Generally, the solid materials are classified into three groups.

1. Conductors (having an abundance of free ēs)
2. Insulator (having hardly any free ē)
3. Semiconductor (Conductivity lies between conductors and Insulators).

The Resistivity is $10^{-8}\ \Omega m$ in case of conductor

$10^{-3}\ \Omega m$ Semiconductor

$10^{12}\ \Omega m$ Insulators.

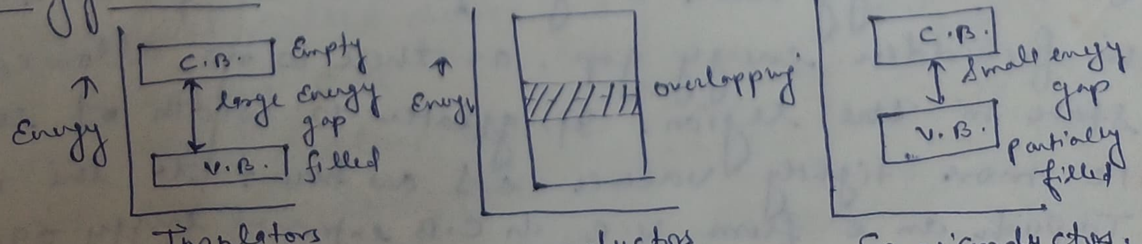
Properties of Semiconductors

1. -ve tempr coefficient of resistance
2. Resistivity lies between conductor & Insulators.
3. when a suitable impurity is added, its conductivity change

At 0K a semiconductor acts as an insulator, because all ēs are tightly held by semiconductor atoms. No ēs in conduction band and valence band is completely filled.

when tempr increase, some of covalent bonds in s/c break up due to thermal energy supplied. If Potential difference is applied across the crystal. Some of free ēs enters in conduction band.

Energy Level:-

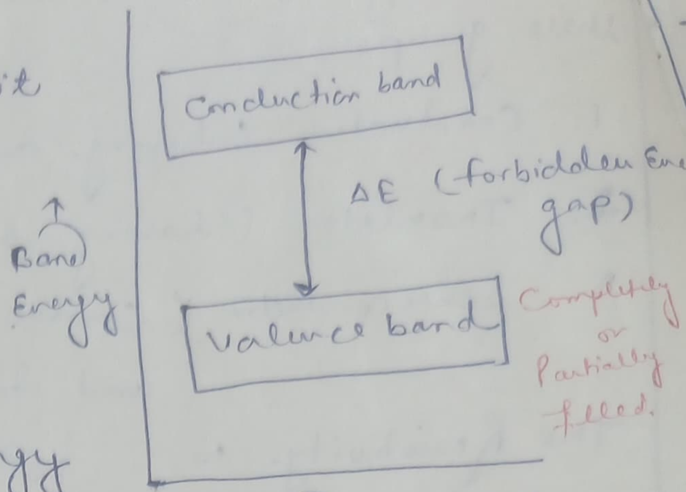


Insulators — $\Delta E \simeq$ 3 ev to 6 ev

conductors

Semiconductors. — $\Delta E =$ 0.1 ev to 1ev

Energy bands in solids:-



• The $\bar{e}$s in outermost orbit of an atom are known as valence electrons. These electrons have highest energy. In solid valence $\bar{e}$s are confined in a band or energy range. "The range of energy possessed by valence $\bar{e}$s is known as valence band". This band may be completely or partially filled OR we can say the uppermost energy band of solid which is partially or completely filled by $\bar{e}$s is called valence band.

• In certain materials (metals) the valence $\bar{e}$s are loosely attached to the nucleus. Even at ordinary temp^r. some of valence $\bar{e}$s may get detached to become free $\bar{e}$s. These free $\bar{e}$s are resposible for conduction of current in a conductor. That's why they are called conduction $\bar{e}$s. "The range of energy possessed by conduction $\bar{e}$s is known as conduction band." All the electrons are free in conduction band. If any substance has empty conduction band i.e. there will no flow of current.

