CHAPTER II
THEORETICAL BACKGROUND

2.1. Introduction

Most semiconducting materials for opto-electronic applications must be in the form of single crystals with exceptional crystalline perfections and purity. Typically large boules are sliced into wafers and devices are prepared by either diffusing dopants into them and/or by depositing them on compounds of either similar composition (homoeptaxy) or different composition (hetroepitaxy). Some semiconductors in polycrystalline thin film or bulk form have also been useful for many applications. Semiconducting thin films have been assuming increasingly complex structure in view of their applications which demand tailor made properties. As a result, sophisticated techniques have emerged for coating thin films. Among these methods, chemical deposition techniques are the most important methods for the growth of films owing to their versatility for depositing a very large number of elements and compounds at relatively lower temperatures. Both in the form of vitreous and crystalline layers, with high degree of perfections and purity, these films can be deposited with required stoichiometry. Large or small and even or uneven surfaces of all types of conducting or insulating can be coated with relative ease. The processes are very economical and have been industrially exploited to a large scale.

Electrochemical preparative methods can be conveniently divided into two categories (1) low temperature techniques (usually aqueous solution, but organic electrolytes are sometime used) (2) higher temperature techniques (molten salt solutions). By far, the greater effort has been given to lower temperature process, because these systems are simple to construct, operate and control, therefore aqueous solution chemistry is much better understood than complex molten salts. The large metal plating industry is based on aqueous electrochemical techniques. The ability to produce thin uniform films on both simple and complex shapes has been one of the traditional strength of electrochemical methods, and it is not surprising that the majority of semiconductor electrodeposition studies have been concentrated on thin film deposition.
An attempt has been made in this thesis to prepare FeSe, FeSe$_2$, CdSe and Cd$_{1-x}$Fe$_x$Se thin films using low temperature electrodeposition process.

In recent years, electrodeposited semiconductor thin films are increasingly used in the field of opto-electronic devices, photoelectrochemical solar cells and solar selective absorber coatings. The important reason is that the requirement of a solar cell for large scale terrestrial use, such as high efficiency, stability and low cost are met with electrodeposited semiconductor solar cells. The electrodeposition technique has got several advantages over other physical and chemical deposition techniques. No costly equipments are required and hence this process is simple and can be easily scaled up. Materials conservation is achieved as deposition takes place only on the desired area. It is not necessary to have very pure starting materials as in the case of other methods. The semiconductor properties like type of conductivity, band gap variation, control of stoichiometry, doping etc., could be controlled with high degree of accuracy. Hence, electrodeposition has become one of the emerging and frequently used techniques for the deposition of semiconducting thin films in many fields of solid state technology.

Hence, in this chapter, the principle of electrodeposition technique with theory pertaining to elemental and alloy semiconductors are explained in detail. Relevant theoretical background for structural, microstructural, compositional, optical, electrical and magnetic properties are also given in detail.

2.2. Theoretical aspects of electrodeposition

Electrochemistry is re-emerging as a vital scientific discipline after many years of relative obscurity. Scientists are optimistic of identifying electrochemical avenues that can cater to the needs of the modern technology like more compact electronic devices, achieving higher purity of materials, with improved crystal uniformity etc. The basis of electrodeposition technique and its potential advantages over thermally driven processes are discussed.

2.2.1. Principles of electrodeposition

Electrodeposition is a process of depositing a substance upon an electrode by electrolysis (i.e) the production of chemical changes by the passage of current through an
electrolyte. The phenomenon of electrolysis is governed by the following Faraday’s laws of electrolysis enunciated by Faraday in 1833.

1. The magnitude of chemical change occurring is proportional to the quantity of electricity passed and

2. The masses of different species deposited or dissolved from electrodes by the same quantity of electricity are in direct proportion to their chemical equivalent weights.

Mathematically the two laws may be combined and expressed as

\[ W = \frac{ITZ}{F} \]  \hspace{1cm} (2.1)

where \( W \) is the substance (in grams) deposited, \( I \) is the current (in amperes), \( Z \) is the equivalent weights (in grams), \( T \) is the time (in seconds) and \( F \) is a constant called Faraday and it is equal to 96,500 Coulombs and is the amount of charge required to deposit one equivalent of any ion from the solution.

2.2.2. Single metal electrodeposition

The electrodeposition of semiconductor compounds like any other chemical process is governed by thermodynamic considerations. In the case of electrodeposition, the reactions are thermodynamically unfavourable, if the overall free energy change (\( \Delta G \)) for the reaction is positive and the electrical energy supplies the needed energy to drive the reaction. Consider the case of an ion \( M^{+m} \) being reduced to \( M \) given in Eq.(2.2)

\[ M^{+m} + me^- = M \]  \hspace{1cm} (2.2)

The change in free energy is given by Eq. (2.3)

\[ \Delta G = \Delta G^0 + RT \ln(a_m / a_m^{+m}) \]  \hspace{1cm} (2.3)

where \( R \) is the gas constant, \( T \) is the absolute temperature and ‘\( a_m \)’ is the activity of species (i.e) activity is used instead of concentration in Eq.(2.3) to account for the interaction of ions in solution or for the difference in reactivity of an atom in a molecule versus that of an atom in the elemental state where the activity would be 1. In the solution case, activity is related to the concentration by the activity coefficient \( a=[M^{+m}] \). Barrow [1] has given a more complete discussion of activity and activity coefficients.
Using concentration, we can write Eq.(2.3) as

$$\Delta G = \Delta G^0 + RT \ln \left( \frac{1}{M^{m}} \right)$$  \hspace{1cm} (2.4)

It can be shown that

$$\Delta G = -nFE$$  \hspace{1cm} (2.5)

where \( n \) is the number of moles of electrons involved in the reaction, \( F \) is Faraday’s constant and \( E \) is the potential. Eq.(2.4) can be rewritten as

$$\Delta E = \Delta E^0 - \left( \frac{RT}{nF} \right) \ln \left( \frac{1}{(M^m)} \right)$$  \hspace{1cm} (2.6)

where \( E^0 \) is the standard electrode potential for reaction in Eq.(2.2) referenced to the standard electrode with \([M^{m}]=1 \text{ mole/litre} \).

A single electrode reaction such as given in Eq.(2.2) cannot stand alone, since there must be a compensating reaction involving an oxidation process. The overall reaction can be represented by Eq.(2.7)

$$bA^{+a} + aB^{+b} = bA + aB$$  \hspace{1cm} (2.7)

and the electrode reactions are given by Eq.(2.8) and (2.9)

$$A^{+a} + ae^- = A \quad \text{(reduction at cathode)}$$  \hspace{1cm} (2.8)

$$B^{+b} = B + be^- \quad \text{(oxidation at anode)}$$  \hspace{1cm} (2.9)

The cell potential is given by Eq.(2.10)

$$E = E_A^0 + E_B^0 - \left( \frac{RT}{abF} \right) \ln \left( \frac{1}{[A^{+a}][B^{-b}]} \right)$$  \hspace{1cm} (2.10)

### 2.2.3. Alloy electrodeposition

Alloys can be deposited by co-electrolysis for which the electrode potentials should be brought very close to each other by suitably complexing them and by reducing the concentration of the more noble metal ion.

Co-deposition of two or more metals leads to alloy or compound or intermetallic deposits. An alloy is an intentional mixture of two or more chemical elements which have metallic properties. A compound is a homogeneous, pure substance composed of two or more essentially different chemical elements which are present in definite proportions.
Intermetallic compound has metallic atoms are joined by metallic bonds. If the two metals constituting the intermetallic compound contribute just sufficient electrons to fill the valence band, the compound may become semiconducting. Fig. 2.1 (a) shows a polarization curve for a metal reduction. The deposition of metal is associated with a standard reduction potential and can be represented by Eq. (2.2)

\[ M^+ + Ze^- = M \text{ at potential } \phi_0 \]  

(2.11)

The polarization curve shows that little current flows up to potential \( \phi_0 \) and then current starts flowing due to the reduction of metal at the cathode. It is usually followed by diffusion limited current and then hydrogen evolution. The use of non-aqueous organic solvents like DMF (dimethyl formamide), DMSO (dimethyl sulfoxide) or ethylene glycol avoids the problem of \( \text{H}_2 \) evolution at the cathode. By changing the bath composition, substrate or by the addition of surfactants or additives, the potential associated with the above reduction reaction can be varied.

