CHAPTER II

DEPOSITION METHODS AND CHARACTERIZATION TECHNIQUES
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2.1 Introduction

The recent trends in the field of modern technology are based on the miniaturization; therefore, thin films become very important for hybrid hetero-structure integration. The advantage of thin film devices are low material consumption and possible use of flexible substrates. In order to satisfy these requirements, various thin film preparation techniques were employed by researchers\(^1\). The choice of a particular method depends on several factors like; (a) material to be deposited, (b) nature of the substrate, (c) required film thickness, (d) structure of the film and (e) applications of the film.

The thin film deposition can be broadly classified as physical and chemical methods and is outlined in the Fig. 2.1\(^2\). The physical methods include physical vapor deposition (PVD), laser ablation, molecular beam epitaxy and sputtering which are employed to deposit many binary and ternary compounds and different alloys. The chemical methods comprise of gas phase deposition methods and solution techniques. The gas phase methods can be further classified into chemical vapor deposition (CVD) and atomic layer epitaxy (ALE) which utilize the gas phase reactants for deposition. The liquid phase reactant methods include spray pyrolysis, sol-gel, spin and dip-coating techniques utilize precursor solutions for thin film preparation\(^3\). The techniques mentioned under the category of physical methods are overwhelmed with certain drawbacks and difficulties. However, physical methods are expensive but give relatively more reliable and reproducible results. Chemical methods have been studied extensively for the preparation of thin films due to their simplicity and inexpensiveness. Moreover, they facilitate materials to be designed on a molecular level. To fully exploit this, one requires a good knowledge of surface processes as well as nucleation, growth and morphology of the films prepared. The chemical methods have some drawbacks and advantages over other methods. However, there is no ideal method to prepare the compounds and alloys in thin film form which will satisfy all the requirements\(^4\). Three basic steps are followed in the film formation in all the above mentioned techniques. These steps are; creation of the species required for film formation, transport of the species through a medium and condensation of the species on the substrate and subsequent coalescence to form the film.

2.2 Spray Pyrolysis

Among the chemical methods, the spray pyrolysis technique is the most popular one today because large number of conducting and semiconducting thin films can be prepared by this technique. It is also popular due to its simplicity and low cost. In this technique, the thin
Deposition Methods and Characterization Techniques

Films can be deposited on different substrates like glass, ceramic, metallic etc. Many studies have been conducted for the past three decades on spray pyrolysis process and preparation of thin films. It has the capability to produce high quality well adherent films of uniform thickness. The present section describes the theoretical background, physical and chemical aspects of the spray pyrolysis method.

Fig. 2.1 Various types of thin film deposition techniques

2.2.1 Theoretical Background

Chemical spray pyrolysis (CSP) is used for depositing a wide variety of thin films, which are used in devices like solar cells, sensors, solid oxide fuel cells etc. It has evolved into an important thin film deposition technique and is classified under chemical methods of...
deposition. This method offers a number of advantages over other deposition processes like; scalability, cost-effectiveness, easiness of doping, operation at moderate temperatures (100-500°C), variety of substrates, control of thickness, variation of film composition and the possibility of multilayer deposition.

Many studies were done on chemical spray pyrolysis (CSP) process since the pioneering work by Chamberlein and Skarman in 1966 on CdS films for solar cells\textsuperscript{24,25}. Several reviews on this technique have also been published. B.R. Bamplin reviewed CSP technique in which properties of specific films (particularly CdS) in relation to deposition parameters and their device applications were discussed in detail\textsuperscript{26}. Tomar and Garcia\textsuperscript{27} discussed the preparation, properties and applications of spray-coated thin films. Albin and Rishbud\textsuperscript{28} presented a review of equipment’s, processing parameters and opto-electronic materials deposited using this technique. Krishnakumar et al., did an exclusive review of sprayed thin films for solar cells in which a variety of solar cell materials and their preparative parameters were detailed\textsuperscript{29}. Different atomization techniques and properties of metal oxide, chalcogenide and superconducting films prepared using CSP were discussed by Patil\textsuperscript{30}. Recently, Perednis and Gaukler\textsuperscript{31} gave an extensive review on the effect of spray parameters on films as well as models for thin film deposition by CSP.

