Chapter II

Experimental methods used

2.1 Introduction

Chapter I give an explanation about the theoretical background necessary for the research work given. The literature survey reveals the importance of the present scenario of the polymer thin films in the development of various applications.

As per the aim and scope of the present work stated in chapter I, the present chapter deals with the experimental methods for the synthesis of the polythiophene and poly (3-methyl thiophene) powder, which have been used as the source material for the thin film deposition. The deposited thin films were characterized for structural, surface morphological, optical (optical absorbance, refractive index, band gap), mechanical (adhesion and intrinsic stress) and optical waveguiding properties. The chapter consists of,

- Synthesis of polythiophene (PTh) and poly (3-methyl thiophene) (P3MeT) powder.
- Deposition techniques used for the deposition of PTh and P3MeT thin films.
- Characterization techniques used.

2.2 Synthesis of PTh and P3MeT powder

Number of methods has been reported earlier by some authors for the synthesis of polythiophene [1-5], polythiophene can be prepared by means of chemical as well as electrochemical polymerization, between which the chemical
oxidative polymerization with iron chloride (FeCl$_3$) and chloroform is a better route because it gives higher yield [6].

### 2.2.1 Polymerization of PTh

#### A) Preparation of solutions

- The monomer solution was prepared by dissolving 0.1M thiophene (AR, Alfa Aesar) in 100 ml of chloroform.
- The oxidant solution was prepared by dissolving 0.2M FeCl$_3$ (Sd-Fine) in 100 ml of chloroform.

#### B) Experimental procedure

- The oxidant solution was kept for half an hour under constant stirring
- A monomer solution of thiophene was added drop-wise to this solution for 8 hours.
- The reaction was carried out under a nitrogen atmosphere at constant stirring.
- After the complete addition of the monomer the reaction mixture was kept at room temperature under a nitrogen atmosphere for 24 h with constant stirring.
- A black brown precipitate of polythiophene was formed, to which a known quantity of methanol was poured.
- The precipitate was washed with methanol, chloroform and HCl over and over again to remove residual oxidant and unreacted monomer and collected in a filter paper.
- During this process the dark brown color of the precipitate changed to brown; then the precipitate was deprotonized by 0.5M ammonia, further washed with 0.5 M HCl, acetone and chloroform and collected by filtration.
- The obtained PTh powder was dried under vacuum at 60$^0$C for 24 hours.

#### C) Reaction mechanism

The polymerization of PTh takes place through the free radical polymerization process in terms of i) initiation, ii) propagation and iii) termination.

When the monomer solution is added in the oxidant solution the free Fe$^{3+}$ ions present in the oxidant solution initiate the polymerization by attacking the
weak bonds ($\pi$-bond) of the one of monomer site, creating another free electron in the monomer, which attacks the weaker bond of another monomer making another electron free, in this way the initiation takes place. Which results in the linking of first monomer with second monomer and propagation takes place, this process is continuous to form a long polymer chain. Finally the free electrons interlinked with each other and the chain, this coupling causes stabilization of polymerization. The reaction mechanism is shown in figure 2.1.

Fig. 2.1 Chemical polymerization of thiophene.

2.2.2 Chemical synthesis of Poly (3- methyl thiophene)

Poly (3-methyl thiophene) was synthesized in similar way of polythiophene using FeCl$_3$ and Chloroform [4]. The polymerization process can be explained as per section 2.2.1; figure 2.2 shows the reaction mechanism of synthesis of poly (3-methyl thiophene).

The experimental procedure and reaction mechanism is similar to the polymerization of thiophene with FeCl$_3$ (Fig.2.1).
Chapter II: Experimental methods used

2.3 Thin film deposition

2.3.1 Introduction

As already mentioned in chapter I, thin film deposition techniques can be classified as physical and chemical. In physical deposition techniques, the source material is deposited without any chemical reaction e.g. vacuum evaporation technique, sputtering etc. In chemical deposition technique, the films are deposited by using chemical reaction in source materials or source material with the environmental factors. In the present work, vacuum evaporation and chemical bath deposition techniques have been used for the deposition of PTh and P3MeT thin films. The PTh powder and P3MeT powders were synthesized as described in previous section of this chapter, which used for the deposition of thin films. Vapor chopping technique was used for the vacuum evaporated polymer thin films only.

