Chapter II

2. 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 [133,134] 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

\[
2d \sin \theta = n\lambda 
\]  
(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, \( \beta \) 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 [135].

2.3 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, 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,

$$E_k = h \nu - E_b \quad (2.3)$$
The experimentally measured energies of the photoelectrons are given by,

\[ E_k = h\nu - E_b - E_w \]  \hspace{1cm} (2.4)

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-ray 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 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 raster scanning to produce images with a spatial resolution of 20 microns. By sputtering materials from the surface, it generates 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 [136],

$$\alpha = \frac{2.303 A}{t} \quad (2.5)$$

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

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (2.6)$$

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.

Resistivity and Hall measurements were used to evaluate mobility and concentration of charge carriers. Resistivity was determined by Van der Pauw technique [137,138]. Here the 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

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

(2.7)

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.

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

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

(2.8)

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 (2.8) can also be written as
\[ \mu_H = \frac{t}{B \rho} \left( \frac{\Delta V}{I} \right) \]  \hspace{1cm} (2.9)

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

\[ R_H = \frac{\mu_H}{\rho} \]

\[ \frac{1}{Nq} = \mu_H \sigma \]  \hspace{1cm} (2.10)

\[ N = \frac{1}{\sigma \cdot q \cdot \mu_H} \]

### 2.7 PHOTOELECTROCHEMICAL STUDIES

**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 1.5eV to 3.0eV (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 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.
**Photocurrent:**

p-n photocells (consisting of p-n junction) and Schottky photocells (consisting of semiconductor-metal junction) are the two principle types of solid state devices. The following equation gives the current-potential dependence of these cells [139, 140],

\[ I = I_o \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] - I_{ph} \]  \hspace{1cm} (2.11)

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.

**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 $I = 0$,

$$V_{ph} = \frac{kT}{q} \ln \left( \frac{I_{ph}}{I_o} + 1 \right) \quad (2.12)$$

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

**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 [141] 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.
**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. Information related to this work are given here in brief [142 - 144].

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.

**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 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.

2.8 PHOTOELECTROCHEMICAL 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 [145-152].

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 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 [153] and Pleskov [154] 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 upto 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.

**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,

$$W = \left( \frac{2 \varepsilon \varepsilon_0 V_b}{qN} \right)^{\frac{1}{2}} \quad (2.13)$$

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.

**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 [155], 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.

**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 \( V_b \),

\[
V_b = V - V_{fb}
\]  
(2.14)

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,

\[
V_{fb \ (NHE)} = (\chi - \Delta E_f + V_H) - 4.5 \]  
(2.15)

\[
= (\phi_{sc} - V_H) - 4.5
\]
(2.16)

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.
2.9 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.

**PEC Cell Parameters:**

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

**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.

**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,

\[
V_{oc} = \frac{n k T}{q} \left( \ln \frac{I_{sc}}{I_o} + 1 \right)
\]  

(2.17)
**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 $V_{\text{max}}$.

$$P_{\text{max}} = V_{\text{max}} \cdot I_{\text{max}}$$

(2.18)

**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,

$$ff = \frac{V_{\text{max}} \cdot I_{\text{max}}}{V_{\text{oc}} \cdot I_{\text{sc}}}$$

(2.19)

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

**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.,

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

(2.20)

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 [156, 157]. The ideality factor can also be determined from the slope by plotting the graph between $V_{oc}$ and $\ln J_{sc}$.

$$\text{Ideality factor 'n' } = \frac{q}{kT} \left( \text{Slope} \right)$$  \hspace{1cm} (2.21)

where $q$ is the electronic charge,

$K$ is the Boltzmann constant,

$T$ is the temperature.

**Efficiency ($\eta$):**

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

$$\text{Efficiency } = \eta = \frac{V_m I_m}{P_{in} A}$$  \hspace{1cm} (2.22)

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

**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 $1/R_s$. 

52
**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 ohm.

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

**2.10 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 scattering, but a tiny portion (~ 1 in $10^7$) of the scattered radiation is shifted to a different wavelength. These wavelength shifted photons are called Raman scattered. 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 spectrum 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.

**Dye Sensitized solar cell:**

A schematic presentation of the operating principles of Dye Sensitized solar cell (DSSC) is given in Fig.2.1. At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO₂ (anatase) although alternative wide band gap oxides such as ZnO [158], and Nb₂O₅ [159] have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. Photo
excitation of the latter results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counterelectrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation.

