence of electrical conductivity on electron concentration:

3. DEPENDENCE OF ELECTRICAL CONDUCTIVITY ON ELECTRON CONCENTRATION

SINCE $\sigma = ne^2\tau/m$, $\sigma \propto n$

METAL	VALENCY	$\sigma(\times 10^7) / (\Omega m)$	$n (\times 10^{28}) / m^3$
Cu	1	5.88	8.45
Ag	1	6.3	5.85
Zn	2	1.09	13.10
Cd	2	0.15	9.28
Al	3	3.65	18.06
Ga	3	0.67	15.30

• CONDUCTIVITY IS **NOT** $\propto n$

As per the classical free electron theory, the electrical conductivity ' σ ' is given by,

$$\sigma = \frac{ne^2\tau}{m}$$

where n : concentration of the electrons, therefore

$$\sigma \propto n$$

If we consider the specific cases of Zinc and Cadmium which are divalent metals, the electrical conductivities are respectively $1.09 \times 10^7 / \Omega m$ & $0.15 \times 10^7 / \Omega m$ which are much lesser than that for Copper and Silver, the values for which are $5.88 \times 10^7 / \Omega m$ & $6.3 \times 10^7 / \Omega m$ respectively. On the other hand,

the electron concentration for Zinc and Cadmium are $13.10 \times 10^{28} / \text{m}^3$ & $9.28 \times 10^{28} / \text{m}^3$ which are much higher than that for Copper and Silver, the values for which are $8.45 \times 10^{28} / \text{m}^3$ and $5.85 \times 10^{28} / \text{m}^3$ respectively.

LESSON-3

Objectives:

At the end of this lesson we shall understand that:

- All the free electrons cannot receive energy
- The electrons are not completely free as assumed in classical theory
- The free electrons obey Pauli's exclusion principle
- The energy levels of an electron in a metal are quantized

Introduction:

In this lesson, we will study Quantum free electron theory of metals, Fermi – Dirac distribution function and Fermi energy and Fermi factor,

Quantum Free Electron Theory of Metals

One of the main difficulties of classical free electron theory of metals is that, it allows all the free electrons to gain energy (as per Maxwell-Boltzmann statistics). Hence value obtained are much higher than experimental values. After development of quantum statistics, it is realized that only one percent of free electrons can thus absorb energy. This brings importance of Pauli's exclusion principle.

In the year 1928 Arnold Sommerfeld applied quantum mechanical conditions and Pauli's exclusion principle to explain failures of classical free electron theory of metals.

The following are some of the assumptions of quantum free electron theory:

- 1) The energy levels of free electrons in metals are quantized
- 2) The free electrons obey Pauli Exclusion Principle
- 3) The electrons travel in side metal with constant velocity, but they are confined within boundaries
- 4) The distribution of electrons are among various levels as per Fermi-Dirac statistics.
- 5) The force of attraction between electrons and positive ionic lattice also force of repulsion among electrons is neglected

Fermi-Dirac Statistics

According to Sommerfeld the electrons are not completely free in the metal as predicted in the free electron theory, i.e they are partially free and bound to the metal as a whole, hence electrons in metal can not be compared to gas

molecules; therefore, we cannot apply Maxwell-Boltzmann statistics. Moreover electrons are assumed to obey Pauli's exclusion principle hence they are governed by Fermi –Dirac statistics .

The electrons obeying Pauli's exclusion principle are identical and indistinguishable particles called 'Fermions'. The Fermi–Dirac distribution function gives most probable distribution of electrons. Hence in equilibrium at a temperature T , the probability that an electron has an energy E is given Fermi function $f(E)$.

E is energy level whose occupancy is being considered, E_F = Fermi level, it is constant for a particular metal.

At absolute zero $f(E) = 0$ for $E > E_F$ and $f(E) = 1$ for $E < E_F$

The Fermi level is highest state for the electrons to occupy at absolute zero, that mean at absolute zero Fermi level divides the occupied states from the unoccupied states.

Fermi Energy

In quantum free electron theory, the energy of electron in metal is quantized, therefore according to quantization rules, if there are N numbers of electrons, then there must be N number of allowed energy levels, since these electrons obey Pauli's exclusion principle.

An energy level can accommodate at most only two electrons, one with spin up and other with spin down, thus while filling energy levels, two electrons occupy the least level, two more next level and so forth, until all electrons are accommodated as shown in figure.

The energy of the highest occupied level at absolute zero temperature is called Fermi Energy and the corresponding energy level is called Fermi Level. The Fermi energy can also be defined as maximum kinetic energy possessed by free electron at absolute zero temperature, it is denoted by E_F .

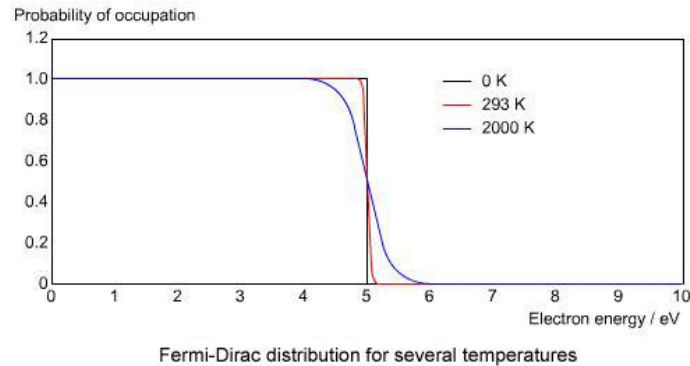
At absolute zero temperature, metal does not receive energy from surroundings, therefore all the energy levels below Fermi level is completely filled up and above the Fermi level all the energy levels are empty, If there are N electrons in the metal then highest occupied level is $N/2$ this level is called Fermi level and corresponding energy is called Fermi energy.

Fermi Factor

When the temperature is greater than the 0 K, metal receives thermal energy from the surroundings; however, at room temperature thermal energy received by metal is very small ($k_B T = 0.025$ eV, k_B = Boltzmann's constant), hence the electrons in the energy levels far below Fermi level cannot absorb this energy because there are no vacant energy levels above them, however the electrons just below Fermi level absorb this energy and may move to unoccupied energy

levels above Fermi level, though these excitations seems to be random, the occupation of various energy levels takes place strictly as per Fermi –Dirac distribution law.

Fermi function, $f(E) = 1/(1+e^{(E-E_F)/kT})$, where $f(E)$ is the probability of an electron occupying energy state E .



(i) For $T = 0K$ and $E > E_F$

$f(E) = 1/(1+e^{\infty}) = 1/\infty = 0$. ie no electron can have energy greater than E_F at 0K.

(ii) For $T = 0K$ and $E < E_F$

$f(E) = 1/(1+e^{-\infty}) = 1/1+0 = 1$. ie all electrons occupy energy states below E_F at 0K.

(iii) For $T > 0K$ and $E = E_F$

$f(E) = 1/(1+e^0) = 1/1+1 = 1/2$. ie 50% electrons can occupy energy states below E_F

above 0K.

Fermi level is defined as energy level at which the probability of electron occupation is one half or 50 %.

Summary of Lesson

Here we learnt that, in metal, free electrons are partially free, because they are bound to the metal as a whole, hence they cannot be compared to molecules of gas.

In metal there is extremely larger number of energy levels. The distribution of electrons among various energy levels is strictly as per Fermi -Dirac function. At 0 K all the energy levels below Fermi level is occupied and above Fermi level, energy levels are empty.

LESSON 4

Objectives

At the end of this lesson we shall understand that:

- The free electrons in metal can be treated as particles in a box
- The Fermi temperature is only theoretical concept
- The total energy of free electron is $\frac{3}{5} E_F$

Introduction

In this lesson, we will study number of available energy states in the range E and $E + dE$, Number of electrons per unit volume, Fermi energy, Fermi temperature and Fermi velocity.

Density of states

The electron energy levels in a material are in terms of bands. The number of levels in each band is extremely large and these energy levels are not evenly distributed in the band. At the highest energy the difference between neighboring levels is of the order of 10^{-6} eV. That means in a small energy interval dE there are still many discrete energy levels. Hence for easy calculations we introduce the concept of 'Density of States'. It is denoted by $g(E)$. The density of state can be defined as follows:

'It is the number of available states per unit volume per unit energy range'.

Number of available states per unit volume between energy range,

E and $E+dE = g(E) dE$.

Summary

Here we learnt that, in metal, free electrons are partially free, because they are bound to the metal as a whole, hence they cannot be compared to molecules of gas. In metal there is extremely larger number of energy levels. The distribution of electrons among various energy levels is strictly as per Fermi -Dirac function.

At 0 K, all the energy levels below Fermi level are occupied and above Fermi level, energy levels are empty.

LESSON-5

Objectives

At the end of this lesson we shall understand that:

The electron moving in metal under influence of external field possesses effective mass. The effective mass varies from solid to solid and it is a function of energy.

The drift velocity of free electrons in metal is equal to Fermi velocity.

Introduction

In this lesson, we study the merits of Quantum free electron theory.

Concept of effective mass

According to Sommerfeld, Quantum free electron theory of metals, the motion of free electrons in metals is considered not as motion of particles, but as passage of waves among periodic lattice. Hence the motion of electrons in metal can be treated as a wave packet. Hence velocity of electron is treated as group velocity. When field is applied to an electron; the wave packet travels under combined action of applied field and potential due to periodic lattice and due to this superposition of these fields the electron responds as if it possesses effective mass; this mass is different from its true mass with which it moves under the influence of external field alone. The effective mass is interpreted in terms of true mass. The Concept of Effective Mass shows that it is possible to deal with the motion of electrons in metal as semi classical manner. In vacuum the effective mass of electron is same as true mass and the Effective Mass varies from solid to solid.

Electrical Resistivity or Conductivity

According to Sommerfeld, Quantum free electron theory of metals the electrons are partially free not completely as assumed in classical free electron theory. Hence free electrons in metals obey Fermi –Dirac statistics. By applying Boltzmann transport equation and Fermi –Dirac statistics he got the equation for electrical conductivity of metals as,

In classical free electron theory it is assumed that Electrical Resistivity in metals is due to scattering of electrons and the scattering of electrons takes place due to lattice defects, dislocations, impurities etc, but according to Sommerfeld the motion of electrons in metals nothing but passage of waves in periodic lattice, if there is perfect periodicity and all ions are at rest, then the waves pass across the arrays without being scattering at all in such case mean free path is infinite, but no metal is free from impurities or lattice defects, that means there is always deviations from periodicity due to this, scattering of electron waves takes place, therefore lattice defects becomes major cause of electrical resistivity in metals and scattering of electron waves becomes the deciding factor for the mean free path of electrons.

Merits of quantum free electron theory

(1) Specific Heat :

According to quantum free electron theory, it is only those electrons that are occupying energy levels close to E_F which are capable of absorbing the heat energy to get excited to higher energy levels. Thus only a small percentage of the conduction electrons are capable of receiving the thermal energy input and hence the specific heat value becomes very small for the metals.

Therefore on the basis of quantum free electron theory

$$C_V = \left(\frac{2k_B}{E_F} \right) RT$$

Taking a typical value of $E_F = 5\text{eV}$ we get

$$\left(\frac{2k_B}{E_F} \right) = 10^{-4}$$

$$\therefore C_V = 10^{-4} RT$$

This agrees with the experimental values. Since C_V is very small, the energy of electrons is virtually independent of temperature.

(2) Temperature dependence of electrical conductivity:

The experimentally observed fact that electrical conductivity ' σ ' has a dependence on $\left(\frac{1}{T} \right)$ but not on $\frac{1}{\sqrt{T}}$ can be explained as follows.

The expression for electrical conductivity is given by

$$\sigma = \frac{ne^2 \tau_F}{m^*}$$

As per quantum free electron theory, $\tau_F = \frac{\lambda_F}{v_F}$

$$\therefore \sigma = \frac{ne^2 \lambda_F}{m^* v_F} \text{ ----- (1)}$$

As per quantum free electron theory E_F and v_F are essentially independent of temperature. But λ_F is dependent on temperature, which is explained as follows.

As the conduction electrons traverse in the metal, they are subjected to scattering by the vibrating ions of the lattice. The vibrations occur such that the displacement of ions takes place equally in all directions. If 'a' is the amplitude of vibrations, then the ions can be considered to present effectively a circular cross-section of area πa^2 that blocks the path of the electrons irrespective of the direction of approach. Since vibrations of larger area of cross-section should scatter more efficiently, it results in a reduction in the value of mean free path of the electrons,

$$\therefore \lambda_F \propto \frac{1}{\pi a^2} \text{ ----- (2)}$$

Considering the facts that,

- (a) the energy of a vibrating body is proportional to the square of the amplitude
 - (b) the energy of ions is due to thermal energy
 - (c) thermal energy is proportional to the temperature (T).
- Therefore we can write,

$$a^2 \propto T$$

$$\therefore \lambda_F \propto \frac{1}{T} \text{ ----- (3)}$$

From (1) & (3) we get,

$$\sigma \propto \left(\frac{1}{T} \right)$$

Thus the dependence of 'σ' on 'T' is correctly explained by the quantum free electron theory.

(3) Electrical conductivity and electron concentration:

By classical free electron theory, it was not possible to understand why metals such as Al and Ga which have 3 free electrons per atom have lower electrical conductivity than metals such as copper and silver which possess only one free electron per atom. But according to quantum free electron theory the same can be explained. We have the equation for electrical conductivity as:

$$\therefore \sigma = \frac{n e^2 \lambda_F}{m^* v_F}$$

From this equation it is clear that, the value of σ depends on both 'n' and the ratio $\frac{\lambda_F}{v_F}$. If we compare the cases of copper and aluminum, the value of 'n'

for Al is 2.13 times higher than that of copper. But the value of $\frac{\lambda_F}{v_F}$ for copper is about 3.73 times higher than that of Al. Thus, the conductivity of copper exceeds that of aluminum.