2.3.2. Substrate cleaning

In the present work, the substrates used were micro slides of size 75 mm × 25 mm and of thickness 1.25 mm ± 0.1 mm (Micro-Aid micro slides and Blue star micro slides). The refractive index of the glass substrate used was 1.515. The substrates used for intrinsic stress measurement were soda glass cover slips (Blue star) of diameter 1.9 cm and of thickness 0.022 cm. Initially the glass slides were

Fig.2.2 Chemical polymerization of (3-methyl thiophene).
cleaned by tap water for few minutes so that the macroscopic impurities will removed and then the substrates was soaked in dilute chromic acid for 15 min and again cleaned in distilled water. The greasy particle on the substrates were removed using soap solution (Balzers substrate cleaner, BD481 901) and rubbing with cotton taking care that the substrate do not get scratched. The substrates were again rinsed in distilled water. The surface layer soap solution was completely removed. Same procedure was carried out for two three times for each substrate. During all these process, the substrate was handled by holding them at the corners with stainless steel forceps. The substrates were later dried under an infra-red lamp and wiped with lintless tissue paper and mounted on the substrate holder inside the vacuum coating chamber immediately.

2.3.3. Deposition techniques

In this present work, the deposition techniques were used are 1) vacuum evaporation technique and 2) chemical bath deposition technique.

2.3.3.1. Vacuum evaporation technique

The HindHiVac (model 12A4D) manufactured vacuum evaporation system was used during this experiment is shown in figure 2.3. The experimental set up of this technique is divided into different parts.

- **Vacuum chamber**

The vacuum chamber is also known as experimental chamber and it is made up of glass or stainless steel. Only the requirement is that, it should not degas under high vacuum. The deposition of the films is taken in this section. This chamber consists of the evaporating system and substrate holder. In resistive heating system, the evaporation was done by using the filament or boat. It is made up of the refractory materials like tungsten, molybdenum or tantalum etc. The use of the refractory material depends on the evaporating temperature range (melting temperature) of the source material. This chamber also consists of substrate holder, which is fixed on suitable distance from the evaporator. The chopper is also fixed inside the chamber.
Pumping system

The pumping system is used to evacuate the gas molecules from the vacuum chamber and reduces the pressure. According to the range of vacuum to be obtained, the vacuum system consists of different types of pumps. Generally vacuum evaporation system consists of two pumps, one is mechanical and another is diffusion pump. Direct drive oil sealed van type rotary mechanical pump (Model-ED-15) is used. It can evacuate the chamber pressure up to $10^{-3}$ to $10^{-4}$ Torr, depending on the evacuation speed. To obtain the pressure up to $10^{-6}$ Torr diffusion pump is used. It works on the principle of momentum transfer from the streaming to diffusing molecules. The work fluid inside the chamber is heated in a boiler and their hot vapor rises to the chimney. The direction of the flow is reversed at the jet cap so that the vapor comes out from the nozzle directed away from the high vacuum side or in downward direction. The vapor stream comes out from the higher pressure to lower so that it expands and acquire maximum velocity than the gas molecules at thermal equilibrium. Thus the zone of more reduced molecules generates at the point of nozzle and maximum number of gas molecules diffuses in that region and acquire the velocity. Thus the pressure in the lower region increases and it can be evacuated by using a backing pump such as rotary pump.

Pressure gauges

The pressure inside the chamber was measured on the basis of different principles by using different instruments. Some instrument measure the pressure as a force exerted by the gas per unit area or change in the physical quantity with respect to change in gas density is used.

