CHAPTER - 3

EXPERIMENTAL TECHNIQUES AND PROCEDURES USED IN
THE CHARACTERIZATION OF SnO₂ AND PSi MATERIALS

3.1 INTRODUCTION

The prepared SnO₂, SnO₂:F, SnO₂:Sb films and porous silicon (PSi) on glass substrates and silicon wafers have been systematically analyzed to identify their structural, surface morphological, optical and electrical properties. In this chapter, the characterization techniques, instruments used for these studies are briefly explained. Simultaneously, the instrumental details and the experimental procedures that have been adopted to carry out these studies are elaborated.

3.2 NATURE OF THE FILM BY HOT PROBE METHOD

Any semiconductor material film, after preparation has to be identified for its nature. The n-type and p-type semiconductors differ by the nature of their majority carriers, 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 as the “Hot Probe Technique”. The experimental 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 formed into a tip (usually a soldering iron) is taken. The tip is heated and with the heated tip one end of the semiconductor is to
Fig. 3.1 Hot Probe Technique
be touched for a short time, while the other end of the rod is connected to 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 MEASUREMENT BY NON-DESTRUCTIVE STYLUS METHOD

The surftest SJ-301 is a stylus type surface roughness and thickness measuring instrument. It can be easily used to measure the thickness of a coating developed on any uniform surface. Figure 3.2 shows the instrument, which is self explanatory. The stylus of the SJ-301 detector unit traces the minute irregularities of the coating surface. Surface roughness is determined from the vertical displacement produced during the detector traversing over the surface irregularities.

When the thickness is to be measured, the stylus is placed over the uncoated surface and made to move towards the coating. Then it steps over the coating and moves over the coating surface for some distance. There is an upward shift in the trace as shown in Fig.3.2 near the stylus. The vertical displacement gives the thickness of the coating. The measurement results are displayed digitally/graphically in jam on the tour panel. The thicknesses of all the SnO₂ coatings are found using this instrument. It is a non-destructive technique and the coating may be used for further studies without any damage.
Fig. 3.2 Surftest SJ-301 stylus instrument for thickness measurement.
3.4 RESISTIVITY MEASUREMENT BY FOUR-POINT PROBE TECHNIQUE

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.

3.4.1 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.3.3 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

\[
\rho = \frac{V}{I} \left( \frac{2\pi}{\frac{1}{s_1} + \frac{1}{s_2} - \frac{1}{s_1 + s_2} - \frac{1}{s_2 + s_3}} \right) \quad \text{--------3.1}
\]

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

If the distance between the adjacent probes is made equal i.e., \( s_1 = s_2 = s_3 = s \), then

\[
\rho = \frac{V}{I} \left( 2\pi s \right) \quad \text{--------3.2}
\]
Fig. 3.3 Block diagram of four probe resistivity measurement setup
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

\[ \rho = \frac{\rho_0}{G(t/s)} \quad \text{--------------------3.3} \]

where \( t \) is the film thickness, and the function

\[ G(t/s) = 1 + 4(s/t) \sum_{n=1}^{\infty} \frac{1}{\left(\frac{s}{t}\right)^2 + (2n)^2} \frac{1}{\left(\frac{2s}{t}\right)^2 + (2n)^2} \quad \text{--------------------3.4} \]

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

\[ \rho = \frac{\pi V}{\ln 2 I} \quad \text{--------------------3.5} \]

\[ \rho \approx 4.53 I V / I \quad \text{--------------------3.6} \]

3.5 CARRIER DENSITY AND MOBILITY MEASUREMENTS BY HALL EFFECT STUDIES

The free carrier density (carrier concentration) \( n \) and their mobility \( \mu_H \) 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 of the sample mounting for a Hall effect measurements is given in Fig.3.4.

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 $\mu_H$ represent the carrier concentration and Hall mobility of the free charges. Then the voltage developed in the $Y -$ direction

$$V_y = \frac{-I_x}{cne} B_z$$

$$cV_y/(-I_x B_z) = (-1/ne)$$

$(-1/ne)$ is called the Hall coefficient and expressed as

$$R_H = (-1/ne)$$

$$R_H = (cV_y/(-I_x B_z))$$

For a film of thickness $t$, if the magnetic induction $B_z$ is applied perpendicular to the plane of the film

$$R_H = \left(\frac{t}{B_z}\right) \left(\frac{V_H}{I_x}\right)$$

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

$$\mu_H = \sigma / |R_H|$$

where $\sigma$ is the conductivity.

$$\sigma = 1/\rho$$

where $\rho$ is the resistivity

$$\mu_H = |R_H| / \rho$$
Fig. 3.4 Schematic setup for a Hall effect measurement
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 2 mm thick rectangular hylam sheet of dimensions of 4 x 44 cm is taken. At 4.5 cm 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 2.3 cm between their tips. Along the breadth wise side with 1.2 cm 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 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.

