CHAPTER 2
CHARACTERIZATION TECHNIQUES

Helical conducting polymers have been obtained usually as bulk powders and characterized by many different analytical and spectroscopic techniques in solutions. The basic principles and the instrumentations of these techniques have been discussed in this chapter. The phase purity and crystallinity of these samples were determined by powder X-ray diffraction (PXRD). The surface morphology, coiling (helicity) and size were obtained using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The thermal stability of the polymers was determined by thermogravimetric analysis (TGA). Optical absorption properties were studied by using UV-Visible spectroscopy and Circular Dichroism (CD) spectroscopy. The samples were also characterized by using Fourier Transform Infra Red (FTIR) spectroscopy. The conductivity of samples was measured by Four probe method and data were related with the band gap value which has been obtained from Tauc’s plot [2.1-2.2].

2.1. Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) is an analytical technique used for phase identification of a crystalline material and it provides information on unit cell dimensions and other related parameters. The powder X-ray diffraction patterns of the samples were recorded on Rigaku miniflex diffractometer employing CuKα1 radiation at a scan rate of 1°/min and step size 0.02 from 2θ range 5-60°C. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline solid sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. These diffracted X-rays are then detected by a detector as shown in Figure 2.1. The interaction of the incident rays with the sample produces constructive interference and a diffracted ray, provided that the Bragg’s Law (nλ=2d sinθ) is satisfied. Here, λ is the wavelength, d is the inter-planar spacing, and θ is the angle between the sample and the incident ray. This law relates the wavelength of the electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. By scanning the sample through a range of 20 angles, all possible diffraction directions of the lattice are attained due to the random orientation of the powder material [2.3-2.6]. Conversion of the diffraction peaks to d-spacings allows identification of the material because each structure has a set of unique d-spacings. This is
achieved by the comparison of d-spacings with standard reference patterns listed in the powder diffraction file.

An X-ray diffractometer consists of three basic elements: an X-ray tube, a sample holder and an X-ray detector as shown in Figure 2.2. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage and bombarding the target material with the electrons. When the electrons have sufficient energy to knock out inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K_{\alpha}$ and $K_{\beta}$. $K_{\alpha}$ consists of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Crystal mono-chrometers are normally useful to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weight average of the two is used. Copper is the most common target material for powder X-ray diffraction, with the wavelength of CuK$\alpha$ radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. While the sample and/or detector are being rotated, the intensity of the diffracted X-rays is recorded. When the geometry of the incident X-rays falling on the sample satisfies the Bragg equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is connected to an output device such as a computer. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle $\theta$, while the X-ray detector rotating at an angle $2\theta$ is mounted on an arm to collect the diffracted X-rays.

Figure 2.1: Schematic diagram of powder X-ray diffraction
X-ray powder diffraction is the most widely used technique for the identification of crystalline materials such as minerals or inorganic compounds. Applications include characterization of crystalline materials, measurement of sample purity, and determination of unit cell dimensions [2.3].

Figure 2.2: Digital photograph of powder X-ray diffractometer

2.1.1. Refinement of the Powder X-ray Data

The following informations are obtained from the powder X-ray diffraction pattern:

(1) Peak positions give the information about the space group and lattice parameters.
(2) Peak intensities give the information about the crystal structure and quantitative analysis.
(3) Profile width and shape gives the information about the instrument contributions, microstructure (size, strain, stacking faults).
(4) Background gives the scattering from the sample environment (air, sample holder), local order/disorder, amorphous phase content, i.e., the degree of crystallinity [2.3].

When coupled with refinement procedures, such as Le Bail [2.7] and Rietveld refinement [2.8], it provides structural information on unknown materials. The calculated powder X–ray diffraction pattern is compared point by point to the experimental diffraction pattern and selected parameters (defining the structural model and describing the profile) are adjusted by a least-squares method to give the best fit.
2.1.2. Method of Least Squares

The common method of refinement is based on the principle of least squares. The principle of least squares states that the best values for the i parameters, p₁, p₂,…pi, which define a function, are those that minimize the sums of the squares of the properly weighted differences between the observed and calculated values of the function for all observational points. Thus, the quantity to be minimized is given by,

\[ S_y = \sum_i W_i (Y_i - Y_{ci})^2 \]

Where, \( W_i \) is the corresponding weight to be assigned to an observation, \( Y_i \) is the observed intensity at step i and \( Y_{ci} \) is the calculated intensity at step i.

