CHAPTER 2

SYNTHESIS AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

This chapter describes the samples preparation method and experimental techniques utilized for the characterisation of materials. In the present investigation, nanoparticles compositions were prepared by sol-gel method, and the thin film was fabricated by the sol-gel spin coating technique. This chapter describes all the techniques, starting from samples preparation to the techniques which were used to study the structural, optical and magnetic properties of the prepared systems. This chapter starts with the techniques and steps needed in the preparation of ZnO-based nanomaterials and thin film, which is followed by a discussion on the experimental techniques used for the measurement of different properties of transition metal and rare earth doped ZnO nanoparticles and thin films.

2.2 SYNTHESIS OF THE COMPOSITIONS

In order to the processing of low dimensional materials (nanoparticles and thin film) two syntheses route were adopted namely, sol-gel for nanoparticles and sol-gel spin coating for thin film preparation.

2.2.1 Nanoparticles Preparation

Sol-gel method has been employed for synthesis of ZnO based nanoparticles compositions. The sol-gel reaction route is the most widely used method for the preparation of nanoparticles from a mixture of acetates as starting materials. The sol-gel method exhibit several advantages over other preparation techniques, such as easy synthesis process at normal temperature and pressure, easy control of chemical compounds and required chemical are easily available etc. The following flow chart (Figure2.1) explains the steps involved in the synthesis of a samples. For synthesis of various compositions, high purity raw materials were used. Detailed process has been given in individual chapters.

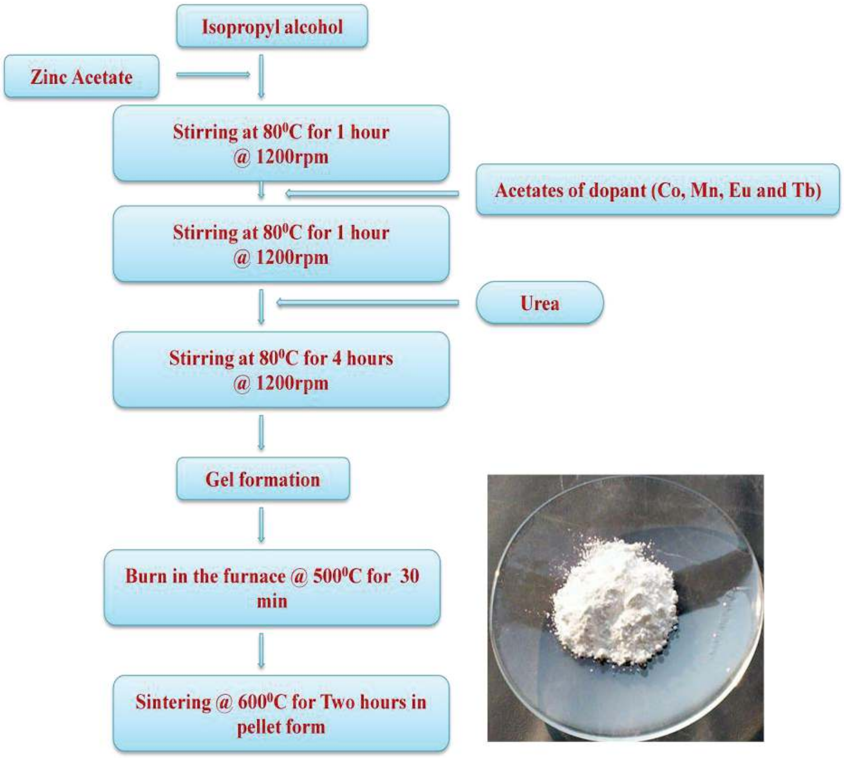

Figure 2.1: Flow chart of nanoparticles preparation.

2.2.2 Thin Film Preparation

The Thin films of pure ZnO and doped ZnO have been prepared by spin coating techniques. Gels of the compositions obtained from sol-gel reaction route have been taken for coating of films on glass substrate. ZnO thin film can be prepared by different techniques, such as pulse laser deposition, thermal evaporation, chemical vapour deposition and sol-gel spin coating method. Among all preparation method, the sol-gel spin coating process is better due to easy control of chemical components, precise control on the thickness of the film, and fabrication of smooth surface thin film at low cost. Following flowchart (Figure 2.2) indicates the details of thin film preparation. Figure 2.3 shows the spin coater, deposition steps and prepared thin film on glass substrate.

