2.1 Introduction

In the past three decades thin film growth techniques have changed day to day life of society. There are numerous thin film technologies used to grow the integrated circuits in our computers, cell phones and palm pilots and many more new methodologies continued to be discovered and explored by the physicists. Today’s routine life has an impact of physics based thin film applications [1]. It is necessary to a technocrats and researchers to evolve new materials possessing combination of both physical and mechanical properties [2]. Deposition methods of thin films can be categorized mainly into two parts viz., physical and chemical techniques.

Chemical methods are economical and easier than that of the physical methods among the methods mentioned in the Fig. 2.1. But there is no ideal method to prepare thin films, which will satisfy all possible requirements. Among the chemical methods, the dip coating technique is the most popular today because large number of conducting and semiconducting thin films can be prepared by this technique. It is also popular due to its simplicity and low cost. In this technique, the thin films can be deposited on different substrates like glass, ceramic, metallic etc.
**Fig. 2.1 Classification of thin film deposition techniques**

In the present study, the synthesis of Polyaniline (PANI) is carried out by chemical polymerization method. The detailed description of this method is mentioned in the previous chapter. Depositions of the films were done by using the simple and cost effective dip coating technique.

**2.2 Dip Coating**

Dip coating is the precision controlled immersion and withdrawal of any substrate into a reservoir of liquid for the purpose of depositing a layer of material. Many chemical and nonmaterial engineering research projects in academia and industry make use of the dip coating technique.
The dip coating process can be separated into five stages:

1. Immersion: The substrate is immersed in the solution of the coating material at a constant speed (preferably jitter-free).

2. Start-up: The substrate has remained inside the solution for a while and is starting to be pulled up.

3. Deposition: The thin layer deposits itself on the substrate while it is pulled up. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating (faster withdrawal gives thicker coating material).

4. Drainage: Excess liquid will drain from the surface.

5. Evaporation: The solvent evaporates from the liquid, forming the thin layer. For volatile solvents, such as alcohols, evaporation starts already during the deposition and drainage steps.
Advantages Of Dip Coating Technique

1. It is very simple and cost effective technique.
2. It does not require any sophisticated instrument.
3. Easy preparative parameters like temperature, concentration, pH, deposition cycles etc.
4. Depositions can be carried out on both conducting and nonconducting substrates.
5. Film thicknesses can be easily changed mere by changing the number of dipping cycles, or switching to a different viscosity fluid.
6. Using dip coating technique we can deposit multilayered film on the same substrate.

2.3 Characterization Techniques

Introduction

Nanoscience and nanotechnology is considered to be the key technologies of the modern era. The discovery of novel materials contributed to the progress of materials science and technology. It is essential to have sophisticated and trustworthy characterization techniques for the analysis of the physical and chemical properties of materials. Characterizations of thin films will certainly help to develop exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. This section deals with different analytical instrumental techniques used to characterize thin films with their operation and working principles.
2.3.1 Thickness Measurement

Profilometer is a measuring instrument used to measure a surface's profile, in order to quantify its roughness. Vertical resolution is usually in the nanometer level, though lateral resolution is usually poorer.

**Contact Profilometers**

A diamond stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance and specified contact force. A profilometer can measure small surface variations in vertical stylus displacement as a function of position. A typical profilometer can measure small vertical features ranging in height from 10 nm to 1 mm. The height position of the diamond stylus generates an analog signal which is converted into a digital signal stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nm to 25 µm and the horizontal resolution is controlled by the scan speed and data signal sampling rate. The stylus tracking force can range from less than 1 to 50 mg [3].

**Non-Contact Profilometers**

An optical profilometer is a non-contact method for providing much of the same information as a stylus based profilometer. There are many different techniques which are currently being employed, such as laser triangulation (triangulation sensor), confocal microscopy (used for profiling of very small objects) and digital holography. In the present work, a contact profiler was used to measure the thickness of PANI thin films.

Roughness is a measure of the texture of a surface. It is quantified by the vertical deviations of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth. Roughness is typically considered to be the high frequency, short wavelength component of a measured surface.
2.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Introduction

FT-IR spectroscopy is a tool for qualitative and quantitative analysis of the various chemical groups present in the material. Instead of recording the amount of energy absorbed when the frequency of the infrared (IR) light is varied (using monochromator), the IR light is guided through an interferometer. Then the Fourier transform is performed on this signal from interferometer, which results in a spectrum similar to that from conventional infrared spectrometer. FTIR spectroscopy is used to study the infrared region of the electromagnetic spectrum, which lies between the visible and microwave regimes. Infrared radiation is broken up into five sub-regions [4]: the near infrared (near-IR) spanning from 0.75 \( \mu \text{m} \) to 1.4 \( \mu \text{m} \) the short-wave infrared (SWIR) spanning from 1.4\( \mu \text{m} \) to 3\( \mu \text{m} \), the mid-wave infrared (MWIR) spanning from 3\( \mu \text{m} \) to 8\( \mu \text{m} \), the long-wave infrared (LWIR) spanning from 8\( \mu \text{m} \) to 15\( \mu \text{m} \), and the far infrared (FIR) spanning from 15\( \mu \text{m} \) to 1000\( \mu \text{m} \). Although the infrared spectrum covers a wide range in the electromagnetic spectrum, FTIR spectroscopy is typically used for viewing MWIR and LWIR.

