Chapter 2

Experimental Techniques

In this dissertation I have presented results of studies on polystyrene (PS) films and gold-polystyrene (AuPS) nanocomposite films. I have prepared the PS films by spin-coating on suitable substrates. I have studied two types of AuPS films. In the first I have sputter deposited Au on the spin-coated PS film using a DC magnetron. In the other type of films, I have prepared dodecanethiol-capped Au nanoparticles in toluene solution and spin-coated these nanoparticles on the PS film surface. For the study of molecular and supramolecular structural characteristics of these films I used a combination of real and reciprocal space measurement techniques – spectroscopy, x-ray scattering and scanning probe microscopy. In this chapter I shall give a brief overview of the working principle of these techniques and discuss the instruments used for present study.

2.1 Spin Coating

Spin coating is a technique by which very thin films are deposited onto a solid substrate. To fabricate thin polymer films, the polymer is first dissolved in a volatile solvent (e.g. toluene for polystyrene). If a drop of solution is placed on a substrate, it can flow to form a metastable, continuous film or form a droplet on the surface, depending on the “wettability” of the substrate. By spinning the substrate, the droplet is forced to spread
out while the solvent evaporates. If deposition conditions such as choice of solvent, solution concentration and spin speed are chosen correctly, a thin film of uniform thickness is deposited on the substrate. The basic mechanism governing the spin coating process was elucidated after the pioneering work on the flow of Newtonian fluid on a rotating disk by Emslie, Bonner and Peck in 1958 [42], which was further extended by Acrivos, Shah and Petersen for non-Newtonian fluids [43]. Later on, Meyerhofer introduced the evaporation of the solvent as an important controlling mechanism in the process [44].

2.1.1 Principle and Theory

Film formation by spin coating technique is accomplished by dispensing a fixed amount of polymer solution onto a wafer. The wafer is then rotationally accelerated up to a preset speed. The resist solution flows radially outward due to centrifugal force, reducing the fluid layer thickness. Evaporation of solvent from the resist solution continuously changes the fluid composition, and thereby the rheological properties of the fluid. The topmost layer of the fluid has the highest radial velocity which decreases gradually towards the substrate, the fluid layer in contact with substrate having zero radial velocity. According to hydrodynamics, two opposite forces act between the adjacent fluid layers, the centrifugal force, which acts radially outward and viscous force, which acts exactly in the opposite direction. The force balance (viscous and centrifugal forces per unit volume) equation in cylindrical polar coordinates (r, θ, z) rotating with the spinning disk at angular velocity \(\omega\) is [42]

\[
\frac{\partial \tau}{\partial z} = -\rho \omega^2 r
\]  

(2.1)

if radial symmetry is postulated. Here \(z\) is the position along the axis of rotation, \(r\) is the radial distance from the axis of rotation and \(\rho\) is the density of the liquid. The shear stress \(\tau\) is related to the velocity gradient \(\frac{\partial v}{\partial r}\), where \(v\) is the radial velocity of the liquid at any point \((r, \theta, z)\). For Newtonian fluids the viscosity is independent of the rate of
shear and we have,
\[ \tau = \eta \frac{\partial v}{\partial z} \] (2.2)
and the equation of motion (Eqn. 2.1) becomes,
\[ \frac{\partial^2 v}{\partial z^2} = -\rho \omega^2 r \] (2.3)
Here \( \eta \) is the viscosity of the liquid. When the centrifugal force is larger than the frictional force on a fluid layer, the flow of mass occurs radially outwards. On the other hand, when the viscous force is exactly balanced by the centrifugal force, the flow of mass does not occur.

For non-Newtonian fluids, \( \tau \) often be approximated by the power law [43],
\[ \tau = K \frac{\partial v}{\partial z} \left| \frac{\partial v}{\partial z} \right|^{n-1} \] (2.4)
where \( K \) and \( n \) are characteristic parameters of the fluid. All non-Newtonian fluids approach Newtonian behaviour if the rate of strain \( \frac{\partial v}{\partial z} \) is made sufficiently small.

The earliest modeling of the process was performed by Emslie et al. [42], who solved the equation of motion for a Newtonian fluid in the lubrication limit and showed that for any initial distribution of fluid on the disk, the film thickness eventually becomes uniform. But for non-Newtonian fluid approximation [43], where effects of shear thinning is considered, analytical solution showed that the fluid film thins more rapidly near the edge of the disk than at the centre. In the light of these results, theory is unable to explain the practical success of the spin coating process for such shear-thinning liquids. This difficulty arises because of the assumption of the power-law dependence of the viscosity on the shear rate. For many non-Newtonian fluids, in particular polymer solutions, a power-law dependence is observed in an intermediate range of shear rates, while at very low shear rates such fluids usually exhibit nearly Newtonian properties. In the spin coating process, the shear rate in the fluid decreases with film thickness, so that in the late stages of spinning, the
2.1. Spin Coating

fluid may behave in a Newtonian manner and the thickness variation will be smoothed out [45].

Eqn. 2.3 may be integrated employing the boundary conditions that \( v = 0 \) at the surface of the disk \((z = 0)\) and \( \frac{\partial v}{\partial z} = 0 \) at the free surface of the liquid \((z = h)\) where the shearing force must vanish. Thus

\[
v = \frac{1}{\eta} \left( -\frac{1}{2} \rho \omega^2 r^2 + \rho \omega^2 rh z \right)
\]

The radial flow \( f \) per unit length of circumference is

\[
f = \int_0^h v \, dz = \frac{\rho \omega^2 r^3 h^3}{3 \eta}
\]

Then applying equation of continuity, differential equation for \( h \) is obtained

\[
\frac{\partial h}{\partial t} = -\frac{\partial (rf)}{\partial r}
\]

Thus from Eqn. 2.6

\[
\frac{\partial h}{\partial t} = -K' \frac{1}{r} \frac{\partial (r^2 h^3)}{\partial r}
\]

where \( K' = \rho \omega^2 / 3\eta \)

With this simple picture including the other physical mechanisms, which affect the final state, viz., solute diffusion, and solvent evaporation, the final dry film thickness can be expressed only in terms of spin speed and initial polymer concentration \((C_0)\) [45].

\[
h_f \propto C_0^m \omega^{-m}
\]

The theoretical calculations suggest the value of \( m \) to be 0.5 and a number of polymeric systems follow \( m = 0.5 \) power law behaviour. However the power law \( m = 0.5 \) is not unique and may depend on the polymer solution chosen. For highly viscous liquids the value of \( m \) can be as large as 0.8. Meyerhofer's [44] calculation suggests \( \nu = 1.67 \), which also have substantial agreement with his extensive experimental results. On the other
hand, Lai's [46] and other's [47] results suggest \( \nu = 2.1 \) and 2.47 respectively.

The spin coating process for non-Newtonian fluids can be described in three consecutive phases. The first phase begins by deposition of the coating fluid onto the substrate surface using a nozzle. A substantial excess of coating solution is usually applied compared to the amount that is required. The substrate is accelerated up to its final, desired, rotation speed as schematically shown in Fig. 2.1.

![Figure 2.1: The schematic diagram representing thin film preparation by spin coating.](image)

Most of the fluid is thrown off the substrate immediately after the spinning is started. During first few seconds, Coriolis forces and fluid inertia are dominant. At this stage the shear rate is quite large and the shear thinning may occur. The second phase of the process begins after these first few seconds when the initial non-Newtonian effects become negligible. During this phase, the decrease in film thickness is mainly due to fluid flow radially outward. The phase ends when the increase in the viscosity is significant and flow of fluid is almost stopped. In the final phase the thickness reduction is entirely governed by solvent evaporation. The spinner is stopped when the films are completely dry and the samples are then stored in desiccators.

### 2.1.2 Instrumentation

The device generally used for spin coating is called a photoresist spin coater. This is very popular in microlithography and the semiconductor industry. It basically consists of a
high speed motor with a vacuum plate attached on top. I have used a EC101 Photoresist spin-coater from Headway Research Inc., USA. The spin coating unit (spin coater) consists of a coating chamber which is mounted on a stage as shown in the left panel of Fig. 2.2. The coating chamber houses a vacuum chuck, which can be rotated with a high speed motor (maximum angular speed $\sim 10,000$ RPM) attached below the horizontal stage as shown in the figure. A close view of the vacuum chuck is shown in the right panel of Fig. 2.2. An array of groves are present on the upper face of the chuck and a rotary vacuum pump (not shown in the figure) sucks the air between the the chuck and the substrate to create a vacuum between the substrate and the chuck so that the substrate is held to chuck while spinning. During film preparation the coating chamber is covered with a glass cover to avoid contamination from atmosphere. An electronic control unit adjusts the spinning speed, acceleration and duration of spinning. The timer can be set to rotate the chuck for a given span of time and the spinning speed is displayed on the panel of control unit. This instrument can be used to create films with thickness below 10nm with surface roughness $\sim 0.5$nm was used to prepare ultrathin polymeric films in our study.
2.2 Magnetron Sputtering

2.2.1 Principle and Theory

Magnetron sputtering has developed rapidly over the last decade to the point where it has become established as the process of choice for the deposition of a wide range of industrially important coatings [48-50]. The driving force behind this development has been the increasing demand for high-quality functional films in many diverse market sectors. In many cases, magnetron sputtered films now outperform those deposited by other physical vapour deposition (PVD) processes, and can offer the same functionality as much thicker films produced by other surface coating techniques. In this method the sputtering process uses ion bombardment to remove the surface atoms of a relatively cool source material (figure 2.3). A plasma is initiated by applying a large negative potential to the target (the substrate being at the ground potential) placed in a vacuum chamber containing an inert gas (e.g. argon, nitrogen, etc.) at low pressure. The required breakdown voltage \( V_{bd} \) is given by Paschen's law [51]

\[
V_{bd} \propto \frac{PL}{\log PL + b}
\]  

(2.10)

where \( P \) is the chamber pressure, \( L \) is the target-substrate distance and \( b \) is a constant.

Once a plasma is formed, positive ions in the plasma are accelerated towards the negatively charged target. Upon striking the target surface, secondary electrons are released, which are accelerated away from the target. These electrons may collide with neutral plasma species while crossing from target to the substrate. If the energy transfer is less than the ionization potential of the gaseous species, the atom can be excited followed by de-excitation through an optical transition, providing the characteristic glow. If the energy transfer is high enough, however, the atom will ionize and accelerate towards the target eventually giving rise to sputtering. This gives rise to the sputtering phenomenon at the target. For each target material, there exists a threshold energy, below which no
sputtering occurs. This energy is typically in the range of 10 - 30 eV. For target atomic masses \((m_1)\) greater than five times the incident ion mass \((m_2)\) (as is the case for heavy metals and Argon ions), the threshold energy is given by

\[
E_{th} = \frac{U_0}{\gamma(1 - \gamma)}
\]

where \(U_0\) is the heat of vaporization of the target material and \(\gamma\) is the energy transfer parameter given by

\[
\gamma = \frac{4m_1m_2}{(m_1 + m_2)^2}
\]

In a magnetron sputtering system, magnets are positioned behind the target. The electrons are therefore forced by the electric field \((E)\) and the magnetic field \((B)\) to travel in a cycloid path in front of the target. The motion of the electrons increases the probability of collision with neutral species and create more ions. This increased ion density decreases the Crooke’s dark space and increases the rate of ion bombardment of the target. Typical ion densities in normal sputtering systems are 0.0001%, while in magnetron systems it often approaches 0.03%. The use of magnetron also allows the formation of plasma at lower chamber pressure, typically \(\sim 10^{-5} - 10^{-3}\) torr. The sputtered target atoms are directed towards the substrate and consequently a film of the sputtered material is obtained. The I-V characteristic of all magnetron sputtering systems can be expressed by the equation [52]

\[
I = k(V - V_0)^n
\]

where \(V_0\) is the minimum voltage necessary to maintain the plasma, and \(n\) is a positive number between 1.5 and 8, whose value depends on the geometry of the target and the pressure of the chamber.