2.2.2 Basics of spray pyrolysis

The basic principle involved in spray pyrolysis technique is that, when droplets of spray solution reach the hot substrate, owing to the pyrolytic decomposition of solution, well adherent pin-hole free, uniform film is deposited on to 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 and sintering, recrystallization of the crystallites are provided by the hot substrate. It is different for the different materials and solvents used in the spray process.

Apart from its simplicity, spray pyrolysis technique has a number of advantages.

- Spray pyrolysis is a simple and low cost technique for the preparation of semiconductor thin films.
- It has capability to produce large area, high quality adherent films of uniform thickness.
- Spray pyrolysis 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.
The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters.

A major advantage of this method is the moderate operating temperature (100-500°C) and can produce films on less robust materials.

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.

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\textsuperscript{32,33}.

2.2.3 Factors governing spray pyrolysis

Thin film formation by using SPT depends upon various parameters. SPT consists of a thermally stimulated chemical reaction between clusters of liquid or vapour atoms of different chemical species. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic decomposition and forms a single crystallite or cluster of crystallites as a product on the substrate. The substrates provide thermal energy for the thermal decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thereby resulting in coherent film. The number of factors governing the film formation mechanism depends on,

- The automation of the spray solution into a spray of fine droplets which depends on the geometry of the spraying nozzle and pressure of a carrier gas.
- The properties of thin films depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition.
- The film thickness depends on the distance between the nozzle and substrate, solution concentration, quantity and substrate temperature.
- The film formation depends upon the process of droplet landing, reaction and solvent evaporation which are related to droplet size and its momentum\textsuperscript{34}.

2.2.4 Outline of spray pyrolysis and formation of thin films

In spray pyrolysis, the process parameters like precursor solution, atomization of precursor solution, aerosol transport and decomposition of precursor are very important while studying the structural, optical & electrical properties, morphology and crystallinity of the thin films. The schematic diagram of spray pyrolysis technique is shown in Fig. 2.2. These four process parameters are discussed in the following section.
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i. Precursor solution

Precursor solution plays a vital role in the formation of thin films 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 high solubility, which increases the 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. In general, metal chlorides and oxy-chlorides have the highest water solubility relative to other metal salts and are used for industrial production. The corrosive nature of the product gases at the adverse effect of residual chlorine on ceramic sintering decreases the general attractiveness of these salts for advanced ceramic solution synthesis, but the technology for handling such systems is available. Other water-soluble metal salts such as nitrates, acetates and sulfates can also introduce impurities, which may adversely affect subsequent processing, sintering or properties. The low solubility of metal acetates and high decomposition temperature of metal sulfates, limit the use of these water-soluble salts. Therefore, hybrid systems in which one of the components is added via a solution and remainder as particles have also been reported. Physical and chemical characteristics of the soluble chemical precursors strongly influence the characteristics of particles formed by spray pyrolysis.

ii. Atomization of precursor solution

The critical operation of the spray pyrolysis technique is to produce uniform and fine droplets by thermal decomposition. A variety of atomization techniques have been used for solution aerosol formation, including pneumatic, ultrasonic and electrostatics. Some of spray atomization techniques include improved spray pyrohydrolysis, microprocessor based spray pyrolysis, electrostatic spray pyrolysis, corona spray pyrolysis, ultrasonic nebulized atomization technique etc. These atomizers differ in droplet size, rate of atomization and droplet velocity. The velocity of the droplet when it leaves the atomizer is very important as it determines the heating rate and the residence time of the droplet during spray pyrolysis. The size of the droplets produced 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. The quality of film also depends on the compressed air used to guide the solution from the nozzle. When the
air pressure is more, smaller droplets are likely to form. However, this causes the substrate temperature to drop due to rapid splashing of smaller droplets. On the other hand, if the air pressure is too small, the larger droplets fall onto the substrates. Hence, it is essential to optimize the air pressure.

![Schematic Diagram of Spray Pyrolysis Technique](image)

*Fig. 2.2 Schematic diagram of spray pyrolysis technique*

### iii. Aerosol transport

In spray pyrolysis, precursor solution is atomized through a nozzle. The nozzle converts the solution into small droplets known as aerosols. These aerosols are allowed to incident on to the preheated substrates. The pyrolytic decomposition of the aerosols depends on the substrate temperature. The formation of thin films with desired properties is possible only at optimum substrate temperature. In an aerosol, the droplet is transported and eventually evaporates. In case dense films are desired, it is important that during transportation as many droplets as possible fly to the substrate without forming particles before reaching the surface as shown in Fig. 2.3.