2.1.3. Indexing the Powder Pattern

Powder indexing of the raw powder pattern, requires sophisticated profile shapes, and background reproduction. A process using iteratively the Rietveld decomposition formula for the whole powder pattern decomposition (WPPD) purposes was first applied in 1988 by Le Bail et al. and called much later the “Le Bail method” or “Le Bail fit,” or “pattern matching” as well as “profile matching” in the FULLPROF Rietveld program (Rodriguez-Carvajal, 1990) [2.9]. Individual intensities were extracted from the powder pattern by a profile fitting procedure which does not need any structural model but constrained the angular position of the reflections to be consistent with the cell parameters. After this stage, the modified Rietveld method is applied with the structural model. This is necessary because some of the intensities previously obtained are subject to caution due to very near overlapping with others. One can combine Le Bail intensity extraction along with refinement of non-structural parameters because if the intensities and parameters are changing significantly, refinement is prone to go bad. Therefore, it is best to converge intensity extraction before refining parameters. Refinement of parameters coupled with Le Bail extraction can provide best possible profile R-factor. A list of programs (1990-1995) applying this method (either exclusively or added inside of a Rietveld code) includes MPROF (Jouanneaux et al., 1990) [2.10], later renamed WINMPROF, FULLPROF (Rodriguez-Carvajal, 1990) [2.10], EXTRACT (Baerlocher, 1990) [2.11], EXTRA (Altomare et al., 1995) [2.12], and EXPO (Altomare et al., 1999) [2.13] which is the integration of EXTRA and SIRPOW for solution and refinement of crystal structures. After that followed the well known Rietveld codes (GSAS [2.14], TOPAS [2.15], etc.) or standalone programs, AJUST [2.14]. In the first application of Le Bail fit used for the structure solution of LiSbWO₆, the fit was realized with the

2.2. Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature or time. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gases. Some materials can gain weight by reacting with the atmosphere gases in which the experiment is being performed. Thus, the behavior of the material can be investigated in different atmospheres such as inert or oxidizing. This technique is used to investigate the thermal stability of a material.

The characteristics or properties which can be measured are drying, the release of structural water, structural decomposition, carbonate decomposition, gas evolution, sulphur oxidation, fluoride oxidation, and re-hydration. Most ceramic samples are normally heated from ambient to the maximum temperature. Slow heating rates are preferred so that the weight changes can occur over a narrower time span and temperature range. The resulting curve is steeper and the onset temperature of the process taking place in the material due to heating is closer to the actual. Fast heating rates spread the weight change over a wider time span and temperature range, and generate less steep curves and shift the onset temperature above the actual [2.18, 2.19].

![Digital photograph of thermogravimetric analyser](image)

Figure 2.3: Digital photograph of thermogravimetric analyser
Figure 2.3 shows a picture of TGA instrument (Model Q50) of TA instruments, New Castle, Delaware, USA. The instrument uses software universal analysis V4.5A for control and result analysis. All samples were tested in the temperature range of 25 to 700 °C at a heating rate of 10 °C/min in N₂ atmosphere.

2.3. Spectroscopic Techniques

Spectroscopy is the study of the interaction between matter and radiated energy as a function of its wavelength or frequency. The data are represented by a spectrum which is a plot of the response or a variation of interaction as a function of wavelength or frequency. There are several spectroscopic techniques which can be used for the characterization of the samples. Few of these techniques have been used in the present work and reported in the following sections.

2.3.1. UV-Visible Absorption Spectroscopy

UV-Visible spectroscopy investigates the interactions between ultraviolet or visible electromagnetic radiation and matter. Ultraviolet-Visible spectroscopy refers to absorption spectroscopy in the ultraviolet-visible spectral region as many molecules absorb ultraviolet or visible light. The Beer-Lambert law states that the absorbance, $A$, of a solution is directly proportional to the concentration, $C$, of the absorbing species in the solution of the path length, $l$ [2.20]. According to Beer-Lambert’s law;

$$A = -\log_{10} \left( \frac{I_t}{I_0} \right) = \varepsilon \cdot l \cdot C$$

where, $I_0$ and $I_t$ are the intensity of the incident light and the transmitted light, respectively as shown in inset of Figure 2.4 and $\varepsilon$ is a constant of proportionality, called the absorptivity.

