CHAPTER X

Experimental Techniques
Sample Preparation Techniques

10.1. Introduction

In general, the deposition of films is by one of the various processes under the broad classification of physical and chemical methods. Experimental techniques, that includes choice of the substrates and its cleaning, preparation of films and measurement of film thickness is the primary process for any sort of application. The substrates on which the films are formed were chosen according to the characterizations and the type of application. Film preparation technique is outlined as a part of this chapter. The in-situ thickness measurement and various measurement techniques for film characterization implemented in the present work are also outlined.

10.2. Base Materials (Substrates)

10.2.1. Choice of Substrates

The function of the substrate is to provide the base onto which thin film circuits are fabricated and various thin film multilayers are deposited. The need for long-term stability in thin film substrates makes it imperative that no chemical reactions occur which could change the properties of the film. The substrate must therefore fulfill certain requirements as to mechanical strength and there must be adequate adhesion of the film to the substrate, not only at normal temperature but also during relatively large temperature changes. Further, to form the films with defined and reproducible electrical and other parameters, the surface of the substrate should be flat and smooth.

It is, in general, possible to say that there is no material that would satisfy all the requirements. The most widely used substrates for polycrystalline films are glass, fused silica, beryllia or beryllium oxide – based ceramic, aluminium nitride and metals. Organic materials such as Mylar and Teflon owing to their low thermal conductivity are used only in special cases. Recently, interest in solar cells on lightweight flexible metallic substrates is increasing as it offers several advantages.
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compared to the heavy and damage prone glass based devices. Use of metallic substrates will allow annealing at higher temperatures and hence film with larger grains can be prepared [1]. In the present work we have used Blue-Star glass micro slides as substrates to form ZnPc thin film. Indium Tin Oxide (ITO-10 Ohms of resistance) coated glass slides has been used as substrate to fabricate solar cells.

10.2.2. Substrate Cleaning

For durable and adherent coating a substrate must be adequately clean. The proper cleaning technique depends on the nature of the substrate, the nature of the contaminants, and the degree of cleanliness required. Expected contaminants include those from manufacturing procedures, human contact, and airborne dust, lint, and oil particles. Cleaning involves the breaking of adsorption bonds between the substrate and the contaminants without damaging the substrate surface itself. The energy to perform this step may be provided directly as heat or ion bombardment, by chemical reaction or solvation, or by mechanical scrubbing [2].

10.2.2.1. Cleaning of Glass Substrates

The procedure used for cleaning glass substrates, which has been found to consistently enable blemish-free films to be produced, is as follows:

1. The substrates were first treated with sodium hydroxide (NaOH) solution. This alkaline agent dissolves fatty material by saponification and menders them wet.
2. After chemical treatment the substrates are washed by hand using a cotton pad and a solution of a detergent.
3. The substrates are then rinsed in distilled water, and placed in an ultrasonic cleaner where they are agitated for 30 minutes in a solution of detergent and distilled water.
4. A second agitation in distilled water follows, and the substrates are dried in a hot-air oven.
5. Finally, the substrates were pre-cleaned with isopropyl alcohol and then heated in an oven for about one hour at a temperature of 100°C.
10.3. Mask

Many applications of thin film lead to the requirement of forming thin film 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 to prevent removal of an already deposited film from certain regions.

10.3.1. Preparation and Cleaning

In the fabrication of Metal-Semiconductor-Metal (MSM) structure, masks have been immensely made use of. For the electrode, dielectric layer, and heterojunction formation masks of thin brass and mica were used respectively. The brass masks of precise dimensions with vertical edges have been prepared by the photolithographic technique. The masks should also be cleaned prior to use in order to avoid the formation of defects in the deposited films for the reason that during deposition the masks are in contact with the substrates. The masks were cleaned with acetone to remove the organic contaminants.

10.4. Thin Film Deposition Techniques

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 been employed [3,4]. The deposition technique and its associated process have a characteristic effect on the nucleation and growth-dominated microstructure of a thin film and thereby on its physical properties [5].

A thin film deposition process involves three steps:

1. Creation of atomic /molecular / ionic species,
2. Transport of these species through a medium,
3. Condensation of the species on a substrate.

