CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

This chapter describes the experimental techniques used in the present investigations for the preparation and characterization of PbPc thin films. Thin films can be defined as a solid layer having a thickness varying from a few angstroms (Å) to about 10 µm or so. The vital role of thin film results from their finite thickness and unique microstructure. The methods of deposition and environment have great influence on the characteristics of thin film. In general, the deposition of films is by one of the various processes under the broad classification of two types. They are

1) Chemical methods and
2) Physical methods.

Experimental techniques, that includes preparation of films, choice of the substrates and measurement of film thickness is the primary process for any sort of applications. The various film preparation techniques, in-situ thickness measurement and a detailed explanation of vacuum evaporation technique for film characterization implemented in the present work are outlined in this chapter.
2.2 FILM DEPOSITION

Thin films can be prepared from a variety of materials such as metals, semiconductors, insulators or dielectrics etc., and for this purpose various preparative techniques have also been developed. The choice of a preparative technique is guided by several factors particularly the melting point of the charge, its stability, desired purity and characteristics of thickness, etc., (Goswami (1996)). A thin film deposition process (Chopra (1969)) involves three steps:

(i) creation of atomic / molecular / ionic species
(ii) transport of these species through a medium and
(iii) Condensation of the species on a substrate.

2.2.1 Chemical Methods

The chemical method depends on the deposition of films from aqueous solutions either by passing a current or by chemical reactions under appropriate conditions. Chemically deposited films are not generally of high purity; however this technique is widely used for the fabrication of conducting connectors, magnetic memory elements, etc., (Chopra (1969)).

The different types of chemical methods for the film formation are chemical reduction plating, solution growth (sol-gel), spray pyrolysis, chemical vapour deposition (CVD), thermal growth, anodization and electroplating (Gould and Shafai (2000)). In sol-gel thin film formation via dipping, inorganic or organic solutions are deposited on the substrate surface by a complex steadily state process combining gravitational drawing, solvent evaporation and continued condensation reaction (Sakuri and Haya (1973)).
Deposition of films from gaseous phase by thermal decompositions or chemical reaction in substrate surface at high temperature is known as chemical vapour deposition (CVD) (Chopra (1969)). Important CVD methods are metal organic chemical vapour deposition, low pressure metal organic chemical vapour deposition, plasma enhanced chemical vapour deposition, aerosol-assisted chemical vapour deposition, and high temperature chemical vapour deposition and thermal chemical vapour deposition (Goswami (1996)).

2.2.2 Physical Methods

The important methods used for thin film preparation in physical methods are vacuum evaporation and sputtering.

Vacuum evaporation is a simple process wherein uniform films of high purity can be deposited under different experimental conditions. It is the most commonly used technique adopted for the deposition of metals, alloys and also many compounds. This involves the evaporation or sublimation of the material in vacuum by thermal energy and allowing the vapour stream of the charge to condense on a substrate so as to form a continuous and adherent deposit of desired thickness. The quality and the characteristics of the deposit will depend on the rate of deposition, substrate temperature, ambient pressure, etc., and the uniformity of the film depends on the geometry of the evaporant source and its distance from the substrate (Goswami (1996)).

Evaporation methods are simple, easy to control, and can produce uniform films of high purity under varied experimental conditions. In this method the amount of impurities included in the growing layer will be minimized and the tendency to form oxides will be considerably reduced. But this method is expensive and requires constant and continuous power supply.
There are different methods for evaporating the material namely, resistive heating, flash evaporation, arc evaporation, laser evaporation, R.F. heating and electron bombard heating.

Sputtering is a process in which the surface of the material will be ejected by the bombardment of energetic and nonreactive ions under reduced pressure. The ejection process takes place as a result of momentum transfer between the impinging ions and the atoms of the target surface (Chopra (1969)). Ion beam deposition has been used effectively in sputtering technique (Barrent (1987)). In this process, ions formed in a glow discharge maintained in an atmosphere of inert gas inside the chamber are accelerated to impinge on the incident particle enables target atoms to be released and these knocked off atoms condensed on the substrates. It has become a commercial process and is applied on a large scale for various coatings (Peter Zorg (1973)). Ion plating is a new deposition technique which is a combination of thermal evaporation on to a substrate (cathode) which is simultaneously bombarded with positive ions from a glow discharge or an ion source, which results in compactness and strong adherence of the films.