![Figure 2.4: Schematic of illustration of (a) sample assembly and (b) digital photograph of UV-Visible spectrophotometer](image)
Thus, for a fixed path length, UV-Visible spectroscopy can be used to determine the concentration of the absorber in a solution. The absorption in the visible range directly affects the perceived color of the chemicals involved. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials. Diffuse reflectance relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material. The back reflected, diffusely scattered light (some of which is absorbed by the sample) is then collected by the accessory (integrating sphere attachment) and directed to the detector optics. Only the part of the beam that is scattered within a sample and returned to the surface is considered to be the diffuse reflection. The specular reflectance component in the diffuse reflectance spectra cause changes in the band shapes, their relative intensities, and, in some cases, it is also responsible for the complete band inversions.

Dilution of the sample with a non-absorbing matrix minimizes these effects. Diluting ensures a deeper penetration of the incident beam into the sample which increases the contribution of the scattered component in the spectrum and minimizes the specular reflection component. Particle size and sample loading mechanics also play an important role. Other factors related to high spectral quality for diffuse reflectance sampling are listed below:

1. **Particle Size**: Reducing the size of the sample particles reduces the contribution of reflection from the surface. Smaller particles improve the quality of the spectra (narrow bandwidths and better relative intensity). The recommended size of the sample/matrix particles is 50 µm or less comparable to the consistency of the finely ground flour.

2. **Refractive Index**: This result in specular reflectance contributions since the spectra of highly reflecting samples will be more distorted by the specular reflectance component. This effect can be significantly reduced by sample dilution.

3. **Homogeneity**: Sample preparations for the diffuse reflectance measurements should be uniform. Non-homogenous samples will lack reproducibility and will be difficult to quantify.
(4) Packing: The required sample depth is governed by the amount of sample scattering. The minimum necessary depth is about 1.5 mm. The sample should be loosely but evenly packed in the cup to maximize beam penetration and minimize spectral distortions.

Even with all these sample preparation practices, the raw diffuse reflectance spectra will appear different from its transmission equivalent. A Kubelka-Munk conversion can be applied to a diffuse reflectance spectrum to compensate for these differences [2.21]. The Kubelka-Munk (K-M) equation is expressed as follows:

\[ f(R) = \left( \frac{1 - R^2}{2R} \right) = \frac{K}{S} \]

Where, \( R \) is the absolute reflectance of the sampled layer, \( K \) is the molar absorption coefficient and \( S \) is the scattering coefficient.

The Kubelka-Munk equation creates a linear relationship for spectral intensity relative to sample concentration. It assumes infinite sample dilution in a non-absorbing matrix, a constant scattering coefficient and an “infinitely thick” sample layer. All UV-Visible spectra of doped and undoped solutions were recorded using a double beam UV-Vis spectrophotometer (Model UV5704SS) ECIL, India over the range of 250-900 nm.

2.3.2. Circular Dichroism (CD) Spectroscopy

Figure 2.5: Digital photograph of circular dichroism spectrometer

Circular dichroism (CD) is the difference in the absorption of left-handed circularly polarised light (L-CPL) and right-handed circularly polarised light (R-CPL) and occurs when a molecule contains one or more chiral chromophores (light-absorbing groups).

Circular Dichroism = \( \Delta A(\lambda) = A(\lambda)_{LCPL} - A(\lambda)_{RCPL} \)

Where, \( \lambda \) is the wavelength
Circular dichroism spectroscopy is a spectroscopic technique where the CD of molecules is measured over a range of wavelengths. CD spectroscopy is used extensively to study chiral molecules of all types and sizes, but it is in the study of large biological molecules where it finds the most important applications [2.22, 2.23]. A primary use is in analysing the secondary structure or conformation of macromolecules, particularly proteins as secondary structure is sensitive to its environment, temperature or pH. CD can be used to observe how secondary structure changes with environmental conditions or on interaction with other molecules. Structural, kinetic and thermodynamic information about macromolecules can be derived from CD spectroscopy. CD instrument as shown in Figure 2.5 is being used for the present work. Circular Dichroism spectra of the solutions were recorded at chira-scan circular dichromator (Applied Photophysics Ltd., UK) at 50 kHz frequency and wavelength step size 1 nm. Measurements carried out in the visible and ultra-violet region of the electro-magnetic spectrum monitor electronic transitions and if the molecule under study contains chiral chromophores then one CPL state will be absorbed to a greater extent than the other and the CD signal over the corresponding wavelengths will be non-zero. A circular dichroism signal can be positive or negative, depending on whether L-CPL is absorbed to a greater extent than R-CPL (CD signal positive) or to a lesser extent (CD signal negative).

