CHAPTER – IV

4. CHARACTERIZATION

4.1. Introduction

Materials in the nanometer scale, such as colloidal dispersions and thin films, have been studied over many years and many physical properties related to the nanometer size, such as colouration of gold nano particles, have been known for centuries. One of the current challenge for researchers in the nanotechnology and nano science fields is the inability and the lack of instruments to observe, measure and manipulate the materials at the nanometer level by manifesting at the macroscopic level.

The past studies focused mainly on the collective behaviours and properties of nano structured materials and the properties and behaviours observed and measured are typically group characteristics. A better fundamental understanding and various potential applications increasingly demand the ability and instrumentation to observe, measure and manipulate the individual nanomaterials and nanostructures. Characterization and manipulation of individual nanostructures require extreme sensitivity and accuracy, with atomic-level resolution.

It leads to various microscopies that will play a central role in characterization and measurements of nano structured materials and nanostructures. Miniaturization of instruments, the physical properties and the short-range forces are the challenges faced in characterising the nanophase materials. Nanostructures and Nano materials not playing a noticeable role in macroscopic level characterization may have significant impacts in the nanometer scale. The development of novel tools and instruments is one of the greatest challenges in nanotechnology.
In this chapter, various structural characterization methods that are most widely used in characterizing nanomaterials and nanostructures, are first discussed. These include: X-ray diffraction (XRD), various electron microscopy (EM) including scanning electron microscopy (SEM) and transmission microscopy (TEM) and scanning probe microscopy (SPM). Then some typical chemical characterization techniques are discussed. Examples include optical and electron spectroscopy and ionic spectrometry. Then the relationships between the physical properties of nanomaterials and dimensions are briefly discussed. The physical properties discussed in this chapter include thermal, mechanical, optical, electrical and magnetic properties. The discussion in this chapter is focused mainly on the fundamentals and basic principles of the characterization methods and physical properties.

4.2 Structural Characterization

Characterization of nanomaterials and nanostructures has been largely based on the surface analysis techniques and conventional characterization methods developed for bulk materials. For example, 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; optical spectroscopy is used to determine the size of semiconductor quantum dots. SPM is a relatively new characterization technique and has found widespread applications in nanotechnology.

The two major members of the SPM family are scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Although both STM and AFM are true surface image techniques that can produce topographic images of a surface with atomic resolution in all three
dimensions, combining with appropriately designed attachments, the STM and AFM have found a much broadened range of applications, such as nanoindentation, nanolithography, and patterned self-assembly. Almost all solid surfaces, whether hard or soft, their electrical characterization can be studied with STM and AFM. In the following, we will briefly discuss the aforementioned characterization techniques and their applications in nanotechnology.

4.3 X-ray diffraction (XRD)

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayers, and atomic arrangements in amorphous materials (including polymers) and at interfaces. XRD offers unparalleled accuracy in the measurement of atomic spacings and is the technique of choice for determining strain states in thin films.

XRD is noncontact and nondestructive, which makes it ideal for in situ studies. The intensities measured with XRD can provide quantitative, accurate information on the atomic high-Z elements, since the diffracted intensity from these is much larger than from low-Z elements. As a consequence, the sensitivity of XRD depends on the material of interest. With lab-based equipment, surface sensitivities down to very lowest thickness are achievable, but by synchrotron radiation (because of its higher intensity) all-the characterization of much thinner films, and for many materials, monatomic layers can be analyzed. While the structure as a function of depth is not normally measured in XRD, this is possible using specialized methods.

XRD is important in many technological applications, because of its abilities to accurately determine strains and to uniquely identify, the presence and composition of phases. In
semiconductor and optical materials applications, XRD is used to measure the strain orientation, and defects in epitaxial thin films, which affect the film’s electronic and optical properties. For magnetic thin films, it is used to identify phases and to determine preferred orientations, since these can determine magnetic properties. For packaging materials, XRD can be used to investigate diffusion and phase formation at interfaces. In a typical experiment, the diffracted intensity is measured as a function of 2θ and the orientation of the specimen, which yields the diffraction pattern.

