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2.1 Introduction

In this chapter we discuss different techniques utilized to prepare and characterize the phthalocyanine films and heterostructures. Thin films are deposited using organic molecular beam epitaxy as well as by drop cast method. Films are characterized by a host of techniques, such as, atomic force microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transforms spectroscopy and UV-Vis spectroscopy, X-ray diffraction, Kelvin probe method etc. We present the details of the electrical characterization of the films.

2.2 Deposition of phthalocyanine films

In this section we present the details of the phthalocyanine films preparation using MBE as well as solution process.

2.2.1 Molecular beam epitaxy

Conceptually organic molecular beam epitaxy is technologically an improved version of the conventional thermal evaporation technique. MBE offers additional advantages to the other deposition techniques, particularly in terms of ultra high vacuum (UHV) environment that allows growth of epitaxial layer with extremely high purity. Other unique characteristics of MBE are:

(i) The beam nature of the mass flow from source to substrate: The molecules evaporated from a source in a vacuum chamber assume the features of a beam when the mean free path ($\lambda$) of the molecules is much larger than the source-to-substrate distance. The occurrence of beam nature, therefore, depends on $\lambda$ of evaporating molecules and concentration of residual gas molecules in the
evaporation chamber. Both these conditions are associated with vacuum conditions of the growth chamber. The $\lambda$ is related with pressure ($p$) as

$$\lambda = 3.11 \times 10^{-24} \frac{T}{pd^2} \quad (2.1)$$

where $d$ is the diameter of the molecules [69]. The growth chamber is maintained at better than $10^{-8}$ torr vacuum level during growth and at this pressure mean free path ($\lambda$) for the phthalocyanine molecule is $4 \times 10^4$ m as calculated using eq. 2.1. The value of $\lambda$ is clearly greater than the typical source to substrate distance (40 cm) and thus ensuring the beam nature of the molecule. Apart from the pressure during growth the residual gas pressure is also pumped down to better than $10^{-9}$ torr which ensure the low concentration of residual gas molecules which affect the beam nature of the molecule. This low residual gas pressure also confirms that no monolayer of residual gas formed during deposition even when the film is deposited at very slow growth rate.

(ii) High degree of control over growth parameters: The molecular beams are usually produced by effusion cells, where constituent materials are evaporated under a fine temperature control [69]. The beam flux and hence, the deposition rate, is monitored by a gauge located near to the substrate. The beam flux can be precisely controlled by temperature of source, with a stability of better than 1%. The precise control over the molecular beams enables to keep the growth rate of the film as low as 1 monolayer per second. The continuous rotation of the substrate and thus confirming excellent uniformity in film thickness as well as in composition on a large area substrate and high reproducibility of film preparation.
Molecular beam can be individually blocked by beam shutter and therefore complex heterostructure with sharp interface can be produced.

(iii) \textit{In-situ growth characterization of the films:} MBE is usually equipped with characterizations tool such as reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) etc. which enables an \textit{in-situ} analysis of the films.

\textbf{2.2.1.1 Configuration details of RIBER-32 EVA MBE system}

The photograph of the MBE system (RIBER EVA 32 E) used for thin film deposition in the present study is shown in Fig. 2.1. It consists of three chambers namely, Introduction Chamber, Analysis Chamber and Growth Chamber. All of them are UHV chambers and are made of stainless steel. All seals are made of OFHC copper gaskets. This construction allows high temperature baking (~200°C) of the entire system to reduce out gassing from the walls. Analysis and Growth chambers are situated in a line, whereas, the Introduction Chamber is situated at 37° off the line joining Analysis and Growth Chambers. Introduction chamber is connected with Analysis chamber and similarly Analysis chamber with Growth chamber are connected through gate valves. There are two magnetically coupled sample transfer mechanisms. One is used to transfer the sample from Introduction to Analysis Chamber and the second is used to transfer sample from Analysis to Growth Chamber. Therefore, substrate cleaning and characterization, film deposition and characterization are performed in-situ under UHV conditions. The details of the three chambers are presented below.
Figure 2.1 Photograph of the MBE deposition system used for the deposition of MPc films.

