Basics of intrinsic semiconductors:

- Chemically pure semiconductors are known as intrinsic semiconductors.

- A semiconductor (solid) can be considered to be extremely pure if it contains one impurity atom out of one billion pure semiconductor atoms.

- In a semiconductor, conduction band and valence band are separated by a small forbidden energy gap (E_g) of the order of 1eV.

- Pure semiconductors of the elements silicon (Si) and germanium (Ge) can be obtained from naturally available Silicon oxide (SiO_2) and Germanium oxide (GeO_2) respectively.

Intrinsic semiconductors at 0K:

- At 0K and close to 0K, valence electrons are tightly bound to the nucleus. These valence electrons are present in covalent bonds. All covalent bonds are completely filled. Therefore, valence bands are full. There are no free electrons at 0K. This means that conduction band is empty. Thus an intrinsic semiconductor behaves as a perfect insulator at 0K.

Intrinsic semiconductors at temperature greater than 0K:

- Thermal energy supplied can rupture covalent bonds and covalent bonds can be broken; the bonded electrons will become free. If the energy available to the liberated free electrons is sufficient, they are excited to the conduction band.

- In principle, for one free electron present in the conduction band, one vacant site of electron in covalent bond (one hole in the valence band) is created.

- In pure semiconductors, a single event of bond breaking leads to two carriers, namely an electron and a hole. The electron and hole are

created as a pair and the phenomenon is called electron-hole pair generation.

Energy gap (E_g) in semiconductors:

- It is the amount of energy required to convert a bound electron into a free electron.

- The energy required to break a covalent bond in germanium crystal and to produce a free electron is about 0.72 eV and that in silicon crystal is 1.12 eV.

Generation and recombination:

- After thermal generation of charge carriers, electrons move randomly in conduction band and holes move randomly in valence band in the absence of electric field.

- The free electrons moving randomly in conduction band may lose their energy on collision with the positive lattice ions fixed in lattice and fall into valence band. These electrons merge with holes. This process is called recombination.

- When the event of recombination occurs, the free electron enters into ruptured covalent bond and re-bridges it. Thermal energy released during this process is used to create electron-hole pair.

- At any constant temperature 'T' (thermal dynamic equilibrium), the number of electrons generated will be therefore equal to the number of holes generated.

- $n = p = n_i$

- 'n' denotes the number density of electrons in the conduction band

- 'p' denotes the number density of holes in the valence band

- 'n_i' denotes the number density of intrinsic charge carriers.

When a radiation (containing photons of energy equal to or greater than the energy gap) is incident on the surface of semiconductor, electron-hole pairs are produced.

Density of electrons in conduction band.

'dn' is the number of free electrons per unit volume in the energy interval between 'E_c' and an energy level 'E' of interest in the conduction band.

Z(E).dE is the number of electron energy states per unit volume in the energy interval between 'E_c' and 'E' in the conduction band.

GROUND ENERGY LEVEL
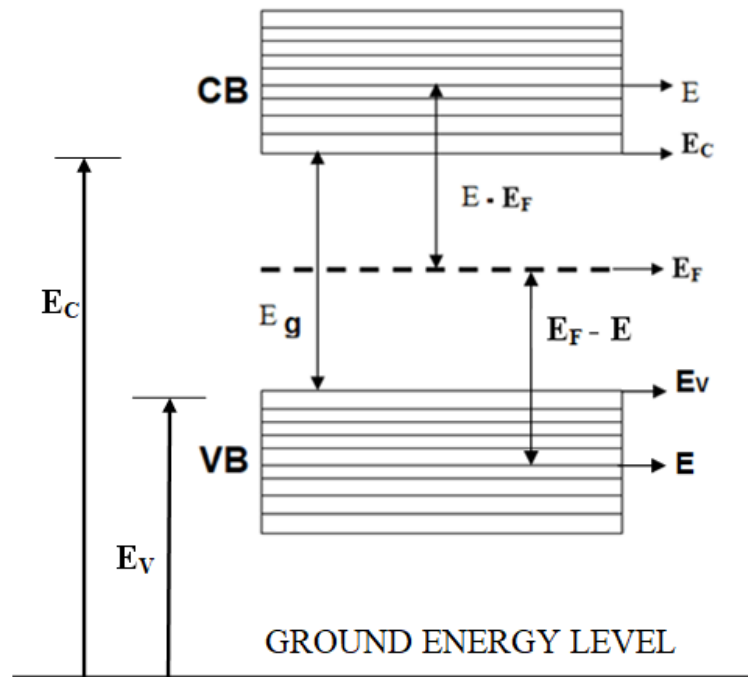
'f(E)' is Fermi-Dirac function indicating the probability of finding electron in the energy interval between 'E_c' and 'E' in the conduction band.