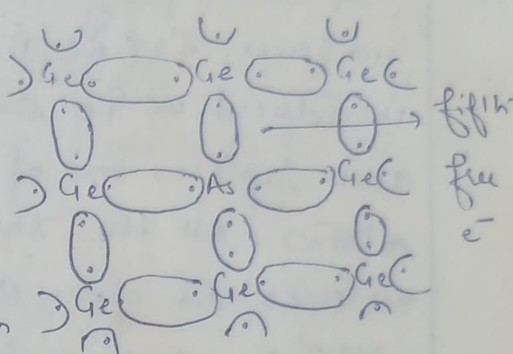
• Separation between conduction band and valence band on the energy level diagrams is called forbidden energy gap. No $\bar{e}$ of a solid can stay in forbidden energy gap, as there is no allowed energy state in the region. If greater is width of energy gap i.e more tightly valence $\bar{e}$s are bound to the nucleus. To push an $\bar{e}$ from V.B. to C.B external energy equal to forbidden gap must be supplied.

Types of Semiconductors

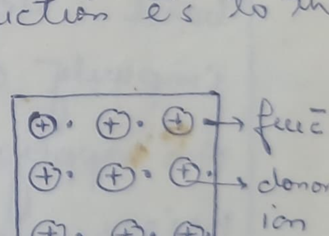
Ge-32- 2,8,18,4
As-33- 2,8,18,5

1. Intrinsic or Pure Semiconductors (Hole - e pairs are created even at room temp^r)
2. Extrinsic or Impure Semiconductors. - If a very small quantity of substance of valency 5 or 3 is introduced as an impurity in a pure germanium (or silicon), its conductivity is increased and called extrinsic semiconductor. It is again divided into two types. — 1. N-Type S/C
2. P-Type S/C.

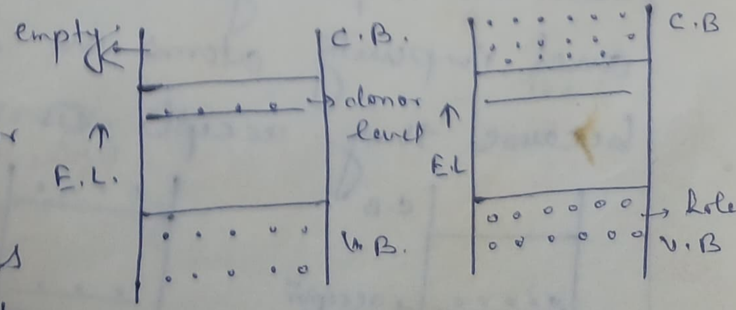
1. N-Type Semiconductors:-



· An impurity of 5 valence $\bar{e}$s (As, Sb, P) is added. It replaces one of the Ge atom. four of five valence $\bar{e}$s of the impurity atom form covalent bonds with Ge atom and V ~~impurity atom~~ becomes free, acts as a charge carrier. The conductivity of the crystal increase. The impurity atoms are called donor atoms because they provide conduction $\bar{e}$s to the crystal. N-type S/C crystal has freely moving electrons and equal no. of stationary +vely charged donor ions. The ions are +vely charged donor ions. The ions are +vely charged because they lost one $\bar{e}$ each. The crystal as a whole is neutral.



· The pentavalent impurity atoms introduce a new energy level called donor level near the C.B.
At room temp^r, valence $\bar{e}$s receive enough energy to jump the gap and enter in CB.



At absolute temp^r

At room temp^r.

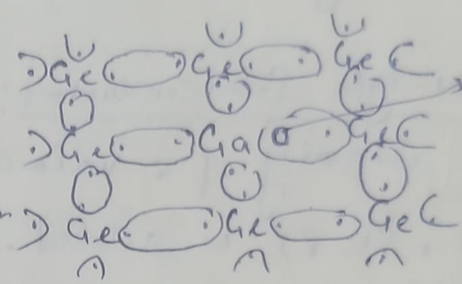
leaving hole behind. Similarly donor ēs at donor level easily absorb energy and jump into C.B. but these free ēs leave no holes behind as they break no covalent bond. Hence, there are more free ēs in C.B. than holes are in valence band. In n-type S/C, ēs are majority carrier and holes are minority carrier.