(i) **Introduction chamber:** In this chamber, shown in Fig. 2.1, the substrates are loaded through the front opening flange. The substrates are fixed on a heater assembly using silver paste, and the substrates can be cleaned by degassing the substrate up to a temperature of 800°C. After loading the sample it is rapidly pumped down from atmospheric pressure to ~$10^{-9}$ Torr with sorption and ion pumps. The heater assembly having the substrate is transferred to the Analysis and/or Growth Chambers using the transfer rods.

(ii) **Analysis chamber:** This chamber serves the following two purposes i.e. cleaning of the substrates by ion etching and (ii) surface characterization of substrates and grown films using X-ray photoelectron spectroscopy. This chamber is equipped
with a substrate heater which can be heated up to 800°C. In order to determine the level of cleanliness of the substrate and, chemical state and composition of the substrate and grown films the chamber is equipped with X-ray photoelectron spectroscopy (XPS) techniques.

(iii) **Growth chamber:** The growth chamber is the most important part of the MBE system. In this chamber all the controlling elements, such as, beam sources with their individual shutters, a main shutter, and manipulator with substrate heater and rotation, pressure control system etc. are located.

The growth chamber can be evacuated to better than $10^{-9}$ torr by using a combination of turbomolecular pump and ion pump with a fully cryoshrouded titanium sublimation pump. A helium closed-loop cryopump is also mounted for supplementary pumping.

Effusion cells are the key components of an MBE system, because they must provide excellent flux stability and uniformity, and material purity [69]. The chamber contains three effusion cells. In the present study, we have used them for CoPc (99.99%), FePc (99.99%) and F$_{16}$CuPc (99.98%). Each effusion cell includes an oven (filament + thermocouple) and fully degassed thick PBN crucible, surrounded by adequate tantalum shielding for use in proximity of a cryoshroud. PBN crucibles are designed to provide a very stable flux during charge depletion. The heating filament is made of high purity tantalum foil. The contact thermocouple is located at the bottom of the crucible. Electrical insulators are made of PBN. The cell can be operated up to 1400°C, and its temperature can be controlled with an accuracy of 1°C. The source mounting flange houses
power and thermocouple feedthroughs. Power supply and temperature control are implemented by the use of microprocessor-based controllers.

The manipulator consists of a gauge head and a substrate heater which can be heated up to 800°C. The manipulator allows the azimuthal rotation of the substrate during growth. The substrates are positioned to maximize growth uniformity for a substrate of size 1 inch diameter.

Quartz crystals monitor are mounted near the substrate to monitor the deposition rate. Alternatively, deposition rate can also be monitored by the flux gauge.

2.2.1.2 Deposition procedure

Following two steps are involved in the deposition of phthalocyanine films.

(i) Substrate preparation: Substrate preparation is very important step before growth studies. In the present studies we have used indium tin oxide (ITO) coated glass, twinned (001) LaAlO$_3$, (0001) Al$_2$O$_3$ and (100) SrTiO$_3$ substrates. Prior to the introduction in the MBE chamber the substrates are thoroughly cleaned in different organic solvents. In the first step the substrates were ultrasonicated in trichloroethylene bath for 10 minutes to remove oil, grease etc. Thereafter the substrates were sonicated in acetone and methanol separately to remove polar and non-polar organic, inorganic impurities and dust particles. To remove the solvent, the substrates were dried under the jet flow of dry high purity Ar gas. Finally, films are loaded in the introduction chamber of MBE system.

(ii) Loading into MBE system and deposition: In the second step, pre-cleaned substrates were loaded into the introduction chamber, which was subsequently
evacuated to $10^{-7}$ torr. The substrates were heated to 500°C to remove the residual solvent particle and other impurities. The substrates were then transferred to analysis chamber, where XPS studies were carried out to examine their cleanliness. If the substrates are found to be clean, they were transferred in-situ to the growth chamber for deposition. Otherwise, they were taken back to introduction chamber for further heat treatment to remove the impurities. Prior to the deposition the, source materials (FePc, CoPc or F_{16}CuPc) were degassed at 200 °C for 2 to 3 times for the removal of volatile impurities. During deposition the pressure of the growth chamber was maintained better than $10^{-9}$ torr. The films were deposited at various substrate temperatures (25°C to 250°C) and the substrate heater can be controlled within ±1°C accuracy of temperature. The deposition rate of the film is monitored by the flux gauge and the deposition rate was varied between 0.02 and 0.5 nm/s by controlling the effusion cell temperature. In order to achieve excellent uniformity in composition and thickness, the source-to-substrate distance was kept comparatively large (40 cm) and the substrates were rotated during the deposition. After the deposition, the films were transferred to the analysis chamber again and films were characterized by XPS. Finally the films were taken out through the introduction chamber for further ex-situ characterization and charge transport measurements.

