Chapter – II

Thin Film Deposition and Characterization Techniques

Part – A

Thin film deposition techniques

2.A.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 [1,2]. Modern technology requires thin films for different applications.

Thin films are thin material layers ranging from fractions of a nanometer to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. Some work is being done with ferromagnetic thin films as well for use as computer memory. Ceramic thin films are also in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools may extend the life of these items by several orders of magnitude. The engineering of thin films is complicated by the fact that their physics is in some cases not well understood. In particular, the problem of rewetting may be hard to solve, as there is ongoing debate and research into some processes by which this may occur.So a thin film is defined as a low dimensional material created by condensing, one by one, atomic/molecular/ionic

species of matter. The thickness is typically less than several microns[3].

Thin - less than about one micron (10,000 A^0, 1000 nm)

Film - layer of material on surface. If no substrate it is foil.

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analysed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are: microelectronic devices, magnetic thin films in recording devices, magnetic sensors, gas sensor, A. R. coating, photoconductors, IR detectors, interference filters, solar cells, polarisers, temperature controller in satellite, super conducting films, anticorrosive and decorative coatings[4].

Thin film technology is a relatively young and ever growing field in the physical &chemical sciences which is confluence of materials science, surface science, applied physics, applied chemistry. Thin film technology has its objectives in the provision for scientific bases for the methods & materials used in thin film electronics.Additionally; it provides a sufficient data in the area of applications to permit for understanding of those aspects of the subject that might still be termed an ‘art’. Thin film of metals were probably first prepared in a systematic manner by Michael Faraday, using electrochemical methods. Thin films have a no. of applications in various fields.Few of them are A.R.coatings,solar energy converters,transistors,coating, technology, interference filters, polarisers,narrow band filters,solar cells,photoconductors,IR detectors, waveguide coatings ,temp. Controlled aerospace devices, photothermal solar coatings (such as black chrome, Nickel, cobalt etc.) Magnetic films in recording device, superconducting films, microelectronic devices, diamond films, and high coatings are used for engineering applications, corrosion resistive thin film coatings and decorative thin film coatings etc. The enormous flexibility provided by the thin film growth processes allows the fabrication of desired geometrical, topographical, physically crystallographic & metallurgical microstructures into two or less dimensions and to study the structure sensitive properties[5].

2.A.2 Practical applications of thin films

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of microminiaturisation made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin films[6].

Secondly as well as generating ideas for new devices, fundamental research has led to a dramatic improvement in understanding of thin films and surfaces. This in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties[7].

The cleanliness and nature of the substrate, the deposition conditions, post deposition heat treatment and passivation are vital process variables in thin film fabrication. Therefore, prior to this improvement in our understanding of thin films, it had not really been possible to apply them to real devices.

Thirdly, much of the finance for early thin film research originated from space and defence programmes to which the device cost is less important than its lightweight and other advantages, the major applications of thin film technology are not now exclusively in these areas but rather often lie in the domestic sector in which low cost is essential [8,9].

Thin film materials have already been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto-optic discs, lithography, microelectromechanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technologies[10].

2.A.3. Preparation techniques for thin film deposition

The properties of thin films are extremely sensitive to the method of preparation, several techniques have been developed (Depending on the desired film properties) for the deposition of the thin films of the metals,alloys,ceramic,polymer and superconductors on a variety of the substrate materials.Each methods has it’s own merits & demerits and of course no one technique can deposit the thin films covering all the desired aspects such as cost of equipments, deposition conditions & nature of the substrate material etc. The vast varieties of thin film materials, their deposition, processing and fabrication techniques, spectroscopic characterization, optical characterization probes, physical properties, and structure-property relationships are the key features of such devices and basis of thin film technologies. Underlying the performance and economics of thin film components are the manufacturing techniques that are used to produce the devices.

Physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on a specific chemical reaction [11]. Thus chemical reactions may depend on thermal effects as in vapour phase deposition and thermal growth. However, in all these cases a definite chemical reaction is required to obtain the final film. When one seeks to classify deposition of films by chemical methods, one finds that are available, into two more classes. The first of these classes is concerned with the chemical formation of the film from medium, and typical methods involved are electroplating, chemical reduction plating and vapour phase deposition. A second class is that of formation of this film from the precursor ingradients e.g. anodisation, gaseous anodisation, thermal growth, sputtering ion beam implantation, CVD, MOCVD and vacuum evaporation.

The methods summarized under the classifications given are often capable of producing films defined as thin films, i.e. 1 µm or less and films defined as thick films, i.e. 1 µm or more. However, there are certain techniques which are only capable of producing thick films and these include screen printing, glazing, electrophoretic deposition, flame spraying and painting.Thin film deposition techniques are broadly classified under two heading as listed in Table 2.A.1 [12].

2.A.3. 1 Physical techniques

A) Physical Vapour Deposition (PVD)

PVD processes proceed along the following sequence of steps:

a) The solid material to be deposited is physically converted to vapour phase;

b) The vapour phase is transported across a region of reduced pressure from the source to the substrate;

c) The vapour condenses on the substrate to form the thin film.

The conversion from solid to vapour phase is done through physical dislodgement of surface atoms by addition of heat in evaporation deposition or by momentum transfer in sputter deposition. The third category of PVD technique is the group of so called augmented energy techniques including ion, plasma or laser assisted depositions [13,14].

B). Evaporation

Evaporation or sublimation techniques are widely used for the preparation of thin layers. A very large number of materials can be evaporated and, if the evaporation is undertaken in vacuum system, the evaporation temperature will be very considerably reduced, the amount of impurities in the growing layer will be minimised. In order to evaporate materials in a vacuum, a vapour source is required that will support the evaporant and supply the heat of vaporisation while allowing the charge of evaporant to reach a temperature sufficiently high to produce the desire vapour pressure, and hence rate of evaporation, without reacting chemically with the evaporant. To avoid contamination of the evaporant and hence of growing film, the support material itself must have a negligible vapour pressure and dissociation temperature of the operating temperature [15,16].

C). Sputtering

If a surface of target material is bombarded with energetic particles, it is possible to cause ejection of the surface atom: this is the process known as sputtering. The ejected atoms can be condensed on to a substrate to form a thin film. This method has various advantages over normal evaporation techniques in which no container contamination will occur. It is also possible to deposit alloy films which retain the composition of the parent target material. DC sputtering, radio frequency sputtering and magnetron sputtering methods are the oldest types of sputtering used. High pressure oxygen sputtering and facing target sputtering are the two new methods introduced for deposition of thin films for applications in superconducting and magnetic films[17].

D). Ion plating

In this atomistic, essentially sputter-deposition process the substrate is subjected to a flux of high energy ions, sufficient to cause appreciable sputtering before and during film deposition. The advantages of physical methods are laid in dry processing, high purity and cleanliness, compatibility with semiconductor integrated circuit processing and epitaxial film growth. However, there are certain disadvantages such as slow deposition rates, difficult stoichiometry control, high temperature post deposition annealing often required for crystallization and high capital expenditure.

2.A.3. 2*. Chemical and electrochemical techniques*

A] Electro deposition

It is a process of depositing a substance on the electrode by electrolysis, the chemical changes being brought about the passage of a current through an electrolyte. The phenomenon of electrolysis is governed by the Faraday’s laws, when a metal electrode is immersed in a solution containing ions of that metal, a dynamic equilibrium M. M_n + x (M- Metal atom & X =S, Se, Te) is set up.

The electrode gains a certain charge on itself which attracts oppositely charged ions & molecules holding them at electrode / electrolyte interface. A double layer consisting of an inner layer of water molecules interposed by preferentially adsorbed ions & outer layer of the charge opposite to that of the electrode is formed. During deposition ions reach the electrode is formed. During deposition ions reach the electrode surface, stabilizes on it, release their ligands, release their charges and undergo electrochemical reaction. The rapid layer depletion of the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk of the electrolyte. The factors influencing the electro deposition process are, I] current density, I] bath composition, iii] pH of the electrolyte, IV] Temp.of the bath v] agitation VI] electrode shape[18].

Thin Film Deposition Techniques

PHYSICAL

Sputtering	**Evaporation**
1)Glow discharge DC sputtering	**1)**Vacuum evaporation
2) Triode sputtering	**2)** Resistive heating
3) Getter sputtering	**3)** Flash evaporation
4)Radio Frequency sputtering	**4)** Electron beam evaporation
5) Magnetron sputtering	**5)** Laser evaporation
6) Ion Beam sputtering	
7)A.C. Sputtering	**6)** Arc evaporation
	7)Radio frequency (RF) heating

CHEMICAL

Gas Phase	**Liquid Phase**
1)Chemical vapour deposition	**1)** Electro-deposition
2)Laser Chemical vapour deposition	**2)Chemical Bath Deposition (CBD)**
3)Photo-chemical vapour deposition	**3)** Electro less deposition
4)Plasma enhanced vapour deposition	**4)** Anodisation **5)** Liquid phase Epitaxy
5)Metal-Organo Chemical Vapour Deposition (MO-CVD)	**6)** Sol- gel
	7) Spin Coating
	8) Spray-pyrolysis technique (SPT)
	9) Ultrasonic (SPT)
	10) Polymer assisted deposition (PAD)

Fig. 2.A.1 - **Broad classification of thin film deposition techniques**

B] Spray pyrolysis:

This is a thermally stimulated reaction between the clusters of liquid vapour atoms of different spraying solutions of the desired compound onto a substrate maintained at elevated temperature. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or cluster of crystallites of the product. The other volatile byproducts and excess solvents escape in the vapour phase.

The thermal energy for decomposition, subsequent recombination of the species, sintering & recrystallisation of the crystallites is proved by hot substrate. The nature of the fine spray droplets, with the help of a carrier gas depends upon spray nozzle. The growth of a film by a spray pyrolysis is determined by nature of the substrate, solution as well as spray parameters. The films are general strong and adherent, mechanically hard, pinhole free & stable with temperature and time. The morphology of the films is general rough and that will depend upon the spray conditions. The surface of the substrate gets affected in the spray process and the choice is limited to glass, quartz, ceramics or oxides, nitride or carbide coated substrates.

C). Chemical vapour deposition

Chemical vapour deposition can be defined as a material synthesis method in which the constituents of vapour phase react to form a solid film at surface. The chemical reaction is an essential characteristic of this method; therefore, besides the control of the usual deposition process variables, the reactions of the reactants must be well understood. Various types of chemical reactions are utilised in CVD for the formation of solids are pyrolysis, reduction, oxidation, hydrolysis, synthetic chemical transport reaction etc.

D). Cathodic deposition

This is a standard method of electroplating. Two metal electrodes are dipped into an electrolyte solution and on application of an external field across the electrodes; metal ions from the solution are deposited on cathode as a film. Deposition of the films is mainly controlled by the electrical parameters such as, electrode potential and current density.

E). Anodic oxidation

This is an electrolytic method for producing oxide films on the surface of metal. These metals form the anode that dips into a liquid electrolyte such as a salt and acid solution. Oxide ions are attracted to the anode to form a thin layer of metal oxide. On increasing the field strength, more oxide ions diffuse through the oxide layer to the metal surface and, hence, the oxide layer grows thicker.

