CHAPTER - III
PREPARATION AND MEASUREMENT TECHNIQUE.

3.1. IMPORTANCE OF THIN FILMS

Thin film science has received tremendous attention because of numerous applications of films on diverse fields such as electronic industries, solar energy utilization military weapon systems, space science, high memory computer elements, sensor, microelectronic and hybrid circuits etc., Rapid developments in thin film technologies have been spurred by the growing importance of microelectronics. Semiconductor science and technology have been developed considerably in the direction of devices by utilizing thin film material, which offers the advantages over bulk crystals in many aspects and in terms of material requirements.

Thin films have become a significant part of microelectronic circuitry by virtue of their small size that is their two dimension in nature and of course this permits the fabrication of very small device structures or micro circuits (1) Many semi conducting material of interest are difficult to prepare bulk crystal without serious in homogenous, strain, inclusion or other defects. The preparation of this crystalline film therefore makes possible a side range of devices, which could not be
possible or economically feasible if only bulk crystal were considered.

Photovoltaic has emerged as a fast developing field due to the global search for alternative sources for power generation. Ever abundant solar energy can be harnessed by suitable devices called photovoltaic cells or solar cells for low cost conversion of solar radiations into electrical energy. Thin film based photo electrochemical solar cells have wide applications due to their low fabrication cost, high throughput processing techniques and ease of junction formation with electrolyte. Among the material that have attached attention in thin film polycrystalline from are II-IV and I-III-IV ternaries and multi ternaries. These electrical and optical properties can suitable by tailored and tuned to the specific need in a given structure.

Devices or components made from films have advantage over those made from the bulk materials because of low cost of production, high reliability superior performance, extreme compactness and corresponding reduction in sizes and weights, low power consumption etc.
3.2. THIN FILM MATERIALS

It is well known that various thin film properties such as structural, optical, electrical, dielectric, mechanical etc., depend not only on the purity of the material but also on their preparation technique and other parameters such as rate of evaporation, substrate temperature, annealing, the thin film thickness etc. There are a large number of methods for preparing thin films of different types of materials but each one has its own limitations. Since individual atomic, molecular or ionic species of matter may exist in the vapor or in the liquid phase. The techniques of thin film deposition can be broadly classified under two main categories:

1. Vapour – phase deposition
2. Liquid – phase / solution deposition

But generally the methods of preparation of thin films are classified as chemical method and physical methods. Thin film devices would typically be about 5μm to 50μm thick in contrast to bulk materials, which are about 150μm to 250μm thickness. In this films deviation from the properties of the corresponding bulk materials because of their small thickness, larger surface to volume. Its wide application leads separate branch of physics known as thin film technology [2]
For the preparation of thin film a support is very much required. General quartz plate or glass plate or a metallic plate is used as a substrate depending upon the requirements. In many thin film preparation quartz plate is preferred because of the optical transparency, non-reactive nature with many elements and available in pure form.

3.3. VAPOUR PHASE DEPOSITION

It can be broadly divided into two categories.

1. Physical Vapour Deposition (PVD)

2. Chemical Vapour Deposition (CVD)

3.3.1. PHYSICAL VAPOUR DEPOSITION

The basic PVD processes are those currently known as evaporation, sputtering and ion plating. In recent years, a significant numbers of specialized PVD process based on the above have been developed and extensively used. Reactive ion plating activated reactive evaporation, reactive sputtering etc. As an example, if the activated reactive evaporation (ARE) process is used with an negative bias on the substrate, it is very often called Reactive ion plating. Simple evaporation using and R.F. heated crucible has been called Gasless ion plating.
Step1:

- Creation of vapor phase species – There are three ways to put a material into the vapor phase evaporation sputtering or chemical vapors and gases.

Step2:

- Transport of the vapor species from the source to the substrate can occur under line of slight or molecular flow-conditions.

- Alternately, if the partial pressure of the metal vapor and gas species in the vapor state is high enough or some of these species are ionized, the square many collisions in the vapor phase transport to the substrate.

Step3:

- This involves the deposition of the film by nucleation and growth processes.

- The microstructure and composition of the film can be modified by bombardment of the growing film by uniform vapor phase resulting in sputtering and condensation of the film atoms and enhanced surface mobility of the atoms in the near surface and surface of the film.

ADVANTAGES:

- Extreme versatility in composition of deposit virtually and metal, alloy, refractory or inter- metallic compound, some polymeric type materials and their mixtures can be easily...
deposited. In this regard, they are superior to any other deposition process.

- The ability to produce unusual microstructures and new crystallographic modification. E.g. amorphous deposits.
- The substrate temperature can be varied within very wide limits from subzero to high temperatures.
- Ability to produce coating or self- supported shapes at high deposition rates.
- Deposits can have very high purity.
- Excellent bonding to the substrate.

3.3.1.1. THERMAL EVAPORATION IN VACUUM

It is the most commonly used technique adopted for the deposition of metals, alloys and also many compounds such as oxides (Al₂O₃ [3], MoO₃ [4], SnO₂ [5], ZnO [6],) sulphides (CdS [7], PbCdS [8,9]) and halide (PbCl₂ [5]).

The principle involves the evaporation or sublimation of the material placed in the refractory element like W, Mo or Ta in vacuum by thermal energy and allowing the vapour stream of the charge to condense on a substrate so as to form as continuous and adherent deposit of desired thickness. Hind Hivac thermal evaporation coating unit Model 12A4 consists of three main parts, namely, the vacuum chambers, the pumping
system, and the electrical gadgets. The vacuum chamber is coupled with the pumping system of a three-stage oil diffusion pump packed by a double stage rotary pump. Silicon oil having low vapour pressure is used as the charge for diffusion pump.

Pirani and Penning gauges are provided for the measurement of pressure inside the vacuum chamber. The substrate temperature is monitored by digital thermometer using Cr-Al thermocouple. Using this method, Indium metal contacts on lithium oxide films are made in the present work for electrical measurement. Molybdenum is used as boat material. The choice of the boat material or filament is primarily determined by the evaporation temperature and the resistance to alloying and or chemical reaction with the evaporant.

