Chapter 3

Analytical techniques employed for characterization

3.1 Swift heavy ion irradiation
3.2 Structural Characterisation Techniques
3.3 Composition
3.4 Magnetic measurements

Ever since optical microscopy enabled the first scientific study of phase transformation in metals and steels, the role of characterisation and importance of various characterisation tools is increasingly being felt in the realm of materials science. The advent of nanotechnology really boosted the use of various analytical tools for characterisation and tools like AFM, MFM, XPS and HRTEM thus have become household names. It is very essential that a proper understanding of the working principle of various tools is necessary and this chapter takes a look at some of the analytical tools employed for characterising samples at various stages.

3.1 Swift Heavy Ion Irradiation

The 15 UD Pelletron of Inter University Accelerator Centre, New Delhi, India was used for the ion beam irradiation experiment in the present study. It is a versatile, heavy ion tandem type electrostatic accelerator. In this machine, negative ions are produced and pre-accelerated to 300 KeV in Ion sources. Source of negative ions by caesium sputtering (SNICS) is a widely used source for negative ions. The negative ions are then injected into a strong electrical field inside an accelerator tank filled with sulphur hexafluoride insulating gas. At the centre of the tank there is a terminal shell,
which is maintained at a high voltage (~ 15 MV). The negative ions on traversing through the accelerating tubes from the top of the tank to the positive terminal get accelerated. On reaching the terminal, they pass through a stripper, which removes some electrons from the negative ions, thus transforming the negative ions into positive ions.

![Fig.3.1 Schematic showing the principle of acceleration of ions in Pelletron](image)

These positive ions are then repelled away from the positively charged terminal and are accelerated to ground potential to the bottom of the tank. In this manner, same terminal potential is used twice to accelerate the ions. After coming out from the tank, the ions are bend into horizontal plane by an analyzing magnet, which also selects a particular beam of ion. The switching magnet diverts the high energy ion beams into various beam lines for the different experimental areas of the beam hall.
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The entire machine is computer controlled and is operated from the control room. These ions are accelerated to high vacuum chamber in the materials science beam hall, where the samples are loaded in the sample holder, made of thick block of copper. The pressure in the chamber is maintained at $1 \times 10^{-6}$ Torr during the irradiation. A schematic of the Pelletron accelerator at IUAC, New Delhi is shown in figure 3.1. Further experimental details of ion beam irradiation are included in chapter 6.

3.2 Structural characterization techniques

3.2.1 Glancing angle x-ray diffraction (GAXRD)

It is sometimes very difficult to analyze thin films due to their small diffracting volumes, which result in low diffracted intensities compared to the substrate and background. This combination of low diffracted signal and high background make it very difficult to identify the phases present. So, special techniques must be employed when analyzing thin films. The most common technique for analyzing thin films as thin as 100 Å is to use a grazing incidence angle arrangement. Glancing angle diffraction techniques are used when the information needed lies within a thin top layer of the material [72]. Figure 3.2 shows Seemann-Bohlin parafocusing geometry which is commonly used in the study of thin films.

For the Seemann-Bohlin geometry (Figure 3.2) the incident X rays impinge on a fixed specimen at a small angle, $\gamma_G$ (typically $1^\circ$ to $3^\circ$) and the diffracted X rays are recorded by a detector that moves along the focusing circle. This method provides good sensitivity for thin films, due to parafocusing and the large diffracting volume, which results from $\gamma_G$ being small and the X-ray path length in the film being large (proportional to $1/\sin \gamma_G$). By increasing the path length of the incident X-ray beam through the film, the intensity from the film can be increased, while at the same time, the diffracted intensity from the substrate can be reduced. Overall, there is a dramatic increase in the film signal to the background ratio. Since the path length increases when the grazing incidence angle is used, the diffracting volume increases.
proportionally. This is the reason for the increased signal strength. During the collection of the diffraction spectrum, only the detector rotates through the angular range, thus keeping the incident angle, the beam path length, and the irradiated area constant.

Fig. 3.2 Seemann-Bohlin diffractometer. The point F is either the focal point on an x-ray tube or the focal point of a focusing monochromator.