Fig.2.1 – Schematic of the Dye Sensitized solar cell
Photoluminescence:

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties.

Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the band gap. Band gap determination is particularly useful when working with new compound semiconductors.
Radiative transitions in semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.

The return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism.

In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination.

Special features of photoluminescence spectroscopy are:

- Various excitation wavelengths allow for varying penetration depths into the material, and thus, varying levels of volume excitation.
- Detection of photoluminescence from 0.4 to 2.8 micrometers using diffraction and Fourier-transform-based systems.
- Mapping capabilities with 1-micrometer spatial resolution on the Fourier-transform-based system.
- Sample temperatures of 4 to 300 K.
Sensitivity down to the level of parts per thousand, depending on impurity species and host.

**Semiconducting Metal oxide gas sensors**

Gas sensors are used essentially to detect the presence or concentration of toxic gases like CO, inflammable gases like H\textsubscript{2} or pollutants (like CO\textsubscript{2}) in the atmosphere. Detection range depends on the type of gas. For hydrogen gas in air, it may range from 2 ppm to 100 ppm. For combustible gases like methane, it may range from 200 ppm to 10,000 ppm. There are different techniques used to detect the gases viz: (a) using a sintered ceramic sensors (b) gas sensing electrodes and (c) based on absorption of IR radiation. Wide band-gap semiconducting oxides such as SnO\textsubscript{2}, ZnO, Ga\textsubscript{2}O, Fe\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3} and TiO\textsubscript{2} have been exploited for their well-known gas sensing properties. Metal oxide based sensors have been widely used for the detection of gases, which include toxic, inflammable and pollutant gases like CO, H\textsubscript{2}S, CH\textsubscript{4}, H\textsubscript{2}, NH\textsubscript{3} and alcohol.

The sensor responds to all the gases, which reacts with oxygen. Individual sensitivities differ due to the difference in their affinities at different temperatures. As such the response of the sensor is the cumulative effect of changes in the concentration of all such gases in the vicinity. Sensing becomes meaningful only when the concentration of only one of the constituents changes conspicuously. In some cases, this is ensured using suitable molecular sieves or selected reagents or absorbents, which absorb the other constituents.
Since Seiyama and Taguchi used the dependence of the conductivity of ZnO on the gas present in the atmosphere for gas sensing applications, many different metal oxides have been proposed for gas detection. It has been proved that semiconductor gas sensors have highly improved performance for a higher precision and a reduced analysis time. Heated semiconductor metal oxides are kind of the electrochemical class of chemical sensors [160]. Gas sensors based on different metal oxides (SnO₂, TiO₂, In₂O₃, WO₃) are often called Semiconductor Metal Oxide sensors (SMO).

In their simplest configuration, SMO sensors consist of a substrate with heater, electrodes and a sensitive layer in contact with the electrodes. According to Williams and Moseley, most target gases are detected due to their influence on the oxygen stoichiometry of the surface. Many studies have revealed that the key reaction involves modulation of the concentration of surface oxygen ions. Some metal oxides, such as SnO₂, TiO₂ or WO₃, are intrinsically n-type bulk semiconductors, for which, the metal stoichiometric excess is due to oxygen vacancies.

![Fig. 2.2(a) SMO sensor working principle](image)

Fig. 2.2(a) SMO sensor working principle
Under normal sensor operating conditions, the conductivity of the surface has revealed to be much less than that of the bulk. This has been attributed to the formation of surface oxygen ions that trap electrons, inducing a surface depletion layer and thus the development of Schottky barriers at inter-particle contacts. In the case of n-type metal oxides, since the electrons come from ionized donors via the conduction band, the charge carrier density at the interface is thereby reduced and a potential barrier to charge transport is developed. Figure 2.2 (a) and Figure 2.2 (b). As the surface charge is developed, the adsorption of further oxygen is inhibited, the adsorption rate slows down because charge must be transferred to the adsorbate over the developing surface barrier and the coverage saturates at a very low value. At the junction between the grains of the solid, the depletion layer and associated potential barrier lead to high-resistance contacts, which dominate the resistance of the solid. The resistance is then
sensitive to the coverage on the surface of adsorbed oxygen ions and any factor that changes this, will change the resistance.