![The electromagnetic spectrum showing the infrared region and other regions of the spectrum](BeyondBeds.com)

**Fig.2.3** The electromagnetic spectrum showing the infrared region and other regions of the spectrum [5]
IR radiation is typically referred to as heat radiation, since objects at room temperature emit radiation at around 8µm to 10µm. Although not visible to the human eye, the detection of infrared radiation present all around us is useful for many purposes, ranging from military applications, such as night vision and homing systems, to general use applications, such as short-range wireless communication, weather forecasting and spectroscopy. Although several other methods do exist for observing IR radiation, the advent of FTIR systems has eliminated the need for its predecessors. In physics and astronomy, FTIR spectroscopy is used to study celestial bodies and learn more about the composition of the objects in space. In semiconductor processing, it is used as a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic [6]. It is used to identify unknown materials present in the sample. In forensics, it is used for identification of polymer degradation and as a non-destructive method of probing paints, coatings, drugs, and contaminants [7, 8]. FTIR spectroscopy plays its most important role in chemistry, where it can identify different types of chemical bonds. There are six different ways an organic compound can vibrate: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging, and twisting [9]. Therefore, the spectrum of each compound is unique, similar to a fingerprint.

The FTIR not only allows us to detect IR radiation, but it allows us to measure and analyze the exact composition of the radiation, which provides us with essential data to solve problems.

**History**

Infrared radiation was first discovered by Sir William Herchel in the year 1800 with the use of a prism [4]. He used a thermometer to measure the temperature of each region of the spectrum, from violet to red and noted that the temperature increased as he traversed the colors. He continued to move the thermometer past red and noticed that the temperature continued to increase. The region past red became known as infrared (meaning “below red”). Soon after,
Macedonio Melloni made the first thermopile IR detector in 1835. Further development of thermal detectors grew throughout the 1800s. Then, with Albert Einstein’s explanation of the photoelectric effect in 1905 [10], it did not take long until the first photon detectors were created and used to measure IR radiation in the early 1900s.

In 1949, an astrophysicist by the name of Peter Fellgett first used an interferometer to measure the light from extraterrestrial bodies, thus creating the very first FTIR spectrum. However, due to the fact that very few research groups had access to large and expensive computers and that it took nearly 12 hours to transform an interferogram into a spectrum, FTIR was not really used much. The dispersive IR spectrometer was faster and cheaper.

Prior to discussing the workings of an FTIR system, it is important to recognize the various sources of IR generation and detection. During most spectroscopy measurements, the sample we wish to study will be placed between the IR source and detector in order to measure transmission and absorption characteristics of the material. The same FTIR setup can also be pointed towards the sky to record data in our atmosphere.

**Working**

Infrared spectroscopy works on the principle that the chemical bonds have characteristic frequencies at which they vibrate. These resonant frequencies are dependent on the length of the bond and the masses of the atoms at either ends of it. For a diatomic molecule the natural frequency of vibration is: [11]

\[
\omega = \left(\frac{K}{m_r}\right)^{1/2}
\]  

(2.1)

Where, \( k \) is the force constant and \( m_r \) is the reduced mass and is given by the equation:

\[
m_r = \frac{m_1m_2}{m_1 + m_2}
\]

(2.2)

When the incident IR frequency matches with the resonant frequency, absorption takes place, resulting in an absorption peak in the IR spectrum.

In a conventional IR (or “continuous wave”) spectrometer, a sample is
exposed to electromagnetic radiation and the response (usually the intensity of the transmitted radiation) is monitored. The energy of the radiation is varied over the desired range and the response is plotted as a function of radiation energy (or frequency). At certain resonant frequencies characteristic of the specific sample, the radiation will be absorbed resulting in a series of peaks in the spectrum, which can then be used to identify the sample.

Instead of varying the energy of the electromagnetic radiation, Fourier Transform spectroscopy exposes the sample to a single pulse of radiation and measures the response. The resulting signal, called free induction decay, contains a rapidly decaying composite of all possible frequencies. Due to resonance by the sample, resonant frequencies will be dominant in the signal and by performing a mathematical operation called a Fourier transform on the signal the frequency response can be calculated. In this way the Fourier transform spectrometer can produce the same kind of spectrum as a conventional spectrometer, but in a much shorter time. FTIR spectrometers are cheaper than the fabrication of a monochromator. In addition measurement of single spectrum is faster for the FTIR technique because the information of all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity.

For the present work, FTIR spectrometer; Perkin Elmer Model Spectrum one was used and the ray diagram of the FTIR is shown in Fig.2.4.
The interferometer that is used is a Michelson interferometer. It is comprised of a fixed mirror, a movable mirror, and a beam splitter. The IR radiation leaves the source and is directed onto the beam splitter. Here, half the IR is transmitted to the fixed mirror while the other half is sent to the moving mirror. After each sub-beam is reflected back to the beam splitter, they recombine. Based on the location of the movable mirror, there may be constructive or destructive interference. The recombined beam then exits the interferometer and travels to the detector.

For a single frequency source, as the mirror is moved between its extreme positions at a constant velocity, the intensity of the radiation picked up by the detector in the time-domain changes sinusoidally. The detector measurement is recorded along with the position of the movable mirror for each scan. If the sample absorbs at this frequency, the amplitude of the sinusoidal wave is reduced by an amount proportional to the amount of sample in the beam [12]. For a broadband IR source, the interferogram is far more complex, since it is the summation of superimposed sinusoidal waves, with each wave corresponding to a single frequency or wavelength. Likewise, the amplitudes of the frequencies that are absorbed by the sample decrease, modifying the interferogram. The
signal intensity at the detector for a single frequency source can be written as:

$$I(x) = B(v) \cos(2\pi vx)$$ \hspace{1cm} (2.3)  

Similarly, for a source with two distinct frequencies, we have:

$$I(x) = B(v) \cos(2\pi v_1 x) + B(v) \cos(2\pi v_2 x)$$ \hspace{1cm} (2.4)  

For the case of a real instrument, we have:

$$I(x) = \int_{-\infty}^{\infty} B(v) \cos(2\pi vx) \, dv$$ \hspace{1cm} (2.5)  

and its complement in the frequency domain:

$$B(v) = \int_{-\infty}^{\infty} I(x) \cos(2\pi vx) \, dx$$ \hspace{1cm} (2.6)  

The magnitude of Equation 2.5 is constant during the mirror scan, except for when the movable mirror distance from the beam splitter is equal to the distance between the beam splitter and the fixed mirror. At this location, all the waves interfere constructively, producing a burst in the middle of the interferogram. This is illustrated below.

