CHAPTER 2

EXPERIMENTAL TECHNIQUES

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2.1 INTRODUCTION

The electrodepositon of the cadmium based thin films was carried out and the films were characterized by several techniques to identify the chemical composition, stoichiometry, thickness of the films developed and their optical and conducting properties for the material characterization. During the electrodepositon several factors were considered before optimizing the nature of the films obtained. This chapter aims at providing an insight into the methods and techniques followed, the instrumentation and methods of analysis.

The techniques involved is categorized as

a. Preparation of the films

b. Material characterization of the films

Preparation of the films involve the techniques of electrodepositon such as the equipment used and their precision, the selection of the substrate and the counter electrodes, understanding and application of the various parameters necessary to obtain the required nature of the electrodeposit.

Material characterization **[32]** involve the study of the morphology of the films obtained, their optical and electrical properties so as to identify their effectiveness in the preparation of solarcells. The chemical nature and morphology of the films has been studied using the techniques of x-ray diffraction, scanning electron microscopy and energy dispersive electron microscopy, UV-VIS spectrophotometry. The semiconducting nature of the films obtained was carried out by the study of their conductivity measurements. The photovoltaic nature was studied by measuring the photovolotaic current and potential. The detailed procedures followed in the preparation and characterization of the films is discussed below to enhance their importance in the analysis of the results obtained in the later chapters. **Table 2.1** gives an idea of the techniques and their applications in the present study.

Table 2.1 Lay out of the techniques and their application

Sl No	**Technique used**	**Application**
1	Electrodeposition	To obtain the thin films of CdS and CdSSe
2	X- Ray diffraction	Sample identification and chemical data
3	EDAX & SEM	Composition and surface morphology
4	UV-VIS spectrophotometry	Optical characterization
5	Four Probe Method	Resistivity Or conductivity measurements
6	I-V Characterization	Photovoltaic Activity

2.2 Preparation of the thin films by electrodeposition

2.2.1 Preparation of the substrate surface

ITO coated glass of and silicon wafers obtained as rejects from a semiconducting materials factory were chosen as the substrates. Before coating the substrates the surfaces were chemically cleaned to remove all adherents which may interfere in the preparation of good films for the study.

a. Preparation of ITO glass substrate

The ITO glass films were cut to a standard dimension of 2 cm x 1.5 cm. The films were cleaned in clean distilled water in a ultra sonic cleaner for a few minutes and later with methanol and 1-propanol. The films were air-dried and carefully handled using tweezers. These films were basically used to ensure the formation of the films, which have an orange yellow colour [33].

b. Preparation of silicon wafer substrate surface: The n- type silicon wafers were cut using a glass cutter to a dimension of 2 cm x 1.5 cm . The pieces obtained were cleaned thoroughly by a detailed process as discussed below basically to remove the oxide impurities and fingerprints normally left during handling.

The silicon wafers cut to the required size were rinsed with distilled water in an ultrasonic cleaner for about 10 minutes. Then it was boiled in a H_2O: H_2O_2: HCl bath taken in the ratio 86:11:3 for another 10 minutes. After this the wafers were again rinsed with deionised water. The films were then kept immersed in a solution of H_2O: H_2O_2: NH_4OH in the ration 4:1:1 for a few minutes.

The films were removed from this bath and again rinsed with deionised water. The films thus cleaned were kept immersed again in a bath of H_2O: HF mixed in the ratio 10:1. Finally the films were rinsed with deionised water and air-dried. The films were later kept in a dessicator to avoid any moisture accumulation on their surface **[34]**.

