CHAPTER 3

EXPERIMENTAL SETUP AND CHARACTERIZATION

3.1 INTRODUCTION

Thin film applications in optics and electronics have made rapid progress in recent past. Consequently a variety of thin film techniques are available, offering a great flexibility for thin film preparation. Growth techniques play a significant role in governing the properties of thin films, because the same material, deposited by two different techniques, has usually very different physical properties. This is due to the fact that the electrical and optical properties of these films strongly depend on the structure, morphology and the impurities present. Moreover films grown by any particular technique may often have different properties due to the involvement of various deposition parameters. Properties of the thin films, however can be tailored by controlling the deposition parameters viz., substrate temperature, rate of deposition, background pressure, evaporation temperature and angle of incidence of evaporate. Many applications in modern technology require film properties like high optical transmission/reflection hardness, adhesion, non-porosity, high mobility of charge carriers, chemical inertness towards corrosive environments and stability with respect to temperature, stoichiometry and orientation. In fact application and properties of a given material determine the most suitable technique for the preparation of thin film of that material.
Deposition of thin films involves three steps:

A) Creation of atomic/molecular/ionic species.
B) Transport of these species through medium and
C) Condensation of these species on a substrate

Depending on, whether the vapour species has been created by physical or chemical process.

3.2 SUBSTRATE SELECTION AND CLEANING

The substrate selection and cleaning procedures are the special art in thin film deposition. The cleanliness of the substrate is a pre-requisite for obtaining good quality films with reproducible properties. It exerts a decisive influence on the film growth and adhesion.

3.2.1 Substrate Selection

Substrate selection mainly depends on the type of thin film to be deposited and also the process by which the film is prepared. Many times a thin film scientist has to restrict his experiments because of lack of proper substrate for the desired process. In general the following information may be noted before selecting the substrate for the thin film deposition (Pulker 1984, Rancourt 1987 and Maissel 1970).

1. Type of substrates
   a. Glass or crystalline materials like silicon and germanium
   b. Organic and plastics
   c. Metals

2. Rigid or flexible

3. Structure
4. Melting point
5. Hardness
6. Thermal conductivity
7. Thermal expansion
8. Transmitting region
9. Refractive index and extinction coefficient
10. Dielectric strength

3.2.2 Substrate Cleaning

The selection of the substrate decides the type of cleaning to be adopted in the process. The cleanliness of the substrate surface exerts a decisive influence on film growth and adhesion. The choice of the cleaning technique depends on the nature of the substrate, the type of contaminants and degree of cleanliness required.

Pre-cleaning involves the breaking of the adsorption bonds between the substrate and the contaminants without damaging the substrate. This is common for all types of materials. Some of the cleaning methods for the substrates are described below.

3.2.3 Ultrasonic Cleaning

Electrical energy from an oscillator circuit is fed to transducers at the bottom or side of the stainless steel tank. These piezoelectric transducers convert electrical oscillations to mechanical vibrations and cause the tank bottom to vibrate, resulting in intense agitation of the liquid contained in the tank. This intense disturbance in the liquid will cause to form and collapse millions of microscopic cavities or implode to release tremendous energy and
produce an intense local scrubbing action on the objects immersed in the liquid for cleaning.

3.2.4 Chemical Treatment

This method is likely to attack the substrate surface. Acid cleaners react with contaminants such as grease and some oxides to convert them into more soluble compounds. The effectiveness of the solvent is probably more dependent on the ability to wet the substrate than the solvent action.

3.2.5 Vapour Degreasing

The sample to be cleaned is to be inserted in the vapour degreasing chamber. The samples are kept in the bath until they reach the vapor temperature and then they are removed. The residual alcohol on the surface is evaporated immediately and the sample is ready for use.

3.2.6 Glow Discharge Cleaning

This is used as a method of surface preparation before depositing the film. After the chamber has been evacuated to a good vacuum in a reasonable amount of time a gas is introduced into the chamber to reduce the pressure in it about $10^{-3}$ mbar. A high voltage ranging from about 0.5 to 2 kV is applied to the electrodes in the chamber. The voltage causes to breakdown and forms a glow discharge. This results in a flood of excited atoms and ions in the chamber. The gas frequently used to strike the discharge is oxygen because it will remove organic contaminants on the surface of the substrate by oxidizing them. When the oxygen plasma damages the surface, another gas such as argon is used. The argon atoms bombard the surface and can remove some materials in a manner analogous to sputtering.
3.2.7  Washing and Drying

This process occurs many times in the cleaning process. Generally, distilled water is recommended but in semiconductor industry deionized water is recommended. After a careful cleaning and washing process, Lenin cloth or hot oven or acetone is recommended for drying the cleaned surfaces.

The above techniques are frequently used in combination with one another depending on the contaminants and the substrate.

In the present work, the 7059 corning microscopic glass substrates are used.

The glass substrates were degreased by the following cleaning procedure to remove the unwanted impurities normally present on the surface of the glass plates when exposed to the atmosphere.

(i) The glass substrates are washed in soap solution by scrubbing the surfaces with the cotton swab dipped in liquid soap till they pass the breathe figure test to remove oil, grease etc.

(ii) The glass slides are then rinsed thoroughly in deionized water to remove any traces of the soap solution left on the surface.

(iii) Then the substrates are soaked in chromic acid and heated to about one hour to dissolve the fine silica layer formed on the surface and to make a new surface for deposition of the film.

(iv) Finally the substrates are rinsed thoroughly in deionized water and dried with acetone. Now the glass substrates are ready for the deposition of the films.
3.3 THIN FILM DEPOSITION TECHNIQUES

3.3.1 Vacuum Evaporation Technique

Vacuum evaporation technique is one of the most widely used techniques for thin film preparation. The material whose film is required is kept in vacuum environment, heated to a temperature where large number of atoms or molecules leaves the surface of the material. These atoms/molecules deposit on a substrate kept at suitable temperature and distance in the vacuum environment. Deposition process consists of three distinguishable steps:

1. Transition of the condensed Phase (Solid or liquid) into gaseous state.
2. Transportation of vapor source to the substrate.
3. Condensation of vapor at the substrate (deposition at the substrate).

Substrates are made from variety of materials and may be kept at a suitable temperature depending on the properties of the film required. When evaporation is done in vacuum, evaporation temperature will be considerably lowered. Again the formation of Oxides as well as incorporation of impurities in the growing layer will be reduced usually the pressure used for normal evaporation work is about $10^{-5}$ torr. This also ensures a straight line path for most of the emitted vapour atoms for a substrate to source distance of approximately 10 cm in the vacuum system. The rate of deposition of the vapour on a substrate depends of the source geometry, the position of the source relative to the substrate and the condensation coefficient.
3.3.2 Sputtering

Sputtering is a process of ejection of atoms from the surface of a material by bombardment with energetic particles. In this process the substance to be deposited (target) is kept in the form of an electrode whose surface atoms (or molecules) are ejected by momentum transfer from the bombarding ions. The ejected or sputtered atoms are allowed to condense on a substrate to form a thin film (Figure 3.1). If the ejection is due to bombardment by positive ion, the process is known as cathodic sputtering. The ions required for bombardment is usually obtained by maintaining a glow discharge due to an applied electric field within the vacuum chamber. Over the years various sputtering techniques have been developed. The techniques are reactive sputtering, R-F sputtering, triode sputtering, ion plating, magnetron (direct and reactive) sputtering, ion beam sputtering etc (Wasa 1985, Chopra 1969 and Goswami 1995).

