Chapter 2

Processing of Al-doped-based TCOs

2.1 Introduction

ZnO-based TCOs have been processed through a wide range of deposition approaches; sputtering [99–103], PLD [12,104,105], ALD [106–108], CVD[89,109], solution spray [32,33,67,110], dip coating [28,111–113], spin coating [114–117], ink jet printing [118], chemical bath deposition [30,119], being some of the most prominent method of deposition. The deposition techniques can be classified into two broad categories: Vapor-based and solution-based techniques. Ease in processing and lower cost are the main focus of the technologies which are to be implemented for large-scale manufacturing. In addition, for large-scale production, the process should be repeatable, stable, and most importantly, cost-effective. In this chapter, a brief survey of important deposition techniques, their advantages, issue, and some important results are discussed.

2.2 Vapor-based deposition techniques

Vapor-based deposition techniques are attractive due to their controlled stoichiometry and potential for achieving higher uniformity on the lab scale. However, the installation and maintenance costs of these techniques are quite high.

2.2.1 Magnetron sputtering

In sputtering, the material to be deposited is made into a dense, compact target placed in a vacuum chamber filled with Ar-gas, while the substrate is placed at a

distance facing the target. A high voltage is applied across the target (cathode) and the substrate (anode). Under the influence of high voltage, the Ar gas is ionized to Ar^+, a glow discharge is established, and Ar^+ bombards the target. As a result, the target atoms are ejected as atomic vapor and get deposited over the substrate. A schematic of the RF Magnetron equipment is shown in **Figure 2.1**. In the case of insulator targets, the glow discharge will not sustain under the DC field due to the immediate formation of a positively charged surface on the target. Therefore, a radio frequency (RF) power supply is utilized for insulator targets. Since the deposition takes place inside the closed chamber under a controlled atmosphere, the purity of the films is not compromised. The magnetron sputtering technique has a huge advantage over the solution-processed film in terms of uniformity, composition, and homogeneity across the film thickness.

Aluminum-doped ZnO (AZO) was first deposited by Minami et al.[120] in 1984 on the Corning glass 7059 substrates using RF magnetron sputtering technique having RF power of 50 W and applied dc magnetic field of 50 G. Effect of varying concentration, chamber pressure, and temperature variation on the resistivity of the film was studied. The minimum resistivity of ~2 x 10^{-4} **Ω**-cm was obtained in the 1 wt% Al_2O_3 doped films deposited at the chamber pressure of 0.008 Torr. The charge concentration and mobility were ~5 x 10^{20} cm^{-3}, and ~45 cm^2/Vs, respectively, while the film was more than ~80% transparent in the visible range. It was found that the resistance of sputter-deposited Al-doped ZnO film remained unchanged on annealing in an inert and nitrogen atmosphere up to 400 °C. On annealing in oxygen at a higher temperature, charge concentration and mobility were decreased due to a

decrease in Zn_i and $V_O^{\cdot}$ defect concentration and oxygen annihilation. On the other hand, on annealing in a hydrogen atmosphere at temperatures > 400°C, film resistivity decreased [29]. Hydrogen, at temperatures around 400 °C, forms shallow donor levels and passivates oxygen vacancies. The deposition rate was found to increase from 6 to 32 nm/min when the RF power was increased from 25 W to 80 W, while no effect of RF power on the resistivity was observed [121]. The AZO, with doping levels varying from 0.1 to 10 wt.%, showed that the resistivity is generally higher at lower Al doping levels. On increasing the Al-doping levels, the carrier concentration increase; however, if the Al is greater than the solubility limit, the formation of Al_2O_3 and segregation to grain boundaries was observed. An increase in carrier concentration and formation of Al_2O_3 reduces the mobility, which results in increasing the resistivity of the film. [67,122,123]. An increase in the dopant concentration results in increased optical bandgap due to Burstein Moss Effect [124,125]. An increase in the bandgap from 3.28 eV for undoped to 3.38 eV for 5 wt% Al-doped ZnO was observed [126,127]. Tansley et al.[128] deposited ZnO film by reactive RF Sputtering in the presence of oxygen to obtain resistivity of the film was high ~10^3 Ω-cm. Minami et al.[129] deposited AZO film by RF magnetron sputtering and showed the effect of external magnetic field on the arrangement of target and substrate. Lyubchyk et al.[15,79] deposited AZO film by RF Magnetron Sputtering and AZO: H film by reactive magnetron sputtering in the presence of hydrogen and thoroughly investigated the effect of post-thermal annealing in ambient pressure, vacuum, forming gas, H_2 and Ar atmospheres, and plasmas. It was found that the resistivity decreased (up to $\rho \approx 3 \times 10^{-4}$ Ω-cm) in the case of AZO: H film after annealing in hydrogen, at 150-250°C. At the same time,

the average optical transmittance was 88% in the visible region. Jin et al. [130] reported 2 at% Al-doped ZnO film with resistivity as low as ~5 x 10^{-4} Ω-cm for the sputtered film thickness of 300 nm, while the charge carrier concentration was 4.5 x 10^{20} cm^{-3}. Bandgap was observed to increase from 3.40 eV in undoped ZnO to 3.90 eV in 2 at% Al-doped ZnO for 300 nm film, having optical transparency of ~85% on Corning glass 7059 substrate. Igasaki et al.[131] deposited AZO film on Tenpax glass substrate at 100°C, using reactive RF sputtering in the presence of 5% to 10% oxygen, it was observed that resistivity of the film was reduced by six-fold when RF power was varied from ~50W to ~200W. Kim et al. [132] deposited 2 wt% Al-doped ZnO film on glass substrate at 400 °C in oxygen partial pressure of 5 mTorr to achieve an electrical resistivity of 8.7 x 10^{-4} Ω-cm and close to 86% optical transmittance in the visible range. A list of published electrical and optical properties and the parameters of deposition by magnetron sputtering is listed in **Table 2.1**.

