CHAPTER - III

ELECTRICAL PROPERTIES OF AMORPHOUS SEMICONDUCTOR

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3.1 D.C. ELECTRICAL CONDUCTIVITY :

In the preceding chapter, it was pointed out that two different starting points have been adopted to describe the transport properties of amorphous semiconductors. One way is based on the acceptance of the Davis-Mott model and other is based on small polaron model. Here we shall treat some of the most commonly used transport properties which may provide some information about the amorphous solids.

The essential features of the Davis and Mott model for the band structure of amorphous semiconductors, are the existence of narrow tails of localized states at the extremities of the valence and conduction bands and localized levels near the middle of the gap. This leads to three different conduction mechanisms (Figures 3.1a,b,c,d).

3.1.1 EXTENDED STATE CONDUCTION :

The conductivity of semiconductor is given by,

$$\sigma = - e \int N(E)\ \mu(E) kT \frac{\partial f(E)}{\partial E}\ dE \qquad \ldots (3.1)$$

where f(E) is the Fermi-Dirac distribution function

$$f(E) = \frac{1}{1 + \exp\left[(E-E_F)/kT\right]}$$

N(E) - density of state, $\mu(E)$ - mobility of carriers using above equation,

$$\frac{\partial f(E)}{\partial E} = - f(E) \left[1 - f(E) \right] /KT$$

From this σ can be written as :

$$\sigma = e \int n(E) \mu(E) f(E) \left[1 - f(E) \right] dE \qquad \ldots (3.2)$$

In Davis and Mott[3.1] model Fermi level is situated near the middle of the band gap and far from conduction band i.e. the energy which separates the extended states from the localized states. So that Boltzmann statistics is used to describe the occupancy of states.

Thus $f(E) = \exp (- (E - E_F) / kT)$

According to Mott, mobility drops at critical energy E_c or E_V but at present it is not exactly known how mobility depends on the energy in both conduction regimes. In non-degenerate case the conductivity due to electrons excited beyond the mobility edge into extended state is given by,

$$\sigma = eN (E_c) kT \mu_c \exp\left[- (E_c - E_F) / kT\right] \qquad \ldots (3.3)$$

where μ_o is average mobility. The number of electrons in conduction band is,

$$n = \int_{E_c}^{\infty} N(E_c) \exp \left[-(E-E_F)/kT\right] dE$$

$$= N(E_c) kT \exp \left[- (E_c - E_F)/kT\right] \qquad \ldots (3.4)$$

We dedine $\sigma(E_c) = eN\langle E_c \rangle \mu_c kT$

If $N(E_c) = \langle N(E) \rangle /3$

where $N(E)$ is the average density of state over band using this we get,

$$\sigma(E_c) = e \langle N(E) \rangle \mu_c \, kT/3$$

Mott[3.2] has given minimum metallic conductivity by the equation,

$$\sigma_{min} = \text{constant} \frac{e^2}{\hbar a} \qquad \ldots (3.5)$$

where constant = 0.026 and 0.1, $\sigma_{min} = 200 - 300 \ \Omega^{-1} \ cm^{-1}$ using constant = 0.026.

$$\mu_c = 0.078 \ \left(\frac{e}{ha} \right) \Big/ \langle N(E) \rangle \ kT$$

where a is interatomic distance.

The maximum energy E_{max} of the band is given by,

$$E_{max} = \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{and} \quad k_{max} = \frac{\pi}{a}$$

This equation gives

$$N(E) = \frac{km}{2\pi^2 \hbar^2} = \frac{1}{a^3} \ B$$

Substituting in equation of μ_c we get,

$$\mu_c = 0.078 \ \frac{ea^2 B}{\hbar kT} \qquad \ldots (3.6)$$

Taking $a = 2A^{o}$, $B = 5eV$

$$\mu_c = 10 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$$

This value corresponds to mean free path comparable or less than the interatomic distance. Cohen[3.3] suggested that conduction is diffusive or Brownian type. In this regime mobility can be obtained with the help of Einstein equation,

$$\mu = \frac{eD}{kT} \; ; \quad D - \text{Diffusion coefficient.}$$

$$D = \left(\frac{1}{6} \right) \nu a^2$$

ν - jump frequency, a - interatomic distance.

$$\mu_c = \left(\frac{1}{6} \right) \frac{ea^2}{kT} \nu \qquad \dots (3.7)$$

$$\mu_c \propto \frac{1}{kT}$$

Therefore equation for conductivity is of the form,

$$\sigma = \sigma_o \exp\left[- (E_c - E_F) / kT \right] \qquad \dots (3.8)$$

This equation is used for calculation of activation energy. Optical absorption of amrophous semiconductors has shown that band gap decreases with increasing temperature. The energy distance $(E_c - E_F)$ shows similar behaviour under the assumption of linear temperature dependence.

$$E_c - E_F = E(0) - \gamma T \qquad \dots (3.9)$$

$$\sigma = \sigma_o \exp\left(\frac{\gamma}{k}\right) \exp\left[-\frac{E(0)}{kT}\right] \qquad \ldots (3.10)$$

Here E(O) is energy distance at $T = 0\ ^{o}K$.

