CHAPTER-II

Thin Film Deposition and Characterization Techniques
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CHAPTER-II
Thin Film Deposition and Characterization Techniques

2.1 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. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film [1].

Thin films can be deposited by number of physical and chemical techniques and can be classified as shown in Table 2.1. Among the methods mentioned in the Table 2.1, the chemical methods are economical and easier than that of the physical methods. Physical methods are expensive but give relatively more reliable and more reproducible results. Most of the chemical methods are cost effective, but their full potential for obtaining devise quality films has not been fully explored [2]. But there is no ideal method to prepare thin films, which will satisfy all possible requirements. Among the chemical methods, the electrodeposition technique (ED) is the most popular today because large number of conducting and semiconducting thin films can be prepared by this technique.

Electrodeposition, also known as electrochemical deposition or electocrystallization, is one of the most useful technique for preparing thin films on the surface of conducting substrate. Besides advantages such as cost effective, ease of processibility, large area deposition, relatively low temperature synthesis etc, the technique is directly related to many academic challenges in materials physics. Electrochemical technique such as cyclic voltammetry (CV) and chronoamperometry (CA) play dual roles, firstly, being
the methods for deposition and secondly, being utilized for determination of reaction mechanism [3].

Table 2.1

**Thin Film Deposition Techniques**

<table>
<thead>
<tr>
<th>PHYSICAL</th>
<th>CHEMICAL</th>
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<td>1) Glow discharge DC sputtering</td>
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<td>9) Ultrasonic (SPT)</td>
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<td>2) Resistive heating Evaporation</td>
<td>10) Polymer assisted deposition (PAD)</td>
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<td>3) Flash Evaporation</td>
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<td>4) Electron beam Evaporation</td>
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<td>5) Laser Evaporation</td>
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<td>6) Arc R. F. Heating</td>
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<td>7) R. F. Heating</td>
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<tr>
<td>1) Electro-deposition</td>
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<td>3) Electrolysis</td>
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<td>4) Anodisation</td>
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<td>5) Liquid phase Epitaxy</td>
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<td>9) Ultrasonic (SPT)</td>
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<tr>
<td>10) Polymer assisted deposition (PAD)</td>
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The electrodeposition is the simplest of the chemical methods, and it has many advantages [2] like;

1. Structurally and compositionally modulated alloys and compounds can be deposited, which are not easy to deposit with other deposition techniques.
2. In most of the cases the film deposition can be carried out at room temperature enabling to form the semiconductor junctions without interdiffusion.
3. Deposition on complex shapes is possible.
4. Toxic gaseous precursors need not to be used (unlike gas phase methods).
5. The deposition process can be controlled more accurately and easily.

Electrodeposition of metallic films has long been known and used for preparing metallic mirrors corrosion resistant surfaces, etc. During last two decades, electrodeposition has become a tool of materials technology for obtaining films of wide variety of materials including binary-ternary semiconductors, high $T_c$ superconductors, polymer films etc.

2.2. Basics of electrochemical processing

2.2.1 Mechanism of Electrodeposition

Electrodeposition is a process of depositing metal atoms on a conducting substrate by passing direct current through solution containing the metal(s) ions to be deposited. The schematic experimental setup explaining the electrodeposition is shown in figure 2.1.

The typical electrodeposition set up consists of the following components;

1. Electrolyte
2. Cathode and anode

When direct current is passed through cathode and anode, immersed in electrolyte containing the metal(s) ions, the metal ions get attracted towards the cathode, neutralized electrically by receiving electrons and get deposited on cathode. The deposition is controlled by monitoring the amount and the
rate of charge passing through the electrolyte. Thus the electrical energy is used to cause chemical change.

Figure 2.1 The schematic experimental setup explaining the electrodeposition.

2.2.2 Faraday's Laws of Electrolysis

Michael Faraday (1834) established the relationship between the electricity passed through the electrolyte and the chemical change produced in terms of solid material liberated/deposited at the electrode.

**Faraday’s first law**

"The amount of substance liberated or deposited on the electrode is proportional to the quantity of electricity passed."