$$dn = Z(E).dE \times f(E)$$

The density of electron in conduction band is given by

$$\int dn = n = \int_{E_c}^{\infty} Z(E).dE \times f(E)$$

When $E = E_c$, $f(E_c) = 1$

Here E_c is the energy corresponding to the energy level at the bottom edge of the conduction band.

When $E = \infty$, $f(E = \infty) = 0$

'E' is considered to be equal to infinity at the top energy level in the conduction band.

Thus the lower limit in the above integration is 'E_c' and the upper limit is infinity.

The bottom edge of conduction band corresponds to potential energy of electron at rest.

Then $(E - E_c)$ is the kinetic energy of an electron in any energy level 'E' located between 'E_c' and '$E_c + dE$'.

$$Therefore, Z(E).dE = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \times (E - E_c)^{1/2}.dE$$

When the temperature 'T' is small, the average kinetic energy available to free electrons ($K_B.T$) is small and consequently the number of energy levels lying between 'E' and 'E_c' is more compared to the number of kinetic electrons.

This situation exists as long as $(E - E_F) \gg (3K_B.T)$.

For this condition, the probability of an electron energy state being occupied by more than one electron is very small.

Therefore, the Fermi-Dirac function becomes as follows.

$$f(E) = \frac{1}{1 + exp\left(\frac{E - E_F}{k_B T}\right)} = \exp\left(\frac{E_F - E}{k_B T}\right) \; as \; exp\left(\frac{E - E_F}{k_B T}\right) \gg 1$$

$$Therefore, n = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(\frac{E_F - E}{k_B T}\right).dE$$

$$n = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(\frac{E_F - E + E_c - E_c}{k_B T}\right).dE$$

$$n = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_F - E_c}{k_B T}\right) \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(\frac{-(E - E_c)}{k_B T}\right).dE$$

The integration is solved by substitution. Putting $x = E - E_c, \; dx = dE$

Changing the limits: *When $E = E_c, x = 0$ and when $E = \infty, x = \infty$.*

$$n = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_F - E_c}{k_B T}\right) \int_{0}^{\infty} x^{1/2} \exp(-ax).dx$$

$$In \; the \; above \; equation, a = \frac{1}{k_B T}$$

The integral $\int_{0}^{\infty} x^{1/2} \exp(-ax).dx$ is known as Gamma function. The solution of the integral is as follows.

$$\int_{0}^{\infty} x^{1/2} \exp(-ax).dx = \frac{\sqrt{\pi}}{2a\sqrt{a}} = \frac{\sqrt{\pi}}{2} \times (k_B T)^{3/2}$$

$$n = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_F - E_c}{k_B T}\right) \times \frac{\sqrt{\pi}}{2} \times (k_B T)^{3/2}$$

On simplification of the equation, we get

$$n = 2\left(\frac{2\pi m_e^* k_B T}{h^2}\right)^{3/2} \times \exp\left(\frac{E_F - E_c}{k_B T}\right)$$

In the above equation, the rest mass of electron 'm' is replaced by its effective mass m_e^*. *The term $N_C = 2\left(\frac{2\pi m_e^* k_B T}{h^2}\right)^{3/2}$* is temperature dependent material constant. It is called effective density of electron energy states in the

conduction band.

$$n = N_c \times \exp\left(\frac{E_F - E_c}{k_B T}\right)$$

At T=300K, N_c = 2.8 x 10^{25} effective electron energy states per unit volume in silicon. 'Effective density of electron energy states in conduction band' means the electron energy states most probably occupied at particular temperature.

Density of holes in valence band.

- 'dp' is the number of holes per unit volume in the energy interval between 'E_v' and 'E' in valence band.