The properties of the film deposited depend on the evaporation rate of the source material, the temperature of the substrate on which the material is to be deposited and vacuum maintained during deposition. The thickness of the film depends upon the distance between the source and source and substrate and time of deposition.
3.4. CHEMICAL VAPOUR DEPOSITION (CVD)

Chemical vapour deposition is a chemical process which takes place in the vapour phase very near the substrate (or) on the substrate so that a reaction product is deposited onto the substrate. The deposition can be a metal, semiconductor, alloy (or) refractory compound the history of CVD techniques dates back to the early nineteenth century when the reduction of silicon tetrafluoroide or silicon tetrachloride by sodium or potassium [10] was utilized. In the 1930s increasing emphasis was laid on utilizing the CVD technique to prepare refractory compounds such as metal carbides, nitrides, silicides, borides, and oxide as well as sulfides selenides, telluride’s, outer metallic compounds and alloys. CVD gained wide acceptance as means of growing thin layers. The process has since been extended to deposit a wide variety of films, including insulators, conductors, resistors, varistors and ferrites.

Chemical vapour deposition involves essentially exposure of the substrate to one or several vaporized compounds or reagent gases, some or all of which obtain constituents of the desired deposited substance. A chemical reaction is the initiated at or near the substrate
surface producing the desired material as a solid-phase reaction product which condenses on the substrate.

The chemical reaction may be activated by the application of heat, an rf field, light or X-rays, a glow discharge electron bombardment, or catalytic action of the substrate surface. It should be emphasized that the morphology of the deposited layer is strongly influenced by the nature of the chemical reaction and the activation mechanism. It is important to attain deposition conditions which enable the reaction to take place near or on the substrate surface (heterogeneous reactions) in order to avoid powdery deposits, which result when the reaction occurs in the gas phase (homogenous reaction).

The film growth in the CVD process takes place in an atom/molecule or atom/molecule condensation process. The growth process is in many ways similar to that of physical vapour deposition processes such as evaporation and sputtering. A clear distinction between chemical vapour deposition and physical vapour deposition (PVD) process is that in CVD the formation of a film results from a heterogeneous chemical reaction without involving a mean free path of the gas molecules larger than or comparable with the dimensions of the deposition chamber as a necessary condition for the
deposition process. However CVD may be carried out at low pressures or in high vacuum depending on the requirements are reviewed [11].

The major advantages of the CVD technique are:

In general, no vacuum or pumping facilities are required, and thus a relatively simple setup and fast recycle times are possible.

It is possible to grow multi component alloys

1. Refractory materials can be deposited at relatively lower temperatures compared to vacuum evaporation.

2. It is relatively easy to dope the deposits with controlled amounts of impurities.

3. High deposition rates are possible

4. It is possible to deposit compounds and control their stoichiometry easily.

5. In-sites chemical vapour etching of the substrates prior to deposition is possible.

6. Objects of complex shapes and geometries can be coated and

7. Epitaxial layers of high perfection and low impurity content can be grown.
However, the technique suffers from several drawbacks namely.

The thermodynamics and reaction kinetics involved in the deposition process are frequently very complex and poorly understood.

1. The reactive gases used for the deposition process and reaction products are, in most cases, highly toxic, explosive, or corrosive.

2. The corrosive vapors may attack the substrate the deposited film and material of the deposition set up and volatile products generated during the deposition process may lead to incorporation of impurities in the growing film.

3. Usually higher substrate temperatures are required than in the corresponding CVD technique.

4. It is difficult to control the uniformity of the deposit and

5. Masking of the substrate is usually difficult.

6. The high temperatures may lead to diffusion alloying or is limited.
3.4.1. CHEMICAL ASPECTS OF CVD

Chemical vapour deposition involves, essentially, exposure of the substrate to one (or) several vaporized compounds (or) reagent gases, all of which constitute for the desired deposited substances. Any chemical reaction between one or several reactive vapour, which yields a solid phase reaction product, can be used for chemical vapour deposition. The substrate may in some cases, take part in the reaction mechanism if the temperature is sufficiently high.

For example, Si or Al substrates when exposed to an oxygen atmosphere grow SiO₂ or Al₂O₃ layers, respectively. The selection of a practical reaction however is dictated by the constraints imposed by the substrate and the reaction. Moreover, one has to be aware of and take into account the fact that the actual course of the reaction may be much more complex and involve formation of intermediate reaction species in accordance with the reaction kinetics. The reaction kinetics depends on several factors, notably flow rates, partial gas pressure, deposition temperature, temperature gradients, and nature and properties of the substrate surface.

The chemical reactions utilized in CVD process can be classified as
i. Decomposition reactions.

ii. Hydrogen or metal reduction of halogens

iii. Polymerization and

iv. Transport reactions.

Four brief summaries of these reactions follow:

**Decomposition:**

If high energy is supplied to the vaporized plating compound sufficiently steaming over or being adsorbed on the substrate surface. It decomposes and a solid-phase reaction product condenses on the substrate. This reaction can be written as

\[ AB\text{ (gas)} \rightarrow A\text{ (Solid)} + B\text{ (gas)} \]

Both the organic and inorganic as well as polar and non-polar plating compounds are suitable for this process. A typical example of a decomposition process is

\[ SiH_4 \rightarrow Si + 2H_2 \]

The decomposition process, also termed pyrolysis, can be classified as a high-temperature pyrolysis requiring a substrate temperature exceeding 600°C or a low-temperature process at temperatures between room temperature and 600°C primarily metal halides, in particular the iodides, undergo high-temperature decomposition. Compounds which decompose at low
temperatures include metal hydrides, metal carbonyls and some of the more unstable metal halides and carbonyl halides.