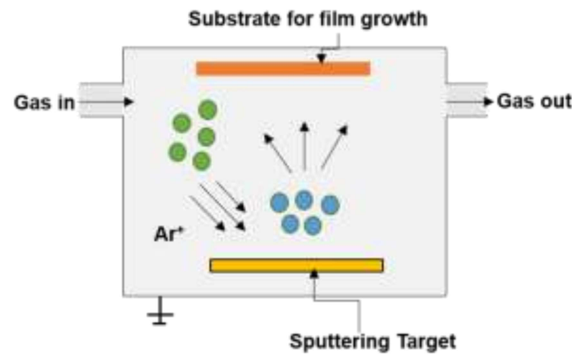

Figure 2.1 Schematic diagram of RF Magnetron Sputtering

Table 2.1 Electrical and optical properties achieved by various researchers on AZO films deposited using RF/DC magnetron sputtering technique

Al/Al_2O_3 Doped% / Thickness (nm)	Temp. (°C)	ρ(Ωcm) (x 10^{-4})	n(cm^{-3}) (x 10^{20})	μ (cm^2/Vs)	T (%) @550 nm	Ref.
-/90-200	-	2.5	5	6-7	80-90	[99]
2 wt%/400	30	10	6.26	9.98	85-95	[100]
0.7-8.7 at% / 300±50	200-500	23	6	46	-	[101]
2 wt%/ 200	RT-250	56	5.2	2.2	80-85	[102]
2 wt% /300	600	36	3.7	4.6	80-85	[103]
0-4 at% /500	RT-80	4	8	22	80	[133]
2 at% /200-700	RT-75	3.5	8	22	70-80	[134]
2 wt%/ 176-485	100	58.4	8.7	1.3	80-90	[135]
2 wt% /680-780	30-250	29.4	10.7	19.8	75-80	[136]
2 wt% /200	300	18	5.1	6.8	80	[137]
0.25-2wt% /50-800	250	2.5	6.8	36	-	[138]
2 wt%/300±30	600	12	3.2	17	-	[139]
1.3 wt%/-	RT-250	3	8	23.5	60-80	[121]
1 wt% /-	300-600	1.35	6.9	67	-	[140]
2 wt% /115-348	350	9.13	4.1	16.3	85-90	[141]
2 wt% /500	RT	5.6	10	-	70-80	[142]

ρ = Resistivity, n = charge carrier concentration, μ = mobility, T=Transparency

2.2.2 Pulse Laser Deposition

In PLD, the material to be deposited is made as a dense target, while the high-power ruby, Nd: YAG laser is used to evaporate the target material. The target is placed close to the substrate in a vacuum chamber. When the high-power laser pulse strikes the target, a plume of vapors emerges from the target and gets deposited over the relatively cool substrate surface to create a thin film. Multi-element stoichiometry is easier to obtain with this technique. The schematic of the PLD diagram is shown in **Figure 2.2**. PLD was initially used to deposit films of the semiconductor compounds such as CdTe, PbTe, and ZnTe [143]. Agura et al. [14] deposited AZO film with varying laser energy (15-40 mJ), energy density (0.75-2 J/cm^2), and

substrate temperature (165-300°C). The minimum resistivity was obtained at the substrate temperature of 200°C [144]. The resistivity of the deposited film increased when the laser energy was raised from 0.75 mJ to 2.25 mJ, while charge concentration and mobility both decreased. The effect of Al doping % on the optoelectronic properties was investigated for films deposited using PLD [16,145,146]. On increasing wt.% of Al up to 0.8, resistivity reduced; however, for Al doping concentration >0.8 wt% the resistivity again increased, while the charge concentration almost remained constant. At 0.8 wt.% Al doping, the electrical resistivity was 3.7×10^{-4} Ω-cm. The application of a magnetic field during PLD was found to promote (002) orientation in AZO films [16]. Yang et al. [144] utilized a magnetic field during PLD to enhance the performance. The AZO film was deposited on a Corning glass 7059 substrate using a Nd: YAG laser (λ=355 nm) of 2 Jcm^{-2} power (10 Hz), while the post-deposition annealing was carried out in the temperature range 100-400°C at an oxygen pressure of 2 Pa for 30 min. Agura et al. [14,147] deposited 1.8 wt% Al-doped ZnO film at 230 °C using an ArF excimer laser (λ=193 nm, power density = 0.75 J/cm^2). By applying a magnetic field perpendicular to the plume, a highly transparent (91%) film with minimum resistivity of 8.54×10^{-5} Ω-cm was achieved, while the highest mobility and carrier concentration were 47.6 cm^2/V-s, and 1.54×10^{21} cm^{-3}, respectively. The deposition rate is higher in the case of PLD as compared to other vacuum-based processing routes.