The X-ray wavelength λ is typically 0.7-2 Å, which corresponds to X-ray energies (E = 12.4 keV/A) of 6 ~17 keV. Before considering the conditions for XRD, we will briefly review some important properties of crystalline materials. Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d-spacing. To distinguish between these, we introduce a coordinate system for the crystal whose unit vectors a, b, and c are the edges of the unit cell. For the familiar cubic crystal, these form an orthogonal system. Any atomic plane can now be uniquely distinguished by its Miller indices. These are the three reciprocal intercepts of the plane with the a-, b-, and c-axes and are reduced to the smallest integers having the same ratio.

Thus, an (hkl) plane intercepts the crystallographic axes at a/h, b/k, and c/l when there is constructive interference from X rays scattered by the atomic planes in a crystal, a diffraction peak is observed. The condition for constructive interference from planes with spacing dhH is given by Bragg’s law:

\[ \lambda = 2d_{hkl} \sin \theta_{hkl} \]

where \( \theta_{hkl} \) is the angle between the atomic planes and the incident X-ray beam. For diffraction to be observed, the detector must be positioned so the diffraction angle is 28hu, and
the crystal must be oriented so that the normal to the diffracting plane is coplanar with the incident and diffracted X-rays, so that the angle between the diffracting plane and the incident X-rays is equal to the Bragg angle. For a single crystal or epitaxial thin film, there is only one specimen orientation for each (hkl) plane where these diffraction conditions are satisfied. Crystals may consist of many grains or crystallites (small crystalline regions) having a distribution of orientations. If this distribution is completely random, then diffraction occurs from any crystallite that happens to have the proper orientation to satisfy the diffraction conditions. The diffracted X-rays emerge as cones about the incident beam with an opening angle of $2\theta_{hkl}$ creating a “powder” diffraction pattern.

The Bragg-Brentano geometry \cite{1,2} is used widely for preferentially and randomly oriented polycrystalline materials. In this geometry slits collimate the incident X-rays, which impinge on the specimen at an angle $\theta$. After passing through receiving slits, the diffracted X-rays are detected. The specimen is rotated at one half the angular velocity of the detector. Since the incident and diffracted X-rays make the same angle to the specimen surface, structural information is obtained only about (hkl) planes parallel to this surface. When the receiving slits, the specimen, and the focal point F lie on a circle, the diffracted X-rays are approximately focused on the receiving slitsing), which considerably improves the sensitivity.
4.4 Scanning Electron Microscope (SEM)

The SEM provides the investigator with a highly magnetised image of the surface of a material that is very similar to what one would expect if one could actually "see" the surface visually. This tends to simplify image interpretations considerably, but reliance on intuitive reactions to SEM images can, on occasion, lead to erroneous results. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from about 10—300,000 times. Not only is topographical information produced in the SEM, but information concerning the composition near surface regions of the material is provided as well. In the SEM, a source of electrons is focused (in vacuum) into a fine probe that is rastered over the surface of the specimen.

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.

If the amplitude of the saw-tooth voltage applied to the x- and y-deflection amplifiers in the SEM is reduced by some factor while the CRT saw-tooth voltage is kept fixed at the level necessary to produce a full screen display, the magnification, as viewed on the screen, will be increased by the same factor. The principle images produced in the 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. They are produced by different mechanisms. When a high-energy primary electron interacts with an atom, it undergoes either inelastic scattering with atomic electrons or elastic scattering with the atomic nucleus. In an inelastic collision with an electron, some amount of energy is transferred to the other electron. If the energy transfer is very small, the emitted electron will probably not have enough energy to exit the surface. If the energy transferred exceeds the work function of the material, the emitted electron can exit the solid. When the energy of the emitted electron is less than about 50 eV, by convention it is referred to as a secondary electron (SE), or simply a secondary. Most of the emitted secondaries are produced within the first few nm of the surface. Secondaries produced much deeper in the material suffer additional inelastic collisions, which lower their energy and trap them in the interior of the solid.

Higher energy electrons are primary electrons that have been scattered without loss of kinetic energy (i.e., elastically) by the nucleus of an atom, although these collisions may occur after the primary electron has already lost some of its energy to inelastic scattering. Backscattered electrons (BSEs) are considered to be the electrons that exit the specimen with an
energy greater than 50 eV, including Auger electrons. However most BSEs have energies comparable to the energy of the primary beam. The higher the atomic number of a material, the more likely it is that backscattering will occur. Thus as a beam passes from a low-Z (atomic number) to a high-Z area, the signal due to backscattering, and consequently the image brightness, will increase.

