CHAPTER III

EXPERIMENTAL TECHNIQUES

3.1. Introduction

Once the films are prepared, their material properties are to be studied in order to find their utility for the intended use. In this chapter an account of the experimental techniques to study the material properties of the developed thin films is given. These studies provide the structural, electrical, optical and surface morphological properties of the film.

3.2. The Nature Of the film- Hot Probe Methods

A simple test can be performed to find the nature of the films deposited. The n-type and p-type semiconductors differ by the nature of their majority carries, for the former it is the electrons and for the latter it is the holes. The simple technique for assessing the nature of the carriers in a semiconducting film is based on the fact that when a piece of semiconductor is momentarily heated at one end while the other end being cold, carriers flow from the hot end to the cold end. So for the n-type, the conventional current will be from the cold end to the hot end while for the p-type it will be the other way round. Therefore if a technique is developed to find the direction of electron flow through a semiconductor in an electric circuit it may be possible to determine the nature of the semiconductor and this
technique is called “the Hot Probe Technique”. The arrangement is shown in the Fig.3.1.

The semiconductor thin film coated substrate is placed on a metal plate. A fairly long metal rod with one end ending into a tip (usually a soldering iron) is taken. The tip is to be heated and with the heated tip the one end of the semiconductor is to be touched for a short time while the other end of the iron is connected the metal base/other end of the thin film through a Galvanometer The end of the metal base, which is connected to the Galvanometer is called the cold junction and the hot tip, the hot junction. When the hot probe momentarily touches the semiconductor film, a current passes from the cold junction to the hot junction for a n-type semiconductor; whereas for the p-type, the current passes from the hot junction to the cold junction. All the deposited films have been tested by this technique to find their semiconducting nature.

3.3. Thickness Measurements Weight Gain Method

Thickness is the most important parameter which controls the film properties. Different techniques are available for the measurement of thickness of the films. They can be broadly classified into the following categories; mechanical, electrical, magnetic, radiation and optical methods. Of these methods, the mechanical method is simple and straightforward and hence it has been used for the present study. The method used can also
Fig. 3.1

Hot Probe Technique

1. Hot probe
2. Semiconductor film
3. Metal base
4. Galvanometer
5. Cold junction
be called the weight gain method. If a film of thickness $V$ deposited uniformly over an area, $A$ has a mass, $M$ density, $D$ and volume, $V$ then

$$D = \frac{M}{V} \frac{M}{At} \quad \text{3.1}$$

Therefore, the thickness of the film can be measured using the relation,

$$t = \frac{M}{DA} \quad \text{3.2}$$

The density, $D$ of the film is approximated to the standard density of the bulk material. $A$ is the area over which the film is deposited. ‘$M$’ is the mass of the film i.e. the mass gained by the substrate and is the difference in the masses of the substrate before and after deposition. Since the mass gain 'M' is very small of the order of a few mg or less a sensitive electronic analytical balance will have to be used. For the present work, a Mettler Toledo AG 245 electronic analytic balance with a precision of 0.01mg is used.

3.4.1. Resistivity Four-point **Probe Techniques**

The Resistivity of the films is usually measured using the Four-Point Probe Technique. The principle, a short account of
the theory, the instrumentation developed and the method of measurement are given below.

3.4.2. Principle

To determine the Resistivity of samples of different sizes and shapes, the method uses a four-point probes in a line on the study sample, passing a constant current through the outer pins (probes) and measuring the floating potential difference across the inner pins (probes). Fig.3.2 shows the arrangement for the technique.

A constant current source can be used to send the current and the voltage can be measured either potentiometrically or using a sensitive voltmeter.

