Chapter 11

TECHNIQUES AND MEASUREMENTS
CHAPTER - II

TECHNIQUES AND MEASUREMENTS

Materials characterization using X-ray diffraction, Scanning Electron Microscopy, Atomic Spectroscopy techniques plays a vital role in all aspects of semiconductor technology from fundamental research to manufacturing (application). Measurements of energy gap, resistivity, Hall mobility, carrier concentration and photosensitivity of semiconducting materials are described below.

2.1 X-Ray Diffraction (XRD)

X-Ray diffraction is a well established [63,64] technique for determining crystalline order in three dimensional solids. The measurements indicate the identification of individual crystalline phases by their characteristic diffraction patterns. Further analysis of XRD patterns yields information regarding the orientation and size distribution of the crystallites.

The well known relationship between the wavelength of the X-ray beam, $\lambda$, is the angle of diffraction, $2\theta$ is the distance between each set of atomic planes of the crystal lattice, $d$ is given by Bragg’s law

$$n\lambda = 2d \sin \theta$$

Where, $n$ is the order of diffraction and $d$ is the interplanar distance of the crystalline material being calculated from the above equation. The interplanar spacings depend solely on the dimensions of the crystal unit cell while the intensities of the diffracted rays are a function of the placement of
the atoms in the unit cell. Also the crystalline size calculated using Scherrer’s equation
\[ t = \frac{k \lambda}{B \cos \theta} \] ... (2)

Where, B is the breadth of the diffraction line at its half intensity maximum (FWHM) and K is the shape factor which usually takes a value of about 0.9 [65].

2.2 Atomic Absorption Spectroscopy (AAS)

AAS is a technique for determining the concentration of the metallic elements in solution. Atomic absorption is specific and characteristic for each element. Here the sample may be either liquid or solid, but must be diluted or dissolved in a suitable medium. The quantity required may vary and is dependent upon the element(s) sought and the anticipated concentration level. Extremely low concentrations may be determined by using evaporation or solvent extraction.

2.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope is one of the most versatile instruments available for the examination and analysis of micro structural characteristics of solid objects. In SEM, the areas to be examined or the micro volume to be analyzed, is irradiated with a finely focused electron beam which may be static or swept in a raster across the surface of the specimen. The types of signals produced when the electron beam impinges on the specimen surface include secondary electrons, back scattered electrons, Auger electrons,
characteristic X-rays, and photons of various energies. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample (surface topography, crystallography etc). If the sample is not electrically conducting, it is usually necessary to coat it with carbon, gold or some other metal to provide a conducting surface.

2.4 Atomic Force Microscopy (AFM)

AFM stands for Atomic Force Microscopy or Atomic Force Microscope and is often called the “Eye of Nanotechnology”. AFM, also referred to as SPM or Scanning Probe Microscopy, is a high-resolution imaging technique that can resolve features as small as an atomic lattice in the real space. It allows researchers to observe and manipulate molecular and atomic level features. AFM works by bringing a cantilever tip in contact with the surface to be imaged. An ionic repulsive force from the surface applied to the tip bends the cantilever upwards. The amount of bending, measured by a laser spot reflected on to a split photo detector, can be used to calculate the force. By keeping the force constant while scanning the tip across the surface, the vertical movement of the tip follows the surface profile and is recorded as the surface topography by the AFM. The predecessor of AFM is STM, Scanning Tunneling Microscopy or the Scanning Tunneling Microscope, was invented in 1981 by G. Binnig and H. Rohrer who shared the 1986 Nobel Price in Physics for their invention. An excellent technique, STM is limited to imaging conducting surfaces. AFM has much broader potential and application
because it can be used for imaging any conducting or non-conducting surface. The number of applications for AFM has exploded since it was invented in 1986 and now encompass many fields of nanoscience and nanotechnology. It provides the ability to view and understand events as they occur at the molecular level which will increase our understanding of how systems work and lead to new discoveries in many fields. These include life science, materials science, electrochemistry, polymer science, biophysics, nanotechnology, and biotechnology.

2.5 X-Ray Photoelectron Spectroscopy (XPS)

XPS is also called Electron Spectroscopy for Chemical Analysis (ESCA). This is an electron spectroscopy method that uses x-rays to eject electrons from the inner shell orbitals. The kinetic energy, $E_k$, of these photoelectrons is determined by the energy of the x-ray radiation $h\nu$, and the electron binding energy $E_b$, given by,

$$E_k = h\nu - E_b$$

The experimentally measured energies of the photoelectrons are given by,

$$E_k = h\nu - E_b - E_w$$

Where $E_w$ is the work function of the spectrometer. The electron binding energies are dependent on the chemical environment of the atom, making XPS to identify the oxidation states and ligands of an atom. In XPS, the sample is illuminated with soft x-radiation (1.5kV) in an ultrahigh vacuum. The
photoelectric effect leads to the production of photoelectrons, the energy spectrum of which can be determined in a beta ray spectrometer.

XPS instrument consists of an energy analyzer for the photoelectrons and an electron detector. The analysis and detection of photoelectrons requires that the sample be placed in a high vacuum chamber. Since the photoelectron energy depends on the x-ray energy, the excitation source must be monochromatic. The energy of the photoelectrons is analysed by an electrostatic analyzer, and the photoelectrons are detected by an electron multiplier tube or a multichannel detector such as microchannel plate. XPS evaluates the valence states, bonding environments and the molecular composition of surface layers. Identifies elements from lithium to uranium, with detection levels down to 0.5 at %. To produce images with a spatial resolution of 20 microns roaster scanning is used. By sputtering materials from the surface, generates composition distribution for materials. Evaluate the surface of catalysts to determine reactive species. High vacuum of order of $10^{-10}$ Torr reduces contamination for reliable analysis. The small spot size facilitates analysis of small areas and features.

2.6 Optical Properties

In semiconductors the equilibrium situation can be distributed, by generation of carriers due to optical absorption. Optical photons incident on any material may be reflected, transmitted or absorbed. The absorption of light in a semiconductor can lead to:
a. Photo ionization of semiconductor atom: this is excitation of valence electrons to the conduction band. The energy required is greater than or equal to the band gap.

b. Photo ionization of impurity atoms: this leads to the transition of an electron from the donor level to the conduction band or from the valence band to the acceptor level.

c. Formation of excitons.

d. Excitation of free carriers to a higher energy state in the same band.

e. Excitation or absorption of photons.

The optical absorption studies are useful for the identification of band gap, impurity states etc. Further, processes like (a) and (b) result in generation of electrons/holes and hence photoconductivity, photovoltage etc. 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 the valence band to the conduction band. The conservation of energy and momentum must be satisfied in optical absorption processes. Considering the opto-electronic applications of thin films, the optical absorption studies are very important which give an insight into the nature of transitions either direct or indirect. To measure the band gap of the semiconductor, the following procedure has to be adopted. From the optical measurements, the absorbance of the semiconducting film for each wavelength can be obtained. The absorption coefficient $\alpha$ is calculated by using the relation,
\[ \alpha = 2.303 \text{ A / t} \] ... (3)

Where, \( A \) is the absorbance value at a particular wavelength and \( t \) is the thickness of the semiconductor film thickness is estimated by adopting a non destructive technique, namely gravimetric method.

The absorption coefficient \( \alpha \) for a band to band transition between parabolic bands is given by

\[ \alpha = A(h\nu - E_g)^{n/2} / h\nu \] ... (4)

Where, \( A \) is the constant depending upon the transition probability, \( h\nu \) is the radiation energy and \( n = 1 \) or \( 4 \) depending upon direct or indirect transition respectively. A plot of \( (\alpha h\nu)^2 \) or \( (\alpha h\nu)^{1/2} \) against \( (h\nu) \) whose intercept on the \( h\nu \) axis is the band gap for the direct or indirect transition respectively and the slope is \( A \).

### 2.7 Hot Probe Technique

This technique [66] based on the principle of Seebeck effect. It is used to measure the direction of electron flow in a semiconductor in an electric circuit, from the direction it is possible to determine the type of the semiconductor.

### 2.8 Resistivity and Hall Measurements

The electric behavior of polycrystalline semiconductors show similarities to that of single crystalline materials since the microscopic regions of crystallinity (domains) have a short–range order or a microscopic periodicity. Poly crystalline semiconductors can therefore be considered to be
quasi-periodic. For studying the transport properties of polycrystalline thin films, the Hall effect has been used as an important tool.

