CHAPTER II

TECHNIQUES AND MEASUREMENTS

2.1 INTRODUCTION

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

2.2 X-RAY DIFFRACTION (XRD)

X-Ray diffraction is a well established [21, 22] 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 yield informations regarding the orientation and size distribution of the crystallites.

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

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

(2.1)

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 unit cell while the intensities
of the diffracted rays are a function of the placement of the atoms in the unit cell. The crystalline size can be calculated using Scherrer’s equation

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  
(2.2)

where, \( \beta \) = 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 [23].

### 2.3 ATOMIC FORCE MICROSCOPY

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, which was invented in 1981 by G. Binnig and H. Rohrer. Though STM is an excellent technique it is limited to imaging conducting surfaces. AFM has much broader potential and applications 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 encompasses 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, material science, electrochemistry, polymer science, biophysics, nanotechnology, and biotechnology.

2.4 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 ultra high 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 require 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 and identifies elements from lithium to uranium, with detection levels down to 0.5%. XPS uses roaster scanning to produce images with a spatial resolution of 20 microns. By sputtering materials from the surface, it generate composition distribution for materials. It evaluated 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.

2.5 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. Photoionization 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. Photoionization 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 [24],

$$\alpha = \frac{2.303 A}{t}$$  \hspace{1cm} (2.3)

where, $A$ is the absorbance value at a particular wavelength and $t$ is the thickness of the semiconductor film and 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

$$\alpha = \left( \frac{A(h\nu - E_0)^{\frac{3}{2}}}{h\nu} \right)^\frac{2}{5}$$  \hspace{1cm} (2.4)
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 gives the band gap for the direct or indirect transition respectively and the slope is $A$.

### 2.6 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. Polycrystalline 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.

![Figure 2.1 Hall Effect](image)

Resistivity and Hall measurements were used to evaluate mobility and concentration of charge carriers. Resistivity was determined by Van der Pauw technique [25,26]. Fig 2.1 shows the schematic diagram that has been normally used for these measurements. 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 $R_{AB,CD}$, $R_{BC,DA}$ and $t$ can be written as

$$\rho = \pi t \left( \frac{R_{AB,CD} + R_{BC,DA}}{2 \ln 2} \right) \cdot f \left( \frac{R_{AB,CD}}{R_{BC,DA}} \right)$$

(2.5)

where the resistance $R_{AB,CD}$ is the potential difference $V_D - V_C$ 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 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.

Figure 2.2 Hall Effect
The illustration of Hall effect is shown in fig 2.2 and the circuit diagram used for hall effect studies is shown in fig 2.3. The Hall mobility can be determined by introducing the film into the electromagnetic field. Here, the change in the resistance $R_{BD,AC}$ is measured when a magnetic field is applied perpendicular to the film. The Hall mobility is then given by

$$
\mu_H = \frac{t}{B\rho} \Delta R_{BD,AC}
$$

(2.6)

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

$$
\mu_H = \frac{t}{B\rho} \left( \Delta V \right)
$$

(2.7)

Consider the magnetic field applied across AC when current (I) is passing perpendicular to AC (i.e.,BD). The electric field induced 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
\[ R_\mu = \frac{\mu_\mu}{\rho} \]

\[ \frac{1}{Nq} = \mu_\mu \sigma \]

\[ N = \frac{1}{\sigma q \mu_\mu} \]  \hspace{1cm} (2.8)

**2.7 PHOTOCONDUCTIVE MEASUREMENTS**

Photoconductivity is the increase in electrical conductivity of a substance caused by radiation incident on it. The effects of illumination are to increase the number of mobile charge carriers in the substance. If the energy of the incident photon absorbed in the sample will excite an electron to the conduction band producing a hole in the valence band, and thereby, increasing the conductivity of the sample. 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 [27].

2.7.1 Recombination Model

The concept of hole or electron traps is important in the recombination theory of photoconductivity. Because of 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.

2.7.2 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.

