CHAPTER 4: CHARACTERIZATION TECHNIQUES FOR NANOMATERIALS
4.1 Introduction

Nanomaterials behave differently as the size changes with respect to the bulk. It is necessary to characterize physical, structural and optical properties of a material to qualify as nanomaterial. Various characterization techniques are used to know the characteristics of the nanomaterials.

4.2 Characterization techniques

Characterization techniques are classified as:

a) Chemical characterization
b) Structural characterization

4.2.1 Chemical characterization techniques

To study the internal chemical structural details, chemical characterization is done.

i) Optical Spectroscopy:

a) Optical absorption spectroscopy (OAS)
b) Photoluminescence (PL)
c) Fourier Transform Infrared Spectroscopy (FTIR)
d) Raman Spectroscopy

ii) Electron Spectroscopy:
a) Energy Dispersive X-ray Spectroscopy (EDS)
b) X-ray Photoelectron Spectroscopy (XPS)
c) Auger Electron Spectroscopy (AES)
d) Ultraviolet photoelectron spectroscopy (UPS)

iii) Ionic Spectrometry

iv) Rutherford Backscattering Spectrometry (RBS)
v) Secondary Ion Mass Spectrometry (SIMS)

4.2.2 Structural characterization techniques

Variation in the size of nanoparticle determines the optical properties of the material. Similarly, for different applications of the nanomaterial, the information about the shape, lattice constants and crystallinity are important. To know the size, shape, lattice constants and crystallinity of the material, structural characterization is done. The techniques are [1,2]:

i) X-ray diffraction technique

ii) Electron microscopy:
a) Scanning Electron Microscopy (SEM)
b) Transmission Electron Microscopy (TEM)/High Resolution (HR)TEM with Selected Area Electron Diffraction (SAED)
c) Small Angle X-ray Scattering (SAXS)

d) Environmental Transmission Electron Microscopy (ETEM)

e) Scanning Probe Microscopy (SPM):
   i) Atomic Force Microscopy (AFM)
   ii) Scanning Tunneling Microscopy (STM)

iii) Dynamic light Scattering

4.3 Characterization techniques adopted in the present work

4.3.1 Chemical Characterizations:

4.3.1(a) Optical Spectroscopy:

Optical spectroscopy uses the interaction of light with matter as a function of wavelength or energy in order to obtain information about the material. Absorption or emission experiments with visible and UV light tend to reveal the electronic structure. Vibrational properties of the lattice (i.e., phonons) are usually in the IR and are studied either using IR absorption or Raman spectroscopy. Optical spectroscopy is attractive for materials characterization because it is fast, nondestructive and of high resolution.
UV-visible spectroscopy

This technique involves the absorption of near-UV or visible light. Absorption spectroscopy is employed to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present [3]. When organic compounds absorb UV or visible light, energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump needs more energy than a small one. Figure 4.1 showing the possible electron jumps that light may cause.

![Figure 4.1 Possible electron jumps](http://www.chemguide.co.uk/analysis/uvvisible/theory.html)

Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps,
then that wavelength will be absorbed its energy will have been used in promoting an electron.

The relationship between the frequency of light absorbed and its energy

\[ E = h \nu \]  \hspace{1cm} (4.1)

Where, \( E \) is the energy of each quanta of light, \( h \) is the Planck's constant and \( \nu \) is the frequency of light. For higher energy jump, light of a higher frequency is to be absorbed.

UV-visible spectrophotometer measures both intensity and wavelength. It is usually applied to molecules and inorganic ions in solution. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as \( I_o \). The intensity of the light, \( I \) passing through the sample cell is also measured for that wavelength. If \( I \) is less than \( I_o \), then obviously the sample has absorbed some of the light.

The Beer-Lambert Law gives, the relationship between \( A \) (the absorbance) and the two intensities is given by:

\[ A = \log_{10} \frac{I_o}{I} \] \hspace{1cm} (4.2)

An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. An absorbance of 1 happens when 90% of the light at that wavelength has been absorbed that means that the intensity is 10%
of what it would otherwise be. A spectrophotometer can be either single beam or double beam.