2.2.2 Solution process

Deposition of organic films requires solubility of the organic molecules in an appropriate solvent. Unfortunately, the solubility of FePc, CoPc and F_{16}CuPc in majority of
organic solvents as well as in water is very poor, therefore their films cannot be prepared by solution process. (CuPcTs) is soluble in water, and therefore we have chosen this material for making thin films by drop casting method. First, the substrates (quartz and sapphire) were carried out by sonicating them in try-chloro-ethylene, acetone and methanol for 10 min each, respectively. Substrates were then dried using argon gas jet stream. In the second step, the solution, prepared by dissolving 5 mg. of CuPcTs in 0.1 ml of de-ionised water and 0.4 ml of methanol and sonicated for 10 min, was spread on substrate. Deposited films were dried for few hours under ambient conditions and finally vacuum annealed at 250°C for 15 min.

2.3 Characterization techniques

2.3.1 Atomic force microscopy (AFM)

AFM measures the interatomic forces acting between a fine tip and a sample surface, as schematically depicted in Fig. 2.2. The tip is attached to the free end of a cantilever or tuning fork and is brought very close to a surface. Attractive or repulsive forces resulting from interactions between the tip and the surface will cause a positive or negative bending of the cantilever. AFM operates in three different modes: contact mode, non-contact mode and tapping mode. At relatively large distance from the sample surface, the force of attraction between the tip and the sample surface dominants, whereas repulsive force is most significant at very small distance (less than few angstroms).

In non-contact mode or dynamic mode, the tip is held order of tens to hundreds of angstroms from the sample surface, and the interatomic force between the tip and sample is attractive (largely a result of the long-range van der Waals interactions). In contact mode or static, the tip is brought in to close contact with sample surface less than a few angstroms, so
that force between tip and sample becomes repulsive. The resulting deflection by cantilever is monitored and measured by different detection techniques. For organic material, the major problem with this mode of operation is that, surfaces can be easily scratch or damaged due to the direct contact with the tip. These drawbacks are overcome by tapping mode. Though, since the force of attraction is much weaker than the repulsion, the resolution is usually lower than the contact mode of operation.

![Diagram](image)

**Figure 2.2** (a) Interaction of the AFM tip with sample surface. (b) Force versus separation between AFM tip and the sample surface.

The tapping mode combines the advantages of contact and non-contact mode. In tapping mode-AFM the cantilever is oscillating close to its resonance frequency (100-500 kHz) with amplitude of approximately 20 nm so that the tip just touching (tapping) the
surface. An electronic feedback loop ensures that the oscillation amplitude remains constant, such that a constant tip-sample interaction is maintained during scanning. The resolution of this tapping mode is almost the same as that of contact mode, but it is faster and much less damaging.

Figure 2.3 (a) Photograph showing the AFM tip and sample stage. (b) Block diagram of AFM.
The atomic force microscope used in the present studies was Nanonics 4000SPM/AFM system, as shown in Fig. 2.3 (a). In this case, the probe is made of the glass fiber tip (diameter 10nm) which is attached to tuning fork with pizocrystal [70]. The images are recorded in the tapping mode by oscillating the tip at resonance frequency (20-50 kHz depending on the tips). The probe was scanned in phase mode. During scan, phase changes due to tip surface interaction. The difference in signal called an error signal; this signal is sent to proportional, integrator and differentiator (PID) controller. PID sends the feedback via high voltage pizo driver to make constant phase by moving pizodriver in z direction at that x, y point. This way an image is generated. A schematic diagram of signal processing is shown in the Fig. 2.3 (b). The image so generated was processed (like smoothing, flattening etc) by NWS software [71]. This software was also used to study surface roughness by extracting line profile from the image.

2.3.2 Scanning electron microscopy (SEM)

SEM provides information relating to topographical features, morphology and phase distribution [72, 73]. The operation of SEM is described in Fig 2.4. The scanned electron beam is produced in an electron microscope column. Electrons are emitted from heated cathode and arranged through electric and magnetic fields in a proper direction to achieve the required incident beam at sample surface. The principal elements of electron column are electron gun, the condenser lens, and the scanning and deflecting coils. Electrons in the SEM are accelerated at voltages in the range 2-40 kV.