For decomposition at low pressure with a large concentration of decomposition products, increased substrate temperature may be required. An increase in substrate temperature is beneficial in obtaining improved crystalline composition, purity or adhesion of the deposited layer. Despite the simplicity of the decomposition process, certain difficulties may arise, associated with the formation of more than the non-volatile residual reaction product such as carbon from carbonyls and organic metallic compounds boron from borohydrides and oxides from oxygen containing compounds.

Electron bombardment, used in activated decomposition, converts various silicon oils adsorbed to a substrate surface to SiO or SiO$_2$ with incorporated organic constituents [12].

Reduction

A decomposition process aided by the presence of a second reaction species can be considered as a reduction process. Consequently, deposition occurs at a temperature lower than that for pyrolysis of the first
component. Hydrogen or metal vapors are employed as reducing agents while metal halides, oxyhalides, or other oxygen-containing compounds are used to obtain the material to be deposited. In some cases, addition of a reducing agent to a reactive vapour from which the layer is formed mainly pyrolysis. Server to prevent Co-deposition of undesired oxides or carbides the strength of the reducing reaction in chemical vapour deposition from metal halides is influenced by the reducing agent and increases in the sequence.

\[ \text{H}_2 \rightarrow \text{Cd} \rightarrow \text{Zn} \rightarrow \text{Mg} \rightarrow \text{Na} \rightarrow \text{K} \quad (\text{if } < 1000^\circ \text{C}) \]

However, a very strong reducing reaction leads to premature reduction in the gas phase, yielding powdery deposits. A typical example of chemical vapour deposition by reduction is the preparation of Si from the corresponding halide vapour using H\textsubscript{2} or Zn as the reducing agents according to the reaction.

\[ \text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl} \]

Hydrogen, although less strongly reducing, offers the advantage that it can be premixed with the metal is used in stoichiometric proportions and the process is carried out at a reduced pressure. If the reductant metal forms a halide in the reaction that is less volatile than the parent metal and may therefore be co-deposited operating
conditions have to be maintained such that the pressure of the halide of the reductant metal is lower than its saturation pressure at the deposition temperature.

In this context for the reductant metals mentioned above, the fluorides, the chlorides land the bromides (except those of Zinc) and the iodides (except those of Zinc & Magnesium) being the least volatile than their parent metals with fluoride being the least volatile and the iodides the most volatile. Further alkali metal halides are least volatile relative to the parent metal. Thus iodide is preferable as deposition media and alkali metals are least suitable reductants.

For thermally activated deposition the reduction process may require high substrate temperatures. However, too high a temperature may lead to pyrolysis of a reaction product such as hydrogen halide leading to a reversal of the reaction or etching of the substrate polymerization.

In the polymerization technique, organic and inorganic composites from the monomers where molecules are linked together by one of the following activation processes.

1. Irradiation with light, X-rays, or Y-rays.

2. Electron or ion bombardment
3. Surface catalysis or surface recombination of monomers having free radicals.

4. Electrical discharge in the monomer vapour

The films can also be produced by

1. Depositing the monomer film of the substrate by other means and then activating the polymerization.

2. Condensing monomer vapors on the substrate and subjecting them simultaneously or sequentially to the activation process.

3. Activating in the gas phase and allowing the polymerized product to deposit on the substrate or

The polymerized films have electrical properties ranging from semi-conducting to insulating and have certain desirable characteristics such as complete surface coverage, good adhesion, low stress, and high plasticity.

Transport reactions:

From the source location to the substrate location utilized a relatively highly volatile chemical vapour. The chemical transport technique involves the transfer of a relatively non-volatile material. The three basic steps are:
1. Conversion of the source material into a volatile compound through a chemical reaction.

2. Transport of the vapour to the substrate and

3. Decomposition of the chemical vapour over or on the substrate leading to deposition of the source material onto the substrate.

To achieve chemical transport the reaction equilibrium is usually shifted to opposite sites in the source and substrate locations let us consider the example of an indirect distillation system.

\[
\text{Ti (Solid)} + 2\text{NaCl (gas)} \rightleftharpoons \text{TiCl}_2 (\text{gas}) + 2\text{Na (gas)}
\]

The direction in which the reaction occurs is controlled by the temperature and pressure conditions. Thus different conditions of temperature and pressure are maintained at the source and substrate regions. Another method of shift the reaction equilibrium is to introduce an additional chemical to perform either a reduction or an oxidation of the transport vapour near the substrate surface, leading to the deposition of a compound. e.g. the transport of SiO$_2$ with more volatile SiO as the transport medium according to the reaction.

\[
\text{Si (solid)} + \text{SiO}_2 (\text{solid}) \rightarrow 2\text{SiO (gas)}
\]

\[
2\text{SiO (gas)} + \text{O}_2 (\text{gas}) \rightarrow 2\text{SiO}_2 (\text{solid})
\]
The various reactions utilized for chemical transport, the disproportionate reactions. Particularly the halide disproportionate reaction, are the most widely used. Transfer is accomplished by treating the non volatile metal with the vapour of its own higher-valent halide at a high temperature to yield a lower-valent, volatile halide which after transport into a cooler zone of the system disproportionate back into the higher valent, volatile halide and the non-volatile metal. The higher valent halide is recycled by feeding back the hotter zone in which the source material is kept. Thus the system can operate as a closed system. A typical example is the transport of silicon in an iodine vapour atmosphere [13].

\[
\begin{align*}
\text{Si (solid) + 2I}_2\text{(gas) } & \rightarrow \text{SiI}_4\text{(gas)} \\
\text{Si (Solid) + SiI}_4\text{(gas) } & \rightarrow 2\text{SiI}_2\text{(gas)} \\
2\text{SiI}_2\text{(gas) } & \rightarrow \text{SiI}_4\text{(gas)}
\end{align*}
\]

An additional advantage of transport reactions as that refinement of the material also occurs in those cases. Such as they are above where the corresponding iodine vapors of the major contaminant the source materials have vapour pressures sufficiently different from those of the major transporting species.
Transport reactions exist where oxidation occurs on one side of the reaction equilibrium and reduction on the other such as

\[ \begin{align*}
2\text{Ga (solid)} + \text{H}_2\text{O (gas)} & \rightarrow \text{Ga}_2\text{O} \text{(gas)} + \text{H}_2 \text{(gas)} \\
\text{Ge (solid)} + \text{H}_2\text{O (gas)} & \rightarrow \text{GeO (gas)} + \text{H}_2 \text{(gas)}
\end{align*} \]

We may note here that transport reactions have been used for gaseous etching e.g. Ge or Si with HCl [14,15] and Al\textsubscript{2}O\textsubscript{3} with fluorinated hydrocarbons [16] to remove contaminants and surface damage prior to the deposition of epitaxial films and also to obtain a thin film by thinning (gaseous etching) a relatively thick deposit [17].

