CHAPTER 3

Deposition and Characterisation Techniques
Abstract

This chapter presents the various deposition techniques used for the growth of transparent conducting oxide thin films. The chapter also describes the various characterisation tools employed for analyzing the grown films.
3.1 Introduction

Transparent conducting oxide thin films exhibit high electrical conductivity, high optical transmittance in the visible region and high reflectance in the IR region. These unique properties make them suitable for a variety of applications. So various techniques for the growth of these films have been intensively investigated during the recent past. The same material deposited by two different techniques usually has different properties. So, growth techniques play a significant role in governing the properties of these films. This is due to the fact that electrical and optical properties of the films strongly depend on the structure, morphology and the nature of the impurities present [1]. Also, the films grown by any particular technique may often have different properties due to the involvement of various deposition parameters. The properties of the films, therefore, can be tailored by controlling the deposition parameters.

3.2 Thin Film Preparation Techniques

Generally any thin film deposition follows the sequential steps: a source material is converted into the vapour form (atomic/molecular/ionic species) from the condensed phase (solid or liquid), which is transported to the substrate and then it is allowed to condense on the substrate surface to form the solid film [2]. Depending on how the atoms/molecules/ions/clusters of species are created for the condensation process, the deposition techniques are broadly classified into two categories, viz. Physical methods and Chemical methods [3]. The general physical methods that have been used to grow the transparent conducting oxide films are vacuum evaporation and sputtering [4,5]. The vacuum evaporation techniques include, thermal evaporation by resistive heating and electron beam evaporation. All these physical methods of deposition of thin film were done in a high vacuum system in which a vacuum of $10^{-5}$ mbar was created using a
diffusion pump backed by a rotary pump. The chemical methods include chemical vapour deposition, spray pyrolysis and dip coating [6-8]. The following sections discuss the methodology and experimental set-ups used in various thin film deposition, especially techniques used for the growth of films used in the present investigation.

### 3.2.1 Vacuum Evaporation

It is the most widely used technique for the preparation of thin films for the deposition of metals, alloys, and also many compounds, as it is very simple and convenient. Here the only requirement is to have a vacuum environment in which sufficient amount of heat is given to the evaporants to attain the vapour pressure necessary for the evaporation. The evaporated material is allowed to condense on a substrate kept at a suitable temperature. A resistively heated tungsten or tantalum source is used to evaporate the charge. The important control parameters are the substrate temperature, evaporation rate, source to substrate distance and the oxygen partial pressure. Transparent conductors can be evaporated in three ways (i) by directly evaporating the metal oxides, (ii) reactive evaporation of the metal in the presence of oxygen and (iii) post oxidation of metal films. Always some deficiency of oxygen will be there when an oxide material is evaporated. To avoid this, the films must either be evaporated in the partial pressure of oxygen or some post deposition heat treatment in air must be done.

Reports on the growth of ITO thin films by evaporation involve reactive evaporation of either metallic alloy or an oxide mixture [9-12]. Films grown by vacuum evaporation using oxide mixtures are usually deficient in oxygen and an oxygen partial pressure of $10^{-4}$ Torr is necessary to have transparent thin films. X-ray diffraction studies of vacuum evaporated ITO films revealed no trace of any oxide phase of tin even for highly doped films [13]. The preferred
orientation observed in the vacuum evaporated films was (111). Thermal evaporation technique has been used for the deposition of metal electrodes in the present study.

3.2.2 Sputtering

Sputtering is one of the most versatile techniques used for the deposition of transparent conductors when device quality films are required. Sputtering process produces films with higher purity and better controlled composition, provides films with greater adhesion and homogeneity and permits better control of film thickness. The sputtering process involves the creation of gas plasma usually of an inert gas such as argon [14] by applying voltage between a cathode and anode. The cathode is used as a target holder and the anode is used as a substrate holder. Source material is subjected to intense bombardment by ions. By momentum transfer, particles are ejected from the surface of the cathode and they diffuse away from it, depositing a thin film onto a substrate. Sputtering is normally performed at a pressure of $10^{-3} - 10^{-7}$ Torr.

There are two modes of powering the sputtering system; dc and rf biasing. In dc sputtering system a direct voltage is applied between the cathode and the anode. This method is restricted for conducting targets only. RF sputtering is suitable for both conducting and non-conducting targets; a high frequency generator (13.56 MHz) is connected between the electrodes of the system.

In the process of sputtering, the material is knocked out of a surface by heavy argon ions and travel across the system to condense onto the substrate surface. For the sputtered material to arrive at the substrate surface with the high energy necessary to give a good coating, and for the process to be efficient, it is important for the material to travel without collision with the residual gas in the vacuum. However, the residual gas pressure needed to maintain a simple
electrical discharge, in order to provide the argon ions for bombardment, is too high to allow transfer of the sputtered material without many collisions. This give rise to a very slow deposition rate and poor quality coating. A magnetron uses a magnetic field to confine electrons close to the cathode, making it easier to sustain an electrical discharge at low pressure. Magnetron sputtering is particularly useful when high deposition rates and low substrate temperatures are required [15].

Both reactive and non-reactive forms of dc, RF and magnetron sputtering have been employed for the deposition of semiconducting transparent thin films. In reactive sputtering, the reactive gas is introduced into the sputtering chamber along with argon to deposit oxide films. The deposition rates and properties of the films strongly depend on the sputtering conditions such as the partial pressure of the reactive gas, the sputtering pressure, substrate temperature and target to substrate spacing.

In sputter deposition, the material arrives at the substrate mostly in atomic or molecular form. The atom diffuses around the substrate with a motion determined by its binding energy to the substrate, which is influenced by the nature and temperature of the substrate. The depressions on the substrate surface act as adsorption sites for the diffusing atoms. At each hop, the atom will either jump over the barrier into an adjacent site or will re-evaporate. After a certain time, the atom will either evaporate from the surface or will join another diffusing single atom to form a doublet. These doublets will be joined by other single atoms to form triplets, quadruplets and so on. This stage is known as the nucleation stage of thin film growth and it leads to the formation of quasi-stable islands. The islands will grow in size and it will lead to the coalescent stage. Coalescence proceeds until the film reaches continuity.
Sputtering may be carried out in a variety of systems, which may differ in sputtering configuration, geometry, target type etc. Experimental sputtering systems usually have small targets and low production rates, whereas commercial production systems have large targets and rapid substrate transport to maximize production rate. Irrespective of the sputtering system used, the basic sputtering process remains the same. Figure 3.1 shows a typical sputter deposition system.

