Theoretical background

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2.1 Introduction

In this chapter we describe about the theoretical background of semiconductors, conduction mechanism and characterization techniques. It also describes the chemistry of photoelectrode-electrolyte interface. The photoelectrode i.e. semiconducting material is discussed with the help of band theory. The mechanisms of charge transfer are studied in electrolyte as well as semiconductor material. The formations of junction are discussed with the reference to space charge layer, Helmholtz layer and Butler-Volmer reaction for charge transfer mechanism.

The photoelectrochemical cell is constructed by using semiconductor photoelectrode, counter electrode and electrolytic solution. The semiconductor photoelectrode is immersed in electrolyte and then exposed to sunlight which converts solar radiation into electrical energy. The charge transfer process across the photoelectrode-electrolyte interface in dark and in light results in current flow in junction.

2.2 Semiconductors

2.2.1 Concept of energy bands

Semiconductor materials at zero Kelvin have basically the same structure as insulators, a filled valance band separated from empty conduction band by energy gap containing no allowed energy states [1]. Fig 2.1 shows typical band structure at zero Kelvin. The difference lies in the size of band gap Eg which is much smaller in semiconductors than in insulators. The band gap in case of metals is high as compared to semiconductors. Metals show promotion of electron from partially filled valence band to empty conduction band. In case of insulators the conduction mechanism is absent as the band gap is very high (Eg=10eV), which shows negligible number of electronic excitations.

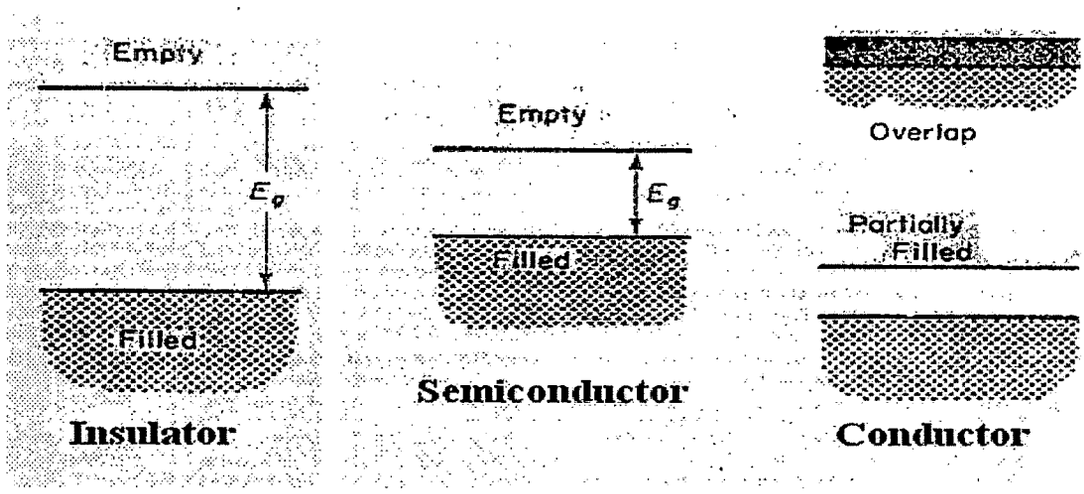


Fig 2.1 Typical band structure at zero Kelvin

An important difference between semiconductors and insulators is that, the number of electrons available for conduction can be increased greatly in semiconductors by means of thermal or optical energy.

Depending on the type of electron transition, there exist two types of semiconductor energy bands [2],

i) Direct band gap semiconductors,

ii) Indirect band gap semiconductors.

In direct band gap semiconductors, an electron in the conduction band can fall to an empty state in the valence band giving off the energy difference Eg as a photon of light. In case of indirect band gap semiconductors an electron in conduction band minimum can not fall directly into the valence band maximum, but must go through some defect state within the band gap. In an indirect transition, the energy is given largely as heat to the lattice rather than as an emitted photon. Fig 2.2(a) and (b) shows direct and indirect type of transition s in semiconductors.

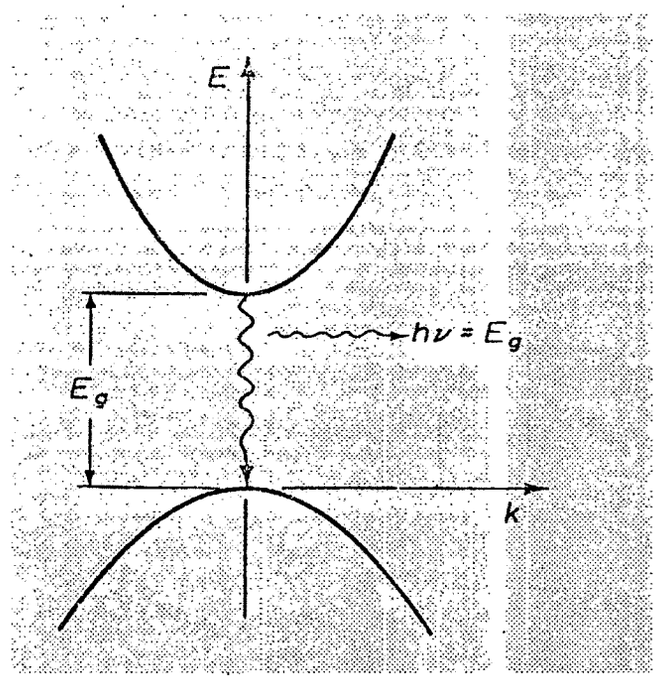


Fig 2.2(a)