3.2.2 Electron Microscopy

An electron microscope is employed to magnify things on a fine scale. Electron microscopes use a beam of electrons to illuminate a specimen and create a highly-magnified image. They have much greater resolving power than light microscopes. Both electron and light microscopes have resolution limitations, imposed
by the wavelength of the radiation they use. The greater resolution and magnification of the electron microscope is because the de Broglie wavelength of an electron is much smaller than that of a photon of visible light. The electron microscope uses electrostatic and electromagnetic lenses in forming the image by controlling the electron beam to focus it at a specific plane relative to the specimen. This is analogous to a light microscope using glass lenses to focus light on or through a specimen to form an image.

3.2.2.1 Scanning Electron Microscopy

**Operation**

In SEM, a source of electrons is focused in vacuum into a fine probe that is rastered over the surface of the specimen. The electron beam passes through scan coils and objective lens that deflect the beam horizontally and vertically so that the beam scans the surface of the sample (Figure 3.3). As the electrons penetrate the surface, a number of interactions occur that can result in the emission of electrons or photons from or through the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose x- and y- inputs are driven in synchronism with the x-y voltages rastering the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen [72]. As a result, the magnification system is simple and linear magnification is calculated by the equation:

\[ M = \frac{L}{l} \]

where \( L \) is the raster’s length of the CRT monitor and \( l \) the raster’s length on the surface of the sample. SEM works on a voltage between 2 to 50 kV and its beam diameter that scans the specimen is 5nm-2µm. The principle images produced in SEM are of three types: secondary electron images, backscattered electron images and elemental X-ray maps. Secondary and backscattered electrons are conventionally
separated according to their energies. When the energy of the emitted electron is less than about 50 eV, it is referred to as a secondary electron and backscattered electrons are considered to be the electrons that exit the specimen with an energy greater than 50 eV [73]. Detectors of each type of electrons are placed in the microscope in proper positions to collect them.

3.2.2.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen [72]. The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses. The geometry of TEM is shown in figure 3.4. The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture
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and “hits” the sample surface. The electrons that are elastically scattered consists of the transmitted beams, which pass through the objective lens. The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose the elastically scattered electrons that will form the image of the microscope. Finally, the beam goes to the magnifying system that consists of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens. The formed image is shown either on a fluorescent screen or in monitor or both and is printed on a photographic film.

**Operation**

The operation of TEM requires an ultra high vacuum and a high voltage. TEM offers two methods of specimen observation, diffraction mode and image mode. In diffraction mode, an electron diffraction pattern is obtained on the fluorescent screen, originating from the sample area illuminated by the electron beam. The diffraction pattern is entirely equivalent to an X-ray diffraction pattern: a single crystal will produce a spot pattern on the screen, a polycrystal will produce a powder or ring pattern (assuming the illuminated area includes a sufficient quantity of crystallites), and a glassy or amorphous material will produce a series of diffuse halos. The image mode produces an image of the illuminated sample area. The image can contain contrast brought about by several mechanisms: mass contrast, due to spatial separations between distinct atomic constituents; thickness contrast, due to non uniformity in sample thickness; diffraction contrast, which in the case of crystalline materials results from scattering of the incident electron wave by structural defects; and phase contrast. If the unscattered beam is selected for image formation, one obtains the Bright Field Image. Dark Field Images are attained if diffracted beams are selected by the objective aperture. Also in TEM, analysis can be done with EDS (Energy Dispersive X-ray spectroscopy), EELS (Electron Energy Loss Spectrum) and EFTEM (Energy Filtered Transmission Electron Microscopy) data.
3.2.3 Atomic Force Microscopy

The Atomic Force Microscope was developed to overcome a basic drawback of the STM (scanning tunneling microscope) - that it can only image conducting or semi-conducting surfaces. The AFM, however, has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples. Binnig, Quate, and Gerber invented the Atomic Force Microscope in 1985 [74]. Their original AFM consisted of a diamond tip attached to a strip of gold foil. The diamond tip contacted the surface directly, with the interatomic van der Waals forces providing the interaction mechanism. Detection of the cantilever’s vertical movement was done using a second tip - an STM placed above the cantilever.
**AFM probe deflection**

Today, most AFMs use a laser beam deflection system, introduced by Meyer and Amer, where a laser is reflected from the back of the reflective AFM lever and onto a position-sensitive detector (figure 3.5). AFM tips and cantilevers are microfabricated from Si or Si$_3$N$_4$. Typical tip radius is from a few to 10s of nm [77].

