Chapter 3

Thin Film Deposition Methods and Characterization Techniques

3.1 Thin film: Introduction

Thin films have been used in the study of the relationship between the structure of solids and their physical properties. Thin films are formed by depositing material onto a clean supporting substrate to build up film thickness, rather than by thinning down bulk material.

“Any solid or liquid object with one of its dimensions very much less than that of the other two is called a thin film”.

The mechanical properties of thin films are quite different from those of the bulk material, e.g. the strengths exhibited by some films appear to be as much as 200 times as great as for well annealed bulk samples and are usually several times as great as the strengths of severely cold worked bulk material.

The emerging technology needs various types of thin films for variety of applications. Many materials have been prepared in the form of thin films over a century because of their potential technical value and scientific curiosity in their properties. Thin films have very wide range of applications and extend from the superhydrophobic coatings on glass and metals, micrometer dots in microelectronic, photoelectronic, thermoelectronic, superconductivity, information-storage media, fuel cells and bio-compatible coatings.

3.2 Thin film deposition methods

The properties of thin films depend on the method of deposition. The required properties and versatility can be obtained by choosing proper method of thin films deposition. Thin film deposition methods can be broadly classified as either physical or chemical. In physical methods the film material is moved from a target source with some form of energy to the substrate. This technique is widely used in one-component films, like metal films. Under physical methods, we have vacuum evaporation and sputtering, where the deposition takes place after the material to be deposited has been transferred to a gaseous
state either by evaporation or an impact process. Chemical film fabrication methods involve chemical reactions and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Under chemical methods, we have the gas phase chemical processes such as conventional chemical vapor deposition (CVD), laser CVD, photo CVD, metal organo-chemical vapor deposition (MOCVD) and plasma enhanced CVD. Liquid phase chemical methods include sol-gel process, electrodeposition, chemical bath deposition (CBD), modified chemical bath deposition (M-CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, etc.

The broad classification of thin film deposition methods is outlined in Table. 3.1. The physical methods are plugged with certain drawbacks and difficulties. A careful and precise control of the boat temperature is an essential requirement for obtaining good stoichiometric films. Chemical methods are relatively economical and easier ones as compared to physical methods.

Among all the thin film deposition methods, sol-gel process offers a wide range of advantages over other methods of thin film deposition as shown below:

1. Low temperature processing
2. Requires considerably less equipment and is potentially less expensive
3. Easy coating of large surface
4. Small thickness
5. High optical quality
6. High purity

However, the most important advantage of sol-gel processing over conventional coating methods is the ability to control precisely the microstructure of the deposited film, i.e. the pore volume, pore size, and surface area.
Table 3.1: Broad Classification of Thin Film Deposition Methods

<table>
<thead>
<tr>
<th>Physical Deposition Methods</th>
<th>Chemical Deposition Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum evaporation</td>
<td>Gas Phase</td>
</tr>
<tr>
<td>- Resistive heating</td>
<td>- Chemical vapour deposition</td>
</tr>
<tr>
<td>- Flash evaporation</td>
<td>- Laser chemical vapor deposition</td>
</tr>
<tr>
<td>- Electron beam evaporation</td>
<td>- photochemical vapor deposition</td>
</tr>
<tr>
<td>- Laser evaporation</td>
<td>- Plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>- Arc evaporation</td>
<td>- Metal organochemical</td>
</tr>
<tr>
<td>- Radio frequency (RF) heating</td>
<td>Liquid Phase</td>
</tr>
<tr>
<td>- Sputtering</td>
<td>- Sol gel process</td>
</tr>
<tr>
<td>- Glow discharge DC sputtering</td>
<td>- Electrodeposition</td>
</tr>
<tr>
<td>- Triode sputtering</td>
<td>- Chemical bath deposition</td>
</tr>
<tr>
<td>- Getter sputtering</td>
<td>- Successive ionic layer adsorption and reaction (SILAR)</td>
</tr>
<tr>
<td>- Radio frequency (RF) sputtering</td>
<td>- Electroless deposition</td>
</tr>
<tr>
<td>- Magnetron sputtering</td>
<td>- Anodization</td>
</tr>
<tr>
<td>- Face target sputtering</td>
<td>- Spray pyrolysis</td>
</tr>
<tr>
<td>- Ion beam sputtering</td>
<td>- Liquid phase epitaxy</td>
</tr>
<tr>
<td>- AC sputtering</td>
<td></td>
</tr>
</tbody>
</table>

Chapter 3 Thin Film Deposition Methods and Characterization Techniques
3.3 Thin film deposition techniques

Certainly one of the most technologically important aspects of sol-gel processing is that, prior to gelation, the fluid sol or solution is ideal for preparing thin films by such common processes as dipping, spinning, or spraying.

