3.1 Thin Film Deposition Techniques

3.1.1 Introduction

Technological progress of modern society depends on the material science and engineering community's ability to conceive the novel materials with extraordinary combination of physical and mechanical properties [1]. Modern technology requires thin films for different applications [2]. Thin films can be deposited by number of physical and chemical techniques and can be classified as shown in Table 3.1.

Among the methods mentioned in the table 3.1, the chemical methods are economical and easier than that of the physical methods. But there is no ideal method to prepare thin films, which will satisfy all possible requirements. Among the chemical methods, the spin coating technique is the most popular today because large number of conducting and semiconducting thin films can be prepared by this technique. It is also popular due to its simplicity and low cost. In this technique, the thin films can be deposited on different substrates like glass, ceramic, metallic etc. Many studies have been conducted over about three decades on spray pyrolysis processing and preparation of thin films. It is simple and low cost technique and has capability to produce high quality adherent films of uniform thickness.
Table 3.1

**Thin Film Deposition Techniques**

<table>
<thead>
<tr>
<th>PHYSICAL</th>
<th>CHEMICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>Gas Phase</td>
</tr>
<tr>
<td>1) Glow discharge DC sputtering</td>
<td>1) Vacuum Evaporation</td>
</tr>
<tr>
<td>2) Triode sputtering</td>
<td>1) Chemical vapour deposition</td>
</tr>
<tr>
<td>3) Getter sputtering</td>
<td>2) Laser Chemical vapour deposition</td>
</tr>
<tr>
<td>4) Radio Frequency sputtering</td>
<td>3) Photo-chemical vapour deposition</td>
</tr>
<tr>
<td>5) Magnetron sputtering</td>
<td>4) Plasma enhanced vapour deposition</td>
</tr>
<tr>
<td>6) Ion Beam sputtering</td>
<td>5) Metal-Organo Chemical Vapour Deposition (MO-CVD)</td>
</tr>
<tr>
<td>8) A.C. Sputtering</td>
<td>6) Sol- gel</td>
</tr>
<tr>
<td>6) Arc</td>
<td>7) Spin Coating</td>
</tr>
<tr>
<td>7) R. F. Heating</td>
<td>8) Spray-pyrolysis technique (SPT)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaporation</td>
<td>Liquid Phase</td>
</tr>
<tr>
<td>1) Vacuum Evaporation</td>
<td>1) Electro-deposition</td>
</tr>
<tr>
<td>2) Resistive heating Evaporation</td>
<td>2) Chemical bath deposition (CBD)</td>
</tr>
<tr>
<td>3) Flash Evaporation</td>
<td>3) Electro less deposition</td>
</tr>
<tr>
<td>4) Electron beam Evaporation</td>
<td>4) Anodisation</td>
</tr>
<tr>
<td>5) Laser Evaporation</td>
<td>5) Liquid phase Epitaxy</td>
</tr>
<tr>
<td>6) Arc</td>
<td>6) Sol- gel</td>
</tr>
<tr>
<td>7) R. F. Heating</td>
<td>7) Spin Coating</td>
</tr>
<tr>
<td>9) Ultrasonic (SPT)</td>
<td></td>
</tr>
<tr>
<td>10) Polymer assisted deposition (PAD)</td>
<td></td>
</tr>
</tbody>
</table>
3.1.2 Spin coating Technique (SCT)

Spin coating technique has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of a liquid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm). Centripetal acceleration will cause the resin to spread to, and eventually off, the edge of the substrate leaving a thin film of resin on the surface. Final film thickness and other properties will depend on the nature of the resin (viscosity, drying rate, percent solids, surface tension, etc.) and the parameters chosen for the spin process.

The spin coating process can be broken down into the four stages as shown in Fig. 3.1. The deposition, spin up, and spin off stages occur sequentially while the evaporation stage occurs throughout the process, becoming the primary means of thinning near the end.

![Fig. 3.1 The Four Stages of the Spin Coating Process](image)

The deposition process involves dispense of an excessive amount of fluid onto a stationary or slowly spinning substrate. The fluid is deposited through a nozzle at the center of the substrate or over some programmed path. An
excessive amount of fluid is used to prevent coating discontinuities caused by the fluid front drying prior to it reaching the wafer edge.

In the spin up stage, the substrate is accelerated to the final spin speed. In this stage rotational forces are transferred upward through the fluid, a wave front forms and flows to the substrate edge by centrifugal force, leaving a fairly uniform layer of fluid on substrate.

The spin off stage is the spin coating stage where the excess solvent is flung off the substrate surface as it rotates at speeds between 2000 and 8000 RPMs. The fluid is being thinned primarily by centrifugal forces until enough solvent has been removed to increase viscosity to a level where flow ceases. The spin off stage takes place for approximately 10 seconds after spin up [3]. Though present throughout the spin coating process, evaporation becomes the primary method of film thinning once fluid flow ceases. Evaporation is the complex process by which a portion of the excess solvent is absorbed into the atmosphere. If significant evaporation occurs prematurely, a solid skin forms on the fluid surface which impedes the evaporation of solvent trapped under this skin and, when subjected to the centrifugal forces of the spinning substrate, causes coating defects. A variety of film thicknesses can be deposited by spin coating, due to film thickness being roughly inversely proportional to the square root of spin speed. As coating thicknesses increase, it becomes harder to find a solvent/solute mixture which will not dry before reaching the substrate edge. For this reason, thick films are occasionally formed by spinning on multiple thinner, more reliable coatings [4, 5].

### 3.1.2 (a) Modeling Spin Coating

The fluid flow on the spinning substrate is governed by the continuity equation and the conservation of mass. Assuming solvent density and fluid viscosity are constant, the continuity equation for the conservation of mass states the excess of fluid flux leaving a control volume must result in an equal rate of fluid thinning. The equation based on this law is given below.

\[
\frac{\partial h}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \cdot \rho \cdot \omega^2 \cdot r \cdot h^3 \right) + \frac{m}{\rho} \sqrt{1 + \left( \frac{\partial h}{\partial r} \right)^2} \quad \text{........................................(3.1)}
\]
The variables here are thickness \((h)\), radical distance \((r)\), angular velocity \((\omega)\), solvent density \((\rho)\), film viscosity \((\mu)\), and mass flux of solvent \((m)\). The first term on the right in equation 3.1 is the net flux leaving the control volume by centrifugal forces and the second term is the net flux leaving the control volume by evaporation.

