Chapter 2

Experimental Techniques

2.1 Introduction

In nanotechnology and nanoscience the greatest challenge for the researchers is inadequate instruments to observe, measure and manipulate the materials at the nanometer level. Earlier studies have focused on the collective behaviour and properties of nanostructured materials. However for better understanding and for various applications, it is desired to characterize and manipulate individual nanostructures.

In this chapter, various structural characterization methods which are most widely used in characterizing nanomaterials and nanostructures, have been discussed. These include: X-ray diffraction (XRD), transmission electron microscopy (TEM) and Field emission scanning electron microscopy (FESEM). XRD has been widely used for the determination of crystallinity, crystal structures and lattice constants of nanoparticles, nanowires and thin films; SEM and TEM together with electron diffraction have been commonly used in characterization of nanoparticles.

2.2 X-ray Diffraction

X-ray diffraction is a very significant experimental technique that has been used to analyze the crystal structure of the solids, including crystalline size, lattice constants and geometry identification of unknown materials, preferred orientation of polycrystals, defects, stresses etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen. When an
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X-ray strikes an atom, it will be weakly scattered in all directions. If it encounters a periodic array of atoms, the waves scattered by each atom will reinforce in certain directions and cancel in others. Geometrically, crystal is made up of a group of lattice planes and the scattering from a given family of planes can only be strong if the X-rays reflected by each plane arrive at the detector are in phase. This leads to a relationship called Bragg's law:

$$\lambda = 2d \sin \theta$$

(2.1)

where $d$ is the spacing between atomic planes in the crystalline phase and $\lambda$ is the X-ray wavelength. The intensity of the diffracted x-rays is measured as a function of the diffraction angle $2\theta$ and specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. In material characterization XRD is considered as a vital technique as it is nondestructive and does not require elaborate sample preparation. XRD measures the accurate positions of diffraction peaks, which makes it excellent for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the positions of diffraction peaks. From this peak shift one can calculate the change in $d$ spacing, which is the result of the change of lattice constants under strain. Inhomogeneous strains may cause a broadening of the diffraction peaks that increase with $\sin \theta$ and these vary from crystallite to crystallite or within the crystallite. Peak broadening is also caused by the finite size of crystallites, but here the broadening is independent of $\sin \theta$. In case where both crystallite size and inhomogeneous strain contribute to the peak width, then from the analysis of peak shapes these can be determined separately.

In the absence of inhomogeneous strain, the crystallite size, $D$, can be calculated from the peak width by using Scherrer's formula:

$$D = \frac{K\lambda}{B \cos \theta}$$

(2.2)

where $\lambda$ is X-ray wavelength, $B$ is the full width at half maximum (FWHM) of diffraction peak, $\theta$ is the diffraction angle, and $K$ is the Scherrer's constant of the order of unity for usual crystal. However, in case of nanoparticles sizes calculated from Scherrer's formula may be different from the true particle size because nanoparticles often produce twinned structures. In addition, X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizable amount of powder. Since the estimation would work only for very small particles, this technique is very useful in characterizing nanoparticles.
Powder diffraction can be useful at various situations. In the following text I have discussed some points, in which the importance of XRD can be seen.

1. The intensities and positions of diffraction peaks can be compared to a standard database of known materials in order to identify the contents of the sample and to determine the presence or absence of any particular phase.

2. In a quantitative phase analysis, a mixture of two or more crystal line phases can be easily and accurately analyzed in terms of its phase fractions, whether or not the crystal structures of all phases are known.

3. The crystal structure of a new or unknown material can be determined when a similar structure with a known structure exists. Depending on the degree of similarity between the new and the old structure, this is fairly straightforward.

4. The lattice parameters can be calculated by using plane spacing equation (Cullity & Stock (2001)):

\[ d^2 = \frac{4(h^2 +hk +k^2)}{a^2 + l^2 c^2} \]  

5. The variation in the peak positions with sample orientation can be used to deduce information about the internal strain of the sample.

