CHAPTER 2

EXPERIMENTAL DETAILS OF SPRAY PYROLYSIS DEPOSITION AND CHARACTERIZATION METHODS

2.1 INTRODUCTION

In this chapter, the details of an indigenously developed spray pyrolysis system along with its components are discussed. Details have also been given on different characterization techniques employed to study the films. The description and experimental background of each technique have been given with regard to the present study on transparent conducting oxides. More details about individual methods are described in the literature (Mayer and Nicolet 1986, Feldman and Mayer 1986, Warren 1990, Ertl and Küppers 1985, Dosch 1992, Cullity 1978, Pankove 1971, Wooten 1972). In this work, Al and Cd doped Zinc oxide (ZnO:X, X= Al and Cd), Zn doped tin oxide (SnO$_2$:Zn) and Zinc stannate (Zn$_2$SnO$_4$) films were prepared by chemical spray pyrolysis method. To deposit the films, we have used a home made spray pyrolysis experimental setup and characterized the films by a variety of techniques. The elemental composition analysis of the films was studied by using energy dispersive X-ray spectrometer (EDX) attached to a Hitachi S-4800 high resolution field emission scanning electron microscope (HR-SEM). The structural properties of the films were studied by the X-ray diffraction (XRD) technique employing a RINT Rigaku 2500 X-ray diffractometer with CuK$_\alpha$ radiation. The optical properties of the films were studied by UV-Visible and spectroscopic ellipsometry methods. The Hall coefficient combined with resistivity measurement setup in the van der Pauw
configuration has been used the electrical measurements. The principle, functioning and importance of the above measurements and techniques are briefly outlined in this chapter.

2.2 SPRAY PYROLYSIS

2.2.1 Physical and Chemical Aspects of Spray Pyrolysis

The chemical reaction that provides the basis for the spray pyrolysis technique is the thermal decomposition of the initial material. The oxidation of the decomposition products and the formation of the desired layer material ensure that the pyrolysis takes place directly on the substrate surface, keeping the temperature of the initial material well below the decomposition temperature. This can be achieved by dissolving the initial material in a solvent, atomizing into droplets and carrying these droplets to the hot substrate with a carrier gas. During the continuous vaporization of the solvent, temperature of the dissolved initial material is held almost at the boiling point of the solvent until the solvent is entirely vaporized. Initially the solvent has to cool the starting material and thus prevent the material from decomposing very soon. Next, it is possible to obtain the desired particle size for the optimum chemical reaction at the substrate surface using a well defined composition and optimization of the solution flow.

Viguie and Spitz (1975) pointed that this method involves liquid droplets of the solution, whose constituents can either vaporize before they reach the substrate or react on the substrate after splashing. Several intermediate compounds can form depending on the nature of the reaction between these two extremes, and the physical properties of the coating can thereby be strongly affected. During the process, if the reaction takes place just above the surface of the substrate, then it is called heterogeneous reaction. If both the reactant and the product molecules form either in the gas phase or
on the substrate then it is called homogeneous reaction. The homogeneous reaction impede the growth rate, leading to powder formation (Chopra et al 1983, Siefert 1984a, b). The chemicals used for spray pyrolysis have to satisfy the following conditions (Shanthi et al 1980).

(i) on thermal decomposition, the chemicals in the solution form must provide the species / complexes that will undergo a thermally activated chemical reaction to yield the desired thin film material.

(ii) the reminder of the constituents of the chemicals, including carrier liquid should be volatile at the spray temperature.

2.2.2 Experimental set up

The chemical technique of liquid phase hydrolysis (spray pyrolysis) was devised by Chamberlin and Skarman (1966). A similar method of gas phase hydrolysis has been developed in our laboratory to deposit a variety of simple oxide thin films on different substrates. The essential constituents of the spray pyrolysis set up are a furnace to heat the substrate and a spray gun to spray the aqua-alcoholic solution on to the substrate. The schematic diagram of the spray pyrolysis experiment developed in our laboratory and employed to prepare the films for this study is shown in Figure 2.1. The different constituents of the spray pyrolysis experimental set up are discussed below.