When alloy of two metals are required, the standard reduction potential of them should be considered. If only a small difference in potential exists, alloy of two metals can be obtained by changing the ratio of their ionic concentration in the solution of the corresponding simple salts. The resulting equilibrium can be written as given by Eq. (2.12)

\[
\phi_0^a + \left( \frac{RT}{ZF} \right) \ln(a^a) = \phi_0^b + \left( \frac{RT}{ZF} \right) \ln(a^b)
\]  

(2.12)

where \( \phi_0^a \) and \( \phi_0^b \) are the standard metal potentials

\( a^A \) and \( a^B \) are the activities of the discharging ions

\( R \) is universal gas constant

\( F \) is Faraday’s constant

\( Z \) is the valency of the ion

\( T \) is absolute temperature

In most of the alloy formation processes, the metals at the cathode do not interact with each other according to Eq. (2.12). This is due to the large difference in reduction potential of the metals forming the alloy. Because of this, the ions of nobler metals
(more positive) deposit preferentially compared to that of ions of baser metals (less positive). Thus for co-depositing metals to form alloys, the concentration of the more noble metals at the cathode/electrolyte interface should be considerably reduced relative to that of less noble metal. This is achieved by adjusting the concentration of noble metals ions or by changing the activity of discharging ions by complex formation or by inhibiting the rate of reduction of more noble metal by introducing suitable surfactants. The co-deposition requires that the electrode potential for the two ions should close (260 mV) to each other. Fig.2.1 (a,b) shows the polarization curve for two metals A and B and an alloy formed with (A+B). Individually the reduction of A and B occurs at their corresponding reduction potentials. However, when two such solutions are mixed up, polarization curve changes to Fig.2.1 (c) which shows the co-deposition of A and B to form an alloy.

2.3. Mechanism of electrodeposition

The steps in the mechanism of compound semiconductor electrodeposition are as follows [2]

1. The aqueous-or complexed metal ion is transferred or deposited as an adion (still partly bound) to a surface site. Such sites include the plane surface, edges, corners, crevices or holes with the plane surface providing the primary sites.
2. The adion diffuses across the surface until it meets a growing edge or step, where further dehydration occurs.
3. Continued transfer or diffusion steps may occur into a kink or vacancy or co-ordinate with other adions, accompanied by more dehydration until it is finally co-ordinates with other ions (and electrons) and becomes a part of the metal and being incorporated into the lattice.
4. Deposition of metal ions results in depletion in the solution adjacent to the surface. These ions must be replenished if the deposition process is to continue. This replenishment or mass transport of ions can be accomplished in three ways such as migration, convection and diffusion.
Fig. 2.1. Cathodic polarization curves for: (a) Metal A (b) Metal B (c) Metal (A+B)
Electrodeposition of compound semiconductors comprise of placing two or more elements in a solution as cations. One of these elements may be a semimetal such as Te, As or Sb and the other element may be any substance which has a deposition potential less noble than that of the semimetal when both elements are in solution. The formation of such compound involves the following order of occurrences [3].

1. Transfer of solvated cations to the cathode with a resulting polarization according to commonly accepted principles.
2. Neutralization of a nobler ion.
3. Conversion of the cathode surface to the layer of adsorbed ions. Complete depolarization of the cathode with respect to the less noble ion.
4. Reduction of the less noble ion at the rate of first-order electron conductance.
5. Polarization of the cathode as the neutral character of surface is restored.
6. Building of the crystal lattices and macro-crystals of a compound of the two or more participating elements through repetition of the polarization and depolarization steps.

2.4. Practical aspects of electrodeposition

An electrochemical deposition is achieved by passing an electric current between two electrodes separated by an electrolyte. By definition, the synthesis takes place at the electrode-electrolyte interface. A typical electrodeposition system consists of

(1) a substrate
(2) an electrolytic bath
(3) an applied field for electrolysis
(4) counter electrode

This section emphasizes the practical aspects of electrodeposition.

2.4.1. Substrate

Substrates play a vital role in semiconductor electrodeposition. Their influences are not restricted to imparting certain morphological characteristics to the growing layer. In a more subtle way, electronic or optical properties may also be affected. Therefore, in choosing a suitable substrate, in addition to considering the necessity to provide
mechanical support to the electrodeposits, consideration must be given to the possible influence of the substrate on the properties of the deposit.

(a) Choice of substrate

Broadly speaking the following criteria should be applied for the selection of a substrate:

1. It should have good conductivity. This is essential, because the substrate is one of the electrodes in electrodeposition. One can use an insulating substrate provided a suitably conductive coating is first applied on its surface. Good conductivity of the substrate is also beneficial in improving the carrier collection efficiency.

2. The thermal expansion of the substrate should match well with that of the electrodeposited film. Usually, in semiconductor electrodeposition, the film requires annealing treatment at temperatures that may be fairly high to improve the grain size or stoichiometry or to fabricate junctions. A mismatch in the thermal expansion often leads to strains that result in cracking or peeling off the film.

3. The substrate should have good mechanical strength.

4. In many applications, cost is an important consideration.

5. The semiconductor-metal contact may be ohmic or rectifying, so care should also be given to the type of interface one desires to obtain.

6. In some cases, the atoms of the substrates tend to diffuse inside the electrodeposited semiconducting films, especially during post-deposition annealing treatment. The film purity, doping concentration, electronic properties, etc., may consequently be altered. The solid solubility, diffusion coefficient and other properties of the substrate atoms in the semiconductor bulk should be examined to avoid such problems.

7. The substrates should be stable in the electrolytic bath.

8. The substrate surface should be smooth. One should avoid surface waviness, porosity, voids and other irregularities as these influence the local current distribution. Also, the electrodeposits usually tend to
reproduce the surface morphology of the substrate. An uneven, porous surface with voids will not be useful for any device applications.

Subject to the foregoing considerations, one may use single-crystal, polycrystalline, or amorphous substrates of metals, or semiconductors in the form of foils, sheets, wafers or thin films. Uncoated insulating glass cannot be used, but insulating glass that has been coated with a transparent conducting film has been used to electrodeposit a number of semiconductors. When single-crystal semiconductors are used as substrates, a back ohmic contact is normally formed by using a conducting paint, a suitable solder or an evaporated film. Metals have been widely used as substrates for electrodeposition because of their good conductivity, easy availability, lower cost and relative ease of handling.

(b) Substrate surface preparation

The preparation of a smooth scratch-free substrate surface is extremely important in semiconductor electrodeposition as surface inhomogeneities tend to be amplified during electrodeposition. On the atomic scale, surface defects may be point defects, dislocations etc., while on the microscopic scale they can be scratch marks left from polishing operations, grain boundaries etc., Substrate surface preparation is a substrate-specific operation consisting of three major steps: grinding and polishing, cleaning and testing the surface cleanliness.

2.4.2. Electrolytic bath

The electrolytic bath is the medium that supplies the ions that move upon application of an electric field. In general, ionic transport is facilitated in an aqueous solution, non-aqueous solution and molten salt solution. Some practical aspects are discussed below: The choice of solvent depends upon many factors. The primary factors are: (i) solubility (ii) non-reactivity. Water is nature’s best gift as a solvent and was once used for almost all electroplating work. Now both aqueous and non-aqueous solvents are used. Aqueous solvents are suitable for a large number of salts, complexing agents and other compounds. Barring a few hydrolysis reactions, water is generally a non-reactive solvent. However, an aqueous solution necessarily contains $H^+$ (or $H_3O^+$) and $OH^-$ ions,
which complicate the electrodeposition process by resulting in the evolution of H₂ and/or O₂ at the electrode.

2.4.3. Preparation of the electrolytic bath

(a) Selection of the solvent

The choice of a particular solvent depends on the following criteria:

1. Electrodeposition solvents are stable in only a limited potential range, beyond which reduction-oxidation reactions take place. The range is termed the working potential range or the window. The potential at which the electrodeposition is to be carried out should be within this range.

2. The morphology and rate of growth depends upon the temperature at which the electrodeposition is being carried out. The solvent should remain liquid at the desired temperature. Therefore, solvents with a large liquid range are preferred to provide greater flexibility.

3. High vapor pressure solvents are preferred because the electrolytic concentration remains more constant.

4. The dielectric constant should generally be more than 10 [4]. Too low dielectric constant facilitates ion-pair formation, giving poor conductivities and ionization in the solution.

