CHAPTER 1

INTRODUCTION TO TRANSPARENT CONDUCTING OXIDES AND THIN FILM PREPARATION METHODS

1.1 INTRODUCTION

In recent years, the demand for thin film coatings on large area substrates has been rapidly increasing. Coating is sometimes required to make an object harder, or to provide the surface with particular electrical and optical properties. Hence, research on thin film science has received much attention due to its tremendous applications in modern technology. The importance of coatings and the synthesis of new materials for industrial applications have resulted in considerable development of novel thin film processing and characterization technologies. Currently, the development goes hand in hand with the explosion of scientific and technological breakthroughs in microelectronics, optoelectronics and nanotechnology.

A thin material created by atoms / molecules / ions / cluster of species by condensation process is defined as thin film growth (Chopra and Das 1983). This involves in the process of placing a thin layer of one substance on another (ex. substrate) in order to modify the properties of the second material, e.g. to increase the hardness or to change electrical conduction or to modify the optical properties of the underlying substrate material.

Studies on transparent and highly conducting semiconducting oxide films have attracted many research groups due to their wide range of
applications both in research and industry. Thin films of metal oxides like cadmium oxide (CdO) and indium oxide (In$_2$O$_3$), are the well known classical examples for optically transparent and electrically conducting materials. Thin films of CdO, produced by thermal oxidation of sputtered cadmium films were first reported by (Badeker 1907). Thin films (~100-200 Å) of metals such as Ag, Mg, Cu, Fe, etc. have also been reported to have similar properties. These films, in general, are not very stable and sensitive to the environment, and their optical and electrical properties change with time. On the other hand, some metal oxide coatings are widely applied because of their stability and hardness that are superior to those of thin metallic films.

The applications of transparent conductive oxide (TCO) coatings have prompted enormous research on their deposition and characterization methods. Various TCO films are applied in optoelectronics, including touch panels, electroluminescent, plasma, and field emission displays. In addition, these coatings are also used as heat reflective mirrors, energy efficient windows, gas sensors, as transparent electrodes in photovoltaic cells, and as fire retarding materials. As transparent conductors, these films find applications in vehicle and aircraft windscreen defrosters.

Heterojunction solar cells with an integral conducting transparent layer offer the possibility of fabrication of low-cost solar cells with performance characteristics suitable for large scale terrestrial applications. The conducting transparent film permits the transmission of solar radiation directly to the active region with little or no attenuation. In addition, the TCO films can also serve as a low resistance conductor to the junction and as an antireflection coating for the active region. Solar cells utilizing these types of coatings are now widely fabricated, e.g. SnO$_2$/Si, In$_2$O$_3$/Si. Furthermore, these films can be used as gas sensors, by utilizing the large changes in their conductance produced by the charge exchange with absorbed gas molecules.
The electron concentrations in the conduction band in a semiconductor sensor can vary approximately linearly with the pressure of the gaseous environment, for a range up to eight orders, while the variations in carrier mobility are generally small. This large and reversible variation in conductance with active gas pressure has made semiconducting materials very attractive for the gas sensing devices (Hartnagel et al 1995).