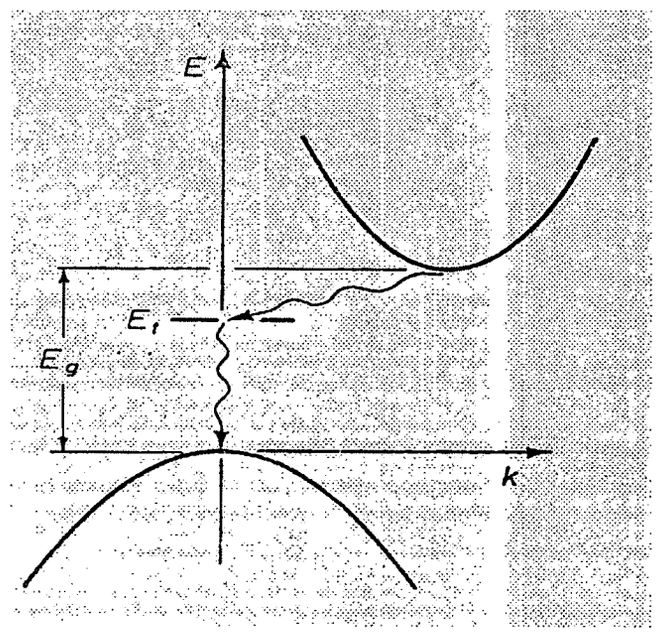


Fig 2.2 (b)

Fig 2.2: a) Direct type of transitions in semiconductors.

b) Indirect type of transitions in semiconductors.

The difference between direct and indirect band structures is important for deciding which semiconductor can be used in devices requiring light output. For example, semiconductor light emitters and lasers generally made of materials capable of direct band to band transitions or indirect material with vertical transitions between defect states.

2.2.2 Types of semiconductors

Semiconductors are classified into two types depending on the impurity or defects [3],

i) Intrinsic semiconductor,

ii) Extrinsic semiconductor.

i) Intrinsic semiconductor

A perfect semiconductor crystal with no impurities or lattice defects is called as an intrinsic semiconductor. It is extremely pure form of semiconductor. In such materials there are no charge carriers at 0K, since the valence band is filled and the conduction band is empty. At higher temperatures, electron-hole pairs are generated, as valence band electron are excited thermally across the band gap to the conduction band. The EHPs are the only charge carriers in the intrinsic semiconductors as shown in fig 2.3.

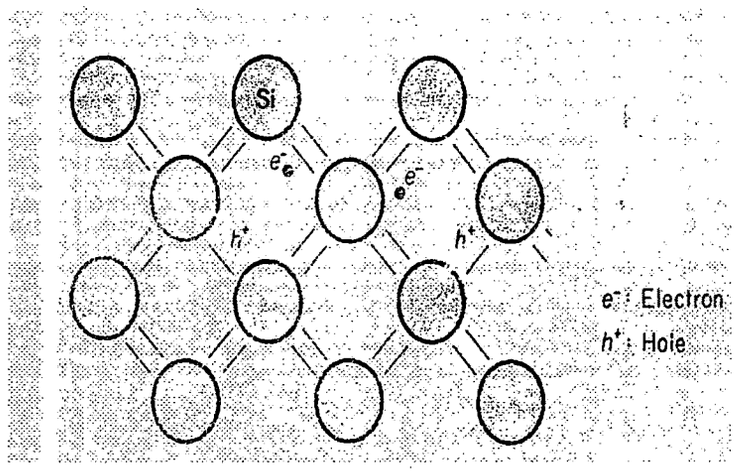


Fig 2.3: A model of electron hole pair formation in covalent bonding.

ii) Extrinsic semiconductor

The intrinsic semiconductor has little current conduction capability at room temperature. It is possible to create carriers in semiconductors by purposely introducing impurities into the crystal. This process called 'doping' and material formed is called as extrinsic or impurity semiconductor. The amount and type of such an impurities can be controlled during the preparation of extrinsic semiconductor. When impurities or lattice defects are introduced

into a perfect crystal, additional levels are created in the energy band structure usually within the band gap. This increase either the number of electrons or holes in the semiconductor crystal.

Depending upon the type of impurity added, extrinsic semiconductors are classified into [4],

i) n-type semiconductor,

ii) p-type semiconductors

i) n-type semiconductors

Fig 2.4(a) shows band diagram for n-type of semiconductor. When a small amount of pentavalent impurity is added to a pure semiconductor, it is known as n-type semiconductor. The addition of pentavalent impurity like P, As, Sb provides a large number of free electrons in the n-type semiconductor crystal. The current conduction in n-type semiconductor is chiefly by negative charges i.e. electrons.