Emslie, Bonner, and Peck (EBP) were the first group to investigate the spin coating process using Newtonian fluids [8]. They assumed an initially uniform film of thickness \(h_o\) and the absence of evaporation in order to develop the analytic solution for thickness \(h\) shown below.

\[
h = \left( h_o + 4 \rho \omega^2 h_o t / 3 \mu \right)^{1/2}
\] ...............................(3.2)

When the time derivatives of the equations are taken, and substitutions made, the following equation for film thinning rate is just the first term on the right of Equation 3.1 using the assumption height is not dependent on radial position.

\[
- \frac{dh}{dt} = \frac{2 \rho_0 \omega^2 h^3}{3 \mu_0}
\] ...............................(3.3)

In equations 3.2 and 3.3, \(\rho\) is fluid density, \(m\) is fluid viscosity, and \(\omega\) is the angular velocity of the substrate. In addition, EBP observed that a sufficiently smooth fluid layer will become more uniform as it thins, and profiles that are not sufficiently smooth develop a wave of fluid that is swept outward, leaving a fairly uniform layer behind the front [8]. This second phenomenon is the definition of the spin up stage given in the previous section.

The EBP assumption of no evaporation over simplifies the physical process, since the fluid properties change as a result of evaporation. Meyerhofer [9] developed a more accurate model for film thickness \((h)\) which included evaporation as function of spin speed. This inclusion of evaporation came at the cost of losing the analytic solution to Equation 3.1 and having to settle for the approximate solution shown below.

\[
h_f = \left( 1 - \frac{\rho_0}{\rho} \right) \left( 3 \mu_0 e^f \left( 2 \rho \omega^2 \left( \frac{\rho_0}{\rho} \right) \right) \right)^{1/3}
\] ...............................(3.4)
The variables in equation 3.4 are fluid density ($\rho$), fluid viscosity ($\mu$), and angular velocity ($\omega$), and evaporation rate ($e$), with the subscript 0 indicating the value of the parameter at the onset of spin off.

In approximating the solution of the continuity equation, Meyerhofer assumed the spin off stage and the evaporation stage were distinct. In the first stage, the film thins by centrifugal forces only, followed by the second stage where the film thins by evaporation only. The transition point between the spin off and evaporation stages was taken to be the point where the thinning rate due to evaporation was the same as the thinning rate due to centrifugal forces. Although thinning by evaporation occurs constantly, the assumption of better approximates the physical process when, as seen in the early stages of spin coating, the rate of thinning by centrifugal force is much greater than the rate of thinning by evaporation. This can be seen in Equation 3.1, as the film thins as the thickness cubed in the centrifugally driven flux. The assumption of the evaporation rate being independent of substrate position is not appropriate when coating larger substrates or odd shaped substrates due to the large pressure variations over the substrate surface. Several studies have been carried out to determine the evaporation rate as a function of position using round substrates [10].

3.1.2 (b) Advantages of spin coating

As evidenced by its maturity, spin coating has many advantages in coating operations with its biggest advantage being its lack of coupled process variables. Looking at Equation 3.3, although it is only an approximation of the actual spin coating process, the spin speed ($w$) and the fluid viscosity ($\mu$) are the only degrees of freedom, making the spin coating process very robust. Therefore, film thicknesses are easily changed by changing the spin speed, or switching to a different viscosity fluid. In the alternative coating techniques described later, many have multiple coupled parameters, making coating control more complex.

Another advantage of spin coating is the ability of the film to get progressively more uniform as it thins, and if the film ever becomes completely uniform during the coating process, it will remain so for the duration of the process [8]. The maturity spin coating implies many of the
issues involved in spin coating have been studied and a lot of information exists on the subject.

3.1.2 (c) Disadvantages of spin coating

The disadvantages of spin coating are few, but they are becoming more important as substrate sizes increase and fluid costs rise. First of all, as substrate sizes get larger, the throughput of the spin coating process decreases. Large substrates cannot be spun at a sufficiently high rate in order to allow the film to thin and dry in a timely manner resulting in decreased throughput.

The biggest disadvantage of spin coating is its lack of material efficiency. Typical spin coating processes utilize only 2-5% of the material dispensed onto the substrate [11], while the remaining 95-98% is flung off into the coating bowl and disposed. Not only are the prices of the raw fluid increasing substantially, but disposal costs are increasing as well. As a rule of thumb, the disposal costs of fluid waste is about 60 percents dollar of resist resulting in a net cost of 160% of the cost of the used resist [11]. If economically feasible manufacturing costs are to be maintained, a method for improving this material utilization is of primary importance, especially in the flat panel display area.

The diverse and application rich properties of metal oxide thin films such as high-temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity and semiconductivity, continue to receive significant attention. Metal oxide films are conventionally grown by physical and chemical vapour deposition [3, 4]. All growth methods have their advantages and disadvantages. Vacuum techniques provide high quality materials and excellent thickness control, but production rates are restricted by the cost of scaling vacuum systems. A chemical solution deposition such as sol–gel are more cost-effectively scaled and since vacuum is not required oxygen stoichiometry is easy to maintain [5]. However, chemical-solution techniques are limited in that not all types of metal oxides can be deposited and the control of stoichiometry is not always possible owing to differences in chemical reactivity among the metals. In addition, the formation of high density films employing chemical-solution techniques is often difficult.
3.2 Chemical solution methods

Sol–gel processing is perhaps the most well known and extensively studied method for chemical solution deposition of thin films and as such has received much attention. However; other solution techniques have been developed and provide viable alternatives to the physical deposition methods.

3.2 (a) Sol–gel

In general, the sol–gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase. The starting materials used in the preparation of the “sol” are usually reactive inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a “sol”. Thermal treatment of the sol results in the complete loss of the alkoxides as alcohol and formation of the metal oxide.

3.2(b) Chemical bath techniques (CBT)

This is perhaps the oldest known chemical method for the formation of thin films; dating back to 1884 when PbS was deposited using thiourea. This technique usually involves the simple immersion of a substrate into a solution containing both a metal salt and a chalcogenide precursor. As such it has generally been dominated by the formation of sulfides and selenide films. However, in recent years considerable work on the formation of oxide films has been carried out. CBT require that the product of the metal ion concentrations and the chalcogenide must exceed the solubility product of the desired product, thus the maximum obtainable thickness is limited by the supply of the reactants in solution. Control of film thickness, composition and density require complex control of the solution composition, pH and temperature.

Overall, one of the greatest challenges in solution-based processes of complex metal oxide films are to produce high-quality films with desired chemical composition. Several years ago, metal complexes of the polymer poly (ethyleneimine) (PEI) as a route to metal oxide film deposition began. Polymer assisted deposition (PAD), has the traditional advantages of
chemical-solution deposition systems and has the added feature of producing high quality films comparable to physical vapour deposition (PVD). Binding the metals directly to the polymer has several advantages including homogeneous distribution of metal precursors, and sequestering the metal until the polymer is decomposed. Sequestering the metal eliminates metal oxide formation in solution and results in a true bottom-up film formation that yields crack-free, epitaxial metal oxides. The precursors are air- and water-stable and the metal polymer can be spun, dipped or spray coated on to the substrate. Thermal decomposition of the metal polymer results in the formation of high density, even epitaxial, films of metal oxides.