2.2.2 Preparation of the electrolyte solutions

a. Preparation of the electrolyte solution for the deposition of the **Binary CdS** Thin films

The electrolyte solution for the deposition of CdS films was prepared using analytical grade cadmium chloride ($CdCl_2.21/2H_2O$), Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) crystals, and hydrochloric acid (HCl-approximately 10M). Sodium thiosulphate solution containing 10 m moles per dm^3 of solution [0.01M],was prepared in distilled water using standard glass apparatus and electronic balance. Cadmium Chloride solution was prepared from its salt by carefully weighing $CdCl_2$ crystals such that the solution would contain 20 m moles per dm^3[0.2M], of the solution. Calculated volumes of the two solutions were transferred for each trial into the electrolytic cell using standard graduated pipette. The electrolyte solutions were changed after each deposition to avoid any impurity content and also to maintain the concentration of the ions **[35]**.

b. Preparation of electrolyte solution for the deposition of Ternary **CdS/CdSe** thin films:

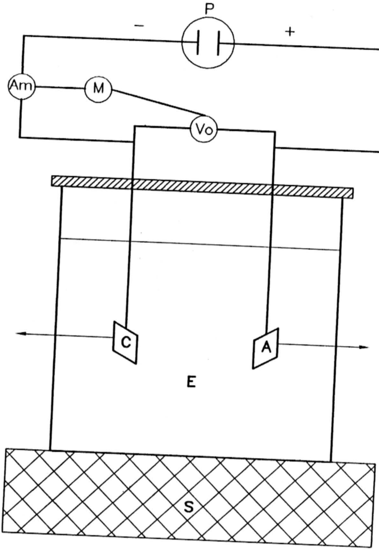
The electrolyte solution for the deposition of the ternary CdS_xSe_{1-x} was prepared using analytical grade cadmium chloride and sodium thiosulphate crystals. The aqueous solution of selenium dioxide [SeO_2] was prepared using standard analar grade selenium dioxide.

As in the earlier case aqueous solutions of 0.01M sodium thio sulphate and 0.02 M cadmium chloride solution was prepared. The three solutions were mixed in different proportions by volume and the deposition conditions were optimized . The solution compositions were varied and the deposition of the films was carried out at different concentrations of the electrolyte. The solutions were prepared fresh and changed after each deposition [**36**].

2.2.3 The electrolytic cell preparation :

An electrolytic cell consists of two electrodes and the electrolytic solution of known concentration. Normally the electrodeposition is carried out with a DC source.

The electrolytic cell used for the study consisted of a platinum anode and the substrate as the cathode. The electrolytic solution was placed in the container and the electrodes dipped into it [**Fig 2.1**].



ELECTRICAL CONNECTIONS SETUP FOR ELECTRODE POSITION

Fig.2.1

P: POWER SUPPLY
Am: AMMETER
Vo: VOLTMETER
M: MULTIMETER
E: ELECTROTYPE
C: CATHODE (SUBSTRATE)
A: ANODE (COUNTER ELECTRODE)
S: MAGNETIC STIRRER

Electrodepositon was carried out at constant laboratory conditions of temperature [298K] and pressure so as to simplify the procedure. A magnetic stirrer was employed to provide mixing of the components and constant deposition current. Several conditions were varied during the deposition and the films obtained thereof were studied to arrive at better deposition parameters.

2.2.4 The parameters taken under consideration are mentioned below:

a. Deposition Potential: Deposition potential range was obtained from standard voltammograms for the electrolyte combination. The deposition was carried out within this range and the optimum deposition range was obtained.

b. Concentration of the electrolyte solution: The concentration of the electrolytes was varied by adding different proportions by volume. The nature of the films obtained was studied so as to obtain the most suitable film thickness.

c. Deposition Time: The quantity of deposition in terms of the thickness of the deposit obtained is found to vary linearly with time. **[37]**. The deposition time was varied between 10 and 90 minutes.

d. Substrate material: ITO coated glass was used due to its transparency, which is useful to study some of the properties, such as optical characterization. Further visual observation of the nature of coating would be easily identified. Coatings on silicon wafers cut to suitable size was used to study the photocell activity of the films and to obtain larger areas of deposition.

e. Counter Electrode: Platinum electrode was employed as the counter electrode due to its non-interactive nature. Subsequently copper electrode was used as the

2.3 Material characterization of the deposited films:

The characterization of the deposited films were carried out using the techniques of x-ray diffractometry[XRD] , Scanning electron microscopy[SEM] and Energy dispersive analysis of x-rays[EDAX] and UV-VIS spectrophotometry .

XRD was employed to identify the nature of the deposit i.e., either as amorphous or crystalline.