Two types of interactions occur in SEM between the electrons beam and the sample structure. These interactions may be either elastic, if the electron beam strikes the sample and
there is a change in its direction without changing its energy (backscattered electrons), or an inelastic interaction, which occurs when the beam of electron strike an orbiting shell electron of the sample, causing ejection of new electrons (secondary electrons). If the vacancy due to the creation of a secondary electron is filled from a higher level orbital, an X-Ray characteristic of that energy transition is produced. In addition, Auger electrons, and cathodoluminescence are produced, as shown in Fig. 2.5. These interactions reveal the important information about the sample to find out the surface characteristics and the chemical nature of the sample.

**Figure 2.4** Block diagram of a typical SEM setup.
The most widely utilized signal is the secondary electron signal. Nearly all of secondary electrons come from a region very closer to the sample surface. Secondary electrons are characterized from other electrons by having energy of less than 50 eV. The secondary electron is emitted from an outer shell of the specimen atom upon impact of the incident beam. It is the most useful signal for examining surface structure and gives the best resolution image of 10 nm or better. Since the secondary electron intensity is a function of the surface orientation with respect to the beam and the secondary electron detector and thus, produces an image of the specimen morphology. The secondary electron intensity is also influenced by the chemical bonding, charging effects and back scattered electron intensity, since the back scattered electron generated secondary electrons are significant part of the secondary electric signal.

\[\text{Sample} \quad \text{Electron beam} \quad \text{Cathodoluminescence} \]

\[\text{Auger electrons} \quad \text{Backscattered electrons} \quad \text{Secondary electrons} \]

\[\text{X-rays} \quad \text{Secondary electrons} \]

\[\text{Sample} \]

**Figure 2.5** Interaction of the electron beam with sample.

The detector is Everhart-Thornley detector composed of a scintillator, collector, light pipe, and photo multiplier tube. First electrons striking the positively biased scintillator and
converted to a burst of photons, that travel through the light pipe to a photomultiplier tube which converts the photons of light into a voltage. The strength of this voltage depends on the number of secondary electrons that are striking the detector. Thus the secondary electrons produced from a small area of the specimen give rise to a voltage signal of a particular strength. The voltage is led out of the microscope column to an electric console, where it is processed and amplified to generate a point of brightness on the cathode ray tube screen. Contrast in the SEM image is the difference in intensity, or brightness of the pixels that make up the image. The difference in intensity represents difference in signal from corresponding picture elements on the sample. A photograph of SEM, (Tescan make VEGA MV2300T/40 system) used in the present study is shown in Fig. 2.6.

Backscattered electrons consist of high-energy electrons (greater than 50 eV) originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume. The intensity of their signals increases with increase the atomic number. Backscattered electron signal is often used to show atomic number contrast, in which areas of higher average atomic number produce more back scattered electrons, and thus appear brighter than lower atomic number regions. The contrast in this image is not due to colour differences but is produced by different intensities of electrons back scattering from the layers with different average atomic number.

The characteristics X-rays signal depends exclusively on the atoms that produced it, hence can be used for chemical identification analysis. The EDS X-ray detector (also called EDS or EDX) measures the number of emitted x-rays versus their energy. The energy of the X-ray is characteristic of the element from which the X-ray was emitted.
Cathodoluminescence (CL) is the emission of photons of characteristic wavelengths from a material that is under high-energy electron bombardment is used to study the internal structure of the material.

![SEM photograph](image)

**Figure 2.6** The photograph of the SEM (model: Tescan VEGA MV2300T/40).

### 2.3.3 X-ray photoelectron spectroscopy (XPS)

XPS was developed as a surface analysis technique in the mid-1960s by Siegbahn and his coworkers [74]. Core level electrons have the binding energies matching to the energies of the photons that lie in X-ray region [74, 75]. XPS are based on the photoelectric effect, through which an atom absorbs a photon with energy \( h\nu \) in excess of binding energy \( E_b \) of an electron; a photoelectron is emitted with kinetic energy

\[
K.E. = h\nu - E_b
\]

In XPS a soft X-ray source (Al-K\(_\alpha\) and Mg-K\(_\alpha\)) is used to ionize electrons (by knocking out the core-level electron) from the surface of a solid sample (top few atomic
layers). The binding energies of these electrons are measured, which are characteristics of the elements. Binding energies of core electrons are not only element-specific but also contain chemical information, because the energy levels of core electrons depend slightly on the chemical state of the atom. Such shift in the energies of core level electrons arising due to chemical state of electrons is known as chemical shift. The advantages of XPS technique are (i) quantitative analysis of elements and chemical states of all elements except hydrogen and helium, (ii) typical element detection limits are 0.1 atomic percentage from the top few nm, and (iii) samples can be conductors, semiconductors or insulators [76-78].