2.7.3 Photoconductivity

The photoconductivity covers the entire 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 as 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
\[ \sigma = qN\mu \]  (2.9)

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

\[ \Delta \sigma = q(\mu \Delta N + N \Delta \mu) \]  (2.10)

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 lifetime. They lose energy through different processes of relaxation and recombination.

Any photoconductivity phenomenon basically involves three processes of energy transfer as 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.

\subsection*{2.7.4 Photosensitivity}

The concept of photosensitivity may be defined in several ways. The quantity specific sensitivity (SS) is the one way of defining photosensitivity [28]. 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 = $P/(l \times b \times t)$, where $P$ is the power.

Hence,

$$SS = \Delta \sigma \ast l \ast b \ast t / P$$

$$= \Delta i \ast l \ast l \ast b \ast t / (V \ast b \ast t \ast P)$$

$$= \Delta i \ast l^2 / (V \ast P) \quad (2.11)$$

where $\Delta i$ is the photocurrent, $V$ is the applied voltage, $l$ is the electrode spacing and $P$ is the absorbed radiation power. Here, $SS$ is expressed in mho-cm² 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,

$$S = (\sigma_L - \sigma_D) / \sigma_D$$

$$= \Delta \sigma / \sigma_D \quad (2.12)$$

where $\sigma_L$ – Light conductivity and $\sigma_D$ – dark conductivity

But $\sigma = 1 / (R \ast A)$ where $R$ – resistance, $l$ – length and $A$ – area of cross-section of the photoconductor. Substituting this in (2.12), then
\[ S = \frac{(R_D - R_L)}{R_L} \]  \hspace{1cm} (2.13)

\[ = \frac{R_D}{R_L} - 1 \]

\[ = \frac{R_D}{R_L} \quad \text{if } R_D \gg R_L \]

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 \( G = \frac{\Gamma}{t} \). But, \( \mu = \frac{l^2}{Vt} \)

\[ t = \frac{l^2}{\mu V} \]

\[ G = \frac{\Gamma \mu V}{l^2} \]  \hspace{1cm} (2.14)

### 2.8 PHOTOELECTROCHEMICAL (PCE) STUDIES

#### 2.8.1 Semiconductors

In the light energy conversion discussed in the following pages, the substance that absorbs the radiant energy and transduces it to an electron hole pair is a semiconductor. The nature and properties of a semiconductor make this possible.

The colour of a semiconductor roughly indicates the portion of the solar spectrum that 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 dioxide, 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 a smaller spectral range of the terrestrial solar radiation producing smaller currents than smaller band gap materials, which absorb more radiation 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.

2.8.2 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 [28, 29],

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

(2.15)

Here,  
\( I_o \) 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.

### 2.8.3 Photopotential

At a certain illumination, the photopotential $V_{ph}$ as measured under open circuit condition, occurs at the potential at which the photocurrent is equal to the corresponding dark current, i.e., when the total current is zero. Under this condition, then $I = 0$,

$$V_{ph} = \frac{kT}{q} \ln \left( \frac{I_{ph}}{I_o} + 1 \right)$$  \hspace{1cm} (2.16)

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

### 2.8.4 Liquid Junction Photovoltaics

The photovoltaic properties of the semiconductor liquid junction are the basis of the liquid junction photovoltaic cells known as the photoelectrochemical (PEC) cells. In fact, it was in a semiconductor – electrolyte junction (or interface) that Bequerel [30] 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.
2.8.5 Semiconductor- Electrolyte Junction

The semiconductor electrolyte interface, has been the subject of intense study and many excellent treatises and reviews are available on this subject. Informations related to this work are given here in brief [31 - 33].

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 of 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.

2.8.6 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 so that a potential barrier is formed at the interface 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 interface determines the nature of the space charge layer which may be a depletion, accumulation 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 layer results if the surface acquires excess of majority carriers and 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 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.
2.9 PHOTO ELECTRO CHEMICAL 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 photoelectrochemical cell. Many reviews are available in the literature on the subject of PEC cells [34-41].