3.3. A. Basics of dip coating technique

Dip coating technique can be described as a process where the substrate to be coated is immersed in a coating sol and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. The schematics of the dip coating process are shown in Figure 3.1.

![Dip coating process](image)

**Figure 3.1** Dip coating process: dipping the substrate in the solution, formation of the wet layer and gelation of the layer by solvent evaporation.

In the dip coating process, the atmosphere controls the evaporation of the solvent and subsequent destabilization of the sols by solvent evaporation leads to a gelation process and the formation of a transparent film due to the small particle size in the sols (nanometer range). The gelation process during
dip coating process is shown in Figure 3.2. The resulting film has to be densified by thermal treatment and the densification temperature depends on the composition.

![Diagram of gelation process during dip coating process](image)

**Figure 3.2.** Gelation process during dip coating process obtained by evaporation of the solvent and subsequent destabilization of the sol.

The coating thickness is defined mainly by the withdrawal speed, the solid content and the viscosity of the liquid. There are six forces acting on the coating during withdrawing [1]:

1. viscous drag upward on the liquid by moving substrates
2. force on gravity
3. resultant force of surface tension in the concavely shaped meniscus
4. inertial force of the boundary layer liquid arriving at deposition region
5. surface tension gradient and
6. the disjoining or conjoining pressure (important for films less than 1 µm thick)

When the liquid viscosity (η) and substrate speed (U) are high enough to lower the curvature of the gravitational meniscus, the deposition film thickness (h) is the thickness that balances the viscous drag (cηU/h) and gravity force (ρgh) [2, 3] the thickness is given by,

\[
h = c_1 \frac{(\eta U)}{\rho g}^{1/2}
\]

(3.1)

where proportionality constant, \( c_1 \), is about 0.8 for Newtonian liquids.

When the substrate speed and liquid viscosity are not high enough (often the case for sol-gel deposition), this balance is modulated by the ratio of viscous drag to liquid-vapor surface tension (\( \gamma_{LV} \)) according to the following relationship derived by Landau and Levich [4],

\[
h = 0.94 \frac{(\eta U)^{2/3}}{\gamma_{LV}^{1/6} (\rho g)^{1/2}}
\]

(3.2)

The interesting part of dip coating processes is that by choosing an appropriate viscosity the thickness of the coating can be varied with high precision from 20 nm up to 50 nm while maintaining high optical quality.

In sol-gel film deposition, evaporation is generally relied upon to solidify the coating. The most significant factor in the rate of evaporation is the rate of diffusion of the vapor away from the film surface [2] This in turn depends on the movement of the gas within a very thin layer (l ~ 1 mm), because even a tiny bit of convention can greatly enhance diffusion. The rate of evaporation, \( m \), is generally expressed in terms of an empirical mass transfer coefficient, k, according to [5]:

\[
m = k (p_c - p_i)
\]

(3.3)

where, \( p_c \) is the partial pressure of the volatile species in local equilibrium with the surface and \( p_i \) is its partial pressure a distance, l, away. To a first approximation the evaporation rate is independent of the liquid depth.
During dip coating, the movement of the substrate can strongly influence the evaporation rate, but in practice $k$ and $p_c - p_i$ are probably dominated by large-scale, uncontrolled currents above the bath [2].

Although the composition of the liquid bath may be relatively unaffected by evaporation, the much thinner film experiences a substantial increase in concentration. The slower the substrate speed, the thinner the film and the greater the overlap of the deposition and drying stages. Since condensation continues to occur during sol-gel film formation, the relative condensation and evaporation rates will dictate the extent of further cross-linking that accompanies the deposition and drainage stages. The evaporation rate can, of course, be controlled by the deposition ambient. The condensation rate may be controlled by varying the pH of the coating bath.

### 3.3. B. Basics of spin coating technique

In the spin coating process, the substrate spins around an axis that should be perpendicular to the coating area. The stages of the spin coating process are shown schematically in figure 3.3. The spin coating process is carried out in four stages: deposition of the sol, spin up, spin off and gelation by solvent evaporation. An excess of liquid is dispensed on the surface during the deposition stage. In the spin up stage, the liquid flows radially outward, driven by centrifugal force. In the spin off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin off slows down, because the thinner the film, the greater the resistance to flow, and because the concentration of the nonvolatile components increases raising the viscosity. In the fourth stage, evaporation takes over as the primary mechanism of thinning.
An advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin off and, once uniform, tends to remain so provided that the viscosity is not shear dependant and does not vary over the substrate [2]. This tendency arises due to the balance between the two main forces: centrifugal force, which drives flow radially outward and viscous force (friction), which acts radially inward [6]. During spin-up, centrifugal force overwhelms the force of gravity, and the rapid thinning quickly squelches all inertial forces other than centrifugal force. The quality of the coating depends on the rheological parameters (rheology is complex parameter and depends on particle shape, temperature, solvent, concentration and particle interaction) of the coating liquid.