In the present vacuum system two types of gauges were used depending on the range of measurement. Pirani gauge is used for the pressure measurement up to a range of $10^{-4}$ Torr and above that penning gauge is used up to $10^{-7}$ Torr.
Fig. 2.3 Vacuum coating unit.

**Valves**

Vacuum chamber, diffusion pump and rotary pump are separated by means of different types of valves. High vacuum valve is used for the separation of vacuum chamber and diffusion pump. Roughing valve is used to separate the vacuum chamber from the rotary pump. It is used to roughly evacuate the vacuum
chamber by using only rotary pump therefore nominated as roughing valve. Backing valve is used to separate the diffusion pump and rotary pump.

**Vapor chopping technique**

The vapor chopping technique (Fig. 2.4) has been reported to improve the quality of thin films [7, 8, and 9]. It consists of a metallic vane of aluminum cut into circular shape of 10 cm diameter. This circular sheet was given a V-cut (155°) shape as shown in figure 2.4. This thin circular vane was fixed to a light aluminum rod of 6.5 cm height. This aluminum rod was attached to the shaft of 6 V DC motor having a broad base and fixed inside the vacuum system. The variable power supply of 0-4 V (DC) was used to vary the voltage by means of which the speed of rotation could be controlled and hence the chopping speed. The rate of chopping was kept 5-6 rot/sec in all of the experiments. As the chopper rotated, the filaments were exposed to the substrates with regular time interval. The vane was kept at the center between the source and substrate.

![Fig. 2.4 Vacuum evaporation technique with vapor chopper.](image)

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2.3.3.2. Chemical Bath Deposition [10]

Introduction

The chemical bath deposition method is one of the economical methods to deposit thin films and nanomaterials, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. The major advantage of CBD is that it requires only solution containers and substrate mounting devices. One drawback of this method is the wastage of solution after every deposition but among various deposition techniques, chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. Chemical bath deposition method is one of the suitable methods for preparing highly efficient thin films in a simpler manner. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution, and topographical and chemical nature of the substrate.

Preparation of solutions and experimental set up of CBD

The monomer (thiophene and 3-methyl thiophene) (AR grade) was purified by distillation before prior use. Iron chlorides FeCl₃, Chloroform (CH₂Cl), Methanol (CH₃OH) were used for the preparation of the polythiophene thin films. An inert atmosphere is required for the deposition of poly (3-methyl thiophene) thin films so that the conventional CBD method was modified as shown in Fig. 2.5. The oxidant solution was prepared by dissolving FeCl₃ in chloroform and the glass slides were immersed in this beaker under constant stirring and kept in the glass chamber consisting of three ports as shown in figure 2.5. Nitrogen was introduced from first port and the second port for outlet of nitrogen, the monomer solution prepared in chloroform was added drop wise in the oxidant solution by a funnel from the third port of the glass chamber. Initially the ratio of oxidant to the monomer was kept 1:1. During the precipitation, heterogeneous reaction occurred and the deposition of polymer took place on the glass substrate. The substrates coated with polymer thin films were removed after a time interval of 1 h from the bath, washed with methanol followed by chloroform and acetone over and over.
again to remove residual oxidant and unreacted monomers, dried in air and preserved in a vacuum dessicator. The experiment was repeated by changing oxidation concentration.

**Reaction Mechanism**

The CBD is based on the formation of solid phase from a solution, which involves the two steps of nucleation and particle growth. In nucleation, the heterogeneous reaction at the substrate surface takes place when clusters of the molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film [11].