**Polarization**

Linearly polarised light is the light whose oscillations are confined to a single plane. All polarised light states can be described as a sum of two linearly polarised states at right angles to each other, usually referenced to the viewer as vertically and horizontally polarised light as shown below.

![Vertically Polarised Light](image)
If for instance we take horizontally and vertically polarised light waves of equal amplitude that are in phase with each other, the resultant light wave (blue) is linearly polarised at 45 degrees, as shown below:

If the two polarisation states are out of phase, the resultant wave ceases to be linearly polarised. For example, if one of the polarised states is out of phase with the other by a quarter-wave, the resultant will be a helix and is known as circularly polarised light (CPL). The helices can be either right-handed (R-CPL) or left-handed (L-CPL) and are non-superimposable mirror images. The optical element that converts between linearly polarised light and circularly polarised light is termed a quarter-wave plate. A quarter-wave plate is birefringent, i.e., the refractive indices seen by horizontally and vertically polarised light are different. A suitably oriented plate will convert linearly polarised light into circularly polarised light by slowing one of the linear components of the beam with respect to the other so that they are one quarter-wave out of phase. This will produce a beam of either left- or right-CPL.
The difference in absorbance of left-hand and right-hand circularly polarised light is the basis of circular dichroism (CD). A molecule that absorbs LCP and RCP differently is optically active, or chiral.

** Relationships Between Absorbance and Ellipticity 

Circular dichroism (CD) is usually understood and actually measured as the differential absorbance of left ($A_{LCP}$) and right circularly polarised ($A_{RCP}$) light, and so can be expressed as:

$$\Delta A = A_{LCP} - A_{RCP}$$

Taking into account cell path length and the compound concentration, we can arrive at a molar circular dichroism ($\Delta \varepsilon$).

$$\Delta \varepsilon = \varepsilon_{LCP} - \varepsilon_{RCP} = \Delta A / (C \times l)$$

Where, $\varepsilon_{LCP}$ and $\varepsilon_{RCP}$ are the molar extinction coefficients for LCP and RCP light respectively, $C =$ molar concentration and $l =$ pathlength in centimeters.

Further, the relationship between $\Delta A$ and $\theta$ (degrees of ellipticity) is explained. The description of ellipticity is somewhat more complex than $\Delta A$. Linearly polarised light
when passed through a circular dichroic sample will become elliptically polarised. Elliptically polarised light is the light that is not fully circularly polarised but instead is elliptical in shape. This is because the circular polarised components of the original linear polarised light are now not of equal magnitudes due to differential absorbance (circular dichroism). The advantage of circular dichroism ellipticity as a measurement unit is that it is more easily related to optical rotation measurements and polarimetry. Both ellipticity and optical rotation are measurements of changes in polarisation state of a linear polarised analyzer beam and both have the same units and similar amplitudes for a given sample. This similarity aids in comparison of optical rotation and circular dichroism measurements, a useful ability when circular dichroism spectroscopy first started to be widely used back in the 1960’s. Fortunately, it is very easy to inter-convert between $\theta$ and $\Delta A$:

$$\Delta A = \frac{\theta}{32.982}$$

[Note: Due to the small size of many measurements, $\theta$ is often quoted as millidegrees ($\text{m}^\circ$) or 1/1000 of a degree.]

Molar ellipticity can be manipulated in the same way as $\Delta A$. For instance taking into account concentration and cell pathlength according to Beer Lambert’s law, we can derive a measurement of molar ellipticity $[\theta]$. Following polarimetric conventions, molar ellipticity is reported in degrees cm$^2$ dmol$^{-1}$ or degrees M$^{-1}$ m$^{-1}$, which are equivalent units as shown below.

$$M^{-1}m^{-1} = \frac{\text{1000 cm}^2}{\text{mol} \cdot \text{100 cm}} = \frac{\text{10 cm}^2}{\text{mol}} = \text{cm}^2 \text{dmol}^{-1}$$

Molar ellipticity can be calculated using the following equation:

$$[\theta] = 100x\theta/(Cxl)$$

Where, $C$ is the concentration in molar and $l$ is the cell pathlength in cm. The factor of 100 converts to path length in meters.