Shown in the figure 4.2, a single beam UV-visible spectrophotometer.

![Figure 4.2 Schematic of single beam UV-visible Spectrophotometer](http://nelchem.kaist.ac.kr/chem-ed/spec/uv-vis/uv-vis.htm)

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament (300-2500 nm), a deuterium arc lamp, continuous over the ultraviolet region (190-400 nm), xenon arc lamps, continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths [4]. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode
arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

In a single beam spectrophotometer the light passes through the sample cell. $I_0$ must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time shown in figure 4.3. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

![Figure 4.3 Schematic of a dual-beam UV-visible spectrophotometer](http://www.files.chem.vt.edu/chem-ed/spec/uv-vis/dualbeam.html)
The Tauc's plot is used to determine optical bandgap. Tauc plot shows the quantity $hv$ (the photon energy) on the abscissa and the quantity $(ahv)^r$ on the ordinate, where $a$ is the absorption coefficient of the material [5]. The value of the exponent $r$ denotes the nature of the transition; for example, $r = \frac{1}{2}$ for indirect transitions [5]. The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical bandgap of the material. However, if the material does not have a single phase, it will likely not have a single distinct absorption onset, which corresponds to a more gradually sloping curve in the Tauc's plot.

(ii) Photoluminescence Spectroscopy:

Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon.

If a light particle (photon) has an energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap. In this process of photoexcitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron energy eventually falls back down to the valence band. As this
happens, the energy it loses is converted back into a luminescent photon which is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap energy, $E_g$. The process of photon excitation followed by photon emission is called photoluminescence [6].

There are many types of photoluminescent process:

a) *Resonant radiation*: When a photon of a particular wavelength is absorbed and equivalent photon is immediately emitted. This process is extremely fast about 10ns, and no significant transition of the internal energy of the chemical substrate between absorption and emission occurs.

b) *Fluorescence*: When the chemical substrate undergoes internal energy transitions before re-emitting the energy from the absorption. This process is also fast, but some of the original energy is dissipated so that the emitted light photons are of lower energy than those absorbed.

c) *Phosphorescence*: In phosphorescence the energy from absorbed photons undergoes intersystem crossing into a state of higher spin multiplicity, generally a triplet state. When the energy is trapped in the triplet state, transition back to the lower singlet energy states is forbidden quantum mechanically. This leads to a slow process of radiative transition back to singlet state that last from minutes to hours [7]. The lifetime of phosphorescence is usually from $10^{-4}$-$10^{-2}$s, much longer than that of Fluorescence [8]. Therefore, phosphorescence is even rarer than fluorescence, since a molecule in the triplet state has a good chance of undergoing intersystem crossing to ground state before phosphorescence can occur.
A spectrometer is an instrument used for measuring the intensity of light as a function of wavelength. Spectrometers usually contain a diffraction grating (or prism) to disperse the light, thereby spreading out the light of differing wavelengths into different positions. The spectrometer unit has an internal CCD (charged coupled device) silicon detector, essentially a digital camera detector, to measure the light intensity at various positions along its length. From the emission patterns, photoluminescence spectroscopy is used in other fields of analysis, especially semiconductors.

a) **Band gap determination**

Band gap is the energy difference between the lowest state in the conduction and the highest state in the valence bands, in semiconductors. The spectral distribution of PL from a semiconductor can be analyzed to nondestructively determine the electronic band gap and this provides a means to quantify the elemental composition of compound semiconductor [8].

b) **Impurity levels and defect detection**

Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration. The PL spectrum at low sample temperatures often reveals spectral peaks associated with impurities contained within the host material. Fourier transform photoluminescence microspectroscopy, which is of high sensitivity, provides the potential to identify extremely low concentrations of intentional and unintentional impurities [8].
c) **Surface structure and excited states**