We write this formula as,

$$\sigma = C_o \exp\left[\frac{-E(0)}{kT}\right] \qquad \ldots (3.11)$$

where $C_o = eN\ (E_c)\ kT\ \mu_c \exp\left(\frac{\gamma}{k}\right)$ ... (3.12)

Mott[3.4] has shown that σ_o lies between 10 and $10^3\ \Omega^{-1}cm^{-1}$ in most of amorphous semiconductors. In chalcogenide glasses, the temperature coefficient of optical gap lies between 4×10^{-4} and 8×10^{-4} eV deg^{-1}. As the Fermilevel is situated near the middle of the gap the values of $\exp\left(\frac{\gamma}{K}\right)$ lie in the range 10-100.

3.1.2 CONDUCTION IN BAND TAILS :

If the wave functions are localized $\sigma(E) = 0$ conduction occurs only by thermally activated hopping. Every time electrons move from one localized state to another, it will exchange energy with phonons. Therefore, mobility will have a thermally activated nature;

$$\mu_{hop} = \mu_o \exp\left[\frac{-W\ (E)}{kT}\right] \qquad \ldots (3.13)$$

where $\mu_o = \left(\frac{1}{6}\right) \gamma_{ph} \frac{e\ R^2}{kT}$ ... (3.14)

W - excitation energy, μ_o - mobility at T = 0 γ_{ph} -

phonon frequency, R - distance covered in one hop.

The conductivity being an integral over all available energy states, will depend on the energy distribution of the density of localized states. If we assume that the density of state N(E) behaves as power 'S' of E,

$$N(E) = \frac{N(E_c)}{(\Delta E)^s} (E - E_A)^s \qquad \ldots (3.15)$$

$\Delta E = E_C - E_A$,

then conductivity σ_{hop} due to electron can be easily calculated using equation,

$$\sigma = e \int N(E)\, \mu(E)\, f(E) \left[1-f(E) \right] dE$$

$$\sigma_{hop} = \sigma_{o\,hop} \left(\frac{kT}{\Delta E} \right)^s C \exp\left[-(E_A - E_F + W)/kT \right] \ldots (3.16)$$

where $\sigma_{o\,hop} = \left(\frac{1}{6} \right) \nu_{ph}\, e^2 R^2 N(E_c)$ and

$$C = S! - \left(\frac{\Delta E}{kT} \right)^S \exp\left(\frac{-\Delta E}{kT} \right) \left[1 + S \left(\frac{kT}{\Delta E} \right) + \right.$$

$$\left. + S\,(S-1) \left(\frac{kT}{\Delta E} \right)^2 + \ldots \right] \qquad \ldots (3.17)$$

for linear vibration S = 1, the conductivity is given by

$$\sigma_{hop} = \sigma_{o\,hop} \frac{kT}{\Delta E} (C_1 \exp\left[-(E_A - E_F + W)/kT \right] \ldots (3.18)$$

where

$$C_1 = 1 - \exp\left(-\frac{\Delta E}{kT} \right) \left(1 + \frac{\Delta E}{kT} \right) \qquad \ldots (3.19)$$

3.1.3. CONDUCTION IN LOCALIZED STATES AT THE FERMI ENERGY.

The fermi energy lies in a band of localized state, the carriers move between states via tunnelling process. The temperature dependence of the hopping conductivity at E_F has been given by Mott[3.5]. Let us consider the electrons scattered by phonons from one localized state to another. W be energy difference between states. P be probability that an electron jumps from one state to another state is given by three factor -

(1) The probability of finding a phonon with excitation energy equal to W is given by Boltzmann equation $\exp\left(-\frac{W}{kT}\right)$

(2) An attempt frequency ν_{ph} which cannot be greater than the maximum phonon frequency.

(3) The probability of electron transfer from one state to another state, depends upon overlapping of wave function and given by $\exp(-2\alpha R)$.

Here R - jumping distance, α - Rate of fall of wave function.

The probability P that an electron jumps will be expressed by

$$P = \nu_{ph} \exp\left(-2\alpha R - \frac{W}{kT}\right) \qquad \ldots (3.20)$$

By using Einstein relation for mobility,

$$\mu = \frac{eD}{kT} \quad \text{with } D = \left(\frac{1}{6}\right) PR^2$$

$$\sigma = \left(\frac{1}{6}\right) e^2 R^2 PN(E_F) \qquad \ldots (3.21)$$

where $N(E_F)$ is the density of states at the fermi level. Using equation (3.20), the conductivity is represented by,

$$\sigma = \left(\frac{1}{6}\right) e^2R^2 \ \nu_{ph} N(E_F) \exp(-2\alpha R) \exp\left(-\frac{W}{kT}\right) \qquad ...(3.22)$$

As the temperature is lowered the number and energy of phonons decrease and the more energetic phonon assisted hops will progressively become less favourable. Carriers will tend to hop to larger distance in order to find sites which lie energetically closer than nearest neighbour. The factor $\exp\left(-2\alpha R - \frac{W}{kT}\right)$ will not have its maximum value for the nearest neighbour. In order to find most probable hopping distance, Mott used an optimization procedure. If $N(W)$ is the density of state per unit volume and per unit energy, then the number of states with energy difference W within a distance R from a particular atom is given by,

$$\frac{4\pi}{3} R^3 N(W) W$$

The electron can leave its site only if the number of accessible sites is at least one. Taking this into account one gets for the average energy spacing between states near Fermi lev-el,

$$W = \frac{3}{4\pi R^3 N(E_F)} \qquad ... (3.23)$$

and for the jump probability

$$P = \nu_{ph} \exp\left[-2\alpha R - \left(\frac{4\pi}{3}\right) N(E_F) R^3 kT\right]^{-1} \qquad ... (3.24)$$

