CHAPTER 3

Theoretical aspects of thin film and thin film junction

Theoretical background is the essential part of any experimental work. Unless we understand the proper theory related to any experiment the result explained is not completed. In this chapter it is aimed to highlight the related theories for calculating and explaining the results of different parameters of the proposed studies. Theories applied for the studies of structural, electrical, optical properties of semiconducting films, Schottky and heterojunction junctions are discussed and explained here.

3.1 Structural properties

Varieties of experimental procedures have been adopted to study the microstructural, compositional and thermal degradation of thin films. These may be classified as X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetry analysis (TGA) etc. However, for organic semiconductors one important analysis is IR spectra where molecular bonding phenomena are accurately studied.

X-ray diffraction analysis is the one of the main techniques and tools to study the structures of any materials. Using this XRD technique the nature of the material whether it is amorphous, crystalline or polycrystalline can be detected. Lattice parameters, orientations of crystal planes, grain size, composition, defects, stress and strain etc. can also be studied using this XRD technique [129-131].

Bragg [132] considered X-ray diffraction from crystal as a problem of reflection from atomic planes and considered a set of parallel atomic planes of miller indices (hkl), the distance between successive planes being $d_{hkl}$. When an X-ray beam is reflected by
an atomic plane the condition for reflection or diffraction from the set of plane under consideration is

\[ 2d_{hkl} \sin \theta = n\lambda, \quad \text{with } n = 0, 1, 2, 3 \ldots \]

Where \( n \) is the order of reflection, \( d \) is the interplanner spacing of a particular set of crystal plane, \( \lambda \) is the wavelength of the incident X-ray and \( \theta \) is the angle makes by the incident ray with the plane called angle of diffraction. This condition shows immediately that for a given values of \( d_{hkl} \) and \( \lambda \) and \( n \) having integer values, only a particular angle \( \theta \) would produce such a reflection. Thus it can be concluded that when a beam of monochromatic X-rays incident on a crystal with an arbitrary angle \( \theta \) is in general not reflected. Also, because \( \sin \theta \leq 1 \) and \( d \sim 10^{-8} \) cm, reflection or diffraction can be observed only for \( \lambda \) of the order of \( 10^{-8} \) cm or less.

3.1.1 Lattice constant

Lattice constant or parameters are the characteristics of a crystal, defined as the distances of the neighbouring unit cells in three dimensions generally denoted by ‘a’. For a cubic lattice the distance between successive planes is given by [133],

\[ d_{h} \sqrt{h^2 + k^2 + l^2} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad (3.01) \]

Where \( hkl \) are the miller indices and \( d \) is the interplanner distance. Several factors like divergence of the X-ray beams, refraction and absorption of X-rays by the specimens etc. may affect the accurate measurement at ‘a’. So, accuracy of determination of lattice constant is dependent upon the accuracy in measurement of \( d \)

From Bragg’s law, \( d = \lambda/2\sin \theta \) \quad (3.02)

The Nelson-Riley curve is plotted for accurate measurement of lattice constant at \( \theta = \pi/2 \). Here curve is plotted between calculated lattice constant ‘a’ for different planes and the error function [134],

76
\[ f(\theta) = \frac{1}{2} \left( \cos^2 \theta / \sin \theta + \cos^2 \theta / \theta \right) \quad (3.03) \]

The intercept of this plot with X-axis gives the corrected value of lattice constant.

### 3.1.2 The grain sizes

The size of a crystallite is an important structural property of the materials. If \( \beta_{2\theta} \) is the width of the diffraction line of the half of the maximum peak intensity for diffraction angle \( \theta \) then according to Scherrer’s formula, the average grain size \( D_{\text{hkl}} \) at the films for most preferred plane (hkl) will be,

\[ D_{\text{hkl}} = \frac{K \lambda}{\beta_{2\theta} \cos \theta} \quad (3.04) \]

Where \( \lambda \) is the wavelength of X-ray used, \( K \) is the proportionality constant which is taken as 0.99 [135].

### 3.1.3 Average stress and strain

Stress may be computed from the measurement of changes in lattice parameters and line broadening using X-ray and electron diffraction technique. Halliday et al.[136] gave a detailed treatment of determination of stress. The relation used to evaluate the stress is,

\[ S = \frac{E_F}{2 \Psi} \frac{a_0 - a}{a_0} \quad (3.05) \]

Where ‘\( a_0 \)’ and ‘\( a \)’ are the lattice constants of the bulk material and the strained film, respectively. \( E_F \) and \( V_F \) are the Young’s modulus and Poisson’s ratio of the bulk material respectively. Here ‘\( a \)’ refers to the lattice constant perpendicular to the film plane. If ‘\( a \)’ is the lattice constant in the plane of the film, the stress is given by,

\[ S = \frac{E_F}{1 - \Psi} \frac{a_0 - a}{a_0} \quad (3.06) \]
If broadening of the diffraction lines is used for the determination of stress, stress gradient and micro strain, contributions to broadening due to all the small crystallite size must be taken into account [137]. The micro strain ($\varepsilon$) developed in thin film in different preferred orientations are calculated from the relation,

$$\varepsilon_{hkl} = \frac{\beta_2 - \varepsilon \cos \theta}{4}$$

(3.07)

The presence of strain in the thin film may be responsible for the broadening of the X-ray diffraction peaks. Considering the entire broadening of a diffraction profile to be due to both particle size and strain, Williamson and Hall developed the following relation for the corrected value of full width at half of the maximum ($\beta$) of a broadened profile [138, 139],

$$B = [\lambda/D \cos \theta] + [4\varepsilon \tan \theta]$$

Or, $[\beta \cos \theta/\lambda] = [1/D] + [4\varepsilon \sin \theta/\lambda]$  

(3.08)

Where $D$ is the average grain size and $\varepsilon$ is the average strain developed in the film.