In powder diffractometer, a small disc like container is filled with powder sample and surface of powder carefully flattened with the help of glass slab. The disc is put on one axis of the diffractometer and tilted by an angle $\theta$ while a detector rotates around it on an arm at twice this angle. This configuration is known under the name Bragg-Brentano. Another configuration is the theta-theta configuration in which the sample is stationary while the x-ray tube the detector are rotated around it. The angle formed between the tube and the detector is $2\theta$. This configuration is most convenient for powder. The image of X-ray diffractometer is shown in Fig. 2.1.
2.2 X-ray Diffraction

Figure 2.1: X-ray Diffractometer.
2.3 Transmission Electron Microscope

In this section, we will see how electrons can be used to probe the microstructures of the materials. Electron microscopy is the most powerful tool for characterization of materials. The electron beam methods are capable of determining crystal structure, shapes, orientations, defects within the crystals, and the distribution of atoms within these individual crystals. In transmission electron microscope (TEM), accelerated electrons are projected onto a thin specimen by means of the condenser lens system, and penetrate the sample thickness either undeflected or deflected. The greatest advantage that TEM offers is the high magnification ranging from $50$ to $10^6$ and its ability to provide both image and diffraction information from a single sample.

The scattering processes experienced by electrons during their passage through the specimen determine the kind of information obtained. Diffraction patterns are obtained due to elastic scattering without the loss of energy. Inelastic interactions between primary and sample electrons at heterogeneities such as grain boundaries, dislocations, second-phase particles, defects, density variations, etc., cause complex absorption and scattering effects, leads to the spatial variation in the intensity of the transmitted electrons. By changing the strength of the intermediate lens one can switch between imaging the sample and viewing its diffraction pattern.

The high magnification or resolution of all TEM is a result of the small effective electron wavelengths, $\lambda$ is given by the De Broglie relationship as follows

$$\lambda = \frac{h}{\sqrt{2mqV}},$$

where $m$ and $q$ are the electron mass and charge, $h$ is Planck’s constant, and $V$ is the potential difference through which electrons are accelerated. For example, electrons of 100 KeV energy have wavelengths of 0.37 nm and are capable of effectively transmitting through 0.6 $\mu$m of silicon. Higher the operating voltage of a TEM instrument, the greater its lateral spatial resolution. The theoretical instrumental point to point resolution is proportional to $\lambda^{3/4}$. High voltage TEM instruments (with e.g. 400 KV) have point to point resolutions better than 0.2 nm. High voltage TEM instrument have the additional advantage of greater electron penetration, because high energy electrons interact less strongly with matter than lower energy electrons. So it is possible to work with thicker samples on a high voltage TEM. One shortcoming of TEM is its limited depth resolution. Electron scattering information in a TEM image originates from a three
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dimensional sample, but is projected onto a two dimensional detector. Therefore, structure information along the electron beam direction is superimposed at the image plane. The most difficult aspect of TEM technique is sample preparation for TEM analysis (Cao (2004)).

TEM instrument, consists of an emission source, which may be a tungsten filament, or a lanthanum hexaboride (LaB$_6$) source. For tungsten, this will be of the form of either a hairpin style filament, or a small spike shaped filament. LaB$_6$ sources utilize small single crystals. By connecting this gun to a high voltage source (typically $\sim$100-300 kV) the gun will, given sufficient current, begin to emit electrons either by thermionic or field electron emission into the vacuum. This extraction is usually aided by the use of a Wehnelt cylinder. Once extracted, the upper lenses of the TEM allow for the formation of the electron probe to the desired size and location for later interaction with the sample.

Manipulation of the electron beam is performed using two physical effects. The interaction of electrons with a magnetic field will cause electrons to move according to the right hand rule, thus allowing for electromagnets to manipulate the electron beam. The use of magnetic fields allows for the formation of a magnetic lens of variable focusing power, the lens shape originating due to the distribution of magnetic flux. Additionally, electrostatic fields can cause the electrons to be deflected through a constant angle. Coupling of two deflections in opposing directions with a small intermediate gap allows for the formation of a shift in the beam path, this being used in TEM for beam shifting, subsequently this is extremely important to STEM. From these two effects, as well as the use of an electron imaging system, sufficient control over the beam path is possible for TEM operation. The optical configuration of a TEM can be rapidly changed, unlike that for an optical microscope, as lenses in the beam path can be enabled, have their strength changed, or be disabled entirely simply via rapid electrical switching, the speed of which is limited by effects such as the magnetic hysteresis of the lenses (Wikipedia (2012b)). Tem image of transmission electron microscope is shown in Fig. 2.2.
2.3 Transmission Electron Microscope