Resistivity and Hall measurements were used to evaluate mobility and concentration of charge carriers. Resistivity was determined by Van der Pauw technique [67, 68]. Here, current contacts A and B, and voltage contacts C, D, E and F are connected to the semiconducting film, deposited on clean glass substrate provided with metal contacts. The resistivity is then derived from the potential drop between the points C and D or E and F and from the dimensions of the sample. On the other hand, Hall voltage can be measured between the points C, D, E and F in order to ensure that the lines of flow are sufficiently parallel and are not changed on application of a magnetic field. For measuring the resistivity of a flat sample it is sufficient to make four small contacts along its circumference to measure the two resistances \( R_{AB,CD} \) and \( R_{BC,DA} \). The equation for \( \rho \) as a function of \( R_{AB,CD} \) and \( R_{BC,DA} \) and \( t \) can be written as

\[
\rho = \pi t (R_{AB,CD} + R_{BC,DA}) f(R_{AB,CD} / R_{BC,DA})/2\ln2 \quad \ldots \quad (5)
\]

Where \( R_{AB,CD} \) is the resistance and \( V_D - V_C \) is the potential difference between the contacts D and C per unit current through the contacts A and B. The current enters the sample through the contact A and leaves it through the contact B. Similarly, the resistance \( R_{BC,DA} \) can be defined. \( \rho \) is the specific resistance of the material and \( t \) is the thickness of the film. The Van der Pauw function \( f \) plotted as a function of \( R_{AB,CD} / R_{BC,DA} \) has been taken from the literature.
The Hall mobility can be determined by introducing the film into the electromagnetic field. Here, the change of the resistance $R_{BD,AC}$ is measured when a magnetic field is applied perpendicular to the film. The Hall mobility is then given by

$$\mu_H = \frac{t (\Delta R_{BD,AC})}{B \rho} \quad \text{... (6)}$$

where, $\mu_H$ is the Hall mobility, $B$ is the magnetic induction and $\Delta R_{BD,AC}$ is the change of the resistance $R_{BD,AC}$ due to the magnetic field. The equation (6) can also be written as

$$\mu_H = \frac{t}{B (\Delta V / \rho I)} \quad \text{... (7)}$$

Consider the magnetic field applied across AC when current ($I$) is passing perpendicular to AC (i.e., BD). The electric field included along the direction perpendicular to both of them is measured as potential here. This can be done for both forward and reverse direction of the applied magnetic field. The difference in these two values is measured as $\Delta V$. If the current carriers are predominantly of one type only, then the Hall coefficient $R_H$ is equal to the product of the conductivity and the Hall mobility. The relation can be written as

$$R_H = \frac{\mu_H}{\rho}$$

$$1 / (Nq) = \mu_H \sigma$$

$$N = \frac{1}{(\sigma q \mu_H)} \quad \text{... (8)}$$

### 2.9 Photoconductive Measurements

Photoconductivity is the increase in electrical conductivity of a substance caused by radiation incident on it. The effect of illumination is to
increase the number of mobile charge carriers in the substance. If the energy of the incident photon absorbed in the sample excite an electron to the conduction band producing a hole in the valence band, then the conductivity of the sample increases. Holes and electrons will eventually recombine but the time spent between release and recombination depends upon the trapping centres.

Trapping centres are those where the captured carriers have a greater probability of being thermally re-excited to the free state. If the reverse is true they are called recombination centres. Although a centre with energy level near one of the band edges is likely to act as a trap rather than as a recombination centre (and vice versa, for centres with levels, lying near the middle of the forbidden gap) the distinction between traps and recombination centres is based on the relative probabilities of thermal ejection and recombination respectively. A recombination centre at one condition of light level and temperature may act as a trap at another condition of light and temperature. The dynamics of photogeneration of carriers is well understood in terms of the transitions taking place between the electronic states.

To explain photoconductivity of the semiconductor, two models such as recombination and barrier have been proposed [69].

2.9.1 Recombination Model

The concept of hole or electron traps is important in the recombination theory of photoconductivity. Due to the presence of impurities and other lattice imperfections, localized levels having energy in the energy gap exist in the
crystal. Most recombination occurs through these recombination centres or traps. Only at high carrier densities and therefore at high intensities of illumination does the direct recombination process compete with trapping. The photoconductivity in equilibrium will be determined by a balance between processes which create charge carriers and those by which they disappear. The generation processes by which carriers are produced include:

a. Generation of hole-electron pairs by thermal and radiant energy.

b. Creation of free electron by thermal or radiant energy leaving a trapped hole behind.

c. Creation of a hole by thermal or radiant energy, leaving a trapped electron behind.

d. Release of a trapped electron and
e. Thermal release of trapped hole.

The recombination processes by which carriers disappear include:

a. Direct recombination of a free electron and a free hole.

b. Trapping of a free electron.

c. Trapping of a free hole.

(d. Recombination of a free electron and a trapped hole.

e. Recombination of a free hole and a trapped electron.

2.9.2 Barrier Model

This model applies to polycrystalline semiconductors, which possesses a high surface state density. It is assumed that illumination produces little or no change in the density of charge carriers but the effective mobility of such
carriers is increased. It is also assumed that a large number of surface states are produced along the crystalline boundaries, for instance, by oxidation of these boundaries. These surface states capture electrons from the interior of the single crystalline domains and produce space charge barriers. Illumination reduces the number of electrons in the surface states and, thereby lowers the barrier height between domains, which may then be observed as an increase in conductivity. This model predicts that the photosensitivity is independent of light intensity and proportional to temperature.

2.9.3 Photoconductivity

The photoconductivity covers all the phenomenon by which a conductivity change, increase or decrease, follows absorption of light in the considered material. Photoconductivity is not an elementary process. It includes several successive or simultaneous mechanisms: optical absorption, hot carrier relaxation, charge carrier transport and recombination.

The observation of any photoconductivity phenomenon requires the presence of at least one type of mobile charge carrier. If the conductivity due to these carriers is written as

\[ \sigma = qN\mu \]  \hspace{1cm} ... (9)

Where, \( q \) is the magnitude of electronic charge, \( \mu \) is the mobility and \( N \) is the carrier concentration. The photoconductivity or variation of conductivity upon light variation, has the general form

\[ \Delta\sigma = q(\mu \Delta N + N \Delta \mu) \]  \hspace{1cm} ... (10)
Thus photoconductivity may arise due to change in carrier concentration and/or carrier mobility. These changes result from the generation in the semiconductor of electronic excited states by absorption of light energy. Either these excited states represent the excess carrier concentration $\Delta N$, or they induce a mobility variation $\Delta \mu$. The excited states have a finite life time. They lose energy through different processes of relaxation and recombination.

Any photoconductivity phenomenon basically involves three processes of energy transfer: generation, relaxation and recombination. Hot excited states are directly generated by optical absorption from the ground states. They relax to excited states of lower energy (cold states) but can also undergo recombination to ground states. Photoconductivity is due to electrical transport by hot and cold excited states.

### 2.10 Photosensitivity

The concept of photosensitivity may be defined in several ways. The quantity specific sensitivity (SS) is the one way of defining photosensitivity [70]. Specific sensitivity is the photoconductivity per unit excitation intensity, i.e., the change in conductivity caused by excitation divided by the excitation intensity. The radiation is absorbed by the volume of the photoconductor. Excitation intensity is the power absorbed per unit volume $= P / (l \cdot b \cdot t)$, where $P$ is the power.

Hence,
\[ SS = \Delta \sigma \frac{I \cdot b \cdot t}{P} \]
\[ = \Delta i \cdot I \cdot b \cdot t / (V \cdot b \cdot t \cdot P) \]
\[ = \Delta i^2 / (V \cdot P) \quad \ldots (11) \]

Where, \( \Delta i \) is the photocurrent, \( V \) is the applied voltage, \( I \) is the electrode spacing and \( P \) is the absorbed radiation power. Here, \( SS \) is expressed in mho-cm\(^2\) per watt. The highly sensitive CdSe type photoconductors have values of specific sensitivity around unity. The specific sensitivity is an intrinsic property of the material, which is independent of applied voltage and light intensity, if the photoconductivity varies linearly with voltage and light intensity.

The relative photosensitivity, \( S \), is defined as the ratio of the change in conductivity to the dark conductivity.

\[ S = \frac{(\sigma_L - \sigma_D)}{\sigma_D} \quad \ldots (12) \]

Where \( \sigma_L \) is the light conductivity and \( \sigma_D \) is the dark conductivity.

But \( \sigma = I / (R \cdot A) \)

Where \( R \) is the resistance, \( I \) is the length and \( A \) is the area of cross-section of the photoconductor. Substituting this in (12), then

\[ S = \frac{(R_D - R_L)}{R_L} \quad \ldots (13) \]
\[ = \frac{R_D}{R_L} - 1 \]
\[ = \frac{R_D}{R_L} \quad \text{if } R_D >> R_L \]

The term photoconductive gain is also used for expressing photosensitivity of a photoconductor in terms of the number of charge carriers that pass between the electrodes per second for each photon absorbed per
second. If the life of majority carrier is $\Gamma$, and the time required for one transit between the electrodes is $t$, then

$$G = \Gamma / t \quad \text{But, } \mu = \frac{i^2}{Vt}$$

$$t = \frac{i^2}{\mu V}$$

$$G = \frac{\Gamma \mu V}{i^2}$$

... (14)

2.11 A.C. PHOTOCONDUTIVITY MEASUREMENTS

2.11.1 A.C. Photosensitivity

The experimental set up used to measure A.C photosensitivity employs a load resistor ($R_L$) (equal to the resistance of the photoconductor) in series with the photoconductive cell and the biasing source of DC power supply APLAB 7321. The source radiation was a 100 W tungsten filament lamp kept at a fixed distance with an intensity of illumination (5000 lux). The incident radiation was chopped at 90 Hz frequency using a chopper, and by applying various bias voltages, the A.C signal was measured using HIL digital multimeter.

Switching on the light, results in a decrease in resistance of the photoconductive cell, which in turn causes a decrease in voltage across the cell, and a corresponding increase in voltage across the load resistor ($R_L$). This increase in voltage across the load is called the signal voltage [71].

