CHAPTER - 4
CHAPTER (4)

DEPOSITION AND CHARACTERIZATION OF ZnO AND ZnO:Al THIN FILMS

4.1: INTRODUCTION

ZnO is an n-type wide band gap semiconductor; the nature of n-type conduction can be controlled by two methods: (i) the creation of intrinsic donors by lattice defects, such as interstitial Zn, and (ii) the introduction of an appropriate extrinsic dopant. Despite of considerable efforts, the nature of donor in intrinsically doped ZnO films is still a controversial topic (zinc interstitial or oxygen vacancy) [1]. Such films exhibit a resistivity of about $10^{-2} - 10^{-3}$ Ω-cm. As deposited films have unstable electrical properties at ambient conditions due to the reoxidation of the oxygen-deficient film [2]. They show poor opto-electronic properties and are not useful for practical applications, hence need doping of appropriate impurity ions.

ZnO:Al is emerging as an alternative candidate to expensive ITO because it has a number of advantages over the more commonly used TCOs. ZnO consists of cheap and abundant elements, which may be contrasted with the more expensive In based films, e.g. Zn is far more abundant than In [2]. ZnO is non-toxic, whereas Cd based TCOs have potential health hazards. ZnO shows stability in hydrogen plasma and heat cycling. Therefore, ZnO has gained significant practical interest for the use as a TCO instead of ITO for applications in photovoltaic devices.

ZnO thin films were deposited using CSP technique on soda lime glass at different deposition conditions. The process parameters were optimized to get best quality TCO films. Optimization was achieved by varying one parameter at a time and keeping all other parameters constant. Quality of ZnO film was ensured on the basis of the criteria of figure of merit and sheet resistance. In this chapter, the results related to structural, optical and electrical properties of undoped ZnO and ZnO:Al films are discussed.

4.2: EXPERIMENTAL: UNDOPED ZnO FILMS

ZnO films were synthesized by spray pyrolysis of solution of zinc acetate (Zn(CH₃COO)₂·2H₂O) in ethanol on soda lime glass substrates. The precursor solution was pumped to spray nozzle using liquid flow control peristaltic pump. The soda lime glass substrates were chemically and ultrasonically cleaned before
deposition. The spray nozzle of optimized diameter 0.3 mm was used for all the depositions. The substrate to nozzle distance was kept 30 cm (optimized) in all depositions. The SS plate (thickness: 1.5 cm) with a 3 kW heater (Make: Baker UK) attached at its base was used for heating the substrate. An electronic temperature controller unit fitted with Cromel–Alumel thermocouple connected to heater was used for temperature measurement and control during deposition. Properly insulated housing was used around the substrate to ensure that the deposition temperature remains constant during film synthesis. Ultra filtered compressed air was used as the carrier gas. It was also ensured that the air pressure (8 kg/cm²) at nozzle remains constant for all depositions. At the end of deposition process, films were kept on the heater at the deposition temperature for 10 min in order to provide sufficient time and temperature for recrystallization. The films were then allowed to cool to ambient temperature before they were taken off for further characterization. The experimental variables considered for optimizing different process parameters for undoped ZnO are summarized in Table (4.1).

Table 4.1: CSP Process parameters optimized for the deposition of undoped ZnO thin films.

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Optimization</th>
<th>T_s (°C)</th>
<th>S_f (ml/min)</th>
<th>S_c (M)</th>
<th>A_f (lit/min)</th>
<th>V (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Temperature (T_s: °C)</td>
<td>▼</td>
<td>325-500</td>
<td>3</td>
<td>0.3</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Solution flow rate (S_f: ml/min)</td>
<td>▼</td>
<td>450</td>
<td>1.5-3.5</td>
<td>0.4</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>Precursor Concentration (S_c: M)</td>
<td>▼</td>
<td>450</td>
<td>2.5</td>
<td>0.1-0.7</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Air Flow Rate (A_f: lit/min)</td>
<td>▼</td>
<td>450</td>
<td>2.5</td>
<td>0.3</td>
<td>8-20</td>
<td>50</td>
</tr>
<tr>
<td>Precursor Volume (V : ml)</td>
<td>▼</td>
<td>450</td>
<td>2.5</td>
<td>0.3</td>
<td>15</td>
<td>30-100</td>
</tr>
<tr>
<td>Variation Interval</td>
<td>▼</td>
<td>25</td>
<td>0.5</td>
<td>0.1</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Optimized Parameters</td>
<td>▼</td>
<td>450</td>
<td>2.5</td>
<td>0.3</td>
<td>15</td>
<td>50</td>
</tr>
</tbody>
</table>

The process parameters play a crucial role in determining the structural and optoelectronic properties of ZnO films in CSP technique. The optimized process parameters for pyrolytic deposition do not necessarily apply universally for all CSP systems, but can serve as a valid guideline. In the present study, we have varied substrate temperature (T_s), solution flow rate (S_f), air flow rate (A_f), volume (V) of solution sprayed and molarity of precursor solution (S_c). The thickness independent
effect of $T_s$, effect of $S_f$ and $S_C$ on structural and optoelectronic properties of undoped ZnO thin films is discussed in detail in the present chapter.

4.2.1: Thickness Independent Effect of Substrate Temperature ($T_s$)

CSP technique was employed to synthesize films of approximately same thickness at different $T_s$ (325–500 °C). In order to understand the thickness independent effect of $T_s$ on optoelectronic properties of ZnO films the substrate temperature was varied from 325 °C to 500 °C at the interval of 25 °C. The structural, optical and electrical properties were studied using techniques discussed in chapter (3). The results are summarized below.