The XPS system which we have used is mounted in the analysis chamber of the MBE system, and thus the in-situ (i.e. without breaking vacuum) and ex-situ (i.e. exposing to ambient) study of the deposited films were carried out. The XPS system (RIBER system model: FCX 700) consists of Al-K$_\alpha$ (1486.6eV) and Mg-K$_\alpha$ (1253.6eV) X-ray sources and MAC-2 electron analyzer. The binding energy scale was calibrated to Au-4f$_{7/2}$ line of 83.95eV. For charge referencing adventitious C-1s peak set at 285eV was used. Each data set was first corrected for the non-linear emission background. The data was then fitted with Gaussian function to find the peak positions.

2.3.4 Fourier transform infrared spectroscopy (FTIR)

The frequencies and intensities of the vibrational modes observed in FTIR provide detailed information about the nature of the bonding in the molecule [79]. FTIR spectra were recorded using Bruker system (vertex 80V). The necessary condition for the infrared absorbance is the presence of permanent dipole moment or change in dipole moment of the chemical bond (between two atoms) when it interacts with IR. The absorption of IR leads to
change in vibration level. So IR absorption helps to identify the characteristic vibrational frequencies of organic functional group. Most of the organic molecules have vibrational frequencies in the mid infrared range of 4000 to 400 cm$^{-1}$. FTIR works on the principle of interferometer that gives an interferogram, a plot of light intensity versus optical path difference. The ray diagram of formation of interferogram is shown in the Fig. 2.7. This interferogram is finally Fourier transformed to give a spectrum of infrared radiation intensity versus wave number.

![Ray diagram of recording FTIR spectra along with electronic circuit of system vertex 80V.](image)

**Figure 2.7** Ray diagram of recording FTIR spectra along with electronic circuit of system vertex 80V.

For our experimental purpose, FTIR spectra were recorded in two different spectroscopy modes: attenuated total reflection (ATR) and diffuse reflectance mode. In the ATR mode, an infrared beam is directed onto an optically dense crystal with a high refractive
index at a certain angle. This internal reflectance creates an evanescent wave (see Fig. 2.8) that extends beyond the surface of the crystal into the sample held in contact with the crystal. This evanescent wave protrudes only a few microns (0.5 - 5 µm) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum. This mode is very good technique to measure FTIR spectra of the film.

**Figure 2.8** Ray diagram of recording FTIR spectra in ATR mode. The accessory used for ATR spectra is also shown in the inset of the diagram.

### 2.3.5 UV-Visible spectroscopy

Absorption of the ultraviolet or visible light by molecules containing \( \pi \)-electrons, \( \sigma \)-electrons or even non-bonding electrons (\( n \)-electrons) leads to electronic excitation among
various energy levels within the molecule; as a consequence, the wavelength of absorption peaks can be correlated with the type of bonds in the spices [80]. A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown in Fig. 2.9. The transition between bonding and antibonding are two types:

(i) $\sigma - \sigma^*$ transition, requires large energies corresponding to absorption, most of the transitions occurs below 200nm.

(ii) $\pi - \pi^*$ transition, occurs with molecules containing conventional double bond or triple bond.

Similarly the transitions between non-bonding and antibonding orbitals are $n - \pi^*$ and $n - \sigma^*$. The absorption may sometime occur due to the $d$ and $f$ electron and also due to charge transfer electrons. So this absorption study is very important tool to indentify the molecule or functional group in the molecule.