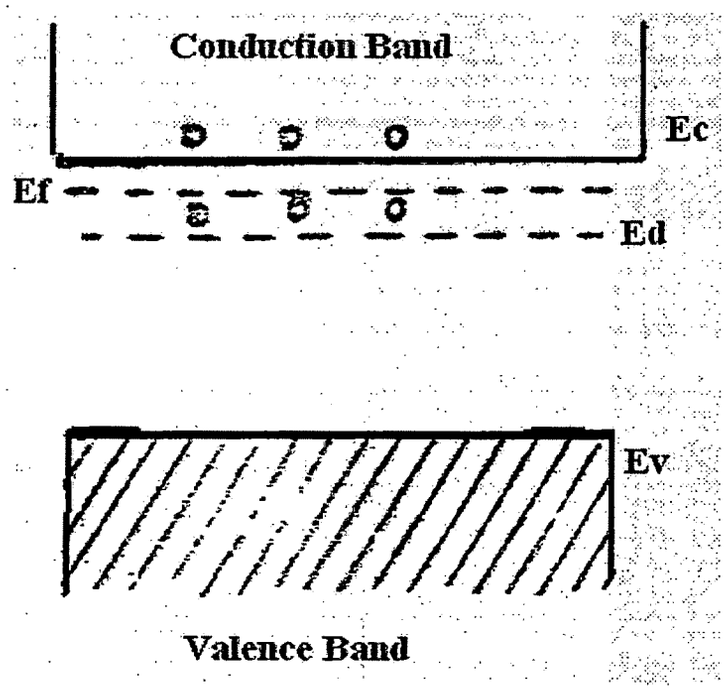


Fig 2.4 (a) Band diagram for n-type of semiconductor.

ii) p-type type semiconductor

When a small amount of trivalent impurity is added to pure semiconductor, is called as p-type semiconductor. The addition of trivalent impurity provides a large number of holes in the semiconductor. For example

Ga and In produces p-type semiconductors which are known as acceptor impurities, because the holes created can accept the electrons. Fig 2.4(b) shows band diagram for p-type of semiconductor

The current conduction in p-type semiconductor is predominantly by holes i.e. positive charges.

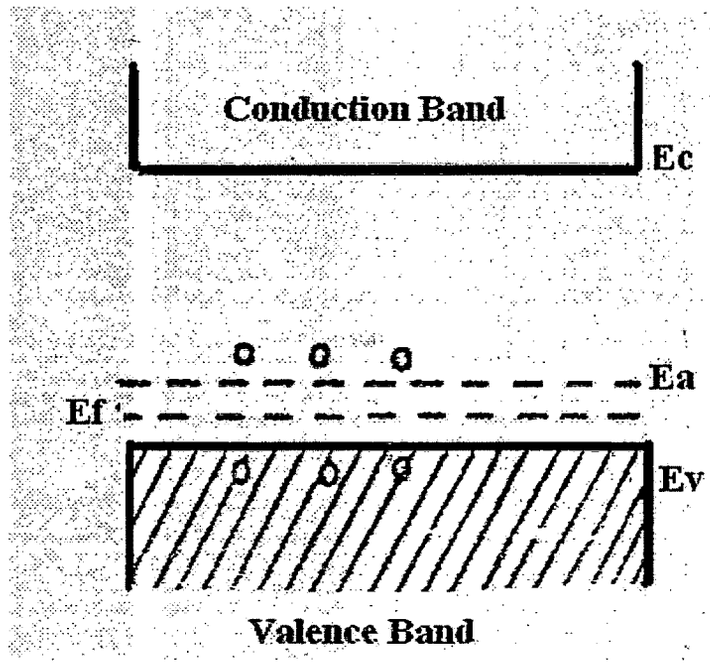


Fig 2.4 (b) Band diagram for p-type of semiconductor.

2.3 Theoretical background of Chemical bath deposition

The deposition of thin film on the substrate surface is a two step process:

1. Formation of nucleus
2. Subsequent growth of nucleus

When a sparingly soluble salt XY is placed in water, saturated solution containing X^+ and Y^- ions in contacts with the undissolved solid electrolyte, XY is obtained and an equilibrium is established between solid phase and the ions in the solutions thus,

$$XY(s) \longleftrightarrow X^+ + Y^- \qquad (2.1)$$

Applying law of mass action to this equilibrium,

$$K = Cx^{+} Cy^{-} / Cxy\,(s) \qquad (2.2)$$

Where Cx^{+} Cy^{-} and Cxy are concentration of X^{+}, Y^{-} and XY respectively.

The concentration of pure solid phase is constant number i.e. Cxy(s) = const = k' Equation (2) becomes.

$$K = Cx^{+} Cy^{-} / K'$$

$$KK' = Ksp = Cx^{+} Cy^{-} \qquad (2.3)$$

The constant Ksp is called solubility product and the product Cx^{+}, Cy^{-} is called ionic product. Now three different situations may arise:

1. When the ionic product is equal to the solubility product, the solution is saturated.
2. When the ionic product exceeds the solubility product the solution becomes supersaturated and precipitation occurs.
3. When the ionic product is less than the solubility product, the solution will be unsaturated.

