Chapter II

Theory of Crystalline and Amorphous Semiconductors

2.1. Introduction:-

A crystalline solid is distinguished by the fact that the atoms making up the crystal are arranged in a periodic fashion i.e there is some basic arrangement of atoms that is repeated throughout the entire solid. Thus the crystal appears exactly the same at one point as it does at a series of other equivalent points, once the basic periodicity is discovered. However not all solids are crystalline; some have no periodic structure at all (amorphous solids) and others are composed of many small regions of single crystal material (polycrystalline solids). The three types of solids have been illustrated in figure 2.1

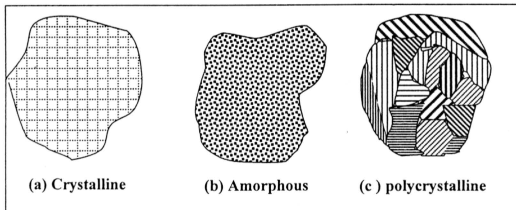

Figure. 2.1 The three types of solids classified according to atomic arrangement: a) Crystalline b) Amorphous are illustrated by microscopic views of the atom whereas c) Polycrystalline structure is illustrated by a more macroscopic view of adjacent single crystalline regions. [19]

In this chapter we are going to discuss the relevant theories of crystalline and amorphous materials which we shall be using in analyzing our experimental results.

2.2 Crystalline Semiconductors:-

The basic lattice structure of many important semiconductors is the diamond lattice which is characteristic of Si and Ge, and is shown in fig 2.2. The basic difference between the case of an electron in a solid and that of an electron in an isolated atom is that in a solid, the electron has a range or a band of available energies. The discrete energy levels of the isolated atoms spread into bands of energies in the solid because in the solids the wave functions of electrons in neighboring atoms overlap, and an electron is not necessarily localized to a particular atom. In a solid many atoms are brought together so that the split energy levels form essentially continuous bands of energies. Every solid has its own characteristic energy band structure. This variation in the band structure is responsible for the wide range of electrical characteristics observed in various materials.

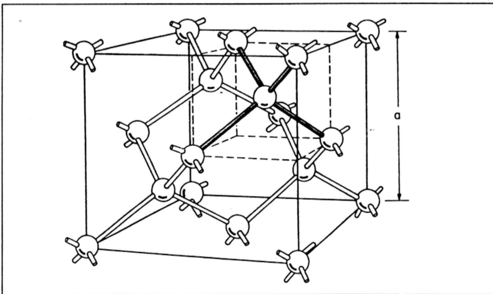

Figure 2.2 The Basic Diamond Lattice Structure [20]

2.3 Band Structure of Crystalline Semiconductors:-

Semiconductor materials at 0°K, have a filled valence band separated from an empty conduction band by a band gap containing no allowed energy states (Figure. 2.3).

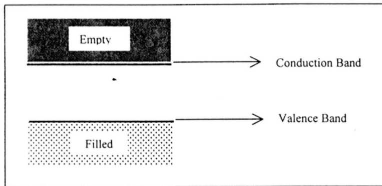

Figure 2.3 Typical band structure in semiconductor at 0 k. [21]

The difference in various material properties is determined by the size of the band gap E_g. This is much smaller in semiconductors than in insulators. For example Silicon has a band gap of about 1.12eV [22] compared to 5eV for diamond. The relatively small band gap of semiconductors allows excitation of electrons from the lower valence band to the upper conduction band by a reasonable amount of thermal or optical energy. Because of reasonably smaller energy gaps, the number of electrons available for conduction in semiconductors can be increased greatly by thermal or optical excitations.

An ideal semiconductor will have an energy gap without any state existing within it. But in practical semiconductors, the situation is much different from this. There are several reasons to explain the departure:-

1. A semiconductor crystal obtained from industry is never perfectly crystalline in the sense that it may have a number of point defects, different impurities and crystal defects.
2. A semiconductor surface represents the termination of an infinite semiconductor crystal and as such the semiconductor crystal will contain surface states due to incomplete covalent bonds and other effects.

The presence of these defects is taken care of by placing appropriate energy states within the energy gap of an otherwise perfect crystal. But in crystalline semiconductors, their densities are usually smaller relative to the free carrier densities.