The A.C photosensitivity is expressed as,

$$\%S = \left( \frac{\Delta R}{R_C} \right) \times 100 = \frac{(E - \Delta V)}{V_1(E - V_2)} \times 100 \quad \ldots (15)$$

Where, $E$ is the applied bias
$R_c$ is the photoconductor dark resistance

$\Delta R_c$ is the change in resistance of the photoconductor on illumination.

$V_1$ is the voltage across the photoconductor in dark

$V_2$ is the voltage across the photoconductor on illumination.

$$V_2 = V_1 + \Delta V; \Delta V \text{ is the signal voltage.}$$

The A.C photosensitivity can be expressed as follows:

$$\%S = \left[ \frac{2 \times \Delta V}{V_2} \right] \times 100 \quad \ldots (16)$$

### 2.11.2 Noise

While calculating the sensitivity of the photoconductor at least seven different sources of noise mechanism must be considered and the conditions for achieving the ultimate performance of photoconductor by limiting the noise factor is discussed [73].

i) Johnson’s noise

ii) Low frequency noise

iii) Noise due to generation and recombination of charge carriers.

iv) Fluctuation in background radiation falling on the photoconductor.

v) Fluctuation in signal radiation received by the photoconductor.

vi) Fluctuation in effective temperature of hot electron photoconductive cell.

vii) Noise in the amplifier followed by a photoconductor.

Noise due to frequency and noise due to amplifier followed by photoconductor are caused by gross imperfections, in the design of the apparatus, but others are of a more fundamental nature.
2.12 Photoelectrochemical Studies
2.12.1 Semiconductors

In the light energy conversion discussed in the following pages, the substance that absorbs the radiant energy and transducers it to an electron hole pair is a semiconductor. The nature and properties of a semiconductor make this possible. The basics are dealt within several excellent text books [70, 74, 75].

The colour of a semiconductor roughly indicates what portion of the solar spectrum is absorbed by it. The energy gap, therefore, determines the colour of the semiconductor. The visible region of the spectrum extends in the energy from about 1.5 eV to 3.0 eV (red to violet). Silicon, gallium arsenide, Indium phosphide, cadmium telluride and other low band gap materials appear black, since visible light is entirely absorbed by them. Zinc oxide, titanium di oxide, tin oxide, strontium titanate etc., appear white because they absorb only in the ultraviolet region, reflecting the visible spectrum.

The energy contained in sunlight is distributed over a wide range of wavelengths and efficient conversion requires a wide spectral response. Wider band gap materials absorb in a smaller spectral range of the terrestrial solar radiation producing smaller currents than smaller band gap materials, which absorb more producing larger short circuit current.

The basic properties of these junctions are described under the solid-liquid junctions, since this work has a direct bearing on electrochemical conversion of light energy.
A short account of the solid state photovoltaics would be in order before going into the wet photovoltaic cells.

2.12.2 Photocurrent

p-n photocells (consisting of p-n junction) and Schottky photocells (consisting of semiconductor- metal junction) are the two principal types of solid state devices. The following equation gives the current- potential dependence of these cells [75],

\[ I = I_0 \left( \exp \frac{qV}{n kT} - 1 \right) - I_{ph} \]  \hspace{1cm} (17)

Here, \( I_0 \) is the reverse saturation current

\( q \) is the electronic charge

\( n \) is the ideality factor

\( V \) is the externally applied voltage

\( I_{ph} \) is the photocurrent

Light excitation produces electron-hole pairs. The charge carriers are separated by the field in the space charge layer and they move in opposite directions. The resultant photocurrent in the reverse direction is proportional to the light intensity.

2.12.3 Photopotential

At a certain illumination, the photopotential \( V_{ph} \) as measured under open circuit condition, occurs at that potential at which the photocurrent is equal to the corresponding dark current, i.e., when the total current is zero. Under this condition, then \( I = 0 \),
\[ V_{ph} = kT/q \ln(I_{ph}/I_o + 1) \] ... (18)

The ratio of photocurrent and reverse saturation current thus closely determines the photovoltage.

2.12.4 Liquid Junction photovoltaics

The photovoltaic properties of the semiconductor liquid junction are the basis of the liquid junction photovoltaic cells known as the photo electrochemical (PEC) cells. In fact, it was in a semiconductor – electrolyte junction (or interface) that Bequerel [76] first discovered the photovoltaic effect as mentioned earlier.

In the solid state cells, light pumps electrons through an external circuit and no chemistry occurs. In the semiconductor electrolyte junction cells, electron transfer occurs across the semiconductor electrolyte interface, resulting in chemical reaction at the interface. Charge is transported by ionic movement in the electrolyte, as in electrochemical cells.

2.12.5 Semiconductor- Electrolyte Junction

The semiconductor electrolyte interface, has been the subject of intense study and many excellent treatises and reviews are available on the subject information related to this work is given here in brief [77 - 79].

The instant a semiconductor is immersed in an electrolyte solution, a junction between the two known as the semiconductor- electrolyte junction is formed, with a space charge layer in the semiconductor. The origin of the space charge layer lies in the difference in the chemical potential of electrons on the semiconductor side and the electrolyte side.
The Fermi level of the semiconductor and the redox potential of the electrolyte give the chemical potential of electrons in the respective phases.

2.12.6 Space Charge Layer

To visualize the formation of the space charge layer, consider an n-type semiconductor, whose Fermi level is above that of the redox system. On placing the semiconductor in the redox system, equilibrium of the Fermi level occurs by transfer of electrons from the semiconductor to the electrolyte. This produces a positive space charge layer in the semiconductor, which is also called a depletion layer, since the region is depleted of majority carriers. The transfer of electrons into the electrolyte causes the conduction and valence bands bend in such a way at the interface that a potential barrier results and further electron transfer from the semiconductor to the electrolyte is prevented.

A similar phenomena at a p-type semiconductor results (with the initial Fermi-level of the semiconductor lower than that of the electrolyte) in a negative space charge layer, the valence and conduction bands bending in such a way to produce a potential barrier for further hole transfer into the electrolyte.

The manner in which charge transfer occurs across the semiconductor electrolyte determines the nature of the space charge layer which may be a depletion, accumulation or inversion or a deep depletion layer.
A depletion layer caused by the depletion of majority carriers in a semiconductor leads to the upward band bending in an n-type semiconductor, and a downward band bending in a p-type semiconductor.

An accumulation of enrichment layer results if the surface acquires excess majority carriers and gets enriched (in majority carriers). This situation leads to a downward band bending in an n-type semiconductor.

An inversion layer results if the number of charge carriers extracted is excessive, so much that the majority carrier band cannot supply all the majority carriers required without resulting in excessive band bending. In this situation the carriers come from the minority carrier band also. Considering an n-type semiconductor, the majority carriers (electrons) are not only extracted from the conduction band but also from the valence band (hole injection). This would mean that the n-type semiconductor has actually been inverted to p-type at the surface.

A deep depletion layer is induced by an applied voltage.

2.12.7 Photo electrochemical cells

A semiconductor immersed in a solution of a redox electrolyte will form a photovoltaic junction. If the electrochemical potential of the solution (\(E_{\text{redox}}\)) lies within the band gap of the semiconductor. This junction is capable of converting light to electrical or chemical energy and it is the heart of a photo electrochemical cell. Many reviews are available in the literature on the subject of PEC cells [80-87]. The list is by no means exhaustive, due to limitations of space.
A PEC cell in its simplest form consists of a semiconductor photoelectrode and a counter electrode immersed in a suitable redox electrolyte solution and shorted through the load. The process by which semiconductor liquid junction solar cells sunlight into electric power resembles that of a p-n junction silicon cell except that the circuit involves redox reactions at the photoelectrode and counter electrode. In a regenerative cell, these are equal but opposite in direction and thus do not introduce any net chemical change. Books by Morrison [88] and the latest book by Pleskov [89] published in 1990 gave a lot of information about PEC cells.

Initial charge transfer at the interface leads to band bending in the absence of illumination, the conduction band and the valence band are bent upto a maximum value of $E_f - E_{\text{redox}}$, $E_f$ being the Fermi level of the semiconductor and $E_{\text{redox}}$ be the potential of the redox couple in solution. This difference, the barrier height, represents the upper limit of the open circuit voltage, $V_{oc}$, which can be obtained under high irradiance. $V_{oc}$ cannot exceed $E_f - V_b$ for photoanodes and $E_f - V_c$ for photocathodes.

### 2.12.8 Space Charge layer width

The width of the depletion layer depends on the electrical conductivity of the semiconductor and the extent of band bending at the surface (In contrast in a metal electrode mainly reside on the surface). From knowledge of the charge carrier density and band bending, the space charge layer width can be calculated from the relationship,

$$W = (2\varepsilon\varepsilon_0 V_b/qN)^{1/2}$$

... (19)
Where, $W$ is the width of the depletion layer

$V_b$ is the band bending

$q$ is the electronic charge

$N$ is the charge carrier density

$\varepsilon$ is the dielectric constant of the semiconductor

$\varepsilon_0$ is the permittivity of free space.