Comparison between Classical free electron theory and quantum free electron theory

Similarities:

- 1) The valence electrons are treated as though they constitute an ideal gas.
- 2) The valence electrons can move easily throughout the body of the solid.
- 3) The mutual repulsion between the electrons and the force of attraction between electrons and ions are considered insignificant.

Differences between the two theories:

Sl.no	Classical free electron theory	Quantum free electron theory
1.	The free electrons which constitute the electron gas can have continuous energy values.	The energy values of the free electrons are discontinuous because of which their energy levels are discrete.
2.	It is possible that many electrons may possess same energy.	The free electrons obey the 'Pauli's exclusion principle'. Hence no two electrons can possess same energy.
3.	The patterns of distribution of energy among the free electrons obey Maxwell-Boltzmann statistics.	The distribution of energy among the free electrons is according to Fermi-Dirac statistics, which imposes a severe restriction on the possible ways in which the electrons absorb energy from an external source.

Solved Problems

1. Calculate the drift velocity and thermal velocity of free electrons in copper at room temperature, (300 K), when a copper wire of length 3 m and resistance 0.022 Ω carries a current of 15 A.

Given: $\mu = 4.3 \times 10^{-3} \text{ m}^2/\text{Vs}$.

Solution: Given that $L = 3 \text{ m}$, $R = 0.022$, $I = 15 \text{ A}$, $T = 300 \text{ K}$, $\mu_{\text{Cu}} = 4.3 \times 10^{-3} \text{ m}^2/\text{Vs}$. $V_d = ?$ and $V_{\text{th}} = ?$

Voltage drop across the copper wire is given by

$$V = IR = 15 \times 0.022 = 0.33 \text{ V}$$

$$\text{Electric Field, } E = V / L = 0.33 / 3 = 0.11 \text{ V/m}$$

$$\text{Drift velocity, } V_d = E \times \mu = 0.11 \times 4.3 \times 10^{-3} = 0.473 \times 10^{-3} \text{ m/s.}$$

$$\text{Thermal Velocity, } V_{\text{th}} = \sqrt{3kT / m}$$

$$= \sqrt{3 \times 1.387 \times 10^{-23} \times 300 / 9.11 \times 10^{-31}}$$

$$= \mathbf{1.17 \times 10^5 \text{ m/s.}}$$

2. Find the relaxation time of conduction electrons in a metal of resistivity $1.54 \times 10^{-8} \text{ ohm-m}$, if the metal has $5.8 \times 10^{28} \text{ electrons /m}^3$

$$\text{Given } \rho = 1.54 \times 10^{-8} \text{ ohm-m} \quad n = 5.8 \times 10^{28} \text{ electrons /m}^3$$

$$\text{Resistivity of metal} = \rho = \frac{m}{n e^2 \tau}$$

$$\mathbf{\text{Relaxation time} = \tau = 3.97 \times 10^{-14} \text{ s}}$$

CONDUCTIVITY IN SEMICONDUCTORS

LESSON-6

Objectives:

- To study the semiconductor energy level diagram
- To derive an expression for hole and electron concentration.
- To observe the Hall Effect in a semiconductor.

Based on the electrical conductivity of the materials they can be classified into three categories. Conductors- conductors are the materials that allow the electricity to pass through them. Eg: aluminum, copper, silver, etc. Insulators- insulators are the materials that do not allow the electricity to pass through them. Eg: paper, glass, etc.

Semiconductors- semiconductors are materials whose electrical conductivity lies between that of conductors and insulators. Eg: silicon and germanium.

Conductivity in semiconductors:

Atoms of silicon and germanium have four electrons in their outer most shell. These electrons form covalent bond with the neighbouring atom and not free at low temperature. Hence they behave like insulators. However when a small amount of thermal energy is available from the surroundings a few covalent bonds are broken and few electrons are set free to move. Even at room temperature good number of electrons is dissociated from their atoms and this number increases with rise in temperature. This leads to conductivity. When an electron is detached from the covalent bond, it leaves a vacancy which behaves like a positive charge. An electron from a neighbouring atom can move onto this vacancy leaving a neighbor with a vacancy. Such a vacancy is called a hole. Hole acts as a positive charge.

Types of semiconductors:

In a semiconductor there are two kinds of current carriers- Electrons and Hole. In a pure semiconductor electrons and holes are always present in equal numbers and it is called intrinsic semiconductor.

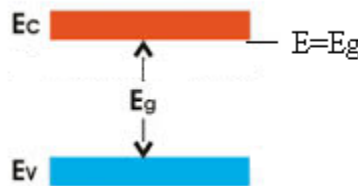
Conductivity of the semiconductors can be changed by adding small amount of impurities (other elements) to it. These impurities are called dopants. Such semiconductors are impure or extrinsic semiconductors. When a few atoms of trivalent or pentavalent element is added into pure crystals of Ge or Si an extrinsic semiconductors are produced. The process of adding impurity atoms is called Doping. When pentavalent impurity atoms like arsenic, antimony, phosphorous, etc are added to pure germanium or silicon crystal, we get an extrinsic semiconductor known as n-type semiconductor. When trivalent impurity atoms like indium, boron, gallium, aluminum, etc are added to pure

germanium or silicon crystal, we get an extrinsic semiconductor known as p-type semiconductor.

Concentration of electrons and holes in intrinsic semiconductors:

With an increase in temperature covalent bonds are broken in an intrinsic semiconductor and electron-hole pairs are generated. We expect that a large number of electrons can be found in the conduction band and similarly, a large number of holes in the valence band. As electrons and holes are charged particles, they are together called charge carriers. Charge carriers are the number of electrons in the conduction band per unit volume (n) and number of holes in the valence band per unit volume (p) of the material. Carrier concentration is known as the density of charge carriers.

Expression for concentration of electrons in intrinsic semiconductor:



Let dn be the number of electrons whose energy lies in the energy interval E and $E+dE$ in the conduction band. Then,

$$dn = g(E)f(E)dE$$

where $g(E)dE$ is the density of states in the energy interval E and $E+dE$ and $f(E)$ probability that a state of energy is occupied by an electron.

The electron density in the conduction band is given by integrating the above equation between the limits E_C and ∞ . $E_C \rightarrow$ energy corresponding to bottom edge of the conduction band and $\infty \rightarrow$ energy corresponding to the top edge of the conduction band. Since $f(E)$ of the electrons occupying the upper levels of conduction band rapidly approaches 0 for higher energies, the upper limit is taken as ∞ . Then,

$$n = \int_{E_C}^{\infty} g(E) f(E) dE$$

The density of states in the conduction band is given by,

$$g(E) dE = \frac{4\pi}{h^3} (2m_e^*)^{3/2} E^{1/2} dE \quad \text{for } E > E_C$$

E_C corresponds to the potential energy of the electron at rest. Thus $(E-E_C)$ will be the kinetic energy of the conduction electron at higher energy levels. Thus,

$$g(E) dE = \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_C)^{1/2} dE$$

The probability of electron occupying an energy level is given by,

$$f(E) = \frac{1}{1 + \exp \left[(E - E_f) / k_B T \right]}$$

When the number of particles is very small compared to the available energy levels, $f(E)$ occupied by more than one electron is very small thus it can be written as

$$f(E) = \exp \left[-(E - E_f) / k_B T \right]$$

Using the value of $g(E)$ and $f(E)$ we can write

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} \int_{E_C}^{\infty} (E - E_C)^{1/2} e^{(E_f - E_C) / k_B T} dE$$

or

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_f - E_C) / k_B T} \int_{E_C}^{\infty} (E - E_C)^{1/2} e^{-(E - E_C) / k_B T} dE$$

This integral is of the standard form which has a solution of the form,

$$\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{\sqrt{x}}{2a\sqrt{a}}$$

where $a = 1/k_B T$ and $x = (E - E_C)$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} e^{(E_f - E_C)/k_B T} \left[\frac{\sqrt{\pi}}{2} (k_B T)^{3/2} \right]$$

Rearranging,

$$n = 2 \left[\frac{2\pi m_e^* k_B T}{h^2} \right]^{3/2} e^{-(E_C - E_f)/k_B T}$$

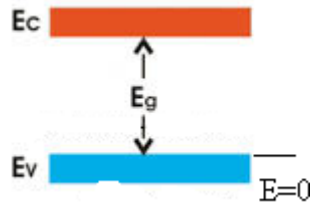
This is the expression for the electron concentration in the conduction band of an intrinsic semiconductor. Designating N_C to be the effective density of states in the conduction band as,

$$N_C = 2 \left[\frac{2\pi m_e^* k_B T}{h^2} \right]^{3/2}$$

The electron concentration in the conduction band of an intrinsic semiconductor can be written as,

$$n = N_C e^{-(E_C - E_f)/k_B T}$$

Expression for concentration of holes in intrinsic semiconductor:



Let dp be the number of holes whose energy lies in the energy interval E and $E+dE$ in the valence band. Then,

$$dn = g(E)[1 - f(E)]dE$$

where $g(E)dE$ is the density of states in the energy interval E and $E+dE$ and $[1 - f(E)]$ probability that a state of energy is occupied not by an electron. Since $f(E)$ is the probability of occupancy of an electron, then the probability that the energy state is vacant is given by $[1 - f(E)]$.

Thus,

$$f(E) = 1 - \frac{1}{1 + e^{-(E_f - E)/k_B T}} \approx e^{-(E_f - E)/k_B T}$$

the density of states in the valence band is given by,

$$g(E)dE = \frac{4\pi}{h^3} (2m_h^*)^{3/2} E^{1/2} dE$$

The top edge of the valence band E_V corresponds to the potential energy of a hole at rest. Thus $(E_V - E)$ will be the kinetic energy of the hole at lower energy levels. Thus,

$$g(E)dE = \frac{4\pi}{h^3} (2m_h^*)^{3/2} (E_V - E)^{1/2} dE$$

Number of holes in the energy interval E and $E+dE$ is given by,

$$dp = \frac{4\pi}{h^3} (2m_h^*)^{3/2} (E_V - E)^{1/2} e^{-(E_f - E)/k_B T} k_B dE$$

To calculate the hole density this equation should be integrated between limits $-\infty$ and E_V . Thus the hole density is given by,

$$\begin{aligned} p &= \frac{4\pi}{h^3} (2m_h^*)^{3/2} \int_{-\infty}^{E_V} (E_V - E)^{1/2} e^{-(E_f - E)/k_B T} dE \\ &= \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{-(E_f - E_V)/k_B T} \int_{-\infty}^{E_V} (E_V - E)^{1/2} e^{-(E_V - E)/k_B T} dE \end{aligned}$$

This integral is of the standard form which has a solution of the form,

$$\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{\sqrt{\pi}}{2a\sqrt{a}}$$

where $a=1/kT$ and $x=(E_V - E)$, thus $dx=-dE$. The lower limit of the x becomes ∞ when $E=-\infty$. If we change the order of integration we introduce another minus sign,

$$p = \frac{4\pi}{h^3} (2m_h^*)^{3/2} e^{-(E_f - E_V)/k_B T} \left[\frac{\sqrt{\pi}}{2} (k_B T)^{3/2} \right]$$

Rearranging,

$$p = 2 \left[\frac{2\pi m_h^* k_B T}{h^2} \right]^{3/2} e^{-(E_f - E_V)/k_B T}$$

This is the expression for the hole concentration in the valence band of an intrinsic semiconductor. Designating N_V to be the effective density of states in the valence band as,

$$N_V = 2 \left[\frac{2\pi m_h^* k_B T}{h^2} \right]^{3/2}$$

The hole concentration in the conduction band of an intrinsic semiconductor can be written as, $p = N_V e^{-(E_f - E_V)/k_B T}$

Law of mass action:

Statement: for a given semiconductor, the product of the electron and hole concentration is a constant at a given temperature and is equal to the square of the intrinsic carrier concentration.

Considering the electron concentration (n) and hole concentration (p) in a semiconductor,

$$n = N_C e^{-(E_C - E_f)/k_B T}$$

$$p = N_V e^{-(E_f - E_V)/k_B T}$$

Therefore, $np = N_V e^{-(E_f - E_V)/k_B T} N_C e^{-(E_C - E_f)/k_B T}$

$$np = N_C N_V e^{E_g/k_B T}$$

for an intrinsic semiconductor $n=p=n_i$,

$$np = n_i^2$$

Fermi level in intrinsic semiconductor:

In a pure semiconductor, the electrons in the conduction band clusters very close to the bottom edge of the band, and the electrons are located at the bottom edge of the conduction band. Similarly the holes are at the top edge of the valence band. The electron concentration is given by,

$$n = N_C e^{-(E_C - E_f)/k_B T}$$

And the hole concentration is given by,

$$p = N_V e^{-(E_f - E_V)/k_B T}$$

for an intrinsic semiconductor $n=p$

therefore,
$$N_C e^{-(E_C - E_f)/k_B T} = N_V e^{-(E_f - E_V)/k_B T}$$

taking log on both sides,

$$-\frac{(E_C - E_f)}{k_B T} = \ln \frac{N_V}{N_C} - \frac{(E_f - E_V)}{k_B T}$$

Considering the value for N_V and N_C and rearranging,

$$E_f = \frac{3}{4} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right) + \frac{(E_C + E_V)}{2}$$

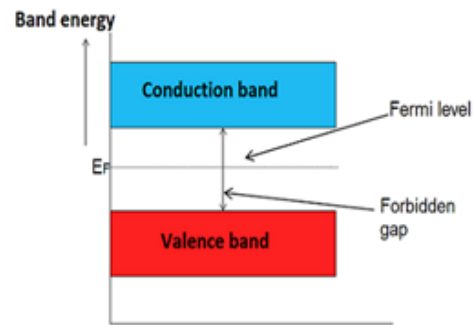
If the effective mass of free electron is equal to the effective mass of free hole,

$$m_h^* = m_e^*$$

We get,

$$E_f = \frac{(E_C + E_V)}{2} = \frac{E_g}{2}$$

Figure below shows the Fermi level in an intrinsic semiconductor.



