EXPERIMENTAL DETAILS

This chapter describes the preparation of thin film semiconducting metal oxide such as ZnO, Cu_2O, SnO_2 and Co_3O_4 by chemical bath deposition method on microscopic glass substrate. The prepared metal oxide films were characterized by X-ray diffraction analysis, FT-IR analysis, scanning electron microscopy (SEM) analysis and UV-Visible spectroscopy analysis. The thickness of the films was measured by weight gain method and the nature of the thin films was determined by hot probe method; and its electrical resistivity was measured by four probe method. Finally the optical energy band gap of the thin films was measured by optical studies.

3.1. MATERIALS USED

Materials used for the deposition of thin film semiconducting metal oxides are given below;

3.1.1. Zinc oxide thin film

Zinc acetate dihydrate (Merck)

Disodium salt of ethylenediamine tetra acetic acid (Merck)

Sodium hydroxide (Himedia)

3.1.2. Copper oxide thin film

Copper sulphate (Fisher Scientific)

Anhydrous potassium carbonate (Merck)

Anhydrous potassium sulphite (Himedia)

3.1.3. Tin oxide thin film

Stannus chloride (Merck)

Ammonia solution (Qualigen)

Sodium hydroxide (Merck)

3.1.4. Cobalt Oxide thin film

Cobalt acetate (Fisher Scintific)

Hydrogen peroxide (Merck)

Ammonia solution (Merck).

3.2. SELECTION OF THE SUBSTRATE

When selecting substrate, certain parameters like surface characteristics, chemical composition, stability, roughness, mechanical strength and other important properties also to be considered. There should not be any chemical reaction between the substrate and the metal oxides which is to be deposited. The nature and surface finish of the substrate are extremely important as they greatly influence the properties of thin films deposited onto them. Glass, quartz, silica wafer and ceramic substrate were used for polycrystalline films. The most commonly used glass slide is of Pyrex. Thermal and mechanical stability of the substrates are required to prevent the damage during the formation of thin films. Glass is found to possess the smoothest possible surface and hence to achieve uniform coatings on it.

3.3. CLEANING METHOD

Microscopic slide of dimension 75 mm x 25 mm x 2.5 mm was purchased from Blue star company, Mumbai. The following procedure was adopted to get ultra pure and hydrophilic surface;

(i)   The substrate was kept in concentrated sulfuric acid bath and heated to 60 ^{o}C for 30 minutes.

(ii)   The substrate was then kept in chromic acid for 24 hours and washed with deionized water.

(iii)   The plates were then cleaned with acetone and deionized water using ultrasonic method at 72 $^{\circ}$C for 50 min. The treated plates were dried at 30 $^{\circ}$C and used for thin film deposition [1].

3.4. PREPARATION OF ZINC OXIDE (ZnO) THIN FILM

Zinc oxide thin film was prepared by a simple chemical bath deposition method from an aqueous solution of 0.1 M of zinc acetate and 0.5 M of disodium salt of ethylenediamine tetra acetic acid (EDTA) (Table 3.1). The pH of the solution was raised to 10.5 by adding few drops of aqueous NH_3 solution. During the addition of ammonia, the solution turns turbid and then it was clear and homogeneous. The solution containing beaker was kept in a water bath, and the bath temperature was slowly raised to 80 $^{\circ}$C. The cleaned microscopic glass substrate was kept in the bath. After 35 min, the glass slide was coated with zinc hydroxide [$Zn(OH)_2$]. The substrate was taken out and dipped in distilled water, dried and stored in a desiccator. The films were then annealed at 300 $^{\circ}$C for 2 hours in air to convert into ZnO. Fig.3.1 shows the experimental setup for the preparation of metal oxide thin films.

3.4.1. Effect of substrate contact time on film thickness

In the chemical bath deposition method, the cleaned substrate was immersed in chemical bath. The contact time is the duration of the substrate in contact with reaction medium, while the reaction was progress and the other reaction conditions remain the same. The effect of substrate contact time on film thickness was

determined using mass gain method. It was observed that the film thickness varied smoothly with the contact time and the optimum contact time was predicted.

Table 3.1 The optimized parameters for chemical bath deposition of ZnO thin film

Parameter	Condition
Bath composition	0.01 M Zinc acetate 0.05 M EDTA Aqueous NH_3 solution
pH	10.5
Temperature	80 ^{o}C
Deposition time	35 min

3.4.2. Effect of pH on film formation

The zinc oxide was formed at different pH, because the composition and appearance was inadequate. Hence, an optimum pH of the medium was found out by trial and error method. At the optimum pH of the medium, zinc oxide thin films were prepared.