Valdes has shown that the resistivity of an infinitely large sample can be given by the relation

\[ \rho = \frac{V}{I} \left( \frac{2\pi}{\frac{1}{s_1} + \frac{1}{s_2} - \frac{1}{s_1 + s_2} - \frac{1}{s_2 + s_3}} \right) \]

where

- \( \rho \) - Resistivity of the film
- \( V \) - floating potential difference between the inner probes
- \( I \) - Current through the outer probes and
- \( s \) - distance between the adjacent probes
Fig. 3.2

Four-point Probe technique
If the distance between the adjacent probes is made equal i.e $s_1 = s_2 = s_3 = s$, then

$$\rho = \frac{V}{I} (2\pi s) \quad \text{---Equation 3.4}$$

This equation holds good for samples whose thickness are in the range of 0.6 cm. In the case of samples which are thin and are on non-conducting substrates, Valdes/1/ has shown that

$$\rho = \frac{\rho_0}{G(t/s)} \quad \text{---Equation 3.5}$$

where $t$ is the film thickness, and the function

$$G(t/s) = 1 + 4(s/t) \sum_{n=1}^{\infty} \frac{1}{\left(\frac{s}{t}\right)^2 + (2n)^2} \frac{1}{\left(\frac{2s}{t}\right)^2 + (2n)^2} \quad \text{---Equation 3.6}$$

When $t/s$ is far smaller than 0.1, which will be the case in respect of thin films, (infinitely thin film), Valdes/1/ has shown that the above relation can be reduced to $G(t/s) = 2s/t$, and in such a case the resistivity $\rho$ of the thin film is given by

$$\rho = \frac{\pi V}{\ln 2 I} \quad \text{---Equation 3.7}$$

$$\rho \approx 4.53 \frac{V}{I} \quad \text{---Equation 3.8}$$
3.4.3. Fabrication of Four-point Probe Apparatus:

A simple novel and yet sensitive Four-point probe apparatus has been developed for the present study and the constructional details of the developed apparatus are given below.

The arrangement consists of a set of Four-point metallic probes arranged along a line equidistant from each other. When laid up, it is essential that all the four probes touch the study film. Through the outer probes a current is sent and the voltage developed is measured between the inner probes. When there is even a slight unevenness in the film, the tips of all the probes may not touch the film. If pressure is applied to ensure that the tips of all probes touch the film, the sharp tips may pierce the film developing small pin-holes in the film leading to discontinuity in the film. To avoid this, each probe must be a spring loaded system, and the entire set of 4 probes must be capable of being moved up or down by a suitable screw arrangement. The spring loaded system ensures that when the probe set is laid even on a slightly uneven film, good contact of the probe-tips can be established because by moving the screw, the tips already in contact will transfer the pressure to the spring and compress the spring thus moving up to the required small extent still maintaining the contact and the ones originally not in contact will establish contact. Thus the spring loaded system ensures contact of all pin tips without puncturing the
film. In the present work a very simple, low cost spring loaded probes have been used. Wrist watch strap pins are spring-loaded systems and they have been used as probes in developing the Four-point Probe setup.

A wrist watch strap pin essentially consists of a 1.4cm long and 1mm dia chromium plated brass stem into which moves two chromium plated brass pins of diameter 0.8mm length 2mm one on either side of the stem. One pin is removed and a suitable tight fitting needle of 7mm inserted. This serves as the upper portion of the probe and the pin serves as the bottom portion of the probe. The movement of the pin into the stem is controlled by a fine spring. The pin can move to a maximum of about 1mm inside the stem under pressure, which is more than that required for meeting the unevenness in thin films.