There is a built-in contrast caused by elemental differences. One further breaks down the secondary electron contributions into three groups: SEI, SEII and SEIII. SEIS result from the interaction of the incident beam with the sample at the point of entry. SEIIs are produced by BSEs on exiting the sample. SEIIIs are produced by BSEs which have exited the surface of the sample and further interact with components on the interior of the SEM usually not related to the sample. SEIIs and SEIIIs come from regions far outside that defined by the incident probe and can cause serious degradation of the resolution of the image.
4.5 Transmission Electron Microscope (TEM)

In TEM, a focused electron beam is incident on a thin (less than 200 nm) sample. The signal in TEM is obtained from both undeflected and deflected electrons that penetrate the sample thickness. A series of magnetic lenses at and below the sample position are responsible for delivering the signal to a detector, usually a fluorescent screen, a film plate, or a video camera. Accompanying this signal transmission is a magnification of the spatial information in the signal by as little as 50 times to as much as a factor of 10'.

This remarkable magnification range is facilitated by the small wavelength of the incident electrons, and is the key to the unique capabilities associated with TEM analysis. The high lateral spatial resolution in a TEM instrument is a consequence of several features of the technique. First, in the crudest sense, TEM has high spatial resolution because it uses a highly focused electron beam as a probe. This probe is focused at the specimen to a small spot. More importantly, the probe's source is an electron gun designed to emit a highly coherent beam of monoenergetic electrons of exceedingly small wavelength. The wavelength,$\lambda$, of 100 keV electrons is only 0.0037 nm, much smaller than that of light, X rays, or neutrons used in other analytical techniques. Having such small wavelengths, since electrons in a TEM probe are in phase as they enter the specimen, their phase relationships upon exiting are correlated with spatial associations between scattering centers (atoms) within the material. Finally, high lateral spatial resolution is maintained via the use of extremely thin samples.

In most TEM experiments, samples are thinned usually to less than 200 nm. For most materials this insures relatively few scattering events as each electron traverses the sample. Not only does this limit spreading of the probe, but much of the coherency of the incident source is also retained. The higher the operating voltage of a TEM instrument, the greater its lateral spatial
resolution. The theoretical instrumental point-to-point resolution is proportional to $\lambda^{3/4}$. This suggests that simply going from a conventional TEM instrument operating at 100 kV to one operating at 400 kV should provide nearly a 50% reduction in the minimum resolvable spacing ($\lambda$ is reduced from 0.0037 to 0.0016 nm in this case). Some commercially available 300 kV and 400 kV instruments, classified as high-voltage TEM instruments, have point-to-point resolutions better than 0.2 nm. High-voltage TEM instruments have the additional advantage of greater electron penetration, because high-energy electrons interact less strongly with matter than low-energy electrons. So, it is possible to work with thicker samples on a high-voltage TEM.

Electron penetration is determined by the mean distance between electron scattering events. The fewer the scattering events, either elastic (without energy loss) or inelastic (involving energy loss), the further the electron can penetrate into the sample. For an Al sample, for instance, by going from a conventional 100-kV TEM instrument, to a high-voltage 400 kV TEM instrument, one can extend the mean distance between scattering events (both elastic and inelastic) by more than a factor of 2 (from 90 to 200 nm and from 30 to 70 nm, respectively, for elastic and inelastic scattering). This not only allows the user to work with thicker samples but, at a given sample thickness, also reduces deleterious effects due to chromatic aberrations (since inelastic scattering is reduced).

One shortcoming of TEM is its limited depth resolution. Electron scattering information in a TEM image originates from a three-dimensional sample, but is projected onto a two-dimensional detector (a fluorescent screen, a film plate, or a CCD array coupled to a TV display). The collapse of the depth scale onto the plane of the detector necessarily implies that structural information along the beam direction is superimposed at the image plane. If two microstructural features are encountered by electrons traversing a sample, the resulting image
contrast will be a convolution of scattering contrast from each of the objects. Conversely, to identify overlapping microstructural features in a given sample area, the image contrast from that sample region must be deconvolved.