## 3.4.3. Effect of temperature on film formation

Bath temperature plays an important role during the deposition of thin film. Hence, the variation of film thickness with temperature at constant time duration was studied and the optimum temperature was found out. At the optimum temperature, the ZnO thin films were prepared for characterization.

Fig.3.1 Experimental set up for the preparation of metal oxide thin films

3.5. PREPARATION OF CUPROUS OXIDE (Cu$_2$O) THIN FILM

Cuprous oxide thin film was prepared by chemical bath deposition method from an aqueous solution of 0.02 M copper sulphate, 0.01 M sodium carbonate and 0.01 M sodium sulphite and the pH of the solution was 6.7. The solution was prepared using analytical grade chemicals and deionized water, and taken in a 100 ml beaker. To this, microscopic glass slide with the dimension of 75 x 25 x 0.25 mm was dipped as substrate. It was kept in a water bath and heated slowly upto 90 ^{o}C. The digital pH meter (Milwaukee) was used to adjust the pH of the bath. The substrate was removed from the bath after 30 min, and then dipped in deionized water and annealed in the oven between 350 ^{o}C for 2 hours. A reddish brown cuprous oxide thin film coating on the substrate was obtained. This procedure was repeated for several times to stabilize the conditions. The probable stoichiometric reaction that might occur in the bath is given below;

$$2CuSO_4(aq) + 2Na_2CO_3 \ (aq) + Na_2SO_3(aq) \longrightarrow Cu_2O(s) + 3Na_2SO_4(aq) + 2CO_2(g)$$
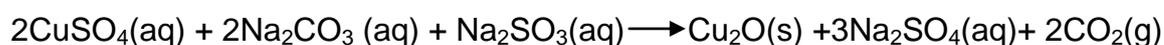
This procedure was repeated for different time duration. The deposited Cu$_2$O films were found to be uniform without any pinhole. The resultant thin films were subjected to various studies.

3.5.1. Effect of substrate contact time on film thickness

The contact time is defined as the duration of the substrate in contact with the reaction medium while the reaction was progress and the other reaction conditions remain the same. The contact time was varied and the film thicknesses were determined.

Table 3.2 The optimized parameters for chemical bath deposition of Cu_2O thin film

Parameter	Condition
Bath composition	0.02 M $CuSO_4$ 0.02 M Na_2CO_3 0.01 M Na_2SO_3
pH	6.7
Temperature	90 ^{o}C
Deposition time	30 min

3.5.2. Effect of pH on film formation

The copper oxide was formed at different pH. An optimum pH of the medium was found out by trial and error method. At this pH, the copper oxide thin films were prepared.

3.5.3. Effect of temperature on film formation

Bath temperature plays an important role during the deposition of thin film. Hence, the variation of film thickness with temperature at constant time duration was studied and the optimum temperature was found out. At the optimum temperature, the Cu_2O thin films were prepared for characterization.

3.6. PREPARATION OF TIN OXIDE (SnO_2) THIN FILM

The tin oxide thin films on microscope glass substrate were obtained by chemical bath deposition method. The precursor solution was prepared from 0.01M stannic chloride dissolved in deionized water and a few drops of isopropyl alcohol were added. The resultant solution was refluxed for 30 minutes to activate the solution (Table 3.3). A well cleaned substrate was kept inside the bath with proper

support or clamped on the top. The bath solution was heated up to 70 ^{o}C. The pH of the bath solution was raised to 6.5 by adding aqueous ammonia in to the bath. The temperature of the bath was maintained to 70 ^{o}C. The addition was done for every 10 minutes duration with constant stirring. After 30 minute, the substrate was removed from the bath and dipped in deionized water and then annealed at 400 ^{o}C for 2 hours [2]. The substrate was covered with a transparent, homogeneous tin oxide thin film. This substrate was taken out and dipped in deionized water, dried and stored in a desiccator. The slides were removed. After the post deposition treatment, the film thickness was estimated and it was found that the thickness had linear relationship with time of immersion.

Table 3.3 The optimized conditions for chemical bath deposition of SnO$_2$ thin film

Parameter	Condition
Bath composition	0.01 M Stannic chloride Few drops of Isopropyl alcohol Aqueous NH$_3$ solution
pH	6.5
Temperature	70 ^{o}C
Deposition time	30 min

3.6.1. Effect of substrate contact time on film thickness

The contact time is the duration of the substrate in contact with the reaction medium while the reaction was in progress and the other reaction conditions remained same. The contact time was varied and the film thicknesses were determined. The film thickness varied smoothly with the contact time.