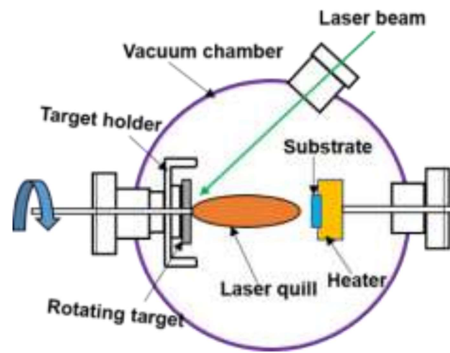

Figure 2.2 Schematic diagram of Pulse Laser Deposition

A list of published articles on pulse laser deposition of AZO film with obtained electrical and optical properties is summarised in **Table 2.2**.

Table 2.2 Doping percentage, thickness, substrate/annealing temperature, resistivity, charge concentration, mobility, and %T values reported in various scientific studies on AZO films deposited using PLD technique

Al/Al_2O_3 Doped% /Thickness (nm)	Temp. (°C)	ρ(Ωcm) (x 10^{-4})	n (cm^{-3}) (x10^{20})	μ (cm^2/Vs)	T (%) @550nm	Ref.
1-2 wt% / 280	230	8.54	15	24	90	[14]
3 wt%/ 150-200	170-500	4.7	19	7.2	90-95	[144]
0-4 wt%/300	200	4.3	9	18	80-90	[16]
3 wt%/200	30- 680	2.2	8.8	32	85-95	[148]
0-5 at%/ 300-350	750	30	0.4	49	80	[149]
0.5-5 wt%/ 280	200	2.5	5	49	85	[150]
2-5 at% /250	400	6	8	13	75-80	[151]
2 wt% /200	30-400	1.4	20	-	85-90	[105]
0.5-4 wt%/-	300	-	20	26	85-90	[152]
0.75-7wt%/150-200	30-300	1.43	14	32	90	[153]
4 at% /450	300-600	7.4	1.89	43.5	-	[154]

ρ = Resistivity, n = charge carrier concentration, μ = mobility, T=Transparency

2.2.3 Chemical vapor deposition(CVD)

Chemical vapor deposition is a process in which the reactive precursor vapors, along with suitable carrier gases, are fed into a closed heating zone, where the precursor decomposes or reacts with another gas/precursor over a preheated substrate resulting in the formation of film over the substrate. A schematic diagram of CVD is shown in **Figure 2.3**. Hu et al. [155] deposited AZO films on soda lime glass substrates and studied the role of different processing parameters during CVD. It was observed that the growth rate increases with the hot zone temperature, while a maximum growth rate of 24 Å/s was reported at 440 °C when the reactor nozzle-substrate distance was 9.5 cm. An increase in growth rate was also observed in increasing the dopant concentration. A minimum resistivity of 3.0 x 10^{-4} Ω-cm along with mobility 35.5 cm^2/Vs were obtained for 0.3 at% Al, while the charge concentration of the film was in the order of 10^{20} cm^{-3}. As the film thickness increased (thickness above 700 nm), grain boundary scattering decreased with the thickness and the role of ionized impurity came into play. Natsume et al. [156] deposited pure ZnO film on soda lime glass, while Ar and O_2 gases flow rates were 500 and 10 ml/min, respectively. The films were annealed in the temperature range of 500 to 600 °C, to obtain a minimum resistivity of 2.44 **Ω**-cm on annealing at 550 °C. Kim et al. [157] showed that the roughness and texture of films could be tailored in CVD to generate trigonal prism-like morphology for increased light-trapping ability. Volintiru et al. [158] deposited AZO film by plasma-enhanced MOCVD and observed its characteristics under different gas pressures of 0.38, 0.85, and 1.5 mbar. The film deposited at higher pressure was more crystalline and thicker resulting in higher mobility and lower resistivity. Hu et al. [155] deposited 0.5 at%

Al-doped ZnO film on soda lime glass substrate having a thickness of 700 nm by chemical vapor deposition technique at 367-444°C having minimum resistivity of ~3.0×10^{-4} Ω-cm and transmittance of 85%. A list of published articles having electrical and optical properties and the parameters of deposition by chemical vapor deposition has been mentioned in **Table 2.3**.

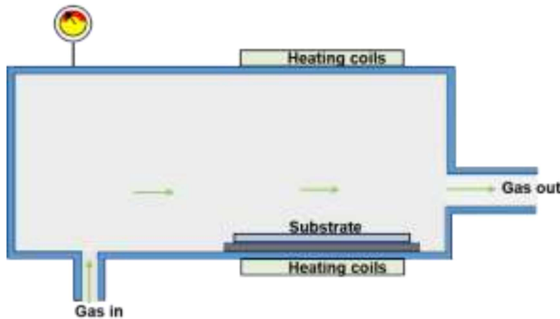

Figure 2.3 Schematic diagram of chemical vapor deposition

Table 2.3 Doping percentage, thickness, substrate/annealing temperature, resistivity, charge concentration, mobility, and %Transmittance values reported in various studies on AZO films deposited using a chemical vapor deposition technique

Al Doped at% /Thickness(nm)	**Temp. (°C)**	**ρ(Ω-cm) ($\times 10^{-3}$)**	**n (cm^{-3}) ($\times 10^{20}$)**	**μ (cm^2/Vs)**	**T(%) @550 nm**	**Ref.**
3 /160	400	1.52	1	52.0	88	[159]
4.8/210	400	252	-	-	82	[160]
2 /447	550	1400	-	-	65	[161]
1 /-	425	10	-	-	80	[162]
4.2 /-	450	13	1	7.9	80	[163]
1.2/850	420	0.3	2	35	90	[155]
2 /-	450	1.1	0.19	7.2	90	[164]
1 / 400	370	0.59	5	24	95	[165]