Sputtered atoms are condensed on a substrate to form a film. This process has the following unique characteristics:

i. Sputtered species are predominantly neutral and atomic. A small (less than 1%) of the species is charged, both positively and negatively.

ii. Sputtering yield (defined as number of ejected atoms per incident ion) increases with the energy and mass of the ions.

iii. Yield depends on the angle of incidents of the ions and increases a $(\cos \theta)^{-1}$ where $\theta$ is the angle between the normal to the target surface and the beam direction.
iv. Yield display an adulatory behavior with periodicity corresponding to the group of elements in the group of elements in the periodic chart.

a. Glow discharge sputtering,
b. Triode Sputtering,
c. Magnetron sputtering and
d. Ion beam sputtering,

![Figure 3.1 Schematic diagram of sputtering](image)

### 3.3.3 Epitaxial Deposition

Oriented growth of one material over another is commonly called “epitaxy” and Epitaxial growth is of particular interest in many semiconductor applications. As a result of nature of deposition process, thin films are invariably fine-grained and have a frozen-in high concentration of structural defects. Solar cell applications require large oriented grains or mosaic monocrystals, if single crystal films are not possible. By selecting an
appropriate single-crystal substrate, mosaic crystal substrate, mosaic crystals are epitaxially grown in sizes up to tens of micrometers and small-angle grain boundaries. Epitaxial film deposition may be achieved by a variety of techniques from solution as well as vapour.

Commonly used Epitaxial deposition techniques are the following:

i. Molecular Beam Epitaxy (MBE),

ii. Liquid Phase Epitaxy (LPE),

iii. Hot Wall Epitaxy (HWE) and


MBE is an ultra high vacuum evaporation process. Here atomic or molecular beams of the element or constituent elements of the compound are created and directed onto clear heated single crystal substrates to form the film. Beam intensities are controlled by the temperature of the emission ovens, chosen to provide necessary flex of the various elements arriving at the surface. In many cases the composition is controlled by the flux ratio, with fluxes controlled via the source temperature. Fast shutters introduced between the sources and the substrates, interrupt the beam fluxes, and by controlling the shutters one can grow layers of precisely controlled characteristics (thickness, dopant profile etc). The MBE unit contains sophisticated analytical tools like mass spectrometer, Low Energy Electron Diffraction (LEED) system etc. LPE is thermally controlled technique for the preparation of high purity Epitaxial films of semi conductor compounds and alloys. HWE is a vacuum deposition technique in which Epitaxial films are grown under condition as near as possible to thermodynamic equilibrium.
3.3.4 Electro Deposition

Electro deposition is the process of depositing a substance by the passage of the electric current through electrolyte, producing a chemical change. Properties of electrodeposited films depend on electrolyte, electrodes and current density when a metal electrode is dipped in a solution containing ions of that metal, a dynamic equilibrium is set up.

\[
M \rightarrow M^{n+} + xe^{-} \quad (3.1)
\]

Where M denotes the metal atom

Resultant potential between the electrode and electrolyte in the absence of the external voltage is called “electrode potential”. With the establishment of dynamic equilibrium the electrode gains a certain charge on itself, which attracts oppositely charged ions and molecules, holding them at the electrode/electrolyte, interface by electrostatic process. During deposition, ions reach the electrode surface, move to stable positions on it and release their charges and undergo electro-chemical reaction. Using this method various metals like Copper, Silver, Gold etc., are electroplated for electrical contracts in solar cells.

3.3.5 Chemical Vapour Deposition (CVD)

Chemical Vapour Deposition is an important and popular technique for the preparation of wide variety of materials (elements as well as compounds) on various substrates. CVD essentially involves exposure of the substrate to one or several vaporizing compounds or reagent gases, some or all of which contains constituents of the desired substance. A chemical reaction is then initiated at or near the substrate surface, producing the desired material as a solid face reaction product, which condenses on the substrate.
The chemical reaction may be activated by the application of heat, an RF field, liquid or X-rays, an electric arc, a glow discharge etc. CVD has many advantages over other methods of thin film deposition. Films with high degree of purity, better stoichiometry and doping levels can be prepared. The need for high expensive vacuum equipment can be avoided, since many reactions can be accomplished at ambient pressures. Higher deposition temperature improves crystal perfection also.

The deposition of thin film from gaseous phases by thermal decomposition or chemical reactions on substrates at high temperature is known as the CVD process. The basic principle involves decomposition or partial dissociation of the vapour phase species and their subsequent deposition on substrates or reactions amongst the vapour species in a neutral atmosphere or otherwise and the deposition of the products. Sometimes a carrier gas is also introduced either to control the rate of reaction or to prevent undesired reactions at the prevailing elevated temperature. Again the CVD process is achieved by a variety of techniques viz thermal decomposition, vapour phase reaction, vapour transportation method etc (Vankar 1985, Chopra 1969 and Goswami 1995).

### 3.3.6 Chemical Bath Deposition (CBD)

Chemical Bath Deposition is a solution growth process used for depositing thin films of compound materials. An aqueous solution of a metal complex, when mixed with a solution of chalcogen bearing compound, precipitation of the chalcogenide occurs under certain conditions. When the precipitation is controlled, compound gets deposited on the wall of the container and surface of the substrate. This method has been used successfully to deposit binary and ternary semiconductors. Parameters that control the deposition process are temperature, pH value, concentration of
ions, the nature of the substrate, nature of the complexing agents and salts used. Impurities that may be present in the starting chemicals have generally no effect on the growth process, unless the concentration is such that it satisfies the condition for precipitation. So, high purity chemicals are not required in this process. Moreover, large area films can be obtained and vacuum is not needed. So, it is clear that this technique is very simple and low cost. One negative aspect is that there can be reaction between substrate and the solution and hence all substrates cannot be used.

In chemical deposition method, thin films are deposited on the substrate from aqueous solution either by passing a current or by chemical reaction under appropriate conditions. Large or small and even or uneven surfaces of all types — conducting or insulating can be coated with relative ease by this cost effective method. The electro deposition, spray pyrolysis, closed space sublimation (CSS), anodization, solution growth, screen printing etc. are different chemical deposition techniques normally used for the deposition of thin films (Vankar 1985, Chopra 1969 and Goswami 1995).

3.3.7 Sol-Gel Method

In sol-gel thin film formation via. Dipping, inorganic or metal-organic films are deposited on the substrate surface by a complex steady state process combining drawing, solvent evaporation and continued condensation reaction (Brinker 1990).

3.3.8 Spray Pyrolysis

Chemical spray pyrolysis (CSP) is commercially attractive method for the production of high quality, uniform and well-crystalline compounds in a short time at low cost (Elidrissi et al 2001, Patil 1999 and Chen et al 1998).
The Spray pyrolysis technique is a simple technology in which an ionic solution containing the constituent elements of a compound in the form of soluble salts is sprayed onto over heated substrates using a stream of clean, dry air. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as carrier gas. In the process, the spray rate the size of the sprayed particles and the spray pattern are strongly influenced by the geometry of the spray nozzle used, in this method low cost and simple handling. The ability to produce good films depends on to proper choice of various process involved in the technique. These include the substrate nature, spray-nozzle diameter, nozzle substrate distance, substrate temperature (Ts) during film deposition and solution concentration (c). The present work deals with the fabrication of spray pyrolysis unit and the characteristics of such films are studied and reported.

Figure 3.2 Schematic diagram of spray pyrolysis
3.4 Spray Pyrolysis Technique

3.4.1 Introduction

Numerous materials have been prepared in the form of thin films over a century because of their potential and technical value and of scientific curiosity in their properties. They have very wide range of applications extending from micrometer dots in microelectronics to coatings of several square meters on window glasses. Various techniques have been examined in the search for the most reliable and cheapest method of producing such thin films. These include oxidation of an evaporated metal film, reactive and non-reactive sputtering techniques, thermal evaporation, molecular beam epitaxy, electron beam evaporation, ion plating, electro deposition, electro less deposition, anodization, and chemical vapour deposition etc. Owing to their simplicity and inexpensiveness, chemical techniques have been studied extensively for the preparation of thin films. Moreover they facilitate materials to be designed on a molecular level.