The quality of the deposited film depends upon the plasma gas pressure, the potential applied, substrate-to-target distance, substrate temperature, etc [53–56]. Another factor
2.2. Magnetron Sputtering

Figure 2.3: Schematic of the magnetron sputtering phenomenon

that plays a significant role in the film growth is the reflected plasma gas atoms from
the target [57-62]. These hyperthermal atoms reach the film surface and transfer their
energy to the growing surface of the film, thereby affecting its structure, crystallinity,
composition, etc.

2.2.2 Instrumentation

The instrument used for depositing Au on polystyrene films discussed in Chapter 5 is a
high vacuum sputter coating unit (PLS 500) from Pfeiffer Vacuum, Germany (figure 2.4).
The main chamber can be evacuated to a base pressure of \( \sim 1 \times 10^{-6} \) mbar with the help
of a turbomolecular pump (Pfeiffer, TMH 520) backed by a rotary pump (Pfeiffer, DUO
016 B). Different types of gases can be introduced into the main chamber for plasma
discharge. The gas flow rate is controlled by a mass flow controller (MKS Instruments,
647B). The instrument is equipped with two d.c. and one r.f. sputtering units which
can be operated at different wattages. The maximum power that can be applied to the
d.c. magnetron is 500W. The diameter of targets used in the present set-up is 2.0 inch.
Sample stage rotation during deposition is possible using this machine. This is useful to
get smooth films while depositing at higher wattage and gas flow rates. The instrument is also equipped with a glow discharge facility for cleaning the substrate surface prior to deposition.

2.3 Analysis Probes Used

Fundamental phenomena involved in the interaction of radiation with matter depend on the wavelength-range of the radiation for a given matter. The main process of interaction in the visible region of the electromagnetic spectrum is the polarisation of the molecule (at least for an insulator). At higher energies as with x-rays, it is generally sufficient to take into account the interactions with the atoms and at the highest x-ray energies only the electrons need be considered in the interaction process.

A photon which meets an atom or molecule can undergo one of the three following events: elastic scattering, with no change in energy; inelastic scattering: part of the energy is transferred to the atom or molecule; absorption: all the energy is transferred to the atom or molecule and the photon vanishes. Another photon can be emitted, but with a lower energy; this is fluorescence.

In my work to get the structural, molecular and atomic level information of the samples (PS and Au-PS nanocomposite) I have used absorption spectroscopy to get information...
2.4 Spectroscopy

about electronic and vibrational levels of the molecule and *elastic scattering* of x-ray, more specifically *x-ray reflectivity*, to get electron density variation along depth of the film. I have also used Atomic Force microscopy (AFM) to get topographic and mechanical properties of the surface of the film from tip-sample interaction. These techniques are discussed in the following sections.

2.4 Spectroscopy

Spectroscopy is a science dealing with the energy states in matter, atoms, molecules, atomic nuclei and large molecular aggregates (crystals, high molecular-weight polymers and colloidal materials). The energy difference between initial and final states is linearly related to the frequency of spectral line. Molecular spectroscopy may be defined as the study of the interaction of electromagnetic waves and molecules.

2.4.1 Regions of the electromagnetic spectrum

In an order of increasing frequency the regions of the electromagnetic spectrum are:

1. **Radio frequency**: $\nu$(frequency) $\sim 10^8 - 10^{10}$ Hz; $\lambda$(wavelength) $\sim 10m - 1cm$. The energy change involved is that arising from the reversal of spin of a nucleus or electron, and $\sim .001$ to 10 Joules/mole. Nuclear Magnetic Resonance (n.m.r) and electron spin resonance (e.s.r) spectroscopy

2. **Microwave**: $\nu \sim 10^{10} - 10^{12}$ Hz; $\lambda \sim 1cm - 100\mu m$. Separation between the molecular rotational levels are $\sim 100$ J/mole. Rotational spectroscopy of molecules.

3. **Infrared**: $\nu \sim 10^{12} - 10^{14}$ Hz; $\lambda \sim 100\mu m - 1\mu m$. Separation between molecular vibrational levels are $\sim 10^4$ J/mole. Vibrational spectroscopy of molecules and condensed matter.
4. Visible and ultraviolet: $\nu \sim 10^{14} - 10^{16}$ Hz; $\lambda \sim 1\mu m - 10nm$. Separation between the energies of valence electrons are $\sim 10^5$ J/mole. Electronic spectroscopy of atoms, molecules and condensed matter.

5. X-ray: $\nu \sim 10^{18} - 10^{19}$ Hz; $\lambda \sim 1nm - 1Å$. Energy changes involving the inner electrons of an atom or a molecule, which may $\sim 10^7$ J/mole. Element identification.

I have used the Infrared and Visible and ultraviolet regions in my work extensively. Basic principles of absorption and reflection spectroscopy and instrumentation are discussed below.

### 2.4.2 Absorbance and Transmittance

The process of absorption can be expressed as follows [63]:

$$A + h\nu \rightarrow A^*$$

A is the absorbing medium, $A^*$ is the material in a higher energy level attained after absorption of energy ($h\nu$). The excited state $A^*$ is not a stable state and the material rapidly returns to the ground state.

There is no direct method for measuring absorbed light. This information is obtained indirectly by measuring the light which is not absorbed by the sample, i.e., the transmitted light (and reflected light). Measuring transmittance ($T$) of a film of given sample of known thickness, the absorption coefficient ($\alpha$) as well as the extinction coefficient ($\kappa_{ext}$) of the sample can be determined. The absorption coefficient $\alpha = 4\pi \kappa_{ext}/\lambda$ is the ratio between the intensity that is absorbed by a slab of unit thickness and the total incoming intensity $I$ for a given wavelength ($\lambda$). The absorbed intensity $dI$ through a slab of thickness $\Delta x$ is given by Lambert's law

$$dI = -\alpha \cdot I \cdot dx$$

(2.15)
2.4. Spectroscopy

then, the transmittance can be expressed in terms of extinction coefficient \( k \)

\[
T = \frac{I_T}{I_0} = \exp(-a \cdot x') = \exp\left(-\frac{4\pi \kappa_{ext} x'}{\lambda}\right)
\]

(2.16)

where \( I_T \) and \( I_0 \) represent the transmitted and incident beam intensities respectively through the film of absorbing material of thickness, \( x' \).

The Beer-Lambert law relates the absorbance \( A \) to the incident \( (I_0) \) and transmitted \( (I_T) \) intensities as well as the concentration \( (c) \) and path length \( (x') \) of the absorbing material, such that:

\[
A = \log(I_0/I_T) = \log(1/T) = ax'c
\]

(2.17)

here \( A \) is the absorbance and is the quantity normally measured in a spectrometer while \( a \) is the absorptivity given by \( a = \alpha/c \). Eqns (2.16), (2.17) are true only when reflectance of the slab is negligible with respect to its transmittance for a given wavelength range.

2.4.3 Infrared Spectroscopy

Basic Principle

Infrared radiation is another name for heat. All objects in the universe at the temperature above absolute zero give off infrared radiation. When infrared radiation interacts with matter it can be absorbed, causing the chemical bonds in the material to vibrate. The infrared spectra in the \( 2 - 50 \ \mu m \) region originate essentially in the vibrational motion of the atoms within molecules [63, 64]. Like all spectral process, they are due to a transition from one energy state to another; one or more vibrational quanta may be absorbed from radiation, superimposed on which, in gases, there is often a change in the rotational state of the molecule. The presence of chemical bonds in a material is a necessary condition for infrared absorbance to occur. A nonlinear (or linear) \( N \) atomic molecule can have \( 3N-6 \) (or \( 3N-5 \)) different internal vibrations. Here two approximations are implicit (i) each...
vibration is simple harmonic and (ii) each is independent of the others. Each of these independent modes of vibrations, the normal vibrations, is quantized and, if the change from one vibrational level to another in any mode causes a change in the position of the electric centre of the molecule, it can be excited by radiation of frequency ν given by the universal law $hν = E_2 - E_1$. The expression for the frequency (in Hz) of vibration of mass $m_1$ and $m_2$ vibrating about an equilibrium point with simple harmonic motion is [65]

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k'}{\mu}}$$  \hspace{1cm} (2.18)

where $k'$ is the restoring force per unit displacement from the equilibrium point and $\mu (= \frac{m_1m_2}{m_1+m_2})$ is the reduced mass. In order to be infrared active, there must be a change in the dipole moment during the vibration and this change may take place either along the line of symmetry axis (parallel to it) or at right angles to that (perpendicular).

A complex molecule is likely to have an infrared spectrum exhibiting a large number of normal vibrations, of which some involve all the atoms to much the same extent, called skeletal vibrations and others involve only a small portion of the molecule denoting the characteristic group vibrations.

It may seem that a polymer molecule with tens of thousands of atoms has tens to hundreds of thousands of normal modes and it's infrared spectra is expected to be impossibly complicated. But in practice this is not so, because the molecule of a homopolymer consists of a large number of chemically identical units, each of which usually contains only tens of atoms or fewer. This leads to a considerable reduction in the complexity of the infrared spectrum.

Types of Infrared Spectrometer

There are two distinct types of infrared spectrometers in common use for studying materials, including polymers: Dispersive instruments and Fourier transform instruments. In my studies the latter has been used.
2.4. Spectroscopy

A. Dispersive infrared spectrometer

In the dispersive instruments the radiation is physically split up into its constituent wavelengths by a monochromator either before or more usually after, it passes through the sample and the different wavelengths are processed in sequence.

B. Fourier transform infrared (FTIR) spectrometer

In the Fourier transform instrument radiation of all wavelengths passes through the sample to the detector simultaneously. The detector measures the total transmitted intensity as a function of the displacement of one of the mirrors in a double beam interferometer, usually of the Michelson type, and the separation of the sample response at different wavelengths is subsequently done mathematically.

![Schematic diagram of Michelson Interferometer](image)

Figure 2.5: Schematic diagram of Michelson Interferometer

The purpose of an interferometer is to take a beam of light, split it into two beams, and make one of the light beams travel a different distance than the other. The difference in distance travelled by these two light beams is called the optical path difference ($x$). The Fourier transform infrared (FTIR) spectrometer is usually based on Michelson inter-
ferometer shown schematically in Fig. 2.5. At the intersection of the four arms is a beam splitter, which is designed to transmit half the radiation that impinges upon it, and reflect half of it. Movement of the mirror $M_1$ causes a path difference between the two beams of monochromatic radiation of wavelength $\lambda$ that pass through the interferometer. Totally constructive interference will occur for radiation transmitted in the direction of the detector whenever $x = n \lambda$, where $n$ is an integer, and the measured intensity of the recombined beams will be maximum. When $x = (n + \frac{1}{2}) \lambda$, the two beams destructively interfere, to give zero intensity. At path differences other than those, a combination of constructive and destructive interference takes place, and the intensity is somewhere between very bright and very weak. The intensity measured by the detector varies cosinusoidally with the displacement of the mirror.