2.12.9 Helmholtz and Gouy layers

At the interface on the electrolyte side in the Helmholtz layer, a few angstrom thick. This is made up of charged ions from the electrolyte absorbed on the semiconductor electrode surface. These ions are of opposite sign to the charge induced in the solid electrode.

Beyond the Helmholtz layer is the Gouy-Chapman diffuse double layer, caused by the like charges in the solution side of the Helmholtz layer attracting unlike charges, resulting in a more extensive disturbance of the bulk charge distribution near the phase boundaries. In this region, there would be a non-linear fall in potential away from the interface.

The difference between the Fermi levels of the solid phase and liquid phase will be equal to the band bending but for the potential drop across the Helmholtz layer. This effect is similar to that of surface states on the potential barrier in Schottky junctions.

2.12.10 Flat band potential and Donor density

The flat band potential of a semiconductor electrode correlates the energy levels of the electrolyte and the semiconductor. It is the electrode
potential at which there is zero space charge in the semiconductor and the semiconductor bands are flat from the bulk of the surface. It is measurable with respect to a standard electrode like NHE or calomel electrode. The difference between the electrode potential \( V \) in the dark at equilibrium and the flat band potential \( V_{fb} \) gives the band bending \( V_b \),

\[
V_b = V - V_{fb} \quad \ldots \quad (20)
\]

The value of the flat band potential takes into account the effect on Helmholtz layer on the band bending. The flat band potential is a property of the bulk of the semiconductor as well as the electrolyte,

\[
V_{fb}(\text{NHE}) = (\chi - \Delta E_f + V_H) - 4.5 \quad \ldots \quad (21)
\]

\[
= (\phi_{sc} - V_H) - 4.5 \quad \ldots \quad (22)
\]

Where, \( \chi \) is the electron affinity

\( \phi_{sc} \) is the work function

\( \Delta E_f \) is the difference between the Fermi level and the majority carrier band edge.

\( V_H \) is the potential drop across the Helmholtz layer.

### 2.13 PEC cell configuration and measurements

The PEC cell was constructed as follows. The photoelectrode and a counter electrode of graphite was positioned 2 cm apart in a 100 ml pyrex cell containing the alkaline polysulphide redox electrolyte of composition 1M \( \text{Na}_2\text{S} \), 1M S and 1M NaOH, prepared using argon purged triple distilled water. Prior to the experiments argon was bubbled through the electrolyte, and during the experiments too, gently.
The two electrodes immersed in the electrolyte about 2 cm apart were externally connected through a multimeter (HIL 2102) to measure the current and a decade resistance box. The photoelectrode was positioned as close as possible to the cell facing the light source to minimize light attenuation due to solution absorption. The PEC cell voltage was measured using a HIL 2161 digital multimeter. Solar cell measurements were made with the two electrode system in a single compartment cell. An ORIEL model 6432 tungsten halogen lamp was the light source. The beam was passed through a 5 cm water filter and an ORIEL model 7165 IR absorbing filter fitted to a condensing lens system. The intensity of the light incident on the electrode was measured using Suryamapi, reading the intensity in mWcm\(^{-2}\). Intensity variations were achieved by employing the neutral density filters and by adjusting the path length of the light beam from the source to the cell. I-V characteristics were determined by recording the current and voltage from the PEC cell under illumination by progressively decreasing the load resistance. The current was measured as a function of load resistance only under irradiation and no external power source was used.

### 2.13.1 PEC cell parameters

Short circuit current, open circuit voltage, fill factor, power maximum and conversion efficiency are the main cell parameters.
2.13.2 Short circuit current ($I_{sc}$)

It is the current flowing through the illuminated junction under zero bias. In an ideal case, this current should equal to the light generated current and proportional to the number of incident photons.

In practice the short circuit current is the current flowing through a precision load resistor such that the voltage across the cell is less than 20 mV. The intercept of I on the x-axis at $V = 0$ gives the short circuit current.

2.13.3 Open circuit potential ($V_{oc}$)

It is the voltage at zero current through the device i.e., it is the voltage developed in the cell under illumination, when no current flows through the cell.

$V_{oc}$ is measured across the unloaded cell with a voltmeter having an internal resistance of at least 20 kilo ohms. $V_{oc}$ can be calculated from the equation,

$$V_{oc} = n k T / q \left[ \ln\left( I_{sc} / I_0 + 1 \right) \right] \quad \ldots (23)$$

2.13.4 Power maximum ($P_{max}$)

This is determined by calculating the product of I and V over the entire current -voltage output curve. A maximum value is observed at the particular point on the I-V curve, which corresponds to the maximum power output. At this point the current and voltage are designated $I_{max}$ and $V_{max}$.

$$P_{max} = V_{max} \times I_{max} \quad \ldots (24)$$
2.13.5 Fill Factor (ff)

It is the ratio of the maximum power output of the cell to the product of the open circuit voltage and short circuit current,

\[ ff = \frac{V_m I_m}{V_{oc} I_{sc}} \quad \text{... (25)} \]

Fill factor indicates the extent of deviation from the ideal output.

2.13.6 Ideality factor (n)

In practice, the junction behaviour is not always ideal. Therefore, a factor ‘n’ known as the ideality factor is introduced in the exponential term, i.e.,

\[ I = I_o \left[ \exp\left(\frac{qV}{nkT}\right) - 1\right] - I_{ph} \quad \text{... (26)} \]

The deviation of the slope of the current potential dependence under the forward bias causes deviations from ideal junction behaviour.

Detailed information on the junction behaviour can be found in the standard text books [90,91]. The ideality factor can also be determined from the slope by plotting the graph between \( V_{oc} \) and \( \ln J_{sc} \).

Ideality factor ‘n’ = \( \frac{q}{kT} \) (slope)

Where, \( q \) is the electronic charge,

\( K \) is the Boltzmann constant,

\( T \) is the temperature.

2.13.7 Efficiency (\( \eta \))

This is given by the ratio of the electrical energy output to the light energy input.
Efficiency = \( \frac{V_m I_m}{P_{in} A} \)

Where, \( P_{in} \) denotes the optical power incident on the electrode and \( A \) is the illuminated area of the electrode.

### 2.13.8 Series Resistance (\( R_s \))

It is composed of electrical resistance due to metal contact and semiconductor layer, semiconductor, electrolyte and the connecting leads. For a carefully designed solar cell, the series resistance will be very low.

Series resistance can be determined from the inverse of the slope of the I-V curve at \( I = 0 \). The slope is equal to \( 1/R_s \).

### 2.13.9 Shunt Resistance (\( R_{sh} \))

If the semiconductor layer is defective with pin holes and cracks and impurities, it will provide a shunting path for the photo generated current. Its value should be high. For good cells it should exceed 1000 ohms.

Shunt resistance is determined from the slope of the I-V curve at \( V = 0 \). The inverse of the slope gives \( R_{sh} \).

### 2.14 Laser Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy, much like infrared (IR) spectroscopy. However, whereas IR bands arise from a change in the dipole moment of a molecule, Raman bands arise from a change in the polarizability. In many cases, transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary. This note
briefly explains the Raman effect, some advantages of Raman spectroscopy, and the basics of Raman instrumentation.

When a beam of light is impinged upon a sample, photons are absorbed by the material and scattered. The vast majority of these scattered photons has exactly the same wavelength as the incident photons and is known as Rayleigh scatter, but a tiny portion (approximately 1 in $10^7$) of the scattered radiation is shifted to a different wavelength. These wavelength shifted photons are called Raman scatter. Most of the Raman scattered photons are shifted to longer wavelengths (stokes shift), but a small portion are shifted to shorter wavelengths (anti-stokes shift). In each case, the incident photon excites an electron into a higher virtual energy level (or virtual state) and then the electron decays back to a lower level, emitting a scattered photon. In Rayleigh scattering the electron decays back to the same level from which it started. In both types of Raman scattering the electron decays to a different level than that where it started. Stokes Raman scattering occurs when the final energy level is higher than the initial level, while anti-stokes Raman scattering occurs when the final energy level is lower than the starting level. Stokes scattering is much more common than anti-stokes scattering because at any given time an electron in the most common temperature range is most likely to be in its lowest energy state, in accordance with the Boltzmann distribution. Only stokes Raman scattering is commonly used in spectroscopy. As mentioned above, Raman is a form of vibrational spectroscopy. This means that these energy transitions arise from molecular vibrations. Because these vibrations involve identifiable functional groups,
when the energies of these transitions are plotted as a spectrum, they can be used to identify the molecule.

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wave numbers, cm$^{-1}$). This difference is called the Raman shift. Note that, because it is a difference value, the Raman shift is independent of the frequency of the incident radiation. Typically, only the Stokes region is used (the anti-Stokes spectrum is identical in pattern, but much less intense). Raman spectroscopy is useful for chemical analysis for several reasons: it exhibits high specificity, it is compatible with aqueous systems, no special preparation of the sample is needed, and the timescale of the experiment is short.

Because Raman detects fundamental vibrations, Raman bands have a good signal-to-noise ratio and are non-overlapping. This allows a Raman spectrum to be used for everything from fingerprinting of samples to constructing complex chemical models of reaction processes.

The IR spectrum of water is strong and relatively complex, making IR inadequate for analysis of aqueous solutions due to heavy interference by the water bands. However, the Raman spectrum of water is weak and unobtrusive, allowing good spectra to be acquired of species in aqueous solution.