In some cases, it is possible to obtain limited depth information using TEM. One way is to tilt the specimen to obtain a stereo image pair. Techniques also exist for determining the integrated depth (i.e., specimen thickness) of crystalline samples, e.g., using extinction contours in image mode or using convergent beam diffraction patterns. Alternatively, the width or trace of known defects, inclined to the surface of the foil, can be used to determine thickness from geometrical considerations. Secondary techniques, such as EELS and EDS can in some cases be used to measure thickness, either using plasmon loss peaks in the former case, or by modelling X-ray absorption characteristics in the latter. But no TEM study can escape consideration of the complications associated with depth.

4.6 X-ray Photoelectron Spectroscopy (XPS)

A photon of sufficiently short wavelength (i.e., high energy) can ionize an atom, producing an ejected free electron. The kinetic energy KE of the electron (the photoelectron) depends on the energy of the photon \( h\nu \) expressed by the Einstein photoelectric law:

\[
KE = h\nu - BE
\]

where \( BE \) is the binding energy of the particular electron to the atom concerned. All of photoelectron spectroscopy is based on Equation (1). Since \( h\nu \) is known, a measurement of \( KE \) determines \( BE \). The usefulness of determining \( BE \) for material analysis is obvious when we remember the way in which the electron shells of an atom are built up. The number of electrons in a neutral atom equals the number of protons in the nucleus. The electrons, arranged in orbitals
around the nucleus, are bound to the nucleus by electrostatic attraction. Only two electrons, of opposite spin, may occupy each orbital.

The energy levels (or eigenvalues E) of each orbital are discrete and are different for the same orbital in different atoms because the electrostatic attraction to the different nuclei (i.e., to a different number of protons) is different. To a first approximation, the $BE$ of an electron, as determined by the amount of energy required to remove it from the atom, is equal to the $E$ value (this would be exactly true if, when removing an electron, all the other electrons did not respond in any way). So, by experimentally determining a $BE$, one is approximately determining an $E$ value, which is specific to the atom concerned, thereby identifying that atom.

**Elemental Analysis**

The electron energy levels of an atom can be divided into two types: core levels, which are tightly bound to the nucleus, and valence levels, which are only weakly bound. For the carbon atom of Figure 1, the C Is level is a core level and the C 2s and 2p levels are valence levels. The valence levels of an atom are the ones that interact with the valence levels of other atoms to form chemical bonds in molecules and compounds. Their character and energy is changed markedly by this process, becoming characteristic of the new species formed. The study of these valence levels is the basis of ultraviolet photoelectron spectroscopy (UPS) discussed in another article in this encyclopedia. The core-level electrons of an atom have energies that are nearly independent of the chemical species in which the atom is bound, since they are not involved in the bonding process.

Thus, in nickel carbide, the C Is $BE$ is within a few eV of its value for elemental carbon, and the Ni 2p $BE$ is within a few eV of its value for Ni metal. The identification of core-level $Bi$
thus provides unique signatures of the elements. All elements in the periodic table can be identified in this manner, except for H and He, which have no core levels. Approximate BEs of the electrons in all the elements in the period table up to Z= 70 are plotted in Figure 2, as a function of their atomic number Z, up to the usual 1486.6-eV accessibility limit.* Chance overlaps of BE values from core levels of different elements can usually be resolved by looking for other core levels of the element in doubt.

Quantitative analysis, yielding relative atomic concentrations, requires the measurement of relative peak intensities, combined with a knowledge of Z, plus any experimental measurements. Cross section values are known from well-established calculations from experimental measurements of relative peak areas on materials of known composition. A more practical problem is in correctly determining the experimental peak areas owing to variations in peak widths and line shapes, the presence of subsidiary features (often caused by the breakdown of the independent electron model), and the difficulty of correctly subtracting a large background in the case of solids. There are also instrumental effects to account for because electrons of different KE are not transmitted with equal efficiency through the electron energy analyzer. This is best dealt with by calibrating the instrument using local standards, i.e., measuring relative peak areas for standards of known composition in the same instrument to be used for the samples of unknown composition. Taking all the above into account, the uncertainty in quantification in XPS can vary from a few percent in favorable cases to as high as 30% for others. Practitioners generally know which core levels and which types of materials are the most reliable, and in general, relative differences in composition of closely related samples can be determined with much greater accuracy than absolute compositions.
4.7 Optical Studies

4.7.1 UV – Vis Spectral analysis

Ultra – violet- visible (UV- Vis) absorption spectra for all the nano crystalline samples prepared in the present study using a CARY- 5E model instrument.

![Graph showing UV-Vis absorption spectra](image)

**Fig 4.3 Model UV-Vis Spectrum**

Absorption against wavelength values were used to determine the bandgap energy. The absorption co-efficient was determined using the relation.

\[ \alpha = 2.303 \log \left( \frac{\text{abs}}{\text{particle size}} \right) \]

Of the sample. \( \alpha^2 \) values are plotted against the corresponding \( h \nu \) values. The bandgap energy was calculated by determining the \( h \nu \) value corresponding to the linear portion of the curve extrapolated to \( h \nu \) (axis)
4.7.2 Photoluminescence Spectrometer

Luminescence refers to the emission of light by a material through any process other than blackbody radiation. The term Photoluminescence (PL) narrows this down to any emission of light that results from optical stimulation. Photoluminescence is apparent in everyday life, for example, in the brightness of white paper or shirts (often treated with fluorescent whiteners to make them literally glow) or in the light from the coating on a fluorescent lamp. The detection and analysis of this emission is widely used as an analytical tool due to its sensitivity, simplicity, and low cost. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed.

Precise quantitative concentration determinations are difficult unless conditions can be carefully controlled, and many applications of PL are primarily qualitative. PL is often referred to as fluorescence spectrometry or fluorometry, especially when applied to molecular systems. Uses for PL are found in many fields, including environmental research, pharmaceutical and food analysis, forensics, pesticide studies, medicine, biochemistry, and semiconductors and materials research.

In PLY a material gains energy by absorbing light at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal (electron-hole pair creation). The system then undergoes a nonradiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes, and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state.
If the cross-coupling is strong enough this may include a transition to a lower electronic level, such as an excited triplet state, a lower energy indirect conduction band, or a localized impurity level. A common occurrence in insulators and semiconductors is the formation of a bound state between an electron and a hole (called an exciton) or involving a defect or impurity (electron bound to acceptor, exciton bound to vacancy, etc.) After a system-dependent characteristic lifetime in the excited state, which may last from picoseconds to many seconds, the electronic system will return to the ground state.

In luminescent materials some or all of the energy released during this final transition is in the form of light, in which case the relaxation is said to be radiative. The wavelength of this emission is longer than that of the incident light. This emitted light is detected photoluminescence, and the spectral dependence of its intensity is analyzed to provide information about the properties of the material. The time dependence of the emission can also be measured to provide information about energy level coupling and lifetimes. In molecular systems, we use different terminology to distinguish between certain PL processes that tend to be fast (submicrosecond), whose emission we call fluorescence, and other, slower ones ($10^{-4}$ s to 10 s) which are said to generate phosphorescence.

The light involved in PL excitation and emission usually in the range 0.6- 6 eV (roughly 200-2000 nm). Many electronic transitions of interest lie in this range, and efficient sources and detectors for these wavelengths are available. To probe higher energy transitions, UPS, XPS, and Auger techniques become useful. X-ray fluorescence is technically a high-energy form of PL involving X rays and core electrons instead of visible photons and valence electrons. Although lower energy intraband, vibrational, and molecular rotational processes may participate in PL, they are studied more effectively by Raman scattering and IR absorption.Since the excited
electronic distribution approaches thermal equilibrium with the lattice before recombining, only features within an energy range of -kT of the lowest excited level (the band edge in semiconductors) are seen in a typical PL emission spectrum.

It is possible, however, to monitor the intensity of the PL as a function of the wavelength of the incident light. In this way the emission is used as a probe of the absorption, showing additional energy levels above the band gap. Scanning a range of wavelengths gives an emission spectrum that is characterized by the intensity, line shape, line width, number, and energy of the spectral peaks. Depending on the desired information, several spectra may be taken as a function of some external perturbation on the sample, such temperature, pressure, or doping variation, magnetic or electric field, or polarization and direction of the incident or emitted light relative to the crystal axes. The features of the spectrum are then converted into sample parameters using an appropriate model of the PL process.