![Figure 3.1 Schematic sketch of RF sputter deposition system](image)

The process of RF sputter deposition is made possible due to the large difference in mass, and hence mobility, of electrons and inert gas ions. Because electrons are many times less massive than ions, electrons attain much greater velocities
and travel much further than ions during each cycle of the applied RF voltage waveform. Since electrons travel much further, they eventually accumulate on the target, substrate and chamber walls such that the plasma is the most positive potential in the system. These induced negative voltages or “sheath voltages”, cause acceleration of positive ions toward the negatively charged surfaces, which subsequently leads to sputtering events. The volume adjacent to a surface tends to be relatively free of electrons because of the negatively charged surface. This leads to a “dark space” because electrons are not available to excite gas atoms [8].

The target is selectively sputtered by controlling the relative surface areas of the target and the substrate holder. If space charge limited current is assumed, the ion current flux, \( J \) can be estimated by the Child- Langmuir equation [8],

\[
J = \frac{KV^{3/2}}{D^2 m_{ion}}
\]  

(3.1)

where \( D \) is the dark space thickness, \( V \) is the sheath voltage, \( m_{ion} \) is the ionic mass and \( K \) is the proportionality constant. Since the positive ion current must be equal at both the electrodes,

\[
\frac{A_A V_A}{D_A^2} = \frac{A_B V_B}{D_B^2}
\]  

(3.2)

where \( A_A \) and \( A_B \) are the surface areas of electrodes A and B respectively (Fig 3.2). It should be noted that this step differs from the assumption of treating the positive ion current densities equal.
If the positive ion current densities were equal, there would be a much greater positive ion current flowing during one half cycle of the applied voltage waveform than the other due to the much greater area of the grounded substrate electrode. Therefore, because this system is assumed to be in steady state, the total positive ion current per half cycle should be the relevant quantity.

The glow discharge itself is a region where large quantities of positive and negative charge exist and can be modelled as a wire. Since most of the voltage in the glow discharge is dropped across the dark space, and they have small conductivities, they can be modelled as capacitors such that the capacitances,

$$C \propto \frac{A}{D} \quad (3.3)$$
Furthermore, an AC voltage will divide across two series capacitors such that,

\[
\frac{V_A}{V_B} = \frac{C_B}{C_A}
\]  

(3.4)

From equations (2.1), (2.2) and (2.3),

\[
\frac{V_A}{V_B} = \left( \frac{A_B}{A_A} \right)^2
\]  

(3.5)

This equation tells that smaller area will see larger sheath voltage, whereas larger area will see a smaller sheath voltage by a power of 2. The usefulness of this result is that \( A_B > A_A \) must hold to selectively sputter the target. This is done in practice by grounding the substrate holder to the entire chamber resulting in a very large \( A_B \). For this reason it is extremely important that the substrate holder and the system are well grounded to ensure that resputtering of the growing film does not occur.

We have used an in-house made magnetron for the rf sputtering of tin doped Indium oxide thin films. A magnet of 2000 gauss was used to deflect the ions. A schematic diagram of the magnetron is shown in figure 3.3. The vacuum system consists of a six-inch diameter diffusion pump backed by a rotary pump (make – Indovision, Bangalore). The rf supply was connected to the magnetron through a capacitive matching network (make – Digilog Instruments, Bangalore). The flow of argon gas into the vacuum chamber was controlled using a mass flow controller (make Bronkhorst, Holland).

The reports on ITO films by sputtering of oxide target show that the use of oxide target helps in controlling the stoichiometry of the films [16,17]. Usually, oxygen added to the sputtering gas mixture improves the structural, electrical and optical properties of the films provided the oxygen partial pressure is low and is within a narrow range [18]. The films deposited at lower deposition rates show (400) peak while those deposited at higher deposition rates are reported to show (222) peak [19].
3.2.3 Pulsed laser deposition

Pulsed laser deposition (PLD) is a relatively new technique used for depositing superconducting and transparent conducting oxide thin films. PLD provides several advantages compared to other deposition techniques in the growth of multicomponent oxide thin films [20]. For a multi component target, the composition of films grown by PLD reproduces that of the target. PLD film crystallize at lower substrate temperature relative to other physical vapour deposition techniques due to the high kinetic energy (>1 eV) of the ionised and ejected species in the laser produced plasma. Also the surface of the TCO film
grown by PLD is very smooth. ITO films grown by PLD, have already been used as the anode contact in organic light emitting diodes (OLEDs). The main issues confronting PLD technology is the small substrate coverage, low deposition rates and non-uniformity of film thickness.

3.2.4 Chemical vapour deposition

Chemical vapour deposition (CVD) is one of the most important methods used for producing semi conducting transparent thin films. The technique involves a reaction of one or more gaseous reacting species on a solid substrate. Here, metallic oxides are grown by the vaporization of a suitable organometallic compound. A vapor containing the condensate material is transported to a substrate surface, where it is decomposed by a heterogeneous process [21]. The decomposition condition should be such that the reaction occurs only at or near the substrate surface and not in the gaseous phase, to avoid the formation of powdery deposits, which may result in haziness in the films.

The quality of the films deposited by CVD depends on various parameters such as substrate temperature, gas flow rate and system geometry. All these parameters should be optimized and controlled in order to get best quality films. The main advantage of using the CVD process are simplicity, reproducibility and ease with which it can be adopted for large scale production without requiring vacuum as an essential requirement. The cost of production of thin films by this technique is very low. Films of high purity, stoichiometry and structural perfection can be obtained. The main disadvantage is that the morphology of the films deposited by CVD is strongly influenced by the nature of the chemical reaction and the activation mechanism.