4.2.2: Results and Discussion

4.2.2. A: Structural Properties

Figure 4.1 shows low angle X-ray spectra of ZnO films prepared at various substrate temperatures ($T_s$). As seen from the figure, all films are polycrystalline in nature having hexagonal wurtzite structure with most preferred orientation along c-axis [002] direction. The other planes (100), (101), (102) and (103) were also observed in the X-ray diffractogram. However, their intensities are weaker than that of the (002) plane. The intensity of (002) plane increases with increase in $T_s$, however, the intensity of (100) and (101) plane shows a decreasing trend and almost disappears for higher $T_s$. The preferred orientation along [002] direction increased with increase in $T_s$. Furthermore, with increase in $T_s$, the width of (002) peak becomes narrower which indicates an improvement in the structural order of ZnO films. The improvement in the structural order can be attributed to better crystallinity and lower defect density at high deposition temperature ($T_s > 425 °C$) [3].

The variation observed in the texture coefficient TC of (h k l) planes for ZnO films and measured Standard Deviation ($\sigma_g [h k l]$) values were compared with ASTM data [4] and strengthens above inference. Figure 4.2 shows the variation of Texture Coefficient TC[002], TC[101] and Standard Deviation $\sigma_g$ of [002] plane with $T_s$. As seen from figure 4.2, with increase in $T_s$, TC[101] attenuates whereas TC[002] increases. This shows that the growth of ZnO film becomes increasingly preferred along [002] direction with increase in $T_s$. From figure 4.2, it is clear that Standard Deviation ($\sigma_g$) initially increases gradually with significant rise from 400 °C and
exhibits an average constant value above 450 °C. This could be governed by the nucleation process during film formation [5]. If the nucleation is preferred in the initial stage of deposition, a strict improvement in preferred growth is observed. This results in an average constant value of standard deviation. However, if nucleation takes place randomly on the growing surface and/or growth of nuclei takes place due to surface diffusion of impinging flux, then it will result in decreased standard deviation.

**Figure 4.1** XRD patterns of ZnO films deposited at different Substrate Temperatures ($T_s$).

**Figure 4.2**: Variation of Texture coefficient $TC[002]$, $TC[101]$ and Standard Deviation $\sigma_g$ of [0 0 2] plane with $T_s$. 

CHAPTER - 4: DEPOSITION AND CHARACTERIZATION OF ZnO AND ZnO:Al THIN FILMS 48
4.2.2.B: Surface Morphology

Figure 4.3 (A) (B) and (C) shows SEM images of ZnO thin films synthesized at $T_s = 350$, 400 and 450 °C respectively. The SEM images shows that films are uniform consisting of homogeneous distribution of quite small grains over the scanned area. The size distribution of grains appears less homogeneous at lower temperatures ($T_s = 350$ °C). With increasing temperature, the grain size of the films becomes larger and the films feature an improved crystallinity. At 400 °C, a granular structure can be observed in Figure 4.3 (B), whereas the films develop a columnar structure consisting of regularly aligned nanorods of ZnO when deposited at 450 °C, (figure 4.3 (C)). Granular formation was observed and the surface topography becomes smoother as the substrate temperature increases, getting a compact array at the higher substrate temperature. The average feature size measured on the surface was approximately constant. No voids or pinholes were detected, which is expected to be the major disadvantage of spray pyrolyzed samples.

![SEM images of ZnO films synthesized at different $T_s$ temperatures.](image)

*Figure 4.3: SEM images of the ZnO film synthesized at (A) $T_s = 350$ °C (B) $T_s = 400$ °C (C) $T_s = 450$ °C using CSP technique.*

4.2.2.C: Optical Transmission and Absorption

Figure 4.4 shows the transmission curves (%T versus $\lambda$) for ZnO films prepared at different $T_s$ in the spectral range of 270 to 1100 nm. A sharp cutoff was observed near $\lambda = 370$ nm in the transmission spectra. The inset graph in Figure 4.4 shows the variation of transmittance (%T) and film thickness (t nm) at different $T_s$. It is observed from inset of Figure 4.4 that ZnO films show high transmittance (91 to 95%) in the spectral range 400 to 1100 nm. The thickness of the films is approximately constant and varies within 280 – 325 nm.
Figure 4.4: Spectral dependence of transmittance for ZnO films synthesized at different $T_s$. The inset shows variation of film thickness and % transmittance at different $T_s$.

Figure 4.5: Spectral dependence of absorptance for ZnO films synthesized at different $T_s$. The inset is plot of $(ahv)^2$ vs. $hv$ of ZnO films synthesized at different $T_s$.

Figure 4.5 illustrates the variance of absorptance in the range 270 to 1100 nm. It is evident that the absorption coefficient decreases with an increase in wavelength, and a sharp decrease in absorption coefficient near the band edge indicate better crystallinity of the films and lower defect density. The analysis of the transmission
and absorption spectra in the vicinity of the fundamental absorption edge shows that the variation of the absorption coefficient is in accordance with the following relation which implies the direct transitions.

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

The inset graph in Figure 4.5 shows the variation of \((ah\nu)^2\) vs. \(h\nu\). The bandgap of the material from graph is x-axis intercept obtained by extrapolating the linear portion of the exponential curve.

Figure 4.6 shows the dependence of film thickness (\(t\) nm), grain size (\(D\) nm) and bandgap (\(E_g\) eV) of the films synthesized at various \(T_s\). With increase in \(T_s\) grain size was found to be increased. The grain size of the films synthesized at various \(T_s\) is found to vary from 45 nm to 60 nm. Band gap energy was found to be decreased from 3.272 to 3.242 eV with increase in \(T_s\).