Mathematically, \( W \propto Q \) where, \( W \) is the amount of substance liberated in grams, and \( Q \) is the quantity of electricity passed through electrolyte, in coulombs. If current strength \( I \) is passed for \( t \) seconds, then the quantity of electricity.

\[
\text{Quantity of electricity} = \text{Current strength} \times \text{time}
\]

\[
Q = I \times t
\]

\[
W \propto I \times t \quad \text{or} \quad W = z \times I \times t
\]
Here $z$ is the proportionality constant, known as 'Electrochemical equivalent'. It can be defined as, "The amount of substance liberated (in g) on the electrode on passing a current 1 A for 1 sec. or passing 1 coulomb of charge".

**Faraday's Second Law**

"If same quantity of electricity is passed through different electrolytes, then the amounts of substance liberated on the respective electrodes are in the ratio of their equivalent weights."

An important implication of the Faraday's second law is that the ratio of the mass of electrodeposit to its gm-equivalent weight is a constant equivalent to 1 Faraday or 96,500 Coulombs (c) or 26.3 ampere-hour (Ah).

### 2.2.3 Electrode-Electrolyte interface

The electrode-electrolyte interface plays an important role in electrodeposition process. The electrode used in electrodeposition should necessarily be a good conductor. When an electrode is immersed in the liquid electrolyte, the anisotropic forces developed at the interface, results in a new arrangement of solvent dipole and ions of the electrolyte. At the beginning, the charge comes in two phases (one electrode and other electrolyte), start accumulating at the phase boundary and giving rise to the interface, acting as a barrier to flow of charge in either direction. As the built-up grows on the two sides, the electrical forces overpower the barrier, resulting in the flow of charges. The charge flow stops when the electrochemical potential on the two sides of the interface become equal. The interfacial region thus acquires a potential gradient that acts as a barrier to the further flow of charges. The whole process occurs at about 1000 Å region at the phase boundary. The layer of charges is developed on both sides of the boundary and hence termed as an "electrical double layer."

The electrode-electrolyte interface according to Stern's model can be divided into two parts:

1. A compact double layer, known as Helmholtz double layer adjacent to the electrode, and
2. A diffuse layer known as Gouy-Chapman layer.
The Helmholtz layer

The Helmholtz double layer is a dense layer of ions stuck to the electrode. In this region the potential varies linearly with distance as shown in fig. 2.2(b). This dense layer is divided into inner and outer Helmholtz planes. The inner Helmholtz Plane (IHP) is adjacent to the electrode surface and consists of completely oriented solvent dipoles and specifically adsorbed (or contact-adsorbed) ions. The orientation of solvent dipoles depends on the specific interaction with the electrode surface as well as the electric field. Large ions with negative free energy of contact adsorption are expected to be contact adsorbed. In aqueous system, the cations react rather strongly with the water molecule, and their inner hydration sphere is retained. This limits their closest distance of approach to the electrode. They are thus separated from the electrode by approximately one or two electrolyte molecules. On the other hand, anions interact weakly with electrolyte; hence hydration sheath is not covered on them. Thus the closest distance of approach could correspond to direct contact; they can be a part of IHP. The Outer Helmholtz Plane (OHP) consists of solvated ions (usually cations) at the closest distance of approach from the electrode surface. The OHP thus consists of partly ionized electrolyte molecule dipole layers.

Bockris et al. [4] developed a model of electrode-electrolyte interface and is shown in figure 2.2(a). In presence of contact adsorbed ions, it can be seen from figure 2.2(b) that the potential distribution (\( \phi \)) changes across the double layer. The schematic of electrode immersed in electrolyte is shown in figure 2.2(c). OHP is the site at which non-specifically adsorbed ions arrive to take part in the charge transfer processes.