The thickness of an initially uniform film during spin off is described by [2, 7]:

\[ h(t) = h_0 / \left(1 + 4\rho \omega^2 h_0^2 \frac{t}{3\eta}\right)^{1/2} \]  

(3.4)
where $h_0$ is the initial thickness, $t$ is time, $\eta$ is the liquid viscosity and $\omega$ is the angular velocity: $\rho$ and $\omega$ assumed constant. Even films that are not initially uniform tend monotonically toward uniformity, sooner or later following equation above.

The thinning procedure creates a steady forced convection in the vapor above the substrate that causes the mass transfer coefficient, $k$, to be quite uniform. Thus the evaporation rate in spin coating tends to be quite uniform also. A spun film arrives at its final thickness by evaporation after the film becomes so thin and viscous that its flow stops. According to a model of spin coating by Meyerhofer [8] that separates the spin off and evaporation stages, the final thickness and total elapsed time to achieve this thickness are,

$$
h_{\text{final}} = (1 - \frac{\rho_A}{\rho_A^0}) \times (3\eta m / 2\rho_A \omega^2)^{1/3} \quad (3.5)
$$

and

$$
t_{\text{final}} = t_{\text{spin-off}} + h_{\text{spin-off}} \frac{\rho_A^0}{m \rho_A} \quad (3.6)
$$

where $\rho_A$ is mass of volatile solvent per unit volume, $\rho_A^0$ is initial value of $\rho_A$, $h$ is final thickness, $\eta$ is viscosity, $\omega$ is angular speed, $m$ is evaporation rate of the solvent, $m$ has to be determined empirically.

Scriven [9] described the thickness of an initially uniform film during spin off by,

$$
h(t) = \frac{h_0}{\left(1 + 4 \rho \omega^2 d_0^2 t / 3\eta \right)^{1/2}} \quad (3.7)
$$

where $h_0$ is the initial thickness, $t$ is time, $\rho$ is the density, and $\omega$ is the angular velocity. Lai and Chen [10, 11] independently determined the thickness of films obtained by spin coating, using different angular speeds, and their results could be fitted very well with the equation,

$$
d = A \omega^B \quad (3.8)
$$

where $A$ and $B$ are constants to be determined empirically.

Equations (3.4 – 3.6) pertain to Newtonian liquids that do not exhibit a shear rate dependence of the viscosity during the spin off stage. If the liquid is shear thinning, the lower shear rate experienced near the center of the substrate
Chapter 3 Thin Film Deposition Methods and Characterization Techniques

causes the viscosity to be higher there and the film to be thicker. This is often the case for particulate sols and gel-forming systems. In order to overcome this situation, commercial spin coating apparatus employs sophisticated dispensing systems that meter out liquid from a radially moving arm.

3.3. C. Basics of spray technique

The basic principle involved in spray technique is that, when the droplets of spray solution reach to the hot substrate, owing to the pyrolytic decomposition of solution, well adherent pin–hole free, uniform, film is deposited on the substrates. The other volatile byproducts and excess solvent escape in the form of vapors. The thermal energy for decomposition and subsequent recombination of the species is provided by the hot substrate. It is different for the different materials and for the different solvents used in the spray process.

The schematic diagram of the spray technique is shown in Figure 3.4. It mainly consists of spray nozzle, rotor for spray nozzle, liquid level monitor, hot plate, gas regulator value and air tight fiber chamber.

a) Spray nozzle

It is made up of glass and consists of the solution tube surrounded by the glass bulb. With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle and the solution is automatically sucked in the solution tube and the spray starts.

b) Rotor for spray nozzle

Stepper motor based microprocessor controller is used to control the linear simple harmonic motion of the spray nozzle over the required length of the hot plate.

c) Liquid level monitor

The spray rate at a fixed air pressure depends upon the height of the solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitor.
d) Hot plate

The iron disc, with diameter 16 cm and thickness 0.7 cm to which 2000 Watt heating coil is fixed is used as a hot plate. Maximum temperature of 500 ± 5°C can be obtained with this arrangement. The chromel-alumel thermocouple is used to measure the temperature of the substrates and is fixed at the center of the front side of the iron plate. The temperature of the hot plate is monitored with the help of temperature controller (Aplab make Model No. 9601).