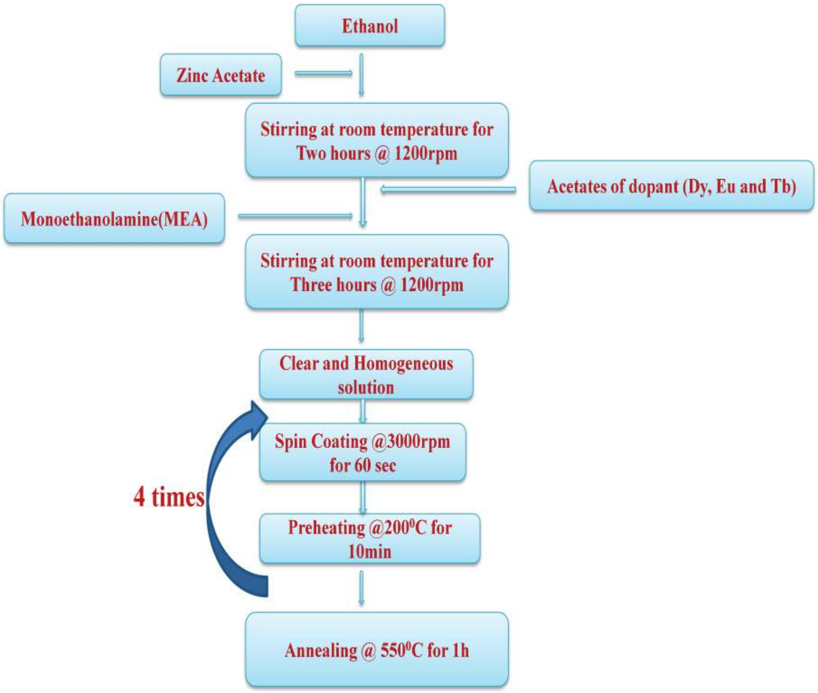

Figure 2.2: Flow chart of thin film preparation.

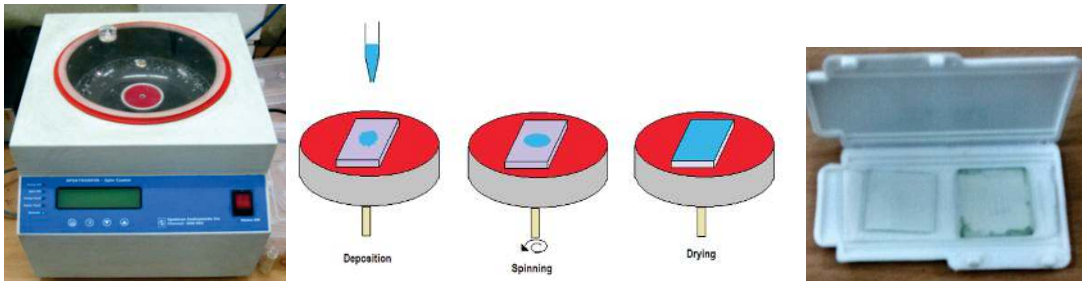

Figure2.3: **(a)** Spin coater **(b)** Deposition technique **(c)** Prepared thin film on glass substrate.

2.3 CHARACTERIZATIONS TECHNIQUES & THEIR WORKING PRINCIPLE

The Characterization techniques used to study the structural optical and magnetic properties of the samples are listed below and detail description in different sections.

- ☐ Thermal properties: TGA -DSC
- ☐ Structural properties: XRD, HR-XRD, Raman, FTIR, XPS
- ☐ Local structure: EXAFS, XANES
- ☐ Elemental analysis: EDS
- ☐ Surface morphology: SEM, TEM, AFM

☐ Optical properties: UV-Vis spectroscopy, Photoluminescence spectroscopy

☐ Magnetic properties: Magnetic property measurement system (MPMS)

☐ Thickness of thin film: M Probe Thin film measurement system

2.3.1 Thermo Gravimetric Analysis and Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measures the temperature and heat flow associated with a transition in material as a function of time and temperature in a controlled atmosphere. This measurement provides quantitative and qualitative information about the physical and chemical change that involves endothermic or exothermic processes or change in heat capacity. Thermo gravimetric analysis (TGA) is a technique for measuring the change in weight of a substance as a function of temperature or time. The sample usually a few milligrams in weight is heated at a constant rate, typical in the range 1 to 20^{o}C min^{-1} and has a constant weight until it begins to decompose at a certain temperature. Under dynamic heating, decomposition occurs over a range of temperature and after certain temperature, no weight loss is observed leading to the completion of the decomposition reaction. The weight losses are fundamental properties of the sample and can be used for quantitative calculations of compositional changes. A phase transition in the sample may also be confirmed by using this technique. TGA and DSC analysis of samples have been carried out by METTLER TOLEDO Japan in nitrogen atmosphere as shown in Figure 2.4.

Figure 2.4: TGA-DSC set up.