3.4.2 Fundamentals of Spray Pyrolysis Technique

Spray pyrolysis is essentially a thermally stimulated reaction between clusters of liquid and vapour atoms of different chemical species. This atomization technique of chemical species involves spraying a solution containing soluble salts of the constituent atoms of the desired compound with the help of a compressed gas or air through a nozzle. During this process, precursor solution is pulverized by means of a neutral gas (e.g. nitrogen) so that it arrives at the substrate in the form of very fine droplets. The compressed air or gas called as the carrier gas, which carries the atomized fine droplets may or may not play an active role in the pyrolytic reaction. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. Thus the sprayed fine
droplets on reaching (or hitting) the surface of the hot substrate, they undergo the chemical decomposition and reaction to form the required compound, which get adsorbed with the substrate, producing a thin film. These adsorbed molecules form the nucleus for the growth of crystallites or crystals contained in the thin films. As more and more droplets reaching the substrate, clusters of nuclei cling together to form the crystallites. Hence the film grows. The liquid solvent serves to carry the reactants and distribute them uniformly over the substrate area during the process.

Spray pyrolysis has been developed extensively by Chamberlin 1966 and co-workers. After that, many research articles and review articles (Pamplin 1979, Viguie 1975, Krishnakumar 1987 and Kern 1980) related to spray pyrolysis processing and the range of thin films deposited by this method for various applications have appeared in the literature. A comprehensive review of all possible thin film materials that could be deposited by spray pyrolysis technique for various applications has been published (Pramod 1999).

3.4.3 Physical Aspects of Spray Pyrolysis

Spray pyrolysis involves spraying a solution, usually aqueous containing soluble salts of the constituent atoms of the desired compound onto a heated substrate. Every sprayed droplet reaching the hot substrate surface undergoes pyrolytic (endothermic) decomposition and forms thin films with cluster of crystallites.

A block diagram of a general spray pyrolysis set-up is shown in Figure 3.3. Filtered carrier gas and solution are fed into a spray nozzle at a predetermined constant pressure and flow rate respectively. Substrate is placed inside a tubular furnace, which is powered by an external heater supply. The thermocouple in the feedback network delivered proportional
output to the temperature monitor unit. Uniform coating over larger area on a substrate can be achieved by mechanical / electromechanical movement of either the nozzle or substrate holder or both. The spray set-up should be inside an enclosed chamber with an exhaust duct to remove vaporized constituents and to provide a stable flow pattern. The droplet size and distribution of droplets in the spray cone mainly depend on the geometry of the spray nozzle. The typical mode of droplet formation in a spray head is shown in Figure 3.4.

![Figure 3.3 Chemical spray pyrolysis set-up](image)

In the spray cone, there exist three regions. Region A is in front of the nozzle, where the liquid is being lifted off the tip and accelerated into the main air cone turbulent-vortex region and the length of this region mainly depend on the flow rate of the precursor. The expanding helical shape of the aerosol envelope is seen at the confluence of regions A and B, where the
droplets are formed by the turbulence of the air stream. Region C is the outside region of the main aerosol cone, where low velocity droplets are seen when the nozzle is not suitably designed.

For uniform deposition, researchers have gone for modifications in the spray nozzle

Figure 3.4 Droplet formation at the spray nozzle

Kulaszewick et al (1980) has employed a rotating sprayer having a swing motion resulted in homogeneous films with reproducible properties. Pommier et al 1981 have modified the spray technique to grow films of uniform thickness over a large surface area (10 x 10 cm$^2$). For this, they made mechanical arrangement to move the nozzle in the x-y directions above the substrate. The upward and downward spray mechanism has been conducted by Arya 1986, whereas Unaogu and Okeke 1990 have used a rotating sprayer for the spray action. Peaker and Horsley 1971 have applied a method in which preheating of the spray mist took place too apart from the substrate heater.
This has resulted in the relatively small temperature fall at the substrate surface in comparison with other pyrolytic processes. Gottlieb et al 1991 have reported that size of the droplets generated by the ultrasonic vibrations can be calculated using Lang’s formula:

\[ d = k \left( \frac{8\pi \sigma}{\rho f^2} \right)^{1/3} \]  

(3.2)

Where ‘d’ is the diameter of the droplets, ‘\(\sigma\)’ is the surface tension, ‘\(\rho\)’ is the density of the precursor, ‘f’ the frequency of vibration and ‘k’ a constant that depends on the system used.

### 3.4.4 Chemical Aspects of Spray Pyrolysis

The chemicals used as solvent for spray pyrolysis must satisfy a variety of conditions for obtaining good quality films. The required conditions are (i) they should have lower surface tension (ii) they should undergo a thermally activated chemical reaction leading to proper thermal decomposition and good quality thin films and (iii) the remainder of the constituents of the chemical should be volatile at the pyrolytic temperature. These conditions are met by a number of combinations of chemicals and each combination has its own thermodynamic and kinetic considerations.

During pyrolytic decomposition, the constituents of the droplets vaporize during their transit towards the substrate or reacts on the surface after splashing. The pyrolytic process, in which the reaction occurs just above the surface of the heated substrate, is called heterogeneous reaction. If both the reactant and the product molecules are present in the gas phase or on the heated substrate then it is termed as homogeneous reaction. The homogeneous reaction is not desirable, which impede the film growth rate leading to irregular surfaces with powder formation (Chopra 1983 and Siefert 1984).
In heterogeneous reaction, the droplets undergo pyrolytic (endothermic) decomposition leading to formation of films with single crystallites or cluster of crystallites. The other volatile by-products and the excess solvent escape in the vapor phase. The substrate provides the required thermal energy for this type of decomposition and subsequent recombination of the constituent species by thermal diffusion. This reaction process results in the sintering and recrystallization of the clusters of crystallites giving rise to coherent films.

3.4.5 Atomization Process

During the spray, the region between the atomizing nozzle and the substrate could be divided into three sections as shown in Figure 3.5. Region ‘A’ is in front of the nozzle where liquid is being lifted off to the tip of the nozzle and accelerated into the main air core turbulence – the vortex region. Region ‘B’ is the space where the expanding helical shape of the rest of the aerosol envelope is seen due to the vortex formed by the turbulence of the air stream. Region ‘C’ is the space outside the main aerosol cone where the low velocity droplets are seen when the nozzle design is not optimized.

Figure 3.5 Atomization Process and Vortex Region
The critical operations for the spray pyrolysis technique are: (i) Preparation of uniform and fine droplets and (ii) the controlled thermal decomposition of these droplets in terms of environment location and time.

Generally commercialized nozzle atomizers are used to spray solutions for thin film preparations. However, such nozzle atomizers are sufficient neither to obtain reproducibly micrometer or sub-micron size droplets nor to control their size distribution. Consequently, some new or modified atomization technique had been developed recently and used effectively for thin film preparations.

3.5 SPRAY PYROLYSIS EXPERIMENTAL SETUP

The schematic diagram and photography of the experimental set up used in the present study is shown in Figure 3.6 and Figure 3.7 respectively. Various components required for the process of depositing thin films by this technique is explained as follows. The main part of this set up is a cylindrical chamber. The top of the chamber is connected to an exhaust fan fitted onto a wall of the room to exhaust the smoke produced inside the chamber while spray deposition is going on. The electric oven which heats up the sprayed solution is used to heat the substrate and its holder. This electric oven is made up of a ceramic tube of length 30 cm with inner and outer radii 10 cm and 12 cm respectively and is wounded with kanthal wires as shown separately in Figure 3.8(a). The upper portion of this tube is open and the lower portion is closely wound so that a temperature gradient could be obtained such that the substrate and its holder could be kept at a higher temperature while the region through which the sprayed solution comes will be kept relatively at lower hotness. This cylindrical oven is placed vertically. The substrate holder could be suspended from the top of the oven. A thermo couple is inserted into the oven through the top side and placed such that the tip of the thermo couple is touching the surface of the substrate surface to sense the hotness. The other
side of the thermocouple is connected to the temperature controller and indicator. The heater is connected through a variac to adjust the rate of heating.