For the multiple ordered diffraction pattern of a sample, for each peak found at different 20, $\beta$ values are different. Now, when $\beta \cos \theta/\lambda$ versus $4\sin \theta/\lambda$ is plotted according to above relation (3.08) and will be straight line (called Williamson and Hall plot). Therefore, the Y-intercept of the linear plot will give the average grain size ($D$) and the slope of this plot will give the average strain ($\varepsilon$) of the sample [140].

3.1.4 Dislocation density

The density of dislocations is the number of dislocation lines that intersect a unit area in the crystal [141]. A single dislocation line sweeping across a slip plane gives rise to a displacement of the order of few Angstroms; thus any appreciable plastic deformation must be the result of a large number of dislocations sweeping across many
slip planes. The rate of flow may be expected to be proportional to the total length of all active dislocation lines and the average velocity with which the elements of these lines move. Hence, the concept of dislocation density $\rho$ is introduced,

$$\text{i.e. } \rho = \frac{S}{V} \quad (3.09)$$

Where $S$ is the total length of the dislocation lines and $V$ is the volume of the crystal [142].

3.2 Conduction processes in semiconductor

Conductivity of the semiconductors is mainly attributed to number of electrons and holes present in the material. The mobility of the charge carriers are important factors in conductivity process in the materials.

3.2.1 Conductivity of intrinsic semiconductor

The total conductivity in intrinsic semiconductor due to combined effect of free electrons and holes is,

$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

Or, $\sigma = en(\mu_e + \mu_h) \quad (3.10)$

Where $\mu_e$ is the mobility of electron, $\mu_h$ is the mobility of hole, $n_e$ is the density of electrons in conduction band and $n_h$ is the density of the holes in the valence band. But for intrinsic semiconductor $n_e = n_h = n$. The density of electrons in conduction band is given by,

$$n_e = 2 \left( \frac{2\pi m^*_e k_B T}{\hbar^2} \right)^{3/2} \exp \left[ \frac{E_F - E}{k_B T} \right] \quad (3.11)$$

The density of holes in the valence band is given by

$$n_h = 2 \left( \frac{2\pi m^*_h k_B T}{\hbar^2} \right)^{3/2} \exp \left[ \frac{E_F - E}{k_B T} \right] \quad (3.12)$$
Where $m_e^*$ and $m_h^*$ are the effective mass of electron and hole respectively, $E_F$, $E_V$ and $E_C$ are the energy of Fermi level, top of the valence band and bottom of the conduction band respectively and $K_B$ is the Boltzmann constant and $T$ is the absolute temperature. The Fermi level is given by,

$$E_F = \frac{E_C + E_V}{2} + \frac{3}{4} K_B T \ln \frac{m_h^*}{m_0^*}$$

If $m_h^* = m_e^*$ we find that

$$E_F = \frac{E_C + E_V}{2} \quad (3.13)$$

Since log1 is zero. This means Fermi level exactly half way between the top of the valence band and bottom of the conduction band.

In terms of band gap energy, the density of carriers $n_e = n_h = n$ in a band is given by,

$$n = 2 \left[ \frac{2\pi K_B T}{\hbar^2} \right]^{3/2} (m_e^* m_h^*)^{3/4} \exp \left[ -\frac{E_F}{k_B T} \right] \quad (3.14)$$

and the conductivity of an intrinsic semiconductor is given by,

$$\sigma = 2 \left[ \frac{2\pi K_B T}{\hbar^2} \right]^{3/2} (m_e^* m_h^*)^{3/4} \exp \left[ -\frac{E_F}{k_B T} \right] e(\mu_e + \mu_h) \quad (3.15)$$

The mobilities $\mu_h$ and $\mu_e$ have temperature dependence and will largely cancel the $T^{3/2}$ temperature variation of the term,

$$\left[ \frac{2\pi K_B T}{\hbar^2} \right]^{3/2} (m_e^* m_h^*)^{3/4}$$

So that the conductivity, $\sigma$ is dominated by the exponential term, $e^{-\frac{E_F}{k_B T}}$.

Therefore we can write the equation as,

$$\sigma = \text{Constant} \; e^{-\frac{E_F}{k_B T}} \quad (3.16)$$
Or, $\rho = \text{Constant} \ e^{\frac{E_g}{k_B T}}$  \hspace{1cm} (3.17)

Or, $\log_e \rho = \log_e \text{Constant} + \frac{E_g}{2 \ k_B T}$

which is the equation of a straight line. This is confirmed by plotting $\log_e \rho$ against $\frac{1}{T}$ for some intrinsic semiconductor. The slope of the line $\frac{E_g}{2 \ k_B}$ will provide the value of energy gap $E_g$.

3.2.2 Extrinsic semiconductor (impurity semiconductor)

n-type dopant or donor impurity

In impurity semiconductor impurity atoms reduce the energy gap $E_g$. Donors represent isolated energy levels located so close to unfilled band that very little energy is required to lift an electron from the donor level into the unfilled band i.e. conduction band, where it is available for the conduction of electricity.

There the Fermi level lies exactly halfway between the donor levels and bottom of conductor band. As $T$ increases, Fermi level drops [143].

In n-type semiconductor of donor concentration $N_d$, the density of electron in the conduction band is,

$$n_e = \left[2N_d\right]^{1/2} \left[\frac{2 \ \pi \ \Phi \ k_B T}{\hbar^2}\right]^{3/4} \exp\left[-\frac{\Delta E}{2 \ k_B T}\right]$$  \hspace{1cm} (3.18)

Where $\Delta E = E_c - E_d$ the ionization energy is also called activation energy.

$E_d$ is the donor level.

p-type dopant or acceptor impurity

In the case of p-type, doping involves by a trivalent impurity. They are called acceptor atoms as they accept electrons. The majority carries in this type of doping are holes. In a p-type semiconductor, as there is a low concentration of electrons than that of holes, the Fermi level lies closer to the valence band.
For p-type semiconductor, the density of holes is,

\[ n_h = \left[2N_a\right]^{1/2} \left[\frac{2\pi \frac{\hbar^2}{2m_e} N_a \Delta E}{\hbar^2}\right]^{3/4} \exp \left[\frac{-\Delta E}{2k_BT}\right] \tag{3.19} \]

Here \( \Delta E = E_a - E_v \) and \( N_a \) is the acceptor concentration.

