CHAPTER 2 SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1. INTRODUCTION

This chapter in-detail discusses all the synthesis techniques and the characterization techniques used in this thesis, their theoretical background, the main principle and working mechanism of the particular technique.

2.2. SYNTHESIS TECHNIQUES

The most general approach for nanomaterial production is a ‘top-down’ or a ‘bottom-up’ method. ‘Top-down’ approach involves generating nanomaterials by reducing the size of bulk materials. ‘Top-down’ method is usually a physical process or a combination of physical and chemical processes. The most common examples of ‘top-down’ method are sputtering [166], evaporation techniques [167, 168], vapour condensation [169], laser ablation [170], high-energy milling [171] etc. However, ‘bottom-up’ approach involves material generation from atomic or molecular level. The most common examples for ‘bottom-up’ are processes like the traditional precipitation reactions, precursor decomposition method, along with advanced techniques like sol-gel method [172, 173], chemical vapour deposition (CVD) [174-176], template-assisted method [177], electrochemical method [178], solvo-thermal method [179, 180], hydrothermal method [181, 182], etc.

2.2.1. Simultaneous Reduction Method

Simultaneous reduction is a method involving reduction of two or more metal salts into formation of bi-metallics, composites or alloys. Precursors are taken in required stoichiometric quantities and are then dissolved in suitable solvent and stirred to make a homogeneous solution. The pH of the solution in regulated in order to assist the
formation of free metal ions. These free ions thus formed diffuse through the solvent and distribute throughout the solvent. To this ionic suspension, necessary reducing agent is added in required proportions to reduce the metal ions to their zero-valent states.

### 2.2.2. Solvo-thermal Method

Solvo-thermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes. Typically solvo-thermal process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis. The process can be used in the preparation of nanomaterials like thin films, bulk powders, single crystals, and nanocrystals. In addition, the morphology of the crystals formed can be controlled by manipulating the solvent.

Recent reviews [180] reveal the degree to which solvo-thermal synthesis techniques are now an essential technique for controlled synthesis of many semiconductor materials. Zinc oxide nanoparticles prepared by solvo-thermal method are found to exhibit quantum dot effects [181]. Typically, a shell of one composition (e.g., ZnS) can be synthesized over a core of another nanocrystal (e.g., CdS) [182]. The core can also be used as a seed to grow larger particles by adjusting the concentration after the initial growth. Many quantum dot applications are optimized by size and shape control, and solvo-thermal synthesis is a key technology for achieving this control.

### 2.2.3. Sol-Gel Technology

Sol-gel is a useful self assembly process for nanomaterial formation. A colloid that is suspended in a liquid is called a sol. A suspension that keeps its shape is called a gel. Thus sol gels are suspensions of colloids in liquids that keep their shape.
The sol-gel process involves the evolution of networks through the formation of a colloidal suspension (sol) and the gelation of the sol to form a network in a continuous liquid phase (gel) [183].

Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks. The critical size of the colloid particles (or particle diameter) typically ranges from tens of angstroms ($10^{-10}$ m) to a few micrometers ($10^{-6}$ m).

Under certain chemical conditions (typically in base-catalyzed sols), the particles may grow to sufficient size to become colloids, which are affected both by sedimentation and forces of gravity. Stabilized suspensions of such sub-micrometer spherical particles may eventually result in their self-assembly, yielding highly ordered microstructures reminiscent of the prototype colloidal crystal: precious opal [184]. Under certain chemical conditions (typically in acid-catalyzed sols), the inter-particle forces have sufficient strength to cause considerable aggregation and/or flocculation prior to their growth. The formation of a more open continuous network of low density polymers exhibits certain advantages with regard to physical properties in the formation of high performance glass and glass/ceramic components in 2 and 3 dimensions.

In either case (discrete particles or continuous polymer network) the sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

The precursors for synthesizing these colloids normally consist of ions of a metal. Metal alkoxides and alkoxy silanes are popular because they readily react with water. Additionally because water and alkoxides are immiscible, a mutual solvent such as an alcohol is used.
Metal alkoxides are members of the family of organometallic compounds, which are organic compounds which have one or more metal atoms in the molecule. Metal alkoxides (R-O-M) are like alcohols (R-OH) with a metal atom, M, replacing the hydrogen H in the hydroxyl group. They constitute the class of chemical precursors most widely used in sol-gel synthesis. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

\[
\text{M-O-R} + \text{H}_2\text{O} \rightarrow \text{M-OH} + \text{R-OH (hydrolysis)} \quad (2.1)
\]

\[
\text{M-OH} + \text{HO-M} \rightarrow \text{M-O-M} + \text{H}_2\text{O (water condensation)} \quad (2.2)
\]

\[
\text{M-O-R} + \text{HO-M} \rightarrow \text{M-O-M} + \text{R-OH (alcohol condensation)} \quad (2.3)
\]