3.2.1 Polymer assisted deposition method (PAD)

Polymer assisted deposition (PAD) is a chemical solution route to high quality thin films of metal oxides. This technique employs metal ions coordinated to polymers as the film precursor. The use of polymer bound metals has several advantages. The polymer controls the viscosity and binds metal ions, resulting in a homogeneous distribution of metal precursors in the solution and the formation of uniform metal oxide films.

The key to PAD is the inherent stability of the metal polymer solutions. The simplest view of the metal polymer interactions is the formation of covalent complexes between the lone pair on the nitrogen atom and the metal cation. This classic Werner-type chemistry is clearly the simplest method for the formation of first-row transition metals, using nitrates, acetates or chlorides. One of the key features in the formation of the complexes is the use of Amicons filtration to remove non-coordinated species [13].

For example the first-row transition metals bind well to the simple PEI polymer, presumably in a manner as shown in Fig. 3.2 (left). Other hard metals such as titanium require PEI functionalized with carboxylic acids to provide a stable coordination environment (Fig. 3.2, right). Another method for binding metals utilises the ability of protonated PEI to coordinate anionic metal complexes as shown in Fig. 3.3 (right).
Fig. 3.2 Putative structures of PEI and carboxylic acid functionalized PEI metal complexes.

Fig. 3.3 Putative structures of PEI binding EDTA complexes by hydrogen bonding and electrostatic binding.

The major advantage of the EDTA route is that EDTA forms stable complexes with almost all metals. The EDTA complexes bind to the PEI via a combination of hydrogen bonding and electrostatic attraction as seen in Fig. 3.3 (left). This hydrogen bonding is sufficiently stable that the Amicons filtration can also be used to purify these polymers. These solutions can remain stable for months even when multiple metals are used. Once the metal polymers have been prepared their viscosity can be adjusted by the simple removal of water under vacuum or by dilution with deionized water [13].
3.2.2 Colloidal solution method

(a) True Solutions:

A true solution is a homogeneous solution in which the solute particles have diameters between 0.1 nm to 1 nm i.e., the solute particles are of molecular dimensions. Such dispersed particles dissolve in solution to form a homogenous system. These do not settle down when the solution is left standing. The particles are invisible even under powerful microscopes and cannot be separated through filter paper, parchment paper or animal membranes. For example, sodium chloride in water is a true solution. Most ionic compounds form true solutions in water. Organic compounds like sugar and urea also form true solutions in water.

(b) Suspensions:

Suspensions consist of particles of a solid suspended in a liquid medium. Suspensions are systems with two distinct phases. The particles in suspensions are bigger than 100 nm to 200 nm across. The particles of a suspension may not be visible to the naked eye but are visible under a microscope. Suspensions are heterogeneous systems. They stay only for a limited period i.e. these are not stable as the particles have a tendency to settle down under the influence of gravity. The particles of a suspension can neither pass through ordinary filter paper nor through animal membranes. Examples of suspensions are sodium chloride in benzene, turmeric in water, silver chloride, barium sulphate or sand in water.

(c) Colloids:

Colloidal solution or colloidal state or colloidal dispersion, represent an intermediate kind of a mixture between true solution and suspension. The size of a colloidal particle lies roughly between 1-100 nm. Colloids are also a two-phase heterogeneous system consisting of the dispersed phase and dispersion medium. However, colloidal particles present in small amount as the dispersed phase component behave like a solute in a solution when suspended in a solvent phase or dispersing medium, because of their small size. Since the dispersed phase in a colloidal system is uniformly distributed in the dispersion medium, the colloidal state appears homogenous to the naked eye or even an ordinary microscope (due to particles being invisible).
However it is a heterogeneous dispersion of two immiscible phases and this is proved by viewing it under an ultra-microscope, where the light reflected by colloidal particles can be seen. Colloidal particles do not settle down under gravity: a colloidal solution of gold prepared by Faraday over 125 years ago continues to be in excellent condition even today. Colloids can pass through ordinary filter paper but do not pass through animal membranes [14]. The difference between true, suspensions and colloidal solution are given in table 3.2. Fig.3.4 shows the types of solution.

Table 3.2 Difference between True Solutions, Suspensions and Colloidal Solutions

<table>
<thead>
<tr>
<th>Property</th>
<th>True Solutions</th>
<th>Suspensions</th>
<th>Colloidal Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Less than $10^{-7}$ cm</td>
<td>Greater than $10^{-5}$ cm</td>
<td>Between $10^{-5}$ and $10^{-7}$ cm</td>
</tr>
<tr>
<td>Visibility of particles</td>
<td>Invisible to naked eye not visible under powerful microscope</td>
<td>Easily visible</td>
<td>Invisible to naked eye. Visible under powerful microscope.</td>
</tr>
<tr>
<td>Sedimentation of particles</td>
<td>Do not settle down</td>
<td>Settle down due to gravity</td>
<td>Settle down under high centrifugation</td>
</tr>
<tr>
<td>Filtration through filter power</td>
<td>No residue is formed</td>
<td>Residue is formed</td>
<td>No residue is formed</td>
</tr>
</tbody>
</table>

Fig.3.4 Types of solution
3.3 Characterization Techniques

Introduction

In the past years the advancement in science has taken place mainly with the discovery of new novel materials. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the filed of materials science. In this section different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation and working.

3.3.1 Differential Thermal Analysis and Thermo Gravimetric Analysis (DTA -TGA)

Thermal analysis includes a group of techniques in which physical and chemical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program in different gas environments. Modern thermal analysis instrument measures phase transition temperature, weight losses in materials, and energies of transitions, dimensional changes, modulus and viscoelastic properties. Current applications include environmental measurements, product reliability, compositional analysis, stability, chemical reactions and dynamic properties.