2.3.2 Phase Formation and Crystal Structure Studies by Powder X-Ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the crystallographic structure of materials. The copper emitted X-ray radiations are most commonly used with characteristic wavelength (Cu-K_α =1.5418Å). When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ. The diffracted beam can be detected by using a movable detector (Geiger counter) which is connected to a chart recorder. The X-ray diffraction setup is shown in Figure2.5 (b). In regular use, the counter is set to scan over a range of 2θ values at a constant angular velocity. Generally, a 2θ range of 10 to 90 degrees is sufficient to cover the most useful part of the powder pattern. The identification of single or multiple phases helps us to understand the mechanism behind the formation of these samples. The interaction of electromagnetic radiation with a periodic structure creates a diffraction pattern. The distance of the periodic structure must be about the same wavelength of the radiation. X-rays wavelengths order (few angstroms) is approximately equal to typical inter-atomic distance in crystalline solids. When X-rays are scattered from a crystalline solid they can constructively interfere, producing a diffracted beam.

Bragg's Law

The relationship describing the angle at which a beam of X-rays of a particular wavelength diffracts from a crystalline surface was discovered by Sir William H. Bragg and Sir W. Lawrence Bragg and is known as Bragg’s Law

$$2d\sin\theta = n\lambda \tag{2.1}$$

λ = wavelength of the X-rays
θ = scattering angle
n = integer representing the order of the diffraction peak
d = inter-plane distance

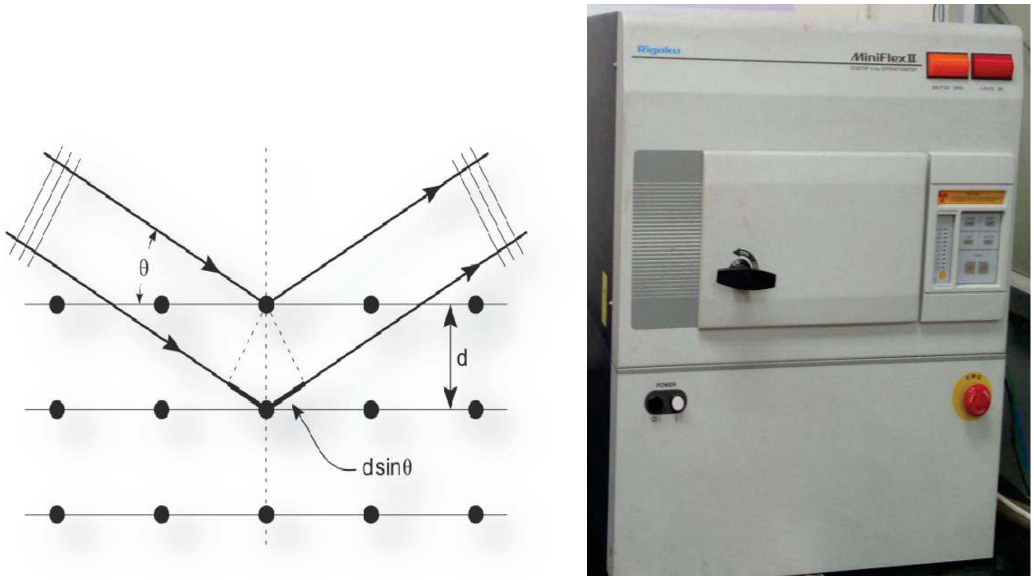

Figure 2.5 (a) Schematic diagram of X-ray diffraction **(b)** XRD set up.

The phase formation of synthesized samples has been confirmed using Rigaku-MiniFlex-II DESKTOP powder X-ray diffractometer with Cu K_α radiation (λ= 1.54 Å) at 30 kV and 15 mA. The diffraction patterns were recorded over the range $20^\circ \leq 2\theta \leq 90^\circ$ with a step size of 0.02º. The XRD data analysis provides the important parameters such as crystallite size, lattice parameter, unit cell volume, atomic packing fraction etc.

2.3.3 High-Resolution X-Ray Diffraction (HR-XRD)

Phase confirmation and nature of crystalline quality of thin film samples were measured using High-Resolution X-ray diffraction (Rigaku) with monochromatic Cu-K_α radiation (λ= 1.54 Å) at inclination angle 1°. All the patterns were recorded over the range of $20° \leq 2\theta \leq 90°$ with a step size of 0.02°. The HR-XRD instrument is shown in Figure2.6

Figure 2.6: HR-XRD set up.

