

Physics Practical Experiment Manual
B.Sc. VI Semester (Electronics)
Lab Name-Semiconductor Materials lab
List of experiments:



- 1. To measure the resistivity of semiconductor crystal with temperature by four -probe method.**
- 2. To determine the Energy Band gap (E_g) of silicon Crystal using energy band gap measurement setup.**
- 3. To determine the type (n or p) and mobility of semiconductor material using Hall-Effect System.**
- 4. To Characterize the optical characteristics using UV-VIS Spectrometer.**
- 5. To find out the chemical bond present in deposited thin films using FTIR.**
- 6. To Synthesize the Thin Films using Sol-Gel Spin Coating system.**
- 7. To Synthesize the Thin Films using Chemical Route Synthesis method.**
- 8. To Deposit the Thin Films of Conductors using CVD System.**

Four Probe Method

Aim:

Study the temperature dependence of resistivity of a semiconductor (Four probe method) and to determine band gap of experimental material (Ge).

Apparatus Required:

Four probe apparatus, sample (a Ge crystal in form of a chip), oven, thermometer (260°) constant power supply, oven power supply, panel meters for measurement of current and voltage.

Formula Used : Resistivity of a semiconductor is

$$\rho = A \exp\left(\frac{E_g}{2k_B T}\right)$$

Where E_g is Band Gap in eV

k_B is Boltzman constant = 8.617×10^{-5} eVK⁻¹

and T is absolute Temperature

Principle :

Ohm's law: If physical conditions (like temperature, mechanical stress) remains unchanged, then potential difference across two ends of a conductor is proportional to current flowing through it

$$V \propto I$$

$$V = IR$$

The constant of proportionality, R, is called resistance of the conductor.

Resistivity: At a constant temperature, the resistance, R, of a conductor is (i) proportional to its length and (ii) inversely proportional to its area of cross-section,

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

The constant of proportionality, ρ , is called resistivity of material of the conductor. Resistivity of a material is equal to the resistance offered by a wire of this material of unit length and unit cross-sectional area. Unit of resistance is ohm (Ω), and unit of resistivity is ohm-meter ($\Omega\text{-m}$)

Four probe method: The 4-point probe set up (Fig.I & Fig.II) consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements. A high impedance current source is used to supply current through the outer two probes, a voltmeter measures the voltage across the inner two probes to determine the sample resistivity. Typical probe spacing ~ 2 mm. These inner probes draw no current because of the high input impedance voltmeter in the circuit. Thus unwanted voltage drop ($I R$ drop) at point B and point C caused by contact resistance between probes and the sample is eliminated from the potential measurements. Since these

contact resistances are very sensitive to pressure and to surface condition (such as oxidation of either surface).

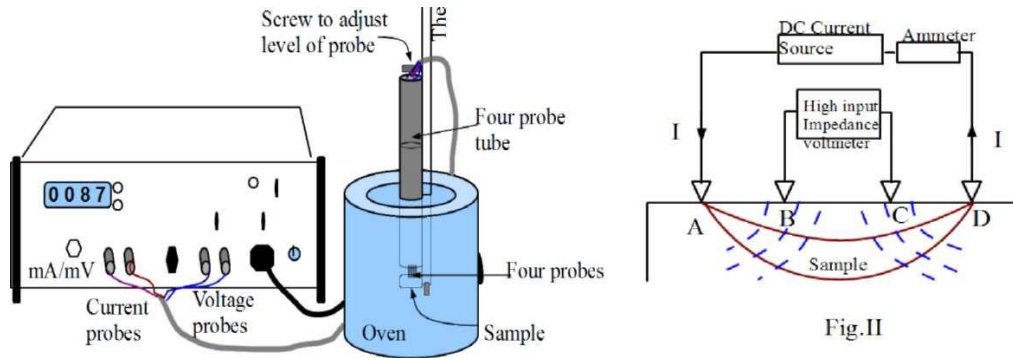


Fig.I Schematic diagram of a Four Probe

Resistivity of Germanium (semiconductor) crystals or slices:

In order to use this four probe method in germanium crystals or slices it is necessary to assume that: The resistivity of the material is uniform in the area of measurement and a non conducting boundary is produced when the surface of the crystal is in contact with an insulator. The derivation of equations given below are involved. For each case it is assumed that the probes are equally spaced (spacing =s).

Case I: Resistivity Measurements on a Large Sample:

We assume that the metal tip is infinitesimal and sample are semi infinite in lateral dimensions. For bulk samples where the sample thickness, $W \gg S$, the probe spacing, we assume a spherical protrusion of current emanating from the outer probe tips. The resistivity is computed to be

$$\rho_o = \left(\frac{V}{I}\right) * 2\pi s$$

where

V = floating potential difference between the inner probes, unit: volt

I =current through the outer pair of probes, unit: ampere

s = spacing between point probes, unit: meter

ρ_o = resistivity, unit: ohm meter

Case II: Resistivity Measurements on a Thin Slice-Nonconducting Bottom Surface:

For the case of a nonconducting bottom on a slice the resistivity is computed from

$$\rho = \frac{\rho_o}{G_7\left(\frac{W}{S}\right)}$$

$G_7\left(\frac{W}{S}\right)$ can be calculated from graph (1) or from Table (1) given below or using formula

$$G_7(w/s) = \frac{2s}{w} \log_e 2$$

Table 1

| S.No. | W/S | G ₇ (W/S) | S.No. | W/S | G ₇ (W/S) |
|-------|-------|----------------------|-------|-------|----------------------|
| 1. | 0.100 | 13.863 | 6. | 1.000 | 1.504 |
| 2. | 0.141 | 9.704 | 7. | 1.414 | 1.223 |
| 3. | 0.200 | 9.631 | 8. | 2.000 | 1.094 |
| 4. | 0.330 | 4.159 | 9. | 3.333 | 1.0228 |
| 5. | 0.500 | 2.780 | 10. | 5.000 | 1.0070 |

Temperature dependence of resistivity of a semiconductor:

Intrinsic semi-conduction The process in which thermally or optically excited electrons contribute to the conduction is called intrinsic semi-conduction. In the absence of photonic excitation, intrinsic semi-conduction takes place at temperatures above 0 K as sufficient thermal agitation is required to transfer electrons from the valence band to the conduction band. Conductivity for intrinsic semi-conduction. The total electrical conductivity is the sum of the conductivities of the valence and conduction band carriers, which are holes and electrons, respectively. It can be expressed as

$$\sigma = e(n_e\mu_e + n_h\mu_h) \tag{1}$$

where n_e, μ_e are the electron's concentration and mobility,
and n_h, μ_h are the hole's concentration and mobility, respectively.

Drift mobility determines the average drift velocity in the presence of an applied external field. It also depends on the temperature. The mobility is a quantity that directly relates the drift velocity v_d of charge carriers to the applied electric field E across the material, i.e.,

$$\mu = v_d / E \dots\dots\dots \tag{2}$$

In the intrinsic region the number of electrons is equal to the number of holes, $n_e=n_h=n_i$, so Equation (1) implies that,

$$\sigma = en_i (\mu_e + \mu_h) \tag{3}$$

The electron density (electrons/volume) in the conduction band is obtained by integrating (density of states x probability of occupancy of states) from the bottom to top of the conduction band. The detailed calculations reveal that

$$n_i = NT^{\frac{3}{2}} \exp\left(-\frac{E_g}{2k_B T}\right) \tag{4}$$

Where N is a constant substituting n_i in eq (3)

$$\sigma = e (\mu_e + \mu_h) NT^{\frac{3}{2}} \exp\left(-\frac{E_g}{2k_B T}\right) \tag{5}$$

This shows that conductivity depends on temperature it decreases exponentially with decrease in temperature.