2.4 Electrical Properties:-

It is the temperature dependence of semiconductor conductivity that distinguishes semiconductors from metals and insulators. To analyze the variation of semiconductor conductivity, it may be expressed as:

$$\sigma_n(T) = q\mu_n(T)n(T) \tag{2.1}$$

Presuming the mobility $\mu_n(T)$ to be determined by lattice scattering it may be written as [23]

$$\mu_n(T) = \frac{A_1}{T^{\frac{3}{2}}} \tag{2.2}$$

But the carrier density in 'n' type semiconductor may be expressed as [24]

$$n(T) = A_2 T^{\frac{3}{2}} \exp\left[-\left(\frac{E_C - E_F}{kT}\right)\right] \tag{2.3}$$

On combining above equations, we finally get,

$$\sigma(T) = A\exp\left[-\left(\frac{E_c - E_F}{kT}\right)\right] \tag{2.4}$$

if we ignore the variation of E_F with 'T',

σ according to equation (2.4) should exhibit an exponential variation up to about 60°K. With further rise in temperature, the supply of electrons from the donor states decreases around room temperature. 'σ' deviates from its exponential dependence when $n \cong N_d$. In that case the semiconductor conductivity according to equation (2.1) is given by,

$$\sigma(T) = q\left(\frac{A_1}{T^{\frac{3}{2}}}\right)N_d \tag{2.5}$$

Thus, when the carrier density has stopped increasing, σ(T) according to equation (2.5) must drop off with increasing 'T'. However, if the temperature of the semiconductor is increased sufficiently so that the direct excitation of carriers from the valence band to conduction band takes place, the specimen tends to become

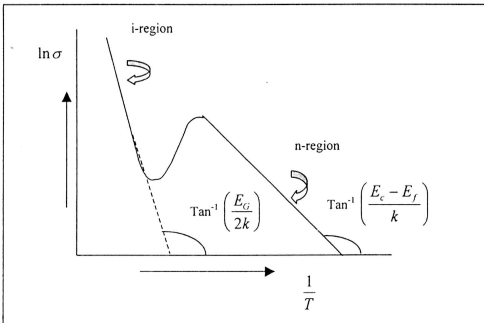

Fig. 2.4 The variation of ln σ as a function of temperature 'T' [25]

intrinsic. It then starts displaying a characteristic exponential dependence once again as expressed by,

$$\sigma_i = q(\mu_n + \mu_p)n_i = q[\mu_n(T) + \mu_p(T)]\left[(N_c N_v)^{\frac{1}{2}} \exp\left(\frac{-E_g}{2kT}\right)\right] \quad (2.6)$$

The variation of ln σ as a function of (1/T) is shown in Fig: (2.4)

2.5 Optical Properties:-

Optical measurements constitute one of the most important means of determining the band structure of semiconductors. Photon induced electronic transitions can occur between different bands which lead to the determination of the energy band gap or within a single band such as the free carrier absorption. Optical measurements can also be used to study lattice vibrations. The transmission coefficient 'T' and the reflection coefficient 'R' are the two important quantities generally measured. For normal incidence they are given by [26]

$$T = \frac{(1 - R^2)\exp(-4\pi x/\lambda)}{1 - R^2\exp(-8\pi x/\lambda)} \quad (2.7)$$

and

$$R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \quad (2.8)$$

Where λ is the wavelength, n is the refractive index of air with respect to the semiconductor, k is the extinction coefficient and x is the thickness of the sample. The absorption coefficient per unit length α is given by,

$$\alpha = \frac{4\pi k}{\lambda} \quad (2.9)$$

So, by analyzing T Vs λ and R Vs λ at normal incidence, both 'n' and 'k' can be estimated. Near the absorption edge, the absorption coefficient can be expressed as

[26]

$$\alpha = (h\nu - E_g)^{\nu} \quad (2.10)$$

Where $h\nu$ is the photon energy, E_g is the band gap and ν is a constant.

In the one electron approximation $\nu = 1/2$ and $3/2$ for allowed direct transitions and forbidden direct transitions respectively.

2.6 Amorphous Semiconductors:-

Amorphous semiconductors are non-crystalline in the sense that they lack long-range periodic ordering of their constituent atoms. They contain covalently bonded atoms arranged in an open network with correlations in ordering up to third or fourth nearest neighbors. This short-range order is directly responsible for the observable semiconductor properties such as optical absorption edges and activated electrical conductivities.

A distinction has to be made between amorphous and polycrystalline materials. Polycrystalline semiconductors are composed of grains with each grain containing a periodic array of atoms surrounded by a layer of interconnective boundary of atoms (Figure.2.1c). For smaller and smaller grains that i.e microcrystallites the surface layer of each grain contains a larger and larger number of atoms relative to the periodically arranged interior atoms. Eventually for smaller grains the distinction between the interior and the surface is lost and the concept of microcrystallites with a definable periodic region looses its meaning. The material is then said to make a transition to the amorphous state.