For monochromatic illumination of wavenumber $\tilde{\nu}(= 1/\lambda)$ and path difference $x$, the measured intensity, $I(x)$, is related to the incident intensity, $I_0(\tilde{\nu})$, from the source by the equation [66]

$$I(x) = \frac{1}{2} I_0(\tilde{\nu}) T(\tilde{\nu})(1 + \cos 2\pi x \tilde{\nu})$$

(2.19)

where $T(\tilde{\nu})$ is the transmittance of the sample at $\tilde{\nu}$. The path difference is equal to twice the mirror displacement, measured from the position where the two paths are equal. When polychromatic radiation passes through the interferometer, as it does when the interferometer is used for recording infrared spectra, the intensity measured for any value of $x$ is the integral of the above expression over the range of wavenumber involved. The intensity expressed as a function of $x$ is then apart from a constant added term $\frac{1}{2} \int I_0(\tilde{\nu}) T(\tilde{\nu}) d\tilde{\nu}$, proportional to the Fourier transform $\int I_0(\tilde{\nu}) T(\tilde{\nu}) \cos(2\pi x \tilde{\nu}) d\tilde{\nu}$, of the spectrum $I_0(\tilde{\nu}) T(\tilde{\nu})$ and this is called the interferogram. The detector signal and corresponding mirror displacement are fed to an on-line computer which calculates the inverse Fourier transform to provide a spectrum in the conventional form. The effect of a double-beam instrument (useful to eliminate the background effect) is obtained by recording an additional interferogram corresponding to $I_0(\tilde{\nu})$ after removing the sample to provide a new path from the...
2.4. Spectroscopy

interferometer to the detector which does not pass through the sample but is otherwise equivalent to the original path. In both methods the transmittance or absorbance of the sample is obtained by calculation from the stored spectra.

Modes of Operation

There are basically two modes of operation of IR Spectrometer - Transmission mode and Reflection mode. There are again two different modes in reflection spectroscopy, viz., Attenuated Total Reflection (ATR) and Specular Reflection mode. Depending on the sample type the appropriate mode should be used to extract the infrared spectra. For my studies transmission and ATR modes are important and discussed below.

A. Transmission mode

When infrared radiation passes through a homogeneous and isotropic sample the intensity is reduced by the same factor for each equal increase in distance traveled. If the reduction in intensity is due only to absorption rather than scattering, then according to Eqn. (2.17), absorbance can be calculated from the transmittance measurement. The transmission mode is mostly used in my experimental work.

B. Reflection (ATR) mode

If the sample is very thick the transmittance will approach zero and the absorbance will tend to infinity for all wavelengths, and even for thinner samples there may be wavelength regions where \( A > 3 \), the practical limit for most spectrometers [66]. For some materials it is very difficult to produce samples with suitably low absorbance and for some investigations, such as those for surface coatings, it is not even possible to obtain the appropriate material free from a substrate. For such samples the method of attenuated total reflection (ATR) spectroscopy may be useful because in this method the radiation passes only through a limited thickness of the sample.

Although specular or diffuse reflectance spectra may be recorded, as yet they are little used and ATR spectroscopy dominates the reflectance approach. The basic optical principle involved here, first observed by Newton, is that if light propagating in one optical
medium meets the boundary with a less dense medium at a suitable angle of incidence, it will traverse a small distance above few micrometer within the second medium before being reflected back into the first material without penetrating the second. There have subsequently been many elegant demonstrations of the effect, which may be described in terms of a standing wave normal to the surface in the denser medium and an evanescent, non-propagating field in the rarer medium, whose electric field amplitude decays exponentially with distance from the surface. In practice, the effective depth of penetration is usually a few micrometers, and depends on the angle of incidence and the difference between the refractive indices of the two media. The sample under examination is the medium of lower refractive index and a hybrid type of reflection/absorption spectrum, commonly known as an ATR spectrum, is obtained. The medium of higher refractive index must be transparent to infrared radiation. As the difference between the refractive indices of the sample and the other medium increases the ATR spectrum approximates more closely to the absorption spectrum, but the peak intensities decrease.

Instrumentation

Figure 2.6: PerkinElmer Spectrum GX FTIR Spectrometer set-up. Position of source, detector and sample compartment inside the box are denoted by 'S', 'D' and 'SC' respectively. (a) Whole set-up. (b) Inside of the sample compartment is shown, where white arrow shows the direction of light from source to Detector through sample.
A PerkinElmer Spectrum GX FTIR Spectrometer, USA (Fig. 2.6) is used for my measurements. The whole operation range of this instrument is $10000 - 30 \text{ cm}^{-1}$ with resolution $0.2 - 4 \text{ cm}^{-1}$, enabling the use of near (part), mid and far infrared options. Scan speed can be varied by varying optical path difference (OPD) velocity between 0.05 and 5.0 cm/s. This has a single beam Michelson interferometer with rotary bi-directional scan and stationary beamsplitter with interferometer auto alignment. Two types of voltage-stabilized and air-cooled sources are used here for different region of infrared radiation: near infrared radiation is produced by a tungsten-halogen lamp with a quartz envelope, mid and far infrared radiation is produced by a temperature stabilized, wire coil that operates at 1350K. Wide Range KBr and Far IR grid beamsplitters are used for the ranges $10000 - 370 \text{ cm}^{-1}$ and $710 - 30 \text{ cm}^{-1}$ respectively. These beam splitters are interchangeable. Fast Recovery Deuterated TryGlycine Sulphate (FR-DTGS) with calcium fluoride window, KBr window, and polyethylene window are used as detectors for near, mid, and far infrared region respectively.

In our measurement FTIR spectroscopy in transmission mode is used. The data had taken in the $10000 - 370 \text{ cm}^{-1}$ range with a resolution of $4.0 \text{ cm}^{-1}$, at $20^\circ\text{C}$.

### 2.4.4 Ultraviolet-visible Spectroscopy

In the visible and ultraviolet regions, excitation of a valence electron causes movement of electronic charges in the molecule. The consequent change in the electric dipole gives rise to spectrum by its interaction with the electric field of radiation.

The spectral region of our concern, ultraviolet and visible ($140 - 800 \text{ nm}$), is part of the so called “optical spectrum” region, which can be roughly subdivided as follows:

1. Vacuum ultraviolet: $10 - 185 \text{ nm}$
2. Far ultraviolet: $185 - 200 \text{ nm}$
3. Short ultraviolet: $200 - 300 \text{ nm}$
4. Near ultraviolet: 300 – 400 nm

5. Visible: 400 – 700 nm

In my studies, lab sources were used to obtain spectra in visible, near ultraviolet, short ultraviolet, and far ultraviolet regions, while a Synchrotron source was used to collect spectra at far ultraviolet and vacuum ultraviolet regions.

Basic Principle

A. Electronic Spectroscopy

As a first approach to the electronic spectra of molecules we may use the Born-Openheimer approximation; in the present context this may be written as [65]:

\[ E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} \]  

(2.20)

This implies that the electronic, vibrational and rotational energies of a molecule are independent of each other. Then a change in the total energy of the molecule is:

\[ \Delta E_{\text{total}} = \Delta E_{\text{electronic}} + \Delta E_{\text{vibration}} + \Delta E_{\text{rotation}} \]  

(2.21)

The approximate order of magnitude of this changes are:

\[ \Delta E_{\text{electronic}} \approx \Delta E_{\text{vibration}} \times 10^3 \approx \Delta E_{\text{rotation}} \times 10^6 \]  

(2.22)

and so we see that vibrational changes will produce a 'coarse structure' and rotational changes a 'fine structure' on the spectra of electronic transitions. We should also note that whereas pure rotation spectra are shown only by molecules possessing a permanent electric dipole moment, and vibrational spectra require a change of dipole during the motion, electronic spectra are given by all molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change. This means that homonuclear
molecules (for e.g., $H_2$ or $N_2$), which shows no rotation or vibration-rotation spectra, do give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequencies may be derived. The energy required for transition between electronic levels in molecules corresponds to visible and ultra-violet radiation.

Electrons in the vast majority of molecules fall into one of the three classes: $\sigma$ electrons, $\pi$ electrons and non-bonding electrons ($n$ electrons). In chemical terms a single bond between atoms contains only $\sigma$ electrons, a multiple bond contains $\pi$ electrons in addition, while elements to the right of carbon in periodic table, notably nitrogen, oxygen and halogens, possess $n$ electrons. In general the $\sigma$ electrons are most firmly bound to the nuclei and hence require a great deal of energy to undergo transitions, while the $\pi$ and $n$ electrons require less energy, the $n$ electrons usually (but non invariably) requiring less than the $\pi$ electrons. Thus, in an obvious notation, $\sigma \rightarrow \sigma^*$ transitions fall into the vacuum ultraviolet, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ appear at the border line of near and far ultra violet regions and the $n \rightarrow \pi^*$ come well into the near ultra violet and visible regions. These generalizations are indicated schematically on Fig. 2.7. Theory and analysis schema of

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Chapter. Experimental Techniques
this spectroscopy are discussed in detail in Chapter 3

B. Plasmon Spectroscopy

The absorption of a photon by a semiconductor or insulator creates an electron in the LUMO band and a hole in the HOMO band. The oppositely charged particles, under the right conditions, become a bound electron-hole pair. This neutral bound pair is called an exciton [67]. A metal, on the other hand, consists of a fixed lattice of positive ions together with a gas of free electrons, which exactly cancels the charge of the ions. Thermal or other low energy excitations would cause displacement of the free electron gas. Again, the coulomb coupling between the electron gas and the ionic lattice would finally cause the whole electron gas to oscillate with respect to the fixed ionic lattice. These oscillations are called plasma oscillations and it has been observed that in metals these oscillations are quantized. These quantized plasma oscillations are called plasmons [67].

A neutral gas of ions and electrons is called plasma. The polarization given by moving charges \( e \) of volume density \( n \) from their equilibrium position by a distance \( x \) is

\[
P = n e x
\]  

(2.23)

This gives rise to an electric field \( E \). Each charge is then returned to equilibrium by a force \( e E \), so that the equation of motion is given by

\[
m \ddot{x} = -4\pi ne^2 x
\]  

(2.24)

This describes a simple oscillatory motion of frequency

\[
\omega_p = \left( \frac{4\pi ne^2}{m} \right)^{1/2}
\]  

(2.25)

At the density of free electrons in metals, this frequency is \( \sim 10^{16} \sec^{-1} \). The density of the free electrons is equal to the density of metal atoms multiplied by the valency.