Photoluminescence, is very sensitive to surface effects or adsorbed species of semiconductor particles and thus can be used as a probe of electron-hole surface processes [8].

d) **Recombination mechanisms**

Recombination mechanism, can involve both radiative and non-radiative processes. The quantity of PL emitted from a material is directly related to the relative amount of radiative and non-radiative recombination rates. Non-radiative rates are typically associated with impurities and the amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process [8]. When samples is exposed to photons, the photoexcitation of electrons from the valence band to conduction band occurs and, the electrons losses excess energy through non-radiative relaxation before falling to the lowest energy in the conduction band. The electrons may radioactively recombine with holes of the valence band and if the sample is completely free of impurities i.e. pure an exciton gets formed between these two carriers with a small binding energy. The characteristic of the energy levels is the energy of the emitted photons due to band-to-band transition, an exciton recombination or any other possible transitions [9].

If the sample is impure or doped, radiative recombination also may occur via shallow donor or acceptor levels. In case of impure sample three types of transition may occur, conduction band to acceptor level, donor level to valence band and donor level to acceptor level.
Thus, analysis of photoluminescence pattern can give information about the impurity, energy transfer, bandgap of the material.

4.3.1(b) Energy Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive Spectrometry (EDS) was first introduced in the late 1960s, when solid state detectors were first interfaced to microanalyzers [10]. The chemical composition of the sample is done by energy dispersive X-ray spectroscopy (EDS). EDS systems are typically integrated into either an SEM or EPMA instrument. EDS systems include a sensitive X-ray detector, a liquid nitrogen is use for cooling, and software to collect and analyze energy spectra. 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. In all EDS all photons emitted by the sample are collected and measured simultaneously by a solid state X-ray detector. The common EDS detector is a lithium- drifted silicon, Si(Li) [1]. The detectors 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 [11]. Figure 4.4 is a schematic representation of EDS.

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 [11].
When the electron beam from the source strikes the sample, various excitation in sample occurs and these are the characteristics of the elements present and can be used for elemental identification.

When an electron approaches the atom it gets decelerated due to coulombic field. This results in a loss of energy of the electron and that energy appears as photon, referred to as bremsstrahlung or 'breaking radiation'. This radiation contains photons of all energies till the energy of the original electron, as an electron can lose any energy, from zero to the energy of primary electrons. The characteristic X-rays emitted by atoms will appear as spikes on these large, smoothly varying photon intensity. From the X-ray lines the atom can be identified. The intensities of these lines is related to concentrations of the emitting species in the sample [1].

EDS has certain limitations, the 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. 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 [11]. 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.

4.3.2 Structural Characterization

4.3.2 (a) X-ray Diffraction Technique

X-ray Diffraction (XRD) is one of the classical methods for identification and characterization of crystalline solids. Each crystalline solid has its unique characteristic X-ray powder pattern which is used as a "fingerprint" for its identification. The method is based on the diffraction of X-rays by the sample in different directions. Waves of wavelength comparable to the crystal lattice spacing are strongly scattered (diffracted).

The X-ray source is Cu X-ray having a wavelength of Cu $K\alpha$ lines, 1.54 Å. The diffracted rays are detected by a detector placed on the opposite side shown in figure 4.5. The X-ray source, sample and the detector are placed in a particular configuration given by the Bragg-Brentano geometry that gives a 0-2θ scan. The source is stationary and the sample and the detector are mobile. When the sample moves by an angle $\theta$, the detector moves by angle 2θ. The rotation rate is kept at 1°/min and the sample is scanned for 10°-80° scan. The sample is loaded on a soda glass substrate [3].
The schematic of X-ray diffractometer is shown in figure 4.6. The angle and intensities of the diffracted X-rays are used to perform crystallographic studies. The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ (Fig.4.7). The intensities of the spots provide information about the atomic basis. The sharpness and shape of the spots are related to the perfection of the crystal [12].
The structure of the material can be obtained from intensity Vs 20 plot.