![Beam deflection system](image)

**Fig.3.5** Beam deflection system, using a laser and photo detector to measure the beam position.

**Measuring forces**

Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook’s law gives $F = -kz$, where $F$ is the force, $k$ is the stiffness of the lever, and $z$ is the distance the lever is bent. Figure 3.6 depicts the force–distance curve which shows the different forces that an AFM tip can experience from a sample.

**AFM Modes of Operation**

Because of AFM’s versatility, it has been applied to a large number of research topics. The Atomic Force Microscope has also gone through many modifications for specific application requirements.
Contact-mode

The first and foremost mode of operation, contact mode is widely used. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height above the surface. It is this adjustment that is displayed as data. However, the ability to track the surface in this manner is limited by the feedback circuit. Sometimes the tip is allowed to scan without this adjustment, and one measures only the deflection. This is useful for small, high-speed atomic resolution scans, and is known as variable-deflection mode.

![Fig.3.6 Force-distance curve](image)

Because the tip is in hard contact with the surface, the stiffness of the lever needs to be less that the effective spring constant holding atoms together, which is on the order of 1 - 10 nN/nm. Most contact mode levers have a spring constant of < 1N/m.

Non-contact Mode

Noncontact mode belongs to a family of AC modes, which refers to the use of an oscillating cantilever. A stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it (hence, “noncontact”). The
forces between the tip and sample are quite low, on the order of pN ($10^{-12}$ N). The detection scheme is based on measuring changes in the resonant frequency or amplitude of the cantilever.

**Dynamic Force / Intermittent-contact / “tapping mode” AFM**

Commonly referred to as “tapping mode” it is also referred to as intermittent-contact or the more general term Dynamic Force Mode (DFM).

A stiff cantilever is oscillated closer to the sample than in noncontact mode. Part of the oscillation extends into the repulsive regime, so the tip intermittently touches or “taps” the surface. Very stiff cantilevers are typically used, as tips can get “stuck” in the water contamination layer.

The advantage of tapping the surface is improved lateral resolution on soft samples. Lateral forces such as drag, common in contact mode, are virtually eliminated.

**AFM Instrumentation**

Figure 3.7 shows a schematic of the atomic force microscope. The important components are:

(Z) Coarse Z motion translator- This translator moves the AFM head towards the surface so that the force sensor can measure the force between the probe and sample. The motion of the translator is usually about 10 mm.

(T) Coarse X-Y translation stage - The XY translation stage is used to place the section of the sample that is being imaged by the AFM directly under the probe.

(X-P) X and Y piezoelectric transducer - With the X and Y piezoelectric transducer the (Y-P) probe is moved over the surface in a raster motion when an AFM image is measured.

(FS) Force Sensor - The force sensor measures the force between the probe and the sample by monitoring the deflection of a cantilever.

(ZP) Z piezoelectric Ceramic - Moves the force sensor in the vertical direction to the surface as the probe is scanned with the X and Y piezoelectric transducers.
(FCU) Feedback control unit - The feedback control unit receives the signal from the light lever force sensor and outputs the voltage that drives the Z piezoelectric ceramic. This voltage refers to the voltage that is required to maintain a constant deflection of the cantilever while scanning.

(SG) X-Y signal generator - The motion of the probe in the X-Y plane is controlled by the X-Y signal generator. A raster motion is used when an image is measured.

(CPU) Computer - The computer is used for setting the scanning parameters such as scan size, scan speed, feedback control response and visualizing images captured with the microscope.

(F) Frame - A solid frame supports the entire AFM microscope. The frame must be very rigid so that it does not allow vibrations between the tip and the surface.

**Fig.3.7** Schematic of components and subsystems of an atomic force microscope system
Resolution in an Atomic Force Microscope

Traditional microscopes have only one measure of resolution; the resolution in the plane of an image. An atomic force microscope has two measures of resolution; the plane of the measurement and in the direction perpendicular to the surface [75].

**In Plane Resolution:** The in-plane resolution depends on the geometry of the probe that is used for scanning. In general, the sharper the probe the higher will be the resolution of the AFM image.

**Vertical Resolution:** The vertical resolution in an AFM is established by relative vibrations of the probe above the surface. Sources for vibrations are acoustic noise, floor vibrations, and thermal vibrations. Getting the maximum vertical resolution requires minimizing the vibrations of the instrument.

### 3.2.4 Magnetic Force Microscopy (MFM)

Magnetic force microscopy detects the force (or force derivative) acting on a small magnetic probe in the stray field close to the specimen [81]. The technique can give a resolution below 20 nm with comparable low effort in sample preparation. It does not need ultra clean sample surfaces and ultra high vacuum. Also magnetic fields can be applied to the specimen during measurements.