Of all the factors, pH and concentration of catalyst, molar ratios of the precursors and temperature have been identified as most important. By controlling these factors it is possible to vary the structure and properties of the sol-gel derived inorganic network over wide ranges. In hydrolysis the reactions occur through the addition of water which results in the replacement of alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions involving the (R-OH) produce R-O-R bonds plus the by-products water or alcohol. Upon drying trapped volatiles such as water or alcohols are driven off and the network shrinks further as condensation occurs.

2.3. CHARACTERIZATION TECHNIQUES

2.3.1. X-Ray Powder Diffraction

X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. The method has been used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized and average bulk composition is determined.
2.3.1.1. Fundamental Principle [185]

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law \( n\lambda=2d \sin \theta \). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 20 angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

2.3.1.2. X-Ray Powder Diffraction (XRD) Instrumentation

X-rays generated in a cathode ray tube are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg equation given in equation 2.1, 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 then output to a device such as a printer or computer monitor.

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

(2.1)

Where

- \( d \) - interplanar distance
- \( \theta \) - angle of the maximum of diffraction
- \( \lambda \) - Wavelength of the radiation

The geometry of 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 is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2\( \theta \). The instrument used to maintain the angle and rotate the sample is termed a Goniometer. For typical powder patterns, data is collected at 2\( \theta \) from ~5° to 70°, angles that are preset in the X-ray scan.

2.3.1.3. X-Ray Powder Diffraction

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being \( K_a \) and \( K_b \). \( K_a \) consists, in part, of \( K_{a1} \) and \( K_{a2} \). \( K_{a1} \) has a slightly shorter wavelength and twice the intensity as \( K_{a2} \). The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. \( K_{a1} \) and \( K_{a2} \) is sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK\(_a\) radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging 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 then output to a device such as a printer or computer monitor. An illustrative powder XRD setup is shown in fig. 2.1.

![Image: X-ray powder diffractometer (20 setup)]

**Figure 2.1: X-ray powder diffractometer (2θ setup)**

### 2.3.1.4. Crystallite Size

If the crystallites of the powder are very small the peaks of the pattern will broaden. From the broadening it is possible to determine the average crystallite size, in Å, by Debye-Scherrer formula given in equation 2.2,

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.2)

where,

- **K** - 0.9 (sphere constant)
- **λ** - wavelength of the radiation
- **β** - full width half maxima (FWHM) in radians
- **θ** - angle of maximum diffraction
2.3.2. Field Emission Scanning Electron Microscope

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). Fig 2.2 shows an illustrative diagram of A SEM.

Figure 2.2: Illustrative diagram of SEM

2.3.2.1. Fundamental Principles of SEM
Accelerated electrons in an 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 decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescent), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbital’s (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. Fig 2.3 represents a schematic diagram of a field emission SEM.
2.3.2.2. Components of FESEM

a. Vacuum

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

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 (FESEM).

Thermionic Emitters use electrical current to heat up a filament; the two most common materials used for filaments are Tungsten (W) and Lanthanum Hexaboride (LaB₆). 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. FESEM uses Field Emission Source producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM).

c. Anodes

The FESEM 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 μA). A voltage (1 ~ 30KV), 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 resolves two closely spaced point as two separates entities). As voltage increases, better point-to-point resolution can be reached
d. 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 it 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 Field Emission Source is smaller, a lower level of the beam condensation is necessary to have a probe useful for image processing. This makes the FESEM the highest resolution instrument.

2.3.3. Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS or EDX) systems are typically integrated into SEM instrument. EDS systems include a sensitive x-ray detector, a liquid nitrogen dewar for cooling, and software to collect and analyze energy spectra. EDS can be used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader raster area.

2.3.3.1. Fundamental Principles

Interaction of an electron beam with a sample target produces a variety of emissions, including X-rays. An energy-dispersive (EDS) detector is used to separate the characteristic x-rays of different elements into an energy spectrum, and EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. EDS can be used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for a wide variety of materials. EDS systems are typically integrated into either an SEM instrument. The detector is mounted in the sample chamber of the main instrument at the end of a long arm, which is itself cooled by liquid nitrogen. The most common detectors are made of Si(Li) crystals that operate at
low voltages to improve sensitivity, but recent advances in detector technology make available so-called "silicon drift detectors" that operate at higher count rates without liquid nitrogen cooling. Fig 2.4 shows typical liquid nitrogen EDS.