A wide variety of different mechanisms may participate in the PL process and influence the interpretation of a spectrum. At room temperature, PL emission is thermally broadened. As the temperature is lowered, features tend to become sharper, and PL is often stronger due to fewer nonradiative channels. Low temperatures are typically used to study phosphorescence in organic materials or to identify particular impurities in semiconductors.

PL is generally most useful in semiconductors if their band gap is direct, i.e., if the extrema of the conduction and valence bands have the same crystal momentum, and optical transitions are momentum-allowed. Especially at low temperatures, localized bound states and phonon assistance allow certain PL transitions to appear even in materials with an indirect band gap, where luminescence would normally not be expected.
For this reason bound exciton PL can be used to identify shallow donors and acceptors in indirect GaP, as well as direct materials such as GaAs and InP, in the range $10^{13}$-$10^{14}$ cm$^{-3}$. Boron, phosphorus, and other shallow impurities can be detected in silicon in concentrations approaching $10^{11}$ cm$^{-3}$. Copper contamination at Si surfaces has been detected down to $10^{10}$ cm$^{-3}$ levels. The most common configuration for PL studies is to excite the luminescence with red-wavelength light and to measure the intensity of the PL emission at a single wavelength or over a range of wavelengths. The emission characteristics, either spectral features or intensity changes, are then analyzed to provide sample information.

### 4.7.3 PL Excitation Spectroscopy

Instead of scanning the emission wavelength, the analyzing monochromator can be fixed and the wavelength of the incident exciting light scanned to give a PL excitation (PLE) spectrum. A tunable dye or Ti:Sapphire laser is typically used for solids, or if the signals are strong a xenon or quartz-halogen lamp in conjunction with a source monochromator is sufficient. The resulting PL intensity depends on the absorption of the incident light and the mechanism of coupling between the initial excited states and the relaxed excited states that take part in emission. The spectrum is similar to an absorption spectrum and is useful because it includes higher excited levels that normally do not appear in the thermalized PL emission spectra. Some transitions are apparent in PLE spectra from thin layers that would only be seen in absorption data if the sample thickness were orders of greater magnitude. This technique assists in the identification of compounds by distinguishing between substances that have the same emission energy but different absorption bands. In semiconductors, it can be valuable for identifying impurity PL peaks, especially donors, by enhancing certain PL transitions through resonant excitation. It is useful for determining the energy levels of thin-film quantum structures, which, when combined
with appropriate models, are used to simultaneously determine well widths and effective masses. Information about higher energy transitions can also be obtained by Modulation Spectroscopy techniques such as photoreflectance and electroreflectance.

4.7.4 Time-Resolved PL

By monitoring the PL intensity at a chosen wavelength as a function of time delay after an exciting pulse, information can be obtained about the electron relaxation and recombination mechanisms, including nonradiative channels. The time scales involved may vary from two hundred km to seconds to tens of seconds. A 111 emission spectrum may be measured also at successive points in time. Spectral analysis then yields, for example, the evolution of a carrier distribution as excitonic states form and as carriers are trapped by impurities. The progress of chemical reactions with time can be followed using time-dependent data. By monitoring the depolarization of luminescence with time of PL from polymer chains, rotational relaxation rates and segmental motion can be measured.

A useful application of time-dependent PL is the assessment of the quality of thin 111-V semiconductor alloy layers and interfaces, such as those used in the fabrication of diode lasers. For example, at room temperature, a diode laser made with high-quality materials may show a slow decay of the active region PL over several ns, whereas in low-quality materials nonradiative centers (e.g., oxygen) at the cladding interface can rapidly deplete the free-carrier population, resulting in much shorter decay times. Measurements of lifetime are significantly less dependent on external conditions than is the PL intensity.
4.7.5 PL Mapping

Spatial information about a system can be obtained by analyzing the spatial distribution of PL intensity. Fluorescent tracers may be used to image chemical uptake in biological systems. Luminescence profiles have proven useful in the semiconductor industry for mapping impurity distributions, dislocations, or structural homogeneity in substrate wafers or epilayers. Similar spatial information over small regions is obtained by cathodoluminescence imaging. For mapping, the sample (or the optical path) is translated, and at each position PL at a single wavelength or over an entire spectrum is measured. The image is formed from variations in intensity, peak energy, or peak line width. Lateral resolution of 1 pm is possible.