In our present work, thin film of PbPc were prepared by vacuum evaporation technique and the experimental details about the vacuum coating unit and the selection and preparation of the substrates are presented in this chapter. The experimental details pertains to the evaluation of various properties using analytical techniques viz., X-ray diffraction (XRD), Energy Dispersive Analysis of X-rays (EDAX), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Optical properties, Photoluminescence (PL), photoconduction, Dielectric and AC conduction studies and Current Voltage analysis (IV) are also presented in this work. The Figure 2.1 shows the schematic diagram of Research Umbrella.
Lead Phthalocyanine thin films

Glass substrate
150 nm, 300 nm and 450 nm

450 nm thickness
annealed at 303, 323 K and 373 K

KCl substrate
150 nm

Structural and Compositional Studies
XRD, EDAX, FTIR, SEM, AFM, PL, Opti, AC, IV

Surface Studies

Optical Studies

Conduction Studies

Structural and Compositional Studies
XRD, EDAX, SEM, AFM, IV, PC

Surface Studies

Conduction Studies

Figure 2.1 Research umbrella
2.3 VACUUM COATING UNIT

Figure 2.2 shows the photograph of the vacuum coating unit. Figure 2.3 shows the schematic representation of the conventional coating unit. In the present study, a conventional unit (12 A 4D Hind Hivac, India) was used in the film preparation. The unit comprises of three main parts namely,

i) vacuum chamber

ii) pumping or evaporating system

iii) electrical equipments.

The vacuum chamber is evacuated by a three stage oil diffusion pump and is backed by a double stage gas ballast rotatory pump with an evacuating capacity of 200 litres / unit. A magnetic isolation cum air admittance valve in the system serves as a safety accessory. The pirani gauge which works on the basis of thermal conductivity is used for measuring the chamber pressure for low vacuum (0.5 to \(10^{-3}\) Torr) and for measurements of higher vacuum (\(10^{-2}\) to \(10^{-6}\) millibar); a penning gauge (ionization gauge) is employed. The resistively heated source has been energized by a L.T. transformer with high current supply. The heating of the substrate is brought about by a heater arrangement. Molybdenum boat was used as the source for evaporating the PbPc material. Three circular glass windows enable visual inspection of the coating process. A cooling water pipeline is coiled on the outer wall of the chamber to prevent over heating, especially at the chamber windows. The oil diffusion pump is connected to the coating chamber, which permits the diffusion pump to be kept under vacuum and at operating temperature when the coating chamber is at atmospheric pressure. The rate of evaporation was properly controlled and maintained constant during the evaporations.
Figure 2.2 Vacuum coating unit
Figure 2.3 Schematic representation of vacuum coating unit

1 – Rotary Pump  2 – Magnetic Isolation Valve
3 – Butterfly valve  4 – Pirani Gauge I
5 – Pirani Gauge II  6 – Penning Gauge
7 – Backing Line  8 – Glass or Metal Bell Jar
9 – Diffusion Pump  10 – Diffusion Pump Heater
11 – Liquid Air Trap  12 – Air Admittance Valve
13 – Needle Valve  14 – Baffle Valve
2.4 MASKS

Many applications of thin film lead to the requirement of forming thin films of complicated forms with a high lateral resolution. For this purpose suitable masks are used to prevent deposition on the areas, which we want to keep clean or on the contrary preventing removal of an already deposited film from certain regions.

2.4.1 Preparation of masks

In the fabrication of Metal-Semiconductor-Metal (MSM) structures masks have been used to prepare the electrode and the dielectric layer. Masks were prepared from brass and thin mica sheets respectively. The brass masks of precise dimensions with vertical edges have been prepared by the photolithographic techniques (Bogulavaskii and Vannikov (1970)) with the use of double negatives causing etching on both the surfaces.

2.4.2 Mask Cleaning

The masks should be cleaned to avoid the formation of defects in the deposited film for the reason that during deposition the masks are in contact with the substrates and any contaminant on it affects the film growth. In turn this may give rise to weak spots in the film structure. The masks were initially cleaned with acetone to remove the organic contaminants.