Temperature dependence of resistivity

$$\rho = \frac{\exp\left(\frac{E_g}{2k_B T}\right)}{e (\mu_e + \mu_h) NT^{\frac{3}{2}}} \tag{6}$$

Or,

$$\rho = A \exp\left(\frac{E_g}{2k_B T}\right) \quad (7)$$

Where A is a constant Taking Log

$$\ln \rho = \ln A + \frac{E_g}{2k_B T} \quad (8)$$

or

$$\log \rho = C + \frac{1}{2.3026} * \frac{E_g}{2k_B T} \quad (9)$$

where C is a constant . Rewriting eq (9)

$$\log \rho = C + \frac{1}{2.3026 * 10^3} * \left(\frac{E_g}{2k_B}\right) \left(\frac{1000}{T}\right).$$

Therefore, if a graph is plotted $\log \rho$ vs $\left(\frac{1000}{T}\right)$ it should be a straight line and band gap E_g can be determined from its slope as follows :

1. Slope = $\frac{AC}{BC} = \frac{1}{2.3026 * 10^3} * \frac{E_g}{2k_B}$,
2. Band gap $E_g = 2.3026 * 10^3 * 2 * k_B * \text{slope}$ eV, (Take Boltzman constant $k_B = 8.617 * 10^{-5}$ eVK⁻¹).

Method :

- (1) The setting of 4-point probes on the semiconductor chip is a delicate process. So first understand well the working of the apparatus. The semiconductor chip and probe set is costly.
- (2) Note the values of probe spacing (S) and the thickness (W) of the semiconductor chip. Note the type of semiconductor (germanium or something else).
- (3) Make the circuit as shown in Fig.1. Put the sample in the oven (normally already placed by lab instructor) at room temperature.
- (4) Pass a milliampere range current (say 5 mA) in the sample using constant current power supply.
- (5) The reading of the current through the sample is measured using milliammeter provided for this purpose. The voltage is measured by a high impedance milli voltmeter connected to the inner probes. The readings can be taken alternately on digital meter provided for this purpose.
- (6) Note temperature of sample (oven) using thermometer inserted in the oven for this purpose.
- (7) The oven temperature is increased a little, and its temperature noted after reaching steady state. Again the constant current reading (advised to be kept the same) and the corresponding voltage readings are taken.

(8) Repeat the procedure for different temperatures. Note the data in the observation table.

(9) For each temperature, calculate the resistivity by using the relation.

$$\rho = \frac{\rho_0}{G_7 \left(\frac{W}{S}\right)} = \left(\frac{V}{I}\right) \left(\frac{2\pi S}{G_7 \left(\frac{W}{S}\right)}\right)$$

(10) Compute $\log \rho$ and $10^3 / T$ and write it in the observation table.

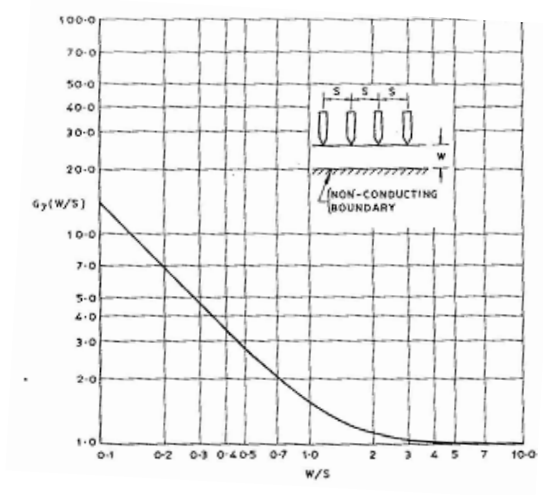
(11) Plot a graph between $\log \rho$ and $10^3 / T$. It is a straight line. Find its slope.

(12) Calculate the band gap using formula

$$E_g = 2.3026 \cdot 10^3 \cdot 2 \cdot k_B \cdot \text{slope eV}$$

Use Boltzman constant $k_B = 8.617 \cdot 10^{-5} \text{ eVK}^{-1}$

($k_B = 1.3806 \cdot 10^{-23} \text{ JK}^{-1}$ and $1\text{eV} = 1.6 \cdot 10^{-19} \text{ J}$)



Graph 1

Observations:

1. Semiconductor chip material = Germanium
2. Spacing (distance) between the probes, $s = 2.0 \text{ mm} = \dots\dots\dots \text{ m}$.
3. Thickness of the sample, $w = 0.5 \text{ mm} = \dots\dots\dots \text{ m}$.

Table : Voltage across the inner probes for a constant current at different sample temperatures

Current (I) =mA

| S.No. | Temperature T (K) | Voltage across inner probes (mV) | $\frac{1000}{T} K^{-1}$ (calculated) | Resistivity $\rho = \left(\frac{V}{I}\right) \left(\frac{2\pi S}{G_7\left(\frac{W}{S}\right)}\right)$ (ohm-cm) | Log ρ (calculated) |
|-------|---------------------|----------------------------------|--------------------------------------|--|-------------------------|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| .. | | | | | |
| .. | | | | | |

Calculations:

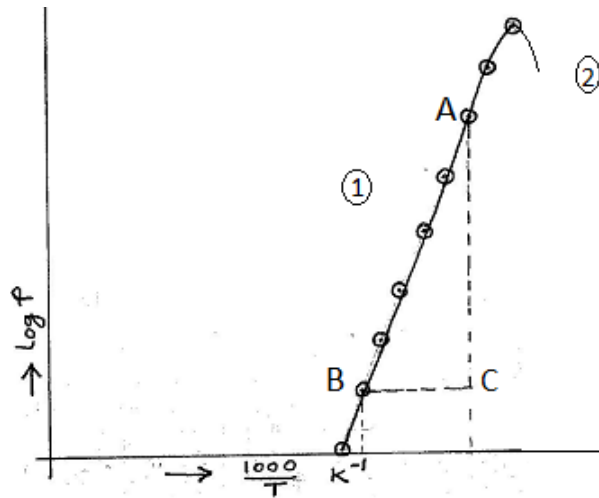
- For the given sample $\left(\frac{W}{S}\right) = \dots\dots\dots$
- The correction factor $G_7(w/s) =$ (from table 1 or graph 1) or calculate $G_7(W/S)$ as follows:

$$G_7(w/s) = \frac{2 * s}{w} \ln 2$$

- Calculation of $T (K^{-1})$, ρ (ohm-m) and $\log \rho$

$$\rho = \frac{\rho_0}{G_7\left(\frac{W}{S}\right)} = \left(\frac{V}{I}\right) \left(\frac{2\pi S}{G_7\left(\frac{W}{S}\right)}\right)$$

- The graph between $\frac{1000}{T}$ and $\log \rho$ is plotted as shown in graph (2)
- Slope of the straight line is $\frac{AC}{BC}$
- Energy band gap $E_g = 2.3026 * 2 * k_B * \text{slope} * 10^3$ (in eV)



Graph 2 Variation of $\log \rho$ with $\frac{1000}{T}$

Explanation of Graph-2

The resistivity of a Germanium crystal as a function of inverse temperature. For this sample when $T < T' \text{ } ^\circ\text{K}$ i.e. region (2), conduction is mainly due to the impurity carriers (extrinsic region). For $T > T' \text{ } ^\circ\text{K}$ conduction is due to electrons transferred to the conduction band and the corresponding holes created in the valence band (this is the intrinsic region).

Result:

1. The temperature dependence of the resistivity of semiconductor (germanium) chip is as shown in the graph (2). The resistivity decreases exponentially with the increase in T . That is as at low temperatures resistivity is more and at high temperatures the resistivity is less.
2. The energy band gap for the given semiconductor (germanium) is =eV.