![Diagram showing various electronic transitions](image)

**Figure 2.9** Electronic energy levels and possible electronic transitions of $\pi$, $\sigma$, and $n$ electrons.
For our experiment we have used JASCO B430 spectrometer. The schematic of the double beam single monochromator spectrometer is shown in Fig 2.10. In this spectrometer the intensity (I) of the beam passing through the sample is compared with a reference beam (I₀) and in output we get absorbance \( A = \log_{10}(I/I₀) \) vs wavelength. Absorbance is directly proportional to the numbers of absorbing molecules (concentration) in the light-path and path length. This is called Beer-Lambert law, can be expressed as

\[
A = \varepsilon lc
\]  

(2.2)

where \( \varepsilon \) is the molar extinction coefficient, \( c \) concentration of absorbing species and \( l \) is path length.

**Figure 2.10** Block diagram of a typical double beam single monochromator UV-spectrometer.

### 2.3.6 Raman spectroscopy

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic)
spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecules electric field. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. Thus, by analyzing the scattered photons information on the vibrational motions of atoms in molecules is obtained. These motions are a function of molecular conformation, of the distribution of electrons in the chemical bonds, and of the molecular environment. Thus, interpretation of the Raman spectrum provides information on all these factors [81, 82].

Raman spectra were recorded using LABRAM–1 micro/macro Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany). The 488-nm line of an Ar$^+$ laser was used for excitation and the scattered Raman signals were analyzed in a back-scattering geometry using a single monochromator spectrometer equipped with a Peltier-cooled CCD detector for multichannel detection.

2.3.7 Kelvin Probe method

The Kelvin Probe is a non-contact, non-destructive vibrating capacitor device used to measure the work function difference, or for non-metals, the surface potential, between a conducting specimen and a vibrating tip. The Kelvin method was first postulated by the renowned Scottish scientist W. Thomson, later Lord Kelvin, in 1861[83, 84]. He described the movement caused by coulomb repulsion within a gold leaf electroscope when zinc and copper plates brought into close proximity while the plates were electrically connected as shown in Fig. 2.11. In 1932, this technique is modified by Zisman as a vibrating capacitor [85].
The Work Function is usually described as being the ‘least amount of energy required to remove an electron from a surface atom to infinity or equivalently the vacuum level’. The Kelvin probe measures the work function indirectly, i.e. via equilibrium not via extracting electrons [84]. The Kelvin probe (KP) technique measures the contact potential difference (CPD) between surface of sample and KP tip in close proximity. The principle of the KP techniques is shown in Fig 2.12. The electronic energy level diagram for two conducting but isolated materials (sample and tip) of different work functions is shown in Fig 2.12 (a). $\phi_{\text{tip}}$ and $\phi_{\text{sample}}$ represent the work functions of the tip and sample respectively, with $\phi_{\text{sample}} < \phi_{\text{tip}}$. If an external electrical contact is made between them, electrons flow from the sample with the smaller work function to the tip with the larger work function. This causes the tip to charge positively while the sample charges negatively to equalize their Fermi level. This creates an electric potential between them, shifting their electronic states relative to each other as shown in Fig. 2.12 (b). This electric potential called contact potential difference ($V_{\text{CPD}}$) and is exactly equals to the sample and tip work function difference. If $\phi_{\text{tip}}$ is known
then $\phi_{\text{sample}}$ can be calculated by measuring $V_{\text{CPD}}$. The $V_{\text{CPD}}$ is calculated by applying a variable “backing potential” $V_{b}$ in the external circuit. At the unique point where $V_{b} = - V_{\text{CPD}}$ the electric potential between the plates vanishes and a null output signals obtained as shown in Fig. 2.12 (c).

![Diagram showing Kelvin probe measurement](image)

**Figure 2.12** Principle of Kelvin probe measurement.

Traditionally, the $V_{\text{CPD}}$ was determined by vibrating the reference electrode (KP tip) above the sample and adjusting $V_{b}$ until a zero or null output resulted. This method of detection is extremely sensitive to noise since the Kelvin Probe signal is diminishing with respect to the noise background. In addition, KP measurements can only detect the CPD, real work function measurements are only possible through calibration i.e. the KP needs to be calibrated against a surface with known work function.

For our measurement, we have used Scanning Kelvin Probe system SKP5050 manufactured by KP technology as shown in Fig. 2.13 (a). The Kelvin probe tip (made of
gold) and sample mounting stage is shown in Fig 2.13 (b). In this system $V_{CPD}$ is measured by off-null detection method or 'Baikie Method' where the signal is measured at high signal levels far from balance is correspondingly much less sensitive to noise than traditional systems, with work function resolution 3-5 meV. In our measurements, standard gold/aluminum sample manufactured by KP technology was used for calibration purpose.