3.3.1 (a) Differential Thermal Analysis (DTA)

In DTA, the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature). Any phase transition that the sample undergoes will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. This differential temperature ($\Delta T$) versus the programmed temperature ($T$) at which the whole system is being changed yields the temperature of transitions and the nature of the transition such as exothermic or endothermic.
3.3.1 (b) Thermo Gravimetric Analysis (TGA):

It provides a quantitative measurement of any weight change associated with a transition. Thermogravimetry can directly record the loss or gain in weight with time or temperature due to oxide phase formation, dehydration or decomposition. Thermogravimetric curves are characteristic for a given compound or systems because of the unique sequence of physiochemical reactions, which occur over definite temperature ranges and at rates that are function of the molecular structures. Changes in weight are due to rupture or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical reactions, reaction mechanism and the intermediate and final reaction products. The usual temperature range is from ambient to 1200°C with inert or reactive atmospheres. All weight-change processes absorb or release energy and are thus measurable by DTA or DSC, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a clear distinction to be made between physical and chemical changes when the samples are subjected to both DTA and TGA tests. In general, each substance will give a DSC or DTA curve whose shape, number and position of the various endothermic and exothermic features serve as a means of qualitative and quantitative identification of the substance. When an endothermic change occurs the sample temperature lags behind the reference temperature because of the heat in the sample. The initiation point for a phase change or chemical reaction is the point at which the curve first deviates from the base line. When the transition is complete thermal diffusion brings the sample back to equilibrium quickly. The peak (or minimum) temperature indicates the temperature at which the reaction is completed. Endotherms generally represent physical rather than chemical changes. Sharp endotherms are indicative of crystalline rearrangements, fusion, or solid-state transition for relatively pure materials. Broader endotherms cover behavior ranging from dehydration, temperature-dependent phase behaviors to melting of polymers. Exothermic behavior (without
decomposition) is associated with the decrease in enthalpy of a phase or chemical system. Narrow exotherms usually indicate crystallization (ordering) of a metastable system, whether it is supercooled organic, inorganic, amorphous polymer or liquid, or annealing of stored energy resulting from mechanical stress. Broad exotherms denote chemical reactions, polymerization or curing of thermosetting resins. Exotherms with decomposition can be either narrow or broad depending on kinetics of the behavior. The area of exotherms or endotherms can be used to calculate the heat of the reaction or the heat of a phase formation.

**Specifications:**

It is SDT-2960 from TA Instruments, USA. It is capable of performing both differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) at the same time. Differential Thermal Analysis (DTA) can also be carried out using SDT 2960. It measures the heat flow and weight changes associated with transitions and reactions in material over the temperature range from RT to 1500°C. These experiments can be carried out in either of the optional environment like N2, O2, Ar or air at pre decided flow-rate (ml/min) and heating rate (°C/min). The gas-switching accessory is used to turn on and off or to switch between two different purge gases during SDT experiment. Heat-flow accuracy is equal to 1% where as DTA sensitivity is 0.001°C and that of weight is 0.1 µgm. This SDT-2960 controller is connected to PC and the special software makes the thermal analysis. It stores the data as well as runs the analysis programs [15].

**Applications:**

Melting point, crystallization behavior, glass transition temperature, thermal stability, dehydration, oxidation, phase-transition, specific heat, reaction kinetics etc can be determined.

### 3.3.2 X-ray Diffraction technique (XRD)

X-ray diffraction is a very powerful and suitable technique for characterizing the microstructure of thin films. It is non-destructive, non-contact and provides useful information, such as presence and composition of phases, film thickness, grain size and orientation and strain state. The basic principles of
X-ray diffraction are found in textbooks e.g. by Buerger [16], Klug and Alexander [17], Cullity [18], Tayler [19], Guinier [20], Barrett and Massalski [21].

Fig.3.5 shows the Schematics of X-ray diffractometer. Diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg’s law and is given as

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

where,

- \( d \) = interplaner spacing
- \( \theta \) = diffraction angle
- \( \lambda \) = wavelength of x-ray
- \( n \) = order of diffraction

In crystalline solids the atoms are ordered in particular repeated pattern referred as unit cell with its interatomic spacing comparable to wave length of x-rays (0.5 to 2.5Å). Hence crystals are the best gratings for the diffraction of x-rays. The directions of diffracted x-rays give information about the atomic arrangements and hence the crystal structure and phase formation can be confirmed by x-ray diffraction studies.
The way of satisfying Bragg’s condition is devised and this can be done by continuously varying either $\lambda$ or $\theta$ during the experiment. The way, in which these quantities are varied, distinguish the three main diffraction methods and tabulated in table 3.3.

**Table 3.3 X-ray diffraction methods.**

<table>
<thead>
<tr>
<th>Method</th>
<th>$\lambda$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laue Method</td>
<td>Variable</td>
<td>Fixed</td>
</tr>
<tr>
<td>Rotating crystal Method</td>
<td>Fixed</td>
<td>Variable (in part)</td>
</tr>
<tr>
<td>Powder Method</td>
<td>Fixed</td>
<td>Variable</td>
</tr>
</tbody>
</table>

In powder method the crystal to be examined is reduced to a fine powder and placed in a beam of a monochromatic x-rays. Each particle of the powder is the tiny crystal, or assemblage of smaller crystals, oriented at random with respect to incident beam. Some of the crystals will be correctly oriented so that their (100) planes, for example, can reflect the incident beam. Other crystals will be correctly oriented for (110) reflections and so on. The result is that every set of lattice planes will be capable of reflection. This is the principle of a powder diffractometer.

Ideally, according to Bragg’s law, for the particular $d$ value, the constructive interference of x-rays should occur only at particular $\theta$ value i.e Bragg’s angle and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum there.

**Identification of Phases**

From the $d$-spacings, phases can be identified in a film using the standard JCPDS powder diffraction file and the reflections can be indexed with Miller indices.

However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at $\theta \pm d\theta$, which broadens the peak corresponding to diffracted beam in proportion to the size of the tiny crystal.
This can be used to calculate the particle size. The relation for the same is
given by Debye Scherrer and formulated [19] as,

$$t = \frac{0.9\lambda}{\beta \cos \theta_B} \quad \text{(3.6)}$$

where, $t =$ particle size, $\theta_B =$ diffraction angle, $\lambda =$wavelength of x-rays and $\beta$
line broadening at Full Width at Half Maxima (FWHM).

Further, the powder diffractometer can also be used for x-ray diffraction
from thin films. Epitaxial or polycrystalline (may or may not be oriented) thin
films can be considered as single crystal or powder (crystals or assembly of
crystals spread on substrate) respectively. Hence, a typical epitaxial or
oriented film may not show all corresponding reflections and show only few
reflections for example say, a c-axis oriented film will show only (hkl) for which
h and k indices are zero and l is non zero. However, these hidden peaks can
be detected by small angle x-ray diffraction technique.

### 3.3.3 Scanning Electron Microscopy (SEM)

Interaction of electrons with elements is well understood and has been
extensively used for characterizing the materials. As the electrons can be
focused to micron or sub-micron size, it is well suited for analyzing sub-micron
sized areas or features. When an electron strikes the atom, variety of
interaction products are evolved. Fig. 3.6 illustrates these various products
and their use to obtain the various kinds of information about the sample.
Scattering of electron from the electrons of the atom results into production of
backscattered electrons and secondary electrons. Electron may get
transmitted through the sample if it is thin. Primary electrons with sufficient
energy may knock out the electron from the inner shells of atom and the
excited atom may relax with the liberation of Auger electrons or X-ray
photons. All these interactions carry information about the sample. Scanning
electron microscope is an instrument that uses electron beams to observe the
morphology of a sample at higher magnification, higher resolution and depth
of focus. Of these, backscattered electrons, secondary electrons and
transmitted electrons give information about the microstructure of the sample.
Auger electron, ejected electrons and x-rays are energies specific to the
element from which they are coming. These characteristic signals give information about the chemical identification and composition of the sample.