Figure 2.4: An EDS detector, showing liquid nitrogen dewar, cold arm and detector tip that is mounted in the sample chamber

An EDS detector contains a crystal that absorbs the energy of incoming x-rays by ionization, yielding free electrons in the crystal that become conductive and produce an electrical charge bias. The x-ray absorption thus converts the energy of individual x-rays into electrical voltages of proportional size; the electrical pulses correspond to the characteristic x-rays of the element.

2.3.3.2. Limitations

1. There are energy peak overlaps among different elements, particularly those corresponding to x-rays generated by emission from different energy-level shells (K, L and M) in different elements. For example, there are close overlaps of Mn-Kα and Cr-Kβ, or Ti-Kα and various L lines in Ba. Particularly at higher energies, individual peaks may correspond to several different elements; in this case, the user can apply deconvolution methods to try peak separation, or simply consider which elements make "most sense" given the known context of the sample.
2. Because the wavelength-dispersive is more precise and capable of detecting lower elemental abundances, EDS is less commonly used for actual chemical analysis although improvements in detector resolution make EDS a reliable and precise alternative.

3. EDS cannot detect the lightest elements, typically below the atomic number of Na for detectors equipped with a Be window. Polymer-based thin windows allow for detection of light elements, depending on the instrument and operating conditions.

2.3.4. High Resolution Transmission Electron Microscopy

High resolution transmission electron microscopy (HRTEM) is one of the most effective instrumentation techniques for studying micro-structural characteristics of solid objects including crystal defects, grain boundaries, inter-phases, interfaces, intrinsic & extrinsic dislocations etc.

2.3.4.1. Fundamental Principle of TEM

Unlike SEM, TEM uses high energy electrons transmitted through sample to analyze the sample. The electron microscope can use three different electron sources, a plain tungsten (W) filament, a W filament with a LaB6 crystal tip and a field emission gun. Each offers different levels of brightness, with W filament being the lowest and field emission being the brightest. The filament is held in an uncharged Wehnelt cap (0 kV) and is heated in vacuum to excite the electrons. The anode, situated below the Wehnelt cap, allows for the excited free electrons to be directed through it due to the positive voltage, typically 200 kV. The electrons, when located at the filament, will have a high potential energy and a low kinetic energy until the electron reaches the anode, and beyond, where they will have no potential energy and high kinetic energy. Fig. 2.5 shows the schematic diagram of TEM working principle
The electron beam, as it moves down the column, passes through a series of lenses and apertures. The first lens the beam encounters is the condenser lens; this focuses the beam onto the sample. The contrast of the sample can also be changed by using different sizes of the condenser apertures, located below the lens. After the specimen, the beam is refocused by the objective lens, which allows for the diffraction plane to be viewed. The objective aperture can also be used to increase sample contrast and to view dark field imaging. The beam finally passes through the projector lens, which gives the resulting image on the viewing screen.

There are three main contrasts in TEM imaging; mass-thickness, diffraction and phase contrast. For mass-thickness contrast, the thicker the sample, the darker the contrast, however the mass of the material has to be taken into account. Materials of high mass, such as heavy atoms and dense crystals, will have an increased chance at scattering the electrons at a high angle. These high angle scattered electrons tend to be removed.
by the use of an aperture. If only a small amount of information is obtained then the data will have a low intensity, and therefore darker contrast.

Diffraction contrast is normally seen with crystalline material. This contrast is mainly from the stresses in crystal planes that shift the atomic column out of alignment. The resulting effect, which is caused by the interference of the electron waves, is contrast within the image at these locations. The amount of strain on the atoms will differ from one crystal plane to the next, so this contrast will be affected by crystal orientation. Other effects include; sample preparation, crystal thickness and defects within a crystal. The defects amplify this atomic distortion, making the diffraction contrast very useful for defect investigation.

Diffraction contrast has a limited resolution of 1-3 nm since it is based on the crystal structure stresses. To use the HRTEM to view atomic columns, phase contrast is required. When the electron passes through a crystal, the individual atoms cause the wavelength to change, thus changing the phase of the electron. The electrons that are less affected will result in a different contrast to those that are more affected. The density and thickness of the sample will greatly alter the phase of the electron and therefore show very dark contrasts for both. Additionally, if the sample is too thin, only one atom deep, the effect on the phase of the electron will be too small for a contrast difference.