(i) The presence or absence of a certain set of planes gives us the crystal structures.

(ii) The shift of the peaks from its original positions in case of bulk crystals gives the strains in the material.

![Figure 4.7 X-ray Diffraction Pattern](image)

Although the method of X-ray diffraction is quantitative, in general, it is used for qualitative analysis. This form of analysis extends to all crystalline solids including ceramics, metals, insulators, organic, polymers, thin film powders etc. X-ray diffractometers can be used either for single crystals or for powders. While single crystal diffractometers are used for the study of molecular structure, powder diffractometers are used for analysis of phases, though the latter can also be used to derive molecular information [1].

Two approaches are generally used for the analysis of X-ray diffraction data.

i) **Laue equations**: In Laue equations, diffraction from one-dimensional crystal may be treated in the same way as the diffraction by an optical grating.
Upon projection, the grating is like an array of points similar to a crystal. The diffraction condition is again, \( n \lambda = d \sin \theta \). In a crystal arrangement of atoms is periodic in all three directions and three independent Laue equations can be written. The three equations have to be satisfied simultaneously for diffraction to occur [1].

(ii) **Bragg’s law:** In Bragg’s law, a crystal is viewed as a plan containing several lattice points. When X-rays are incident on a crystal, different lattice planes causes simultaneous reflections of the X-ray beam. These simultaneous reflections may cause constructive or destructive interference depending on the angle of incidence of X-rays, interlayer separation, wavelength of X-rays. The reflection being equal to the angle of incidence as shown in fig. 4.8. The reflected beams are in phase when the path length between the beams is an integral multiple of the wavelength. The planes of light travelling after reflection will be in phase only when this condition is satisfied. This means that distance \( ABC = n \lambda \) or \( 2d \sin \theta = n \lambda \). But for all other angles other than \( \theta \) destructive interference occurs. Few specific directions along which the interference is constructive are given by the Braggs law [1].

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

(4.3)

Where \( d \) is the separation between the planes of the crystal, \( \theta \) is the angle of incidence of X-ray and \( \lambda \) is the wavelength of the X-ray.

For all angle other than \( \theta \), destructive interference will occur leading to cancellation of the intensity. For crystals containing thousands of such planes, Bragg’s law imposes severe restrictions on \( \theta \) and the cancellation of intensities.
is usually complete. However, in cases where number of diffraction planes is limited, diffraction peak will broaden.

Homogeneous and inhomogeneous strains can be characterized by studying the diffraction peak positions of the XRD [2]. The shift in the peak positions is due to homogeneous strain that leads to change of lattice constants and the change in the d-spacing can be calculated.

Due to inhomogeneous stains broadening of the diffraction peaks are observe that increases with increase in Sinθ. Peak broadening is also caused by the finite size of crystallites, in this case the broadening is independent of sinθ. From peak shapes contribution of crystallite size and inhomogeneous strain to the peak width can be determined. The crystallite size D, can be estimated from the peak width by Debye Scherrer's formula [13]

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(4.4)
Where $\beta$ is the Full Width at Half maximum in radians, $\theta$ is the peak position, $D$ is the average grain size, $\lambda$ is the wavelength of incident X-ray, $K$ is the Scherrer's constant, having value 0.9.

The accuracy of size by Scherrer's formula is limited to the cases where instrument and stress-related broadening are negligible. The lattice strain on the particles is obtained by using the formula [5] between strain and particle size, given by,

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\eta \sin \theta}{\lambda}$$  \hspace{1cm} (4.5)

Where $\beta$ is the Full Width at Half maximum in radians, $\theta$ is the peak position $D$ is the average grain size, $\lambda$ is the wavelength of incident X-ray, $\eta$ is the effective strain. The strain is determined from the slope of the plot between $\beta \cos \theta / \lambda$ and $\sin \theta / \lambda$, whereas average particle size is obtained from the inverse of the y-axis intercept obtained by extrapolating the above mentioned plot.