Amorphous semiconductors are prepared by atomic deposition procedures such as: Evaporation, Sputtering, Chemical Vapour Deposition (CVD), Plasma Decomposition of gases and Electroplating. [27-30]

2.7. Band Structure of Amorphous Semiconductors:

In recent times, exciting advances have been made in understanding the problem of how the disorder in a semiconductor influences the band structure and hence the electrical properties. Observed experimental data of electrical transport properties can only be properly interpreted if a model for the electronic structure is available. For crystalline semiconductors as already discussed, the main features of the energy

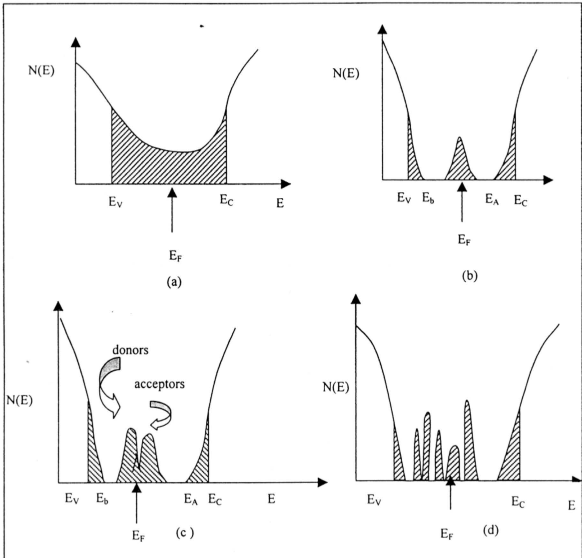

Figure 2.5. Schematic density of states diagrams for amorphous semiconductors. (a) The Cohen-Fritzche-Ovshinsky model, (b) the Davis-Mott model showing a band of compensated levels near the middle of the gap, (c) modified Davis-Mott model, (d) a "real" glass with defect states [31]

distribution of the density of electronic states N(E) are the sharp structure in the conduction and valence bands and the abrupt terminations at the valence band maximum and the conduction band minimum. The sharp edges in the density of states produce a well-defined forbidden energy gap. Within the band, the states are extended which means the wave functions occupy the entire volume. This specific feature of the band structure is a consequence of the perfect short range and long range order of the crystal. In an amorphous solid, the long-range order is destroyed where as the short range order somewhat exists. The inter atomic distance and the valence angle are only slightly changed. The concept of density of states is also applicable to the non-crystalline solids. Based on Anderson's [32] theory, Mott [33] argued that the special fluctuations in the potential energy caused by the configurational disorder in an amorphous material may lead to the formation of localized states which do not occupy all the different energies in the band but form a tail above and below the normal band. Mott postulated further that there should be a sharp boundary between the energy ranges of extended and localized states. The states are called localized in the sense that electrons placed in that region have their wave functions extending over only a short distance and not the entire region. Several models have been proposed for the band structure of amorphous semiconductors. Figure 2.5 illustrates schematically the main features of various band models.

2.7.1 The Cohen-Fritzsche-Ovshinsky (CFO) Model:-

The CFO model [34] shown in Figure 2.5a assumes that the tail states extend across the gap in a structureless distribution. This gradual decrease of the localized state destroys the sharpness of the conduction and valence band edges. One of the major

objections against the CFO model was the high transparency of the amorphous chalcogenides below a well-defined absorption edge.

2.7.2 Davis-Mott Model:

According to the Davis-Mott model [35] the tails of the localized states should be rather narrow and should extend only to a few-tenths of an electron volt into the forbidden gap. They also proposed the existence of a band of compensated levels near the middle of the gap, originating from the defects in the random network namely dangling bonds, vacancies etc. Figure 2.5b sketches the Davis-Mott model. Here E_C and E_V represent the energies, which separate the ranges where the states are localized and extended. The central band may be split into a donor and an acceptor band, which will also pin the Fermi level (Figure 2.5c). Mott suggested that at the transition from extended to localized states the mobility drops by several orders of magnitude producing a mobility edge. The interval between the energies Ec and Ev acts as a pseudogap and is defined as the mobility gap.

Experimental evidences coming from luminescence, photoconductivity and drift mobility studies suggest the existence of various localized gap states, which are split off from the tail states and are located at well defined energies in the gap (2.5d). These states are associated with defect centers, whose nature is not always known.

The interpretation of electrical transport properties is dependent on the energy distribution of the density of states. On the basis of the Davis-Mott model, there can be three processes leading to conduction in amorphous semiconductors. Their relative contributions to the total conductivity will predominate in different temperature ranges. At very low temperatures, conduction can occur by thermally assisted tunneling between states at the Fermi level. At higher temperatures, charge

carriers are excited into the localized states of the band tails. Carriers in these localized states can take part in the electrical charge transport only by hopping. At still higher temperatures, carriers are excited across the mobility edges into the extended states. The mobility in the extended states is much higher than in the localized states. It, therefore, follows that the electrical conductivity measurements over a wide temperature range are needed to study the electronic structure of amorphous semiconductors.