Fig. 3.6 Variety of interaction products evolved due to interaction of electron beam and sample.

**Principle of Scanning Electron Microscope**

A well-focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM application, their intensity being dependent on the atomic number of the host atoms. Each may be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube. To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the C.R.T. beam in synchronization with this. The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor C.R.T. screen. Change in brightness represents change of a particular property within the scanned area of the specimen [21]. The ray diagram of scanning electron microscope is shown in Fig.3.7.
Interaction of energetic electron beam with solid surface leads to several signals like elastically scattered electrons (i.e., change of direction without change of energy) from the coulomb field of the nucleus whereas some others includes inelastically scattered electrons (with change of energy) from the electrons of the host atoms giving rise secondary electrons, Auger electrons and x-rays characteristics to host lattice. The secondary electrons (signal from approximately top 100 Å) are used to get contrast from surface morphology.

The scattering cross section for back-scattered electrons is given as [22],

\[
Q = 16.2 \times 10^{-30} \left( \frac{Z}{E} \right)^2 \cot \left( \frac{\phi}{2} \right) \quad \text{(3.7)}
\]
where, Z is atomic number and E is electric field.

Here the cross-section is proportional to $Z^2$. Hence, the back-scattered electrons are used for the Z contrast or for compositional mapping.

### 3.3.4 Field Emission Scanning Electron Microscope (FESEM)

**FESEM History and Principle:**

FESEM is the acronym for Field Emission Scanning Electron Microscope. It was Ernest Ruska (1906 - 1987) whom in his PhD. thesis mentioned the potential for electrons to be used in a microscope. In 1933 Ruska and Knoll constructed the first electron microscope and in 1935 Knoll wrote the first work describing the concept of a SEM. In 1938 Von Ardenne built a scanning transmission microscope (STEM) adding coils to a transmission electron microscope. The first SEM used to study a solid surface was described by Zworykin et al (1942) working for the RCA laboratories in the United States. As a practice in the early days the gun was located in the bottom so the specimen chamber and was high enough for the operator but the specimen might fall down the column. A resolution of 50 nm was achieved with this microscope. The first micrographs showing the striking three-dimensional imaging capability were obtained in Cambridge at the Engineering Department in 1952 by Dennis McMullan who was continuing the work by Ken Sander (both under C. W. Oatley supervision). The next important step was also in Cambridge when Oatley improved the secondary electron detector by adding a scintillator to convert electrons to photons, and let the way for improvement in signal to noise ratio.

Nowadays, three-dimensional features can be observed due to the large Depth of Field available in the FESEM. The addition of energy dispersive X-ray detector combined with digital image processing is a powerful tool in the study of materials, allowing good chemical analysis of the material. The FESEM is a major tool in materials science research and development.
**Principle:**

Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through Electromagnetic Lenses, focusing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. The ray diagram of Field Emission Scanning Electron Microscope is shown in Fig.3.8. And the ray diagram of emission of different types of electrons during scanning is shown in fig.3.9.

![Fig.3.8 The ray diagram of Field Emission Scanning Electron Microscope](image-url)
Basic Concepts

Vacuum

The FESEM can be classified as a high vacuum instrument (less than $1 \times 10^{-7}$ Pa in the ions pumps 1 and 2). The vacuum allows electron movement along the column without scattering and helps prevent discharges inside the instrument. The vacuum design is a function of the electron source due to its influence on the cathode emitter lifetime.

Field Emission Source

The function of the electron gun is to provide a large and stable current in a small beam. There are two classes of emission source: thermionic emitter and field emitter. Emitter type is the main difference between the Scanning Electron Microscope (SEM) and the Field Emission Scanning Electron Microscope (FESEM). Thermionic Emitters use electrical current to heat up a filament; the two most common materials used for filaments are Tungsten (W) and Lanthanum Hexaboride (LaB$_6$). When the heat is enough to overcome the work function of the filament material, the electrons can escape from the material. Thermionic sources have relatively low brightness, evaporation of cathode material and thermal drift during operation. Field Emission is one way of generating electrons that avoids these problems. A Field Emission Source
(FES); also called a cold cathode field emitter, does not heat the filament. The emission is reached by placing the filament in a huge electrical potential gradient. The FES is usually a wire of Tungsten (W) fashioned into a sharp point. The significance of the small tip radius (~ 100 nm) is that an electric field can be concentrated to an extreme level, becoming so big that the work function of the material is lowered and electrons can leave the cathode. FESEM uses Field Emission Source producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM). The FESEM S-800 has two anodes for electrostatic focusing. A voltage (0 ~6.3 KV) between the field emission tip and the first anode, called the extraction voltage, controls the current emission (1 ~ 20 mA). A voltage (1 ~ 30KV), called the accelerating voltage, between the cathode and the second anode increases the beam energy and determines the velocity at which the electrons move into the column. This voltage combined with the beam diameter determines the resolution (capacity to resolves two closely spaced point as two separates entities). As voltage increases, better point-to-point resolution can be reached.

**Electromagnetic lenses**

To resolves a feature on the specimen surface, the beam diameter must be smaller than the feature (still containing high current density). Therefore is necessary to condense the electron beam. To assist in the demagnification of the beam, electromagnetic lenses are employed. Since, the cross over diameter in the Field Emission Source is smaller, a lower level of the beam condensation is necessary to have a probe useful for image processing. This makes the FESEM the highest resolution instrument. Aperture Variable apertures are used to refine the beam. Increases in the objective aperture size cause a drop in the irradiation current. Small objective aperture sizes will produce better resolution, good depth of field and minimal charging. It is the responsibility of the user to choose the correct aperture size. Work Distance

The objective lenses can focus the probe at various specimen working distances (the Z axis from the lenses to the specimen surface). Long working distance and small aperture shown an image that appears in focus over a large change in Z. Depth of Field depth of Field is important in routine
microscopy and represents the ability to maintain the focus even with large changes in specimen topography. Long working distance and small aperture yields images that appear in focus over a large change in Z-axis. A common practice is to select the current in the objective lenses and move the specimen vertically until it becomes in focus. The FESEM capability must often used in routine microscopy and represents the ability. Long working distance and small aperture yields images that appear in focus over a large change in Z-axis. Select the current in the objective lenses and move the specimen vertically until it becomes in focus.