![Graph showing variation of film thickness, grain size, and bandgap with substrate temperature.](image)

**Figure 4.6:** Plot shows variation of film thickness (\(t\)), grain size (\(D\)) and band gap (\(E_g\)) of ZnO films synthesized at different substrate temperatures (\(T_s\)).

### 4.2.2.D: Electrical Properties

The Hall Effect (Van der Pauw geometry) technique of determining electrical resistivity was used to determine the dark resistivity of the ZnO films. The dependence of conductivity on \(T_s\) was studied for all ZnO films. The variation observed in electrical conductivity (\(\sigma\)), mobility of charge carriers (\(\mu\)) and carrier concentration (\(\eta\)) of the deposited ZnO films with \(T_s\) is shown in figure 4.7. It was
found that the conductivity increases with increase in $T_s$ and becomes maximum (91.8 $\Omega^{-1}\text{cm}^{-1}$) at $T_s=450$ °C, above which there is steady decrease in conductivity. This increase in conductivity can be attributed to the increase in carrier concentration and mobility of the charge carriers. Also, it was found that the carrier concentration and mobility of charge carriers increases up to 450 °C, above which it slightly decreases. The maximum value of carrier concentration $3.26 \times 10^{19}$ cm$^{-3}$ and mobility 15.85 cm$^2$V$^{-1}$S$^{-1}$ corresponds to deposition temperature 450 °C at which resistivity 0.011 $\Omega$-cm is lowest. The early increase in conductivity can be attributed to improvement in the crystallinity and the modification in properties of the grain boundaries. For higher temperatures, the slight decrease in conductivity may be due to increase in rate of diffusion of alkali ions because of softening of soda lime glass. It is reported by different authors that the scattering of carriers by grain boundaries plays the dominant role for electrical conduction mechanism in ZnO films [6-8]. It is important to point out that as per the claim of Mustafa Özats [9], even when more sophisticated techniques were used, 0.011 $\Omega$-cm is within the lowest resistivity value range reported in the literature for undoped ZnO thin films [10, 11].

![Figure 4.7: Plot shows variation of mobility ($\mu$), conductivity ($\sigma$) and charge carrier concentration ($n$) in ZnO films synthesized at different substrate temperatures ($T_s$).](image)

Figure 4.8 shows the variation of sheet resistance ($R_s$) in $\Omega$/cm$^2$ and figure of merit ($\Phi_{TC}$) with deposition temperature. From figure 4.8 it can be observed that $R_s$ decreases with increase in $T_s$, becomes minimum at $T_s = 450$ °C and then increases slightly. With increase in $T_s$, $\Phi_{TC}$ increases up to $T_s = 450$ °C after which it suddenly
decreases. The highest figure of merit obtained is $1.77 \times 10^{-3} \ \Omega^{-1}$ for deposition temperature $450 \ ^\circ C$. The corresponding value of sheet resistance is minimum $3.31\times10^2 \ \Omega/cm^2$ along with a transmittance of 95 % for 400 to 1100 nm spectral region.

**Figure 4.8:** Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different substrate temperature ($T_s$).

### 4.2.3: Effect of Solution Flow Rate ($S_f$)

It was observed that for $S_f > 5$ ml/min generally the films tend to be powdery in nature. The lower $S_f < 4$ ml/min are purposefully chosen in order to provide sufficient time for nucleation and to reduce the drop in temperature due to large rate of spraying the precursor. ZnO films were deposited by spray pyrolysis of $0.4 \ \text{M, } 50 \ \text{ml solution of zinc acetate (Zn(CH}_3\text{COO})_2.2\text{H}_2\text{O)} in ethanol on glass substrates for different solution flow rate at optimized $T_s = 450 \ ^\circ C$. The results obtained are discussed below:

### 4.2.4: Results and Discussion

#### 4.2.4.A: Structural Properties

Figure 4.9 shows low angle X-ray spectra of ZnO films prepared at different solution flow rate ($S_f$). As seen from XRD pattern, all films are polycrystalline in nature having hexagonal wurtzite structure with most preferred orientation along c-axis [002] direction. The intensities of plane (100), (101), (102) and (103) are very weak as compared to that of the (002) peak. With increase in $S_f$ the intensity of (002)
plane increases. Similarly the intensities corresponding to all other planes in the diffraction pattern were found to increase with increase in $S_f$. Further, for low $S_f$, XRD pattern reveals that the intensities of (100), (101), (102) and (103) planes become very weak when compared with corresponding peaks observed for higher $S_f$. At low $S_f$, during the film synthesis nucleation takes place so as to govern the growth predominantly along [002] direction improving the crystallinity. This indicates the strict improvement in the structural order of the film for low $S_f$. The improvement in the structural order can be attributed to better crystallinity and lower defect density.

The variation observed in the TC (h k l) planes of ZnO films and measured standard deviation ($\sigma_g$) of (002) plane obtained after comparison with ASTM data also strengthens above inference. Figure 4.10 shows the variation of TC [002], TC [100] and standard deviation ($\sigma_g$[002]) with $S_f$. As seen from figure 4.10, TC [002] initially takes average constant value and then attenuates with increase in $S_f$. Whereas with increase in $S_f$, TC [100] decreases initially and then increases after $S_f = 2.5$ ml/min. This shows that the ZnO film becomes increasingly preferred oriented along the c-axis [002] direction perpendicular to the surface of substrate for lower $S_f$. From figure 4.10, it is clear that standard deviation ($\sigma_g$) of [002] initially decreases slowly with significant decrease after $S_f = 2.5$ ml/min. This confirms the fact that the strict improvement in the preferred orientation occurs for lower $S_f$. This could be governed by the nucleation process during film formation [5].