2.3.4 Scanning Electron Microscope and Energy Dispersive X-Ray Spectroscopy

Scanning electron microscope (SEM) is used to investigate the morphology (texture), crystallite structure, grain size and orientation of materials making up the sample. OXFORD Instrument SEM EVO 18 Research has been used for SEM and EDS analysis, (shown in Figure2.7). Energy dispersive X-ray spectroscopy (EDS) has been employed for qualitative and quantitative analysis of the entire elements present in the samples. The interaction of electron beam with an atom at various depth within sample generates different signals such as secondary electron, backscattered electron, characteristic X-ray, cathodoluminescence, absorbed current (specimen current) and transmitted electrons. The signals are used by SEM to produce an image. Detecting all signals in an instrument is difficult. The standard equipment in all SEM is secondary electron detector. In case of secondary electron imaging, the secondary electrons are emitted from very close to the specimen surface. SEM analysis can be used to produce very high-resolution images of a sample surface. The beam electrons that are reflected from the sample by elastic scattering are known as backscattered electrons. The resolution of backscattered electrons (BSE) is less than secondary electron due to its origin from deeper locations within the specimen. The intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen and BSE images can be used to get information about the distribution of different elements in the sample. The sample in powder, as well as, palette form can be used for SEM analysis.

Energy-dispersive X-ray spectroscopy (EDS, EDX) is used to get information about the presence of element as well as atomic and a weight percentage of an element in the sample. The energy-dispersive spectrometer measure number and energy of the X-rays emitted from a specimen, which are arises due to a difference in energy between the higher-energy shell and the lower energy shell. Since the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element. Therefore, EDS allows the elemental composition of the specimen to be measured. The EDS is equipped with SEM set up.

Figure 2.7: SEM- EDS set up.

2.3.5 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. The interaction of the electrons transmitted through the specimen creates an image. This image is magnified and focused onto an imaging device, such as a fluorescent screen, a sensor and a CCD camera. TEM is capable of imaging at a significantly higher resolution because of the small De Broglie wavelength of an electron. This enables the instrument to examine fine details even as small as a single column of atoms. A TEM is composed of several components, which include a vacuum system (in which the electrons travel), an electron emission source (for generation of the electron stream), a series of electromagnetic lenses and electrostatic plates. TEM is used in all major area of science including material as well as biological sciences. Standard TEM grid sizes is a 3.05mm diameter ring, with a thickness and mesh size ranging from a few to 100µm. The properly dispersed sample is placed onto the inner meshed area having the diameter of approximately 2.5mm. Generally, grid materials are copper, molybdenum, gold or platinum. This grid is placed into the sample holder which is paired with the specimen stage. A wide variety of designs of stages and holders exist, depending upon the type of experiment being performed. The most common mode of operation for TEM is the bright field imaging mode. In this mode, the contrast is due to occlusion and absorption of electrons in the sample (classically). Thicker regions of the sample or region with a higher atomic number will appear dark, whilst regions with no sample in the beam path will appear bright (hence the term bright field). The TEM images have been collected with TECNAI G^2 200kV (FEI) Transmission Electron Microscope to investigate morphology and particle sizes of samples (Figure2.8). The copper grid with 300 meshes has been used for TEM sample measurement.

Selected area electron diffraction (SAED) is an experimental technique that can be performed inside a TEM. In a TEM, a thin crystalline specimen is subjected to a parallel beam of high-energy electrons. As TEM specimens are typical ~100 nm thick, and the electrons typically have the energy of 100-400keV, the electrons pass through the sample easily. In this case, electrons are treated as wave-like, rather than particle-like because the wavelength of high-energy electrons is a fraction of a nanometre, and the spacing between atoms in a solid is only slightly larger, the atoms act as a diffraction grating to the electrons, which are diffracted. That is, some fraction of them will be scattered to particular angles, determined by the crystal structure of the sample, while others continue to pass through the sample without deflection. As a result, the image on the screen of the TEM will be a series of spots. The selected area diffraction patterns each spot corresponding to a satisfied diffraction condition of the sample's crystal structure. SAED patterns are a projection of the reciprocal lattice, with lattice reflections showing as sharp diffraction spots. SAED patterns can be used to identify crystal structures and measure lattice parameters.

Figure 2.8: TEM set up.

2.3.6 X-Ray Absorption Spectroscopy (XAS)

XANES and EXAFS Analysis

The X-ray absorption spectroscopy analysis exhibit two parts, namely X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS). XANES is strongly sensitive to formal oxidation state and coordination chemistry (e.g. octahedral and tetrahedral coordination) of the absorbing atom, while the EXAFS is used to determine the distances, coordination number, and species of the neighbours of the absorbing atom. X-ray absorption fine structure (XAFS) analysis indicates how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. Specifically, XAFS is the modulation of an atom's X-ray absorption probability due to the chemical and physical state of the atom. The high sensitivity of XAFS spectra for oxidation state, coordination chemistry, distances, coordination number and species of the atoms immediately surrounding to the selected element lead towards a practical way to determine the chemical state and local atomic structure for a selected atomic species. XAFS is used in various fields such as biology, environmental science, catalysts research, and material science. Since XAFS is an atomic probe, it places few constraints on the samples that can be studied. All atoms have core level electrons, and XAFS spectra can be measured for almost all element except for element whose absorption edge energy does not lie in the range of beamline specification (such as Li). XAFS for non-crystalline and highly disordered materials can also be measured.