SEM and EDAX studies were carried out to obtain the morphology and composition of the deposits.

The UV-VIS technique was required to identify the transmission and absorption parameters as well as the thickness of the coatings obtained.

In order to understand the application of these techniques it is essential to understand the principle and procedure involved in each of these . The next part of this chapter aims at providing a brief outlay of ideas involving the principles and experimental aspects of these techniques.

The conducting nature of the films was studied by measuring the conductivity and further the photocell activity was studied by obtaining the I-V characteristics.

2.4 X-RAY DIFFRACTOMETRY

X-ray diffractometry or XRD is useful in the study of the differentiation and determination of phases such as crystalline or amorphous nature , unit cell dimension , space group, crystal systems and crystal sizes. Emphasis has been attached for this technique in the study.

2.4.1 X-rays and their production

X-rays are short wavelength electromagnetic radiation produced by the deceleration of high -energy electrons or by electronic transitions involving electrons in the inner orbital of atoms.Their wavelength ranges from 10^{-5} to 100 Ang.

X-rays are obtained in three ways:

1. By bombardment of a metal target with a beam of high-energy electrons
2. By exposure of a substance to primary beam of X-rays so as to generate a secondary beam of fluorescent X-rays.
3. By employment of a radioactive source whose decay results in X-ray emission.

X-ray sources like UV and visible emitters, often produce both a continuous and a discontinuous spectrum. In an X-ray tube, the electrons produced at a heated cathode are accelerated toward the target anode with a potential in the range of 100KV.

Upon collision, part of the energy of the electron beam is converted to X-rays. The continuous radiation from the electron beam source results from collisions between the electrons of the beam and the atoms of the target material. At each collision the electron is decelerated and a photon of X-ray energy is produced. The energy of the photon will be equal to the difference in kinetic energies of the electron before and after collision.

2.4. 2 Crystal structure and applications of XRD technique

A crystal is defined as a homogeneous and anisotropic part of a crystalline solid with a regular geometry independent of the size. The crystal lattice is the array of points showing the arrangement of molecules, atoms or ions in a three dimensional space. Based on the symmetry aspects, 230 crystal forms are identified. They are further identified into 7 crystal systems based on a specific set of crystallographic axis and symmetry operations. They are cubic, rhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral.[**39**].

2.4.3 PRINCIPLE

The idea of using x-rays in the analysis of nature of crystals was given by Max Von Lave. Accordingly, if the wavelength of X-rays is of the same order of magnitude as the spacing between the ions of the crystal, then a diffraction effect should be observed. Further, the works of W.H. Bragg and Co led to the idea of the crystal being composed of a series of equally spaced atomic planes or lattices, which can not only act as a transmission grating, but also as reflection grating.

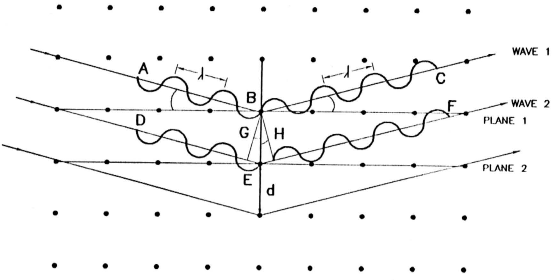


Fig 2.2 X-RAYS DIFFRACTION FROM CRYSTALS

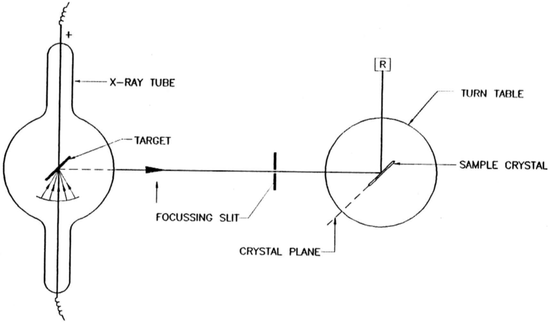


Fig 2.3 X-RAY SPECTROMETER (ROTATING CRYSTAL TECHNIQUE)