Depending on whether the vapor species has been created by a physical process, by a chemical, electroless, or electrochemical process, the deposition process can broadly classified into two main groups, namely, chemical methods (including electro chemical methods) and physical methods.
10.4.1. Chemical and Electrochemical Methods

Among chemical and electrochemical methods the most important are electrolytic deposition, electroless deposition, anodic oxidation, and chemical vapor deposition (CVD) [6]. The properties of the films prepared by these methods are not easily reproducible and hence the chemical methods are of limited use. In cathode electrolytic deposition, the substance to be deposited is present in a solution or melts in the form of ions. The properties of the deposited films as, its adhesion to the substrate, its crystal structure, etc., may be influenced by the composition of the electrolyte. By this method, it is, of course, possible to deposit films only on conducting substrates and substances in the electrolyte may contaminate the films. Electroless deposition, based upon the similar principle, involves the deposition from the solution by electrochemical processes without the presence of an externally applied field. The rate of deposition depends on the temperature of the bath and in some cases the deposition needs to be stimulated by a catalyst. Anodization is a field-assisted form of thermal growth [7]. The anodization can be accomplished galvanostatically as well as potentiostatically. The pH of the electrolyte plays an important role in obtaining a coherent film. Chemical vapor deposition (CVD) is a widely used method in semiconductor technology for the preparation of thin monocrystalline films of high purity. Chemical vapor deposition, involves essentially, exposure of the substrate to one or several vaporized compounds or reagent gases, some or all of which contain constituents of the desired deposited substance. A chemical reaction is then initiated, at or near the substrate surface, producing the desired material as a solid-phase reaction product, which condenses on the substrate.

10.4.2. Physical Methods

The most important physical methods for the preparation of thin films are sputtering and vacuum evaporation. Both methods require lowered pressure in the working space and therefore make use of vacuum techniques.

10.4.2.1. Sputtering Techniques

The ejection of atoms from the cathode surface by impinging of energetic positive ion of noble gases such as helium, argon, neon, and krypton, at a reduced
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pressure under a high dc voltage gives rise to the sputtering phenomenon. The ejection process, known as sputtering, takes place as a result of momentum transfer between the impinging ions and the atoms of the target surface. An increasing interest in the deposition of films of technological importance for devices fabricated from metals, alloys, oxidic and other compounds of refractory nature has led to a detailed study of this process [4,8] and it is now possible to make various resistive, semi conducting, super conducting and magnetic films by this technique in a better way.

The different methods of sputtering are,

1. Glow discharge sputtering
2. Magnetron sputtering
3. rf sputtering
4. Ion beam sputtering
5. Reactive sputtering and
6. Triode sputtering

Thermal evaporation technique employed in the present work is described as a separate topic of interest in this chapter and is as follows.

10.5. Vacuum Evaporation

Vacuum evaporation is currently the most widely used method for the preparation of thin films. This method is comparatively simple, but it can in proper experimental conditions provide films of extreme purity and, to a certain extent, of preselected structure.

The process of film formation by evaporation consists of several physical stages:

1. Transformation of the material to be deposited by evaporation or sublimation into the gaseous state
2. Transfer of atoms or molecules form the evaporation source to the substrate
3. Deposition of these particles on the substrate and
4. Rearrangement or modifications of their binding on the surface of the substrate.
The rate of condensation / deposition of the vapor atoms depends on the vapor-source-substrate geometry and the condensation coefficient on the surface under given physical conditions. Deposition of films at normal rates from 1 to 10Å/sec must be carried out in a vacuum better than 10^{-5} Torr if significant gas contamination of the film is to be avoided. Vaporization of alloys and compounds is usually accompanied by dissociation or association, or both processes. The tendency to dissociate is greater with higher evaporation temperatures and lower pressures [5].

The temperature of a material for evaporation may be raised by direct or indirect heating. There are different methods for evaporating the material, namely

1. Resistive heating
2. Flash evaporation
3. Arc evaporation
4. Exploding-wire technique
5. Laser evaporation
6. RF heating and

10.5.1. Flash Evaporation

Flash evaporation is one of the easiest and flexible techniques for the deposition of thin films. The objective of film-composition control is well accomplished by evaporating to completion even small quantities of the constituents in the desired ratio. The figure 10.1 shows the flash evaporation setup. In the present setup only one filament was used at a temperature sufficiently high to evaporate the less volatile material. Although fractionation occurs during the evaporation of each particle, the latter are so small that stratification in the film is limited to a few atomic layers. These potential in homogeneities are further reduced by dispensing the evaporant in a steady trickle, thus there are several different particles at all times. Hence maintaining the uniform composition of that of the source material and accordingly excellent control of film composition can be achieved by this method of film preparation.
10.6. Vacuum Coating Unit

The photograph of “HIND HIVAC” coating unit (12A4D) used in the present work is shown in figure 10.2.