2.8. Electrical Transport Properties:

To describe the transport properties of amorphous semiconductors, one may start from the Davis-Mott model. As already explained, the essential features of Davis-Mott model or 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 a band of localized levels near the middle of the gap to account for the presence of dangling bonds and vacancies. This leads to three basically different conduction mechanisms.

2.8.1 Extended State Conduction:

Conductivity for any semiconductor can be written in the following form:-

$$\sigma = e\int N(E)\mu(E)f(E)[1-f(E)]dE \tag{2.11}$$

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

$$f(E) = \frac{1}{1+\exp^{[(E-E_F)/kT]}} \tag{2.12}$$

Using the relationship,

$$\frac{\partial f(E)}{\partial E} = -f(E)[1-f(E)/kT] \tag{2.13}$$

σ can be written as,

$$\sigma = e\int N(E)\mu(E)kT\frac{\partial f(E)}{\partial E}dE \quad (2.14)$$

In the Davis-Mott model, the Fermi level E_F is situated near the middle of the gap and thus sufficiently far from E_C, the energy which separates the extended state from the localized state, so that the Boltzmann statistics can be used to describe the occupancy of states,

$$f(E) \approx \exp[-(E-E_F)/kT] \quad (2.15)$$

According to Mott [36], the mobility drops sharply at the mobility edge E_C [or E_V] but it is not exactly known how the mobility depends on energy in both conduction regimes. In the non-degenerate case under the assumption of constant density of states and constant mobility the conductivity due to electrons excited beyond the mobility edge into the extended states is given by:-

$$\sigma = e\,N(E_C)\,kT\mu_C \exp[-(E_C-E_F)/kT] \quad (2.16)$$

where μ_C is the average mobility. The number of electrons is given by;

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

$$= N(E_C)kT \exp[-(E_C-E_F)/KT] \quad (2.17)$$

In order to get an idea of the order of magnitude of μ_C, we define

$$\sigma(E_C) = e\,N(E_C)\,\mu_C kT \quad (2.18)$$

If $N(E_C) \cong \langle N(E)\rangle/3$, where $\langle N(E)\rangle$ is the average density of states over the bands, then

$$\sigma(E_C) = e\langle N(E)\rangle\,\mu_C KT/3 \quad (2.19)$$

Mott calculated the lowest value of the electrical conductivity before the start of the activated process i.e just at E_C. This quantity is called the minimum conductivity. He derived the expression,

$$\sigma_{(min)} = \text{Constant.}\frac{e^2}{\hbar a} \tag{2.20}$$

where the constant lies in the range between 0.026 and 0.1; $\sigma_{(min)}$ is usually of the order of 200 to 300 $\Omega^{-1}cm^{-1}$, 'a' in the above expression represents the lattice spacing. Taking the constant to be 0.026 one finds for the mobility,

$$\mu_C = \frac{0.078e}{\hbar a(\langle N(E)\rangle)kT} \tag{2.21}$$

The density of states function for a crystalline semiconductor may be expressed as:

$$N(E) = \frac{km}{2\pi^2\hbar^2} \tag{2.22}$$

On the other hand the maximum energy E_{max} of the band which also yields the width 'B' of the band is expressed by:

$$E_{max} = \frac{\pi^2\hbar^2}{2ma^2} = \text{'B' and } k_{max} = \frac{\pi}{a} \tag{2.23}$$

Combining (2.22) and (2.23) one may obtain,

$$N(E) = \frac{\pi}{4a^3b} \cong \frac{1}{a^3B} \tag{2.24}$$

Introducing the above result in the expression for μ_C one gets:

$$\mu_C = \frac{0.078e \times B \times a^2}{\hbar kT} \tag{2.25}$$

Taking A= 2 $\mathring{A}$; B works out to be 9.4ev. One then finds that at room temperature μ_C = 0.17cm^2/V.Sec. This value corresponds to a mean free path comparable to or less than the interatomic distance. In this regime the mobility can be obtained with the help of Einstein's relation,

$$\mu = \frac{eD}{kT} \tag{2.26}$$

and the diffusion constant 'D' may be written as:

$$D = \frac{1}{6}\upsilon a^2 \tag{2.27}$$

where υ is the jump frequency.