Figure 2.2: Transmission Electron Microscope (TEM).
2.4 Field Emission Electron Microscope

The scanning electron microscope (SEM) permits the observation and characterization of heterogeneous organic and inorganic materials on a nanometer to micrometer scale. SEM can be used for a wide variety of materials for obtaining three-dimensional-like images of their surfaces. The major use of SEM is to obtain topographic images in the magnification range of 10-10000×.

In SEM, the finely focused electron beam is allowed to fall on the area to be examined, either it swept in a raster across the surface of the specimen to form images or may be static to obtain an analysis at one position. During interaction of the electron beam with the sample, the signals produced are: secondary electrons, backscattered electrons, characteristic x-rays and other photons of various energies. These signals can be used to examine surface topography, crystallography, composition etc. Among these signals secondary and backscattered electrons are more important for the imaging signals because these vary primarily as a result of differences in surface topography. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signal results from the interactions of the electron beam with atoms at or near the surface of the sample. The scanning electron microscope is one of the most useful instruments available for the examination and analysis of the microstructural characteristics of solid objects. SEM can produce very high resolution images of a sample surface, it can obtain the details about 1-5 nm (Goldstein (2003)).

Another major feature of the SEM is the depth of field, which is responsible for the three dimensional appearance of the specimen image. The greater depth of field of the SEM provides much more information about the specimen. Usually in SEM electron source uses high temperature to enable the electrons in the cathode to overcome the work function energy barrier. These thermionic sources are relatively inexpensive and need no special vacuum, but have the limitations of low brightness, limited lifetime and large energy spread. Field emission is an alternative way of generating electrons which is free from these limitations (Goldstein (2003)).

The field emission cathode is usually a wire fashioned into a sharp point and supported by a tungsten hairpin. Negative potential is applied to the cathode so that electric field can concentrate at the tip. When the electric field at the tip reaches a magnitude of about 10 V/nm, the potential barrier is lowered in height and also becomes so narrow that the electrons can “tunnel” directly through it.
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and leave the cathode. Tungsten as a cathode is strong enough to withstand the high mechanical stress produced on the tip by the electric field, but carbon and silicon nanotubes have also been employed successfully. A cathode current density of as high as $10^5$ A/cm$^2$ may be obtained from a field emitter as compared with about 3 A/cm$^2$ from a thermionic source (Goldstein (2003)).

Field emission gun may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide. The electron beam having energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot of about 0.4 nm to 5 nm in diameter. The beam passes through the pairs of scanning coils or pairs of deflector plates in the electron column, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within the teardrop shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron’s landing energy, the atomic number of the specimen and the specimen’s density. The energy exchange between the electron beam and the sample results in the reflection of high energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines it is digitally captured and displayed on a computer monitor and saved to a computer’s hard disc (Wikipedia (2012a)). The image of field emission electron microscope is shown in Fig. 2.3.
Figure 2.3: Field Emission Scanning Electron Microscope.
2.5 Sensor Fabrication

Following procedure was followed to fabricate thick film sensors. A pinch (2-3 mg) of ZnO powder was mixed properly with two drops of distilled water to make a paste. The paste was painted with a fine brush onto an alumina substrate (12 mm×5 mm size) having pre-deposited gold electrical contacts to obtain a thick film of thickness around 25-27 µm. For deposition of gold contacts, liquid bright gold (manufactured by Hobby Colorobbia Bright Gold) was painted with brush on alumina substrates leaving a 2 mm gap in the middle which followed heat treatment to convert the paint into metallic gold. To obtain sensors of identical geometry, alumina substrates were appropriately masked using commercially available cellulose tape and after painting them with sensing material, extra wet material was removed. No material as a binder was used since, fine particles of zinc oxide were “self-binding”. The sensor design is shown in Fig. 2.4. Above procedure was followed to fabricate the sensor for each powder, which followed curing at 350°C for 30 min.