F). Deposition by chemical reactions

Chemical reaction either takes place on the surface of the dipped substrate or in the solution itself, where a mixing of components on the surface to be coated is required. Most of the coatings are formed in a two step fashion;

i) "Sensitizing" the surface for the nucleation reaction of the adhering coating layer.

ii) Deposition of coating by selected reactions.

The most widely used deposition methods are listed below

A) *Homogeneous chemical reduction* of a metal ion solution by a reducing agent regardless the substrates.

B) *Electroless plating* for the deposition of metallic coating by controlled chemical reduction that is catalysed by the metal or alloy being deposited.

Among the various chemical deposition systems, chemical bath deposition has attracted a great deal of attention because of its overriding advantages over the other conventional thin film deposition methods.

The chemical bath deposition method for the preparation of thin films has recently been shown to be an attractive technique because of its simplicity, convenience, low cost and low temperature, and it has been successfully used for depositing ternary metal chalcogenide thin films [19].

Understanding of the chemistry and physics of the various process involved in a deposition processes has now made possible to obtain undoped/doped, multicomponent semiconductor thin films of usual/unusual and metastable structure.

G). Arrested precipitation technique

Arrested precipitation technique (APT) is modified chemical bath deposition method. The arrested precipitation technique based on Ostwald ripning law is simple and inexpensive method used for deposition of wide variety of metal chalcogenide thin films. Arrested precipitation technique can be distinguished from other conventional techniques as follows:

- It is ideally suited for large area thin film depositions; substrate surfaces of both accessible and non-accessible nature could easily be deposited.
- It is simple, inexpensive and does not require sophisticated instrumentation.
- The deposition is usually at low temperature and avoids oxidation or corrosion of the metallic substrates.
- Stoichiometry of the deposits can be maintained since the basic building blocks are ions instead of atoms.
- Slow film formation process facilitates better orientation of the crystallites with improved grain structures over the substrate surface.
- Doped and mixed films could be obtained by merely adding the mixant / dopant solution directly into the reaction bath.
- Electrical conductivity of the substrate material is not an important criterion.
- An intimate contact between reacting species and the substrate material permits pinhole free and uniform deposits on the substrates of complex shapes and sizes.
- Wide varieties of conducting / nonconducting substrate materials can be used.
- Dissociation rate of organometallic complex to release free metal ions for reaction is well control by maintaining the pH of reacting solution.

H).Chemical bath deposition:

Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reactions usually reduction of metal ions in solution by a reducing agent. If this occurs on a catalytic surface, it is called an electro less deposition.

Among the methods mentioned in the Table 2.1, 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 chemical bath deposition(CBD) method 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 chemical bath deposition(CBD) method for the preparation of thin films. Thereafter, due to good productivity of this technique on a large scale and simplicity of the apparatus, it offered most attractive way for the formation of thin films of metal oxides, metallic spinal type oxides, binary chalcogenides, ternary chalcogenides, superconducting oxides etc. It is simple and low cost technique and has capability to produce large area of high quality adherent films of uniform thickness[20-27].

2.A.4. Basics of Chemical bath deposition technique.

Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reactions usually reduction of metal ions in solution by a reducing agent. If this occurs on a catalytic surface, it is called an electro less deposition (autocatalytic). Silvering is the most widely used for this technique, metallic as well as mixed film sulphides, and selenides) and other alloys can be deposited. For nonmetallic surfaces a sensitizer has to be used. The growth rate & degree of crystallinity depends upon the temperature of the solution. The main advantage of this method is to deposit the films on non-accessible surfaces such as rounded glass tubes.

The chemical bath deposition is the simplest of the chemical methods, and it has many advantages as;

1] It is simple & does not require any sophisticated instrumentation.

2] It is ideally suited for large area depositions & substrate surfaces of both accessible & non accessible nature could easily be deposited.

3] The deposition is usually at low temperature and avoids the oxidation or corrosion of the metallic substrates.

4] It is possible to obtain uniform & large area semiconductor deposits on a variety of substrate materials.

5] Thickness of the deposits can be controlled from few nanometers to micrometer by variation in the preparative parameters.

6] As compared to the other thin film deposition techniques, chemical bath deposition process can be used conveniently for deposition of a variety of materials.

A). Factors governing the chemical bath deposition:

It is the most suited method for deposition thin films. However, the growth of film is found to be governed by the various factors such as bath composition, the pH, and deposition time & deposition temperature.

a) Bath composition

The growth rate and quality of the deposited films was greatly influences by the concentration of the reacting species. The films deposited by using low concentration are thin and nonuniform.This observation can be relates to the insufficient supply of ionic species at such concentration levels. On the other hand when concentration of the species was increased, the quality and uniformity of the films goes on increasing and the films were thick. This is true up to a certain level of concentration and then saturation in the growth process was observed.

b) The pH:

It is the most important factor in the Chemical bath deposition. Thus the desired films were obtained on the substrate surface by optimizing the P^H value of its bath solution which avoids the deleterious effects.

c) Deposition time:

Growth of the thin film by chemical bath deposition is time dependent. The deposition time of the film affects film thickness.

d) Deposition temperature:

The temperature dependence of growth rate shown by literature survey that the rate of deposition increases with bath temperature resulting into formation of fine grained structure.

2.A.5. Selection of deposition process

No single technique is ideally suited for preparation of large area thin films with all the desired properties. Hence choice and selection of deposition process plays a vital role in the formation of good quality thin films, and while selecting a particular technique it should be tested satisfactorily for the following aspects:

- Cost effectiveness.
- It should be able to deposit desired material.
- Film microstructure and deposition rate should be controlled.
- Stoichiometry should be maintained as that of the starting materials.
- Operation at reduced temperature.
- Adhesive at reduced temperature.
- Abundance of deposit materials
- Scaling up of the process.
- Masking of the substrates.
- Control on film substrate interface and defects created in the film.

Among the various techniques discussed above, chemical bath deposition technique is employed in present investigation.

Part - B

Characterization Techniques.

2.B.1. Introduction

In the past years the advancement in science has taken place mainly with the discovery of new 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 and surface characterization, which have strong bearing on the properties of materials. In this section different analytical technique used to characterize our thin films are described with relevant principles of their operation and working.

2.B.2. Electrochromic Characterization Techniques:

Electro analytical techniques are concerned with the measurement of time related electrical quantities, such as charge or current and potential their relationship to the chemical reactions concerned.

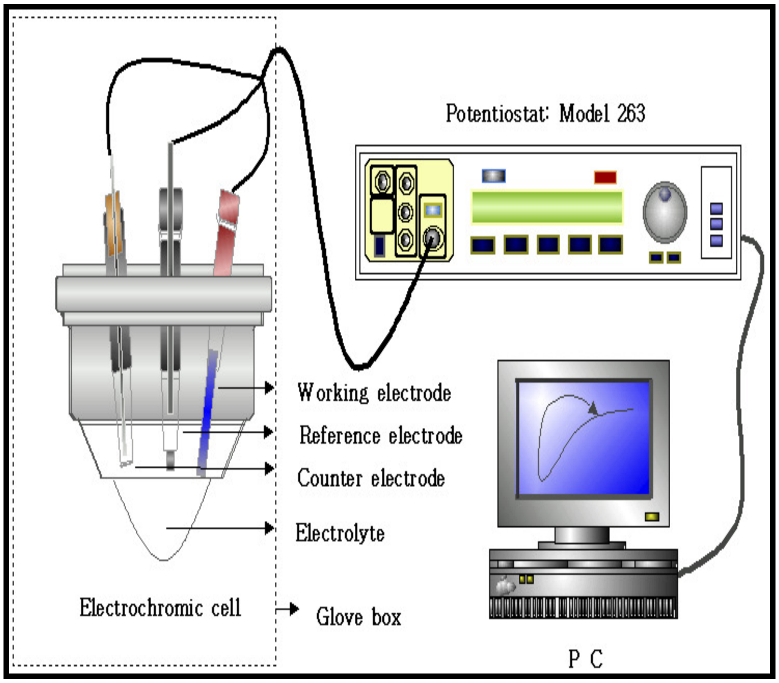


Fig. 2.B.1 Schematic diagram of the EC cell apparatus prepared for EC property measurements.

Commercial Potentiostat CHI 400 electrochemical Analyser can be used for electrochromic characterizations of thin films.[28,29]The measurements requires an electrochemical cell with the three electrodes namely working, counter, and the reference, versus which the electrode potential are measured

2. B.2.1 Cyclic voltammetry (CV) and Linear sweep techniques (LSV)

Cyclic voltammetry is often the first experiment performed in an electro analytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect 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 and resulting current response versus a reference electrode (SCE) is measured.

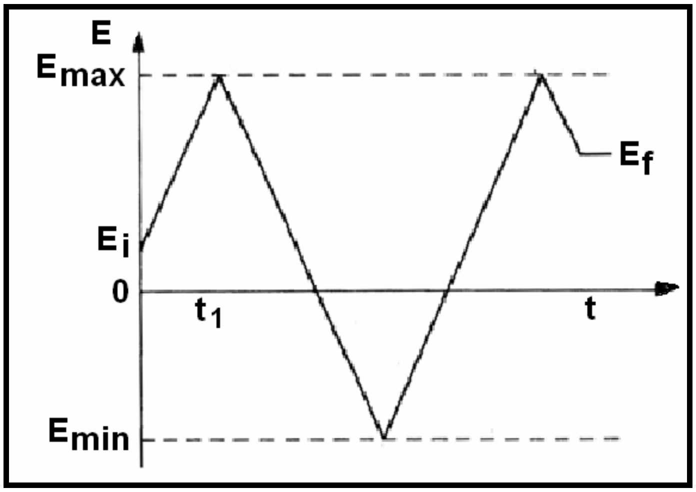


Fig.2.B.2 Variation of Applied Potential for Cyclic Voltametry

In cyclic voltammetry, on reaching $t = t_1$ the sweep direction is inverted as shown in figure 2.B.2 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 ν
- The maximum potential, E_{max}

- The minimum potential, E_{min}
- The final Potential, E_f

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

A) Reversible system

Fig. 2.B.3 shows a typical curve for linear sweep voltammetry (LSV) recorded for reversible reaction of the type O + ne^-→ R.

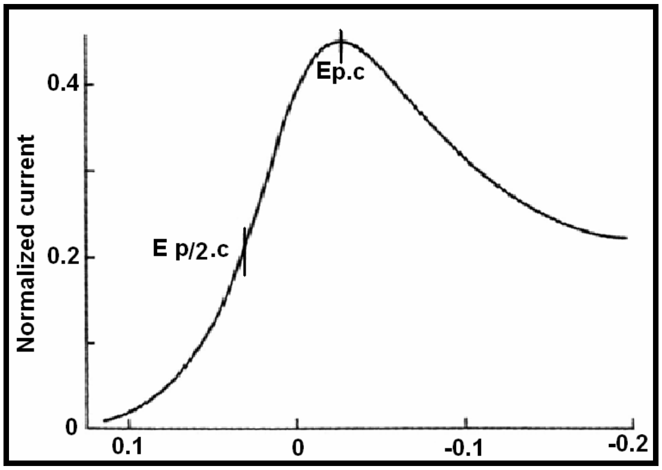


Fig. 2.B.3 A typical curve for linear sweep voltammetry (LSV)

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.B.3, similar to application of potential step. Fig. 2.B.4 shows the typical cyclic voltammetry (CV) for reversible system.