Combining (2.26) and (2.27) we get

$$\mu_C = \frac{ea^2\upsilon}{6kT} \tag{2.28}$$

This equation gives the same temperature dependence as equation (2.25) derived by Mott. The expression for extended state conductivity may now be written from equation (2.16) in the following form.

$$\sigma = \sigma_0 \exp\left[-\left(\frac{E_C - E_F}{kT}\right)\right] \tag{2.29}$$

where $$\sigma_0 = eN(E_C)\,\mu_C kT = \frac{0.078N(E_C)ea^2B}{\hbar} \tag{2.30}$$

2.8.2 Conduction in Band Tails:

Hopping Conduction:

If the wave functions are localized, conduction can only occur by thermally activated hopping. Every time an electron moves from one localized state to another, it will exchange energy with a phonon. It may then be expected that the mobility will have a thermally activated nature,

$$\mu_{hop} = \mu_0 \exp[-W(E)/kT] \tag{2.31}$$

The pre exponential factor μ_0 has the form: (see 2.28)

$$\mu_0 = \frac{eR^2(\vartheta_{ph})}{6kT} \tag{2.32}$$

where ϑ_{ph} is the phonon frequency and 'R' is the distance covered in one hop. For a typical phonon frequency ϑ_{ph}, which is $10^{13}sec^{-1}$ and W of the order of KT, equation (2.31) yields mobility of the order of $10^{-2}cm^2V^{-1}sec^{-1}$ at room temperature.

The conductivity being an integral over all available energy states, will depend upon the energy distribution of the density of localized states. If one assumes the density of state function of localized states to be,

$$N(E)=\frac{N(E_C)(E-E_A)}{(\Delta E)} \tag{2.33}$$

With $\Delta E = E_C - E_A$, then the conductivity σ_{hop} due to electrons can be easily calculated from equation (2.11) as,

$$\sigma_{hop}=\sigma_{0(hop)}\frac{kTC_1\exp[-(E_A-E_F+W)/kT]}{\Delta E} \tag{2.34}$$

$$\text{Where } \sigma_{0(hop)}=\left(\frac{1}{6}\right)\left(\vartheta_{ph}e^2R^2N(E_C)\right) \tag{2.35}$$

2.8.3 Conduction in Localized States at the Fermi Energy:-

If the Fermi Energy lies in a band of localized states, as predicted by the Davis and Mott model, the carriers can move between these states via the phonon assisted tunneling processes. An estimate for the temperature dependence of the hopping conductivity at E_F has been given by Mott [37]. Consider an electron that is scattered by phonons from one localized state to another. The energy difference between the states is denoted by 'W'. The probability 'p' that an electron jumps per unit time should be given by,

$$p=\vartheta_{ph}\exp(-2\alpha R-W/kT) \tag{2.36}$$

Since, the probability function at E_F is 1, it follows from equation (2.16) that the conductivity in localized states at the Fermi energy is,

$$\sigma = e\mu kTN(E_F) \quad (2.37)$$

By making use of Einstein's relation

$$\mu = \frac{eD}{kT}$$

since, $D = \frac{1}{6}pR^2$, the conductivity can be written

$$\sigma = \frac{e^2 pR^2}{6} N(E_F) \quad (2.38)$$

Here $N(E_F)$ is the density of states function at the Fermi Energy. And $N(E_F)KT$ is the density of electrons that contribute to conductivity. Using equation (2.36) in equation (2.38) we get,

$$\sigma = \frac{1}{6} e^2 R^2 \vartheta_{ph} N(E_F) \exp(-2\alpha R - W/KT) \quad (2.39)$$

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 then tend to hop to larger distances in order to find sites, which lie energetically closer than the nearest neighbours. This mechanism is the so-called 'Variable Range Hopping'. In order to find the most probable hopping distance, Mott used an optimizing procedure, which is as follows:

Since, $N(E_F)$ is the density of states 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,

$$\frac{4\pi}{3} R^3 N(E_F) W \quad (2.40)$$

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 the Fermi energy level to be,

$$W = \frac{3}{4\pi R^3 N(E_F)} \tag{2.41}$$

and for the jump probability;

$$p = \vartheta_{ph} \exp\left[-2\alpha R - \left(\frac{3}{4\pi R^3 N(E_F) kT}\right)\right] \tag{2.42}$$

The most probable jump distance is found by minimizing the exponent of the above expression as a function of 'R'. One then finds,

$$R = \left[\frac{9}{8\pi\alpha N(E_F) kT}\right]^{\frac{1}{4}} \tag{2.43}$$

On combining equation (2.42) and equation (2.43), we get the jump frequency of the form,

$$p = \vartheta_{ph} \exp\left(\frac{-A}{T^{\frac{1}{4}}}\right) \tag{2.44}$$

where

$$A = 2.1[\alpha^3 / kN(E_F)]^{\frac{1}{4}} \tag{2.45}$$

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

$$\sigma = \sigma_0(T) \exp\left(\frac{-A}{T^{\frac{1}{4}}}\right) \tag{2.46}$$

where

$$\sigma_0(T) = \frac{e^2 \vartheta_{ph} N(E_F)}{6}\left[\frac{9}{8\pi\alpha N(E_F)kT}\right]^{\frac{1}{2}} = \frac{e^2}{2(8\pi)^{\frac{1}{2}}}\vartheta_{ph}\left[\frac{N(E_F)}{\alpha kT}\right]^{\frac{1}{2}} \quad (2.47)$$

In principle, the two parameters 'α' and $N(E_F)$ can be evaluated from the slope of a plot of $\ln\left(\sigma\sqrt{T}\right)$ vs $T^{-1/4}$ and from the intercept at $T^{-1/4} = 0$, if one makes a reasonable assumption for ϑ_{ph}. Also one can get an idea of most probable hopping distance 'R' at a given temperature from equation (2.43).