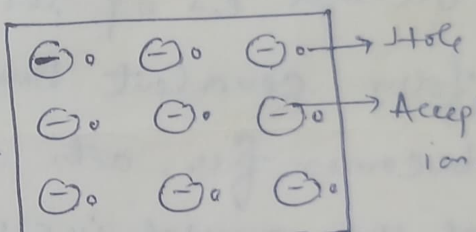
Ga31 - 2,8,18,3

Ga → gallium
B → Boron
Al → aluminium

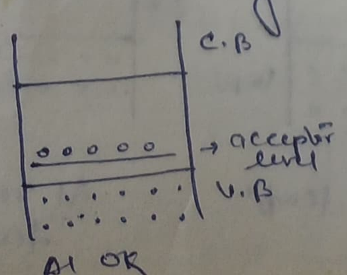
P-Type Semiconductors :-

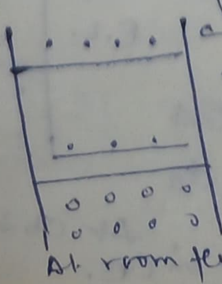
· If an impurity atom with 3 valence ēs (Al, B, Ga) is introduced in Ge crystal, it also replaces one of the germanium atoms. All the three of its valence ēs form covalent bonds with one each valence ē of the three nearest Ge atoms while the valence ē of the IV nearest Ge atom is not able to form the bond. Hence on one side of the impurity atom, there is an empty space is called 'hole'.





On applying an electric field, a valence ē from a neighboring atom can drop into this hole, thereby creating a hole in the next atom. In this way hole can move across the crystal from one atom to another. Such an impure germanium crystal is called P-type S/C and impurity atoms are called acceptor atoms because they accept ēs from the pure semiconductor.





· There is an acceptor level near the V.B. The energy required for this jump is < as compared to jump to C.B.

→ Majority carriers are holes in P-type S/C.

INTRINSIC SEMICONDUCTORS:-

The semiconductors in which the transformation of electrons to the conduction band and the generation of holes in the valence band are achieved purely by thermal excitation are called intrinsic semiconductors. It means this effect is temperature dependent and produces equal numbers of electron and hole carriers. It is assumed that the electrons in the conduction band may have energy lying between E_c and ∞ while the electrons in valence band have energy lying from $-\infty$ to E_v. E_g is the width of the forbidden gap.

(i) <u>Electron Concentration in Conduction Band:-</u>

The density of $\bar{e}$s in the conduction band i.e. total number of $\bar{e}$s per unit volume, is given by

$$n_c = \int_{E_c}^{\infty} D(E)\, F(E)\, dE \quad \text{——— (I)}$$

where $D(E) \rightarrow$ energy density of states at the bottom of conduction band of the semiconductor is

$$D(E) = \frac{4\pi}{h^3}(2m_e)^{3/2}(E-E_c)^{1/2} \quad \text{——— (II)}$$

$D(E)dE$ gives the total no. of available states in the range E & $E+dE$.

$F(E)$ is the fermi energy function giving the probability of occupation occupancy of allowed energy states by the $\bar{e}$s under the condition of thermal equilibrium and given by

$$F(E) = \frac{1}{e^{(E-E_F/k_BT)}+1} \quad \text{——— (III)}$$

Where K_B is Boltzmann constant, T is ... in Kelvin, E_F is the fermi level.

Putting the values of D(E) & F(E) from (ii) & (iii) in (i).

$$n_c = \frac{4\pi}{h^3}(2m_e)^{3/2}\int_{E_c}^{\infty}\frac{(E-E_c)^{1/2}\,dE}{e^{(E-E_F/K_BT)}+1}$$

If $E - E_F >> K_BT$, the unit term is denominator is negligible

$$n_c = \frac{4\pi}{h^3}(2m_e)^{3/2}\int_{E_c}^{\infty}(E-E_c)^{1/2}\left(e^{(E_F-E)/K_BT}\right)dE$$

$$n_c = \frac{4\pi}{h^3}(2m_e)^{3/2}\int_{E_c}^{\infty}(E-E_c)^{1/2}\left\{e^{\left(\frac{E_F-E_c}{K_BT}\right)}\cdot e^{\frac{(E_c-E)}{K_BT}}\right\}dE$$