4.7.6 Sample Requirements

PL measurements are generally nondestructive, and can be obtained in just about any configuration that allows some optically transparent access within several centimetres of the sample. This makes it adaptable as an in situ measurement tool. Little sample preparation is necessary to eliminate any contamination that may contribute its own luminescence. The sample may be in air, vacuum, or in any transparent, nonfluorescing medium. Small probed regions down to 1-2 pm are possible using microscope lenses. Lasers can supply as much pump power as needed to compensate for weaker signals, but a limit is reached when sample heating or nonlinear optically induced processes become significant.

For semiconductor work, either whole wafers or small pieces are used, the latter often being necessary for insertion into a cryostat. Bulk solids may be analyzed in manyform, but scattered light may be reduced and the signal increased if the emitting surface is specular. Photoluminescence finds its greatest strengths as a qualitative and semiquantitative probe. Quantification based on absolute or relative intensities is difficult, although it is useful in
applications where the sample and optical configurations may be carefully controlled. The necessary conditions are most easily met for analytical applications of molecular fluorescence, where samples may be reproducibly prepared in the form of controlled films or as dilute concentrations of material in a transparent liquid solvent, and where reference standards are available PL intensities are strongly influenced by factors like heating, photochemical reactions, oxygen incorporation, and intensity, power density and the wavelength of the exciting light. If these factors are carefully controlled PL intensities can be used to study various aspects of the sample, but such control is not always possible.

Other aspects that can cause intensity variations are the focal region of the incident and collection optics, the relationship of the sample's image to the monochromator entrance slit, and the spectral response of the detector and optical path. Nevertheless, quantification is possible, a good example being the evaluation of the composition of chromatographic separations adsorbed onto glass, alumina, polyethylene, or paper.

4.7.7 Instrumentation

A variety of commercial instruments are available for PL measurements. These include spectrofluorometers intended primarily for use with liquids in a standard configuration, and simple filter-based systems for monitoring PL at a single wavelength. For use with opaque samples and surfaces, a few complete commercial systems are available or may be appropriately modified with special attachments, but due to the wide range of possible configuration requirements it is common to assemble a custom system from commercial optical components. Four basic components make up a PL system: 1 A source of light for excitation. Sur& studies generally require a continuous or pulsed laser. A dye laser is used if tunability is needed and a sample holder, including equipments for focusing the incident light and collecting the
Iuminescence. Efficient light collection is important, and the sample holder may need to allow for a cryostat, pressure cell, magnet, or electrical contacts and a dispersive element for spectral analysis of PL. This may be as simple as a filter, but it is usually a scanning grating monochromator. For excitation spectroscopy or in the presence of much scattered light, a double or triple monochromator (as used in Raman scattering) may be required. Photomultiplier tubes supply good sensitivity for wavelengths in the visible range, and Ge, Si, or other photodiodes can be used in the near infrared range. Multichannel detectors like CCD or photodiode arrays can reduce measurement times, and a streak camera or nonlinear optical techniques can be used to record ps or sub-ps transients.

4.8 The Vibrating-Sample Magnetometer

The vibrating sample magnetometer has become a widely used instrument for determining magnetic properties of a large variety of materials: diamagnetics, paramagnetics, ferromagnetics, ferrimagnetics and antiferromagnetics. The vibrating-sample magnetometer (VSM) is based on Faraday’s law which states that an emf will be generated in a coil when there is a change in flux linking the coil. We may write for a coil with $n$ turns of cross-sectional area $a$:

$$ V = -na \frac{d\Phi}{dt} $$

If the coil is positioned in a constant magnetic field, then

$$ B = \mu_0 H $$

When we bring a sample having a magnetization $M$ into the coil, we have

$$ B = \mu_0 (H + M) $$

The corresponding flux change is

$$ \Delta B = \mu_0 M $$

From this we get,
\[ V_{dt} = - n_0 \mu_0 M \]

This means that the output signal of the coil is proportional to the magnetization \( M \) but independent of the magnetic field in which the size of \( M \) is to be determined. In the VSM, the sample is subjected to a sinusoidal motion (frequency and the corresponding voltage is induced in suitably located stationary pickup coils.)