The factors which affect the solubility product are temperature, solvent and particle size [5]. To determine solubility products, a variety of techniques like colorimetric, conduct metric, polarography, thermodynamics etc. are used [6-9].The mechanism of thin film deposition process involves two types,

a) By ion -by-ion mechanism
b) By cluster-by-cluster mechanism

a) By ion -by-ion mechanism

In case of ion –by-ion growth the deposition process involves the ion-by-ion deposition at nucleation sites on the immersed surfaces. Many researchers have obtained the thin films by ion-by-ion mechanism [10-11].

b) By cluster-by-cluster mechanism

According to Lundin and Kitaev [12] nucleation takes place by adsorption of colloidal particles and growth takes place as a result of surface coagulation of these particles, which gives thin, adherent films. This is known as cluster-by-cluster growth of thin film.

The particle size of a precipitate is controlled by the experimental conditions, prevailing at the time of its formation, such as temperature, rate of

mixing of reagents, ion concentration, of reagents and the solubility of the precipitate. All of these can be related to relative of super saturation of the system. The various steps involved in precipitation are,

1) Super saturation

A solution is said to be supersaturated when it contains more ions than that permitted by solubility product.

Super saturation = Q-S

Relative super saturation = Q -S /S (2.4)

Where Q is the concentration of a solute in solution at any instant and S is an equilibrium concentration in a saturated solution of the same solute.

2) Nucleation

For any precipitate there is some minimum number of the ions or molecules required to product a stable phase in contact with a solution, called as nucleus. The formation of nuclei is necessary for a precipitate formation. The rate at which nuclei form in a solution is dependent upon the degree of supersaturation. In highly super saturated solution, the velocity of nucleation increases rapidly. The rate of nucleation increase exponentially with the supersaturation as,

$$\text{Rate of nucleation} = K\,(Q-S)^{r} \qquad (2.5)$$

The next step that can occur during precipitation is the growth of particles already present in the solution (i.e. nucleation centers). The growth of nuclei or other seed particles should occur so that film and precipitate can be obtained. In case of an ionic solid, the process involves deposition of cations and anions on appropriate sites.

$$(XY)_{n+} + X^{+} + Y^{-} \longleftrightarrow (XY)_{n+2} \qquad (2.6)$$

$$(XY)_{n+1} + X^{+1} + Y^{-} \longleftrightarrow (XY)_{n+2} \qquad (2.7)$$

Where n is the minimum number of X and Y ions that must combine in order to yield the stable particles (XY)n. The rate of growth is found to be directly proportional to the super saturation and can be expressed by the equation.

Rate of growth = K'A (Q-S) (2.7)

Where A is the surface area of the exposed solid and K' is a constant that is characteristic of particular precipitate.

3) Precipitation and Co-precipitation from Homogeneous Solution

The lowering of degree of supersaturation in order to form crystalline precipitate by slow and drop wise addition of reagent and use of dilute solution of ions to be precipitated, however cannot entirely eliminate high supersaturation and rapid precipitation. This is because at the point in the solution where a new drop of precipitating agent first makes a contact. There is at least momentarily, relatively high concentration of reagent is established, which results in the high degree of local supersaturation and a consequent rapid precipitation. In precipitation from homogeneous solution by slow chemical reaction. This avoids the local reagents excess and the relative supersaturation is thus kept low. In general homogeneously formed precipitate is better suited for analysis than solids formed by direct addition of reagent [15-17].

Co-precipitation is phenomenon in which some extraneous material is precipitating along with the actual precipitate. In ternary system the mixed crystal formation occurs. One of the ions in the crystal lattice of a precipitate is replaced by the other ion resulting in mixed crystal formation. The exchange is possible if two ions have same charge and size. For co-precipitation, two salts must also have similar crystal structure. The size of ions should not very more than 5%.

2.4 Theoretical background of characterization techniques

2.4.1 X-ray diffraction

It was in 1912 that V. Laue [18] pointed out that a crystal might be expected to diffract X-rays. The first diffraction patterns from crystals were obtained in the same year by Freidrich and Knapping and the first analyses of crystal structures were published by W.L. Bragg shortly afterwards. At first, only the simplest structures could be analyzed but great advances in techniques have been made since those early days, and it has been possible to determine in detail the arrangement of atoms in many quite complicated molecules.

15875

The eight faces corresponding to the octahedron are said to constitute a form. A face which is parallel to a plane whose intercepts on the three area are Ha, Kb, Lc, where h, k, l are whole numbers is possible face of crystal, and for the planes which commonly occur. The numbers h, k, l define the plane to which a symbol (hkl) may be given and are called its Miller indices.