3.6.2. Effect of pH on SnO$_2$ film formation

The tin oxide was prepared at different pH and an optimum pH of the medium was found out by trial and error method. At this pH, the tin oxide thin films were prepared.

3.6.3. Effect of temperature on film formation

Bath temperature plays an important role in determining the film thickness of the deposit. Hence, variation of film thickness with temperature at constant time duration was studied and the optimum temperature was found out. At the optimum temperature, the Sn$_2$O thin films were prepared for characterization.

3.7. PREPARATION OF COBALT OXIDE (Co$_3$O$_4$) THIN FILM

Cobalt oxide thin film, Co$_3$O$_4$ was prepared by chemical bath deposition method. The precursor solution was prepared from 0.01 M cobalt acetate and 0.05 M disodium salt of ethylene diamine tetra acetic acid. To this, a few drops of aqueous ammonia was added to maintain the pH of 6.8 and then 2 ml of 30% hydrogen peroxide was added drop by drop with constant stirring. The temperature of the bath was maintained at 60 ^{o}C. A well cleaned glass substrate was kept in the bath. After 25 min, bottom and side wall of the beaker was coated with bluish black material and similar coating was also deposited on the side of the substrate as a homogeneous thin film. The substrate was washed with deionized water and annealed at 400 ^{o}C for 2 hours. The annealed films were bluish black in colour, homogeneous and free from pin hole.

The resultant thin films were subjected to various studies. This procedure was repeated for different time intervals from 20 mins to 50 mins. The slides were

removed and thickness were estimated after the post deposition treatment of Co_3O_4 films and it was found that the thickness varied linearly with time.

Table 3.4 The optimized conditions for chemical bath deposition of Co_3O_4 thin film

Parameter	Condition
Bath composition	0.01M Cobalt acetate 0.05 M EDTA 2 ml 30 % H_2O_2 Aqueous NH_3 solution
pH	6.8
Temperature	60 ^{0} C
Deposition time	25 min

3.7.1. Effect of substrate contact time on film thickness

The contact time is the duration of the substrate in contact with the reaction medium while the reaction was in progress and the other reaction conditions remained the same. The contact time was varied and film thicknesses were determined. The film thicknesses varied smoothly with the contact time.

3.7.2. Effect of pH on Co_3O_4 film formation

The cobalt oxide was formed at different pH. An optimum pH of the medium was found out by trial and error method. At this pH, the cobalt oxide thin films were prepared.

3.7.3. Effect of temperature on film formation

Bath temperature also plays an important role in determining the film thickness of the deposit. Hence, variation of film thickness with temperature at

constant time duration was studied and the optimum temperature was found out. At the optimum temperature, the Sn_2O thin films were prepared for characterization.

3.8. CHARACTERIZATION TECHNIQUES

3.8.1. X-Ray diffraction analysis

X-ray region is a part of electromagnetic spectrum ranging between 0.1 to 100 A° (equivalent to an energy of 0.1 – 100 KeV). The breaking of X-rays into dark and bright bands caused by the interference of one part of the beam with another when the ray is deflected by an opaque object with accompanying variation in the intensity of X-rays in different directions is called X-ray diffraction. X - ray diffraction method is one of the most important tools applied in solid-state chemistry, since it constitutes a powerful and readily available method for determining atomic arrangements in matters.

Structural identification and the determination of lattice parameter are based on interpretation of the X-ray diffraction pattern using Bragg's law [3];

$$2\ d\ \sin\theta = n\lambda$$

Where, "d" is the interplanar distance of the material which can be calculated from the equation. The "d" spacing was varied by the crystal assembly and the intensities of the diffracted rays depend upon the crystal size of the material. By using Scherrer's equation [4] one can calculate the crystallites size using the formula;

$$D = 0.9\lambda\ /\ \beta\cos\theta$$

Where, the wavelength (λ) of the monochromatic X-ray, θ is the Bragg angle and β is the breadth of the diffraction peak at full width half maximum of X-ray diffraction peak. The crystalline peaks observed in the X-ray diffraction patterns are indexed by assigning Miller indices namely (hkl) using standard analytical methods [5]. Precise

values of α spacing and estimated line intensities were compared with the JCPDS data. The lattice parameter 'a' for the cubic structure was calculated using;