Group III – IV semi conductors [18] such as Ga As, AlAs, GaSb, InP, InAS, GaP and GaN have been obtained from CVD Processes by the hydride method, the chloride method and the organo metallic method. Ternary alloys such as Ga\textsubscript{x} In\textsubscript{1-x} As\textsubscript{1-x} P\textsubscript{x} have been prepared with precisely tailored band gaps determined by the compositional variable x. The CVD process has been extended to prepare quaternary alloys [19] such as Ga\textsubscript{x} In\textsubscript{1-x} As\textsubscript{y} P\textsubscript{1-y} with desired band gap and lattice constants.

Films of II-IV compounds have been obtained by employing [18] the reaction of metal vapors with group VI hydrides, an open tube transport of II-VI compounds by
HCl or HBr, and the reaction of organo metallic diethyl or dimethyl compounds of metals with group hydrides.

Transparent conduction oxides films namely, SnO$_2$, In$_2$O$_3$, VO$_2$, V$_2$O$_3$, V$_2$O$_5$, SnO$_2$ Sb, and In$_2$ O$_3$. Sn has been prepared either by hydrolysis of the metal chlorides or by pyrolysis of metal organic compounds.

**Metals:**

The following major processes are involved in the arrangement of CVD of metals and metal alloys

1. Reduction of metal hydrides with vapors of thermodynamically appropriate metals and chemical transport reaction.

2. Thermal decomposition of pyrolysis of organo metallic compounds, generally at low temperature.

3 Hydrogen reduction of metalhalides, oxyhalides, carbonylhalides, and other oxygen reduction of metalhalides, oxyhalides, carbonylhalides and other oxygen containing compounds.

**Insulators:**

In many cases, CVD produces higher quality dielectric films than other deposition methods for such application as optical coatings, surface passivation, insulation between multi layer arrangements, diffusion,
and photo etching masks and corrosion preventing coatings. Insulating films deposited by the CVD process include silicon dioxide (SiO₂) silicon nitride (Si₃N₄) boron nitride (BN) alumina (Al₂O₃) aluminum nitride (AlN) tantalum pentoxide (Ta₂O₅) niobium pentoxide (Nb₂O₅) and titanium dioxide (TiO₂) close-spaced vapor transport (CSVT). The use of a close spacing in chemical transport systems for growing epitaxial layers of pure and compound semiconductors has been demonstrated by several workers [20, 21]. In this CSVT technique a temperature gradient is maintained between the closely spaced (~1mm) source and substrate.

A gas is used to react with the sourced to form a volatile compound that is subsequently decomposed at the surface of the substrate to form a thin film. As expected, the deposition rate is strongly dependent of the kinetics of transport of this reactive gas. The source and substrate temperature, the substrate surface and of course, the thermodynamics of the reactions involved. The various processes occurring have been analyzed theoretically by Bailly et al [22].

Using the CSVT technique may [23] reported epitaxial deposition of Si by using a low pressure i₂ atmosphere for transport of Si from a source held at a
temperature lower than the substrate. Epitaxial films of CdS and GaAs grown at rates of approximately min have been obtained by Curtis and Brunner [24] by exploring the displacement of the equilibrium of the reaction

\[
\text{CdS (solid) + H}_2 \text{ (gas)} \rightleftharpoons \text{H}_2\text{S (gas) + Cd (gas)}
\]

Epitaxial films of CdTe [25] and GaAs [26] have been obtained by this technique using water vapour as the transporting agent.

3.4.2. MORPHOLOGY OF FILMS PREPARED BY CVD

Depending on the nature of the substrate and the surface conditions, the deposition conditions prevailing during growth and the nature and amount of impurities. The microstructure of CVD-grown films range from very porous to impermeable from amorphous to epitaxial single crystal and from powdery to strongly adherent,

In general, in analogy with PVD high substrate temperatures and low vapour concentrations lead to coarsely crystalline coating whereas low substrate temperatures and high vapour concentrations yield amorphous or microcrystalline layers.

It should be emphasized that this general principle is influenced to a great extent by the nature of the
reacting vapors the nature of the substrate, the vapour velocities, and the impurities in the system.

Nucleation process occurring in the early growth stages largely determines the morphology of CVD films. Filby et al [27] have pointed out that a relatively high nucleation rate yields a smooth layer whereas high lateral growth rate leads to the formation of facts or steps. The smoothness of epitaxial films may also be influenced by the substrate orientation.

The substrate temperature plays an important role in the microstructure of the films. At very low temperature, microcrystalline, amorphous or porous layers are obtained, owing to slow or incomplete reactions, with increase in deposition temperature, rapid growth occurs. However, the integrity of the coatings in generally inferior to that of low-temperature deposited coatings.