Among the several types of TCOs, the SnO$_2$, ZnO, In$_2$O$_3$, Ga$_2$O$_3$, and CdO are the well-known binary compounds. Doping element is generally introduced to improve their electrical conductivity, and the frequently used doped TCOs are In$_2$O$_3$:Sn, In$_2$O$_3$:F, SnO$_2$:F, SnO$_2$:Sb, ZnO:Al, In$_2$O$_3$:Sn (ITO) because of its excellent electrical and optical properties. However, several problems have been encountered while using ITO, particularly, the high cost, scarcity of In, and also the tendency to fracture on flexible substrates. For the last two decades, efforts have been taken to develop alternative materials to replace ITO. These efforts emerged with the development of a variety of ternary and even more complex TCO materials, such as Zn$_2$SnO$_4$, Cd$_2$SnO$_4$, In$_4$Sn$_3$O$_{12}$, and GaInO$_3$, based on combinations of binary compounds like ZnO, CdO, In$_2$O$_3$, and SnO$_2$, producing multicomponent oxides beyond the ternary compounds. But the applications of these multicomponent oxides are rarely reported. The use of ternary and multicomponent oxides makes possible to design TCO films suitable for specialized applications due to the fact that their electrical, optical, chemical and physical properties can be controlled or modified by altering their chemical composition. Although they have low resistivity, the thin films containing Cd, such as In-doped CdO, Cd$_2$SnO$_4$, and CdSnO$_3$, are of lower practical use due to their toxicity and material cost (Minami 2000). Some of the important TCO materials and their properties are listed in Table 1.1.
Recently, there are efforts to improve and develop new TCO compounds by doping zinc oxide (ZnO), tin oxide (SnO$_2$) and zinc stannate (ZTO) using a variety of deposition techniques, e.g., spray pyrolysis, Chemical vapour deposition (CVD), sputtering, pulsed laser deposition (PLD) and chemical spray pyrolysis methods, as the TCO characteristics are mainly depend on its deposition methods.

Table 1.1 Some the important TCO materials and their properties
(Dekker Thesis 2007)

<table>
<thead>
<tr>
<th>TCO</th>
<th>Deposition method</th>
<th>$\rho$ (Ωcm)</th>
<th>T %</th>
<th>$E_g$ (eV)</th>
<th>n ($cm^{-3}$)</th>
<th>$\mu$ (cm$^2$/s.V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>Sputtering</td>
<td>6.1x10$^{-3}$</td>
<td>95</td>
<td>4.13</td>
<td>1.3x10$^{20}$</td>
<td>7.7</td>
</tr>
<tr>
<td>SnO$_2$: Sb</td>
<td>Spray</td>
<td>10$^{-3}$</td>
<td>85</td>
<td>3.75</td>
<td>7.0x10$^{20}$</td>
<td>10</td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$</td>
<td>Sputtering</td>
<td>5x10$^{-4}$</td>
<td>93</td>
<td>2.7</td>
<td>5.0x10$^{20}$</td>
<td>22</td>
</tr>
<tr>
<td>CdIn$_2$O$_4$</td>
<td>Sputtering</td>
<td>2.7x10$^{-4}$</td>
<td>90</td>
<td>3.24</td>
<td>4.0x10$^{20}$</td>
<td>57</td>
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<tr>
<td>In$_4$Sn$<em>3$O$</em>{12}$</td>
<td>Sputtering</td>
<td>3.5x10$^{-4}$</td>
<td>&gt;80</td>
<td>3.5</td>
<td>7.0x10$^{20}$</td>
<td>11.5</td>
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<tr>
<td>In$_2$O$_3$</td>
<td>PLD</td>
<td>2x10$^{-4}$</td>
<td>86</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>7.0x10$^{20}$</td>
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<tr>
<td>ITO</td>
<td>CVD</td>
<td>1.7x10$^{-4}$</td>
<td>90</td>
<td>3.9</td>
<td>8.8x10$^{20}$</td>
<td>43</td>
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<tr>
<td>ITO</td>
<td>Sputtering</td>
<td>2.4x10$^{-4}$</td>
<td>95</td>
<td>4.0</td>
<td>1x10$^{20}$</td>
<td>12</td>
</tr>
<tr>
<td>ITO</td>
<td>PLD</td>
<td>8.5x10$^{-5}$</td>
<td>85</td>
<td>&gt;80</td>
<td>1.4x10$^{21}$</td>
<td>53.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>Reactive ev</td>
<td>10$^{-3}$</td>
<td>88</td>
<td>3.3</td>
<td>1x10$^{20}$</td>
<td>10</td>
</tr>
<tr>
<td>ZnO</td>
<td>Sputtering</td>
<td>2x10$^{-3}$</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>1.2x10$^{20}$</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>Sputtering</td>
<td>10$^{-2}$</td>
<td>90</td>
<td>3.52</td>
<td>4.7x10$^{20}$</td>
<td>1.47</td>
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<td>&gt;85</td>
<td>3.59</td>
<td>10x10$^{20}$</td>
<td>10</td>
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<tr>
<td>ZnO:In</td>
<td>Sputtering</td>
<td>2x10$^{-2}$</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>7x10$^{19}$</td>
<td>1.9</td>
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<tr>
<td>ZnSnO$_3$</td>
<td>Sputtering</td>
<td>4x10$^{-3}$</td>
<td>&gt;80</td>
<td>&gt;80</td>
<td>1x10$^{20}$</td>
<td>10</td>
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</tbody>
</table>
1.2 THIN FILM DEPOSITION METHODS