The unit cell in crystal is produced by continued repetition of a single 'unit' since all the units are to be identical can identically placed, the whole collection of points obtained by intersections of three sets of parallel or equally spaced planes is called space lattice. The idea of space lattice as underlying the structure of crystals was first worked out in detail by Bravais.

The important discovery of von Laue which made it possible to investigate the crystal structure by means of X-rays was based directly on the idea of the crystal as a repeating pattern in space. It is well known that if a beam of light falls on a screen perforated with holes arranged in a regular pattern whose spacing are comparable with wave-length of the light, diffraction occurs, the light after passing through the screen, consists non only of a same what weakened beam in the direction of the incident beam but also of other regularly arranged, separate beams, deviated from original direction through angles, depending on the ratio of wavelength of light to the spacing of pattern. The diffraction is due to the interaction of the regularly periodic pattern with the regularly periodic light waves.

Another way of regarding this stringency of condition was pointed out by W.L. Bragg in 1912 if parallel beam of X-rays is incident in a direction making a glancing angle θ with the surface of the planes; each plane must be thought to be as reflecting a very small fraction of incident beam [19]. Fig 2.5 shows the diffraction of a beam of X- rays from the crystal containing planes with'd' spacing .Any diffracted beam which does occur must therefore in a direction correspondent to reflection. The path difference between reflected beams, derived from the same incident beam and reflected at successive planes at a glancing angle θ is easily calculated by Bragg's Law,

$$n\lambda = 2\, d \sin\theta \qquad (2.8).$$

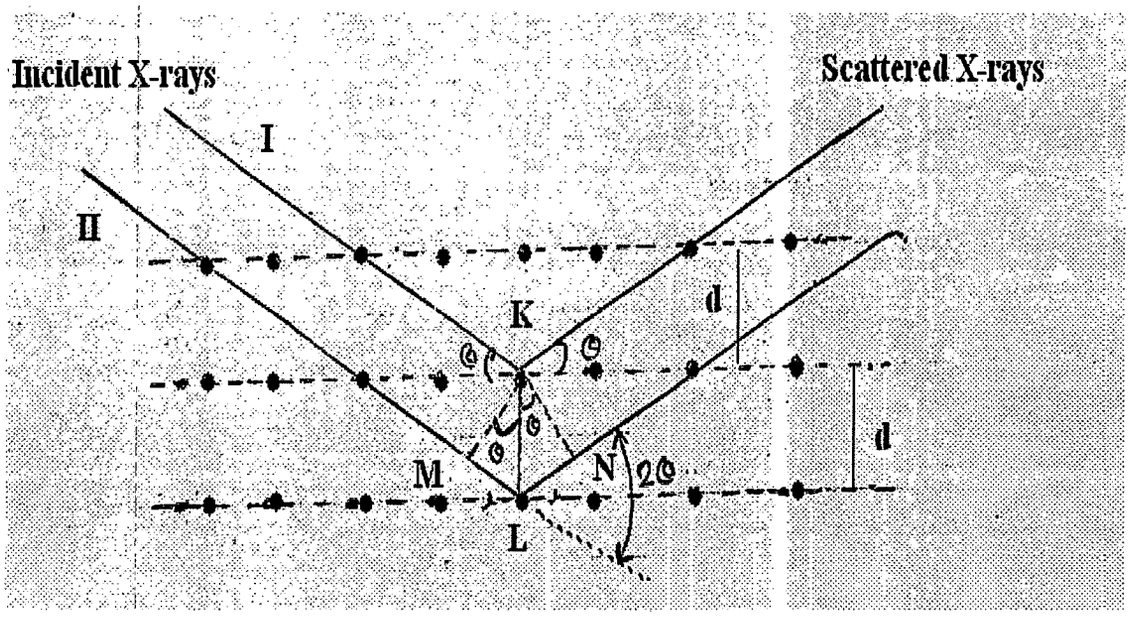


Fig 2.5: The diffraction of a beam of X- rays from the layers of atoms in a crystal.

There are four methods of observing the X-ray diffraction spectra -

1. The Laue Method
2. The X-ray spectrometer
3. The rotating crystal method.
4. The powdered crystal method.

The intensity of X-rays i.e. a beam in which the energy passing per unit area per unit time is I_0 falls on a small crystal, bathing it completely in radiation.

The X-ray diffractogram of as deposited and annealed films were obtained. From XRD data we can calculate unit cell parameters, and grain size intensity. The identification and analysis of phases can be obtained from XRD data. The crystallite size is determined by using Full width at half maximum (FWHM). The average crystallite size is determined by Scherrer's formula [21].

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (2.9)$$

Where D is the grain size, λ is the wavelength used β the angular line width of half maximum intensity and θ Bragg's angle. K is the constant. The value of K

varies from 0.9 to 1.3. It is best approximated to value of 0.9, when little is known about crystallite shape.