A sprayer nozzle whose dimensions are shown in Figure 3.8(b) is held above the oven with the help of a holder attached with an iron rod. The nozzle could be titled sideways, by rotating the iron rod from outside such that deposition may be made uniform on the microscopic slide which is the substrate placed on its holder. Flexible PVC tubes are used to connect the solution reservoir (the graduated burette) and the air compressor respectively to the corresponding inputs of the nozzle.

Figure 3.6 Experimental Set-up of Spray Pyrolysis Technique
Steps involved in the spraying procedure are given below.

1. Exhaust fan and Electric oven are switched on
2. Temperature controller is switched on. Manually the required temperature is set.
3. Variac is adjusted to the required voltage.
4. Substrate is cleaned well, placed on the holder and the holder is suspended into the oven. The thermocouple is made to touch the surface of the substrate.
5. The prepared solution is taken into the burette and it is allowed to fill up till the tip of the nozzle. Then closed with the stopcock.
6. Compressed air is opened slowly. The valve is adjusted till the required air pressure is obtained and kept constant.

7. The stopcock is on to maintain the flow rate of the solution. The temperature is noted.

8. Every time the initial adjustments are made such that for a required flow rate of solution, the substrate temperature is maintained a constant with a fluctuation of ± 5°C.

![Figure 3.8 Cross Section of (a) Tubular Electric Oven (b) Spray Nozzle](image)

The formation of the required compound by the heterogeneous reaction is mostly affected by all the above said parameters. Initially it is essential to understand about the effective area within which uniform deposition could be made with this experimental set up. The substrate temperature and the concentration of the spraying solution will not affect much the area of deposition. Therefore the effect of other parameters (via nozzle diameters, compressed air pressure, solution flow rate and the distance...
between the nozzle and the substrate) on the area of spray was studied by varying one parameter while keeping others as a constant.

First of all, the spray was carried out on a sheet of paper at room temperature with this experimental set up using water alone as the spray solution and the diameter and hence the area over which the paper was made wet, was measured. The effective area of spray as a function of distance was plotted as shown in Figure 3.9. The effective area increases as the distance increases, but at large distances the gravitational force dominates and hence limits the rate of increase of the effective area with distance. The region outside the main aerosol containing low velocity particles of smallest sizes may get evaporated completely and they may not reach the substrate. This reason may also be attributed to the limit of increase in the effective area of spray.

![Figure 3.9 Effect of Nozzle to Substrate Distance on the Area of Spray for various Air Pressure](image-url)
Then experiments were done with the thermocouple, compressed air and the radiant heater with variac arrangement to understand the voltage setting to be made along with the studied parameters to carry on the spray without much fluctuation ($\Delta T$) in the substrate temperature. The formation of the required compound (Reaction kinetics) and the thickness of the film deposited as a function of the corresponding parameters.

### 3.5.1 Characteristic Features of Spray Pyrolysis

The preparation parameters involved in this spray method are many, whose interaction or even existence is sometimes difficult to access. The spraying method involves the decomposition (at high temperature, around 300-500°C) of a mineral compound such as tin chloride penta hydrate or indium chloride dissolved in a solution of water and alcohol. Water is used as an oxidizing agent. The most important parameters of film preparation are as follows.

### 3.5.2 Growth Rate

In spray pyrolytic decomposition process, the growth and nature of the film surface depend on chemical nature and concentration of precursors, temperature of the substrate, droplet size during atomization and the various spray parameters. As mentioned in the previous section, chemicals used for spray pyrolysis must satisfy a variety of conditions. Usually, a number of combinations of chemicals meet these conditions. Each combination has its own thermodynamic and kinetic considerations. An oxide film can be prepared from variety of starting materials including nitrates, carbonates, halides etc. The choice of anion in the metal salt depends on the thermodynamic driving force and these salts are in decreasing order of thermodynamic force (Aranovich 1979). The heat of reaction is also a required thermodynamic factor and a non-equilibrium reaction proceeds
towards accumulation of anion/cation species. Organometallic compounds have also been used because of its low temperature decomposition. In addition to this, their high vapor pressure allows the use of vapor transport rather than a liquid transport technique (Kane 1975 and Korzo 1967). The variation of growth rate as a function of molarities of precursor also been discussed and the growth mechanism is discussed viz. Rideal-Eley and Langmuir-Hinshelwood mechanism (Ghostagore 1978). The continuous increase in growth rate with molarity indicates that the growth rate is governed only by the cation containing species.

Moreover, in the case of transparent oxide films, the thickness increases linearly with time of spray (that is, with the amount of sprayed solution). Also, the growth of thin films is temperature dependent (Yi 1995, Song 1998 and Vink 1995). At low temperatures, the growth rate is controlled by activated processes, such as adsorption, surface diffusion, and chemical reaction and desorption. The growth rate is thus controlled by the reaction kinetics and the molecules are accumulated in front of the substrate. However, at high temperatures, the activated processes occur so fast and the molecules do not dam up on the substrate (that is, growth rate is diffusion limited) (Bryant 1977). Growth rate also depends on the size of the droplets, because the decomposition of droplet is temperature dependent. If the droplet size is large, the heat absorbed from the surroundings will not be sufficient to vaporize entirely the solvent on the way to the substrate and adversely affect the kinetics of the reaction.

3.5.3 Substrate Temperature Effect

Since the dynamics of the evaporation and pyrolytic reactions are strongly temperature-dependent process, the substrate temperature has the most significant effect on the quality of the films. The role of the substrate
temperature on film formation and microstructure are investigated by Viguie et al 1975. Films grown at lower temperature are amorphous (Manifacier 1979 and Maudes 1980), whereas deposited at higher temperature are polycrystalline (Shanthi 1981).

There is an optimum temperature at which the required compound will be formed with the best compromise between overall transparency and conductivity. When the substrate temperature is too low to evaporate the solvent the adherence will be absent, resulting to powdery and amorphous films. At very high substrate temperature the cations will react with oxygen to form the corresponding oxides.

3.5.4 Substrate Effect

Neutral surfaces are not taking part in pyrolytic reactions and the choice of such surface is limited to glass, quartz, ceramics, oxide/nitride/carbide coated substrates, Ge, Si, etc. Oxide films on Si sometimes induce etching and in general, deposition of coherent films on metallic substrate is difficult. Even if the substrate is chemically inactive, it may contain mobile alkali and other rare earth ions, which will be readily incorporated in the film. In transparent oxides, Na\(^+\) and Li\(^+\) ions are incorporated substitutionally and Ca\(^{2+}\) and Si\(^{2+}\) ions are interstitially. Inclusion of these ions would increase with the increasing substrate temperature. The nature of the substrate particularly glass is an important parameter as it has been demonstrated by Manifacier and Fillard 1981 that the substrate is a diffusion source for alkali ions. Amorphous nature of the substrates will mostly produce preferential growth of thin films; whereas the crystalline nature of the substrate may produce epitaxial growth.
3.5.5 Film Composition

Film composition is expected to depend on the kinetics of the spray process and the thermodynamics of the pyrolytic processes. Incomplete pyrolytic reactions yield intermediate compounds, which is trapped as impurity in the film. These impurity concentration decreases with increasing substrate temperature during pyrolysis. For chloride salts, addition of HCl to the solution has been found to reduce the chlorine content in the film. The conductivity of TO film is attributed to the multi-valency tin ions and/or chlorine ions. The deviation from stoichiometry is controlled by the water and alcohol content in the spray solution. Water molecules provide oxygen and alcohol acts as a reducing agent. Use of a carrier gas does not seem to affect the concentration of incorporated oxygen vacancies.