It is well known that the thin film properties are strongly dependent on several parameters like method of deposition, substrate materials, substrate temperature, rate of deposition, background pressure etc. Specific applications in modern technology demand film properties such as high optical reflection/transmission, hardness, adhesion, non-porosity, high mobility of charge carriers, chemical inertness towards corrosive environments, and stability with respect to temperature. The need for the new and improved optical and electronic devices stimulated the study of thin solid films of single elements, binary and ternary systems, with controlled composition and specific properties.

The thin film deposition methods can be broadly classified into two categories: (i) Physical deposition techniques and (ii) Chemical deposition techniques. In physical deposition techniques, atoms or molecules of the source material are vaporized by physical processes such as thermal evaporation or by bombardment from an energetic beam of electrons, photons or ions. Whereas, in chemical techniques, a chemical reaction of one or more vapour species incident on a substrate surface produces a film of desired composition. Physical deposition is typically carried out in a vacuum environment to avoid contamination of the film by the ambient atmosphere, while chemical deposition often utilizes an inert carrier gas, and may even be carried out at atmospheric pressure. Details on thin film deposition techniques are well explained (Ohring 1992, Campbell 1996). The following steps are involved in the thin film deposition process and are common to both PVD and CVD techniques.
1. Generation of atoms or molecules from a source, which may be in solid, liquid or vapour phase. This is accomplished by supplying energy to the source in the form of heat or incident energetic particles or from chemical reaction.

2. The important part of the deposition process is the transport of constituent atoms or molecules to the substrate that determines the uniformity of the films.

3. Deposition of atoms or molecules on the substrate. The condition of the substrate surface is the key issue in this phase. If the substrate surface is contaminated with a fraction of monolayer of impurity atoms, the surface mobility of the arriving film atoms may be reduced to an extent.

4. Post growth treatment. In this process, a prolonged annealing of the film at elevated temperatures may yield a film with superior properties as a result of crystal grain growth in the film.

5. Post growth analysis. Modern film analytical methods are essential to improve the deposition process parameters that enable to achieve better film quality.

The different thin film deposition methods can be classified according to the scheme shown in Figure 1.1.
Figure 1.1 Classification of different thin film deposition methods

The most common techniques that have been used to grow TCO films include Chemical Vapor Deposition (CVD), Spray Pyrolysis, Reactive Evaporation, Magnetron Sputtering, Plasma Assisted Reactive Evaporation, Ion Beam Sputtering, Ion Plating and Filtered Vacuum Arc Deposition. Each of these techniques has its own advantages and disadvantages. However, the use of these coatings for commercial applications will be feasible only if they can be produced in large area at low cost. Even though different methods are proposed from time to time for the production of TCO in industrial scale, spray pyrolysis and sputtering are the most widely used techniques due to their simplicity, reproducible results and capable to coat on large area substrates. In the following sections some of the important thin film deposition methods, used for TCO deposition are discussed in detail.
1.2.1 Physical Vapour Deposition (PVD)

Physical vapour deposition (PVD) is a process for transferring atoms or molecules from a source to a substrate that relies on physical methods to produce the vapour species. Some of the physical deposition methods are discussed in the following sections.