- Z (E).dE is the number of electron energy states per unit volume in the energy interval between 'E_v' and 'E' in valence band.

- '(1 - f(E))' is the Fermi function indicating the probability of not finding electron in the energy interval between 'E_v' and 'E' in valence band.

$$dp = Z(E).dE \times (1 - f(E))$$

The density of holes in valence band is given by

$$\int dp = p = \int_{-\infty}^{E_V} Z(E).dE \times (1 - f(E))$$

When $E = -\infty, f(E = -\infty) = 0$

'E' is considered to be equal to infinity at the bottom energy level in the valence band.

When $E = E_V, f(E_V) = 1$

Here E_V is the energy corresponding to the energy level at the top edge of the valence band.

Thus the lower limit in the above integration is minus infinity and 'E_V' is the upper limit.

The top edge of valence band corresponds to potential energy of hole at rest. Then (E_v - E) is the kinetic energy of a hole in any energy level 'E'

located between 'E$_v$' and 'E'. The kinetic energy of hole increases from the top edge of valence band towards the bottom edge of valence band.

$$Therefore, Z(E). dE = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \times (E_V - E)^{1/2}. dE$$

When the temperature 'T' is small, the average kinetic energy available to free holes (K$_B$.T) is small and consequently the number of energy levels lying between 'E' and 'E$_v$' is more compared to the number of kinetic holes. This situation exists as long as (E$_F$ - E) >> (3K$_B$.T).

For this condition, the probability of an electron energy state being occupied by more than one hole is very small. Therefore, the Fermi-Dirac function becomes as follows.

$$1 - f(E) = 1 - \frac{1}{1 + exp\left(\frac{E - E_F}{k_B T}\right)} = exp\left(\frac{E - E_F}{k_B T}\right) as \ exp\left(\frac{E_F - E}{k_B T}\right) \gg 1$$

$$Therefore, p = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \int_{-\infty}^{E_V} (E_V - E)^{1/2} \exp\left(\frac{E - E_F}{k_B T}\right). dE$$

$$p = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \int_{-\infty}^{E_V} (E_V - E)^{1/2} \exp\left(\frac{E - E_F + E_V - E_V}{k_B T}\right). dE$$

$$p = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_V - E_F}{k_B T}\right) \int_{-\infty}^{E_V} (E_V - E)^{1/2} \exp\left(\frac{-(E_V - E)}{k_B T}\right). dE$$

The integration is solved by substitution. Putting $x = (E_V - E), \ dx = -dE$

Changing the limits: $When \ E = -\infty, x = \infty \ and \ when \ E = E_V, x = 0.$

$$p = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_V - E_F}{k_B T}\right) \int_0^\infty x^{1/2} \exp(-ax). dx$$

$$In \ the \ above \ equation, a = \frac{1}{k_B T}$$

The integral $\int_0^\infty x^{1/2} \exp(-ax). dx$ is known as Gamma function. The solution of the integral is as follows.

$$\int_0^\infty x^{1/2} \exp(-ax) \, . \, dx = \frac{\sqrt{\pi}}{2a\sqrt{a}} = \frac{\sqrt{\pi}}{2} \times (k_B T)^{3/2}$$

$$p = \left(\frac{4\pi}{h^3}\right) \times (2m)^{3/2} \exp\left(\frac{E_V - E_F}{k_B T}\right) \times \frac{\sqrt{\pi}}{2} \times (k_B T)^{3/2}$$

On simplification of the equation, we get

$$p = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} \times \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

In the above equation, the rest mass of electron 'm' is replaced by its effective mass m_h^*. *The term* $N_V = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2}$ is temperature dependent material constant. It is called effective density of states of holes in the valence band.

$$p = N_V \times \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

At T=300K, $N_V = 10^{25}$ effective hole energy states per unit volume in silicon. 'Effective density of hole energy states in valence band' means the energy states most probably not occupied by electrons at particular temperature.