The unit consists of three main sections namely

1. The vacuum chamber
2. The pumping system
3. The electrical equipment with connection

The vacuum chamber could be evaluated by a three-stage oil diffusion pump backed by a double stage gas ballast rotary pump capable of evaluating 200 liters / minute. The silicon oil, DC704, is having a low vapor pressure (10\(^9\) Torr) have been used as the charge for the diffusion pump.
The chamber pressure could be measured from a thermal conductivity gauge (pirani gauge) for low pressures ($0.5 - 10^{-3}$ mbar) and an ionization gauge (penning gauge) for still lower pressures ($10^{-2} - 10^{-4}$ mbar). The evaporation of the material from the filament or boat has been facilitated by a LT supply obtained from the secondary of a transformer.

**10.7. Sample Preparation**

**(a) ZincPhthalocyanine (ZnPc)**

ZincPhthalocyanine (98% pure) obtained from Fluka Chemie Company, Germany was evaporated by resistive heating method. The powder form of ZnPc was placed in a molybdenum boat (100amps) and heated with high current by energizing transformer. The transformer capable of supplying 150 amperes at 20 Volts is used to provide the necessary current for heating the molybdenum source. Prior to evaporation, the evaporant material was carefully degassed at a lower temperature for about thirty minutes with the shutter closed. Deposition of the material on to pre-cleaned glass and metallic substrates under the pressure of about $\sim 10^{-6}$ mbar was achieved by slowly varying the current. A constant rate of evaporation 1Å/sec was maintained throughout the study. The adhesion of the films to the substrate seems to be extremely good. For the preparation of heterostructures
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The as deposited films were placed in the substrate holder with appropriate masks. The in situ substrate heater arrangement has been used to prepare the ZnPc thin films at various substrate temperatures and the copper-constant thermocouple has been employed to measure the temperature.

(b) TiO\textsubscript{2} sol preparation

The Sol-gel TiO\textsubscript{2} nano particle synthesis is based on hydrolysis and condensation of metal alkoxide. The reaction can be represented as follows:

\[
\text{Ti(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{Ti(OR)}_3(\text{OH}) + \text{ROH} \quad \text{(Hydrolysis)}
\]

\[
\text{Ti(OR)}_4 + \text{Ti(OR)}_3(\text{OH}) \rightarrow \text{Ti}_2\text{O(OR)}_6 + \text{ROH} \quad \text{(Condensation)}
\]

The reaction stops with the inclusion of two water molecules:

\[
\text{Ti(OR)}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{ROH}
\]

Where R is the alkaline group.

In the first step 3.2 ml of \([\text{TiO}_2\text{CH}_3]_4\) (Aldrich chemicals, Germany) is added to the mixture of C\textsubscript{2}H\textsubscript{5}OH, iso-propanol, and HCl in the volumetric ratio of 4ml: 6 ml:0.5 ml respectively. The Solution is stirred vigorously for 1 hour. In the second step, the mixture of C\textsubscript{2}H\textsubscript{5}OH (2ml), iso-propanol (4 ml) and deionized water (0.8ml) was prepared and stirred for 1 hour. The resultant compounds from the first step and second step are added together and stirred well for 1 hour, further 0.4 ml HNO\textsubscript{3} (69-72\% Pure Chem Labs India) was added in the above mixture as a catalyst, and TiO\textsubscript{2} transparent sol was obtained as a end product from the mixture.