ρ = Resistivity, n = Charge carrier concentration, μ = Mobility, T=Transparency

2.2.4 Atomic layer deposition

Atomic layer deposition (ALD) involves vaporizing precursor materials to deposit a thin film on a substrate surface. The precursors are introduced sequentially in pulses such that the precursors react over the substrate in a self-limiting manner to form the film. ALD delivers a very precise thickness control at angstrom levels. ALD was first used by Suntola et al. [166] in 1977 to deposit ZnS for flat panel displays. Later, Yousfi et al. [167] deposited 2 at% Al-doped ZnO and investigated the effect of temperature on the deposition rate. It was observed that the deposition rate increases linearly with room temperature up to 140 °C and then remains constant at (0.25 nm/cycle) up to 180 °C, while any further increase in temperature results in a reduced rate of deposition. The resistivity of the ZnO and 2 at% Al-doped ZnO decreased with an increase in temperature from 120 to 280 °C with minimum resistivity of 4×10^{-3} Ω-cm and maximum transparency of ~>85%. Kwon et al.[168] investigated the effect of several factors, such as the precursor pulse ratio, purge time, and the source gas injection time, on the electrical, structural, and optical properties of AZO films. Resistivity was found to decrease while the growth rate increased with the precursor pulse ratio. An increasing trend of resistivity was observed with source injection time. Minimum resistivity of 9.7×10^{-4} Ω-cm and transparency above 80% were reported for TMA/DEZ pulse ratio 1/10. Park et al.[169] deposited Al-doped ZnO film at the substrate temperature of 180°C, ZnO film was deposited by a mixture of DEZ and H_2O was inducted with the help of carrier gas. The film deposited on the Si substrate was (100) oriented, smooth (roughness ~21.9-23.9 Å), and transparency of more than 80% on Si substrate 300-800 nm. The work function of the film was 4.53 eV, while the sheet resistance was

91.2 Ω/cm^2. Elam et al.[107] discussed the different thickness-controlling procedures during ALD. Saarenp et al.[170] deposited AZO film as transparent electrode material for organic light emitting diode (OLED) application with a sheet resistance of 500 Ω/cm^2 having a thickness of 60-80 nm thickness. Lujala et al.[171] deposited AZO film by atomic layer epitaxy at a low substrate temperature of 120-350°C and demonstrated a resistivity as low as 1.8x10^{-4} Ω-cm for 1.5 at% Al-doped ZnO with the transmittance >85%.

2.3 Solution-based processing techniques

In typical solution-based processing, the precursor of the material to be deposited is prepared in solution form. The solution-based processing methods are classified depending upon the way of deposition and decomposition of the liquid solution. Spin coating[172,173], dip coating[174,175], spray pyrolysis[176,177], chemical bath deposition [29,178], screen printing [179,180], inkjet printing [181], and doctor blade [182] are some of the preferred solution-based deposition techniques. **Figure 2.4** shows a schematic of some popular solution-based deposition techniques. The key benefits of the solution-based techniques over the vapor-based techniques include (i) low establishment and maintenance cost, (ii) simpler operation and handling (iii) flexibility to change the dopant together with the host material concentration and solvent, (iii) low power consumption (iv) high-throughput and efficient in roll-to-roll processing. However, generally, solution-based processing techniques result in poor electrical and optical properties in comparison to vapor-processed films. The major draw backs of the solution-based processing methods include: (i) non-homogeneous grain growth and distribution,

(ii) usually high surface roughness, (iii) presence of undecomposed precursors/impurities, (iv) less dense films and contamination, and (v) randomly oriented grains. Therefore, the solution-based processing routes almost always require additional post-deposition annealing in an appropriate atmosphere to enhance the properties to acceptable levels. Therefore, devising strategies for achieving properties of solution-processed AZO films at par with the films processed by vapor-based techniques is an active area of research.

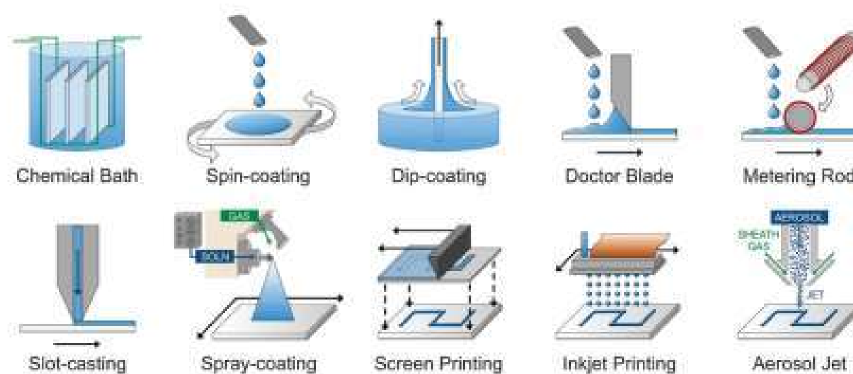

Figure 2.4 Available solution-based deposition techniques used for precursor solution deposition with the help of proper solvent. Reproduced with permission [183]. Copyright 2011, Royal Society Of Chemistry

2.3.1 AZO deposited by sol-gel dip coating/ spin coating

Dip coating is a simple way of deposition onto a substrate in which the substrate is dipped into a precursor solution for a stipulated time, which is pulled out slowly at a specified rate so that a uniform thin film of liquid forms over the substrate. The solution-coated substrate is then annealed at pre-defined temperatures to get the desired film. Viscous force, capillary (surface tension) force, and force due to gravity determine the thickness of the film on the substrate. It has been shown that

the kinetics of growth depends on the ionic product and solubility product of the solution at pre-defined pH. The ionic product of the solution, slightly greater than the solubility product, supports the deposition of the film [184].