The experimental set up for CVD consists of a quartz tube of diameter 18mm in which two separate temperature zones are maintained using resistance furnaces:
the evaporation zone (Temperature varies from 150 to 200°C) and the reaction zone (Temperature varies from 350 to 450°C). Vapors from the reactants are transported into the reaction zone by a carrier gas (N₂). The reactants used for the process were indium and tin acetyl acetonates mixed in the ratio 43:57 wt%. The films grown by this technique were found to be polycrystalline and showed (222) diffraction peak [22].

### 3.2.5 Spray pyrolysis

This is one of the relatively simple and cheap methods that can be easily adopted for the mass production of large area coatings for industrial applications. The method is based on the pyrolytic decomposition of a metallic compound dissolved in a liquid mixture when it is sprayed onto a preheated substrate [23]. The method depends on the surface hydrolysis of a metal chloride on a heated substrate surface in accordance with the reaction

\[
\text{MCl}_x + y\text{H}_2\text{O} \rightarrow \text{MO}_y + x\text{HCl}
\]

in which M is any host metal such as Sn, In or Zn of the oxide film.

The atomisation of the chemical solution into spray of fine droplets is accomplished by the spray nozzle with the help of a filtered carrier gas. The carrier gas and solution are fed into the spray nozzle at predetermined pressures and flow rates. The geometry of the gas and the liquid nozzles strongly determine the spray pattern, size distribution of droplets and spray rate which in turn determine the growth kinetics and hence the quality of the films grown. The other important parameters that affect the film quality are the nature and temperature of the substrate, the solution composition, the gas and solution flow rates and nozzle to substrate distance.
3.3 Characterization Tools

The optimisation of the preparation conditions is the main task in order to get device quality films. This is to be done on the basis of detailed structural, compositional, morphological, optical and electrical properties of the films obtained at different growth conditions. In the following sections the techniques used for the film characterizations are discussed briefly.

3.3.1 Thin film thickness

Thickness plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the film thickness and the deposition parameters are kept constant. Film thickness may be measured either by in-situ monitoring of the rate of deposition or after the film deposition. In the present work, the film thickness was determined by employing optical interference technique.

3.3.1a Optical interference method

Film thickness can be measured accurately from interference fringes using multiple beam interferometry. This technique was first used by Weiner [24] and later was modified by Tolansky [25]. Two reflecting surfaces are brought in close proximity such that a small wedge with a small air gap in between them is formed. If a monochromatic light falls at normal incidence on it, interference of light due to the multiple reflected beams results in a series of fringes (Fizeau). The distance between the fringes depends on the air gap as well as on the wavelength of the monochromatic light.
The film for thickness measurement is deposited on a flat surface so as to leave a sharp edge between the film and the uncoated region of the substrate. Over this film a highly reflecting coating of aluminium forms a sharp step on the film edge. Another optically flat glass slide known as the reference plate with a partially transparent aluminium film is then placed over the specimen with the metal coated surfaces in contact with each other so as to leave a small air gap at the step. A monochromatic parallel beam of light is then incident on this two plates assembly and reflected light is then observed through a microscope. A set of sharp fringes perpendicular to the step with equal displacements will be observed and the thickness \( t \) can be determined using the relation,

\[
  t = \frac{b \lambda}{2a}
\]

where \( b \) is the displacement of the fringes at the step and \( a \) is the distance between consecutive fringes. The sharpness of the fringes depends on the reflectivity of the metal coating, the spread of the incident beam, air gap etc.

### 3.3.2 Surface morphology

The uniformity and roughness of the thin film surface plays an important role in the optical properties of thin films. When the surface is rough, the films will be less transparent and the grain boundaries will affect the electrical properties of the thin films. The surface morphology of the films is studied using scanning electron microscopy (SEM).

Scanning electron microscopy (SEM) is one of the most widely used techniques for obtaining micro structural and surface features of thin films. An electron beam is focused onto the surface of the specimen and results in the ionization of the atoms in the specimen. This will cause the ejection of the secondary electrons from the surface, very close to the incident beam position. These secondary electrons can be attracted to a positively charged detector with high
efficiency. The secondary electron yield per primary electron is high and increases as the angle between electron beam and the surface normal increases [26]. The secondary electrons generated from the specimens are used for Z-modulation in a corresponding raster on an oscilloscope. In order to avoid charging problems a thin layer of gold is deposited on the specimen without altering the surface features. The secondary electron mode is generally preferred for topographical feature determination since these electrons generate only from about 10Å0 or less from the film surface and hence the picture obtained is a faithful reproduction of the surface features.

The scanning electron microscopy can be effectively used for the surface analysis to know the details regarding the grain size, presence of minor or secondary phases, the orientation of the grains, uniformity, porosity of the sample etc. SEM gives a pictorial overview of the grains on the thin film surface.

### 3.3.3 Energy dispersive x-ray analysis (EDX)

EDX was used to estimate the composition of the thin film samples. x-rays are generated by the incident electrons within a volume similar to but rather larger than that for the backscattered electrons. Peak x-ray energies corresponding to the characteristics of the elements within that volume can be identified and the relative compositions of elements can be estimated. Thus the bulk composition of the sample and of the individual grains in a polycrystalline sample can be determined [26].
3.3.4 X-ray diffraction studies

Electrical and optical properties of the materials are influenced by the crystallographic nature of the films. X-ray diffraction (XRD) studies were carried out to study the crystallographic properties of the thin films prepared.

A given substance always produces a characteristic x-ray diffraction pattern whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. The particular advantage of x-ray diffraction analysis is that it discloses the presence of a substance and not in terms of its constituent chemical elements. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is much faster, requires only very small sample and is non destructive [27,28].

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic x-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of $\lambda$. This condition is called Bragg’s law and is given by the relation,

$$2d\sin \theta = n\lambda$$  \hspace{1cm} (3.8)

where $n$ is the order of diffraction, $\lambda$ is the wavelength of the x-rays, $d$ is the spacing between consecutive parallel planes and $\theta$ is the glancing angle (or the complement of the angle of incidence)[29].
x-ray diffraction studies gives a whole range of information about the crystal structure, orientation, average crystalline size and stress in the films. Experimentally obtained diffraction patterns of the sample are compared with the standard Powder Diffraction Files published by the International Centre for Diffraction Data (ICDD).