(c) Preparation of TiO\textsubscript{2} thin film layer

Usually sol-gel growned TiO\textsubscript{2} films develop macro cracks in its surface. Formations of macro cracks are controlled by a desired deposition rate during deposition. In the present work an attempt have been made to control the macro cracks developed in the film through micro controller assembly. The TiO\textsubscript{2} films were coated on the well-cleaned glass substrate by dip coating technique. A dip coating apparatus (figure 10.3) equipped with a micro controller assisted stepper motor to
control the pullout rate, was used to dip in and pull out the substrate at a constant rate of withdrawal. The constant pull out rate was maintained at 0.3 mms⁻¹ throughout the deposition.

![Figure 10.3 Schematic diagram of the Sol-Gel dip coating apparatus.](image)

### 10.8. Fabrication of thin film capacitors

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

#### 10.8.1. Electrode Material

Electrode should adhere well to the substrate to form a stable structure. The electrode material should be such that it should not react with the material of the dielectric 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 these, 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 posses both qualities.
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Apart from aluminium (Al), Copper and Silver has been used as electrodes in order to study the electrode effect on the ZnPc thin films.

10.8.2. Thin Film Capacitor Preparation

Aluminium (99.999% purity) obtained from Aldrich chemicals, USA, was evaporated at a pressure of $10^{-5}$ mbar from a helical tungsten filament through brass masks to form the bottom as well as top electrodes. The required structure of the electrode was attained with the aid of brass masks. The electrode shapes and the final MSM structure are shown in figure 10.4.

![Figure 10.4](image)

**Figure 10.4** Formation of (a) top electrode (Al) (b) dielectric layer over the top electrode (c) bottom electrode (Al) and (d) the final MSM structure.

10.9. Thickness Measurement

Thickness is one of the most important thin film parameters since it largely determines the properties of film. Methods of monitoring thickness can be divided into several groups, including gravimetric, optical, electrical, magnetic and radiation. Some methods can only be used for finished films, while others enable to monitor thickness during the actual process of film formation.
**10.9.1. In-situ measurements**

Monitoring methods are very valuable because they allow the preparation of a thin film of selected thickness. Moreover, they can be used for measurement of deposition rate by measuring the thickness increment over unit time. The thickness of the films was measured by employing quartz crystal thickness monitor.

**10.9.1.1. Theory**

The quartz crystal monitor utilizes the thickness shear mode of a piezoelectric quartz crystal. In this, the major crystal surfaces are antinodal, and mass added on either one or both sides shifts the resonance frequency irrespective of the thickness, density, elastic constants, or stiffness of the added material. A 35° 20' quartz crystal cut, called the AT cut, is generally used for the monitor because of its low temperature coefficient (±5X10^-6 between -20 and +60°C) for the resonant frequency. The frequency of the fundamental resonance of a thickness made for an AT cut crystal is given by

$$f = \frac{1}{2d} \left( \frac{c}{\rho_q} \right)^{1/2} = \frac{N}{d} = \frac{1670}{d} \text{mmKc/Sec} \quad (10.1)$$

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

$$N = \left( \frac{c}{4\rho_q} \right)^{1/2} = 1,670 \text{ mmkc/sec}.$$ 

Warner and Stockbridge showed that a 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

$$\Delta f = -f \frac{km}{\rho_q Ad} \quad (10.2)$$

Where the constant \(k = 1\) and the negative sign implies a decrease in the frequency. Combining equations (10.1) and (10.2),

$$\Delta f = -f^2 \frac{km}{N\rho_q A} = -C, \frac{m}{A} = C, t \rho_{film} \quad (10.3)$$
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Where \( C_f = \left( \frac{f^2 k}{N \rho_{\text{film}}} \right) \) is a constant of the crystal, and \( m = A t \rho_{\text{film}} \) assuming a uniform film of thickness \( t \) and a constant density \( \rho_{\text{film}} \). Thus \( t = \frac{\Delta f}{C_f \rho_{\text{film}}} \) yields average film thickness.

Any predeposit can easily be removed by dissolving the under layer in NaOH solution, and the same crystal may be used again. The sensitivity of the crystal does not increase appreciably by depositing over an area larger than the electrode, except when the conductive coating also increases the active area of the electrode. For a deposit covering areas smaller than the electrode area, the mass sensitivity decreases slightly.

The standard method of operation of an AT-cut crystal is by perpendicular excitation using metal electrodes on the central area of each face. The crystal is operated at series resonance where parallel capacitance has a smaller effect. However, the capacitance should be kept small to maintain high frequency stability and a high Q value. 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. Water cooling of the crystal holder can easily be incorporated and may be necessary for excessive heating due to lengthy deposition times from extended sources. The crystal monitor may be used not only to monitor the deposition rate but also to control conveniently the evaporation rate from a vapor source.