![Interferogram showing plot of intensity measured at the detector as a function of retardation](image)

**Fig.2.5 Interferogram showing plot of intensity measured at the detector as a function of retardation** [12]

Performing a Fourier Transform or Fast Fourier Transform on the
interferogram will show the data in the frequency domain, allowing us to see what wavelengths of light are transmitted and what are absorbed by the sample. Studies of the spontaneous orientation of dipole moment in semiconductors are carried out with a non destructive tool of analysis by infrared spectroscopy which can give information on atomic arrangement and inter atomic forces in the crystal lattice itself. It is possible to investigate how the infrared vibrational frequencies and thus the inter-atomic forces are affected by the onset of the semiconductor states. If the two energy levels $E_1$ and $E_2$ are placed in an electromagnetic field and the difference in the energy between the two states is equal to a constant ‘h’ multiplied by the frequency of the incident radiation $\nu$, a transfer of energy between the molecules can occur, giving therefore $\Delta E = h\nu$.

Where, the symbols have their usual meanings. When the $\Delta E$ is positive the molecule absorbs energy; when $\Delta E$ is negative, radiation is emitted during the energy transfer and emission spectra are obtained. When the energies are such that the equation is satisfied, a spectrum unique to the molecule under investigation is obtained. The spectrum is usually represented as a plot of the intensity Vs the frequencies and peaks occur when the condition is satisfied. Frequency ranges that can be encountered in this spectrum vary from those of ‘$\nu$’ rays, which have wavelength of about $10^{-10}$ cm to radio waves which have wavelength of $10^{10}$ cm. The most of spectroscopic investigation are carried out in a relatively small portion of spectrum close to visible light. This region includes UV, visible and IR region and is arbitrarily defined as being between wavelength of $10^{-6}$ cm and $10^{-3}$ cm. Both the atoms and molecules give rise to spectra but they differ from each other. The difference between the atomic and molecular spectra lies in the nature of energy levels involved in the transitions. In the atom, the absorption represents transition between the different allowed levels for the orbital electrons. In case of molecules, however, the atoms within the molecules vibrate and the molecule as a whole rotates and the total energy contributions are represented by the equation, [14]

$$E_{\text{tot}} = E_{\text{ele}} + E_{\text{vib}} + E_{\text{trans}}$$  \hspace{1cm} (2.7)
Where, $E_{\text{elect}}$ is the electronic energy, $E_{\text{vib}}$ is the vibrational energy, $E_{\text{rot}}$ is the rotational energy and $E_{\text{trans}}$ is the translation energy. The separate energy levels are quantized and only certain transitions of electronic, vibrational and rotational energy are possible. Translational energy is usually sufficiently small to be ignored. The vibrational spectrum of a molecule is considered to be a unique physical property and is a characteristic of the molecule. As such the infrared spectrum can be used as a fingerprint for identification, in support of X-ray diffraction technique for the purpose of characterization [15].

2.3.3 Fourier Transform Raman Spectroscopy (FT-Raman)

Introduction

Raman spectroscopy is different from the rotational and vibrational spectroscopy considered above in that it is concern with the scattering of radiation by the simple, rather than an absorption process. It is named after the Indian physicists who first observe it in 1928, C. V. Raman. Both rotational and vibrational spectroscopes are possible. The energy of the exciting radiation will determine which type of the transition occurs-rotational transitions are lower in energy than vibrational transitions.

In addition to this, rotational transitions are around three orders of magnitude slower than vibrational transitions. Therefore, collisions with other molecule may occur in the time in which the transition is occurring. A collision is likely to change the rotational state of the molecule and so the definition of the spectrum obtained will destroyed. Rotational spectroscopy is therefore carried out on gases at low pressure to ensure that the time between the collisions is greater than the time for transition.
Fig. 2.6 Schematic of actual setup of FT-Raman spectroscopy [16]

The vibrational states probed by Raman spectroscopy are similar to those involved in infrared spectroscopy. However, the two vibrational spectroscopy techniques are complementary, in that vibrations that are strong in an infrared spectrum (those involving strong dipole moments) are typically weak in a Raman spectrum. Likewise, non-polar functional group vibrations that give very strong Raman bands usually result in weak infrared signals. As an example, hydroxyl- or amine-stretching vibrations and the vibrations of carbonyl groups are usually very strong in an FT-IR spectrum and are weak in a Raman spectrum. The stretching vibrations of carbon double and triple bonds and the symmetric vibrations of aromatic groups give a very strong Raman signal.

Raman spectroscopy provides key information about the structure of molecules. The position and intensity of features in the spectrum reflects the molecular structure and can be used to determine the chemical identity of the sample. Spectra may also show subtle changes depending on the crystalline form. With the extensive spectral libraries that are now available, it is very straightforward to identify compounds by spectral library searching.