5. Lower viscosity is always preferred because of the better conductivity and diffusion. Furthermore, many irreversible electrochemical reactions limited by mass transport become reversible in a medium with lower viscosity.

(b) Selection of the supporting electrolyte

The supporting electrolyte performs several functions in an electrochemical process: (i) It increases the conductivity of the electrolyte. This minimizes Joule heating and provides more uniform current distribution and IR compensation. (ii) It reduces the electrode double layer thickness and also influences adsorption and ion pairing. (iii) It effectively eliminates the effect of migration in the mass transport. The criteria for selection of supporting electrolyte are its solubility in the solvent and a dissociation constant sufficiently high to yield good conductivity and the electrochemical oxidation of anion and electrochemical reduction of cation at more anodic or cathodic potentials.
(c) Additives in the electrolyte

Additives (brightening agent, surfactant, complexant etc.,) are often added to the plating bath to obtain a smoother and brighter deposit, controllable reaction rate, better adhesion and better texture. The role of additives in the electrodeposition process through still a mystery is broadly either (i) control the rate of deposition process (ii) influence deposit morphology. It is common knowledge that the electronic and optical properties of semiconductors are strongly influenced by inclusion of any additive or impurity. More work on the extent of inclusion and their role in electronic and optical properties is very desirable.

(d) Solvent purity

The presence of impurities in the solvent interferes with electrochemical process. In many cases, electrodeposition may not be possible or the deposit morphologies may be affected by the impurities. The electronic properties of the semiconductors are also extremely sensitive to impurities that co-deposit. It is therefore essential to purify the solvent. Some commonly used methods employ deionization using ion-exchange resin and/or distillation from an alkaline permanganate solution. However, this is not a very satisfactory method, and many organic contaminants may still be present. Further purification by passing the water vapors through a column of platinum gauge heated from 750 to 800°C in a stream of oxygen is necessary to remove oxygen followed by pre-electrolysis at a constant potential may also be employed to remove heavy metal ions.

(e) Counter electrode

Generally, the counter electrode is not functional but merely serves to complete the circuit. It may in some cases, serve to replenish the electrolyte with ions to be deposited. The distribution of current across the electrode and hence the uniformity of the deposited films is affected by the shape of the active electrode. Higher current densities at edges and projections compared to crevices and hollows lead to thicker deposit on the edges.
2.5. Electrodeposition technique

Electrodeposition technique can be classified according to the nature of the electric field applied across the electrolysis cell:

1. Deposition at a constant DC potential (Potentiostatic)
2. Deposition at a constant DC current (Galvanostatic)
3. Deposition using a periodic pulsed source

2.5.1. Potentiostatic deposition

In potentiostatic mode (i.e., constant DC potential) electrodeposition, different charge transfer reactions proceed under a steady state condition at rates approximate to the steady state interfacial over potential $\eta$ and exchange current density $j_0$. The choice of over potential is dictated by the composition of the bath, the substrate and the reversible potential of the species to be deposited. Potentiostatic deposition is carried out under either pure activation, diffusion or mixed control depending on the choice of the deposition potential. The schematic diagram (Fig.2.2) of apparatus for potentiostatic measurements: P- potentiostat, E - controlled potential, e₁- test electrode, e₂- reference electrode, e₃-counter electrode.

Potentiostatic d.c deposition has been used to grow layers of a large number of elemental, binary and ternary semiconductors. In the case of semiconductor electrodeposition, it is desirable to obtain large-grained (preferably oriented) polycrystalline deposits. However, very low over potential may not be suitable, as they may lead to a spongy or porous deposits due to low nucleation rates. As the over potential is increased, the supersaturation increases and a large number of nuclei are formed. The deposit thus acquires a fine grained morphology. Very high overpotentials may, however, lead to the growth of whiskers and dendrites.

2.5.2. Galvanostatic deposition

The constant current between the working and counter electrodes required for electrodeposition at a constant direct current can be obtained from a galvanostat. The initial guideline for choosing the required deposition current density can be obtained from the knowledge of (1) The Faradaic efficiency (2) The maximum permissible growth rate.
for a good crystal. The former can be obtained by a series of preliminary deposition experiments. The latter is to be obtained from the available crystal growth data.

The schematic diagram of apparatus (Fig. 2.3) for galvanostatic measurements: P- constant current power supply, e₁- test electrode, e₂- reference electrode, e₃- counter (auxiliary) electrode, V- potential time recording instrument. In galvanostatic technique the current between the test electrode and the auxiliary (counter) electrode is held constant with a current source (galvanostat) and the potential between the test electrode and the reference electrode is determined as a function of time. The potential is the dependent variable, which is recorded with suitable recording systems such as recorders or oscilloscopes.

2.6. Parameters influencing electrodeposition

2.6.1. Bath characteristics

The composition of the bath plays an important role in the deposition process. Usually, the main constituent of the deposition bath is the electrolyte, which essentially serves to provide ions either in their simple form or in the form of a complex. Depending on whether the process is cathodic or anodic, the nature of the anions or cations can strongly influence the structure of the film deposited, particularly so if the ions are preferentially absorbed at the electrode/electrolyte interface forming a part of the inner row of the double layer. For the same reason, certain organic molecules can afford a similar control. In some cases, suitable wetting agents may be used to promote the detachment of the hydrogen bubbles from the cathode surface and thus prevent pitting caused by hydrogen evolution in a cathodic deposition. If the electrolyte itself is not very conductive, acids, alkalies or suitable salts that are highly ionizable are used to achieve the required conductivity and to control the pH value of the bath. The pH controls the overall conductivity of the electrolyte. However, a suitable optimum value has to be determined, because too low pH value may result in hydrogen evolution whereas too higher value may cause the inclusion of hydroxides in the deposits. The temperature of the bath controls the rate of diffusion of the ions, the convection current in the bath, the nature and stability of any complex and the decomposition of additive, if any.
Fig. 2.2. Schematic diagram of apparatus for potentiostatic deposition

Fig. 2.3. Schematic diagram of apparatus for galvanostatic deposition
2.6.2. Electrodes

Generally, the counter electrode is not actively functional but merely serves to complete the circuit. It may in some cases, serve to replenish the electrolyte with ions to be deposited. The distribution of current across the electrode and hence the uniformity of the deposited films is affected by the shape of the active electrode. Higher current densities at edges and projections compared to crevices and hollows lead to thicker deposit on the edges.

2.6.3. Current density

Current density is the total current divided by the electrode area. It is one of the principal variables that determine the overall nature of the deposit, particularly the microstructure, efficiency of deposition and the deposition rate. The optimum range of current densities can be experimentally determined for each individual deposition process to yield deposits suited to a particular need. Usually, the current is in the order of mA. It decreases with the increase of deposition time.

2.6.4. Agitation and temperature

The convection current in the bath are generated by externally provided agitation to reduce the possibility of concentration over voltage arising. The temperature of the bath controls the rate of diffusion of the ions, the convection current in the bath, the nature and stability of any complex and decomposition of any additives.

2.7. Theoretical aspects of various studies

The properties of electrodeposits and mechanical aspects of growth can be best understood if the films are characterized while they are growing or after the electrodeposition process has ended. As such, characterization techniques can be classified as (i) in-situ techniques (used as the film grow) and (ii) ex-situ techniques (used after final film growth). The use of these techniques for the characterization of semiconducting films is still scanty although they have been often used for metal electrodeposits. In this section, the theoretical background of various studies has been discussed.

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2.7.1. Voltammetric studies

The current-voltage curve for an electro-chemical reaction obtained with electrodes is called ‘voltammograms’. The study of different types of voltammograms is called ‘voltammetry’. Cyclic voltammetry has become an important analytical technique for studying electrochemical reaction. It can be ingeniously used for the analysis of materials employed and products obtained in the electrodeposition work. This technique finds almost importance in understanding the mechanism of electrodeposition, in finding the formal redox potential, growth pattern of the deposit and the influence of different additional agents on this process. The basic principles are explained in detail so that a non-expert in this growing field will appreciate the study and may even adopt this fascinating field for the development of thin films.