\( E_a \) is the acceptor level.

3.3 Temperature dependence of conductivity of semiconductor

In a pure semiconductor no donor or acceptor level occurs at 0 K, the valence band is full and conduction band is empty. The Fermi level lies midway between the two i.e. \( E_F = \frac{E_C + E_v}{2} \). As the temperature is raised the electrons are transferred into the conduction band, and then if the density of states at the bottom of the conduction band is equal to that at the top of the valence band, \( E_F \) will remain in the middle of the gap. If however, density of states is not same for few bands then \( E_F \) will move to higher or lower energies as \( T \) is raised.

For n-type semiconductor, if donor states be at an energy \( E_d \) above the valence band, then at 0 K all the states up to \( E_d \) are filled and all states above \( E_d \) are vacant. Thus \( E_F \) will lie midway between the donor level and bottom of the conduction band i.e. \( E_F = \frac{E_C + E_v}{2} \). In this case, however, since density of states will not remain same for the donor level as well as for conduction band, when temperature is increased, the Fermi level will not remain constant.

As temperature is increased \( E_F \) slowly shifts downwards and cross the donor level. At sufficiently high temperature all the donors will be ionized and most of the electrons are excited from the valence band to conduction band just as in intrinsic semiconductor. An analogous situation occurs for p-type semiconductor also.
At low temperature, the majority carrier concentration in an n-type semiconductor is a strong function of temperature, determined essentially by the ionization of the dopant impurities i.e. by the position of $E_F$. The expression,

$$\sigma = \sigma_0 e^{\left(-\frac{E}{k_BT}\right)}$$  \hspace{1cm} (3.20)

is generally used to obtain the activation energy $E$ of impurity semiconductor from its logarithm of conductivity versus $\frac{1}{T}$ curve. At higher temperature the donor levels may be exhausted or acceptor levels saturated, since these level generally contain fewer state than either in conduction or valence band. The carrier concentration then becomes insensitive to temperature. At sufficiently high temperatures electrons are excited from valence to conduction band in large numbers since sufficient energy is available for that. The equal quantities of electrons and holes are liberated and exceed by far limited number of extrinsic carriers. The conduction therefore, becomes intrinsic. At this range the slop of $\ln\sigma$ vs $\frac{1}{T}$ curve as per above relation will give the value of forbidden energy gap.

3.4 Optical properties of semiconductor

Energy band gap is an important property of any semiconductors. It is measured by a beam of light of selected frequencies passed through the semiconductors. The intensity may be reduced by scattering and by absorption. The extent of reduction by absorption depends on the path length of the beam through the semiconductor, the nature of the atoms of the semiconductor and the wave length of the incident beam. When photons of selected wavelength are passed through the semiconductor, the relative transmission of the various photons is measured. It is observed that photons with energies greater than the band gap energy of the semiconductor ($\hbar\nu \geq E_g$) are absorbed while photons with energies less than the band gap of semiconductor are
transmitted. From the measurement of transmitted (or absorbed) photons one can derive the band gap energy of the semiconductor.

In semiconductor, the atoms in the lower energy level can absorb radiation and get excited to the higher energy level, when it is exposed to radiation. This absorption occurs when the frequency of radiation $\nu$ is such that $\hbar \nu$ is equal to or greater than the energy difference between the two concerned levels. The dependence of $I$, the intensity of radiation transmitted through the semiconductor of thickness ‘t’ is of the form,

$$I = I_o \exp (-\alpha t) \quad (3.21)$$

Where $I_o$ is the initial intensity of radiation and $\alpha$ is the absorption co-efficient.

There are four main types of transition which can be induced by radiation: (a) intrinsic absorption, (b) carrier absorption, (c) localized states and (d) lattice absorption.

In intrinsic absorption electrons are excited to conduction band from valence band directly. The carrier absorption occurs from the excitation of free carrier in the valence or conduction band into vacant states of higher energy within the energy band. The localized state occurs due to presence of impurity levels within the energy gap. Electrons and holes bound to the localized states (impurity levels) can be excited to the conduction and valence bands as well as to higher bound states by radiation of smaller energy than that needed to create free carriers intrinsically. The interaction of optical radiation with lattice vibration results in lattice absorption and is ascribed to phonon interaction [144].

### 3.4.1 Optical constants of thin films

Films are ideal specimens for reflectance, transmittance and interferometric types of measurement. Optical constants of thin films are however, influenced by
various factors such as the rate of evaporation, the substrate temperature, film thickness, and crystallinity or otherwise. n and k are also found to vary with the film thickness and the wavelength of the incident light. The electromagnetic field that describes light traveling in X-direction through a material of refractive index ‘n’ is given by [145],

$$E_x = E_0 \times \exp \left[ iw \left\{ \frac{nx}{(c - \omega)} \right\} \right] \exp (-w/kx/c) \quad (3.22)$$

Where k is the extinction co-efficient also known as the imaginary part of the complex refractive index of the medium. The optical behaviour of a material is generally utilized to determine its optical constants such as complex refractive index ($n^* = n - ik$), real part of complex refractive index (n), imaginary part of complex refractive index (k), absorption co-efficient ($\alpha$) and dielectric constant ($\varepsilon$) of the films. Real part of refractive index ‘n’ is related to the reflectance spectrum, which is in turn is connected with the band structure [146]. Also the knowledge of this parameter is important for multilayers structures and antireflection coatings. From above equation it is seen that the wave is attenuated by $\exp (-w/kx/c)$. The attenuation of the intensity is thus given by $\exp (-2w/kx/c)$. The absorption co-efficient ‘$\alpha$’ defined by relative decrease of intensity per unit distance in the propagation direction through,

$$I = I_0 \exp (-\alpha x),$$

is then given by,

$$\alpha = \frac{2 \omega k}{c} = \frac{4\pi k}{\lambda}, \quad (3.23)$$

where $\lambda$ is the wave length of the incident light.
3.5 Organic semiconductor