If we now consider a lightly damped system of a free electron under the influence of
an electric field, then the equation of motion for the electron is given by

$$m\ddot{x} = -e\varepsilon(t) = -e\varepsilon_0 \exp(-i\omega t)$$  \hspace{1cm} (2.26)

where $\omega$ is the frequency of the radiation and $\varepsilon_0$ is its amplitude. The solution to the above equation is given by

$$x(t) = \frac{e\varepsilon(t)}{m\omega^2}$$  \hspace{1cm} (2.27)

The polarization $P$ of the gas is equal to $-ne\varepsilon$. Therefore, the electric displacement $D$ and the relative dielectric constant $\varepsilon_r$ is given by

$$D = \varepsilon_r\varepsilon_0 P$$

$$= \varepsilon_0\varepsilon + P$$

$$= \varepsilon_0\varepsilon - \frac{ne^2\varepsilon}{m\omega^2}$$

Therefore taking Eqn. (2.25) into consideration,

$$\varepsilon_r(\omega) = 1 - \frac{ne^2}{\varepsilon m\omega^2}$$

$$= 1 - \frac{\omega_p}{\omega^2}$$  \hspace{1cm} (2.29)

Now the reflectivity $R$ expressed in terms of the complex dielectric constant $\tilde{n} (=\sqrt{\varepsilon_r})$ is given by

$$R = \left|\frac{\tilde{n} - 1}{\tilde{n} + 1}\right|^2$$  \hspace{1cm} (2.30)

The above equation suggests that for frequencies below $\omega_p$ there is 100% reflection. At $\omega_p$, the medium absorbs the incident radiation and above $\omega_p$, the radiation is transmitted through the medium. Thus all metals will eventually become transmitting if we go far enough into the ultra-violet so that $\omega > \omega_p$. Thus the plasma oscillations correspond to oscillations in the condition where $\varepsilon_r = 0$. The quantized plasma oscillations are called
2.4. Spectroscopy

Plasmons. They can be excited upon the passage of a beam of electrons through the metal. The energy $E_{\text{out}}$ of the transmitted electrons is given by

$$E_{\text{out}} = E_{\text{in}} - n'\hbar\omega_p$$

(2.31)

where $n'$ is the number of plasmons emitted during the passage through the metal. Thus, by measuring the energy of the electrons emerging, the plasma frequency can be determined.

Ultraviolet and visible (uv-vis) spectroscopy takes recourse of the above concepts for the detection of plasma resonant frequencies in metals. This technique is employed to characterize nanoparticles, the basic idea being the fact that there exists a strong band in the visible region of the absorption spectra of noble metal nanoparticles arising from the surface plasmons in response to an external electromagnetic field [68]. It has been observed that as the nanoparticle size decreases there is a dramatic increase in the plasmon resonance bandwidth which may be accompanied by shifts in the resonance position. The intensity is however proportional to the metal concentration. This necessitated the introduction of size dependent dielectric constant, at least for free electron metals, when the particle diameter ($a$) becomes smaller than the electron mean free path ($l$) in the bulk metal. For $a < l$, the electrons are scattered by the surface, strongly affecting their response to the incident electromagnetic field. This results a inversely proportional dependence of the plasmon bandwidth on particle diameter [69, 70]. In fact, for particle diameters substantially smaller than a wavelength of light, samples prepared without a matrix generally appear to be black. The size of a metallic nanoparticle can be obtained from the width of its absorption peak and is given by [71]

$$\Gamma = \frac{2v_F}{a}$$

(2.32)

where $\Gamma$ is the full-width at half-maximum (FWHM) of the absorption spectrum, $v_F$ is the Fermi velocity of the metal and $a$ is the particle diameter. It is assumed here that the
2.4. Spectroscopy

particles are spherical in shape. Theories however exist for non-spherical particles also. The bulk crystal absorption has a small step at a particular threshold frequency and then shows a smooth, continuous absorption rising towards higher energies. With the decrease of particle size, a blue shift is observed in the absorption spectra.

Instrumentation

A. Ultraviolet-Visible region: Lab source

![Schematic diagram of a spectrometer suitable for operation in the ultraviolet visible region](image)

Figure 2.8: Schematic diagram of a spectrometer suitable for operation in the ultraviolet visible region

![GBC UV-Visible Cintra 10e Spectrometer set-up](image)

Figure 2.9: GBC UV-Visible Cintra 10e Spectrometer set-up. Position of source, detector and sample compartment inside the box are denoted by ‘S’, ‘D’ and ‘SC’ respectively. (a) Whole set-up. (b) Inside of the sample compartment is shown, where white arrows show the direction of light from source to detector through sample and reference.
2.4. Spectroscopy

Fig. 2.8 shows the basic construction of ultraviolet-visible spectrometer schematically. I have used GBC UV-Visible Cintra 10e Spectrometer, Australia (Fig. 2.9) for my experiment. The scan range of this instrument is 190 — 1000 nm. The instrument can be used in the transmission modes and diffuse reflection mode for solids and liquids.

![Spectrophotometer Diagram]

Figure 2.10: (Left) Transmittance accessory. (Right) Reflectance accessory

Tungsten-Iodine lamp is used for visible and near uv radiation (300 — 1000 nm) and Deuterium discharge lamp is used for (190 — 300 nm). A Czerny-Turner monochromator is used to select the precise wavelength of interest. Accessories for transmittance and Reflectance are shown in Fig. 2.10. Silicon photo diode is used as detector for transmittance measurement and Photo multiplier tube is used in case of reflectance measurement.

B. Vacuum Ultraviolet region: Synchrotron source

I am presenting first a very brief discussion on synchrotron radiation. Then I will discuss about the vuv experiment as well as the synchrotron beamline, which was used for performing my experiment.

Figure 2.11 shows the schematic of origin of synchrotron radiation. Wherever the path of electrons bends, acceleration causes them to produce electromagnetic radiation. In the lab rest frame, this produces a horizontal fan of radiations that is highly collimated.
in the vertical direction and extends to high energies. Synchrotron radiation is highly collimated, hence very bright, are tunable in energy and are linearly polarized in the horizontal plane. I have used synchrotron source to perform spectroscopy in far and vacuum uv regions with polarized light and very high resolution in energy. The measurements in the vuv region were performed at the BEAR (Bending magnet for Emission, Absorption and Reflectivity) beamline at ELETTRA (Trieste, Italy). The experimental station of the BEAR beaml ine [72, 73] is a UHV chamber conceived to fully exploit the spectroscopic possibilities offered by the light spot produced by the beamline (Figure 2.12). Spectroscopies include reflectivity (specular and diffuse), optical absorption, fluorescence and angle resolved photoemission. The chamber can be rotated around the beam axis to select the s (TE) or p (TM) incidence conditions and/or the position of the ellipse of polarization with respect to the sample. Photon detectors (e.g. photodiodes) and electron detector (hemispherical analyzer - 1° angular resolution, 20 meV energy resolution) cover about completely the full $2\pi$ solid angle above the sample surface in any light incidence condition.

The conceptual diagram of the experimental station, mainly from the point of view of rotations and translations of sample and detectors, is shown in Figure 2.13, where $\Omega_L$ is the laboratory frame of reference, $\Omega_C$ is the vacuum vessel frame of reference, rotating around the beam, $x_L$ axis, $\Omega_M$ is the manipulator frame of reference.
2.4. Spectroscopy

The whole system rotation $\Psi_C$ around the light beam axis $x_L - x_C$ covers $90^\circ$ in order to align the $y_C$ axis (manipulator frame axis) parallel or perpendicular to $y_L$ axis of $\Omega_L$. Positioning of the ellipse of polarisation of the incident beam in any position with respect to the sample is achieved in this way.

The analyser/detector primary rotation around the $y_C$ axis and the rotation of the sample manipulator around the $y_C$ axis are coaxial. The rotation $\Theta_M$ of the sample manipulator and the rotation $\Theta_A$ of the analyser/detectors primary arm around the $y_C$ axis both cover angle of $360^\circ$.

The rotation $\Phi_A$ of the analyser secondary goniometer is fixed to and rotates together with the primary arm around the $y_C$ axis; it covers an angle of $220^\circ (+110^\circ, -110^\circ$ with respect to the plane passing through the normal to the secondary goniometer and $y_C$). This secondary arm holds the electron hemispherical analyser and photodiodes directed towards the centre of the assembly.

The transmittance measurements were performed at BEAR beamline (Figure 2.12)
with spectral resolution 0.01 eV in the range 4 – 9 eV. The experimental chamber was at 10^{-10} Torr vacuum level. The spot size on the sample was 0.4 \times 0.2 \text{ mm}^2. The transmission and their relative direct signals were measured using an IRD SXUV-100 silicon photodiode. The background signal was recorded by measuring the dark signal of the photodiode. The normalization of the measurements took into account the ring current \( C \) or the monitor current \( I_0 \) from a 100V biased W-mesh, for possible fluctuations of the photon beam. The experimental transmittance \( T_{\text{ring}} \) and \( T_{\text{mesh}} \) obtained respectively by normalizing with the ring and the monitor current, are given by
\[ T_{\text{ring}} = \left( \frac{I_D - I_{D,B}}{C} \right) / \left( \frac{I^D_{B} - I^D_{0,B}}{C^D} \right) \]  
\[ T_{\text{mesh}} = \left( \frac{I_D - I_{D,B}}{I_0 - I_{0,B}} \right) / \left( \frac{I^D_{B} - I^D_{0,B}}{I^D_{0} - I^D_{0,B}} \right) \]

Where \( I_D \) and \( I^D_{B} \) represent the diode currents given by the beam passes through the sample and the direct beam respectively. \( I_{D,B} \) and \( I^D_{0,B} \) represent the background diode currents with sample and without sample respectively. \( C \) and \( C^D \) represent the ring current during the measurements. Similarly \( I_0 \) and \( I^D_{0} \), \( I_{0,B} \) and \( I^D_{0,B} \) represent the mesh currents in same convention as mentioned above. The differences between the two kinds of normalizations were 2% at maximum, apart from the region of overlapping of the two channels (40-50 eV) and at higher energies (> 800 eV) where the mesh signal was too noisy. The appropriate normalization was used depending on the situation. Absorbance of the sample can be measured using this transmittance in Eqn. (2.17).

### 2.5 X-ray Scattering

The scattering of electromagnetic waves is used in basic research, materials science, and industry for investigations of surfaces and interfaces on length scales covering several orders of magnitude. X-ray scattering is a probe to investigate surfaces on angstrom scales. Nowadays x-ray reflectivity has emerged as a powerful tool for the investigation of the structural properties of thin polymer films. This technique provides excellent spatial resolution, down to ~ 0.5 nm with penetration depths over hundreds of nanometers. It probes the variation in the electron density. This technique is non-destructive and, consequently, repetitive measurements on one specimen can be performed. The specimen does not required special conditioning and measurements can be done under ambient conditions. The non-destructive nature of x-ray scattering technique and its ability to explore structural properties of crystalline and non-crystalline solids [40, 74–77], liquids [24, 78–80],
thin films and their buried interfaces [81–83] makes this technique an indispensable tool for structure determination. Moreover, using x-rays in grazing incidence the sensitivity to the surface can be increased [40, 76, 77].

\[ q = k_f - k_i \]  

(2.34)

The components of \( q \) in \( x \), \( y \) and \( z \) directions are given by

\[ q_x = k_0(\cos \theta_f \cos \psi - \cos \theta_i) \]  

(2.35)

\[ q_y = k_0(\cos \theta_f \sin \psi) \]  

(2.36)

\[ q_z = k_0(\sin \theta_f + \sin \theta_i) \]  

(2.37)

Fig. 2.14 shows the scattering geometry in the general case of a surface experiment. The plane of incidence contains the incident wave-vector \( k_i \) and the normal to the surface. If \( k_f \) is the scattered wave vector, then the momentum transfer vector \( q \) is given by

\[ q = k_f - k_i \]  

(2.34)

The components of \( q \) in \( x \), \( y \) and \( z \) directions are given by

\[ q_x = k_0(\cos \theta_f \cos \psi - \cos \theta_i) \]  

(2.35)

\[ q_y = k_0(\cos \theta_f \sin \psi) \]  

(2.36)

\[ q_z = k_0(\sin \theta_f + \sin \theta_i) \]  

(2.37)
2.5. X-ray Scattering

where $k_0 = 2\pi/\lambda$, $\lambda$ being the wavelength of the incident radiation. In a reflectivity experiment, we work in the plane of incidence and thus have the in-plane angle $\psi = 0$. In specular reflectivity, incident angle ($\theta_i$) and the scattered angle ($\theta_f$) are kept equal. This gives information about the thickness and electron density profile of the individual layers and the interfacial roughness [40, 76, 82, 84]. Off-specular diffuse scattering ($\theta_i \neq \theta_f$) provides better understanding about the in-plane correlation and also the correlation between the interfaces [40, 79, 85]. In case of grazing incidence diffraction (GID) experiments, one varies $\psi$. This gives in-plane lattice structure of the sample [86–88]. Specular reflectivity technique is discussed below in detail.