Precautions:

1. The surface of the semiconductor should be flat.
2. All the four probes should be collinear.
3. The adjustment of 4-point probes should be done gently, as the semiconductor chip is brittle.
4. The voltage should be measured using inner probes only using a high impedance millivoltmeter.
5. Temperature of the oven should not exceed the limits set by manufacturer of the probes and chip.

ENERGY GAP OF SEMICONDUCTOR

Aim: To determine the Energy gap of the semiconductor (Thermistor)

Apparatus: Thermistor, power supply, resistor, voltmeter and milli-ammeter.

Formula:

$$E_g = \frac{2.303 \times 2K \times S}{1.601 \times 10^{-19}} \text{ eV}$$

where, E_g = Energy gap of given semiconductor, eV

K = Boltzman's constant, $1.38 \times 10^{-23} \text{ Jk}^{-1}$

S = Slope of the graph

Procedure: An Ohmmeter is connected across the thermistor (Red to Red & Black to Black) and the resistance of the thermistor at the room temperature is noted. Then the thermistor is immersed in oil bath and heated to a temperature of 95°C . Then while cooling the resistance of the thermistor is noted from Ohmmeter for different temperatures starting from 90°C till 50°C for every 5°C reduction in temperature. The readings are tabulated. A plot of $\text{Log } R$ versus $1/T$ is made. Slope (S) of the curve is determined. The energy gap of the given semiconductor is calculated using the formula.

$$E_g = \frac{2.303 \times 2K \times S}{1.601 \times 10^{-19}} \text{ eV}$$

[**Note:** Thermistors are made of semiconductors. The variation of resistance (R) of a thermistor with temperature (T) is given by

$$R = R_0 e^{\frac{E_g}{2KT}} \quad \text{Taking Log}_{10} \text{ on both the sides} \quad \left(R = R_0 \exp \left[\frac{E_g}{2KT} \right] \right)$$

$$\text{Log } R = \text{Log } R_0 + \frac{E_g}{2KT} \quad \text{Log } e^{\frac{E_g}{2KT}} \quad \ln R = \ln R_0 + \frac{E_g}{2KT}$$

A plot of $\text{Log } R$ versus $1/T$ must be a straight line with slope.

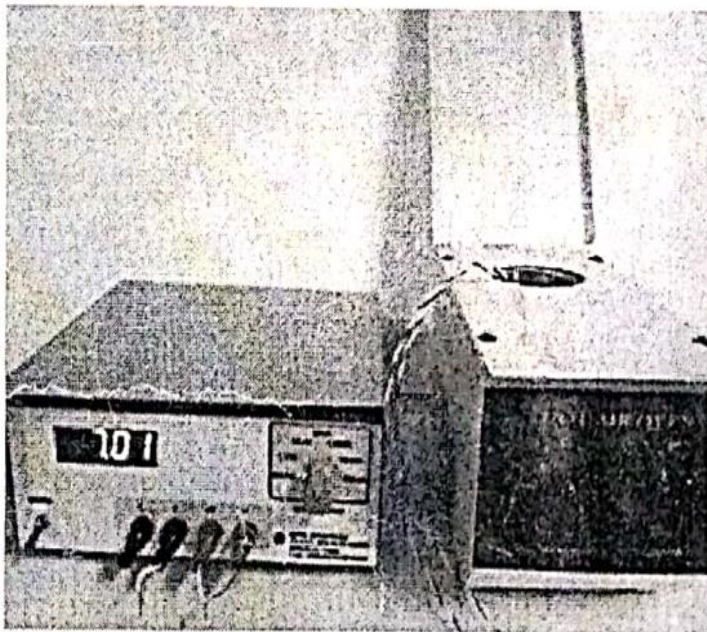
$$S = \frac{E_g}{2K} \text{Log } e$$

$$E_g = \frac{2KS}{\text{Log } e} = 2.303 \times 2KS \text{ J}$$

$$E_g = \frac{2KS}{\text{Log } e} = \frac{2.303 \times 2KS}{1.601 \times 10^{-19}} \text{ eV}$$

Procedure:

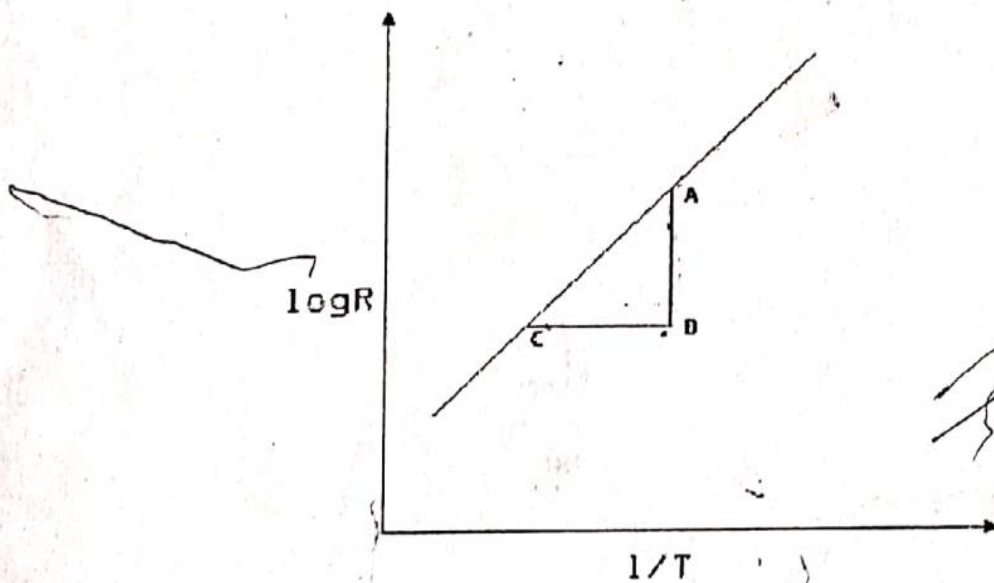
1. Connect the thermister to the main unit (Red connector to red connector and black connector to black connector). Keep the selector knob at suitable range.
2. Place the thermistor into the beaker having silicon oil and put it into the Hot Air Oven with thermometer. Keep Energy Control knob of oven at 80.



3. Switch ON the heater and heat it upto 90 deg C and switch off the heater.
4. Now allow the temperature to cool down and tabulate the resistance at different temperature as shown below:

| Sl No | Temp(°C) | Temp (K) | Resistance (in Ω) | Log R | 1/T (K ⁻¹) |
|-------|-----------|----------|-------------------|-------|------------------------|
| 1 | 90 | | | | |
| 2 | 85 | | | | |
| 3 | 80 | | | | |
| 4 | 75 | | | | |
| 5 | 70 | | | | |
| 6 | 65 | | | | |
| 7 | 60 | | | | |

5. Plot the Graph between Log R and 1/T. It will be a straight line. Calculate the slope from the graph



Boltzman Constant $k=1.38 \times 10^{-23} \text{ JK}^{-1}$

6. Calculate energy gap using relation

$$E_g = \frac{2.303 \times 2k \times S}{1.601 \times 10^{-19}} \text{ eV}$$

Result: Energy gap of the material given semiconductor is, $E_g = \dots\dots\dots \text{eV}$

DETERMINATION OF HALL COEFFICIENT BY USING HALL APPARATUS

Requisites

| | |
|--|--------------------------------|
| Hall Probe (Ge crystal & InAs Crystal) | Hall effect setup (Digital) |
| Electromagnet | Constant current power supply. |
| Digital Gaussmeter. | |