Raman spectroscopy offers some major advantages in comparison with other analytical techniques. Raman is a light scattering technique, so all that is
required for the collection of a spectrum is to place the sample into the excitation beam and collect the scattered light. There are few concerns with sample thickness and little interference from the ambient atmosphere, so there is no need for high-vacuum or desiccated sample holders. Glass, water and plastic packaging have weak Raman spectra, making the technique even easier to use. Samples usually can be analyzed directly inside a glass bottle or plastic bag without having to open the package and risk contamination. Aqueous samples are readily analyzed without having to remove water and because there is no interference from ambient humidity, there is no need to purge the instrument.

No two molecules give exactly the same Raman spectrum, and the intensity of the scattered light is proportional to the amount of material present. Thus Raman provides both qualitative and quantitative information about the sample, allowing for spectral interpretation, library searching, data manipulation and the application of chemometric methods. Raman spectroscopy is non-destructive. There is no need to dissolve solids, press pellets, compress the sample or otherwise alter its physical or chemical structure. This makes Raman spectroscopy ideal for investigating physical properties such as crystallinity, phase transitions and polymorphs. The lack of sample preparation also minimizes cleanup and the possibility of cross-contamination. Raman spectroscopy also has several additional advantages. Unlike other vibrational techniques, its operational wavelength range is usually independent of the vibrational modes being studied. Since Raman spectroscopy measures the shift in frequency from that of the excitation laser, it can be performed using any operating range from UV to NIR. It thus permits access to vibrational mode information normally associated with wavelengths ranging from 2–200 µm. This makes Raman ideal for the study of inorganic materials that have vibrational frequencies in the far-infrared that are otherwise difficult to reach.

Dispersive Raman microscopy using visible excitation wavelengths delivers 1 µm spatial resolution and is widely used in the analysis of micron-level sample contaminants. Raman spectrometers are based on one of two
technologies: dispersive Raman and Fourier transform Raman. Each technique has its unique advantages and each is ideally suited to specific types of analysis.

**Working**

**Raman Effect**

When a sample is irradiated with an intense monochromatic light source (usually a laser), most of the radiation is scattered by the sample at the same wavelength as that of the incoming laser radiation in a process known as **Rayleigh** scattering. However, a small proportion of the incoming light – approximately one photon out of a million – is scattered at a wavelength that is shifted from the original laser wavelength.

![Fig.2.7 Various steps involved in Raman Effect](image)

As illustrated in the simplified energy level diagram, a molecule at rest resides in the ground vibrational and electronic states. The electric field of the laser beam raises the energy of the system for an instant by inducing a polarization in the chemical species. The polarized condition is not a true energy state and is referred to as a “virtual state”. Relaxation from the virtual state occurs almost instantaneously and is predominantly to the initial ground state. This process results in Rayleigh scatter, which is scattered light of the same wavelength as the excitation laser. Relaxation to the first excited vibrational level results in a Stokes-Raman shift. Stokes-Raman shift scattered light is of lower energy (longer wavelength) than that of the laser light. In addition, most
systems have at least a small population of molecules that are initially in an
excited vibrational state. When the Raman process initiates from the excited
vibrational level, relaxation to the ground state is possible, producing scatter of
higher energy (shorter wavelength) than that of the laser light. This type of
scatter is called anti-Stokes Raman scatter.

To observe the Raman spectrum, it is necessary to separate the collected
Raman scattered light into its composite wavelengths. In dispersive Raman
instruments, this is accomplished by focusing the Raman scattered light onto a
diffraction grating, which splits the beam into its constituent wavelengths. These
are directed onto a silicon charge-coupled device or CCD detector.

\[ \text{Electronic} \]
\[ \text{Excited State} \]
\[ \text{Vibrational Levels} \]

\[ \text{Vibrational States} \]

\[ \text{Rayleigh} \]

\[ \text{1} \]

\[ \text{2} \]

\[ \text{Stokes} \]

\[ \text{1} \]

\[ \text{2} \]

\[ \text{Electronic} \]

\[ \text{Level 10} \]

\[ \text{Electronic} \]

\[ \text{Ground State} \]

\[ \text{Vibrational Levels} \]

\[ \text{IR Absorption} \]

\[ \text{And Emission} \]

\[ \text{Fig. 2.8} \]

Energy level diagram of vibrational and electronic states at
ground and excited state respectively

Dispersive Raman usually employs visible laser radiation. Typical laser
wave-lengths are 780 nm, 633 nm, 532 nm, and 473 nm; others are also used.
The intensity of the Raman scatter is proportional to \( \frac{1}{\lambda^4} \), so short excitation
laser wavelengths deliver a much stronger Raman signal. Although this would
suggest that all Raman should be collected using the shortest wavelength lasers,
fluorescence is also much more likely to occur under these conditions. It is
possible to use software and other strategies to correct for low-level fluorescence
interference and still be able to obtain usable Raman spectra. However, strong fluorescence saturates the CCD and makes Raman measurements impossible. Fluorescence is excitation wavelength-dependent, so a sample that fluoresces at one wavelength is less likely to do so at another. When selecting a Raman spectrometer, it is important to look for one that integrates multiple laser sources and makes it easy to exchange lasers rapidly and effortlessly. Spectral resolution determines the amount of detail that can be seen in the spectrum. If the resolution is too low, it may be impossible to distinguish between closely related compounds. When the resolution is unnecessarily high, the data become noisy without providing any increase in useful information. Spectral resolution is determined by the diffraction grating dispersion and by the optical design of the spectrograph. Gratings have many lines or grooves blazed into the surface, which disperse the incoming light. The higher the number of grating lines per unit length, the broader the dispersion angle and the higher the spectral resolution obtained. With a fixed detector size, there is a resolution beyond which not all of the Raman wavelengths fall on the detector in one exposure. To achieve higher resolution, it is necessary to move either the grating or the detector to collect sequential segments of the spectrum. Spectral resolution can also be increased by extending the optical path length of the spectrograph or by improving the spectrograph design.