3.5.1 Charge transport in organic semiconductor

Organic semiconductors are hydrocarbon molecules with backbone of carbon atoms. The strong bonds that form the molecular backbone arise from $sp^2$ hybridized atomic orbitals of adjacent carbon atoms that overlap yielding a bonding and antibonding molecular $\sigma$ and $\sigma^*$ orbitals. The remaining atomic $p_z$ orbitals overlap to a lesser degree, so that the resulting molecular $\pi$ and $\pi^*$ orbitals are less binding or antibinding, thus forming the frontier orbitals of the molecule. The bonding and antibonding molecular orbitals are delocalized over both the atoms and the bonding molecular orbital possesses lower energy than the parent atoms, while the antibonding orbital has higher energy. The energy band that results from the bonding orbital of the molecule is known as the valence band, while the conduction band is the result of the antibonding orbitals of the molecules. The width of the individual bands across the range of energy is called band width. The valence band (VB) represents the highest occupied molecular orbital (HOMO) and the conduction band (CB) represents the lowest unoccupied molecular orbital (LUMO) [147]. In the ground state of the molecule, all bonding orbitals up to the highest occupied molecular orbital, the HOMO, are filled up with two electrons of anti parallel spin while the antibonding orbitals, form the lowest unoccupied molecular orbitals LUMO, onwards are empty. Neutral excited states can be formed for example by light absorption in a molecule, when an electron is promoted from the HOMO to the LUMO. In general, any configuration with an additional electron in an antibonding orbital and a missing electron in a bonding orbital i.e. a hole corresponds to a neutral excited state.
In terms of an energy band description, the $\sigma$-bonds form completely filled bands, while $\pi$-bond would correspond to a half-filled energy band. The molecular orbitals of a polymer form a continuous energy band that lies within a certain energy range. The antibonding orbitals be rated higher in energy $\pi^*$ form a conduction bond where as the lower energy lying bonding orbitals form the valance band. The two bands are separated by the energy gap known as band gap as shown in Figure 3.1.

![Diagram of energy bands](image)

**Figure 3.1:** Two bands are separated by the energy gap

For charge transport in organic solids to take place, there must be a charge on the molecular unit. This may either be an additional electron that is accommodated in antibonding orbital (HOMO) or one that is removed from a bonding orbital (LUMO). The molecule is then no longer in the ground state but rather in a charged excited state.

The common electronic feature of conductive polymers is the $\pi$ conjugated system. Due to p-orbital overlapping of neighbouring molecules of the conjugated structure, the electrons have gained the freedom to move along the entire chain, which provides their semiconducting and conducting properties. In these materials, the p-
electrons are delocalized within molecules and the carrier transport occurs through hopping of charge from one molecule to other. Since the \( \pi \) conjugated system in conducting polymers extend over the whole polymer chain, the conducting polymer can be regarded as one dimensional polymer semiconductor. Due to overlap of \( P_z \) orbitals and \( \pi \) electron delocalized within the molecule the gap between HOMO and LUMO is small and transition frequency is within the visible range. In this material apart from electrons and holes, there exist solitrons, polaron, soliton-polaron, bi-polarons and polaron-excitons etc.

### 3.5.2 Doping of polymer

Doping of polymer produce similar results as doping of inorganic semiconductors. The acceptor species give rise to p-type and donor species give rise to n-type conductivity. The doping of polymer is however achieved by oxidation and reduction. For p-type conductivity, oxidation by halogen and for n-type conductivity, reduction by alkali metals is used. Doped polymer is in general a salt of the compound. In conducting polymers, the influence of chemical dopant or the morphology of the polymer layer and the charge transporting states are still a matter of research. The (Quasi) one dimensional nature of the conducting states however can explain the exceptionally high conductivity in doped conjugated polymer system. It has been observed that the physics of undoped amorphous conjugated polymer film cannot be very different from that of other disordered organic system.
3.5.3 Junction of polymer device

There are various ways and designs used to fabricate a device from these polymers. The mechanical flexibility, easy low temperature processing and low consumption of power are some important points that necessitate the organic polymers are being extensively researched in present day electronic world. The opening of new market in sensors, large area flexible displays and smart card are some possibilities leading to low cost electronics. Since the invention of light emitting diode from organic materials in 1980, there has been a rapid expansion of organic electronics based on conjugated polymers, oligomers and other molecular devices.

![Diagram of a metal polymer junction](image)

Figure 3.2: Schematic representation of metal polymer (p-type) junction

The simplest form of polymer based device is the sandwich structure of polymer layer between two metal electrodes. Other structures include multilayers and Schottky barrier (metal semiconductor) devices. This Schottky barrier junction is made by depositing a metal electrode of suitable work function onto the polymer film. The base electrode is a suitable metal or conducting oxide layer (most cases Indium Tin Oxide)
showing low contact resistance. Since the device performance is greatly affected by interface states of the metal and polymer, the Schottky contact is important (i.e. Schottky diode) phenomenon in device fabrication of polymer material. The junction parameters on which the performance is based are: work function, band gap, surface states, doping, thickness, pressure of an interfacial layer etc. The schematic representation of metal-polymer junction is shown in Figure 3.2. The main physical parameters to be evaluated in the junction are activation energy, barrier height, diode ideality factor, band gap, doping concentration, saturation current density, series resistance etc. Other devices include heterojunction where two types of polymer materials are in contact with each other similar to inorganic heterojunction device.