Theory

When an electrical current passes through a sample placed in a magnetic field, a voltage develops across the sample in a direction perpendicular to both the current and the magnetic field. This is known as Hall effect. The basic experimental setup for study of Hall effect is shown in Fig. 9.1. A rectangular slab of a semiconducting sample with its *width* (w) along y -direction and *thickness* (d) along z -direction is placed in a magnetic field of strength B directed along the z -direction. Now an electric current, I_H is made to pass through the sample along its length by maintaining a potential difference along x -direction. The corresponding current density is,

$$J_x = \frac{I_H}{wd} \quad (1)$$

Suppose that the charge carriers are positive, each having charge $+q$, and are moving along $+x$ direction with velocity \vec{v} . Then the Lorentz force experienced by the carriers due to themagnetic field is,

$$\vec{F}_B = q(\vec{v} \times \vec{B}) = -(qvB)\hat{y} \quad (2)$$

This force \vec{F}_B along $-\hat{y}$ direction deflects the positive charge carriers towards the *bottom surface* of the sample. This makes the *bottom surface* positively charged while leaving the *top surface* negatively charged. This

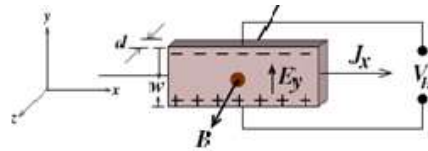


Fig. 9.1

accumulation of charges near the bottom and top surfaces of the sample leads to the development of a transverse electric field $\vec{E} = E_y\hat{y}$ along the y -direction. Force due to this electric field, $q\vec{E}$ opposed the Lorentz force \vec{F}_B and prevents further charge accumulation. In the steady state condition, these two forces balance out each other and we get,

$$qE_y = qvB \quad (3)$$

Now we define a quantity called *Hall coefficient* R_H , as the ratio of the electric field E_y to the current density J_x multiplied by magnetic field B , that is

$$R_H = \frac{E_y}{J_x B} = \frac{1}{nq} \quad (4)$$

where we have used Eq. (3) and the fact that $J_x = nqv$, n being the number density (m^{-3}) of charge carriers. In order to determine R_H , we proceed as follows. Writing $v = J_x/nq$ and multiplying both sides of Eq. (3) by wd , we get

$$E_y wd = \frac{J_x wd B}{nq} \quad (5)$$

But $E_w = V_H$, the voltage across the top and bottom surfaces called the Hall voltage and $J_x w d = I_H$. This gives,

$$V_H = \left(\frac{R_H B}{d}\right) I_H \quad (6)$$

Therefore, if we measure the Hall voltage V_H against Hall current I_H for a fixed magnetic field B and plot V_H versus I_H , the curve will be a straight line with the slope m being,

$$m = \frac{R_H B}{d} \quad (7)$$

The Hall coefficient R_H can be calculated from the value of this slope, m if the thickness d of the sample is known. Once R_H is determined, the carrier density n can be calculated using Eq. (4). Now assume the situation where the charge carriers are negative with $q = -e$. In that case, for current direction along $+x$, the charges will be moving with velocity $\vec{v} = -v\hat{x}$. The Lorentz force, $\vec{F}_B = q(\vec{v} \times \vec{B}) = -(evB)y\hat{y}$ will still be along negative y direction as before. However this time, the bottom surface acquires negative polarity and consequently, the sign of the Hall voltage V_H will be opposite to what was observed in case of positive charge. Thus for given directions of the Hall current and the magnetic field, we can determine the type of charge carriers (whether +ve or -ve) by looking at the sign of the Hall voltage V_H .

Description of apparatus

The experimental setup is complete unit (Fig. 9.2) consisting of the followings - an electromagnet, constant current power supply, a Gauss and Tesla meter, a Hall current & voltage measurement unit and the sample connected with contact leads for passing Hall current and measuring Hall voltage.

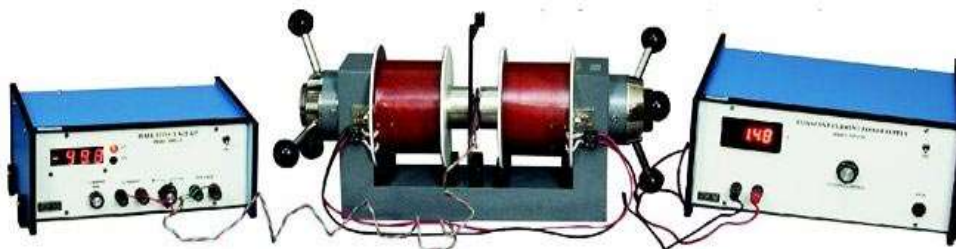


Fig. 9.2. Hall effect set-up

Experimental procedure:

1. Connect the width wise contacts of the Hall probe to the terminals marked 'voltage' and Length wise contacts to terminals marked 'current'.
2. Switch 'ON' the Hall effect setup and adjustment current (say few mA).
3. Switch over the display to voltage side. There may be some voltage reading even outside the magnetic field. This is due to imperfect alignment of the four contacts of the Hall probe and is generally known as the 'Zero field potential'. In case its value is comparable to the Hall voltage it should be adjusted to a minimum possible (for Hall probe (Ge) only). In all cases the error should be subtracted from the Hall voltage reading.
4. Switch on the constant current power supply at any desired value.

5. Measure the magnetic field between the pole pieces of the electromagnet using digital Gaussmeter and also measure the distance between two pole pieces.
6. The Hall probe is placed in between the pole pieces of the electromagnet as shown in Fig. 9.2 and rotate the Hall probe till it becomes perpendicular to the magnetic field so that the Hall voltage will be minimum in this adjustment.
7. Measure the Hall voltage as a function of current in the Hall effect setup keeping the magnetic field constant and plot a graph.
8. The slopes (V_1 / I_1) & (V_2 / I_2) is to be calculated from the graph.

Determination of Hall Coefficient

The thickness of the semiconductor $d = 0.58\text{mm}$
Constant Power Supply: 1.5 A and 2 A

Data Sheet:

| Sl. No. | Const. Magnetic Field | | Const. Magnetic Field | |
|---------|-------------------------------------|----------------------------|-------------------------------------|----------------------------|
| | $B_1 = \dots\dots\dots\text{Gauss}$ | | $B_2 = \dots\dots\dots\text{Gauss}$ | |
| | Current in mA (I_1) | Voltage in mV (V_1) | Current in mA (I_2) | Voltage in mV (V_2) |
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |
| 9 | | | | |
| 10 | | | | |

Graph: A graph is plotted between Hall current (I) and Hall voltage (V) for two constant magnetic fields.

Calculation :

The value of Hall coefficient is calculated applying the formula $R_H = \frac{V_H d}{IB}$

From graph $\frac{V_1}{I_1} = \dots\dots\dots$ and $\frac{V_2}{I_2} = \dots\dots\dots$

$$R_{H_1} = \frac{V_1 d}{I_1 B_1} =$$

$$R_{H_2} = \frac{V_2 d}{I_2 B_2} =$$

$$R_H = \frac{R_{H_1} + R_{H_2}}{2} =$$

Conclusion

Precautions

1. The current through the sample should not be large enough to cause heating.
2. The pressure contacts should be clean and firm to avoid noise.

UV-Vis Spectroscopy

Aim- To characterize the optical characteristics using UV-VIS Spectrometer.

Apparatus required- cuvette.

Introduction - Ultraviolet-visible (UV-Vis) spectroscopy is mainly used to study the optical properties and to find the optical parameters of any organic and inorganic nano scale molecules. This is based on the principles of electronic transition in between different orbitals of different molecules. When Ultraviolet and Visible range EM waves are incident on any sample then the sample absorbs the energy, which is sufficient to excite the electrons of the molecules to the higher energy orbital and displayed their corresponding peaks as a graph in between intensity vs. wavelength. The intensity of absorption peaks is dependent on the concentration of the sample solution and also the energy gap in between molecular orbitals.

Principle - Ultraviolet-visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet visible spectral region. This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transition. In UV-visible spectroscopy, only the valence electrons absorb the energy and the molecule goes for transition from ground state to excited state. This characteristic absorption depends on the nature of electrons present. The intensity of absorption depends on the concentration and pathlength as given by Beer-Lambert's law.