The most probable jump distance is found by minimizing the exponent of the above expression as function of R,

$$R = \left[\frac{g}{8\pi\alpha \; N(E_F) \; kT} \right]^{1/4} \qquad \ldots (3.25)$$

This gives a jump frequency of the form,

$$P = \nu_{ph} \exp \left(\frac{-A}{T^{1/4}} \right) \qquad \ldots (3.26)$$

$$\text{where } A = 2.1 \left[\alpha^3 / kN \, (E_F) \right]^{1/4} \qquad \ldots (3.27)$$

Mott's treatment of variable hopping leads to a temperature dependence for the conductivity of the form,

$$\sigma = \left(\frac{1}{6} \right) e^2 \, R^2 \; \nu_{ph} \, N(E_F) \, \exp \left(- \frac{A}{T^{1/4}} \right) \qquad \ldots (3.28)$$

$$\text{or} \qquad \sigma = \sigma_o \, (T) \, \exp \left(\frac{- A}{T^{1/4}} \right) \qquad \ldots (3.29)$$

In Motts derivation the prefactor σ_o (T) is given by

$$\sigma_o \, (T) = \frac{e^2 \; \nu_{ph} \, N(E_F)}{6} \left[\frac{9}{8\pi\alpha N(E_F) kT} \right]^{1/2}$$

$$= \frac{e^2}{2(8\pi)^{1/2}} \; \nu_{ph} \left[\frac{N(E_F)}{\alpha kT} \right]^{1/2} \qquad \ldots (3.30)$$

Assuming $\alpha^{-1} = 10A^o$; $N\,(E_F) = 10^{10}\ cm^{-3}\ eV^{-1}$,

one finds $R = 250\ T^{-1/4}\ A^o$ which yields $80A^o$ at 100^ok.

Several authors have investigated the effect of

Departure from a constant density of states and have clearly demonstrated that energy distribution of the density of states is of major importance in the theory of variable range hopping. A review of article on hopping conductivity in disordered solids has recently been published by Overhof[3.6].

3.2. THERMO-ELECTRIC EFFECT IN SEMICONDUCTOR :

Fundamental information about the mechanism of conduction in solids can be obtained from studies of the thermoelectric effect. In 1821, Thomas seeback found that if a metal is connected at its two ends with a second metal, and if one of the junctions is heated, a voltage is developed across the open ends of the second metal. The schematic circuit for the measurement of thermoelectric voltages for a semiconductor is given in Figure (3.2). If the metal contacts are applied to the two ends of a semiconductor rod and if one junction is maintained at a higher temperature than the other, a potential difference will be developed between the two electrodes. This thermoelectric or seeback voltage is produced partly because of the majority carriers in semiconductor defused from hot to cold junction per second, thus giving a potential difference between the two ends. This voltage builds up a value such that the return current just balances the diffusion current, when a steady stage is reached.

In the experimental arrangement of Figure (3.2), if the charge carriers in semiconductors are predominantly electrons, the cold junction becomes negatively charged, if the carriers are positive holes, the cold junction becomes positively charged. The magnitude of the voltage V_s is proportional to the difference in temperature between the hot and the cold junction.

From the sign of thermoelectric voltages, it is thus possible to deduce whether a specimen exhibits n-type or p-type conductivity; further from the magnitude of the thermoelectric voltage one can determine the concentration of charge carriers in the specimen.

Semiconductors exhibit thermoelectric behaviour in circuits with metals the magnitudes of the thermoelectric quantities exhibited by semiconductors are often much larger than those exhibited by metals. The electric properties of semiconductors can be used to know the position of Fermi level with respect to band edges.

A typical thermoelectric circuit containing a semiconductor is shown in Figure (3.2). The semiconductor is shaped into long thin rod with metal contacts at its two ends. One end of the bar is kept at a reference temperature To while the other end is placed at To + ΔT. Let us suppose that a linear temperature gradient exists along the bar, which is P type. Under these conditions, the Fermi level in the metal and semiconductor and the edges of the semiconductor band assume the position shown in the lower part of figure. The semiconductor band edges become tilted as indicated. While the Fermi level also becomes tilted, with a somewhat different slope. The Fermi level in the semiconductor is continuous with the Fermi levels in the metals at two contacts. The Fermi level in metal wires leading away from the contacts do not change with temperature as compared to the magnitude of change in Fermi level in semiconductor; hence the Fermi level in metal wires are shown horizontal in Figure (3.3) and seeback voltages of the circuit is essentially given by the difference in the Fermi level from one end of the semiconductor bar to the other end. In the case of uniform P-type semiconductor taken as an example, the right end of bar becomes negative with respect to left hand side. The tilting of the energy levels in the figure is greatly exagerated in order to illustrate the arguments to be presented.

If the temperature difference is small the effects depicted in figure (3.3) will be linear with temperature and hence linear with horizontal distance across the diagram. The quotient between V_s and ΔT is called the "thermoelectric power". Its physical dimensions are volt per degree, it is designated by a symbol Q. If both the hot and cold junctions are raised or lowered in temperature keeping T same, it will be found that Q varies with mean temperature. The variation of Q with temperature can just be well observed by keeping the cold junction at temperature, To and plotting the thermoelectric voltage V_s against the variable temperature To + ΔT of the hot junction. The slope of this plot at temperature T gives the value of Q at that temperature.