3.5.4 Optical studies of organic polymer films

Optical absorption studies are important methods for various investigations of the properties of organic semiconductors. The processes of optical phenomena in organic semiconductors are different from their inorganic counterpart. Organic polymer has conjugated p-electron system formed by p_2 orbitals of sp^3-hybridized C atoms in the molecule. In comparison to the σ bond constituting the backbone of the molecules, π bonding is significantly weaker (Figure 3.3). Therefore, the lowest electron excitations of conjugated molecules are the π-π* transitions with an energy gap typically between 1.5 eV to 3 eV leading to light absorption or emission in the visible spectral range [148]. Usually, the ground state of an organic molecule is a singlet state (S_0) and absorption of photon leads to the first excited state (S_1). The lifetimes of (S_1) states are very small and finally lead to the transition back to the ground state via non radiative transition. In the
excited singlet state, there is a small probability for intersystem crossing to the triplet state, from which the excitation energy can be released either by phosphorescence or non radiatively. Apart from other properties, polyaniline has good switching properties between two oxidation states. The addition of an acid or a base that protonates and deprotonates the base (-NH-) sites in polyaniline causes switching of the material between oxidation states. This influences the absorption in UV-Vis range of the spectrum [149]. However, the absorption or emission in organic films depends on several factors like, conjugated length, bonding structure, doping materials used etc.

The optical spectroscopy is an important method of probing the structural and dynamical process taking place in matter interacting nonlinearly with laser fields. However, it is often practiced to take help of other tools for information regarding structural, bonding, optical band gaps etc. These are generally, X-ray spectroscopy, nuclear magnetic resonance (NMR), IR spectroscopy, UV-Vis spectroscopy etc.
3.6 Metal - semiconductor junctions

3.6.1 Ohmic contact to a semiconductor

When a metal contacts with the semiconductor, it will form either a Schottky barrier or an ohmic contact depending on the work functions of the two. The term “ohmic” refers in principle to a contact that is non-injecting has linear I-V characteristics in both directions. Its important significance is that the voltage drop across this contact must be negligible as compared to across the device or specimen and the I-V characteristics is independent of this contact.

Generally for n-type semiconductor ohmic contact can be made by a metal having work function $\phi_m$ less than the work function of the semiconductor $\phi_s$ i.e. ($\phi_m < \phi_s$). In p-type semiconductor ohmic contact can be made by the metal having work function $\phi_m$ greater than the work function of the semiconductor $\phi_s$ i.e. ($\phi_m > \phi_s$). But there are a few number of metal semiconductor combinations that satisfy these conditions. Mostly the ohmic contact is so designed that the charge carrier can easily tunnel through heavily doped semiconductor immediately adjacent to the metal [150]. Energy band diagram of an ideal ohmic contact between a metal and a p-type semiconductor has been shown in Figure 3.4.

3.6.2 Metal-semiconductor junction and Schottky barrier

When a metal is in contact with any semiconductor it forms either Schottky barrier or ohmic contact depending upon the values of work function of both metal and semiconductor. The barrier affects flow of charge carriers, it allows easier flow in one direction and lesser (almost no) flow in the opposite direction, called the Schottky barrier. A metal can form Schottky barrier with n-type or p-type if the work function of both the materials fulfill the required conditions. To form a Schottky barrier with n-type
semiconductor the work function of the metal $\phi_m$ should be greater than the work function of the semiconductor $\phi_s$.

For a Schottky junctions with p-type semiconductor the work function of the metal is less than the work function of the semiconductor (i.e. $\phi_m < \phi_s$). The energy band diagram of a metal-(p)semiconductor is shown in Figure 3.5. Here the Fermi level of the semiconductor ($E_{F_s}$) which is closer to valence band edge lies below the Fermi level of the metal ($E_{F_m}$) prior to contact as shown in Figure 3.5(a). When a metal and a semiconductor are brought into contact, charge carriers readjustment take place and flow from metal into the semiconductor to bring the system into equilibrium and a potential barrier occurs in the interfacial space charge region. It is effectively a flow of holes from the semiconductor, leaving ionized acceptor atoms near the semiconductor surface, which bends the bands forming a barrier to further movement of holes across the interface.
Figure 3.4: An Ohmic contact between a metal and a p-type semiconductor with $\phi_m > \phi_s$; (a) band diagram before contact; (b) after intimate contact at thermal equilibrium, $\phi_m$, work function of metal; $\phi_s$, work function of semiconductor polymer film; $E_v$, valence band edge; $E_F$, Fermi energy level; $E_c$, conduction band edge; $E_{\text{vac}}$, vacuum level; $\chi_s$, electron affinity of the semiconductor; $E_g$, band gap of the semiconductor.
Figure 3.5: A Schottky barrier between a metal and a p-type semiconductor with $\phi_m < \phi_s$; (a) band diagram before contact; (b) after intimate contact at thermal equilibrium, $\phi_m$, work function of metal; $\phi_s$, work function of semiconductor polymer film; $E_v$, valence band edge; $E_F$, Fermi energy level; $E_c$, conduction band edge; $E_{vac}$, vacuum level; $\phi_{bo}$, barrier height; $\chi_e$, electron affinity of the semiconductor; $E_g$, band gap of the semiconductor; $D$, depletion width; $\xi = E_{Fm} - E_v$ (for p-type semiconductor)

In Schottky junction, majority charge carriers can flow to both the directions from the metal to semiconductor and from semiconductor to metal. The net current is the difference between the two opposite flows of current between the metal and semiconductor. An applied bias $V$ determines the dominant process and hence the overall current flows.
In Schottky junction the flow of current is governed mainly by three mechanisms viz.

(1) Thermionic emission of majority carriers (electrons for n-type, holes for p-type) from the semiconductor to the metal.

(2) Tunneling of majority charge carriers from semiconductor to metal.

(3) Thermionic emission of minority charge carriers (electrons for p type and holes for n-type semiconductor) from the metal into the semiconductor.