Unlike most other chemical analysis techniques, Raman requires no special preparation of the sample. In fact, no contact with the sample is
needed at all because Raman involves only illuminating a sample with a laser and collecting the scattered photons. Note especially that this makes Raman spectroscopy non-destructive.

Because a Raman spectrum can be acquired in as little as a few seconds, Raman can be used to monitor chemical reactions in real time.

A typical Raman spectrometer is made up of three basic parts: the laser, the collection device, and the spectrograph.

A laser is used to excite Raman spectra because it gives a coherent beam of monochromatic light. This gives sufficient intensity to produce a useful amount of Raman scatter and allows for clean spectra, free of extraneous bands. Lasers used for Raman spectroscopy must exhibit good wavelength stability and low background emission.

The probe is a collection device that collects the scattered photons, filters out the Rayleigh scatter and any background signal from the fiber optic cables, and sends the Raman scatter to the spectrograph. Many probes also focus and deliver the incident laser beam.

When Raman scattered photons enter the spectrograph, they are passed through a transmission grating to separate them by wavelength and passed to a detector, which records the intensity of the Raman signal at each wavelength. This data is plotted as the Raman spectrum.

2.15 Theory of Electrodeposition

The art of electroplating metals and metallic alloys has been in vogue for nearly a century and the earlier efforts are well documented. Most of the
development has been more by way of art rather than science, which started to merge only recently. Further the viability of using the electro deposition technique as a tool of materials technology is attracting attention as a means of obtaining films of a wide variety of materials including semiconductors, superconductors, polymer films, materials for biostimulation, specific electronic device application materials and others.

Some of the key advantages of the electro deposition technique are:

1. It is possible to grow films over large areas as well as irregularly shaped surfaces.
2. Compositionally modulated structures or nonequilibrium alloys can be electroplated.
3. A wide range of industrial experience can be drawn upon.
4. It is specially attracted in terms of cost, high throughput and scalability.

Electro deposition was originally used for the preparation of metallic mirrors and corrosion resistant surfaces among other things. In its simplest form electrodeposition consists of an electrolyte containing metal ions, an electrode or substrate on which the deposition is desired, and a counter electrode. When a current flows through the electrolyte, the cations and anions move towards the cathode and anode respectively, and may deposit on the electrode after undergoing a charge transfer reaction. The discovery of electrodeposition can be traced back to Michael Faraday and his famous laws of electrolysis.

The first law states that the total amount of chemical change produced by an electric current is proportional to the total charge passing through the
electrolyte. The second law states that the masses of the different substances liberated in the electrolysis are proportional to their chemical equivalent weights.

A simple electrodeposition system consists of the following components:

Electrolyte: The electrolyte or bath provides the ions to be electrodeposited. It has to be electrically conductive, it can be aqueous, nonaqueous or molten; and it must contain suitable metal salts. Sometimes an additive is included to improve the quality of the electrodeposit. An ideal additive should not become incorporated in the film but should lead to improvement of its adhesion, surface finish, uniformity etc.

Electrodes: At least two electrodes (cathode and anode) are needed. An applied electric field across these, provide the main driving force for the ions. The positive and negative ions deposit at the cathode and anode respectively. Cathodic deposition is more popular in electroplating because (1) most metal ions are positive ions and (2) anodic deposition has been found to give poor stoichiometry and adhesion.

Power Supply: The power supply can be (1) direct current at constant voltage, which leads to potentiostatic deposition (2) direct current at constant current which leads to galvanostatic deposition and (3) a current or voltage waveform or pulse.

The process leading to electrodeposition can be outlined in simple terms as below. On the application of an electric field, $M^{n+}$ would move to the cathode, and the chemical electrodeposition process can be written as
On the other hand, if the electrolyte contains more than one species that can be simultaneously deposited, then the electrodeposition process, for say, two

Types of ionic species can be written as

\[ M^{n+} + n\text{e} \rightarrow M \]

\[ N^{n+} + n\text{e} \rightarrow N \]

or

\[ M^{n+} + N^{n+} + 2\text{e} \rightarrow MN \]

Accordingly we can deposit a compound or an alloy of a multicomponent system.

As the electrodeposition proceeds, the ionic concentration in the bath is depleted and has to be replenished by adding the salt. Another alternative is to use one of the electrodes as a sacrificial electrode, one that corrodes during electrodeposition to maintain the ionic concentration constant.

The ionic discharge process can be summarized as follows:

1. Ionic species move in the electrolyte bulk toward the electrode on which the deposition is to occur. This is regarded as the reactant zone.

2. The moving ionic species approach the electrode (pre-reaction site) at, say, the Outer Helmholtz Plane (OHP) without actually being discharged. The charge transfer that ultimately leads to electrodeposition starts at this interface. This is regarded as the charge transfer zone.

3. The charge transfer is completed at the electrode, and the electrodeposit is obtained.
According to the Butler-Volmer model, the discharge of the electroplating ions is assumed to take place only when the latter have arrived at the Outer Helmholtz Plane. While calculating the rate of charge transfer reaction, it assumes that the rate at which the ions are consumed by the discharge reaction is equal to the rate at which they arrive at the OHP. In the charge transfer zone or prereaction zone the ions are transported from the electrolyte bulk to be discharged at the electrode. The concentration term in the Butler Volmer equation should be the ionic concentration in the charge transfer zone at $x = 0$, i.e. $c_{x=0}$ and not the bulk concentration $c_0$ at $x = \infty$. These two will be equal only when the ionic discharge rate is equal to the rate of ionic transport. If the charge transfer rate is greater than the rate of ionic transport, then the interface region will become depleted of the discharging ionic species. On the other hand, if the ionic transport processes are much faster, this will lead to the accumulation of ions in the interface region. This inequality between the transport flux and the charge transfer flux gives rise to concentration polarization or over potential.

2.15.1 Importance of diffusion limited transport

Diffusion limited transport has been found to be useful in electrodeposition work. A discussion of the important implications is follows.

Diffusion limited transport enables oppositely charged ionic species to move in the same direction. One can thus perform cathodic electrodeposition with negatively charged ions also. Diffusion limited transport enables one to change the equilibrium potential over a range of values depending upon the
ionic activities. According to Nernst equation, a decrease in ionic activity of the discharging species results in a negative shift in the deposition potential. This possibility has been used by a number of workers to electrodeposit two or more components with different equilibrium potentials.

The current density under the influence of diffusion is given by

\[ j = j_0 \left[ 1 - \exp \left( \frac{nF\eta}{RT} \right) \right] \]

Suppose in a cathodic electrodeposition experiment the electrode potential is continuously driven in the negative direction. Initially when the electrode potential is made more negative than the equilibrium potential of the ionic species transported by diffusion, the current will rise. The cathodic current will continue to rise with increasingly negative electrode potential, and the interfacial ionic activity will decrease continuously. When the rate of diffusion becomes equal to the rate of discharge, the interfacial ionic activity will be practically zero and the current density will attain a value \( j_1 \). The higher efficiency of the cathodic process results from the higher value of \( j_1 \). This value can be increased by (1) increasing the concentration \( c_0 \), (2) increasing the diffusion coefficient by working at a higher temperature, and (3) lowering the diffusion layer thickness by forced convection (stirring).

### 2.15.2 Transfer Coefficient

In the derivation of the Butler – Volmer equation, the movement of ions across the interface was assumed to be the only necessary condition for the charge transfer reaction. The role of electrons in the metal electrode as dynamic entities capable of crossing the interfacial barrier was completely
ignored. The electron in general quantum mechanically tunnel through the interfacial barrier to the ionic species in the electrolyte [92-95]. As the electron transfer process is nonradiative, the tunneling should take place without a change in the energy of the system within the restraints of the uncertainty principle. This requires sufficient stretching of the bonds between the reactant and the surrounding ligand to create an acceptor state of energy equal to the electron energy in the metal.

The transport coefficient (symmetry factor) $\alpha$ for quantum mechanical tunneling has been defined as the ratio of the energy required to stretch the ion ligand bond to the critical state and the energy gap between the electron state in the metal and the solution side of the interface. The energy gap should be closed to make tunneling possible. We thus see that $\alpha$ can be correlated to some physically meaningful parameters such as the ion- solvent interaction and the structure of the double layer.

The charge transfer reaction activated by a bridging ion can be treated quantum mechanically. In bridge assisted tunnelling, the transmission probability may be large. Also if the bridging ion is of opposite charge to reacting species, this may lead to a higher concentration of the latter at the OHP.

### 2.15.3 Surface Coverage Factor

The electrode surface immersed in the electrolyte is generally with contact adsorbed ions, solute molecules etc., broadly of two categories: non blocking and blocking. The effect of blocking species can be incorporated into
the Butler-Volmer equation by considering only the fraction $\theta$ of the electrode surface that is not available for charge transfer reaction when a current $j$ is flowing. $\theta$ is called the surface coverage factor for all adsorbed species. Frumkin [96] gave a detailed account of the role of contact adsorption in the electrode process.

The binding energy of the contact adsorbed species is of practical interest in electrodeposition. For example, during aqueous electrodeposition, the discharging hydrogen is often strongly bound to the cathode surface with energy on the order of 50 kcal/mol. On the other hand the water molecules are only weakly adsorbed. Interfacial tension has also been used as parameter to express the interaction of the solvent-electrode system.