POSITION OF FERMI ENERGY LEVEL IN AN INTRINSIC SEMICONDUCTOR

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

$$2\left(\frac{2\pi m_e^* k_B T}{h^2}\right)^{3/2} \times \exp\left(\frac{E_F - E_c}{k_B T}\right) = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} \times \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

$$\exp\left(\frac{E_F - E_c - E_V + E_F}{k_B T}\right) = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

$$\exp\left(\frac{2E_F - (E_c + E_V)}{k_B T}\right) = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$
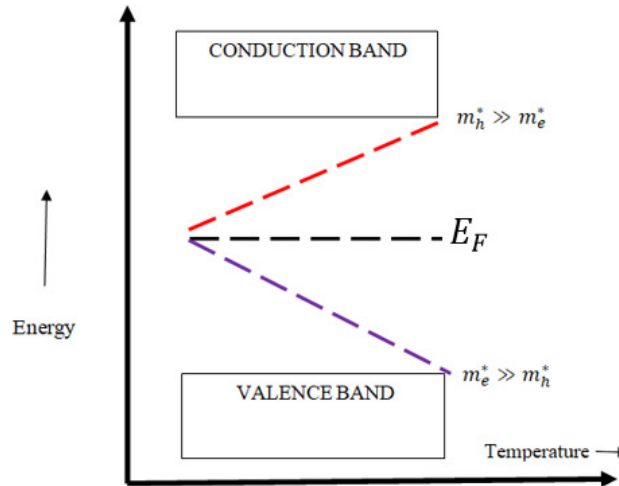
Taking natural logarithm on both sides,

$$\left(\frac{2E_F - (E_c + E_V)}{k_B T}\right) = \frac{3}{2} log_e \left(\frac{m_h^*}{m_e^*}\right)$$

On rearranging the equation,

$$E_F = \left(\frac{E_c + E_V}{2}\right) + \left(\frac{3k_B T}{2}\right) log_e \left(\frac{m_h^*}{m_e^*}\right)$$

When $T = 0K$, $E_F = \left(\frac{E_c + E_V}{2}\right)$.

This equation shows that the Fermi energy level lies at the midpoint of the energy gap in an intrinsic semiconductor.

Expression for intrinsic carrier concentration

At any constant temperature 'T' (thermal dynamic equilibrium), the number of electrons in the conduction band is equal to the number of holes in the valence band.

$$n_i^2 = n \times p = N_c \exp\left(\frac{E_F - E_c}{k_B T}\right) \times N_V \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

$$n_i^2 = 4\left(\frac{2\pi k_B T}{h^2}\right)^3 \times (m_e^* m_h^*)^{3/2} \exp\left(\frac{-(E_c - E_V)}{k_B T}\right)$$

$$n_i = 2\left(\frac{2\pi k_B T}{h^2}\right)^{3/2} \times (m_e^* m_h^*)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right) \; as \; E_g = E_c - E_V$$

Interpretation of the above equation

- The concentration of intrinsic charge carriers is independent on Fermi level.

- The concentration of intrinsic charge carriers has an exponential dependence on the energy band gap value E_g.

- It strongly depends on the temperature.

- The factor 2 in the exponent indicates that two charge carriers are produced when one covalent bond is broken.

Limitations of intrinsic semiconductor:

- Conductivity is low. Germanium has conductivity 10^7 times smaller than that of copper.

- Conductivity is a function of temperature and increases exponentially as the temperature increases.

- Conductivity cannot be controlled from outside.

ELECTRICAL CONDUCTIVITY IN INTRINSIC SEMICONDUCTORS

- In an intrinsic semiconductor, electrical conduction is due to both electrons and holes. Electrons drift in conduction band and holes drift in valence band when an electric field is applied

- Electrical conductivity in intrinsic semiconductors (σ_i) is given by

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

$$\sigma_i = 2 \left(\frac{2\pi k_B T}{h^2} \right)^{3/2} \times (m_e^* m_h^*)^{3/4} \exp \left(\frac{-E_g}{2 k_B T} \right) e (\mu_e + \mu_h)$$

μ_e and μ_h – Mobility of electrons and holes respectively;

T- Temperature of semiconductor

Theoretical calculations reveal that the mobility in non-polar

semiconductors, such as silicon and germanium, is dominated by acoustic phonon interaction. The resulting mobility is expected to be proportional to $T^{-3/2}$.