Molar Circular Dichroism and molar ellipticity can be converted directly by:

$$\Delta \varepsilon = [\theta]/3298.2$$

This factor is a hundred fold larger than between raw absorbance and ellipticity due to the conversion between molar extinction defining path lengths in centimeters and ellipticity having path length defined in meters.
2.3.3. Fourier Transform Infra-red Spectroscopy (FTIR)

Infrared spectroscopy deals with the infrared region of the electromagnetic radiation which interacts with the matter. FTIR spectra of all the samples were recorded in transmission mode with KBr pressed pellets using a Perkin–Elmer (Model No.2000, UK) spectrometer as shown in Figure 2.6. The spectra of all samples were recorded in frequency range of 400 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\) with 32 step count. Infra-red radiation has a longer wavelength and lower frequency than visible light. The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e., the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates [2.24]. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and the associated vibronic coupling.

In order to establish a vibrational mode in a molecule to be "IR active", it must be associated with changes in the dipole. A permanent dipole is not necessary, as the rule requires only a change in dipole moment. A molecule can vibrate in many ways, and each way is called a vibrational mode. For molecules with \(N\) atoms in them, linear molecules have \(3N - 5\) degrees of vibrational modes, whereas nonlinear molecules have \(3N - 6\) degrees of vibrational modes (also called vibrational degrees of freedom). As an example \(\text{H}_2\text{O}\), a non-linear molecule, will have \(3 \times 3 - 6 = 3\) degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g., \(\text{N}_2\), the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, e.g., \(\text{CO}\), absorb in the IR spectrum. The exact frequency at which a given vibration occurs is determined by the strength of the bonds involved and the mass of the component atoms. In practice, infrared spectra do not normally display separate absorption signals for each of the \(3N-6\) fundamental vibrational modes of a molecule. The number of observed absorption may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations. Furthermore, the number of observed absorption may be decreased by molecular symmetry, spectrometer limitations and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions is
that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode, as shown in Figure 2.7.

Figure 2.6: Digital photograph of infrared spectrophotometer

Figure 2.7: Absorption band corresponding to single, double and triple bond stretching

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier Transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be
produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR radiation is the same as the vibrational frequency of a bond, absorption occurs. The basic components of an FTIR are shown schematically in Figure 2.8. Most interferometers employ a beam splitter which takes the incoming infrared beam and divide it into two optical beams. The other beam reflects off from a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which allows this mirror to move a very short distance (few mm) away from the beamsplitter. The two beams reflect off of their respective mirrors and they are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signals which exist the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point which makes up the signal has information about every infrared frequency which comes from the source. Because there need to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the “percent transmittance”.

Figure 2.8: A simple layout of an FTIR instrument
This technique results in a spectrum which has all the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A signal background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

2.4. Microscopic Techniques

Microscopy is the technical field of using microscopes to view samples and objects that cannot be seen with the naked eye and hence the objects that are not within the resolution range of the normal eye. There are three well-known branches of microscopy, optical, electron, and scanning probe microscopy. Optical and electron microscopy involve the diffraction, reflection, or refraction of electromagnetic radiation/electron beams interacting with the sample, and the subsequent collection of this scattered radiation or another signal in order to create an image. Scanning probe microscopy involves the interaction of a scanning probe with the surface of the sample.

2.4.1. Scanning Electron Microscopy (SEM)

The surface morphology of samples was studied using scanning electron microscopy (Hitachi scanning electron microscope, Model S-3700N) at an acceleration voltage of 10 kV. All samples were plasma coated with a thin layer of gold to provide electrical conduction and reduce the surface charging. The scanning electron microscope as shown in Figure 2.9 uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens which reveal information about the sample including external morphology (texture), and chemical composition.

A schematic layout of SEM is given in Figure 2.10. SEM is also capable of performing analyses of selected point locations on the sample and this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions using energy dispersive X-ray (EDX) analysis, crystalline structure and crystal orientations using electron backscattered diffraction (EBSD). Accelerated electrons in SEM carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are de-accelerated by the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons, photons (characteristic X-rays that are used for elemental analysis), visible light (cathodoluminescence, CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples. X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals.
of atoms in the sample. SEM analysis is considered to be non-destructive, i.e., X-rays generated by the electronic interactions do not lead to a volume loss of the sample and so it is possible to analyze the same material repeatedly [2.25].

For conventional imaging in SEM, specimens must be electrically conductive, at least at the surface and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Non-conductive specimens tend to charge when scanned by the electron beam and especially in secondary electron imaging mode; this causes scanning faults and other image artifacts.