3.5.6 Carrier Gas Pressure

The carrier gas is used to atomize the solution into fine particles. Higher pressure yields fine particles increasing which can produce mist of the particles. By controlling the pressure, the required size could be obtained but to have uniformity in the size, corona spray should be adopted. This pressure also affects the substrate temperature and hence it has to be optimized.

3.5.7 Nozzle – Substrate Distance

Heterogeneous reaction is critically decided by this parameter. Closer to the substrate will lower the substrate temperature resulting to powdery deposits. The area of spray increases as this distance increases but not constantly. The flow rate and compressed air pressure will also affect the area along with this parameter.
3.5.8 The Solution and its Concentration

Higher concentrations of the solution will yield mostly powdery deposits. There is a chance of the nozzle to be blocked when the hotness of the substrate reaches it at lower flow rates. Lower concentrations will alter the substrate temperatures and hence to be optimized. The stoichiometry of the film formed depends completely on the concentration and its ratio of the various species in it.

Other parameters like nozzle diameter, the type of carrier gas, rate of flow of the solutions, time of spray and the volume of the solutions also affect the film and its quality. The texture of the films, its transparency and the thickness could be controlled by controlling these parameters.

3.6 OTHER TYPES OF SPRAY PYROLYSIS METHOD

- Upward Spray Pyrolysis
- Ultrasonic Nebulized Atomization
- Improved Spray Pyrohydrolysis
- Corono Spray Pyrolysis
- Electrostatic Spray Pyrolysis
- Microprocessor Based Spray Pyrolysis

3.7 ADVANTAGES OF SPRAY PYROLYSIS METHOD

The chemical versatility of spray pyrolysis technique is demonstrated relating to metal oxides, metallic spinal oxides, binary, ternary, quaternary chalcogenides, and superconducting films (Pramod 1999). Despite its simplicity, spray pyrolysis has the following advantages.
(1) It offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it to the spray solution. (2) Spray pyrolysis does not require high quality targets and/or substrates nor require vacuum at any stage which is a great advantage if the technique is to be scaled up for industrial applications. (3) The deposition rate and the thickness of the film can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical method such as sol-gel which produces films of limited thickness. (4) Operating at moderate temperatures (100-500 °C) spray pyrolysis can produce films on less robust materials. (5) Unlike high power methods such as radio frequency magnetron sputtering, it does not cause local overheating. There is virtually no restriction on selecting substrate material. (6) By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradient throughout the thickness, (7) Prepared films are compact and uniform and the necessary reliable kinetic data can be obtained from the film surface (8) Large area coating and high reproducibility are quite possible and (9) It can be in-built in the laboratory with greater ease and the film production cost is very low when comparing with the other deposition techniques.

SP technique is useful for the production of thin films of simple oxides, mixed oxides, metallic spinel type oxides, group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI binary chalcogenides, group I-III-VI, II-III-VI, II-III-VI, II-VI-VI and V-II-VI ternary chalcogenides, adamantine copper compounds such as Cu$_2$ZnSnS$_4$/Se$_4$, Cu$_2$CdSnS$_4$/Se$_4$, CuGaSnS$_4$/Se$_4$, CuInSnS$_4$/Se$_4$, CuIn$_5$S$_9$/Se$_4$ etc. Recently chemical SP technique is also been successfully employed for the formation of superconducting oxide films.

Pramod S. Patil (1999) also stated that thin films of such metal oxide and metallic spinel oxide materials prepared by SP technique have
matching properties for wide varieties of potential applications. Chalcogenide semiconductor compounds of group II-VI and V-VI have applications in precise temperature control of laser diodes, optical recording system, electrochemical devices, strain gauges and thermoelectric devices. These thin films have great technological importance owing to their potential applications in photo electrochemical cells, solar selective and decorative coatings, opto-electronic devices and thermoelectric coolers (Krishnakumar et al 1987, George and Radhakrishnan 1980).

Since the discovery of high temperature superconductivity in oxides such as Y-Ba-Cu-O, a lot of work has been done on their preparation into thin films by SP technique. Thin films of these compounds have applications in electronic devices such as superconducting quantum interference devices (SQUID) (Schilling et al 1993).

This method is preferred because it is easy to adopt, economically cheaper and can be used for commercial purpose also. Amorphous or polycrystalline thin films can be obtained depending on the droplet mobility, chemical reactivity of various constituents, and substrate temperatures.

3.8 THICKNESS MEASUREMENT

Thickness is the most important film parameter, which controls the film properties. Hence, precise knowledge of the film thickness is necessary for the intensive study of the properties of thin films. Wide varieties of methods are available for measuring thin film thicknesses. Some of the thickness measurement methods available are Stylus profilometry, multiple beam interferometry, ellipsometry, spectrometry, X-ray microanalysis, microgravimetry and Scanning Electron Microscopy (SEM). Complete information about merits and demerits of these methods, measuring range and accuracy can be found in the literature (Chopra 1969, Heavens 1969 and

The Mitutoya surftest SJ-301 is a stylus type surface roughness and thickness measuring instrument. It can be used to measure the thickness of thin film coatings on any uniform surface. The stylus of the SJ-301 detector unit traces the minute irregularities of the vertical displacement of the fine needle, when the detector is traversing over the film surface irregularities. For measuring film thickness, the stylus is placed over the uncoated surface and made to move towards the coating. Then it steps over the coating surface and moves over it. The vertical displacement gives the thickness of the coating. The thicknesses of the prepared thin film samples were found using this instrument. It is a non-destructive technique and the coatings may be used for further studies without any damage.

The picture of the device along with the stylus is shown in Figure 3.10 and their technical specifications are listed below:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model number</td>
<td>SJ-301 4 mN type</td>
</tr>
<tr>
<td>Measuring range x-axis</td>
<td>12.5 mm</td>
</tr>
<tr>
<td>Z-axis</td>
<td>350 μm</td>
</tr>
<tr>
<td>Measuring speed</td>
<td>0.5 mm/s</td>
</tr>
<tr>
<td>Stylus tip radius</td>
<td>5 μm</td>
</tr>
<tr>
<td>Stylus tip material</td>
<td>Diamond</td>
</tr>
<tr>
<td>Measuring force</td>
<td>4 mN</td>
</tr>
<tr>
<td>Detecting method</td>
<td>Differential inductance</td>
</tr>
<tr>
<td>Recording magnification</td>
<td>10-100 K</td>
</tr>
</tbody>
</table>
Figure 3.10 External view of the surface profiler SJ-301

3.9 THIN FILM CHARACTERIZATION TECHNIQUES

3.9.1 Introduction

The deposited metals and oxide films were characterized for their structural, surface morphological, compositional analysis, electrical and optical properties. X-ray diffraction used for studying the structural properties of the films. Scanning electron microscopy and atomic force microscopy are used to identify the surface morphology of the prepared films. The EDAX and XPS are used to identify the elemental content in the films. The optical parameters were analyzed from the transmittance and absorbance spectra obtained using UV-Vis-NIR spectrophotometer. The Van der Pauw technique is employed to measure electrical resistivity and Hall mobility of the films. The principle, functioning and importance of each technique are briefly outlined in this section with related theory.
3.9.2 X-Ray Techniques

In X-ray works, one can choose between white and monochromatic radiations. With white radiation a “Laue Pattern” is obtained and the lattice planes are easily recognizable. The Laue technique is mainly used to determine the orientation of single crystals. It is a convenient tool because a pattern can be recorded on Polaroid film within a few minutes. X-ray techniques based on monochromatic radiations are generally more important because the \(d\) spacing can be calculated from the observed diffraction angles.

An important feature of X-ray diffractometer is its ability to focus in to a sharp diffraction line with the radiation, which is Bragg-reflected from an extended specimen area. This considerably improves the sensitivity and the signal to noise ratio. Focusing is achieved by making the specimen a part of the circumference of a circle, so called focusing circle, so that all the beams diffracted in different areas by the same family of \((hkl)\) planes, cross over again and are detected on this circle. Two different designs of diffractometers namely Bragg-Brentano diffractometer and Seemann-Bohlin diffractometer are used in thin film work.