2.3.5. Selected Area Electron Diffraction

SAED determines whether the sample is amorphous or crystalline, and if crystalline whether it is polycrystalline (made up of lot of different crystals) or single crystal (made up of just one crystal). There are three basic patterns for SAED; solid rings that indicate amorphous material, dotted rings indicate polycrystalline material and a 2 dimensional pattern indicates a single crystal. To obtain the best diffraction pattern for a crystal, the specimen needs to be tilted in both the x and y direction.

By measuring the distance between the diffraction rings or spots, the reciprocal d-spacing can be calculated using equation 2.3 where d is the reciprocal d-spacing, D is the distance between spots on the negative and L is the camera length. Unlike XRD,
the relationship between two spots on a pattern can be directly related to each other and as such, only two independent spots need to be indexed to work out all spot indexes of the pattern. If the unit cell is known then the diffraction pattern can be indexed. If the unit cell is unknown then two or more diffraction patterns of one crystal with different zone axes are required to calculate the unit cell.

\[ d = \frac{2 \sin \theta}{\lambda} = \frac{D}{L\lambda} \]  

(2.3)

The use of the selected area aperture allows for selecting large or small areas of a crystal. Small apertures are normally quite beneficial for the studying of defects or for removing residual background spots from other crystals. Twin defects can be studied using this method as the aperture can be used either side of the defect and on the defect. The circles represent the selected area aperture and are attached to a corresponding diffraction pattern. The centre pattern is the twin defect pattern, whereas the left and right patterns are from either side of the defect. The diffraction spots are colored differently so the two patterns can be seen how they make up the twin defect pattern.

With the diffraction pattern, the TEM can be switched from bright field, which is the standard for imaging, to dark field imaging which distinguishes between amorphous and crystalline material. This is a very simple technique and is especially useful when looking for nanoparticles in mesoporous silica\textsuperscript{11} or crystalline domains in soft templated mesoporous metal oxide.

A diffraction pattern is obtained for the material using the smallest aperture. Normally the (000) spot is moved to the centre, but for dark field imaging a spot that is in the surrounding area is needed. The objective aperture is inserted and is centered on the selected spot, reducing the aperture size until the smallest is obtained. The selected area aperture is then removed and the microscope is switched to imaging. Amorphous material and light atoms will appear dull and hazy whereas the crystalline material or heavy atoms will shine.
The reason for this is due to the majority of amorphous material and the lighter elements only changes the angle of the beam very slightly, whereas the heavier atoms and crystalline material will deflect the beam to a higher angle. As the deflected beam moves further from the central position, the amount of signal from amorphous material will decrease. By setting the aperture to a diffraction spot, it removes information from the low angle bright field imaging. The information that does get through will have the majority coming from the crystal that has that spot and a minor signal from the amorphous material. Similarly, if you have defects in a crystal, there is a possibility of using dark field imaging of one of the defect areas by blocking out the diffraction spots using the aperture of the areas you are not interested in.

2.3.6. Atomic Force Microscopy

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s at IBM Research - Zurich, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first atomic force microscope (also abbreviated as AFM) in 1986. The first commercially available atomic force microscope was introduced in 1989. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface, but this is much more challenging with very few groups reporting reliable data.

2.3.6.1. Instrumentation
The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip is scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x, y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area \( s = f(x,y) \) represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated. Fig 2.6 represents the schematic diagram of the working principle of AFM.
Typical tips used are silicon or silicon nitride tips depending on the necessary applications.

2.3.7. Fourier Transform Infrared Spectroscopy

2.3.7.1. Principle

FT-IR stands for Fourier Transform Infra-Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The basic principle of an IR spectroscope is illustrated in fig 2.7.
The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum.