2.5.1 X-Ray Reflectivity (XRR)

In x-ray reflectivity measurements, a well collimated monochromatized x-ray beam is made to be incident on sample surface at a grazing angle $\theta_i$ (starting from few milliradians) and the reflected intensity is recorded in the plane of incidence at an angle $\theta_f$. If the angle of incidence of impinging x-rays is sufficiently small, the penetration depth and the scattering is limited to the near surface region. Reflectivity data is generally taken at angles considerably larger than the critical angle of total external reflection and therefore penetration depth is of the order of thousands of angstroms. The sensitivity is then obtained by interference of x-rays scattered by layers with different electron densities at different depths in the sample.

Basic Formalism

An electromagnetic plane wave given by its electric field vector $\Psi(r) = \Psi_0 \exp(ik\cdot r)$, which penetrates into a medium characterized by an index of refraction $n(r)$, propagates according to the Helmholtz equation

$$\, (\nabla^2 + k^2n^2)\Psi(r) = 0 \quad (2.38)$$
where \( k = 2\pi/\lambda \) is the modulus of the wave vector \( k_1 \) and \( \lambda \) denotes the wavelength of the radiation. In general, the index of refraction for an arrangement of \( N \) atoms per unit volume, which may be assumed to be harmonic oscillators with resonance frequencies \( \omega_j \), is expressed as \[89\]

\[
n^2 = 1 + \left( \frac{Ne^2}{\varepsilon_0 m} \right) \sum_{j=1}^{N} \frac{f_j}{\omega_j^2 - \omega^2 - 2i\omega\eta_j} \tag{2.39}
\]

Where \( \omega \) is the frequency of the incoming electromagnetic wave, \( e \) is the charge and \( m \) is the mass, respectively, of the electron, the \( \eta_j \) are damping factors, and the \( f_j \) denote the forced oscillation strengths of the electrons of each single atom. It should be noted that in general the \( f_j \) are complex numbers, \( f_j = f_j^0 + f_j'(E) + f_j''(E) \), where \( f_j'(E) \) and \( f_j''(E) \) take into account dispersion and absorption corrections depending on the radiation energy \( E \) \[90\]. For x-rays \( \omega > \omega_j \), and Eqn. (2.39) may be replaced by \[91,92\]

\[
n = 1 - \delta + i\beta \tag{2.40}
\]

with the dispersion and absorption terms

\[
\delta = \frac{\lambda^2 r_0 \rho_{el}}{2\pi} \sum_{j=1}^{N} \frac{f_j^0 + f_j'}{Z} = \frac{r_0 \lambda^2}{2\pi} \sum_{j=1}^{N} \frac{\rho_j}{A_j} (Z_j + f') \tag{2.41}
\]

and

\[
\beta = \frac{\lambda^2 r_0 \rho_{el}}{2\pi} \sum_{j=1}^{N} \frac{f_j''}{Z} = \frac{r_0 \lambda^2}{2\pi} A_j \sum_{j=1}^{N} \frac{\rho_j}{A_j} f_j'' \tag{2.42}
\]

It should be emphasized that \( \delta \) is always positive. In Eqns. (2.41) and (2.42) we have introduced: (1) the classical electron radius \( r_0 = e^2/(4\pi\varepsilon_0 mc^2) = 2.814 \times 10^{-8} \) Å, (2) the total number of electrons \( Z = \sum_j Z_j \), where \( Z_j \) denotes the number of electrons of each elementary component of the material i.e., with \( j^{th} \) atomic number and (3) the electron density \( \rho_{el} \) as a function of the spatial co-ordinates \( r = r(x, y, z) = r(r_j, z) \). The quantities \( f_j^0 \) are \( q \) dependent, where \( q = k_f - k_i \) is the wave vector transfer (\( k_i, k_f \))
are the wave vectors of the incident and scattered plane x-ray waves). This has to be taken into account when measurements over a large $q$ region are analyzed [90]. However in the region of grazing incidence and exit angles, $\theta_i$ and $\theta_f$, respectively, the wavevector transfer is small, and $f_j^0$ may be approximated with high accuracy by $f_j^0 \approx Z_j$. $N_A$ is Avogadro's number, $\rho_j$ is the density of element $j$ with atomic weight $A_j$ [40,76]. For x-rays $\delta \sim 10^{-6}$ and $\beta$ is usually one or two orders of magnitude smaller. In case of a homogeneous medium and far away from absorption edges, Eqns. (2.41) and (2.42) can be rewritten in terms of the electron density $\rho_{el}$ and the linear absorption coefficient (or mass absorption coefficient), $\mu$ as

$$\delta = \lambda^2 \rho_{el} r_0 / 2\pi \tag{2.43}$$

and

$$\beta = \mu \lambda / 4\pi \tag{2.44}$$

In vacuum, the $z$ component of the momentum transfer vector, normal to the surface or $x$-$y$ plane, is given by

$$q_{z,0} = 2\pi \left( \frac{\sin \theta_i + \sin \theta_f}{\lambda} \right) \tag{2.45}$$

In specular condition $\theta_i = \theta_f$, we can write,

$$k_{z,0} = q_{z,0} / 2 = 2\pi \sin \theta_i / \lambda \tag{2.46}$$

For a single vacuum/medium interface, Snell's law of refraction gives

$$\cos \theta_i = (1 - \delta) \cos \theta_r \tag{2.47}$$

where $\theta_r$ is the exit angle of the refracted radiation as shown in Fig. 2.15. Thus if $\theta_r = 0$, and since $\delta$ is very small, the critical angle is

$$\theta_c \approx \sqrt{2\delta} = \lambda \sqrt{r_0 \rho_{el} / \pi} \tag{2.48}$$
Now we consider a perfectly smooth surface of a medium on which x-ray hits at a grazing angle $\theta_i$. For incident angles $\theta_i \leq \theta_c$ the phenomenon of *total external reflection* occurs. The x-rays do not penetrate far into the medium and all incoming radiation is reflected. When $\theta_i > \theta_c$, the incident beam is reflected and transmitted at angles $\theta_f$ and $\theta_r$ respectively. As mentioned earlier, in specular condition $\theta_i = \theta_f$ and only the $z$-component of momentum transfer vector $q$ will survive (i.e. $q_x = q_y = 0$). The critical value of momentum transfer vector $q_c$ corresponding to $\theta_c$ can be written as

$$q_c^2 = \left(\frac{4\pi}{\lambda}\right)^2 \theta_c^2 = 16\pi \rho_e r_0$$  \hspace{1cm} (2.49)

The $z$-component of momentum transfer vector in the medium $q_{z,1}$ can be written as

$$q_{z,1} = (q_{z,0}^2 - q_{c,1}^2)^{1/2}$$  \hspace{1cm} (2.50)

Here we have used the suffix '0' and '1' for air (or vacuum) and medium, respectively. By using the appropriate boundary conditions for the electric field and its derivative at the air/medium interface one can obtain the Fresnel formulas for reflection and transmission coefficients as [40, 81–84]
2.5. X-ray Scattering

\[ r_{01} = \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}} = \frac{q_{z,0} - q_{z,1}}{q_{z,0} + q_{z,1}} \]  

(2.51)

and

\[ t_{01} = \frac{2q_{z,0}}{q_{z,0} + q_{z,1}} \]  

(2.52)

The specular reflectivity can then be written as

\[ R = r_{01} \cdot r_{01}^* \]  

(2.53)

\[ R \] is simply the Fresnel reflectivity and can be written in terms of \( q_z \) as

\[ R_F(q_z,0) = \left| \frac{1 - [1 - (q_{z,1}/q_{z,0})^2]^{1/2}}{1 + [1 - (q_{z,1}/q_{z,0})^2]^{1/2}} \right|^2 \]  

(2.54)

Figure 2.16: Reflectivity curve for Si substrate and a 100 Å thick Au film on Si substrate. Inset: Film/substrate structure for which the reflectivity curve is shown.

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2.5. X-ray Scattering

This is shown in Fig. 2.16 for the interface between silicon and air. For \( q_{s,0} > 3q_{c,1} \), the Fresnel reflectivity may be well approximated by

\[
R_F(q_{s,0}) \propto (q_{c,1}/q_{s,0})^4 \tag{2.55}
\]

Therefore for an infinitely sharp interface the reflectivity will vary with \( q_{s,0}^2 \) at high values of \( q_{s,0} \).

**Reflectivity from Multiple Interfaces using the Parratt Formalism**

The Parratt formalism is based on solving Fresnel equations at multiple interfaces. Let us consider a film of thickness \( d \) on a substrate as shown in the inset of Fig 2.16. The reflectivity profile shown contains Kiessig fringes i.e., interference fringes originating from the variation in electron density. The difference between successive minima of these fringes is inversely related to the thickness of the film. We will denote the air, film and the substrate as media 0, 1 and 2 respectively. If we denote the reflection coefficients at the air-film interface \((z = 0)\) and film-substrate interface \((z = d)\) as \( r_{01} \) and \( r_{12} \) respectively, then the reflectance from this air-film-substrate system can be written as

\[
r' = \frac{r_{01} + r_{12}}{1 + r_{01}r_{12}} \tag{2.56}
\]

The continuity condition at the substrate-film interface at \( z = d \) gives rise to an extra exponential factor in the expression of \( r_{12} \) as

\[
r_{12} = \frac{k_{z,1} - k_{z,2}}{k_{z,1} + k_{z,2}} \exp(-2ik_{z,1}d) = \frac{q_{z,1} - q_{z,2}}{q_{z,1} + q_{z,2}} \exp(-iq_{z,1}d) \tag{2.57}
\]

We can extend the above calculation to the case of reflectivity for stratified homogeneous media having \( M \) such thin layers [93]. Starting from air/vacuum as medium 0, we will denote the topmost layer as medium 1 and so on. Thus \( M \)-th layer is the bottom most layer and \((M+1)\)th layer is the substrate. Let us denote the thickness of each layer by \( d_n \). A set of equations similar to Eqn. (2.56) can be obtained for each interface and one
can arrive at a recursive formula given by [40, 81–84, 94]

\[ r_{n-1,n} = \frac{r_{n,n+1} + F_{n-1,n}}{1 + r_{n,n+1}F_{n-1,n}} \exp(-i \frac{q_z}{n} d_{n-1}) \]  

(2.58)

where

\[ F_{n-1,n} = \frac{q_{z,n-1} - q_{z,n}}{q_{z,n-1} + q_{z,n}} \]  

(2.59)

The reflectance is first calculated using Eqn. (2.58) between the layer closest to the substrate and the substrate, i.e., the M th and (M+1) th layer respectively with the assumption that \( r_{M+1,M+2}=0 \), as the thickness of this layer (substrate) is taken as infinite. The calculated reflectivity is then fitted to the experimental data to obtain the electron density profile (EDP) of the multilayer structure. The above calculation is not only used for multilayer thin films, but also widely utilized to approximate realistic electron density profile of a monolayer film. This is done by subdividing the continuous electron density profile of the film into a series of discrete layers each having thickness \( d_n \) and electron density \( \rho_n \).