The electrical output signal of these latter coils has the same frequency Its intensity is proportional to the magnetic moment of the sample, the vibration amplitude, and the frequency A simplified schematic representation of the VSM is given in Fig.4.4 The sample to be measured is centered in the region between the poles of a laboratory magnet, able to generate the measuring field A thin vertical sample rod connects the sample holder with a transducer assembly located above the magnet. The transducer converts a sinusoidal ac drive signal, provided by an oscillator/amplifier circuit, into a sinusoidal vertical vibration of the sample rod. The sample is thus subjected to a sinusoidal motion in the uniform magnetic field \( H_0 \)

![Fig 4.4 Schematic representation of VSM](image-url)
Coils mounted on the poles of the magnet pick up the signal resulting from the motion of the sample. This ac signal at the vibration frequency is proportional to the magnitude of the moment of the sample. However, since it is also proportional to the vibration amplitude and frequency, the moment readings taken simply by measuring the amplitude of the signal are subject to errors due to variations in the amplitude and frequency of vibration.

In order to avoid this difficulty, a nulling technique is frequently employed to obtain moment readings that are free of these sources of error. These techniques (not included in the diagram shown in the figure) make use of a vibrating capacitor for generating a reference signal that varies with moment, vibration amplitude, and vibration frequency in the same manner as the signal from the pickup coils. When these two signals are processed in an appropriate manner, it is possible to eliminate the effects of vibration amplitude and frequency shifts. In that case, one obtains readings that vary only with the moment of the sample.

4.8.1 The Hysteresis Loop and Magnetic Properties

A great deal of information can be learnt about the magnetic properties of a material by studying its hysteresis loop. A hysteresis loop shows the relationship between the induced magnetic flux density (B) and the magnetizing force (H). It is often referred to as the B-H loop. An example hysteresis loop is shown below.
Fig 4.5 Hysteresis Curve (B-H)

The loop is generated by measuring the magnetic flux of a ferromagnetic material while the magnetizing force is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as $H$ is increased. As the line demonstrates, the greater the amount of current applied ($H^+$), the stronger the magnetic field in the component ($B^+$). At point "a" almost all of the magnetic domains are aligned and an additional increase in the magnetizing force will produce very little increase in magnetic flux. The material has reached the point of magnetic saturation. When $H$ is reduced to zero, the curve will move from point "a" to point "b." At this point, it can be seen that some magnetic flux remains in the material even though the magnetizing force is zero. This is referred to as the point of retentivity on the graph and indicates the remanence or level of residual magnetism in the material. (Some of the magnetic domains remain aligned but some have lost their alignment.) As the magnetizing force is reversed, the curve moves to point "c", where the
flux has been reduced to zero. This is called the point of coercivity on the curve. (The reversed magnetizing force has flipped enough of the domains so that the net flux within the material is zero.) The force required to remove the residual magnetism from the material is called the coercive force or coercivity of the material.

As the magnetizing force is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (point "d"). Reducing \( H \) to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing \( H \) back in the positive direction will return \( B \) to zero. Notice that the curve did not return to the origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back to the saturation point where it completes the loop.

From the hysteresis loop, a number of primary magnetic properties of a material can be determined.

1. **Retentivity** - A measure of the residual flux density corresponding to the saturation induction of a magnetic material. In other words, it is a material's ability to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation. (The value of \( B \) at point b on the hysteresis curve.)

2. **Residual Magnetism** or **Residual Flux** - the magnetic flux density that remains in a material when the magnetizing force is zero. Note that residual magnetism and retentivity are the same when the material has been magnetized to the saturation point. However, the level of residual magnetism may be lower than the retentivity value when the magnetizing force did not reach the saturation level.
3. **Coercive Force** - The amount of reverse magnetic field which must be applied to a magnetic material to make the magnetic flux return to zero. (The value of $H$ at point $c$ on the hysteresis curve.)

4. **Permeability** - A property of a material that describes the ease with which a magnetic flux is established in the component.

**Reluctance** - Is the opposition that a ferromagnetic material shows to the establishment of a magnetic field. Reluctance is analogous to the resistance in an electrical circuit.
4.9 REFERENCES