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 convert 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 [42] and Pleskov [43] have given 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 up to a maximum value of $E_f - E_{\text{redox}}$, $E_f$ being the Fermi level of the semiconductor and $E_{\text{redox}}$, the potential of the redox couple in solution. This difference, the barrier height, represents the upper limit of the open circuit voltage, $V_{oc}$ that can be obtained under high irradiance. $V_{oc}$ cannot exceed $E_f - V_a$ for photoanodes and $E_f - V_c$ for photocathodes.
2.9.1 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. From the knowledge of the charge carrier density and band bending, the space charge layer width can be calculated from the relationship,

\[
W = \left( \frac{2e \varepsilon \varepsilon_0 V_b}{qN} \right)^{\frac{1}{2}}
\]  

(2.17)

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.

2.9.2 Helmholtz and Gouy layers

There is a Helmholtz layer at the interface on the electrolyte side which of few angstroms 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 [44], 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.

### 2.9.3 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 \( V_b \),

\[
V_b = V - V_{fb} \tag{2.18}
\]

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,

\[
V_{fb} \ (NHE) \ = \ (\chi - \Delta E_f + V_H) - 4.5 \tag{2.19}
\]

\[
= (\phi_{sc} - V_H) - 4.5 \tag{2.20}
\]

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.
2.10 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 Na$_2$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 used as 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. The 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.
2.10.1 PEC Cell Parameters

Short circuit current, open circuit voltage, fill factor, power maximum and conversion efficiency are the main cell parameters.

2.10.2 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 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.

2.10.3 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,

$$V_{oc} = \frac{n k T}{q} \left( \ln \frac{I_{sc}}{I_o} + 1 \right)$$  \hspace{1cm} (2.21)
2.10.4 Power Maximum ($P_{\text{max}}$)

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 $I_{\text{max}}$ and $V_{\text{max}}$.

$$P_{\text{max}} = V_{\text{max}} \cdot I_{\text{max}} \quad (2.22)$$

2.10.5 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,

$$ff = \frac{V_{\text{m}} \cdot I_{\text{m}}}{V_{\text{oc}} \cdot I_{\text{sc}}} \quad (2.23)$$

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

2.10.6 Ideality factor

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.,

$$I = I_o \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] - I_{\text{ph}} \quad (2.24)$$

The deviation of the slope of the current potential dependence under the forward bias causes deviations from ideal junction behaviour.
Detailed informations on the junction behaviour can be found in the standard text books [45,46]. The ideality factor can also be determined from the slope by plotting the graph between $V_{oc}$ and $\ln J_{sc}$.

\[
\text{Ideality factor } 'n' = \frac{q}{kT} \cdot (\text{Slope})
\]  

(2.25)

where  
q is the electronic charge,  
k is the Boltzmann constant,  
T is the temperature.

2.10.7 Efficiency ($\eta$)

This is given by the ratio of the electrical energy output to the light energy input

\[
\text{Efficiency} = \eta = \frac{V_m I_m}{P_{in} A}
\]  

(2.26)

where $P_{in}$ denotes the optical power incident on the electrode and A is the illuminated area of the electrode.

2.10.8 Series Resistance ($R_s$)

It is composed of electrical resistance due to metal and semiconductor layer, semiconductor and 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 $1/R_s$. 

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2.10.9 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 \(R_{sh}\).

2.11 LASER RAMAN SPECTROSCOPY

Raman spectroscopy is a form of vibrational spectroscopy, much like infrared (IR) spectroscopy. However, IR bands arise from a change in the dipole moment of a molecule whereas Raman bands arise from a change in the polarizability. In many cases, transitions that are allowed in Raman are forbidden in IR, and hence the 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 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. Since 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 wavenumber, cm\(^{-1}\)). This difference is called the Raman shift, and since it is a difference value, the Raman shift is independent of the frequency of the incident radiation. Typically, only the Stokes region is used where as 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.

Since Raman lines are of 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. Hence the technique 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.