e) Gas regulator value

The gas regulator value is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. A glass tube of length 25 cm and of diameter 1.5 cm is converted into gas flow meter. Since air pressure depends upon the size of the air flow meter, the air flow meter should be calibrated from nozzle to nozzle.

f) Air tight fiber chamber

Since the number of toxic gases is evolved during the thermal decomposition of sprayed solution, it is necessary to fix the spraying system inside with air tight fiber chamber. An air tight fiber chamber of the size (2’ x 2’ x 2’) was fabricated. The fiber avoids the corrosion of the chamber. The outlet of chamber is fitted to exhaust fan to remove the gases evolved during thermal decomposition.
Important parameters involved in spray technique are precursor solution, evaporation period, thermolysis, and atomization for studying the structure and morphology of the thin films. These four process parameters are discussed in the following section.

Figure 3.4: Schematic diagram of spray technique.
1) Precursors

A precursor solution plays a vital role in the formation of thin film of various compounds. The true solutions, colloidal dispersions, emulsions, and sols can be used as aerosol precursors. Aqueous solutions are usually used due to ease of handling safety, low cost, and availability of a wide range of water soluble metal salts. The solute must have a high solubility which increases in particle yield of the process. Increasingly, alcoholic and organic solutions have been studied due to the interest in the synthesis of organic materials from metal organic and undergo polymerization and for the synthesis of non-oxide ceramic solutions.

2) Atomization

A variety of atomization techniques have been used for solution aerosol formation, including pneumatic, ultrasonic, and electrostatics. These atomizers differ in droplet size, rate of atomization and droplet velocity. The velocity of the droplet when it leaves the atomizer is important because it can determine the heating rate and the residence time of the droplet during spray. The size of the droplets products with pneumatic or pressure nozzles decreases when the pressure difference across the nuclei is increased. For a specific atomizer the droplet characteristics depend on the solution density, viscosity and surface tension.

3) Evaporation Period

In first stage of spray, evaporation of the solvent from the surface of the droplet, diffusion of the solvent vapor away from the droplet in the gas phase, change in droplet temperature and diffusion of solute towards the centre of the droplet have important role concerns with the stoichiometry of films. The factors controlling the particle growth and ultimately film formations of well adherent surface is due to

1) evaporation of liquid droplets
2) evaporation from solution droplets
3) temperature of liquid droplets
4) temperature of solution droplets
5) solute diffusion in a droplet
6) solute condensation.

Apart from its simplicity, spray technique has a number of advantages.
1. Spray is a simple and low cost technique for the preparation of thin films.
2. It has capability to produce large area, high quality adherent films of uniform thickness.
3. Spray technique does not require high quality targets and/or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
4. The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters.
5. It offers an extremely easy way to dope films with virtually any elements in any proportion, by merely, adding it in some form to the spray solution.
6. By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.

Spray technique has been used to prepare the thin film on a variety of substrates like glass, ceramic or metals. Many studies have been conducted over about three decades on SPT and the mechanism of thin film formation and influence of variables on the film formation process has been comprehensively reviewed in the literature [12]. Due to the simplicity of the apparatus and the good productivity of this technique on a large scale, it offered a most attractive way for the formation of thin films.

3.4 Substrate cleaning

Substrate cleaning is the process of breaking the bonds between substrates and contaminants without damaging the substrates. In thin film deposition process substrate cleaning is an important factor to get reproducible films as it affects the smoothness, uniformity, adherence and porosity of the
films. The substrate cleaning process depends upon the nature of the substrate; degree of cleanliness required and nature of contaminants to be removed. The common contaminates are grease, adsorbed water, air borne dust, lint, oil particles etc. The micro slides supplied by Blue Star of dimensions 7.5 cm x 2.2 cm x 0.1 cm have been used as the substrates. The following process has been adopted for cleaning the substrates.

1. The substrates were washed with detergent solution ‘Labolene’ and then with water.
2. These substrates were boiled in chromic acid for about ten minutes.
3. Substrates were cleaned with double distilled water.
4. These substrates were kept in NaOH solution to remove the acidic contaminations.
5. The substrates were again washed with distilled water and cleaned ultrasonically.
6. Finally substrates were dried in alcohol vapors.

3.5 Thin Film Characterization Techniques

A wide variety of characterization techniques were used to evaluate the material quality of the thin films before using the films in applications. The structural properties of the films were studied by scanning electron microscopy (SEM). The RMS roughness of the films was studied by atomic force microscopy (AFM). Chemical composition measurements were made by fourier transform infrared (FT-IR) spectroscopy. The static and dynamic water contact angle against water was measured using a contact angle meter. The percentage of optical transmission was studied by spectrophotometer.

3.5.1 Scanning Electron Microscopy

- **Introduction**

  Scanning Electron Microscopy (SEM) technique is used to observe the morphology of a sample at higher magnification, higher resolution and depth of focus [13] compared to an optical microscope. In this technique, an accelerated
beam of mono-energetic electrons is focused onto the surface of the sample and it is scanned over a small area. Several signals are generated and appropriate ones are selected depending on the mode of its operation. This signal is amplified and made to form synchronous image on a cathode ray tube. A camera is used to photograph the image or it may be processed on the computer. The magnification of the displayed image is defined as the ratio of the size of the image on the cathode ray tube (CRT) to the size of the electron beam scanning on the specimen surface. The type of information obtained can be changed by switching the signal. In this way, the specific desired characteristics of the specimen surface can be seen on the CRT on a magnified scale.

- **Principle of working**

A line diagram of typical scanning electron microscope is given in figure 3.5. A well focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals as mentioned above. Back-scattered electrons and secondary electrons are particularly pertinent for SEM applications their intensity being dependent on the atomic number of the host atoms. Each may be collected, amplified and utilized to control the brightness of the spot on the cathode ray tube.

To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electromagnetic deflection coils and so is the C.R.T. beam in synchronization with this. The signals are transferred from point to point and signal map of the scanned area is displayed on a phosphor C.R.T. screen. Changes in brightness represent the changes of a particular property within the scanned area of the specimen.
Figure 3.5: Line diagram of a typical Scanning Electron Microscope

1. Cathode
2. Anode
3. Electron beam
4. Magnetic lens
5. Scanning lens
6. Magnetic lens
7. Specimen
8. Secondary electrons
9. Back scattered electrons
10. Detectors
11. Video amplifier
12. Scanning generator
13. Magnification generator
• Resolving power of SEM

To get the knowledge of the various microstructural properties of a substance like surface geometry, pore structure, particle size distribution, dislocation and defects etc., various characterization methods like microscopy and scattering experiments with light, electrons and ions are used. Scanning Electron Microscope uses electrons to form an image. Since electrons are charged particles they can be accelerated and deflected using electromagnetic fields and the wavelength of the electron beam can be altered as per the de-Broglie relation

\[ \lambda = \frac{h}{2 e V M_e^{1/2}} \]  

(3.9)

Where, \( h \) = Planck’s constant, \( e \) = electron charge, \( V \) = applied potential and \( M_e \) = mass of the electron. Therefore, for an accelerating potential \( V = 80 \) kV, the wavelength is \( \lambda = 4.3 \) pm.

If this value of \( \lambda \) is put into the Rayleigh’s criterion for the resolving power of a microscope

\[ R = 0.61 \frac{\lambda}{n \sin \alpha (M_e)^{1/2}} \]  

(3.10)

Where \( \alpha \) = semi angle subtended by the objective lens or limiting aperture at object point and \( n \) = refractive index of the object space.

The theoretical value of \( R \) is of the order 1 pm for a numerical aperture of 1.4. However, in practice a highest resolution of 100 pm is attainable because of the limitations of the numerical aperture.

The SEM produces the images of high resolution with a large depth. The sample preparation is relatively easy and non-conducting samples can also be scanned by coating a few nanometer of a conducting layer such as Au-Pt or Au-Pd alloy.

Pre-Requisites for SEM characterization

• Vacuum: Electrons being charged particles, require vacuum environment for traversing without change in their number and density.
The sample under the investigation needs to be conducting, otherwise there is a charge build up due to the impinging electrons which gives rise to the jumping of the beam and hence instability. Therefore, for the SEM characterization, the sample has to be vacuum compatible and electrically conducting as well.

**Sample preparation**

Surface of non-conducting materials is rendered conducting usually by coating a thin (100Å) metal film aluminium/gold/gold-palladium. Biological samples are specially treated to immobilize them and render them vacuum compatible without appreciable change in their surface morphology. Entire sample preparation consists of mounting of the sample on a metallic platform via a conducting path.

**Operating Modes**

The SEM can be operated in many different modes where each mode is based on a specific type of signal. The choice of operating mode depends on the properties of the sample and on what features one wants to investigate. The more common modes are:

a) Secondary electrons
b) Back scattered electrons
c) X-rays

a) Electrons with energies between 0 – 30 eV are detected and used to form the image. These electrons come from a layer within 5 nm of the surface.

b) Elastically scattered electrons with energies ranging from a few KeV to the energy of the incident electrons (typically 15 – 30 KeV) are detected. Such electrons come from a volume extending down to 0.5 µm below the surface and therefore give information also about the “bulk” properties of the materials.

c) A material irradiated with high-energy electrons will emit X-rays; both as characteristic radiation and as continuous spectrum (brehmsstrahlung). The characteristic X-rays are, as the name implies, characteristic of the emitting element and can therefore be used to perform a compositional analysis of the specimen.
3.5.2 Atomic Force Microscopy

- **Introduction**

The ability of the atomic force microscope (AFM) to create three-dimensional micrographs with resolution down to the nanometer to the angstrom scales has made it essential tool for imaging surfaces [14]. A key of AFM is its micrographic force sensor or cantilever. One or more beams of silicon or silicon nitride of length 100 to 500 µm and about 0.5 to 5 µm thick usually form the cantilever. At the end of the cantilever, a sharp tip is mounted which is used to sense a force between the sample and tip, for continuous or intermittent contact with the sample and raster-scanned over the surface. Fine motion piezoelectric scanner is used to generate images and force measurements. A piezoelectric scanner is a device that moves by a microscopic amount when a voltage is applied across its electrodes. A piezoelectric scanner for AFM’s can translates in three dimensions (x, y and z axes) and come in different sizes to allow maximum scan ranges of 0.5 to 125 µm in the x, y and several microns in the vertical (z) axis. A well-built scanner can generate stable motion on the scale below 1 Å.

- **Principle of working**

By scanning the AFM cantilever over a surface (or scanning a sample under the cantilever) and recording the deflection of the cantilever, local height of the sample is measured. The measured cantilever deflection allows a computer to generate a map or surface topography [15]. Three-dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position. Other imaging techniques are also used including measuring the change in amplitude or phase of an oscillating cantilever, using tapping mode. This tapping mode is useful to study the surface morphology of thin films. Along with study of surface morphology and roughness of the film, it is possible to study the growth stages in thin film. A line diagram of typical atomic force microscope is given in figure 3.6.
Components of the atomic force microscope

1) Piezocrystals

Piezocrystals are ceramic materials that expand or contract in the presence of voltage gradient and conversely, they develop an electrical potential in response to mechanical pressure. In this way, movements in x, y and z direction are possible.

2) Probe

The probe represents a micromachined cantilever with a sharp tip at one end, which is brought into interaction with the sample surface. Each probe has different specifications and shape. V-shaped cantilevers are the most popular
(but also there are rectangular), providing low mechanical resistance to vertical deflection, and high resistance to lateral torsion. Integrated cantilevers are usually made from silicon (Si) or silicon nitride (Si₃N₄). They are characterized by their force constant and resonant frequency, which have to be chosen according to the sample to be studied. Additionally an optical detection system and electronics for the management of scanning procedures and data acquisition are necessary.

3) Beam Deflection Detection

To detect the displacement of the cantilever, a laser is reflected off the back of the cantilever and collected in a photodiode.

- Operating Modes

  1) Contact Mode

  In the so-called contact-AFM mode, the tip makes soft “physical contact” with the surface of the sample. The deflection of the cantilever is proportional to the force acting on the tip, via Hook’s law. In contact-mode the tip either scans at a constant small height above the surface or under the conditions of a constant force. In the constant height mode the height of the tip is fixed, whereas in the constant-force mode the deflection of the cantilever is fixed and the motion of the scanner in z-direction is recorded. By using contact-mode AFM, even “atomic resolution” images are obtained. For contact mode AFM imaging, it is necessary to have a cantilever which is soft enough to be deflected by very small forces and has a high enough resonant frequency to not be susceptible to vibrational instabilities. Silicon Nitride tips is used for contact mode.

  2) Non Contact Mode

  In this mode, the probe operates in the attractive force region and the tip-sample interaction is minimized. The use of non-contact mode allowed scanning without influencing the shape of the sample by the tip-sample forces. In most cases, the cantilever of choice for this mode is the one having high spring constant of 20-100 N/m so that it does not stick to the sample surface at small amplitudes. The tips mainly used for this mode are silicon probes.
3) Tapping Mode (intermittent contact Mode)

The force measured by AFM can be classified into long-range forces and short range forces. The first class dominates when we scan at large distances from the surface and they can be Van der Waals force, capillary forces (due to the water layer often present in an ambient environment). When the scanning is in contact with the surface the short range forces are very important, in particular the quantum mechanical forces (Pauli Exclusion Principle forces). In tapping mode-AFM the cantilever is oscillating close to its resonance frequency. An electronic feedback loop ensures that the oscillation amplitude remains constant, such that a constant tip-sample interaction is maintained during scanning. Forces that act between the sample and the tip will not only cause a change in the oscillation amplitude, but also change in the resonant frequency and phase of the cantilever. The amplitude is used for the feedback and the vertical adjustments of the piezoscanner are recorded as a height image. Simultaneously, the phase changes are presented in the phase image (topography). The advantages of the tapping mode are the elimination of a large part of permanent shearing forces and the causing of less damage to the sample surface, even with stiffer probes. Different components of the sample which exhibit different adhesive and mechanical properties will show a phase contrast and therefore even allow a compositional analysis. For a good phase contrast, larger tip forces are of advantage, while minimization of this force reduces the contact area and facilitates high-resolution imaging. So in applications it is necessary to choose the right values matching the objectives. Silicon probes are used primarily for Tapping Mode applications.