The tilting of the energy bands and Fermi level in the semiconductor sustaining a temperature gradient can be explained as follows :

Suppose the temperature T and To + ΔT written within the impurity dominated temperature range of the semi-conductor, assuming the specimen to be uniformly doped. Then the concentration of the impurity carriers, positive holes, will be higher at right hand end than at left hand end in figure (3.3). Consequently there will be a diffusion of positive holes down the temperature gradient from right to left. The cooler end of the specimen, therefore, becomes positively charged and a steady state potential difference just counter balances the diffusion flow. The potential difference in question is given by the vertical distance S on the diagram.

Even if there were no concentration gradient of majority carriers (as would be the case if the temperature To and To + ΔT were in such a range that the acceptor were all saturated), there would still be a small potential difference generated between the two ends of the specimen. This difference would result from the fact that those holes thermal motion would be going alightly faster in the right to left direction than in left to right because they come from a warmer region of the specimen and hence have higher thermal kinetic energies. For semi-conductor in the impurity dominated and intrinsic temperature range, however, this effect is small compared with the effect of diffusion and may be neglected in approximate theory.

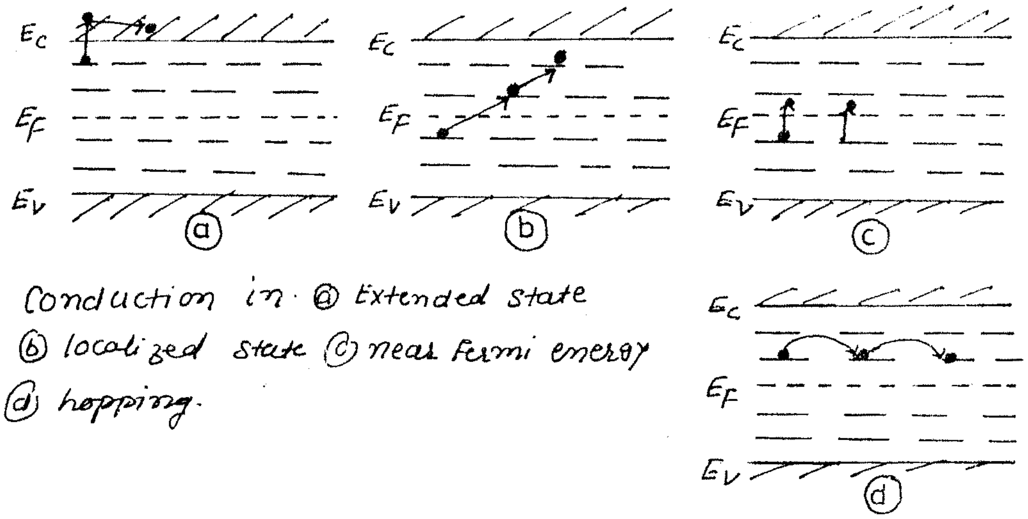
3.3. SEEBACK EFFECT AND THERMOELECTRIC POWER :

The Fermi level in P type semiconductor rises with temperature towards the middle of the forbidden gap. Hence the total rise of the Fermi level in figure (3.3) from cold of the specimen to the warm end is given by the sum of rise in the upper edge of the valence band and the additional increase due to the rise of the Fermi level above the valence band edge. In other wards,

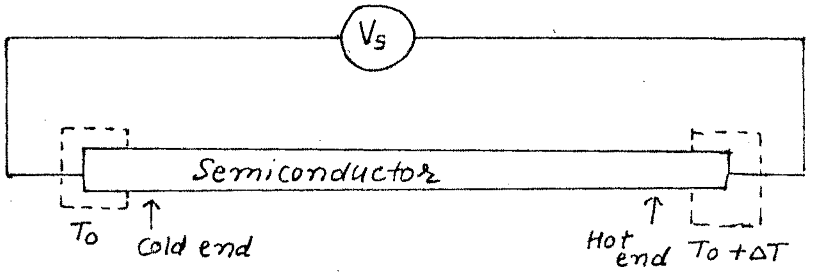
$$V_s = S + \frac{dV_F}{dT} \Delta T \qquad \ldots (3.31)$$

This V_s is voltage which would be indicated by a high resistance voltmeter in the metallic part of the circuit.

The calculation of the thermoelectric quantity V_s in terms of basic physical quantities is straight forward for simple cases of semiconductors in which only one type of conducting particles need be considered. In the p-type specimen indicated in figure (3.3) the right to left current density due to diffusion is,



FIG·3·1 Conduction in ⓐ Extended state ⓑ localized state ⓒ near Fermi energy ⓓ hopping.