Indexing a diffraction pattern (also called a diffractogram or spectrum) involves determining the lattice constant and structure and labeling each peak with its appropriate $hkl$ designation. In Bragg's law, $d$ can be in terms of lattice parameter $a_0$ and then the equation becomes

$$\eta \lambda = 2d \sin \theta = 2 \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \sin \theta$$  \hspace{1cm} (4.6)

The structure factor calculations give the relationship for allowed reflections for cases of FCC and BCC structures [14].
4.3.2(b) Scanning Electron Microscope (SEM)

The first Scanning Electron Microscope was debuted in 1942 and commercially produced in 1965. SEM is popular because of its versatility, various modes of imaging, ease of sample preparation, possibility of spectroscopy and diffraction as well as easy interpretation of the images. The best image resolutions is in the range of 0.5 nm [1]. SEM images have a characteristic three dimensional appearance and can be used to judge structure [15].

In SEM, a monochromatic electron beam with a very fine spot size of ~ 5nm and having energy from a few hundred eV to 50 KeV is passed over the surface of the specimen which induces various changes in the sample. The resulting particles from the sample are used to create an image of the specimen. The information is derived from the surface of the sample.

The schematic of SEM is shown in the figure 4.9. SEM consists of an electron gun at the top, the "Virtual source" that produces a stream of monochromatic electrons. The stream is then condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to form beam and also to limit the amount of current in the beam. The condenser aperture along with the first condenser lens works to eliminate the high–angle electrons from the beam. The second condenser lens forms electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob". The objective aperture further eliminates high-angle electrons from the beam. A set
of coils "scan" or sweep the beam in a grid like fashion, dwelling on points for a period of time determined by the scan speed. The last objective lens, focuses the scanning beam onto the part of the specimen desired. The beam of electrons strikes the sample and interactions occur inside the sample and are detected by various instruments. The instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number of interactions. Then beam moves to the next dwell point. This process is repeated until grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second [15].

![Figure 4.9 Schematic of Scanning Electron Microscope](www.unl.edu/CMRAcfem/semoptic.html)

In SEM, high spatial resolution microanalysis of materials is possible. The spatial resolution of the analysis is made possible by the small dimensions of excitation beam, of the order of a few nanometer [1]. The electron beam causes various excitations in the sample that are the characteristic of the elements present in the material. Characteristic X-rays emitted by the sample
as a result of core hole decay is used for elemental identification. The intensity of the signal can be used for quantitative analysis.

Microanalysis is done in two ways namely, "energy dispersive spectroscopy" (EDS) and "wavelength dispersive spectroscopy" (WDS). EDS corresponds to energy analysis and WDS corresponds to wavelength analysis. WDS is more time consuming and cumbersome than EDS but improved energy resolution is possible in comparison to EDS [1].

4.3.2(c) Transmission Electron Microscopy (TEM) & Selected Area Electron Diffraction (SAED)

The first TEM was built by Max Knoll and Ernst Ruska with resolving power greater than that of light, in 1933 and the first commercial TEM in 1939. TEM is used to reveal the internal structure of materials. Magnifications of greater than 300k is possible in all TEM. Latest TEM has magnification of 50 million times.

Figure 4.10 is the schematic of Transmission electron microscope. The four basic components of TEM microscope are (i) an electron gun, that emits a beam of monochromatic electrons as the illumination source, (ii) a set of condenser lenses to focus the illumination onto specimen, (iii) an objective lens used to form first image of the specimen, (iv) a series of magnifying lenses to create the final magnified image [16].
Electrons are emitted by heating a filament (thermionic emission, tungsten or LaB₆ filament) or from an unheated filament that has an extremely high potential gradient placed across the filament (field emission, fine-tipped single-crystal tungsten) [16]. The stream of monochromatic electrons move along the optical axis of the microscope are focused to a small, thin, coherent beam by the use of condenser lenses. The beam is restricted by the condenser aperture, knocking out high angle electrons. The beam then strikes the specimen and parts of it are transmitted. This transmitted portion is focused by the objective lens into an image. The objective aperture enhances the contrast by blocking out high-angle diffracted electrons, whereas the selected area aperture enables to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample. The image is then passed down the column through the intermediate and projector lenses. The image strikes the phosphor image.
screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through. The lighter areas of the image represent those areas of the sample that more electrons were transmitted through [15].