![Figure 2.13](image)

**Figure 2.13** A photograph of (a) Scanning Kelvin probe system SKP5050 manufactured by KP technology and (b) Kelvin probe tip and sample stage.

### 2.3.8 X-ray diffraction (XRD)

For the determination of the structure of the deposited films, X-ray diffraction in different configurations are carried out. These are discussed as follows.
2.3.8.1 Powder XRD

We have used powder X-ray diffractometer (Seifert XRD 3003TT) in θ-2θ scan mode to characterize the orientation and structure of the grown Pc thin films. Fig. 2.14 shows the schematic diagram of the diffractometer, which consists of an X-ray source, and a goniometer for mounting sample and X-ray detector. The X-ray source used was Cu Kα having wavelength of 1.54056Å, which has been selected using a Graphite monochromator. For mounting thin films, a specially designed Perspex holder (having a groove of dimension 10 mm×10 mm×1 mm) was employed. The films were mounted on this groove using red wax in such a way that X-rays fall on the film plane. Since the wavelength (λ) of X-rays coincides with the atomic spacing (d) in the solids, it diffracts in those orientations of 2θ, where the Bragg condition of diffraction [86] i.e. $2d \sin \theta = n\lambda$ (θ being the angle which incident beam makes with the plane of sample) is satisfied. While recording the diffraction pattern with
detector, the sample is synchronously rotated along with the detector, such that the incident X-ray incident beam makes an angle $\theta$ with the plane of sample whereas detector is at angle $2\theta$ with respect to incident beam. This is commonly known as $\theta$-2$\theta$ scan of X-ray diffraction. The recorded diffraction pattern is compared with standard pattern to get information about the phase of the samples. The lattice parameters are obtained by fitting the recorded diffraction peaks using least-square fitting software.

### 2.3.8.2 Grazing angle XRD

In powder or normal geometry contribution from the substrate to diffraction can sometimes overshadow the contribution from the thin films. Therefore the structures of the very thin films (typically less than 20 nm) were investigated by Grazing angle X-ray diffractometer. The schematic of this diffraction configuration is shown in the Fig. 2.15. In this configuration, incident X-ray falls at a very small angle (e.g. 0.1º) which is fixed with the sample surface and detector does 2$\theta$ scan. The sampling depth (D) is related with angle of incidence ($\phi$) by the formula,

$$D(\phi) = \frac{\lambda}{4\pi q}$$

where $\lambda$ is the x-ray wave length (1.541Å), and

$$q = \left[\sqrt{(\phi^2 - \phi_c^2)} + 4(\delta_i)^2 + \phi_c^2 - \phi^2\right]^{1/2} \left(\sqrt{2}\right)^{-1}$$

$\delta_i = \lambda(\frac{\mu}{4\pi})$, $\phi_c$ is the critical angle of incidence and $\mu$ is the linear absorption coefficient [87]. In the present studies, we have employed $\phi = 0.1^\circ$, which leads to a sampling depth of ~ 10 nm; and thus this technique becomes ideal for analyzing the structure of very thin films without having interference from the substrates.
2.3.9 X-ray reflectivity

When X-ray beam falls on a surface it undergoes total external reflection below certain critical angle ($\theta_c$). Above the $\theta_c$, the X-ray starts penetrating inside the layer and the reflectivity of the sample falls off with a slope depending on the incidence angle and the roughness of the interface. The oscillation on the reflectivity spectrum above $\theta_c$ (generally known as the Kiessig oscillations) is due to the finite thickness of the layer. In general, the thickness of the film can be obtained from the frequency of oscillation, while the slope of the curve gives the roughness of the interface [88]. Grazing incidence X-ray reflectivity (GIXRR) for Pc thin films was carried out using CuK$_\alpha$ radiation (1.54 Å) on a computer-controlled reflectometer (Kristalloflex 710 D X-ray generator (SIMENS) and D5000 diffractometer) and the obtain reflectivity data fitted theoretically to extract thickness and interface roughness.
2.3.10 Secondary Ion Mass Spectrometry (SIMS) and Matrix-assisted laser desorption/ionization (MALDI)

Both techniques (SIMS and MALDI) give information about the molecular mass. In SIMS technique, sample is bombarded with high energy Ar ion (~ 5-40 keV), which sputter the films in the forms of ionized molecules / their fragmented parts. The resulting of ionized molecules / their fragmented are accelerated into a mass spectrometer, where they are mass analyzed by measuring their time-of-flight (TOF) from the sample surface to the detector as schematically shown in Fig. 2.16 (a).