Figure 2.4: Schematic of gas sensor.
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2.6 Gas Sensing Unit and Data Acquisition System

The measurements of gas sensor response were carried out with a home built apparatus consisting of a simple potentiometer arrangement, a 40 L test chamber in which a sample holder, a small temperature controlled oven and a circulating fan were installed. For monitoring ambient moisture a humidity meter has been placed inside the testing chamber to operate all the samples under similar conditions. Schematic of testing chamber is shown in Fig. 2.5(a). I have checked all samples at about 20% humidity. Fabricated sensor was placed in the test chamber oven at a desired temperature and a known quantity of alcohol species (e.g. 25 µL of ethanol gives 250 ppm in 40 L chamber) was injected into test chamber using Hamilton syringe. Due to small quantity of VOC, it instantaneously vapourizes and mixes with air in the chamber. After keeping it in the chamber for about 40 s, the mixture is allowed to exhaust out of lab through chamber door. The chamber door is kept open for 30 min to replenish the lost oxygen on the sensor surface and recovery of sensor resistance to the base value. Variation of real time voltage signal across the resistance connected in series with the sensor, was recorded with an experimental set up consisting of Keithley Data Acquisition Module KUSB-3100 shown in Fig. 2.5(b). The image of the sensor testing chamber is shown in Fig. 2.6. The sensor response magnitude was determined as Ra/Rg ratio, where Ra and Rg are the resistances of sensor in air ambiance and air-gas mixture, respectively. Figure 2.7 shows the response and recovery time of any gas sensor. The response time is defined as the time required for the conductance to reach 90% of the equilibrium value after test gas is injected. The recovery time is the time necessary for the sensor to attain a conductance 10% above the original value in air. All the sensors were tested three times by following same procedure by varying temperature from 250 to 450°C with 50°C intervals.

Gas sensing mechanism is based on the principal that, the interaction of ethanol vapour with the surface of semiconducting oxide brings about the change in material resistance. This change in resistance is termed as the gas sensing response of the sensor.
2.6 Gas Sensing Unit and Data Acquisition System

Figure 2.5: Schematic of (a) Testing Chamber and (b) Data Acquisition System.

Figure 2.6: Image of sensors testing chamber.
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Figure 2.7: Response and recovery time.

2.6.1 ppm Calculations

In order to calculate the ppm of the known volume of ethanol following calculations have been made:
Volume of chamber = 40 L
Molecular weight of ethanol = 46
Let 0.025 ml of ethanol has been injected into the chamber
Density of ethanol = 0.8 g/ml
At NTP volume of ethanol becomes = Mol. Wt./Density
\[ \frac{46}{0.8} = 57.5 \text{ ml} \]
If 57.5 ml of ethanol has number of molecules = \(6.023 \times 10^{23}\)
Then 1 ml of ethanol has number of molecules = \(\frac{6.023 \times 10^{23}}{57.5}\)
Therefore, 0.025 ml of ethanol has number of molecules = \(\frac{6.023 \times 10^{23}}{57.5} \times 0.025 = 2.61 \times 10^{20}\) molecules

For 40 L chamber containing air,
If 22.4 L at NTP has number of molecules = \(6.023 \times 10^{23}\)
Then 1 L at NTP has number of molecules = \(\frac{6.023 \times 10^{23}}{22.4}\)
Therefore 40 L at NTP has number of molecules = \(\frac{6.023 \times 10^{23}}{22.4} \times 40\)
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Then 40 L chamber has $10^{24}$ molecules of air
Now $2.61 \times 10^{20}$ molecules of ethanol will become ppm in the $10^{24}$ molecules of air

\[ \frac{2.61 \times 10^{20}}{10^{24}} \times 10^6 \]

\[ = 261 \text{ ppm} \]

Hence 0.025 ml of ethanol would become 261 ppm in the 40 L chamber.