![Diagram of Chemical Bath Deposition Technique](image)

**Fig. 2.5 Schematic diagram of Chemical Bath Deposition Technique used for preparation of PTh and P3MeT thin films.**
The film thickness is found to depend upon deposition time, molar concentration of reactants and temperature of bath and speed of rotation. It is interesting to note that film thickness can also vary with oxidant concentration this can be understood as follows: as soon as monomer is added to the oxidant solution, the free Fe$^{3+}$ ions initiates the polymerization of monomer [12] by attacking on the weak bonds of monomer ($\pi$-bond). When the glass substrates are immersed into the chemical bath the ions get adsorbed on the substrate due to the forces of attraction between free ions in the solution and surface of the substrate. These forces may be cohesive forces or Vander Waals forces or chemical attractive forces. Increase in the concentration of FeCl$_3$, which results into more number of free Fe$^{3+}$ ions resulting in increase in the adsorption between glass and ions in the solution, which helps to increase the film thickness. The possible growth mechanism is shown in figure 2.6

![Fig. 2.6 Reaction mechanism of polymerization.](image)

**2.4 Ambient air ageing study**

Vacuum evaporated and chemical bath deposited polythiophene and poly (3-methyl thiophene) thin films (nonchopped and vapor chopped) were kept in air ambient for fixed period of time (30 days) at room temperature and the measurements were taken again. The films were protected from dust.
2.5 Characterization techniques

The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. In this section different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation and working.

2.5.1 Fourier Transform Infrared Spectroscopy [13-14]

Infrared spectroscopy is an important tool for the identification of unknown substances, which deals with the infrared region of the electromagnetic spectrum that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

2.5.1.1 Principle of working

It well known fact those atoms in the molecule are not stationary but rotate in a number of ways, also bonds between atoms in the molecule are not rigid but elastic in nature. They vibrate and rotate in specific energy levels. The energy difference between these energy levels is quantized. When such molecule expose to IR radiation, it absorb IR radiation. Absorption of IR radiation takes place only when there is change in dipole moment of the molecule. The absorption of IR radiation involves excitation of molecules to higher energy vibrational levels. This energy is quantized. The IR spectrophotometer measures this absorption and gives directly IR spectrum in the form of graph. Generally, IR spectrum is percentage transmittance Vs wave numbers in cm$^{-1}$. According to Hooke’s law for diatomic molecules, absorption frequency depends on the mass of atoms and strength of the bond.
\[
f = \frac{1}{2\pi c} \left[ \frac{(m_1 + m_2)}{(m_1 m_2)} \right]
\]

Where,
- \( f \) - Vibrational frequency.
- \( c \) - Wavelength of light.
- \( f \) - Force constant.
- \( m_1, m_2 \) - mass of atoms.

The vibration frequency of atoms in molecules corresponds to the frequencies found in the IR region of the electromagnetic spectrum. In this order of interaction, atoms undergo vibration by absorbing radiation and shows absorption spectra in that frequency region. The vibration must involve an oscillation in electric dipole moment. Only under these circumstances IR radiation of the same frequency are absorbed and the absorption intensity is,

\[
\int a \, dv = \left( \frac{N \cdot \pi}{3 \cdot C} \right)^2 \left( \frac{\delta \pi}{\delta Q} \right)^2
\]

where,
- \( a \) - The absorption coefficient at frequency ‘\( v \)’.
- \( N_1 \) - Number of molecules per cm\(^3\)
- \( \pi \) - Bond moment.
- \( Q \) - Normal co-ordinates for the vibration

2.5.1.2 Instrumentation

In the present work, FTIR spectra were recorded using Perkin Elmer Spectrum1 spectrometer in the range 400 - 4000 cm\(^{-1}\). Films were scratched from glass substrate and mixed with KBr and used for FTIR spectra study. The schematic block diagram of the FTIR instrument is shown in figure 2.7.

Its main components are as follows: The interferometer with the electronics for controlling the spectrometer and communicating with an external computer, the IR-ray source, the transfer optics and the IR detector, and the cell.
1. **Interferometer**

   The interferometer modulates the IR light along with the light from the laser and from the white-light source. The latter two are used for scaling the spectrum. The complete interferometer unit comprises the above light sources, their power supplies, the detectors for laser light and white light, the beam splitter, the retro reflectors, the transfer mirrors and the interferometer arm. The interferometer arm is distinguished by its twin-pendulum design, which contributes to the spectrometers robustness and freedom from over sensitivity.