Fermi Level in an Intrinsic Semiconductor

LESSON -7

Hall Effect:

When a conductor carrying a current is placed in a transverse magnetic field, an electric field is produced inside the conductor in a direction normal to both the current and the magnetic field. This phenomenon is known as Hall Effect and the generated voltage is called as Hall voltage.

Illustration of Hall effect:

Consider a thin rectangular semiconductor wafer mounted on an insulating strip and the two pairs of electrical contacts are provided on the opposite sides of the wafer. A pair of contacts is connected to a constant current source and the other pair is connected to a sensitive voltmeter. The whole arrangement is mounted between two pole pieces of an electromagnet so that the magnetic field acts perpendicular to the lateral faces of the semiconductor wafer.

Hall coefficient:

Hall coefficient ' R_H ' is defined as Hall field per unit current density per unit magnetic induction. When a potential difference is applied across the ends of a p-type semiconductor, the current (I) is given by,

$$I = peAv_d$$

where p - concentration of holes, e - charge of a hole, A - area of cross-section of the end face, v_d average drift velocity

Current density J is

$$J = \frac{I}{A} = pev_d$$

When the force due to the magnetic field F_L is in equilibrium with the force due to the transverse electric field F_E

$$eE_H = ev_dB$$

i.e.
$$\frac{E_H}{B} = \frac{1}{v_d}$$

since $v_d = \frac{J}{pe}$, therefore, $\frac{E_H}{JB} = \frac{1}{pe}$

the ratio $\frac{E_H}{JB}$ is known as Hall co-efficient, given by,

$$R_H = \frac{E_H}{JB}$$

For a p-type semiconductor the carriers are positively charged holes,

$$R_H = \frac{1}{pe}$$

For an n-type semiconductor the carriers are negatively charged electrons,

$$R_H = \frac{1}{ne}$$

Hall voltage (V_H):

If a rectangular slab of semiconductor of thickness t and width w is taken. A current I is passed through it with potential difference V . when the slab is placed between two pole pieces of an electromagnet, the Hall voltage V_H is given by,

$$V_H = E_H w = R_H JBw$$

Hall voltage is given by,

$$V_H = \frac{R_H IBw}{wt} = \frac{R_H IB}{t}$$

where $J=I/A$, $A=wt$.

Two Probe method and four probe method

In four probe (four probes or wires are used) resistance or conductivity measurements, you send current through two probes and measure the resulting voltage with two other probes. The voltage drop in the current wires does not contribute error to the voltage measurement. There is very little current flow in the voltage sense wires. With two probes, the voltage drop from the current flow will not be separable from the voltage drop in the device under test. It may be a significant error in low resistance devices.

Summary:

By studying the energy level diagram we can derive an expression for hole and electron concentration. With the help of Hall Effect one can find that whether the given material is n-type or p-type.

SUPERCONDUCTIVITY

LESSON-8

The conductors at normal conditions have some resistance in spite of their highest purity. But certain metals and alloys, the resistance drops to zero or a negligible value at very low temperature close to absolute zero (0K) and the metal is said to be superconductor. The resistance of metal drops suddenly to zero value at a particular temperature called critical temperature (T_c) Transition temperature. This value is different for different materials. Superconductivity is an electrical phenomenon due to which the electrical resistivity of some metals falls suddenly to zero when they are cooled below their critical temp, and will have 100% conductivity. Till now 33 elements, alloys ceramic materials and organic compounds have been identified.

Ex: Hg, Liquid He, Liquid nitrogen, lead, Thorium, Thallium, Nb, Sn, Zn, Al etc.

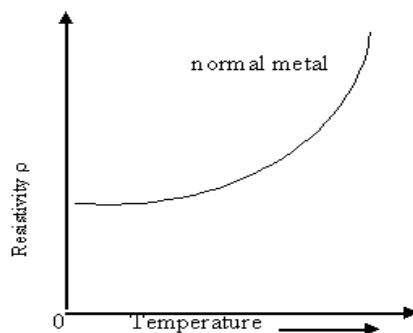
The phenomenon of superconductivity was first discovered by H Kamerlingh onnes in 1911.

The superconducting state of metal can be destroyed by

- when the temperature of the metal is increased above critical temp.
- when a strong magnetic field is applied to super conducting state
- when a high current density exists in the conductor

Many materials have critical temperature in the range of 1K to 20K. In certain ceramics the critical temp. Will be closed to 100 K and is termed as high temperature Superconductors.

Temperature Dependence electrical resistivity:



Not all metals and good conductors are superconductors. Most superconductors are relatively poor conductors at room temp. Even the ferromagnetic elements are not superconductor Electric current is the flow of

electron amongst the positive ion in a metallic crystal. Increase in temperature will increase the thermal agitation of ions above their mean position and hence the conductivity decreases. On the other hand, as the temperature decreases the thermal agitation decreases, hence electrons are more mobile, which reduces the resistance of the conductor. In normal conductors the resistance decreases with decrease in temperature, reaches a fixed minimum value at absolute temperature. In case of super conductors basically have higher resistivity at room temperature than the good conductors, the resistance gradually decreases with decrease in temperature, at a particular temperature the value of resistance suddenly drops to zero and the metal will have 100% conductivity. The temperature at which the resistance suddenly drops at zero is called the critical temperature. The critical temperature is different for different super conductors. Pure metal will have a fixed value

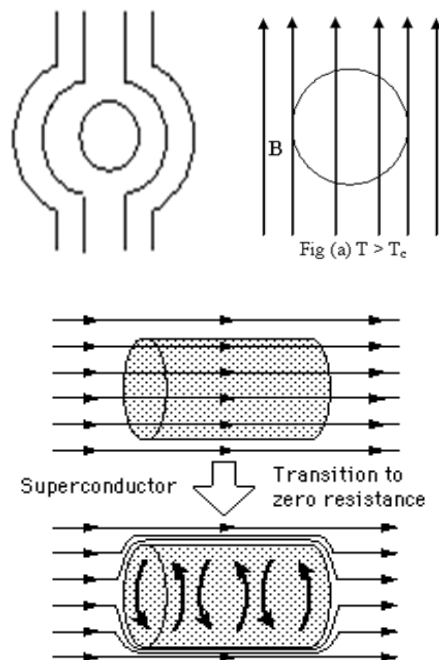
EFFECT OF MAGNETIC FIELD:

MEISSNER EFFECT:

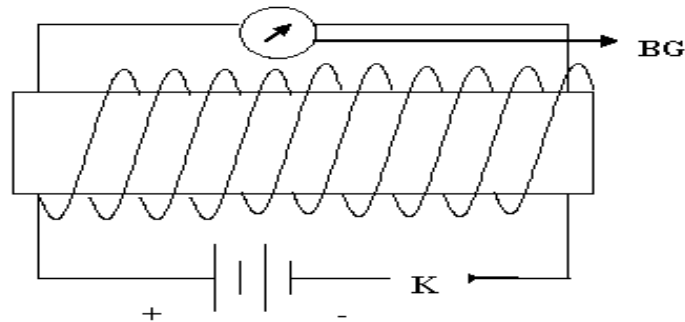
A Super conductor kept in a magnetic field expels the magnetic flux out of its body when it is cooled below critical temperature and becomes perfect diamagnetic. This is known as Meissner effect. When the magnetic field is increased or its temperature rises above T_c it becomes normal conductor and allows the magnetic field to pass through it when the temperature of the specimen increases the value of the critical magnetic field decreases correspondingly.

The critical field is different for different substances

Meissner Effect



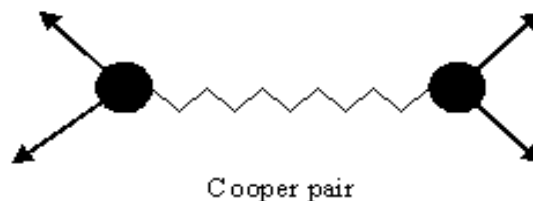
Demonstration of Meissner effect:



Consider two coils, a primary and a secondary are wound on a superconducting material, which is kept above its critical temperature. Connect a DC battery with a plug key. The secondary coil is connected to galvanometer BG. When the key is closed current flows in the primary coil and sets up a magnetic field in it. The magnetic flux immediately links with the secondary coil. This amounts to the change in magnetic flux in the secondary coil and therefore, momentary current flows through BG which shows deflection. When the current in the primary coil reaches a steady value, the magnetic flux also become steady. Hence there will be no change in the magnetic flux linked with secondary coil. The BG now does not show any deflection. Now the temperature of the superconductor is gradually decreased. As soon as temperature reaches below the critical temperature, the BG suddenly shows a momentary deflection indicating a change in the magnetic flux linked with the secondary coil. This change in the magnetic flux can be attributed to expulsion of the magnetic flux from the body of superconducting material. This magnetic expulsion continues for all values of $T \leq T_c$.

LESSON-9

B C S THEORY of Superconductivity:



During the flow of current in a superconductor, when an electron comes near a positive ion core of the lattice, it experiences an attractive force because of the opposite charge polarity between the electron and the core. The ion core will be displaced from its position which is called lattice distortion. The ion core while returning to original site from distorted, position overshoots and hence oscillates around its mean position before it comes to rest. While doing so, a phonon is created (quantized mechanical/ elastic oscillation in a solid, need a medium). Now an electron which comes near that place will also interact with the distorted lattice, which tends to reduce the energy of the electron. Because of the reduction of energy during the interaction the electrons are in their lower energy states get attracted and form a bound pair called cooper pair (is a bound pair of electrons formed by the interaction between electrons with opposite spin and momenta in a phonon field. This pair formation takes place through phonon interaction and it is called Electron-lattice-electron interaction. The attractive force between the electrons is maximum when the two electrons forming a pair have equal and opposite momenta and spin. The interaction of electron is attractive only when the phonon energy is more than the electronic energy. Temperature below T_c close to 0K, electron- lattice-electron interaction with the help of phonons continues and all the electrons form a cloud of cooper pair, which in turn moves through the crystal. This forms an ordered state of the conduction electrons. There is no scattering on the lattice atoms, have no resistance to flow. Therefore the conductivity becomes infinity which is named as superconductivity.

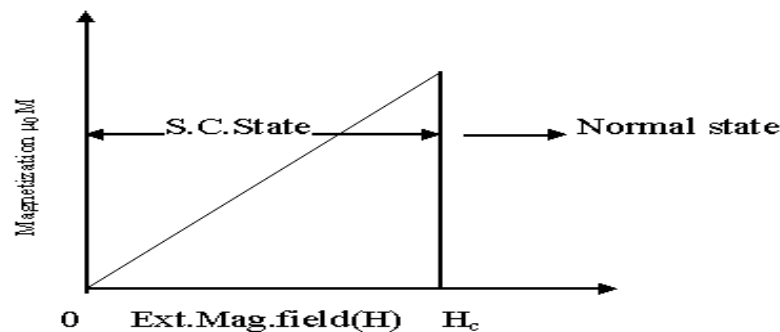
TYPES OF SUPERCONDUCTORS:

They are of two types:

- Type 1 (Soft) superconductors
- Type 2 (Hard) superconductors

Type 1 (soft) Superconductors:

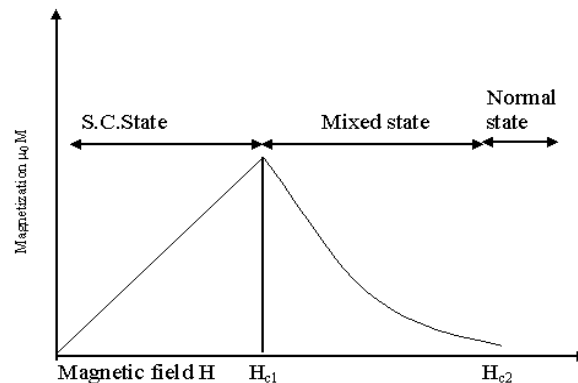
Type1 or soft superconductors are those in which the destruction of the sc state by a magnetic field occurs sharply.



The magnetic field at which a superconductor transits to a normal state is called the critical magnetic field (H_c). The critical field value for type 1 sc are found to be very low. The dependence of magnetic moments on H for type 1 sc is as shown in fig. If the applied field exceeds (H_c) then the material becomes normal conductor. Hence they are not used for coil in superconducting magnets. Examples: Al, Pb, tin, mercury.

Type II (Hard) superconductors:

Type II superconductors are those in which the destruction of the sc state by a mag. field takes place gradually. The transition from the sc state to normal state occurs between lower critical field H_{c1} and upper critical field H_{c2} . At H_{c1} the magnetic flux lines begin and H_{c2} the field penetrates completely.



Between H_{c1} & H_{c2} , the material exists in a mixed state. It exhibits both normal & sc

Type II superconductors have higher values of T_c & H_c and hence require a greater magnetic field. Type II superconductor has a higher resistance to magnetic field induced and therefore widely used in the coils of superconducting magnets. Examples: Niobium, Tantalum, alloys of Niobium, Zn, Chromium, niobium-tin (Nb_3Sn), Nb-Al, Nb-Ge etc.

HIGH TEMPERATURE SUPER CONDUCTOR (HTSC):

With the low temperature superconductor practical application becomes limited as they use expensive liquid helium (BP=4.2K) to reach the sc state. HTSC have a T_c value around 100K such superconductors can be achieved using liquid nitrogen (BP=77K) which is 500 times cheaper than liquid helium. High temperature superconductors are not metals & intermetallic compounds, but are oxides which fall under the category of ceramics. Ceramics are mostly anti ferromagnetic. Most of them are based on copper oxides with other metallic elements.