Gouy-Chapman layer or diffuse layer

The size of the ions forming the outer Helmholtz plane (OHP) is such that the sufficient number of them cannot neutralize the charge on the electrode. Therefore, the remaining charges are held with increasing disorder as the distance from the electrode surface increases and the electrostatic forces become weaker and dispersion by thermal motion is more effective. These less ordered charges forcing opposite to that on the electrode
constitutes the diffuse part of double layer. Thus, all the charges, which neutralize on the electrode, are held in a region between OHP and the bulk of electrolyte. The additional charges required to neutralize the total charge on the electrode forms the Gouy-Chapman layer or diffuse layer.

Figure 2.2 (a) Electrode Electrolyte Interface, (b) Potential Distribution across the double layer & (c) The schematic of electrode immersed in electrolyte
2.2.4. Steps involved in electrodeposition process

Electrodeposition of ionic species from the electrolyte occur in following successive steps (fig. 2.3)

1. Ionic transport
2. Discharge
3. Breaking of ion-ligand bond (if the bath is complexed)
4. Incorporation of adatoms on the substrate surface followed by nucleation and growth.

All above steps occur within 1–1000Å from the substrate; however each has its own region of operation. These various processes can be classified with respect to distance from the electrolyte as:

a. In the electrolyte
b. Near the electrode
c. At the electrode

![Diagram showing various stages of ion transport]

**Fig. 2.3** Approximate region in which various stages of ion transport occur leading to various steps involved in electrodeposition process.

a. Process in the electrolyte

The ions in the electrolyte can move towards the electrode under the influence of:

1. Potential gradient leading to ion drift, d\(\psi\)/dx
2. Concentration gradient leading to diffusion of ions, dc/dx
3. A density convective current, dp/dx due to consumption of ions at the electrode.

The general mathematical equation including all these processes can be written as Nernst-Planck equation,
Thin Film Deposition and Characterization Techniques

\[ j = zF \left( \frac{D_e}{RT} \frac{d\varphi}{dx} + D \frac{dc}{dx} + cv \right) \]  

[2.1]

Where, \( F \) is the Faraday's constant, \( \nu \) is the viscosity of the electrolyte, \( R \) is the gas constant and \( D \) is the diffusion coefficient. The three terms in the parenthesis respectively describe the contributions of migration, diffusion and convection processes to the mass transport towards the electrode.

b. Processes near the electrode but within electrolyte

Ionic species are normally surrounded by hydration sheath or by other complex forming ion or legand present in the electrolyte. They move together as a single entity and arrive near the electrode surface where the ion-legand system either accepts electrons from the cathode (or donates electrons to the anode). This ionic discharge occurs between 10 to 1000 Å from the electrode.

c. Processes that occur on the electrode surface

The discharged ions arrive near the electrode, where step by step they lead to the formation of a new solid phase or the growth of an electrodeposit. The atoms deposited have a tendency to form either an ordered crystalline phase or a disordered amorphous phase.

The electrodeposition formation steps of transport, discharge, nucleation, and growth are interlinked.

2.2.5. Mechanism of Ionic discharge at the Electrode

Consider a positively charged ion \( M^{z+} \) just after it has arrived at the electrolyte side of the electrode-electrolyte interface. The metallic electrode surface offers several pathways for the charge transfer between the ion and electrons of the metal [2].

1. The electron transfer can take place between the metal electrode and the ionic species at the OHP. This is therefore the prereaction site.
2. The prereaction site is the IHP
3. The charge transfer reaction between the ion at the OHP and the metal electrode is mediated via a bridging ion.
The first case is similar to the homogeneous charge transfer reaction between two reacting species in the solution. One can visualize two possible reactions for the case of charge transfer between the approaching $M^{2+}$ ion and the electron of the metal.