Spray gun: A double nozzle spray gun of glass material is used for the spraying process (Figure 2.1). The spray gun is a coaxial assembly of a glass tube and a capillary tube. The inner and outer diameters of the spray gun are 0.2mm and 0.5mm respectively. In order to form the spray nozzle, both the capillary and glass tubes are tapered at one end to minimize the inner diameter to a maximum possible extent. Whereas, the other end of the capillary is provided beyond the glass tube and the glass tube is fused with the
outer surface of capillary. The capillary is used as the inlet for solution and a separate inlet is made on the glass tube to pass carrier gas (filtered compressed air). Hence when the carrier gas is allowed to pass through the tube, it will gain more pressure due to the tapered end and results in spraying the solution droplets that comes out of capillary.

![Schematic diagram of home made spray pyrolysis equipment used for thin film preparation.](image)

Figure 2.1 Schematic diagram of home made spray pyrolysis equipment used for thin film preparation.

**Heater and temperature controller:** A well equipped resistive heating set up is employed for the substrate heating. The set up includes (i) an iron plate of 15 cm diameter and 3 mm thickness that has been placed over the heater as the controller to achieve required temperature.

**Solution container:** A glass vessel is used as a solution container and is covered with two-holed cork. Through one hole, a capillary tube is inserted well inside the solution which is connected to the capillary of spray gun using a PVC pipe. A glass tube is inserted in the other hole and is connected to the compressor outlet to provide the capillary rise. During the spray interval, the solution in the capillary of the spray gun may either drop
out of the spray gun or may flow back to the solution container. This problem can be resolved by adjusting the height level of the solution container.

**Air compressor:** An air compressor with the container capacity of 18.0 litres has been employed for our experiments to supply the carrier gas. A pressure regulator that is fixed at the outlet of the container is used to achieve specific regulation on the pressure of the carrier gas. This can be used to vary the pressure of carrier gas, which is an essential parameter of spray pyrolysis technique in the film growth. The outlet of this regulator is connected to air filter that filters the oil content or other impurities mixed with the carrier gas. The outlet of the air filter is connected with an open/close valve. With the aid of this valve the spraying action can be started or stopped. The total pressure and flow rate of the carrier gas have been optimized for each material and it vary between 40-60 kg/cm².

### 2.2.3 Mechanism of Spray Pyrolysis Deposition

The optimization of spray condition is indeed a complicated process and it needs deeper theoretical understanding of the spray steps. The thermal behaviour of the sprayed droplets depends on their mass, and the deposition process is governed by different mechanism depending on the size of the droplets. Figure 2.2 shows the various deposition processes that occur above the required decomposition temperature depending on the droplet size.

In process A, the droplet is so large that the heat absorbed from the surrounding will not be sufficient to vaporize the entire solvent on the way to the substrate. The droplet hits the substrate, where the solvent vaporized completely leaving a dry precipitate. The temperature would now increase above the boiling point of the solvent and decomposition occurs. Also the vaporization of the solvent locally removes a lot of heat and the substrate temperature would decrease at this point. This affects adversely the kinetics of
the reaction and the equalization of the particle concentration does not occur at this point. The surface becomes rough and the transmission decreases drastically.

**Figure 2.2** Spray deposition processes in relation to the droplet size (Siefert 1984a)

Process B (medium droplet size) is distinguishable that the droplet dries up entirely before reaching the substrate and then hits the surface on the basis of statistical distribution. At this stage, some of the particles, evaporate and condense in the gaps between the particles, where the surface reaction starts. In this process also, the vaporization of the particle locally removes a lot of heat, but not the same amount as in the process A.

Process C (ideal droplet size) includes the classical chemical deposition process leading to the optimum film properties. In this process the solvent is entirely vaporized just above the substrate. Before the particle reaches the substrate, there is sufficient time for it to warm up to ambient temperature. The particle melts or vaporizes (or sublimes) and undergoes a
heterogeneous reaction. During this reaction there are several processes involved and the process steps are listed below (Kumar 1976, Hosack 1972).

(i) Diffusion of the reactant molecules to the surface.

(ii) Absorption of one or several reactant molecules on the surface.

(iii) Surface diffusion, chemical reaction, and incorporation into the lattice.

(iv) Desorption of the product molecules from the surface and

(v) Diffusion of product molecules away from the surface.

![Figure 2.3](image)

**Figure 2.3** Growth rate ($r$) as a function of inverse temperature during spray deposition optimization

Figure 2.3 shows the temperature dependence of the growth rate ($r$) in process C. At low temperatures (area III), the growth rate is controlled by activated processes such as adsorption, surface diffusion, chemical reaction and desorption. The growth rate is thus controlled by the reaction kinetics. This means that the molecules, which are flowing by diffusion, accumulate in
front of the substrate and hence the concentration gradient flattens. This supports the possibility of homogeneous reaction.