2. **IR-radiation source**

   The source of the IR radiation is a glowbar, a resistor with positive temperature characteristics, made from silicon carbide.

3. **IR detector**

   The IR detector is a DTGS detector (deuterized triglyceride sulphate).

4. **Cell**

   It is connected to the spectrometer is the heated long-path cell. Via an optical transfer device located above the cell, the IR ray passes into the cell. In the cell, it is reflected several times by three mirrors, increasing the length of the optical path before leaving the cell again and arriving at the detector. The optical path length is fixed in the factory through the setting of the mirrors. It is normally 6.4 m.

2.5.2 **Scanning Electron Microscopy (SEM)**

2.5.2.1 **Principle of working**

   The Scanning Electron Microscopy (SEM) has been widely used for characterization of two dimensional surface topography of thin film. The scanning microscope used in this work was JSM-6360, 9JEOL), Japan. figure 2.8 shows the ray diagram of scanning electron microscope.

   In Scanning Electron Microscope, a well-focused mono-energetic (~25KeV) beam incident on a solid surface and gives various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM
application, their intensity being dependent on the atomic number of the host atoms. Each may be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube. To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the C.R.T. beam in synchronization with this. The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor C.R.T. screen. Change in brightness represents change of a particular property within the scanned area of the specimen [15]. The ray diagram of scanning electron microscope is shown in figure 2.8.

![Ray diagram of scanning electron microscope](image)

**Fig. 2.7 Schematic and block diagram of FTIR instrument.**

The interaction of energetic electron beam with solid surface leads to several signals like elastically scattered electrons (i.e change of direction without change of energy) from the coulomb field of the nucleus, whereas some other includes inelastic scattered electrons (with change of energy) from the electrons of
the host atoms giving rise secondary electrons, Auger electrons and x-rays characteristics to host lattice. The secondary electrons (signal from approximately top 100 Å) are used to get contrast from surface morphology.

Fig. 2.8 The ray diagram of scanning electron microscope.

2.5.3 X-Ray photoelectron spectroscopy

After World war II, Kai Siegbahn and his group in Uppsala (Sweden) developed several significant improvements in the equipment and in 1954 recorded the first high energy resolution XPS spectrum of cleaved sodium chloride (NaCl) revealing the potential of XPS[16]. A few years later in 1967, Siegbahn published a comprehensive study on XPS bringing instant recognition of the utility of XPS. In cooperation with Siegbahn, Hewlett-Packard in the USA produced the first commercial monochromatic XPS instrument in 1969. Siegbahn received the Nobel
Prize in 1981 to acknowledge his extensive efforts to develop XPS into a useful analytical tool.

2.5.3.1 Working principle

Figure 2.9 shows the block diagram of X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra high vacuum (UHV) conditions [17]. The emitted electrons have measured kinetic energies given by:

\[ \text{K.E.} = h \nu - \text{B.E.} - \Phi_s \]

Where,

- \( h \nu \) is the energy of the photon,
- \( \text{B. E.} \) – Binding energy of the atomic orbital from which the electron originates.
- \( \Phi_s \) – Is the spectrometer work function.

The binding energy may be regarded as the energy difference between the initial and final states after photoelectron has left the atom. Due to verity of possible final states of the from each type of the atom, there is a corresponding verity of kinetic energies of the emitted electrons. Moreover there is a different possibility for each final state [18]. Since each element has a unique set of binding energies, XPS can be use to identify and determine the concentration of the elements in the surface. Variation in the elemental binding energies (the chemical shifts) arise from differences in the chemical potential and polarizability of compounds. These chemical shifts can be used to identify the chemical state of the materials being analyzed.
2.5.4 Atomic Force Microscopy

Any surface of thin film has irregularities on the surface. These irregularities depend on various parameters. Such irregularities can observe by using SEM or FESEM. But atomic force microscope (AFM) gives the proper view of those irregularities in the form of surface roughness. Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Figure 2.10 shows the block diagram of AFM.