$$1/d^2 = (h^2+k^2+l^2)/a^2$$

Where, h, k and l represents the Miller indices and 'd' is the interplanar distance. In X-ray diffraction studies, a monochromatic Kα radiation (1.5404 A$°$) was used. This was obtained from an X-ray tube using copper as the target. As nickel strongly absorbs K$_\beta$ (1.39A$°$) radiation, monochromatic K$_\alpha$ radiation can be obtained by using a nickel foil as filter [6]. The powder X-ray diffraction method involves the diffraction of a collimated monochromatic beam from a powder sample containing an enormous number of tiny crystals having random orientation. The diffracted beams from the sample passes through the receiving slit and enter the Geiger counter. A chart recording the amplified output of the Geiger counter gives directly a plot of intensity versus scattering angle (2θ).
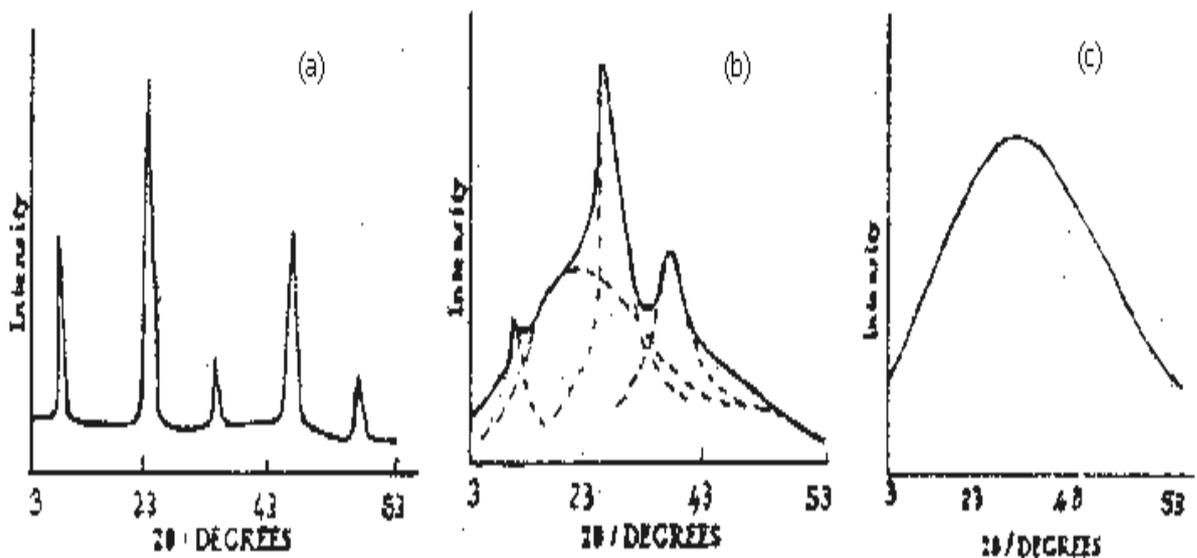

Fig.3.2 Typical X-ray diffraction patterns of (a) crystalline, (b) semi crystalline metal oxides and (c) amorphous

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One of the important uses of XRD to differentiate between crystalline, amorphous and semi-crystalline metal oxide powders as shown in Fig.3.2.

In the present studies, X-ray diffraction measurements were made from JEOL - (Model: JDX8030) X-ray diffractometer using nickel-filtered Cu-Kα radiation as shown in Fig.3.3. The diffraction patterns were taken at room temperature and the range of 2θ between 10° and 80° .The step size and scan rate were set at 0.1^o and 2°/ min, respectively.

3.8.2. FT- IR spectral studies

Infrared spectroscopy used not only in the elucidation and identification of molecular structure but also in application of quantitative analysis. IR radiation is usually defined as that electromagnetic radiation whose frequency is between ~12800 and 10 $cm^{-1.}$ (0.78 and 1000 μm). Within this region of the electromagnetic spectrum, chemical compound absorb IR radiation provided there is a pole moment change during a normal molecular vibration, molecular rotation, molecular rotation-vibration or a lattice mode, or from combination, difference and overtones of normal molecular vibration. IR spectroscopy is unique in that spectra can be recorded for materials in any physical sate (solid, liquid, vapour) and in solution over a wide temperature range. Each material exhibits its own unique IR spectrum under a specified set of condition.

Frequencies and intensities of the IR bands exhibited by a chemical compound uniquely characterize the material, and its IR spectrum can be used to identify the particular substance in unknown sample. Different classes of chemical compounds contain chemical groups which absorb IR radiation at identical frequencies and have the same band intensity.