The reflectivity of this layered system is calculated using the above mentioned recursion relation. The reflectivity profile calculated using this model is modified iteratively until it matches the experimental data. The layer thickness and electron densities are used to construct the electron density profile along film depth.

**Reflectivity using distorted-wave Born approximation**

We have also used a method of extraction EDP, based on Distorted wave Born approximation (DWBA), that has proved to be particularly useful in detecting small variations in density, which occur due to layering in liquids or polymers. This scheme, unlike the Parratt scheme, does not require any a priori model of the electron density profile, other than the average electron density of the total film. In this scheme we consider the film to be composed of a number of thin slices of equal thickness with electron density of \( j \) th slice (or box), \( \rho_j = \rho_0 + \Delta \rho_j \) where \( \rho_0 \) is the average electron density over the total thickness of
2.5. X-ray Scattering

the film and \( \Delta \rho_j \) varies with slices but is constant in the \( j \)th slice. We can then write \( \Delta \rho(q_z) \) in terms of \( \Delta \rho(z) \), where \( \Delta \rho(z) \) is the variation of electron density as a function of the film depth \( z \) (the film surface is taken as \( z = 0 \), with \( z \) positive into the substrate) [27],

\[
\Delta \rho(q_z) = \int_{-\infty}^{+\infty} \Delta \rho(z) \exp[iq_z z] dz
\]

(2.60)

For our scheme Eqn. (2.60) gives the result as,

\[
\Delta \rho(q_z) = \frac{i}{q_z} \left[ \left( \sum_{j=2}^{N} \left( \Delta \rho_j - \Delta \rho_{j-1} \right) \exp(iq_z(j-1)d) \right) + \Delta \rho_1 - \Delta \rho_N \exp(iq_zNd) \right]
\]

(2.61)

Where, \( N \) is the total number of boxes used in the calculation. In the above expression \( q_z = 2(k_z^2 - k_z^2)^{1/2} \) is the \( z \)-component of momentum transfer vector in the film, \( k_c \) being the critical wave vector for the average film of electron density \( \rho_0 \).

Here we have derived the expression for specular reflectivity of a thin film on a substrate in terms of \( \Delta \rho(q_z) \) using the DWBA formalism. The expression of \( \Delta \rho(q_z) \) given in Eqn. (2.61) is used to calculate specular reflectivity. First we have derived the expression for specular reflectance \( r'(q_z) \) and Fresnel transmission \( a(q_z) \) and reflection coefficients \( b(q_z) \).

The wave function \( \Psi(z) \) satisfying the Helmholtz equation of the form Eqn. (2.38), for the x-rays in a one dimensional potential \( V(z) \) due to the film of thickness \( d \) on a substrate can be written as

\[
\Psi(z) = \exp(ik_{z,0}z) + r'(q_z) \exp(-ik_{z,0}z) \quad z < 0
\]

\[
= a \exp(ik_{z,1}z) + b \exp(-ik_{z,1}z) \quad 0 < z < d
\]

\[
= T \exp(ik_{z,2}z) \quad z > d
\]

(2.62)

where \( k_{z,0}, k_{z,1} \) and \( k_{z,2} \) have already been defined earlier, to be the \( z \) component of
wavevector transfer in air, film and substrate respectively. $T$ is the Fresnel transmission coefficient in the substrate. By definition we take the top of the film to be at $z = 0$ and the direction into the film as $z$ positive. Applying the conditions of continuity of the wavefunction and its derivative at $z = 0$ we arrive at the following set of equations

\begin{align*}
1 + r'(q_z) &= a + b \quad (2.63) \\
k_{z,0}(1 - r'(q_z)) &= k_{z,1}(a - b) \quad (2.64)
\end{align*}

Similarly applying the boundary conditions at $z = d$ we get

\begin{align*}
a \exp(ik_{z,1}d) + b \exp(-ik_{z,1}d) &= T \exp(ik_{z,2}d) \quad (2.65) \\
k_{z,1}(a \exp(ik_{z,1}d) - b \exp(-ik_{z,1}d) &= Tk_{z,2} \exp(ik_{z,2}d) \quad (2.66)
\end{align*}

Using Eqns. (2.65) and (2.66) we can write,

\begin{align*}
k_{z,1} &= \frac{a \exp(ik_{z,1}d) + b \exp(-ik_{z,1}d)}{a \exp(ik_{z,1}d) - b \exp(-ik_{z,1}d)} \quad (2.67)
\end{align*}

Which on further simplification gives

\begin{align*}
b &= ar_{12} \quad (2.68)
\end{align*}

again using Eqns. (2.63), (2.64), (2.68) and (2.51) we can write

\begin{align*}
r'(q_z) &= \frac{r_{01} + r_{12}}{1 + r_{01}r_{12}} \quad (2.69)
\end{align*}

Using Eqns. (2.63), (2.68) and (2.69) we can write

\begin{align*}
a &= \frac{1 + r_{01}}{1 + r_{01}r_{12}} \quad (2.70)
\end{align*}
Let us define the potential $V$ as $V_1 + V_2$ where

$$
V_1 = 0 \quad z < 0 \\
= r_0 \rho \quad 0 < z < d \\
= r_0 \rho_s \quad z > d \tag{2.71}
$$

$\rho_s$ being the electron density of the substrate, and

$$
V_2 = 0 \quad z < 0 \\
= r_0 \Delta \rho \cdot \quad 0 < z < d \\
= 0 \quad z > d \tag{2.72}
$$

Here $r_0$ is the classical electron radius for x-ray scattering. Let us also define a time reversed wavefunction corresponding to the one defined in Eqn. (2.62) above as

$$
\tilde{\Psi}(z) = \exp(-ik_{z,0}z) + r^*(q_z) \exp(ik_{z,0}z) \quad z < 0 \\
= a^* \exp(-ik_{z,1}z) + b^* \exp(ik_{z,1}z) \quad 0 < z < d \\
= T^* \exp(-ik_{z,2}z) \quad z > d \tag{2.73}
$$

The specular reflectivity, $R(q_z)$, in DWBA is given by

$$
R(q_z) = |\langle \tilde{\Psi}|V_1|\phi \rangle + \langle \tilde{\Psi}|V_2|\tilde{\Psi} \rangle|^2 \tag{2.74}
$$

Here $|\phi \rangle = \exp(ik_{z,0}z)$. The first term can be shown to be equal to $ir'(q_z)$. The second term can be written as

$$
\langle \tilde{\Psi}|V_2|\tilde{\Psi} \rangle = \frac{2\pi r_0}{k_{z,1}} \left[ a^2 \Delta \rho(q_{z,1}) + b^2 \Delta \rho^*(q_{z,1}) + 2ab \int dz \Delta \rho(q_z) \right] \\
= \frac{4\pi r_0}{q_{z,1}} \left[ a^2 \Delta \rho(q_{z,1}) + b^2 \Delta \rho^*(q_{z,1}) \right] \tag{2.75}
$$
where $\int dz \Delta \rho(z) = 0$ since $\Delta \rho$ is defined about the mean density and $\Delta \rho(qz)$ is the Fourier transform of $\Delta \rho(x)$.

Hence the specular reflectivity in DWBA for a film on a substrate can be written as

$$R(qz) = \left| r'(qz) + \frac{4 \pi r_0}{qz} \left[ a^2 \Delta \rho(qz) + b^2 \Delta \rho'(qz) \right] \right|^2$$  \hspace{1cm} (2.76)

Here, $r'$ is the specular reflectance coefficient of the average film of electron density $\rho_0$, $r_0$ is the classical electron radius ($= 2.8 \times 10^{-8}$ Å), $a$ and $b$ are the coefficients for transmitted and reflected amplitudes of the average film. By selecting an appropriate number of slices and $\rho_0$ for the film we fit Eqn. (2.76), after convolution of the Gaussian resolution function, to the data, keeping $\Delta \rho$'s as the fit parameters.

**Effect of Roughness**

So far we have discussed the reflectivity profile for ideally smooth surfaces/interfaces. For a real system one has to include the effect of roughness in reflectance of each interface which reduces the reflectivity of the surface by scattering x-rays in non-specular direction. In most of the cases, we assume that deviations of the actual interface from the average value of the interface can be described by gaussian statistics. This is equivalent to convoluting the infinitely sharp profile with a Gaussian smoothing function. Let us consider roughness at the interface separating media $n - 1$ and $n$ to be $\sigma_n$, i.e. the standard deviation of the actual interface from the average value of the interface is $\sigma_n$. Then Eqn. (2.58) will be modified as [40]

$$r_{n-1,n}^{\text{rough}} = r_{n-1,n} \exp\left(-\frac{1}{2} \frac{q_{n(n-1)} q_m \sigma_n^2}{q_m^2} \right),$$  \hspace{1cm} (2.77)

These reflectances can then be used to calculate the reflectivity of the entire film in either of the above mentioned analysis schemes. In general, the reflectivity from a surface having roughness $\sigma$ is given by
\[ R_{\text{rough}} = R_F \exp(-q_z^2 \sigma^2) \] (2.78)

where \( R_F \) is the Fresnel reflectivity given by Eqn. (2.54). It is clear from Eqn. (2.78) that the reflectivity from a rough surface is smaller compared to the smooth surfaces and this deviation increases as \( q_z \) increases. The interfacial roughness reduces the density contrast between two layers and thus reduces the amplitude of the oscillation in the reflectivity profile. The x-y average EDP as a function of depth, \( \rho(z) \) can be written as [84]

\[ \rho(z) = \sum_{1}^{M} \Delta \rho_n f(z_n, \sigma_n) \] (2.79)

where \( \Delta \rho_n \) is the change in electron density at \( n \)-th interface located at a position \( z_n \) and \( f \) is an error function given by

\[ f(z_n, \sigma_n) = f(z - z_n, \sigma_n) = \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{z-z_n} \exp(-t^2/2\sigma^2) \, dt \] (2.80)

where \( \sigma_n \) is the roughness of the \( n \)-th interface which is a parameter for the estimation of interfacial width. It can be noted that these error functions of Eqn. (2.79) come as Debye-Waller like functions for the reflectance of each interface in reciprocal space as given in Eqn. (2.77).