**Electron beam and Specimen interaction**

The specimen and the electron beam interact in both elastic and inelastic fashion giving different types of signals. Elastic scattering events are those that do not affect the kinetic energy of the electron even when its trajectory had been affected. Inelastic scattering events are a result of the energy transference from the electron beam to the atoms in the specimen, as result the electrons have energy loss with small trajectory deviation. Some of the signals created in this way are: secondary electrons (SE), Auger electrons and X-Rays. Each of these signals gets specific information about topography, crystallography, surface characteristics, specimen composition and other properties.

**3.3.5 X-ray Photoelectron Spectroscopy (XPS)**

The foundation to electron spectroscopy was laid way back in the year 1887 when Heinrich Hertz discovered the photoelectric effect. However, it had taken more than half a century further to establish photoelectron spectroscopy as a technique. In 1950, Kai Seigbahn was reported the first successful study in photoelectron spectroscopy for which he received the Nobel Prize for Physics in 1981 [53, 54]. They coined the term Electron Spectroscopy for Chemical Analysis (ESCA). But since other methods also give chemical information, it is more commonly known as XPS today.

The term electron spectroscopy is generic and covers a large number of techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES),
electron energy lens spectroscopy (EELS) and so on. The techniques wherein monochromatic photons are used as the probing signal and the characteristic of the electrons emitted from the surface are studied, falls under the section photoelectron spectroscopy [55].

Electrons with low energies do not have the penetrability in the specimen and hence only those from atoms on the first few layers of the specimen (surface) leave the surface without losing a part of their energy. Those electrons arising from deep inside the specimen will lose part of their energy and form the background in the energy spectrum of the emitted electrons. The inelastic mean free path, (IMPF), of the electrons in a specimen depends on the energy of the electrons and the nature of the specimen. It is given by

$$\lambda = \frac{538a_A}{E_A^2 + 0.41a_A(a_AE_A)^{1/2}} \quad \text{...................}(3.8)$$

where, $E_A$ is electron energy in eV and $3$ is the volume of the atom in mm$^3$ and $\lambda$ is IMFP and is in nm.

The intensity of electrons emitted from the depth of the specimen is reduced following Beer-lamberts law and the angular distribution follows cosine law. Hence, almost 95 percent of electrons emitted from the surface is from atoms within a depth of $3\lambda$. In photoelectron spectroscopy, the depth of penetration of a probing signal is larger than that of the emitted electrons and hence the limitation on the layers analyzed is not restricted by the penetrability of the probing signal. Any species has electrons in them existing in certain states with corresponding binding energies. A measure of the binding energies leads to the identification of the species and the number of electrons associated with the energy leads to the quantification of the states and in turn of the number of electrons as a function of the binding energy in a given sample. Measurement of the kinetic energy of the electrons that are emitted from the solid will lead to the measurement of bound electron spectrum in the solid.
When a monochromatic beam of photons of energy $h\nu$ is launched on an isolated atom, the photons may get scattered elastically or inelastically. When the energy of photons is more than the binding energy $BE$, of the electron in the atom, the electron may get knocked out with kinetic energy, K.E. As the recoil energy of the atom due to the emission of electron is negligible due to the heavy mass differences between the two particles, KE may be given by,

$$KE = h\nu - BE \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.9)$$

Here, the binding energy is the ionization potential of the atom. Hence, the kinetic energy of the electron gives the binding energies of electrons in the atom. The same experiment may be extended to a solid specimen with appropriate correction for the work function, of the spectrometer.

This correction is necessary as the solid specimen is in electrical contact with the spectrometer.

**XPS Measurements**

Photoelectron spectrometer consists of a source of electromagnetic radiation, either an X-ray source or a UV source, electron kinetic energy analyzer and an electron counter all housed in an ultra high vacuum system. A schematic illustration is given in Fig. 3.10. The line width of the X-ray source should be as narrow as possible. The X-ray source could be an x-ray tube or radiations from a synchrotron. Synchrotron is an excellent source of high fluxes of x-rays whose wavelength can be tuned but not readily available. An x-ray tube with a metallic target such as aluminum operated at voltages needed to excite the K-electron will give the characteristic family of x-rays. The characteristic lines are almost a hundred times in intensity over Bremstrahlung radiation that forms the background. And hence x-ray tubes are directly used as photon sources in x-ray photoelectron spectrometers. Appropriate filter can be used to cut off other lines such as Kβ. Normally aluminum, magnesium and zirconium are used as targets in the source of radiation with energies 1486.6 eV, 1253.6 eV and 2042.4 eV respectively [56].
Different types of electron spectrometers analyze the spectrum of electrons from the specimen.

Figure 3.10 Basic components for XPS measurements.

**Applications**

The major use of XPS is for identification of compounds using energy shifts due to change in the chemical structure of the sample atoms. For example, an oxide exhibits a different spectrum than a pure element (SiO\textsubscript{2} on Si for example). Chemical compounds or elements are identified by the location of energy peaks on the undifferentiated XPS spectrum. Concentration determination is more difficult. Peak heights and peak areas can be used with appropriate correction factors to obtain concentrations but the method is primarily used for identifications [26].

**3.3.6 Fourier Transform Infrared Spectroscopy (FT-IR)**

**Introduction**

FT-IR spectroscopy is a tool for qualitative and quantitative analysis of the various chemical groups present in the material. Instead of recording the amount of energy absorbed when the frequency of the infrared (IR) light is varied (using monochromator), the IR light is guided through an interferometer. Then the Fourier transform is performed on this signal from
interferometer, which results in a spectrum similar to that from conventional infrared spectrometer.

**Working**

Infrared spectroscopy works on the principle that the chemical bonds have characteristic frequencies at which they vibrate. These resonant frequencies are dependent on the length of the bond and the masses of the atoms at either ends of it. For a diatomic molecule the natural frequency of vibration is:

\[
\omega = \left( \frac{K}{m_r} \right)^{1/2} \tag{3.10}
\]

Where, \( k \) is the force constant and \( m_r \) is the reduced mass and is given by the equation:

\[
m_r = \frac{m_1 m_2}{m_1 + m_2} \tag{3.11}
\]

When the incident IR frequency matches with the resonant frequency, absorption takes place, resulting in an absorption peak in the IR spectrum.

In a conventional IR (or “continuous wave”) spectrometer, a sample is exposed to electromagnetic radiation and the response (usually the intensity of the transmitted radiation) is monitored. The energy of the radiation is varied over the desired range and the response is plotted as a function of radiation energy (or frequency). At certain resonant frequencies characteristic of the specific sample, the radiation will be absorbed resulting in a series of peaks in the spectrum, which can then be used to identify the sample.

Instead of varying the energy of the electromagnetic radiation, Fourier Transform spectroscopy exposes the sample to a single pulse of radiation and measures the response. The resulting signal, called free induction decay, contains a rapidly decaying composite of all possible frequencies. Due to resonance by the sample, resonant frequencies will be dominant in the signal and by performing a mathematical operation called a Fourier transform on the signal the frequency response can be calculated. In this way the Fourier transform spectrometer can produce the same kind of spectrum as a conventional spectrometer, but in a much shorter time. FTIR spectrometers are cheaper than the fabrication of a monochromator. In addition measurement of single spectra is faster for the FTIR technique because the
information of all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity.