The spin coating, on the other hand, is a more recently developed way of obtaining a film onto a small flat substrate [92]. In spin coating, the film of the precursor is formed by dropping a stipulated amount of precursor solution which is spread over the substrate by high-speed rotation. Unsteady radial spilling of liquid solution takes place, during which centrifugal and viscous forces compete to give a uniform film. The centrifugal force increases with speed, while the viscosity of the solution can be adjusted by changing the chemistry of the solution. Volatile solvents are commonly used because it leads to faster evaporation with the desired residue on the substrate, which on further coating becomes uniform and homogeneous. Thickness and uniformity depend on the rotation speed, evaporation of solvents, and rheology of the solidifying liquid.

Tsuchiya et al. [185] deposited AZO film on a quartz substrate and studied the effect of the number of dips on film thickness, and showed that film thickness increases linearly with the number of dipping. The effect of doping concentration on electrical properties was studied after varying Al/Zn 1-7 mol%. The resistivity and mobility of the film decreased while the charge concentration increased with doping. Ohya et al. [186] deposited AZO film with 30 and 8 dips of 0.2 M and 0.5 M ZnAc solution. A decrease in grain size was observed with increasing Al doping in ZnO. Lesser number of dips is required with higher concentrations to get similar resistivity as compared to lower concentrations. Nishio et al. [187] deposited AZO

film on a quartz substrate and studied the effect of different additives on the thickness and electrical properties. It was observed that faster thickness built-up took place in the solution containing diethylenetriamine as an additive compared to diethanolamine, mono-ethanolamine, and acetylacetone additives. The resistivity of the film was minimum in the case of the acetylacetone additive. Srinivasan et al. [188] deposited ZnO film by spin coating. He observed the optical bandgap energies 3.239, 3.247, and 3.262 eV for ZnO thin films coated on glass, quartz, and sapphire substrates, respectively. Ghomrani et al. [189] investigated the effect of chloride and nitrate precursor of aluminum on the electrical properties of the film. The minimum resistivity of the film was obtained in the case of nitrate precursor after annealing at 450°C. It was also observed that with an increase in temperature, resistivity decreases minimum at 450 °C in nitrate precursor. The minimum resistivity of 4.18 x 10^{-3} Ω-cm was obtained at 3 at% dopant concentration. The bandgap remained unchanged with varying annealing temperatures; however, the bandgap decreased from 3.25 to 3.08 eV with the increase in Al concentration, most probably due to conduction band filling. Tonny et al. [117] deposited AZO film by spin coating and investigated the effect of the thickness of the film on structural, optical, and electrical properties; with an increase in thickness (002) peak becomes more intense, transparency of the film decreases with the film thickness, resistivity and sheet resistance of the film decreases with the film thickness. Minimum resistivity was ~10^{-5} Ω-cm however, transparency of the film was below 60%. Znaidi et al. [92] described the effect of additives and different fluid properties on AZO films in brief. The film prepared by spin coating or dip coating is cheaper and simple; however, the use of additives like stabilizers and the requirement of several

repetitive coating cycles to build the thickness make this processing route complex and cumbersome.

2.3.2 Spray pyrolysis

Spray pyrolysis is a liquid solution-based deposition technique where the precursor solution is atomized and sprayed over a preheated substrate. Precursor atomization is the primary step for the deposition of a film on a substrate by spray pyrolysis. It involves the creation of aerosol of a precursor solution which is propelled with some initial velocity towards the heated substrate surface where

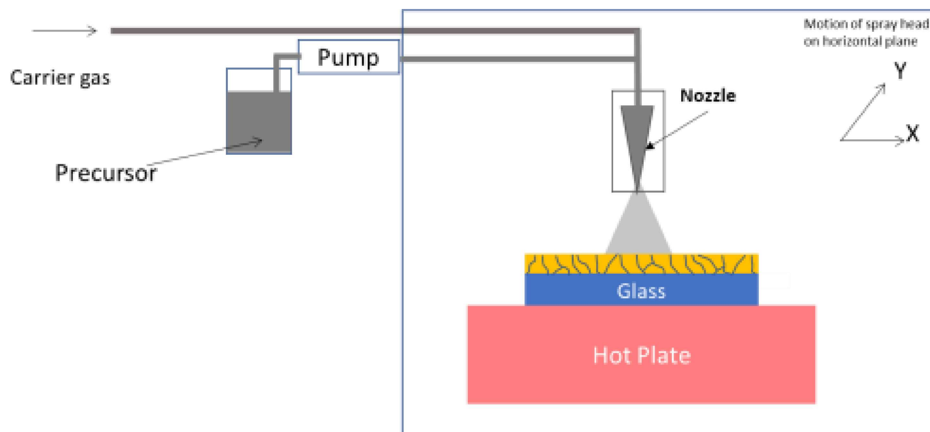

Figure 2.5 Schematic of the spray pyrolysis deposition procedure

the precursor reacts/decomposes. A schematic of spray pyrolysis is shown in **Figure 2.5**. Spray pyrolysis generally uses pressurized air, ultrasonic, or electrostatic atomizers to create a spray of the solution. Different types of atomizers and their typical droplet size, velocity, and atomization rate are listed in **Table 2.4**.