Gratings are designed for optimum throughput over a relatively narrow wavelength range, so gratings should be selected for the desired resolution and for the correct laser wavelength. Using a single grating for more than one laser wavelength requires a compromise in instrument throughput and sensitivity. Ideally, gratings should be matched specifically to each laser. The CCDs commonly used for dispersive Raman are highly sensitive silicon devices. The detecting surface of the CCD is a two-dimensional array of light-sensitive elements, called pixels (typically each pixel is < 30 µm). Each pixel acts as an individual detector, so each dispersed wavelength is detected by a different pixel (or closely spaced group of pixels). CCD detectors commonly have a large wavelength response region, routinely extending from 400 nm up to
approximately 1000 nm. Specialized detectors extend the response up to approximately 1100 nm and down into the UV range. This means that the longest excitation wavelength that can be used with a silicon CCD detector, without loss of the higher shifted wavenumber portions of the Raman spectrum, is about 780 to 785 nm. (A 3300 cm$^{-1}$ Stokes shift from 780 nm corresponds to 1050 nm.) The low end cutoff of the Raman spectrum is determined by the ability of the Rayleigh filters to exclude Rayleigh scattering (light at the excitation laser wavelength) from the spectrograph. The performance of a Raman spectrometer at the low shifted wavenumber end of the spectrum also depends on the adequacy of the laser line filters. Good modern instruments should be able to attain at least a 100 cm$^{-1}$ cutoff. Since inorganic compounds display important Raman bands below 100 cm$^{-1}$, an instrument that can deliver a 50 cm$^{-1}$ low end cutoff is ideal.

![Ray diagram of FT-Raman Spectrometer.](image)

**Fig. 2.9 Ray diagram of FT-Raman Spectrometer.**

The basic set up of Raman spectrometer is shown in Fig 2.9. Note that the detector is orthogonal to the direction of the incident radiation, so as to observe only scattered light. The source needs to provide intense monochromatic
radiation, and usually laser. The criteria for a molecule to be Raman active are also different to other types of spectroscopy, which required permanent magnetic dipole moment, at least for diatomic molecules [15].

In place of visible excitation lasers, an FT-Raman spectrometer uses a laser in the near infrared – usually at 1064 nm. At this wavelength fluorescence is almost completely absent, however because of the $1/\lambda^4$ relationship between Raman scattering intensity and wavelength, the Raman signal is weak. In addition, silicon CCD detectors cannot be used in this region of the spectrum. FT-Raman uses sensitive, single-element, near-infrared detectors such as indium gallium arsenide (InGaAs) or liquid nitrogen-cooled germanium (Ge) detectors. An interferometer converts the Raman signal into an interferogram, permitting the detector to collect the entire Raman spectrum simultaneously. Since at low signal levels the spectral noise is predominantly detector dark noise and is independent of the intensity of the Raman signal, delivering the entire spectrum at once onto the detector greatly improves the signal-to-noise ratio. Application of the Fourier transform algorithm to the interferogram converts the results into a conventional Raman spectrum. In addition to freedom from fluorescence interference, another advantage of FT-Raman spectroscopy is its exceptionally good x-axis (shifted wavenumber) accuracy as a result of the internal interferometer calibration supplied by the built-in helium-neon laser. Both of these attributes make FT-Raman the ideal technique for collecting spectra for reference libraries. FT-Raman spectroscopy is particularly well-suited for bulk sample analysis and can be configured to accept samples in most common formats, including vials, cuvettes, tubes, plastic bags, bottles, powders, films and solids. The Thermo Scientific NXR FT-Raman Microstage allows users to mount samples horizontally for easier handling and features an integrated video camera. With a minimum laser spot size of 50 µm, the Microstage provides microscope capabilities and sufficient spatial discrimination to be able to analyze heterogeneous samples.
2.3.4 X-ray Photoelectron Spectroscopy (XPS)

The foundation to electron spectroscopy was laid way back in the year 1887 when Heinrich Hertz discovered the photoelectric effect. However, it had taken more than half a century further to establish photoelectron spectroscopy as a technique. In 1950, Kai Siegbahn was reported the first successful study in photoelectron spectroscopy for which he received the Nobel Prize for Physics in 1981 [16, 17]. They coined the term Electron Spectroscopy for Chemical Analysis (ESCA). But since other methods also give chemical information, it is more commonly known as XPS today.

The term electron spectroscopy is generic and covers a large number of techniques such as XPS, ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), electron energy lens spectroscopy (EELS) and so on. The techniques wherein monochromatic photons are used as the probing signal and the characteristic of the electrons emitted from the surface are studied, falls under the section photoelectron spectroscopy [18].

Electrons with low energies do not have the penetrability in the specimen and hence only those from atoms on the first few layers of the specimen (surface) leave the surface without losing a part of their energy. Those electrons arising from deep inside the specimen will lose part of their energy and form the background in the energy spectrum of the emitted electrons. The inelastic mean free path, (IMPF), of the electrons in a specimen depends on the energy of the electrons and the nature of the specimen. It is given by

\[ \lambda = \frac{538 \sigma_A}{E_A^2 + 0.41 \sigma_A (\alpha_A E_A)^{1/2}} \]

(2.8)

Where, \( E_A \) is electron energy in eV and 3 is the volume of the atom in mm\(^3\) and \( \lambda \) is IMFP and is in nm.