Many non aqueous solvents interact fairly strongly with the electrode surface and $\theta$ becomes a dominant factor. Apart from solvent adsorption, the role played by the contact-adsorbed additives is also significant in controlling $\theta$ (and hence the electro-deposition).

Multi step reaction:
So far, only a single step reaction,

$$r + 2e \rightarrow p$$

The above reaction may comprise the two steps

$$r + e \rightarrow I, I + e \rightarrow r$$

Where, $I$ refers to an intermediate species formed during the reaction.

Generally the step with the lowest exchange current density qualifies as the rate determining step (RDS). Suppose $j$ is the current density corresponding to the RDS for an $s$-step reaction. The total current density
would be $s_j$. The electrode potential will have only one value, but the overpotentials corresponding to the $s$ different steps may be different. The overpotential is the difference between the electrode potential and the reverse potential. The different values for overpotential can be attained at different steps simply because of the differences in the reversible potentials of each step, which are governed by the respective concentration ratios of the intermediates.

The exchange current density $j_0$ and the transfer coefficients $\alpha_c$ and $\alpha_a$ are two important parameters related to the kinetics of the charge transfer reaction. For a given electrode potential, the net current density will be higher for the process with the higher exchange current density. The exchange current density depends on the nature of the reaction, the electrode material, and the bath composition. The transfer coefficient describes the effect of the electric field on the charge transfer step and the symmetry of the cathodic and anodic processes. Its dependence on the electrode material is usually small.

2.16 Electrodeposition of semiconductors

In principle the theory of metallic electrodeposition can be applied to semiconductor film deposition. However, some typical problems of semiconductors have to be considered.

First, semiconductor films are relatively resistive (in comparison with metals). As a consequence, the interfacial potential and charge distribution may drastically change over the first few layers of semiconductor have been formed. For thicker films this may even lead to morphological changes.
Second, the resistivity of a semiconductor is highly sensitive to defects, orientation, and other factors. As the electrodeposition proceeds, the semiconductor resistivity may continue to vary. In an extreme situation, a non degenerate semiconductor may even become a degenerate semiconductor.

Third, in metal electrode- electrolyte contact, the space charge layer within the electrode plays an insignificant role, whereas for semiconductor electrolyte contact the space charge layer is dominant.

Fourth, the presence of the space charge layer, the high density of surface states and/or surface defects, and the resistivity of the semiconducting film can also exercise controlling effects on the charge transfer reactions. As a result the Tafel plot for semiconductors may not be the same as was originally envisaged for metallic deposits.

The above remarks are applicable to both elemental and compound semiconductors. Apart from a few elemental semiconductors (Si, Ge, Se,Te) most of the semiconductors of interest are compound semiconductors. Three problems are typical of compound semiconductor electrodeposition:

1. Most of the compound semiconductors have at least one metallic (Ga,Cu,In,Cd,Zn, etc.,) and one nonmetallic (S,Se,Te,P,As etc.,) component as in GaAs, GaP, CdS and CuInSe$_2$. Unfortunately, the reduction potentials of the nonmetals are widely different from those of the metal ions. The general condition for co-depositing the different components of the compound requires that the constituents have equal reduction potentials. This is difficult to attain for compound semiconductors.
2. Most compound semiconductors have a very negative Gibbs free energy of formation. This may shift the deposition potential of the more noble component to more positive value, helping the co-deposition.

3. Many compound semiconductors exhibit multiple phases. The possibility of such multiphase formation may lead to additional complexities in the activity term controlling the electrodeposition.

2.17 Practical Aspects of Electrodeposition

2.17.1 Choice of substrate

Substrates in semiconductor electrodeposition are expected to play an important role. Their characteristics are not restricted to impart certain morphological characteristics to the growing layer. In a more subtle way electronic or optical properties may also be affected. Therefore, in choosing a suitable substrate, in addition to considering the need to provide mechanical support to the electrodeposits, due consideration must be given to the possible influence of the substrate on the properties of the deposit. Broadly speaking the following criteria should be applied for the selection of the substrate.

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

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

3. The substrate should have good mechanical strength.

4. In many applications cost is an important consideration.

5. For epitaxial films, it is necessary to match the lattice parameters between the single crystal substrate and the growing film.

6. The semiconductor metal contacts may be ohmic or rectifying, so care should be given to the type of interface one desires to obtain.

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

8. The substrate should be stable in the electrolyte bath.

9. The substrate surface should be smooth, one should avoid surface waviness, porosity, voids, and other irregularities as these influence the local current distribution. Also the electrodeposits tend to reproduce the surface morphology of the substrate. An uneven porous surface with voids will not be useful for any device application.
Subject to the foregoing considerations one may use single crystal, polycrystalline or amorphous substrates of metals or semiconductors in the form of foils, sheets, wafers or thin films. When single crystal semiconductors are used as substrates a back ohmic contact is normally formed by using a conducting paint, a suitable solder or an evaporated film. Metals have been widely used as substrates because of their good conductivity, easy availability, lower cost and relative ease of handling.

2.17.2 Substrate surface preparation

The preparation of smooth scratch free substrate surface is extremely in semiconductor electro deposition as surface in homogeneities tend to amplified during electro deposition. On the atomic scale surface defects may be point defects, dislocations etc., while on the macroscopic scale they can be scratches left from polishing operations, grain boundaries etc., and substrate preparation is a substrate specific operation consisting of three major steps, grinding and polishing, cleaning and testing the surface cleanliness. Grinding and polishing are usually employed to prepare a smooth surface with a mirror finish. The grinding operation uses abrasives of different grit sizes. Emery paper can be used for grinding, after grinding the surface is either polished mechanically or electrochemically. Mechanical polishing is performed using polishing wheels with abrasive grains glued to them with the help of adhesives or cement compounds. The glues are available in a wide range of viscosities and flexibilities. The abrasive most commonly used in metal polishing is fused alumina grains, which are available in various grain sizes down to 0.3 µm.
Fused alumina is hard, sharp, fast cutting and long wearing. Silicon carbide can also be employed for certain special operations. However, it is more difficult to bond it firmly to the wheel. The polishing surface is lubricated with a lubricating oil or grease that can be sprayed or friction applied on to the polishing wheel. Lubrication is desirable to minimize heat and produce a fine polish. Typical speeds of polishing wheels range from 6000 to 8000 revolutions per minute.

In some applications electropolishing can also be employed. This is an electrochemical operation in which the substrate is allowed to dissolve slowly by applying an anodic bias to it. The microscopic projections are allowed to dissolve slowly by applying an anodic bias to it. The microscopic projections are dissolved away at a greater rate, resulting in smoothing, leveling and/or deburring. Brightening of the surface takes place simultaneously. The surface brightness achieved by electropolishing is different from that obtained by mechanical means. Electropolishing yields a scratch free, deformation free surface. Time, temperature and current density are the critical parameters that control the surface finish. The surface quality and finish obtained by a prior polishing operation also help to determine the finish resulting from electropolishing. One can remove layers a few micrometers thick using electropolishing.

2.17.3 Cleaning

Surface cleaning in thin film technology is an important step prior to deposition. It is necessary to remove the contaminants that would otherwise
affect the properties of the films. The properties that can be affected by the
presence of the contaminants include adhesion, morphology, nucleation,
electronic properties of the film, and the substrate film interface. The choice
of the cleaning procedure is governed by the substrate as well as by what
contaminants are likely to be present. The composition, physical properties
and chemistry of the substrate should be carefully considered in designing the
cleaning operation. The cleaning process should be chosen to avoid any
undesirable damage to the substrate surface and yet remove the
contaminant. It is easier to select the cleaning procedure when the nature and
origin of the contaminants are known. Some common contaminants are finger
tip grease, glue, dust, leftovers of abrasives, soldering fluxes and similar
materials.

2.17.4 Cleaning by solvents

Solvent cleaning is employed to dissolve or emulsify the contamination.
Solvent cleaning can be performed by soaking the surface in petroleum or
chlorinated solvents. Some common chlorinated solvents are
trichloroethylene, methylene chloride, and perchloroethylene. These
chlorinated solvents may contain hydrochloric acid as a hydrolysis product,
and due care should be exercised to inhibit it. Vapor degreasing units are also
commonly employed for cleaning. Such a unit consists of a chamber in which
a chlorinated solvent is vaporized. Cleaning takes place when the solvent
vapors condense on the colder substrate. Solvent cleaning can also be
accomplished by soaking in an emulsifiable solvent. Detergent cleaning is
useful for metals. Acid cleaning is often employed to remove oxides and oil from inert glass or metal substrates. An aqueous solution of organic or inorganic acid is normally employed in a soaking, painting, brushing or spraying application. The contaminants are first converted into water soluble compounds that are subsequently removed in a water rinse. Alkaline cleaners along with some surface active agents are often employed after detergent cleaning to remove oil smuts and oxides. Cleaning is generally performed at temperatures of 120 – 200 °F. The final cleaning should be done in flowing deionized water.