Application of a bias voltage $V$ across the junction, as in p-n junctions, leads to a difference $qV$ between the Fermi levels in the semiconductor and the metal. For an ideal contact between metal and p-type semiconductor of energy band gap $E_g$, the barrier height is,

$$\phi_{bo} = E_g - (\phi_m - \chi_s) \quad (3.24.a)$$

To make Schottky junction with n-type semiconductor the metal work function should be greater than the work function of the semiconductor (i.e. $\phi_m > \phi_s$). For perfect contact, the limiting value of the barrier height is [151],

$$\phi_{bo} = (\phi_m - \chi_s) \quad (3.24.b)$$

Practically perfect metal semiconductor contact is never formed because a thin insulating oxide layer forms in between the two materials called interfacial layer. But this layer is so thin that the charge carriers can easily flow through it.

### 3.6.3 Capacitance of Schottky barrier

The junction formed at the metal semiconductor interface may behave like a parallel plate capacitor. The measurement of capacitance value of this capacitor under reverse bias condition may provide some information about the junction parameters. For an ideal Schottky barrier with p-type semiconductor, the capacitance under reverse bias
per unit area can be expressed in terms of the diffusion potential \( V_d \) and acceptor density \( N_a \), by the relation, if the effect of electrons can be neglected.

\[
C^{-2} = \left( \frac{2}{\varepsilon_s N_a} \right) \left( V_{b1} + V_r - \frac{kT}{q} \right) \tag{3.25}
\]

Where \( \varepsilon_s \) the permittivity of semiconductor, \( N_a \) is the acceptor density, \( V_{b1} \) is the diffusion voltage at zero bias and \( V_r \) is the applied reverse bias.

This relation shows that a graph of \( C^{-2} \) as a function of \( V_r \) should be a straight line with a slope of \( \left( \frac{2}{\varepsilon_s N_a} \right) \) and a negative intercept on the \( V_r \) axis is equal to, \(-V_i = -V_{b1} + \frac{kT}{q}\) from which \( V_{b1} \) can be calculated. \( N_a \) can be known from the slope of the line if the permittivity of the semiconductor is known. Since the barrier height, \( \Phi_{b0} = V_{b1} + \xi \), relation (3.25) becomes,

\[
C^{-2} = \left( \frac{2}{\varepsilon_s N_a} \right) \left( \Phi_{b0} - \xi + V_r - \frac{kT}{q} \right) \tag{3.26}
\]

If the barrier height \( \Phi_{b0} \) is independent of \( V_r \) (i.e. no interfacial layer is there) a plot of \( C^{-2} \) against \( V_r \) should give a straight line with an intercept \( V_i \) on the horizontal axis equal to \( \left( \Phi_{b0} - \xi - \frac{kT}{q} \right) \).

The barrier height is given by,

\[
\Phi_{b0} = V_i + \xi + \frac{kT}{q} \tag{3.27}
\]

\( \xi \) is known from the relation,

\[
\xi = \left( \frac{kT}{q} \right) \ln \left( \frac{N_e}{N_a} \right)
\]

Where \( N_e \) is the density of the state.
While measuring the capacitive response of the depletion region to the reverse bias the effect of minority carriers has been neglected. This capacitance can also be measured experimentally by superposing an A.C. voltage on the steady D.C. bias $V_r$ and measuring the capacitance in the normal way by a capacitance bridge.

If the barrier height is greater than the $(E_g - \xi)$ then the effect of minority carriers is considerable, thereby the electron density in the adjacent to the metal exceeds the acceptor density and the electric field at the interface is due partly to the holes and partly to the uncompensated acceptors, $C^2$ vs $V_r$ plot will not be linear, the intercept on $V_r$ axis will give less $V_i$ hence $\Phi_b$.

The insulating oxide layer formed at the barrier may change the capacitance value as it modifies the depletion region on the bias voltage. The capacitance formed by the interfacial layer is effectively in series with the capacitance of the depletion region, but the interfacial layer is not linear, hence the resultant capacitance is expected to be a complicated function of parameters related.

### 3.6.4 Schottky barrier with an interfacial layer

When a metal-semiconductor junction is fabricated an interfacial insulating oxide layer is formed in between the metal and semiconductor contact. This thin layer is formed on the semiconductor surface when it is exposed to air. To avoid or minimize this layer the junction should be made in a high vacuum condition. If it is of the order of 10 Å the charge carrier can easily and freely tunnel through it.

The capacitance of Schottky barrier containing an interfacial layer between the semiconductor and the metal can be considered as the series connection of the oxide and semiconductor capacitance. Hence, the interfacial layer reduces the capacitance of the Schottky barrier diode; although a capacitance measurement will have the same
characteristics as an ideal Schottky barrier diode except that the built-in voltage is increased. However, the potential across the semiconductor is decreased due to the voltage drop across the oxide layer, so that at low voltage the barrier for electrons flowing into the semiconductor is reduced yielding a higher current. It has been assumed that the interfacial layer forms a very thin tunnel barrier which at low voltages does not restrict the current. As the voltage applied to the Schottky barrier is more positive, the depletion layer width reduces, so that the field in the oxide also reduces and with it the voltage drops across the oxide. The current under forward bias conditions therefore approaches that of the ideal Schottky diode until the tunnel barrier restricts the current flow. This results in a higher ideality factor for Schottky barrier with an interfacial layer [152, 153].

If an appreciable interfacial layer is present, the barrier height depends on the bias voltage ($V_r$). If the interfacial layer is so thin that the occupation of the surface states is determined by the Fermi level in the metal, then according to Cowley [154], the barrier height found from the intercept ($-V_i$) of the $C^{-2}$ vs $V_r$ plot will be,

$$\phi_h = \phi_{ho}^+ \phi_i/4$$

Where $\phi_{ho}$ is the flat band barrier height and, $\phi_i = 2\alpha q(N_e/\varepsilon_o)$ and $\alpha = (\delta \varepsilon_e/\varepsilon_i) + q\delta D_o$,

$\delta$ and $\varepsilon_i$ being thickness and permittivity of the interfacial layer respectively and $D_o$ is the density of interface states.

For most practical cases $\phi_i$ is less than $\phi_{ho}$ by about two orders of magnitude, the C-V method essentially gives the flat band barrier height.