The intensity of electrons emitted from the depth of the specimen is reduced following Beer-lamberts law and the angular distribution follows cosine law. Hence, almost 95 % of electrons emitted from the surface is from atoms within a depth of \( 3\lambda \). In photoelectron spectroscopy, the depth of penetration of a
probing signal is larger than that of the emitted electrons and hence the limitation on the layers analyzed is not restricted by the penetrability of the probing signal. Any species has electrons in them existing in certain states with corresponding binding energies. A measure of the binding energies leads to the identification of the species and the number of electrons associated with the energy leads to the quantification of the states and in turn of the number of electrons as a function of the binding energy in a given sample. Measurement of the kinetic energy of the electrons that are emitted from the solid will lead to the measurement of bound electron spectrum in the solid.

When a monochromatic beam of photons of energy $h\nu$ is launched on an isolated atom, the photons may get scattered elastically or inelastically. When the energy of photons is more than the binding energy $BE$, of the electron in the atom, the electron may get knocked out with kinetic energy, $KE$. As the recoil energy of the atom due to the emission of electron is negligible due to the heavy mass differences between the two particles, $KE$ may be given by,

$$ KE = h\nu - BE $$

(2.9)

Here, the binding energy is the ionization potential of the atom. Hence, the kinetic energy of the electron gives the binding energies of electrons in the atom. The same experiment may be extended to a solid specimen with appropriate correction for the work function, of the spectrometer.

This correction is necessary as the solid specimen is in electrical contact with the spectrometer.

**XPS Measurements**

Photoelectron spectrometer consists of a source of electromagnetic radiation, either an X-ray source or a UV source, electron kinetic energy analyzer and an electron counter all housed in an ultra high vacuum system. A schematic illustration is given in Fig. 2.10. The line width of the X-ray source should be as narrow as possible. The X-ray source could be an X-ray tube or radiations from a synchrotron. Synchrotron is an excellent source of high fluxes of x-rays whose wavelength can be tuned but not readily available. An x-ray
tube with a metallic target such as aluminum operated at voltages needed to excite the K-electron will give the characteristic family of X-rays. The characteristic lines are almost a hundred times in intensity over Bremstrahlung radiation that forms the background. And hence x-ray tubes are directly used as photon sources in X-ray photoelectron spectrometers. Appropriate filter can be used to cut off other lines such as Kβ. Normally aluminum, magnesium and zirconium are used as targets in the source of radiation with energies 1486.6 eV, 1253.6 eV and 2042.4 eV respectively [19]. Different types of electron spectrometers analyze the spectrum of electrons from the specimen.

![Figure 2.10 Basic components for XPS measurements.](image)

**Applications**

The major use of XPS is for identification of compounds using energy shifts due to change in the chemical structure of the sample atoms. For example, an oxide exhibits a different spectrum than a pure element (SiO$_2$ on Si for example). Chemical compounds or elements are identified by the location of energy peaks on the undifferentiated XPS spectrum. Concentration determination is more difficult. Peak heights and peak areas can be used with appropriate correction factors to obtain concentrations but the method is primarily used for identifications.
2.3.5 Field Emission Scanning Electron Microscopy (FE-SEM)

History And Principle

FE-SEM is the acronym for Field Emission Scanning Electron Microscopy. It was Ernest Ruska (1906 – 1987) whom in his Ph.D. Thesis mentioned the potential for electrons to be used in a microscope. In 1933 Ruska and Knoll constructed the first electron microscope and in 1935 Knoll wrote the first work describing the concept of a SEM. In 1938 Von Ardenne built a scanning transmission microscope (STEM) adding coils to a transmission electron microscope. The first SEM used to study a solid surface was described by Zworykin et al. (1942) working for the RCA laboratories in the United States. As a practice in the early days the gun was located in the bottom so the specimen chamber and was high enough for the operator but the specimen might fall down the column. A resolution of 50 nm was achieved with this microscope. The first micrographs showing the striking three-dimensional imaging capability were obtained in Cambridge at the Engineering Department in 1952 by Dennis McMullan who was continuing the work by Ken Sander (both under C. W. Oatley supervision). The next important step was also in Cambridge when Oatley improved the secondary electron detector by adding a scintillator to convert electrons to photons, and let the way for improvement in signal to noise ratio.

Nowadays, three-dimensional features can be observed due to the large depth of Field available in the FE-SEM. The addition of energy dispersive X-ray detector combined with digital image processing is a powerful tool in the study of materials, allowing good chemical analysis of the material. The FE-SEM is a major tool in materials science research and development.

Principle

Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. As a result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary
electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. The ray diagram of Field Emission Scanning Electron Microscope is shown in Fig. 2.11. And the ray diagram of emission of different types of electrons during scanning is shown in Fig. 2.12.

![Ray diagram of Field Emission Scanning Electron Microscope](image)

**Fig. 2.11 Ray diagram of Field Emission Scanning Electron Microscope**

**Basic Concepts**

**Vacuum**

The FE-SEM can be classified as a high vacuum instrument (less than $1 \times 10^{-7}$ Pa in the ions pumps 1 and 2). The vacuum allows electron movement along the column without scattering and helps to prevent discharges inside the instrument. The vacuum design is a function of the electron source due to its influence on the cathode emitter lifetime.
Field Emission Source