FT-IR can provide the following information:

1. It can identify unknown materials
2. It can determine the quality or consistency of a sample
3. It can determine the amount of components in a mixture

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:

- It is a non-destructive technique
- It provides a precise measurement method which requires no external calibration
- It can increase speed, collecting a scan every second
- It can increase sensitivity – one second scans can be co-added together to ratio out random noise.
- It has greater optical throughput
- It is mechanically simple with only one moving part

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter. The two beams reflect off of their respective mirrors and 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 signal which exits the interferometer is the result of these two beams “interfering” with each other. The schematic diagram of the working principle if FTIR is given in fig 2.8
The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.
2.3.8. Photoluminescence Spectroscopy

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. The excitation energy and intensity can be chosen to probe different excitation types and also different parts of the sample. PL analysis is nondestructive. The technique requires very little sample manipulation or environmental control. When light of sufficient energy is illuminated a material, photons are absorbed and (electronic) excitations are created. These excitations relax and emit a photon. The PL can be collected and analyzed to provide information about the photo-excited states. The PL spectrum reveals transition energies and the PL intensity gives a measure of the relative rates of radiative and non-radiative recombination [186]. Fig 2.9 gives the illustrated image of the basic concept of PL spectroscope.

![Figure 2.9: Typical experimental set-up for PL measurements](image)

Variation of the PL intensity upon change of external parameters, e.g., temperature, excitation energy, power of excitation, can be used to further characterize electronic states and bands. PL investigations can be used to characterize a variety of materials parameters, which will be introduced respectively as follows:

1. Band gap determination
   The most common radiative transition in semiconductors is between states in the conduction and valence bands - bandgap of a semiconductors

2. Impurity levels and defect detection
Radiative transitions in semiconductors also involve localized defect levels. The PL energy associated with these levels can be used to identify specific defects, and the PL intensity can be used to determine their concentration.

3. Recombination mechanisms

As discussed above, the return to equilibrium, also known as "recombination" can involve both radiative and nonradiative processes. The PL intensity and its dependence on the level of photo-excitation and temperature are directly related to the physics of the recombination mechanism.

4. Material quality

In general, non-radiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination. The typical PL experimental set-up is illustrated in Figure 2.10.

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![Figure 2.10: Schematic diagram of PL spectrophotometer](image-url)

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2.3.9. Brunauer-Emmett-Teller Adsorption Analysis

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption. The solid that takes up the gas or vapor or the solute from the solution is called the adsorbent whereas the gas or the solute, which is held to the surface of the solid is called the adsorbate.

The Variation of adsorption with pressure at a given constant temperature, when expressed graphically is called adsorption isotherm [187].

(a) Types of adsorption isotherms

Brunauer, Emmett and Teller classified the isotherms into five types. Type 1 isotherms are followed when adsorption is limited to only few molecular layers. In the case of physical adsorption. The adsorption isotherms are given in fig. 2.11

Type 1 isotherms are encountered with micro porous powders whose pore sizes do not exceed a few adsorbate molecular diameters. The volume of the gas adsorbed approaches a limiting value just enough to complete a uni-molecular layer even when the gas pressure is high.

Type 2 isotherms are most frequently encountered when adsorption occurs on nonporous powders or on powders or on powders with pore diameters larger than micro pores. The inflection point or knee of the isotherm usually occurs near the completion of the first adsorbed monolayer and with increasing relative pressure, second and higher layer are completed until at saturation the number of adsorption layers becomes infinite.

Type 3 isotherm principally by heats of adsorption which are less than the adsorbate heat of liquefaction. Thus, as adsorption proceeds, additional adsorption is facilitated because the adsorbate interaction with an adsorbed layer is greater that the interaction with the adsorbent surface.
Type 4 isotherms occur on porous adsorbent possessing pores in the radius range of approximately 15-1000 Å. The slope increases at higher relative pressure indicates an uptake of adsorbate as the pores are being filled. As is true for the type 2 isotherms, the knee of the type 4 generally occurs near the completion of the first monolayer. Here there is not only multilayer adsorption, but also capillary condensation of the gases in the minute pores of the adsorbent.

Type 5 isotherm results from small adsorbate-adsorbent interaction potentials similar to type 3.

Type 6 is a stepped isotherm not included in the classical classification.

![Figure 2.11: Adsorption isotherms](image)

(b) Determination of specific surface area

The specific surface area is usually determined by using the BET equation which is based on the phenomenon of adsorption. The Langmuir theory of adsorption is restricted to formation of unimolecular layer of gas molecules on the solid surface and disregards the possibility of multilayer adsorption. But in BET theory, it is assumed that multilayer adsorption can take place since the solid surface possesses uniform localized sites.
In the actual BET surface area analysis, we determine the volume of the nitrogen gas adsorbed by a known weight of the sample at liquid nitrogen temperature. Since the area occupied by single adsorbed molecular nitrogen can be estimated, the total surface area can be calculated by multiplying the area of one molecule by the number of molecules requires to form the monolayer. Adsorption varies directly with pressure and inversely with temperature. Here the temperature is held constant and the amount of nitrogen adsorbed at liquid nitrogen temperature is measured at different pressures.