3.5.3 Fourier Transform Infrared Spectroscopy

- Introduction

Fourier transform infrared (FTIR) spectroscopy is a tool for qualitative and quantitative analyses of the various chemical groups present in the material [16-18]. Instead of recording the amount of energy absorbed when the frequency of the infrared (IR) light is varied (using monochromater), the IR
light is guided through an interferometer. Then the Fourier transform is performed on this signal from interferometer, which results in a spectrum similar to that from conventional infrared spectrometer.

- **Principle**

  In physical sciences, we often come across problems involving vibrations, or oscillations and resonances. These oscillatory motions can be described mathematically with the help of sine or cosine functions. For example, a simple harmonic motion of a particle can be represented by \( y = a \sin \omega t \) or \( y = a \cos \omega t \) where, \( \omega \) represents frequency. But, in most of the cases, the vibrations are complex functions which require an infinite series of terms. This type of function can be expressed in terms of sine and cosine series. This representation is called Fourier series.

  Fourier series is the representation of a function of a real variable by means of a series of sines and cosines which is an indispensible technique in mathematical physics. Fourier series for any single valued functions \( f(x) \) defined on the interval \([-\pi, \pi]\) may be represented over this interval by:

  \[
  f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left[ a_n \cos nx + b_n \sin nx \right]
  \]

  Where, the expansion co-efficients,

  \[
  a_0 = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \, dx \quad \text{(3.12)}
  \]

  \[
  a_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \cos nx \, dx \quad (n=0, 1, 2\ldots) \quad \text{(3.13)}
  \]

  \[
  b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} f(x) \sin nx \, dx \quad (n=0, 1, 2\ldots) \quad \text{(3.14)}
  \]
Fourier transforms:

\[
G(\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} f(t)e^{i2\pi\nu t} \, dt \tag{3.15}
\]

\[
f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} G(\nu)e^{-i2\pi\nu t} \, d\nu \tag{3.16}
\]

Equations (3.15 and 3.16) are called the Fourier Transform pair. If \( f(t) \) satisfies the Dirichlet conditions and the integral \( \int |f(t)| \, dt \) is finite, then \( G(\nu) \) exists for all \( \nu \) and is called the Fourier transform of \( f(t) \). The function \( f(t) \) in equation (3.16) is called the Fourier transform (inverse transform) of \( G(\nu) \).

Naturally it is required that \( \nu t \) be dimensionless since it is the argument of an exponential quantity. The combination of \( \nu t \), where \( \nu \) is the frequency with the dimension of inverse time and \( t \) is time, satisfies the above condition. The above Fourier transforms are used in the determination of absorption frequencies in the Fourier Transform Infrared Spectroscopy.

- **Working**

Infrared spectroscopy works on the principle that the chemical bonds have characteristic frequencies at which they vibrate. These resonant frequencies are dependent on the length of the bond and the masses of the atoms at either ends of it. For a diatomic molecule the natural frequency of vibration is:

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_r}} \tag{3.17}
\]

Where, \( k \) is the force constant and \( \mu_r \) is the reduced mass and is given by the equation:

\[
\mu_r = \frac{m_1 m_2}{m_1 + m_2} \tag{3.18}
\]

The force constant \( k \) is given by:

\[
K = \frac{2V}{x^2} \tag{3.19}
\]
Where $V$ is the potential in which the atoms vibrate and $x$ is the distance between the two atoms. The force constant is expressed either in kgs$^{-2}$ or Nm$^{-1}$. When the incident IR frequency matches with the resonant frequency, absorption takes place, resulting in an absorption peak in the IR spectrum.

In a conventional IR (or "continuous wave") spectrometer, a sample is exposed to electromagnetic radiation and the response (usually the intensity of transmitted radiation) is monitored. The energy of the radiation is varied over the desired range and the response is plotted as a function of radiation energy (or frequency). At certain resonant frequencies characteristic of the specific sample, the radiation will be absorbed resulting in a series of peaks in the spectrum, which can then be used to identify the sample.