There are two image modes of TEM, Bright field mode and Dark field mode. In Bright field (BF) image mode an aperture is placed in the back focal plane of the objective lens that allows only the direct beam to pass through [15]. The image results from weakening of the direct beam by its interaction with the specimen. Therefore, mass-thickness and diffraction contrast contribute to image formation. Thick areas, that are areas in which heavy atoms are enriched, and crystalline area appear dark contrast. The image is interpreted by the simultaneous occurrence of the contrast-forming phenomena [16]. In dark field image mode, the direct beam is blocked by aperture while one or more diffracted beams are allowed to pass the objective aperture. As the diffracted beams strongly interacted with the specimen, useful informations about planar defects, stacking faults or particle sizes can be obtain.

In the TEM the electrons pass through the sample as it is thin. The electron that pass through the sample is classified into three categories: the unscattered electrons, the elastically scattered electrons and the inelastically scattered electrons. The unscattered electrons pass right through the sample after inciding with the sample without any interaction with the sample atoms and transmission of these electrons is inversely proportional to the thickness of the sample. So, thicker parts of the sample appear darker while the thinner part of the sample appear lighter [17]. The incident electrons that are deflected due to
their interaction with the sample but do not loss any energy, gives elastically scattered electrons. The incident electrons are scattered during elastic interaction and are scattered according to Bragg's law. The scattered electrons are collated by magnetic lenses and it form a pattern of diffraction spots. These diffraction pattern gives information about orientation and atomic arrangement in the area probed. This mode of operation is known as Selected Area Electron Diffraction (SAED) [17].

When the incident electrons lose energy due to their interaction with the sample atoms, the inelastically scattered electrons are generated. The inelastic loss of energy by the incident electrons is the characteristic of the element of the sample and this confirms the composition and also provide the bonding information of the examined sample region [17].

4.3.2(d) High Resolution TEM (HRTEM)

HRTEM is useful for direct atomic level study like interface, dislocation, defects, etc. It allows imaging of the crystallographic structure of specimen at an atomic scale [15]. The highest resolution is 0.08 nm. HRTEM is an imaging mode of TEM.

In HRTEM, image is formed by the phase contrast due to interference in the image plane of the electron wave with itself [18]. The contrast formation in high resolution TEM (HRTEM) can be explained by the wave nature of electrons. In HRTEM, a virtually planar electron wave is transmits a thin specimen (thickness < 20 nm), in most cases a crystal. During transmission the incident
electron wave is scattered (or diffracted in the case of a crystal) at the potentials of the atoms, and thereby the phase of the electron wave is changed. At the exit surface of the specimen the object wave is formed, which carries direct and highly resolved information on the object. The object wave is magnified in the electron microscope and during this process the wave suffers additional phase shifts due to imperfect lenses (aberrations). Finally, the image recorded on film plates or digital cameras is an interference pattern of the image wave, which itself and it contains essentially phase contrast with all the microscopic aberrations included. As the phase of the electron wave carries the information about the sample and generates contrast in the image, and so known as phase-contrast imaging. A single recorded image in HRTEM consists of electron intensities only the phase of the wave and hence an important information on the object is lost [19]. In conventional HRTEM, image interpretation is performed by an iterative procedure by comparing numerically simulated images with images acquired at the electron microscope. The computer-simulated images are based on atomic model structures, including all imaging parameters that need to be known as precisely as possible. The resolution limit of the structure analysis is determined by the point resolution of the microscope which is the optical resolution of the objective lens [19].