![Figure 4.9: XRD patterns of ZnO thin films deposited by CSP technique for different solution flow rates ($S_f$).](image)
Figure 4.10: A) Variation of TC [002] and TC [100] and standard deviation \( \sigma_g \) of [002] plane and B) TC [101] and TC [103] with solution flow rate \( (S_f) \).

Figure 4.10B shows the variation of TC [101] and TC [103] with \( S_f \). It can be observed from the figure 4.10B that TC [101] decreases with increase in \( S_f \). The intensity of [103] peak decreases with \( S_f \), the increase in TC [103] can mainly be attributed to decrease in intensity of all other peaks in XRD. From figure 4.10A and B it becomes clear that \( S_f \) plays important role in growth mechanism of the ZnO films synthesized by CSP technique. The preferred orientation of the film may be altered at higher flow rates \( S_f > 5 \) ml/min for which the ZnO films tend to be powdery in nature. It can be observed from XRD patterns that with increase in \( S_f \), the width of (002) plane becomes narrower which may be because of higher size of spray droplet at high \( S_f \) resulting in formation of films with larger grain size. The grain size of the films synthesized as determined from XRD was found to increase from 45 nm to 67 nm with increase in \( S_f \). The results obtained are tabulated in table (1) for further comparison.
Figure 4.11: Variation of deposition rate (nm/min) with solution flow rate (Sf).

Figure 4.11 shows variation in deposition rate (nm/min) with solution flow rate (Sf). It can be observed from figure 4.11 that with increase in Sf, deposition rate increases which results in increased thickness of the film. Thus films of desired thickness can be synthesized using chemical spray pyrolysis technique by controlling the precursor solution flow rate (Sf) with the help of peristaltic pump. With increase in Sf (1.5 to 3.5 ml/min) the deposition rate increases by almost eight times. For Sf = 3.5 ml/min the growth rate measured (84.7 nm/min) is maximum. It was also observed that the films synthesized are highly uniform, pinhole free and adherent to the substrate.

4.2.4.B: Surface Morphology

The scanning electron microscopic analysis of the ZnO film synthesized was done to study surface morphology. Figure 4.12 shows SEM image of ZnO thin film synthesized at 450 °C substrate temperature and 2.5 ml solution flow rate. The SEM image shows that film is uniform consisting of regularly aligned nanorods of ZnO. One can observe the homogeneous distribution of quite small grains over the scanned area. The smoother surface of the sample is because of small crystallite size. The formation of well defined ZnO nanorods perpendicular to substrate surface can make these films suitable for applications like dye sensitized solar cells, liquid crystal displays, thin film solar cell and photonics devices.
Figure 4.12: SEM image of the ZnO film synthesized at $S_f = 2.5 \text{ ml/min}$ at $450 ^\circ \text{C}$ using CSP technique.

4.2.4.C: Optical Transmission and Absorption

Figure 4.13, shows the measured transmission curves ($%T$ versus $\lambda$) for ZnO films prepared at different $S_f$. A sharp cutoff was observed near $\lambda = 370 \text{ nm}$ in the transmission spectra for all the films. The inset graph in figure 4.13 shows the variation of transmittance ($400 \text{ nm} - 1100 \text{ nm}$) and film thickness with variation in $S_f$.

Figure 4.13: Spectral dependence of transmittance for ZnO films synthesized at different $S_f$. The inset shows variation of film thickness and transmittance ($400 - 1100 \text{ nm}$) of ZnO films synthesized at different $S_f$. 
It is observed from figure 4.13 that ZnO films prepared at different Sf shows transmittance > 89% in the range 400 to 1100 nm. The transmittance was found to vary from 95% to 89% for ZnO films synthesized with Sf varying between 1.5 ml/min to 3.5 ml/min. The film thickness (t) is found to increase with increase in Sf. Figure 4.14 illustrates the variance of absorbance in the range 350 to 1100 nm. It is evident that the absorption coefficient decreases with an increase in wavelength and a sharp decrease in absorption coefficient near the band edge indicate better crystallinity of the films and lower defect density.

The inset graph in figure 4.14 shows the variation of $(\alpha h \nu)^2$ versus $h \nu$. The bandgap energy of the deposited ZnO films is determined using the inset of figure 4.14. The energy gap of the films synthesized was found dependent on film thickness.

![Figure 4.14: Spectral dependence of absorbance for ZnO films synthesized at different solution flow rate (Sf). The inset is plot of $(\alpha h \nu)^2$ vs. $h \nu$ for ZnO films synthesized at different solution flow rate (Sf).](image)

Band gap energy was found to decrease with increase in film thickness. The bandgap energy values so determined are in good agreement with reported values in literature [12, 13]. Figure 4.15 shows the variation of $E_g$ (eV), grain size (nm) and film thickness t (nm) as a function of Sf. It becomes clear from the figure 4.15 that increase in Sf increases the film thickness as well grain size, whereas the $E_g$ decreases with increase in grain size. The grain size of the films synthesized at various Sf is found to vary between 45 nm to 67 nm. A shift from $E_g = 3.162$ eV to 3.272 eV has been observed for the films synthesized at different Sf.
4.2.4. D: Electrical Properties

The variation observed in electrical conductivity ($\sigma$), mobility of charge carriers ($\mu$) and carrier concentration ($\eta$) of the ZnO films deposited with various $S_f$ is shown in figure 4.16. It was found that the conductivity increases with increase in $S_f$ and becomes maximum (78.8 $\Omega^{-1}\cdot \text{cm}^{-1}$) for $S_f = 2.5$ ml/min, above which there is steady decrease in conductivity. The early increase in conductivity can be attributed to the increase in carrier concentration and mobility of the charge carriers. Also it was found that the carrier concentration and mobility of charge carriers decreases for higher flow rates ($S_f$). The early increase in conductivity can also be seen because of improvement in the crystallinity and the modification of properties of the grain boundaries. It is reported by different authors that the scattering of carriers by grain boundaries plays the dominant role for electrical conduction mechanism in ZnO films [14].