The function of the electron gun is to provide a large and stable current in a small beam. There are two classes of emission source: thermionic emitter and field emitter. Emitter type is the main difference between the Scanning Electron Microscope (SEM) and the Field Emission Scanning Electron Microscope (FE-SEM). Thermionic emitters use electrical current to heat up a filament; the two most common materials used for filaments are Tungsten (W) and Lanthanum Hexaboride (LaB$_6$). When the heat is enough to overcome the work function of the filament material, the electrons can escape from the material. Thermionic sources have relative low brightness, evaporation of cathode material and thermal drift during operation. Field Emission is one way of generating electrons that avoids these problems. A Field Emission Source (FES); also called a cold cathode field emitter, does not heat the filament. The emission is reached by placing the filament in a huge electrical potential gradient. The FES is usually a wire of Tungsten (W) fashioned into a sharp point. The significance of the small
tip radius (~ 100 nm) is that an electric field can be concentrated to an extreme level, becoming so big that the work function of the material is lowered and electrons can leave the cathode. FE-SEM uses FES producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM). The FE-SEM S-800 has two anodes for electrostatic focusing. A voltage (0 ~6.3 KV) between the field emission tip and the first anode, called the extraction voltage, controls the current emission (1 ~ 20 mA). A voltage (1 ~ 30 kV), called the accelerating voltage, between the cathode and the second anode increases the beam energy and determines the velocity at which the electrons move into the column. This voltage combined with the beam diameter determines the resolution (capacity to resolve two closely spaced point as two separates entities). As voltage increases, better point-to-point resolution can be reached [20].

**Electromagnetic Lenses**

To resolve a feature on the specimen surface, the beam diameter must be smaller than the feature (still containing high current density). Therefore is necessary to condense the electron beam. To assist in the demagnification of the beam, electromagnetic lenses are employed. Since, the cross over diameter in the FES is smaller, a lower level of the beam condensation is necessary to have a probe useful for image processing. This makes the FE-SEM the highest resolution instrument.

**Aperture**- Variable apertures are used to refine the beam. An increase in the objective aperture size causes a drop in the irradiation current. Small objective aperture sizes will produce better resolution, good depth of field and minimal charging. It is the responsibility of the user to choose the correct aperture size.

**Work Distance**- The objective lenses can focus the probe at various specimen working distances (the Z axis from the lenses to the specimen surface). Long working distance and small aperture has shown an image that appears in focus over a large change in Z.
**Depth Of Field**- Depth of Field is important in routine microscopy and represents the ability to maintain the focus even with large changes in specimen topography. Long working distance and small aperture yields images that appear in focus over a large change in Z-axis. A common practice is to select the current in the objective lenses and move the specimen vertically until it becomes in focus. The FE-SEM capability must often used in routine microscopy and represents the ability. Long working distance and small aperture yields images that appear in focus over a large change in Z-axis. Select the current in the objective lenses and move the specimen vertically until it becomes in focus.

**Electron Beam And Specimen Interaction**

The specimen and the electron beam interact in both elastic and inelastic fashion giving different types of signals. Elastic scattering events are those that do not affect the kinetic energy of the electron even when its trajectory had been affected. Inelastic scattering events are a result of the energy transference from the electron beam to the atoms in the specimen, as result the electrons have energy loss with small trajectory deviation. Some of the signals created in this way are: secondary electrons (SE), Auger electrons and X-Rays. Each of these signals gets specific information about topography, crystallography, surface characteristics, specimen composition and other properties.

**2.3.6 Energy Dispersive Analysis By X-Rays Spectroscopy (EDS)**

If the sample is made the target in an X-ray tube and bombarded with electrons of suitable energy, it emits characteristics X-rays. This is the basis of a method of chemical analysis. The emitted X-rays are analyzed in an X-ray spectrometer and the elements present in the sample qualitatively identified by their characteristics wavelengths. Quantitative estimation is also possible by measuring relative intensities in the spectra. For compositions greater than or about 1% and elements separated by few atomic numbers, energy dispersion analysis is very useful because the intensities are increased about 100-fold. The resolution however, of an energy dispersion instrument is as much as 50 times less than the wavelength dispersion spectrometer using a crystal; thus
overlapping of lines from nearby elements may occur. The specimen must be either electrically conducting or made so by evaporating a metallic layer on the surface, otherwise surface stray electric fields may divert the incident electron beam. If a sample is irradiated with X-rays of sufficiently high energy, it will emit fluorescent radiation. This radiation may be analyzed in an X-ray spectrometer and the elements present in the sample identified by their characteristics wavelengths. The X-ray fluorescent spectra are simple and more accurate with corresponding optical spectra if the sample contains at least one percent element.

2.3.7 Electrical Resistivity

The use of thin film as a resistors, contacts and interconnections have led to extensive study of conductivity, temperature dependent stability etc. Investigation of critical resistivity as a highly structure sensitive property make it possible to be an insight in to the structural and electrical properties of the metal films which, is important from both the theoretical and practical point of view.

The contact methods are most widely used for the measurement of resistivity; these methods include two-point probe, four point probe and the spreading resistance. The two-point probe method is simple, easy to use and useful for highly resistive thin films. In this method, constant voltage ‘V’ is applied between two-fixed positions probes with separation ‘d’ and current passing through a sample of known dimensions (cross section area A) is measured with an appropriate current meter. For uniform sample the resistivity is given by,

\[ \rho = \frac{A \times V}{d} \times \frac{1}{I} \]  

In case of semiconducting thin films, resistivity decreases with increase in temperature. The thermal activation energy ‘Ea’ is calculated by using resistivity.

\[ \rho = \rho_0 \exp\left(-\frac{E_a}{kT}\right) \]  

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*Thin Film Deposition And Characterization Techniques*
Where, symbols have their usual meanings. The slope of \( \log \rho \) Vs \((1000/T)\) leads to the estimation of activation energy. The resistivity measurement of material gives information of room temperature resistivity, activation energy and type of material (NTC or PTC). However, there is disadvantage of metal contact, which forms a low resistance Ohmic or non-Ohmic junction with material. The metal contacts forms heating effect of current, especially when sample resistivity is high.