MFM consists of a cantilever which is suspended on one side. On the free end a small volume of magnetic material, the tip is mounted. When a magnetic surface is brought close to this tip they will interact by the magnetic stray field. Magnetic force microscopy is a non-contact technique and during scanning, the sample is kept at a distance of several nanometers from the tip. The interaction between tip and sample can be measured by a detector which is placed on the back side of the cantilever. When the sample is moved with respect to the tip a one dimensional array of interaction data is put into computer and stored there. The direction of this motion is called the fast scan direction. A number of parallel scan lines will form a two-
dimensional array of data in the computer. The direction of the offset between these lines is called the slow scan direction. A computer assigns grey-or colour values to different strengths of interaction forming a microscopic image of interaction on the sample surface.

In a MFM two basic detection modes can be applied which are sensitive to two different types of interaction. The static (or DC) mode detects the magnetic force acting on the tip whereas the dynamic (or AC) mode measures the force derivative.

**Static mode**

According to Hooke’s law the displacement $\Delta z$ of the cantilever is proportional to the force that it exerts on the tip.

$$F = -c\Delta z \text{ (N)}$$  \hspace{1cm} 3.1

The proportionality constant $c$ is called the cantilever constant. In this mode the cantilever is used to translate the force acting on the tip to a displacement which can be measured by the detector. The detector signal and thus the magnetic image will be a direct measure of the force acting on the cantilever.

**Dynamic mode**

In the dynamic mode the cantilever is oscillated at or close to its resonance frequency. The cantilever can be treated as a harmonic oscillator having the resonance frequency $f$ which is given by

$$f = \frac{1}{2\pi} \sqrt{\frac{c_{\text{eff}}}{m}} \text{ (Hz)}$$  \hspace{1cm} 3.2

with ‘m’ the effective mass of tip and cantilever. The effective cantilever constant $c_{\text{eff}}$ consists of two contributions

$$c_{\text{eff}} = c - \frac{\partial F}{\partial z} \text{ (N/m)}, \text{ where ‘c’ is the cantilever constant.}$$  \hspace{1cm} 3.3
In the close proximity of the sample, the forces acting on the magnetic tip change when the distance between the tip and sample is changed. This can be described by a force derivative $\frac{\partial F}{\partial z}$. This force derivative on the tip acts on the cantilever just like an additional cantilever constant. Note that in case of a large cantilever oscillation amplitude the force derivative will not be constant over one period, resulting in a non-harmonic oscillation. For low amplitudes, however a constant $\frac{\partial F}{\partial z}$ can be assumed so that the problem can still be treated as a harmonic oscillator:

$$f = \frac{1}{2\pi} \sqrt{\frac{c - \frac{\partial F}{\partial z}}{m}} \text{ (Hz)}$$  \hspace{1cm} (3.4)

From this it can be shown that a force derivative $\frac{\partial F}{\partial z}$ changes the cantilever resonant frequency to

$$f = f_0 \sqrt{1 - \frac{\partial F}{c \partial z}} \text{ (Hz)}$$  \hspace{1cm} (3.5)

with $f_0$, the free resonance frequency of the cantilever in the case of no tip-sample interaction.

The cantilever is oscillated directly at its resonance frequency $f$ using a feedback amplifier with amplitude control. The change in resonance frequency can be directly detected by FM demodulation techniques.

During the MFM measurements, there are two forces acting on the tip; magnetic and Van der Waals forces. Hence, in MFM, the signal contains both information of surface topography (called ‘Topo signal’) and surface magnetic property (called ‘MFM signal’) generated by Van der Waals and magnetic forces, respectively. The dominating force depends on the distance between the tip and the sample surface, because the inter-atomic magnetic force persists for greater tip-to-sample separations than the van der Waals force. These van der Waals forces vary according to the tip-sample distance and therefore are used to measure the surface
topography. If the tip is close to the surface, in the region where standard Non-Contact AFM is operated, the image will be predominantly topographic. As one increase the separation between the tip and the sample, magnetic effects become apparent. Collecting a series of images at different tip heights is one way to separate magnetic from topographic effects.