Various steps during pyrolysis of aerosols are as explained below.

- In the first step, an aqueous precursor solution is converted into aerosols (droplets) by spray nozzle and the solvent evaporation takes place.
- In this step, vaporization of the solvent leads to the formation of precipitate as the droplets approaches the substrate.
Pyrolysis of the precipitate occurs in succession before the precipitate reaches the substrate.

When the precipitate reaches the substrate, nucleation and the growth of metal oxide thin films on the substrate take place.

Finally, the growth of the nuclei leads to the formation of continuous thin layer of metal oxide.

![Mechanism of thin film formation by spray pyrolysis method](image)

**Fig. 2.3 Mechanism of thin film formation by spray pyrolysis method**

### 2.2.5 Deposition parameters

Properties of film deposited depends on various deposition parameters like substrate temperature, nature of spray and movement of spray head, spray rate, type of carrier gas, nature of reactants and solvents used. The effect of some important spray parameters are discussed here.

**i. Substrate temperature**

Substrate temperature plays a major role in determining the properties of the films formed. It is generally observed that higher substrate temperature results in the formation of better crystalline films. Grain size is primarily determined by initial nucleation density and recrystallization. Recrystallization into larger grains is enhanced at higher temperature. By increasing the substrate temperature, the film morphology can be changed from cracked to dense and then to porous. Variation of substrate temperature over different points results in non-uniform films. Composition and thickness are affected by changes in substrate temperature which consequently affect the properties of deposited films. For example, while
preparing SnS films using CSP, single phase films are obtained only in a narrow range of temperatures. Secondary phases like Sn$_2$S$_3$, SnS$_2$, SnO$_2$ etc., are present in films prepared at lower and higher temperatures.$^{39}$

**ii. Influence of precursors**

Precursors used for spraying is very important and it affects the film properties seriously. Solvent, type of salt, concentration and additives influence the physical and chemical properties of the films. Usually, de-ionized water is ideal for a low cost process. Use of alcohol as solvent has also been reported. It was observed that transparency of as deposited ZnO films increased when ethanol was used instead of water as solvent for zinc acetate$^{40}$. Properties of films varied with type of precursors. For example, when In$_2$S$_3$ thin films were deposited from chloride based and nitrate based precursors, their properties differed significantly. Films from chloride based precursors were crystalline and highly photosensitive compared to those formed from nitrate based precursors which were amorphous$^{41}$. Concentration of spray solution also affects the nature of the films formed. Usually it ranges from 0.001 M to 0.1 M and it is seen that smooth films of columnar grains are obtained with low concentration and low spray rates. Chen et al., observed that surface morphology of the films changed from cracked to crack free reticular, after introduction of acetic acid into precursor solution$^{42}$. The change in morphology was attributed to the chemical modification of precursor solution. Caillaud et al., investigated the influence of pH on thin film deposition and found that the growth rate depended on pH. Formation of basic salts, adsorption compounds or precipitates slowed down the growth at higher pH. At low pH, deposition rate decreased drastically$^{43}$.

**iii. Spray rate**

Spray rate is yet another parameter influencing the properties of films formed. It has been reported that properties like crystallinity, surface morphology, resistivity and even thickness are affected by changes in spray rate. It is generally observed that smaller spray rate favours formation of better crystalline films. Smaller spray rate requires higher deposition time for obtaining films of the same thickness prepared at higher spray rate. Also, the surface temperature of substrate may deviate to a lower value at high spray rate. These two factors may contribute to the higher crystallinity at small spray rates. Decrease in crystallinity at higher spray rates was observed in sprayed CuInS$_2$ thin films. Decrease in crystallinity usually results in increased resistivity of the films. Surface morphology of the films varies
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with spray rate. Higher spray rate results in rough films\textsuperscript{44}. Also, it was reported that films deposited at smaller spray rates are thinner due to the higher re-evaporation rate.

iv. Other parameters

Parameters like height and angle of spray head, angle or span of spray, type of scanning, pressure and nature of carrier gas etc., influence the properties of deposited films. Different types of spray heads which produce different spray patterns are commercially available. Relative motion of the substrate holder and spray head should ensure maximum uniformity and large area coverage.

2.2.6 Experimental details

Nebulizer Spray Pyrolysis technique is employed for the fabrication of films. Nebulizer is a small machine that is powered by an air compressor, which has ability to change the precursor solution into very tiny droplets like mist. Though it is portable, it requires electric power to operate air compressor. Tubing connects the compressor to a cub of the Nebulizer that holds the liquid. By applying the compressed air to the Nebulizer, it can convert the liquid into mist form.

Nebulizers are two types; they are Nebulizer Spray Pyrolysis (NSP) and Ultrasonic Nebulizer. Nebulizers are based on the Venturi principle, whereas Ultrasonic Nebulizers use the converse piezoelectric effect to convert alternating current to high frequency acoustic energy. Important variables for both types are treatment time required, particle size produced and aerosol liquid output. Two main parameters are generally used to evaluate the performance of nebulizer, the droplet size distribution of the aerosol and the liquid output rate and are basically determined by the design and user conditions of the nebulizer. A higher gas flow of the compressor in Jet nebulizer or a higher variation frequency of the piezo electric crystal in an ultrasonic nebulizer decreases the droplet size. The major part of the mass of volume distribution should preferably correspond with aerodynamic particle diameters in the range of 1 to 5 mm. The droplet size and rate of flow of solution in nebulizer mainly depends on the geometry of nebulizer and carrier gas pressure. According to the simulations and experiments, it can be inferred that the droplet size distribution of the Jet micro-nebulizer described is finer and more uniform than that of the current conventional devices; furthermore, the system power consumption is lower than that of the ultrasonic-type nebulizer\textsuperscript{45}. An attempt made to use the medical nebulizer as a spray gun for thin film preparation on any kinds of substrate by applying very high carrier gas pressure as inlet for
producing chemical solution’s mist. The schematic diagram and photograph of nebulizer spray pyrolysis technique are as shown in Figs. 2.4 and 2.5.

**Fig. 2.4 Nebulizer spray pyrolysis (NSP) setup**

**Fig. 2.5 Photograph of Nebulizer spray pyrolysis (NSP) setup**
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A specially designed solution flow tube is used as an outlet with 25 cm horizontal length and 15 cm vertical length. The bottom of the vertical tube is designed carefully as a spray nozzle to spray the chemical liquid mist on the substrate smoothly.

2.3 Characterization tools

Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. In this section different analytical instrumental techniques used to characterize the films are described with relevant principles of their operation and working.

2.3.1 Structural analysis

i. X-Ray Diffraction

The analysis of crystal structure is of great importance in the description of materials; such an analysis is typically performed by employing XRD techniques. Other techniques include electron diffraction method and neutron diffraction method. The basic information that can be obtained from such diffraction patterns is the d_hkl spacing, the crystal lattice type, lattice parameters and crystalline phases present in materials, the structural properties of these phases and atomic arrangements of crystalline materials. In general, two interacting waves interfere constructively if they are in phase, i.e., in step, whereas the waves interfere destructively, i.e., cancel each other out, if they are out of phase, this is called diffraction. In XRD, the electron beam strikes a metal target and X-rays are generated. The X-rays is incident on a specimen in an angle θ. If the specimen is crystalline and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, diffraction will occur.

The diffraction condition is illustrated in Fig. 2.6, which demonstrates that the path difference between X-ray waves, which are specularly reflected from two adjoining (parallel) planes, is 2d sinθ. The intensity of diffracted X-rays is measured as a function of the diffraction angle 2θ and the orientation of specimen. This diffraction pattern is used to determine the crystalline phases and structural properties of the specimen according to Bragg’s law.46

\[ 2d \sin \theta = n\lambda \]  

(1)
where, \( n \) (called the order of the corresponding reflection) is an integer, \( \lambda \) is the wavelength of X-rays, \( d \) is the atomic spacing and \( \theta \) is characteristic angle. If the wavelength is known (depends on the type of X-ray tube used) and the angle can be measured (with a camera or diffractometer), the interplanar distance can be calculated from the Bragg equation, so that the reciprocal lattice of the crystal can be directly mapped. International Center Diffraction Data (ICDD) or formerly known as (JCPDS) Joint Committee on Powder Diffraction Standards is the organization that maintains the database of inorganic and organic spectra. The database is available from the Diffraction equipment manufacturers or from ICDD. Currently the database is supplied either on magnetic or optical media.