2.5 SUBSTRATE
2.5.1 Choice of Substrate

The function of the substrate is to provide the base on to which thin film circuits are fabricated and various thin film multilayers are deposited. The substrate had to be optically plain, transparent, electrically non-interfering, chemically stable and comparatively cheap. Further, the nature and surface finish of the substrates are extremely important because they
really influence the properties of films deposited on to them. Out of all the substrates such as glass, quartz, ceramic, halides, mica, minerals, metals etc., glass is found to possess a good smoothness and is very economic (Sakuri and Haya (1973), Veluswamy et al (1984)) and hence widely used. In the present work we have used Blue-Star glass micro slides and KCl as substrates for the deposition of films.

2.5.2 Substrate Cleaning

For durable and adherent coating a clean substrate is needed. The cleanliness of the substrate exerts a decisive influence on film growth and adhesion and hence it is essential for the preparation of thin films with reproducible properties. Cleaning involves the breaking of adsorption bonds between the substrate and the contaminants without damaging the substrate surface itself. Expected contaminants include those from manufacturing procedures, human contact, and airborne dust, lint and oil particles. The cleaning procedure adopted to clean the glass slides is described in detail.

i) The glass substrates were first treated with sodium hydroxide solution. The alkaline agent dissolves fatty materials by saponification and renders them wet and keep the substrates into the distilled water.

ii) The second step is to clean the substrates by the soap solution.

iii) After rinse with distilled water the substrates were subjected to ultrasonic agitation for about 30 minutes in distilled water mixed with some drops of soap solution. The shock waves created in the solvent rendered possible the removal of residues.

iv) The substrates were then dried in an oven for about 45 minutes.

v) The substrates were pre-cleaned with isopropyl alcohol. The isopropyl alcohol vapour condensed on the object to be cleaned and hence enhanced to removal of surface contaminants.
vi) Finally the substrates were heated in an oven for about 45 minutes at a temperature of 373 K.

2.6 SAMPLE PREPARATION

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) was kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts is used to provide the accessory current for heating the molybdenum source which was used for the evaporation process. Prior to evaporation, the evaporant material was carefully degassed at lower temperature for about 45 minutes with the closed shutter. Deposition of PbPc on pre-cleaned glass substrates under the pressure of $10^{-6}$ Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. Rotary drive was employed to maintain uniformity in film thickness. The thickness of the films was measured by Quartz crystal monitor. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties.

2.7 FABRICATION OF THIN FILM CAPACITORS

The capacitors were formed on a substrate with the dielectric layer in between the two metal electrodes so as to form a Metal-Semiconductor-Metal structure.

2.7.1 Selection of Electrode Material

The selected electrode should adhere well to the substrate to form a stable structure; it should not react with the material of the film and should have a low electrical resistance. Generally metals like gold, silver, copper,
aluminium, titanium, lead and tin have been used as electrode materials. Of this gold, silver and copper have very low resistance but their adherence to the substrate is poor. Titanium, lead and tin have good adhesion but offer high resistance. Only aluminium has been established to possess both qualities i.e. low resistance and good adhesion and has been used for electrode deposition in the present work.

2.7.2 Electrode Deposition

Aluminium (99.999% purity, Aldrich chemicals, USA) was evaporated at a pressure of $10^{-6}$ Torr from a helical tungsten filament through masks to form the lower electrode. Aluminium melts, wets the filament and results in uniform coating. The source to the substrate distance was maintained as 13.5 cm prior to the evaporation; aluminium was kept under shutter for two minutes. The required dielectric films have then been coated with the aid of suitable brass masks. Finally the upper electrode was formed with aluminium to complete MSM structure. The electrode shapes and the final MSM structure are shown in Figure 2.4.

![Figure 2.4 Formation of (a) top electrode (Al) (b) dielectric layer (PbPc) over the top electrode (c) bottom electrode and (d) the final MSM structure](image-url)
2.8 **THICKNESS MEASUREMENTS**

Thickness plays an important role in film properties and almost all film properties are thickness dependent. In all thickness measurement techniques it is generally assumed that the films are homogeneous and more or less uniformly deposited on the substrates so that the film will have a mean thickness.

Thickness of the films are measured either by the monitor method (in situ monitoring of the rate of deposition), or after the film is taken out of the deposition chamber. Different types of the thickness measurements can be done which is termed as mechanical, electrical, magnetic, radiation, optical, mass difference etc.