The key to successful MFM imaging lies in separating the magnetic signal from the entire signal. In MFM, this is done by ‘Two Pass’ technique. In this MFM mode, sample is scanned twice to separate the signal. In the first scan, the tip scans the surface as in True Non-Contact AFM to obtain the topography of the sample. In the second scan, the tip-sample distance is increased and the biased tip is scanned along the topography line obtained from the first scan. The tip is only affected by the magnetic force and MFM image is obtained as a result.

The topographical line maintains constant tip sample distance, which equals the line of the constant van der Waals force. So, when the tip follows the topography line in the second scan of 'MFM mode', the van der Waals forces acting on the tip are kept constant. Thus, the only change in force affecting the signal is the change of the magnetic force. So, from the second scan, the MFM image, free of topography signal, can be obtained.

**3.2.5 Scanning Tunneling Microscopy**

The scanning tunneling microscope (STM) was invented by Binnig and Rohrer and implemented by Binnig, Rohrer, Gerber, and Weibel. Figure 3.8 shows its essential elements.

A probe tip, usually made of W or Pt-Ir alloy, is attached to a piezodrive, which consists of three mutually perpendicular piezoelectric transducers: x piezo, y piezo, and z piezo. Upon applying a voltage, a piezoelectric transducer expands or contracts. By applying a sawtooth voltage on the x piezo and a voltage ramp on the y piezo, the tip scans on the xy plane. Using the coarse positioner and the z piezo, the
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Tip and the sample are brought to within a fraction of a nanometer each other. The electron wave functions in the tip overlap electron wave functions in the sample surface. A finite tunnelling conductance is generated [76].

By applying a bias voltage between the tip and the sample, a tunneling current is generated. The most widely used convention of the polarity of bias voltage is that the tip is virtually grounded. The bias voltage $V$ is the sample voltage. If $V > 0$, the electrons are tunneling from the occupied states of the tip into the empty states of the sample. If $V < 0$, the electrons are tunneling from the occupied states of the sample into the empty states of the tip. The tunneling current is converted to a voltage by the current amplifier, which is then compared with a reference value. The difference is amplified to drive the $z$ piezo.

Fig.3.8 Schematic of a STM instrument
The phase of the amplifier is chosen to provide a negative feedback: if the absolute value of the tunneling current is larger than the reference value, then the voltage applied to the $z$ piezo tends to withdraw the tip from the sample surface, and vice versa. Therefore, an equilibrium $z$ position is established. As the tip scans over the $xy$ plane, a two-dimensional array of equilibrium $z$ positions, representing a contour plot of the equal tunneling-current surface, is obtained, displayed, and stored in the computer memory. The topography of the surface is displayed on a computer screen, typically as a gray-scale image. Usually, the bright spots represent high $z$ values (protrusions), and the dark spots represent low $z$ values (depressions). The $z$ values corresponding to the gray levels are indicated by a scale bar. To achieve atomic resolution, vibration isolation is essential. This is achieved by making the STM unit as rigid as possible, and by reducing the influence of environmental vibration to the STM unit [77]

**Modes of Operation**

**Constant Current Mode**

By using a feedback loop the tip is vertically adjusted in such a way that the current always stays constant. As the current is proportional to the local density of states, the tip follows a contour of a constant density of states during scanning. A kind of a topographic image of the surface is generated by recording the vertical position of the tip.

**Constant Height Mode**

In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The current as a function of lateral position represents the surface image. This mode is only appropriate for atomically flat surfaces as otherwise a tip crash would be inevitable. One of its advantages is that it can be used at high
scanning frequencies (up to 10 kHz). In comparison, the scanning frequency in the constant current mode is about 1 image per second or even per several minutes.

3.3 Composition

3.3.1 Energy dispersive x-ray spectroscopy

Photons of X-radiation with wavelength and energy characteristic of the elements in the specimen are emitted under electron bombardment in all forms of electron microscope. The spectrum of radiation can thus be used for elemental identification, using forms of x-ray spectroscopy based on either wavelength or energy (known as wavelength dispersive or energy dispersive x-ray spectroscopy) [73].

![Diagram of electron transitions](image)

**Fig.3.9** Schematic of electron transitions responsible for the production of (a) $K\alpha, K\beta$ and (b) $L\alpha$ and $L\beta$ x-rays.