At higher temperatures (area II) all molecules that are diffusing to the substrate will be deposited. At this stage, the activated processes occur very fast and the molecules flowing to the substrate will not be slowed down. The concentration gradient remains steep, that is the growth rate is diffusion limited. High temperature also causes a strong surface diffusion of the absorbed molecules and thereby leads to a very smooth surface.

Finally, in area I, the part of the homogeneous reaction in the vapour space, which extends in the front of the substrate is so large that the formation of powder will be the growth limiting reaction.

The behaviour of the smallest droplet is shown in process D (Figure 2.2). In this process, because of the relatively small surface area, the solvent is already completely vaporized far away from the substrate. The particle melts and vaporizes (or sublimes) and a chemical reaction will occur in the vapour phase. This is a homogeneous reaction, because all reactant molecules and product molecules are in the vapour phase. The molecules condense as micro crystallites, and form a powdery precipitate on the substrate. This powder disturbs the formation of the layer and leads to a reduction in transmission of the deposited films. In addition, the homogeneous reaction diminishes the deposition efficiency of this procedure.

2.2.4 Optimization of Spray Conditions

In order to optimize the spray conditions of the deposition system, prior to the deposition of pure ZnO and SnO\textsubscript{2} films, various deposition
parameters like initial concentration of the spray solution, spray nozzle substrate distance, spray nozzle angle, carrier gas flow rate, and substrate temperature etc have been varied. It was a very difficult task to adjust all parameters simultaneously and to arrive at a common deposition procedure (condition) for the films. Hence to identify the best deposition conditions, each parameter has been optimized individually. After several trials, it has been identified that the deposition setup is capable of depositing homogeneous films on a 3 cm$^2$ substrate, when the substrate and the spray nozzle are separated by a distance of 20 cm-35cm. After attaining uniformity of the films, the substrate temperature has been optimized to obtain transparent and well crystallized films. As mentioned in the previous section, during deposition, the substrate temperature decrease drastically, which reduces the films quality. Hence, the solution has been sprayed on the substrates for a few seconds at regular time interval. After optimization, the spray time has been fixed at 3 seconds followed by 2 minutes waiting time, to maintain the substrate temperature at a fixed value. Finally, the substrate temperature has been varied from 150 to 450$^\circ$C (maximum capacity of the heating system) in steps of 50$^\circ$C. For each case, the transmission of the deposited films has been measured at 650 nm and is plotted as a function of deposition temperature (Figure 2.4). From this figure it is clear that the transmission of the films increased while increasing the substrate temperature and reaches a maximum value above 350$^\circ$C. During the optimization process, upto 350$^\circ$C, we frequently observed slight powder formation on the substrates. Above 400$^\circ$C, there is no powder formation and the grown films shows good crystalline behavior. Hence we have chosen the optimized 400$^\circ$C for thin film deposition in all our experiments.
Figure 2.4 Transmission of ZnO films deposited at different temperatures. Maximum transmission and very good crystallization has been observed above 350°C.

2.3 CHARACTERIZATION OF THE FILMS

In this study, varieties of characterization techniques were used to evaluate the structural, optical and electrical properties of the thin films. The studies include determination of the structure from X-ray diffraction, film thickness, optical parameters and the conductivity of various films. As important were the investigations on the morphological features by atomic force microscope (AFM), scanning electron microscope (SEM) and determination of grain size. The band gap of the films was calculated from the absorption edge of the transmittance spectra. The Hall coefficient combined with resistivity measurement set up has been used for studying the electrical properties of the films. The most relevant aspects of these analytical techniques are discussed briefly in the following sections.
2.3.1 X-ray Diffraction Analysis

X-ray diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases in material and to measure their structural properties (Cullity 1978). XRD is also used to determine the thickness of thin single or multilayer films, and the atomic arrangements (phase of atoms) in amorphous materials (including polymers) and interfaces. X-ray diffraction method is commonly used because it is non-destructive. The basic principle of X-ray analysis is rather simple: a monochromatic X-ray beam penetrates through the sample and from the scattered signal the real structure is determined. In this way, film thickness, layer density, surface and interface roughness, crystal lattice constants, preferred grain orientation (texture), grain size and lattice strain have been measured. In this study a XRD (model: Rigaku RINT-2500) powder diffractometer with CuKα radiation of wavelength \( \lambda = 1.54056 \text{Å} \) was used for measurements. The X-ray scans were performed between 2θ values of 20° and 80° with a typical step size of about 0.02°.