1.2.1.1 Vacuum Evaporation

Vacuum evaporation (including sublimation) is a physical vapour deposition (PVD) process, where the material is thermally vaporized from a source and deposited on the substrate without collision with the gas molecules present in the space between the source and substrate. Vacuum evaporation experiments are normally conducted in a gas pressure range of $10^{-5}$ to $10^{-9}$ Torr, which determines the level of contamination in the deposited film (Seshan 2002).

Deposition of thin films by vacuum evaporation is a very simple, convenient, and widely used technique. In this method, evaporation of the material takes place in vacuum environment. Sufficient amount of heat is supplied to the evaporant to attain the desired vapour pressure, and the evaporated material is allowed to condense on the substrate maintained at a required temperature (Hartnagel et al 1995). Vacuum evaporation is possible for a wide range of materials, particularly for metals except the refractory metals with low vapour pressures. By heating the materials, the vapour pressure of the charge is raised to a level at which the evaporation and sublimation occurs. The important process parameters are the substrate material, source and substrate temperatures, source-substrate distance, background gas composition and pressure. Using this method, evaporants with the extraordinary range of chemical reactivity and vapour pressures can be deposited. This method leads to a large diversity in source designs including resistance-heated filaments, electron beams, crucibles heated by conduction, radiation, or rf-induction, arcs, exploding wires, and lasers.
1.2.1.2 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is an evaporation technique in which a focused laser pulse is directed onto the target of material in a vacuum chamber. The laser pulse locally heats and vaporizes the target surface, producing an ejected plasma or plume of atoms, ions, and molecules. The plume of material is deposited onto an adjacent substrate to produce a crystalline film. The plasma contains both energetic molecular clusters and macroparticles. The emission of macroparticles is a serious drawback that affects the film quality. The crossed laser induced evaporation plumes are used to discriminate macroparticles ejected from the target. The energy of the incident laser pulse determines the energy of the evaporated material. The majority of the energy spectrum of plasma particles consists of low-energy component (1-100 eV) and a fraction of high-energy component (up to a few keV) (Gorbunov et al 1996) can also be observed in the plasma. The energetic impact of the evaporated material determines the growth rate and also the surface roughness of the films. Therefore, a choice of proper laser pulse energy is required to achieve quality films. Each laser pulse evaporates a well-defined amount of material and hence it is very easy to maintain the growth rate precisely. Using this method, multicomponent alloy films can also be uniformly deposited by varying the number of laser pulses (Vossen and Kern 1978, Chopra 1969).

1.2.1.3 Sputtering Process

Sputter deposition is a widely used technique based on glow discharge for the deposition of thin films. The schematic of the Sputter process is shown in Figure 1.2, sputtering occurs whenever a high energetic particle strikes a surface to dislodge an atom from the surface (Seshan 2002). The ejected (or) sputtered atoms condense on a substrate and form a thin film. When the ejection is due to positive ion bombardment, it is referred to as cathode sputtering. In addition to the ejection of target material, other
processes that are associated with the bombardment of a target by highly energetic ions include:

a) Secondary electron ejection.

b) Ion reflection at the target surface.

c) Ion implantation, with the ion being permanently buried into the target.

d) Radiation damage in the target with structural rearrangement varying from simple vacancies and interstitial to more gross lattice defects, and

e) Emission of X-rays and photons.

Figure 1.2 Process generated by the impact of highly energetic particle on the target surface (Chapman 1980)
The sputter process is the widely practiced physical vapour deposition method for industrial applications of large area coatings. Both reactive and non-reactive forms of DC and RF sputtering and, recently, magnetron and ion beam have also been used for special purposes.