Bragg-Brentano diffractometer is commercially available and most widely used (Figure 3.11). The specimen is mounted in the centre of the diffractometer and rotated by angle \(\theta\) around an axis of the film plane. The counter is attached to an arm rotating around the same axis by angle twice as large as those of the specimen rotation. It can be seen that the focusing circle continuously shrinks with increasing diffraction angle. Only \(\text{‘hkl’ planes parallel to the film plane contribute to the diffracted intensity.}

In Seemann-Bohlin X-ray diffractometer (Figure 3.12) the specimen and the focusing circle remains stationary while the detector tube moves along the circumference of the focusing circle itself. In order to face
the specimen, always the tube rotates around an axis going through the circle with half the speed of the rotation of the tube carrier around the circle centre.

Figure 3.11 XRD Experimental Setup

Figure 3.12 Seemann-Bohlin X-ray Diffractometer
Bragg-Brentano diffractometer has been used extensively in thin film research where as Seemann-Bohlin X-ray diffractometer has been employed only for a few studies.

The main advantages of Seemann-Bohlin X-ray diffractometer is a constant angle of incidence which can be kept as small as 5 degree thus giving higher diffracted intensities than Bragg-Brentano diffractometer in the whole angular range and particularly in the back reflection region. Seemann-Bohlin arrangements are limited to polycrystalline specimen of random orientation.

It is worthwhile to note that for X-ray diffraction a film can remain on its substrates and allows ‘nondestructive testing’ of the film-substrate system. the ‘d’ spacings of films attaches to the substrate usually contain contribution of homogeneous strains caused either by intrinsic stresses in the film or by differential thermal expansion if the temperature of the fabrication and observation are different. One of the main applications of X-ray diffractometer techniques in thin films is in fact to make use of their good resolution of ‘d’ spacing to investigate strains in thin films (Culity 1967).

**Bragg’s law**

The layers of a crystal act like weak reflecting mirrors for the X-rays. Only if the path difference of the reflected X-rays is a whole number of wavelengths does constructive interference occur. This is described by Bragg's Law:

\[ n\lambda = 2dsin\theta \]  \hspace{1cm} (3.3)

Where, \( n \) is the order of reflection, \( \lambda \), the wavelength of the X-rays, \( d \), the distance between the atomic planes parallel to the axis of the incident beam, \( \theta \)- Angle of incidence relative to the planes.
Uses of X-Ray Powder Diffraction

The most wide spread use of X-ray powder diffraction is the identification of crystalline compounds by their diffraction pattern. Some other specific uses are

- Identification of single materials, minerals, chemical compounds, ceramics or other engineering materials.
- Identification of multiple phases in micro crystalline mixtures.
- Determination of the crystal structure of identified materials.
- Identification and structural analysis of clay minerals.
- Recognition of amorphous materials in partially crystalline mixtures.
• Determination of crystallite size from the analysis of peak broadening.

• Determination of crystallite shape from study of peak symmetry.

• Study of thermal expansion in crystal structures using in-situ heating stage equipment.

• Quantitative determination of amounts of different phases in multiphase mixtures by peak-ratio calculation.

3.9.3 Structural parameters

3.9.3.1 Grain size (D)

The grain size (D) was calculated using the Scherrer’s formula (Klug 1954 and Culity 1967) from the full width at half maximum (FWHM)

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(3.4)

Where  
\( k \) - shape factor \( \approx 0.94 \),  
\( \lambda \) - Wave length of the X-rays (1.54060 Å for Cu Kα)  
\( \theta \) - Bragg’s angle  
\( \beta \) - Full Width Half Maximum

3.9.3.2 Dislocation density (\( \delta \))

The dislocation density (\( \delta \)) can be evaluated from crystallite size (D) by the following relation (Klug 1954)

\[ \delta = \frac{1}{D^2} \]  

(3.5)
3.9.3.3 Strain ($\varepsilon$)

The origin of the micro strain is related to the lattice misfit, which in turn depends upon the deposition conditions. The micro strain ($\varepsilon$) can be calculated from the following relation (Klug 1954, Dhanam 2002 and Velumani 1998)

$$\varepsilon = \frac{\beta \cos \theta}{4}$$ (3.6)

3.9.3.4 Interplanar Spacing (hkl)

From XRD profiles, the interplanar spacing $d_{hkl}$ was calculated using the Bragg’s relation (Klug 1954, Dhanam 2002 and Velumani 1998)

$$d_{hkl} = \frac{n\lambda}{2\sin \theta}$$ (3.7)

Where $\theta$ - Bragg’s angle

$n$ - Order of diffraction

Also using grain size ‘$D$’ and film thickness ‘$t$’, number of crystallites ‘$N$’ has been estimated using the relation (Dhanam 2002 and Velumani 1998)

$$N = \frac{t}{D^2} / \text{unit area}$$ (3.8)

From X-ray diffraction (XRD) study, information about lattice parameters, orientations of crystal planes, grain size, structure (i.e. epitaxial, polycrystalline, amorphous etc), composition (with the help of standards), defects and stress and strain in thin films can be studied (Pradip K. Kalita 2000, and De 1993).
3.9.4 Powder Method

The powder diffraction method represents the easiest procedure for the identification of an unknown materials based on diffraction analysis. This is also known as Debye-Scherrer method. Powder diffractometers come in two varieties θ-θ, in which X-ray tube and detector move simultaneously or θ-2θ, in which the X-ray tube is fixed and the specimen moves at half (1/2) the rate of detector to maintain θ-2θ geometry.

In the present work, x-ray diffraction studies were carried out on CuInS₂, Sb doped CuInS₂, Zn doped CuInS₂ and Bi doped CuInS₂ films deposited with different deposition parameters. The technical details of the X-ray diffractometer used in the present study are:

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
Detector : Xe proportional counter

In this sophisticated diffractometer, diffracted beams are collected by the Xe proportional counter, whose output is directly fed into a chart recorder. The beam of the X-ray source is automatically rotated with the help of a motor so that the X-ray beam incident angle can be precisely recorded. The detector, collecting the diffracted beam is mounted co-axially with source rotator and coupled to it in such a way that when the source moves through an angle of ‘θ’, the detector moves through an angle of ‘2θ’, so that it is in the right position to collect the diffracted X-rays from crystalline samples. The chart recorder plots the diffracted X-ray intensity as a function of ‘2θ’. The
plot consists of a series of peaks of different intensities depending on the magnitude of the diffracted x-ray intensity in that direction.

From the XRD pattern one can determine the interplanar spacing (d), lattice parameters and hence the structure of the films. Usually, the diffraction peak positions are compared with the data from JCPDS cards. In the present case, the JCPDS standard data were compared with the obtained CuInS$_2$, Sb doped CuIns$_2$, Zn doped CuIns$_2$ and Bi doped CuIns$_2$ films data for fixing the structure of the prepared films.

In general, diffraction peak from a lattice plane is labeled as Miller indices (hkl) and these indices are related to inter-atomic spacing or ‘d’ spacing. For an orthogonal system (ie, $\alpha = \beta = \gamma = 90^\circ$), the ‘d’ spacing for any set of planes is given by the formula:

$$\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (3.9)

Where, ‘a’, ‘b’ and ‘c’ are the cell edges.