A 5.8 x 4.9cm hylam sheet is taken. A separation of 2mm between the adjacent probes is envisaged. So, four fine holes of 1mm dia have been drilled in the hylam sheet with a separation of 2mm between the adjacent ones. Through the holes, the top ends of the stems of the wrist watch strap pins have been inserted such that a small length of 1mm of each projects out of the top of the hylam sheet. The hylam sheet is firmly mounted on an old traveling microscope frame available in the lab so that the fine screw movement intended for vertical motion could be utilized. The top of the pins have been soldered to the ends of a
4 wire flat cable, the other ends of the cables have been attached to 4 terminals fixed at the base of the microscope on another firmly fitted hylam sheet. The tips of the pins have been aligned using the following procedure. An optically plane glass plate has been arranged on a flat surface tested by a sprit level. The probe set holder (microscope holder) is moved down adjusting the pins until the reflected images of the pin tips in the glass plate coincide with the pin tips and line along a lie. This ensures that the pin-tips are along a line and are at the same level. The alignment is checked using a microscope and fine adjustments, if necessary, are made so that all tips are tangential to the horizontal cross wire. Finally arranging the pin tips on a plane metal plate, direct contact if any between the pins is checked with a multimeter. After these operations, the positions of the pins passing through the hylam sheet are glued using araldite to ensure that the pins fit into the holes firmly without even the slightest ply. Even though there is no direct contact between the pins, a short length of fine insulating tapes has been pasted over the top of each pin (above the hylam sheet) as an additional precaution. The developed set up is shown in Plate No.3.1.

3.4.4. Measurement Method:

For measuring the resistivity of a film, first the probe system is moved up releasing the upward movement screws and fixed. The study film is arranged on a good flat surface below the
Plate 3.1
Four point probe resistivity apparatus
probe set. A Systronics Model No.613 power supply (which can function as a constant current source) is connected to the end terminals through a 4-Ya digit Philips DM341 Digital Multimeter and set in 2mA range where it can have an accuracy of 0.001mA. Another 4 1/2 digit Philips DM341 Digital Multimeter set in 2V range where it can have an accuracy of 0.00IV is connected between the middle terminals, connected to the middle pins for measuring the voltage between them. The probe set is moved down by releasing the screw and fixed very close to the film surface but not touching it. The film is adjusted, if necessary, so that the probe set is not near the edges of the film. The probe sets gently moved down using the tangential screw until the current and voltage readings are seen in the meters used. At this stage, the current I and voltage V are noted. High currents of the order of 100 mA or so will produce heating effect in the film which will result in variation in the film properties. So, only low currents of the order of 10 mA or less will be ideal and only such currents have been used in the present study. For each film, at 5 different locations of the film (not close to edges of the film) keeping more or less a constant current I, the voltage V are measured. The resistivity of the film is calculated using the Eqn.3.8.
3.5. Carrier Density (N) and Mobility (μ) – Hall effect measurements studies

The free carrier density (carrier concentration) N and their mobility μ_H have been measured using Hall effect studies.

When a current carrying specimen is placed in a transverse magnetic field, a voltage is developed across the specimen in a direction perpendicular to both the current and the magnetic field. The phenomenon by which this voltage is developed is called the Hall effect and the voltage, the Hall voltage. The schematic diagram for a Hall effect measurements is given in Fig.3.3.

Let a, b and c be the dimensions of a rectangular specimen. Let a current I_x be passed through the specimen along the X-direction and a magnetic field of flux density B_z applied along the Z-direction. Let V_y be the Hall voltage developed in the Y-direction. Let N and μ_H represent the carrier concentration and Hall mobility of the free charges. Then the voltage developed in the Y-direction

\[ V_y = \frac{-I_x}{cN_e} B_z \]

\[ cV_y/(-I_x B_z) = \frac{-1}{N_e} \]

(-1/N_e) is called the Hall coefficient R_H.
Fig. 3.3
Schematic setup for a Hall effect measurement
\[ R_H = (-1/Ne) \] \[ (cV_y/I_x B_2) = R_H \]

For a film of thickness \( t \), if the magnetic induction \( B_2 \) is applied perpendicular to the plane of the film

\[ R_H = (-t/B_2) (V_H/I_x) \]

Where \( V_H = V_y \)

Using \( 1/R_H = -Ne \),

the carrier concentration (\( N \)) can be determined.

Therefore \( N = -1/R_H e \)

The mobility can be calculated using the relation

\[ \mu_H = \sigma \left| R_H \right| \]

where \( \sigma \) is the conductivity.

\[ \sigma = 1/\rho \]

where \( \rho \) is the resistivity

\[ \mu_H = \left| R_H \right| / \rho \]

For the present work, Control System and Devices Electromagnet capable of producing a magnetic induction of 2 tesla (20 kgauss) at 1.0 cm pole gap has been used. A simple film holder has been made. A 2mm thick rectangular hylam sheet of dimensions of 4 x 44cm is taken. At 4.5cm from the top edge along the central line two gold plated brass tempered
pins bent at the edges for ensuing good contacts have been fixed with a separation of 2.3cm between their tips. Along the breadth wise side with 1.2cm separation, two similar pins have been fixed along a line perpendicular to the line joining the length wise pins symmetric with respect to it and at the middle of the line so that when the pins are in contact with the film Vander Pauw geometry is obtained. The pins are tempered and gold plated to ensure good contact. The lengthwise pins are intended for sending a current through the film and the breadth wise pins for measuring the voltage developed on account of the transverse magnetic field. When measurements are to be made, the gap between the pole faces is adjusted so that the film holder (hylam sheet) can be easily inserted between the pole pieces such that the field when switched on will be perpendicular to the plane of the film. This separation between the pole faces is 3.3cm. The magnetic induction between the pole faces of the magnet has been measured using the Scientific Equipment Services Digital Gauss meter DGM102.

The film is mounted on the holder. A Systronics power supply Model 613 (which can serve as a constant current source) is connected to the lengthwise pins through a DC milliammeter and a 4% digit PHILIPS DM 341 Digital multimeter is connected across the breadthwise pins for measuring the Hall voltage developed. As the films may get heated up when high current of the order of 100 mA and more is used, currents of the
order of 10 mA or less have to be used. The selected current I is sent through the film.

A constant current ($I_{ac}$ is applied to the terminals a and c and the corresponding voltage $V_{bd}$ is measured between the terminals b and d with magnetic field (B), which is given as

$$V_{bd} = V_o + V_H$$

Where $V_o$ is the zero-field voltage and $V_H$ the Hall voltage. The measurement is repeated by reversing the magnetic field. Since the zero field voltage does not change its phase when the magnetic field is reversed, but the signal of the Hall voltage changes. Hence the voltage $V_{R_{bd}}$ across the terminal (b and d) becomes

$$V_{R_{bd}} = V_o + V_H$$

Where the super script ‘R” denotes that the direction of the magnetic field is reversed.

From Eqns. (3.14) and (3.15) the Hall voltage can be estimated as

$$V_H = \frac{1}{2} (V_{bd} - V_{R_{bd}})$$

If $B_z$ is the magnetic induction, the Hall coefficient $R_H$, Can be calculated using the relation

$$R_H = (-t/B_z) (V_H/I_x)$$

The carrier concentration (N) and Hall mobility $\mu_H$ are found using the relations, $N = -1/R_H e$

and

$$\mu_H = \sigma |R_H|$$
3.6. X-Ray Diffraction Studies

The structure of the crystallites of the thin films developed are to be studied to assess whether the films could be used for the intended applications. The X-ray Diffraction (XRD) technique is a very powerful tool for the crystal structure determination. X-rays are a form of electromagnetic radiation, which can be diffracted by the atom bearing planes of a crystal.

Using X-ray diffraction, information about the crystal structure can be obtained from the positions and intensities of the diffracted beams. Taking that the scattering centers (atoms) are located in a set of crystal planes whose directional properties are described by the Miller indices hkl, the distance between the planes (dhkl) can be related to the scattering angle (θ_hkl) between the planes and the incoming beam, by the Bragg equation

\[ 2d_{hkl} \sin \theta_{hkl} = n\lambda \]

where \( \lambda \) is the wavelength of the X-rays and \( n \) is the order of diffraction. For diffraction it is also necessary that \( \theta_{hkl} \) is the angle between the diffracted beam and the planes. Further, the incoming and diffracted beams must be in a plane normal to the set of diffracting planes.

Once the diffraction angles \( \theta \) are measured, the corresponding \( d \)'s and [hkl] values can be fixed. In the geometry of the practical diffractometers, only \( 2\theta \) can be measured. So from the photographed X-ray pattern, the 2θ values and the
intensity of the maxima can be found and a plot between $2\theta$ and intensity made for studies. However, the modern X-ray diffractometers (XRD) make use of a built in computer, which is programmed to give directly the print out of a plot of $2\theta$ versus intensity of the diffracted beam.

Of the various X-ray diffraction methods, the powder diffraction method is the simplest and most useful for the immediate determination of the nature of the sample, phase identification, quantitative analysis of a mixture of phases, particle size analysis, characterization of physical imperfections, etc. The powder diffraction methods are particularly exciting because it is possible to arrive at the structure of the sample if “$d$”, the inter planar distance and the Bragg angle $\theta$ are known. For a thin film, the powder diffraction method is the one that could be used. For the present work, the high precision X’pert, Pro, Netherlands X-ray diffractometer available at the Regional Research Laboratory (RRL), Thiruvananthapuram has been used. It employs filtered Cu K alpha 1 radiation of wavelength 1.54056 Å.

3.7. Surface Morphological Studies;

The Scanning Electron Microscopy and Atomic Force Microscopy are two most versatile and powerful tools for the surface morphological studies.
3.7.1. **Scanning Electron** Microscope (SEM) studies:

When techniques based on simple reflection mode of the optical microscopy are used for the surface morphological studies, very limited spatial resolution of the order of a few tens of a millimeter alone can be obtained and hence these techniques are unsuited for such studies. However very high resolution can be obtained in electron beam techniques. The most versatile among these electron microscopes, is the Scanning Electron Microscope (SEM).

The primary reason for the SEM’s usefulness lies in the high resolution which can be obtained when objects are examined; values of the order of $10^{-7}$ m (100 Å) are usefully quoted for commercial instruments. Another important features of SEM images is the three dimensional appearance of the specimen, which is a direct result of the large depth of focus. The greater depth of focus of the SEM provides much more information about the specimen than that could be obtained from any other techniques. The SEM is also capable of examining very small objects. The convenience of the SEM also lies in the long working distance between the final lens and the sample surface.

SEM offers several modes of operation. The most widely employed one is secondary electron imaging, which gives images of better than 100 Å resolution almost unlimited depth of field.
and good contrast between most components of the specimen. The basic components of the SEM are the electromagnetic lens system, electron gun, electron collector, visual and recording Cathode Ray Tube (CRTs), and the electronics associated with them.

The low energy (50eV) secondary electron emitted from the surface of the specimen provide the basis for the imaging. The beam can be concentrated to a small probe (say 20 Å diameter) that may be deflected across the specimen in the raster fashion using scanning coils. The secondary electrons can be detected above the specimen, and an image showing the intensity of secondary electrons emitted from the different parts of the specimen can be displayed on a CRT. There is facility to photograph the image with the help of a high resolution recording cathode ray tube and a roll film camera.

This scanned image is particularly useful for examining the morphology of metal alloys, thin films of metal and semiconductors and crystalline materials as well (Cheetan and Peter Day (1987)/2/).

JSM 35 CF JEOL Model SEM which is capable of taking highly magnified pictures of solid, dry conducting and non-conducting specimen which make up metallurgical, biological and chemical samples has been used in the present study. The
The maximum magnification of the equipment is 1,80,000 times with a resolution of 60 Å. A specimen size may be 2 cm in diameter and 1 mm in thickness or 1 cm x 1 cm area with 1 mm thickness.

The SEM studies provide the nature of the surface, (about the uniformity, smoothness, cracks) and the nature of the grains (shape, particulate or interconnected crystallites and grain size) (Coles (1987)/3/)

3.7.2. Atomic Force Microscopy (AFM)

AFM is unique modern tool available for a real space view of the atomic structure and surface morphology of materials (9). It is a surface structural technology, which is truly local in that, it images the individual atoms and does not rely upon long-range order to produce a signal. The technique is based on electron tunneling between a sharp metal tip and the surface of a conducting/semiconducting solid surface. When the tip is brought close to the sample surface (as close as 5 to 10 Å), the wave function of the tip and the sample overlap and electrons tunnel between the tip and the surface of the solid. If sufficient voltage is applied to the solid sample, there will be a net flow of electrons across the gap, which varies exponentially with the separation between the tip and the sample. The flow of electrons gives the tunneling current. The direction of electron flow depends on the sign of the bias voltage applied.
Scanning the tip over the surface from side to side in parallel lines, keeping a constant tunneling current, generates a map of the film/solid surface. Features in the map correspond to vertical displacements of the tip as it follows a contour of constant density of states at the surface of the sample.

The Nanoscope® E Scanning Probe Microscopy systems Model No 3138 J has been used for the surface analysis of the films. Fig.3.4 shows the experimental set-up for the AFM measurements. In the AFM measurements, a Topometrix Explorer system is operated in air in contact mode, with a typical scanning frequency of 0.5-lHz. In order to make electrical measurements, commercial Si tips are coated with a conductive layer of boron-doped diamond. These wear-resistant conductive AFM tips have a radius of about 100nm and a spring constant of 4N/m. In order to establish a good electrical contact between the tip and the sample, a load of about 50nN has to be applied. Under these conditions, the contact resistance between the tip and an evaporated gold film is typically 50kΩ. Though a load of 50 nN is relatively high, no damage appears on the films, even after intense scanning. The current is measured with an external high band pass (>10^4 Hz) Keithley K429 current amplifier. The noise level for the current measurement is below 10 pA. The AFM electronics enable simultaneous acquisition of topography information and tip-sample current, as well as
Fig. 3.4
Schematic diagram of the AFM Experiment
curren-voltage measurements at specific locations on the surface.

### 3.8. Optical Properties:

The high optical transparency of TCOs in the visible and near-IR regions of the solar spectrum is a direct consequence of their being wide band gap semiconductors \((\text{Eg} > 3.0 \text{eV})\). Nowadays development of TCO films with controlled bandgap has become a necessity owing to the increased applications of these films. So the optical transmission and band gap studies of these films are essential for characterizing them. As the lattice arrangements of the crystallites of the films play as important role in conduction and reflections of radiation, the optical absorption and transmission of the films are to be studied at different wavelengths (i.e. at different photon energies \(E = hv\), where \(v\) is the frequency of the photon) and the absorption coefficient calculated for each photon energy \((E)\).

The absorption coefficient data can be analyzed using the theory of Bardeen et al./4/ and Smith/5/. The theory predicts that the absorption coefficient \((a)\) due to band to band transition can be expressed as

\[
a = A \ (hv - \text{Eg})^r
\]

for direct transition, where \(r = \frac{1}{2}\) for the allowed and \(r = \frac{3}{2}\) for the forbidden transition.

For indirect transition,
\[ a = B (hv - Eg' \pm Ep)^r \]

where \( Eg' \) is the indirect energy gap and \( Ep \) is the absorbed(+) or emitted(-) phonon energy. In this case \( r=2 \) represents allowed and \( r=3 \) represents a forbidden transition.

For direct allowed transition TCO films a plot of \( a^{-2} - hv (=E) \), will be a straight line and its intercept along the \( E=hv \) axis will give the direct band gap value, shown in the Fig.3.5. A typical transmittance spectrum for a TCO film is shown in Fig.3.6. A sharp decrease in the transmittance in the lower wavelength region is due to the fundamental absorption and the decrease in transmittance at higher wavelength region is due to the free carrier absorption. In such a case; the \( a^{-2} \) Vs \( hv \) curve will have a linear portion corresponding to the fundamental absorption which when extrapolated to the \( hv \) axis will give \( E_g \) the direct band gap.

The transmittance spectra of the film has been recorded using the PerkinElmer Lambda 35 UV/Vis spectrometer.
Fig. 3.5
A typical graph of $E$ vs $\alpha^2$
Fig. 3.6

A typical transmittance spectra of a TCO
References;