FIG·3·2

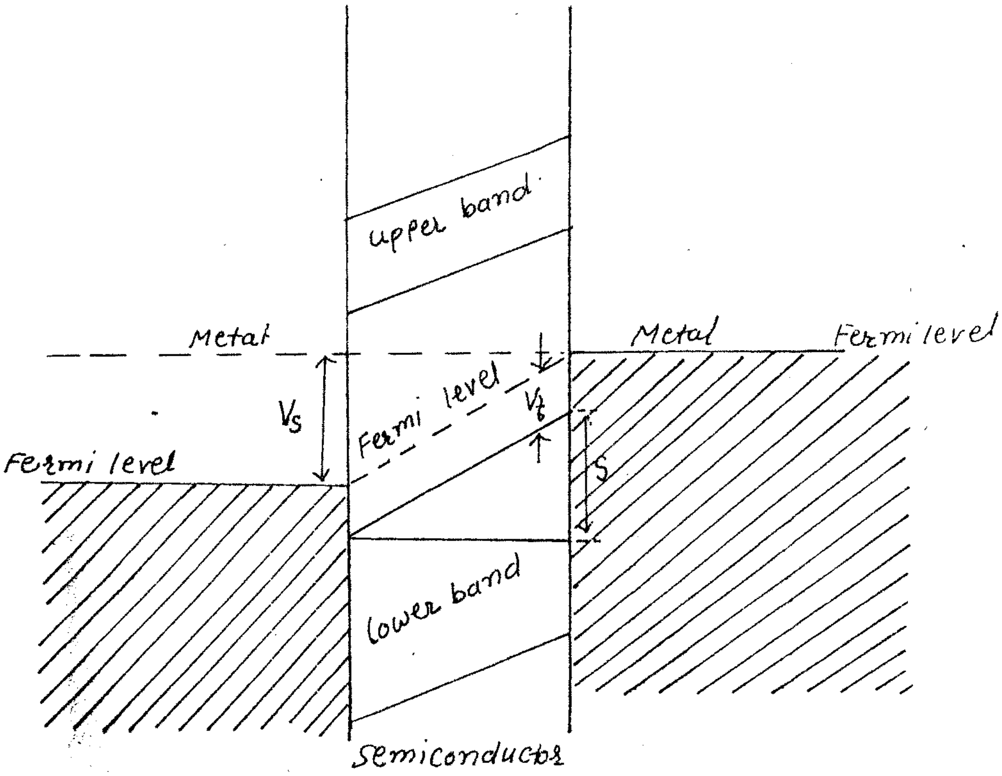


FIG 3·3

variation of Fermi level in ptype material.

$$I_{RL} = D_p\, q.\, \frac{dp}{dx} \qquad \ldots (3.32)$$

where D_p - Diffusion constant

$\frac{dp}{dx}$ = rate of change of holes with distance.

q - charge on hole.

The left to right return current due to electric field set up by this process is,

$$I_{RL} = P\, \mu_p\, q\, E_x$$

where E_x - is electric field, p-number of holes

μ_p - hole mobility

In steady state, these two currents are equal giving,

$$D_p . q \,.\, \frac{dp}{dx} = P_{\mu_p}\, q . E_x \qquad \ldots (3.33)$$

For D_p we may write KT μ_p/q from the Einstein relationship and assuming the electric field to be uniform (as it will be for a small temperature difference and uniform gradient) we may set S/L for E_x where L is the length of the specimen with these substitutions, and rearranging equation 3.33 becomes,

$$\frac{dp}{dx} = \frac{pq}{kT} \,.\, \frac{S}{L} \qquad \ldots (3.34)$$

However $\frac{dp}{dx} = \frac{dp}{dT} \,.\, \frac{dT}{dx} = \frac{dp}{dT} \,.\, \frac{\Delta T}{L}$

So equation (3) becomes,

$$\frac{dp}{dT} = \frac{pq}{kT} \cdot \frac{S}{\Delta T} \qquad \ldots (3.35)$$

From the Fermi statistics,

$$P = 2UT^{3/2} e^{-q V_F/KT}$$

where $U = 2.42 \times 10^{15}$ cm^{-3} Ab s$^{-3/2}$

Differentiating with respect to T, and substituting the result into equation (3.35) and simplifying we get,

$$S = \left(\frac{-dV_F}{dT} + \frac{V_F}{T} + \frac{3K}{2q} \right). \Delta T \qquad \ldots (3.36)$$

Combining equations (3.36) and (3.31)

$$V_s = \left(\frac{V_F}{T} + \frac{3k}{2q} \right) \Delta T \qquad \ldots (3.37)$$

Since $Q = \frac{V_s}{\Delta T}$

$$Q = \frac{V_F}{T} + \frac{3\ k}{2\ q} \qquad \ldots (3.38)$$

These last two equations for seeback voltage and thermoelectric power are only approximate. Their deviation neglected the effect described earlier in which a small contribution to S comes from the difference in mean thermal kinetic energy of particles diffusing randomly in two directions in the specimen. The correction to take account of this effect yields for V_s and Q.

$$V_s = \left(\frac{V_F}{T} + \frac{2k}{T} \right) \Delta T \qquad \ldots (3.39)$$

$$Q = \frac{V_F}{T} + \frac{2k}{q} \qquad \ldots (3.40)$$

$$Q = \frac{K}{g} \left(2 + \frac{E_F}{kT} \right) \qquad \ldots (3.41)$$

A similar derivation holds for a n type semiconductor leading to equations similar to the two above except that the signs of V_s and Q will be negative and that $(V_g - V_F)$ will appear instead of V_F

Equation (3.40) gives us an independent method for determining V_F in a p type semiconductor sample and hence for obtaining by calculation a value for the hole concentration P. Therefore, from equation (3.40),

$$P = 2UT^{3/2} \, e^{-qQ/k + 2} \qquad \ldots (3.42)$$

In case of an n-type Semiconductor above formula becomes,

$$Q = \frac{-K}{q} \left(2 + \frac{E-E_F}{KT} \right)$$

3.4. THERMOELECTRIC POWER :

Important information about the transport mechanism in amorphous semiconductor has been obtained from thermopower data. In this section we shall derive the formulas for thermoelectric power associated with the three processes of conduction.