Let $\frac{E-E_c}{K_BT} = x$ $\qquad K_\beta = 1.38\times10^{-23}\ J/K$

$E - E_c = xK_BT$

$dE = K_BT\,dx$ $\qquad E = eV$

when $E=E_c$, $x=0$; $E=\infty$, $x=\infty$

$(E-E_c)^{1/2} = (x^{1/2})(K_BT)^{1/2}$ $\qquad 1J = 6.2\times10^{18}\ eV$

$$n_c = \frac{4\pi}{h^3}(2m_e)^{3/2}\int_0^{\infty}(x)^{1/2}(K_BT)^{1/2}e^{-x}e^{+\frac{(E_F-E_c)}{K_BT}}\cdot K_BT\,dx$$

$$n_c = \frac{4\pi}{h^3}(2m_e)^{3/2}(K_BT)^{3/2}e^{\left(\frac{E_F-E_c}{K_BT}\right)}\int_0^{\infty}e^{-x}x^{+1/2}dx$$

$$\therefore \int_0^{\infty}x^{1/2}e^{-x}dx = (\pi/4)^{1/2}$$

$$n_c = \frac{4\pi}{h^3}(2m_eK_BT)^{3/2}e^{\left(\frac{E_F-E_c}{K_BT}\right)}\cdot(\pi/4)^{1/2}$$

$$n_c = 2\left(\frac{2\pi m_e K_BT}{h^2}\right)^{3/2}\exp\left\{\frac{E_F-E_c}{K_BT}\right\}$$

$$\boxed{n_c = 2\left(\frac{2m_e K_B T\pi}{h^2}\right)^{3/2} \exp\left\{\frac{E_F - E_c}{K_B T}\right\}} \quad \text{---(iv)}$$

(ii) Hole Concentration in Valence Band:-

Since a hole signifies a vacancy created by removal of an electron i.e an empty energy level, the fermi function for a hole is $1 - f(E)$. Here $f(E)$ represents the probability that the level is occupied by an electron

$$1 - f(E) = 1 - \frac{1}{\exp\frac{(E-E_F)}{K_B T} + 1}$$

$$= \frac{\exp\left\{\frac{E-E_F}{K_B T}\right\}}{\exp\left\{\frac{E-E_F}{K_B T}\right\} + 1}$$

$\because E < E_F$ being in valence band, so the exponential term < 1 and can be neglected in the denominator,

$$\therefore 1 - f(E) = \exp\left\{\frac{E-E_F}{K_B T}\right\}$$

Thus density of holes in the valence band can be given by

$$n_h = \int_{-\infty}^{E_v} D(E)\left[1 - f(E)\right] dE$$

$$= \frac{4\pi}{h^3}(2m_h)^{3/2} \int_{-\infty}^{E_v} (E_v - E)^{1/2} \exp\left\{\frac{E-E_F}{K_B T}\right\} dE$$

$$\left(e^{\frac{E-E_v}{K_BT}} < e^{\frac{E_v-}{K_BT}}\right.$$

$$\frac{E_v - E}{K_B T} = x.$$

$$E_v - E = x K_B T$$

$$dE = -dx\,(K_B T)$$

$$(E_v - E)^{1/2} = (x^{1/2})(K_B T)^{1/2}$$

$$n_h = \frac{4\pi}{h^3}(2m_h)^{3/2}\int_{\infty}^{0} x^{1/2}(K_BT)^{1/2}\exp\left\{\frac{E_v - E_F}{K_BT}\right\} e^{-x}(-K_BT)\,dx$$

$$n_h = \frac{4\pi}{h^3}(2m_h)^{3/2}\exp\left\{\frac{E_v - E_F}{K_BT}\right\}(K_BT)^{3/2}\int_0^{\infty} x^{1/2} e^{-x}\,dx$$

$$\boxed{n_h = 2\left(\frac{2 m_h \pi K_B T}{h^2}\right)^{3/2}\exp\left\{\frac{E_v - E_F}{K_B T}\right\}} \quad -(4)$$