Figure 4.17 shows the variation of sheet resistance ($R_s$) in $\Omega/cm^2$ and Figure of Merit ($\Phi_{TC}$) with solution flow rate. The sheet resistance decreases with increase in $S_f$ and becomes minimum for $S_f = 2.5$ ml/min after which it increases slowly. Whereas $\Phi_{TC}$ increases with increase in $S_f$, becomes maximum for $S_f = 2.5$ ml/min and then further decreases. The highest figure of merit obtained is $2.92 \times 10^{-3} \Omega^{-1}$ for $S_f = 2.5$ ml/min.
ml/min. The corresponding value of sheet resistance is minimum $2.04 \times 10^2 \, \Omega/cm^2$ with the transmittance of 95% within the spectral range of 400 to 1100 nm.

**Figure 4.16:** Plot shows variation of mobility ($\mu$), conductivity ($\sigma$) and charge carrier concentration ($n$) in ZnO films synthesized at different solution flow rate ($S_f$).

**Figure 4.17:** Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different solution flow rate ($S_f$).

### 4.2.5: Effect of Molarity of Precursor Solution ($S_c$: M)

ZnO films were deposited to optimize the molarity of precursor solution ($S_c$: M) using optimized $T_s = 450^\circ C$, $S_f = 2.5 \, \text{ml/min}$. The other process parameters $A_f = 16$
lpm, V=30ml and substrate to nozzle distance = 35cm, were constant for all
depositions. The results obtained are discussed below:

4.2.6: Results and Discussion

4.2.6.A: Structural Properties

Figure 4.18 shows low angle X-ray spectra of ZnO films prepared at different
precursor concentration. As seen from XRD, all films are polycrystalline in nature
having hexagonal wurtzite structure with most preferred orientation along c- axis
[002] direction. The other planes observed are (100), (101) and (103), however their
intensity is low. The intensity of (002) plane initially increases slightly till $S_c = 0.3M$
and then decreases. Whereas, intensities of (100) and (101) planes found to be
increased with increase in $S_c$. For $S_c < 0.4M$, XRD observation reveals that the
intensities of (100), (101) and (103) peaks become very weak when compared to
(002) peak. This indicates the strict improvement in the structural order of the film
for $S_c < 0.4M$. This means, for $S_c < 0.4 M$, nucleation takes place so as to govern the
growth predominantly along [002] direction. The improvement in the structural order
can be attributed to better crystallinity and lower defect density [5]. However, for $S_c >
0.4 M$ the intensity of (100) and (101) planes increases rapidly with substantial
decrease in intensity of (002) plane.

![XRD patterns of ZnO thin films deposited by CSP technique for different
molarity of precursor solution.](image)

*Figure 4.18: XRD patterns of ZnO thin films deposited by CSP technique for different
molarity of precursor solution.*
Figure 4.19 shows the variation of TC [002], TC [100] and standard deviation ($\sigma_g$) of [002] plane with $S_f$. As seen from figure 4.19 TC [002] plane initially takes average constant value and then attenuates with increase in $S_C$, whereas TC [100] increases. This shows that for lower $S_C$, the ZnO film becomes increasingly preferred along the c-axis [002] direction perpendicular to the surface of substrate. The standard deviation $\sigma_g$ [002] initially increases slightly with significant decrease after $S_C = 0.4$ M. This indicates that at higher $S_C > 0.4$ M and $S_f > 5$ ml/min the preferred orientation of film could be altered. This confirms the fact that the strict improvement in the preferred orientation occurs for lower $S_C$ and $S_f$.

![Figure 4.19: Variation of TC [002], standard deviation $\sigma_g$ of [002] and TC [100], TC [103] with molarity.](image)

### 4.2.6.B: Optoelectronic Properties

Figure 4.20, shows the measured transmission curves (%T versus $\lambda$) for ZnO films prepared at different $S_C$. A sharp cutoff was observed near 370 nm wavelength in the transmission spectra for all the films. The inset graph in figure 4.20 shows the variation of transmittance, film thickness and growth rate with variation in $S_C$. The ZnO films prepared at different $S_C$ show transmittance $> 90\%$. The film thickness ($t_s$) is found to be increased with increase in $S_C$. The growth mechanisms involved in deposition of ZnO films are Rideal-Eley and Langmuir-Hinshelwood mechanism [7]. With increase in molarity of the precursor solution, the growth rate increases till 0.5M indicating that Zn-containing species dominate the growth rate. This is Rideal-Eley mechanism in which film grows by a continuous adsorption followed by reaction of
Zn containing species with the chemisorbed oxygen molecules at the growing surface. This type of growth has been observed in SnO_2 thin film prepared by Chemical Vapor Deposition method. In CSP technique, it is difficult to control the incorporation of oxygen into the film because the growth occurs in atmospheric conditions. Thus Zn-containing species not only control the growth but also the film stoichiometry. For molarity > 0.5 M, the availability of oxygen from air is insufficient for a further increase in the growth rate. The saturation of surface concentration of reactants limits the rate of formation of ZnO layer. Hence, growth rate decreases slightly beyond a 0.5M concentration of the solution. This is the Langmuir-Hinshelwood growth mechanism which may be possible for the growth of ZnO layer. The lack of sufficient oxygen from the surrounding atmosphere may lead to a considerable competition for the adsorption sites as a function of reactant ratio. Thus, the growth rate of ZnO films is primarily controlled by Rideal-Eley and Langmuir-Hinshelwood mechanisms. However, the influence of Rideal-Eley mechanism was found dominant in ZnO growth processes.