1. Electronation reaction,
   \[ M^{2+} + ze \rightarrow M \]
2. Deelectronation reaction
   \[ M \rightarrow M^{2+} + ze \]

2.2.6. Multi step electron transfer

In many reduction or oxidation half reactions, the oxidation state changes by value greater than one. Examples for metallic cations are $\text{Tl(III)} \rightarrow \text{Tl(II)}$, $\text{Cu(II)} \rightarrow \text{Cu(O)}$. Even single electron transfer may sometimes involve the number of steps [5]. For example, the deposition of silver from cyanide bath can be expressed by the overall reaction

\[ \text{Ag(CN)}_2^- + e^- \rightarrow \text{Ag} + 2(\text{CN})^- \]

The above reaction may consist of the steps as follows,

\[ \text{Ag(CN)}_2^- \rightarrow \text{AgCN} + \text{CN}^- \quad (\text{step I}) \]
\[ \text{AgCN} \rightarrow \text{Ag}^+ + \text{CN}^- \quad (\text{step II}) \]
\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \quad (\text{step III}) \]

Thus overall reaction involves steps for dissociation of the cyanide ion, discharge of the silver ion, and removal of the cyanide from the interfacial region. For a two electron system as shown in figure 2.4 the reaction can be represented as

\[ A + e^- \rightarrow B \]
\[ B + e^- \rightarrow C \]

Generally the electron transfer is consecutive. The kinetics of these two steps is conditioned by the medium where they occur and this will determine the type of voltammetric wave that is observed.

Three limiting cases can be distinguished as follows.

1. The second step ($B+e^- \rightarrow C$) occurs at more negative potential than first. It is seen that a one electron reduction until the applied potential is
sufficiently negative for reduction of the second electron. In other words one can have two separated voltammetric waves as shown in figure 2.4(a)

2. First step is rate determining. This case is corresponds to

\[ A + e \rightarrow B \quad \text{rate determining step (RDS)} \]
\[ B + e \rightarrow C \quad \text{fast.} \]

The form of the voltammogram is the same as for \( A + e \rightarrow B \), but the current is multiplied by 2 and the voltammogram is as shown in figure 2.4(b)

3. Second step is rate determining

This corresponds to

\[ A + e \rightarrow B \quad \text{pre-equilibrium} \]
\[ B + e \rightarrow C \quad \text{rate determining step (RDS)} \]

Due to pre-equilibrium step the voltammetric wave is steeper (figure 2.4(c)) than case 2.

Figure 2.4 Voltammogram for the reduction of species A following \( A + e \rightarrow B + e \rightarrow C \) for (a) Second step much more difficult than the first, (b) First step is rate determining second step fast, (c) First step pre-equilibrium second step rate determining
2.2.7. Pathways for the growth of an electrodeposits

The pathway for the growth can be divided into following steps (figure 2.5) [2].

- Transport (Step I): Ion in the electrolyte bulk
- Ion at the interface (Step II)
- Adatom formation and surface diffusion
- Diffusion to a growth site
- Step III (Route A): Cluster
- Step III (Route B): Formation of growth centre
- Step IV (Monolayer formation)

![Figure 2.5 Schematic representation of steps involved in electrodeposition](image)

1. Transport of ions in the electrolyte bulk towards the interface.
2. Discharge of ions reaching the electrode surface, giving rise to generation of adatoms.
3. Nucleation and growth, where again alternative routes are possible
   a. Growth assisted by surface diffusion.
   b. Growth assisted by formation of clusters and critical nuclei.
   c. Formation of monolayer and final growth of electrodeposit.

Surface defects such as steps, kinks and dislocations generally control the growth kinetics. The kinks sites and screw dislocations together sustain the growth of the electrodeposit.

2.3. Electrochemical techniques for film synthesis

2.3.1. Voltammograms

The Butler-Volmer equation predicts the exponential relationship between the current density and overpotential. Such plot is known as Tafel plot. This relationship is very useful in determining the deposition potential of the metal...
species present in the electrolyte. If the overpotential is increased, initially the
current density varies linearly, a point reached at which a small increase in
overpotential causes a large increase in the current density. This overpotential
is called decomposition potential or deposition potential of that species. When
the external potential is applied across the electrolytic cell, the equilibrium is
disturbed and the polarized interface, "double layer" is disturbed, which
causes depolarization of the interface. The curves of overpotential vs. current
density are therefore referred as voltammogram. The voltammogram besides
estimating the deposition potential are also useful in understanding the
cathodic or anodic reactions and their rates, which ultimately controls the rate
deposition of the particular species. Of all the methods available for
studying electrode processes, potential sweep methods are probably most
widely used.