### 2.3.8 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is often the first experiment performed in an electro analytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process. In CV a reversible dc potential sweep (using a triangular potential waveform) was applied between working electrode (film) and counter electrode (platinum wire) and resulting current response versus a reference electrode (SCE) is measured.

![Variation of applied potential for CV](image)

**Fig. 2.13 Variation of applied potential for CV**

In CV, on reaching \( t=t_1 \) the sweep direction is inverted as shown in Fig.2.13 and sweep until \( E_{min} \), then inverted and sweep to \( E_{max} \) etc. The important parameters involved are

- The initial Potential \( E_i \)
- The initial sweep direction
- The sweep rate \( \nu \)
• The maximum potential, \( E_{\text{max}} \)
• The minimum potential, \( E_{\text{min}} \)
• The final Potential, \( E_{f} \)

A faradic current, \( I_{f} \) due to the electrode reaction, is registered in the relevant zone of applied potential where electrode reaction occurs. There is also a capacitive contribution: on sweeping the potential, the double layer charge changes: This contribution increases with increasing sweep rate [22]. The total current is

\[
i = I_{c} + I_{f} = G_{d} \left( \frac{dE}{dt} \right) + I_{f} = vG_{d} + I_{f} \quad \quad \quad \quad (2.12)
\]

Thus \( I_{c} = v \) and it can be shown that \( I_{f} = v^{2} \). This means that at very high sweep rates capacitive current must be subtracted in order to obtain accurate values of the rate constant.

The applicability of Nernst equation and therefore, reversibility has to do with time allowed for the electrode to reach equilibrium. The concentration of the species at the interface depends on the mass transport of these species from bulk solution, often described by mass transfer coefficient \( K_{d} \). A reversible reaction corresponds to the case where the kinetics of the electrode reaction is much faster than the transport. The kinetic is expressed by standard rate constant, \( K_{0} \) which is the rate constant when \( E=E^{\circ} \)

\( E^{\circ} \)- Actual potential and \( E^{\circ} \)- Formal potential \([E^{\circ} \text{- standard potential}]\)

The kinetics of electrode reactions does not measure the rate of electron transfer itself, as this is an adiabatic process, following Frank-Condon principle, and occurs in approx \( 10^{-16} \)s. What it measures is the time needed for the species, once they have reached the interfacial region, to arrange themselves and their ionic atmospheres into position for electron transfer to be able to occur. According to kinetics of the reactions there are three types of reactions

1. Reversible
2. Irreversible
3. Quasi reversible
1. Reversible System

Fig. 2.14 shows a typical curve for linear sweep voltammetry recorded for reversible reaction of the type \( O + n \text{e}^- \rightarrow R \). The curve can be understood in the following way. On reaching a potential where the electrode reaction begins, the current rises as in a steady state voltammogram. However, the creation of a concentration gradient and consumption of electroactive species means that, continuing to sweep the potential, from a certain value just before the maximum value of the current, peak current, the supply of electroactive species begins to fall. Owing to depletion, the current then begins to decay, following a profile proportional to \( t^{-1/2} \) which is shown in Fig. 2.15, similar to application of potential step.

![Fig. 2.14 The typical curve of Linear Sweep Voltammetry for reversible system.](image)

![Fig. 2.15 The typical curve of CV for reversible system](image)
Information as a diagnostic for linear sweep and CV of reversible reactions are [21]

- $I_p \propto \nu^2$
- $E_p$ independent of $\nu$
- $E_p - E_{p/2} = 56.6/n$ mV
  
  and for CV alone
- $E_{pa} - E_{pc} = 59.0/n$ mV
- $I_{pa}/I_{pc} = 1$

Another practical factor affecting the voltammogram is the solution resistance between working and reference electrode. This resistance leads to a shift in the potential of the working electrode by $I_pR_\Omega$ where $R_\Omega$ is the resistance (uncompensated) of the solution.

2. Irreversible System

In the case of an irreversible reaction of the type $O + ne^{-} \rightarrow R$, linear sweep and CV lead to the same voltammetry profile, since no inverse peak appears on inverting the scan direction.

![Voltammogram for irreversible system](image)

**Fig. 2.16 Voltammogram for irreversible system**

Fig. 2.16 shows a voltammogram for irreversible system. With respect to reversible system, the waves are shifted to more negative potential (reduction), $E_p$ depending on the sweep rate. The peaks are broader and lower.
3. Quasi-Reversible Systems

The extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increasing separation between anodic and cathodic peaks. On increasing sweep rate, there is less time to reach equilibrium at the electrode surface; reactions, which appear as reversible at low sweep rates, can be quasi reversible at high sweep rates. Fig. 2.17 shows the effect of increasing irreversibility on the shape of CV.

![Fig. 2.17 Effect of increasing irreversibility on the shape of cyclic voltammogram.](image)

![Fig. 2.18 Comparison of ideal and real cyclic voltammograms](image)
CV provides a measure of a supercapacitors charge-response With regard to a changing voltage, and is therefore a means of evaluating capacitance. The procedure for obtaining a voltammogram is simple and requires no specialized equipment. To perform CV tests a series of changing voltages at a constant sweep rate (dV/dt) is applied and the response current is recorded. An ideal capacitor with no resistance would display a rectangular shape, but most real electric double layer capacitor voltammograms take the shape of a parallelogram with irregular peaks (Fig. 2.18). Prominent peaks that occur within narrow voltage windows are usually evidence of pseudocapacitive behavior. Faster sweep rates correspond to charging and discharging at higher power levels.
2.4 References