The partial pressure of the reactants in the system influences the deposition rate and hence the grain size. With increase in deposition rate the deposited layer can vary from column or (at low rates) to porous (at higher rates) [28].
3.5 LIQUID PHASE / SOLUTION DEPOSITION:

The unit species of the material to be deposited are dispersed in a liquid medium (generally aqueous) and are always present in ionic form by this technique. Solution deposition techniques, therefore involves chemical and or electrochemical reactions in the formation of film. Some general advantages of solution deposition techniques over vapor deposition techniques are

1. Experimental setups are much less sophisticated compared to those in vapor deposition techniques.

2. No expensive equipment such as vacuum systems is required for deposition and

3. Deposition can be carried out at lower temperature.

3.5.1. ELECTRO DEPOSITION:

The occurrence of chemical changes owing to the passage of electric current through an electrolyte is termed electrolysis and the deposition of any substance on an electrode as a consequence of electrolysis is called electro-deposition. The principle involves the deposition of substance on an electrode as a consequence of
chemical change due to the passage of electric current through an electrolyte.

The mechanism of deposition involves the dissociation of metal salts to anions and cations, the deposition of the latter at the cathode surface and consequent neutralization of their charges to form metallic films. In electroplating the anode is generally of the same metal which is to be deposited on the cathode. The amount of metal deposited at the cathode can be expressed by the first and second laws of electrolysis i.e. 

\[ W = ZI\tau \]

where 'W' is the weight of the metal deposited, 'Z' is the electrochemical equivalent, 'I' is the current passed, '\tau' is the time of deposition and '\alpha' is the cathode efficiency. Same amount of metal from the anode goes into solution. Electrode reactions for a divalent metal (M) salt bath can be expressed by the following equation.

\[
\begin{align*}
\text{M}^{2+} + 2e^- & \rightarrow \text{M at the cathode} \\
\text{M} & \rightarrow \text{M}^{2+} + 2e^- \text{ at the anode}
\end{align*}
\]

Similar types of reactions also take place for mono and trivalent metals. The dissolution of metal anode to form the metallic salt can be treated as the oxidation process where as the deposition of metal at the cathode
surface as the reduction process. Thus when a metal is deposited at the cathode an equal amount of metal ions goes into the solution from the anode. Quality of the film depends upon the deposition parameters such as bath composition, temperature, pH, current density etc. Alloys such as AlSb [29] can be deposited by coelectrolysis for which the electrode potentials should be brought very close to each other. Electro deposition of compound like CdSe [30]. CaAs [31] is also possible by co-depositing the two components in elemental form by cathodic reduction of their corresponding ions and their subsequent reaction to form the corresponding compound. For example, the deposition of CdSe film involves electrolytic co deposition of Cd$^{2+}$ and SeO$_3^{-2}$ ions. The reaction involved at the cathode in the case of CdSe film is as

$$\begin{align*}
\text{Cd}^{2+} + 2e^- & \rightarrow \text{Cd} \\
\text{SeO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- & \rightarrow \text{Se} + 6\text{OH}^- \\
\text{Cd} + \text{Se} & \rightarrow \text{CdSe}
\end{align*}$$

Baranski and Fawcett [31] have used to deposit thin films of semi conducting metal chalcogenides such as CdS, HgS and PbS on various substrates. Detailed review of this technique is given by Milazzo [32] and Brenner [33].
3.5.2. ELECTROLESS DEPOSITION:

Electroless technique also involves the reduction of metal ions to form the deposits, but no external power supply is required to provide electrons. In this process, films can be deposited without passing any current. The substrates can be both metals and non-conductors. The basic principle of this process is the reduction of a metal on a substrate surface by a reducing agent and once an initial coating is formed, further deposition can go on auto-catalytically. The reducing agent normally used is sodium hypophosphite. This process is originally developed by Brenner and Riddell [34] for metals like nickel, platinum, but Goswami [35] observed metal such as brass, copper, lead could be coated by electro less process when these were in contact with iron or nickel, and now a days not only metals but also non-conductors are coated by electroless plating technique with the help of suitable sensitizing SnCl₂ and activating PdCl₂ solution treatment [36]. Also compounds like ZrO₂ [37] and CdS [38] are prepared by this method.

3.5.3. SPRAY PYROLYSIS TECHNIQUE:

A large number of metallic salt solutions when sprayed on to a hot substrate decomposed to yield oxides films. It was used as early as 1910 to obtain transparent
oxide films. In the 1960's Chamberlin et al [39-41] extended the technique to produced sulphide and selenide films. The technique involves a thermally stimulated reaction between clusters of liquid/vapour atoms of different chemical species. Spray pyrolysis method lies somewhere in the regime between a thin film and a thick film technique depending on the atom cluster size.

The spray pyrolysis technique has been developed extensively by Chambering et al [39-43], Bube et al [44-50] at Stanford University and Savalli et al [51, 52] at Montpellier University. A review on this technique has been published by Chopra et al [53].

3.6.1. GROWTH KINETICS

The aerodynamics of the atomization and droplet impact process and has correlated the dynamic features of the spray process with the kinetics of film growth and surface topography has been studied by Limpkin [54]. When both the size and momentum of the spray droplets are uniform, optically good quality and smooth films are obtained.

According to Banerjee et al [55, 56] the liquid droplet tends to flatten out into a disk on impact with the
substrate surface. The disk geometry depends on the momentum and volume of the droplets, the substrate temperature and the balance of the dynamical surface, energy and thermal process. The deposition process is a resultant of the following steps i) spreading of a drop into a disk ii) Pyrolytic reaction between the decomposed reactants iii) evaporation of the solvent, and iv) repetition of the preceding processes with succeeding droplets. Consequently the film generally contains disks interspersed into each other. The lateral mobility of the droplets and coalescence and sintering kinetics of the super imposed disk crystallite clusters determine the growth kinetics and microstructural features of the spray deposited films. The following important characteristics are observed in this mode a growth i) the random disk-by-disk growth exposed to a continuous flow of pressurized liquid droplets eliminates microscopic and macroscopic voids and cavities in the growing film. Thus spray deposited films are coherent and pinhole free even at very low (1000Å) thickness, provided the substrate temperature is high enough to cause complete pyrolytic reaction ii) the micro structure of the film depends very sensitively on several deposition conditions, notably the spray head geometry, carrier gas and liquid flow pattern,
droplets velocities, sizes and geometries, nature and temperature of the substrate, the kinetics and thermodynamics of the pyrolytic reactions and the temperature profile during the deposition process.