2.5.4.1 Working principle [19]

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample...
lead to a deflection of the cantilever according to Hooke's law. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

![Fig. 2.10 Block diagram of AFM microscope.](image)

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, which can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects.
seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area \( z = f(x,y) \) represents the topography of the sample.

AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated.

### 2.5.5 UV-Vis Spectroscopy

The study of the optical properties of thin films has great importance for a variety of applications. This deals primarily with reflectance (R), transmittance (T) and absorbance (A) properties and their relation to the optical constants of the film. For crystallite materials, the transition of electrons from valence band to conduction band can be grouped into direct and indirect process [20]. In direct inter band optical transitions, the value of wave vector \( k \) for elements remains unchanged in E-k space and momentum also does not change whereas in indirect inter band transition, the wave vector \( k \) for electrons changes in the E-k space. Thus, vertical transitions are important when the valence and conduction bands extreme are located at the same point in the Brillouin zone. For indirect transition, the band extreme differs in their positions in E-k space. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by using classical relation –

\[
\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu}
\]

where,

- \( E_g \) - is the separation between bottom of the conduction band and top of the valence band,
- \( h\nu \) - is the photon energy,
- \( n \) - is constant.

For allowed direct transition, \( n = 1/2 \) and allowed indirect transition, \( n = 2 \). Thus if the plot of \( (\alpha h\nu)^2 \) against \( h\nu \) is linear, the transition is direct allowed. Band gap energy \( E_g \) is determined by extrapolating the linear portion of the curve to the
energy axis at $\alpha = 0$. Though the optical band gap, nature of transition, transmission etc are easily obtained from optical absorption, the reflectance $R$ is assumed to be zero and the equation depends on only classical approach.

The optical transmittance and absorbance of the films deposited on to glass substrates were measured using a spectrophotometer (Hitachi Japan, Model No. 330). The light emitted from the source (deuterium or tungsten lamp) is passed through the two grating monochromators for obtaining monochromatic beam and then it is splitted in to two beams. After passing through the sample and reference compartment, the monochromatic beams are converged and then converted in to an electrical signal by a detector or photomultiplier tube. The detected signal is digitized by a 16 bit A/D converter. The wavelength range used was 300 nm to 850 nm. The internal block diagram is shown in the figure 2.11.

![Fig. 2.11 Block diagram of UV-Vis Spectrophotometer.](image)

2.5.6 Refractive index measurement [9]

2.5.6.1 Abele’s method

Refractive index of the thin film can be measured by Abele’s method based on the principle of measurement of Brewster’s angle. At the Brewster’s angle, the reflection of parallel component of light at the films-air interface vanishes. This method requires the substrate to be grounded on the back side to avoid back side
reflection and films should be coated on half surface of the substrate with sharp demarcation. If $\Phi_B$ is the Brewster’s angle and ‘$n_f$’ is the refractive index of the films, then the refractive index of thin films can be calculated by using following formula.

$$\phi_B = \tan^{-1}(n_f)$$

In present work, the refractive index of the films is measured by using Abele’s method using spectrometer (COSLAB MAKE). This could be measured up to the accuracy 20 sec. of arc. The sodium vapor lamp was used as the source of monochromatic light ($\lambda=589$ nm). A polaroid sheet (Jain Laser-tech) was used as polarizer. All the alignment for spectrometer, collimator, and telescope and prism table was followed. The spectrometer was initially aligned to get plane of polarization of incident light in the plane of incidence by finding the Brewster’s angle of glass. All the substrate used in this method were grounded on backside using surface grinding machine to avoid the back reflection. To compare the intensities from the two half (coated and uncoated), stainless steel blades were used as a mask in order to obtain the clear demarcation of films. The half coated substrate was fixed on the specially made substrate holder. To measure the angle of incidence accurately, a cross wire was fitted very near to the objective end of the telescope. Removing the eyepiece for viewing the films, the cross wire was made to coincide with the coated-uncoated demarcation. The angle of incidence adjusted till the illumination from the substrate half and films half were found to be equal. This was measured by keeping the eyepiece and coinciding the cross wire with the centre of slit. The adjustment was done number of times to get the cross wire in the centre of slit and coincide with demarcation.