The modern high temperature superconductors have a complex unit cell structure with oxygen. such cells are made of 1 atom of rare earth metal, 2

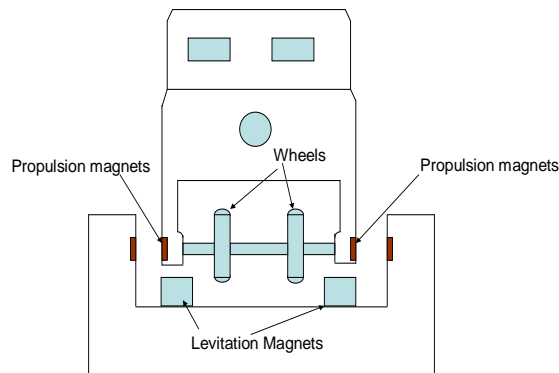
atom of barium, 3 atoms of copper and 7 atoms of oxygen, referred to as 1-2-3 superconductors.

Two compounds using bismuth, strontium, calcium, copper and oxygen had $T_c = 100\text{K}$ and using mercury, thallium barium, calcium, copper and oxygen had $T_c = 139\text{K}$.

LESSON-10

APPLICATION OF SUPER CONDUCTORS:

MAGLEV VEHICLE:



Magnetically levitated vehicles are called Maglev vehicles. They are made use of in transportation by being set afloat above a guideway. Here the friction is eliminated. With such arrangement, great speeds could be achieved with low energy consumption. It works based upon Meissner effect. The vehicle consists of superconducting magnets built into vehicles base. There is an Aluminum guideway over which the vehicle will be floating. The levitation is produced by enormous repulsion between two powerful fields, one produced by the superconducting magnet in the vehicle and the other one by the electric currents in the aluminum guideway. Vehicle wheels will be retracted into the body, when it starts levitation. While stopping, the wheels are drawn out. The speed is around 400km/h in test drives in Japan.

UNIT-4

Objectives

- At the end of lesson we shall understand about,
 - Static dielectric constant.
 - Types of Polarizations.
 - Internal or local fields in solids and liquids.
 - Lorentz field in cubic materials.
 - Clausius Mossotti equation.
 - Frequency dependence of dielectric constant.
 - Ferroelectric materials and applications.

Introduction

A **dielectric** is a substance that is highly resistant to the flow of an electric current. In other words a dielectric is electrically non conducting material that provides electrical insulation between two media (conductors) which are at different potentials. Eg - Glass, Wax paper, Ceramics, Porcelain. When a dielectric medium interacts with an applied electric field, charges are redistributed within its atoms or molecules. This redistribution alters the shape of an applied electrical field both inside the dielectric medium and in the region nearby. When two electric charges move through a dielectric medium, the interaction energies and forces between them are reduced.

Dielectric Constant

Faraday discovered that the capacitance of the condenser increases when the region between the plates is filled with dielectric. If C_0 is the capacitance of the capacitor without dielectric and C is the capacitance of the capacitor with dielectric then the ratio C / C_0 gives ϵ_r called relative permittivity or Dielectric constant, Also for a given isotropic material the electric flux density is related to the applied field strength by the equation $D = \epsilon E$, Where ϵ is Absolute

permittivity. In SI system of units the relative permittivity is given by the ratio of absolute permittivity to permittivity of free space. $\epsilon = \epsilon_0 \epsilon_r$. ϵ_0 is permittivity of free space. ϵ_r is relative permittivity or dielectric constant. For an isotropic material, under static field conditions, the relative permittivity is called static dielectric constant. It depends on the structure of the atom of which the material is composed.

Dipole: A dipole is an entity consisting equal number of positive and negative charges separated by a small distance. A dipole moment is a vector directed from positive field.

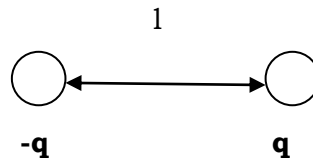


Fig 1. Charges separated by small distance

Polarization: The displacement of charges in the atoms or molecules of a dielectric under the action of applied field leading to the development of dipole moment is called polarization.

Electrical polarization

The polarization of the dielectric is the process of formation of dipoles or alignment of already existing dipoles by the application of an electric field on the dielectric material. The ratio of induced dipole moment to the effective applied electric field is called polarizability.

Polar and non-Polar dielectrics

In dielectrics there are no free electrons, the center of positive charges are centered or concentrated at the center of atom and center of negative charges are concentrated in the electron cloud. With the center of gravity positive charges coincide with center gravity of negative charges, then it neutralizes each other effects; hence their dipole moment is zero. Such dielectrics are called

non-polar dielectrics. In some other dielectrics like water, center of gravity of positive charges never coincides with center of gravity of negative charges even in the presence of applied field. In such dielectrics each molecule behaves as if it contains a pair of positive and negative charges separated by a distance (10-30m). Hence they have permanent dipole moment. They are known as **polar** dielectrics.

Consider a dielectric material placed between two plates of a parallel plate capacitor as shown in figure 2. Let a *dc* potential be applied between the plates; the atomic dipoles in the material align in the electric field. The mean position of electrons will align towards the positive plate of capacitor and mean position of positively charged nucleus will align towards negative plate of capacitor. Inside the material the dipoles formed, align such that positively charged particles are attracted towards the negatively charged particles. In fact, at the surface of dielectric layer, negative charge is formed near positively charged plate of capacitor; a layer of positive charge is formed adjacent to the negatively charged plate of capacitor, these charges on the surface of dielectric material is called polarized charges.

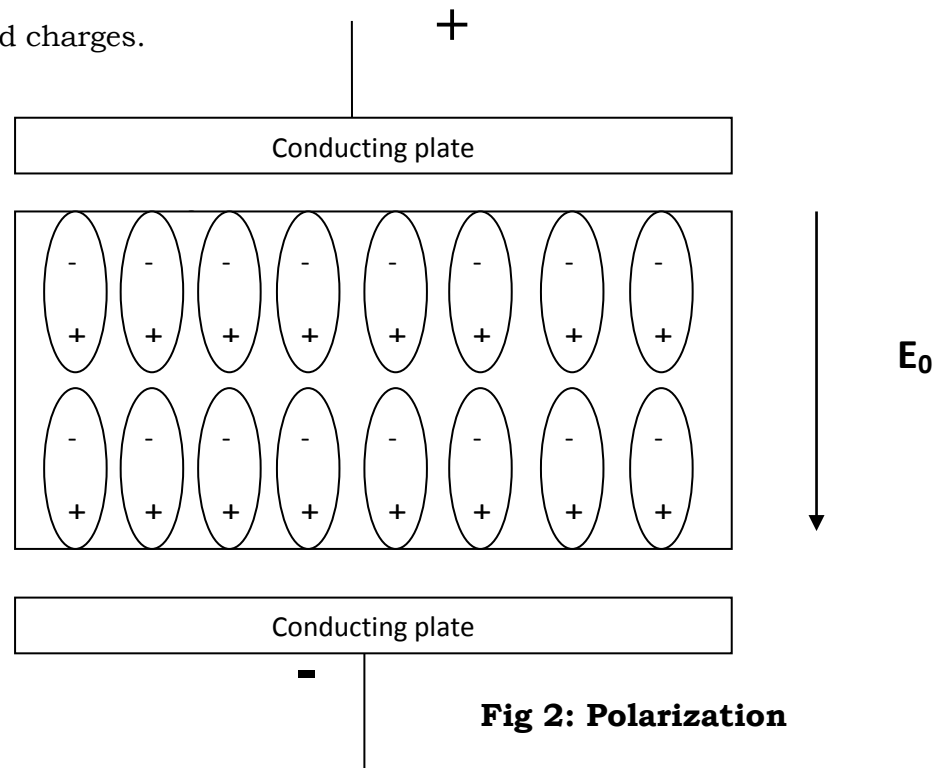


Fig 2: Polarization

Different Types of Polarization Mechanisms

The polarization is alignment of permanent or induced atomic or molecular dipoles under action of applied field; hence depending on dielectric material and manner of applied electric field, there are four types of polarization mechanisms:

1. Electronic polarization.
2. Ionic polarization.
3. Orientation or molecular polarization.
4. Space charge polarization.

Electronic Polarization

This is the most common type of polarization, which occurs in most of the dielectrics. The electronic polarization is due to displacement of center of gravity of negatively charged particles relative to center of gravity of positive charges. This is called electronic because the dipole moment results due to shift of the electron cloud relative to the nucleus as shown in Fig 3. This type of polarization is due to induced dipole moments. The electrons has very high natural frequencies of order 10^{15}Hz , hence light of frequency 10^{15}Hz can cause electronic polarization. The electronic polarization is temperature independent. The electronic polarization occurs in over short interval of time 10^{-15}sec .

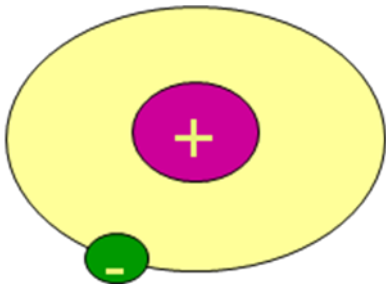
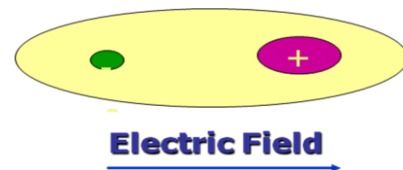


Fig 3: Atom without Electric field



Atom with Electric field

Since the induced dipole moment is directly proportional to applied field strength E

$$\mu_e \propto E \text{ or } \mu_e = \alpha_e E \text{ or } \alpha_e = \mu_e / E$$

α_e is called electronic polarizability. $\alpha_e = \frac{\mu_e}{E}$

Electronic Polarization $P_e = N \mu_e$ $N =$ number of atoms per m^3

$$P_e = N \alpha_e E \quad \alpha_e = \frac{4 \pi \epsilon_r R^3}{3}$$

Macroscopic equation is $P = \epsilon_r (\epsilon_r - 1) E$

$$N \alpha_e E = \epsilon_r (\epsilon_r - 1) E$$

$$\text{Electronic polarizability. } \alpha_e = \frac{\epsilon_r (\epsilon_r - 1)}{N}$$

2. Ionic Polarization.

The ionic polarization occurs only in ionic materials like NaCl etc. In this type of materials under equilibrium conditions, the cations and anions remain at their mean equilibrium conditions. When the field is applied the cations and anions get displaced from their mean positions in opposite directions and give rise to a net dipole moment as shown in Fig 4. As the dipole moment occurs only under an applied electric field, ionic polarization is due to induced dipoles; also ions are heavier than electrons. This type of polarization is slow process and ionic polarization is limited to frequencies up to 10^{13} hertz and hence light frequencies of 10^{15} cannot cause ionic polarization.

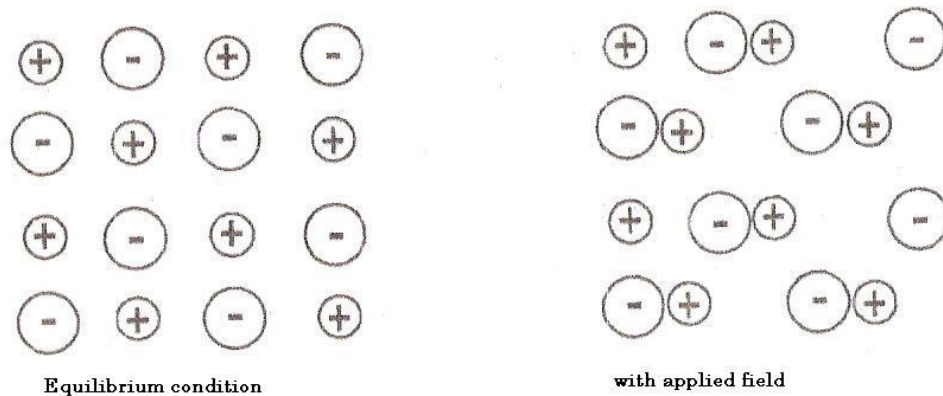


Fig 4: Ionic polarization

3. Orientation Polarizations or molecular polarization

The orientation polarization occurs in polar dielectrics in which there are molecules with permanent dipole moment. The orientation of these molecules are random due to thermal agitation, because of randomness in orientation, the material has net zero dipole moment in the absence of electric field. When electric field is applied each dipole undergo rotation so as to orient along the direction of the field, which exert a torque in them, thus material itself develops the dielectric polarization as shown in Fig 5. In the orientation polarization restoring forces do not exist, however dipole alignment is balanced by thermal agitation and this type of polarization is strongly temperature dependent.

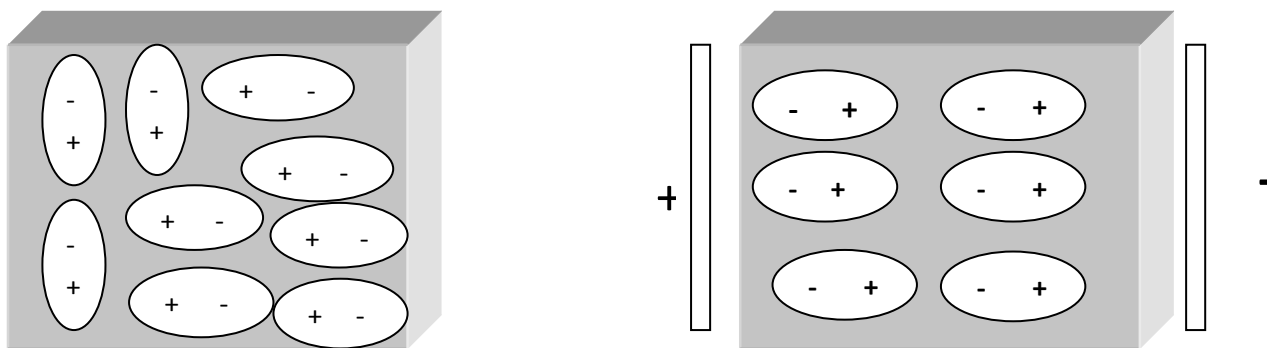


Fig 5: Randomly oriented permanent dipoles

Aligned dipoles in an electric field

The orientation polarizability is given by $\alpha_0 = \mu^2/3kT$

The orientation polarization P_o is given by $P_o = N \mu^2 E/3kT$

4 Space Charge Polarizations

The space charge polarization occurs in multiphase dielectric substances in which there is a change of resistivity between different phases when electric field is applied at high temperature. The electric charges get accumulated at the interface due to sudden change in conductivity. This accumulation of charges with opposite polarities at opposite parts in low resistivity phase leads to development of dipole moment (Fig 6).