10.10. Structure and Surface

Structural characterization of these films was carried out by X-ray diffractometer (JEOL Japan, JDX8030 model). Scanning Electron Microscope (JOEL 840 SEM) was employed in the present study to analyze the surface morphology of the film surface. Microstructural analysis was performed in a HRTEM microscope JEOL 2010FEG, with spherical aberration \( C_s = 0.5 \) mm and ultimate resolution of 1.9 Å. Before the analysis, the ZnPc powders stripped from the substrate was grinded in an agate mortar and dispersed in ethyl alcohol by sonic bath. A drop of this suspension was deposited on a 300-mesh carbon coated Cu grid. The images were digitalized in-situ using the Gatan camera in the microscope, and a digital processing
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was used in the Fourier space in order to enhance the structure of the observed individual reflections. The AFM analyses were performed using the Multimode Scanning Probe Microscope (SPM) nanoscope IV, Digital Instruments.

10.11. Optical Measurements

The optical transmittance measurements were made in the UV, visible and IR regions at near normal incidence for all the films deposited on glass substrates. In the present work, JASCO – UV/VIS/NIR double beam spectrophotometer (JASCO - V570 model) was used. The spectrophotometer has a wavelength range of 190nm to 2500nm with an accuracy of ± 0.3nm. Since the spectrophotometer was interfaced with computer the recorded spectrum is obtained directly from the computer.

10.12. Electrical Measurements

The figure 10.5 and 10.6 shows the electrical measurement setup for DC and AC respectively. Current – Voltage characteristics of the junctions (Al-CdTe/CdS-Al structure) were studied by employing Digital pico ammeter (DPM 111,Scientific equipment, Roorkee) in series with the capacitor and voltage source. Figure 10.5 shows the experimental dc conduction set up employed in the present study. All the studies were performed under a vacuum of about 680 mmHg. The I-V behaviour of the junctions was studied in the temperature range 300-500K and the temperature during measurements was maintained using continuously variable voltage autotransformer. A Copper-Constantan thermocouple is used for the temperature measurements. A potential of 1-20 volts was applied using DC regulated power supply in series with a digital voltmeter. The Capacitance-Voltage measurements were made at room temperature in dark using digital LCR meter (LCR 819, GW Instek, Good Will Instrument Company Ltd., Taiwan). The bias dependent capacitance of the junctions was studied by applying reverse bias voltages (0-2 volt) for frequencies in the low (50Hz) to high (100KHz) values. For this purpose the internal bias of the LCR meter was switched OFF and the external bias was switched ON. Through out the study, the equivalent series capacitance (Cs) of the dielectric material was measured.
10.13. Photoconduction studies

The photoconductive property of the film has been analyzed by subjecting the deposited ZnPc films by irradiation of light from a tungsten lamp. The photocurrent has been measured using a multifunctional optical power meter (ORIEL - Model 70310 USA). The variations of photocurrent with applied voltage and light intensity have been studied. The spectral response of films has been recorded in the wavelength region 400 to 800nm. Electrical conductivity was measured by taking silver paste as a contact electrode at 1cm separation applied on the film surface. The samples are kept in the measurement chamber. An ELH lamp was used for white light and a series of oriel VIS-NIR interference filters were used for monochromatic
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light. The incident light intensity was measured in mW/cm² by placing a suryampi at the position of the sample.


In the present study ZnPc solar cells with the structure ITO/ZnPc-CdS/Ag and ITO/ZnPc-TiO₂/Ag have been fabricated. Polycrystalline p-type ZnPc films have been deposited on to the ITO substrates by the vacuum evaporation method. CdS window layer n-type has been formed on the ZnPc films by thermal evaporation technique, which results in the formation of n-CdS/p-ZnPc heterojunction solar cells. The TiO₂ layer have been prepared by the sol-gel method on the ZnPc films to form TiO₂/ZnPc heterojunction solar cells. The characteristics of the solar cells have been studied by illuminating the white light using a tungsten lamp. The light intensity has been measured using a suryampi.
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