This angle and the straight reading were observed and the angle of incidence was found, the tangent of which gave the measurement up to an accuracy of $\pm 0.002$.

2.5.6.2 Spectrophotometric method

Spectrophotometric method is also used in this present work, for the calculation of the refractive index of thin films. This method is based on the
spectrometric results, by measuring the simultaneous absorption and transmittance of thin film at eye sensitive 621 nm wavelength, the reflectance has been calculated by using relation,

\[
\text{Transmittance} + \text{Absorption} + \text{Reflectance} = 1
\]

The refractive index (n) of thin films calculated by using the following formula [21].

\[
n = \left[ \frac{n_s^2 T_f + n_s \left(1 + \sqrt{R_f}\right)^2}{T_f + n_s \left(1 - \sqrt{R_f}\right)^2} \right]^{1/2}
\]

Where,

- \( n \) = refractive index of the film.
- \( n_s \) = refractive index of the substrate.
- \( T_f \) = transmittance of the film.
- \( R_f \) = reflectance of the film.

### 2.5.7 Direct pull off method for adhesion measurement

The adhesion of the thin film with the substrate is an important parameter, which can affect the reliability and the performance of the device. In the present work, the adhesion was measured by a simple and convenient direct pull off (DPO) method [9]. The adhesion testing apparatus for adhesion measurement used is shown in figure 2.12.

This adhesion testing apparatus consists of two hard metal chucks aligned on the same axis with one movable and other fixed.

The movable chuck was attached to a spring balance of maximum capacity of 50 Kg, with an accuracy of ±0.5 Kg. The spring arm of balance was connected to a pulling mechanism through a metal cable. Aluminum studs of 0.5 cm diameter and 5 cm length attached to the film side and back side of the substrate with an adhesive ‘Araldite’. In order to align the studs during curing a special stud fixture was made which is shown in the Figure 2.5. After curing the adhesive, the adhesion was measured by monitoring the load when the failure occurred at the film substrate interface.
The adhesion was calculated using the formula.

\[ \sigma = \left( \frac{g \times F}{A} \right) \]

Where,
- \( g \) = gravitational force
- \( F \) = load in kg used to occur failure at film substrate interface
- \( A \) = area of stud (0.005 m).

**Fig. 2.12** Schematic diagram of (A) adhesion testing apparatus (B) sample holder for stud alignment.

**2.5.8 Intrinsic stress by interferometric method**

The deposition of the thin film leads into bending of the substrate, this bending caused because of intrinsic stress originated in the thin film, and this bending can be concave or convex depends upon whether the stress is tensile or compressive.
2.5.8.1 Principle of working and instrumentation

The working of this method is based on the Newton’s rings. When a Plano-convex lens is placed on a optically plane glass plate, a wedge shaped air films of gradually increasing thickness from the point of contact is formed in between glass plate and lens.

![Photographic Camera](image)

![Partially Silvered Mirror](image)

![Monochromatic Light](image)

![Substrate](image)

![Optical flat](image)

Fig. 2.13 Schematic of intrinsic stress measurement method.

If the monochromatic beam of light is allowed to fall normally and films viewed in a reflected light, then we will get circular alternating dark and bright band, concentrated around the point of contact. The radius of the circular interference fringes varies with the radius of the curvature of Plano-convex lens.
The experimental setup consist of optical flat glass plate (λ/10), monochromatic source, beam splitter and traveling microscope as shown in figure. 2.13. Thin films were deposited on the convex side of cover slip by placing them carefully on substrate holder.