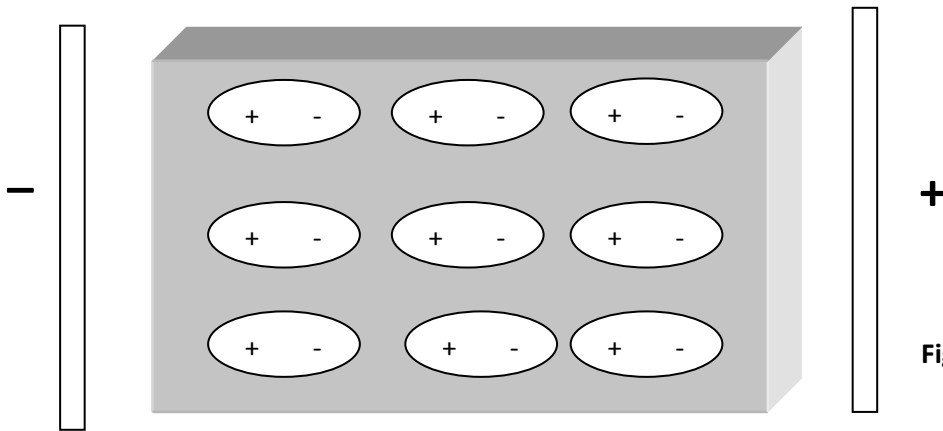


Fig 6: Space charge polarization

The space charge polarization is not an important factor in most common dielectrics. The total polarization α of a material is thus given by the sum of electronic, ionic and orientation polarizations,

$$\text{i.e. } \alpha = \alpha_e + \alpha_i + \alpha_o$$

Internal Field

When the electric field is applied to dielectric material either liquid or solids, each atom in the material develops dipole moment and acts like electric dipole, since atoms either in liquids or solids are surrounded on all sides by polarized atoms, the internal field at given point inside the material is equal to the electric field created by the neighboring atoms and the applied field.

“The internal field is defined as the electric field that acts at the site of any given atoms of a solid or liquid. Dielectric field subjected to an external field and is resultant of the applied field and the field due to all the effects of the surrounding atoms.”

Expression for Internal or local fields in solids and liquids.

Consider a dielectric material solid or liquid the under action of electric field of intensity ‘E’. In dielectric imagine an infinite string of similar equidistant atomic dipoles parallel to field,

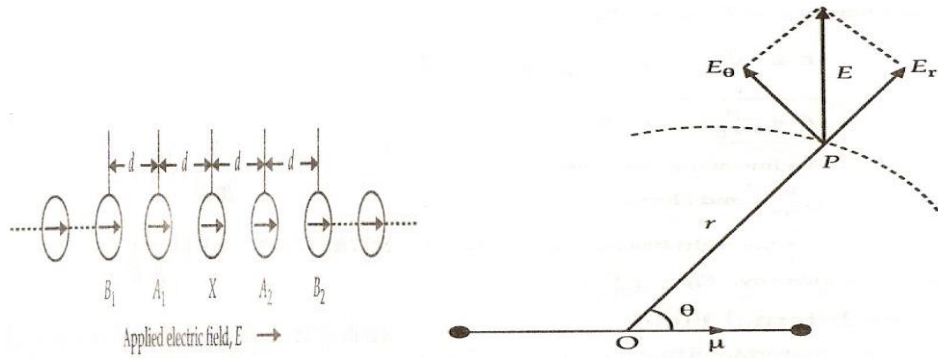


Fig 7: Internal field

The components of the electric field at ‘P’ due to an atomic dipole in polar form are given by

$$E_r = \frac{\mu \cos \theta}{2\pi \epsilon_0 r^3} \quad E_\theta = \frac{\mu \sin \theta}{2\pi \epsilon_0 r^3} \quad (1)$$

Dipole at A₁:

The distance of X from A₁ is d. i.e., $r = d$ and $\theta = 0$

$$E_r = \frac{\mu}{2\pi \epsilon_0 d^3} \quad E_\theta = 0 \quad (2)$$

Field at X due to A₁: $\mathbf{E_r + E_\theta} = \frac{\mu}{2\pi \epsilon_0 d^3}$

Dipole at A₂:

Since it is situated symmetrically on the other side of X its field at X will

also be $\frac{\mu}{2\pi\epsilon_0 d^3}$

Field at X due to A₂:

$$\frac{\mu}{2\pi\epsilon_0 d^3} \quad (3)$$

Therefore field at X due to both dipoles A₁ and A₂

i.e

Field at X due to A₁ & A₂:

$$E_1 = \frac{\mu}{\pi\epsilon_0 d^3}$$

Field at X due to B₁ & B₂, located at a distance of 2d:

$$E_2 = \frac{\mu}{\pi\epsilon_0 (2d)^3}$$

The Total Field E' at X due to all dipoles:

$$\begin{aligned} E' &= E_1 + E_2 + E_3 + \dots \\ &= \frac{\mu}{\pi\epsilon_0 (d)^3} + \frac{\mu}{\pi\epsilon_0 (2d)^3} + \frac{\mu}{\pi\epsilon_0 (3d)^3} + \dots \\ &= \frac{\mu}{\pi\epsilon_0 d^3} \left[1 + \frac{1}{2^3} + \frac{1}{3^3} + \dots \right] \\ &= \frac{\mu}{\pi\epsilon_0 d^3} \sum_{n=1}^{\infty} \frac{1}{n^3} \end{aligned}$$

where n = 1, 2, 3, ..., ∞

But we know that by summation of infinite series $\sum_{n=1}^{\infty} \frac{1}{n^3} = 1.2$

$$\therefore E' = 1.2 \frac{\mu}{\pi\epsilon_0 d^3} \quad (5)$$

The total field at X which is the internal field E_i , is the sum of the applied field E and the field due to all the dipoles, i.e. E' .

$$E_i = E + E' \quad (6)$$

If α_e is the electronic polarizability for the dipoles, then

$$\mu = \alpha_e E_i \quad (7)$$

$$E_i = E + \frac{1.2 \alpha_e E_i}{\pi \epsilon_0 d^3}$$

By rearranging the terms in the above equation we have

$$E_i = \frac{E}{1 - \frac{1.2 \alpha_e}{\pi \epsilon_0 d^3}} \quad (8)$$

This is the expression for internal field in case of one-dimensional array of atoms in dielectric solids or liquids.

Lorentz Field for a cubic lattice:

In 3D the general equation for internal field is expressed as

$E_i = E + (\gamma/\epsilon_0) P$, where P is the polarization and γ is a proportionality constant called internal field constant.

In the 3D if it is a cubic lattice then, $\gamma = 1/3$ and the internal field is named as **Lorentz Field** given by

$$E_{\text{Lorentz}} = E + P/3\epsilon_0$$

The above equation is known as Lorentz relation. One of the important results that follow from this relation is Clausius-Mossotti relation.

CLAUSIUS-MOSSOTTI RELATION

Consider an element solid dielectric of a dielectric constant ϵ_r . If N is the number of atoms/unit volume of the material, μ is the atomic dipole moment, then we have ,

Dipole moment,

$$\mu = \alpha E_i \quad (1)$$

Polarization of the medium is

$$\mathbf{P} = N\alpha E_i \quad (2)$$

Therefore

$$E_i = \frac{P}{N\alpha} \quad (3)$$

For a medium with dielectric isotropy

$$P = \epsilon_0 (\epsilon_r - 1) E \quad (4)$$

Therefore

$$E_i = \frac{P}{\epsilon_0 (\epsilon_r - 1)} \quad (5)$$

In 3D

$$E_i = E + \gamma \frac{P}{\epsilon_0} \quad (6)$$

Using (3), (5) and (6),

$$\frac{P}{N\alpha} = \frac{P}{\epsilon_0 (\epsilon_r - 1)} + \gamma \frac{P}{\epsilon_0} \quad (7)$$

$$\frac{1}{N\alpha} = \frac{1}{\epsilon_0} \left(\frac{1}{(\epsilon_r - 1)} + \frac{1}{3} \right)$$

$$\frac{\epsilon_0}{N\alpha} = \left(\frac{\epsilon_r + 2}{3(\epsilon_r - 1)} \right)$$

$$\left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{N\alpha}{3\epsilon_0}$$

This is Clausius-Mosotti equation.

Dielectric losses:

It is the loss of energy in the form of heat by a dielectric medium due to the internal friction that is developed as consequences of switching action of molecular dipoles under certain ac conditions.

Dipolar Relaxation:

Relaxation time is the time required for the dipole to reach the equilibrium orientation from the disturbed position in alternating field conditions.

Frequency dependence of dielectric constant:

The dielectric constant ϵ_r for a material remains unchanged when subjected to a d.c voltage. But it is subjected to a.c voltage the value of ϵ_r undergoes changes depending on the frequency of the applied voltage. In addition, ϵ_r becomes a complex quantity. It is then represented as ϵ_r^* and is expressed as,

$$\epsilon_r^* = \epsilon_r' - j\epsilon_r'' \text{ -----(1)}$$

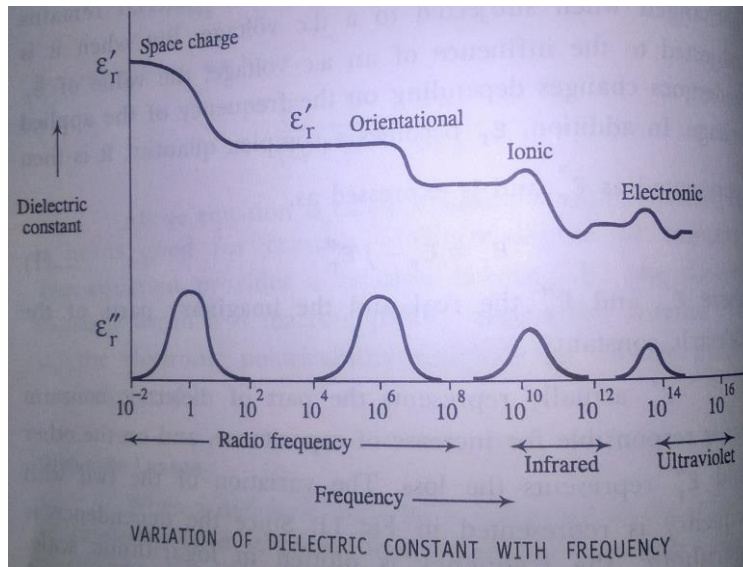
where ϵ_r' and ϵ_r'' are the real and the imaginary parts of the dielectric constant. ϵ_r' actually represents the part of dielectric constant that is responsible for

increase of capacitance and on the other hand ϵ_r'' represents the loss. The variation of the two with frequency is represented in Fig 8 .Since the dependence is logarithmic; the frequency is plotted in logarithmic scale. As there is a direct relation between various polarizations and the dielectric constant, the variations shown in the Fig could be understood easily once we know the dependence of various mechanisms on the frequency of the applied field.

All the four different polarization mechanisms that occur in a dielectric material will be effective in static field conditions. But, each of them responds differently at different frequencies under alternating field conditions since the relaxation frequencies of different polarization processes are different. If τ_e , τ_i , τ_o are the relaxation times for the electronic, ionic and orientation polarizations, then in general,

$$\tau_e < \tau_i < \tau_o$$

When the frequency of the applied field matches with the relaxation frequency of a given polarization mechanism the absorption of energy from the field becomes maximum. But, when the frequency of the applied field becomes greater than the relaxation frequency for a particular polarization mechanism, the switching action of the dipole cannot keep in step with that of the changing field, and the corresponding polarization mechanism is halted. Thus the frequency of the applied a.c. is increased, different polarization mechanisms disappear in the order, - orientation, ionic and electronic.



In the figure, it can be observed that in the beginning (i.e., when the frequency variation starts from a value 10^{-2} Hz), all the four polarization mechanisms will be responding and hence the total polarization will be maximum. Accordingly ϵ_r' value starts increases. But as the frequency increases from low frequency to higher frequencies in the radio frequency range, the space charge polarization mechanism and the orientation polarization mechanism come to a halt in order, through the other two mechanisms remain active throughout. Accordingly ϵ_r' experiences decrement at the corresponding stages. When the frequency crosses the infrared range, ϵ_r' will be next step down in its value as the ionic polarization steps. Finally the electronic polarization fades away while the frequency crosses the ultraviolet limit and ϵ_r' steps down for the last time to stabilize at its least value. The peaks in the variation of ϵ_r'' over frequency regions corresponding to the decrements in ϵ_r' indicates the losses that the material suffer over those frequencies.

The loss that occurs in a dielectric material is essentially due to the phase lag of voltage behind the current in the capacitor between the plates of which the dielectric material lies. Such a loss in a capacitor is expressed by a factor called

$\tan \delta$. A large value for $\tan \delta$ signifies higher dielectric loss. It is also referred to as **tangent loss**.

It can be shown that for a capacitor with a dielectric material,

$$\tan \delta = \epsilon_r'' / \epsilon_r'$$

Solved examples:

1. Find the polarization produced in a dielectric medium of relative permittivity 15 in the presence of an electric field of 500V/m.

Solution:

Given: $\epsilon_r = 15$, we know that, $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$

$$E = 500 \text{ V/m}$$

$$P = ?$$

$$P = \epsilon_0 (\epsilon_r - 1) E$$

$$= 8.854 \times 10^{-12} (15 - 1) 500$$

$$= 6.195 \times 10^{-8} \text{ C/m}^2$$

2. A parallel plate capacitor of area 650 mm^2 and a plate separation of 4mm has a charge of $2 \times 10^{-10} \text{ C}$ on it. What should be the resultant voltage across the capacitor when a material of dielectric constant 3.5 is introduced between the plates?

Solution:

Given

Area of the capacitor $s = 650 \text{ mm}^2 = 650 \times 10^{-6} \text{ m}^2$

Distance of separation between the plates, $d = 4 \text{ mm} = 4 \times 10^{-3} \text{ m}$

Charge on the capacitor, $Q = 2 \times 10^{-10} \text{ C}$

Dielectric constant $\epsilon_r = 3.5$

We know that,

$$C = \epsilon_0 \epsilon_r s / d$$

$$\text{Also, } C = Q/V$$

Equating the above relations,

$$Q/V = \epsilon_0 \epsilon_r / d$$

$$\text{Or } V = Q d / \epsilon_0 \epsilon_r s$$

$$= 2 \times 10^{-10} \times 4 \times 10^{-3} / 8.85 \times 10^{-12} \times 3.5 \times 650 \times 10^{-6}$$

$$= 39.73 \text{ V}$$

3. The dielectric constant of sulphur is 3.4. Assuming a cubic lattice for its structure calculate the electronic polarizability of sulphur.

Solution:

Since the crystal structure of sulphur is cubic we can apply Clausius – Mossotti equation,

$$\text{Hence } \alpha_e = \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \frac{3\epsilon_0}{N}$$

and

$$\left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{N\alpha}{3\epsilon_0}$$

Now, N the number of atoms/unit volume can be written as,

$$N = \frac{N_A * 10^3 * D}{atomicnumber}$$

$$N = \frac{6.025 * 10^{26} * 2.07 * 10^3}{32.07}$$

$$N = 3.89 * 10^{28} / m^3$$

$$\text{Hence } \alpha_e = \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \frac{3\epsilon_0}{N}$$

$$\alpha_e = \left(\frac{3.4 - 1}{3.4 + 2} \right) \frac{3 * 8.854 * 10^{-12}}{3.89 * 10^{28}}$$

$$\alpha_e = 3.035 * 10^{-40} \text{ Fm}^2$$

5. A elemental solid dielectric material has polarizability $7 * 10^{-40} \text{ Fm}^2$. Assuming that internal field to be Lorentz, calculate the dielectric constant for the material if the material has $3 * 10^{28} \text{ atoms/m}^3$.

Solution:

$$\alpha_e = 7 * 10^{-40} \text{ Fm}^2$$

$$\text{No of atoms/m}^3 = 3 * 10^{28}$$

The internal field is Lorentz field

Since the internal field is Lorentz field, we can apply Clausius –Mossotti equation,

$$\left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{N\alpha}{3\epsilon_0}$$

$$\left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \left(\frac{3 * 10^{28} * 7 * 10^{-40}}{3 * 8.854 * 10^{-12}} \right)$$

$$= 0.7906$$

$$(\varepsilon_r - 1) = (\varepsilon_r + 2) * 0.7906$$

$$\varepsilon_r - 1 = 0.7906 \varepsilon_r + 1.5812$$

$$\varepsilon_r (1 - 0.7906) = 2.5812$$

$$\varepsilon_r = 2.5812 / 0.2094$$

$$\varepsilon_r = 12.33$$

UNIT-5

Nano science

Objectives

- At the end of lesson we shall understand about,
 - nano science.
 - Density of states (1D, 2D, 3D)
 - Synthesis (Top-down and bottom-up)
 - Ball milling method.
 - Sol-Gel methods.
 - Carbon nano tube (CNT)- Properties, synthesis)
 - Applications of carbon nano tubes.

Introduction:

Nanotechnology is the science and technology of small things that are less than 100nm in size. One nanometer is 10^{-9} meters or about 3 atoms long. For comparison, a human hair is about 60-80,000 nanometers wide. When the dimensions of the material such as its, length, breadth, thickness fall in the range of 1-100 nm, the resulting structures exhibit characteristics that are specific to their sizes and dimensions. Such materials are called as nanomaterials. Further Nanoparticles are particles between 1 and 100 nanometers in size. Thus confining the dimensions of a bulk can show different physical and chemical properties. The confinement of dimensions of a bulk can result in 2D, 1D, 0D.

Density of states (DOS) in 0D, 1D, 2D and 3D:

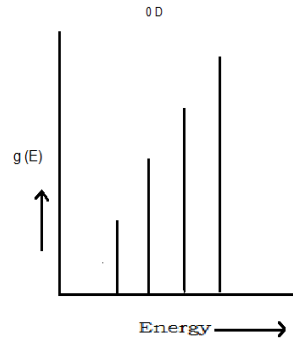
In case solid-state and condensed matter physics, the density of states (DOS) of a system gives the number of states per interval of energy at each energy level that is available to be occupied.

Basically the nanoparticles are classified on the basis of dimensions as zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D) nano particles.

Zero dimensional (0D): A zero dimensional structures the simplest building block that may be used for nonmaterial design.

Eg: Quantum dots

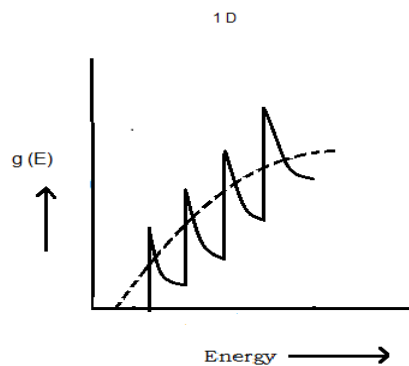
Density of states for 0D is as shown below,



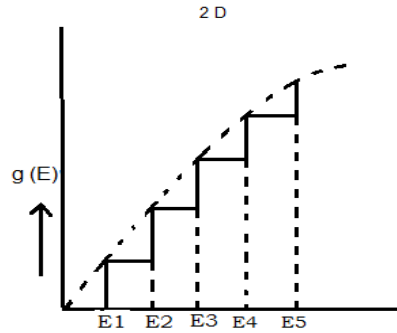
One dimensional (1D): In one dimensional structure only one dimension of the material is reduced to nanometer range and the other dimensions remain large.

Eg: nanorod, nanowire.

Density of states for 1D is as shown below,



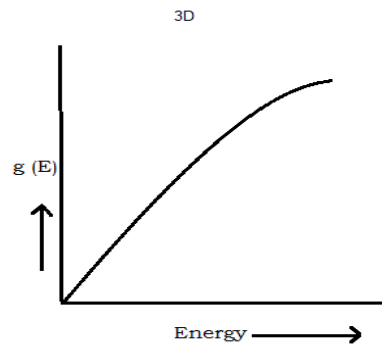
Two dimensional (2D): In 2D structures two of dimensions of the material are reduced to nanometer range and one dimension remains large called quantum wire. Eg: Quantum wire, fibers, plate lets etc. Density of states for 2D is as shown below:



Three dimensional (3D): If bulk material there is no confinement in any of its material dimensions.

Eg: Any bulk structure

Density of states for 3D is as shown below:



Synthesis of materials:

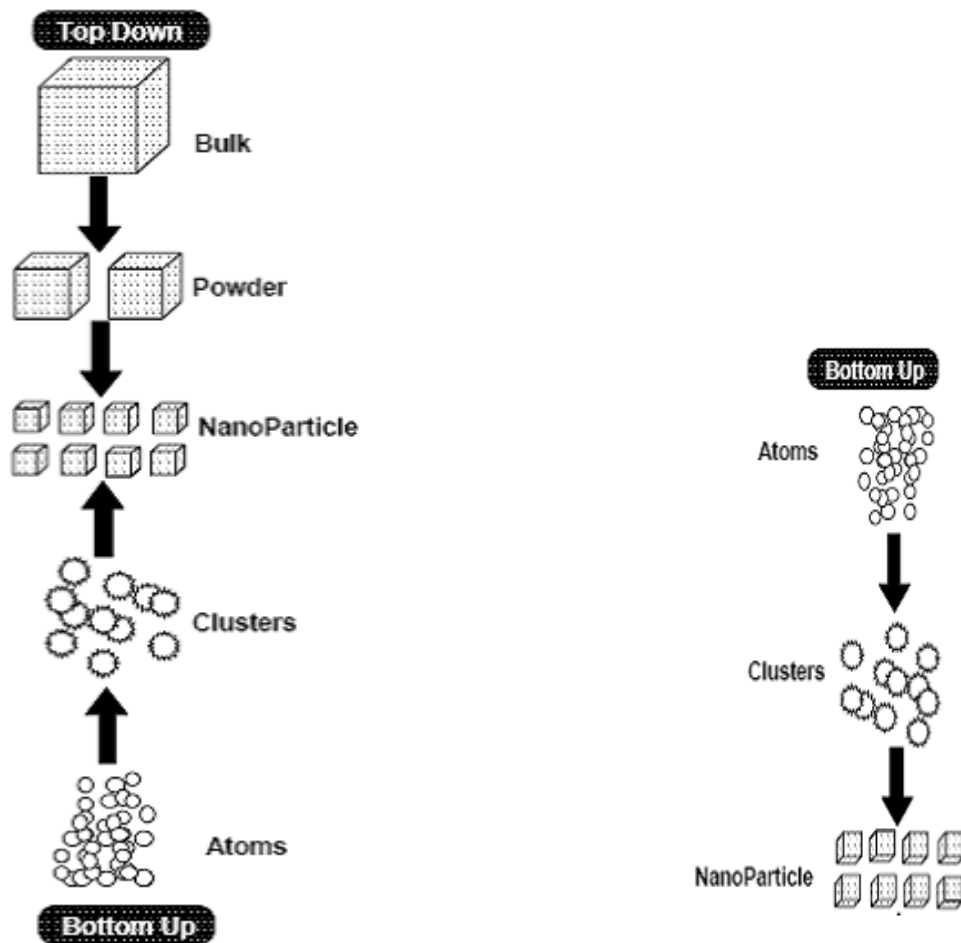
Nanomaterials can be natural or can be synthesized by various processes that can be categorized into two approaches namely,

1. Top-down
2. Bottom-up

In case of Top-Down approach the synthesis is initiated with the bulk material and undergoing size reduction becomes powder and then a nano particle and cluster finally yielding atoms. One of the examples of top-down approach is Ball milling method.

Where as in Bottom-up approach the synthesis is initiated with atoms as the starting element and undergoes polymerization giving nano particles as the end product. One of the examples of approach is Ball milling method.

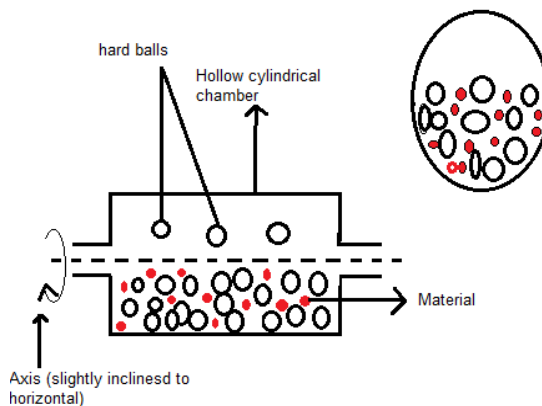
The steps of synthesis of nanoparticles are represented in the diagram given below:



Example of Top-Down method: Ball milling method.

Example for Bottom-up method: sol-gel method.

Ball milling method: (Top-Down method)



The ball mill consists of a hollow cylindrical chamber that can rotate about axis. There are hard and heavy balls made of tungsten/steel inside the chamber. Larger balls are used for milling to produce smaller particle size. The chamber is mounted such that, its axis is slightly inclined to the horizontal to enable the material inside to slide and accumulate around in one region. The given material is crushed into small grain size and fed into the chamber. As the cylindrical chamber is rotated around its own axis, the balls get carried upwards. But under gravity they drop down and hit the sample with high speed. This happens repeatedly and the material will be pounded to get reduce to nano size particles. However the speed of the rotation must be less than a critical speed beyond which the balls instead of falling down will be carried along the periphery of the chamber all along. Then the material size misses the hit and reduction in size stops before attaining the nano particle size.

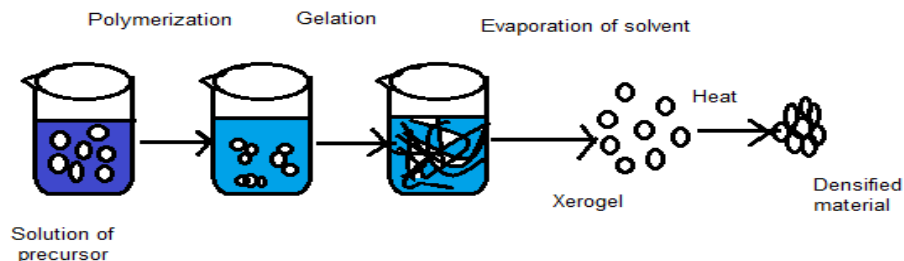
Advantages:

- This method is suitable for large scale production at low cost.
- It can be used to grind material irrespective of hardness

Disadvantages:

- Because of the nature of use, the purity of the material is affected

Sol-gel method: Bottom-up method



Sol-gel is a process in which precipitated tiny solid particles agglomerate to form long networks which spread continuously throughout a liquid in the form of a gel. Sols are solid particles suspended in liquid medium. Gels comprise of long networks of particles like polymers in which the interspaces form pores that contain liquid.