Figure 2.9: Digital photograph of scanning electron microscope
They are therefore usually coated with an ultrathin coating of electrically conducting material, commonly gold deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conducting materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium and graphite. Coating prevents the accumulation of static charge on the specimen during electron irradiation. Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z). The improvement in resolution arises because backscattering secondary electron emission near the surface are enhanced and thus an image of the surface is formed.

2.4.2. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a technique for imaging solid materials at atomic resolution. Structural information can be acquired both by imaging
(high resolution) as well as by electron diffraction. Additional detectors allow for elemental and chemical analysis up to nanometer scale. The evaluation of morphologies were done on a HRTEM (Philips Tecnai G² 30 transmission electron microscope) with 300 kV accelerating voltage.

In a TEM (Figure 2.11 to Figure 2.13) high-energy (>100 kV) electrons and electromagnetic lenses are used instead of photons and glass lenses. The electron beam passes through an electron-transparent sample and a magnified image is formed using a set of lenses. This image is projected onto a fluorescent screen or a CCD camera. Whereas the use of visible light limits the lateral resolution in an optical microscope to a few tenths of μm, the much smaller wavelength of electrons allows for a resolution of 0.2 nm in a TEM. Scattering from the crystal planes introduces diffraction contrast which is due to the interaction of the electron beam with the sample. In diffraction mode, another intermediate lens is inserted to image on the screen the diffraction pattern of the back focal plane. This contrast depends on the orientation of a crystalline area in the sample with respect to the electron beam. As a result, a TEM image of a sample consisting of randomly oriented crystals will have its own grey-level. In the resulting TEM, image denser areas and areas containing heavier elements appear darker due to scattering of the electrons in the sample. Electron diffraction pattern can also be obtained from this technique.

Figure 2.11: Interactions between electrons and materials in TEM technique
In case of a crystalline material, electron diffraction will only occur at specific angles, which are characteristic for the crystal structure present. As a result, a diffraction pattern of the irradiated area is created which can be projected onto the CCD camera. In this way, electron diffraction can provide crystallographic information. As a result of the interaction of the electron beam with the specimen, some energy is transferred from the electrons to the sample. The excitation and de-excitation of atoms and molecules in the sample allow (local) chemical analysis [2.26].

Figure 2.12: An optical view for a transmission electron microscope
2.5. Four Probe Method for Conductivity Measurement

Organic polymers, as insulating materials are used to isolate components of an electrical system from each other and from the ground. For this purpose, it is generally desirable to have the surface resistivity as high as possible. Control of surface resistivity of polymers is of great importance for the integration of these materials in a wide range of industrial applications such as packaging, conductors, sensors and active electrodes etc.

Resistivity and conductivity are fundamental properties of semiconductors and are critical parameters in both materials research and wafer fabrication. A semiconductor’s resistivity depends primarily on the bulk doping, but can be modified through device processing. The resistivity can affect a device’s series resistance, threshold voltage, capacitance, and other parameters. Measuring a semiconductor material’s resistivity is one of the most common electrical tests. Determining the conductivity type (or sign of the majority carrier) of a wafer is common in both research and fabrication. A four-point collinear probe and the appropriate test equipment shown in Figure 2.14 can be used to determine both resistivity and conductivity. The four-probe set up (Model DRF-02 Owen 1038-Optochem. International, New Delhi) was used for the conductivity measurement.
Figure 2.14: Digital photograph of Four-Point collinear probe resistivity tester

The four-point, or Kelvin, probe method is the most common way to measure a semiconductor material’s resistivity. Two of the probes are used to source current and the other two probes are used to measure voltage drop as shown in Figure 2.15. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the semiconductor material. This technique involves bringing four equally spaced probes into contact with the material of unknown resistance. The probe array is usually placed in the centre of the material.

Figure 2.15: Four-Point Collinear probe resistivity method

The two outer probes sense current while the two inner probes sense the resulting voltage drop across the sample. The volume resistivity is calculated with this equation:

\[ p = \frac{\pi}{ln2} \times \frac{V}{I} \times t \times k \]
Where, $\rho = $ volume resistivity ($\Omega$-cm)

$V =$ the measured voltage (volts)

$I =$ the source current (amperes)

$t =$ the sample thickness (cm)

$k =$ a correction factor based on the ratio of the probe spacing to wafer diameter and on the ratio of wafer thickness to probe spacing.

A differential electrometer measurement method must be used for characterizing higher resistance materials.
2.6. References