The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle with the help of a filtered carrier gas, which may be air (as in the case of oxide films) or may not (as in the case of sulphide films) be involved in the pyrolytic reaction. The carrier gas and the solution are fed into the spray nozzle at predetermined constant pressure and flow rates. The substrate temperature is maintained with the help of a feedback circuit, which controls a primary and auxiliary heater power supply. Large area uniform coverage of the substrate is effected by scanning either or both the spray head and the substrate, employing mechanical or electromechanical arrangements. The geometry of the gas and liquid nozzles largely determines the spray pattern, the size distribution of droplets, and the spray rate. A wide variety of nozzles have been designed and employed for spraying stationary and moving substrates.

3.6.2. OXIDES DEPOSITION

The metal oxide films are obtained by an aqueous metal salt solution is sprayed onto a hot substrate in air
Generally metal chloride such as SnCl₄ for SnO₂ [57], InCl₃ for In₂O₃ [58] AlCl₃ for Al₂O₃ [59] FeCl₃ for Fe₂O₃ [60] CoCl₃ for Co₂O₃ [61] and ZnCl₂ for ZnO [62] have been used. In addition nitrates, carbonates, acetates and bromides have also been employed [63].

Organo metallic compounds have also been used to obtain oxide films. Although more expensive, these compounds offer the advantage of low decomposition temperature, thereby reducing substrate / vapor film interaction. Some of these compounds are dibutyltindiacetate (C₄H₉)₂ Sn (CH₃COO)₂ for SnO₂ [57] indium acetylacetonate in (C₂H₅O₂) for In₂O₃ [64-66] Cd (CH₃COO)₂ dihydrate in methanol for CdO [67].

3.7. FEATURES OF THE SPRAY PYROLYSIS PROCESS

3.7.1. GROWTH RATE

The growth rate is determined by the chemical nature, temperature of the substrate, and concentration of the spray solution, its additives, and the spray parameters the growth rates can be as large as 100 Å min⁻¹ for oxide films and 50Å min⁻¹ for sulphide films.

3.7.2. SUBSTRATE EFFECTS

The spray pyrolysis process is affected by the substrate surface. When it is not desirable for the
substrate to take part in the pyrolytic reactions, neutral substrates such as glass, quartz, ceramics or appropriate oxide/ carbide coated substrates are employed. In the case of certain oxide films on Si some desirable etching takes place during deposition. Metallic substrates [56] have not been found suitable for this process.

Mobil alkali and other alkaline earth metal ions such as Li⁺, Na⁺, Ca²⁺, Sr²⁺ and Mg²⁺ contained in the chemically inactive substrates may be incorporated into the films and the extent of inclusion would increase with the substrate temperature.

Generally, at lower substrate temperature foggy and diffusely scattering films are obtained. High substrate temperature yields thinner, continuous, hard and spectrally scattering films. Moreover, at higher temperatures, re-evaporation of anionic species may occur, leading to metal rich deposits.

3.7.3. FILM COMPOSITION

Depending on the kinetics of the spray process and the thermodynamics of the pyrolytic process the composition of the film is expected. Stoichiometric sulphide and selenide films and nearly stoichiometric oxide films have been obtained under appropriate
conditions. The stoichiometry of sulphide films does not vary appreciably with the metal to sulphur ratio in the spray solution for ratio ranging from 1:1 to 1:5 but the microstructure of the films is strongly influenced by this ratio [68, 69, 70].

At low temperature, if the pyrolytic reactions have not been completed, some by-products or intermediate compounds will be trapped as impurities in the film. In the case of chloride salts, residual chlorine is often present [62] in films the chlorine concentration in SnO₂ films decreases with increasing substrate temperature during pyrolysis. Consequently, owing to the cooling effect at the growing film surface, a higher concentration of chlorine [71] is sensitively dependent on the ratio of chlorine to Sn ion in the spray solution.

The Stoichiometry of the oxide films is dependent on relatively more complex reactions [58,72,73]. The presence of oxygen ion vacancies in tin oxide films is associated with the conversion of Sn⁴⁺ to Sn²⁺.

The Oxygen content in films is also influenced by the rate of cooling of the films after the spray is over, owing primarily to the adsorption of oxygen.
3.8. SUBSTRATE SELECTION

3.8.1. SUBSTRATES

Thin films cannot generally work independently and they must be support themselves, and thus some form of carrier must be provided. This carrier, or "substrate", would ideally have no interaction with the thin film except for sufficient adhesion to provide support. If the film is to be part of a circuit the substrate may also be called upon to conduct any heat generated in the film to a heat sink. In addition, the substrate must be compatible with the deposition processes and all subsequent processing or handling necessary for the use of the films. Another consideration is cost, particularly if the films are to be utilized commercially. Metals and semiconductors may be coated with insulating films, but these are generally discounted because of parasitic capacitance. Another requirement is mechanical strength, and on this basis all the nonmetallic elements may be eliminated. The requirement of thermal stability essentially eliminates the organic plastics, which deform or decompose below 250°C. The inorganic compounds which remain include amorphous, polycrystal, and single crystal structures such as glass, ceramics, and sapphire. These examples are
also the most commonly used substrate materials, and this discussion is limited to them.

3.8.2. SUBSTRATE CLEANING

Through the proper cleaning technique depends on the nature of the substrate, the nature of the contaminants, the nature of the substrates and the degree of cleanness required before cleaning any substrate [74] must used it must adequately cleaned. Expected contaminants include those from manufacturing procedures, human contact (such as protein), and airborne dust, lint, and oil particles. If the substrates have received any prior processing, a host of new contaminants may be present a knowledge of the processing steps may provide the list of those to be expected. As a minimum, the substrate surface must be made clean enough that contaminants do not interfere with the adherence of a vacuum deposited film. The ability to pass the water-break test is usually a necessary but not a sufficient condition to insure adherence. On visual inspection, using dark field illumination, there should be no lint or other particles and no film visible on any area.