1.2.1.3.1 Reactive sputtering

Reactive sputtering is the widely used process for producing coatings of compounds. Most metal atoms are sputtered from a metallic target, and sufficient reactive gas, like Ar-O₂ or Ar-N₂ gas mixture is added to the chamber to form the desired component on the substrate. In addition, when compounds with multiple elements are to be deposited, the composition of the deposited film often differs from the composition of the target due to the fact that the compounds decompose during the sputtering, though the situation varies according to the chemical bond strength between the components. The concentration of the volatile components, such as oxygen and nitrogen, is reduced in the deposited film. Simultaneously, during deposition the target surface composition also changes. To maintain the stoichiometry, reactive gas of the volatile components is added into the plasma. The reactive sputter process in general possess higher growth rate typically in the range of 10 to 30 nm/min when an Ar-O₂ mixture is used and is about 5 nm/min for pure O₂ atmosphere.

1.2.1.3.2 Sputtering from oxide targets

If the sputter cathode is an oxide or an insulator material, the DC sputtering is not possible due to the building up of positive (Ar⁺) surface charges. However, a high frequency alternating potential may be used to neutralize the insulator surface periodically with plasma electrons, which have much higher mobility than the positive ions. It is an indispensable technique for deposition of thin films of semiconductor and insulators. The DC and RF diodes are similar in basic configuration, but differ in the power supply
frequency. Sputtering at lower pressures ($10^3$ torr) is possible if the RF configuration is used due to their higher plasma density.

1.2.2 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is a surface reaction on a solid surface, where one or more gaseous reacting species are involved. When the vapourized species is incident on a substrate, it produces a film of desired composition. CVD process entirely differs from PVD process, which does not require high vacuum (or) unusual levels of electric power. This technique is versatile for synthesizing both simple and complex compounds. The main control parameters are gas flow, gas composition, substrate temperature and the geometry of deposition apparatus. The deposition rate depends mainly on both the gas flow rate and substrate temperature. The typical growth rates ranges from 30 to 100 nm/min. In CVD process, the geometry of the deposition system is more important for large-scale applications (Blocher 1981, Kalbskopf 1981). Secondly, the chemical reaction is an important part of this technique and requires lot of understanding about the reaction mechanism. Various types of chemical reactions are utilized in CVD (Figure 1.3) for thin film deposition.

![Figure 1.3 A schematic drawing of the CVD technique (Hartnagel et al 1995)](image-url)
In one type of reaction, a vapour precursor that contains the material to be deposited is decomposed by reduction, e.g. using hydrogen at an elevated temperature. Decomposition is accomplished by thermal activation. Alternatively, plasma activation may be used to reduce or decompose the precursor at a lower temperature than the thermal activation. The different steps involved in a CVD process.

(i) Convective and diffusive transport of reactants from the gas inlets to the reaction zone.

(ii) Chemical reaction in the gas phase to produce the product and by products. Transport of the initial reactants and their products to the substrate surface.

(iii) Adsorption (chemical and physical) and diffusion of these species on the substrate surface.

(iv) Heterogeneous reactions catalyzed by the surface leading to film.

(v) Desorption of volatile by-products of the surface leading to film.

(vi) Convective and diffusive transport of reaction by products away from the reaction zone.

A variety of modified CVD processes exists namely metalorganic CVD (MOCVD) when a plasma is used to induce or enhance decomposition and reaction; low pressure CVD (LPCVD) when the pressure is less than ambient; and low pressure plasma enhanced CVD (PECVD) when the pressure is low enough that ions can be accelerated to appreciable energies from the plasma.
1.2.3 Epitaxial Growth of Thin Films

Epitaxy describes the extended single-crystal growth of a film on a crystalline substrate. Depending on the growth conditions and the substrate quality, the epitaxial films are extremely perfect in crystalline quality and defect free. Epitaxial growth methods are generally used for semiconductor device fabrication, as they can be produced with greater purity than bulk material.

