Chapter 2

APPARATUS AND EXPERIMENTAL TECHNIQUES USED IN THE PRESENT STUDY

2.1. Introduction

Phthalocyanines are the most extensively studied materials among the organic semiconductors\(^1,2,3\) after anthracene.\(^4\) They are very stable and can be sublimed without decomposition. They retain high purity, and are relatively easily crystallised. Copper phthalocyanine, Cobalt phthalocyanine and Lead phthalocyanine have wide range of applications in gas sensors\(^5\), artificial solar cells\(^6\) and pigment industry. There are a number of deposition techniques\(^7\) used for making these films. In this chapter, the apparatus and experimental techniques used in the present study are dealt with.

2.2. Methods of Preparation of Thin Films

Methods of preparing thin films may be divided into (i) chemical methods (ii) physical methods and (iii) sputtering. Chemical methods include (1) chemical vapour deposition (2) spray pyrolysis (3)
electrodeposition (4) anodisation (5) solution growth and (6) screen printing. The formation of very pure and well-defined films is possible using physical vapour deposition techniques. Physical vapour deposition is classified into (1) thermal evaporation (2) electron beam evaporation (3) molecular beam epitaxy (4) activated reactive evaporation and (5) ion plating. Sputtering can be further classified into (i) d.c. sputtering, (ii) rf sputtering, (iii) magnetron sputtering and (iv) ion beam sputtering.

Each of the above-mentioned methods has its own advantages and disadvantages, and we will restrict our discussion only to the method which we have used in this study. We have employed the thermal evaporation method for the preparation of thin films in this thesis.

2.3. Thermal Evaporation

One of the most widely used techniques for depositing thin films is thermal evaporation.\(^3\) Basically it involves three steps; boiling or subliming of source to form its vapour, transport of the vapour from the source to the substrate and condensation of the vapour on the substrate. The basic physics of the process contains elements of thermodynamics, kinetic theory of gases and condensation phenomena.
Solid materials are sublimed under high vacuum when heated to sufficiently high temperature. The condensation of the vapour onto a cooler substrate yields thin solid films. This method has the following advantages.

1. Impurity concentration in the film will be minimum.
2. Material boils at lower temperature under vacuum.
3. Growth can be effectively controlled.
4. Mean free path of the vapour atom is considerably larger at low pressure and hence a sharp pattern of the film is obtained.
5. Selection of the substrate is wide.

The evaporation rate and hence condensation have wide limits, depending upon the type of source and material used. Characteristics of the prepared film can be varied by parameters such as temperature, type of substrate, deposition rate and residual atmosphere. All these parameters can be controlled in the thermal evaporation method. More than that single evaporation can give films of different thicknesses. We have used here molybdenum boats and tungsten baskets for evaporation of phthalocyanine thin films. Films of high purity can readily be produced with a minimum of interfering conditions. The different factors which are to be expected to have some influence on the nature and properties of an evaporated film are the following.
2. Vapour beam intensity
3. Nature and conditions of substrate
4. Temperature of the vapour source and velocity of the impinging molecule.
5. Material contamination from vapour source.

2.4. Effect of Residual Gases

Because of the collisions with ambient gas molecule, a fraction of the vapour, proportional to \( \exp(-d/\lambda) \) is scattered and hence randomised in direction within a distance 'd' during their transfer through the gas.

The mean free path \( \lambda \) for air at 25°C is given in Table 2.4.1. Table 2.4.1. shows that a pressure of \( 10^{-5} \) Torr is necessary to ensure straight line path for most of the evaporated species and for substrate source distance of 10 to 50cm in vacuum chamber. The residual gas atoms also strike the substrate during the deposition.

Table 2.4.1: Data on the Residual Air at 25°C in a Typical Vacuum used for Film Deposition

<table>
<thead>
<tr>
<th>Pressure Torr</th>
<th>Mean free path ( \lambda ) (between collision) cm</th>
<th>Number of collisions/sec (between molecules)</th>
<th>Number of molecule/cm(^2) sec (striking surface)</th>
<th>Monolayer/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-2} )</td>
<td>0.5</td>
<td>9x10(^4)</td>
<td>3.8x10(^{18})</td>
<td>4400</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>51.0</td>
<td>900</td>
<td>3.8x10(^{16})</td>
<td>44</td>
</tr>
<tr>
<td>( 10^{-5} )</td>
<td>510</td>
<td>90</td>
<td>3.8x10(^{15})</td>
<td>4.4</td>
</tr>
<tr>
<td>( 10^{-7} )</td>
<td>5.1x10(^4)</td>
<td>0.9</td>
<td>3.8x10(^{13})</td>
<td>4.4x10(^{-2})</td>
</tr>
<tr>
<td>( 10^{-9} )</td>
<td>5.1x10(^6)</td>
<td>9x10(^{-3})</td>
<td>3.8x10(^{11})</td>
<td>4.4x10(^{-4})</td>
</tr>
</tbody>
</table>
2.5. Effect of Vapour Beam Intensity

The rate of evaporation and hence condensation can vary over wide limits depending upon the type of material and source being used. There exists a critical vapour beam density below which no condensation occurs and also a critical substrate temperature above which no film could be formed except at very high beam intensities.

2.6. Effect of Substrate Surface

The nature of the condensed film depends on the structure of the substrate, its temperature and cleanliness. Condensing atoms tend to take the structure of underlying surface, forming amorphous or polycrystalline layers on amorphous substrate and a single crystal film on single crystal substrate. The adhesion of a film to the substrate is strongly dependent on the cleanliness and microscopic topography of the substrate surface. Presence of the contaminants on the substrate surface may increase or decrease the adhesion depending on whether absorption energy is increased or decreased.

2.7. Effect of Evaporation Rate

The rate of free evaporation of vapour atoms from a clean surface of unit area in vacuum is given by Longmuir–Dushman equation
\[ N_e = 3.513 \times 10^{22} P_e (1/MT)^{1/2} \text{ moles/cm}^2 \text{ sec} \]

\( P_e \), the equilibrium vapour pressure of evaporant under saturated vapour conditions at a temperature \( T \) and \( M \) is the molecular weight of vapour species. Rate of condensation of the vapours or the deposition rate depends not only on the evaporation rate but also on the source geometry, its position relative to the substrate and condensation coefficient. An increase in the source temperature increases the kinetic energy of the incident species\(^{10}\) also increases the surface mobility and grain size. The grain size may also be modified by giving the film a post-deposition annealing treatment at a temperature higher than the deposition temperature. It should be noted that grain growth obtained during post deposition annealing is significantly reduced from that obtained by depositing the film at annealing temperature because of the involvement of high activation energy process of thermal diffusion. For a given set of material–substrate combination and under a given set of deposition conditions, grain size increases as film thickness increases. Beyond a certain thickness grain size remains constant suggesting coherent growth without underlying grain growing further. The effect of increase in grain size with thickness is more prominent at high substrate temperatures.
2.8. Contamination from Vapour Source

Heating of materials can be carried out directly or indirectly by a support. Vapour sources of various types, geometries and sizes can be made easily or commercially obtained. Choice of the element is mainly determined by the evaporation temperature and the chemical reaction of the support with evaporant which may contaminate the film. The vapour sources used in this thesis for film growth are silver, aluminium, copper phthalocyanine, cobalt phthalocyanine and lead phthalocyanine.

2.9. Purity of the Evaporating Materials

The deposited thin films will be contaminated if the evaporant itself is impure. Usually high purity materials are used in evaporation work. The materials used in the present work is supplied by Aldrich Company INC., WI. The elementary analysis of the supplied materials is carried out and results are given below in Table 2.9.1.
Table 2.9.1: Comparison of the Calculated and Obtained (by Elementary Analysis) Percentage Composition of Elements

<table>
<thead>
<tr>
<th>Materials</th>
<th>Elements</th>
<th>Calculated (%)</th>
<th>Analysed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper Phthalocyanine</td>
<td>C</td>
<td>66.72</td>
<td>66.40</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.799</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>19.45</td>
<td>19.70</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>11.02</td>
<td>11.02</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>—</td>
<td>0.58</td>
</tr>
<tr>
<td>Cobalt Phthalocyanine</td>
<td>C</td>
<td>67.26</td>
<td>66.30</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.822</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>19.61</td>
<td>19.80</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>10.31</td>
<td>11.01</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>—</td>
<td>0.59</td>
</tr>
<tr>
<td>Lead Phthalocyanine</td>
<td>C</td>
<td>53.40</td>
<td>52.8</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.24</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>15.57</td>
<td>16.10</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>28.79</td>
<td>28.10</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>—</td>
<td>0.70</td>
</tr>
</tbody>
</table>

2.10. Production of Vacuum

The evaporation of thin films with controlled properties requires an operating environment which interferes as little as possible with the process of film formation. It is possible to obtain high vacuum in a closed chamber to minimise interaction between residual gases and the surface of growing films. A wide variety of vacuum components, materials and assembly techniques are now available. Various degrees of vacuum are given below according to their pressure ranges.\(^\text{11}\)

- Coarse or rough vacuum: 760–1 Torr
- Medium vacuum: 1–10\(^{-3}\) Torr
- High Vacuum: 10\(^{-3}\) – 10\(^{-6}\) Torr
Very High Vacuum \[ 10^{-6} - 10^{-9} \text{ Torr} \]

Ultra High Vacuum \[ 10^{-9} \text{ Torr and below} \]

The advantages of using a vacuum system for thermal evaporation are:

1. The material will boil at lower temperature in vacuum.
2. Oxide formation in the boiling surface can be reduced.
3. Impurities in the deposited film will be little.

To reduce the pressure in a vacuum enclosure, two different principles are employed (1) Physical removal of gases from the vessel by exhausting the gas load to outside and (2) the condensation or trapping of gas molecules on some part of the inner surface of the enclosure without discharging the gas. Oil sealed rotary pump is the former type and diffusion pump, the latter which are discussed in detail in sections 2.11 and 2.12 respectively.

2.11. Oil Sealed Rotary Pump

The cross section of the pump used in the present work (Hind Hivac ED 12) is as shown in Figure 2.11.1. The gas transport is effected as the keyed shaft rotates the eccentric and piston. Then the gas is isolated from the inlet after one revolution, then compressed and exhausted during the next cycle. The rotary pump contains an
Figure 2.11.1: Schematic diagram of the cross section of an oil sealed rotary pump

1. Outlet valve
2. Seal
3. Rotar
4. Inlet
5. Vanes
6. Stator
eccentrically mounted rotor with spring loaded vanes. Friction, wear and tear are minimised by a thin oil film which lubricates all parts of the pump and also seals the minute gap at the seat. The exhaust end is closed by a pressure valve (1 in Figure 2.11.1) leading into the oil reservoir. During rotation, vanes slide in and out within the cylindrical interior of the pump, enabling a quantity of gas to be confined. The crescent shaped air volume is compressed and discharged through an exhaust valve into the atmosphere.

A vented outlet valve admitting a small airflow into the compression section which is called gas ballasting reduces condensation of water vapour by lowering the compression ratio. The fluid in the rotary pump can be either mineral oils or diphenyl ethers, as the high vapour pressure oils decompose during their operation. The problem of backstreaming of oil vapours is solved by installing fore-line traps. These operate by condensation on liquid nitrogen traps or by adsorption on surface active materials. Adsorption traps containing activated alumina is also used which is superior to charged zeolite and activated charcoal. The most important characteristics of the rotary pump is the speed at which it removes the gas from the system. The lowest pressure to which it can exhaust the vacuum system is \( \sim 10^{-3} \) mbar.
The idea of evacuating a vessel by molecular momentum transfer from streaming to diffusing the molecule was first described by Gaede.\textsuperscript{12} There are various traps and baffles to eliminate the problem of backstreaming of pump fluid vapours. The basic elements of a diffusion pump used in our plant (Hind Hivac 114D) are shown in Figure 2.12.1. The work fluid is heated by a heater and boiler, 6 and 7 in Figure 2.12.1 and hot vapour rises in the chimney. The direction of flow is reversed at the jet cap so that the vapours issue through a nozzle with supersonic speed. In passing from a region of higher to lower pressure, vapour expands. The expansion of the gas alters the normal distribution of the molecular velocities by creating a component in the direction of expansion which is larger than the velocity associated with a static gas at thermal equilibrium. The molecule emerging with a normal velocity distribution would spread omnidirectionally and yield no pumping action. Gas molecules from the high vacuum side diffuse through the throat and receive velocity components directed towards the fore-vacuum side; (5 in Figure) by colliding with molecules of the working fluid. Thus the zone of reduced pressure is generated in the vicinity of the nozzle 9, and more gas from high vacuum side diffuses towards this region. The high speed jet of fluid imparts momentum to the random
Figure 2.12.1: Schematic diagram of the cross section of a diffusion pump

1. High vacuum intake
2. Jet cap
3. Throat
4. Vapour jet
5. Fore-vacuum
6. Heater
7. Boiler
8. Oil
9. Nozzle
10. Water cooled casing
moving incoming gas molecules. Thus the gas molecules move towards the outlet where it is removed by a backing pump. The vapour jet condenses on the cooled pump walls and returns to the boiler. The gas molecules diffuse to the vapour molecules, hence the name diffusion pump.

The working fluid should have high molecular weight, low vapour pressure and necessary thermal stability. Commonly used fluids are hydrocarbons, silicon fluids, polyphenyl ether and perfluropolyether. We have used silicon oil 704 DC as the working fluid. This oil is superior to other fluids because of its low vapour pressure and high resistance to oxidation at high working temperatures.

To prevent backdiffusion of gas from dense to the rare zone vapour jet should retain as much of its density as possible. To reconcile this requirement with wide throat area for maximum gas intake, the cross section of the lower zone is narrowed through aerodynamically shaped tapering stacks. The outer walls are water cooled to recover the workfluid back and to produce a denser boundary layer by removing vapour molecules which travel laterally without contributing to the jet action. To enhance the directionality and speed of the vapour the pumps employ multistage stacks, with three jets working in series.
2.13. Vacuum Coating Unit

The type of vacuum equipment needed obviously depends on the desired purity of the film. Detailed reviews on various types of vacuum systems and their ultimate pressures are given by Holland, Caswell, Dushman, and Roth. The vacuum system employed to deposit and characterise thin films in the present work contain an assortment of pumps, tubings, valves and gauges to establish and measure the required reduced pressure as shown in Figure 2.13.1. Basically the vacuum system, "Hind HiVac" Vacuum coating unit model No. 12A 4 consists of 0.4 m diffusion pump backed up by an oil sealed rotary pump. Ultimate pressure obtained in a 0.3 m diameter steel bell jar is of the order of $8 \times 10^{-6}$ mbar. It has set ups for electron beam evaporation and flash evaporation. Most of the evaporations are carried out at a pressure of $(1 - 2) \times 10^{-5}$ Torr. It has provisions for ion bombardment cleaning of substrates. The pressure measurement in the system is done by means of Pirani and Penning Gauges (7 and 12 in Figure 2.13.1) provided with the system.

The Pirani gauge model Hind HiVac-A6STM is used for measuring vacuum in the range $0.5 - 10^{-3}$ Torr with two heads. Change of pressure in vacuum system brings about a rise or fall in number of gas molecules present and hence a rise or fall in the thermal conductivity of
Figure 2.13.1: Schematic diagram of a vacuum coating unit

1. Bell jar
2. Substrate
3. Thickness monitor
4. Source shutter
5. Electron beam gun
6. Current feed through
7. Penning Gauge
8. Roughing valve
9. Baffle valve
10. Diffusion pump
11. Highvac
12. Pirani Gauge
13. Fore-line trap
14. Isolation valve
15. Rotary pump
the gas. Thus the heat loss of constant voltage electrically heated filament in the system varies with the pressure. The Pirani gauge head element has high temperature coefficient of resistance. So a slight change in the system pressure brings about useful change in filament resistance resulting in an out of balance current which can be read as pressure on a meter as in Figure 2.13.2. The filament is often reconditioned if the gauge behaves erratically when it is filled with any contaminants. The gauge head is flushed with acetone and thoroughly dried. 10V AC or DC is applied across the filament to volatise the deposits on the filament. The Penning gauge model STM4 is used to measure vacuum in the range $10^{-2}$ to $10^{-6}$ Torr in two ranges with instant range-changing provided by a toggle switch. This is a cold cathode ionization gauge consisting of two electrodes; anode and cathode as given in Figure 2.13.3. A potential difference of about 2.3 kV is applied between the cathode and anode through current limiting resistors. A magnetic field is introduced at right angles to the plane of electrodes by a permanent magnet having nearly 800 gauss magnetic field which will increase the ionisation current. The electrons emitted from the cathode of the gauge head are deflected by means of magnetic field applied at right angles to the plane of the electrodes and are made to take helical path before reaching the anode loop. Thus following very long path, the chance of collision with gas molecules is high even at low pressures.
Figure 2.13.2: Schematic representation of Pirani Gauge

1. High vacuum
2. Reference wire
3. Sensing Wire
4. Vacuum system

Figure 2.13.3: Schematic representation of Penning gauge

1. Magnetic field
2. Anode (+)
3. Cathodes (-)
4. Ballast resistor
The secondary electrons produced by ionisation, themselves perform similar oscillations and the rate of ionisation increases rapidly. Eventually the electrons are captured by anode and equilibrium is reached when the number of electrons produced per second by ionisation is the sum of positive ion current and electron current to the anode and is used to measure the pressure of the gas. If the gauge shows unstable pressure reading due to the contamination of the gauge head by forming a thin layer of deposits on the anode loop and cathode liner, it is cleaned chemically by heating for 20 minutes in a solution of 20–30% HNO₃ and 2–3% HF acids. Figure 2.13.4 shows the photograph of the coating unit along with the accessories. We have used oil sealed rotary pump¹⁵ and diffusion pump¹⁰ for the production of high vacuum. In our coating unit the diffusion pump has an evacuating speed of 500 lit./sec. The coating unit has provisions for ion bombardment cleaning of substrates.

2.14. Preparation of Films

Thermal evaporation method of PVD techniques is used for the film preparation. Thin films are evaporated onto clean substrates. Thermal evaporation is a simple method in which the material is created in vapour form by means of resistive heating. On heating a material in vacuum, sublimation takes place and the atoms are transported and get
Figure 2.13.4: Photograph of the coating unit and accessories
deposited onto cleaned substrates held at suitable distance at desired temperatures. The material for deposition is supported on a source which is heated to produce desired vapour pressure. The requirements for the source are that it should have a low vapour pressure at the deposition temperature and should not react with the evaporant. The shape of the source is designed and fabricated in such a way as to hold the evaporant material. We have used both tungsten baskets and tungsten helix as the sources for coating electrodes. The evaporant material in the powder form is deposited using a molybdenum boat. The low tension (LT) supply for evaporation source is obtained from a 230 V input transformer by means of parallel or series connections in the secondary side of the transformer. The LT output from transformer is fed through a current meter and a selector switch to LT feed through and filament holders. The unit is connected for 10V/100A ratings from the transformer.

2.15. Substrate Cleaning

For deposition of films, highly polished and thoroughly cleaned substrates are required. A variety of cleaning processes are available. First the substrates are cleaned using liquid detergent. Then it is kept in dilute nitric acid for some time. After this the substrates are cleaned using distilled water. Then the substrates are agitated ultrasonically in
acetone. They are then rinsed in isopropyl alcohol and dried in hot air. Inside the bell jar the substrates are subjected to ionic bombardment for five minutes as a final cleaning before deposition. The ions are produced inside the bell jar by H. T. discharge at medium pressure.

2.16. Thickness Measurement

There are different techniques to determine the film thickness. We employ the optical techniques for measuring the thickness of the films. It can be used for both opaque and transparent films. The basic principle underneath this technique is the interference of two or more beams of light reflected or transmitted from the bottom and top of the film whose thickness is to be measured. The condition for maxima in reflection will be the condition for minima in transmission and vice versa. In the case of multiple beam interference by reflection, the interference pattern is formed. There is sharp bright fringes on a dark background in the case of transmission whereas sharp dark fringes on bright background in reflection.

For opaque films a sharp step down to substrate plane must be first generated either by a deposition through a mask or by subsequent etching. For practical purposes the fringes formed are classified as the two cases of multiple beam interferrometry. Fizeau fringes are generated by monochromatic light and represent contours of equal
thickness in an area of varying thickness 't' between two glass plates. This is accomplished by contacting the two glass plates such that they form a slight wedge at an angle $\alpha$ so that the thickness between the two plates can be varied. The angle $\alpha$ is made very small so that consecutive fringes are spaced as far apart as possible. For normal incidence of monochromatic light, the spacing between the fringes correspond to a thickness difference of $\lambda/2$, $\lambda$ is the wavelength of the monochromatic light used.

Another method to determine the film thickness is the Fringes of Equal Chromatic Order (FECO). In this case white light is used at angle of incidence zero degree and the reflected or transmitted white light is dispersed by a spectrograph. Here the fringes are formed for certain values of $t/\lambda$. $^{17}$ FECO fringes are obtained with two silvered glass surfaces parallel to each other, where the plate is adjusted to get Fizeau fringes. The spacing between the interferogram is inversely proportional to the thickness 't'. We have used the Tolansky's multiple beam interference method for the determination of the thickness of the film.

2.17. Tolansky's Multiple Beam Fizeau Fringe Method

The schematic representation of Fizeau fringes produced by multiple beam interference is as shown in Figure 2.17.1. The technique
Figure 2.17.1: Schematic representation of the multiple beam interference method

a) Fringe pattern
b) Arrangement
c) Sample with step and a match-flat
can be employed when the film to be studied remains stable in vacuum and can be coated with highly reflective layer. The film is deposited onto the glass substrate. A sharp edge within the film is produced by shadowing with sharp masks during deposition. The film is then coated with a highly reflecting silver layer. A second glass plate with a silver coated surface and having some percentage of transmission is lowered onto the glass substrate and the whole system is illuminated with a parallel beam of monochromatic light of wavelength (\( \lambda = 5893 \, \text{Å} \)) from a sodium vapour lamp. At small distance between two glass plates, when the cover glass is tilted slightly, multiple beam interference fringes appear with a distance 'x'. In the region of sharp edge, the fringes are shifted by a distance 'Ax'. A shift 'Ax' in 'x' corresponds to a thickness step of \( \lambda/2 \) and hence the thickness of the film.

\[
t = \frac{\Delta x}{x} \left[ \frac{\lambda}{2} \right]
\]

2.17.1

2.18. Substrate Heater

Nichrome wires wound over thick mica sheets sandwiched between two mica sheets is used as the substrate heater. Substrates are held against the heater surface. The maximum temperature attainable is 500°C. Substrates can be uniformly heated with this arrangement. Temperature of the substrate is measured by copper-
constantan thermocouple and substrate temperature is controlled by a variable voltage transformer.

2.19. Sample Annealing

The samples have been annealed in a specially designed furnace. It consists of a coil of Kanthal (A1 grade temperature range 1150–1350°C). To avoid heat loss it is surrounded by a thick package of fire brick silica whose working temperature is 1100°C and the melting point is 1710°C. The width of the heating element is about 20 cm. The filament is also covered with sillmate (Al₂O₃–SiO₂) tube, maximum working temperature is 1500°C and melting point is 1710°C. It helps to provide uniform heating region at the centre of the tube. In addition it avoids any thermal shock during the annealing process. The temperature of the heater is controlled and recorded by a digital temperature controller cum recorder.

Figure 2.19.1. shows the block diagram of the temperature controller. The thermocouple used is chromel–alumel type. The output of the thermocouple is calibrated to 0.04 mV/°C and fed directly to the comparator circuit as shown in the block diagram. The comparator consists of the IC LN324 and its associated circuitry. By adjusting the hysteresis loop of the comparator, using a hysteresis voltage regulator one can control, set and reset voltage for the relay switch. The voltage
Figure 2.19.1: Block diagram of the temperature controller cum recorder
corresponding to the setting temperature is referred by the comparator. The heater coil is connected through the relay switch and the power to the heater and thereby the temperature is controlled by the comparator circuitry.

The analog signal from the thermocouple is converted to a digital one with the help of an A/D converter, using a 3 digital single chip A/D converter IC 7107 (intersil) having high accuracy. The A/D converter provides a built-in-seven segment display unit. The temperature can be displayed digitally. When the temperature reaches the pre-set temperature, the heater cuts off automatically, by action of the relay switch. After a few seconds, the heater is again switched on and the process is repeated, thus maintaining a constant temperature at the centre of the furnace. Figure 2.19.2 shows the photograph of the furnace and temperature controller for the post deposition annealing experimental set up.

2.20. Conductivity Cell

A schematic diagram of the conductivity cell fabricated is as shown in Figure 2.20.1. The cell consists of a thick walled cylindrical chamber with a bottom flange and four side tubes made of stainless steel. Three side tubes are closed air-tight with glass windows and are
Figure 2.19.2: Photograph of the post deposition annealing furnace and controller cum recorder set up
Figure 2.20.1: Schematic diagram of the cross section of the conductivity cell

1. Cylindrical chamber
2. Inner tube
3. Liquid nitrogen cavity
4. Copper finger
5. Mica insulator
6. Heater coil
7. Sample holder
8. Glass window
9. Side tube
10. Bottom flange
11. To rotary pump
12. Neoprene "O" ring
13. BNC
14. Thermocouple
15. Connecting leads to
16. Substrate with film
used in spectroscopic studies. The remaining side tube is connected to a rotary vacuum pump and the chamber can be evacuated to a low pressure of $10^{-3}$ mbar. The inner tube is made of stainless steel pipe which has been welded to a large copper finger. The liquid nitrogen cavity and the heater coil help the sample to attain the required temperature very quickly. The outer enclosure is made leak proof by using a neoprene 'O' ring which rests inside the groove on the flanges. A sample holder fixed at the copper finger can hold the film on a substrate in the form of a strip with the help of screws. Mica sheets are placed in between the sample holder and substrate. The outer surface of the copper finger is covered with mica sheets and the heater coil is wound over it. The electrical leads are taken out through teflon insulation. A d.c. power supply is used to heat the heater coil. The electrical leakage current through the mount is by-passed to earth by grounding the inner tube. The leads of the electrodes are taken out using BNC connector. A copper-constantan thermocouple in contact with the sample senses the temperature. Temperature of the sample in the cell can be varied from liquid nitrogen temperature to 400°C.

2.21. Keithley Programmable Electrometer 617

Electrical conductivity measurements are carried out using Keithley programmable electrometer model No. 617. It is a highly
sensitive instrument designed to measure voltage, current, charge and resistance. The instrument has a sensitivity of 0.05%, 0.15%, 0.4% and 0.15% of the reading for the measurement of voltage, current, charge and resistance. The very high input resistance, low input offset current and sensitivity allows accurate measurement. The measuring range is between 10μV and 200V for voltage measurements, 0.1 pA and 20mA in the current mode and 10fC to 20nC in coulomb mode. The resistance can be measured in two modes (i) constant current mode and (ii) constant voltage mode. Due to the high input resistance, a resistance as high as 200 GΩ can be measured in the constant current mode. Using constant voltage mode resistance as high as 10^{16} Ω can be measured. In this mode, the measured resistance is automatically calculated from the applied voltage. The built in voltage source of the instrument can be used to apply a current I, through the unknown resistance R. The insulation resistance is then automatically calculated by the instrument as \( R = \frac{V}{I} \); where \( I \) is the current through the resistance and \( V \) is the programmed voltage. The schematic diagram for the measurement of electrical resistance by two probe method and four probe method are as shown in Figure 2.21.1(a) and 2.21.1(b). Figure 2.21.2 gives the photograph of electrical conductivity experimental set up used in the laboratory.
Figure 2.21.1: Schematic diagram for the electrical conductivity measurement (a) two probe method (b) four probe method
Figure 2.2.1.2: Photograph of the electrical conductivity experimental set up
The model 617 has a built-in voltage source. The voltage can be programmed between \(-102.35\) V and \(+102.4\) V in steps of 50 mV and the maximum measurable output current is 2 mA. The instrument is capable of an internal 100 point data store mode that can be used to log in a series of readings. The fill rate of data store can be set to specific intervals according to the experimental conditions.

2.22. UV–Visible Spectrophotometer

To study the optical transmittance of the films in the ultraviolet-visible range, Shimadzu 160A spectrophotometer has been employed. It is a double beam system employing a static beam splitting half mirror which sends the light beam from the monochromator equally through the sample and the reference substrate. The light beam emitted from the light source (Deuterium lamp \(D_2\) or halogen lamp \(W_1\)) is reflected by the mirror \(M_1\) and is directed into the monochromator. The deuterium lamp produces wavelength from 200 nm. The halogen lamp produces wavelength up to 1100 nm. The light source switching wavelength can be set to any value within the range of 295 to 364 nm. Its initial value is 350.5 nm. The lamps can be automatically interchanged according to the wavelength range needed. All the optical elements except the light source are isolated from the external atmosphere by the window plate \(W\) so as to be dust free. The slit width of the monochromator is fixed at
2 nm. G is a 900 line/nm aberration corrected concave holographic grating. The light beam from the monochromator is passed through the stray light cut off filter F, reflected by the mirror $M_2$ and split by the half mirror $M_3$ into the sample and the reference beams. Each beam passes through the respective cells to the detector. Two voltages are produced by the detector which are proportional to the light intensities of the reference and sample beams respectively. These two voltages are amplified and fed to the electrical system. Figures 2.22.1., 2.22.2 and 2.22.3 give the simplified block diagram of the optical system and electrical system of the Shimadzu 160A spectrophotometer and photograph of the optical set up. The output absorbance or transmittance can be seen in the video display and printed out using the chart recorder.

2.23. X-ray Diffractometer

Shimadzu Model XD-610 diffractometer is used for the X-ray diffraction measurements. The block diagram of the XD 610 system is shown in Figure 2.23.1. The main components of the system are the X-ray tube, the X-ray generator, goniometer, controller/counter and recorder. X-ray tube has a copper anode target. X-ray power generator provides a high voltage from 20 to 60 kV and current ranging from 5 to 60 mA. The goniometer can scan in the range between $20^\circ$. 
Figure 2.22.1: Block diagram of the optical system of the spectrophotometer (Shimadzu 160 A)
Figure 2.22.2: Block diagram of the electrical system of the spectrophotometer (Shimadzu 160 A)
Figure 2.22.3: Photograph of the Shimadzu 160 A spectrophotometer
Figure 2.23.1. Block Diagram of XD 610 diffractometer
and 159°. In the diffractometer X-rays are diffracted from the sample and are concentrated on the detection slit located at a position symmetrical to the sample about the X-ray focus of the tube. The X-rays are detected by scintillation detectors and converted into electrical signals. The signal is picked up by the pulse height analyser after eliminating its noise components. A chart recorder running synchronous with the goniometer gives the recorded spectra. The scattered intensities are angle dependent in the Bragg–Brentano geometry where the x-ray beam falls at an angle θ to the substrate and the detector is placed at an angle 2θ. The specimen and the detector are rotated at angular velocities ω and 2ω respectively to get various diffracting planes. In this geometry when the films of thickness 't' are used atomic spacing between planes can be calculated using Bragg's condition.

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} 2.23.1

where θ is the angle of incidence and λ the wavelength of the Cu Kα radiation. Consequently the scattered intensities will be angle dependent and this has to be taken into account while comparing the intensities with ASTM data.
Since space between atoms are fixed by atoms and ions, the material with which the sample is composed can be detected. Photograph of the XD 610 set up for the structure studies is as shown in the Figure 2.23.2.

Figure 2.23.2 : Photograph of the XD 610 diffractometer
References