2.4.2 Compositional study

Atomic absorption spectrometry is based on the absorption of radiation by valence electron of atoms in the vapour state. The measurement of the absorption of radiation by ground state atoms gives rise to the technique of AAS. The principle of Atomic absorption spectrometry is based on the Beer Lambert's Law relating the absorption of the monochromatic radiation with the concentration of the absorbing agnate species [22].

$$I = I_0 E^{-\epsilon cl}. \qquad (2.10)$$

Where,

I_0 = Intensity of incident beam

I = Intensity of transmitted beam

ϵ = molar absorptivity coefficient

C = concentration moles per lit

l= Path length.

The burner used in AAS is slot burners to increase the path lengths as well as to produce the desired gas flow patterns to prevent flame flash back. A mixture of fuel and oxidant in the appropriate proportion is used to produce the flame and sample in the form of an aerosol is introduced. The amount of radiation absorbed by the atoms in the flame is measured and then related to the concentration measured by using calibration curve [23].

2.4.3 Optical Study

A fundamental property of semiconductor compounds is band gap i.e. energy separation between valence band and conduction band. The absorption of radiation in a material is considered to be due to inner shell electrons, valence band electrons, free carriers of electron bound to localized impurity centers or defects of some type. An optical excitation of electrons across the band gap is strongly allowed producing an abrupt increase in absorptivity at the wavelength corresponding to the band gap energy. This feature in optical spectrum is known as the optical absorption edge.

The absorption coefficient near the absorption edge was given by [24],

$$\alpha \sim (h\nu - Eg)^r \qquad (2.11)$$

Where hν is a photon energy, Eg is a band gap, r is the constant.

The most convenient way to explaining the optical band gap is to determine the wavelength at which the extrapolations of the base line and the absorption edge cross. By plotting the graph of $(\alpha h\nu)^2$ versus hν for various values of r, it becomes possible to determine the nature of transition involved. The extrapolation of lines and intercepts of the straight line portion of the respective plot corresponding to zero absorption on the energy axis give values of energy gaps [25].

2.4.4 Electrical properties measurements

1) Electrical conductivity

The electrical conductivity measurements play a vital role in determining all the parameters related to thin films. For the measurement purpose, contact method is widely used. The method includes two probe .The two probe method is simple, useful for high resistive thin films and easy to use. In this method constant DC voltage V is applied between two fixed positions on the surface of the thin film. The current passing through the sample of known dimensions is measured with an appropriate current meter. For uniform sample, the conductivity is given by [26-27].

$$\sigma = (d/A)\,(I/V) \qquad (2.12)$$

$$A = t.b$$

Where t=thickness, b= width of the film.

2) Thermoelectric power measurements

It is also known as Seeback Coefficient. It is defined as the ratio of thermally generated voltage to the temperature difference across the piece of semiconductor.

TEP is negative for n-type semiconductor and positive for p-type semiconductor. This fact is often used to determine the conduction type of a semiconductor. The TEP can also be used to determine the Fermi level relative to band edges.

2.4.5 Scanning Electron Microscopy

It is capable of producing high resolution images of sample surface. SEM has been widely used for characterization of low dimensional surface topography of thin specimens.

All SEM have facilities for detection of secondary and backscattered electrons. They used incident electrons beam with energy between 2 and 40 Kev. The secondary electrons are orbital electrons knocked out of sample atoms by collision with incident electrons beam. The escape depth of secondary electron is low due to its lower energy (50eV). Consequently these electrons are generated at a specimen depth of few nano meters in metal and few tens of nano meters in insulators. The region, from which they originate, is a little larger than beam diameter. Typical resolution may be approximately 5nm [28].

SEM photograph is also used to calculate grain size of film using Cottrell's method [29]. This method relates number of intercepts of grain boundaries per unit length. It also provides information regarding the particle size and shape [30].

2.4.6 Photoelectrochemical cell studies

Photoelectrochemical cell consists of semiconductor photo electrode, electrolyte and counter electrode. Semiconductor photo electrode is most important part of PEC cell & any modification in its properties reflects consecutive changes in electrical properties of cell. The counter electrode should have large surface area low over potential, high rate of charge transfer, etc. the electrolyte is another important parameter in PEC cell. It consists of oxidisable and reducible species. This ionic species help to scavenge photo generated holes form photo electrode to counter electrode. Thus electro chemical performance and the conversion deficiency depend on the nature of electrolyte used.

2.4.6.1 Electrochemistry of Semiconductor electrolyte interface

The electrochemical potential of electrons in semiconductor electrode is generally represented by it Fermi level and in liquid electrolyte containing a redox couple, by its redox potential. As a consequence of the equalized electron

energies, the transfer of electric charge produces a region on each side of the junction is known as space charge double layer. In order to observe the space charge double layer interface is divided into two groups,

1. A semiconductor side of the interface
2. An electrolyte side of the interface.

1. The semiconductor side of the interface:

The investigation of the photo electrode material-electrolyte interface was carried out by Brattain et al [31]. Later on much more information about photo electrode-material-electrolyte was available.