A beam of x-rays striking the atoms, which constitute these planes, will be diffracted in such a manner so as to cause either interference with or reinforcement of the beam diffracted from the first or outer plane. The whole beam will behave as if it had been reflected from the surface of the crystal **[40]**

The situation is illustrated in **Fig. 2.2 [ref.39]**

It can be seen from the diagram that **rays 1** and **2** are incident on a set of parallel equidistant **[d]**, planes **AA^1** and **BB^1**. According to the Snell's law, the angle of incidence is equal to angle of reflection in one plane. The rays can reinforce in the direction of reflection only when their path difference is an integer multiple of λ the wavelength. In other words the condition for reflection from the set of planes under study is, $\mathbf{n\,\lambda = 2\,d\,sin}\,\theta$ where n= 0,1,2,3, which indicates the order of reflection For a given set of values of d and λ , only a particular angle θ produces such a reflection. Since sin θ <1 and d< 10^{-8} cm the reflection can be observed only for λ of the order of 10^{-8} cm or less. This is one other reason for the x-rays being used in the study of crystal lattice structure. Such a method makes use of a rotating crystal method or Bragg's method where reflection occurs for discrete set of θ values. **[40,41]**

The schematic diagram of the arrangement is given in **Fig. 2.3**. and **Fig. 2.4** gives the goniometer x-ray path. **[40,41]**

2.4. 3 Application of XRD technique in the study of the deposited films

The present study employed XRD to identify the structural characteristics of the deposited films using Compact X-ray Diffractometer PW 1840, Philip.

The films were cleaned and air dried and placed on a sample holder and firmly fixed. Trial scans were run with the start angle of 10^0 and end angle of 120^0. Later scans were carried out between 10^0 and 90^0 for obtaining the preferred orientation of the samples.

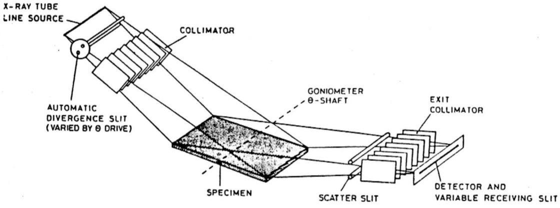


FIG. 2.4 GONIOMETER X-RAY PATH

2.5 SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ANALYSIS

2.5.1 Principle

The major purpose of the technique of scanning electron microscope or SEM is for morphological surface analysis. The information is reflected from the sample surface similar to the viewing of images by reflectance in optical microscopy. The difference between an optical microscope and a scanning electron microscope is that while the optical microscope reflects photons SEM analyses electrons released from the specimen. The choice of electrons is due to their being high energy particles which may induce other information signals within the sample such as cathodoluminiscence and x-rays. **[42]**

2.5.2 Arrangement of SEM operating system:

A SEM basically consists of five systems

1. Illuminating system, consisting of the electron gun and magnetic lenses. It produces the electron beam and focuses it onto the sample. The electron gun has an electron source held at a negative potential. The electrons produced on the application of high current are attracted down the microscope column by the potential difference of the anode. Normally a heated tungsten filament is used as the electron source. The demagnifying lens serves the dual function of demagnifying and focusing the electron beam. **Fig. 2.5** gives an illustration of this system.

2. Information system , which holds the sample releases a variety of information signals. While SEM is capable of generating data of three different electron signals,

a typical SEM can only detect secondary electrons and back scattered electrons.

3. Detection system, which is responsible for collecting and amplifying the information signals generated by the probe-specimen interaction.

4. Display system, serves the purpose of reproducing the topography of a specimen in the same sequence as it was electronically scanned.

5. Vacuum system is designed to remove gases from the column as the gases may contaminate the sample or react with the filament causing its eroding or they may scatter the high velocity electrons. [43]

The schematic diagram of the SEM is given in **Fig. 2.6**

2.5.3 Working of the SEM operating system:

A high negative voltage accelerates electrons produced at the filament by thermionic emission so that the filament will not capture them in its attempt to maintain electrical neutrality. As the electron beam enters the electron lens system, its diameter is reduced to nearly 5 mm. The electron lens consists of a coil of wire with its axis aligned along the beam's path. When current is passed through the coil an electro magnet is produced. The magnetic lines produced thereby converge the electron beam to a focal point below the lens. When this beam hits the specimen surface, electrons are emitted from the surface of the sample. These electrons are collected by the detector, which converts them into an electrical signal.