The average grain size of the film can be calculated using the Scherrer’s formula [27],

\[ d = \frac{0.9\lambda}{\beta \cos \theta} \]  

(3.9)

where, \( \lambda \) is the wavelength of the x-ray and \( \beta \) is the full width at half maximum intensity in radians. The lattice parameter values for different crystallographic systems can be calculated from the following equations using the (hkl) parameters and the interplanar spacing \( d \).

For cubic system,

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \]  

(3.10)

x-ray diffraction measurements of the different films were done using Rigaku automated x-ray diffractometer. The filtered copper Kα (\( \lambda = 1.5418\text{Å} \)) radiation was used for recording the diffraction pattern.

### 3.3.5 Optical characterisation

#### 3.3.5a Determination of optical band gap

An important technique for measuring the band gap of a semiconductor is by studying the absorption of incident photons by the material. In this, photons of selected wavelength are directed at the sample and the relative transmission of the various photons is observed. Since photons with energies greater than the
band gap energy are absorbed while photons with energies less than band gap energy are transmitted, the experiment gives an accurate measure of band gap [30].

According to Bardeen et al. [31] for the parabolic band structure, the relation between the absorption coefficient ($\alpha$) and the band gap of the material is given by,

$$\alpha = \frac{A}{h \nu} (h \nu - E_g)^r$$  \hspace{1cm} (3.11)

where, $r = 1/2$ for allowed direct transitions, $r = 2$ for allowed indirect transitions, $r = 3$ for forbidden indirect transitions and $r = 3/2$ for forbidden direct transitions. $A$ is the parameter which depends on the transition probability. The absorption coefficient can be deduced from the absorption or transmission spectra using the relation,

$$I = I_0 e^{-\alpha t}$$  \hspace{1cm} (3.12)

where, $I$ is the transmitted intensity and $I_0$ is the incident intensity of the light and $t$ is the thickness of the film. In the case of direct transition, $(\alpha h \nu)^2$ will show a linear dependence on the photon energy ($h \nu$). A plot of $(\alpha h \nu)^2$ against $h \nu$ will be a straight line and the intercept on energy axis at $(\alpha h \nu)^2$ equal to zero will give the band gap.

3.3.5b Determination of optical constants

The optical constants, the refractive index ($n$) and the extinction coefficient ($k$) of the films are calculated using the theory of Manificer et al. [32] for weakly absorbing films.
Since ITO is a very weakly absorbing film, the measurement of transmission of light through the film in the region of transparency is sufficient to determine the real and imaginary parts of the complex refractive index \( n^* = n - ik \). For such films the following method can be used for determining the optical constants.

If the incident light has unit amplitude then the amplitude of the transmitted wave is

\[
A = \frac{t_1 t_2 \exp\left(-2\pi i n^* t/\lambda\right)}{1 + r_1 r_2 \exp\left(-4\pi i n^* t/\lambda\right)}
\]  
(3.13)

Where \( t_1, t_2, r_1 \) and \( r_2 \) are the transmission and reflection coefficients of the front and rear surfaces respectively and are given by

\[
t_1 = \frac{2n_0}{n_0 + n}, \quad t_2 = \frac{2n}{n + n_1}
\]  
(3.14a) & (3.14b)

\[
r_1 = \frac{n_0 - n}{n_0 + n} \quad \text{and} \quad r_2 = \frac{n - n_1}{n + n_1}
\]  
(3.14c) & (3.14d)

\( n_0, n \) and \( n_1 \) are the refractive indices of the substrate, film and the medium respectively.

Transmission coefficient of the layer is \( T = \frac{n_1}{n_0} A^2 \)  
(3.15)

If we consider the case of normal incidence and weak absorption (where \( k^2 << (n - n_0)^2 \) and \( k^2 << (n - n_1)^2 \)).

Transmission coefficient is given by
\[ T = \frac{16 n_0 n_1 n^2 \alpha_i}{c_1^2 + c_2^2 \alpha_i^2 + 2 c_1 c_2 \alpha_i \cos(4 \pi n t / \lambda)} \]  

(3.16)

where \( c_1 = (n + n_0)(n + n_1) \)  
\( c_2 = (n - n_0)(n_1 - n) \)  

(3.17)
(3.18)

and \( \alpha_1 = -4\pi kt / \lambda = \exp(-\alpha t) \)  

(3.19)

Here \( \alpha \) is the absorption coefficient of the thin film, \( t \) is the thickness, \( k \) is the extinction coefficient and \( \lambda \) is the wavelength of light.

The extreme values of \( T \) are

\[ T_{\text{max}} = \frac{16 n_0 n_1 n^2 \alpha_i}{(c_1 + c_2 \alpha_i)^2}, \]  

(3.20)

and

\[ T_{\text{min}} = \frac{16 n_0 n_1 n^2 \alpha_i}{(c_1 - c_2 \alpha_i)^2}. \]  

(3.21)

where \( n = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \)  

(3.22)

\[ N = n_0^2 + n_1^2 + 2 n_0 n_1 \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}} \]

Knowing \( T_{\text{max}}, T_{\text{min}}, n_0 \) and \( n_1 \) at the same wavelength refractive index \( n \) of the film can be calculated.
3.3.6 Electrical characterization

3.3.6a Resistivity by two probe method

The resistivity of the films is determined by the two-probe method with the electrodes in planar geometry. Evaporated indium layers or high conducting silver paste was used as the electrodes. The current voltage measurements were carried out using a Keithley’s source measure unit (Model SMU236). The resistivity (ρ) of the films is calculated applying ohm’s law, by the relation \( \rho = RA/L \) where R is the resistance given by the slope of the current-voltage characteristic curves. A is the area of the film in planar geometry which is given by the product of the film thickness and the width of the film. L is the spacing between the electrodes.