2.3.2 Crystallite Size Measurement

Phase identification using X-ray diffraction relies mainly on the positions of the peaks in a diffraction profile as well as the relative intensities of these peaks to some extent. Another aspect of the diffraction from material is the importance to consider how diffraction peaks are changed by the presence of various types of defects such as small number of dislocations in crystals with dimensions of millimeters. Small grain size can be considered as another kind of defect and can change diffraction peak widths. Very small crystals cause peak broadening. The well known Scherrer equation explains the peak broadening in terms of incident beam divergence, which makes it possible to satisfy the Bragg condition for non-adjacent diffraction planes. Using Scherrer equation the crystallite size can be easily calculated as a function of peak width specified as the full-width at half maximum peak.
intensity (FWHM), peak position and wavelength. The Scherrer equation is written as,

\[ D = \frac{0.9\lambda}{\omega \cos \theta} \]  

(2.1)

where \( \omega \) is the FWHM of the diffraction peak in radians and \( \lambda \) is wavelength of the X-rays and \( \theta \) is the position of the diffraction peak.

### 2.3.3 Optical Measurements

One of the versatile methods for studying the condensed matter is optical spectroscopy measurement. This measurement relies on the interaction of light with matter, in which the electron distribution, change of molecular configuration, molecular orientation, change of spin orientation etc. are accompanied by the absorption or the emission of radiation at characteristic frequency and energy. The radiation excitations in the range of 10 nm to 2000 nm are referred to as the ‘electron spectrum’ and it involves the excitation of loosely bound outer electrons of an ion, atom or molecule to other quantized levels and hence the optical spectroscopy provides useful information about these excitations.

The basic principle of any optical spectroscopy measurement is that electromagnetic radiations from a suitable source are dispersed and this dispersed light is passed through the sample of interest. A part of the transmitted radiation is studied as a function of its wavelength with a suitable detecting system. Hence, an optical spectrometer consists of three main components:

(i) Light source with monochromator

(ii) Sample and reference port and

(iii) The detecting unit
There exist various types of sources, monochromators and detecting units. However, their right choice depends upon certain basic requirements (Strobel 1960, Robison 1970 and Willard et al 1965).

In this investigation, in order to study the optical properties of the films, UV-visible spectroscopy and spectroscopic ellipsometry techniques have been used. Both optical spectroscopy and spectroscopic ellipsometric measurements rely on the interaction of light with the sample (Roseler 1990 and Tompkins 1993). In spectrophotometry the intensity of the reflected and transmitted light is measured, whereas, ellipsometry utilizes the polarization state of the light.

2.3.3.1 Optical Spectroscopy

In this work, for the optical spectroscopy measurements, JASCO V500 model spectrometer was used to record the optical transmittance in the spectral range from 200 nm to 900 nm. In this measurement the intensity of the reference beam is defined as \( I_0 \), and the intensity of the sample beam is defined as \( I \). If the sample under investigation does not absorb light of a given wavelength, then \( I = I_0 \). However, if the sample compound absorbs light then \( I \) is less than \( I_0 \), and this difference can be plotted on a graph as a function of wavelength. Absorption may be presented as transmittance \( (T = I/I_0) \) (or) absorbance \( (A = \log I_0/I) \). If the sample under investigation does not have any absorption, \( T=1.0 \) and \( A=0 \), which is considered as an ideal case.

The optical absorption coefficient is defined as

\[
I = I_0 \exp(-\alpha t)
\]  

(2.2)
where \( I \) is the intensity of the transmitted light, \( I_0 \) is the incident light, \( \alpha \) is the absorption coefficient and \( t \) is the thickness of the film. From the optical absorption coefficient (\( \alpha \)) value, one can easily understand the type of the transition associated with the band structure of the thin film under investigation and the band gap value can be calculated by using the equation,

\[
\alpha = \frac{A \left( \frac{h\nu - E_g}{h\nu} \right)^m}{cm^{-1}} \tag{2.3}
\]

where \( m' \) is a constant associated with the type of transition. Depending upon the nature of the transition involved \( m' \) might assumes the values 1/2, 2, 3/2, and 3 for the direct allowed, indirect allowed, direct forbidden and indirect forbidden respectively. Where \( E_g \) is the band gap extracted after extrapolation of the plot at \( \alpha = 0 \), \( A \) is the constant which is related to the effective mass associated with the bands, and \( h\nu \) is the energy of the incident photon.