For the present work, FTIR spectrometer; Perkin Elmer Model Spectrum one was used and the ray diagram of the FTIR is shown in fig.3.11.

![Ray diagram of FT-IR Spectrometer](image)

**Fig.3.11 Ray diagram of FT-IR Spectrometer**

Studies of the spontaneous orientation of dipole moment in semiconductors are carried out with a non destructive tool of analysis by infrared spectroscopy which can give information on atomic arrangement and inter atomic forces in the crystal lattice itself. It is possible to investigate how the infrared vibrational frequencies and thus the inter-atomic forces are affected by the onset of the semiconductor states. If the two energy levels $E_1$ and $E_2$ are placed in an electromagnetic field and the difference in the energy between the two states is equal to a constant 'h' multiplied by the frequency of the incident radiation $\nu$, a transfer of energy between the molecules can occur, giving therefore $\Delta E = h\nu$. 
Where, the symbols have their usual meanings. When the $\Delta E$ is positive the molecule absorbs energy; when $\Delta E$ is negative, radiation is emitted during the energy transfer and emission spectra are obtained. When the energies are such that the equation is satisfied, a spectrum unique to the molecule under investigation is obtained. The spectrum is usually represented as a plot of the intensity Vs the frequencies and peaks occur when the condition is satisfied. Frequency ranges that can be encountered in this spectrum vary from those of ‘$\nu$’ rays, which have wavelength of about $10^{-10}$ cm to radio waves which have wavelength of $10^{10}$ cm. The most of spectroscopic investigation are carried out in a relatively small portion of spectrum close to visible light. This region includes UV, visible and IR region and is arbitrarily defined as being between wavelength of $10^{-6}$ cm and $10^{-3}$ cm. Both the atoms and molecules give rise to spectra but they differ from each other. The difference between the atomic and molecular spectra lies in the nature of energy levels involved in the transitions. In the atom, the absorption represents transition between the different allowed levels for the orbital electrons. In case of molecules, however, the atoms within the molecules vibrate and the molecule as a whole rotates and the total energy contributions are represented by the equation,

$$E_{tot} = E_{elect} + E_{vib} + E_{trans}$$ \hspace{2cm} (3.12)

Where, $E_{elect}$ is the electronic energy, $E_{vib}$ is the vibrational energy, $E_{rot}$ is the rotational energy and $E_{trans}$ is the translation energy. The separate energy levels are quantized and only certain transitions of electronic, vibrational and rotational energy are possible. Translational energy is usually sufficiently small to be ignored. The vibrational spectrum of a molecule is considered to be a unique physical property and is a characteristic of the molecule. As such the infrared spectrum can be used as a finger print for identification, in support of X-ray diffraction technique for the purpose of characterization [24].

### 3.3.7 Raman Spectroscopy

**Introduction:**

Raman spectroscopy is different from the rotational and vibrational spectroscopy considered above in that it is concern with the scattering of
radiation by the simple, rather than an absorption process. It is named after the Indian physicists who first observe it in 1928, C. V. Raman. Both rotational and vibrational spectroscopes are possible. The energy of the exciting radiation will determine which type of the transition occurs-rotational transitions are lower in energy than vibrational transitions.

In addition to this, rotational transitions are around three orders of magnitude slower than vibrational transitions. Therefore, collisions with other molecule may occur in the time in which the transition is occurring. A collision is likely to change the rotational state of the molecule, and so the definition of the spectrum obtained will destroyed. Rotational spectroscopy is therefore carried out on gases at low pressure to ensure that the time between the collisions is greater than the time for transition.

The basic set up of Raman spectrometer is shown in fig 3.12.
Note that the detector is orthogonal to the direction of the incident radiation, so as to observe only scattered light. The source needs to provide intense monochromatic radiation, and usually laser. The criteria for a molecule to be Raman active are also different to other types of spectroscopy, which required permanent magnetic dipole moment, at least for diatomic molecules. A molecule will only be Raman if the following gross selection rule is fulfilled [24].

3.3.8 Optical Absorption Studies

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is altogether considered to be due to 1) inner shell electrons 2) valence band electrons 3) free carriers including holes as well as electrons and 4) electrons bound to localized impurity centers or defects of some type. In study of the fundamental properties of some semiconductors, the absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons so that electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer the electrons from valence band to conduction band. The optical absorption spectra of semiconductors generally exhibits a sharp rise at a certain value of the incident photon energy which can be attributed to the excitation of electrons from valence to conduction band (may also involve acceptor or donor impurity levels, traps etc.). The conservation of energy and momentum must be satisfied in optical absorption process. Basically there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rose across the fundamental gap in the conduction band. However, indirect transition also involves simultaneous interaction with lattice vibration. Thus the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. The direct interband
optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Figures 3.13 (a). Hence a wave vector $k$ for electron remains unchanged in $E$-$K$ space. The optical transition is denoted by a vertical upward narrow.

![Figure 3.12 E-K diagrams showing (a) direct and (b) indirect inter-band transition.](image)

Let’s visualize a situation in Figure 3.12 (b), where interband transition takes place between different $k$-states. Since these must satisfy the momentum conservation laws. The only way such a transition can take place is through the emission or absorption of a phonon with wave vector $q$ as;

$$K' = k + K \ldots \ldots \ldots \ldots (3.13)$$

Absorption coefficient $\alpha$ for simple parabolic bands and for direct transition is given by the relation (3.14) [25].

$$\alpha = \alpha_0 \left( \frac{h \nu - E_g}{h \nu} \right)^n \ldots \ldots \ldots \ldots (3.14)$$
Where, $E_g$ is band gap energy. For allowed transition $n = 2$ and for forbidden transition $n = 3$. The band gap energy is determined by extrapolating the linear portion of the plot $(h\nu)^n$ versus $h\nu$ to the energy axis at $\alpha=0$.

### 3.3.9 Cyclic voltammetry (CV)

Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process. In cyclic voltammetry a reversible dc potential sweep (using a triangular potential waveform) was applied between working electrode (film) and counter electrode (platinum wire) and resulting current response versus a reference electrode (SCE) is measured.

![Figure 3.13 Variation of applied potential for Cyclic Voltammetry](image)

In cyclic voltammetry, on reaching $t=t_1$ the sweep direction is inverted as shown in fig.3.13 and sweep until $E_{\text{min}}$, then inverted and sweep to $E_{\text{max}}$ etc.