**Cyclic voltammetry (CV) and linear sweep techniques (LSV)**

The basic scheme involves the application of a potential sweep to the
working electrode with respect to a reference electrode [5]. In linear sweep
voltammetry the potential scan is done only in one direction, stopping at
chosen value, $E_f$ for example at $t=t_1$ as shown in figure 2.6

![Variation of applied potential for Cyclic Voltammetry and Linear Sweep Voltammetry](image)

In cyclic voltammetry, on reaching $t=t_1$ the sweep direction is inverted as
shown in figure 2.6 and sweep until $E_{min}$, then inverted and sweep to $E_{max}$ etc.
The important parameters involved are

- The initial Potential $E_i$
The initial sweep direction
- The sweep rate $v$
- 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. The total current is

$$I = I_c + I_f = C_d \frac{dE}{dt} + I_f = vC_d + I_f \quad \cdots \quad (2.2)$$

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 $E=E^{eq}$

$E$- Actual potential and $E^{eq}$- Formal potential [$E^0$- 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
**Reversible system**

Figure 2.7 shows a typical curve for linear sweep voltammetry recorded for reversible reaction of the type $0 + ne \rightarrow R$. 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 fig.2.10, similar to application of potential step. Figure 2.8 shows the typical cyclic voltammetry for reversible system.

![Figure 2.7](image)

**Figure 2.7. The typical curve of Linear Sweep Voltammetry for reversible system.**

![Figure 2.8](image)

**Figure 2.8 The typical curve of Cyclic Voltammetry for reversible system**
Information as a diagnostic for linear sweep and cyclic voltammogram of reversible reactions are [5]

- \( I_p \alpha v^2 \)
- \( E_p \) 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 \( I_p R_\Omega \) where \( R_\Omega \) is the resistance (uncompensated) of the solution.

**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.

![Normalized current](image)

**Figure 2.9 Voltammogram for irreversible system**

Figure 2.9 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.
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 2.10 shows the effect of increasing irreversibility on the shape of cyclic voltammogram.

Figure 2.10 The effect of increasing irreversibility on the shape of cyclic voltammogram.

2.3.2 Pulse techniques

A step in applied potential or current [5, 6] represents an instantaneous alteration to the electrochemical system. Potential and current step give complimentary information because, where as in first case the potential causes a brief capacitive current peak, in second case a part of the applied current, the value of which probably vary with time, is always used to charge the double layer as the potential changes.

Potential Step: Chronoamperometry (C.A.)

The study of variation of the current response with time under potentiostatic condition is chronoamperometry. The current resulting from a potential step from a value of the potential where there is no electrode reaction to one corresponding to the mass transport limited current was calculated for simple system \( \text{O} + n\text{e}^- \rightarrow \text{R} \), where only \( \text{O} \) or only \( \text{R} \) is initially
present. This is the faradic current, $I_f$, since it is due only to faradic electrode process (only electron transfer).

The typical experiment leading to diffusion limited current involves application of a potential step at $t=0$ to an electrode, in a solution containing either oxidized or reduced species, from a value where there is no electrode reaction to the value where all electroactive species that reach the electrode react, as shown in figure 2.11. This gives rise to diffusion limited current whose value varies with time. This current can be expressed by equation

$$I_f(t) = \frac{nFAD^{1/2}c_0}{(nt)^{3/2}} \quad \ldots \quad (2.3)$$

This is known as Cottrell equation [7]. It indicates the decrease of the current with $t^{1/2}$, which is shown in figure 2.12.