**Resolution Function**

The calculated reflectivity profile cannot be compared directly with the experimental reflectivity data because one has to take into account the finite resolution of the experimental setup in the calculation [40,82]. The resolution in reflectivity measurements depends on the wavelength dispersion (\( \Delta \lambda/\lambda \)), the angular divergence of incoming beam (\( \Delta \theta_i \)) and the acceptance of outgoing radiation (\( \Delta \theta_f \)). Before comparing with experimental data, the calculated profile has to be convoluted with a resolution function which is generally modeled as a gaussian function of the type

\[ \text{Chapter. Experimental Techniques} \]
The standard deviation $\sigma_R$ is related to the full-width at half-maximum (FWHM) $\Delta q_z$ of a gaussian function as $\sigma_R = \Delta q_z/(2\sqrt{2\log 2})$ \cite{95}. This $\Delta q_z$ depends on wavelength dispersion as well as on the geometry of experimental setup. In the usual geometry of the experimental setup, the aperture of the detector slits perpendicular to the scattering plane is kept wide open so that the scattered intensity in the $q_y$ direction is integrated out in the XRR experiment. Assuming $x$-$z$ plane as the scattering plane, we take total differential of Eqn. (2.35) and Eqn. (2.37),

$$dq_z = k_0(\cos \theta_i \, d\theta_i + \cos \theta_f \, d\theta_f) + dk_0(\sin \theta_i + \sin \theta_f), \quad (2.82)$$

$$dq_x = k_0(\sin \theta_i \, d\theta_i - \sin \theta_f \, d\theta_f) - dk_0(\cos \theta_i - \cos \theta_f) \quad (2.83)$$

With the assumption that $d\theta_i$ and $d\theta_f$ are randomly distributed the resolution widths in $q_x$ and $q_z$ are given by,

$$\Delta q_x^2 = k_0^2(\sin^2 \theta_i \, \Delta \theta_i^2 + \sin^2 \theta_f \, \Delta \theta_f^2) + \Delta k_0^2(\cos \theta_i + \cos \theta_f)^2, \quad (2.84)$$

$$\Delta q_z^2 = k_0^2(\sin^2 \theta_i \, \Delta \theta_i^2 + \sin^2 \theta_f \, \Delta \theta_f^2) + \Delta k_0^2(\cos \theta_i - \cos \theta_f)^2 \quad (2.85)$$

In our setup the distance between x-ray source and sample was kept equal to that between the sample and the detector. In this geometry $\Delta \theta_i = \Delta \theta_f = \Delta \theta$ (say), which can be obtained from the FWHM of the direct beam profile. Then in specular condition above two equations can be rewritten as,
2.5. X-ray Scattering

\[
\Delta q_z = E \left[ \frac{1}{2} \cos^2 \theta \Delta \theta^2 + \left( \frac{\Delta E}{E} \right)^2 \sin^2 \theta \right]^{1/2}
\]

(2.86)

\[
\Delta q_x = E \left[ \frac{1}{2} \sin^2 \theta \Delta \theta^2 + \left( \frac{\Delta E}{E} \right)^2 \cos^2 \theta \right]^{1/2}
\]

(2.87)

For the monochromatic x-ray source, we do not have to consider the effect of wavelength dispersion and hence the second term in the above equations will vanish and only the first terms in expression of \( \Delta q_z \) and \( \Delta q_x \) will contribute to the resolution function.

2.5.2 Instrumentation

Instrument for X-ray Reflectivity Study

![Grazing incidence x-ray reflectivity set-up used for our experiments.](image)

Figure 2.17: Grazing incidence x-ray reflectivity set-up used for our experiments.

The angle dispersive grazing incidence x-ray reflectivity (XRR) setup in our laboratory is shown in Fig. 2.17. The XRR setup consists of three main parts: (a) the x-ray source - the rotating anode x-ray generator and associated beam optics, (b) the motor controlled 3 circle goniometer, and (c) the x-ray detector and associated electronics.

(a) The X-ray Source
The x-ray generator (Enraf Nonius FR 591) consists of a water-cooled copper rotating anode of cylindrical cross section and a cathode assembly inside a high vacuum chamber. The shaft of the cylindrical anode rotates coaxially inside another cylinder containing ferrofluid material which serves as a lubricant as well as a vacuum seal. The cathode consists of a ceramic coated high voltage connector and the focus assembly containing a filament and focus cup to focus the electron beam. The cathode is continuously cooled with oil flow. The emitted electron beam from the filament impinges on the anode after being accelerated by the set voltages between cathode and anode. Two types of filaments, broad focus and fine focus, can be used in this generator and we have used only fine focus in our experiments. Fine focus filament produces an electron beam of cross section 0.3 x 3.0 mm. The axis of the electron beam is perpendicular to the axis of rotation of the anode. The x-ray beam emerging from the surface of the anode is the characteristic copper emission superimposed on the \textit{bremsstrahlung} radiation. This beam emerging from the chamber through beryllium window is collimated by a slit before it is monochromatized. Si (111) single crystal has been used as monochromator to select the CuK\textsubscript{α} line. The K\textsubscript{α1} or K\textsubscript{α2} line of CuK\textsubscript{α} doublet can be chosen by properly placing a 100 \mu m vertical slit in the x-ray beam path. CuK\textsubscript{α1} radiation of wavelength 1.540562 Å is used in our laboratory experiments. Another horizontal slit having a vertical aperture of 5 mm is also used in the x-ray path.

(b) The Goniometer

A three circle goniometer have been used in our experiment. There are several stepper motors for rotations as well as translational movements. In Fig. 2.18, we have shown the rotation geometry of goniometer. In this setup the two principal motors, \( \theta \) and 2\( \theta \) motors, are mounted coaxially and the axis of rotation is vertical. The goniometer head on which the samples can be mounted houses the X-motor for translational motion along \( z \)-axis, \( \theta_y \) and \( \theta_z \) motors for coarse and short range rotations about \( y \) and \( z \) axes respectively and the \( \phi \) motor for rotations about the \( x \) axis. The movements of \( \theta \), 2\( \theta \) and \( \phi \) motors are controlled by separate microprocessors and all these processors are interfaced with a PC.
The movements of the remaining motors are controlled manually from the motor control panel. The distance from the monochromator to the center of the goniometer and from the goniometer center to the detector is kept nearly same and is equal to 40 cm.

(c) The Detector

A NaI scintillation detector coupled with a photomultiplier tube (PMT) is used in our setup. The detector is mounted on $2\theta$ arm of the goniometer. Each incident photon on the NaI crystal produces an optical pulse with amplitude proportional to the energy of the incident photon. This light pulse is incident onto the photocathode of the PMT and a number of photoelectrons are produced. These electrons from the photocathode is subsequently reflected off successive dynodes to produce secondary electrons and the final output of the PMT at the anode is magnified several times as compared to the incident signal at the cathode. The PMT is coupled to a preamplifier. The purpose of using a preamplifier immediately after the PMT is to match the impedance between the detector and the remaining part of the signal chain by providing a high input impedance to the detector side and a low output impedance to the subsequent circuit. It also minimizes the
2.5. X-ray Scattering

capacitative load on the detector which arises due to interconnecting cables and hence enhances the signal to noise ratio. The pulse from preamplifier is passed through a linear shaping amplifier. The amplifier serves to amplify and shape the signal from the preamplifier to enable counting of the pulses and avoid the pileup problem due to overlap of successive pulses (in case of high counting rates). To count these pulses it is needed to convert the output pulses from linear shaping amplifier to logic pulses for which a differential discriminator or single channel analyzer (SCA) is used. The function of the SCA is to produce a logic output pulse only if the amplitude of the input linear pulse lies between a window of input amplitudes. In our setup we have selected a LLD and a window so that the CuKα line is selected and the signal to noise ratio is optimized. The final steps in the signal processing chain are the counter and timer. In order to reduce the background counts due to air scattering evacuated collimator pipes are placed between the monochromator and the sample and between sample and detector. We have also used a setup to overcome the effect of fluctuation in the incident x-ray beam intensity arising out of inadvertent fluctuation in the x-ray power supply.

2.5.3 Sample-Cell

I have used the home made sample cell [96,97], shown in Figure 2.19, to perform the experiment in elevated temperature with $\sim 10^{-3}$ mbar vacuum. The cell is made of brass and consists of two separate part (top and bottom). The main part contains an inner copper block (for better thermal conductivity) on which the sample was mounted along with the temperature sensor (PT-100 with stability $\pm 0.1K$), very close to the sample. Nickel-Chromium wire, wound around the Cu block, used as heating coil. A Teflon block was used to thermally insulate this inner block from the outer hollow brass cell which was mounted on the goniometer. The temperature of the heater was regulated using a temperature controller (Lake Shore, 331) with temperature stability of $\pm 1K$. After inserting the sample in the position as shown in Figure 2.19, two parts are fitted together with screws. A neoprene o-ring sits as vacuum seal on flat circular flange. Starting from
2.6 Scanning Probe Microscopy

Scanning Probe Microscopy (SPM) is a technique that allows us to obtain three dimensional images of surfaces at the atomic scale [98-100]. This technique is based upon scanning a probe (the tip) within a few nanometers above the surface of interest while monitoring some interaction between the probe and the surface. The interaction is spatially localized according to the shape of the probe and the finite effective range of the interaction. When the probe moves laterally (horizontally) relative to the sample, any change in the height of the surface causes the tip-surface interaction to change. The distance-dependence of a particular tip-sample interaction can be exploited to guide the tip at a finite tip-surface separation over the sample by keeping the interaction strength at a constant preset value with a feedback circuit. By raster scanning the tip, surface contours of constant interaction strength are obtained. Changing the type of interaction

Figure 2.19: Sample cell for reflectivity measurements.

room temperature maximum limit of the cell is 200°C. In the experiments 5K/minute ramp rate was used.
generally leads to changes of the surface contours obtained. Alternatively, the tip can be raster scanned at a fixed height over the sample surface and variations of the interaction strength, resulting from variations of tip-to-sample spacing, can be recorded. Depending on the types of tip-surface interactions monitored, SPM can be operated in different modes. The most commonly used modes are atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The interaction that is monitored in AFM is the van der Waals force, either the very short range repulsive force or the longer range attractive force, between the tip and the surface while in STM the tunneling current between a metallic tip and a conducting substrate is probed. Some other members of the family of scanning probe techniques are Magnetic Force Microscopy (MFM), where the spatial variation of the magnetic force interaction between a magnetic tip and sample is probed; Electrostatic Force Microscopy (EFM), which is used to study the distribution of electrical charge on a surface by probing the long range electrostatic Coulomb forces; Lateral Force Microscopy (LFM) that identifies and maps relative differences in surface frictional characteristics by detecting the torsion of the scanning tip; Chemical Force Microscopy (CFM), where the tip is functionalized with a chemical species and scanned over a sample to detect adhesion differences between the species on the tip and those on the surface of the sample; Scanning Thermal Microscopy (SThM) where a tiny resistance thermometer is used as the scanning probe and the image contrast reflects variations in thermal properties across the sample; Scanning Near-Field Optical Microscopy (SNOM) which scans a very small light source very close to the sample and the detection of the scattered light forms the 3D image of the surface.