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 4/4 digit PFIILIPS 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

$$V_{bd} = V_0 + V_H$$

Where $V_0$ is the zero-field voltage and $V_H$ the Flail 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 $V_{bd}^{R}$ across the terminal (b and d) becomes

$$V_{bd}^{R} = V_0 + V_{bd}$$
Where the super script ‘R’ denotes that the direction of the magnetic field is reversed.

From Eqns. (3.2) and (3.3) the Hall voltage can be estimated as

\[ V_H = \frac{1}{2} (V_{bd} - V_{bd}^R) \]  
--------- 3.14

If \( B_z \) is the magnetic induction, the Hall coefficient \( R_H \) can be calculated using the relation

\[ R_H = \frac{-e}{B_z} \left( \frac{V_H}{I_x} \right) \]  
--------- 3.15

The carrier concentration (n) and Hall mobility \( \mu_H \) are found using the relations,

\[ n = -\frac{1}{R_H e} \]  and

\[ \mu_H = \frac{\sigma}{|R_H|} \]

3.5.1 OPTICAL CHARACTERIZATION: UV-VIS-NIR SPECTROPHOTOMETER

Optical properties are of much importance for thin films. The measurement of transmission or reflection of a sample provides a satisfactory way to determine the form of the absorption edge. The absorption edge and energy band gap can be determined from the transmission measurement [2]. Hence the optical transmittance properties of the films were studied by Hitachi-3400 UV-Vis-NIR spectrophotometer.

When the radiation is incident on a thin film material with energy equal or greater than that of the band gap, absorption of the photons can take place and electrons can be raised in energy from the valence band to the conduction band, creating electron hole pairs. The material absorbs little and can transmit the photons having energy less than the band gap of the semiconductors, as the energy is insufficient to create an electron hole pair. The ability of a material to absorb photons of a given wavelength is measured quantitatively by the optical absorption coefficient \( \alpha \), measured in units of reciprocal distance.
There are two major types of intrinsic absorption processes involved in determining $\alpha$, they are the direct and indirect absorption. As a general rule, the larger the band gap, the smaller is the value of $\alpha$ for a given wavelength but absorption coefficient also depends on the density of states in the conduction and valence bands. The optical absorption coefficient is related with the energy band gap and it is given by the following equation [3]

$$\alpha \nu = B (\nu - E_g)^n$$  \hspace{1cm} 3.16

where $B$ is a constant, $E_g$ is optical band gap and $n$ is the exponent. For crystalline semiconductors, $n$ is $1/2$, $3/2$, $2$ and $3$ when the transition is direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively. Apparently the plot of $(\alpha \nu)^2$ or $(\alpha \nu)^{1/2}$ against $(\nu)$ provides the nature and $E_g$ value of a particular film.

The direct optical absorption is illustrated in Fig.3.5. It is a first-order process involving only the absorbed photon and can be represented approximately as a vertical line on the energy versus wave vector plot. The absorption transition conserves energy so that $\Delta E = h\nu$ (where $h\nu$ is the photon energy), and there is no change in $k$ between initial and final states except for the small momentum of the photon. An indirect optical transition is a second order process involving both the absorbed photon and a simultaneously absorbed or emitted phonon, which occurs when the minimum of the conduction band and the maximum of the valence band occur at different values of the wave vector $k$ as illustrated Fig.3.6. Here the absorption transition conserves energy by requiring $\Delta E = h\nu + E_p$, where $E_p$ is the photon energy and the change in $k$ between the initial and final states $\Delta k$ is just equal to the value of $k$ of the phonon involved.

3.5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectroscopy is one of the most powerful analytical tools for elucidation of the molecular structures of inorganic and organic compounds. It has a very wide range of applications from identification of organic compounds to
Fig. 3.5 Direct transition from the valence band to the conduction band
Fig. 3.6 Indirect transition from the valence band to the conduction band
material science in the semiconductor industry. From the FTIR analysis it is possible to identify the functional groups on surfaces and adsorbates, molecular composition of the materials. Infrared spectroscopy is based on absorption of IR radiation causing transition in the sample from one vibrational state to another, higher energy vibrational state [4],

In the present study, the following FTIR spectrometer configuration has been used to identify the change in functional groups and molecular structures of the S$_{11}$O$_2$ and PSII films after the intercalation/deintercalation of metal ions.