---

**Figure 2.11** Potential step applied in a typical Chronoamperometry study

**Figure 2.12** variation of current with time according to Cottrell equation
2.3.3. Electrochemical Quartz Crystal Microbalance (EQCM)

A computerized time resolved electrochemical quartz crystal microbalance (figure 2.13.) used for the electrochemical applications such as for the determination of amount of mass deposited on to the electrode surface. The system contains a quartz crystal oscillator; fast digital function generator, data acquisition system and potentiostate. The QCM is integrated with potentiostate. The frequency signals of the QCM subtracted from a standard reference frequency during the potential scan. System gives concurrent shift in the frequency of the quartz crystal electrode with applied voltage. According to EQCM theory [7,8], such a shift is proportional to an increase of mass on the electrode surface according to equation 2.4.

\[
\Delta f = \frac{-2f_0^2}{\sqrt{f_0^2 - \Delta m \rho_q \mu_q}} \quad (2.4)
\]

where \(f_0\) is resonant frequency (Hz), \(\Delta f\) is Frequency change (Hz), \(\Delta m\) is mass change (g), \(\rho_q\) is the density of quartz (\(\rho_q = 2.648\ \text{g/cm}^3\)), and \(\mu_q\) is shear modulus of quartz (\(\mu_q = 2.947\times10^{11}\ \text{g/cm.s}^2\)). The above relationship shows that, an increase in mass leads to a decrease in frequency, and that the magnitude of the change in frequency is directly proportional to the mass change. This is the basis for quantitative measurements of mass changes using the EQCM.

Figure 2.13. Schematic of electrochemical quartz crystal microbalance
2.4. Characterization Techniques

2.4.1. Introduction

Characterization is an important step in the development of superior materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, microstructural 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 field 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.

2.4.2. Structural and morphological characterizations:

In general way, the characterization of materials can be classified into several major headings like phase (compositional and structural), physical and chemical properties. The characterization of physical properties of a material is mostly pertaining to electrical, magnetic, dielectric and optical properties. However, prior to any study of a solid-state materials main emphasis are paid on the phase and structural characterizations along with morphological and topographical characterizations, using:

1. X-ray Diffraction Technique (XRD)
2. Scanning Electron Microscopy (SEM)
3. Energy Dispersive X-ray Analysis (EDS)
4. Atomic Force Microscopy (AFM)

The details of these techniques are discussed in the following sections.

2.4.4A (a) X-ray Diffraction technique (XRD):

X-ray diffraction is a very powerful and suitable technique for characterizing structure 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 classic textbooks e.g. by Buerger [9], Klug and Alexander [10], Cullity [11], Tayler [12], Guinier [13], Barrett and Massalski [14].
Figure 2.14 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,

$$2d \sin \theta = n\lambda \quad \ldots \ldots \ldots (2.5)$$

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 2.5 Å). 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 2.2.
Table 2.2 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 \( d \)-spacing, 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 \( 0 \pm d \theta \), 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 [12] as,

\[
t = \frac{0.9 \lambda}{\beta \cos \theta_b} \quad \ldots \ldots \quad (2.6)
\]

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.

**Instrument specifications:**

- **Model:** PW 3710/ PW1710 PHILIPS, Holland
- **Angle (2θ):** 10° to 100°
- **Target:** Cu.
- **Normal mode:** PW3710/PW 1710 APD Controller.
- **Specimen:** Fine Powder (quantity approximately 1 cm³)
- **Applications:** Crystallographic studies, Quantitative analysis of organic, inorganic minerals, metals and alloys.

### 2.4.4A (b) Scanning Electron Microscopy (SEM)

Interaction of electrons with elements is well understood and has been extensively used for characterizing of 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. Figure 2.15 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.

**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.

![Electron Beam Diagram](image)

**Figure 2.15.** Variety of interaction products evolved due to interaction of electron beam and sample
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 [15]. The ray diagram of scanning electron microscope is shown in Figure 2.16.