An inelastic collision between a K shell electron and a primary electron with energy greater than the binding energy of the K shell electron can result in the ejection of a core electron from the atom. The resulting vacancy in the K shell can be filled by an electron from one of the higher energy shells, L, M, etc. The excess energy of this electron, that is the difference between the energy states in the two shells, is irradiated during the transition as a x-ray photon. Thus the energy of the K x-radiation equals
EL-EK if the transition is between L, K shells and EM-EK if it is between M, K shells. The former is designated as $K\alpha$ radiation and later as $K\beta$. A similar situation exists with respect to electrons in the L shell. The energy of the L x-radiation equals EM-EL if the transition is between M, L shells and EN-EL if it is between N, L shells. The former is designated as $L\alpha$ radiation and later as $L\beta$. Figure 3.9 shows a schematic of the electron transitions responsible for the production of $K\alpha$, $K\beta$, $L\alpha$, and $L\beta$ x-rays. Every atom species has, therefore, a characteristic x-ray emission spectrum which can be excited by supplying energy equal to or in excess of the appropriate binding energy, by electron bombardment. The characteristic line spectrum forms the ‘fingerprint’ of the different atomic species. Since the actual energy levels depend on the atomic number of the elements, it follows, therefore, that the elements present in a specimen can be identified by analysis of the emission spectrum. The characteristic lines are superimposed on a background continuum (Bremsstrahlung continuum).

The technique uses a semiconductor detector to classify x-radiation according to energy. The EDS x-ray detector measures the relative abundance of emitted x-rays versus their energy. The detector is a single crystal disc of lithium-drifted silicon [Si(Li)] or high purity germanium [HPGe] having 3-5 mm thickness and with an active area between 10 and 30 mm$^2$. When an incident x-ray strikes the detector, it creates a charge pulse that is proportional to the energy of the x-ray. The charge pulse is converted to a voltage pulse (which remains proportional to the x-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The analyzer may have 1000 channels each 10, 20, 40 or 80 eV wide, so that the total energy range covered by the analysis would be 10, 20, 40 or 80 keV, respectively. Thus ED spectrometer is able to analyze a whole spectrum simultaneously. The spectrum of x-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.
Analytical Information

**Qualitative Analysis** - The sample x-ray energy values from the EDS spectrum are compared with known characteristic x-ray energy values to determine the presence of an element in the sample. Elements with atomic numbers ranging from that of beryllium to uranium can be detected. The minimum detection limits vary from approximately 0.1 to a few atom percent, depending on the element and the sample matrix.

**Quantitative Analysis** - Quantitative results can be obtained from the relative x-ray counts at the characteristic energy levels for the sample constituents. Semi-quantitative results are readily available without standards by using mathematical corrections based on the analysis parameters and the sample composition. The accuracy of standard less analysis depends on the sample composition. Greater accuracy is obtained using known standards with similar structure and composition to that of the unknown sample.

**Elemental Mapping** - Characteristic x-ray intensity is measured relative to lateral position on the sample. Variations in x-ray intensity at any characteristic energy value indicate the relative concentration for the applicable element across the surface. One or more maps are recorded simultaneously using image brightness intensity as a function of the local relative concentration of the element(s) present. About 1 \( \mu \)m lateral resolution is possible.

**Line Profile Analysis** - The SEM electron beam is scanned along a pre-selected line across the sample while x-rays are detected for discrete positions along the line. Analysis of the x-ray energy spectrum at each position provides plots of the relative elemental concentration for each element versus position along the line.
3.3.2 X-Ray Photoelectron Spectroscopy

The detection and energy analysis of photoelectrons produced by radiation whose energy exceeds their binding energies is the subject of an extensively used technique known as photoelectron (PE) spectroscopy. This technique can be conveniently divided into two broad areas, the first employing ultraviolet radiation, hence called ultraviolet photoelectron spectroscopy (UPS) and the second using X-rays, termed X-ray photoelectron spectroscopy (XPS).

Figure 3.10 (a&b) shows a schematic of the process involved in the emission of a photo – or auger electron. XPS involves the removal of a single core electron, while AES is a two electron process subsequent to the removal of the core electron. Auger electrons are produced in XPS along with photoelectrons.