Two database versions available are the PDF I and the PDF II. The PDF I database contains information on d-spacing, chemical formula, relative intensity, quality information and routing digit. The PDF II database contains full information on a particular phase including cell parameters. The database format consists of a set number and a sequence number. The set number is incremented every calendar year and the sequence number starts from 1 for every year. The yearly releases of the database are available in September of each year.

![Fig. 2.6 Representation of XRD pattern](image)
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Model : X’pert PRO

X-ray source : 1.8 kW ceramic copper tubes

Operation potential : 40 kV, 30 mA

Filter : Nickel

Radiation used : CuKα - 1.54056 Å

ii. Fourier Transform-Infra-Red spectroscopy

Studies of the spontaneous orientation of dipole moment in semiconductors are carried out with a non-destructive tool of analysis by infrared spectroscopy which can give information on atomic arrangement and inter atomic forces in the crystal lattice itself. It is possible to investigate how the infrared vibrational frequencies and thus the inter-atomic forces are affected by the onset of the semiconductor states. FT-IR spectroscopy is a tool for qualitative and quantitative analysis of the various chemical groups present in the material. Instead of recording the amount of energy absorbed when the frequency of the infrared (IR) light is varied (using monochromator), 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. 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.

The spectrum is usually represented as a plot of the intensity vs. the frequencies and peaks occur when the condition is satisfied. Frequency ranges that can be encountered in this spectrum vary from those of “ν” rays, which have wavelength of about 10-10 cm to radio waves which have wavelength of 10-10 cm. Most of spectroscopic investigations are carried out in a relatively small portion of spectrum close to visible light. This region includes UV, visible and IR region and is arbitrarily defined as being between wavelength of $10^{-6}$ cm and $10^{-3}$ cm. Both the atoms and molecules give rise to spectra but they differ from each other. The difference between the atomic and molecular spectra lies in the nature of energy levels involved in the transitions. In the atom, the absorption represents transition between the different allowed levels for the orbital electrons. In case of molecules, however, the atoms within the molecules vibrate and the molecule as a whole rotates and the total energy contributions are represented by the equation, Where, $E_{\text{elect}}$ is the electronic energy, $E_{\text{vib}}$ is the vibrational energy, $E_{\text{rot}}$ is the rotational energy and $E_{\text{trans}}$ is the translation energy. The separate energy levels are quantized and only certain transitions of electronic, vibrational and rotational energy are possible. Translational energy is usually sufficiently small to be ignored.
The vibrational spectrum of a molecule is considered to be a unique physical property and is a characteristic of the molecule. As such the infrared spectrum can be used as a finger print for identification, in support of X-ray diffraction technique for the purpose of characterization.

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. FT-IR spectrometers are cheaper than the fabrication of a monochromator. In addition measurement of single spectra is faster for the FT-IR 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. For the present work, FT-IR spectrometer; Perkin Elmer Model Spectrum one was used and the ray diagram of the FT-IR is shown in Fig. 2.7.48.

Fig. 2.7 Ray diagram of FT-IR Spectrometer
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2.3.2 Surface analysis

i. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) can provide a highly magnified image of the surface and the composition information of surface regions of the materials. The resolution of scanning electron microscope can approach a few nanometers and the very high magnifications. In scanning electron microscope, electron beam is accelerated by an electron gun at low voltage of 1-20 kV and is scanned on the specimen surface. As the electron beam strikes the surface, a large number of signals are generated from the surface in the form of electrons or photons. These signals emitted from the specimen are collected by detectors to form images and the images are displayed on a cathode ray tube screen. In scanning electron microscope one can get the three types of images such as, secondary electron images, backscattered electron images and elemental X-ray maps. Secondary electrons (SE) are considered to be the electrons resulted from inelastic scattering with atomic electrons and with the energy less than 50 eV; Backscattered electrons (BSE) are considered to be the electrons resulted from elastic scattering with the atomic nucleus and with the energy greater than 50 eV. The backscattering will likely occur in a material of higher atomic number, so the contrast caused by elemental differences can be built up. After the primary electron beam collides with an atom in the specimen and ejects a core electron from the atom, the excited atom then decays to its ground state and emit either a characteristic X-ray photon or an Auger electron. The schematic diagram of the scanning electron microscope is shown in Fig. 2.8.

In the present study, the HITACHI Model S-3001H model with a greater resolution, is used to observe and analyze surface of the films. In the present study, the SEM used is capable of taking magnified pictures of solid, dry, conducting and non-conducting specimen. Its technical specifications are listed below.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model number</td>
<td>HITACHI Model S-3001H</td>
</tr>
<tr>
<td>Scanning probe diameter</td>
<td>20 Å</td>
</tr>
<tr>
<td>Resolution</td>
<td>60 Å at 30 kV</td>
</tr>
<tr>
<td>Magnification</td>
<td>20 - 65,000</td>
</tr>
<tr>
<td>Voltage</td>
<td>1 - 39 kV</td>
</tr>
<tr>
<td>Required specimen size</td>
<td>5x5 mm² with 1 mm thickness</td>
</tr>
</tbody>
</table>
ii. Atomic Force Microscopy

The working principle of Atomic Force Microscope (AFM) is very simple. The atomic force microscopy is used to scan the surface of the sample using a cantilever with a sharp tip near the sample surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nanometers. Atomic force microscope operates by measuring attractive or repulsive forces between a tip and the sample surface. In its contact mode (repulsive) atomic force microscope can be used to measure the local sample height. In its non-contact mode (attractive), atomic force microscope derives topographic images; the tip does not touch the sample. The tip is fixed at a constant distance from the surface. As the tip raster scans in two dimensions (x,y), a piezo-electric sensor move in the z direction to maintain a constant deflection using a feedback loop. Depending on the difference in the deflection value, a voltage is applied to the piezo-electric sensor to move the sample up or down to maintain the constant deflection.

Fig. 2.8 Schematic diagram of Scanning Electron Microscopy
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The voltage applied to the piezo-electric sensor plotted against the tip movement gives the true height variations on the sample surface. This provides a three dimensional image of the sample topography. The deflection of the tip is detected by a light sensitive detector sensing displacement of laser beam reflecting the back of the cantilever. Various forces such as van der Waals, electrostatic, capillary, adhesive and double layer can act between the tip and the sample\textsuperscript{50}. The schematic diagram of the atomic force microscopy is shown in Fig. 2.9.

In the present study, Nanoscope E scanning profile microscopy model No.3138 J has been used for the surface analysis of the prepared films. The technical features of the instrument are listed below.

- **Model number**: Nanoscope E - 3138 J
- **Mode of operation**: Contact mode, tapping mode
- **Resolution**:
  - In contact mode - atomic level
  - In tapping mode - nm scale laterally
- **Scanning frequency**: 0.5 - 1 Hz
- **Scan area**: 150x150 µm
- **Probe diameter**: 20 Å
- **Spring constant**: 4 N/m
- **Sample size**: 12x12 mm\textsuperscript{2} and 4 mm thick

![Fig. 2.9 Representation of Atomic Force Microscopy](image)

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2.3.3 Chemical composition analysis

i. Energy Dispersive X-ray Analysis

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-rays (Fig. 2.10). The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. The excess energy of the electron that migrates to an inner shell to fill the newly-created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron, and the method for its analysis is known as Auger Electron Spectroscopy (AES)\textsuperscript{51}.

ii. X-ray Photoelectron Spectroscopy

Information on the quantity and kinetic energy of ejected electrons is used to determine the binding energy of these now--liberated electrons, which is element-specific and allows chemical characterization of a sample. X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique, which provides information both about chemical composition and chemical bonding.
The phenomenon is based on the photoelectric effect outlined by Einstein in 1905 where the concept of the photon was used to describe the ejection of electrons from a surface when photons impinge upon it. For XPS, Al Kα (1486.6 eV) or Mg Kα (1253.6 eV) are often the photon energies of choice. Other X-ray lines can also be chosen such as Ti Kα (2040 eV). The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The energy of the photoelectrons leaving the sample is determined and this gives a spectrum with a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element. The peak areas can be used to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. Hence, XPS can provide chemical bonding information as well. XPS is not sensitive to hydrogen or helium, but can detect all other elements. XPS must be carried out in ultra-high vacuum (UHV). The analysis of composition has been widely applied in the thin film research fields. One can obtain the composition of thin films from XPS spectra. The information of all elements in thin film can be gained from the survey scan spectrum of XPS. The detailed information of each element in the thin film can be obtained from the narrow scan spectrum of XPS. In XPS the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron. For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in
the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

Fig. 2.11 Ray diagram of XPS

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study; furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region\textsuperscript{52}. Thus, the technique is capable of yielding a quantitative analysis (Fig. 2.11).