The scattering cross section for back-scattered electrons is given as [16],

\[ Q = 16.2 \times 10^{-30} \left( \frac{Z^2}{E} \right) \cot \left( \frac{\phi}{2} \right) \]  \hspace{1cm} (2.7)

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.
2.4.4A. (c) Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) probes the surface of a sample with a sharp tip, a couple of microns long often less than 100 Å in diameter [14]. The tip is located at the free end of a cantilever, which is 100 to 200 µm long. The forces between the tip and sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as tip is scanned over the sample or the sample is scanned under the tip. The measured cantilever deflection allows a computer to generate a map or surface topography [17].
Several forces typically contribute to the deflection of an AFM cantilever. AFM operates by measuring the attractive or repulsive forces between a tip and the sample. The forces most commonly associated with atomic force microscopy are interatomic force called the Van der Waals force. The dependence of the Van der Waals force upon the distance between the tip and the sample is shown in figure 2.17. The two distance regimes are labeled in the figure are (a) the contact regime and (b) non-contact regime.

In the contact regime, the cantilever is held at a distance less than few angstroms from the sample surface, and the inter-atomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held at a distance of the order of tens to hundred of angstroms from the sample surface, and the inter-atomic force between the cantilever and sample is attractive. Figure 2.18 shows schematic diagram of AFM.

In principle, AFM resembles the record player as well as the surface profilometer. However, AFM incorporates a number of refinements that enable it to achieve atomic-scale resolution: Sensitive detection, flexible cantilever, sharp tips, high-resolution tip-sample positioning and Force feedback.

Figure 2.17 Inter-atomic force versus distance curve for the operation of AFM
Figure 2.18. Schematic diagram of Atomic Force Microscope (AFM)

2.4.4A. (d) 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 Siegbahn was reported the first successful study in photoelectron spectroscopy for which he received the Nobel Prize for Physics in 1981 [18, 19]. 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 [20].
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

\[ \lambda = 538a_A / E_A^2 + 0.41a_A (a_A E_A)^{1/2} \]  

(2.8)

where, \( E_A \) is electron energy in eV and \( a_A \) 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-lambert's 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 \( B_E \), 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,

\[ \text{KE} = h\nu - B_E \]  

(2.9)
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.

\[ KE = h\nu - BE \]  \hspace{1cm} (2.10)

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

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 figure 2.19. 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 Bremsstrahlung 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 K\textsubscript{p}. 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 [23]. Different types of electron spectrometers analyze the spectrum of electrons from the specimen.
Figure 2.19. 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$_2$ 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.

2.4.2A. (e) 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 rise 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 2.20 (a). Hence a wave vector k for electron remains unchanged in E-K space. The optical transition is denoted by a vertical upward narrow. Absorption coefficient α for simple parabolic bands and for direct transition is given by the relation (10) [21,22].

\[ \alpha = \alpha_0 \frac{(hv - E_g)^n}{hv} \]  

where \( E_g \) is the separation between bottom of the conduction and top of the valence band, \( hv \) is the photon energy, \( n \) is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and \( \alpha_0 \) is a constant depending upon the transition probability for direct transition. For allowed direct transitions \( n = 1/2 \) and for allowed indirect transition \( n = 2 \). Thus if the plot of \( (\alpha hv)^2 \) against \( hv \) is linear then the transition is direct allowed. The band gap energy \( E_g \) is determined by extrapolating the linear portion of the curve to the energy axis at \( = 0 \).
Let's visualize a situation in Figure 2.20 (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:

\[
K' \pm q = k + K 
\]

(2.12)

The transition defined by equation (2.9) is termed indirect transition. For indirect transition equation (2.10) prevails.

\[
\alpha = \alpha_0 \frac{(hv - E_g)^n}{hv} 
\]

(2.13)

where, \( E_g = E_g' \pm E_p \), \( E_g \) is indirect band gap energy and \( E_p \) is the phonon 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 \((hv)^n\) versus \( hv \) to the energy axis at \( \alpha = 0 \).

2.4.2A (f) Thickness Measurements

Sample thicknesses were measured using fully computerized AMBIOS Make XP-1 surface profiler with 1 Å vertical resolution. With a low force stylus mechanism that produces stylus loads as small as 0.05 milligrams, the
XP-1 is ideally suited for measurement of soft or delicate films. The unique high resolution optical deflection sensor allows extremely repeatable step height measurements. For instance, measure a 1 micron film ten times in the same location and the standard deviation of the ten measurements will be 10 angstroms or less. The 140mm diameter scan stage and 20mm maximum sample height accommodates many different sample sizes and shapes. Simply position your sample on the scan stage: select a scan recipe, click the scan button, and as soon as the scan is complete, your surface data is immediately available for analysis. With 25 ASME B46 1-1995 defined calculations of surface roughness, waviness, and other features; the XP-1 incorporates all of the required surface measurements for the researcher.