In our study, the local structure has been investigated by XAS measurement at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India, with the Energy-Scanning EXAFS beamline (BL-9) in fluorescence mode at the Indus-2 Synchrotron Source (2.5GeV, 200mA). This beamline uses a double crystal monochromator (DCM) to select photon energy in the energy range of 4-25 keV. The beamline optics is composed a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) (2d=6.2709) based DCM. The horizontal and vertical focusing of the beam at the sample position is done by a sagittal cylinder second crystal of the DCM and a Rh/Pt coated bendable post mirror facing down respectively. For the transmission measurement (Zn K edge), the data has been collected with the help of three ionization chambers (300mm length each). The incident flux (I_0), transmitted flux (I_t) and EXAFS spectrum of a reference metal foil for energy calibration have been measured separately. In order to improve the signal to noise ratio, appropriate gas pressure and gas mixtures have been chosen to achieve 10-20% absorption in first ionization chamber and 70-90% absorption in the second ionization chamber. The absorption coefficient μ is calculated by $I_t = I_0 e^{-\mu\chi}$ Here, χ represent the thickness of the absorber. The XAFS measurements for Eu edge and Tb edge are done in fluorescence mode using a Si drift detector. The sample is placed at 45°, while detector for fluorescence signal (I_f) is placed at 90° to the incident X-ray beam. The incident X-ray flux (I_0) measured by an ionization chamber detector placed prior to the sample. The scanning the monochromator over the specified energy range gives the value of absorbance of the sample $\mu(E) = \frac{I_f}{I_0}$ as a function of energy.

2.3.7 Raman Spectroscopy

Raman spectroscopy is employed to investigate vibrational, rotational, and other low-frequency modes. It relies on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. The Raman spectra have been collected at room temperature with a Renishaw Raman spectrometer equipped with 532 nm lasers shown in Figure 2.9 (a). The diode pumped solid state laser of wavelength 532 nm having maximum power 100mW, 5% of which has been used to avoid laser-induced heating in the sample. The incident laser beam has been focussed on the sample by a 50x long-distance objective attached to the Leica DM 2500M microscope. The Raman scattered light was collected in back-scattering geometry by the same objective and a 2400 grooves/mm grating was used as the dispersion element. The Slit width of 50μ has been maintained throughout the measurement. The resolution of the spectrometer is better than 1 cm^{-1} with a repeat deviation less than ±0.2 cm^{-1}. Spectrometer scanning, data collection and processing were done by a dedicated computer using Wire 4.0 software.

Selection Rule for Raman Spectra

The polarizability (α) can be used to determine the distortion of a molecule in an electric field. The Raman shift can be activated optically only in the presence of non-zero polarizability derivative with respect to the normal coordinate (i.e., the vibration or rotation):

$$\partial\alpha / \partial Q \neq 0$$

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering are filtered out while the rest of the collected light is dispersed onto a detector. The Raman Effect occurs when light impinges upon a molecule and interacts with the electrons of that molecule. In case of spontaneous Raman Effect, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency so that the total energy of the system remains balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an Anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction. Raman spectra are typically expressed in wave numbers, which have units of inverse length. In order to convert spectral wavelength and wave numbers of shift in the Raman spectrum, the following formula can be used:

$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) \tag{2.7}$$

Here Δw is the Raman shift expressed in wave number, λ_0 is the excitation wavelength, and λ_1 is the Raman spectrum wavelength.