Fritzsche[3.7] has given general equation for thermoelectric power,

$$S = \frac{-K}{e} \int \frac{E-E_F}{kT} \frac{\sigma(E)}{\sigma} dE \qquad \ldots (3.43)$$

Substituting value of $\sigma(E)$ from conductivity equation we get

$$S = \frac{-k}{e} \frac{\int \mu(E)\ N(E)\ kT \left[(E-E_F)/kT\right] \frac{\partial f}{\partial E} dE}{\mu\ (E) N(E)\ kT \frac{\partial f}{\partial E}\ dE} \qquad \ldots (3.44)$$

where f is Fermi-Dirac distribution function,

$$\frac{\partial f}{\partial E} = - f(1 - f)\ /\ kT \qquad \ldots (3.45)$$

then

$$S = \frac{-k}{e} \frac{\int \mu(E) N(E) \left[(E-E_F)/kT\right] f(1-f) dE}{\int \mu\ (E) N(E)\ f(1-f)\ dE} \qquad \ldots (3.46)$$

For non-degenerate semiconductor classical Boltzmann statistics is appropriate. In this case f(1-f) in equation (3.46) reduces to Boltzmann factor,

$$f = \exp\left[- (E - E_F)/kT\right]$$

3.4.1 MOTION OF CARRIERS IN EXTENDED STATES :

Under the assumption of a constant density of states and an energy independent mobility the thermoelectric power can be given by integration of equation (3.46).

This gives expression for motion of Electrons

$$S = \frac{-k}{e} \left(\frac{E-E_F}{kT} + A \right) \qquad \ldots (3.47)$$

where A = 1

In crystalline semiconductors the term A depends on the scattering mechanism. Hindley[3.8] has found a similar expression for using the random phase model. If both the electrons and holes contribute to the conductivity, then the thermoelectric power is the algebraic sum of individual contributions S_e and S_h. Thus we have,

$$S = \frac{S_e \sigma_e + S_h \sigma_h}{\sigma_e + \sigma_h} \qquad \ldots (3.48)$$

where S_e - Thermoelectric power of electron

S_h - Thermoelectric power of holes.

σ_e - conductivity of electrons

σ_h - conductivity of holes

3.4.2 MOTION OF CARRIER IN LOCALIZED STATE NEAR THE MOBILITY EDGE :

The thermoelectric power by carrier in the localized state of band tails will be given by,

$$S = \frac{-k}{e} \frac{\int (E-E_F)/kT \ \exp\left[-(E-E_F)/kT\right] N(E) \ dE}{n} \qquad \ldots (3.49)$$

If density of localized state behave like some power 's' of the energy E,

$$N(E) = \frac{N(E_C)}{(E_C - E_A)^s} (E - E_A)^s$$

then we get

$$S = \frac{-k}{e} \left(\frac{E_A - E_F}{kT} + \frac{C^*}{C} \right) \qquad \ldots (3.50)$$

where $C^* = \int_0^{\Delta E/kT} e^{-x} x^{s+1} dx$

Here $\Delta E = E_C - E_A$ is the width of tails and $x = \left(\frac{E - E_A}{kT} \right)$.

The value of C^*/C depends on the energy distribution of the density of localized states. For linear variation of N(E) 's' can be represented by,

$$S = \frac{-k}{e} \left(\frac{E_A - E_F}{kT} + \frac{C_1^*}{C_1} \right) \qquad \ldots (3.51)$$

$$C_1^* = 2 - \left[\exp \left(\frac{-\Delta E}{kT} \right) \left(2 + 2 \left(\frac{\Delta E}{kT} \right) + \left(\frac{\Delta E}{kT} \right)^2 \right] \qquad \ldots (3.52)$$

$$\text{and } C_1 = 1 - \left[\left(\frac{-\Delta E}{kT} \right) \left(1 + \left(\frac{\Delta E}{kT} \right) \right] \right.$$

If the carriers move by hopping in the localized states, the conductivity varies linearly exponentially with temperature and measured activation energy is the sum of the activation energies for carrier creation and for hopping. The activation energy for hopping does not appear in to expression for S and therefore one expects a difference in slopes between the conductivity and thermoelectric power.

3.4.3 MOTION OF CARRIERS IN LOCALIZED STATES AT THE FERMI ENERGY :

At low temperature, charge transport can arise from electron tunneling between states at E_F. Cutler and Mott[3.9] suggested that the thermoelectric power in this regime should be identical to equation used for metallic conduction.

$$S = \frac{\pi^2 k^2 T}{3e} \quad \frac{d\ln \sigma(E)}{dE} \quad E_f \qquad \ldots (3.53)$$

Since the Fermi level lies in a region where the density of states is finite. The thermoelectric power is small. Its sign may be positive or negative depending on whether the major contribution to the current will lie below or above the Fermi energy. Several authors[3.10-3.13] have calculated the thermoelectric power in the variable range hopping regime.

3.5 CONDUCTION BY SMALL-POLARON MOTION :

The formation of small polaron in non-crystalline materials has been discussed by E_{min}[3.14]. He argued that the probability of small polaron formation in disorder state is largely increased as compared to the crystalline state. It may be remembered in Davis and Mott model that existence of mobility edges at the energies which separates the localized tail states from the extended states. The existence of such tail states does not appear in a small polaron band.

If the charge carrier remains in the vicinity of a particular atomic site over a time interval long enough for displacements of the surrounding atoms to take place a potential well may be created which can lead to trapping of the carrier. The unit built up by the trapped carrier and its induced lattice deformation is called a polaron. The polaron has a lower energy than the free electron but has a higher effective mass since it must carry its induced deformation with it, as it moves through the lattice. The decreases in energy of the small polaron relative to that of the electron in the undistorted lattice is called the small polaron binding energy. The reduction in energy of small polaron is the net result of two opposite contributions. On the one hand, a lowering due to the displacements of the surrouhding atoms and on the other hand, an increase due to the strain energy originating from the induced lattice disortion. Holstein[3.15] found that for a crystal the small polaron states overlap sufficiently to form a polaron band.