![Figure 4.20: Spectral dependence of transmittance for ZnO films synthesized at different S_C. The inset shows variation of transmittance, film thickness and growth rate of ZnO films synthesized at different S_C.](image)

Figure 4.21 shows the effect of S_C on R_s and Φ_TC of undoped ZnO films. Initially R_s decreases rapidly with increase in S_C till S_C = 0.3 M concentration after which there is slow but steady increase in Rs. Subsequently Φ_TC increases rapidly till 0.3 M concentration and then decreases with increases in S_C. The highest value of Φ_TC =
12.3 \times 10^{-4} \ \Omega^1 \ \text{was obtained for 0.3 M concentration of precursor solution, for which} \ R_s = 555 \ \Omega \cdot \text{cm}^2.

**Figure 4.21:** Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different solution concentration ($S_C$).

### 4.2.7: Effect of Air Flow Rate ($A_f$)

ZnO films were deposited using CSP technique at optimized $T_s = 450 \ {}^\circ C$, $S_f = 2.5$ ml/min, 0.3 M solution to optimize the air flow rate ($A_f$). The effect of air flow rate on film thickness and optical transmittance of undoped ZnO films is shown in figure 4.22. As seen from the figure the film thickness ($t$) decreases whereas transmittance increases with increase in $A_f$. All films are highly transparent ($T>92\%$). The films of desired thickness can be deposited by controlling $A_f$. Figure 4.23 shows the effect of $A_f$ on sheet resistance and figure of merit of undoped ZnO films. Very high $A_f > 20$ lpm leads to formation of ultrathin and non uniform films. As seen from the figure 4.23 the sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of undoped ZnO films significantly depends on the $A_f$. The minimum value of $R_s = 414 \ \Omega/cm^2$ is observed at $A_f = 15$ lpm. The high value of $R_s$ at low $A_f$ may be because of the low impinging speed of spraying solution which causes less percentage of Zn atoms to reach the hot substrate surface. Whereas at very high $A_f$, the $R_s$ increases drastically due to higher impinging speed of spraying solution, which results in incomplete decomposition reaction of the ZnO. The highest value of figure of merit is obtained at $A_f = 15$ lpm. The figure of merit indicates that the deposited film quality is poor at high air flow.
rates, possibly because of the presence of unreacted species. These results show that the conductive and highly transparent ZnO films can be repeatedly deposited at 15 lpm air flow rate.

![Figure 4.22: Plot shows variation of film thickness (t) and transmittance (%T) of ZnO films synthesized at different $A_f$.](image)

**Figure 4.22:** Plot shows variation of film thickness ($t$) and transmittance ($%T$) of ZnO films synthesized at different $A_f$.

![Figure 4.23: Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different $A_f$.](image)

**Figure 4.23:** Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different $A_f$.

### 4.2.8: Effect of Volume of Precursor Solution (V)

ZnO films were deposited using CSP technique at optimized $T_s = 450^\circ C$, $S_f = 2.5$ ml/min, 0.3 M solution and $A_f = 15$ lpm to optimize the volume (V) of precursor.
solution. The effect of sprayed volume $V$ on film thickness and transmittance of undoped ZnO films is shown in figure 4.24. As seen from the figure the film thickness $(t)$ increases whereas transmittance decreases with increase in volume of precursor. All films are highly transparent ($T > 90\%$). It can be observed that the films of desired thickness can be obtained by spraying required volume of precursor solution.

**Figure 4.24:** Plot shows variation of film thickness $(t)$ and transmittance $(%T)$ of ZnO films synthesized at different volume of precursor.

**Figure 4.25:** Plot shows variation of sheet resistance $(R_s)$ and figure of merit $(\Phi_{TC})$ of ZnO films synthesized at different volume of precursor.

Figure 4.25 shows the effect of $V$ on $R_s$ and $\Phi_{TC}$ for undoped ZnO films. The decrease in $R_s$ with increase in volume of sprayed solution can be attributed to
increased film thickness. The $\Phi_{TC}$ increases initially with increases in $V$, attains maximum value for $V = 50$ ml, and then decreases gradually.

4.3: ALUMINIUM DOPED ZnO FILMS

4.3.1 Experimental

The electrical conductivity of n-type undoped ZnO film is mainly due to stoichiometric deviation (oxygen vacancies) or excess zinc. However, undoped ZnO films are not stable at high temperature. Exposure to environment or heat treatment of these films influences the optoelectronic properties. The structural and optoelectronic properties can be further improved by doping the ZnO films with aluminium at cation sites. The results obtained for aluminium doped ZnO films ($ZnO:Al$) are discussed in detail in this chapter. The observed changes in the structural and optoelectronic properties are investigated as a function of substrate temperature and doping concentration in the starting solution. The aluminium (Al) doped zinc oxide ($ZnO:Al$) films were prepared by thermal decomposition of solution of zinc acetate ($Zn(CH_3COO)_2\cdot2H_2O$) and aluminium chloride ($AlCl_3$) in ethanol on soda lime glass substrates by CSP technique.