In case of MALDI, a sample is mixed or coated with an energy absorbing matrix and subsequently a laser beams (N₂ laser, wavelength ~ 300 nm, energy density ~ 20 µJ/cm²) falls on the films as schematically shown in Fig. 2.16 (b). This process assist in emission of molecular ion, which later analyzed using TOF mass spectrometer, ions are separated and
recorded based on their mass (molecular mass) to charge ratio \((m/z)\). The desorption process in MALDI is soft with very low fragmentation of analyte molecules [89].

![Figure 2.17](image)

**Figure 2.17** A schematic of in plane charge transport measurement geometry.

### 2.4 Charge transport measurement

For electrical and gas sensing measurement gold electrode were deposited by thermal evaporation method. Gold pads (size: 2 mm × 3 mm) were deposited through a metal mask with different electrode spacing (12 μm). The films are loaded in vacuum chamber which is connected to a TMP based vacuum pumping system. To deposit gold electrodes, 99.99% pure gold wire is loaded on a tungsten filament, which was resistively heated by external power supply. To prevent diffusion of gold atoms into the Pc films, electrodes are deposited with very slow rate (0.5 Å/s). The deposition rate and thickness of the deposited electrodes is monitored through a quartz crystal monitor.

The charge transport measurements were carried out using in planar geometry. The in-plane geometry, as shown in Fig. 2.17, has following distinct advantages over the out-of-plane geometry in which films is sandwiched between two electrodes.
(i) In the out-of-plane geometry, metal atoms from the electrode can get incorporated in the films, which can act as charge trapping centers, and hence, can give rise to hysteresis in $J-V$ characteristics [109]. This makes it difficult to isolate the intrinsic hysteretic effect. This problem will not arise in the in-plane geometry, as the electrodes are far apart (12 µm).

(ii) Large electrode spacing also indicates that the contribution of contact resistance is very small compared to the film resistance.

Therefore in our studies we measured $J-V$ characteristics using two-probe in-plane geometry. To measure $J-V$ characteristics a silver wire is attached to the previously deposited electrode by conducting silver paint. Keithley 6487 picoammeter/voltage source and computer based data acquisition system were used to record the $J-V$ characteristics. All measurements were carried out in dark to avoid the problem of photoconductivity. In order to rule out the effect of film inhomogeneities, $J-V$ characteristics were measured on at least three pairs of electrodes deposited on a film at different positions. For measuring the temperature dependence of the resistivity and temperature dependent $J-V$ characteristics, the samples were mounted in a closed cycle cryostat. The cryostat (CCR APD Cryogenics make) consists of a compressor, which compresses the Helium gas and expands it in the vicinity of the sample chamber. Because of Joule Thomson expansion of Helium gas, its temperature falls and it cools the region surrounding it. Platinum resistance sensors (Pt-100) are used to monitor the temperature. Lakeshore temperature controller (Lakeshore 330 auto tuning temperature controller) controls temperature of the sample chamber. A small manganin heater was used to heat the sample for measurements of transport properties at different temperatures.
Figure 2.18 Schematic representation of gas sensing measurement setup.

2.5 Chemiresistive gas sensing measurement

The gas sensitivity of the films was measured using a home-made gas sensitivity measurement setup, as shown in Fig 2.18. The sensor films are mounted on a heater surface. The temperature of the heater was controlled by an external power supply and temperature controller. The sensor assembly was mounted in a leak tight 1000 ml stainless steel container, and the known amount of gas (to be sensed) was injected into the chamber using a micro-syringe. To measure the response of the sensor films for a particular gas, current at a particular bias as a function of time was measured by Keithley make 6487 picoammeter/voltage source and computer based data acquisition system. For the recovery of the sensor, the chamber was exposed to the ambient atmosphere. A photograph of gas sensing setup, used in the present study is shown in Fig. 2.19 (a). The sample was mounted
on a heater in a leak tight stainless steel chamber (net volume: 1000 cm$^3$) as shown in Fig. 2.19 (b).

Figure 2.19 A photograph of (a) gas sensing setup and (b) top view of stainless steel chamber.