The relationship between sensor resistance and the concentration of deoxidizing gas can be expressed by the following equation over a certain range of gas concentration:

\[ R_s = A[C]^{-\alpha} \]

\( R_s \) = Electrical Resistance of the Sensor

A= Constant

C = Gas concentration

\( \alpha \) = Slope of \( R_s \) curve

Some characteristics that make SMO sensors for gas sensor users are:

- Low cost, small size and easy to handle (compared to other gas sensors)
- Fast sensor response and recovery time
- Robust construction, good mechanical strength and high reliability leading to a low failure rate.
- Long operating life and maintenance free
- Good resistance to corrosive gases.
Figure. 2.3 Simple sensor structure

The central surface reaction responsible for most gas responses involves changes in the concentration of surface oxygen species such as $O^2$. Oxygen adsorbates can think of as a trap for electrons from the solid bulk. In case of an n-type semiconductor such as $SnO_2$ the electrons come from ionized donor (stoichiometric defects) via the conduction band. Reducing gases react with oxygen adsorbates, which release trapped electrons and increase the electrical conductance of the n-type semiconductor. Fig. 2.3 shows the schematic diagram of the simplified sensor geometry. The sensing material is deposited on alumina substrate and a pair of electrodes is placed on the active film – alumina interface. Gas access is from the top of the film only.

Tin oxide is a widely used material for gas sensor applications because of its high sensitivity. Chemical inertness, inexpensive material, material stability and relatively low operating temperature with a fast response time though poor selectivity to the gases since it is sensitive to almost all the gases. The selectivity
can be achieved by doping with noble metals, fabrication technologies and other physical parameters. It is an oxygen deficient n-type semiconductor and crystallizes in a rutile structure. It is commonly used as a gas sensor-particularly for reducing gases in industrial and domestic purposes. They require temperature of 300-400°C for their operation and are affected by moisture content. The Tin oxide detects the reducing gases CO, H₂, N₂ and H₂S.

It is well known that the resistance of SnO₂ changes according to various reducing gases environments. In atmosphere, oxygen is adsorbed onto SnO₂ surface by capturing electrons from the conduction band and remains as $O_2^-$, $O^-$ or $O^{2-}$ ions until they desorbs at higher temperature. These adsorbed oxygen species induce a subsequent potential barrier at a grain boundaries and a resistive depletion layer is formed which determines most of the sensor resistance. When a flammable gas is introduced, the adsorbed oxygen is removed by oxidation of the gas and the captured electrons are injected into the conduction band. This results in a reduction of the potential barrier height and decrease in resistance of the sensor.
Materials used for Sensors and their applications.

<table>
<thead>
<tr>
<th>Material</th>
<th>Examples</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramics</td>
<td>SnO$_2$, ZnO</td>
<td>Gas sensors, mainly Hydrocarbon gases</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>Solid analyte, mainly as O$_2$ sensors.</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>O$_2$ Sensors</td>
</tr>
<tr>
<td></td>
<td>BaTiO$_3$, SrSnO$_3$, SrTiO$_3$,</td>
<td>O$_2$ Sensors</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$, ZnCr$_2$O$_4$</td>
<td>Humidity sensor</td>
</tr>
</tbody>
</table>

Metal-oxide gas sensors such as tin dioxide (SnO$_2$), have been popular since the late 1960 [133]. They are simple rugged devices that perform reasonably well with relatively simple electronics support. Bulk metal oxides have electrical properties that change in the presence of reducible gases such as methyl mercaptan (CH$_3$SH) and ethyl alcohol (C$_2$H$_5$OH). When a metal-oxide crystal such as SnO$_2$ is heated at a certain high temperature in air, oxygen is adsorbed on the crystal surface is exposed to reducible gases, the surface potential decreases and conductivity measurably increases. Other materials like Indium oxide and indium tin oxide films.

The sensing performance of the sensors was examined using the “static gas sensing system” (figure.2.4). There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to desired operating temperature. The current passing through the heating element
was monitored using a relay operated with an electronic circuit with adjustable ON–OFF time intervals. The Cr–Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and the current was measured by a digital picoammeter. Air was allowed to pass into the glass chamber after every gas exposure cycle.

Fig.2.4. Block diagram of the gas sensing system