Fig.3.3 Photograph of X-Ray Diffractometer

These bands are termed as 'group frequencies' and they are predictable and allow the analyst to identify molecular structures through functional group identification. Modern instruments allow spectra to be recorded for nanogram samples. No other technique allows examination and identification of materials under such a wide variety of physical conditions. With the recent development of Fourier transform infrared spectroscopy, it is now possible to rapidly record IR spectrum of even coloured substances and also short living compounds. Fourier transform IR spectrometer uses Michelson interferometer to produce an interferogram. The interferogram is related to the IR spectrum by a mathematical operation known as Fourier Transformation. A computer algorithm that was developed to the operation very fast in the FFT (Fast Fourier Transform) program. The FTIR instruments take hardly 0.2 to 0.3 sec to get the spectrum [7, 8].

In the present studies, the thin film metal oxides were characterized by Perkin Elmer FTIR spectrometer and the photograph of the instrument is shown in Fig. 3.4.

3.8.3. Scanning electron microscopy studies

Scanning electron microscopy is used primarily for the study of surface topography of solid material. Scanning electron microscope permits a depth of field for greater than optical or transmission electron microscopy. The resolution of the scanning electron microscope is about 3 nm, approximately two orders of magnitude greater than the optical microscope and one order of magnitude less than the transmission electron microscope. Thus, the SEM bridges the gap between these two techniques [9, 10].

An electron beam passing through an evacuated column is focused by electromagnetic lenses onto the specimen surface. The beam is then projected over the specimen in synchronism with the beam of a cathode ray tube (CRT) display

screen. In elastically scattered secondary electrons are emitted from the sample surface and collected by a scintillator. In this way the secondary electron emission from the sample is used to form an image on the CRT display screen. Differences in secondary emission result from changes in surface topography. If elastically back scattered electrons are collected to form the image, contrast results from the compositional differences. Cameras are provided to record the images on the display screen.

The scanning electron microscope permits not only observation of very fine details (high resolution) but also good focus over a wide range of specimen surfaces (large depth of field). If an element of the specimen has a low atomic number, the incident electrons will show a tear- drop shaped diffusion, while if the element has a high atomic number, the incident electrons will show a hemispheric diffusion. Higher accelerating voltages expand the diffusion area much deeper. In the course of diffusion, the incident electrons gradually lose their energy until absorbed by the specimen (detected as absorbed current). In this process, low energy secondary electrons are reflected outside the specimen, with loosing much of their energy.

In addition, the Auger effect causes Auger elements very near to the specimen surface, when incident electrons collide with constituent atoms of the specimen, most of the electron energy is converted into heat, but a portion of it is consumed to produce X-rays, visible and infrared cathode luminescence together with secondary and Auger electrons. Quanta (Secondary electrons), back scattered electrons, X-rays and so on, carry information which describes the nature of the specimen (its atomic number, elemental distribution, topography, surface potential distribution, magnetic domain, chemical and crystallographic characteristics etc.,).

This information is covered into a video signal and displayed on a CRT as a scanning image

In the present study, surface morphology of the prepared metal oxide thin films were analyzed by JEOL (Model: JSM-840A) - scanning electron microscope as shown in Fig.3.5.

3.8.4. Thin film thickness measurements

The thickness of the thin film deposits was calculated from the weight gain method [11]. The substrate was cleaned thoroughly, dried and its initial weight was measured before deposition. After carrying out the deposition, the weight gain was measured.

$$t = \frac{\Delta_m}{\rho_{B.A}}$$

Where, t = thickness of the film, Δ_m = m_2 - m_1 = mass of the deposited film, m_2 = mass of the substrate after deposition, m_1 = mass of the substrate before deposition, ρ_B = bulk density of thin film material and A= area of the film.

3.8.5. Nature of thin films

Generally the film nature is determined by hot probe method. N-type and P-type semiconductors differ by the nature of the majority carriers. For the former electrons, and for the latter holes as the majority carriers. Therefore, if a technique is developed to measure the direction of electron flow with a semiconductor in an electric circuit, it may be possible to determine the nature of the semiconductor that is called the hot probe technique as shown in Fig.3.6 [12].