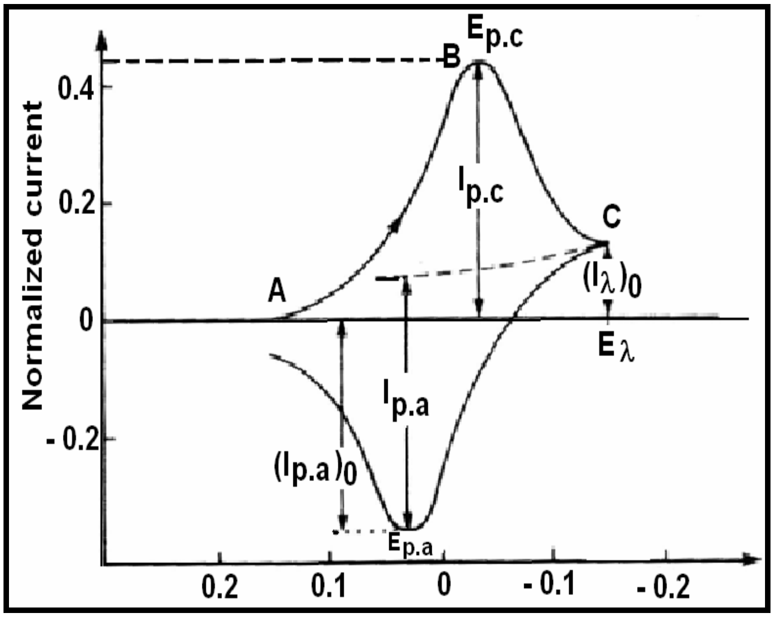


Fig. 2.B.4 The typical cyclic voltammetry (CV) for reversible system.

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_Ω where R_Ω is the resistance (uncompensated) of the solution.

B) Irreversible system

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

C) 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. Fig. 2.B.5 shows the effect of increasing irreversibility on the shape of cyclic voltammogram.

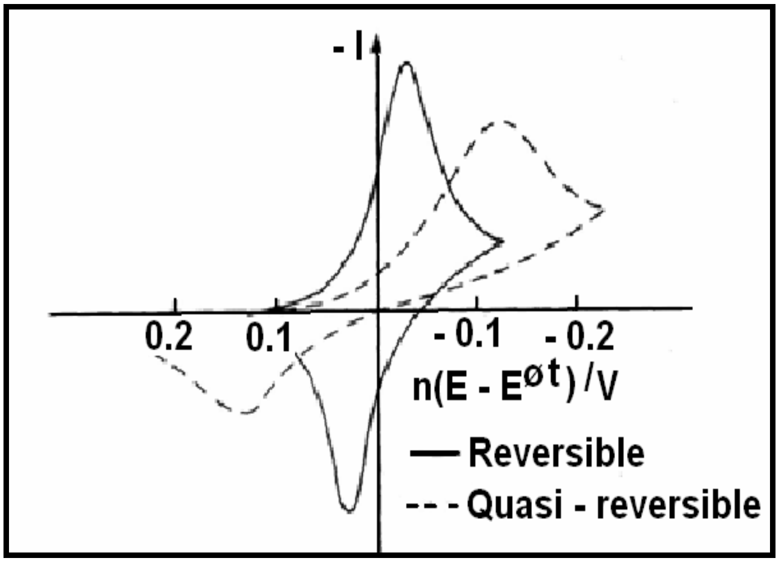


Fig. 2.B.5 The effect of increasing irreversibility on the shape of cyclic voltametery

Cyclic Voltametery (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions taking place at the electrode - electrolyte interface. It offers a rapid location of redox potentials of the electroactive species in agitated or quiescent electrolyte and convenient evaluation of the effect of media upon the redox process[30-34].In CV the potential is continuously changed as a linear function of time in potential window + volts VS SCE and resulting current response is recorded. The resulting current versus potential plot is termed as a cyclic voltammogram. A smooth curve indicates that no well defined phase change occur during the reaction. It is assumed that only the oxidized ionic species are present initially, the mass transfer under concentration gradient is diffusion controlled and Fick's law of diffusion holds good for both oxidized and reduced ionic species. The redox potentials are predicted by Nernst equation given by,

$$E = Eo + (0.059 / n) \log (Co / Cr) \quad \text{-------------} \quad 2.1$$

Where, n = No. of electrons transferred

Co and Cr = concentration of oxidized and reduced ionic species

During a negative potential scan (coloration) in the first half cycle, as the applied potential approaches the characteristic reduction potential (Epc) predicted by Nernst equation, the cathodic current attains a peak value (Ipc). At least 90/n mV beyond the peak, the direction of applied potential is reversed. This helps in locating the presence of another reducible species in the bath.

During the reverse positive scan (bleaching) the reduced ionic species get oxidized and with similar trend the anodic current a peak value (Ipa) at an oxidation potential (Epa). If the redox reaction is reversible i.e. maintain the surface concentrations of oxidized and reduced species as per the Nernst equation, the voltammogram is symmetrical otherwise it is asymmetrical.

D) Diffusion Coefficient;

It is the measure of ease with which an ionic speices can intercalate /deintercalate in the host. It is given by Randles and Sevick equation

$$D^{1/2} = Ip / 2.69 \times 10^5 . n^{2/3} . C.A.V^{1/2} \quad \text{----------} \quad 2.2$$

Ip = Cathodic or anodic peak current

C = Concentration of ionic species

n = Ionic charge

A = Area of film

V = Potential scan rate

2. B.2.2 Pulse techniques

A step in applied potential or current 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.

A) Potential Step: Chronoamperometry (CA)

The study of variation of the current response with time under potentiostatic condition is chronoamperometry [35]. 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 O + ne^- → R, where only O or only R is initially present. This is the faradic current, I_f since it is due only to faradic electrode process (only electron transfer).

In the present study we have used double potential step chronoamperometry to measure the speed of electrochromic response and to apprehend intercalation and de-intercalation. An overview of CA experiment is shown in figure. The potential is altered between two values. We consider an initial step from a potential where there is no electrode reaction to a value to the limiting reduction current (only O initially present in solution); at $t = \tau$ the potential reverts to its initial value and there is oxidation of R that was produced. As mass transport under these conditions is solely by diffusion, the i-t curve reflects the change in the concentration gradient in the vicinity of the surface. This involves a gradual expansion of the diffusion layer associated with the depletion of the reactant and hence decreased slope of the concentration profile as time progresses. Accordingly, the current decays with the time (Fig.2.B.6) as given by Cottrell equation (2.3).

$$I_f(t) = \frac{nFAD^{1/2}c_\infty}{(\pi t)^{1/2}} \quad \text{---------------} \qquad \textbf{(2.3)}$$

It indicates the decrease of the current with $t^{1/2}$, which is shown in Fig.2.B.6. Such a $i(t^{1/2})$ constancy is often termed a “Cottrell behavior”

The time required for the transition from colored to bleached state or vice-versa under the application of voltage pulse is termed as response or switching time. Though the magnitude of response time depends upon end use demand, a minimum switching time is necessary in advanced opto-Electronic EC devices.

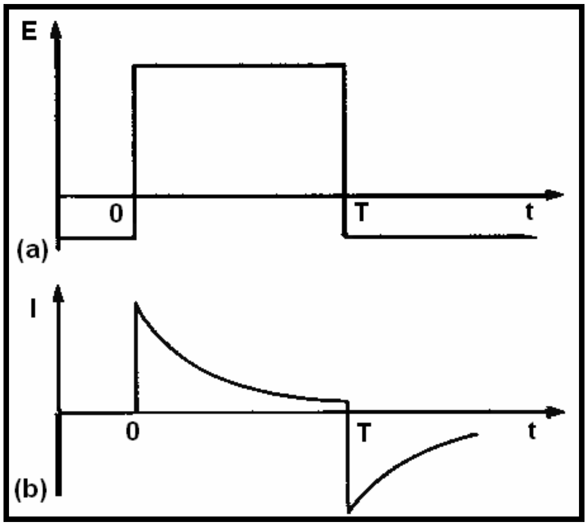


Fig. 2.B.6 Chronoamperometric plot exhibiting I Vs t behavior

B) Chronocoulometry (CC)

Instead of studying the current with time, we can integrate the current and study the variation of charge with time: this is called as Chronocoulometry.

Advantages over chronoamperometry:

1. The signal usually increases with time, facilitating measurement towards the end of transient, when the current is almost zero.
2. Integration is effective to in reducing signal noise.
3. It is relatively easy to separate the capacitive charge, Q_c, from the faradaic charge, Q_f.

Double step chronocoulometry also gives information on the kinetics coupled homogeneous reactions. In the resent study we have used double step chronocoulometry to determine the quantitative information of charges intercalated and deintercalated in the two successive steps applied for constant time.

Reversibility;

From the CC curves the amount of charges intercalated (Qi) and deintercalated (Qdi) during redox process are calculated. The electrochemical reversibility is calculated using the relation-

Reversibility = Q di / Qi ------------- 2.4

From the CV and CC analysis of electrochromic sample parameters like Reversibility, Response or switching time, Diffusion Coefficient and coloration efficiency can be determined.

2.B.3 UV-Vis-NIR spectroscopy

Spectrophotometers are optical instruments that measure the intensity of light transmitted or reflected by objects as a function of wavelength. Light from the lamp enters the monochromator, which disperses the light and selects the particular wavelength chosen by the operator for the measurement. The light beam of selected wavelength is passed alternately through the sample and along the reference path. The ‘reference’ and `sample' light beams pass through the cell compartment, consisting of a `reference space' and a sample space. The two light beams converge on the detector. Quantitative measurements in chemical analysis are done by comparison of the absorption with the absorbance of known concentration of the element.

Extensively used for determination of trace impurities in semiconductors, alloying elements in steel, non-ferrous alloys, trace impurities in ceramic materials, trace impurities in liquids like high purity water, solvents, acids, dyestuffs in food etc. Transmittance or absorbance of solid or liquid and total diffuse reflectance/transmittance of solids like large disks, silicon wafers, plastics, glass etc. can be measured. Band gap determination, electron transition and enzyme activity studies can also be made.

A diagram of the components of a typical spectrometer is shown in figure 2.B.7. The beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

If the sample compound does not absorb light of a given wavelength, $I=I_o$. However, if the sample compound absorbs light then I is less than I_o, and this difference may be plotted on a graph versus wavelength. Absorption may be presented as transmittance ($T = I/I_o$) or absorbance ($A= \log I_o/I$). If no absorption has occurred, T = 1.0 and A= 0.

Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}.