Table 2.4 Characteristics of Atomisers Commonly Used for spray pyrolysis [190]

Atomiser	Droplet size(µm)	Atomization rate(cm^3/min)	Droplet velocity(m/s)
Pressure	10-100	3-no limit	5-20
Nebulizer	0.1-2	0.5-5	0.2-0.4
Ultrasonic	1-100	<2	0.2-0.4
Electrostatic	0.1-100		

Droplet size, rate of atomization, and the initial velocity of the droplets are important parameters. The initial departing velocity decides the rate at which the droplets reach the substrate surface, the time of traverse of the droplets to reach the substrate, and the heating rate decides the quality of the film to be deposited. During its travel from atomized droplet to the substrate surface, it passes through a series of processes to form a dense polycrystalline film, as shown in **Figure 2.6**. The film morphology, microstructure, and compactness of the deposited films boil down to the competition between the two critical factors: the rate of evaporation of the solvent (F_{Evap}) and the rate deposition of precursor (F_{Dep}). When the substrate temperature and spray rate are such that F_{Evap} is greater than F_{Dep}, layers films with very small grain sizes and porosity form. In such cases, preferential orientation of columnar grains is not achieved.

On the other hand, when F_{Dep} is greater than F_{Evap}, a new layer of the precursor is deposited before the complete crystallization of the earlier layer; as a result, the crystallization is retarded, resulting in the build-up of precursor film. When this thick precursor film decomposes, large amounts of gases evolve, resulting in large shrinkage and crack formation. Such films are generally not uniform, and the surface finish is poor. For achieving a large columnar, compact film, F_{Dep} should

be slightly greater than $F_{Evap,}$ as shown in **Figure 2.7**. When the F_{Dep} is slightly greater, the earlier deposited precursor layer is almost crystallized when the new layer of the precursor is deposited. This helps maintain a thin saturated liquid pool of precursor at the top, which assimilates with the new precursor layer and supports continuous growth. A compact columnar, oriented thin film can easily be deposited if appropriately controlled.

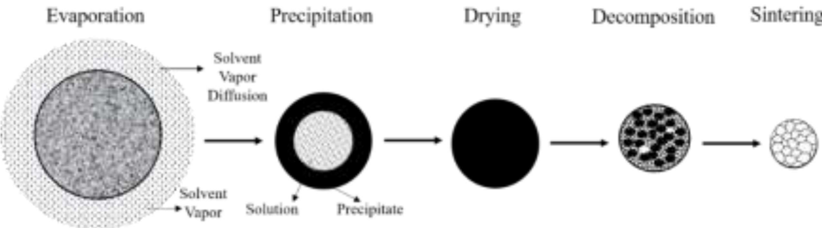

Figure 2.6 Stages during spray pyrolysis process

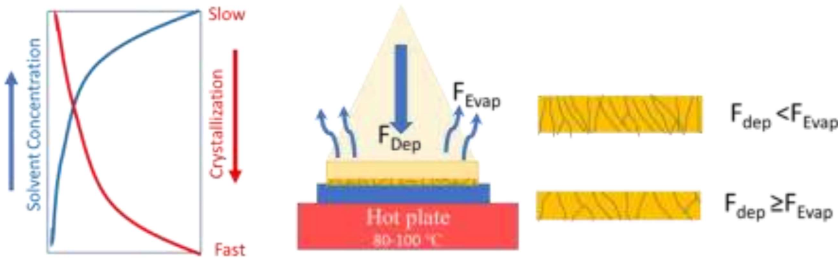

Figure 2.7 Schematic of the competition between deposition and evaporation rate on crystallization

Spray pyrolysis has received considerable attention because of being a simple, economic, and flexible process. Spray pyrolysis initially became popular in early 1944 for depositing TCO films. Merchant et al. [191] deposited ZnO and 0.5 to 6 at% Al-doped ZnO on Corning glass 7059 substrate by ultrasonic nebulised spray

pyrolysis compared the as-deposited result with film annealed in hydrogen. During deposition, the substrate temperature was 150°C, the spray chamber pressure was 8 cm/H_2O, the substrate to nozzle distance was 1.6 cm, and the nebulizing rate was 8 mL/h, at 300, 350, and 400 °C. The film's resistivity was found to be minimum at 1 at% Al-doped ZnO annealed for 5 min at 350°C. The lowest resistivity of the film was ~10^{-3} Ω-cm with a thickness of 300 nm. A higher degree of transparency ~85% for 2 at% Al-doped ZnO thin film with a bandgap of 3.22 eV was obtained. Crossay et al. [192] deposited Al-doped ZnO film by ultrasonic spray pyrolysis on borosilicate glass using a 0.7 MHz ultrasonic nebulizer and nitrogen as a carrier gas. The effect of acetic acid addition in the precursor solution on the electrical and optical properties of AZO film was investigated. The minimum resistivity was 3 x 10^{-3} Ω-cm obtained with a rather thick 3 μm film (0.03 wt% Al) having 74% transparency. Manouni et al. [31] deposited AZO on Pt/Quartz substrate at 400 °C. Partial orientation along [002] was obtained for 1 at% Al-doped ZnO while the minimum resistivity was 0.8 Ω-cm with a transparency of 80%. Muiva et al. [63] reported a widening of the bandgap with an increase in Al concentration from 3.18 to 3.35 eV (for 0-10 % Al), which was attributed to the Burstein-Moss shifting effect. Devasia et al.[193] studied the effect of nozzle-substrate distance. Highly oriented films along [002] were obtained at 10 cm with the minimum resistivity of 3.6 x 10^{-3} Ω-cm. Goyal et al. [194] deposited AZO film on Corning glass 7059 substrates by spray pyrolysis at 500°C substrate temperature to achieve a 2.1x10^{-2} resistivity Ω-cm for 0.8 at% Al-doped ZnO films while the charge concentration and mobility of the film were 8.8 x 10^{19} cm^{-3} and 5.8 cm^2/Vs. Aklilu et al. [195] modified the substrate (Corning glass-7059) with SAM-H_3C to obtain a resistivity