ZnO:Al deposition was carried out in two sets of experiments. At first the substrate temperature ($T_s$) and then dopant concentration ($D_c$: at%) was optimized on the basis of the best quality TCO. The parameters used for deposition of these films are summarized in table (4.2),

**Table 4.2: CSP Process parameters used for the deposition of ZnO:Al thin films.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimization of $\Phi_{TC}$</th>
<th>$T_s$ (°C)</th>
<th>$D_c$ (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Temperature ($T_s$: °C)</td>
<td>SET I: 375-475</td>
<td>375-475</td>
<td>450</td>
</tr>
<tr>
<td>Solution flow rate ($S_f$: ml/min)</td>
<td>2.5</td>
<td>2.5</td>
<td>SET II: 2.5</td>
</tr>
<tr>
<td>Air Flow Rate ($A_f$: lit/min)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Precursor Volume ($V$: ml)</td>
<td>50</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Precursor Concentration ($S_c$: M)</td>
<td>0.3</td>
<td>0.3</td>
<td>1-6 at %</td>
</tr>
<tr>
<td>Dopant Concentration ($D_c$: at%)</td>
<td>3 at%</td>
<td>1-6 at %</td>
<td>1-6 at %</td>
</tr>
<tr>
<td>Variation Interval</td>
<td>25</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>Optimized Parameters</td>
<td>450</td>
<td>3 at %</td>
<td>3 at %</td>
</tr>
</tbody>
</table>
4.3.2 Effect of Substrate Temperature

ZnO:Al films were synthesized at different substrate temperature ($Ts = 375 - 475 \degree C$) by spray pyrolysis of 0.3 M, 50 ml solution of zinc acetate ($Zn (CH_3COO)_2.2H_2O$ 99.9% pure) and $AlCl_3.6H_2O$ (99.9% pure) in ethanol. Appropriate parts of $AlCl_3$ have been added to 0.3 M zinc acetate solution to realize an atomic Al:Zn ratio of 3:97. The results obtained are discussed below:

4.3.3 Results and Discussions

4.3.3.A: Structural Properties

The Al-doping caused no additional X-ray diffraction peaks and $Al_2O_3$ content was below the detection limit. When compared with the theoretical peaks of randomly distributed crystals, the deposited films exhibit a preferred orientation along [002] direction. Figure 4.26 shows low angle X-ray spectra of ZnO:Al films prepared by CSP technique at different substrate temperature. All ZnO:Al films are polycrystalline in nature having hexagonal wurtzite structure with most preferred orientation along c-axis [002] direction. The other peaks corresponding to (101) and (103) planes are also observed in the X-ray diffractogram. However, their intensities are very weak as compared to that of the (002) peak. The intensity of (002) plane increases with increase in $Ts$, however, the intensity of (101) and (103) plane shows a decreasing trend and almost disappears for high deposition temperature. The polycrystallinity of the films was found to be decreased with increase in $Ts$. The improvement in the structural order can be attributed to better crystallinity and lower defect density at high deposition temperature ($Ts > 425 \degree C$).

The variation observed in the texture coefficient of [hkl] planes of ZnO films and measured standard deviation ($\sigma_g$) values compared with ASTM data also strengthens above inference. Figure 4.27 shows the variation of texture coefficient TC[002], TC[103] and standard deviation $\sigma_g$ of [002] plane with substrate temperature ($Ts$). As seen from Figure 4.27, with increase in deposition temperature TC[103] plane attenuates whereas TC[002] plane increases. This shows that the growth of ZnO film becomes increasingly preferred along the [002] plane with increase in $Ts$. From Figure 4.27, it is clear that standard deviation ($\sigma_g$) increases with substrate temperature and above 450 $\degree C$ it exhibits an average constant value. This could be governed by the nucleation process during film formation. If the nucleation is preferred in the initial
stage of deposition, a strict improvement in preferred growth is observed. This results in constant value of standard deviation, which may be due to incorporation of Al in addition to Zn taking place at the regular [002] sites in the ZnO lattices. Thus the improvement of preferred growth along [002] plane at higher $T_s$ for zinc oxide films is controlled and modified by both molar concentration of the Zn(CH$_3$COO)$_2$.2H$_2$O solution and incorporation of Al doping.

Figure 4.26: XRD patterns of ZnO:Al films (3 at % Al doping) deposited at different $T_s$.

Figure 4.27: Variation of Texture Coefficients TC[002], TC[103] and standard deviation $\sigma_g$ of [002] plane for ZnO:Al films with substrate temperature ($T_s$).
4.3.3.B: Optical Transmission and Absorption

Figure 4.28 shows the measured transmission curves (%T versus λ) for ZnO:Al films prepared at different T_s (375 – 475 °C). A sharp cutoff was observed near 370 nm wavelength in the transmission spectra. The inset graph in Figure 4.28 shows the variation of transmittance and film thickness for different substrate temperatures T_s. It is observed from Figure 4.28 that ZnO:Al films are highly transparent (>90%) in the spectral range 400 to 1100 nm. The thickness of the films decreases with increase in substrate temperature. Figure 4.29 illustrates the variance of absorption in the range 350 to 1100 nm. It is evident that the absorption coefficient decreases with an increase in wavelength, and a sharp decrease in absorption coefficient near the band edge indicate better crystallinity of the films and lower defect density. The inset graph in Figure 4.29 shows the variation of (ahu)^2 vs. hν. The energy bandgap of the material from graph is x intercept obtained by extrapolating the linear portion of the exponential curve. Figure 4.30 shows the dependence of bandgap energy (E_g eV) and grain size (D nm) of the ZnO:Al films synthesized at various T_s. With increase in T_s, grain size was found to be increased. The grain size of the films synthesized at various T_s is found to vary from 55 nm to 51 nm. Bandgap energy was found to be increased from 3.228 to 3.299 eV with increase in T_s.