2.7.1.1. Linear Sweep Voltammetry

The current-potential curve obtained by varying the potential linearly with time is called linear potential sweep voltammogram or peak polarogram. Consider a negative going potential sweep, when the reduction potential of species ‘O’ is reached, the current rises sharply as ‘O’ near the electrode surface is reduced, the current then becomes diffusion controlled and begins to fall. When the potential is well apart the half-wave potential, the current falls as \( t^{1/2} \). The peak current for a reversible process at a planar electrode is found to be

\[
i_p = 0.446nFA\left(\frac{nFV}{RT}\right)^{1/2}D^{1/2}C^{1/2}
\]

(2.13)

where ‘V’ is the potential scan rate in V/sec, ‘n’ is the surface atomic density, F is the Faraday’s constant, ‘A’ is the nucleation rate constant, ‘R’ is the gas constant, ‘T’ is the absolute temperature, ‘D’ is the diffusion coefficient and ‘C’ is the concentration of the different species. For a reversible process, the shape of the curve and the peak potential are independent of scan rate, but the peak current is proportional to \( V^{1/2} \). The capacitive charging current produced due to changing potential and the ohmic potential drop in the solution due to large peak current are the two factors which reduce the accuracy of the method.
2.7.1.2. Cyclic Voltammetry

Cyclic Voltammetry usually referred as C-V is one of the simplest and widely employed analytical tools used in the investigation of several process in electrode/ electrolyte interface [5]. Figure 2.4 shows the experimental set up for cyclic voltammetry. Instead of a linear potential variation, if a triangular wave potential is applied to the cell, the indicator electrode potential is swept linearly through the voltammetric wave and then back again. On the forward scan, the current response is just the linear potential sweep voltammogram as O is reduced to R. On the reverse scan, the R molecules near the electrode are reoxidized to O and an anodic peak results. The resulting curve is called a triangular wave cyclic voltammogram. The response on the second and subsequent cycles of a cyclic voltammogram is qualitatively similar to that of the first cycle but with current peaks somewhat reduced in amplitude. The reason for this decrease is that the concentration profiles of O and R do not return to initial conditions at the completion of a cycle. On multiple cycles, a steady state is eventually reached with damped concentration waves propagating out in the solution.

One of the most important deposition parameters of a electrochemical reaction is the determination of the formal reduction potential. It is customary to report the average of the forward and reverse peak potentials as the formal reduction potential of the redox couple. By ‘reversible reaction’ electrochemists mean that the reaction is fast enough to maintain the concentrations of the oxidized and reduced forms in equilibrium with each other at the electrode surface. If the reaction is reversible then the separation in the peak potentials $E_p$ will be close to $58/\text{mV}$ (at $25\degree\text{C}$) from which relationship we can evaluate the value of n. The proper equilibrium ratio at a given potential is determined by the Nernst Equation given below:

$$E = E_0 - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right) = 0$$

(2.14)

where O $\rightarrow$ Oxidized form and

R $\rightarrow$ Reduced form
Fig. 2.4. Experimental set up for cyclic voltammetric arrangement
Another characteristic of reversible system is the dependence of the peak height on the square root of the scan rate. At 25°C, the peak current is given by Eq.(2.15)

\[ i_p = (2.69 \times 10^3) n^{1/2} A D_0 V^{1/2} C_0 \]

(2.15)

The current will be in amperes when \( A \) is in cm², \( D_0 \) is in cm²/sec (scan rate) and \( C_0 \) is the bulk concentration in moles/cm³.

The peak current for a quasi-reversible system is not proportional to \( V^{1/2} \) except when the peaks are so widely separated that the system is described as totally irreversible. The point to remember is that one should use conditions that give the most reversible behaviour is possible. For reversible system, the scan rate should be slowed down to minimize \( E_p \). The type and condition of the working electrode surface can make a difference in the electron transfer kinetics. Solid electrodes need to be polished and or cleaned by exposing them to oxidizing agents. In some cases, workers advocate ‘activating’ the electrode surface by the application of a sequence of extreme positive and negative potentials [6]

### 2.7.2. X-ray diffraction

In crystalline solids, atoms (and molecules) are arranged in a periodic and regular fashion which confirms the standard geometry called crystal lattice. In this crystal lattice, the atoms can be thought of as forming different planes taking part in the coherent scattering process. That is, when an X-ray beam is incident on a set of parallel planes (with in each crystal) of the crystalline bulk, electron clouds of these atoms diffract the X-ray beam in a rational approach. From this, the basic Bragg’s equation is formed as

\[ 2d \sin \theta = n \lambda, \]

where ‘\( d \)’ is the interplanar distance (or) lattice constant, ‘\( \lambda \)’ is the wavelength of the characteristic X-rays and ‘\( \theta \)’ is the incident and diffracted angles and \( n \) is order of the scattered beam. This famous Bragg’s law provides the basic platform for the XRD methods. A crystal is a complex solid, although orderly arrangement of atoms and all the atoms in the path of the X-ray beam scatter the X-rays simultaneously. In general, the scattered rays interfere and destroy one another, but in certain specific direction (2\( \theta \)) they combine to form new wave fronts. This co-operative scattering is known as ‘diffraction’ and instruments that are used to study the diffraction suitable for
The study of polycrystalline materials are called X-ray powder diffractometer.

2.7.2.1. Characterization of a crystalline deposit

A metal deposit over a known crystalline substrate may initially be identified in the following systematic approach. The XRD lines corresponding to the known substrate are first identified. It is done by comparing experimentally observed values of 2θ, d and relative intensities (I/I\text{max}) of the reflections with the standard data available from the Powder Diffraction File (JCPDS-ICDD, 2003) [7]. Once the substrate lines are clearly identified, the remaining lines from the deposit are separately identified. In the case of sufficiently thick deposit, the X-rays won’t reach down to the substrate and hence only the diffraction lines corresponding to the deposit are observed and are used for identification. The equation relating lattice constant (d), Bragg angle (θ) and lattice parameters in the case of hexagonal and orthorhombic structures are given by Eq.(2.17) and (2.18)

\[
\begin{align*}
    d &= \frac{\lambda}{2 \sin \theta} \\
    \frac{1}{d_{hkl}^2} &= \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \left[ \frac{t^2}{c^2} \right] \\
    \frac{1}{d_{hkl}^2} &= \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{t^2}{c^2}
\end{align*}
\]

where \( \lambda \) is the wavelength of X-rays used. For every assigned (hkl) indices, lattice parameters are calculated using Eq.(2.16), (2.17) and (2.18). When all the observed reflections are rightly assigned to compute constant values of the lattice parameters, an average value of lattice parameter is calculated.

2.7.2.2. Crystallite size determination

The effect of line broadening is primarily due to micro residual stress and crystallite size (i.e., crystallites of 1000Å). In case of negligible micro residual stress (and instrumental broadening), the crystallite size (D) is calculated using the following Eq. (2.19)

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]
where $\beta$ is the broadening of the line 'half-width' measured at half of its maximum intensity (in radians) and in case of sufficient instrumental broadening given in Eq.(2.20)

$$\beta = \left(\beta_s^2 - \beta_{sd}^2\right)^{1/2}$$

(2.20)

where $\beta_s$ and $\beta_{sd}$ are the half widths of the sample and standard specimens (at almost same Bragg angle position), respectively.

2.7.3. Microstructural analysis

For a polycrystalline materials consisting of sufficiently large and strain free crystallites, diffraction theory predicts that the lines in the powder pattern will be exceedingly sharp. In actual experiments lines of such sharpness are never observed because of the combined effect of a number of instrumental and physical factors that broaden the pure diffraction line profile. Of more fundamental importance to the present discussion is the fact that the shape and breadth of the pure profile are determined both by the mean crystallite size or distribution of sizes, characterizing the specimen, and by the particular imperfections prevailing in the crystalline lattice [8]. Hence, in principle at least, an appropriate analysis of the line profile should yield such information as the mean crystallite dimension or size of the coherent crystalline domains, distribution of crystallite size, the nature and extent of lattice imperfections. Although, all these factors mainly contribute to the broadening of the line profile, there are some other parameters of the diffraction profile which are also affected by defects. In general the following features of the diffraction profile will be affected by lattice imperfections.

1. Breadth or width of diffraction profile
2. Shape or asymmetry of the diffraction profile
3. Line position
4. Intensity

Since, broadening is affected by all types of defects, this is considered to be the most important feature of the profile in defect analysis and the method of estimation of different lattice imperfections from a study of breadth of the intensity profile is sometimes referred to as X-ray line broadening technique. Thus, we find that by a proper analysis of the X-ray diffraction profile from a specimen, we can identify and estimate
the extent of the different types of lattice imperfection existing in the sample. Such an analysis is known as X-ray line profile analysis and is the basis of the study of lattice defects in solids.