The types of electrons present in any molecule is classified as :

1. σ electrons: These are present in saturated compounds. Such electrons do not absorb near UV, but absorb vacuum UV radiation ($< 200\text{nm}$).
2. π electrons: These electrons are present in unsaturated compounds contain double or triple bonds like $>C=C<$, $-C=C-$.
3. 'n' electrons: These are non bonded electrons which are not involved in any bonding (eg) lone pair of electrons like in S, O, N & halogens (X).

By the characteristic absorption peaks the nature of the electrons present and hence molecular structure can be elucidated.

It was considered that σ , π , n electrons are present in a molecule and can absorb UV radiation to excite from the ground state by the. The various transitions are $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$. The energy required for excitation for different transitions are: $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$. After absorption of UV radiations these electronic structures have greater or lesser polar character than in ground state. Some of them stays as biradicals or as activated structures. In general, re-distribution of electrons in the molecule may take place, like $>C=O \rightarrow >C^+ - O^-$

→ > Cδ+ — Oδ-. Polar solvents shifts n→ π* and n→σ* to shorter wavelengths and π→ π* to longer wavelengths.

Beer-Lambert's Law: Consider a light beam incident on a material, then it can be scattered, absorbed, or transmitted.

- Transmitted light – Light emerges propagating in the same direction as the incident light.
- Absorbed light – Energy from light is absorbed in the volume of the material.
- Scattered light – Light emerges in a different direction from the incident light.
- Absorption and scattering occur at the molecular and atomic level. For light to be absorbed, its energy must equal or more than available energy states in the atoms or molecules, or it can be scattered from the molecule, atom, or electrons, (like billiard balls).
- Light incident upon a material may or may not be removed from the incident beam
- Probability that the light is removed from the incident beam is related to the cross section, σ. Cross section σ is like an effective area of the atom or molecule. σ can be larger or smaller than the geometric cross section. σ takes into account the absorption and scattering of light.
- **There are two laws related to the absorption of radiation:**
 1. Beer's law related to concentration of absorbing species. And
 2. Lambert's law related to thickness or path length of absorbing species.

Two laws are applicable under the condition: $I_0 = I_a + I_t$

Where I_0 = Intensity of incident light, I_a = Intensity of absorbed light and I_t = Intensity of transmitted light; considering no reflection or scattering of light takes place.

- Consider light incident on a material with area A and thickness dx and concentration of molecules C.
- Number of molecules illuminated by light of incident intensity I is CA dx.
- Total “effective” area that the molecules present is σCA dx.
- Probability of light being absorbed or scattered out of the beam in thickness dx is:

$$- dI/I = \sigma C A dx / A;$$

where dI is the change in intensity across dx.

We have $- dI/I = \sigma C A dx / A;$ integrating both sides we get

$$\int_{I_0}^I - dI/I = \int_0^x \sigma C dx$$

$$\ln I - \ln I_0 = \ln\left(\frac{I}{I_0}\right) = -\sigma Cx$$

$$I = I_0 e^{-\sigma Cx} = I_0 e^{-\mu x}$$

The coefficient $\mu = \sigma C$ is the linear attenuation coefficient. If we ignore scattering, we can equate the linear attenuation coefficient with the linear absorption coefficient. Linear attenuation coefficient μ usually expressed in units of cm^{-1} .

Thus the **Beer's law** states that "the intensity of a beam of monochromatic light decreases exponentially with increase in the concentration of absorbing species".

And **Lambert's Law** states that "the rate of decrease of intensity with the thickness of the medium is directly proportional to the intensity of incident light".

μ is a function of wavelength, $\mu = \mu(\lambda)$. So Beer-Lambert's Law is also a function of λ , i.e.

$$I(\lambda) = I_0(\lambda) e^{-\mu(\lambda)x}$$

- **Transmittance** is defined as $T = I(\lambda) / I_0(\lambda)$.
- A quantity called **Absorbance**; $\alpha = \log(1/T) = \log [I_0(\lambda) / I(\lambda)] = \log [e^{\mu x}] = 0.434\mu x$.
- A further definition is the **molecular extinction coefficient**; $\epsilon = 0.434\sigma$.

$$\text{So } \alpha = \epsilon Cx$$

- Absorbance is useful since it can be summed for layers of different materials, each with their own x , C , σ , etc. is given by;

$$\begin{aligned} \alpha_{\text{tot}} &= \alpha_1 + \alpha_2 + \alpha_3 + \dots \\ &= \epsilon_1 C_1 x_1 + \epsilon_2 C_2 x_2 + \epsilon_3 C_3 x_3 \dots \end{aligned}$$

- A specialized device to measure the intensity of light as a function of wavelength is the spectrophotometer. Come in various varieties.

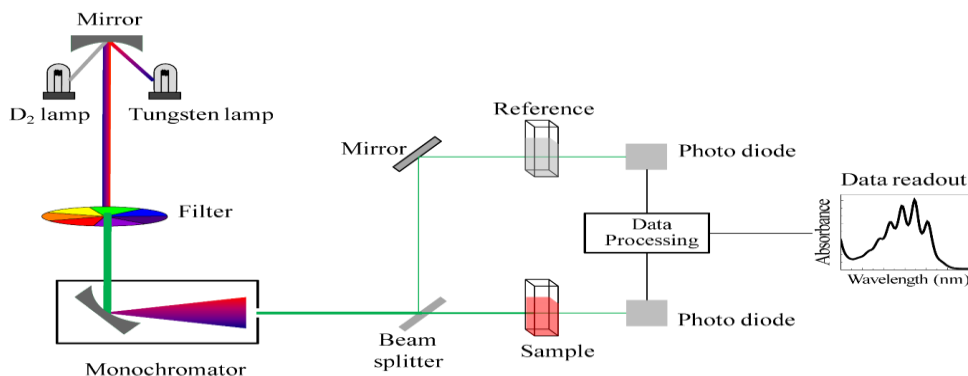


Figure : UV-Vis spectroscopy set up.

When a monochromatic beam of light comes out from the monochromator it is divided into two beams via a beam splitter, one of them is goes through the sample, and the other one is passes via a mirror to a reference. After that the transmitted two beams through the sample and the reference are directed back to the detector circuit where they are compared with each other. UV-Vis spectroscopy is used to evaluate the optical band gap or Tauc gap of the any material using the absorption intensity versus wavelength spectra and for that **Tauc plot** is used. The Tauc gap is often used to differentiate practical optical properties of amorphous materials. Jan Tauc showed that the optical absorption spectrum of amorphous germanium resembles the spectrum of the indirect transitions in crystalline germanium (plus a tail due to localized states at lower energies), and proposed an extrapolation to find the optical gap of these crystalline-like states.

Generally, the absorption coefficient (α) is related to photon energy ($h\nu$) by the known equation as:

$$\alpha h\nu = \beta (h\nu - E_g)^r \quad \text{Or} \quad (\alpha h\nu)^{1/r} = \beta (h\nu - E_g)$$

Typically, a Tauc plot shows the quantity $h\nu$ (the energy of the light) on the abscissa and the quantity $(\alpha h\nu)^{1/r}$ on the ordinate, where α is the absorption coefficient of the material. The value of the exponent r denotes the nature of the transition:

- $r = 1/2$ for direct allowed transitions
- $r = 3/2$ for direct forbidden transitions.
- $r = 2$ for indirect allowed transitions
- $r = 3$ for indirect forbidden transitions

At low photon energies the absorption approaches zero then the material is transparent and near the band-gap value the absorption gets stronger and shows a region of linearity. This distinct linear region that is the the onset of absorption and extrapolating this linear region to

the abscissa will intercept the $h\nu$ - axis yields the energy of the optical band gap of the material.