$$Therefore\ the\ term\ 2e\left(\frac{2\pi k_B T}{h^2}\right)^{3/2}(m_e^* m_h^*)^{3/4}(\mu_e + \mu_h)\ is\ a\ constant$$

$$Let\ \sigma_0 = 2e\left(\frac{2\pi k_B T}{h^2}\right)^{3/2}(m_e^* m_h^*)^{3/4}(\mu_e + \mu_h)$$

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_B T}\right)\backslash$$

DETERMINATION OF ENERGY GAP OF SEMICONDUCTOR

$$\frac{1}{\rho} = \sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_B T}\right)$$

$$\frac{RA}{l} = \rho = \rho_0 \exp\left(\frac{E_g}{2k_B T}\right)\ as\ \rho_0 = \frac{1}{\sigma_0}$$

$$R = \left(\frac{l\rho_0}{A}\right)\exp\left(\frac{E_g}{2k_B T}\right) = C\exp\left(\frac{E_g}{2k_B T}\right)\ as\ C = \left(\frac{l\rho_0}{A}\right)$$

Taking natural logarithm on both sides,

$$log_e R = log_e C + \left(\frac{E_g}{2k_B T}\right)$$

This equation is of the form $y = mx + c$

In the place of y, the term $log_e R$ is present. In the place of x, the term $\frac{1}{T}$ is present. In the place of m, the term $\left(\frac{E_g}{2k_B}\right)$ is present. The constant term is $log_e C$.

The resistance of the given semiconductor is measured at different temperatures. A graph is plotted taking $\frac{1}{T}$ along the X-axis and $log_e R$ along the Y-axis. It will be a straight line with positive slope as shown in the following figure.
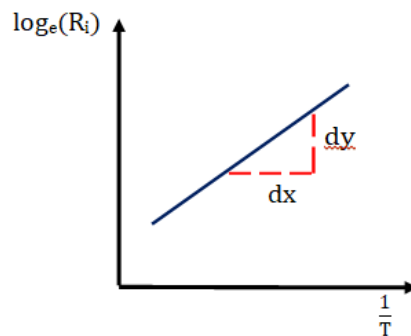
$$Slope\ of\ the\ straight\ line = \frac{E_g}{2k_B}$$

From this equation, $Energy\ gap = Slope \times 2k_B$. Thus the energy gap of an intrinsic semiconductor can be determined.

Carrier mobilities and band gaps for some common semiconductors

Material	μ_e $(cm^2V^{-1}s^{-1})$	μ_h $(cm^2V^{-1}s^{-1})$	E_g (eV)
Ge	3900	1900	0.66
Si	1350	450	1.10
GaAs	8500	400	1.43

Material	E_g (eV)	n_i (cm^{-3})	σ $(\Omega^{-1}\ cm^{-1})$
Ge	0.66	2.3×10^{13}	0.02
Si	1.10	10^{10}	3×10^{-6}
GaAs	1.43	2.4×10^6	3.4×10^{-9}
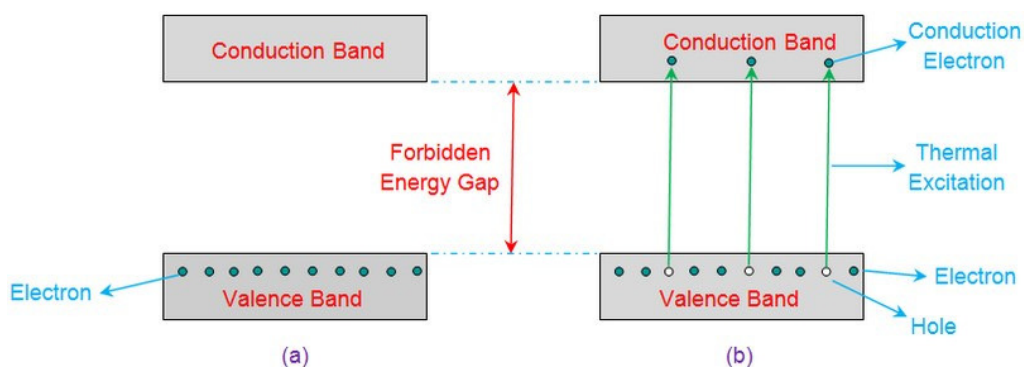
Energy Band Diagram of Intrinsic Semiconductor at (a) 0K (b) Temperature > 0K