The two types of epitaxial growth are: (i) homoepitaxy, in which the film is grown on a crystalline substrate of the same material, and (ii) heteroepitaxy, in which the film and substrate are different. Homoepitaxy has the advantage that the substrate and the film have the same lattice constant, provided the substrate surface is perfectly clean. It can also serve as a template to facilitate the growth of film as a single crystal. Despite the mismatch between the film and substrate in the heteroepitaxy, a clean and oriented substrate provides a template for deposited atoms even though this may introduce strain in the film. The different types of epitaxy are described in the following sections.

1.2.3.1 Molecular-beam epitaxy

Molecular-beam epitaxy (MBE) is the simplest as well as well understood epitaxial process. MBE is a physical deposition process, in which the deposition occurs by the interaction of beams of atoms / molecules with a clean substrate surface maintained in ultra high vacuum (UHV). The beams are generated by the thermal evaporation of the constituent elements contained in refractory crucibles and is arranged such that the beams can be conveniently turned on and off. This setup allows the growth of a specific material to be initiated or terminated extremely rapidly. The UHV
environment prevents contamination of the surface, when growth is not taking place and also allows a variety of in-build analytical tools for characterization in the same vacuum chamber for in-situ surface analysis, beam-flux measurements and film-structure studies (Cho 1994).

1.2.3.2 **Vapour-phase epitaxy**

Vapour-phase epitaxy (VPE) is a chemical deposition process. VPE has evolved from the CVD of Si on Si substrates. VPE has been used from the early days for Si device processing to prepare thin layers of silicon with properties superior to those of the bulk substrate material. The deposition is typically carried out at pressures ranging from a few Torr to atmospheric pressure (Houng 1992). This has the advantage of simplifying the apparatus and increasing the growth rate. However, the complex fluid flow of reactant gases at these pressures is difficult to model.

1.2.3.3 **Liquid-phase epitaxy**

Liquid-phase epitaxy (LPE) involves the growth of an epitaxial film on a substrate that is placed in contact with a saturated solution of the film material. In some cases, the solvent may be one of the film constituents; e.g. GaAs films grown from a saturated solution of as in molten Gallium. When the solution is cooled slightly, it becomes supersaturated and growth occurs on the substrate (Funitoshi et al 1997).

1.2.3.4 **Solid-phase epitaxy**

Solid-phase epitaxy (SPE) describes the re-growth of a polycrystalline amorphous film on a crystalline substrate at an elevated temperature. The most common example of SPE is the re-growth of a semiconductor over an amorphized surface of the same semiconductor.
material. Generally, the amorphization of the semiconductor surface is achieved by ion implantation. Annealing causes re-growth of the films from the unimplanted region.

1.2.4 Solution Methods of Deposition

The solution methods of coatings are inexpensive and relatively easy method, which can be easily scaled up from small scale laboratory experiments to large area industrial applications. Any hydrolysable compounds such as halides, nitrate, nitrides and preferably metallo-organic alkoxide precursors are necessary for this kind of deposition. The three different types of thin film deposition methods are: spin coating, dip coating and spray pyrolysis. Details of these methods are given in the following sections.

1.2.4.1 Spin coating

Spin coating is a simple and widely used technique for depositing thin films on wafer surfaces. In this method, an excess amount of a solution is placed on a substrate, which is then rotated at high speed around an axis perpendicular to the coating area. Due to the centrifugal force, the liquid evenly spreads on the substrate surface and forms thin films. The process involves simple fluid flow and evaporation behaviors, which normally allow the formation of uniform coatings (Birnie and Manley 1997). The spin coating process can be divided into four stages as shown in Figure 1.4. The deposition, spin up, and spin off stages occur sequentially, while the evaporation occurs throughout the process.
Figure 1.4 The four stages of the Spin coating process

The deposition process involves the dispense of an excessive amount of fluid onto a stationary or slowly spinning substrate. The fluid is deposited through a nozzle at the center of the substrate or over some programmed path. An excessive amount of fluid is used to prevent coating discontinuities.