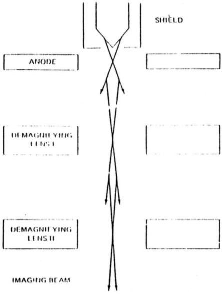


FIG.2.5 ILLUMINATING SYSTEM OF SEM

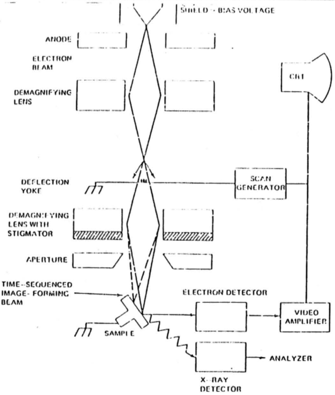


FIG.2.6 SCHEMATIC DIAGRAM OF SEM

[ref.43]

This signal contains a lot of information about the point of focus. When a point - by -point scan is carried through an extent of 1000 points it produces a frame. The scanning is carried through several such frames [**44**]

The micrographs obtained provide information such as

a. Surface deformities

b. Structural faults due to surface and internal mechanical stress

c. Uniformity of deposition

Limitations of the technique

Specimens considered for the SEM studies need satisfy some characteristics :

* The specimen must withstand the vacuum conditions of the vacuum system

* They must be able to sustain the bombardment of the electrons

* The specimens must fit into the specimen chamber. [**45**]

2.5.4 Application of SEM in the present study

SEM was carried out with the Philips 515 scanning electron microscope. The surface analysis of the films deposited in terms of morphology and the extent of uniformity was obtained using this technique. The films were coated with gold before taking their SEM micrographs. The developed photographs were used to identify the morphological characters of the films, which is useful to further identify the optimal conditions for the required type of the deposition. The uniformity of the grain size and chemical nature were studied using these micrographs.

2.6 ENERGY DISPERSIVE X-RAY ANALYSIS

Electrons being relatively energetic particles induce information signals within a sample such a cathodoluminiscenece and x-rays. As a consequence other developments which are direct outgrowths of SEM are identified which includes the energy dispersive x-ray analysis or EDAX. EDAX generally is carried out to obtain information on the chemical nature of the specimen. It is considered as a quantitative and non-destructive technique. The results regarding the composition of the specimen is normally obtained in terms of atomic percentage and weight percentage. The quantifying results are called ZAF, which includes three separate effects viz., atomic number (Z), absorption (A), and fluorescence (F). [46]

2.6.1 Principle and working of the EDAX operating system:

In order to understand the principle behind this technique, it is necessary to know the inner structure of an atom and its electronic transitions. The electrons in an atom are distributed in the various energy shells K, L, M & N. It is well known that the inner shell electrons need more energy to be removed from the atom than the outer shell electrons.

When a lower energy electron such as the K-electron is removed from the atom either by excitation or ionization, a vacancy is created in their inner shell. Electron beams, charged particles like alpha particles or photons from other x-rays or electromagnetic radiation can bring about the excitation.

The high-energy outer shell electrons tend to occupy the vacant space created by such an excitation. Consequently, the difference of energy between these transitions is released as a photon of x-ray and x-rays are emitted. Normally inner electron transitions such as the transitions within the K, L, M shells lead to such a situation. The energy released is a function of the atomic number and each element has a distinct, characteristic energy of transition. The nature of the x-ray produced depends on the kind of transition. If a K shell vacancy is filled by a L- electron, a K_α x-ray is produced similarly if the K shell vacancy is filled by a M electron, K_β x-ray is produced. **Fig.2.7** gives a schematic idea of such transitions.

When these characteristic radiation strike the detector of the EDAX system, a current pulse is produced. It is then preamplified at liquid nitrogen temperature and passed through the main amplifier, electronic processors and multi channel analyzer The pulses are separated according to their amplitudes, counted and stored.