The semiconductor thin film is placed on a metal plate and a metal heater tip (normally a soldering iron) was connected to the metal base through a multimeter.
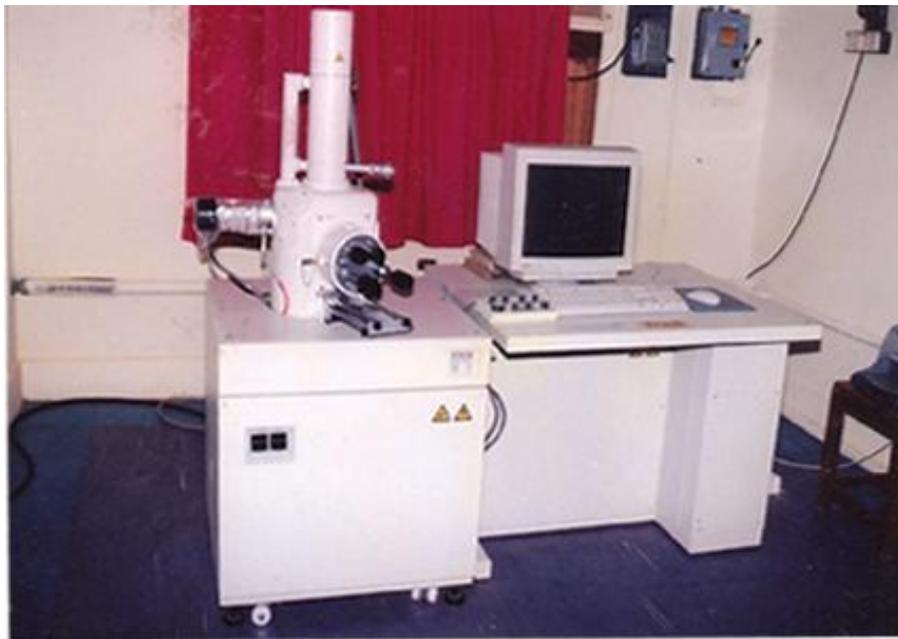
Fig.3.4 Photograph of FTIR Spectroscopy

Fig.3.5 Photograph of Scanning Electron Microscope

One end of the metal base, which is connected to the multimeter was called the cold junction and the hot tip is hot junction. When the hot probe is touched over the semiconductor thin film, current flows from the cold junction to the hot junction for n-type semiconductor and the reverse for p-type semiconductor. The deposited thin films were evaluated by this technique to find out the nature of the semiconductors.

3.8.6. Electrical resistivity measurements [13, 14]

The electrical resistivity of the thin film was measured with a Keithley ohmmeter after making two ohmic contacts with silver paint (Demetron) at 30 ^{o}C. Resistivity is a measure of how strong a material opposes the flow of electric current. A low resistivity indicates a material readily allows the movement of electric charge. This is also known as specific electrical resistance. The S.I. unit of electrical resistivity is ohm meter. The electrical resistivity "ρ" of a material is usually defined as;

$$\rho = \frac{R A}{L}$$

Where, ρ is the static resistivity (ohm meter), R is the electrical resistance of a uniform specimen of a material (ohm), L is the length of the specimen (meter), A is the cross sectional area of the specimen (square meter).

In general, electrical resistivity of metal increases with temperature, while the resistivity of semiconductor decreases with increasing of temperature. At high temperatures, the resistance of a metal increases linearly with temperature. The resistivity of the semiconductor films is very sensitive to deposition conditions, nature of the substrates and the temperature of the substrate at which thin films are prepared.
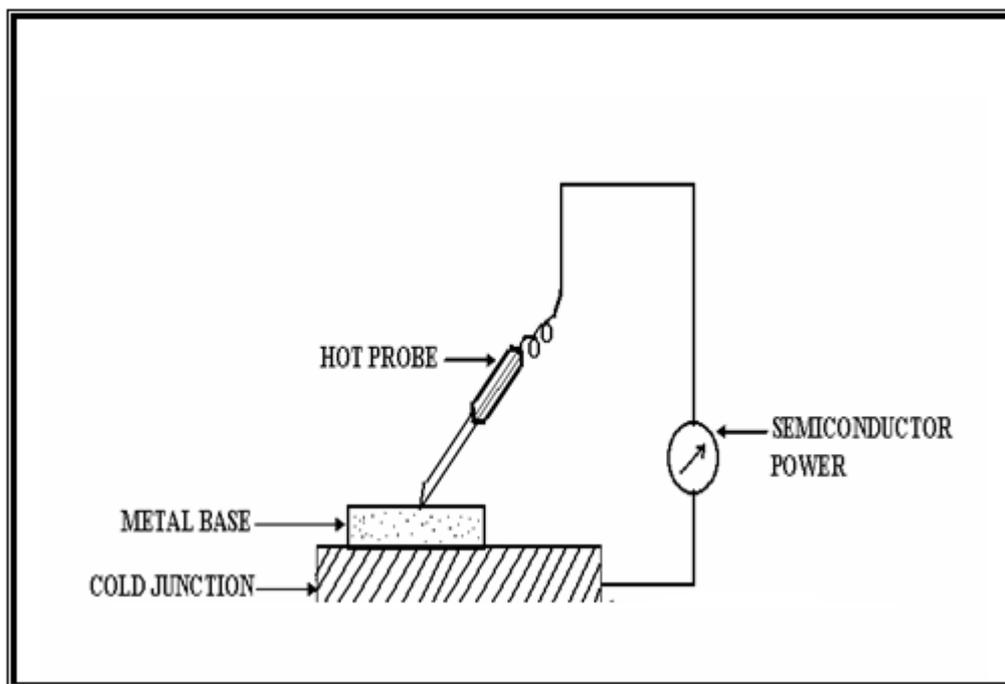
Fig.3.6 Schematic representation of hot probe meter