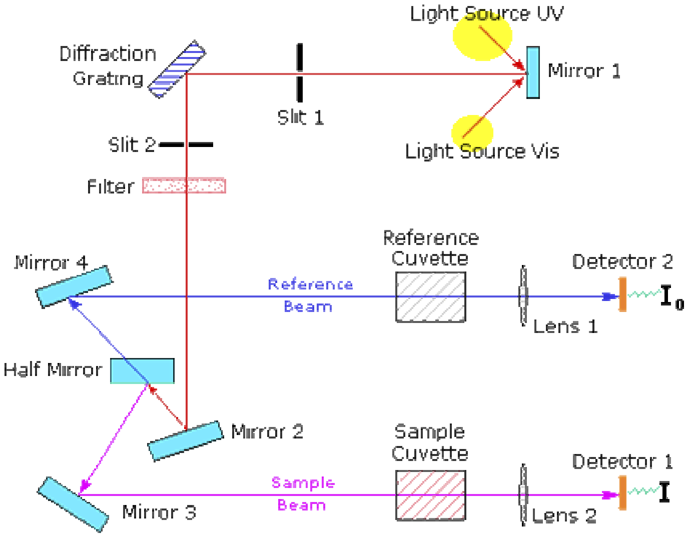


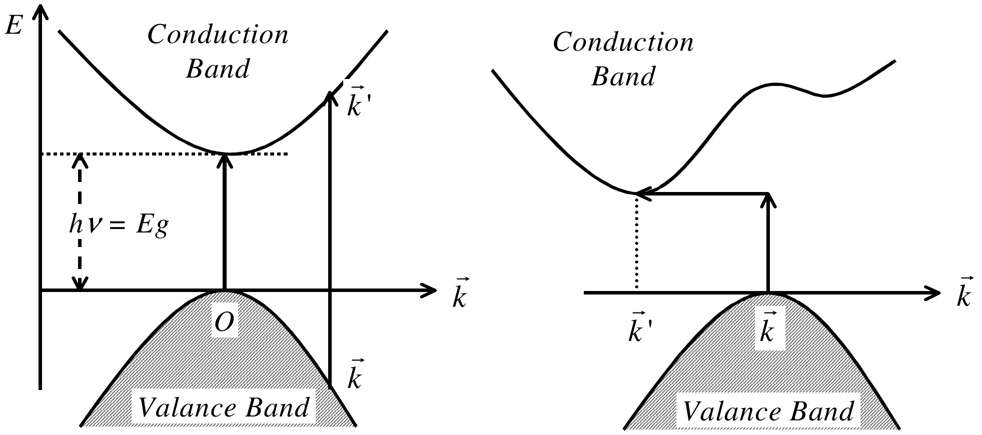
Fig. 2.B.7 Schematic of UV-Vis-NIR spectrophotometer

Different compounds may have very different absorption maxima and absorbance. 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 exhibit 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 figure 2.B.8. Hence a wave vector k for electron remains unchanged in E-K space. The optical transition is denoted by a vertical upward narrow.

For simple parabolic bands and for direct transition, absorption coefficient α is given by the relation [36].

$$\alpha = \frac{\alpha_o (h\nu - E_g)^n}{h\nu} ------------ (2.8)$$

where E_g is the separation between bottom of the conduction and top of the valence band, hν is the photon energy, ν is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and α_o is a constant depending upon the transition probability for direct transition. For allowed direct transitions n =1/2 and for allowed indirect transition ν = 2. Thus if the plot of $(\alpha h\nu)^2$ against hν 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 α =0.



(a)

Fig. 2.B.8.- "Direct interband optical transitions" for a) direct band and b) indirect band semiconductors. The transitions are represented by vertical arrow.

2.B.4 Infrared spectroscopy

Infrared spectroscopy (FT-IR) is a technique for identification of gases released directly from the sample or during thermal treatment. IR spectroscopy is a classical technique, which depends upon the interaction of infrared radiation with the vibrating dipole moments of molecules. It gives, with the exception of homonuclear diatomic and noble gases, a characteristic spectrum for each substance.

2.B.5.. 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, energies of transitions, dimensional changes, modulus and viscoelastic properties. Current applications include environmental measurements, product reliability, compositional analysis, stability, chemical reactions and dynamic properties.

2.B.5.1 (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 (ΔT) 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.

2.B.5.2 (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 behaviour. 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 N_2, O_2, 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 0.1μ gm. 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 [37].

Applications

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

2.B.6. X- ray Diffraction (XRD) Technique

X-ray diffraction (XRD) is a powerful technique for determination of crystal structure and lattice parameters. The basic principles of X-ray diffraction are found in textbooks e.g. by Buerger [36], Klug and Alexander [37], Cullity [38], Tayler [39], Guinier [40], Barrett and Massalski [41].

Much of our knowledge about crystal structure and the structure of molecules as complex as DNA in crystalline form comes from the use of x-rays in x-ray diffraction studies. A basic instrument for such study is the Bragg spectrometer[42].

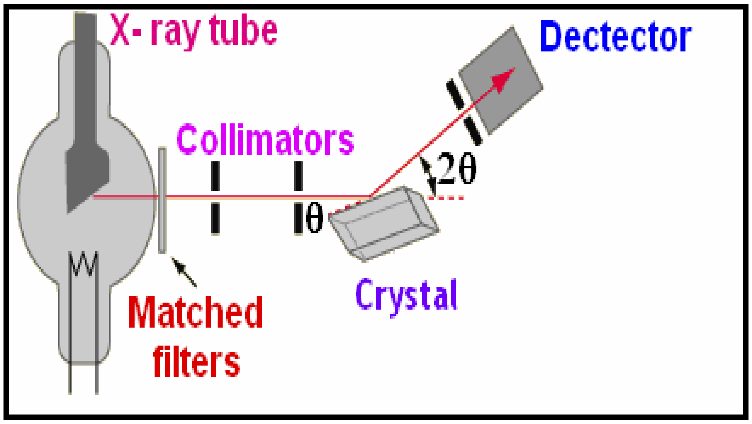


Fig. 2.B.9(a)- Bragg Spectrometer

Fig. 2.B.9(a) and Fig. 2.B.9(b) 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,

$$2d \sin\theta = n\lambda \qquad \text{---------------} \qquad 2.5$$

where,

d = interplaner spacing
θ = diffraction angle
λ = wavelength of x-ray
n = order of diffraction

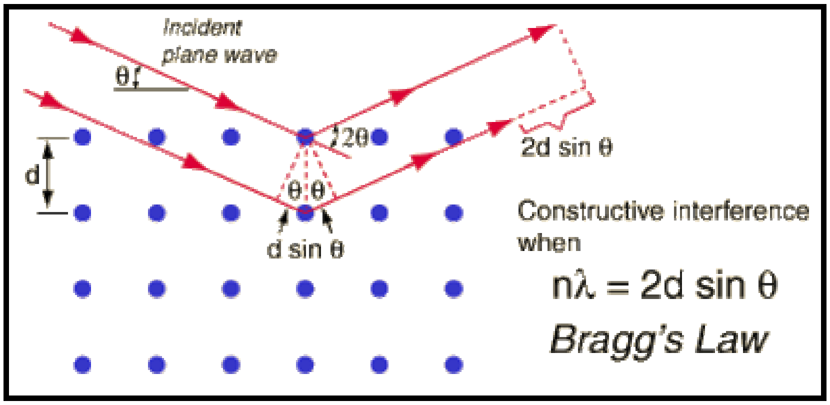


Fig. 2.B.9(b). Schematics of X-ray diffractometer.

For thin films, the powder technique in conjunction with diffractometer is most commonly used. In this technique the diffracted radiation is detected by the counter tube, which moves along the angular range of reflections. The intensities are recorded on a computer system. The'd' values are calculated using relation (2.5) for known values of θ, λ and n. The X- ray diffraction data thus obtained is printed in tabular form on paper and is compared with Joint Committee Power Diffraction Standards (JCPDS) data to identify the unknown material. The sample used may be powder, single crystal or thin film. The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherrer's formula as follows [43]

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad \textbf{2.6}$$

where, D is crystallite size, λ is wavelength of X-ray used, β is full width at half maxima of the peak (FWHM) in radians, θ is Bragg's angle. The X- ray diffraction data can also be used to determine the dimension of the unit cell. This technique is not useful for identification of individuals of multilayers or percentage of doping material.

2.B.7. Scanning Electron Microscopy (SEM)

Scanning electron microscope is an instrument that is used to observe the morphology of the solid sample at higher magnification, higher resolution and depth of focus as compared to an optical microscope [44]. When an electron strikes the atom, variety of interaction products are evolved. Fig. 2.B.10 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. 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.

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 [45]. The ray diagram of scanning electron microscope is shown in Fig. 2.B.11. The scattering cross section for back-scattered electrons is given as [23],

$$Q = 16.2 * 10^{-30} \left[\frac{Z}{E} \right]^2 \cot\left(\phi / 2 \right) \qquad \text{----------} \qquad \mathbf{2.7}$$

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.

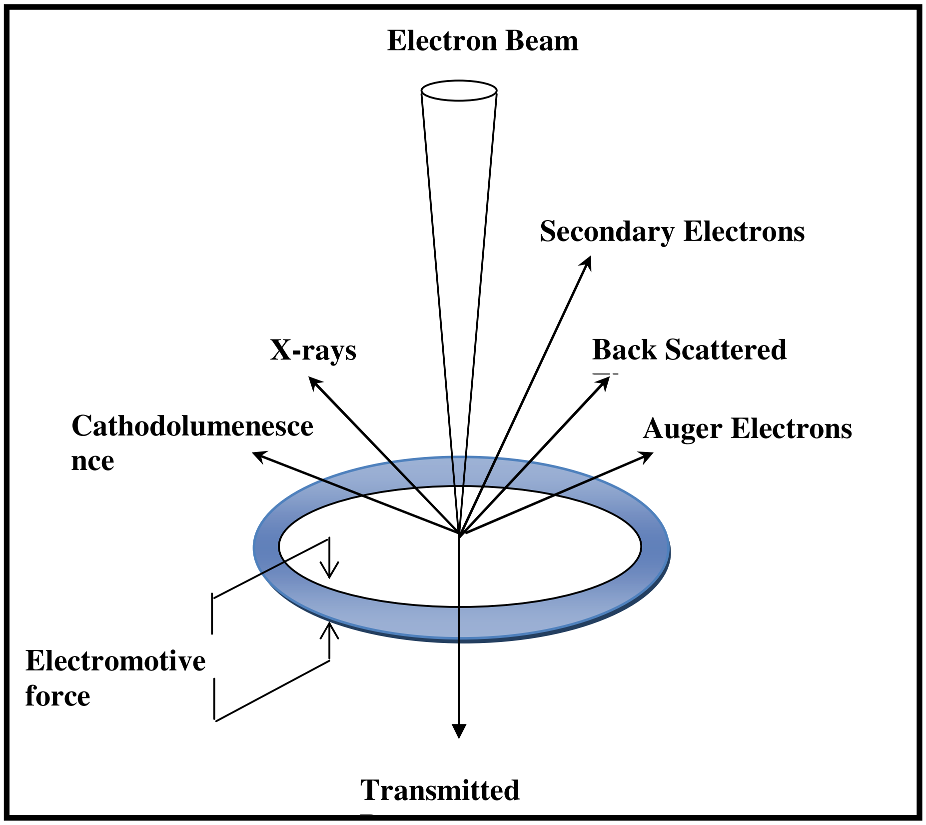


Fig. 2.B.10- Variety of interaction products evolved due to interaction of electron beam and sample