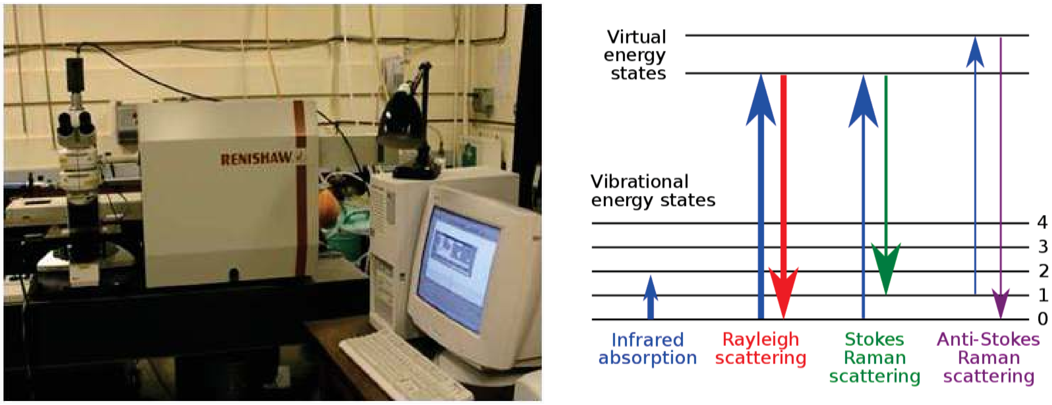

Figure 2.9 (a) Renishaw Micro Raman spectroscope **(b)** Energy level diagram showing states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

2.3.8 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis has been used to obtain information about the functional group, inter or intra-molecular interaction and vibrational modes. Fourier transform infrared spectroscopy can be used to obtain an infrared spectrum of absorption, emission, and Raman scattering of a sample (solid, liquid or gas). An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over another spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR technique has made dispersive infrared spectrometers and opened up new applications of infrared spectroscopy. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical algorithm) is required to convert the raw data into the actual spectrum. Schematic diagram for an FTIR spectrometer is shown in Figure 2.10(a). The horizontal axis is the position of the mirror, and the vertical axis is the amount of light detected. This is the "raw data" which can be transformed into an actual spectrum.

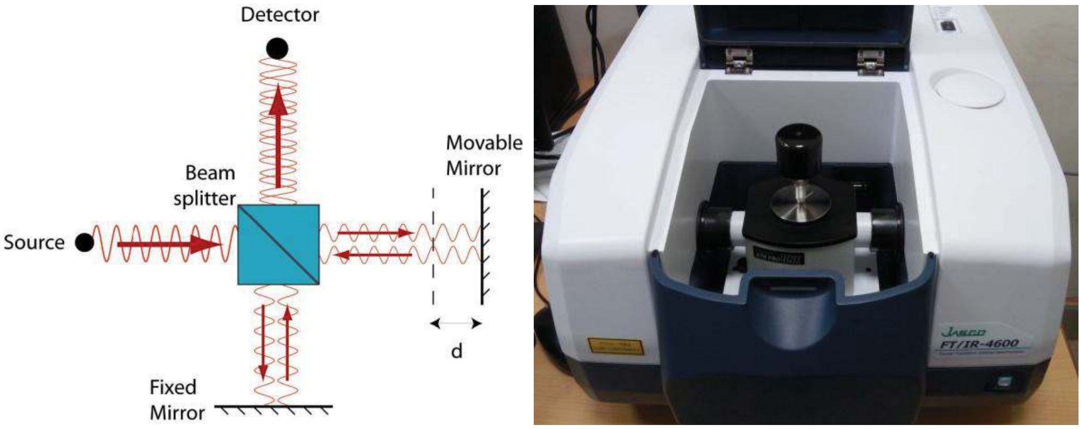

Figure 2.10 (a) Schematic diagram of a Michelson interferometer, configured for FTIR **(b)** Fourier transmission infrared spectrometer (JASCO FT/IR-4600).

The beam is generated by a light source-one containing the full spectrum of wavelengths to be measured. The light shines into a certain configuration of mirrors, called a Michelson interferometer that allows some wavelengths to pass through but blocks others. The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that pass through. In a Michelson interferometer adapted for FTIR, light from the source is collimated and directed to a beam splitter. Ideally, 50% of the light is reflected towards the fixed mirror and 50% is transmitted towards the moving mirror. Light is reflected from the two mirrors back to the beam splitter and (ideally) 50% of the original light passes into the sample compartment. There, the light is focused on the sample. On leaving the sample compartment, the light is refocused on to the detector. The FTIR set up is shown in Figure2.10 (b).

2.3.9 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique. It provides the information about the elemental composition of the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. In XPS spectra measurement process, the X-rays are irradiated on the sample and simultaneous measurement for kinetic energy and numbers of electrons that escape from the top 0 to 10 nm of the material is carried out. XPS spectra are recorded in high vacuum ($P \sim 10^{-8}$millibar) or ultra-high vacuum (UHV; $P < 10^{-9}$millibar) conditions, although a current area of development is ambient-pressure XPS, in which samples are analyzed at pressures of a few tens of millibar. XPS is a non-destructive surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its as-received state, or after some treatment, such as: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some or all of the surface contamination (with mild ion etching) or to intentionally expose deeper layers of the sample (with more extensive ion etching) in depth-profiling XPS, exposure to heat to study the changes due to heating, exposure to reactive gases or solutions, exposure to ion beam implant, exposure to ultraviolet light.