2.7.3.1. Parameters for line profile analysis

We know that the observed diffraction profile from a sample under study is the result of the convolution of geometrical profile and the profiles due to the various lattice imperfections that may coexist in the sample. These line profiles are collectively referred to as diffraction profile. The next step obviously would be to recover the profiles due to each imperfection from the composite pure diffraction profile. Hence, in order to study each individual imperfection, the observed line profile is to be separated out or deconvoluted to get the profiles due to each individual defect. Since, in the absence of precise information on the nature and extend of these defects, deconvolution becomes a formidable task, the more pragmatic approach would be to find the relationship between the different identifiable feature of the line profile and the different lattice imperfections. Among these features, the most important are the line width and line position, the former playing the most dominant role in defect analysis. Hence, it will be the first task of the crystallographer to select out some appropriate parameter for measuring these features of the line profile and then find out the effect of different imperfections on them whose law of addition is well known.

2.7.3.2. Line position measurement

There are several parameters in use for the measurement of line position of a profile of the intensity distribution $I(2\theta)$ as a function of the angle of scattering $(2\theta)$. The experimental profile is obtained either directly from the diffractometer chart recorder or by converting the powder photograph of the sample into diffractogram by using a microphotometer. The recorded intensities at different angles $(2\theta)$ covering the entire range over which intensities are appreciable as shown in Fig.2.5. This gives the experimental line profile. The most obvious and ready measure of line position is the peak of the diffraction profile $(2\theta_0)$ and the peak intensity is largely affected by the experimental conditions and the geometry of the set up. Another parameter for measurement of location line is known as median, a point which divides the profile into
two equal halves on opposite sides of the point. The most fundamental parameters of line position are known as mean or centre of gravity, also called centroid. This is also called the first moment of any distribution of $f(x)$ (say) and is defined in general as given in Eq.(2.21)

$$x = \frac{\int xf(x)dx}{\int xf(x)}$$

(2.21)

With reference to the intensity distribution profile $I(2\theta)$, its centroid $2\theta$ will be given by Eq.(2.22)

$$2\theta = \frac{\int I(2\theta)\phi(2\theta)d(2\theta)}{\int I(2\theta)d(2\theta)}$$

(2.22)

The limits of the integration being the values of $2\theta$ at which $I(2\theta)$ becomes or tends to becomes zero. It has been shown by Wilson [9] that the centroid of the observed profile will be equal to the sum of the centroids of the different profiles which have convoluted to form the observed one. Thus we can write symbolically

$$\Delta_{n} = \Delta_{r} + \Delta_{g}$$

(2.23)

where $\Delta_{r}, \Delta_{f}$ and $\Delta_{g}$ refers to the centroids of the observed, pure diffraction and geometrical profile respectively measured from a common reference $2\theta_{0}$ (say) of the profile. The above Eq.(2.23) can be generalized as

$$\Delta_{n} = \sum_{i=1}^{N} \Delta_{i}$$

(2.24)

where $\Delta_{n}$ is the centroid of the line profile which results from the convolution synthesis of $N$ different profiles whose centroids are $\Delta_{i}$s. This is really a difficult task as the tails of the profiles approach very slowly to the background and even often this is estimated by truncating the profile at some arbitrary level.
Fig. 2.5. Angular distribution of intensities $I(2\theta)$, $2\theta_0$ corresponds to peak position and $2\theta_c$ centroid. Half width $\beta_{1/2} = 2(\theta_2 - \theta_1)$
2.7.3.3. Measurement of line broadening

As discussed in the previous section, an originally geometrically sharp line will be broadened into a bell shaped curve due to the presence of various lattice imperfections and the instrumental functions. There are several measurement of the dispersion of the line profiles are listed below:

a) Half-intensity width ($\beta_{1/2}$)
b) Integral width ($\beta$)
c) Variance ($W$)
d) Fourier coefficient ($A_n$)

(a) **Half-intensity width ($\beta_{1/2}$)**

Of all the parameters in use for the measurement of breadth of a line profile, half width, is the earliest and was used by Scherrer in his famous equation relating breadth with the crystallite size. As shown in Fig.2.5, this is equal to the angular distance between two points of the profile $2\theta_1$ and $2\theta_2$ at in which the intensity falls to half of its maximum or peak value (i.e) $I_{max}/2$, denoting half width as $\beta_{1/2}$ on $2\theta$ scale

$$\beta_{1/2} = 2(\theta_2 - \theta_1)$$ (2.25)

However, this is a parameter which can be measured very easily and hence can be used for routine work, where high accuracy is not needed.

(b) **Integral width ($\beta$)**

The integral of a line profile $I(2\theta)$ on $2\theta$ scale is defined by the following Eq.(2.26)

$$\beta_{2\theta} = \frac{\int I(2\theta)d(2\theta)}{I_{max}}$$ (2.26)

where the subscript $2\theta$ signifies the unit of the abscissa of $I(2\theta)$ curve and $\int I(2\theta)d(2\theta)$ is known as the integrated intensity of the diffraction profile. $I_{max}$ is the intensity at the peak of the profile. Obviously, the integral width is the ratio of integrated intensity to the peak intensity and hence equal to the breadth of the rectangle whose one side is $I_{max}$ and area is equal to the total area under the curve of $I(2\theta)$. The limits of the integral over which intensity is measured should theoretically extend from minus to plus infinity.
(c) Variance (W)

Both $\beta_{1/2}$ and $\beta$ are empirically of devised parameters used by crystallographers for the measurement of dispersion or width of an intensity profile. Mathematically, the most natural measure of dispersion is the second moment or the variance of the line profile which is the mean square deviation from its mean (i.e) centroid, often called the first moment. Hence, the second moment or the variance is measured with respect to the centroid and is defined on $2\theta$ unit as given in Eq.(2.27)

$$W_{2\theta} = \frac{\int (2\theta - \overline{2\theta})^2 I(2\theta) d(2\theta)}{\int I(2\theta) d(2\theta)}$$  \hspace{1cm} (2.27)

where $\overline{2\theta}$ is the centroid or first moment of the line profile. The limits of the integral, theoretically, should be $\pm \infty$. However, in practice, it is taken to be the values of $2\theta$ where the intensity merges or tends to merge into the background level. Variance has the important property of additivity which is also independent of the nature of the distribution of the profiles. Hence, we can easily write the variance $W_n$ of the experimental profile as the algebraic sum of the variances of the different profiles which have convoluted to give the observed profiles. Thus, in general,

$$W_n = \sum W_i$$  \hspace{1cm} (2.28)

where $W_i$'s are the variances of the different profiles and the relation is independent of the nature of distribution of the constituent profiles. This relation is used to correct for instrumental broadening and is found to be most convenient.

However, variance is a range sensitive parameter and consequently depends on the choice of the background level which has a marked influence on the range to be selected for integration. In fact, it is found that the diffraction profiles approach zero, rather asymptotically following an inverse square law. For such a function varying inversely as the square of the distance from the mean, the variance will be a linear function of the total range $\sigma$ (say) and can be written as
\[ W = K\sigma + C \]  
\[(2.29)\]
where \( K \) and \( C \) are constants and are depend upon the physical conditions of the sample and the geometrical factors. As in the case of centroid, here also to make the variance finite and determine, the line profile is truncated at some arbitrary level. This naturally introduces an element of inaccuracy. Nevertheless, centroid and variance are considered to be very useful measure of line position and line width respectively and are being increasingly used now-a-days in line profile analysis.

(d) Fourier-coefficients (\( A_n \))

Like the moments, Fourier co-efficient of a function are also considered to be the natural characteristics of its distribution. This parameter was perhaps first introduced in line profile analysis by Bertaut [10] followed by Warren and Averbach [11]. It can be shown that the diffraction profile from an assembly of polycrystalline aggregate consisting of crystallites of all shapes in all orientations is given by a Fourier series with coefficients given by Eq.(2.30)

\[ A(n) = N(n)J(n) \]  
\[(2.30)\]
where \( J(n) \) is the average value of \( FF^* \) for a pair of cells, \( n \) interplanar distance apart, \( F \) is structure factor in the given direction and \( N(n) \) is the number of such pair of cells. However, if the crystallites are not distorted, but only small in size, then \( J(n) \) is constant and in such case the coefficients are simply given by \( N(n) = N - n \). Fourier method is very rigorous one and is independent of the line shape and can be applied for the analysis of diffraction profiles for crystallites of any shape and size.