In the present investigation, the chemical composition and valence states of constituent elements are analyzed by X-ray Photoelectron Spectroscopy (XPS, Physical Electronics PHI 5400, USA) with monochromatic Mg K\textsubscript{α} (1254 eV) radiation source at University of Madras.

2.3.4 Optical analysis
i. UV-Vis-NIR Spectrophotometer

Spectrophotometers are optical instruments that measure the intensity of light transmitted or reflected by objects as a function of wavelength. Light from the lamp enters the monochromator, which disperses the light and selects the particular wavelength chosen by the operator for the measurement. The light beam of selected wavelength is passed alternately through the sample and along reference path. The ‘reference’ and ‘sample’ light beams pass through the cell compartment, consisting of a `reference space' and a sample space. The two light beams converge on the detector. Quantitative measurements in chemical analysis are done by comparison of the absorption with the absorbance of known concentration of the
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element. Extensively used for determination of trace impurities in semiconductors, alloying elements in steel, non-ferrous alloys, trace impurities in ceramic materials, trace impurities in liquids like high purity water, solvents, acids, dyestuffs in food etc. Transmittance or absorbance of solid or liquid and total diffuse reflectance/transmittance of solids like large disks, silicon wafers, plastics, glass etc. can be measured. Band gap determination, electron transition and enzyme activity studies can also be made. Different compounds may have very different absorption maxima and absorbance. The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical photon absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is altogether considered to be due to 1) inner shell electrons 2) valence band electrons 3) free carriers including holes as well as electrons and 4) electrons bound to localized impurity centers or defects of some type. In study of the fundamental properties of some semiconductors, the absorption by the second type of electrons is of great importance. In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons so that electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer the electrons from valence band to conduction band. The optical absorption spectra of semiconductors generally exhibit a sharp rise at a certain value of the incident photon energy, which can be attributed to the excitation of electrons from valence to conduction band. The conservation of energy and momentum must be satisfied in optical absorption process. Basically, there are two types of optical transitions that can occur at the fundamental edge of the crystalline semiconductor, direct and indirect. Both involve the interaction of an electromagnetic wave with an electron in the valence band, which is rise across the fundamental gap in the conduction band. However, indirect transition also involves simultaneous interaction with lattice vibration. Thus, the wave vector of the electron can change in the optical transition. The momentum change being taken or given up by phonon. The direct interband optical transition involves a vertical transition of electrons from the valence band to the conduction band such that there is no change in the momentum of the electrons and energy is conserved as shown in Fig. 2.12. Hence, a wave vector k for electron remains unchanged in E-k space. The optical transition is denoted by a vertical upward narrow53.
In the present work, optical transmittance properties of the films are analyzed with the Hitachi-3400 UV-Vis-NIR spectrophotometer. Technical specification of the instrument is listed below

- **Model**: Hitachi-3400 (double beam)
- **Wavelength range**: 200 - 2600 nm

### ii. Photoluminescence Spectroscopy

Photoluminescence spectroscopy (PL) is a powerful optical method used for characterizing materials. It can be used to find impurities and defects in semiconductors and to determine semiconductor band gaps. A material absorbs light, creating an electron hole pair; an electron from the valence band jumps to the conduction band leaving a hole. The photon emitted upon recombination corresponds to the energy difference between the valence and conduction bands, and is hence lower in energy than the excitation photon. Luminescence is light that accompanies the transition from an electronically excited atom or molecule to a lower energy state. The forms of luminescence are distinguished by the method used to produce the electronically excited species. When produced by absorption of incident radiation, the light emission is known as photoluminescence. Photoluminescence that is
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short-lived ($10^{-8}$ s or less between excitation and emission) is known as fluorescence. Photoluminescence that is longer-lived (from $10^{-6}$ s all the way up to seconds) is known as phosphorescence. The reason for the difference in lifetime is that fluorescence involves an allowed, high-probability transition while phosphorescence involves a forbidden, low-probability transition. Photoluminescence excitation spectra are determined by measuring emission intensity at a fixed wavelength while varying the wavelength of the incident light used to produce the electronically excited species responsible for emission. The excitation spectrum is a measure of the efficiency of electronic excitation as a function of excitation wavelength. Photoluminescence emission spectra are determined by exciting at a fixed wavelength and varying the wavelength at which emission is observed. Between excitation and emission, electronically excited molecules normally lose some of their energy because of relaxation processes. As a consequence, the emission spectrum is at longer wavelengths, that is, at lower energy, than the excitation spectrum. PL is divided into two major types: Intrinsic and extrinsic depending on the nature of electronic transition producing it.