Figure 3.7: Schematic ray diagram of the (FTIR) spectrophotometer.
Instead of varying the energy of the electromagnetic radiation, Fourier Transform spectroscopy exposes the sample to a single pulse of radiation and measures the response. The resulting signal, called free induction decay, contains a rapidly decaying composite of all possible frequencies. Due to resonance by the sample, resonant frequencies will be dominant in the signal and by performing a mathematical operation called a Fourier Transform on the signal the frequency response can be calculated. In this way the Fourier transform spectrometer can produce the same kind of spectrum as a conventional spectrometer, but in a much shorter time. FTIR spectrometers are cheaper than conventional spectrometers because building of interferometers is easier than the fabrication of a monochromater. In addition measurement of single spectra is faster for the FTIR technique because the information of all frequencies is collected simultaneously.

This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity (signal to noise ratio is very much improved). For the present work, Perkin Elmer Model: Spectrum one FTIR spectrophotometer was used and the ray diagram of the FTIR is shown in Figure 3.7.

3.5.5 Contact Angle Measurement

The wettability property of a solid surface is one of the most important aspects in both theoretical research and industrial application [19]. One of the fundamental methods of characterizing the hydrophobic properties of a solid surface is to determine the contact angle. The contact angle is a measure of the wetting behavior of a particular liquid on the surface under investigation and directly relates to the interfacial energies of the systems. The contact angle on the solid surface gets changed merely by changing the chemistry of the outermost monolayer. Atoms on the surface have higher energy than those within the bulk, so there is energy associated with the existence of any interface. When the specific energy (J/m\(^2\)) of the solid–vapor interface, \(\gamma_{SV}\), is
greater than that of the solid-liquid interface $\gamma_{SL}$, liquid tends to flow over an exposed solid surface.

When a small liquid droplet is put in contact with flat solid surface, distinct equilibrium regions may be found like partial wetting, finite contact angle $\theta$, complete wetting $\theta = 0$, or complete non-wetting [20]. In the case of partial wetting, the wetted portion of the surface is determined by certain ‘contact line’. A layer of liquid on a plane solid surface has two interfaces, solid-liquid '$\gamma_{SL}$' and liquid-vapor '$\gamma_{LV}$' so the change in energy ($\Delta E$) produced by spreading of the liquid film is:

$$\Delta E = \gamma_{SL} + \gamma_{LV} - \gamma_{SV}$$  \hspace{1cm} (3.20)

If $\Delta E<0$ the energy of the system is reduced so that the liquid will spread spontaneously (i.e. $\theta = 0$); otherwise the solid-liquid-vapour will be characterized by a finite contact angle. The balance of the tensions at the point of interaction leads to a relationship between the surface tension that is known as ‘Young’s equation [21]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos (\theta)$$  \hspace{1cm} (3.21)

Hydrophobicity of the thin films was tested in terms of contact angle ($\theta$) of the water droplet with the surface, using the formula,

$$\theta = 2 \tan^{-1} \left( \frac{2h}{\Delta} \right)$$  \hspace{1cm} (3.22)

Where, $h$ is the height and $\Delta$ is the width of water droplet touching the aerogel surface.

Water contact angle measurements were performed using contact angle meter. In this method the contact angle was directly measured using a contact angle meter. A water drop is kept on the surface and the image of the drop is projected on the screen with protractor. This gives directly the value of $\theta$ after the proper adjustment of the tangent to the water drop at the point of contact with the solid surface.
3.5.6 Optical Properties

Optical properties of the films are necessary for applications in opto-electronic devices. The considerable theoretical and experimental investigations on the optical behavior of thin films deal primarily with reflection, transmission and absorption properties and their relation to the optical constants of the film. The Beer-Lambert Law is illustrated in Figure 3.9. The light energy of Intensity 'I₀' passes through a sample with concentration 'C'. Some light energy is absorbed by the sample. The amount of light energy exiting the sample has Intensity 'Iᵣ'.

![Figure 3.9: Beer-Lambert law](image)

The Absorbance and Transmission (or Transmittance) of light through a sample can be calculated by measuring light intensity entering and exiting the sample. The Beer-Lambert Law is given by the following equations:

\[
\text{Light Absorbance (A)} = \log \left( \frac{I_0}{I_r} \right) = KCL \tag{3.23}
\]

\[
\text{Light Transmission (T)} = \frac{I_r}{I_0} = 10^{-KCL} \tag{3.24}
\]
The following terms are defined:
Light Intensity entering a sample is "I_0"
Light Intensity exiting a sample is "I_r"
The concentration of analyte in sample is "C"
The length of the light path in glass sample cuvette is "L".
"K" is a constant for a particular solution and wave length.
Chapter 3 Thin Film Deposition Methods and Characterization Techniques

References