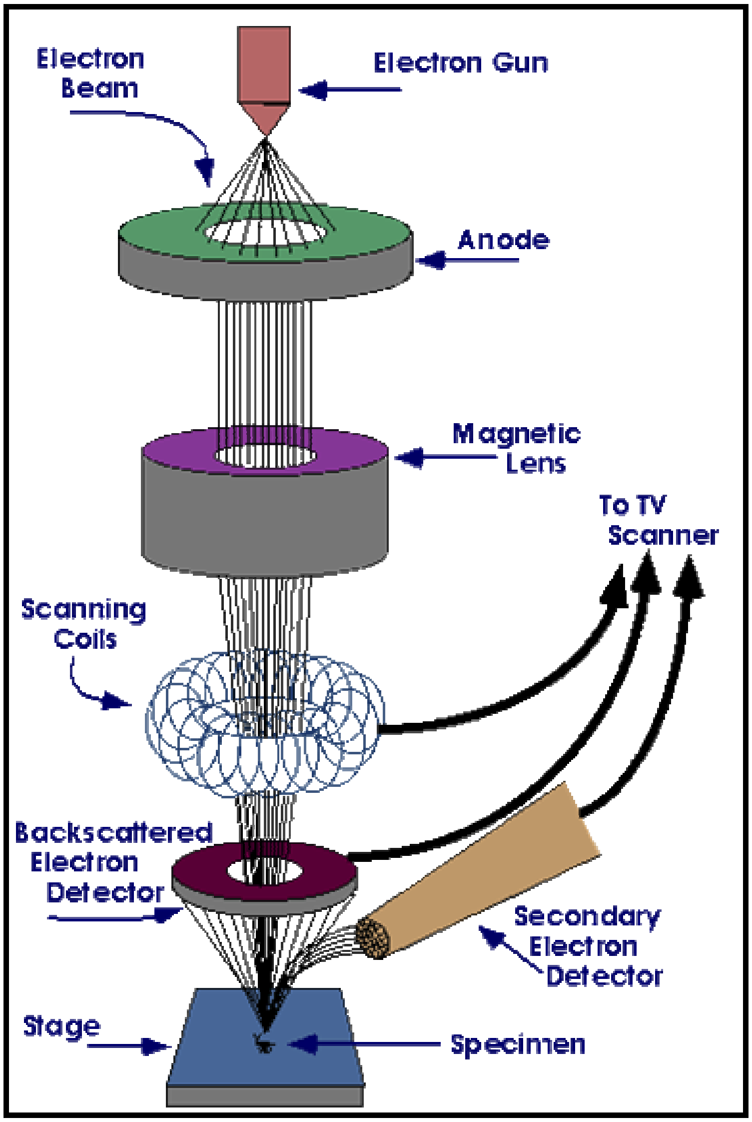


Fig. 2.B.11- The ray diagram of scanning electron microscope.

2.B.8. Energy Dispersive Analysis by X-Rays Measurement (EDS)

In EDS technique a sample is made the target in an X- ray tube and is bombarded with electrons of suitable energy, it emits characteristics X-rays. This is the basis of a method of chemical analysis. The emitted X-rays are analyzed in an X-ray spectrometer and the elements present in the sample are qualitatively identified by their characteristics wavelengths. For compositions greater than or about 1% and elements separated by few atomic numbers, energy dispersion analysis is very useful because the intensities are increased about 100-Fold [46]. The resolution however, of an energy dispersion instruments is as much as 50 times less than the wavelength dispersion spectrometer using a crystal; thus overlapping of lines from nearby elements may occur. If a sample is irradiated with X-rays of sufficiently high energy, it will emit fluorescent radiation. This radiation may be analysized in an X-ray spectrometer and the elements present in the sample identified by their characteristics wavelengths. Study of thin films, ferrites, composites, biological samples and pharmaceutical samples are the common application areas.

2.B.9. Thickness Measurement

The thickness of film is the most significant parameter that affects the properties of the thin films. It may be measured either by in-situ monitoring of the rate of the deposition or after the film is taken out form deposition chamber. Technique of the first type often referred to as monitor methods generally allow both monitoring and controlling of deposition rate of film thickness. Any known physical quantity related to film thickness can be used to measure the thickness. The method chosen should be convenient, reliable and simple. One of the most convenient surfaceprofilometer and reliable method for determining film thickness in this method, area and weight of the film are measured.

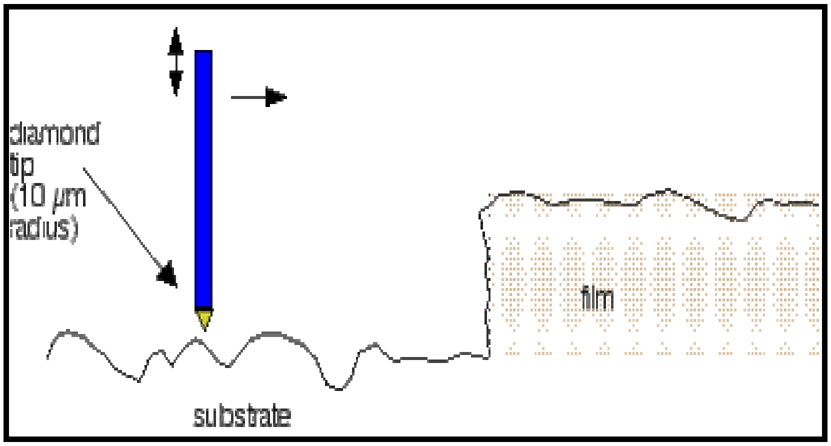


Fig. 2.B.12 Schematic Diagram of Typical Profilometer

Electro-magnetic sensors detect the vertical motion of the stylus as it is moved horizontally across the sample.

measure

A) film thickness (step height)

a) changes of 200 Å to 65 µm

b) vertical resolution of about 10 Å

B) roughness

a) horizontal resolution depends on tip radius

problem: stylus penetrates soft films

In our experiment we used the XP-1 Ambios Technology surface profilometer (contact mode) having 1 A^o resolution.

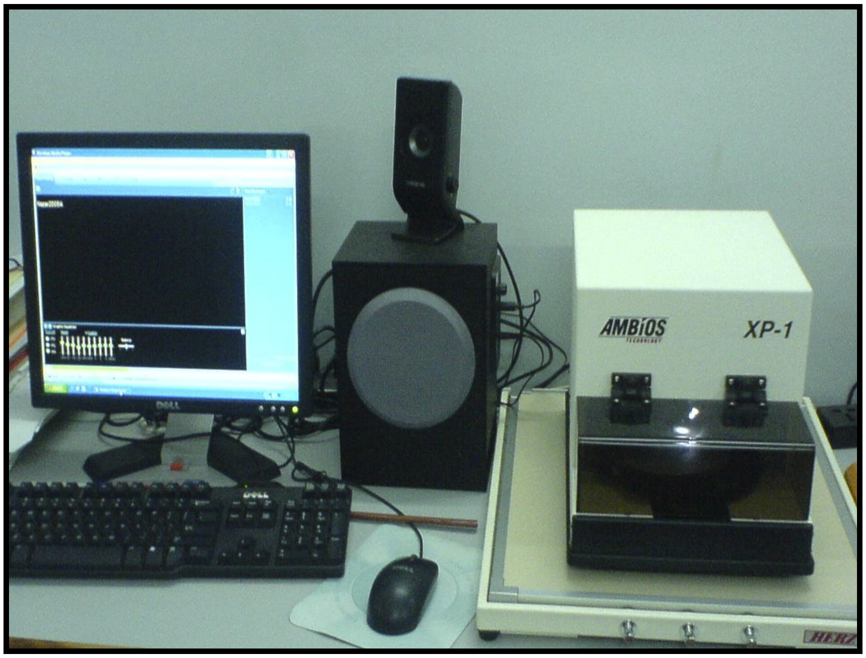


Fig. 2.B.13 XP-1 Ambios Technology surface profilometer

2.B.10. Transport Properties

Surface transport phenomena are well known to have a strong influence on the electronic properties of bulk semiconductors. When transport takes place through thin specimens, the carriers are being subjected to considerable scattering by the boundary surface in addition to normal bulk scattering. This additional scattering will reduce the effective carrier mobility below the bulk value and will thus give rise to quantum size effects. A study of these size effects can yield information on the electronic structure of a surface and is therefore of considerable fundamental and practical importance. These phenomena play an important role in the transport properties of semiconducting film of about 1μm thickness and having carrier concentration upto 10^{18} cm^{-3}. Surface transport phenomena in bulk semiconductor have received much attention in recent years. An excellent review of the subject is given by Pulliam et al. [49]. The important transport properties i.e. electrical resistively, thermoelectric power (TEP) are discussed below.

A) Electrical conductivity

The use of thin films as resistors, contacts and interconnections has lead to extensive study of conductivity, its temperature dependence, the effect of thermal processing stability and so on. Investigations of the electrical resistivity as a highly structure sensitive properties make it possible to gain insight into the structural and electrical properties of the metal film which is important from both the theoretical and practical point of view. The contact techniques are most widely used for the measurement of resistivity. These techniques include two-point probe, four point probe and the spreading resistance methods. The two-point method is simple and easy to use. In this technique a constant current I is passed through a sample of known dimensions (cross-sectional area 'A'). And the d.c. voltage 'V' between two fixed position probes (separation'd') measured either with impedance voltmeter or potentiometrically. For uniform sample resistively is given by

$$\rho = (A / I) (V / d) \quad \text{-----------} \quad 2.11$$

In case of semiconducting thin films, the resistivity decreases with increase in temperature. The thermal activation energies 'E_a' are calculated by using following relation:

$$\sigma = \sigma_0 \exp (-\Delta E / k_B T) \quad \text{----------} \quad 2.12$$

where, σ_0 represent the pre-exponential factor, ΔE is the activation energy for electrical conduction and k_B is the Boltzmann constant Fig. 2.B.14(A) and 2.B.14(B) shows photograph and schematic diagram of the electrical conductivity measurement unit. The two brass plates of the size 10 x 5 x 0.5 cm are grooved at the centre to fix the heating elements. Two strip heaters (65 Watts) were kept parallel in between these two brass plates to achieve uniform temperature. The two brass plates are then screwed to each other. The sample was mounted on the upper brass plate at the centre. To avoid the contact between the film and the brass plate, a mica sheet was placed between the film and brass plate. The area of the film was defined and silver emulsion (paste) was applied to ensure good electrical contact to the films. The working temperature was recorded using a Chromel-Alumel thermocouple (24 gauge) fixed at the centre of the brass plates. Testronix model 34 C (power supply unit) was used to pass the current through the sample.