as low as 8.096 x 10^{-3} Ω-cm with ≥85% transparency. The mobility of the films was 5.40 cm^2/Vs, while the carrier concentration was 1.52x10^{20} cm^{-3}. A list of obtained electrical and optical properties and the parameters of deposition by solution spray pyrolysis is tabulated in **Table 2.5**.

Table 2.5 Doping percentage, thickness, substrate/annealing temperature, resistivity, charge concentration, mobility, and %T values reported in earlier studies on AZO films deposited using spray pyrolysis technique

%Al Doped /Thickness (nm)	Temp. (°C)	ρ (Ω-cm)	n (cm^{-3}) (x 10^{20})	μ (cm^2/Vs)	%T@ (550nm)	Ref.
6.96 at% /-	350	0.066	-	-	90	[196]
3 at% /1126	360	0.0023	3.71	7.46	82	[23]
2 at% /136.5	500	0.0017	9480	-	85	[197]
3 at% /302	350	0.0766	0.14	5.64	85	[198]
3 at% /550	475	0.0147	2.82	1.5	87	[199]
3.5 at% /400	400	0.0081	1.52	5.4	86	[195]
6 wt% /-	400	0.0015	1.56	25.2	70	[200]
3 at% /602	475	0.01	0.78	6	75	[61]
1.2 at% /660	425	0.002	0.67	40.5	85	[201]
5 wt% /600	475	0.02	7	0.4	85	[202]
4.7wt%/300	230	0.004	0.94	13.21	90	[203]
3 at% /520	300	0.0015	0.98	-	78	[204]
2 at% /1490	470	0.0053	1.10	10.7	82	[205]
6 wt% /1120	470	0.0051	0.88	13.9	82	[205]
1.5at% /420	390	0.007	0.15	5.5	-	[206]
3 at% /800	500	0.009	0.83	4.37	-	[207]
3 at% /602	475	0.021	3.11	1.01	77	[208]

ρ = Resistivity, n = charge carrier concentration, μ = mobility, T=Transparency

2.4 Post-deposition annealing

The main aim of the post-deposition annealing is to activate the dopants decompose/remove any unburned precursors, improve crystallinity and grain growth and relieve stresses from the film. On post-deposition annealing, grain

growth takes place voids present in between the grain boundaries decrease. Sometimes, it leads to the generation of micro-cracks and porosity in the film due to in-built stress. Post-deposition annealing can be done either in an ambient atmosphere, vacuum, or in the presence of an inert or reducing atmosphere.

Nunes et al. [66] studied the effect of a post-deposition annealing atmosphere on the pure and doped (In and Al) ZnO thin films deposited by spray pyrolysis. After annealing in the Ar atmosphere, the mobility of the film increased from 1.1 cm^2/Vs to 13.3 cm^2/Vs, which led to a decrease in the resistivity of the film. The transmittance of the film was 80% after annealing the AZO film. Orientation of the ZnO film along (002) was changed to (101) while the intensity X-ray diffraction peaks were found to increase, indicating improved crystallinity, while grains grew by 35% [209]. Chen et al. [210] reported the effects of temperature and post-deposition annealing on AZO film deposited by PLD on a glass substrate and also studied its effect on the structural, electrical, and optical properties of AZO thin films. The experimental results show that the electrical resistivity of films deposited at 240 °C was 6.1×10^{-4} Ω cm, which was further reduced to as low as 4.7×10^{-4} Ω-cm by post-deposition annealing at 400 °C for 2 hours (h) in argon. The average transmission of AZO films in the visible range is 90%. Ohyama et al. [28] deposited AZO film on a silica substrate by dip coating. The films were prepared annealed at 600 °C in two atmospheres: air for 1 h, and nitrogen for 1 h. The resistivity decreased by more than one order of magnitude as the temperature increased, up to 400°C, and showed a minimum value of 6.5×10^{-3} Ω-cm. XRD pattern showed that the film became oriented along [002] direction on post-deposition annealing,

while substantial grain growth was observed in SEM. Ohyama et al. [91] deposited ZnO and AZO thin film by dip coating on a glass substrate, having withdrawal rates of 1.2/7.0 cm/min. Pre and post-annealing temperature ranges were kept (200℃-450°C) and (500°C-800°C), respectively. Followed by (500°C-700°C) for 15 min in a nitrogen atmosphere. Sharp (002) peak orientation was observed in the XRD pattern after final annealing. Obtained resistivity was minimum at 0.5 at% Al-doped ZnO film was ~6.5 x 10^{-3} Ω-cm.

2.4.1 Vacuum annealing

Vacuum annealing of ZnO and AZO films results in the creation of oxygen vacancies which leaves two extra electrons close to the conduction band, which helps in increasing the charge carrier concentration. At the same time, the thermal effect of annealing also improves crystallinity and grain growth, resulting in enhanced mobility. Therefore, vacuum annealing is effective in reducing the resistivity of the ZnO films. On the other hand, annealing in the air can increase the resistivity by filling the oxygen vacancies. Jin et al. [130] reported an increase in resistivity by up to two orders of magnitude on annealing in air, whereas, vacuum annealing has been found to reduce resistivity by up to three-four orders of magnitude [131,211–214]. An increase in resistivity on annealing in the air has been attributed to the two-fold effect of filling oxygen vacancies, and the chemisorbed oxygen at the grain boundaries acts as additional trap sites. On the other hand, vacuum annealing releases oxygen vacancies and causes desorption of oxygen and, as a result, de-trapping of electrons from grain boundaries. Even a small concentration of oxygen vacancy is shown to have a strong effect on the properties

of ZnO. The defect equation for the formation of vacancy of oxygen has been discussed in **Chapter 3**. Kuroyanagi et al.[215] deposited ZnO-based TCOs using electron beam evaporation which had a resistivity of ~ 1.87 x 10^{-3} Ω-cm while charge concentration and mobility of the film were 3.12 x 10^{20} cm^{-3} and 11.1 cm^2/Vs, respectively. On vacuum annealing at 400°C, the resistivity reduced to 10^{-4} Ω-cm, and the films became 90% transparent in the visible range. Vacuum annealing improves crystallinity of films which helps in improving transparency of the films. Vacuum annealing of the sputtered film was found to improve crystallinity and shrinkage in lattice parameter *'c'* [216]. The sputter deposited AZO films at 320 °C had the lattice constants c=5.237 Å, which on vacuum annealed reduced to c=5.229 Å, while the (002) orientation improved to near perfect. As-deposited AZO film prepared by sputtering had a large amount of internal compressive stress. Chang et al.[217], also reported a reduction in the residual stress on annealing in a vacuum. Raviendra et al.[101] deposited (1 to 6 at%) Al-doped ZnO by chemical bath deposition on glass/quartz substrate [184] having a resistivity of ~6.0 x 10^{-2} Ω-cm. On vacuum annealing, the resistivity of the film was reduced to ~2.1 x 10^{-4} Ω-cm. Charge concentration and mobility of the film were ~10^{20} cm^{-3} and 11.9 cm^2V/s. Cameron et al.[218] reported minimum resistivity of ~7 x 10^{-4} Ω-cm and transparency of 90% after doping 0.8 at.% Al in ZnO at post-deposition annealing temperatures of 400 °C (in the air) and 450°C (in vacuum). Vacuum annealing improves the electrical and optical properties of ZnO-based TCO [32]; however, in many cases, the effect of vacuum annealing is reversible, and longer exposure to air or annealing in air results in increased resistivity.

2.4.2 Rapid thermal annealing/Radiative annealing

Rapid thermal annealing (RTA) utilizes lamps for radiative heating of the samples. Since the radiation is used for heating the films, very high ramp rates (up to 50-100°C/s) can be achieved. Rapid thermal annealing results in specific changes in the atomic arrangement of thin layers. Some of the direct consequences of rapid thermal annealing include dopant activation, densification of deposited films, and surface diffusion-enabled grain growth. In the beginning, radiative annealing was used mainly to ramp up the temperature of semiconductor wafers (silicon, germanium, GaAs, and SiC) to activate dopants and thin layer oxidation [219]. Radiative annealing reduces the thermal budget and saves time in the mass production lines. Therefore, this technique is mainly used for applications where the substrate needs to be brought to a certain temperature faster and only for a short period (seconds to minutes). Rapid thermal annealing, in the case of ZnO, was tried first for Ga-doped ZnO film, which was deposited by plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD)[220]. As the grains oriented toward the specific direction in the annealed film, improvement in the crystallinity was indicated by the XRD peak [221]. Rapid thermal annealing of solution-processed aluminium doped zinc oxide thin film was first attempted by Marouf et al. [97]. A significant reduction in strain in AZO film was reported on rapid thermal annealing. The resistivity of ~$4x10^{-3}$ Ω-cm and optical transparency of 87% was achieved after radiative annealing. The biggest change in resistivity was observed in the case of undoped ZnO, which improved from 1.51 Ω-cm in as-deposited condition to 0.54 Ω-cm after rapid thermal annealing. Highly crystalline films with

smoother surface morphology lead to lesser carrier scattering, higher mobilities, and, therefore, improved conductivity [97].

2.5 Concluding Remarks

Resistivity lower than ~10^{-4} Ω-cm and transparency of AZO film ≥ ~90% have been achieved by PLD/sputtering techniques. Although low resistivity and high transparency have been achieved through vapor-based deposition techniques, they are primarily demonstrated in lab-scale film fabrication and are not easily amenable to large-scale production. For large-scale production, vapor-based techniques would lead to a sharp rise in processing costs. Spray pyrolysis is a promising solution-based throughput processing technique due to its low cost and scalability; it can be easily adapted for roll-to-roll large-scale manufacturing. However, the solution spray processed AZO lags behind in terms of electrical properties. The electrical and optical properties of the solution-processed TCOs can be improved by adopting post-deposition annealing.