Cleaning involves the breaking of adsorption bonds between the substrate and the contaminants without damaging the substrate surface itself. The energy to
perform this step may be provided directly as heat or ion bombardment, by chemical reaction or salvation, or by mechanical scrubbing. Chemical cleaning methods ultimately depend on salvation and then removal of solvents. Mechanical action is best conducted in the presence of solvents and is most effective for removing gross contamination. The most logical order for combining the three techniques is to provide mechanical scrubbing in the presence of solvents, chemical reaction and salvation, and finally heat or ion bombardment (usually at reduced pressure).

Mechanical scrubbing has been performed by rubbing the substrate with chalk or cotton swabs, but a more effective procedure is to suspend the substrate in an ultrasonically agitated detergent solution. In this method, ultrasonic waves are transmitted to the solvent from a transducer and cause cavitations or bubble collapse with corresponding local surges of hydrostatic pressure. The stress created when a bubble cavity implodes on the surface of the substrate allows the solvent to penetrate between the contaminant and the substrate. The variable parameters of ultrasonic cleaning are the frequency of vibration and the power applied, as well as temperature, vapor pressure, surface tension, and
viscosity of the cleaning solution. The lower the frequency, the more violent the cavitation, but practical application is limited to frequencies above the audible range. An increase in power increases cavitations, but too much power may limit cavitations to the face of the transducer and reduce the cleaning action at the substrate surface. The effect of temperature on cavitations depends on the physical properties of the solvent used. Optimum results using water occur between 60°C and 70°C. Liquids of low vapour pressure and viscosity produce better cavitations. Surface tension is the most important physical property of the cleaning solution, and greater surface tension leads to a greater energy release on bubble collapse. A quick but subjective test for ultrasonic action is to suspend a piece of aluminum foil in the solution (or in a beaker of water suspend in the solution) for about 15 seconds and then to visually inspect the full for deformation.

Chemical treatment to remove contaminants is often used but is likely to attack the substrate surface. Acid cleaners react with contaminants such as grease and some oxides to convert them to more soluble components, and alkaline cleaners saponify fats and decrease surface tension. The effectiveness of solvents is probably more
dependent on their ability to wet substrate than their solvent action on the contaminants. The two main considerations of a solvent are that it be available in high purity and that any traces left on the substrate be easily removed in the vacuum system by heating to reasonable temperatures. Two effective final solvent rinses in common use are deionized distilled water and isopropanol.

Substrates may become contaminated during and after cleaning. Cleaning tanks and substrate baskets must be immaculate and the surrounding atmosphere should be filtered. Substrate storage after cleaning is risky and should be minimized. Storage overnight beneath boiling, deionized, water is apparently safe for 7059 glass and dry storage is possible for a few hours in a closed, clean glass dish or desiccators. Inside a vacuum system, substrates may be further cleaned by heating at reduced pressures and, with modern vacuum techniques; there is little chance for further contamination other than particulate matter.

The following substrate cleaning procedure has been used with good results on substrates of glass, glazed ceramic, unglazed ceramic, and sapphire. The first step in this system uses room temperature ultrasonic
agitation in a dilute solution of detergent to dislodge gross dirt. The second step is the same as the film but is carried out at 70° C in a separate tank. The room-temperature bath is necessary first to remove protein material since heat natures such contaminants and makes them more difficult to remove. The third operation is to replace the film of detergent solution on the substrate with a film of water. A hot-water spray rinse followed by an overflow rinse is usually effective. The objective of the fourth step is the conversion of organic materials (not previously removed) to water soluble compounds. A boiling solution of hydrogen peroxide is used to perform this function, since it is a strong oxidizing agent and is volatile. The fifth operation replaces the film of peroxide with one of water, and it is carried out in two steps. The first is quick dip in hot distilled water, the second is a 15 minutes soak in overflowing boiling, deionized, distilled water.

Before substrate is to add into a vacuum system they are dried with hot (110°C) clean nitrogen for 15 minutes. A visual examination of glass substrate using oblique illumination will show any remaining particulate matter. No substrate ever appears perfect in these respects and such a test is uncomfortable subjective.
Some residue will almost always be observed at the lower substrate edge, especially where there has been contact with the substrate container during final drying. If the atmosphere used for the inspection is not filtered. Particulate matter will be observed to land on the substrate during examination and further confuse the test. The lack of confidence in this visual that and in other tests usually results in their being used only after trouble has been encountered with the appearance or adherence of deposited films.

3.9 MEASUREMENT TECHNIQUES

INTRODUCTION

Thin film materials are developing by the use of many technological applications. The structural, optical, electrical properties are studied by using X-ray diffraction, UV visible spectrophotometer, Electrical resistance scanning Electron microscopic method are characterized.

3.9.1 X-RAY DIFFRACTION STUDIES

Diffraction of X-rays by a crystal was first observed by Friedrich, Knipping and Laue [75] while experimentation with X-rays. Bragg [76] almost simultaneously observed the reflection of X-rays by a crystal. This discovery leads to study the characteristic of
Materials, and it is a well established technique for determining crystalline order in three dimensional solids. The measurement indicates the identification of individual crystalline phases by their characteristic diffraction patterns. Further analysis of XRD patterns yields information regarding the orientation and size of the crystallites. The JEOL 8030 model X-ray Diffract meter is employed for the XRD analysis. The well known Braggs law gives the relation between the wavelength of X-ray beam and the diffraction angle of it, and is give by

\[ n\lambda = 2d \sin \theta \] (3.1)

When 'n' is the order of diffracted X-ray is d the inter planner distance of the crystalline material the wavelength of X-ray, \( \theta \) is the diffraction angle. The inter-planar spacing depends solely on the dimensions of the unit cell of the crystal the intensities of the diffracted rays are the function of the placement of the atoms in the unit cell. The crystalline size or the average grain size (D) can be calculated using Scherer's formula (66)

\[ D = \frac{K \lambda}{\beta \cos \theta} \] (3.2)

Where '\( \beta \)' is the breadth of the diffraction line at its full width half maximum intensity (FWHM) in radians, \( \lambda \) is the wavelength of the incident X-ray (1.541 A) \( \theta \) is the
angle at which the maximum peak occurs and ‘K’ is the shape factor which usually takes a value of about 0.89.