Ultrasonic cleaning can also be a useful technique, particularly for ceramics. The cleaning is assisted by ultrasonic agitation in which jetting, which accomplishes the collapse of bubbles generated by cavitation near the surface, increases the rate of solvation and emulsification. The cleaning liquid can be a water based or solvent based chemical in which the substrates are immersed. The effectiveness of ultrasonic cleaning depends on the intensity of cavitation achieved. Liquids with higher surface tension and lower viscosity should be preferred. The dissolved gases in the liquid also tend to decrease cavitation intensity, whereas increasing temperature increases it. The ultrasonic frequency and power should also be properly chosen. Higher frequencies require more power to maintain the same level and cavitation intensity. Similarly, the ultrasonic power should be matched to the work desired.
2.17.5 Cleaning by Heating

Heating the substrate may remove the volatile impurities. The temperature should be chosen according to the melting point and/or surface reactivity of the substrate. Heating is not useful if it causes stresses and cracking due to non-uniform heating or oxidation of the surface.

2.17.6 Cleaning by etching

In many cases, a suitable etchant can be used to clean a surface. Etching can be performed in the dark or under illumination. This can be specially used for semiconductor substrates.

2.17.7 Other methods

There are a number of cleaning methods that are more useful than the foregoing for thin film deposition in vacuum systems. Three of these methods are sputter cleaning, plasma oxidation and glow discharge cleaning. Cleaning techniques have been discussed by Brown, Holland [97,98].

(a) Surface Cleanliness Test

The various tests that can be applied for checking the surface cleanliness are:

(b) Breath Figure Test

The substrate is brought near the mouth and a soft breath is blown on it. A poorly reflecting black specular film indicates a clean surface. Breath figures of various shapes appear on an uneven surface.
(c) Atomizer Test

Water is sprayed over the surface of the dried substrate. Surface cleanliness is indicated by the formation of fine mist, while on an unclean surface water coalesces into big drops.

(d) Water Break Test

The substrate is pulled against the surface of water in a beaker. If the water sticks to the substrate surface as a continuous film, a clean surface is indicated.

(e) Contact Angle Test

A contact angle zero between water droplet and the substrate implies that the substrate is clean.

(f) Coefficient of friction Test

Resistance encountered when a glass or metal sheet is slid over the substrate can also be measure of cleanliness. If the coefficient of friction approaches unity then surface is clean.

(g) Indium Adhesion Test

Surface cleanliness is tested by measuring the coefficient of adhesion between the substrate and a piece of indium. It may range from zero for a dirty surface to about two for a clean surface.

(h) Fluorescence Dye Test

Contaminants that can absorb fluorescent dyes can be detected by illuminating the substrate with UV light.
(i) Edge Lighting Effect

It is useful to check transparent substrates such as glass. If the edge of the glass is illuminated the contaminants present on the surface become visible as lighted areas against a dark background.

In addition to the foregoing techniques one can also employ gravimetric or radiotracer methods.

(j) Electrolytic Bath

The electrolytic bath is the medium that supplies the ions that move upon application of an electric field. In general ionic transport is facilitated in aqueous solutions, non aqueous solutions or molten salt bath.

2.18 Aqueous and Nonaqueous Electrolytic Solutions

The choice of solvent depends on primary factors such as solubility and nonreactivity.

Aqueous: These solvents are suitable for a large number of salts, complexing agents and other compounds. Barring a few hydrolysis reactions, water is generally a nonreactive solvent. However an aqueous solution necessarily contains H⁺ and OH⁻ ions, which complicate the electro deposition process by resulting in the evolution of hydrogen and / or oxygen at the electrodes.

Nonaqueous: These can be further classified as protic and aprotic solvents.

Protic Solvents: (Alcohols, formamide etc.,) these solvents are generally strong hydrogen donors and can exchange protons rapidly. Such solvents also sometimes lead to hydrogen evolution.
Aprotic Solvents: They contain hydrogen bonded only with the carbon (propylene carbonate, DMF, DMSO, acetonitrile, tetrahydrofuran etc.).

The nonaqueous solvents have attracted attention for semiconductor electro deposition work due to the greater flexibility they afford in choosing dopants, solutes, complexants, temperature range and working electrode potentials and the absence of hydrogen evolution reaction, among other reasons.

2.19 Preparation of Electrolytic bath
Selection of Solvent: The first step is to choose aqueous or nonaqueous solvents depending on the material to be deposited. Electro deposition solvents are stable in only a limited potential range, beyond which reduction-oxidation takes place. This range is called the working potential range or the window. The potential at which the electro deposition is to be carried out should be within this range. The morphology and rate of growth depends upon the temperature at which electro deposition is being carried out. The solvent should remain liquid at the desired temperature. Therefore solvents with a large range are preferred to provide greater flexibility.

High vapour pressure solvents are preferred because the electrolytic concentration remains more constant. This is particularly true when the solvent is being purged with nitrogen or an inert gas to drive out the dissolved oxygen.

The dielectric constant should be more than 10. Too low a dielectric constant facilitates ion pair formation, giving poor conductivities and ionization in the solution.
Lower viscosity is always preferred because of the better conductivity and diffusion. Furthermore, many irreversible electrochemical reactions limited by mass transport become reversible in a medium with lower viscosity.

2.19.1 Selection of supporting electrolyte

The supporting electrolyte performs several functions in the electrochemical process. (1) It increases the conductivity of the electrolyte. This minimizes Joule heating and provides more uniform current distribution and IR compensation. (2) It reduces the electrode double layer thickness and also influences ion pairing and adsorption. (3) It effectively eliminates the effect of migration in the mass transport. The criteria for selection of a supporting electrolyte are its solubility in the solvent and a dissociation constant sufficiently high to yield good conductivity and the electrochemical oxidation of anion and electro reduction of cation at more anionic or cationic potentials respectively the electrochemical process under investigation.

In aqueous media, KCl, HCl have been commonly used. In organic solvents lithium perchlorate, lithium tetrafluoroborate, trifluoroacetate and quaternary ammonium salts have been employed as supporting electrolytes.

2.19.2 Additives in electrolytes

Additives (brightening agents, surfactants, complexants etc.) are often added to the plating bath to obtain a brighter and smoother deposit, controllable reaction rate, better adhesion and better texture. The role of additives in the electro deposition process though still a mystery is broadly
either (1) to control the rate of electro deposition process or (2) influence deposit morphology.

2.19.3 Solvent Purity

Impurities in the solvent interfere with the electrochemical processes. In many cases electro deposition may not be possible or the deposit morphologies may be affected by the impurities. The electronic properties of the semiconductor are also extremely sensitive to impurities that co-deposit. It is therefore essential to purify the solvent. Purification techniques for water have been discussed by Hughes and Michell [99,100]. Some of the commonly used methods employ deionization using ion exchange resin or distillation from an alkaline permanganate solution. However this is not a very satisfactory method and many organic contaminants may still be present. Further purification by passing the water vapours through a column of platinum gauge heated to 750 – 800°C in a stream of oxygen is necessary to remove these contaminants. In situ purification by flushing an inert gas to remove oxygen followed by pre electrolysis at a constant potential may also be employed to remove heavy metal ions.

Non aqueous solvents also need to be purified by refluxing with strong oxidizing or reducing agents, distillation under reduced pressure, or passage through molecular sieves. A common impurity in nonaqueous solvent is oxygen, which can be removed by purging with nitrogen.
2.20 Molten salt electrolysis bath

The term molten salt includes molten media that may be wholly ionic or derived from simple salts. The conductivity and ionicity of these systems are generally sensitive to temperature, pressure and composition. Molten salts exhibit a wide range of electrochemical stability, high ionic conductivity, high heat capacity and good thermal conductivity. They also exhibit good electrochemical reaction rates. In contrast to aqueous electrodeposition, molten salt electrodeposition can be carried out without the annoying intervention of hydrogen evolution, oxide formation, hydride formation and similar problems.

Some of the commonly used molten salt electrolytes are,

NaCl + KCl + Na₃PO₄, NaF + KF + NaPO₃ + In₂O₃

etc. Molten salt baths suffer from certain disadvantages like high operating temperatures, lack of sufficient thermodynamical and kinetic data.

2.21 Classification of electrodeposition Techniques

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

Deposition at constant dc potential (Potentiostatic)

Deposition at constant dc current (Galvanostatic)

Deposition using a periodic or pulse source.
2.21.1 Potentiostatic deposition

In this technique different charge transfer reactions proceed under a steady state condition at rates appropriate the steady state interfacial overpotential and exchange current density. The choice of the overpotential is dictated by the composition of the bath, the substrate and the reversible potential of the species to be deposited. The table of standard electrode potentials serves as an approximate guide in finding the potentials at which electrodeposition of particular species will be possible, but in practice the actual deposition depends on a number of factors such as substrate deposit interaction the hydrogen overvoltage, the interaction between the components during compound electrodeposition, and the polarization characteristics of the bath. Potentiostatic deposition is carried out under pure activation, diffusion or mixed control depending on the choice of the deposition potential. Potentiostatic deposition has been used to grow layers of elemental, binary and ternary semiconductors. In the case of semiconductors it is desirable to obtain large grained polycrystalline deposits. However, very low overpotential may not be suitable, as they may lead to a spongy or porous deposit due to low nucleation rates. As the overpotential is increased, the supersaturation increases and a large number of nuclei are formed. The deposit thus acquires a fine grained morphology. Very high overpotentials may, however lead to the growth of dendrites or whiskers. In the case of compound semiconductors, more stringent control of the deposition potential is required to maintain the deposit stoichiometry.
2.21.2 Deposition at constant Direct Current

The constant current between the working and counter electrodes required for electrodeposition at a constant direct current can be obtained from a galvanostat.