The EDAX system is capable of simultaneous detection of elements and does not miss even the unexpected elements. It is possible to obtain rapid qualitative and comparative analysis. It can be used against irregular, rough samples as well. It proves to be low power technique with a compact arrangement of the components. **Fig 2.8** gives a scheme for the detection system of the EDAX.

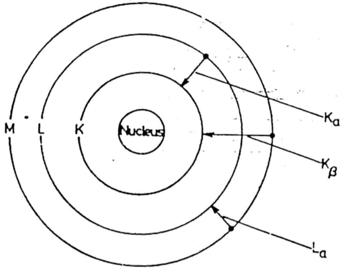


FIG. 2.7 ELECTRON TRANSITIONS & X-RAY PRODUCTION

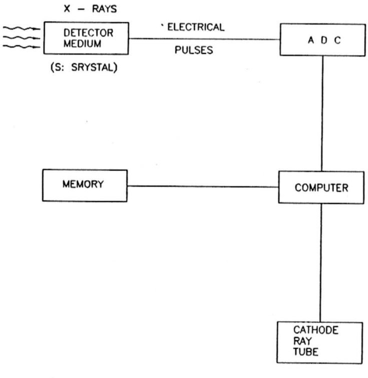


FIG. 2.8 DETECTION SYSTEM OF EDAX

[ref.47]

Limitations of the technique:

The only limitation of the technique is that it cannot distinguish between ionic , non ionic and isotopic species and elements of low atomic number . When used in association with the SEM techniques it can not be used for hydrated samples. Generally elements with Z>5 are identified using the EDAX techniques. Further the production of secondary x-rays, absorption effects and fluorescence may cause some error in the analysis **[46,47]**.

2.6.2 Application of the technique in the present study:

The technique was applied to the present work in order to obtain information on the weight percentage ratio of the elements deposited. Prior to the application of the technique the films were coated with carbon to prevent image defects.

2. 7 UV-VIS SPECTROPHOTOMETRY

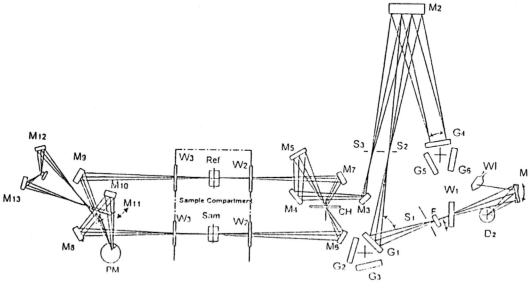
UV -VIS Spectrophotometry is used to identify the optical properties and related optical constants such as refractive index **[n]**, extinction coefficient **[k]** & absorption coefficient **[a]**. Further the characteristic energy **[Eg]** of the electronic transition near the fundamental absorption edge of the sample as well as the thickness can be determined using this technique. An analysis of the UV and visible region would reveal information of electronic transition and vibrations of the fine structure. **[48]**

The optical constants are related to the electronic energy band. It is envisaged therefore that the study of the optical properties will finally lead to the derivation of the energy band diagram of the semiconducting thin films. The important parameters, which can be obtained from this technique, are:

1. The transmission capacity of the thin film
2. The optical constants refractive index and extinction coefficient as well as absorption coefficient
3. The thickness of the film
4. The characteristic energies of electronic transition near the fundamental absorption edge of the sample.

Principle components of the optical system are shown in Fig. **2.9**. The UV source used for most operation below 340 nm is a deuterium arc lamp and for the visible region from 340 nm to 1000nm a tungsten quartz lamp is used .The wavelength scanning is completely software controlled. The rotation beam splitter serves to divide the intensity to two optical paths to pass the reference ad sample position. The beam recombine brings together these two signals and focuses it into a photomultiplier tube. The signal processing manipulation of the data and storage is done through a computer. **[48,49]**

Application in the present study: The present study involved the use of the technique to determine the transmission parameters and thickness of the optimized films. The spectrophotometer used was a double beam instrument controlled by a software and computer.