In the spin up stage, the substrate is accelerated to the final spin speed. As rotational forces are transferred upward through the fluid, a wave front that forms and flows to the substrate edge by centrifugal force forms a fairly uniform layer. In the spin off stage, the excess solvent is flung off the substrate surface as it rotates at speeds between 2000 and 8000 RPMs. The fluid is being thinned primarily by centrifugal forces until enough solvent has been removed to increase the viscosity to a level, where flow ceases. The spin off stage takes place for approximately 10 seconds after spin up.

In this method, evaporation becomes a crucial parameter that determines the film thinning and quality of the final deposits. Evaporation is the complex process by which a portion of the excess solvent is absorbed into the atmosphere. If significant evaporation occurs prematurely, a solid skin
forms on the fluid surface, which impedes the evaporation of solvent trapped under this skin and causes coating defects when subjected to the centrifugal forces of the spinning substrate.

Films of various of film thickness can be deposited by spin coating, due to the fact that film thickness is roughly inversely proportional to the square root of spin speed. As coating thicknesses increases, it becomes difficult to find a solvent / solute mixture, which would not dry before reaching the substrate edge. For this reason, thick films are occasionally formed by spinning on multiple thinner and more reliable coatings.

1.2.4.2 Dip coating

The dip coating method consists of inserting the substrate into a solution containing hydrolysable metal compounds and pulling it out at a constant speed under controlled temperature and atmospheric conditions. In this atmosphere, hydrolysis and condensation processes take place. The coating thickness mainly depends on the withdrawal speed, the solid content and the viscosity of the liquid. In this method, the films are hardened by high temperature treatments. The rate of heating needs to be controlled to avoid cracking of the films (Brinker et al 1991). This method has been commercially used to deposit coatings on both side of a glass substrate on large area coatings (about 10 to 12 m²).

1.2.4.3 Spray pyrolysis

The spray pyrolysis technique involves spraying of a solution (usually aqueous, containing soluble salts of the constituent atoms of the desired compound) onto a substrate maintained at elevated temperatures. The sprayed droplet reacts with the hot substrate surface and undergoes a pyrolytic (endothermic) decomposition and forms single crystallite or cluster of crystallites of the compounds. The other volatile by-products and the excess solvent escape in the vapour phase. The substrate provides the thermal energy
for the thermal decomposition and the subsequent recombination of the constituent species followed by sintering and recrystallisation of the clusters of crystallites to form a coherent film (Shanthi 1999).

Spray pyrolysis has been used to deposit thin films and prepare compound powder material. Even multilayered films can easily be prepared using this versatile technique. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective processing method. It is an extremely easy method for preparing films of any composition. The working principles of spray technique are: (i) the solution either from a reservoir or in vapour phase is carried using some carrier gas like argon, nitrogen or compressed air and (ii) the solution or the vapour is then sprayed by the atomizer onto the hot substrate. The quality of these films depends on parameters such as the spray rate, the substrate temperature and the ratio of various constituents in the solutions. Thin-film deposition using spray pyrolysis can be divided into three main steps: (i) atomization of the precursor solution, (ii) transportation of the resultant aerosol, and (iii) decomposition of the precursor on the substrate (Perednis and Gauckler 2005).

In spray pyrolysis, the important factor is to understand the basic atomization process of the atomization device used. Depending on the application of the films, one can choose the atomizers like air blast, ultrasonic, and electrostatic atomizers, etc.

During aerosol transport, it is important that as many droplets as possible are transported to the substrate without forming powder or salt particles. Sears and Michael (1988) investigated the mechanism of SnO₂ film growth. They studied the influence of forces, which determine both the trajectory of the droplets and evaporation and proposed a film growth model considering the gravitational, electric, thermophoretic and Stokes forces. Sears and Michael (1988), Yu and Liao (1998) developed a model to describe
the evaporation of solution droplets before forming a solid crust by considering the mass transfer, momentum, temperature outside and around the droplet as well as effects of precursor precipitation. The main drawback of this model is the interactions between droplets were ignored. Yu and Liao (1998), Lenggoro et al (2000) investigated the powder production by spray pyrolysis using a temperature-graded laminar flow aerosol reactor and calculated the evaporation rate and the change of the precursor concentration within the droplets, which showed good agreement between the simulated as well as experimental results (Lenggoro et al 2000).