In XPS the sample is irradiated with x-rays of known energy, $h \nu$ and electrons of binding energy (BE) $E_b$ are ejected, where $E_b < h \nu$. These electrons have a kinetic energy (KE) $E_k$ which can be measured in the spectrometer, and is given by [78, 79]

$$E_k = h \nu - E_b - \Phi_{sp}$$  \hspace{1cm} (3.6)
where $\Phi_{sp}$ is the spectrometer work function, and is the combination of sample work function, $\Phi_s$, and the work function induced by the analyzer. Since we can compensate for the work function term electronically, it can be eliminated, leaving

$$E_k = h\nu - E_b$$  \hspace{1cm} (3.7)

or

$$E_b = h\nu - E_k$$  \hspace{1cm} (3.8)

Fig. 3.10 (b) Process involved in Auger electron emission

Thus by measuring the KE of the photoelectrons we can determine the BE of the electrons. An XP spectrum is generated by plotting the measured photoelectron intensity as a function of BE. The resulting series of lines are superimposed on a background caused by the Bremsstrahlung radiation inherent in non-monochromatic X-ray sources. The BEs of these lines is characteristic for each element, and is a direct representation of the atomic orbital energies.

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon the formal oxidation state of the atom and the local chemical and physical environment. Changes in either of the above will give rise to small shifts in the peak positions in the spectrum - so-called chemical
shifts. Such shifts are readily observable and interpretable in XP spectra because the technique is of high intrinsic resolution (as core levels are discrete and generally of a well-defined energy) and is a one electron process (thus simplifying the interpretation). Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photo-emitted electron and the ion core. This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.

XPS is a surface sensitive technique and the surface sensitivity of XPS is due to the low inelastic mean-free path, $\lambda_m$ of the electrons within the sample. For XPS, the main region of interest relates to electron energies from 100-1200 eV, which gives rise to a $\lambda_m$ value of 0.5 to 2 nm. However the actual escape depth $\lambda$ of the photoelectrons depends on the direction in which they are traveling within the sample, such that

$$\lambda = \lambda_m \cos \theta$$

where $\theta$ is the angle of emission to the surface normal. Thus electrons emitted perpendicular to the surface ($\theta = 0^\circ$) will arise from the maximum escape depth, whereas electrons emitted nearly parallel to the surface ($\theta = 90^\circ$) will be purely from the outermost surface layers.

The basic requirements for a photoemission experiment (XPS or UPS) are:

1. A source of fixed-energy radiation (an x-ray source for XPS or, typically, a He discharge lamp for UPS).
2. An electron energy analyzer (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy).
3. A high vacuum environment (to enable the emitted photoelectrons to be analyzed without interference from gas phase collisions).
Analytical techniques employed for characterisation

Such a system is illustrated schematically in figure 3.11

There are many different designs of electron energy analyzer but the preferred option for photoemission experiments is a concentric hemispherical analyzer (CHA) which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy.

![Schematic of XPS system](Fig.3.11 Schematic of XPS system)

3.4 Magnetic measurements

3.4.1 Vibrating sample magnetometer

The magnetic characterization of the samples was carried out using a Vibrating Sample Magnetometer (VSM), model: DMS 1660. The main parts of a VSM and the simplified block diagram are given in figure 3.12 and 3.13. Saturation magnetization ($M_s$), Retentivity ($M_r$) and Coercivity ($H_c$) were evaluated from the hysteresis loops.
The magnetic samples are kept in the sample holder, which is centered in the region between the pole pieces of an electromagnet. A slender vertical sample rod connects the sample holder with a transducer assembly located above the magnet. The transducer converts a sinusoidal ac drive signal into a sinusoidal vertical vibration of the sample rod and the sample thus made to undergo sinusoidal motion in a uniform magnetic field. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion. This ac signal at the vibrating frequency is proportional to the magnitude of the moment induced in the sample. Thus, the pick up coil output accurately gives an account of the moment level of the sample.

![Fig.3.12 Main Parts of VSM](image)

Vibrating sample magnetometry is employed to determine the magnetization of the samples synthesized. When a magnetic material is placed in a uniform magnetic field, a dipole moment is induced which is proportional to the susceptibility of the
sample and the applied field. If the sample is vibrated periodically then it can induce an electrical signal in a pickup coil. The position of the pickup coil is adjusted in such a way as to give the maximum induction without much noise. The induced signal in the pickup coil will be proportional to the magnetic moment produced in the sample and the vibrating frequency of the sample [80].