$$\because \int_0^{\infty} x^{1/2} e^{-x}\,dx = (\pi/4)^{1/2}$$

(III) Fermi Energy and Fermi Level:-

In an intrinsic semiconductor, we know $n_c = n_h$

$$\cancel{2}\left(\frac{\cancel{2\pi} m_e \cancel{K_B T}}{\cancel{h^2}}\right)^{3/2}\exp\left(\frac{E_F - E_c}{K_B T}\right) = \cancel{2}\left(\frac{\cancel{2\pi} m_h \cancel{K_B T}}{\cancel{h^2}}\right)^{3/2}\exp\left(\frac{E_v - E_F}{K_B T}\right)$$

$$(m_e)^{3/2}\exp\left(\frac{E_F - E_c}{K_B T}\right) = (m_h)^{3/2}\exp\left(\frac{E_v - E_F}{K_B T}\right)$$

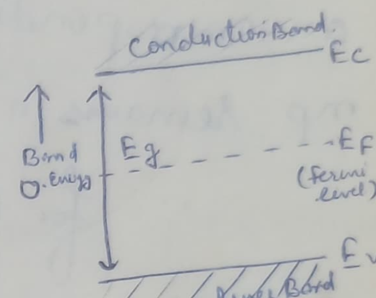
$$\exp\left(\frac{2E_F - E_C - E_v}{K_B T}\right) = \left(\frac{m_h}{m_e}\right)^{3/2}$$

$$\frac{2E_F - E_C - E_v}{K_B T} = \frac{3}{2}\log\left(\frac{m_h}{m_e}\right)$$

$$E_F = \frac{E_C + E_v}{2} + \frac{3}{4} K_B T \log\left(\frac{m_h}{m_e}\right)$$

at absolute zero temperature

$$m_h = m_e \Rightarrow \log 1 = 0$$



$$\boxed{E_F = \frac{E_C + E_v}{2}} \quad \text{— (VI)}$$

⇒ fermi level lies exactly half way between top of valence band and conduction band

(iv) Intrinsic Concentration of charge Carriers:-

Combining equ. (IV) & (V), we get the following expression for the product of $\bar{e}$- hole concentration

$$n_e n_h = 4\left(\frac{2\pi K_B T}{h^2}\right)^3 (m_e m_h)^{3/2} e^{\left(\frac{E_v - E_c}{K_B T}\right)}$$

$$\boxed{n_e n_h = np = A T^3 e^{-E_g/K_B T}} \quad \text{— (VII)}$$

where $E_g = E_c - E_v$ (width of forbidden energy gap)

$$A = \frac{32\pi^3 K_B^3}{h^6} (m_e m_h)^{3/2} \text{ — Constt.}$$

Equ. (VII) shows that the product of holes and electron densities depends on the temperature T and the Eg. but is independent of fermi level E_F. Thus the product of electron and hole concentrations, for a given material, is constant at a given temperature T.

If an impurity is added to increase 'n' there will be a corresponding decrease in p such that the product np remains a constant.

$\therefore$ for intrinsic S/C. $n = p = n$

$$\therefore \boxed{np = n_i^2 = AT^3 e^{-E_g/K_BT}} \quad \text{-(VIII)}$$

Where $n_i \rightarrow$ intrinsic density of either carrier.

This relation is called law of action.

EXTRINSIC SEMICONDUCTOR

The conductivity of an intrinsic semiconductor can be increased by adding certain impurities to it. we get impurity semiconductor which is also known as extrinsic semiconductor.

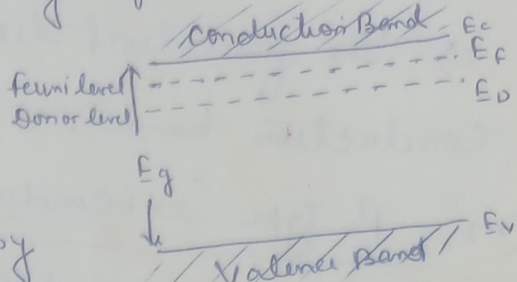
Energy Band and fermi level :-

(1) N-type Semiconductor :- When an amount of pentavalent impurity is added to the crystal, it creates extra $\bar{e}$'s without adding any new holes. N-type semiconductor consists of a conduction band below which there are Nd

forbidden ...