If the interfacial layer is thick enough so that the interface states are partially or fully in equilibrium with the semiconductor, the situation is much more complicated,
because the interface states are indeed filled from the semiconductor. The case is similar to that of an MOS capacitor and the graph of $C^2$ against $(V_t)$ is generally non-linear.

In general, in the metal-semiconductor contact there is always an interfacial oxide layer of atomic layer dimensions and the semiconductor surface has surface states.

### 3.6.5 Electronic transport mechanisms in metal-semiconductor or Schottky barrier junction

![Figure 3.6](image)

Figure 3.6: Schematic diagram of the three current transport mechanisms for current flow from (a) n-type semiconductor to metal, (b) p-type semiconductor to metal; 1. thermionic emission of majority carriers, 2. tunneling, 3. thermionic emission of minority carriers. The same processes hold in the reverse direction from metal to semiconductor. Mechanisms 2 and 3 are generally negligible as compared to 1.

Under the forward bias voltage ($V$), the Fermi level in the semiconductor region will rise by $qV$ in n-type semiconductor and lowered by $qV$ in p-type semiconductor and as a result the barrier will be formed for majority carriers. The current transport in a metal-semiconductor junction is mainly due to majority carriers in contrast to p-n junction where minority carriers are also responsible. The main transport processes
under forward bias condition are, diffusion of carriers from the semiconductor over the potential barrier into the metal, thermionic emission of carriers across the Schottky barrier and quantum mechanical tunneling through the barrier. The diffusion theory assumes that the driving force is distributed over the length of the depletion layer. The thermionic emission theory on the other hand postulates that only energetic carriers, which have energy equal to or larger than the barrier energy at the metal semiconductor interface, contribute to the current flow. Quantum mechanical tunneling through the barrier takes into account the wave-nature of the electrons allowing them to penetrate through thin barriers. In a given junction one finds that a combination of all three mechanisms could exist. However, typically one finds only one to limit the current, making it the dominant current mechanism. If the height of a Schottky barrier on n-type semiconductor is greater than half of the band gap, a region of the semiconductor adjacent to the metal becomes p-type and a high concentration of hole occurs. There are possibilities of these holes to diffuse into the neutral region of the semiconductor under forward bias. This gives rise to the injection of holes. Early works on hole injection of metal semiconductor contact has been summarized by Henisch [155].

The recombination process in metal semiconductor junction normally takes place via localized centers and most effective centers are those with energies lying near the centre of the gap. The recombination current is the common cause of departure from ideal behavior in Schottky diode.

3.6.6 Thermionic emission theory of current transport

For a Schottky barrier junction with moderate doping at room temperature the transport mechanism namely emission of electron over barrier can be adequately described by thermionic emission theory [156]. The current flow mechanisms in metal
semiconductor junction are shown in Figure 3.6. \( J_{in} \) is the current density of electrons flowing from the semiconductor to the metal and \( J_{ms} \) is the current density of electrons flowing from metal to semiconductor. At thermal equilibrium the current density is balanced by two equal and opposite flow of carriers, thus there is zero net current. These current components are proportional to the density of electrons at the boundary. When bias is applied the balance is upset and net current flows through the device.

The current voltage relation according to thermionic emission theory is given by,

\[
J = J_0 \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]  
(3.28)

Where \( J_0 = A^* T^2 \exp \left( -\frac{\Phi_b}{kT} \right) \)  
(3.29)

and \( A^* \) is called the Richardson constant.

The equation (3.28) is similar to J-V expression for p-n junction and correct barrier height is independent of bias. However, in the presence of interfacial layer, the barrier height \( \Phi_b \) depends on the bias voltage. Even in a perfect contact with no interfacial layer, the barrier height is reduced as a result of an image force by an amount \( \Delta \Phi_b \), which depends on the bias voltage. Thus we can write the effective barrier

\[
\Phi_{e,f} = \Phi_{b,0} - (\Delta \Phi_b)_0 + \beta V
\]

Where, \( \Phi_{b,0} \) is the barrier height at zero bias and \( (\Delta \Phi_b)_0 \) is the image force lowering at zero bias. The coefficient \( \beta \) is a positive quantity.

The current density now becomes [157] replacing \( \Phi_b \) by \( \Phi_{e,f} \) in \( (3.28) \),

\[
J = A^* T^2 \exp \left[ -\frac{q\Phi_{b,0} - (\Delta \Phi_b)}{kT} \right] \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]

\[
J = J_0 \exp \left( \frac{qV}{na_x kT} \right) \left\{ 1 - \exp \left( -\frac{qV}{kT} \right) \right\}
\]

(3.30)

Where \( J_0 = A^* T^2 \exp \left[ -\frac{q\Phi_{b,0} - (\Delta \Phi_b)}{kT} \right] \)

(3.31)
And \( \frac{1}{n} = 1 - \beta = 1 - \left( \frac{\delta \Phi_e}{\delta V} \right) \)

\( n \) is called “ideality factor”. It is constant if \( \frac{\delta \Phi_e}{\delta V} \) is constant.

For \( V > \frac{3kT}{q} \), equation (3.30) can be written as,

\[
J = J_0 \exp \left( \frac{qV}{nKT} \right)
\]  

(3.32)

The value of ‘\( n \)’ can be found experimentally by plotting \( \ln \left[ \frac{1}{1 - e^{-\frac{qV}{nKT}}} \right] \) against \( V \). This graph should be straight line of slope \( \frac{q}{nKT} \) if \( n \) is constant even for \( V < \frac{3kT}{q} \). Usually \( \frac{\delta \Phi_e}{\delta V} \) is not constant and \( n \) becomes a function of bias and in that case the \( \ln \left[ \frac{1}{1 - e^{-\frac{qV}{nKT}}} \right] \) vs \( V \) plot is not linear. But still \( n \) is a useful concept and can be obtained from the plot through the relation,

\[
\frac{1}{n} = \frac{kT}{q} \frac{d}{dV} \left[ \ln \left( \frac{1}{1 - e^{-\frac{qV}{nKT}}} \right) \right]
\]

(3.33)

\[
\frac{1}{n} = \frac{kT}{q} \frac{d}{dV} (\ln J) \text{ for } V > \frac{3kT}{q}.
\]

The parameters ‘\( n \)’ is generally a function of \( V \), and can be specified for a particular operating point on the characteristics.