Electrical methods of film thickness measurements involve film resistance method, capacitor monitor method and ionization method. Important optical methods are photometric methods, ellipsometric methods, spectrophotometric methods including Fizeau, Michelson beam interferrometry and polarization interferrometric methods (Goswami (1996), Chopra (1969), Maissel and Glang (1970)). Ellipsometric method is very accurate for its absorption property of radiation such as X-ray, α-ray, β-ray, electron beam etc., and the absorption is generally an experimental function of film thickness. Films of thickness estimated by Tolansky’s method using multiple-beam Fizeau fringes were prepared at room temperature using a high vacuum plant of the type Balzer 121 under a vacuum pressure of $10^{-6}$ Torr (Abd. El-Salam et al (1993)).

2.8.1 **In-situ Measurements**

Monitoring methods are very important because they allow the preparation of a thin film of selected thickness. Moreover, they can be used
for measurements of deposition rate. The thickness of the films was measured by employing quartz crystal thickness monitor.

2.8.2 Theory

The quartz crystal monitor utilizes the thickness shear mode of piezoelectric quartz. In this method thickness measurement depends on the oscillation of a quartz crystal when excited and the frequency of its oscillation depends on its thickness. In this the major crystal surfaces are antinodal and mass added on either one or both sides shifts the resonance frequently irrespective of the thickness, density, elastic constants or stiffness of the added material. A 35°20' quartz crystal cut called the A-T cut, is generally used for the monitoring because of its low temperature coefficient for the resonant frequency. The frequency of the fundamental resonance of a thickness made for an A-T cut crystal is given by

\[ f = \frac{1}{2d} \left[ \frac{C}{\rho_q} \right]^{\frac{1}{2}} = \frac{N}{d} = \frac{1670}{d} \text{ mmkc/sec} \]  

(2.1)

where \( d \) is the crystal thickness, \( \rho_q \), the density, \( C \), the shear elastic constant and

\[ N = \left[ \frac{C}{4\rho_q} \right]^{\frac{1}{2}} = 1,670 \text{ mmkc/sec} \]

Change in frequency \( \Delta f \) due to a deposit of mass \( m \), added to the area \( A \) of the antinodal surface of a mechanical resonator, is given by

\[ \Delta f = -f \frac{km}{\rho_q Ad} \]  

(2.2)
where the constant $k = 1$ and the negative sign implies a decrease in the frequency. Combining equations (2.1) and (2.2)

$$
\Delta f = -f^2 \frac{km}{N \rho_q A} = C_f \times \frac{m}{A} = -C_f \rho_{\text{film}}
$$

(2.3)

where $C_f = \left[ \frac{f^2 k}{N \rho_{\text{film}}} \right]$ is a constant of the crystal, and $m = At \rho_{\text{film}}$ assuming a uniform film of thickness $t$ and a constant density $\rho_{\text{film}}$. Thus

$$
t = \left[ \frac{-\Delta f}{C_f \rho_{\text{film}}} \right]
$$
yields average film thickness.

Any pre-deposit can easily be removed by dissolving the underlayer in NaOH solution and some crystal may be used again. The sensitivity of the crystal does not increase appreciably by depositing over an area larger than the electrode. For a deposition covering an area is smaller than the electrode area results in the slight decrease in mass sensitivity.

The maximum sensitivity of a quartz crystal monitor is limited by variations in the crystal frequency due to the temperature, oscillator drive level and changes in the oscillator circuit. The standard method of operation of an A-T cut crystal is by perpendicular excitation using metal electrodes on the central area of each face. The control is operated at series resonance where parallel capacitance has a smaller effect. However, the capacitance should be kept smaller to maintain high-frequency stability. Water cooling of the crystal holder is necessary to control excessive heating due to long duration deposition. The crystal monitor may be used not only to monitor the deposition rate but also to control conveniently the evaporation rate from a vapour source.
2.9 CONCLUSION

PbPc thin films of thickness 150, 300 and 450 nm on glass substrate and 150 nm on KCl substrate were prepared by thermal evaporation method. The higher thickness 450 nm on glass film is annealed in air at 323 K and 373 K. For dielectric and conduction analysis, sandwich structures of the type Al/PbPc/Al were formed. Al electrodes with 1 mm gap (Al-PbPc-Al) and 10 mm width were deposited onto PbPc films for photoconduction property on glass and KCl substrate.