<table>
<thead>
<tr>
<th>Spectrometer model</th>
<th>Perkin-Elmer make Paragon 500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>Lanthanum, Tantalali</td>
</tr>
<tr>
<td>Wave number used</td>
<td>4000 to 400 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Consequently, the infrared spectrum is a set of absorption bands whose intensity and frequency provides information of structure and bonding in the molecule. FTIR instruments employ interferometer techniques in the collection of spectral information and the spectrum is calculated as an inverse Fourier-Transform of the interferogram. FTIR spectroscopy is non-destructive, structurally specific and, unlike the high vacuum technique, FTIR is able to provide spectral in situ information about solid/liquid interfaces.

3.6 STRUCTURAL CHARACTERIZATION

Structural characterization of thin films using X-ray diffraction (XRD) analysis plays a vital role in all aspects of semiconductor technology from fundamental research to manufacturing. Among the available structural characterization techniques, X-ray diffraction method is very simple, non-destructive and suitable for estimating the crystallographic parameters.

When an X-ray beam falls on matter, scattered X-radiation is produced by all the atoms. These scattered waves spread out spherically from all the atoms in
the sample, and the interference effects of the scattered radiation from different atoms cause the intensity of the scattered radiation, to exhibit maxima and minima in various directions. The equipment consists of a X-ray generator, diffractometer, proportional counter and single channel pulse height analyzer. The specimen is mounted in the center of the diffractometer and rotated by an angle around an axis in the film plane. The counter is attached to an arm rotating around the same axis by angle (2θ). It can be observed that the diameter of the focussing circle continuously shrinks with increasing diffraction angle. Only (hkl) planes parallel to the film contributes to the diffracted intensity.

The X-ray diffraction patterns of all films were recorded by using the following configuration based X-ray diffractometer.

<table>
<thead>
<tr>
<th>X-ray generator (model)</th>
<th>JEOL JDX 803a and PHILIPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter</td>
<td>Nickel</td>
</tr>
<tr>
<td>Radiation</td>
<td>Cu Kα with wavelength = 1.5418Å</td>
</tr>
</tbody>
</table>

The obtained diffraction peaks were indexed with standard JCPDS cards and evaluated the various crystalline parameters like, lattice constants, crystallite size and crystalline phase of the films.

3.7 SURFACE MORPHOLOGY

The surface morphology, homogeneity and grain size of the deposited films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses.

3.7.1 SCANNING ELECTRON MICROSCOPY

Scanning electron microscope is the most versatile and commonly used instrument to study the surface topography of the film. The low energy (50 eV) secondary electrons emitted from the surface of the specimen provide the basis for
a different type of imaging. The beam can be concentrated to a small probe (~ 20 Å diameter) that may be deflected across the specimen in the faster fashion using scanning coils. The secondary electron can be detected above the specimen, and as image showing the intensity of secondary electrons emitted from different parts of the specimen can be displayed on a CRT. This scanning image is particularly useful for examining the morphology of metals, alloys, thin films of metal and semiconductors and crystalline materials. The convenience of scanning microscopy is partly due to the long working distance between the final lens and the sample surface and partly due to the ability to directly study almost any free surface. The schematic diagram of the SEM instrument is shown in Fig. 3.7, which is self-explanatory. Further SEM offers several modes of operation. The most widely employed is secondary electron imaging, which gives images of better than 100 Å resolutions almost unlimited depth of field and good contrast between most cell components [5, 6].

JEOL JSM-5610 LV (Japan) (model) scanning electron microscope has been used for the morphological studies on SnO₂ and PSi films. The SEM micrographs provide information about the surface homogeneity, surface morphology like crack free nature, pinholes, grain size and nature and smoothness of the films [6].

3.7.2 ATOMIC FORCE MICROSCOPY

The unique and modern tool to identify the real view of the atomic structure and surface morphology of the materials is the atomic force microscopy [7]. In the present case the film surfaces were analysed by Nanoscope-III atomic force microscope with STM attachment. The AFM studies also offers the information regarding surface homogeneity, uniformity, nanostructure, nature of grains and other special features of the films, that are in nano meter regime. Also AFM is the basic confirmation tool and plays an important role in nano technology, which
Fig. 3.7 The schematic diagram of the Scanning Electron Microscope (SEM) instrument
deals with the rearrangement / architecture of atoms so as to perform our desired function in the nano meter scale.

This 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 (5 to 10Å), 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 give the tunneling current. The direction of electron flow depends on the sign of the bias voltage applied.

The experimental setup of AFM measurement is shown in Fig. 3.8. In the AFM measurements, a Topomatrix Explorer system is operated in air in contact mode, with a typical scanning frequency of 0.5-1.0 Hz. 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 100 nm and a spring constant of 4 N/m. In order to establish a good electrical contact between the tip and the sample, a load of about 50 nN has to be applied. Under these conditions, the contact resistance between the tip and an evaporated gold film is typically 50 kΩ. 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 (> 10⁴ 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 current-voltage measurements at specific locations on the surface.

3.8 PHOTOLUMINESCENCE STUDIES USING FLUORESCENCE SPECTROPHOTOMETER

Fluorescing sample (both films and solids) can be analyzed, using this spectrophotometer generally on excitation with higher energy radiation such as
Fig. 3.8 Schematic diagram of the AFM Experiment
UV (with wavelength selected). These samples give light in the lower energy region (usually in the visible region), which when wavelength scanned, yields emission spectrum characteristics of the given luminescent species.

VARIAN CARY ECLIPSE Fluorescence Spectrophotometer employing a 15 W Xe plased flash lamp was used for the photoluminescence studies of PSi. Electromagnetic radiation from an Ultraviolet-Visible source passes through a wavelength selected and through the cell as in a spectrophotometer. Unlike the measurement of absorption in a Spectrophotometer, however a portion of the emitted radiation that exists from the cell is measured. Because the luminescent radiation can be emitted in broad band that are centered at different wavelengths, a second wavelength selector is required in the path of the emitted radiation between the cell and the detector. The emitted radiation is not usually measured in-line with the exciting radiation, as in absorptive measurements, owing to possible spectral interference from the exciting radiation. Photoluminescence has been measured at many angles relative to the incident radiation and at many locations within the hole. The most common practice is to measure the emitted radiation of 90 degree from the path of the exciting radiation and at the center of the cell. The signal from the detector is amplified, if required and routed to a read out devices.

High pressure xenon lamps emit a continuum of radiation that useful throughout the ultraviolet-visible and into the near-infrared spectra regions. In order to emit constant intensity radiation at a particular wavelength the lamp requires a stable power supply. Nevertheless, lasers have proved to be useful radiative sources. Spectrophotometers are required, whenever it is necessary to scan the wavelength of either excitative radiation or the luminescent radiation. In general it is required when establishing a new method of fluorescent analysis become the optimal wavelengths of the excitation and emission must be established.

Scanning instruments can be used to obtain two types of spectra. If the wavelength at which the emission observed is held constant, the wavelength at
which excitation occur (excitation spectrum) can be scanned. If the wavelength of the excitation radiation is fixed then the wavelength at which the emission occurs (emission spectrum) can be scanned.

3.9 RAMAN SHIFT STUDIES USING LASER RAMAN SPECTRUM

Renishaw invia Raman Microscope can perform a large number of laser Raman applications. When a beam of light is passed through a substance, a small amount of the radiation energy is scattered, the scattering persisting even if all dust particles or other extraneous matter are vigorously excluded from the substance. If monochromatic radiation, or radiation of a very narrow frequency band is used, the scattered energy will consist almost entirely the radiation of the incident frequency (the so-called Rayleigh scattering). But in addition, certain discrete frequencies above and below that of the incident beam will be scattered; it is referred to as Raman scattering.

The laser is almost ideal as a source for Raman experiments. It gives a very narrow, highly monochromatic coherent beam which can be focused very finely into a small sample. In addition lasers can be extremely powerful, ranging from milli watts to several watts, concentrated into a small energy spread. The laser beam is passed through a cell usually a narrow glass or quartz Tube filled with the sample. Light scattered sideways from the sample is collected by a lens and passed into a grating mono chromator similar to that used in a dispersive infra-red instrument. The signal measured is usually processed by a computer, which plots the Raman spectrum. The use of plane polarized radiation gives, information about the symmetries of molecular vibrations to make these measurements. For vibration measurements the Raman technique has several advantages over infra-red, mainly because both the incident and scattered radiation are at ultra-violet or visible frequencies.
3.10 CURRENT-VOLTAGE CHARACTERISTICS

The circuit for measuring I-V characteristics and the experimental set up is given in the Fig. 3.9. A GE-ELFI lamp of 300 watts power operating at 120 V AC, is used as the light source. This is commonly used light source for solar cell characterization [8]. The distance between the lamp and the test sample is adjusted such that the input intensity on the cell is 100 mW/cm$^2$ as measured by Surya Mapi [CELL laboratories India] with silicon reference cell. The temperature of the Cell during measurement is maintained at 28°C by placing it on a water-cooled metal chamber.

3.11 CONCLUSION

In this chapter, the author has reported briefly the characterization techniques, which were used to characterize the Sn$\text{O}_2$ and PSi films. Also the experimental procedures of these techniques, instrumental specifications and operation procedures are explained in detail. The results are used to interpret the materials properties of coating prepared using the spin coating technique developed by the author.
REFERENCES


5) O, Johari, A.V. Samudra, Characterization of Solid Surfaces