A diagrammatic representation of the three states of conduction in an amorphous semiconductor is shown in figure. 2.6.

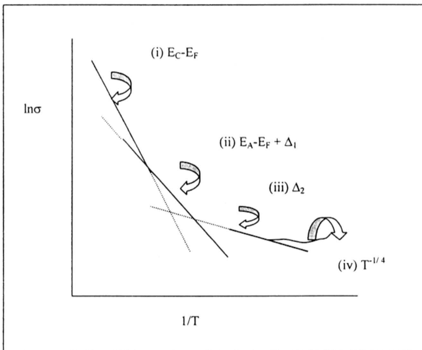

Figure 2.6 A schematic illustration of the temperature dependence of conductivity expected for amorphous semiconductor. The activation energies found in various regimes are indicated [after Mott and Davis [38]]

2.9. Optical Properties:-

The most direct and perhaps the simplest method of proving the band structure of a semiconductor is to measure the optical absorption spectrum. In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state within the semiconductor. By studying the changes in the transmitted optical density as a function of the wavelength, one can investigate some of the possible quantum mechanical transitions that the semiconductor electrons can make and learn much about the distribution of allowed electronic energy levels.

From the optical transmission data one can obtain considerable information on the electronic structure of the material. Among the optical constants that can be determined are refractive index, absorption coefficient, extinction coefficient as well as the thickness of a film. By using these parameters many other useful informations such as energy gap, various characteristic energies, dielectric constant, effective number of valence electrons per anion etc could be obtained. Knowledge of these informations is vital when the suitability of a material as an optical element is considered.

The practical situation for a thin film on a transparent substrate is shown in Fig 2.7, where the film has a complex refractive index and a thickness 'd' bounded by two transparent media with refractive indices N_0 and N_2. The transmittance 'T' and reflectance 'R' of the system is given by [39]

$$T = \frac{T_{23}T_{02}}{1 - R_{20}R_{23}} \tag{2.48}$$

and

$$R = \frac{T^2{}_{20}R_{23}}{1 - R_{20}R_{23}} + R_{02} \tag{2.49}$$

where,

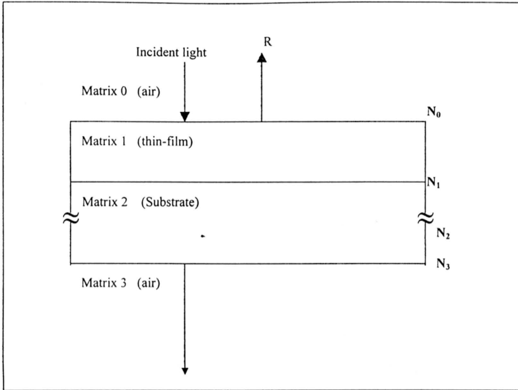

Figure 2.7 Typical Transmission 'T' and Reflectance 'R' of light in a thin film, on a transparent substrate.

$$T_{02} = T_{20} = \frac{n_2}{n_0}\left|\frac{e_1 t_{01} t_{12}}{1 - e^2{}_1 r_{10} r_{12}}\right|^2, \qquad R_{20} = \left|r_{21} + \frac{e_1^2 t_{21} t_{12} r_{10}}{1 - e_1^2 r_{12} r_{10}}\right|^2$$

$$R_{02} = \left|r_{01} + \frac{e_1^2 t_{01} t_{10} r_{12}}{1 - e_1^2 r_{12} r_{10}}\right|^2, \qquad T_{23} = \frac{n_3}{n_2}\left|t_{23}\right|^2$$

$$R_{23} = \left|r_{23}\right|^2, \qquad e_1 = \exp\left(\frac{2i\pi N_1 d}{\lambda}\right)$$

$$t_{kl} = \frac{2N_k}{N_k + N_l}, \qquad r_{kl} = \frac{N_k - N_l}{N_k + N_l}$$

$$N_k = n_k + ik_k.$$

The exact expression of 'T' in air-thin film-substrate-air interfaces where refractive indices $N_0 = N_3 = 1$, $N_1 = n + ik$ and $N_2 = n_s$