The charge distribution across the metal and semiconductor junction widely differs due to following reasons.

a) In case of metals only electrons act as charge carriers while in semiconductors both electrons and holes act as charge carriers.

b) In case of metals the charge carrier density is of the order of $10^{28}/an^3$ while in case of semiconductors it is in the range of 10^{17} to $10^{19}/cm^3$.

c) In case of metals the charge carriers are at the surface, while in case of semiconductor they form a space charge region within the semiconductor near interface.

The nature of space charge layer was decided by the charge transfer that occurs through the electrolyte.

2. An electrolyte side of the interface

The electrolyte side of the interface can be explained by various models like stern, Guoy Champman, Helmholtz and others. [32-35]. According to Helmholtz the charged layer of ions is formed a sheath at the dipped side of the photoelectrode surface as shown in fig 2.6(a). However, it ignores the disrupting effect of the thermal motions of the charged ions, which tend to break up and disperse the rigid wall of the charge. From this model it is clear that the electrode electrolyte interface is similar to a parallel plate of a condenser charged oppositely as shown in fig. 2.6(b).

Term double layers thus originate and all the potential is assumed to be dropped across this double layer of width δ_H fig.2.6 (c). The 'δ_H' is initially

assigned to be independent of the voltage applied to the electrode. The 'δ_H' is initially assigned to be independent of the voltage applied to the electrode. If 'dQ' is the charge on capacitor and 'dV' is the potential drop across the layer, then the differential capacitance is given by,

$$C = dQ/dV = \epsilon_s \epsilon_o / \delta_H \qquad (2.13)$$

Where, ϵ_s, ϵ_0 are the dielectric constant of the material and the free space respectively. This voltage independency of C is however, against the experimental observation.

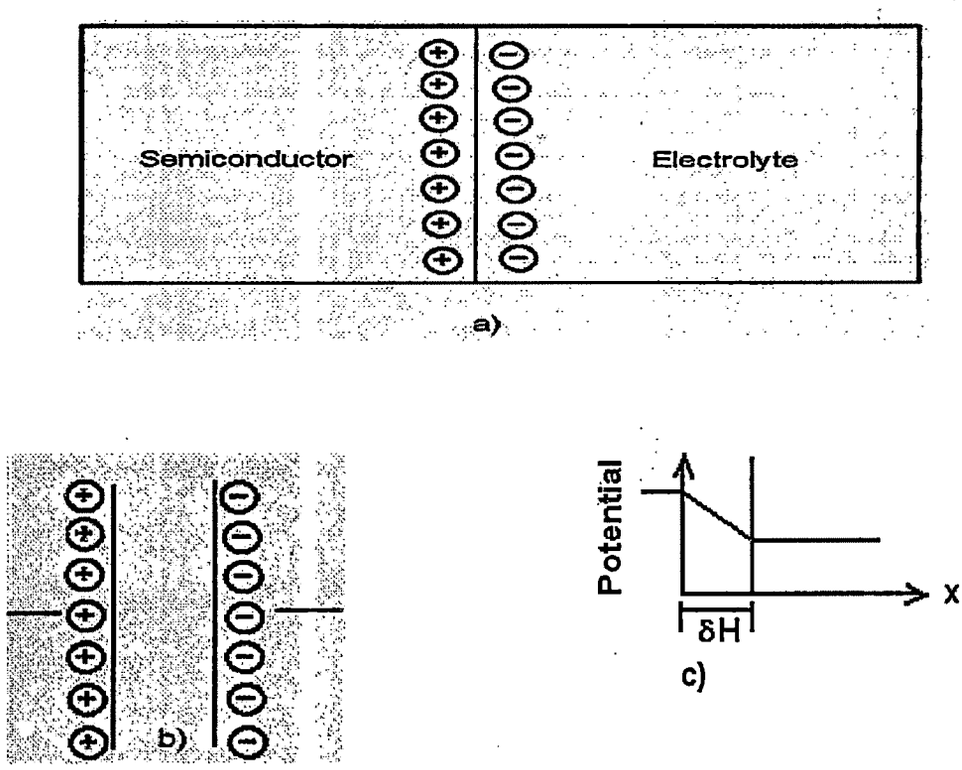


Fig.2.6: A Semiconductor-electrolyte interface (Helmholtz-Perrin model)

a) Helmholtz double layer

b) Electrical equivalence

c) Potential distribution.

According to Guoy and Chapman the electrode surface on which the charges accumulated may be considered as diffused layer. The diffused layers in known as Guoy layer fig.2.7 (a). The charge accumulated on the electrode

surface may be considered as large central ions exerting a planer electrostatic field on the solution side of the interface. This force falls off slowly as we move deep in the bulk of solution. The charge distribution in Gouy Layer, according to the Gouy-Chapman theory decays exponentially with distance as shown in Fig. 2.7 (b).