The important parameters involved are

- The initial Potential $E_i$
- The initial sweep direction
- The sweep rate $\nu$
- The maximum potential, $E_{\text{max}}$
- The minimum potential, $E_{\text{min}}$
- The final Potential, $E_f$
A faradic current, $I_f$, due to the electrode reaction, is registered in the relevant zone of applied potential where electrode reaction occurs. There is also a capacitive contribution: on sweeping the potential, the double layer charge changes. This contribution increases with increasing sweep rate [26]. The total current is

$$I = I_c + I_f = C_d \left( \frac{dE}{dt} \right) + I_f = vC_d + I_f \quad \text{(3.15)}$$

Thus $I_c = v$ and it can be shown that $I_f = v^2$. This means that at very high sweep rates capacitive current must be subtracted in order to obtain accurate values of the rate constant.

The applicability of Nernst equation and therefore, reversibility has to do with time allowed for the electrode to reach equilibrium. The concentration of the species at the interface depends on the mass transport of these species from bulk solution, often described by mass transfer coefficient $K_d$. A reversible reaction corresponds to the case where the kinetics of the electrode reaction is much faster than the transport. The kinetic is expressed by standard rate constant, $K_0$, which is the rate constant when $E=E^\circ$.

E- Actual potential and $E^\circ$- Formal potential [$E^\circ$- standard potential]

The kinetics of electrode reactions does not measure the rate of electron transfer itself, as this is an adiabatic process, following Frank-Condon principle, and occurs in approx $10^{-16}$ s. What it measures is the time needed for the species, once they have reached the interfacial region, to arrange themselves and their ionic atmospheres into position for electron transfer to be able to occur. According to kinetics of the reactions there are three types of reactions

1. Reversible
2. Irreversible
3. Quasi reversible

(I) Reversible system

Figure 3.14 shows a typical curve for linear sweep voltammetry recorded for reversible reaction of the type $O + ne^- \rightarrow R$. The curve can be understood in the following way. On reaching a potential where the electrode reaction begins, the current rises as in a steady state voltammogram. However, the creation of a concentration gradient and consumption of
electroactive species means that, continuing to sweep the potential, from a certain value just before the maximum value of the current, peak current, the supply of electroactive species begins to fall. Owing to depletion, the current then begins to decay, following a profile proportional to $t^{-1/2}$ which is shown in figure 3.14, similar to application of potential step. Figure 3.15 shows the typical cyclic voltammetry for reversible system.

Figure 3.14 The typical curve of Linear Sweep Voltammetry for reversible system.

Figure 3.15 The typical curve of cyclic Voltammetry for reversible system

Information as a diagnostic for linear sweep and cyclic voltammogram of reversible reactions are [26].
- $I_p \propto v^2$
- $E_p$ independent of $v$
- $E_p - E_{p/2} = 56.6/n$ mV

And for cyclic voltammetry alone
- $E_{pa} - E_{pc} = 59.0 /n$ mV
- $|I_{pa}|/I_{pc}| = 1$

Another practical factor affecting the voltammogram is the solution resistance between working and reference electrode. This resistance leads to a shift in the potential of the working electrode by $I_pR_\Omega$ where $R_\Omega$ is the resistance (uncompensated) of the solution.

(II) Irreversible system

In the case of an irreversible reaction of the type $O + ne^- \rightarrow R$. linear sweep and cyclic voltammetry lead to the same voltammetry profile, since no inverse peak appears on inverting the scan direction.

![Voltammogram for irreversible system](image)

Figure 3.16 shows a voltammogram for irreversible system. With respect to reversible system, the waves are shifted to more negative potential (reduction), $E_p$ depending on the sweep rate. The peaks are broader and lower.

(III) Quasi-reversible systems

The extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increasing separation between anodic and cathodic peaks. On increasing sweep rate, there is less time to reach equilibrium at the electrode surface; reactions, which appear as reversible at low sweep rates,
can be quasi reversible at high sweep rates. Figure 3.17 shows the effect of increasing irreversibility on the shape of cyclic voltammogram.

\[
\begin{align*}
\text{Fig. 3.17 Effect of increasing irreversibility on the shape of cyclic voltammogram.}
\end{align*}
\]

Cyclic voltammetry provides a measure of a supercapacitors charge-response. With regard to a changing voltage, and is therefore a means of evaluating capacitance. The procedure for obtaining a voltammogram is simple and requires no specialized equipment. To perform cyclic voltammetry tests a series of changing voltages at a constant sweep rate (dV/dt) is applied and the response current is recorded. An ideal capacitor with no resistance would display a rectangular shape, but most real EDLC voltammograms take the shape of a parallelogram with irregular peaks (Fig. 3.18). Prominent peaks that occur within narrow voltage windows are usually evidence of pseudocapacitive behavior. Faster sweep rates correspond to charging and discharging at higher power levels.
Fig. 3.18. Comparison of ideal and real cyclic voltammograms
References:

<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Publisher</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>G. Carcano; M. Ceriani and F. Soglio</td>
<td>Hybrid Circuits 32</td>
<td>1993</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>D. Bornside, C. Macosko, and L. Scriven</td>
<td>J. Imaging Technology 13</td>
<td>1987</td>
<td>122</td>
</tr>
<tr>
<td>7</td>
<td>T. von Karman, and Z. Angnew</td>
<td>Mathematical Mechanics</td>
<td>1921</td>
<td>233</td>
</tr>
<tr>
<td>9</td>
<td>D. Meyerhofer</td>
<td>J. Applied Physics</td>
<td>49</td>
<td>1978</td>
</tr>
<tr>
<td>11</td>
<td>P. Haaland; J. McKibben and M. Paradi</td>
<td>&quot;Fundamental Constraints on Thin Film Coatings for Flat-Panel Display Manufacturing,&quot;</td>
<td>SID</td>
<td>p. 79</td>
</tr>
<tr>
<td>14</td>
<td>B. G. Prevo, O. D. Velev</td>
<td>Langmuir 20</td>
<td>2004</td>
<td>2099</td>
</tr>
<tr>
<td>15</td>
<td>Willard, Merritt, Dean, Settle</td>
<td>Instrumental methods of analysis</td>
<td>Sixth edition</td>
<td>CBS publishers and distributors</td>
</tr>
<tr>
<td>18</td>
<td>B. D. Cullity</td>
<td>“Elements of X-ray Diffraction”, Addison Wesley, Massachusetts</td>
<td>1956</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>A. Guinier</td>
<td>“X-ray Diffraction”, Freeman, San Francisco</td>
<td>1963</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Scanning Electron Microscopy, Oliver C. Wells, McGraw Hill, Inc. USA. EDAX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>C.M.A. Brett, A. M. O. Brett</td>
<td>“ELECTROCHEMISTRY Principles, Methods, and Application”, Oxford University Press</td>
<td>1993</td>
<td></td>
</tr>
</tbody>
</table>