An Amicus XPS setup was used to performed elemental analysis and chemical state of the compositions and is shown in Figure 2.11.

Figure 2.11: X-ray photoelectron spectroscopy setup (Amicus).

2.3.10 UV-Vis Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) indicates absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. UV-Vis analysis is used to get information about absorption of particular wavelength as well as to calculate band gap of the sample. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I/I_o is called the transmittance and is usually expressed in percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log(T / 100)$$

The UV-visible spectrophotometer can also be used to measure reflectance. In reflectance case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_o) (such as a white tile). The ratio I/I_o are called the reflectance, and are usually expressed as a percentage (%R).

The spectrophotometer exhibit four main components namely a light source, a sample holder, a diffraction grating in a monochromator and a detector. The radiation source is continuous for the visible wavelengths. The photomultiplier tube, a photodiode, a photodiode array or a charge coupled device (CCD) is used as a detector. Single photodiode detectors and photomultiplier tubes are used for scanning monochromator, which filters the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromator is used with CCDs and photodiode arrays. UV-Vis spectrophotometer can be used for nanoparticles as well as a liquid sample.

Figure 2.12: UV-Vis set up.

2.3.11 Photoluminescence Spectroscopy

Photoluminescence spectroscopy (PL) is a powerful technique to study the optical property of a material. In this process, a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. In other words, this process describes an excitation to a higher energy state and then return to a lower energy state accompanied by the emission of a photon. This process of light emission is known as luminescence. The time between absorption and emission is extremely short. The quantum mechanics rules are used to determine the allowed transitions between states. A fundamental principle can be understood by studying the electron configurations and molecular orbital of simple atoms and molecules.

Photoluminescence is an important method for measuring the purity and crystalline quality of semiconductors. The schematic diagram of a general purpose spectrophotometer is shown in Figure 2.13. This spectrophotometer exhibit a xenon lamp as a source of exciting light. This lamp consists high intensity at all wavelengths. The instrument shown is equipped with a monochromator to select both the excitation and emission wavelengths. The excitation monochromator in this schematic contains two gratings, which decreases stray light, i.e. light with wavelengths different from the chosen one. Also, these monochromators use concave gratings, produced by holographic means to further decrease stray light. Both monochromators are motorized to allow automatic scanning of wavelength. The fluorescence is detected with photomultiplier tubes and quantified with the appropriate electronic devices. The output is usually presented in graphical form and stored digitally. The setup of Photoluminescence spectrophotometer is shown in Figure 2.13(b).

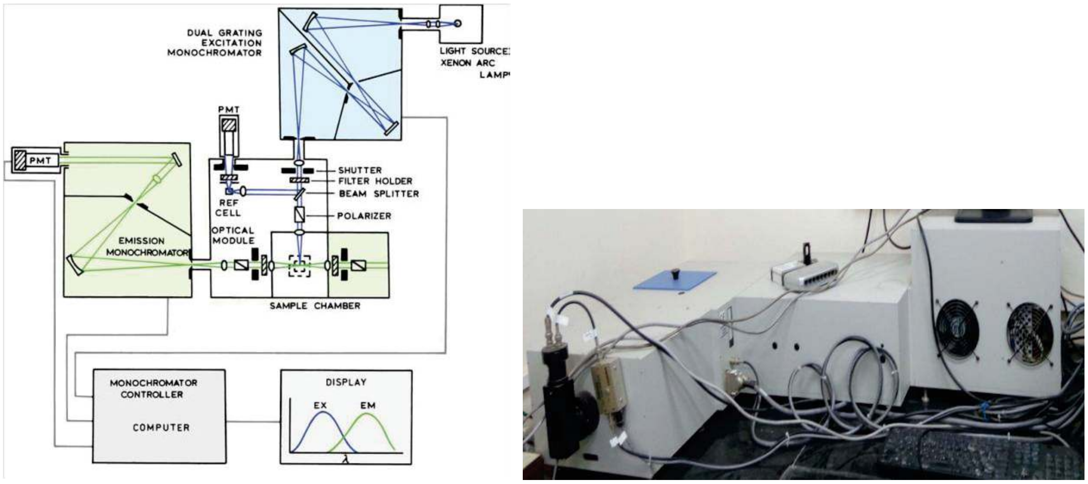

Figure 2.13 (a) Schematic diagram of a Photoluminescence spectrophotometer **(b)** setup of Photoluminescence spectrophotometer.