BET equation is

\[
\frac{p}{V(P - p)} = \frac{1}{VmC} + C - \frac{1(P/Po)}{VmC}
\]

(2.4)

V – volume of the gas adsorbed at the pressure

Vm- Volume adsorbed when the surface of the solid is completely covered with a monolayer of adsorbed gas molecules.

C-A constant ( called BET constant) depending on the nature of the gas.

BET- constant, C is related exponentially to the enthalpy of the adsorption. From the value of the monolayer capacity the BET area can be determined using the equation,

\[
S = \frac{VmA}{M}
\]

where \( A \) – Total Surface area, \( \sigma \)

– Molecular cross sectional area of the adsorbate ( For N2, \( \sigma = 0.162 \)nm at 77K), L-Avagrdno No. Specific surface area, \( S = A/m \) where m-mass of the adsorbent.

(c) Determination of total pore volume
The liquid equivalent to the designed volume adsorbed is the total pore volume (cc/g)

\[ V_{tot} = (V_a)(D) \]  \hspace{1cm} (2.5)

\(V_a\) – Volume of adsorbed at \(P/P_0 = 0.99\)

D-Density of conversion factor

The BET specific surface area of the calcined samples were determined by N2 adsorption at 77K (Micromeritics, Gemini Model No:2360,USA) after degassing the samples in the flowing nitrogen atmosphere at 300 C for 5 hrs in a separate degassing unit attached to the instrument before the measurement.

The total pore volume values are obtained by applying the relative pressure between 0.05 to 0.90.

(d) Determination of average pore size

Assuming that the pores are of cylindrical shape and open at both ends, the average pore size of a given sample is calculated using the equation.

\[ \text{Average pore size} = 4Vp/S_{BET} \]  \hspace{1cm} (2.6)

(e) Pore size distribution curves

Pore size distribution are determined from adsorption/desorption making use of the Kelvin equation, which relates the equilibrium vapor pressure of a curved surface, such as that of a liquid in capillary or pore, to equilibrium pressure of the same liquid on the plane surface.

\[ \ln \left( \frac{p}{P_0} \right) = -\frac{2yVCos\theta}{rRt} \]  \hspace{1cm} (2.7)

Where \(p\) is the equilibrium vapor pressure of the liquid contained in a narrow pressure radius of \(r\) and \(P_0\) is the equilibrium pressure of the same liquid in a
plane surface. The terms \( \gamma \) and \( V \) are the surface tension and the molar volume of the liquid respectively and \( \theta \) is the contact angle of the liquid. When nitrogen is used as the adsorbate at its boiling point of 77K, the Kelvin equation can be written as

\[
Rk = \frac{4.14}{\log\left(\frac{\rho_0}{\rho_p}\right)(A)}
\]  

(2.8)

Rk is the radius obtained from Kelvin equation, which differs from actual pore size since condensation occurs to a core of pore that was already covered by an adsorbed layer.

2.3.10. Gas Chromatography-Mass Spectroscopy (GCMS)

Chromatography is a versatile technique used to physically separate a compound or a mixture of compounds from a solvent or solution. There are two important components in chromatography [188].

1. Mobile Phase
A gas or a liquid that acts as the carrier with steady flow rate. The mobile phase should be an inert substance that shall never react or interact with the sample.

2. Stationary Phase
A solid or a liquid phase that acts as the base for the mobile phase. Stationary phase is usually acts as a adsorbent in separation of the elute.

Fig. 2.12 gives the schematic diagram of the GC instrumentation. The major components of the instrument are

a. Gas flow controllers
Gas flow controllers are used to regulate the gas flow at a constant flow rate throughout the experiment. There are two types of controllers namely manual controllers and electronic controllers. Electronic controllers are known to be more precise and efficient.
b. Injector
Injector is the interface where the sample is inducted in the instrument. The injector is always maintained at a high temperature so that the sample introduced is immediately vaporized. The vaporized sample is then mixed into the carrier gas.

c. Column
Column is the stationary phase in gas chromatography where the sample is separated and processed. There are different kinds of columns for various applications like capillary columns, packed columns, adsorbent columns etc.

d. Detector
Detector analyzes the sample and gives the signal based on retention time. There are different types of detectors based on the detection method. Flame ionization detectors that analyze the sample by ionizing them, thermal conductivity detectors, electron capture detectors etc.

Figure 2.12: Schematic diagram of Gas Chromatogram