Resistivity measurements of semiconductor materials are geometry dependent and quite sensitive to boundary conditions. Many correct ion factors have been calculated and were used in resistivity measurements. Most semiconducting materials have high temperature coefficient of resistivity. For precise measurements, corrections should be made. Temperature coefficient of resistivity changes appreciably with impurity concentration. In the semiconductor industry, the most generally used technique for the measurement of resistivity is the four-point probe method.

In this method, four point probe set in a line are placed on the sample. The usual geometry is to place the probes in a line and use equal probe spacing. A constant current is passed through the "outer" two probes with the help of a power supply and the potential developed across the "inner" two probes is measured using a sensitive digital voltmeter. The resistivity of an infinitely large sample can be determined by the following relation:

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

Where,

ρ = resistivity in ohm.cm

V = floating potential difference between the inner probes, in volts.

I = current through the outer probes, in ampheres.

S = distance between the probes in centimeters.

When the probes are set equidistant i.e., when $S_1 = S_2 = S_3$

$$\rho = \frac{V}{I}\ 2\pi S$$

This equation holds good for samples whose thicknesses are in the range of 0.635 cm. Alternately the probe spacing can be 0.159 cm, so that $2\pi S$ is equal to 1. In such case ρ is given numerically by V / I.

In the present study, four probe resistivity measurement was made using an OSAW AC – DC Four Probe Unit (Model A-4) in conjunction with a UNI – INSTA DC Power supply. The voltage and current were measured using a HIL-2161 Digital multimeter and a Philips (PM 2524) Automatic digital VAΩ meter, respectively [Fig.3.7].

3.8.7. Optical studies

The nature of the material that absorbs the light of a particular wavelength is termed as absorption. The intrinsic absorption in a semiconductor occurs in the vicinity of its energy band gap. The absorbed light in an absorbing medium obeys the Lamberts law given as

$$\mathbf{T = T_o\ e^{-\alpha t}}$$

Where, α is the absorption coefficient, T is the instantaneous transmission, T_o is the transmission at time t = 0 and t is the thickness of the medium. In this, electron transitions occur from the upper part of the valence band to the lower part of the conduction band. Electronic transitions can be "directed" that is without interaction with the phonon as well as crystal momentum of the electron. Similarly, electron transitions can be in "directed" in which change in the crystal momentum of the electron due to interaction with the phonon takes place.
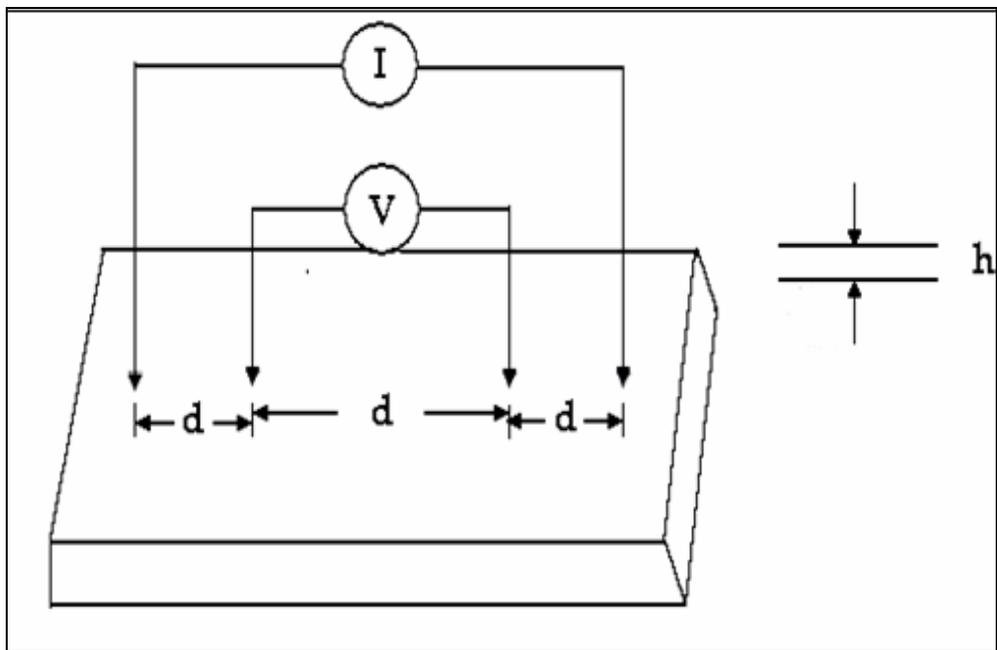
Fig.3.7 Schematic representation of four probe resistivity meter