The value of \( J_0 \) is obtained directly from the intersection of \( \ln \left( \frac{1}{1 - e^{-\frac{qV}{nKT}}} \right) \) vs \( V \) plot with the vertical axis. As \( J_0 \) is a function of temperature \( T \), it can be measured from the forward \( J-V \) characteristics over a range of temperature. A plot of \( \ln(J_0 T^{-\beta}) \) against \( T^{-1} \) should give a straight line with intercept on the vertical axis equal to \( A^* \) and slope \( \Phi_{e0}/k \), where \( \Phi_{e0} \) is the effective barrier height for zero bias.
Therefore the value of effective Richardson’s constant ($A^*$) and the effective barrier height can be calculated from $\ln(J_0T^{-2})$ against $T^{-1}$, the Richardson’s plot.

3.7 Semiconductor heterojunction

A heterojunction is the interface that occurs between two layers or regions of dissimilar crystalline semiconductors. These semiconducting materials have unequal band gaps as opposite to a homojunction. It is often advantageous to engineer the electronic energy bands in many solid state device applications including semiconductor lasers, solar cells and transistors ("heterotransistors") to name a few. Heterojunctions are of two types based on the types of conductivity of the semiconductors used. If both the semiconductors have same type of conductivity, it is said as isotype heterojunction and if the types of conductivity differ, then the junction is said as anisotype heterojunction [158]. Many models have been proposed so far to explain the heterojunction. Out of all these, abrupt heterojunction models are found suitable for many heterojunctions.

3.7.1 Energy band diagram of abrupt anisotype heterojunction

This model was developed by Anderson [158] and commonly known as diffusion model. Energy band diagram of a heterojunction before and after equilibrium have been shown in Figure 3.7. In the Figure two semiconductors of different energy gaps ($E_g$), different dielectric constants ($\varepsilon$), different work functions ($\Phi$) and different electron affinities ($\chi$) are used to form the heterojunction. The discontinuity in the conduction band edges ($\Delta E_c$) is equal to the difference in electron affinity ($\Delta E_c = \chi_1 - \chi_2$) of the two semiconductors. The subscripts 1 and 2 refer to p-type and n-types semiconductors respectively. This type of heterojunction depletion layers form in either sides of the junction, since the interface states are absent on this model, the space
charges of these layers are opposite and equal in magnitude. The built in potential \( V_b \) due to difference in work function \( (\phi_1 - \phi_2) \) is equal to the sum of built in potential on both sides \( V_b = V_{b,1} + V_{b,2} \)

![Energy band diagram](image)

Figure 3.7: Energy band diagram (a) before the formation and (b) after the formation of p-n heterojunction

3.7.2 Transport mechanism of abrupt anisotype heterojunction:

**Thermionic emission model**

This model combines a classical model for evaluation of emission currents with diffusion model for determination of extent of minority carrier built up at the edge of the depletion region. Assuming thermionic emission over the heterojunction barrier to be dominant mechanism, as Schottky diode, current-voltage relation can be expressed as, [159].

\[
J = A^* T^2 \exp \left[ \frac{-q Y_2}{kT} \right] \left[ \exp \left( \frac{-q Y_1}{kT} \right) - \exp \left( \frac{-q Y_2}{kT} \right) \right]
\]
Where $V_1$ and $V_2$ are the voltage distribution in p and n side of the junction respectively. It can be shown that,

$$ J = A^* T^2 q V_b \exp \left( -\frac{q \cdot V}{kT} \right) \left[ 1 - \frac{V}{V_b} \right] \exp \left( \frac{q \cdot V}{kT} \right) - 1 $$

$$ = J_0 \left[ 1 - \frac{V}{V_b} \right] \exp \left( \frac{q \cdot V}{kT} \right) - 1 $$

Where $J_0 = A^* T^2 q V_b \exp \left( -\frac{q \cdot V}{kT} \right)$,

$$ V_{bi} = V_{b1} + V_{b2}, \quad V = V_1 + V_2, $$

and $(V_b) = (\phi_1; \phi_2)$

It is seen that the value of $J_0$ is temperature dependent. The reverse current never saturates and increases linearly with voltage at large bias voltage.

### 3.8 Gas sensitivity in organic semiconductor and junction

Polymer films and their nanocomposites are well known to be sensitive to different analytes and are extensively used in sensing application where their different transduction properties (such as electrical, mechanical and thermal properties) are exploited. Thus in this process, polymer films and junctions with different materials are used in gas sensing devices [160,161]. The interactions between the analytes and the gas sensing materials are multiform depending on different analytes and different active materials of the film. The most common form of phenomena found in gas sensing devices is the absorption of gas molecules by the films or junctions and there by changing the electrical properties of the films or junctions. In addition to absorption, another phenomenon observed in polymer film by vapour molecule is swelling of polymer film. However, sensitivity of the polymer film or junction to different gas molecules depends on the type of polymer film and its physical properties. The most common type of gas sensing polymer device is the resistive type conductive polymer
film and is called chemoresistor. Here the change of conductivity of the film upon exposure to different gases can be suitably measured. The device is made by using the sensitive layer of the polymer film to make contact with the gas molecules and the corresponding change of electrical properties can be transferred by a suitable device called transducer [162]. The gas relative sensitivity $S$ may be written as,

$$S = \frac{\Delta \sigma}{\sigma_{air}} = \frac{\sigma_g - \sigma_{air}}{\sigma_{air}} \quad (3.34)$$

Where, $\Delta \sigma$ is the difference of conductivity of the gas with respect to air and $\sigma_{air}$ is the conductivity of the sample in air.