3.3.6b Hall measurement

The electrical resistivity of a semiconductor thin film can be written using Ohm’s law,

\[
\rho = \frac{1}{en\mu} \tag{3.23}
\]

where ‘\( \rho \)’ is the film resistivity, e is the electronic charge, n is the number of carriers corresponding to the carrier concentration and ‘\( \mu \)’ is the carrier mobility. According to Ohm’s law the carrier mobility affects resistivity. Low resistivity can be achieved by increasing the carrier concentration or mobility or both. Increasing carrier concentration is self-limiting because at some point the increased number of free carriers decreases the mobility of the film due to carrier scattering. Hence there is a trade off between the carrier density and carrier mobility for achieving low resistivity.
In the case of Indium tin oxide films, the resistivity (\(\rho\)), carrier concentration (n), carrier mobility (\(\mu\)), and sheet resistance were measured using vander Pauw four point probe in geometry [33]. Samples used were 1cm x 1cm in size. The ohmic contacts were made using silver paste. The silver paste was applied at the corners of the sample symmetrically as shown in figure 3.4.

![Figure 3.4 Symmetric contacts in vander Pauw geometry](image)

Let \(R_1\) be the potential difference between A and B per unit current through C and D or vice versa. Similarly \(R_2\) the potential difference between B and C per unit current through D and A.

Then sheet resistance \(R_s\) can be calculated using the relation

\[
R_s = \left( \frac{\pi}{\ln 2} \right) \left( \frac{R_1 + R_2}{2} \right) f \left( \frac{R_1}{R_2} \right)
\]  

(3.24)

where \(f \left( \frac{R_1}{R_2} \right)\) is the vander Pauw function and is given by the relation,

\[
f \left( \frac{R_1}{R_2} \right) = 1 - 0.3466 \left( \frac{R_1 - R_2}{R_1 + R_2} \right)^2
\]  

(3.25)

The Hall signal was measured between two ends while passing the current through the other two ends. Hall mobility is,

\[
\mu = \frac{\Delta R \times 10^8}{BR_s}
\]  

(3.26)

where \(\Delta R\) is the change in resistance due to magnetic field (B) which was applied to measure Hall voltage. Carrier concentration was determined using the equation 3.23. The hall coefficient \(R_H\) is given by,

\[
R_H = \mu \times \rho
\]  

(3.27)
The type of carriers can be understood from the sign of the $R_H$. The negative values of $R_H$ correspond to the electrons (n-type) carriers and positive values to holes (p-type).

### 3.4 Plasma Studies

#### 3.4.1 Introduction

Plasma, the fourth state of matter, is a substance in which many of the atoms or molecules are effectively ionized, allowing charges to flow freely. Since more than 99% of the known universe is in the plasma state and has been so since the BigBang, plasma might be considered as the first state of matter. In earlier epochs of the universe, everything was plasma. In the present epoch, stars, nebulae, interstellar spaces etc are filled with plasma. The solar spectrum is also permeated with plasma in the form of solar wind, and the earth is completely surrounded by plasma trapped within its magnetic field. Terrestrial plasma occur in lightning, fluorescent lamps, a variety of laboratory equipments and industrial processes[34].

The distinction between the four states of matter can be expressed in terms of an ascending scale of energy as we pass from solid to liquid to gas and finally to plasma. The atomic theory has made us familiar with the concepts of basic particles like atoms, molecules and combinations of molecules etc; that they are common to the state of matter. The distinction among this states lies in the difference between the bond or the force joining these constituent particles. Thus a strong bonding characterize the solid state, liquid state by a weak bonding and gaseous state by lack of bonding between particles. In microscopic terms it is the kinetic energy of constituent particles that determines the matter state. Because this energy opposes the inter particle binding force and the resultant equilibrium determines its state.
In solid, particles are characterized to a rigid order. In liquid they are free to move around. In gas even though atoms are free to move randomly, the electrons in them performs a harmonic dance over their orbits according to the laws of quantum mechanics. But in plasma, the electrons are liberated from the atoms and acquire complete freedom of motion. In plasma, the ionization increases with increase of temperature. So in plasma, the particles exist in the form of +ve ions and –ve electrons. In hydrogen, at normal pressures ionization becomes complete at about $2 \times 10^4$ to $3 \times 10^4$ K. Fully ionized gas formed in this way is called as high temperature plasma. In this ionized gas there exists some cohesiveness, i.e., the formation of clusters within a very short time after the production of ions. Instead of remaining as singly ionized molecules they soon get attached to other molecules and form clusters; chiefly when polar molecules of other gases or vapors such as H$_2$O are present as impurity. This property is neither the usual characteristics of solids nor fluids. So plasma, in physics, is regarded as the 4th state of matter.

It was Irving Langmuir, who first used the term plasma to describe the oscillations that are observed in a low-pressure mercury discharge[35]. Later, a branch of physics that deals with properties of fully ionized gas was evolved. Developments in many branches of physics, from the time of Langmuir’s work, have contributed directly and indirectly to the present state of plasma physics. After Langmuir, plasma research gradually spread in other directions. The development of radio broadcasting led to the discovery of earth’s ionosphere, a layer of partially ionized gas in the upper atmosphere, which reflects radio waves. Unfortunately, the ionosphere also occasionally absorbs and distorts radio waves. Earth’s magnetic field causes waves of different polarization to propagate at different velocities, which give rise to the ‘ghost signals’ i.e. signals which arrive at a little before or a little after the main signal. In order to understand some of the deficiencies in radio communication, Appleton and
Budden, systematically developed the theory of electromagnetic wave propagation through non-uniform magnetized plasma.