### 2.3.3.2 Spectroscopic Ellipsometry

The spectroscopic ellipsometry is based on measuring the change in polarization state of the reflected light, at multiple wavelengths. This is achieved by determining a complex reflection coefficient \( \rho \) of the sample, which is defined as the quotient of the complex reflection coefficients for light polarized parallel (\( R_p \) – in the plane of incidence) and perpendicular (\( R_s \) – perpendicular to the plane of incidence) to the plane of incidence, illustrated in Figure 2.5.
In the simplest case of the two phase model, which consists of ambient (air or vacuum)/substrate without any additional layers, $R_{p,s}$ represent the Fresenel reflection coefficients of the system. Usually, $\rho$ is transformed into the ‘ellipsometric parameters’ $\psi$ and $\Delta$, which characterize the polarization state of the reflected light according to the relation (Azzam and Bashara 1983, Aspnes 1982 and Aspnes et al 1990).

$$\rho = \frac{R_p}{R_s} = \frac{|R_p|}{|R_s|} e^{i(\delta_p-\delta_s)} = \tan(\psi) e^{i\Delta} \quad (2.4)$$

where $\tan(\psi)$ is the amplitude change and $\Delta$ is the phase difference between $p$- and $s$- components of the electric field. During the measurements, variation in the angle of incidence provides more information on a particular structure, which enables a more accurate structure model to be achieved. This technique is called variable angle spectroscopic ellipsometry (VASE). In this work Woollam-M2000UI ellipsometer was used for the measurements.
instrument enables to record the spectra from 0.7 eV to 5.1 eV (1100 nm to 250 nm). For illumination, a halogen lamp was used in the NIR/VIS region and a deuterium lamp was used for measurements in UV region. The polarized lights were detected by an InGaAs diode array (NIR) and a Si-CCD camera (VIS/UV). The complete measurement was done within 5 minutes, including the sample alignment and three different angles of incidence.

In order to derive the film properties like thickness, wavelength dependent complex refractive index and extinction coefficient values from the acquired ellipsometric data, in principle it is possible to directly extract the refractive index \( n \), extinction coefficient \( k \), and the thickness of the films \( d \). But in practice, however, this is difficult as the sensitivity of \( n \) and \( k \) as a function of angle of incidence is sample dependent and usually very small. Hence, problem arises when trying to extract these three parameters \( n, k \) and \( d \) from the measured ellipsometric parameters \( \psi \) and \( \Delta \). Hence, it has to be solved by regression analysis. In the present study, the manufacturer’s software (WASE39™ 1995) provides a regression analysis, with the “badness of fit” parameter, the “mean-squared-error” designated as MSE, with lower values of MSE for better fitting.

In order to get the best fit, normally the lower region of the spectrum up to 2.5 eV in the case of TCOs (where \( k = 0 \)) will be simulated by using the Cauchy’s dispersion formula (Tompkins 1993) to determine the approximate thickness of the films. The Cauchy’s equation is written as,

\[
\begin{align*}
n(\lambda) &= A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \\
k(\lambda) &= D + \frac{E}{\lambda^2} + \frac{F}{\lambda^4}
\end{align*}
\] (2.5)
After finding the approximate film thickness, the $n$ and $k$ values are calculated by “point–by–point” fitting algorithm. The software supplied by the instrument manufacturer takes care of each and every point of the experimental data and produces better fit. Finally, different oscillator models such as Tauc-Lorentz oscillator model (Tauc et al 1966), Lorntz oscillator model etc are used to derive the accurate optical constant values. The Tauc–Lorentz oscillator model is well suited for dielectric films and is successfully used by many researchers (Tauc et al 1966, Tauc 1969, Jellison et al 2000) to describe ellipsometric data. For the oscillator modeling, in our case, we have considered the following three-layer (five phase) model: substrate/interface-layer/film/roughness/air. The surface roughness was modeled using a Bruggemann effective medium approximation (BEMA) (Bruggemann 1935) mixture of 50% bulk material and 50% voids. As an example, Figure 2.6 (a and b) shows the Psi ($\psi$) and del ($\Delta$) plots of Co:TiO$_x$ sample with the best fits (solid lines) obtained by using Tauc-Lorentz oscillator model (Subramaniam et al 2007). Figure 2.6 (c) shows the variation of $n$ and $k$ as a function of energy. More details about the oscillator modeling is reported by Venkataraj et al (2002).
2.3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. SEM has much higher magnification (>100,000) and greater depth of field (up to 100 times) than that of light microscopy. SEM is used for various purposes:
- Topographic studies
- Microstructure analysis
- Elemental analysis if equipped with appropriate detector (energy/wavelength dispersive X-rays), and
- Elemental mapping.