From the transmission and reflection spectra we able to find the refractive index 'n' of studied samples using the following relation:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

where R is the reflectance and k the extinction coefficient, $k = \frac{\alpha\lambda}{4\pi}$.

The absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as Urbach rule. $\alpha = B e^{\left(\frac{h\nu}{E_a}\right)}$

Where B is a constant and (E_a) , the activation energy. The values of the optical activation energy (E_a) give more detail about the optical behaviour of the studied samples. From the curve of the variation of $\ln(\alpha)$ with the photon energy $(h\nu)$ we can get value of the optical activation energy from the slope of the straight lines of that curves.

Fourier Transform Infrared (FTIR) Spectroscopy

Aim- To find out the chemical bond present in deposited thin films using FTIR

Apparatus required – pelletizer set, hydraulic press machine.

Introduction- Fourier transform infrared (FTIR) spectroscopy is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously gathers high spectral resolution data output over a wide spectral range (infrared radiation in the EM spectrum with frequencies in the range 4000 cm^{-1} to $\sim 200\text{ cm}^{-1}$) for the deduction of various functional groups in a molecule. These frequencies range of. The principles of this technique is relied on absorption or emission of radiation by the samples at a particular frequency that match those of the normal modes of its vibrational motion of molecules frequencies within the macromolecule. These absorption or transmission features are characteristic of the molecular configuration, sequencing, conformation, branching and state of order. Molecular vibration, the coupled motion of atoms within molecules, has the following modes: stretching, bending, wagging, scissoring and rocking, each of which corresponds to an energy level

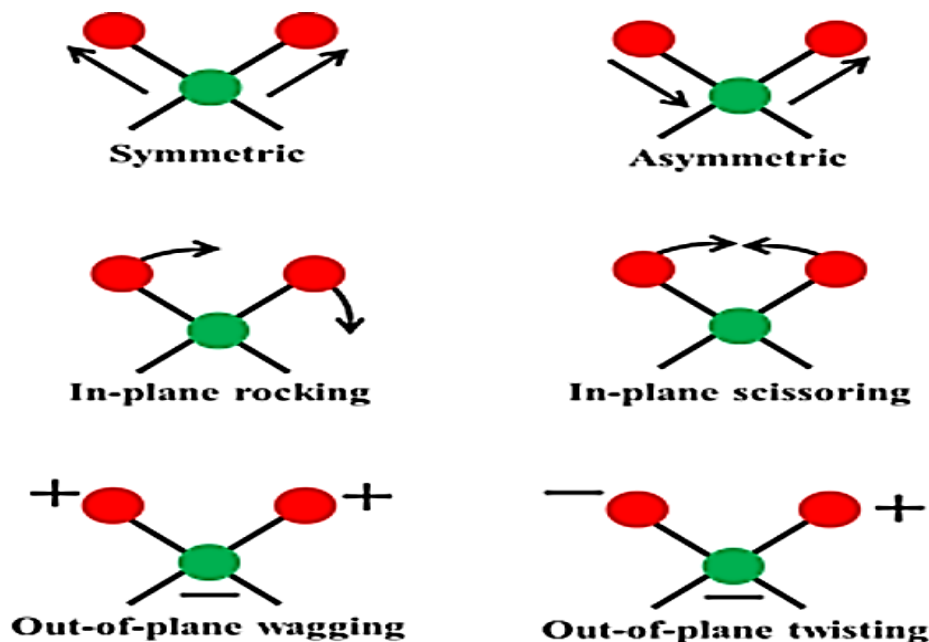


Figure: Types of Molecular Vibrations due to Infra-Red radiation with '+' indicates motion out of the page and '-' indicates motion into the page

IR spectra contains peaks at frequencies where it represent transitions between quantized vibrational energy states, which corresponds to a particular functional group. We are able to identify a pure compound or other functional groups using those unique collection of absorption bands.

Energy difference for transitions between the ground state and first excited state of most of the vibrational modes occurs in the mid-IR range, which is between 4000-400 wavenumber (cm^{-1}). IR spectra is used in both chemical and structural analysis. A substance can be chemically identified by matching the observed IR spectrum with known literature database. Also, structures can be determined as functional groups give rise to characteristic bands from which we can able to find the crystallinity. The intensity of an absorption band is related to the dipole moment change associated with the molecular vibration.

FTIR working principle:

When an IR source sends IR radiation into the interferometer where the radiation goes through the beam splitter and then into a fixed or movable mirror. As the IR radiation interacts a mirror, it travels into the sample compartment and to the IR transducer. An interferogram resulted as the two beams of radiation generated by the beamsplitter, interact with each other. When the signal puts its impact on the transducer, then the interferogram is Fourier Transformed into the resulting spectrum. For calibration technique of the movable mirror in the interferometer laser is used. In FTIR spectroscopy the most commonly used interferometer is a Michelson interferometer. The interferometer modulates IR radiation when it goes through and there occurrence of optical inverse Fourier transformation. Due to passing of modulated IR beam through the sample, there is absorption of different wavelengths to various extents which corresponds to the content of various functional group in the molecules. Finally, liquid nitrogen cooled MCT (Mercury-Cadmium-Telluride) detector is used to detect transmitted IR beam. The interferogram will eventually displayed a spectrum that is the plot in-between absorbed energy and frequency. Corresponding to different vibrations and have unique infrared spectra we able to identify possible substance

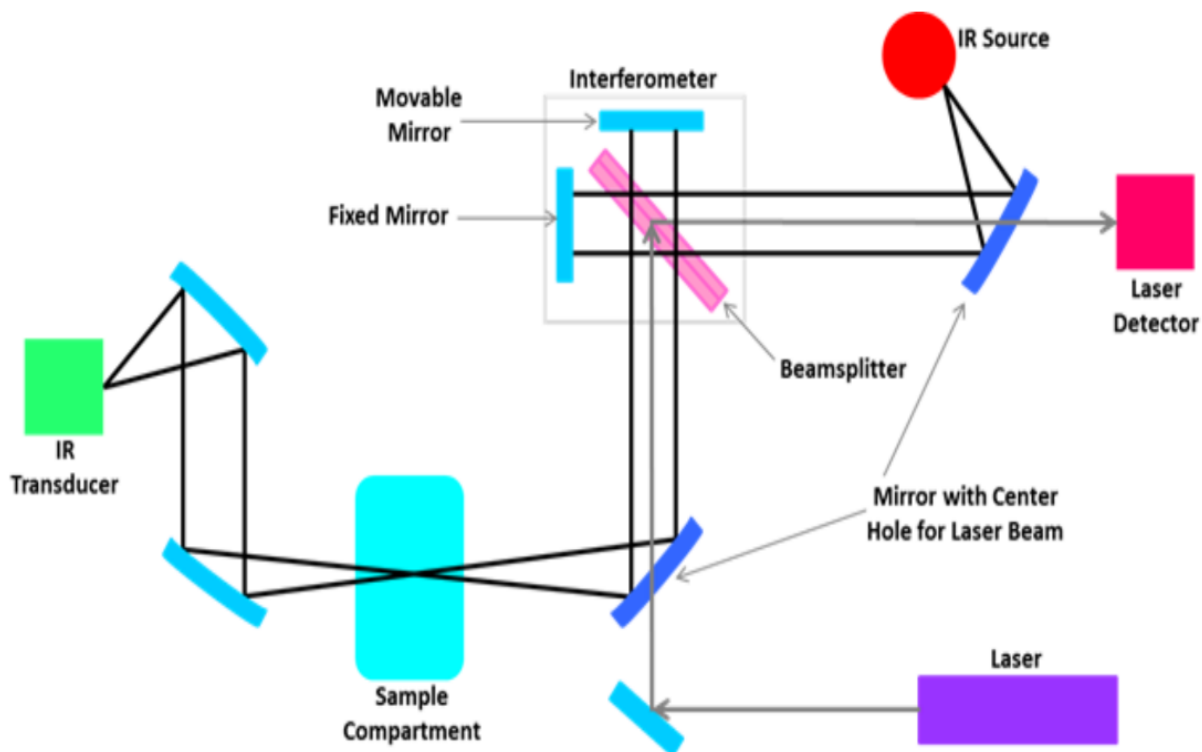


Figure : Instrumental diagram of a Single Beam FTIR spectrometer.