For cubic crystals, $a = b = c$;

$$\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2}$$  \hspace{1cm} (3.10)

For hexagonal crystals,

$$\frac{1}{d^2_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (3.11)

Using these relations, the Miller indices are assigned for each diffraction peak obtained in a diffractogram.
The width of the diffraction peak depends on the phase of the diffracted rays from each plane. If each plane in a crystal diffracts exactly one wavelength later than the preceding plane, all diffracted beams are in phase and constructive interference occurs, resulting zero peak width. If there is a phase lag of slightly greater than one wavelength \( \lambda + \delta \lambda \), for rays diffracted from subsequent planes, a cumulative phase lag \( \Sigma \delta \lambda = \lambda / 2 \) occurs at \((j+1)^{th}\) plane, i.e. \( j \delta \lambda = \lambda / 2 \). Then planes 1 and \((j + 1)\) are exactly ‘\( \pi \)’ out of phase for radiations that is incident and diffracted at ‘\( \theta_1 \)’ and therefore cancel each other. The angular range between the Bragg peak ‘\( \theta \)’ to ‘\( \theta_1 \)’ is the range over which the intensity of the diffracted beam falls from a maximum at ‘\( \theta \)’ to 0 at ‘\( \theta_1 \)’. A similar lower limiting angle ‘\( \theta_2 \)’, occurs for which rays diffracted from adjacent planes have a phase difference of \( \lambda - d \lambda \). The magnitude of the angular range ‘\( \theta_1 \)’ to ‘\( \theta_2 \)’ and hence the breadth of the diffraction peak, is governed by the number of planes \( 2j \), and hence the crystal thickness. If the number of planes is very large, no significant broadening occurs, because ‘\( \delta \lambda \)’ and therefore \( (\theta_2 - \theta_1) \) is negligibly small.

3.10 ELEMENTAL COMPOSITION ANALYSIS

The composition of the surface layer of a material is a property-related parameter that provides information about the elements present and the amount of elements present. Many spectroscopic methods using standard instruments are multi-elemental analyzers, in that; signals from a number of elements can be registered simultaneously. Energy dispersive spectroscopy EDAX and X-ray photoelectron spectrometry (XPS) are the techniques used in this study to identify the elemental content present in the prepared films.

3.10.1 Energy Dispersive Spectroscopy (EDAX)

In energy dispersive spectroscopy, an X-ray spectrum is usually displayed as a function of energy. It consists of a continuous signal with
superimposed characteristic elemental line. The positions of the elemental lines are related to the atomic number of the elements generating them. Elements with increasing atomic number yield lines at successively higher energy. Beyond certain energy, no X-rays are generated and therefore the acceleration voltage has to be high enough to be able to excite the elemental lines. Lighter elements can be analyzed by their K-lines and heavier elements by their L or M lines.

**Figure 3.14 Diagrammatic representation of EDAX**

As X-rays are generated at some depth, they undergo absorption on their way out of the sample. If the sample contains elements that are close to each other in atomic number, X-rays from the heavier elements undergo strong absorption by the lighter elements on their way out. At the same time, this causes fluorescence on the lighter elements. As a result, the observed intensity from the heavier elements is reduced, whilst the intensity from the lighter elements is enhanced. To correct these effects observed X-ray intensity
ratios between sample and standard have to be multiplied by a correction factor K. For that, the data from the spectrometer have to be passed through computer programs that apply ZAF (atomic number, absorption, fluorescence) corrections.

In the present study, X-ray spectrometer attached to the SEM instrument (HITACHI Model S-3001H) is used to perform elemental analysis of all elements down to atomic number 5 with better geometrical resolution.

### 3.11 SCANNING ELECTRON MICROSCOPY (SEM)

To study the surface morphology of thin film samples, the reflection mode of the optical microscope can be used. But this technique is limited in spatial resolution to a few tenths of a millimeter. Very high resolution is required in electron beam technique. The most versatile among these is the scanning electron microscope. The main components of the instrument and the optical system are shown schematically in Figure 3.15.

An electron beam is generated by an electron gun at the top of the column. This beam is focused by two magnetic lenses inside the column and strike the sample in the sample chamber in a very small spot. When these electrons penetrate into the sample, some electrons are scattered back out of the sample and are collected by a suitable detector. These electrons are used to obtain information on the mean atomic number in the part of the sample from which they originated, relative to other part. Secondary electrons with very low energy also be released and are used to obtain information on the topography of the sample.

Usually, the electron beam is not left stationary on the sample, but scans across certain area in a raster pattern. The signal from one of the detector is selected and used to modulate the intensity on a viewing screen,
which is scanned synchronously with the primary beam in the column. Thereby an image is generated on the viewing screen with high brightness in areas with a strong signal from the detector, and darker areas where weak signals are detected. In this way, an enlarged image of the sample is obtained on the screen. To vary the magnification, the size of the scanned area of the sample is varied while the scanning width on the viewing screen is constant. The scanned image is particularly useful for examining the morphology of thin films of semiconductors, insulators and crystalline materials as well. Electrically insulating samples usually have to be given a conducting coating.

**Figure 3.15 Schematic diagram of SEM**
In the present study, HITACHI Model S-3001H is used, which is capable of taking magnified pictures of solid, dry, conducting and non-conducting specimen. Its technical specifications are listed below.

Model number : HITACHI Model S-3001H  
Scanning probe diameter : 20 Å  
Resolution : 60 Å at 30 kV  
Magnification : 20 – 65,000  
Voltage : 1 kV – 39 kV  
Required specimen size : 5 x 5 mm² with 1 mm thickness

Using this instrument, SEM studies have been carried out to identify the morphology of the deposited oxide films. The SEM micrographs provide the nature of the surface (uniformity, smoothness and cracks) and the nature of the grains (Shape, particulate and grain size) (Coles 1987).

3.12 OPTICAL CHARACTERIZATION

In early days, the study of the interactions of light with matter laid the foundations for quantum theory. Today, optical methods are among the most important tools for elucidating the electron structure of matter. Among the many available tools, spectrophotometer, photoluminescence spectrometer and Raman spectrometer are used to explain all the possible transitions such as band-to-band, excitons, between sub bands, between impurities and bands. In addition, the transitions by free carrier within a band and the resonances due to vibrational states of the lattice and of the impurities can be understood.

3.12.1 UV-Vis-NIR Spectrophotometer

The measurement of transmission or reflection of a sample provides a satisfactory way to determine the form of the absorption edge. The
absorption edge and energy band gap can be determined from the transmission measurement (Heavens 1969). Hence, the 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 cm\(^{-1}\)

When light radiation is incident on a thin film material with energy equal or greater than that of the band gap, absorption of photons can take place and electrons are raised in energy from the valance band to the conduction band, creating electron-hole pairs. The ability of a material to absorb photons of a given wavelength is measured quantitatively by the optical absorption co-efficient \((\alpha)\), measured in units of reciprocal distance (Bube 1974) and can be calculated using Lambarts Law

\[
\ln(I_0/I) = 2.303A = \alpha t
\]

(3.12)

Where, \(I_0\) and \(I\) are the intensity of incident and transmitted light respectively, ‘A’ the optical absorbance and ‘\(t\)’ the film thickness.

In order to describe the fundamental absorption edge, the spectral dependence of absorption co-efficient \((\alpha)\) is directly determined using the relation,

\[
\alpha = \frac{4\pi k_f}{\lambda}
\]

(3.13)

Where, \(\lambda\) is the wavelength of incident radiation and ‘\(k_f\)’ the extinction co-efficient.
The extinction coefficient, \( k_f \) was obtained by using the absorption co-efficient value in the relation,

\[
k_f = \frac{2.303 \log_{10}\left(\frac{1}{T}\right)}{4\pi t} \lambda
\]  

(3.14)

There are two major types of intrinsic absorption processes involved in determining \( \alpha \), they are the direct and indirect absorption. As a general rule, the larger the band gap, the smaller is the value of \( \alpha \) for a given wavelength but absorption co-efficient also depends on the density of states in the conduction and valence bands. The optical absorption co-efficient is related to energy band gap and it is given by the following equation (Goswami 1996).

\[
\alpha \nu = B (\nu - E_g)^n
\]  

(3.15)

Where, \( B \) is a constant and \( E_g \) is the optical band gap. For crystalline materials, the exponent \( n \) is 1/2, 3/2, 2 and 3, when the transition is direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively. Apparently, the plot of \((\alpha \nu)^2\) or \((\alpha \nu)^{1/2}\) against \( (\nu) \) provides the nature and \( E_g \) value of a particular film. The direct optical absorption is illustrated in Figure 3.16.