In SEM, primary electrons are thermionically emitted by a cathode filament (W or LaB$_6$) or an emission gun (W-tip) and after that accelerated with high energy potential typically 1 to 30 keV. The accelerated electron beam is steered with scanning coils over the area of interest. The incident beam induces electron emission from the sample surface through elastic and inelastic scattering processes. High energy electrons, which are scattered by elastic collisions are referred as the backscattered electrons. The energy of the backscattered electrons will be comparable to that of the incident electrons. The lower energy electrons that are emitted as a result of inelastic scattering are known as secondary electrons. These secondary electrons can be formed by collisions with the nucleus, where substantial energy loss occurs or by the ejection of loosely bound electrons from the sample atoms. The energy of secondary electrons is typically in the order of 50 eV or less and thus contain the information of only few angstroms deep on the surface of the layer.

To create a SEM image, the incident electron beam is scanned in a raster pattern across the sample’s surface. The emitted electrons are detected at each position in the scanned area by a detector. The intensity of the emitted electron signal is displayed as brightness on a cathode ray tube (CRT). By synchronizing the CRT scan to that of the incident electron beam, the CRT displays the morphology of the sample surface area scanned by the beam. Magnification of the CRT image is the ratio of the image display size to the
sample area scanned by the electron beam. The SEM imaging is performed by keeping the chamber at higher vacuum, typically from $10^{-5}$ to $10^{-7}$ torr. Imaging of non-conductive, volatile, and vacuum sensitive samples can be performed at higher pressures. In this study a Hitachi S-4800 model HR-SEM equipped with a field emission gun and EDX analyzer was used.

2.3.5  **Energy Dispersive X-ray (EDX) Analysis.**

Energy dispersive X-ray spectroscopy (EDX) is a compositional microanalysis technique used in conjunction with scanning electron microscopy (SEM), in which features as small as 1 μm can be analyzed. EDS detects the characteristic X-rays emitted from the sample during bombardment by an electron beam, which characterize the elemental composition of the analyzed volume. When the sample is bombarded by the an electron beam, X-ray photons, which are produced by transitions between deep atomic levels, are ejected from the atoms comprising the sample's surface. The X-ray energy is characteristic of the element from which it was emitted.

When an X-ray strikes the EDX 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 multi-channel analyzer, where the pulses are sorted by voltage. The spectrum of X-ray energy versus counts is evaluated to determine relative abundance of the emitted X-rays versus their energy, and hence the elemental composition of the sampled volume.
**Qualitative Analysis:** The sample X-ray transitions energy derived from the EDS spectrum can be 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 atomic 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 non-standard analysis depends on the sample composition. Greater accuracy can be achieved using known standards with structure and composition similar to that of the unknown sample.

**Elemental Mapping:** Characteristic X-ray intensity can be 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 μm lateral resolution is possible.

**Line Profile Analysis:** The SEM electron beam can be 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.
2.3.6 Atomic Force Microscopy

Atomic force microscopy (AFM) is a method of measuring surface topography on a scale from angstroms to 100 microns. The technique involves imaging a sample through the use of a probe, or tip, with a radius of 20 nm. The tip is held several nanometers above the surface using a feedback mechanism that measures surface–tip interactions on the scale of nano newtons. A detector measures the cantilever movement as the tip moves over the sample. From the tip movements and data from the detector, software is used to reconstruct a map of the surface morphology of the sample under investigation.

The forces responsible for the deflection of the tip are shown in Figure 2.7 as function of tip to sample distance (Force distribution curve). During the measurements only a very few atoms from the tip and sample are involved. Hence the forces between the tip and sample are governed by the inter-atomic forces known as the van der Waals forces.

![Figure 2.7](image)

**Figure 2.7** Intermolecular force vs distance curve (a) repulsive force (b) attractive force
These two regimes are (i) contact regime (soft physical contact) and (ii) the non-contact regime. In the contact regime, the tip is brought until there are few angstroms between the sample and the tip. The force here is usually repulsive. In the non-contact regime the distance between the sample and the tip is held in the order of tens to hundreds of angstroms from the sample surface, and the inter-atomic force between the sample and tip is usually attractive as a result of long-range van der Waals interaction. In this study, the non-contact regime was used for morphological analysis.