![Block Diagram of VSM](image)

**Fig.3.13** Block Diagram of VSM.

This is the basic principle used in the design of a VSM to measure the magnetic properties. The material under study is loaded in the sample holder, and it is placed at the centre region of the pole pieces of a laboratory electromagnet. A slender vertical sample rod connects the sample holder with a transducer assembly located above the magnet, which in turn supports the transducer assembly by means of sturdy adjustable support rods.
A transducer is used to convert the electrical oscillations into mechanical vibrations. An electronic oscillator circuit produces a constant frequency and it is fed to the transducer to vibrate the sample rod. The vibrating sample in the uniform magnetic field induces a signal in the pickup coils mounted to it. The strength of the ac signal at the vibrating frequency is proportional to the magnetic moment induced in the sample. However, vibration amplitude and frequency also will have some contributions to the induced emf. A servomechanism is used to stabilize the amplitude and frequency of the drive so that the output accurately tracks the moment level without degradation due to variation in the amplitude and frequency of the oscillator.

This servo technique uses a vibrating capacitor located beneath the transducer to generate an ac control signal that varies solely with the vibration amplitude and frequency. The signal, which is at the vibration frequency, is fed back to the oscillator where it is compared with the drive signal so as to maintain constant drive output. It is also phase adjusted and routed to the signal demodulator where it functions as the reference drive signal. The signal developed in the pick up coils is then buffered, amplified and applied to the demodulator. There it is synchronously demodulated with respect to the reference signal derived from the moving capacitor assembly. The resulting dc output is an analog signal, which depends only on the magnitude of the magnetic moment, and not influenced by the amplitude and frequency drift. The cryogenic setup attached to the sample assembly can be used to study the magnetization of samples at low temperatures.

### 3.4.2 Ferromagnetic Resonance

FMR is a method to measure magnetic properties by detecting the precessional motion of the magnetization in a ferromagnetic sample. It is thus related to the electron paramagnetic resonance technique. From a macroscopic point of view, the applied static magnetic field $H_0$ causes the total
magnetic moment to precess around the direction of the local field $H_{\text{eff}}$, before relaxation processes damp this precession and the magnetization aligns with $H_{\text{eff}}$ (figure 3.14).

If the sample is irradiated with a transverse rf field (microwaves of typically 1–35 GHz), and if the rf frequency coincides with the precessional frequency, the resonance condition is fulfilled and the microwave power is absorbed by the sample.

Fig.3.14 Precessional motion of magnetic moment in an applied magnetic field

The motion of the magnetization is described by the Landau-Lifshitz-Gilbert equation [40]

$$\frac{\partial M}{\partial t} = -\gamma (M \times H_{\text{eff}}) + \frac{G}{\gamma M_s^2} \left[ M \times \frac{\partial M}{\partial t} \right]$$

3.10

The first part corresponds to the precession. The second part introduces a viscous damping (Gilbert damping constant $G$). The effective magnetic field $H_{\text{eff}}$ includes the applied DC field, the rf microwave magnetic field component, the demagnetizing field (shape anisotropy) and the magnetocrystalline anisotropy field. $\gamma$ is the gyromagnetic ratio $\gamma = g \mu \nu B$/$\hbar$. 

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Microscopically, the $H$ field creates a Zeeman splitting of the energy levels, and the microwave excites magnetic dipole transitions between these split levels (figure 3.15). Since it is difficult to vary the microwave frequency over larger ranges, the DC magnetic field $H_0$ is varied instead [82]. Usually the absorption derivative is measured. The resonance signal resembles a Lorentzian line shape (figure 3.16). The resonance field position $H_{\text{res}}$ depends on the angles, anisotropy parameters, $g$-factor, and magnetization of the sample.

The linewidth $\Delta H$ is directly connected to the relaxation processes. In ultra thin films, Gilbert damping is commonly used to describe the relaxation. But several other possible relaxation paths are also known, e.g. two-magnon scattering, spin-pumping effect, etc., which can contribute to the linewidth. The anisotropy constants can be easily deduced from angle dependent measurements of single crystalline samples. For magnetic multilayers, also the interlayer exchange coupling constant can be determined by FMR in absolute units.

![Fig.3.15 Zeeman splitting of energy levels by a magnetic field](image-url)
Analytical techniques employed for characterisation

Fig. 3.16 A typical FMR spectra

Fig. 3.17 Schematic of the experimental set up for FMR measurements
Figure 3.17 shows a schematic of the experimental setup for FMR measurements. The sample is kept under UHV inside a quartz glass finger connected to the UHV chamber. It fits into the microwave cavity. The microwave components and the electromagnet coils are outside the vacuum and therefore conveniently accessible or removable.