Direct optical absorption is a first order process, involving only the absorbed photon and can be represented approximately as a vertical line on the energy versus wave vector (\( k \)) plot. The absorption transition conserves energy so that \( \Delta E = \hbar \nu \) and there is no change in \( k \) between initial and final states except for the small momentum of the photon. An indirect optical transition is a second order process involving both the absorbed photon and a simultaneously absorbed or emitted phonon, which occurs when the minimum
of the conduction band and the maximum of the valence band occur at different values of the wave vector ‘k’ as illustrated in Figure 3.17. Here the absorption transition conserves energy by requiring \( \Delta E = \hbar \nu + E_p \) where, \( E_p \) is the photon energy and the change in ‘k’ between the initial and final states \( \Delta k \) is just equal to the value of ‘k’ of the phonon involved. Figure 3.18 shows UV-Vis Experimental Setup.

Figure 3.16 Direct transitions from valence band to conduction band

Figure 3.17 Indirect transition from valence band to conduction band
3.12.2 Optical Absorption

Absorption of light by different material can induce various types of transitions such as band to band, between sub bands, resonance due to vibrational state of lattice and impurities. These led to the appearance of bands or absorption peaks in the spectra. Absorption has high values for material where it has low value for dielectrics. In order to produce films with absorption and reflection losses with high transparency, deposition procedure like purity, substrate cleaning, film contamination and thin film quality etc., must be carefully controlled.

3.12.3 Absorption Coefficient

Absorption coefficient was calculated using the transmittance (T) value measured for a particular wavelength and the film thickness (t) using the relation,

\[ \alpha = -\ln \left( \frac{T}{t} \right) \] (3.16)
The absorption coefficient is also given by Lambert’s law

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

(3.17)

Where \( x \) – The distance through which the electromagnetic wave travels to change its intensity from \( I_0 \) to \( I \)

The absorption index or the extinction coefficient \( K_f \), which is the attenuation per unit radiation, may be written as,

\[ K_f = \frac{\alpha \lambda}{4\pi} \]  

(3.18)

Where \( \lambda \) – wavelength of the incident radiation

In insulators and semiconductors the interaction of the electromagnetic radiations with the bound and free charges can explain the absorption and dispersion in the spectral region. The valence band electrons are of about prime importance in the study about semiconductors and insulators. When there is no thermal energy the only possible absorption that can take place is when the quanta of incident radiation have sufficient energy to excite the valence electron across the forbidden zone into the empty conduction band. Because of this, a continuum of intense absorption edge the material is relatively transparent.

If the material under consideration is free from imperfection then from quantum mechanical basis and appropriate selection rule, it is possible to find out the nature of the electronic transition from the relation

\[ \alpha h\nu = A(h\nu - E_g)^n \]  

(3.19)

Where \( A \) – Constant, \( E_g \) – Energy band gap, \( h\nu \) - The photon energy.
And it depends upon the nature of the transition whether it is direct or indirect as well as allowed or forbidden, the magnitude of the exponent ‘n’ characteristics the type of radiation. It takes the value 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively.

### 3.12.4 Direct Transition

When the material is free from any imperfection, only the direct but allowed transition can take value from valance to conduction band.

For direct allowed transition

\[ \alpha = A(h\nu - E_g)^{1/2} \]  \hspace{1cm} (3.20)

For direct forbidden transition

\[\alpha = A(\hbar\nu - E_g)^{3/2} \]  \hspace{1cm} (3.21)

### 3.12.5 Indirect Transition

When the material contains defects such as impurities, dislocations etc, one has to consider the perturbation of the system due to their presences and also their interactions with phonons.

For indirect allowed transition

\[ \alpha = A(h\nu - E_g)^2 \]  \hspace{1cm} (3.22)

For indirect forbidden transition

\[ \alpha = A(h\nu - E_g)^3 \]  \hspace{1cm} (3.23)
3.13 CURRENT-VOLTAGE CHARACTERISTICS

A GE-ELH lamp of 300 watts power operating at 120 V AC is used as the light source. This is commonly used light source for solar cell characterization. The distance between the lamp and the test sample is adjusted such that the input intensity on the cell is 100mWcm\(^2\) as measured by Surya Mapi (CELL laboratories India) with silicon reference cell. The temperature of the Cell during measurement is maintained at 28ºC by placing it on a water-cooled metal chamber.

3.13.1 Two Probe Technique

In this technique, a constant current ‘I’ is passed through two aluminium strip contacts separated by a distance ‘d (=l)’ and the voltage ‘V’, between these strips is measured by using a high impedance voltmeter as shown in Figure 3.19. For a thin film sample of thickness ‘t (=h)’ and breadth ‘b (= w)’ placed between these two aluminum strips, the resistivity is derived from the following equations given by,

\[
\text{Resistance } R = \frac{V}{I} \quad (3.24)
\]

\[
\text{Resistivity } \rho = R \times (\text{Cross sectional area/Length}) \quad (3.25)
\]

\[
\rho = \frac{V \cdot t}{I \cdot b} \Omega \text{cm} \quad (3.26)
\]

In thin film technology, the ratio between the resistivity of the film material to the thickness of the thin film specimen ‘t’ is termed as sheet resistance ‘\(R_{sh}\)’ and thus

\[
R_{sh} = \frac{V \cdot b}{I \cdot t} \Omega/\square \quad (3.27)
\]
Hence, for a square specimen \( l = b \), the resistance of one square of a film is its sheet resistance \( R_{\text{sh}} \), which is independent of the size of the square but depends only on resistivity and film thickness. In such case

\[
\rho = R_{\text{sh}} t \ \Omega \text{cm}
\]  

(3.28)

Figure 3.19 Two point probe set-up

Figure 3.20 Four-point probe set up

3.13.2 Linear four probe technique

The most generally used technique in the semiconductor industry for the measurement of resistivity is the four-point probe. Normally this method is non-destructive; however, the probe points may damage certain film regions when excessive probe pressure is applied. The usual geometry is
to place the probes in a line and use equal probe spacing (Figure 3.20). Current is passed through the outer two probes and the potential developed across the inner two probes is measured. Generally, for probes resting on a semi-infinite medium, the resistivity is expressed as (Wenner 1916).

$$\rho_o = \frac{2\pi \left( \frac{V}{I} \right)}{\frac{1}{S_1} + \frac{1}{S_3} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}}$$

(3.29)

Where, ‘$S_1$’, ‘$S_2$’ and ‘$S_3$’ are probe spacings in centimeters. When the probes are equally spaced then

$$\rho_o = 2\pi S \frac{V}{I}$$

(3.30)

However, for thin film samples with thickness $t < 0.1$ S and boundaries $> 20$ S from probes, the resistivity ‘$\rho$’ is expressed as (Valdes 1954)

$$\rho = \frac{\rho_o}{G(t/s)}$$

(3.31)

The correction factor $G(t/s)$ for infinity thin slice ($t/s < 0.1$) is $\frac{2S}{t} \ln 2$ and therefore

$$\rho = \frac{\pi t V}{\ln 2 I}$$

(3.32)

$$\rho \approx 4.53 \frac{t V}{I}$$

and the sheet resistance $R_{sh}$ is expressed as

$$R_{sh} \approx 4.53 \frac{V}{I}$$

(3.33)
For the present study, the four probe resistivity measurements were carried out on SnO$_2$, SnO$_2$: F, In$_2$O$_3$ and In$_2$O$_3$: Sn thin films using an OSAW AC-DC Four point probe unit, in conjunction with a UNI-INSTA DC power supply. The voltage and current were measured using a HIL 2161 Digital multimeter and a Keithley 2000 multimeter respectively.