is given as [40]

$$T = \frac{Ax}{B - Cx + Dx^2} \quad (2.50)$$

where,

$$A = 16n_s(n^2 + k^2)$$

$$B = \left[(n+1)^2 + k^2\right]\left[(n+1)(n+n_s^2) + k^2\right]$$

$$C = \left[(n^2 - 1 + k^2)(n^2 - n_s^2 + k^2) - 2k^2(n_s^2 + 1)\right]2Cos\left(\frac{4\pi nd}{\lambda}\right) - k\left[2(n^2 - n_s^2 + k^2) + (n_s^2 + 1)(n^2 - 1 + k^2)\right]2sin\left(\frac{4\pi nd}{\lambda}\right)$$

$$D = \left[(n-1)^2 + k^2\right]\left[(n-1)(n-n_s^2) + k^2\right]$$

and $$x = \exp\left(\frac{-4\pi kd}{\lambda}\right) = \exp(-\alpha d)$$

α is the absorption coefficient of thin film at wavelength λ.

A typical transmittance spectrum is shown in figure 2.8. The interference fringes observed are due to interference of the multiply reflected beams in the film.

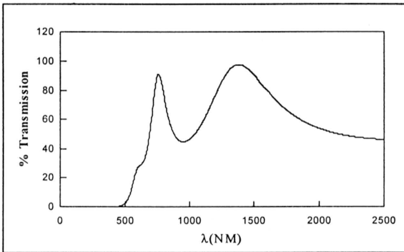

Figure 2.8 A typical transmission spectrum of thin film

Experimentally the number of interference peaks increase with the film thickness. The basic equations for their fringes at maxima and minima are given by,

$$2nd = m\lambda \quad (2.51)$$

and
$$2nd = \left(m + \frac{1}{2}\right)\lambda \tag{2.52}$$

respectively, where the integer 'm' is the order of the interference fringes. The transmission maxima T_{max} and minima T_{min} may be obtained by incorporating equation (2.51) and equation (2.52) in equation (2.50) and are given by,

$$T_{max} = \frac{16n_s n^2 x}{C_1 + C_2 x^2 - 2(n^2 - 1)(n^2 - n^2_s)x} \tag{2.53}$$

and

$$T_{min} = \frac{16n_s n^2 x}{C_1 + C_2 x^2 + 2(n^2 - 1)(n^2 - n^2_s)x} \tag{2.54}$$

where $C_1 = (n+1)^3(n+n_s^2)$ and $C_2 = (n-1)^3(n-n_s^2)$ and $k^2 \equiv 0$ for weak absorption in the medium. An expression that is independent of 'x' could be derived by subtracting the reciprocal of equation (2.54) from the reciprocal of equation (2.53). Then we obtain,

$$\frac{1}{T_{min}} - \frac{1}{T_{max}} = \frac{(n^2 - 1)(n^2 - n_s^2)}{4n_s n^2} \tag{2.55}$$

Solving equation (2.55) for 'n' yields,

$$n = \left[N + (N^2 - n^2_s)^{\frac{1}{2}}\right]^{\frac{1}{2}} \tag{2.56}$$

Equation (2.56) can be used to calculate $n(\lambda)$ from T_{max} and T_{min}

Once $n(\lambda)$ is known α can be determined from both equations (2.53) and (2.54) by solving the quadratic equation for 'x'. Similar results can be obtained by adding the reciprocals of equation (2.53) and equation (2.54). 'x' is then given by,

$$x = \frac{F - \left[F^2 - (n^2 - 1)^3(n^2 - n_s^4)\right]^{\frac{-1}{2}}}{(n-1)^3(n - n_s^2)} = \exp(-\alpha d) \tag{2.57}$$

where ,

$$F = \frac{4n^2 n_s (T_{max} + T_{min})}{T_{max} T_{min}}$$

The thickness of the film can be calculated from two maxima or minima using equation (2.51) and equation (2.52) such that,

$$d = \frac{M\lambda_1\lambda_2}{2[\lambda_2 n(\lambda_1) - \lambda_1 n(\lambda_2)]} \quad (2.58)$$

where, $M = (m_1 - m_2)$ = number of oscillations between two extrema. Knowing d and α the extinction coefficient 'k' can be calculated. Besides the transmitted and reflected energies, part of the impinging photon energy will be absorbed by the electrons in the film leading to different inter and intra band band transitions. The photon energy, which corresponds to the transition of the electrons from the valence to conduction band in a crystal, is often described by:

$$\alpha E = A(E - E_g)^m \quad (2.59)$$

where A is a constant and α, E and E_g represent absorption coefficient, photon energy and energy gap respectively. For amorphous semiconductors the value of 'm' is generally found to be, 2. As a result equation (2.59) may be written as:

$$\sqrt{\alpha E} = \sqrt{A}(E - E_g) \quad (2.60)$$

Therefore, on plotting $\sqrt{\alpha E}$ as a function of the photon energy E, one should expect to get a straight line, the intercept of the line with E= 0 axis gives a measure of the energy gap of the amorphous material.