In sol-gel method, precursors which have a tendency to form gel are selected. A solution of the precursor is obtained by dissolving it in a suitable solvent. The precursors are generally inorganic metal salts or alkoxides which undergo hydrolysis. By poly condensation process, nucleation of solid particles starts and sols are formed.

The sols undergo polymerization which turns the solution into a gel. The sol-gel is then centrifuged from which a form of gel called Xerogel which has no traces of the dispersion medium is obtained. The xerogel is then dried by heating it up to a temperature of 800°C during which time, the pores of the gel network collapse. This is called densification after which we obtain the desired nanomaterials. The steps are represented in the diagram above.

Advantages:

- Highly pure and uniform nanostructures can be obtained in sol-gel processing
- It is an inexpensive technique with fine control of the product's chemical composition

- With this method powder/fiber/thin film coating can be made.

Disadvantages:

- Precursors having a tendency of forming gel can only be selected.

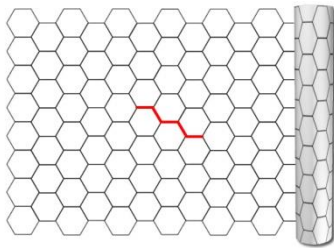
Carbon Nano Tubes (CNTs):

A carbon nanotube is a sheet of carbon (graphite) atoms joined in a pattern of hexagons rolled into a cylinder.

Structure of carbon nano tube:

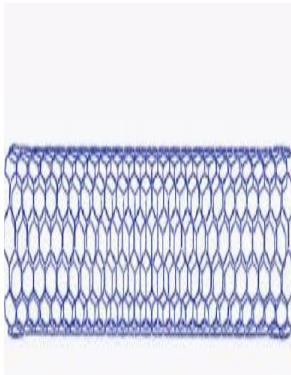
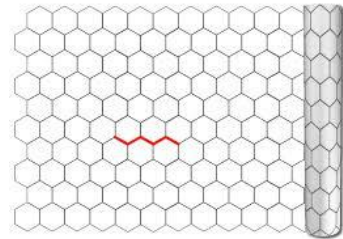
Carbon nano tubes are appearing in 3 different structures namely

- Armchair



- Zigzag

- Chiral



CNTs can be single or multi walled depending on the number of graphene layers present in the formation of tube structure.

Properties of CNT's:

Mechanical properties of CNT'S:

The tensile strength of CNT'S is 100 times as that of steel. The weight of the CNT'S is about 1/10 as that of steel. They have the highest tensile strength of all known materials so far. They are also highly elastic.

Thermal properties of CNT'S:

They possess thermal conductivity which is 2 times that of diamonds. They retain their physical structure in vacuum even up to 2800° C. They are thermally stable.

Electrical properties of CNT'S:

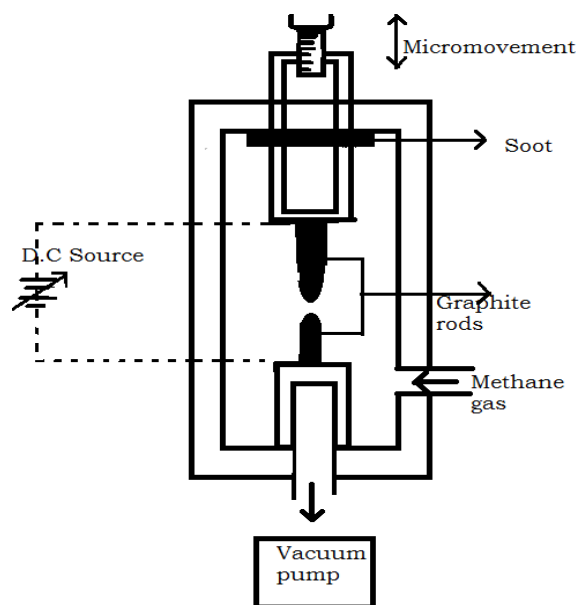
They can be metallic or semiconducting depending on their structure and size. Their current carrying is 1000 times that of copper.

Synthesis of carbon nano tubes:

- Arc discharge method(bottom up approach)
- Pyrolysis method

Arc discharge method:

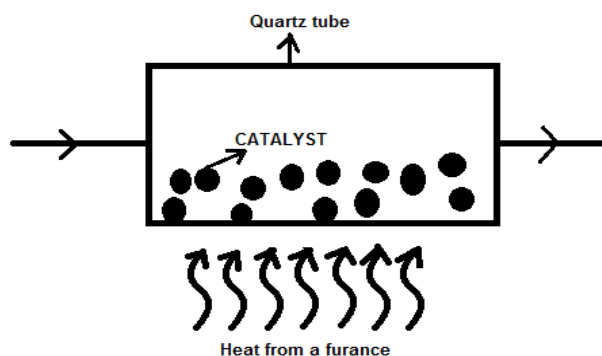
The set-up used in the arc discharge method consists of a vacuum chamber in which two graphite rods are mounted on two supports as shown in the diagram. There is a gap of 1-2 mm between the two tips. The chamber is evacuated by using a vacuum pump and the methane gas at a certain pressure is introduced into the chamber. The two rods are maintained at a suitable dc potential difference (70 A at 18 V) to enable the discharge. On application of the voltage, the arc discharge starts. Carbon evaporates from the anode. Some part of the evaporated carbon, deposits on the cathode tip layer by layer. This is called hard deposit and the rest condenses on the other parts of cathode (called cathode soot) and on the walls of the chamber (called the chamber soot).Both the cathode soot and the chamber soot yield either single or multi walled carbon nanotubes, the hard deposit doesnt yield any product of interest.



Though this method enables production of large quantities of nanotubes, it involves purification of the soot by oxidation, centrifugation, filtration and acid treatment as the products will be highly impure.

Pyrolysis method: (bottom up approach)

Pyrolysis is decomposition of a chemical compound of higher molecular weight into simpler compounds by heating in absence of oxygen so that, no oxidation occurs. It takes place usually at a temperature in the range of 400 °C to 800 °C. The experimental set up is as shown below,



In this method, a hydrocarbon gas such as methane is passed through a heated quartz tube in which a catalyst is present. Due to Pyrolysis, the gas

decomposes. Carbon atoms are freed, which bind with the catalyst such as Ni, Fe, or Co. CNT'S grow on the catalyst and the same is collected after cooling.

Graphene

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale hexagonal lattice. It is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. Graphene has many extraordinary properties. It is about 200 times stronger than steel by weight, conducts heat and electricity with great efficiency and is nearly transparent. Researchers have identified the bipolar transistor effect, ballistic transport of charges and large quantum oscillations in the material.

Scientists have theorized about graphene for decades. It is quite likely that graphene was unwittingly produced in small quantities for centuries through the use of pencils and other similar applications of graphite, but it was first measurably produced and isolated in the lab in 2003. Andre Geim and Konstantin Novoselov at the University of Manchester won the Nobel Prize in Physics in 2010 "for groundbreaking experiments regarding the two-dimensional material graphene."

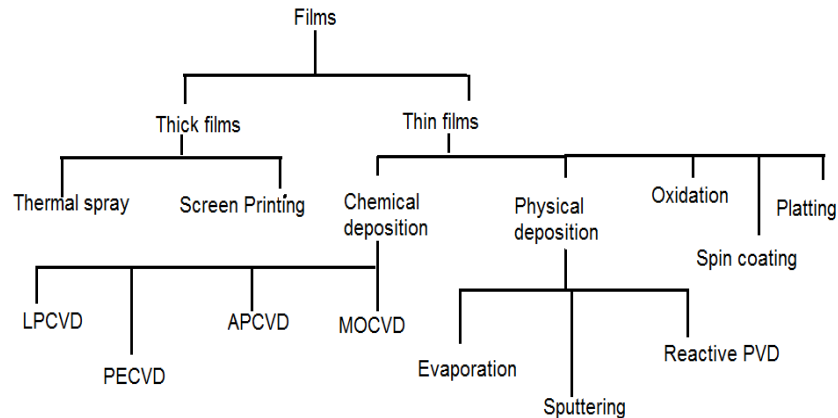
Applications of carbon nanotubes:

- Using semiconducting nano tubes it is possible to make electronic components such as transistors logic gates and nano capacitors, energy storage, super capacitors, field emission transistors, high-performance catalysis, photovoltaic, and biomedical devices and implants.
- Carbon nano tubes are used in medical field for delivering complex natured drugs.
- As these materials are strong as well as light weight, they are being used in building aircrafts and making of Micro Electro Mechanical Systems (MEMS).

Thin films

Introduction

Films can be divided into two categories depending on the thickness of the film and the process of deposition. They are thick films and thin films as explained in the following sections.



Thick films

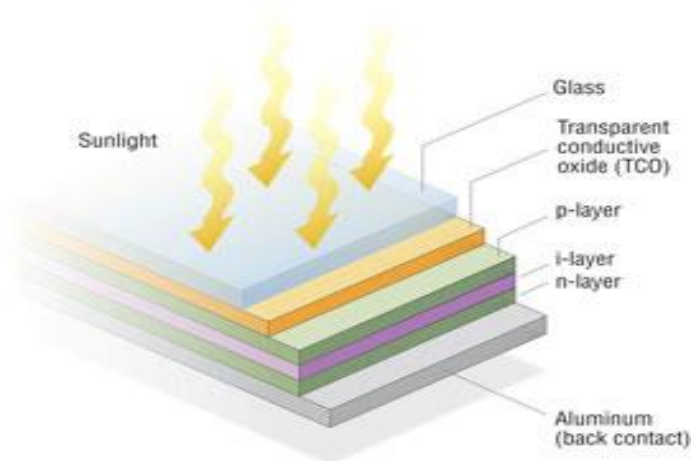
A thick film is the one whose film thickness falls in the range of micrometers (μm) to few millimeters (mm). Major applications of thick films are in the field of electronics as [surface mount devices](#), [sensors](#) and [hybrid integrated circuits](#). Some of the methods used to coat thick films are thermal spray technique, screen printing and so on.

Thin films

Basically a thin film is considered to be a layer deposited of any material whose thickness ranges from a few nanometers (nm) to some micrometers (μm).

Applications: Thin film solar cells

Major applications of thin films are in the field of electronics as semiconductor devices and sensors. In polycrystalline solar cells, layers of n and p type semiconductors are deposited as thin films.



Application Fields	Examples
Electronics	Semiconductor devices, solar cells and sensors
Optics	Antireflection coating; on lenses or solar cells, Reflection coatings for mirrors. Coatings to produce decorations (color, luster), Interference filters, CD's , DVD's and Waveguides.
Chemistry	Diffusion barriers, Protection against corrosion / oxidation. Sensors for liquid / gaseous chemicals.
Mechanical Engineering	"Hard" layers (e.g. on drill bits). Adhesion providers, Friction reduction.

Vacuum ranges

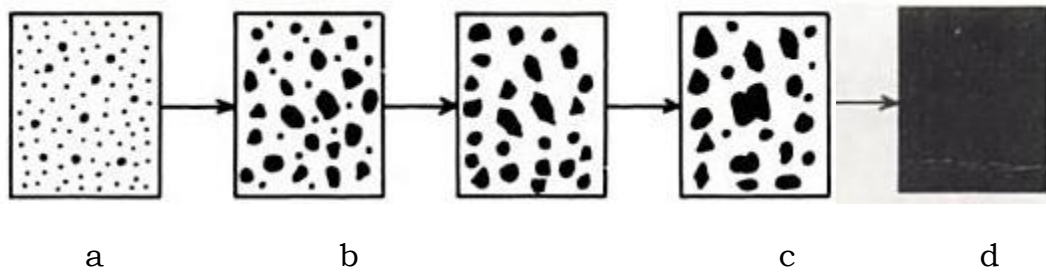
Various degrees of vacuum are mainly classified as follows:

1. Low vacuum - 760 - 25 Torr
2. Medium vacuum - 25 - 10^{-3} Torr
3. High vacuum - 10^{-3} - 10^{-6} Torr

Stages of thin film growth

There are several stages in the growth process of thin film, from the initial nucleation stage to final continuous three dimensional film formation state. These stages of growth were observed

by the scientists using microscopic studies. Nucleation includes condensation of vapours, adsorption of atoms, migration of atoms, formation of critical nuclei and stable clusters. Nucleation is the first step in the formation of a new structure. Nucleation is often found to be very sensitive to impurities in the system. Because of this, it is often important to distinguish between heterogeneous nucleation and homogeneous nucleation.



a: nucleation on glass, b: growth, c: coalescence or agglomeration with island formation d: continuous film.

Coalescence and agglomeration is the action or process of collecting in mass or cluster of materials. Larger islands grow together, leaving channels and holes of uncovered substrate. These islands consist of comparatively larger nuclei with size more than 10 \AA generally with three dimensional nature. The process of formation of these islands takes place either by the addition of atoms from the vapor phase or by diffusion of atoms on the substrate. A nucleus of 5 \AA size is made up of 20 atoms or so and the will be made up of around 100 to 150 atoms. During coalescence many small islands disappear rapidly leading to some definite shapes of larger islands. The time of coalescence is less say about 0.6 sec. As the deposition continues, the gaps disappear to form a continuous film by filling up of the channels and holes in the aggregate mass.