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

The galvanostatic electrodeposition of compound semiconductors is more complex and a straightforward answer for the proper choice of deposition current density is not possible. As discussed earlier, compound semiconductors are usually deposited by the transport of at least one of the constituents under diffusion control. The simplest situation is when the deposition of all the components is diffusion controlled. The rates of deposition will then be directly proportional to the corresponding limiting current densities. As an example, consider the cathodic electrodeposition of a binary compound semiconductor $A_x B_y$. If the electrodeposition of $B$ is under diffusion control, then the maximum current distribution due to species $B$ cannot exceed the corresponding limiting current density. Further, if the deposition of $A$ is under pure activation control, then the current distribution due to $A$ for galvanostatic deposition will depend on the value of exchange current density of $A$ and the steady state overpotential. For the compound
electrodeposition to be favored, the value of the total current density should be chosen that the steady state overpotential satisfies the thermodynamic condition for codeposition of A and B.

Galvanostatic electrodeposition is therefore still an art as it depends on the manipulative experience and ability of the individual worker. Initial trials may be necessary to obtain the final optimum values of the electrodeposition current density.

2.21.2 Electrodeposition from a periodic or pulsed source

The use of non dc signals for electrodeposition is known to improve the deposit quality. However, only a few reports have appeared on its application to semiconductor electrodeposition. Non dc electrodeposition can be carried out by either varying the current or the overpotential. Current variation can be accomplished by using a periodic reverse current, a pulsating current or alternating current without or superimposed over a dc current.

2.22 Morphology of the electrodeposit, applied electric potential and current

The nature and magnitude of the applied electric field across the electrolysis decides (1) grain size (2) surface roughness (3) dendritic growth and (4) formation of powdery or spongy deposit.

2.22.1 Grain size

The grain size depends upon the overpotential which in turn controls whether the deposition is controlled by diffusion, activation or both. The
relevant conclusions can be briefly stated as follows. At low overpotentials initially a small number of nuclei from that grows independently. It is therefore expected that a large grained deposit will be obtained under these conditions. As the overpotential is increased, a large number of nuclei may be formed leading to decrease in grain size.

2.22.2 Surface roughness

At an ideal surface, the value of the diffusion layer thickness and the limiting current are constant throughout, which leads to uniform growth. Some minor variations in thickness may arise due to convective effect, which is neglected here. However the situation is complex for a real surface which is rough consisting of elevation and recesses. The rate of deposition at the elevations may be higher due to shorter diffusional path between the outer plane of the diffusion layer and the elevations. At the tips of the elevations the diffusion conditions may approach those of spherical diffusion. Spherical diffusion is faster than the linear diffusion because of wider diffusional field in the former case. As a result surface roughness gets amplified during electrodeposition.

2.22.3 Dendritic growth

In the case of dc electrodeposition, surface roughness can lead to the initiation of preferential growth at protrusions or dendritics. The mechanism of dendritic growth has been studied by Diggle et al and Popov et al [101,102].
2.22.4 Formation of powdery or spongy deposit

Other than dendritic growth another undesirable type of electrodeposit is a powdery or spongy deposit. Dendritic growth is primarily controlled by overpotential or critical current density; however, powdery/ spongy growth is an interplay of many factors other than the overpotential, such as viscosity and temperature. Powdery deposits are classified by their small particle size and poor adhesion to the electrode surface. They are generally obtained when the deposition is carried out under diffusion limited current conditions or close to transition time. The amorphous nature of the powdery deposit is due to the high nucleation rate. Powder formation is enhanced when the concentration of the depositing species is decreased, the supporting electrolyte concentration is increased, the solution viscosity is decreased, the temperature is decreased or the stirring rate is decreased. The mechanism of formation of a spongy deposit has been discussed by Popov et al [103]. It was shown that a spongy deposit is formed if the radius of the growing grain exceeds a critical value.

2.23 Selective / Brush Plating

An electroplating process performed with hand held portable tool rather than a tank of solution is known as brush plating. The brush plating processes are also called as contact plating, selective plating or swab plating. This is essentially a plating method, deposition of a metal on the surface by electrochemical means, where the work is connected cathodically to the current source. The plating is then applied by means of a brush or swab,
soaked with solution and connected to a flexible anode cable. A direct current
power pack drives the electrochemical reaction, depositing the desired metal
on the surface of the substrate. In practice, movement between the anode
and cathode is required for optimum results when plating, stripping, activating
and so on. Currently a broad range of metals can be plated by brush plating.
The key advantage of selective plating is portability. Many systems can be
moved to various locations in a production facility or be transported to the job
site. Selective plating is also versatile since it permits most electroplate types
to be deposited onto any conductive substrate that can be touched with an
electrode. Cast iron, copper, stainless steel and aluminium can be plated by
this method and exhibit good adhesion. Limited adhesion can be obtained
with other materials such as titanium, tungsten and tantalum.

Selective plating allows higher current densities than tank plating,
which translates into higher deposition rates, upto 0.01 mm/min. In addition,
inherently precise thickness control permits plate buildup or repair without the
need for subsequent machining.

Besides electroplating, selective plating systems can perform several
other ancillary operations:

- Electrostripping for deplating of many metals and alloys
- Anodizing for protecting aluminium alloys
- Electromilling for removing base metal, as in chemical milling
- Electroetching for permanently identifying parts
- Electropolishing for refining a surface chemically
Depending on part size, dimensional considerations and required surface characteristics all of these operations can be done with the same equipment and similar electrodes. Only the solutions are different. In many cases, an operator brush plates only one part at a time. Nevertheless, selective plating is an effective and economical electroplating process when used in application for which it is assigned. These include, plating parts that are too large to immerse in solution, plating a small area of a large component and touching and repair of components, large or small that would cost too much to strip and manufacture. The largest parts ever plated are building domes. The process can also perform at higher production volumes.

Typical selective plating systems include a power pack, plating tools (called as styli or anodes), anode covers, specially formulated plating solutions and any auxiliary equipment required for the particular application. To achieve optimum deposits, equipment should be designed especially for selective plating. Power packs or rectifiers supply the direct current and are specially designed with the features and/or controls required by the process. Output voltage can be typically varied from 0–30 V. Voltage control is extremely important because it regulates the current supplied to the process. In turn, the amount of current consumed over time measured in ampere-hour, determines the deposit thickness. A polarity reversing switch allows the operator to automatically change current flow direction, which is necessary in preparatory operations e.g., etching and desmutting and in stripping.

The plating tool stylus must have an insulating handle and an anode material that is inert, insoluble in plating solutions, and able to carry high
current. Graphite is by far the most practical choice for anode material. Graphite can be machined or shaped to fit the contour of the part being processed. Stainless steel is much more durable, but it dissolves in certain plating solutions. The anode covers (wrapping materials) serve as an insulator between the anode and the cathode and help ensure smooth deposits at higher current densities. Anode covers hold the electrolyte; therefore, they must be free of oil and foreign materials. Various fibre like materials make suitable covers. Cotton works very well if it is sterile. Synthetic fibres such as polyester and nylon do not wet or hold electrolytes as well as cotton, but this does not preclude their use. Polyester felts are typically selected when the same anode is used for numerous parts that are to be plated. Most of these materials work well in the form of tube gaze as covers over cotton. Scotch brite has been used when heavy or hard deposits are required and it can also function as a furnishing tool, improving the surface as plating continues. If a surface is soft and easily scratched, a different wrap should be chosen.

2.24 Key Process Parameters

Controlling continuous movement between the anode and the work piece or cathode, is a key element in obtaining high quality brush plated deposit. However, quality also depends on plating within a specific current density range. The visual appearance of electroplate is also an indicator of quality. A dark grey or black deposit usually corresponds to a burnt deposit, which results from too high current densities or insufficient movement. In
contrast, inadequate current density or too much movement produces a generally shiny surface. Anode to cathode movement may be achieved manually or mechanically, such as by using turning equipment to provide a constant rotational speed for cylindrical parts. Another option is a roto-stylus that rotates the anode instead of the work piece.

For the plating process to be efficient, the plating solution must flow between the anode and the area being plated. Solution can also be supplied by periodically dipping the plating tool into the electrolyte. However, the most efficient method is to pump the solution through the block anode and into the interface between the anode and the work piece. Plating of large areas at high current densities require the use of a pump to re-circulate the solution. This keeps the solution from overheating and results in higher thickness buildup. In addition, the process is faster. The thickness of the deposit can be controlled by monitoring the ampere-hour meter. Each solution has a prescribed energy factor, which indicates how many ampere-hours are required to deposit a given metal thickness on a given area.

In compound semiconductor deposition, however, more than one element is involved and this requires a judicial choice of the concentrations of the precursors for co-deposition of the entities. In the whole world, the first report on semiconductor deposition by brush plating appeared from Central Electrochemical Research Institute (CECRI), Karaikudi, India. Fig.2.1 shows a typical brush plating set up for depositing thin films.
Fig. 2.1 – Brush plating set up