2.4.2A. (g) Photoluminescence (PL)

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process [23].

In order to measure photoluminescence of semiconductors, there are various requirements: (a) a stable, powerful monochromatic light source, (b) optics to focus light on the sample, (c) sample holder, (d) collection optics, (e) monochromator and (f) detector for spectral analysis as shown in figure 21.
Applications

PL can be used to identify surface, interface, and impurity levels and to gauge alloy disorder and interface roughness. The intensity of the PL signal provides information on the quality of surfaces and interfaces. Under pulsed excitation, the transient PL intensity yields the lifetime of nonequilibrium interface and bulk states. Variation of the PL intensity under an applied bias can be used to map the electric field at the surface of a sample. In addition, thermally activated processes cause changes in PL intensity with temperature.

Limitations

The fundamental limitation of PL analysis is its reliance on radiative events. Materials with poor radiative efficiency, such as low-quality indirect band gap semiconductors, are difficult to study via ordinary PL. Similarly, identification of impurity and defect states depends on their optical activity. Although PL is a very sensitive probe of radiative levels, one must rely on secondary evidence to study states that couple weakly with light.

2.4.2A. (h) Transmission Electron Microscope (TEM)

The conventional electron microscopy is nowadays called TEM (transmission electron microscopy). The ray of electrons is produced by a pin-shaped cathode heated up by current. The electrons are vacuumed up by a high voltage at the anode. The acceleration voltage is between 50 and 150
kV. The higher it is, the shorter are the electron waves and the higher is the power of resolution. But this factor is hardly ever limiting. The power of resolution of electron microscopy is usually restrained by the quality of the lens-systems and especially by the technique with which the preparation has been achieved. Modern gadgets have powers of resolution that range from 0.2 - 0.3 nm. The useful resolution is therefore around 300,000 x.

The ray diagram of TEM is shown in figure 22. The accelerated ray of electrons passes a drill-hole at the bottom of the anode. The lens-systems consist of electronic coils generating an electromagnetic field. The ray is first focused by a condenser. It then passes through the object, where it is partially deflected. The degree of deflection depends on the electron density of the object. The greater the mass of the atoms, the greater is the degree of deflection. After passing the object the scattered electrons are collected by an objective. Thereby an image is formed, that is subsequently enlarged by an additional lens-system (called projective with electron microscopes). Thus the formed image is made visible on a fluorescent screen or it is documented on photographic material. Photos taken with electron microscopes are always black and white.

Applications

The TEM is used heavily in both material science/metallurgy and the biological sciences. It is possible to determine the position of defects and to determine the type of defect present. The quantitative interpretation of the contrast shown in lattice images is possible. Crystal structure can also be investigated by High Resolution Transmission Electron Microscopy (HRTEM), also known as phase contrast imaging as the images are formed due to differences in phase of electron waves scattered through a thin specimen. Typical biological applications include tomographic reconstructions of small cells or thin sections of larger cells and 3-D reconstructions of individual molecules via Single Particle Reconstruction.

Limitations

There are a number of drawbacks to the TEM technique. Many materials require extensive sample preparation to produce a sample thin
enough to be electron transparent, which makes TEM analysis a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. Also the field of view is relatively small, raising the possibility that the region analysed may not be characteristic of the whole sample. There is potential that the sample may be damaged by the electron beam, particularly in the case of biological materials.

Figure 2.22. Ray diagram of Transmission Electron Microscope
References

5. Christopher M.A. Brett and Ana Maria Oliveira Brett, "ELECTROCHEMISTRY Principles, Methods, and Application", Oxford University Press, 1993