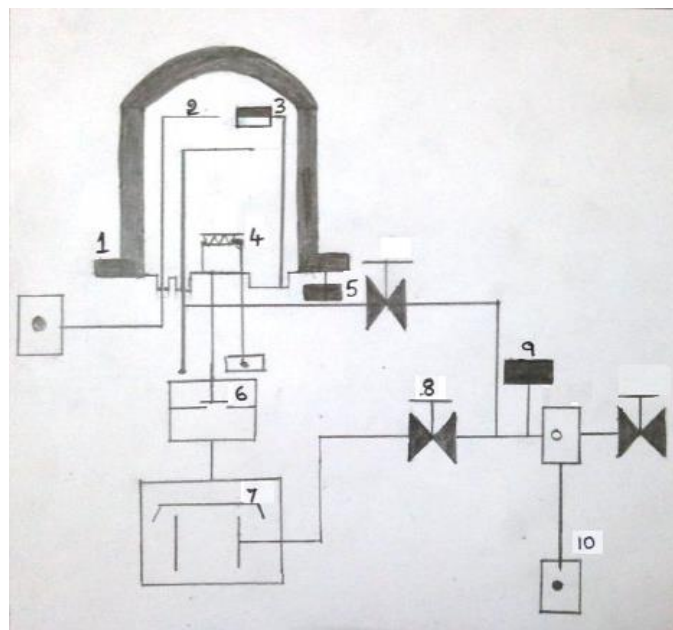
Block diagram of a thin film unit

A standard vacuum coating unit consists of a pumping system which comprises of a rotary vacuum pump, a diffusion pump and additional fully integrated and wired parts like valves, baffles, and gauges.



Photograph of a vacuum coating unit.

Photograph of the vacuum coating unit is shown in the figure above. A schematic diagram of a vacuum coating unit is shown in the figure below. A rotary pump (Pirani gauge to measure vacuum till 10^{-3} Torr) along with a diffusion pump (a penning gauge to measure vacuum above 10^{-3} Torr) is used to ensure clean and better vacuum of the range of 10^{-6} Torr. Thus coating unit is fitted with a Pirani gauge used to measure the roughing vacuum and a Penning gauge to measure very high vacuum.



Schematic diagram of vacuum coating unit.

1. Bell jar 2. Crystal thickness monitor 3. Substrate holder 4. Filament with source material
5. Penning gauge 6. High vacuum valve 7. Diffusion pump 8. Backing valve 9. Pirani gauge

Besides, inside the coating unit, substrates can be cleaned by an ion bombardment facility in partial vacuum. A low tension transformer of 10V-100A is used to heat the filament for resistive

evaporation. Most of the evaporations are processed in a vacuum of about $1-8 \times 10^{-6}$ Torr. Once the high vacuum is reached, resistive heating is done by heating the source (semiconductor or metallic) material with a resistively heated filament or boat (fill the boat or filament with the material to be coated), generally made of refractory metals such as W (tungsten) or Mo (molybdenum). Vapor sources of various types, geometrics and sizes can be easily constructed or obtained commercially. Some forms of these sources are basket, spiral, crucible heater dimple boat, etc. if a material has sufficiently high vapor pressure before melting occurs, it will sublime and the condensed vapors form a film.



a. Boat



b. coils or filament

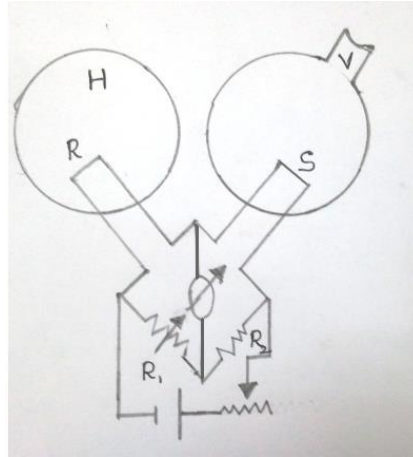
On heating the source material in vacuum, it gets deposited onto the substrate (usually glass) for the required thickness, say 1000 \AA and the film is kept in vacuum for few hours for settling. Later the bell jar can be opened and the films can be used for various studies and characterizations.

Pirani gauge

A heated metal wire (also called a filament) suspended in a gas will lose heat to the gas as its molecules collide with the wire and remove heat. If the gas pressure is reduced the number of molecules present will fall proportionately and the wire will lose heat more slowly. Measuring the heat loss is an indirect indication of pressure. The electrical resistance of a wire varies with its temperature, so the resistance indicates the temperature of wire. In many systems, the wire is maintained at a constant resistance R by controlling the current I through the wire. The resistance can be set using a bridge circuit. The power delivered to the wire is I^2R , and the same power is transferred to the gas. The current required to achieve this balance is therefore a measure of the vacuum. The gauge may be used for pressures between 0.5 Torr to 10^{-4} Torr .

Thus, pressure change in the vacuum unit results in an increase or decrease in the quantity of gas molecules that is there in the chamber. This in turn increases or decreases the thermal conductivity of the given gas. Therefore the loss of heat of the filament that is electrically heated by the constant voltage in the system fluctuates with any variation in pressure. The head filament of the pirani gauge has a temperature coefficient of resistance that is relatively high. So even a small change in pressure of the system can result in a considerable change in the resistance of the filament, as a result of which the current in a Wheatstone's bridge becomes

out-of balance that can be measured as the vacuum on a meter. A schematic diagram of a Pirani gauge is shown in the figure.

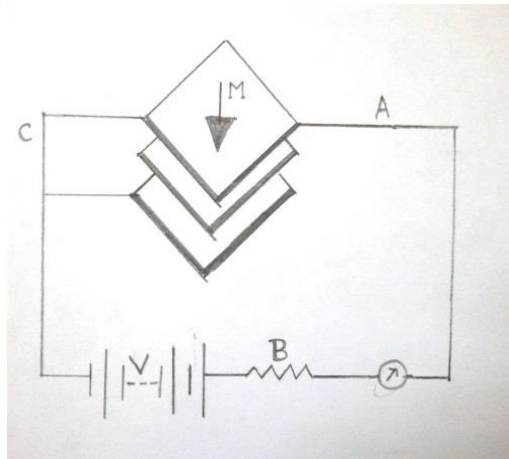


Schematic diagram of a Pirani gauge.

H- High vacuum, V- Vacuum system, R- Reference wire, S- Sensing wire, R_1 and R_2 - Resistances

Penning gauge

It is a cold cathode ionization gauge head and has two electrodes. Through a current limiting resistor, a 2.3 kV potential difference is given between the electrodes. A magnetic field of nearly about 800 gauss is introduced by a permanent magnet which acts at perpendicular to the plane which consists of the electrodes in order to increase the ionization current. Electrons coming out from the cathode (negative electrode) are there by deflected by the applied magnetic field. These electrons are forced to have a course which is helical in shape before they reach the anode loop. There by going through a very long path, even at considerably low pressures the chances of collision with gas molecule are high. Then there is increase in the rate of ionization and also the secondary electrons that are produced by ionization. Eventually, the anode captures the electrons and the equilibrium is said to be attained. This happens when the number of electrons produced per second is the sum of the positive ion current to the cathode and the electron to the anode thus measuring the vacuum. The schematic representation of a penning gauge is shown in figure.



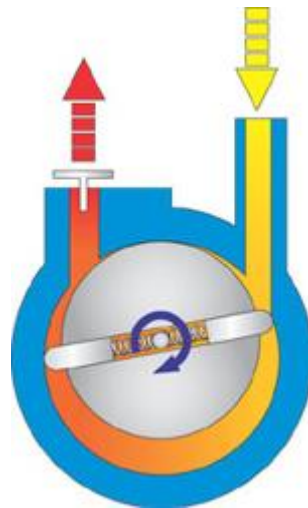
Schematic diagram of a penning ionization gauge

C- Cathode (-), A- Ring anode (+), M- Magnetic field, V- 2kV,
B- Ballast resistor ($1\text{M}\Omega$)

Rotary pump

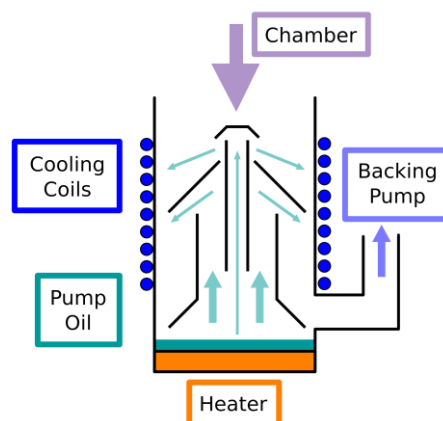
This is considered as the commonly used mechanical pump so as to attain the necessary initial vacuum for high vacuum pumps. This pump comprises of a rotor that is eccentrically mounted within a stator. Pressure valve leading into an oil reservoir closes the exhaust end. At the time of operation the air from the inlet side is drawn into the pump from the rotor when the vanes slide in and out. The volume of air having a crescent-shape is then condensed up to a pressure of about one atmosphere so as to open the outlet valve and to discharge the air out into the atmosphere from the oil seal. An outlet valve which is vented admits a small airflow to the compression section decreases the condensation of water vapor by reducing the value of compression ratio, which is called gas ballasting.

The fluids that are usually preferred to be used in rotary pump are mineral oils or diphenyl ethers because the high vapor is solved by installing fore-line traps.



Schematic representation of an oil sealed rotary pump

Diffusion pump

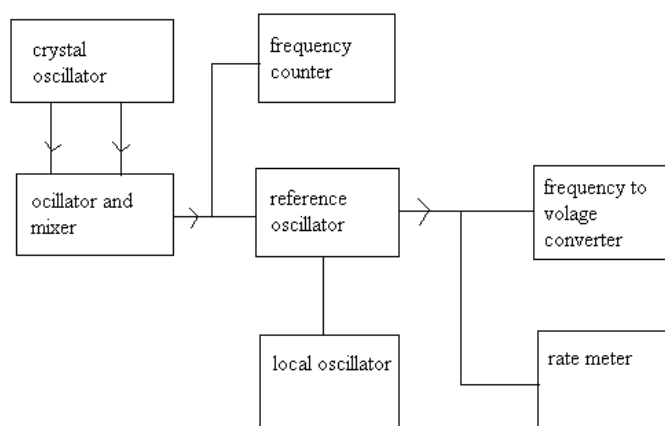


Schematic representation of a diffusion pump

Gaede was the first person to describe the thought of draining a vessel. This process is performed by means of molecular momentum transfer. Oils are used by the diffusion pumps for the purpose of pushing out the gas molecules. Its performance can be improvised by making use of traps and baffles along with the pumps to nullify the effect of streaming back of vapor. The work fluid is vaporized with the help of a heater and the hot vapor rises through a chimney. The jet cap reverses the direction of the flow of vapor and the vapor leaves via a nozzle at a very high speed which is because of the difference in pressure that is present between the inside and the outside of the chimney. Momentum is imparted to the moving incoming gas molecules by this high speed jet of molecules. Thus the gas molecules start moving towards the outlet where they are taken out by means of a backing pump. These vapors will then condense on the pre-cooled walls of the pump eventually and returning to the boiler. This working fluid or diffusion oil is supposed to have a high molecular weight, a relatively low vapor pressure, essential thermal stability and has to be less reactive. The range of vacuum for diffusion pump is about a value of 10^{-2} to 10^{-8} Torr. Usually, the diffusion pump used in the coating unit has a withdrawal speed of about 500 liters/s.

Quartz crystal thickness monitor

A commonly used thickness monitor is the quartz crystal thickness monitor which is employed to measure the thickness of the deposited thin films. It is a digital thickness monitor with a crystal holder cum feed-through and an oscillation box. It has a 3 digit LED auto-ranging display for rate of deposition and 4 digit LED auto-ranging display for thickness deposition.



Block diagram of the quartz crystal thickness monitor.

The concept of this type of measurement and control is that an oscillator crystal can be suitably mounted inside the vacuum chamber to receive deposition in real time and be affected by it in a measurable way. Specifically the oscillation frequency will drop as the crystal's mass is increased by the material being deposited on it. To complete the measurement system, an electronic instrument continuously reads the frequency and performs appropriate mathematical functions to convert that frequency data to thickness data, both instantaneous rate and cumulated thickness.

Process of thermal evaporation

Thin film deposition techniques can be broadly classified into two categories which depend on the process being mainly physical or chemical.

In physical deposition technique, methods include mainly resistive evaporation and electron beam evaporation techniques. In this method mechanical, electromechanical or thermodynamic techniques are used to deposit a thin film of any solid. Starting solid substance that is deposited has to be taken in a vacuum chamber and the source material is heated in vacuum chamber using tungsten coils or baskets so that the particles of the solid substance escape from the surface. Thus the complete unit is placed in the vacuum deposition chamber, so that the particles can move freely. These moving particles when reaches a surface (usually on glass substrate) which is cooler takes away the energy from these particles thereby letting them to shape into a solid thin layer. Examples of physical deposition include vacuum (thermal) evaporation (or resistive heating) and electron beam evaporation.

A thermal evaporation technique uses an electric resistance (tungsten/ molybdenum) coil or a basket so as to liquefy the starting matter and to increase its vapor pressure up to a required level. The process happens in a considerably high vacuum so that the vapor comes in contact with the substrate and does not interact or does not spread with other gas molecules present inside the vacuum chamber. This also reduces the merging of impurities from the remaining gas. Hence, only the materials which are having a vapor pressure much higher than the heating element gets deposited with minimum contamination of the film.

An electron beam evaporation technique also called as EBG evaporation is as same as the thermal evaporation but uses an electron beam to melt and vaporize the source material. When a beam of electron falls on the source material, the atoms of the source material moves to the substrate and settles. Here the temperature of the source material is made above its boiling/sublimation temperature so as to deposit a film on the required surfaces. E-beam evaporation has a major advantage over thermal evaporation that this method yields a higher density film with a better adhesion to the substrate. As the electron beam heats only the source material and does not heat the entire crucible, the level of contamination due to the crucible is relatively less as in the case of thermal evaporation.