Each imaging electron interacts independently with the sample. Above the sample, the wave of an electron can be approximated as a plane wave incident on the sample surface. As it penetrates the sample, it is attracted by the positive atomic potentials of the atom cores, and channels along the atom columns of the crystallographic lattice (s-state model). At the same time, the
interaction between the electron wave in different atom columns leads to Bragg diffraction. As a result of the interaction with the sample, the electron exit wave right below the sample $\varphi_e(x,u)$ as a function of the spatial coordinate $x$ is a superposition of a plane wave and a multitude of diffracted beams with different in plane spatial frequencies $u$ (high spatial frequencies correspond to large distances from the optical axis). The phase change of $\varphi e(x,u)$ compared to the incident wave peaks at the location of the atom columns. The exit wave now passes through the imaging system of the microscope where it undergoes further phase change and interferes as the image wave in the imaging plane (photo plate or CCD). It is important to realize that the recorded image is NOT a direct representation of the sample's crystallographic structure. For instance, high intensity might or might not indicate the presence of an atom column in that precise location. The relationship between the exit wave and the image wave is a highly nonlinear one and is a function of the aberrations of the microscope. It is described by the contrast transfer function [18].

The phase contrast transfer function (CTF) is a function of limiting apertures and aberrations in the imaging lenses of a microscope. It describes their effect on the phase of the exit wave $\varphi e(x,u)$ and propagates it to the image wave. Following Williams and Carter,[20] if we assume the weak phase object approximation (WPOA) holds (thin sample) the contrast transfer function (CTF) becomes

$$CTF(u) = A(u)E(u)\sin(\chi(u)) \quad (4.7)$$
Where $A(u)$ is the aperture function, $E(u)$ describes the attenuation of the wave for higher spatial frequency $u$, also called envelope function. $\chi(u)$ is a function of the aberrations of the electron optical system.

The last, sinusoidal term of the CTF will determine the sign with which components of frequency $u$ will enter contrast in the final image. If one takes into account only spherical aberration to third order and defocus, $\chi$ is rotationally symmetric about the optical axis of the microscope and thus only depends on the modulus $u = |u|$, given by

$$\chi(u) = \frac{\pi}{2} C_s \lambda^3 u^4 - \pi \Delta f \lambda u^2$$

(4.8)

Where $C_s$ is the spherical aberration coefficient, $\lambda$ is the electron wavelength, and $\Delta f$ is the defocus. In TEM, defocus can easily be controlled and measured to high precision. Thus one can easily alter the shape of the CTF by defocusing the sample. Contrary to optical applications, defocusing can actually increase the precision and interpretability of the micrographs.

The *aperture function* cuts off beams scattered above a certain critical angle (given by the objective pole piece for ex), thus effectively limiting the attainable resolution. However it is the *envelope function* $E(u)$ which usually dampens the signal of beams scattered at high angles, and imposes a maximum to the transmitted spatial frequency. This maximum determines the highest resolution attainable with a microscope and is known as the information limit. $E(u)$ can be described as a product of single envelopes:
\[ E(u) = E_s(u)E_c(u)E_d(u)E_v(u)E_D(u) \] (4.9)

Where, \( E_s(u) \) is angular spread of the source, \( E_c(u) \) is chromatic aberration, \( E_d(u) \) is specimen drift, \( E_v(u) \) is specimen vibration, and \( E_D(u) \) is detector.

Specimen drift and vibration can be minimized relatively easily by a suitable working environment. It is usually the spherical aberration \( C_s \) that limits spatial coherency and defines \( E_s(u) \) and the chromatical aberration, together with current and voltage instabilities that define the temporal coherency in \( E_c(u) \). These two envelopes determine the information limit [18].

One of the demerit with HRTEM is that image formation relies on phase-contrast. The image is influenced by strong aberrations of the imaging lenses in the microscope. One major aberration is caused by focus and astigmatism, which often can be estimated from the Fourier transform of the HRTEM image.

Some of the techniques described above are adopted for characterising the as-synthesised samples and those results obtained are presented in the next chapter.
REFERENCE


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