When a light falls on a material, it experiences three kinds of effects namely the absorption, transmission and reflection. Generally, light interacts with a semiconductor by electron transitions and atomic vibrations. Based on these three phenomena, many parameters that are useful in thin film deposition were studied. UV-VIS spectrophotometer was used for optical characterization.

The ability of the material to transmit the light is measured by spectrometer as transmission. The superior optical transmission of the thin film was due to high mobility of the charge carriers and the reduction of free carrier absorption [15]. Light trapping or confinement effect of semiconductor thin film is a very important property to obtain high collection of incident photons in optoelectronic devices especially in solar cells.

Band gap or Energy gap (E_g) between the valence and conduction bands plays an important role in semiconductor material processing. For direct transitions, the optical energy gap or band gap as a function of incident photon energy is given by as;

$$\alpha h\nu \propto (h\nu - E_g)^{1/2}$$

Similarly for indirect transitions, the optical band gap as a function of incident photon energy is defined as;

$$\alpha h\nu \propto (h\nu - E_g)^2$$

Materials having direct transitions are known as direct band gap materials. Similarly materials having indirect transitions are known as indirect band gap materials. Band gap was calculated by using "tauc plot" drawn between $(\alpha h\nu)^2$ and $h\nu$ for direct band gap materials, that is when the linear portion of the graph in the typical plot of

$(\alpha h \nu)^2$ versus $h \nu$ is extrapolated to zero, and the Intercept of " $h \nu$ " axis gives the optical band gap (E_g).

The optical band gap widening or shrinkage are generally attributed to Moss-Burstein shift. The optical band gap widening is due to the optical band filling effect. The optical shrinkage is due to electron – electron interaction and high carrier concentration.

3.8.8. Optical band gap determination

Development of semiconductors with controllable energy gap is necessary for the increased applications of alloys in the solar cell fabrication and other opto-electronic devices. The optical properties of thin films are of much interest due to their alloying nature. Hence, the absorption and transmission properties were studied using spectrophotometer to calculate their band gap variations. The basic principle of the method is given here: Since the generation of both free electrons and free holes is essential to produce a photovoltaic current, intrinsic optical absorption of a single photon across the band gap of the semiconductor is the dominant optical absorption process in a solar cell. Extrinsic absorption by deep, localized states in the band gap may act to affect charge transport (e.g. by charging states to change a junction profile or emptying traps), but it produces negligible net current, since the absorption coefficient associated with extrinsic absorption are many order of magnitude smaller than those of intrinsic process [16, 17].

There are two major types of intrinsic absorption processes involved in determining and they are called direct and indirect absorption. It is a first-order process involving only the absorbed photon and can be represented approximately as a vertical line on energy versus wave vector plot. The absorption transition conserves energy so that $\Delta E = h \nu$ (where $h \nu$ is the proton energy) and there is no

change in initial and final states except for the small momental of the photon. The expected variation of α with photon energy near the minimum energy for absorption, E^d_g is given by

$$\alpha = k(E - E^d_g)^n$$

Where, k is essentially a constant, E is photon energy, E^d_g is the direct band gap and n is a constant which have assigned values, 1/2, 3/2 and 2 for allowed direct transition, forbidden direct transition and allowed indirect transition, respectively.

A plot of $(\alpha h\nu)^2$ as a function of $h\nu$ yields a straight line for a direct absorption, with an intercept on the photon energy axis equal to the direct band gap of the material. At the onset of a direct optical absorption, the absorption coefficient, α increases rapidly with increasing photon energy to values in the range of 10^4 - 10^6 cm^{-1}. For higher photon energies, the absorption coefficient, α remains high and varies only slightly with photon energy depending on transitions to states well above the bottom of the conduction band or to the higher lying bands.

In the present study, optical absorption spectrum of thin film semiconductors were obtained using UV-VIS-NIR spectrophotometer (Hitachi, Model: U3400) in the wavelength range of 400-1000 cm^{-1} in order to determine the band gap of the prepared thin films.

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