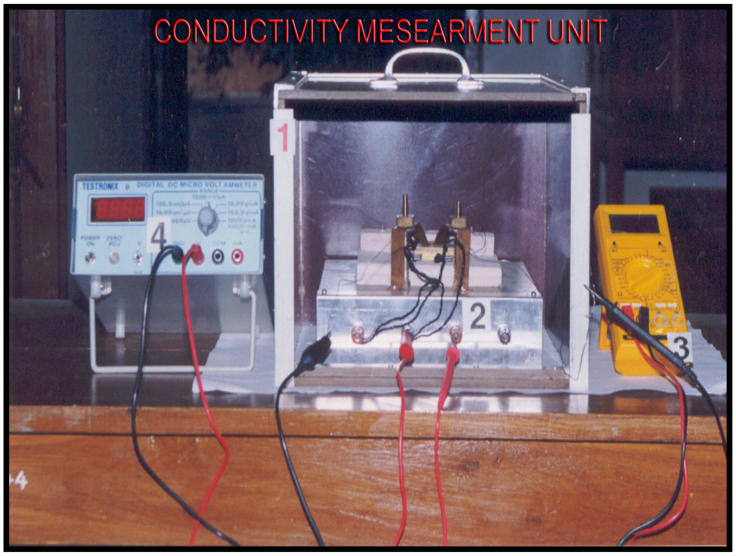


Fig. 2.B.14(A)- Photograph showing the electrical conductivity measurement assembly

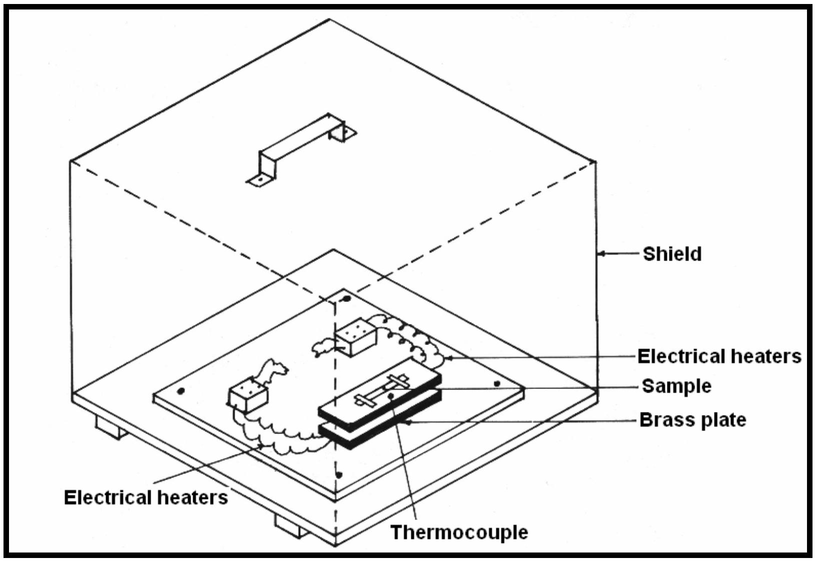


Fig. 2.B.14(B)- Design and schematic arrangement for measurements of electrical conductivity

The potential drop across the film was measured with the help of Meco 801 digital multimeter and current passed through the sample was noted with a sensitive 4 digit picoammeter (Scientific equipment, Roorkee DPM 111).The measurements were carried out by keeping the film system in a light tight box, which was kept at room temperature.

B) Thermoelectric Power (TEP)

If some metal contacts are applied to the two ends of a semiconductor and if one junction is maintained at higher temperature than the other, a potential difference is developed between the two electrodes. This thermoelectric or Seebeck voltage is produced partly because

i) The majority carriers in the semiconductor diffuse from hot to cold junction, thus giving a potential difference between the ends of the specimen. This voltage builds upto a value such that the return current just balances the diffusion current when a steady state is reached.

ii) Other part which contributes to the thermoelectric voltage is the contact potential difference between metal and semiconductor, which occurs at two junctions.

In the semiconductor, if the charge carriers are predominantly electrons, the cold junction becomes negatively charged and if the charge carriers are positive holes, the cold junction becomes positively charged. The magnitude of the developed voltage is proportional to the difference in temperature between the hot and cold junction, if the temperature difference is small. From the sign of the thermoelectric voltage it is thus possible to deduce whether a given specimen exhibits n-or p-type conductivity.

The thermoelectric power (TEP), which is defined as the ratio of thermally generated voltage to the temperature difference across the piece of semiconductor, gives the information about the type of carriers in the semiconductor.

Fig. 2.B.15(A) and 2.B.15(B) shows photograph and schematic diagram of the TEP measurement unit. Thermoelectric power measurement apparatus consist of two brass blocks. One brass block was used as a sample holder-cum-heater. Other brass block was kept at room temperature. The hot and cold junction was kept thermally isolated by inserting an insulated barrier between the junctions. The size of the film used in this study was 40 mm x 12.5 mm x

1.35 mm on amorphous glass substrates, were fixed on two brass blocks. Chromel – Alumel thermocouples (24 gauze) were used to sense the working temperature. A 65 watt strip heater was used for heating the sample. The temperature of the hot junction was raised slowly from room temperature, with a regular interval of 10 K. the thermoemf was noted up to the highest temperature of 500 K. Silver paste contacts were made to films with copper wire. A backellite box was used for proper shielding of the TEP unit, which also minimises to some extent, thermal radiation losses. The mean temperature was measured with a Meco 801 digital multimeter while the differential thermal gradient and thermoelectric voltage were measured with digital Testronix microvoltmeter.

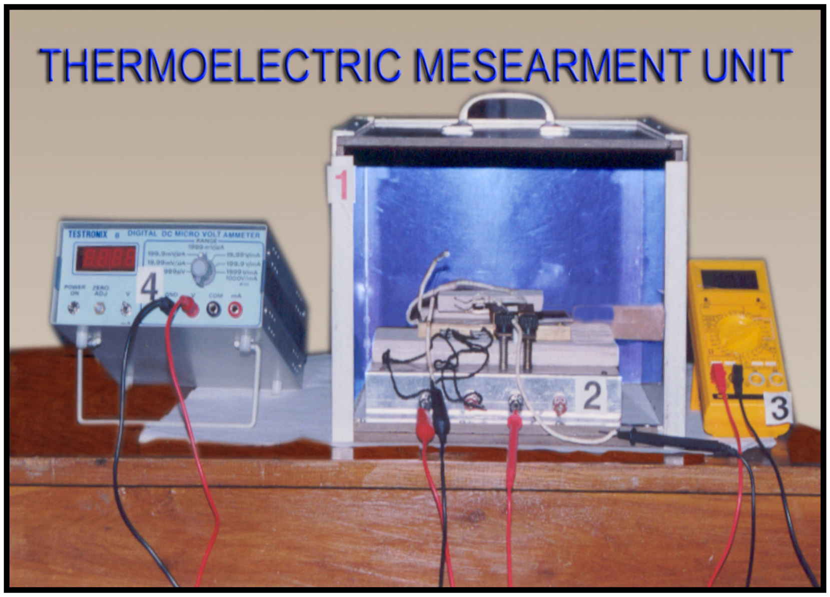


Fig. 2.B.15(A)- Photograph showing the thermoelectric power measurement assembly.

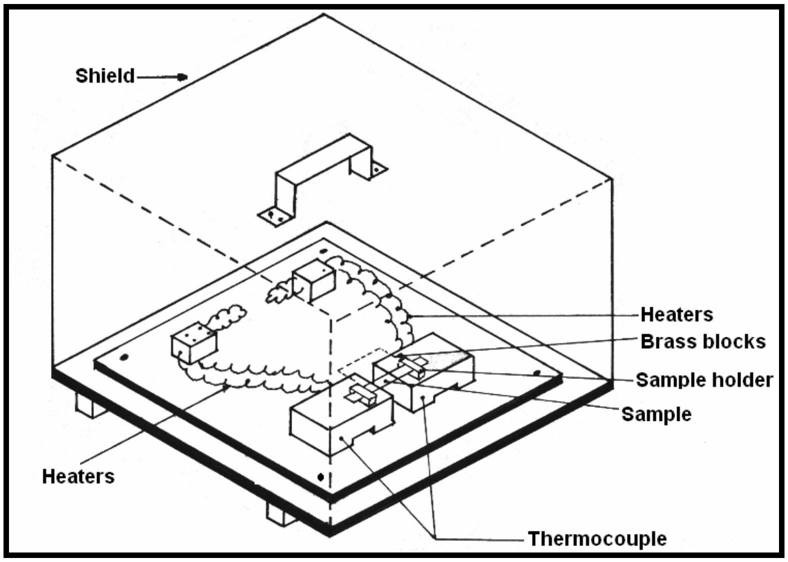


Fig. 2.B.15(B)- Design and schematic arrangement for measurements of the thermoelectric power

2.B.11. Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary, information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector [50-55].

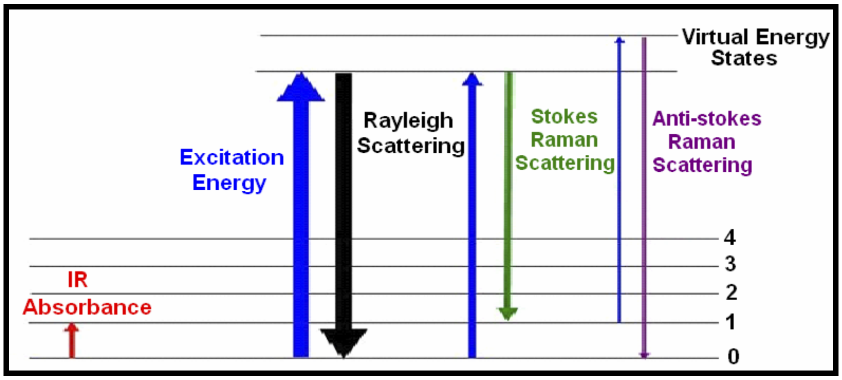


Fig.2.B.16 Raman energy levels

2.B.12 Photoelectrochemical cell (PEC) Study

2.B.12.1 Construction of Photoelectrochemical (PEC) Solar Cell

In the construction of a practical photoelectrochemical cell (PEC) for the conversion of sunlight into electricity (or chemical energy), the most important fact is the long-term stability of cells that show reasonable conversion efficiencies. Thus, an increasing number of studies on photoelectrodes are concerned with their stability. PEC cell consists of a semiconductor photoelectrode, an electrolyte and a counter electrode as shown in Fig. 2.B.18. All parts play an important role in the PEC cell. The distance between photoelectrode and counter electrode is 0.4 cm. When both the electrodes are immersed in the electrolyte, the band bending of the semiconductor photoelectrode may occur. The transfer of electrons to or from the electrolyte can takes place only in the energy region of the conduction band, while the hole transfer can takes place in the region of the valance band. Such a transfer can occurs between two states of the same energy, one empty and other filled. When the interface of the semiconductor photoelectrode-electrolyte is illuminated, the electron-hole pairs are generated in the depletion layer and are separated by the electric field present at the interface. The incident energy of photon should be greater than the band gap energy of the semiconductor. The electron-hole pairs generated in the bulk of the semiconductor are essentially lost through recombination. If a positive potential is applied to the n-type semiconductor photoelectrode and illuminated, the electron-hole pairs are generated and the separated electrons rise to the top of the conduction band and holes in the valence band. This process set up a counter field under open circuit conductions. The counter field is at its maximum and is the open circuit voltage; V_{oc} is given by the equation,

$$V_{oc} = (nKT/e) \log [I_{sc}+1/I_o] \quad \text{--------------} \quad 2.13$$

On the other hand, the counter electrode is being in the same electrolyte, the photo voltage acts as a driving force for the electrons to move under the short-circuit conditions from the semiconductor electrode to the counter electrode and a regenerative cell is formed and is shown in Fig. 2.B.19. The short- circuit current is given by the equation-

$$I_{sc} = I_o [\exp (eV_{oc} /nKT)^{-1}] \quad \text{--------------} \quad 2.14$$

The electrons promoted to the conduction band drift towards the interior, while the holes, the minority carriers, come to the surface of the semiconductor. Here they encounter the reduced form of the redox couple in the solution. The component is oxidized by the holes, transported to the counter electrode and therefore gets reduced. This reduction is driven by the external connection from the semiconductor[57].