In order to find the conductivity for hopping motion of small polarons, one can make use of the Einstein relation which relates the mobility to the diffusion coefficient D

$$\sigma = ne\mu = ne\frac{eD}{kT} \qquad \ldots (3.54)$$

The diffusion coefficient can be written as product of the hopping probability p with square of the interatomic distance a. Thus, dc conductivity for small polarons, being proportional to the probability for hopping and given by

$$\sigma = \left(\frac{ne^2 a^2}{kT} \right) p$$

At coincidence event the carrier will have certain probability to jump. Let P_1 be probability for occurrence of coincidence event and P_2 be the probability of charge transfer during this event.

$$P_1 = \frac{w_o}{2\pi} \exp\left(\frac{-W}{kT} \right) \quad \ldots (3.55)$$

where $\frac{w_o}{2\pi}$ is an average phonon frequency and W is the minimum energy. W is related to small polaron binding energy E_b given by $W = \frac{E_b}{2}$. Then the total probability P becomes

$$P = \frac{w_o}{2\pi} \exp\left(\frac{-W}{kT} \right) P_2 \quad \ldots (3.56)$$

In non-adiabatic regime where the carrier is slow, P_2 1. Holstain derived the following equation,

$$\text{where } P_2 = \frac{2\pi}{\hbar w_o} \left(\frac{\pi}{WkT} \right)^{1/2} J^2 \quad \ldots (3.57)$$

The electronic transfer integral J is measure of the overlapping of wave functions. Using (3.56) we get for non-adiabatic regime,

$$\mu_c = \frac{ea^2}{kT} \cdot \frac{1}{\hbar} \left(\frac{\pi}{WkT} \right)^{1/2} J^2 \exp\left(\frac{-W}{kT} \right) \qquad \ldots (3.58)$$

The mobility will increase exponentially over a broad temperature range. This thermally activated behaviour is essential features of small polaron theory.

For triangular lattice Friedman and Holstein[3.16] derived the following expression for the non-adiabatic case

$$\mu_H = \frac{ea^2}{h} J \left(\frac{\pi}{12kTW} \right)^{1/2} \exp\left(- \frac{W}{2kT} \right) \qquad \ldots (3.59)$$

and

$$\frac{\mu_H}{\mu_c} = \frac{2}{3\sqrt{3}} \frac{kT}{J} \exp\left(\frac{2}{3} \frac{W}{kT} \right) \qquad \ldots (3.60)$$

The Hall mobility is thermally activated with an activation energy which is one-third of that associated with the conductivity mobility since the pre-exponential term decreases with increasing temperature; the Hall mobility will reach a maximum at kT = W/3. The calculation of the Hall mobility of small polarons in a square lattice has been carried out by E_{min}[3.14].

$$\mu_H \propto \left(\frac{\theta}{T} \right)^{3/2} \exp\left(- \frac{W}{3kT} \right) \qquad \ldots (3.61)$$

Another transport property which has received special attention in the experimental studies on small polarons is the thermoelectric power. For small polaron hopping 's' was found[3.17] to be expressed by a formula of classical form

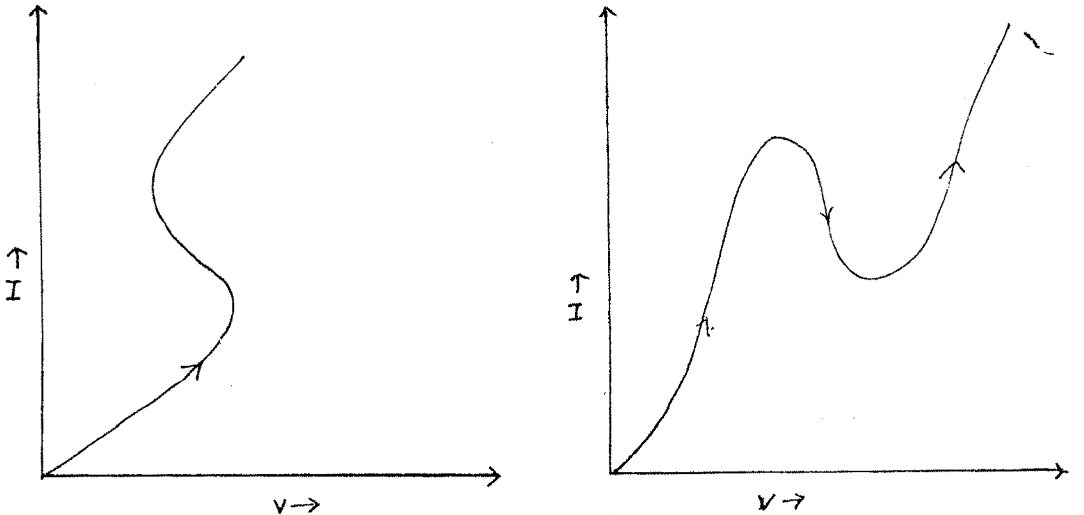
$$S = \frac{-k}{e}\left(\frac{E}{kT} + A\right) \qquad \ldots (3.62)$$

where E is the energy associated with the thermal generation of the carriers. The term A could be very small if there is no transfer of vibrational energy associated with a small-polaron hop.