Later, astrophysicist recognized that much of the universe consists of plasma, and, thus a better understanding of astrophysical phenomena requires a better grasp of plasma physics. The pioneer in this field was Hannes Alfvén, who in 1940’s developed the theory of magneto hydrodynamics (MHD) in which plasma is treated as a conducting fluid. MHD is a physical model describing the properties of electrically conducting fluids interacting with magnetic and electric fields. This theory has been both widely and successfully employed to investigate sunspots, solar flares, solar wind, star formation etc. Two topics of particular interest in MHD theory are magnetic reconnection and dynamo theory. Magnetic reconnection is a process by which magnetic field lines suddenly change their topology. It can give rise to the sudden conversion of a great deal of magnetic energy into thermal energy; as well as the acceleration of some charged particles to extremely high energies. This is thought to be the basic mechanism behind solar flares. Dynamo theory studies show the motion of an MHD fluid can give rise to the generation of a macroscopic magnetic field. This process is important because both terrestrial and solar magnetic fields would decay away comparatively rapidly (in astrophysical terms) were they not maintained by dynamo action. The earth’s magnetic field is maintained by the motion of its molten core, which can be treated as an MHD fluid.

The creation of hydrogen bomb in 1952 generated a great deal of interest in controlled thermonuclear fusion as a possible power source for the future. In the initial years this research was carried out secretly in USA, Soviet Union and Britain. However in 1958 thermonuclear fusion research was declassified, leading to the publication of a number of immensely important and influential papers in the late 1950’s and early 1960’s. Theoretical plasma physics first emerged as a mathematically rigorous discipline in these years. Surprisingly,
fusion physicists are mostly concerned with understanding how thermonuclear plasma can be trapped, in most cases by a magnetic field, and investigating many plasma instabilities which may allow it to escape. The planned International Thermonuclear Experimental Reactor (ITER) is hoped to be the final step before practical fusion energy becomes a reality.

In 1958, James A Allen discovered Van Allen radiation belts surrounding the earth. Radiation belts are plasma regions in the earth’s magnetosphere in which charged particles are trapped by magnetic mirror effect. It is discovered by using data transmitted by the U S explorer satellite, marked the start of the systematic exploration of earth’s magnetosphere via satellite, and opened up the field of space plasma physics.

The development of high-powered lasers in 1960s opened up the field of laser plasma physics. When a high-powered laser beam strikes a solid target material is immediately ablated, and a plasma forms at the boundary between the beam and the target. Laser plasmas tend to have fairly extreme properties (e.g. densities characteristic of solids) not found in more conventional plasmas. A major application of laser plasma physics is the approach to fusion energy known as inertial confinement fusion. In this approach highly focused laser beams are used to implode a small solid target until the densities and temperatures characteristics of nuclear fusion (i.e., the center of a hydrogen bomb) are achieved. Another interacting application of laser plasma physics is the use of extremely strong electric fields generated when a high intensity laser pulse passes through plasma to accelerate particles. High-energy physicist hopes to use plasma acceleration techniques to dramatically reduce the size and cost of particle accelerators.
3.4.2 Different types of plasma

Generally plasma is classified into four types depending upon temperature and density. There are various types of plasma ranging from very high density ($n \approx 10^{36}/m^3$, inside a white dwarf) to a very low density ($n \approx 10^6/m^3$, in interstellar spaces).

3.4.2a Weakly ionized plasma

It is not necessary for every particle to be ionized to be involved in plasma phenomena. In Langmuir’s experiment he named plasma for that part of the discharge remote from boundaries. Physical significance of this is that particles inside plasma region are not influenced by the boundary potential of discharge. In weakly ionized plasma, only a small fraction of the atoms are ionized.

3.4.2b Strongly ionized plasma

As the temperature increases, the kinetic energy of the particles increases and degree of ionization also increases. So the collision behaviour of plasma particle increases and all collisions becomes coulombic interaction. In fully ionized plasma, all atoms are stripped of electrons nearly all the time and all particles are subjected to coulombic interaction.

3.4.2c Hot plasma

In hot plasma, the temperature is that much high so that particles acquires very large kinetic energy and passes each other very quickly without much interference. Such plasma offers almost no resistance to electric current. In hot plasma temperature is of the order of $10^6 \, ^\circ K$ and can be confined in a magnetic field.
3.4.2d Cold plasma

Cold plasma is one with low conductivity. Due to higher interaction there is a charge leakage and the temperature is of the order of 10 or 100 thousand degrees.

3.5 Plasma Diagnostics

Plasma diagnostics plays an important role in all plasma experiments and at the present time represents a rapidly expanding field of research. Plasma is a gas ionized sufficiently so that the charge separation, which can take place in it, is small compared to its microscopic charge density. On a macroscopic scale, therefore, plasma is approximately neutral, although its principal constituents are charged ions and electrons. In order to produce and maintain such a medium, significant amount of energy is required to dissociate and ionize the initially neutral gas to give the electrons and ions with sufficient kinetic energy to prevent immediate reattachment and recombination during the period of the experiment. Most methods for transferring this energy to plasma makes use of developing plasma as a variable electric component. Thus the time dependence of circuit current and voltage parameters gives basic and important information about over-all plasma conditions.

Information about fundamental plasma parameters, like electron temperature, electron density etc., are essential in order to evaluate the energy transport into the plasma. There are several diagnostic techniques employed for the determination of electron density and temperature which includes, plasma spectroscopy, Langmuir probe, Microwave and laser interferometry and Thomson scattering [36]. In the present investigation, Langmuir probe and Optical Emission Spectroscopy were used as the diagnostic tools.
3.5.1 Langmuir Probe

Langmuir probe is one of the simplest techniques for obtaining information about the ions in the plasma. It consists of an electrode of known area inserted in the plasma and connected electrically to a variable-voltage power supply (Fig3.5). This power supply is in turn grounded to a reference electrode inserted in the plasma. The reference electrode in the case of a single Langmuir Probe is much larger than the probe itself and typically consists of the chamber walls or any other convenient conducting surface in contact with the plasma. This apparently simple experimental technique is associated with rather complicated theories that are needed to explain the current-voltage behaviour of these probes in the plasma [37].