2.7.4. Physical techniques and chemical analysis

The characterization of material and devices by physical techniques is done by observing directly or indirectly the imperfections and impurities present in them. In fact, surface characterization has become an indispensable tool for the study of devices and materials. Surface studies do not necessarily exclude study of the bulk, since when it is used in conjunction with other techniques like ion etching, information can be obtained as a function of depth. The various physical techniques for surface studies of our interest are:
CHAPTER - II

1. Scanning electron microscope (SEM)
2. Atomic force microscope (AFM)
3. Energy dispersive analysis by X-rays (EDX)

All these techniques utilize the principle of analysis of characteristic emission (photons, electrons, ions, molecules, atoms) caused by the excitation of surface states from the sample by a primary sources (photons, electrons etc.).

2.7.4.1. Scanning Electron Microscope

The scanning electron microscope (SEM) perhaps, the most widely employed thin film and coating characterization instrument. The SEM provides a direct means of examining surface topography of a sample at higher magnifications with high resolution. Further, SEM offers several modes of operation [12]. The resolution is high as 10 Å have been achieved in SEM by scientists and technologists. Figure 2.6 shows the schematic diagram of a scanning electron microscope. It consists of mainly an electron beam accelerated by a voltage between 5 and 50 kV is scanned in a raster pattern on the specimen surface. An associated cathode ray is scanned in synchronization with the electron beam. A vacuum system is also one of the main parts of the instrument. A pressure of $10^{-5}$ torr is required for tungsten filament and for lanthanum hexa boride (LaB₆) gun we need even less pressure, (i.e) ultra high vacuum.

The vacuum is created by diffusion pump backed by rotary pump. Sometimes getter ion pumps are also used to minimize the contamination of sample depending on the application. The specimen chamber has a stage with goniometer attachment for the movement of the sample in x, y and z direction. The focusing of the electrons from the gun is done by the electromagnetic lens. The electrons impinge on the sample and secondary as well as scattered electrons are ejected which can be visualized on the cathode ray oscilloscope with an attachment of camera for photographing the pictures for record and analysis.

2.7.4.2. Atomic Force Microscope

Atomic force microscope (AFM) is an instrument used for studying surface properties of materials at the atomic to micron level. The AFM is used in electronics,
telecommunications, biological, chemical, automotive, aerospace and energy industries. The AFM can be used to investigate a variety of materials which include thin and thick film coatings, ceramics, composites, glass, synthetic and biological membranes, metals, polymers and semiconductors. The AFM may be used to image surfaces at atomic resolution as well as to measure forces at nano-newton scale. AFM probes the surface of a sample with a sharp tip which is couple of microns long and less than 100 Å in diameters. Tips are typically made from Si$_3$N$_4$ or Si and are located at the free end of a cantilever from 100 to 200 µm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector in the AFM head (Fig.2.7) measures the cantilever deflection as the tip scans the surface of the sample. The force commonly associated with AFM is the Vander Waal’s force. A computer generates a map of the surface topography from the measured cantilever deflection.

AFM can be operated in contact, non-contact and intermittent modes. In contact mode, the tip makes physical contact with the sample. As the tip is moved across the sample, the contact force causes the cantilever to bend according to changes in topography. In non-contact mode, the cantilever is vibrated near the surface of the sample. The distance between the tip and the sample is in the order of tens of thousand of angstroms. Non-contact mode is advantageous because the tip has little or no contact with the sample. Intermittent mode is very similar to non-contact mode. In this mode, the vibrating cantilever tip is drawn closer to the sample surface and the tip just barely hits, or “taps” the sample. Intermittent mode is less likely to damage the film surface in the contact mode. It also eliminates lateral forces between the tip and the sample. It is also more effective than the non-contact mode for imaging large scan sizes that may include large variations in topography. The key measurements of AFM are true 3D surface topographic imaging, complete image analysis all surface features or irregularities, surface elasticity or compressibility measurements and quantitative summary statistics.
Fig. 2.6. Schematic diagram of scanning electron microscope

Fig. 2.7. Schematic diagram of atomic force microscope
The advantages of AFM are given below:

- Quantitative surface roughness measurements.
- Can image any solid surface.
- Measurement of physical forces.
- When compared to scanning electron microscopy, atomic force microscopy provides more accurate topographic contrast, direct height measurements without any coating on the surface.

2.7.4.3. Energy Dispersive Analysis by X-rays

The composition of thin film compounds and alloys have been analyzed using an Energy dispersive analysis by X-rays (EDX). Cliff and Lorimer have derived the following expression for the estimation of composition

\[ \frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B} \]  

where \( I_A \) and \( I_B \) are the characteristic X-ray intensities generated when the specimen is irradiated in vacuum electrons at a particular energy and \( C_A \) and \( C_B \) are the weight fractions of any two elements A and B in the sample. The scaling factor \( K_{AB} \) depends on factors like X-ray absorption and fluorescence in the specimen. Thin films of dimensions 1 cm x 1 cm are used in the measurement of composition by EDX attached with scanning electron microscope. It is to be noted that an EDX technique has an error of about 5 %.

2.7.5. Optical properties

Optical absorption in solid results mainly because of any of the following processes:

1. Excitation of crystal vibration
2. Formation of excitons
3. Excitation of free electrons and holes within allowed bands
4. Excitation of free electrons and holes from one band to another of the same type band
5. Excitation of electrons across the gap from the valence band to an imperfection level and
6. Excitation of an electron from an imperfection level to the conduction band

Of all these absorption processes, only the last three gives rise directly to photoconductivity excitation across the gap. The absorption of radiation that gives rise to transition of electrons between the valence and conduction bands is of two types:

(a) Direct transition

The necessary condition for a direct transition to take place is that in the excitation process no change in the K value of the electron should occur. The absorption coefficient for direct transition is usually $10^4$-$10^5$. The following dependencies are observed during this transition

$$
\alpha \propto (E_v - E_i)^{1/2} \text{ for allowed transitions}
$$

(2.32)

$$
\alpha \propto (E_v - E_i)^{3/2} \text{ for forbidden transitions}
$$

(2.33)

where $\alpha$ is the absorption coefficient, $E_v$ is the energy of the top of the valence band and $E_i$ is the energy of the initial state from which the transition is made. If $(\alpha h\nu)^2$ is plotted against photon energy $(h\nu)$, a straightly line portion is obtained which on extrapolating cuts the energy axis with an intercept equal to the band gap.

(b) Indirect transition

The transition involving a change in the crystal momentum $(k+0)$ are termed as indirect transition. In this case, absorption of both a photon and a phonon or the absorption of a phonon and the emission of phonon takes place. The absorption coefficient is usually $10^{-1}$-$10^3$ cm$^{-1}$. The following dependencies are observed during indirect excitation

$$
\alpha \propto (E_{iy} - E_{ii})^2 \text{ if allowed direct transition at } k=0
$$

(2.34)

$$
\alpha \propto (E_{iy} - E_{ii}) \text{ if forbidden direct transition at } k=0
$$

(2.35)

If $(\alpha h\nu)^{1/2}$ is plotted against photon energy $(h\nu)$, a straight line is obtained, the intercept on energy axis gives the band gap for direct transition.

2.7.5.1. Optical parameters

The optical properties of a crystal are governed by the interaction between the crystal and the electric field of electromagnetic wave. It is convenient to describe the propagation of a plane wave in a solid by a frequency dependent complex refractive
index $N = n - ik$. Where the real part of the refractive index ‘$n$’ is related to the velocity of propagation of the wave and the extinction coefficient ‘$k$’ represents the decay of the amplitude of oscillations of the electric field.

$$E(x,t) = E^0 \exp[i \nu(t - N x / c)] = E^0 \exp[i \nu(t - n x / c)] \exp(-k \nu x / c) \quad (2.36)$$

The optical parameters $n$ and $k$ are related to frequency dependent electrical conductivity $\sigma$ and electrical susceptibility $\chi$. In a static electric field, the conductivity represents the value of the current of free electric charges and the electric susceptibility represents the displacement of bound charges. In an alternating field, the charges oscillate and the distinction between free and bound charges disappears at the microscopic level. However, the current excited by an alternating field can still be represented formally as the sum of the conduction current, varying in phase with the electric field and a displacement current, lagging in phase by $\pi/2$.

$$J = \sigma E + \chi \frac{dE}{dt} \quad (2.37)$$

where $\sigma$ and $\chi$ represent the conductivity and electric susceptibility in an alternating field.