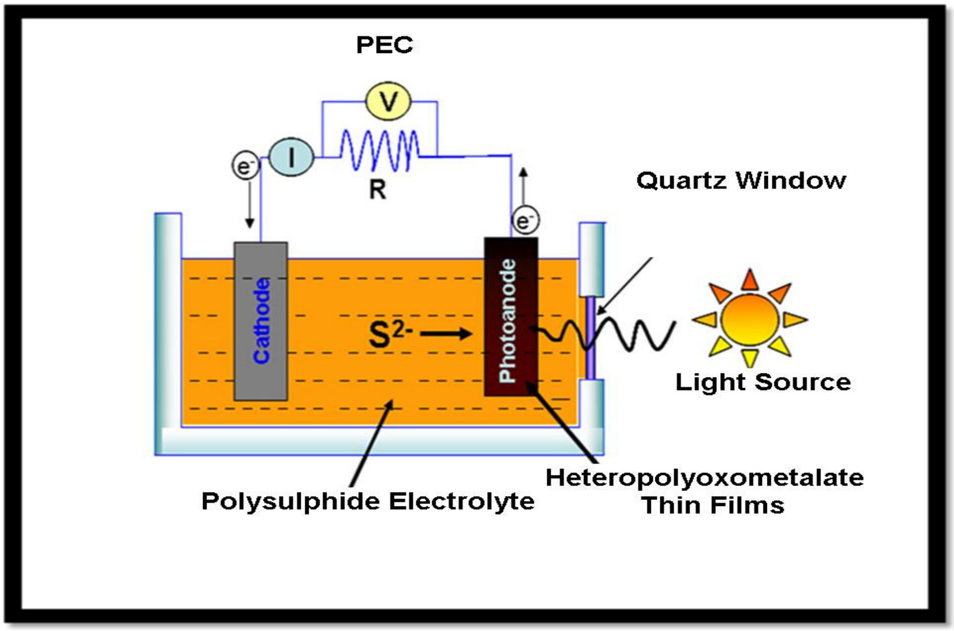


Fig. 2.B.18 Typical electrochemical photovoltaic cell

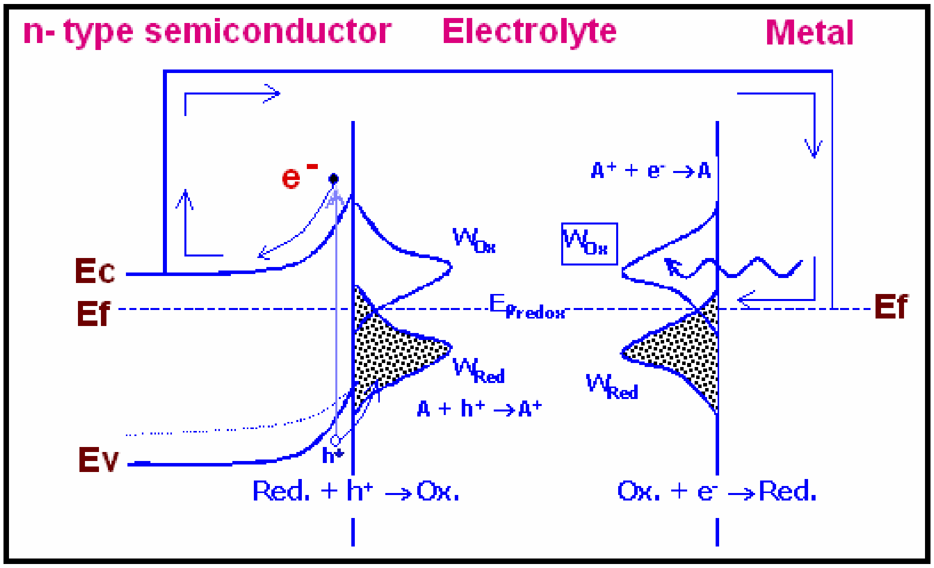


Fig. 2.B.19. Current flow and energy level diagram for n- type semiconductor PEC cell

2.B.12.2 Classification of the Photoelectrochemical (PEC) Solar Cells

The PEC cells are very similar to the Schottky type solid state solar cells. The principle of charge transfer reaction at the semiconductor – electrolyte interface forms the basis of various types, of photoelectrochemical solar cells. Depending on the net free energy change (ΔG) in the overall system, PEC cells can be divided into three categories.

A) Electrochemical photovoltaic cells ($\Delta G = 0$)

These cells consists of such a redox couple that the total cathodic and anodic reactions do not lead to net chemical change i. e. a change in the net free energy, $\Delta G = 0$. The electrodes do not participate in the chemical reaction, they only serve as a “shuttle” for the charge transfer mechanism.

At the semiconductor electrode,

$$(\text{Red.})_{\text{solv.}} + h^{+} \leftrightarrow (\text{OX})_{\text{solv.}} \qquad \text{----------} \qquad 2.15$$

At the metal counter electrode,

$$\mathbf{(Oxi.)_{solv.} + e^- \leftrightarrow (Red)_{solv.}} \quad \text{-----------} \quad \mathbf{2.16}$$

The above cell is the regenerative type PEC cell used for direct production of electricity.

B) Photoelectrolysis cells (∆G > 0)

Effectively two redox couples are present and a net chemical change takes place in the system by converting the optical energy in to chemical energy. The photoelectrolysis cells and some electrochemical storage cells belong to this category. Some examples of reaction for the above type are

$$\mathbf{H_2O \xrightarrow{hv} H_2 + \tfrac{1}{2}\,O_2} \quad \text{---------} \quad \mathbf{2.17}$$

$$\mathbf{CO_2 + H_2O \xrightarrow{hv} CH_2O + O_2} \quad \text{----------} \quad \mathbf{2.18}$$

Chemical energy

C) Photocatalytic cells (∆G < 0)

In these cells, similar to above two redox couples are present such that a net chemical changes take place. Hence ∆G < 0 and the optical energy provides the activation energy for the chemical reaction. Example for photocatalytic cell is

$$\mathbf{N_2 + 3H_2 \xrightarrow{hv} 2\,NH_3} \quad \text{---------------} \quad \mathbf{2.19}$$

2.B.12.3 Requirements of Photoelectrochemical (PEC) Cells

The requirements, expected for achieving good performance of the PEC cells are as follow:

A) Semiconductor photoelectrode

Semiconductor photoelectrode used in PEC cell for the achievement of good performance should satisfy the following requirements:

- It should be of the direct band gap type with high optical absorption coefficient (10^4 to 10^5 cm^{-1}).
- The band gap should be such that, maximum span of the solar spectrum should be utilized.

- Thickness should be thick enough to absorb all the incident radiation.
- The electrode must be stable against corrosion when placed in the specific redox electrolyte. Low band gap semiconductors generally get easily corroded. Therefore, the choice of semiconductor materials is a very important for PEC solar cells.
- Charge carriers in the material should have high mobility and life time.
- Series resistance R_s should as small as possible and shunt resistance R_{sh} should be large enough, ideally $R_s = 0$ and $R_{sh} = \infty$.
- It should remain stable in the dark as well as under illumination.

B) Electrolyte/redox couple

Another important parameter in the PEC cell is the electrolyte. Electrolytes consist of the oxidized species and the reduced species. These species are ionic species which helps to transfer the photo generated holes from photo electrode to counter electrode. The energy levels in the electrolyte are similar to the concept of energy states in the solid and $E_{f\text{-}redox}$ is equivalent to the Fermi energy level of the semiconductor. When the semiconductor electrode is immersed into the electrolyte, the equilibrium situation is achieved by the electron exchange at the surface; the fermi level of the semiconductor adjusts with each other which produces a barrier height depends on the nature of the solution species and particular semiconductor. Electrolyte properties require for the PEC cells are:

- Reduction-oxidation reactions should occur appropriate to the semiconductor band edges.
- Charge transfer rates of oxidized and reduced species at both semiconductor and counter electrode should be high or effective.
- Oxidized, reduced species and solvent components should have photo and thermal stability through useable solar spectrum and operational temperature range.
- The electrolyte should have minimum optical absorption.
- It should be non-corrosive to electrodes.
- Ionic conductance of electrolyte should permit negligible ohmic losses.
- Toxicity, reactivity and cost should preferably below.

C) The counter electrode

The counter electrode is important, it must satisfy regenerative processes, the electrolyte species are oxidized at the counter electrodes giving no net chemical change in the composition of electrolyte. The requirement for the counter electrode for better performance in the PEC cell are:

- The counter electrode should not react with electrolyte. i.e. it should be chemically inert.
- It must be electronically active i.e. the charge transfer between the counter electrode and redox species in the electrolyte must be fast.
- When a counter electrode is immersed into the electrolyte, the half cell potential of the electrode should match with that of the half cell potential of the semiconductor electrode.
- The counter electrode should have a low potential for the reduction reaction.

2.B.12.4 Conversion Efficiency of Solar Cell

A solar cell's energy conversion efficiency (η) is the percentage of power converted (from absorbed light to electrical energy) and collected, when a solar cell is connected to an electrical circuit. This term is calculated using the ratio of the maximum power point, P_m, divided by the input light irradiance (E, in W/m^2) under standard test conditions and the surface area of the solar cell (A_c in m^2)[58,59].

$$\eta = \frac{P_m}{E \times A_c} \qquad \text{------------} \qquad \mathbf{2.20}$$

2.B.12.5 Fill Factor

This is the ratio of the maximum power point (I_{max} maximum short circuit current, V_{oc} Maximum open circuit voltage) divided by the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}):

$$FF = \frac{I_{max} V_{max}}{I_{sc} V_{oc}} \qquad \text{-------------} \qquad \mathbf{2.21}$$

2.B.12.6 Advantages of Photoelectrochemical (PEC) Solar Cell

- The fabrication of PEC cell should be easy and simple.

- Many complicated processing steps in the fabrication of a p-n-junction are simplified or eliminated.
- Growth of single crystal with large are need not be required.
- Since the junction formation is a spontaneous process randomly oriented crystallites can be used.
- The minority carrier diffusion length (LD) and the depletion layer width (W) should be large.
- The most important advantages of an PEC cell is that it has a facility for chemical storage [60].

2.B.13. 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 [61]. 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 [62].