In the present work X-ray diffraction studies have done to determine the crystalline nature of the films prepared at different substrate temperatures and line broadening technique has been used to determine the grain size the content of the doped transition metal in the film is determined by taking into account of the morality of the precursor solution. The ratio of the molarity of the solutions gives the exact percentage of the transition metal content in the film.

3.9.2. FILM THICKNESS MEASUREMENT

True mass difference light absorption, interference effect, Conductivity, Capacitance etc. of the films with increasing thickness are based on the afore said methods. The measurement can be either in a dynamic (or) static condition. In the former film thickness is measured during the deposition process while in the latter, after its completion.

Generally thickness (T) of uniform shape of the material is given by volume of the materials (V) / Area of the material (A). In the present work loss of weight method is used to determine volume of the material which
is based on Archimedes principle. Area of the material is to obtain from graph by counting number of smallest squares occupied by the material.

The following procedure is used to determine film thickness. Films Thickness of the substrate is determined using the relation.

\[ T_{\text{substrate}} = \frac{\text{Volume of the Substrate}}{\text{Area of the substrate}} \]

\[ = \frac{\text{Loss of weight (Wt in air - wt in water)}}{\text{Area of the substrate}} \]

Weight in air is determined using a microbalance and weight in water is determined by immersing the substrate in a beaker containing distilled water similarly. thickness of the Substrate + coated film ( \( T_{\text{Substrate + films}} \)) is determined finally film thickness is obtained from the difference of the above two thickness.

\[ \text{Film Thickness} = T_{\text{Substrate + films}} - T_{\text{Substrate}} \]

3.9.3. SCANNING ELECTRON MICROSCOPE (SEM) STUDIES.

This is one of the most useful and versatile instruments for the investigation of surface topography, grain size, micro structural feature, etc., it provides a pictorial display of the surface layer with a high depth of focus greater than that possible in an electron microscope. The principle involved in imaging is to make
use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the film. The secondary electrons are formed by the interaction of the primary electron beam with the loosely bound electrons of the surface atoms and their emission is very much sensitive to the incident beam direction and the topography of the surface atoms. The more oblique is the surface, the greater will be the surface area from which secondary electrons can emit. The surface morphology of the film is studied using HITACHI S-3000H model. It consists of an electron source, a series of lens system to produce a finely focused electron beam on the film surface and two pairs of deflection coils at right angles to each other. The emitted secondary electrons are collected in a collector, which is amplified and then fed to a CRT. As the electron beam scans the film surface there will be a change in the secondary electron emission according to the surface texture. The scanning picture observed on the CRT represents the image of the surface.

3.9.4 OPTICAL ABSORPTION MEASUREMENTS:

The optical study of solid concerns not only with the physical phenomena such as refraction, reflection, transmission, absorption, polarization and interference of
the light but also the interaction of photon energy with matter and the consequent changes in the electronic states. Absorption of light by different materials can induce various types of transitions such as band to band between sub bands between impurity levels and bands transitions of free carriers within a band and also resonance due to vibration state of lattice and impurities. These lead to the appearance of bands or absorption peaks in the absorption spectra. Absorption of light by an semiconductor or insulator takes place broadly by two process namely i) by raising the electrons from the valence band to conduction band ii) by exciting the lattice vibrations of the material. The later process provides information regarding the bond length of the lattice the effective charge of the lattice atoms and characteristic lattice vibration frequency. From the process (i) it is however possible to find out the electronic band structure.

The optical method provides a very simple way of finding the band gap as compared to the method using thermal excitation which is less reliable. To determine the band gap of the thin film the following procedure has to be adopted from the optical measurements. The absorbance (\(\log \frac{I_0}{I}\) Intensity of the incident light \(I_0\) Intensity of the transmitted light) for each wavelength of
cases it is 3/2. But for the indirect and allowed cases \( n = 2 \) and for the forbidden cases it will be 3 or more.

A plot of \((\alpha h\nu)^2\) or \((\alpha h\nu)^{1/2}\) against \(h\nu\) exhibits a straight line corresponding to direct or indirect transition respectively. The linear portion of the graph above the fundamental absorption edge is extrapolated to \(h\nu\) axis which gives the band gap of the material.

3.9.5. ELECTRICAL MEASUREMENTS

Electrical resistance is the basic property of a material for charge transport. Electrical resistance results from the scattering of charge by the lattice and nature of the material. Sheet resistance is commonly measured in thin films. The most common method to determine the sheet resistance of the film is four-point probe method in the present work film resistance are measured using two point probes spaced 1.3 mm connected to computer controlled Keithley Electrometer Model 6514. A source test current is passed through the probes and the voltage drops are measured. The resistance is then calculated by using Ohm's law. Electrical contacts made on the semiconducting film for measuring film resistance make additional resistance to charge flow. The behaviour of these contacts depends on the relative work functions of the metal and the film. There are three possible types of
cases it is $3/2$. But for the indirect and allowed cases $n = 2$ and for the forbidden cases it will be 3 or more.

A plot of $(\alpha \nu)^2$ or $(\alpha \nu)^{1/2}$ against $\nu \alpha$ exhibits a straight line corresponding to direct or indirect transition respectively. The linear portion of the graph above the fundamental absorption edge is extrapolated to $\nu \alpha$ axis which gives the band gap of the material.

3.9.5. ELECTRICAL MEASUREMENTS

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contacts and these are (i) ohmic (ii) neutral and (iii) blocking contact. Of which ohmic contacts are characterized by a linear dependence of current Vs voltage over a large range and is best suitable for resistance measurement of semi conducting films.
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