donors per unit volume in donor levels having E_d

In intrinsic semiconductor, fermi level lies in the middle of the forbidden energy E_g indicating equal concentrations of free $\bar{e}$s and holes. When a donor type impurity is added to the crystal, a donor level will occupy the states near the bottom of conduction band. Hence, it will be more difficult for the $\bar{e}$s to jump from the valence band to conduction band. Consequently, the no. of holes of the valence band is decreased. Since, fermi level is a measure of the probability of occupancy of the allowed energy states, E_F for n-type semiconductors must move closer to the conduction band, as shown in figure. At usual temperatures all the donor levels will be fully activated and the donor atoms will be ionised. It means the density of electrons in the conduction band will be approximately equal to the density of donor atoms i.e $n_c \simeq N_d$



from eqn.

$$n_c = N_d = 2\left[\frac{2\pi m_e K_B T}{h^2}\right]^{3/2} e^{(E_F - E_c)/K_BT}$$

$$= N_c\, e^{(E_F - E_d)/K_BT}$$

where $N_c = 2\left(\frac{2\pi m_e K_B T}{h^2}\right)^{3/2}$ = constant

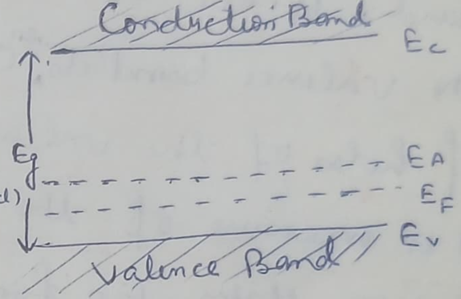
$$\therefore \frac{N_c}{N_d} = e^{-(E_F - E_c)/K_BT}$$

$$-\frac{(E_F - E_c)}{K_BT} = \ln\frac{N_c}{N_d}$$

$$\boxed{E_F = E_C - K_B T \ln \frac{N_c}{N_d}}$$

⇒ The fermi level lies just below the bottom of the conduction band.

(ii) P-Type Semiconductor :- when an acceptor type impurity is added, it also modifies the energy level diagram of semiconductor and makes the conduction easier. The presence of impurity creates new energy levels which are in the gap in the neighbourhood of the top of valence band of energies.



When an intrinsic semiconductor is doped with acceptor type impurity, the concentration of $\bar{e}$s in the conduction band is less than the concentration of holes in valence band, and the fermi level shifts towards the valence band. The acceptor level lies immediately above the fermi level. If we assume that there are only acceptor atoms present and that these are all ionised, we have $p = N_a$, from eqn. (v)

$$p \cdot n_h = N_a = 2\left(\frac{2 m_h \pi K_B T}{h^2}\right)^{3/2} e^{\frac{(E_v - E_F)}{K_B T}}.$$

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

where $N_v = 2\left(\frac{2\pi m_h K_B T}{h^2}\right)^{3/2}$ = Constant

$$\frac{N_v}{N_a} = e^{-(E_v - E_F)/K_B T}$$

or $$\ln \frac{N_v}{N_a} = -\frac{(E_v - E_F)}{K_B T}$$

$$\boxed{E_F = E_V + K_BT \ln \frac{N_V}{N_a}}$$

⇒ fermi level lies above the top of valence band.

(iii) <u>Effect of Temperature:-</u> for an intrinsic s/c $n_i = p_i$ and as temperature increases both n_i and p_i will increase. Thus the fermi level (E_F) will remain approximately at the centre of the forbidden gap. Thus intrinsic semiconductor fermi level is independent of temperature.

If we increase the temperature of an n-type semiconductor, then what happens. Since all the donors have already donated their free electrons at room temperature, the additional thermal energy will only increase the generation of $\bar{e}$-hole pairs. Thus the concentration of minority charge carriers increases. A temperature is ultimately reached when the number of covalent bonds broken is very large such that the number of holes and electrons is almost equal. The extrinsic semiconductor then behaves like an intrinsic semiconductor, although its conductivity is higher. The critical temperature is 85°C for Ge and 20°C for Si. The same arrangement can be put forward for the p-type semiconductor. Thus with an increase in the temperature of an extrinsic (impurity) semiconductor, it behaves almost intrinsically.