Figure 3.5  Langmuir probe and circuit to measure current – voltage characteristics
3.5.1a Theory of Langmuir Probes

The probe current is dependent on the potential imposed on the probe. A typical current-voltage plot is shown in figure 3.6. This characteristic is normally determined by the plasma properties in the immediate vicinity of the probe[39]. The general shape of the $I-V$ characteristic can be divided into three regions. When the probe is biased positively with respect to the local plasma potential the flux of particles reaching the probe will consist of carriers of negative charge (normally electrons). This region is called the electron-accelerating region and is labelled III in figure 3.6. These electrons will be collected from a region called the sheath, which is the region close to the probe surface where the potential exerted by the probe is not shielded by the plasma. When the probe is biased at a potential slightly smaller than the plasma potential only particles with enough energy to overcome the potential barrier will be collected. This region (region II in figure 3.6) is called the electron retarding region. The region I is accessed when the probe is biased increasingly negative relative to the plasma potential. In this region (region I in figure 3.6) only positive ions will reach the probe. This region is called the ion saturation region. The governing theories applicable to these three regions in the $I-V$ plot are discussed in the remainder of this section.
Figure 3.6 Typical current voltage plot, representing the plasma potential ($V_p$) and floating potential ($V_f$)

In the electron-retarding region (region II), the probe actually acts as an energy selector, collecting only those electrons which have large enough kinetic energies to overcome the potential barrier. If the electron distribution is in local thermal equilibrium, the electron energy distribution function can be assumed to be Maxwellian and the current drawn in this regime follows the relation:

$$I_e = n_e e A_p \left( \frac{kT_e}{2 \pi m_e} \right)^{\frac{1}{2}} \exp \left( \frac{e(V - V_p)}{kT_e} \right).$$

(3.22)

where $V_p$ is the plasma potential, $V$ is applied potential, $I_e$ is the electron current, $n_e$ the electron number density, $e$ the electron charge, $A_p$ the probe area, and $k$ the
Boltzmann constant, $T_e$, the electron temperature and $m_e$ the electron mass. The gradient of a plot of $\ln[I_e]$ versus the applied voltage $V$, yields the electron temperature and, given knowledge of the electron current at the plasma potential, substitution of $T_e$ in equation (3.22) yields to the electron number density.

The electron acceleration region (region III) is governed by the orbital motion theory, and an expression for the electron current in this region can be derived as follows: consider a point charge at a bias potential $V_p$, a placed at a distance $r_0$ from an electron with charge $e$, where the potential is $V_p$. Assume that the electron has a forward trajectory, with velocity $v_0$ and impact parameter $p$ as defined in figure 3.7.

![Figure 3.7](image_url)  

**Figure 3.7** Schematic of the input for the orbital motion theory.

The total kinetic energy $T$ of the particle at any time during its trajectory is given by:

$$T = \frac{1}{2} m \left( v^2 + r^2 \left( \frac{d \psi}{dt} \right)^2 \right) \tag{3.23}$$
where the two terms on the right hand side of expression (3.23) are, respectively, the translational and the rotational parts of the total kinetic energy. Given that (conservation of angular momentum):

\[
\frac{d\psi}{dt} = \frac{p v_0}{r^2}
\]  

(3.24)

we can rewrite the expression (3.23) as

\[
T = \frac{1}{2} m v^2 + T_0 \frac{p^2}{r^2}
\]  

(3.25)

Given equation (3.25) we can rewrite the total energy of the system as:

\[
E_T = \frac{1}{2} m v_0^2 - eV_p = \frac{1}{2} m v^2 + T_0 \frac{p^2}{r^2} - eV
\]  

(3.26)

At the point of closest distance to the probe \(r_c\), the translational kinetic energy is totally converted into centrifugal energy \(v = 0\), thus the total energy expression (3.26) can be rewritten as:

\[
\frac{1}{2} m v_0^2 - eV_p = T_0 \frac{p^2}{r_c^2} - eV_c
\]  

(3.27)

Rearranging expression (3.27) gives:

\[
p = r_c \left[ 1 - \frac{e(V_c - V_p)}{T_0} \right]^{\frac{1}{2}}
\]  

(3.28)
Taking $r_c$ as the probe radius $a$, any particle with $p < a\{l + (V_c V_p)/T_0\}^{1/2} = p_a$ will be collected. The expression for the current collected by a cylindrical probe given a Maxwellian electron velocity distribution can also be derived. It takes the form:

$$I_e = n_e e A_p \left( \frac{kT_e}{2\pi m_e} \right)^{1/2} \frac{2}{\sqrt{\pi}} \left( 1 - \frac{e(V - V_p)}{kT_e} \right)^{1/2}$$

(3.29)

Plotting the square of the electron current against the probe voltage yields a straight line, the gradient of which provides a measure of $(n_e)^2$.

The ion saturation current region (I) is a more difficult region to describe. The amount of ion current is governed by the Bohm criterion, since the ion temperature is much lower than the electron temperature in the plasmas under consideration. The Bohm criterion states that the ion velocity must acquire a positive (towards the probe) velocity at the plasma sheet edge even when the ions have very low temperatures. This velocity is provided by the existence of a “pre-sheet” potential drop that occurs at long distances in the plasma. The ion current is thus dependent on the electron temperature and is given by:

$$I_i = 0.6n_{i,\infty} e S \frac{T_e}{m_i}$$

(3.30)

where $n_{i,\infty}$ is the unperturbed (by the electric field of the probe) ion density and $S$ is the surface area of the probe.
Since the ion current is dependent on the electron temperature there is no easy way to deconvolute the total signal into the ion density and the electron temperature without independent measurement of one of the parameters.

The above expressions are strictly only valid in collisionless sheath conditions (i.e. when the mean free path $\lambda >$ sheath dimensions). Higher order corrections have to be included in the expressions in situations where collisions occur within the plasma sheath.

3.5.1b Specifics of the Langmuir probe

The Langmuir probe assembly consists of a Tungsten wire, 200 $\mu$m in diameter and 5 mm in length, supported by a glass sleeve (Fig 3.6). The wire can be biased at voltages in the range of -50 to 50 V, relative to the target and the vacuum chamber. Great care was taken to prevent the probe feed wires being exposed to the plasma since this will contribute to the measured probe current. To ensure a clean probe surface, the probe wire is replaced frequently. The output of the Langmuir probes was measured with a multimeter.