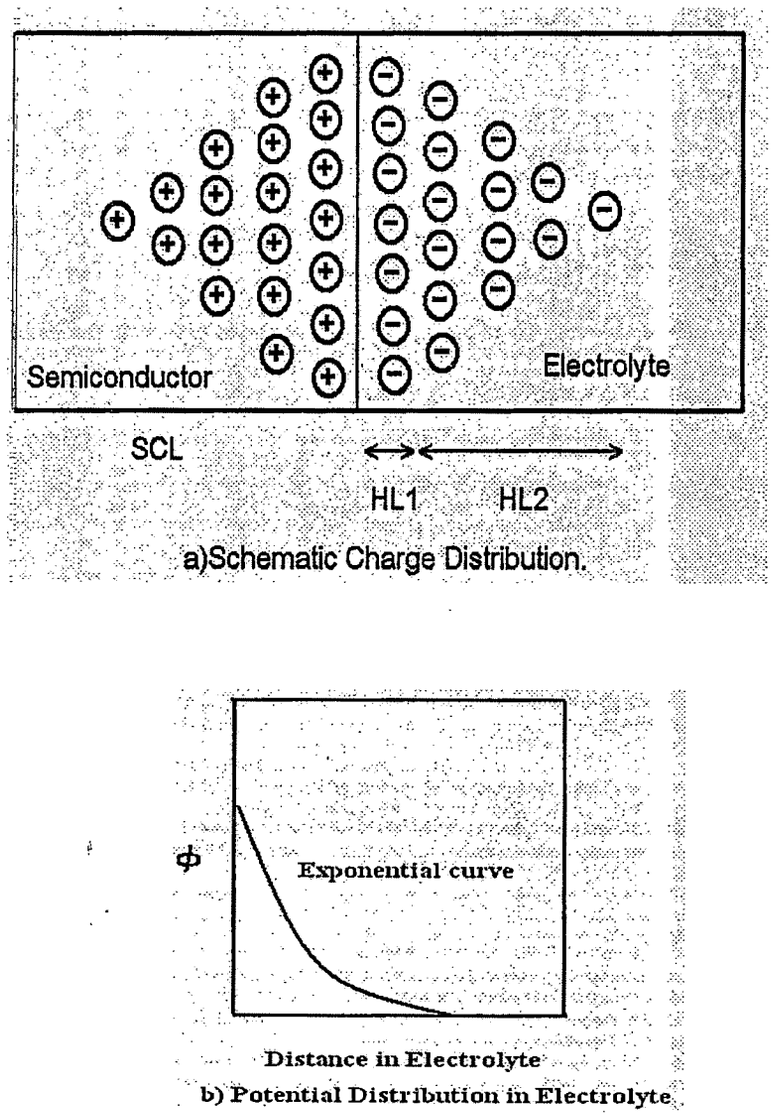
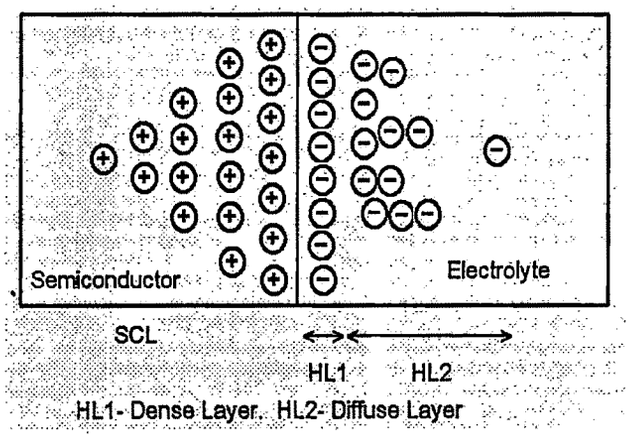


Fig 2.7: Semiconductor –electrolyte interface

Stern given that, the ions being of finite size, keep minimum distance of approach to the electrode surface. Therefore a layer is neither abrupt nor diffuse but a combination of two as shown in fig.2.8 (a). The potential distribution is as shown in fig. According to Stern, the interface distribution is

divided into two layers, viz dense layer and diffused layer. In dense layer, the ions stick to the electrode and the potential variation is assumed to be almost linear, whereas a diffused layer is formed as a result of opposing tendencies of the attractive columbic forces and disordering thermal fluctuations, where the potential decays exponentially as shown in fig 2.8 (b).

In dense layer the ions stick to the electrode and potential variation is assumed to be almost linear, whereas a diffused layer is formed as a result of opposition tendencies of the attractive columbic forces and disordering thermal fluctuations, where the potential decays exponentially [36].



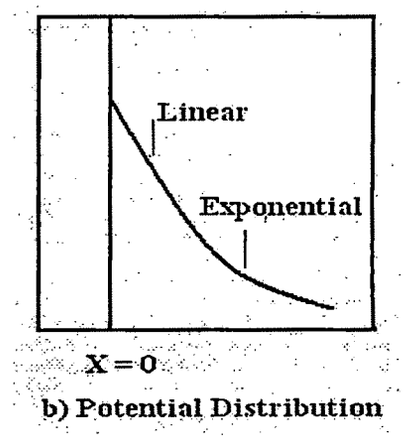


Fig. 2.8 a) **Fig. 2.8 b)**

Fig.2.8: A Semiconductor-electrolyte interface (Stern model)

a) A Schematic charge distribution

b) Potential distribution in electrolyte.

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