3.6 SWITCHING IN NON-CRYSTALLINE SEMICONDUCTORS

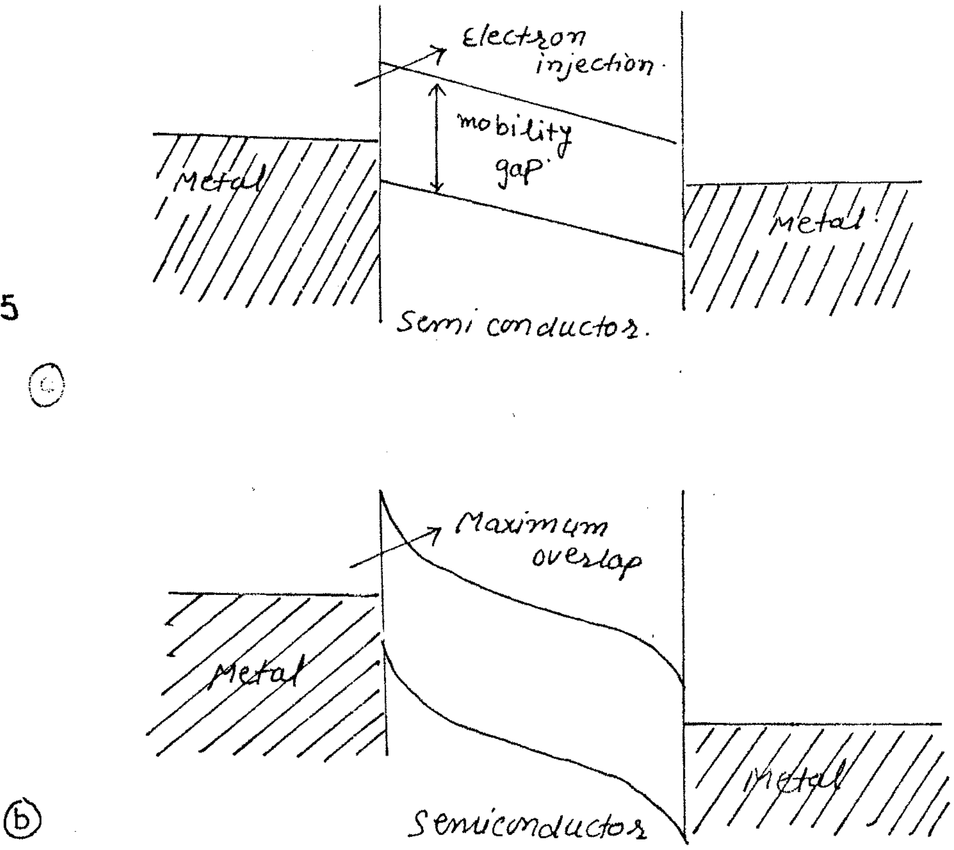
Current-voltage behaviour of a bulk semiconductor showing negative resistance is unstable. This is because of a random fluctuation of charge carrier density at any point in the semiconductor produces momentary space charge which grows exponentially in space and time. The -ve resistance can be divided into two groups (i) voltage controlled negative resistance (ii) current controlled negative resistance, as shown in Figure 3.4. The tunnel diode shows a voltage controlled -ve resistance while a semiconductor controlled rectifier shows the current controlled negative resistance. As we are dealing here the amorphous semiconductor, mostly in these materials the current controlled negative resistance is observed. The earliest mechanism to understand the negative phenomenon was thought in terms of the heterogeneous nature of the material. When the electric field was applied, for current controlled negative resistance, high current filaments are formed in the bulk of the material.

Hanisch, Fagan, Ovshinsky[3.18] explain the -ve resistance phenomena using the concept of energy band model in amorphous semiconductors. It is already discussed in Chapter III, the existence of bands in amorphous material and their overlapping in the forbidden zones. The localized states are near valence and conduction bands. When voltage is applied to metal semiconductor metal (M-S-M) system (Figure 3.5). The electrons are injected from the cathode and holes from the anode. Lampert[3.19] theory of double injection is being used to understand the phenomenon. At very low voltage the density of electrons injected from the cathode is very small. The thermal excitation of carriers from the localized states just below the conduction band will give the current in the circuit. The number of carriers thermally excited is very small and hence current will be small. At low voltage the current is directly proportional to voltage following thereby Ohms Law. As the applied voltage is increased gradually, the number of electrons injected at the electrode will increase. There may be gradual increase in current in the circuit. When the voltage is further increased, the number carriers goes on increasing. All electrons injected by the cathode are not cleared from the electrode quickly and they are held up at electrodes only. This creates an internal negative space charge near the electrodes and because of this the injection of carrier from outside is blocked. In short the electrodes which injected the carrier in the beginning act as blocking electrodes at higher voltages. At the cathode the negative space charge



FIG·3·4 (a) current controlled negative resistance

(b) Votage controlled negative resistance·



FIG·3·5

will be built, because of electrons injection while at anode positive space will be built because of holes injection. The positive and negative space charges are held up at the electrodes till sufficiently high internal field is built up inside the amorphous semiconductor. Because of the internal field the positive and negative space charges move towards each other and they will recombine where the high current will be shown in the circuit. This is the ON state for the material. At this point the material behaves like conductor giving high current in the circuit and the resistance of material become very small.

Recently the non-linear I-V behaviour in such material has been discussed on the basis of charge defect states existing in the material. The details of this mechanism are discussed in Chapter V.

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