This deposited cover slip was placed as it is on the optical flat glass and again adjusted for the circular or oval fringes. The radius or distance between the circular or oval fringes was measured. The difference in the radius or distance between the fringes was used for the measurement of intrinsic stress of thin films. From the fringe pattern, the radii of the fringes are measured in the X and Y direction and plots of \( d_n \) vs \( r_n^2 \) are obtained where \( d_n = n (\lambda)/2 \) is the distance between the curved films and the optical flat which is responsible for fringe of order ‘n’ and \( r_n \) is the radius of the fringe of order ‘n’. The slopes of \( K_X \) and \( K_Y \) of the plots of \( d_n \) vs \( r_n^2 \) are related to the value of the tension per unit area \( T_X \) and \( T_Y \) in the X and Y directions.

\[
K_X = 3t \frac{(T_X - T_Y)}{(Yh^2)}
\]

and

\[
K_Y = 3t \frac{(T_Y - T_X)}{(Yh^2)}
\]

These are used to calculate the intrinsic stress “S” in the films,

\[
S = \frac{Yh^2(K_X - K_Y)}{\left\{6t(1-\nu)\right\}}
\]

Where,

\[
Y = 7 \times 10^{10} \quad \text{Young’s modulus}
\]

\[
\nu = 0.22 \quad \text{Poisson’s ratio}
\]

\[t\] = films thickness
2.5.9 Optical transmission loss by prism coupling method

Optical transmission loss in the films was measured by using prism coupling method. It provides a convenient and efficient method for launching a laser beam into a thin film structure. This method consists of a pair of right angle prism, placed above the thin film guide and separated from it by a small air gap having low refractive index. An incoming laser beam enters the film through one prism and comes out from the film through the other prism. The coupler permits excitation of any one of the films mode by proper orientation of the direction of the incident beam. In prism coupling, the refractive index of the prism should be higher than the refractive index of waveguiding medium (films), and the air gap between the prism and the top of the film surface should be of the order of the wavelength of light used.

Fig. 2.14 Experimental setup of prism coupling method.
Fig. 2.15 Light guiding through thin film waveguide (a) through vacuum evaporated films (INSAT: vacuum evaporated thin film) and (b) through chemical bath deposited films (INSAT: CBD thin film).
The important condition is that the incident laser beam must have the angle of incidence greater than the critical angle so that the evanescent field in the gap travels with the same phase velocity to be excited in the film. Under this condition when the laser beam is incident on the input prism, it will be launched in to the thin films guide and can be taken out by a prism placed at the output end.

In the present work, we have used the two special right angle prism made of extra dense flint glass with a refractive index 1.71. These two identical prisms had a base area of $1 \text{ cm}^2$ and angle $90^0$-$45^0$-$45^0$ (Supreme Optics, Pune). All sides of prism were highly polished and a sharp edge was maintained at the angle of $90^0$. The top of the prism was cut up to the width of 2 mm for mounting purpose.

The prism was pressed from the top of the prism as well as from the back side of the thin film waveguide using the fine brass screws. Care was taken to press the prism slightly away from the sharp edge at the prism angle of $90^0$. Two rectangular brass fixtures were used to mount the input and output prisms. The spacing of the air gap between the base of the prism and the top surface of the films was adjusted in the order of wavelength for effective coupling. The photograph of experimental arrangement is shown in the figure 2.14.

A streak of light observed in thin film waveguide is shown in the figure 2.15. The optical transmission loss was measured by measuring the output intensity from the output prism. The output intensity of 1.5 cm guiding length has been measured in the form of current using the silicon photo diode by keeping the input intensity constant (80 $\mu$A).

The transmission loss has been calculated for 1.5 cm guiding length in decibels using the formula.

$$A = 10 \log \left( \frac{\text{Input intensity}}{\text{output intensity}} \right) \text{ dB/cm}.$$
References:


