2.1 Introduction

Phthalocyanines have attracted much attention during the last decade as active elements in electronic devices and gas sensors. Due to certain properties of these materials, it is possible to prepare stable and homogenous thin films. We have prepared magnesium phthalocyanine (MgPc), iron phthalocyanine (FePc) and zinc phthalocyanine (ZnPc) thin films for investigating the electrical, optical and structural characteristics. These materials satisfy the unique property that they can be sublimed without decomposition. It is known that the performance characteristics of the films depend on its method of preparation. The metal substituted phthalocyanines are found to crystallise using van der Waals force and the growth conditions and substrate material affect the structure and crystallinity of the film.
2.2 Methods of Preparation of Thin Films

Important methods generally used for the deposition of thin films may be classified as (1) physical vapour deposition method (PVD), (2) chemical vapour deposition method (CVD) and (3) cathode sputtering. Physical vapour deposition method is further classified into (a) thermal evaporation, (b) electron beam gun evaporation, (c) molecular beam epitaxy, (d) activated reactive evaporation and (e) ion plating. Chemical vapour deposition methods include (a) chemical deposition, (b) spray pyrolysis, (c) electro-deposition, (d) anodisation, (e) solution growth and (f) screen printing. Cathode sputtering can be further classified into (a) d. c. sputtering, (b) r. f. sputtering, (c) magnetron sputtering and (d) ion beam sputtering.

Each of the above method has its own advantages and disadvantages and we will restrict our discussion only to the method which we have employed in the present study. We have used the thermal evaporation technique by resistive heating for the preparation of the films and is discussed in detail below.

2.3 Thermal Evaporation Technique

Thermal evaporation technique is one of the most widely used techniques for preparation of thin films. The physical stages of film formation consists of several distinguishable steps as (1) sublimation of the material to be deposited to the vapour phase, (2) transfer of vapours from the evaporation source to the substrate, (3) condensation of vapours upon arrival on the substrate and (4) their rearrangement or modifications of their binding on the substrate surface. The basic theory of vacuum evaporation includes the thermodynamics of phase transitions, kinetic theory of gases and kinetic aspects of condensation processes.
Vacuum evaporation method has the following advantages:

1) Impurity concentration in the film will be minimum.
2) Materials sublime at lower temperature under vacuum.
3) Growth can be controlled effectively.
4) Mean free path of the vapour atoms is considerably large at lower 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. We have used molybdenum boats and tungsten baskets as the sources for the evaporation of phthalocyanine thin films. The characteristics of the films are influenced by speed of evaporation, pressure during deposition, thickness of the coating, angle of evaporation, temperature of the substrate and residual atmosphere. All these parameters can be controlled in the thermal evaporation technique. Another advantage of this method is that single evaporation yields a large number of films of different thicknesses. The factors which influence the nature and properties of evaporated films are discussed below.

2.4 Effect of Residual Gases

Because of the collisions with ambient gas molecule, a fraction of the vapour, proportional to \( \exp \left( -\frac{d}{\lambda} \right) \) 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 for different pressures is given in Table 2.4.1. To ensure a straight line path for most of the evaporated atoms a pressure of \( 10^{-5} \) Torr and source to substrate distance of 10 to 15 cm are necessary. The residual gas atoms also strike the substrate during evaporation.
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/cm² sec (striking surface)</th>
<th>Monolayer/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻²</td>
<td>0.5</td>
<td>( 9 \times 10^4 )</td>
<td>( 3.8 \times 10^{18} )</td>
<td>4400</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>51.0</td>
<td>900</td>
<td>( 3.8 \times 10^{16} )</td>
<td>44</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>510</td>
<td>90</td>
<td>( 3.8 \times 10^{15} )</td>
<td>4.4</td>
</tr>
<tr>
<td>10⁻⁷</td>
<td>( 5.1 \times 10^4 )</td>
<td>0.9</td>
<td>( 3.8 \times 10^{13} )</td>
<td>( 4.4 \times 10^{-2} )</td>
</tr>
<tr>
<td>10⁻⁹</td>
<td>( 5.1 \times 10^6 )</td>
<td>( 9 \times 10^{-3} )</td>
<td>( 3.8 \times 10^{11} )</td>
<td>( 4.4 \times 10^{-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.² Presence of 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 atoms from a clean surface of unit area in vacuum is given by Longmuir-Dushman equation

\[ N_e = 3.513 \times 10^{22} \frac{P_e(1/MT)^{1/2}}{\text{moles/cm}^2\text{sec.}} \]  

(2.7.1)

Pe is the equilibrium vapour pressure of evaporant under saturated vapour conditions at a temperature T and M is the molecular weight of vapour. Rate of condensation of the vapour or the rate of deposition 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 vapour atoms and 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. 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 fabricated 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 films. The evaporants used are silver for electrical contacts, magnesium phthalocyanine (MgPc), iron phthalocyanine (FePc) and zinc phthalocyanine (ZnPc) for preparation of thin films.

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 Co., Inc., WI, USA which has an initial purity of 98%. The purity of the evaporant material could be further increased by entrainer sublimation.

2.10 Production of Vacuum

Vacuum is essential in the film production techniques in order to increase the mean free path of the evaporant atoms, to reduce surface as well as bulk contaminations and to protect the vapour source from oxidation and corrosion. A wide variety of vacuum components, materials and assembly techniques are now available. Various levels of vacuum are given below according to their pressure ranges:

- Low vacuum : 760 - 25 Torr
- Medium vacuum : 25 - 10⁻³ Torr
- High vacuum : 10⁻³ - 10⁻⁶ Torr
- Very high vacuum : 10⁻⁶ - 10⁻⁹ Torr
- Ultra high vacuum : Below 10⁻⁹ Torr

Different types of pumps are used for obtaining different levels of vacuum. Similarly for the measurement of vacuum, different gauges are used.
Two different principles are employed to reduce the pressure in a vacuum enclosure. The first one involves the physical removal of gases from the vessel and expelling it. The other method is the condensation or trapping of gas molecules on some part of the inner surface of the enclosure without discharging the gas. Mechanical and vapour-stream pumps operate on the first mode while cryogenic, cryosorption, sublimation and getter ion pumps belong to the latter mode. We have used oil sealed rotary pump as the former type and diffusion pump, the latter and are discussed in detail below.

2.11 Oil Sealed Rotary Pump

This is the most widely used mechanical pump to establish necessary fore vacuum for high vacuum pumps. A cross section of the pump used in the present work (Hind Hivac ED12) is as shown in Figure 2.11.1. The gas transport is effected as the keyed shaft rotates the eccentric rotor. The gas is isolated from the inlet after one cycle and then compressed and exhausted during the next cycle. As shown in the figure, the pump consists of an eccentrically mounted rotor placed inside a stator. Two spring loaded vanes sliding in diametrically opposite slots in the rotor press against the inner surface of the stator. Friction and wear and tear are minimised by an 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 leading into an oil reservoir. During the operation, vanes slide in and out enabling the rotor to draw air through the inlet side into the pump. The crescent-shaped air volume is then compressed to a pressure just above one atmosphere which causes the outlet valve to open and discharge the air through the oil seal into the atmosphere.
Figure 2.11.1  Schematic diagram of the cross section of an oil sealed rotary pump

1. Outlet valve  2. Seal  
3. Rotor  4. Inlet  
5. Vanes  6. Stator

A vented outlet valve admitting a small air flow 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 operation. The problem of back streaming 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 used which is superior to charged zeolite and activated charcoal. The most important characteristic 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 approximately $10^{-3}$ m bar.
2.12 Diffusion Pump

The idea of evacuating a vessel by molecular momentum transfer from streaming to diffusing molecules was first described by Gaede.\(^5\) Diffusion pump uses an oil for pumping out gas molecules. The performance can be improved by using traps and baffles in conjunction with the pumps to eliminate the problem of backstreaming of vapour.

A schematic diagram of the diffusion pump used is shown in Figure 2.12.1. The heater vaporises the work-fluid and hot vapour rises in a chimney. The direction of flow of vapour is reversed at the jet cap so that it issues out through an annular nozzle with supersonic speed. This is due to the pressure difference between the inner and outer side of the chimney. The high speed jet of molecules imparts momentum to the random moving incoming gas molecules. Thus the gas molecules move towards the outlet where it is removed by a backing pump (rotary 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, necessary thermal stability and be the least reactive. Commonly used fluids are hydrocarbons, silicon fluids, polyphenyl ether and perfluoropolyether. 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 temperature.
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
To prevent back diffusion 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 work fluid 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. The working range of pressure for diffusion pump is $10^{-2}$ Torr to $10^{-5}$ Torr.

### 2.13 Vacuum Coating Unit

The type of vacuum equipment needed 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” coating unit (Model No. 12 A4) consists of 0.4 m diffusion pump in conjunction with a backing oil sealed rotary pump. The ultimate pressure achieved in a 0.3 m diameter stainless steel bell jar is of the order of $8 \times 10^{-6}$ m bar. It has set-ups for electron beam evaporation and flash evaporation. Substrates can be cleaned by ion bombardment. A L. T. transformer of 20V-50A is used for filament heating. Most of the evaporations are carried out at a pressure of $(1-2) \times 10^{-5}$ Torr. The pressure obtained by the rotary pump is measured by means of a Pirani gauge and the diffusion vacuum is measured by a Penning gauge.
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. High vac valve  
12. Pirani Gauge  
13. Fore-line trap  
14. Isolation valve  
15. Rotary pump
The Pirani gauge (A6STM) has two gauge heads which facilitate the measurement of the fore vacuum and roughing vacuum. Change of pressure in the vacuum system brings about a rise or fall in the number of gas molecules present and hence a rise or fall in the thermal conductivity of the gas. Thus the heat loss of the constant voltage electrically heated filament in the system varies with the pressure. The Pirani gauge head filament has high temperature coefficient of resistance. So a slight change in the system pressure brings about useful change in the filament resistance resulting in an out of balance current in a Wheatstone’s bridge 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 contaminants. The gauge head is flushed with acetone and thoroughly dried. 10 V a. c. or d. c. is applied across the filament to volatilise the deposits on the filament. The Penning gauge (STP4M-1) is used to measure vacuum in the range $10^{-3}$ to $10^{-6}$ m bar in two ranges with instant range changing provided by a toggle switch. This is a cold cathode ionisation gauge head and consists of two electrodes; anode and cathode as given in Figure 2.13.3. A potential difference of about 2.3 KV is applied between anode and cathode through current limiting resistor. A magnetic field is introduced at right angles to the plane of the electrodes by a permanent magnet having nearly 800 gauss will increase the ionisation current. The electrons emitted from the cathode of the gauge head are deflected by means of the magnetic field and are made to take helical path before reaching the anode loop. Thus following very long path, the chance of collision with gas molecule is high even at low pressures. The secondary electrons produced by ionisation and the rate of ionisation increases rapidly. Eventually the electrons are captured by the anode and equilibrium is reached when the number of electrons produced per second is
the sum of positive ion current to the cathode and the 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 at 140°F 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. The diffusion pump in the coating unit used has an evacuating speed of 500 LS⁻¹.

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

Figure 2.13.4 Photograph of the coating unit along with the accessories
2.14 Preparation of Films

Thermal evaporation method is used for the preparation of thin films. The films are deposited onto clean substrates. In thermal evaporation, the material is created in vapour form by means of resistive heating. On heating the material in vacuum, sublimation takes place and the atoms are transported and get deposited onto the cleaned substrates held at suitable distance at desired temperatures. The material for deposition is supported on a vapour source which is heated to produce desired vapour pressure. The requirements for the vapour 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. We have used tungsten helical baskets and molybdenum boats as the vapour sources. The evaporant material in the powder form is kept in the molybdenum boat. The low tension (LT) supply for evaporation source is obtained from a 230 V input transformer by means of parallel connections in the secondary side of the transformer. The LT output from the transformer is fed through a current meter and a selector switch to LT feed-through and filament holders. The unit is connected to the 10V/100A ratings of the transformer.

2.15 Substrate Cleaning

For deposition of films, highly polished and thoroughly cleaned substrates are required. First the substrates are cleaned using liquid detergent. Then it is kept in dilute nitric acid. After this, they are cleaned using distilled water and agitated ultrasonically in acetone. They are then rinsed in isopropyl alcohol and dried in hot air. Subsequently 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 HT discharge.
2.16 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 with stainless steel clamps. 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.

2.17 Sample Annealing

The samples have been annealed in a specially designed furnace. It consists of a coil of Kanthal (Al 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. The temperature of the heater is controlled and recorded by a digital temperature controller cum recorder.

Figure 2.17.1 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 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.
Figure 2.17.1  Block diagram of the temperature controller cum recorder
The analog signal from the thermocouple is converted to a digital one with the help of an A/D converter, using a three 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 2.17.2 shows the photograph of the furnace and temperature controller.

Figure 2.17.2 Photograph of the annealing furnace and controller cum recorder set up
2.18 Thickness Measurement

There are different techniques to determine the film thickness. We employed the optical technique 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 the case of reflection.

For opaque films, a sharp step down to substrate plane must be first generated either by deposition through a mask or by subsequent etching. For practical purposes the fringes formed are classified as the two cases of multiple beam interferometry. 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 placing in contact the two glass plates so that they form a slight wedge at an angle α so that the thickness between the two plates can be varied. The angle α 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 λ/2 where λ is the wavelength of the monochromatic light used.

Another method to determine the film thickness is by forming Fringes of Equal Chromatic Order (FECO). In this, white light is made to incident on the
film normally and the reflected or transmitted light is dispersed by a spectrograph. Here the fringes are formed for certain values of $t/\lambda$.\textsuperscript{10} FECO fringes are obtained with two silvered glass surfaces parallel to each other, where the plate is adjusted to get the fringes. The spacing between the interferrogram is inversely proportional to the thickness ‘$t$’. We have used the Tolansky’s multiple beam interference technique for the determination of the thickness of the film.

2.19 Tolansky’s Multiple Beam Interference Technique

The schematic representation of the fringes produced by multiple beam interference is as shown in Figure 2.19.1. The technique can be employed when the film to be studied remains stable in vacuum and can be coated with a highly reflecting layer.\textsuperscript{11} During the coating of the film, a sharp edge 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 on to the glass substrate and the whole system is illuminated with a parallel beam of monochromatic light of wavelength ($\lambda = 5893Å$) 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 ‘$\Delta x$’. A shift ‘$\Delta x$’ in ‘$x$’ corresponds to a thickness step of $\lambda/2$ and the thickness of the film is determined as

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

(2.19.1)
Figure 2.19.1  Schematic representation of the multiple beam interference technique

a) Fringe pattern
b) Arrangement
c) Sample with step and a match-flat
2.20 **Conductivity Cell**

A schematic diagram of the conductivity cell fabricated is 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. One side tube is connected to a rotary vacuum pump and the chamber is evacuated to a low pressure of $10^{-3}$ m bar. 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 measures the temperature of the sample. Temperature of the sample in the cell can be varied from liquid nitrogen temperature to 400°C.
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 connector  
14. Thermocouple  
15. Connecting leads to BNC connector  
16. Substrate with film
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% for the measurement of voltage, current, charge and resistance respectively. The measuring range is between 10 µV and 200 V for voltage, 0.1 pA and 20 mA for current and 10 fC to 20 nC for charge measurements. The resistance can be measured in two modes: (1) constant current mode and (2) constant voltage mode. Due to 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. Schematic diagrams of the resistance measurements using the ohms function as a current source and $V/I$ resistance measurement connections are shown in Figures 2.21.1(a) and 2.21.1(b). In the constant voltage 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 resistance is then automatically calculated by the instrument as $R = V/I$, 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 shown in Figures 2.21.2(a) and 2.21.2(b) respectively. A 4½ digit display and IEEE-488 interface make easy access to the instrument data. Autoranging is provided for all functions and ranges. Zero correct, baseline suppression, one shot triggering, isolated ± 100 V voltage source in 50 mV steps, selectable guarding and 100-point data store are also available. Figure 2.21.3 gives the photograph of experimental set-up used in the laboratory for electrical conductivity measurements.
Figure 2.21.1a  Schematic diagram of measuring resistance on Keithley using ohms function

Figure 2.21.1b  Schematic diagram of measuring resistance on Keithley using V/I function

1. Input
2. Voltage source (a - low; b - high)
3. 6011 cable
4. Red wire
5. Black wire
6. Resistance (R)
7. Shield
Figure 2.21.2  Schematic diagram of electrical conductivity measurement (all dimensions are in mm).
(a) Two probe method
(b) Four probe method
2.22 UV-Visible Spectrophotometer

To study the optical transmittance of the films in the ultraviolet-visible range, Shimadzu 160A spectrophotometer has been employed. The block diagrams of the 160A optical and electrical systems are shown in Figures 2.22.1 and 2.22.2 respectively. 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 D₂ or halogen lamp W₁) is reflected by the mirror M₁ 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. The lamps can be automatically interchanged according to the wavelength range needed.
Figure 2.22.1  Block diagram of the optical system of the spectrophotometer (Shimadzu 160A)

D2: Deuterium lamp  W: Window plate
W1: Halogen lamp  M1-M5: Mirrors
M3: Half mirror  F: Filter
L: Lens  G: Grating
Sam: Sample cell  S1: Entrance slit
S2: Exit slit  Ref: Reference cell
P.D.: Photodiode
Figure 2.22.2 Block diagram of the electrical system of the spectrophotometer (Shimadzu 160A)
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 diagrams of the optical system and electrical system of the Shimadzu 160A spectrophotometer and photograph of the instrument respectively. The output absorbance or transmittance can be seen in the video display and printed out using the chart recorder.

**Figure 2.22.3** Photograph of the Shimadzu 160A spectrophotometer
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.

![Block diagram of XD 610 diffractometer](image)

**Figure 2.23.1** Block diagram of XD 610 diffractometer
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. The power supply 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° 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 are 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 'd' can be calculated using Bragg's condition.

\[ 2d \sin\theta = n\lambda \]  

(2.23.1)

where θ is the angle of incidence and λ the wavelength of the CuKα 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 the 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 used in the present study is shown in Figure 2.23.2.

Figure 2.23.2  Photograph of the XD 610 diffractometer
References