During decomposition of the precursor, various processes occur simultaneously (evaporation of residual solvent, spreading of the droplet, and salt decomposition), when a droplet hits the surface of the substrate. Several models have been developed to explain the decomposition mechanism of a precursor. The chemical vapour deposition based process that gives high quality films by spray pyrolysis is claimed as one of the best suited techniques. Figure 1.5 shows the decomposition of the precursor when increasing the substrate temperature (Perednis and Gauckler 2005).

![Diagram](image)

**Figure 1.5** Description of the deposition processes initiated with increasing substrate temperature
In general, among the solution based deposition techniques, spray pyrolysis is a versatile and effective technique to deposit metal oxide films, which could be scaled up from small scale laboratory experiments to large scale industrial applications with less investments. The most important parameter is the substrate temperature and if the substrate temperature is higher, then the films possess more roughness as well as porous. When the temperature is too low, cracks would be observed in the films. The substrate temperature also influences the crystallinity, texture, and other physical properties of the deposited films. Another important spray parameter is the viscosity of the precursor solution that affects the morphology and properties of the deposited films. The film morphology and properties can also be changed by using various additives in the precursor solution (Perednis and Gauckler 2005) with such advantages of this spray pyrolysis technique, we have selected this method for the preparation of thin film samples. More details on the experimental setup and the steps involved in the process optimization are discussed in Chapter 2.

1.3 SCOPE OF THE PRESENT WORK

From the materials science point of view to be able to engineer and optimize transparent conducting oxide (TCO) coatings for modern applications, it is essential to study the material characteristics, in particular the structural, optical and electrical properties, which are essential for the further developments of TCO coatings. In this investigation, we have studied the preparation conditions and properties of Al and Cd doped ZnO, Zn doped SnO$_2$ and Zn$_2$SnO$_4$ films. These films were prepared by chemical spray pyrolysis method with a substrate temperature of 400°C. The effect of the different process parameters on the structure, lattice parameters, thickness, surface roughness, optical and sheet resistance properties has been investigated. In addition, the effect of post growth annealing on the above said properties has also been investigated for Zn$_2$SnO$_4$ films. Energy dispersive
X-ray diffraction (EDX) was employed to determine the chemical composition of the films. The structure of the films has been studied by X-ray diffraction (XRD) method. For the precise determination of optical constants, optical spectroscopy and ellipsometric techniques have been used. The sheet resistance of the films has been measured by four probe method in the van der Pauw configuration. A combination of the results obtained from these measurements is expected to provide an in-depth knowledge on the film properties. This information is important for the understanding of the chemical spray pyrolysis process and for the further development of the performance of the TCOs.

The objectives of the present research are:

- Deposition of Al and Cd doped ZnO, Zn doped SnO$_2$ and Zn$_2$SnO$_4$ thin films by chemical spray pyrolysis method.

- Optimization of deposition conditions for films with high optical transmission, lowest electrical resistivity with good reproducibility.

- Comparison of characteristics of Zn$_2$SnO$_4$ thin films with Al and Cd doped ZnO and Zn doped SnO$_2$ thin films deposited by chemical spray pyrolysis technique.

- It was expected that by optimizing the deposition parameters of Al and Cd doped ZnO, Zn doped SnO$_2$, and Zn$_2$SnO$_4$ thin films, some improvement in the film properties might be achieved. The research for an improved TCO involves the study of structural, electrical and optical properties as a function of the deposition parameters and doping element concentration in the films. These films have the potential to overcome current TCO problems and also would help the scientific community to identify non indium based TCO coatings for modern applications.