3.5.1c Practical complications

Real probe measurement is much more complex, for a variety of reasons. The effective current-collecting area of the probe is not its geometric surface area, but rather the area of the interface between the plasma and sheath around the probe; and the thickness of the sheath. For a given plasma, it is a function of the probe potential. The probe should be small, so that the probe current does not constitute a significant drain on the plasma. With a cylindrical probe, the varying sheath thickness is an even larger effect [38]. Two more complications are associated with additional charge generation. Secondary electrons may be generated at the probe due the direct impact of ions, electrons and photons. The
heating effects caused by such impact, give rise to additional current flow and electron impact ionisation may occur in the sheath, which enhances current flow.

3.5.2 Optical Emission Spectroscopy (OES)

OES examines the light given off by the species in the plasma that have been raised to excited states by impact [39]. Excited species radiates characteristic set of wavelengths that can be used as fingerprints. This unique fingerprint is determined by the fundamental atomic energy levels that are different for each element. OES is an attractive option for plasma process control because it is fast, non-intrusive, monitors multiple elements simultaneously and provides information regarding deposition conditions in the plasma. However, it is just beginning to be used to control deposition processes. This is because the dependence between OES signals and film properties can frequently be a complex function of electron and gas densities, emitting species concentration, electron impact excitation cross section, electron energy distribution function and the probability of inelastic collision between plasma species. The OES system in the present work consist of a spectrometer, monochromator, a CCD detector and a personal computer.

3.5.2a Charge Coupled Device

Charge Coupled Devices (CCD) are multichannel silicon array detectors designed using standard MOS architecture. These are array devices in which individual pixel elements are defined by three electrode gates of varied applied potential (3-phase devices). The electrodes are made from vertically stacked, conductively doped polysilicon and overlay the photosensitive semiconducting silicon. The electrodes are separated from the silicon surface by a thin layer of insulating silicon dioxide. When appropriate voltages are applied to the different electrodes, the electrostatic potentials in the silicon are changed to produce
zones of negative potentials surrounding a potential well. Photoelectrons generated by the incident light are then collected and stored in these localized potential wells (Fig 3.8). CCDs detect and measure light in a three step process [40].

1) Absorption of incident photon energy followed by the creation of electron-hole pairs proportional to the number of absorbed photons. The amount of electron-hole pairs generated in each discrete pixel directly depends on the incident light intensity. However the number of the generated electron-hole pairs is a non-linear function of the incident wavelength. As shown in the figure, the charge resulting from the generated electron-hole pairs in a given pixel is collected in the potential well of that pixel.
2) **Transfer of the resulting charge packets within the array from one pixel to the next.** At the end of an exposure, the charge integrated in each pixel is transferred from one pixel to the next in a column until it finally reaches the readout registers located along one edge of the chip. This charge transfer is accomplished by sequentially changing the applied potential to the different electrodes as shown in figure 3.9. During this process of parallel charge transfer, the charge accumulated in one row of pixel is simultaneously transferred to the corresponding pixel in the next row.

3) **Conversion of charge to voltage and subsequent amplification.** After the parallel charge transfer process, the charge from each row of pixels is accumulated in the readout registers, located at the edge of the chip. The charge from the individual readout registers is then shifted to an output sense node by an analogous serial charge transfer process. Here the charge is converted to an appropriate voltage. The potential level in this “floating diffusion” sense node varies depending on the amount of charge present at the node. The sense node is followed by a charge-to-voltage amplifier, which preserves the linear relationship between the generated charge and the voltage output.
The CCD used in the present investigation for the spectral studies was Spectrum One CCD 3000, 1024×256 pixels (ISA Jobin Yvon – Spex).

### 3.5.2b Spectrometer

Spectrometer used for analysis was Triax 320 (Fig 3.10). The TRIAX 320 is a 1/3 meter instrument offering superb scanning and imaging performance. The large f/4.1 aperture ensures better light gathering. For multichannel detection, the corrected optics and large focal plane offer excellent spectral resolution and spatial separation with wide single exposure wavelength coverage [40].
Figure 3.10 Triax-320 top view

**Specifications of Triax 320**

- **Focal Length** $f$ : 0.32 meters
- **Entrance Aperture Ratio** : $f/4.1$
- **Grating** : 1200 grooves/mm
- **Grating size** : 68 $\times$ 68 mm
- **Blazed at** : 500 nm
- **Image magnification at the exit** : 1.00
- **Spectral dispersion** : 2.64 nm
- **Spectral resolution** : 0.06 nm
- **Wavelength positioning accuracy** : +/- 0.3 nm
3.5.2c Monochromator Calibration

To ensure the accuracy of results, it is important to consider the influence of natural broadening. We have used a mercury lamp to measure the resolution of spectrometer. Spectrum of the mercury lamp in the wavelength range 570 – 580 nm was recorded (Fig 3.11). The peaks were identified and compared with standard wavelength [41].

![Emission spectra of Hg](image)

Figure 3.11 Emission spectra of Hg

The resolution of the spectrometer is given by the equation

$$\Delta \lambda = \frac{FWHM}{a} \times \Delta \lambda$$  \hspace{1cm} (3.31)
where $\Delta A$ (the difference between the standard wavelength) $= 579.065 - 576.965 = 2.1$ mm. Here the FWHM is the full width at half maximum of Hg line (I), which is about 0.4901 nm and $a$ is the distance between the two peaks of the Hg lines recorded using the spectrometer (Figure 3.12), which is, $a = 578.876 - 576.754 = 2.122$ nm. Thus the spectrometer has a resolution of $\Delta \lambda = 0.485$ nm.

### 3.5.2d OES  Recording

The plasma plume is focused to the entrance slit of a monochromatic by means of a convex lens (focal length 17 cm) so as to have one to one correspondence with the sampled area of the plasma and the image. The f-number of the lens is made equal to the f-number of monochromator for better optical coupling. Optical emission from the plasma plume is recorded by means of a scanning monochromator equipped with grating and a CCD array detector. The CCD and spectrometer were interfaced to a PC equipped with Spectra Max for Windows for data acquisition and processing (Fig 3.12). Wavelength dispersed optical spectra within the range 300 – 950 nm have been recorded.

![Figure 3.12 Experimental set up for recording the OES.](image)
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