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.B.20. 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.B.21 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

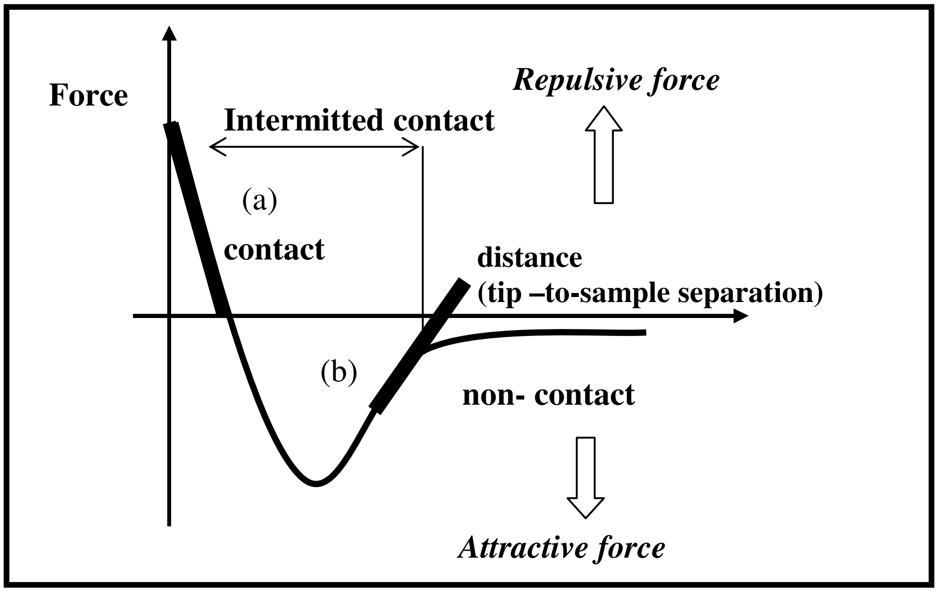


Figure 2.B.20 Inter-atomic force versus distance curve for the operation of AFM

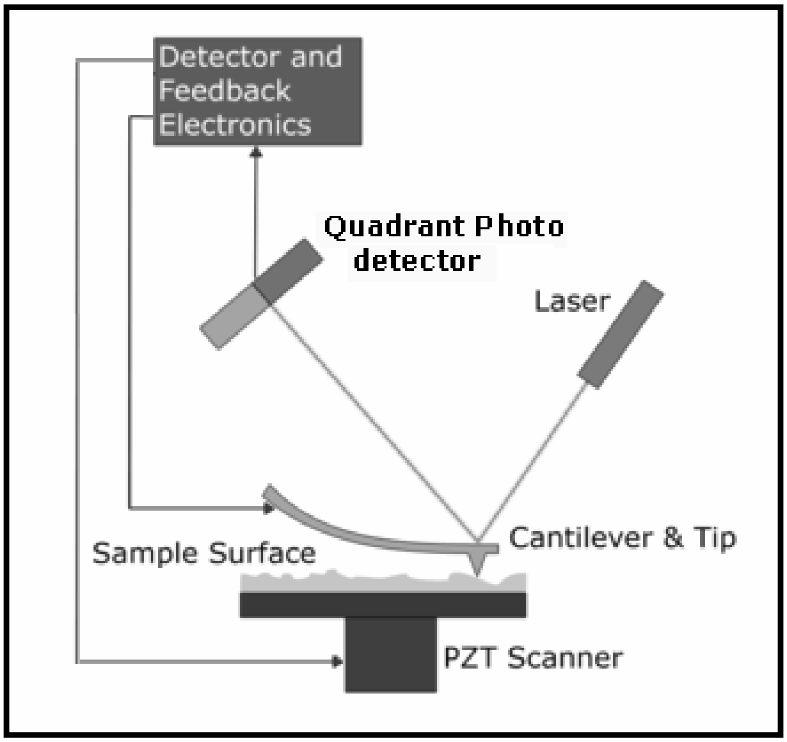


Figure 2.B.21 Schematic diagram of Atomic Force Microscope (AFM)

References

[1] Glocker,and I. Shah (editors), "Handbook of Thin Film Process Technology", Institute of Physics Vol.1&2 (2002).

[2] A. R. West, John Willy & Sons, Singapore, (2003).

[3] Bach, Hans and Dieter Krause (editors) "Thin Films on Glass" Springer-Verlag(2003).

[4] Bunshah, Roitan F (editor). "Handbook of Deposition Technologies for Films and Coatings", second edition (1994).

[5] Glaser, Hans Joachim "Large Area Glass Coating" Von Ardenne Anlagentechnik GmbH (2000).

[6] Willey, Ronald R. "Practical Monitoring and Control of Optical Thin Films " Willey Optical, Consultants ISBN 978-6151-3760-5 (2007).

[7] Willey, Ronald R. "Practical Equipment, Materials, and Processes for Optical Thin Films" Willey Optical, Consultants(2007).

[8] K. L. Chopra and S. R. Das, “Thin Film Solar Cells”, Plenum Press, New York, (1983).

[9] K. L. Chopra, “Thin Film Phenomena”, McGraw Hill, New York (1969).

[10] S.Mohan, “Proc. Advanced Course on Thin Film Processing”, Instrumentation and services unit, I. I. Sc. Banglore, India (1994).

[11] Ohring, Milton "Materials Science of Thin Films: Deposition and Structure" 2nd edition Elsevier, Inc. (2002).

[12] K.Bange, Sol. Energy Mater.Sol.Cells 58 (1999)64.

[13] Mahan, John E. "Physical Vapor Deposition of Thin Films" John Wiley & Sons (2000).

[14] Mattox, Donald M. "Handbook of Physical Vapor Deposition (PVD) Processing" Noyes Publications(1998).

[15] Mattox, Donald M. "The Foundations of Vacuum Coating Technology" Noyes Publications (2003).

[16] Mattox, Donald M. and Vivivenne Harwood Mattox (editors) "50 Years Of Vacuum Coating Technology and the Growth of the Society of Vacuum Coaters", Society of Vacuum

Coaters(2007).

[17] Westwood, William D. "Sputter Deposition", AVS Education Committee Book Series, AVS Vol. 2 (2003).

[18] Christopher M.A. Brett and Ana Maria Oliveira Brett, “Electrochemistry- Principles, Methods, and Applications”, Oxford University Press (1993)..

[19] R. P. Sharma, S. V. Patil, S. V. Bhavsar, A. R. Patil, L Dori. Indian J. Pure Appl. Phys., 37 (1999) 876.

[20]. Yagi, K. Kakizawa, K. Murakami and S. Kaneko, J. Ceram. Soc. Jap., 102 (1994) 296.

[21]. A. I. Y. Tok , F.Y. C. Boey, X. L Zhao, Journal of Materials Processing Technology 178 (2006) 270.

[22]. A. Aoki and G. Nogami, J. Electrochem. Soc., 143 (1996) 191. C. S. Huang, C. S. Tao and C. H. Lee, J. Electrochem. Soc., 144 (1997) 3556.

[23] Hyun-Suk Kim, Chang Sool Kim, Sun-Geon Kim, J. of Non- Crystalline Solids 352 (2006) 2204.

[24] P. S. Patil, E. A. Ennaoui, C. D. Lokhande, M. Muller, M. Giersig, K. Diesner and H. Tributsch, Thin Solid Films, 310 (1997) 57.

[25] C. H. Chem., A. A. J. Buysman, E. M. Kelder and J. Schoonman, Solid State Ionics, 80 (1995) 1.

[26] R. N. Singh, J. F. Koenig, G. Poillerat and P. Chartier, J. Electroanal. Chem., 314 (1991) 214.

[27] A. G. Valyomana, S. Mathew, K. P. Vijaykumar and C. Purushottam, Bull. Mater. Sci., 16 (1993) 55.

[28]. Kill Dong LEE,Journal of the Korean Physical Society, 40, (2005) 1383.

[29]. C.G.Granquist, Handbook of Inorganic Electrochromic Materials. Elsevier, Amsterdam, Netherlands (1995).

[30]. W.Li, F.Cheng, Z.Tao, J.Chen, *J.Phys.Chem.B* 110 (2006) 119.

[31]. T.S. Sian, D.B.Reddy, *J.Appl.Phys.* 98 (2005) 026104.

[32]. V.Bhosale, A.Tiwari, J.Narayan, *J.Appl.Phys.*97 (2005) 083539.

[33]. C.Julien in: G.Pistoria (Ed.), Lithium Batteries: New Materials, Developments and Perspectives, Amsterdam, North-Holland, 1994.

[34]. J.N.Yao.Y.A.Yang, B.H.Loo, *J.Phys.Chem*. B 102 (1998) 59.

[35]. C. R. Brundle and A. D. Baker, Electron Spectroscopy, Theory, Techniques and Applications, Pergamon Press, volume II (1978) Chapter I.

[36] M.Fox.Quantum Optics; An Introduction, Oxford University,Press (2006).

[37] Willard,Merrit, Dean, Settle, Instrumental Methods Of Analysis, Sixth Edition, CBS publishers And Distributors, 606.

[38]. M. J. Buerger, “X-ray Crystallography”, Wiley, New York (1942).

[39]. H. P. Klug and L. E. Alexander, “X-ray Diffraction Procedures”, Wiley, New York (1954).

[40]. B. D. Cullity, “Elements of X-ray Diffraction”, Addison Wesley, Massachusetts (1956).

[41]. A. Taylor, “X-ray Metallography”, Wiley, New York (1942).

[42]. A. Guinier, “X-ray Diffraction “, Freeman, San Francisco (1963).

[43]. C. S. Barrett and T.B. Massalski, “Structure of metals”, McGraw-Hill, New York (1966).

[44]. Thornton, Steven T. and Rex, Andrew, Modern Physics for Scientists and Engineers, Saunders College Publishing, 1993.

[45]. B.D. Cullity, Elements of X-rays 2nd edition Addiso Wesley, London, (1978).

[46]. S. Banerjee, “Proc. of National Workshoip on Advanced Methods for Materials Characterization” (NWMMC-2004) Mat. Res. Soc. India (2004).

[47]. Oatley, D. McMullan and K. C. A. Smith, The Development of the Scanning Electron Microscope,. Advances in Electronics 16 (London: Academic Press) (1985) 443.

[48]. Scanning Electron Microscopy, Oliver C. Wells,. McGraw-Hill, New York, 1974), pp. 9, 139-

[49]. F. Micheltti and P. Mark, J. Appl. Phys. 10 (1967) 136

[50]. E. Becquerel, Comt. Rend. H. A. 9 (1839) 561.

[51]. Gardiner, D.J. Practical Raman spectroscopy.Springer Verlag(1989).

[52]. *Khanna, R.K.* Raman-spectroscopy of oligomeric SiO species isolated in solid methane. Journal of Chemical Physics. doi: 10.1063/1.441393*(1981).*

[53]. Ben Vogel “Raman Spetroscopy portends well for stand off explosive detection“.(29 August 2008).

[54]. Ellis DI, Goodacre R "Metabolic fingerprinting in disease diagnosis: biomedical applications of infrared and Raman spectroscopy". *Analyst* 131 (8): (2006)875.

[55]. Khanna, R.K. *Evidence* of ion-pairing in the polarized Raman spectra of a Ba^{2+}CrO doped KI single crystal. John Wiley & Sons, Ltd. (1957).

[56]. Kneipp K, *et al.* "Surface-Enhanced Non-Linear Raman Scattering at the Single Molecule Level". *Chem. Phys.* 247 (1999)155.

[57]. D. Heiman, Physics U600, Adv Lab I Physics of Waves and Opt ics Summer 2004, Northeastern University, (2004).

[58]. L.D. Partain, “Solar Cells and Their Applications”, John Wiley & Sons, Inc, N.Y. (1995) 600.

[59]. S. Chandra in “Photoelectrochemical Solar Cells” (eds) D. S. Campbell, Gorden and Breach Science Publisher, New York U.S.A. (1985) 225.

[60]. M.T. Gutierrez and J. Ortega, Sol. Energy Mater. 20 (1990) 87.

[61]. A.F. Janzen in “Solar Energy Conversion” Ed. A.E. Dixon, J.D. Leslie, Pergamon Press, G.B. (1978).

[62] T. R. Albrecht, J. Appl. Phy. 69 (1991) 668.

[63] C. S. Barrett and T.B. Massalski, “Structure of metals”, McGraw-Hill, New York, (1966).