2.3.12 Magnetic Property Measurement System (MPMS)

The magnetic properties of samples can be investigated by Quantum Design MPMS 3 magnetometer. MPMS 3 provides three possible measurement modes, DC scan mode, AC susceptibility mode and vibrating sample magnetometer (VSM) mode. In the present work, we have employed VSM mode to study the magnetic behaviour of samples. The recorded data helps to get information about the magnetic behaviour of material using magnetization and susceptibility curve. The basic principle of VSM is based on Faraday's Law of Induction. According to this law, a changing magnetic field will produce an electric field. This measured electric field provides information about the changing magnetic field. The VSM operation starts by placing the sample in a constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains, or the individual magnetic spins, with the field. The magnetization increases with a constant field. The magnetic dipole moment of the sample will create a magnetic field around the sample, sometimes called the magnetic stray field. As the sample is moved up and down, this magnetic stray field is changing as a function of time and can be sensed by a set of pick-up coils. The alternating magnetic field will cause an electric field in the pick-up coils according to Faraday's Law of Induction. This current will be proportional to the magnetization of the sample. The magnetization increases with induced current. The induction current is amplified by a trans-impedance amplifier and lock-in amplifier. The various components are hooked up to a computer interface. Using controlling and monitoring software, the system can tell you how much the sample is magnetized and how its magnetization depends on the strength of the constant magnetic field. A typical measurement of a sample is taken in the following manner:

- the strength of the constant magnetic field is set
- the sample begins to vibrate
- the signal received from the probe is translated into a value for the magnetic moment of the sample

- the strength of the constant magnetic field changes to a new value. no data is taken during this transition
- the strength of the constant magnetic field reaches its new value
- the signal from the probe again gets translated into a value for the magnetization of the sample
- the constant magnetic field varies over a given range, and a plot of magnetization (M) versus magnetic field strength (H) is generated.

Quantum Design MPMS-3 magnetometer used in temperature range 5-300 K is shown in Figure 2.14.

Figure 2.14: MPMS3 setup.

2.3.13 Atomic Force Microscopy

The atomic force microscope (AFM) is an important tool to investigate surface morphology, roughness and quality of a thin film. It is one kind of scanning probe microscopes (SPM). SPMs are designed to measure local properties, such as height, friction, magnetism, with a probe. The image is recorded by raster-scans the probe over a small area of the sample. AFM operate by measuring the force between a probe and the sample. The AFM exhibit a silicon or silicon nitride cantilever with a sharp tip. This sharp tip or probe with a radius of curvature in nm is used to scan the specimen surface. Generally, AFM measures the vertical and lateral deflections of the cantilever with the help of an optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photo-detector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever. The AFM can be operated in many modes, depending on the application such as imaging mode, contact mode tapping mode, and non-contact mode.

Figure 2.15: Atomic Force Microscope.

2.3.14 Thin Film Measurement System

MProbe thin film thickness measurement system by SEMICONSOFT is an effective technique to estimate the thickness of thin film. The complete set up is shown in Figure 2.15. The set up consist a spectrometer, illumination and power source with face up reflection configuration. The device is connected with computer using software TFC companion. The thickness mechanism is based on measurement of reflection. The sample measurement process can be divided in to three parts. The measurement starts with calibration using selected substrate. The software offer variety of substrate and material library. The specific substrate and material should be selected before measurement. The calibration process is followed by measurement of dark current. In the third step, we put the sample below the light spot and software directly gives the thickness of prepared sample with reflectance graph.

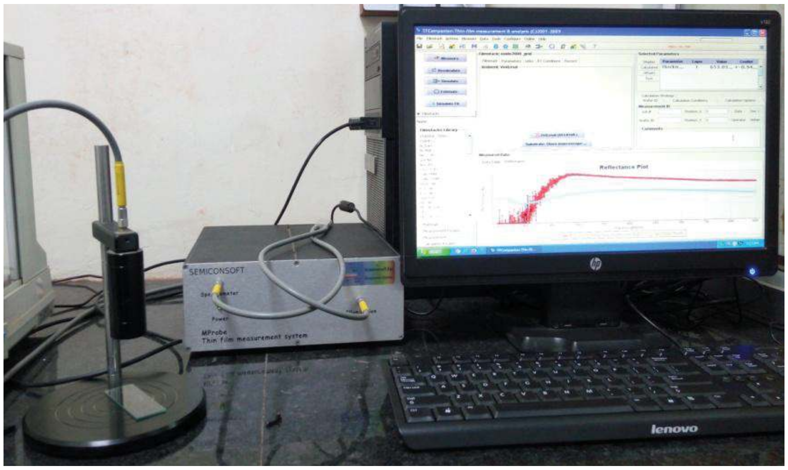

Figure 2.16: MProbe thickness measurement set up.

2.4 CONCLUSION

This chapter describes the sample preparation methods and instrument details used to analyse the properties of the prepared samples. A brief overview of working principle for the different instrument is also included.