**Intrinsic luminescence**

Intrinsic luminescence is of three kinds: i. band-to-band luminescence ii. exciton luminescence and iii. cross-luminescence.

**i. Band-to-band luminescence**

Luminescence owing to the band-to-band transition, i.e., to the recombination of an electron in the conduction band with a hole in the valance band, can be seen in pure crystal at relatively high temperature. This has been observed in Si, Ge and IIIb-Vb compounds such as GaAs.

**ii. Exciton luminescence**

An exciton is a composite particle of an excited electron and a hole interacting with one another. It moves in a crystal conveying energy and produces luminescence owing to the recombination of the electron and the hole. There are two kinds of excitons: Wannier exciton and Frenkel exciton. The Wannier exciton model express an exciton composed of an electron in the conduction band and a hole in the valence band bound together by coulomb interaction. The expanse of the wave function of the electron and hole in Wannier exciton is much larger than the lattice constant. The excitons in IIIb-Vb and IIb-VIb compounds are examples for Wannier exciton. The Frenkel exciton model is used in cases where expanse of electron and hole wave function is smaller than lattice constant. The excitons in organic molecular crystals are examples of Frenkel exciton.
iii. Cross-luminescence

Cross luminescence is produced by the recombination of an electron in the valance band with a hole created in the outer most core band. This is observed in number of alkali and alkaline-earth halides and double halides. This takes place only when the energy difference between the top of valance band and that of conduction band is smaller than the band gap energy\textsuperscript{54}. This type of luminescence was first observed in BaF\textsubscript{2}.

![Block diagram of PL spectroscopy](image)

**Fig. 2.13 Block diagram of PL spectroscopy**

The emission and excitation spectra (Fig. 2.13) of the thin films samples are recorded using Fluorolog-3 spectroflurometer having a 150 W Xenon arc lamp, monochromator and a CCD detector.

- **Model**: Fluorolog-3 spectroflurometer
- **Wavelength range**: 300 - 600 nm
- **Excitation wavelength**: 325 nm

2.3.5 Electrical analysis

i. DC conductivity measurements

In general, the electrical resistivity of oxides is extremely sensitive to its purity and perfection of the crystal. In all cases, the electrical resistivity is very high at low temperatures and decreases rapidly as the temperature is raised, usually in an exponential trend. This type of variation can be due either to ionic conduction or due to electronic semi-conduction. DC conductivity measurements enable us to determine the total conductivity of the samples under investigation originating from grain, grain boundaries and electrode process. In DC measurements, the sample is biased by dc power supply and the variation in current (I) is
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measured (for a fixed voltage (V)) as the temperature of sample under investigation is changed (Fig. 2.14). The resistance \((R = V/I)\) of sample measured as function of temperature is used to calculate resistivity values. Resistivity \((\rho)\) is calculated using simple relation given as,

\[
\rho = \frac{\pi}{\ln(2)} \frac{V}{I} t
\]

(2)

where, \(t\) is the thickness of the sample. The dc conductivity can be represented as Arrhenius relation and is given by,

\[
\rho = \rho_o \exp\left(\frac{E_a}{KT}\right)
\]

(3)

where, \(E_a\) is the activation energy for conduction, \(T\) is the absolute temperature, \(K\) is the Boltzmann constant and \(\rho_o\) is the pre-exponential factor. These oxides follow the modified Arrhenius relation which governs the thermally activated conduction, where the conductivity is observed to be the function of temperature.

![Experimental setup of two probe technique](image)

Figure 2.14 Experimental setup of two probe technique

The instrumentation techniques discussed above have been employed in the present work for analysis and characterization.
References

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Deposition Methods and Characterization Techniques

45. S.-C. Shen, Y.-J. Wang, Y.-Y. Chen, Design and fabrication of medical micro-nebulizer. Department of Systems and Naval Mechatronic Engineering, National Cheng Kung University, Tainan 701, Taiwan.