The magnitude of intensity of the absorption corresponds to the given species is dependent on the concentration of that species. To overcome the limitations of dispersive instruments, FTIR spectrometry was developed.

Sol gel method

AIM- To Synthesize the Thin Films using Sol-Gel Spin Coating system

Apparatus required – Spin coater, substrate, and micro pipette.

What is sol gel process? - sol-gel process is a method used to make solid materials from small molecules. Sol-gel coating is a way to create single- or multicomponent oxide coatings on glass or metals. For sol-gel coating there are basically two methods: a spin coating method for one-sided sol-gel coating or dip coating for double-sided coating. Both sol-gel coating techniques are commonly used in manufacturing thin films.

Theory - Sol-gel processing offers the potentials for a simplified, low cost, low energy, resource efficient processing route. Sol-gel allows the use of a solution or gel as a transition step between a liquid forming into a solid material. This is done through the conversion of liquid chemical solutions into an oxide network via hydrolysis and condensation reactions. This sol gel can then be applied onto a desired substrate through several different techniques. The samples then go through various drying and annealing stages to achieve the desired properties.

Sol - A sol is defined as a stable suspension of colloidal particles or nanoparticles in a liquid. These particles can range from amorphous to crystalline. They can be dense, porous, or even form polymer chains.

Gel - A gel is a porous solid network surrounding and supporting a continuous liquid phase. In typical sol-gel solutions, the formation of gels, or gelation, occurs when the sol particles form covalent bonds. The final structure of the gel network is dependent on the size and shape of these sol particles.

Sol-gel is also known as soft chemistry or solution chemistry. It is the process of taking a solid material, typically a metallic salt or alkoxide known and precursors, and transforming it into a sol or a gel. The transformation converts the metallic precursor into an oxide network through hydrolysis and condensation reactions. This process is typically done at either room temperature or up to no more than 100°C, depending on the solvent used. Figure shows a typical sol-gel process for both thin films and powders.

This process can be broken down into three main steps:

1. Preparation of the solution with a solvent, a precursor, and any additives that may be required.
2. The solution is then applied to a substrate by several techniques with dip-coating; spin coating being the more commonly used. The samples are then pre-heated at an elevated temperature to evaporate the solvent leaving behind a xerogel film or matrix.
3. The process of applying the solution to the film/substrate and then dried is repeated until a desired film thickness is achieved. The sample is then post-heated, or annealed, to form the final crystal structure and remove any leftover organic material.

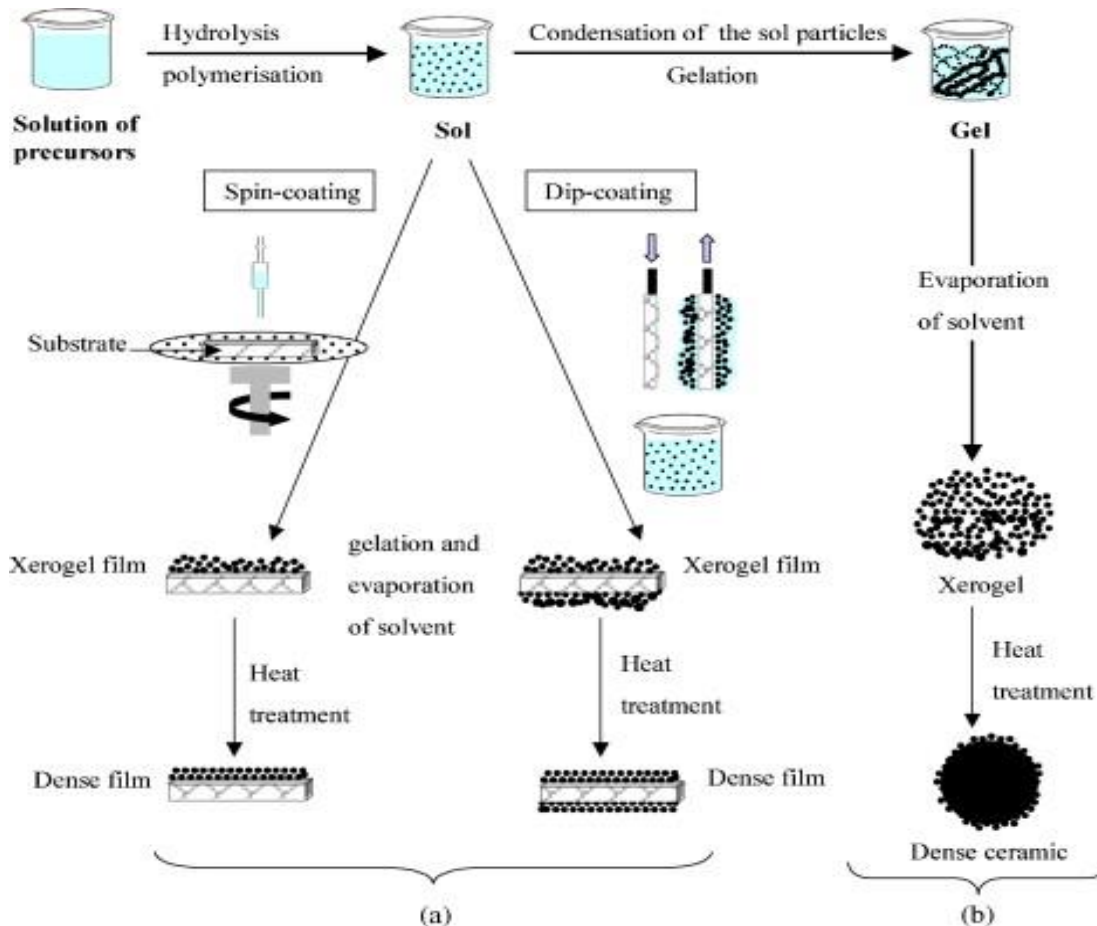


Figure: Image showing two synthesis routes using the sol-gel method. (a) demonstrates the formation of a dense film and (b) shows the formation of a powder or dense ceramic.

A sol-gel solution generally follows five main stages of formation which are hydrolysis, polymerization, condensation, nucleation, and growth (M. Hu, 2000) (Pierre, 1998). Two types of precursors can be used which will typically determine the solution used. Metal alkoxides are generally used with organic solvents and metallic salts are used with aqueous solutions.

Advantages

1. Low processing temperature Ease of manufacture of homogeneous stoichiometric coatings
Control of the coatings chemical composition and microstructure
2. High purity
3. Fairly good adhesion
4. Production of organic-inorganic hybrids
5. Coat complex substrates

Disadvantages

1. Long process times
2. High cost of raw materials

Chemical Route Synthesis method (Spin Coating)

Aim- To Synthesize the Thin Films using Chemical Route Synthesis method.

Apparatus required – Spin coater, substrate, and micro pipette.