If, instead of the current, we consider the polarization and the associated electric induction, we can introduce a complex permittivity $\varepsilon_r = \varepsilon_1 + i\varepsilon_2$ as a coefficient of proportionality between the electric conduction and the field. The relationships between the three pairs of quantities $(n, k, \varepsilon_1, \varepsilon_2, \chi, \sigma)$ are given by the following formulae:

$$n^2 - k^2 = \varepsilon_1 = 1 + 4\pi\chi \quad (2.38)$$

$$2nk = \varepsilon_2 = 4\pi\sigma / \nu \quad (2.39)$$

Estimation of absorption coefficient

The complex refractive index $N$ can be written as

$$N = n + ik \quad (2.40)$$

$$N^2 = \varepsilon_r = \varepsilon_1 + i\varepsilon_2 \quad (2.41)$$

$$\varepsilon_1 = n^2 - k^2 \quad (2.42)$$

$$\varepsilon_2 = 2nk \quad (2.43)$$
where 'n' and 'k' are the refractive index and extinction coefficient, respectively. The fraction of the light transmitted at normal incidence through a plane parallel to film of thickness t is given by Eq.(2.44)[13]

\[ I_t = \frac{(1 - R)^2 + 4R \sin^2 \psi}{\cosh \alpha + R^2 \cosh \alpha - 2R \cos \theta (\psi + Y)} \] (2.44)

and the fraction of incident light reflected is given by Eq.(2.45)

\[ I_R = \frac{R(\cosh \alpha + \cosh \alpha) - 2R \cos \theta Y}{\cosh \alpha + R^2 \cosh \alpha - 2R \cos (\psi + Y)} \] (2.45)

where

\[ R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad \psi = \tan^{-1} \left( \frac{2k}{n^2 + k^2 - 1} \right) \] (2.46)

\( \alpha \) and \( Y \) are absorption coefficient and phase change respectively and are given by

\[ \alpha = \frac{4\pi k}{\lambda} \quad \text{and} \quad Y = \frac{2\pi n t}{\lambda} \] (2.47)

In general, 'n' and 'k' can be determined from \( I_t \) and \( I_R \). In the present work, we have used the following relation [14] in order to determine the value of absorption coefficient

\[ T = (1 - R) \exp(-\alpha t) \] (2.48)

### 2.7.6. Electrical properties

The electrical conductivity of an intrinsic semiconductor at low temperature is due to intrinsic charge carriers (electrons and holes). Such conductivity is sometimes termed as intrinsic conductivity. Since, there are two types of carriers in the intrinsic semiconductor, electrons and holes, its specific conductance is the sum of the conductivities \( \sigma_e = |e| n \mu_e \) due to free electrons, with the concentration 'n' and mobility \( \mu_e \), and the conductivity \( \sigma_h = |e| p \mu_h \) due to the presence of holes, with the concentration p and mobility \( \mu_h \). The mobility is the magnitude of the drift velocity per unit electrical field, (i.e) \( \mu = |V' / E | \). The mobility is defined to be positive for both electrons and holes, although their drift velocities are opposite. In an ideal intrinsic semiconductor the mobility is determined by collisions between electrons and photons, the electrical
conductivity of an intrinsic semiconductor $\sigma = |e|(n\mu_n + p\mu_p)$ and for an intrinsic semiconductor $n = p$, we have $\sigma_i = |e|(n\mu_n + p\mu_p)$. Where $\sigma_i$ denotes the intrinsic conductivity. But the values of $n$ is given by

$$n = n_i = \left(\frac{2\pi K_B T}{h^2}\right)^{3/2} \left(m_e^* m_h^*\right)^{1/4} e^{-E_g/2K_B T}$$

$$\sigma_i = 2|e|\left(\frac{2\pi K_B T}{h^2}\right)^{3/2} \left(m_e^* m_h^*\right)^{1/4} e^{-E_g/2K_B T} (\mu_e + \mu_h)$$

The exponential term $\exp[-E_g / 2K_B T]$ dominates all other temperature dependence, as it seen by writing the above Eq. (2.50) as

$$\log\sigma_i = \left(\frac{-E_g}{2K_B T}\right) + \log\left[2|e|\left(2\pi K_B T / h^2\right)^{3/2} \left(m_e^* m_h^*\right)^{1/4} e^{-E_g/2K_B T} (\mu_e + \mu_h)\right]$$

or

$$\log\rho = \log\sigma_i = \frac{E_g}{-\log\left[2|e|\left(2\pi K_B T / h^2\right)^{3/2} \left(m_e^* m_h^*\right)^{1/4} e^{-E_g/2K_B T} (\mu_e + \mu_h)\right]}$$

where $\sigma$ is the conductivity. If we plot $1/T$ along the $X$-axis and $\log\sigma$ along the $Y$-axis, we will obtain a straight line. The slope of straight line determines $E_g$.

2.7.7. Magnetic properties

Magnetic properties of the deposited films were analyzed using vibrating sample magnetometer (VSM). VSM is an instrument based on the principle of electromagnetic induction. Its basic structure is schematically shown in Fig.2.8 which consists of an electromagnet, a vibration unit with a sample holder, a pair of pick-up coils, and a field sensor. A maximum field of 30 kOe is obtainable from an electromagnet field system. If a field higher than this is required, a superconducting magnet can be used, which is capable of producing a field as high as 160 kOe. The test sample (usually less than 10 mm square in size) in a uniform magnetic field can be treated as a magnetic dipole. The magnetic fluxes from the sample, which vibrates in the direction perpendicular to the applied field, induces an emf in the pick up coil positioned near by. This emf is proportional to the magnetic moment of the sample and is given by Eq.(2.52)
where $M$ is the magnetic moment of the test sample, $\omega$ is the angular velocity of the vibration, and $g_i$ is determined by measuring a sample with a known magnetic moment (calibration sample). After calibration with a standard sample, the output from the pick-up coil represents the value of magnetic moment of the sample, and the output from the field sensor gives the value of applied field. The output of the instrument is therefore a $M$-$H$ loop or more accurately, a curve showing the field dependence of the magnetic moment of the test sample, from which many magnetic parameters can be obtained.

VSM is one of the most commonly used magnetometers for the characterization of magnetic materials in both the research laboratory and the production factory. The ultimate sensitivity of modern VSM is as high as $10^{-6}$ emu and the field resolution can be as small as 1 mOe. It is widely used for the measurements of soft magnetic films ($H_c$ and $M_s$), thin film recording media ($H_c$, $M_s$, $M_r$, $\Delta M$ curve) and giant magnetoresistance (GMR) of spin-valve films ($M$-$H$ loops, $H_{ex}$, $H_I$). When equipped with cryostat or a heating module, VSM can be used to measure the magnetic properties of films at various temperatures ranging from 4 K (with a liquid He cryostat) to high temperature. VSM is particularly useful for the measurement of GMR, spin-valve and tunneling magnetoresistive (TMR) films and antiferromagnet or ferromagnet exchange systems.

**2.7.7.1. Magnetic properties derived from hysteresis loop**

The magnetization/demagnetization curves for a given ferromagnetic material provides a great deal of information during magnetic characterization. The full magnetization curve, is shown in Fig.2.9 and known as a hysteresis loop, illustrates the methodology as well as which properties of the material under scrutiny are observed. The hysteresis loop has the axes of the applied field ($H$) and magnetization of the material ($M$). Often the magnetic induction ($B$) is displayed as a function of applied field ($H$) but $B$ is related to $M$ by the following Eq.(2.53)

$$B = \mu_0 (M + H)$$

(2.53)

where $\mu_0$ is the permeability of free space.
Fig. 2.8. Schematic diagram of vibrating sample magnetometer

Fig. 2.9. Hysteresis loop for magnetic thin films
The hysteresis loop is generated in the following fashion as shown in Fig. 2.9. At point (a) the material is in the virgin or demagnetized state and incurs an applied field (H) until the material achieves magnetic saturation at point (b). From point (b) the field is reduced to zero and the magnetization remaining in the material with zero applied field (remanence) is shown at point (c). From point (c) a negative field is applied to the sample and the induced magnetization is reduced from (c) to (d) which corresponds to the amount of field required to reach zero magnetization in a particular sample. Point (d) is known as the coercive point. The sample is negatively magnetized to point (e) corresponding to magnetic saturation in the opposite direction. When the field is decreased to zero and the magnetization falls to the value at point (f). Lastly, the field is applied in the positive direction to bring the sample back to positive magnetic saturation crossing applied field axis at point (g) and joining the initial saturation at point (b). The area enclosed from point (b) counterclockwise to point (b) is the hysteresis loop.