The refractive index of an amorphous material can be expressed as

[41],

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} \quad (2.61)$$

where n = refractive index, E_0 is the energy of the effective dispersion oscillator, E is the photon energy and E_d is the dispersion energy which measures the average strength of the inter band optical transition. Equation (2.61) can be written as:

$$\frac{1}{n^2-1}=\frac{E_0^2-E^2}{E_dE_0}=\frac{E_0}{E_d}-\frac{E^2}{E_dE_0} \qquad (2.62)$$

If $\frac{1}{n^2-1}$ is plotted against E^2, one expects to get a straight line having a slope $(E_dE_0)^{-1}$ and an intercept $\frac{Ed}{E_0}$. From the slope and the intercept one may easily determine E_0 and E_d. The density of valence electrons, n_v is obtained from a model by C.Ance et al. [42]

$$n_v = 0.0143\frac{E^2{}_d}{(\epsilon\,(0)-1)} \qquad (2.63)$$

where ε (0) is taken to be the square of the saturated refractive index in the long wavelength region. This model enables the estimation of the hydrogen content by using the following relation:

$$C_H=\frac{1}{3}\frac{n_V}{n_S}\left[4-\sqrt{\frac{E_d}{2.8}}\right] \qquad (2.64)$$

where n_S is the density of valence electrons in the crystal silicon which is taken to be 2×10^{23}electrons/cm^3. The dispersion energy was also found to obey [41,43] the empirical relationship,

$$E_d = \beta N_c Z_a N_v \qquad (2.65)$$

where N_c is the coordination number of cation surrounding an anion, Z_a is the formal chemical valence of an anion and N_v is the effective valence electron per anion. The constant β was found to be 0.37 ± 0.04eV for covalent materials and 0.26 ± 0.03eV for ionic materials. Using equation (2.65) one can also find out N_v.

2.10 Hydrogenated Amorphous Silicon and Dangling Bonds:-

Amorphous silicon, for example, contains dangling bonds of about $5 \times 10^{19}/cm^3$ as recorded by ESR measurements [44]. The electron energy levels of the dangling bonds (unpaired electrons) lie in between the valence and conduction band states of the fully paired bonded electrons. These states in the gap contribute to optical absorption and electrical conduction processes masking the measurement of energy gap by either process. Further, there is a large density of gap states, which act as fast non-radiative recombination centers with the result that the photoconductivity or photoluminescence is small in pure a-Si. Finally, the Fermi level, which is essentially pinned by the gap states, does not move significantly when trace impurities of the conventional shallow donor or acceptor types are incorporated. Dangling bond densities may be reduced to some extent by annealing amorphous silicon at higher temperature [45]. The assumption here is that the annealing effects are due to the healing of dangling bonds by reconstruction and rearrangement of the amorphous network. However, it was established that under certain conditions the effects of annealing in reducing dangling bonds are not much.

If dangling silicon bonds cannot be paired to each other, the opportunity still exists to pair them with other atomic orbital. Hydrogen appears to be most suitable for this purpose. Following the success of the glow discharge plasma decomposition of silane (SiH_4), several other procedures have also evolved for incorporating hydrogen into a-Si. These include reactive sputtering with hydrogen containing gas, proton implantation etc. In all cases it is presumed that hydrogen passivates the dangling bonds, thereby revealing the interesting properties of intrinsic a-Si. [46] Nuclear

reaction and infrared transmission studies shows that incorporation of hydrogen atoms in a-Si matrix reduces 5×10^{19} - 2×10^{20} free spin concentration (EPR) of a-Si. [47]. Many intrinsic properties of a-Si:H have already been studied. These include thermally activated conductivity, optical absorption edge, Photoluminescence, electroluminescence and photoconductivity. In addition, the standard shallow donors and acceptors have been shown to dope a-Si:H to be 'n' type or 'p' type respectively. The phenomena of interest to single crystal silicon now become possible to study with a-Si. Extrinsic conductivity, thermopower, Hall effect, photoconductivity have all been measured for a-Si. Schottky barrier and pn junction diodes have been fabricated with amorphous silicon. When operated as solar cells these diodes behave almost like corresponding crystal devices.

Hydrogen and other additives might besides passivating the gap states, also play active roles by enlarging the band gap, changing the electron lattice-coupling etc. How much hydrogenation is needed to reveal the most interesting phenomena is still open to questions.