Theory-

- Spin coating is a procedure used to deposit uniform thin films onto flat substrates.
- Usually a small amount of coating material is applied on the center of the substrate, which is either spinning at low speed or not spinning at all.
- The substrate is then rotated at high speed in order to spread the coating material by centrifugal force.
- A machine used for spin coating is called a spin coater, or simply spinner.
- Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved.
- The applied solvent is usually volatile, and simultaneously evaporates. The higher the angular speed of spinning, the thinner the film.
- The thickness of the film also depends on the viscosity and concentration of the solution, and the solvent

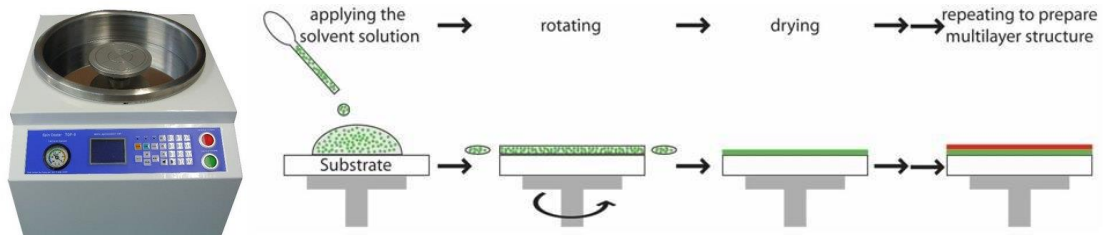


Fig. (A) Spin Coater

(B) Spin Coating Thin Film Deposition Process

Advantages

1. Large-scale production.
2. Size distribution (10-100 nm).
3. It is possible to deposit on a large substrate.
4. No chemical purification is required.

Disadvantages

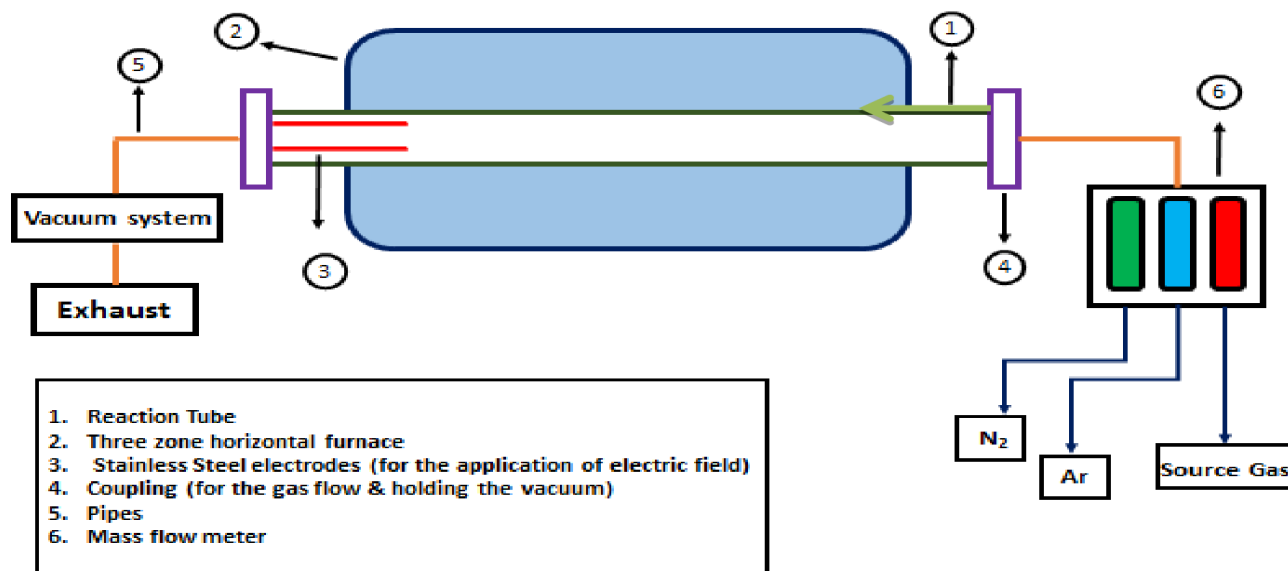
1. Expensive technique.
2. Various particle shapes.
3. Controlling the deposit parameters is difficult to achieve.

Chemical Vapor Deposition

AIM- To Deposit the Thin Films of Conductors using CVD System.

Apparatus required - a gas delivery system, reactor chamber, energy source, vacuum system, and an exhaust system.

Theory- CVD is the deposition of a vapor onto a heated surface. It is part of a class of vapor transfer processing techniques. With CVD, line of sight with the coating surface is not required, which allows for deposition on complex surfaces. It has a high deposition rate and can be used for thick coatings. It can allow for codeposition of elements and does not require a high vacuum. Figure shows a typical CVD process. The first step in CVD is thermal activation of the chemical precursors to form a vapor. This vapor is then transported through a heated chamber where the substrate is located. In this chamber, the desired gas phase reactions occur and the reactants are deposited onto the substrate surface resulting in film formation.



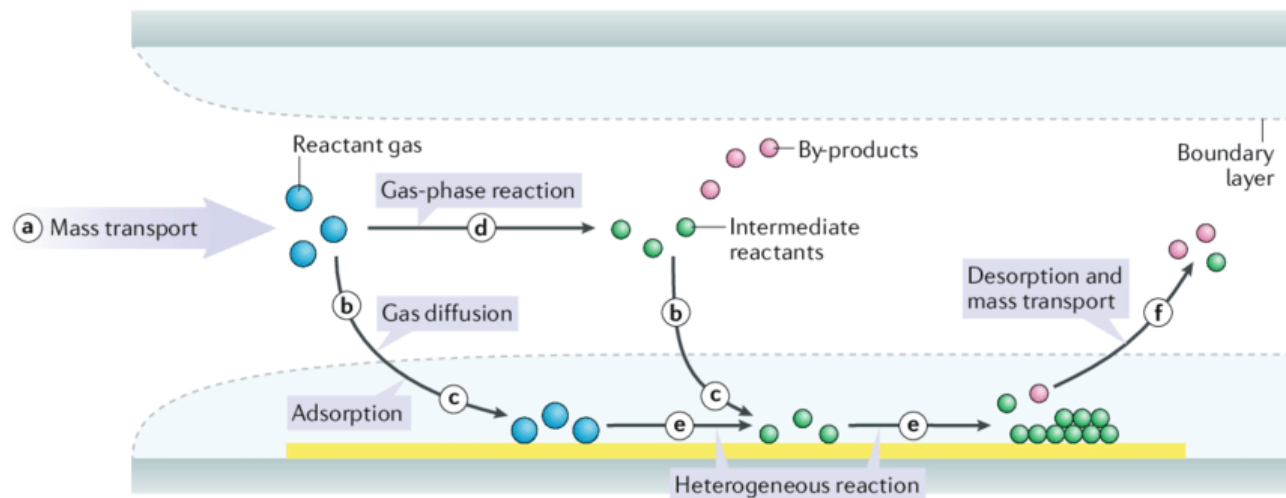
Volatile byproducts are desorbed from the film and removed from the chamber through convection. CVD typically requires high operating temperatures for the gas phase reactions to occur. This not only adds to the cost of processing but limits the types of substrates that the thin film can be grown on. The chemical precursors with high vapor pressures that are needed in CVD are typically toxic and hazardous to work with. Finally, the by-products from the gas phase

reactions that do not remain on the thin films can also be toxic and even corrosion. Often it is required that these by-products be neutralized which adds to the cost of production.

Steps involved in CVD process -

A typical thermally activated CVD (TACVD) process involves

- (1) Mass transport of precursors in the form of vapor to the substrate surface inside a chamber;
- (2) Adsorption of the precursors on the surface of the substrate;
- (3) Chemical reactions on and near the substrate surface;
- (4) Desorption of the chemical by-products from the surface of the substrate; and
- (5) Exhausting the by-products from the chamber along with the unreacted precursor vapor



Advantages

1. The high productivity makes this technique economically very feasible.
2. The low temperature avoids impurity incorporation from the reactor walls and the elimination of auto doping.

Disadvantages

1. for thermal atmospheric CVD is the lack of precursors that are highly volatile, nontoxic and nonpyrophoric.