The word “Hysteresis” comes from Latin verb ‘hyster’, meaning ‘to lag’. The area enclosed by the hysteresis loop represents property known as the energy loss (W_H) in cycling the magnetic field. There are several mitigating factors that determine the shape and size of the hysteresis loop and all of the properties revealed by the hysteresis loop. An important property for characterizing ferromagnetic materials and their subsequent applications is determined in part by the susceptibility or permeability of material. The susceptibility (χ) is defined by the following Eq. (2.54)

\[ \chi = \frac{M}{H} \]  

(2.54)

where M is the magnetization and H is the applied field.

Similarly, the permeability (μ) is defined by the following Eq. (2.55)

\[ \chi = \frac{B}{H} \]  

(2.55)

The susceptibility and permeability are defined as the slopes of M versus H or B versus H, respective behaviour on hysteresis loops. As these slopes change throughout the magnetization process, the most useful information is the initial susceptibility (initial permeability) \( \chi_0(\mu_0) \) which occurs at point (a) in Fig. 2.9 and the maximum susceptibility.
(permeability) $\chi_{\text{max}}(\mu_{\text{max}})$ which occurs at points (d) and (g) corresponding to the corresponding points. The susceptibilities give us important information regarding the case at which a material be magnetized. Saturation magnetization ($M_s$) describes the limit of magnetization in any given material. This occurs when all of the dipole moments in the material are aligned in the direction of the applied magnetic field. Magnetic saturation occurs at point (b) in Fig.2.9. It should be noted that the saturation magnetization depends only on the volume of the autumn being magnetized and it is expected to be a structure insensitive property.

Retentivity ($M_r$) or remanent induction ($B_r$) is the amount of magnetization remaining in a material after a saturating a field has been removed. The retentivity is given by (c). Permanent magnetic theory makes the retention of magnetization to distinguish ferromagnetic materials from paramagnetic material.

The coercivity ($H_c$) is defined, as the applied field required to demagnetize or to bring the magnetization of a saturated material to zero. The coercivity or coercive point is given by point (d). It should be noted that the width of the hysteresis loop is defined as twice the coercivity and as such the coercivity will determine to a great deal the magnetic properties of a material.

The domain structure of the material is magnetically saturated in the direction of the applied field at point (b). The domain structure changes when the magnetic field is applied in the opposite direction to have zero net magnetization at point (d). At point (e), all dipole moment are aligned in the direction of the applied field.

### 2.7.8. Photoelectrochemical solar cell studies

Charge transfer across the semiconductor-electrolyte interface in dark or under illumination results in the flow of current through the junction of electronically (or hole) conducting solids and ionically conducting liquids. This is the key concept in the working of photoelectrochemical solar cells.

The principle of charge transfer reaction at the semiconductor-electrolyte interface forms the basis of various types of photoelectrochemical solar cells. In addition to the semiconductor-electrolyte interface, incorporation of a counter electrode in the
electrolyte to complete the electric circuit gives the desired photoelectrochemical solar cell properties.

Illumination results in the generation of electron-hole pairs, their separation in space charge layer, lowering of the depletion layer barrier and subsequently the hole flux crossing the interface to be captured by the reduced ionic species of the electrolyte increase. On short circuiting, the electron is driven via, the external circuit towards the metal counter electrode where it participates in the reduction reaction of the oxidized species.

A number of theoretical models have been suggested for current-voltage characteristics of photoelectrochemical solar cells but none are able to explain the existing experimental results. In general, theories of regenerative type photoelectrochemical solar cells (direct conversion to electricity) or photoelectrolysis solar cells are similar. The photogenerated electron-hole pairs are separated in the space charge layer giving rise to a photovoltage. So, a theory for current-voltage characteristics of regenerative type photoelectrochemical solar cell (PESC) can be developed by considering the details of charge transport in semiconductor and charge-transfer mechanism at the interface. The two important steps in PESC functioning are:

(a) charge transfer in the semiconductor space charge layer and
(b) charge transfer reaction kinetics at the electrode-electrolyte interface

The two extreme theoretical approaches are based on the assumptions of one of these being dominant and the other is neglected. Thus, the two approaches are:

(a) Bockri and Uosaki theory in which the rate determining step is considered to be the charge-transfer reaction kinetics.

(b) Metal-Semiconductor Schottky-barrier theories in which the electrolyte interface is equated to metal-semiconductor Schottky barrier and the charge transfer reaction kinetics are neglected.

Evidences partially in favour of both types exist but the Schottky barrier theories are more near the real situation. The evidences generally quoted in favour of M-S Schottky barrier theories are [15, 16]
(a) Linear dependency of flat band potential ($V_{fb}$) on pH.

(b) Linear variation of $V_{fb}$ with logarithm of light intensity $I$.

\[ V_{fb} = \left( \frac{KT}{e} \right) \times 2.303(1 + cI) + V_{fb}^D \tag{2.56} \]

where $c$ is a constant and $V_{fb}^D$ is the flat band potential without illumination.

(c) A linear relationship between photocurrent and light intensity.

(d) A linear relationship between (photocurrent)$^2$ versus $V$.

The assumption of Butler’s model [17] is the semiconductor-electrolyte junction resembles a true Schottky barrier between a semiconductor and metal.

Bockris and Uosaki [18] developed a theoretical model for the photoinduced evolution of oxygen and hydrogen in PESC systems taking into account the electrode kinetics and analyzing the charge transfer through the electrode double layer at the semiconductor-electrolyte interface under WKB approximation [19-21]. In the Bockris model the authors assumed that the rate determining step is the reduction of $H_3O^+$ ions at the p-type electrode and the oxidation of either OH$^-$ ion or H$_2$O molecule at the n-type electrode.

Reiss theory [22] is a detailed phenomenological theory of an illuminated semiconductor-electrolyte interface, taking into account the transport phenomenon, reaction kinetics and effects of surface states. However, application of Reiss model to the real situation seems difficult because of enormous calculations involving many parameters.

Wilson’s theory includes, reaction kinetics at the interface in terms of a constant charge transfer velocity ($S_t$) for minority carriers across the semiconductor electrolyte interface and a surface recombination velocity ($S_r$). However, the model only considered the photogenerated current without including the opposing dark current and also neglected recombination in the space charge region. Wilson’s model can be a good approximation for cases where $N_0 > 10^{16}$ cm$^{-3}$, $q\phi_0 < 100$ mA/cm$^2$ and $V < $about one half the band gap. Reichman’s theory [23] included the space charge recombination, the effect of opposing current due to majority carrier and the reaction kinetics. Reichman’s approach
is essentially the same as that of Gärtnert [24] described earlier with a different set of boundary conditions. El Guibaly et al [25, 26] derived expression taking into account reaction kinetics at the interface, surface recombination, recombination in the space-charge region, electronic and hole dark currents.

Most of the theoretical investigation for J-V characteristics of PESC described earlier follows a Gärtnert’s model [24], where the entire semiconducting electrode is divided into two region: a depletion region of width W and the bulk region. The excess charge carrier transport is analyzed using the diffusion-reaction transport model based upon the continuity equation. The continuity equation assumes that the carriers undergo several collisions before recombination occurs. This means that the mean free path for scattering should be small compared with the physical dimensions of the systems.

2.8. Conclusions

In this chapter, important theoretical aspects related to electrodeposition, mechanism and practical considerations of semiconducting compounds are presented. The fundamentals of cyclic voltammetric studies for thin films are briefly described. Theoretical aspects relevant to structural, electrical and magnetic properties of thin films are also given. The informations relevant to theoretical aspects for precise measurement of microstructural parameters are discussed. The necessary information for the process of physical and chemical analyses of thin films is also enunciated. Theoretical aspects relevant to optical and photoelectrochemical properties are also discussed.
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