2.6.1 Atomic Force Microscopy

Basic Principle

For two electrically neutral and non-magnetic bodies held at a distance \( r \) of one to several tens of nanometers, the van der Waals forces usually dominate the interaction
force between them. The force can be derived from Lennard-Jones potential and its distance dependence can be written as

\[ F(r) \propto \left( \frac{1}{r^{13}} - \frac{1}{r^7} \right) \]

The interatomic force vs. distance curve is shown in Fig. 2.20. As the atoms are gradually brought together, the attractive force between them increases until they are so close together that their electron clouds begin to repel each other electrostatically. This electrostatic repulsion progressively weakens the attractive force as the interatomic separation continues to decrease and when the distance between the atoms reaches a couple of angstroms, the total van der Waals force becomes repulsive. In AFM, the local variation of the force acting between the tip and the sample is measured in order to generate the 3D images of the surface. In Fig. 2.21 the operating principle of AFM is shown with the help of a schematic diagram.

The principle of AFM relies on the use of a sharp tip mounted on a cantilever-type spring which is brought into close proximity to the surface and as the tip moves over the surface, the change in local interaction forces acting between them causes the cantilever to bend according to Hooke's law. The cantilever deflection is detected by 'optical lever'
principle and converted into an electrical signal to produce the images. In optical lever method, a laser beam reflected from the backside of the cantilever is made incident on a position sensitive photo detector (PSPD). As the cantilever deflects, the angle of the reflected beam changes and the spot falls on a different part of the photodetector as shown in Fig. 2.22. Generally the detector is made of four quadrants and the signals from the four quadrants are compared to calculate the position of the laser spot. The vertical deflection of the cantilever can be calculated by comparing the amount of signal from the “top” and “bottom” halves of the detector. The lateral twisting of the cantilever can also be calculated by comparing the “left” and “right” halve signals from the detector. This detection system measures the cantilever deflection with sub-angstrom sensitivity. The spring constant of the cantilever should be small enough to allow detection of small forces and its resonant frequency should be high to minimize sensitivity to mechanical vibration. The scanning i.e. tip or sample movement is performed by an extremely
2.6. Scanning Probe Microscopy

Deflection signal
\[(A + B) - (C + D)\]
\[(A + B) + (C + D)\]

Detection laser

Quadrant photodiode

Cantilever deflection

Sample

Figure 2.22: Schematic diagram showing the cantilever deflection in AFM.

precise positioning device made from piezo-electric ceramics, most often in the form of a tube scanner. The scanner is capable of sub-angstrom resolution in x, y and z-directions. To control the relative position of the tip with respect to the sample accurately, good vibrational isolation of the microscope has to be ensured.

Modes of Operation

There are various modes of operation of an AFM - contact mode, tapping mode and non-contact mode being the main three among them.

A. Contact Mode

In contact mode the tip and sample remain in close contact during scanning i.e. the tip is always in the repulsive regime of the intermolecular force curve as shown in Fig. 2.20. The forces range from nano to micro Newtons for solids and even lower (0.1 nN or less) for liquids. In this mode imaging can be done in two ways:

(i) **Constant Force Imaging** in which a feedback circuit adjusts the height of the
tip during scanning so that the cantilever deflection and hence the corresponding force remains constant. The feedback system is connected to the z-piezodrive and the output signal \( U_z \) of the feedback loop adjusts the vertical \( z \) position of the sample or tip to achieve a constant cantilever deflection (constant force). \( U_z \) can be recorded as a function of the \((x, y)\) coordinates which are determined by the corresponding voltages \( U_x \) and \( U_y \) applied to the \( x \) and \( y \) piezoelectric drives. The obtained signal \( U_z (U_x, U_y) \) can finally be translated into the ‘topography’ \( z(x,y) \), provided that the sensitivities of the three orthogonal piezoelectric drives are known.

(ii) **Constant Height Imaging** in which tip is scanned at a fixed height above the sample and the variation in tip-sample interaction force reflects the atomic-scale topography of the sample. This mode is useful when the tip has to be scanned faster than the finite response time of the feedback loop. A significant drawback of this mode lies in the fact that vertical height information is not directly available. Although the constant force mode is generally preferred for most application, constant height mode is often used for taking atomic-scale images of atomically flat surfaces, where the cantilever deflections and thus the variation in force are small. This is also essential for recording real-time images of changing surfaces, where high scan speed is needed. The major problem with contact mode is that the dragging motion of the probe tip, combined with adhesive forces between the tip and the surface, can cause substantial damage to both sample and probe and create artifacts in the image. Thus this mode is not an ideal one to perform high resolution topographic imaging of surfaces of soft materials which can easily be damaged or of overlayers that are loosely held to their substrates.

**B. Non-Contact Mode**

Non-contact AFM (NC-AFM) is a vibrating cantilever technique in which an AFM cantilever is vibrated above the surface of the sample at such a distance that we are no longer in the repulsive regime of the inter-molecular force curve as indicated in Fig. 2.20. Since in non-contact regime, there is no contact between the tip and the sample and the total force acting between them is very low, this mode is advantageous for studying soft
2.6. Scanning Probe Microscopy

or elastic samples. Cantilever used here must be stiffer than those used for contact AFM because soft cantilever can be pulled to contact with the sample surface. The small force values in non-contact regime and the greater stiffness of the cantilevers make the NC-AFM signal small and therefore difficult to measure. Thus a sensitive AC detection scheme is used for NC-AFM operation. Here a stiff cantilever vibrates slightly above its resonant frequency (typically from 100 to 400 kHz) with an amplitude of a few tens to hundred of angstroms. The resonant frequency of the cantilever is decreased by van der Waals force resulting in a change in oscillation amplitude. The system monitors the changes in resonance frequency or vibrational amplitude of the cantilever and these changes can be used as a measure of changes in the force gradient, which reflects changes in the tip-to-sample spacing or sample topography. The resonance frequency or vibrational amplitude of the cantilever is kept constant with the aid of a feedback system that moves the scanner up and down. By keeping the resonant frequency or amplitude constant, the system also keeps the average tip-to-sample distance constant. As with contact AFM, the voltage applied to the scanner \( U_z \) \((U_x, U_y)\) is used to generate the topography. This mode does not suffer from the tip or sample degradation effects that are sometimes observed after taking several scans with contact AFM. However, the attractive Van der Waals forces are substantially weaker than the forces used by contact mode and the attractive forces extend only a small distance from the surface, where the adsorbed fluid layer may occupy a large fraction of their useful range. Hence, even when the sample-tip separation is successfully maintained, non-contact mode provides substantially lower resolution than contact mode.

C. Tapping Mode

Tapping mode imaging overcomes the limitations of the conventional scanning modes by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient by oscillating the cantilever assembly at or near the cantilever's resonance frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude (typically greater than 20nm) when the tip
is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or “tap” the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000 to 500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to energy loss caused by the tip contacting the surface. The amplitude of oscillation changes when the tip scans over the bumps or depressions. A constant oscillation amplitude and thus a constant tip-sample interaction is maintained during scanning with the help of the feedback circuit by adjusting the tip-sample separation. This mode inherently prevents the tip from sticking to the surface and causing damage during scanning. Unlike contact and non-contact modes, when the tip contacts the surface, it has sufficient oscillation amplitude to overcome the tip-sample adhesion forces. Also, the surface material is not pulled sideways by lateral forces since the applied force is largely vertical. This technique has proven to be a valuable tool since it allows reduction of the lateral forces acting on the sample during scanning. Damage and distortion to the sample can be minimized. For these reasons, tapping mode AFM is well suited for the study of polymer, soft matter and fragile objects. An AFM operating in tapping mode can go beyond simple topographic imaging to detect spatial variation in surface composition, adhesion, friction, viscoelasticity and other properties by using a method that is termed as Phase Imaging.

Sample properties can be explored by using the phase lag between the excitation (the signal that drives the cantilever to oscillate) and the response of the cantilever (the cantilever oscillation output signal) as an auxiliary signal [101–103] because phase shift is directly correlated to the tip-sample interaction. Phase imaging is the spatial mapping of this phase lag. Changes in the phase lag often indicate changes in the mechanical properties of the sample surface. Simplified, the system can be modeled by an oscillator consisting of two damped springs representing the cantilever and the sample, respectively. The springs are each described by a characteristic spring constant and a damping constant. In the case of the sample these parameters basically model the viscoelastic
interaction and are assumed to vary locally. The whole system can be described to a first approximation \([104-107]\) by the external driving frequency \(\omega_0\), the effective resonance frequency \(\omega\), and an effective damping \(\alpha\) which may vary locally. These effective quantities dominate the complete resonance behaviour of the system, including the phase shift. Using the approximation in the resonant case \([108]\) the phase shift \(\phi\) is related to the effective parameters by \(\tan \phi = 2\alpha \omega_0/(\omega^2 - \omega_0^2)\). An energy approach \([109-111]\) emphasizes the relation between the phase shift and energy dissipated in the tip-sample interaction volume, implying a dominant role of the damping introduced by the sample. I have used this relation to analyse the phase image in my work and discussed it in detail in Chapter 4 and 5.

Combining the phase signal with the topographical image, surface properties can so be related to sample features. Imaging quality and conditions can be monitored and different interaction mechanisms can be distinguished. This synoptical interpretation of AFM data provides a powerful tool for the investigation of complex sample. Phase imaging is quite effective for contaminant identification, mapping of components in composite materials, differentiating regions of high and low surface adhesion or hardness and regions of different electrical or magnetic properties. In my thesis work, I have studied the surface mechanical properties of pristine polystyrene film and Au-polystyrene nanocomposite by taking phase and topographical image using tapping mode AFM.

### 2.6.2 Instrumentation

The instrument used for my experiments under ambient conditions is a Nanoscope-IV multimode SPM from Digital Instruments, USA (Fig. 2.23). Here, the scanner is attached to the sample holder. For my studies, two types of scanners – 10 \(\mu\text{m} \times 10 \mu\text{m}\) with a vertical range of 2.5 \(\mu\text{m}\) and 0.4 \(\mu\text{m} \times 0.4 \mu\text{m}\) with a vertical range of 0.4 \(\mu\text{m}\) are used. In tapping mode AFM, topographic and phase images are taken using uncoated Si tip with a nominal tip radius of curvature of 5 — 10 nm. The resonant frequency and spring constant of the cantilever attached to the tip for tapping mode measurements are 200 — 400 kHz.
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and 20 – 60 N/m respectively.

Figure 2.24 shows the block diagram of obtaining topographic, phase and frequency modulation (FM) image. In the amplitude and phase detection modes, there is no feedback during the LiftMode scan (the tip lifts above the surface to an adjustable lift height, typically 5-50nm, and scans), i.e., the drive signal that oscillates the cantilever has constant frequency. The 3-D phase or topographic image is generated by plotting the cantilever’s phase or amplitude versus the in-plane coordinates. In the FM mode, the phase of the cantilever oscillation is measured relative to the phase of the drive signal from a high-resolution oscillator. The phase difference is used as an error signal in a feedback scheme, where the frequency of the drive signal is modulated (“Frequency Control lines” in Figure 2.24) to maintain the cantilever oscillation at a constant phase relative to the...
Figure 2.24: Amplitude and phase detection and frequency modulation (FM) techniques with tapping mode AFM.

drive signal. The modulations of the drive signal frequency are then plotted versus the in-plane coordinates, creating the 3-D FM image.