D2: Deuterium lamp
W1 Halogen lamp
F: Filter
G1~ G3: Gratings of first monochromator
G4~ G6: Gratings of second monochromator
S1: Entrance slit
S2: Intermediate slit
S3: Exit slit

W1~ W3: Window plates (W1, W2, 30 mm dia.; W3, 40mm dia.)
CH: Chopper mirror
M1~ M13: Mirrors (M11 is detector switching mirror)
Ref: Reference cell
Sam: Sample cell
PM: Photomultiplier
PbS: PbS cell

FIG. 2.9 OPTICAL SCHEME - UV-VIS SPECTROPHOTOMETE

[ref.48]

2.8 RESISTIVITY / CONDUCTIVITY MEASUREMENTS BY FOUR PROBE METHOD

Several of the conventional methods for measuring resistivity/conductivity of semiconducting materials are often unsatisfactory as the metal-semiconductor contacts are usually rectifying in nature. Further, there is generally minority carrier injection by one of the current carrying contacts and which affects the potential of other contacts and modulate the resistance of the material. The four-probe method overcomes some of these difficulties and also offers some more advantages. It permits measurements of resistivity in samples having a wide variety of shapes, including the resistivity of small volumes within bigger pieces of semiconductor. Also resistivity of sides of p-n junction can be determined with good accuracy.

The setup consists of four sharp probes, which can be placed on a flat surface of the material. Current is passed through the two outer electrodes, and the floating potential is measured across the inner pair. The schematic diagram of the circuit used for the measurements is illustrated in Fig. **2.10.** It is assumed that,

1. The resistivity of the material is uniform in the area of measurements
2. The surface on which the probes rest is flat with no surface leakage
3. The four probes used have contact with the surface at points that lie in a straight line.
4. The material has a conducting base [ITO]

The material whose resistivity/conductivity is to be measured is placed on the base plate of the arrangement and the pipe holding the four probes is gently placed on it.

This set up is placed in the oven and contacts are established. The current is adjusted to desired value say 5mA. The oven is turned on and the temperature is recorded using the thermometer inserted in it. The variation of potential against temperature is recorded at every 5^0 change of temperature in the required. temperature range [30^0-160^0 C]. The cooling temperature s also may be recorded.

The resistivity ρ, is calculated using the formula, $\rho = \rho_0 / t$

where $\rho_0 = V/I \times 2\pi s$, s-the space between the probes[2mm], V-voltage, I-current., t-thickness of the film .

σ, the conductivity of the material,which is the reciprocal of resitivity is calculated

The slope of the plot of log ρ vs. 1/T alternately log σ vs. 1/T gives the value of energy gap, Eg of the material.**[50]**

Application in the present study: The method was applied to study the variations of the conductivity with temperature, a behavior characteristic of semiconducting materials. Further it was applied to calculate the energy gap Eg of the sample to be compared with the one from the UV-VIS spectroscopic data.

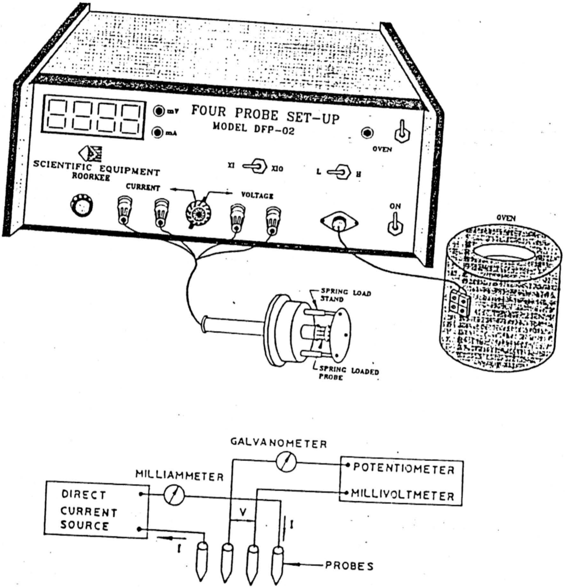


FIG. 2.10 SCHEMATIC DIAGRAM OF FOUR PROBE SET UP

[ref.50]