![Figure 4.28: Spectral dependence of transmittance for ZnO:Al films synthesized at different T_s. The inset shows variation of film thickness and %T at different T_s.](image)

CHAPTER - 4: DEPOSITION AND CHARACTERIZATION OF ZnO AND ZnO:Al THIN FILMS

70
**Figure 4.29:** Spectral dependence of absorptance for ZnO:Al films synthesized at different $T_s$. The inset is plot of $(ahv)^2$ vs. $hv$ for ZnO:Al.

**Figure 4.30:** Variation of film thickness ($t$), grain size ($D$ nm) and bandgap energy ($E_g$ eV) with Substrate temperature ($T_s$).

### 4.3.3.C: Electrical Properties

Generally doping improves the mobility either by increasing the grain size or by passivating the grain boundary barrier [15-16]. The variation observed in electrical conductivity ($\sigma$), mobility of charge carriers ($\mu$) and carrier concentration ($n$) of the ZnO films deposited with $T_s$ is shown in figure 4.31. Al doping has caused increase in conductivity by several orders of magnitude as compared to undoped ZnO films. It
was found that the conductivity increases with increase in $T_s$ and becomes maximum $(4.85 \times 10^3 \ \Omega^{-1}\cdot \text{cm}^{-1})$ at $T_s = 450 ^\circ \text{C}$, above which it decreases. The early increase in conductivity can be attributed to the increase in carrier concentration and mobility of the charge carriers. Also, it was found that the carrier concentration and mobility of charge carriers, slightly decreases for higher $T_s > 450 ^\circ \text{C}$. Interstitial Al atoms contribute to increased carrier concentration. As compared to undoped ZnO films the carrier concentration for ZnO:Al films increased substantially. The maximum value of carrier concentration $8.57 \times 10^{20}/\text{cm}^3$ was observed at $T_s = 450 ^\circ \text{C}$ at which the carrier mobility $35.4 \ \text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ was also maximum. The comparative analysis of figure 4.30 and 4.31 shows that, the variation of energy bandgap and carrier concentration is indicative of Burstein-Moss shift [17-19]. The band gap energy increases due to increase in carrier concentration. The increasing trend of carrier concentration may be attributed to, Al atoms replacing regular zinc sites in the ZnO lattice which produces one free electron. In addition, aluminium atom (Al$^{+3}$) occupying an interstitial position might produce up to three free electrons. It is a well known fact that excellent transparent and conductive coatings with high value of figure of merit should have the maximum carrier mobility value [20]. As seen from the figure 4.31 charge mobility of the ZnO:Al thin films increases linearly with increase in $T_s$ and attains its maxima. The increase in the mobility of a such polycrystalline semiconductor may be due to the improvement in the crystallinity of ZnO:Al film, which reduces scattering of charge carriers from grain boundaries [13]. The lower mobilities at low $T_s$ may be limited by not only the grain boundary scattering but also by ionized impurity scattering. Although aluminium atom (Al$^{+3}$) occupying an interstitial position contributes three free electrons to charge carrier, it has targeted effect on charge mobility. Because interstitial aluminium atom not only produces conduction electron but also ionized impurity scattering centers.

The figure 4.32 shows that, the energy bandgap increases due to increase in carrier concentration. This shifting of band edge towards lower wavelength is known as the Burstein-Moss effect. The positive shifting of absorption edge due to increase in carrier concentration is known as Burstein-Moss band filling [17-19]. The increasing trend of carrier concentration attributes to the fact that, Aluminium ions (Al$^{+3}$) prefer to occupy an interstitial positions in addition to replacing the regular Zn sites. It can be observed from figure 4.32 that bandgap varies linearly with $\gamma^{2/3}$, validating the Burstein-Moss model to explain the results for ZnO:Al thin films. This indicates that
though the dopant concentration (Dc = 3 at%) is constant in precursor solution but actual dopant presence in the deposited film may be less than the desired doping. Similarly the extent of doping must be different at different substrate temperature. From above discussion it is clear that higher deposition temperatures are well suited for the process of doping the metal oxide semiconductors. The incorporation of doping is favored at higher Ts without sacrificing the structural and optoelectronic properties of the ZnO thin films. Thus it is easier to incorporate Al doping in ZnO lattice at higher Ts.

**Figure 4.31:** Plot shows variation of mobility ($\mu$), conductivity ($\sigma$) and charge carrier concentration ($n$) in ZnO:Al films synthesized at different substrate temperature ($T_s$).

**Figure 4.32:** Plot of energy gap (eV) versus $\eta^{2/3}$ for ZnO:Al films deposited at different $T_s$. 

CHAPTER - 4: DEPOSITION AND CHARACTERIZATION OF ZnO AND ZnO:Al THIN FILMS
Figure 4.33 shows the variation of sheet resistance ($R_s$) in $\Omega/cm^2$ and figure of merit ($\Phi_{TC}$) with $T_s$, for ZnO:Al thin films. From figure 4.33 it can be observed that $R_s$ decreases with increase in $T_s$. With increase in $T_s$, $\Phi_{TC}$ increases up to $T_s = 450^\circ C$ after which it decreases. The highest figure of merit obtained is $7.8 \times 10^2 \Omega^{-1}$ for deposition temperature $450^\circ C$ with the minimum sheet resistance $8.75 \Omega/cm^2$.

**Figure 4.33**: Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different substrate temperature ($T_s$).

### 4.3.4: Effect of Doping Concentration

ZnO:Al films were synthesized by spray pyrolysis of 0.3M, 50 ml solution of zinc acetate ($Zn(CH_3COO)_2\cdot2H_2O$) (99.9% pure) and AlCl$_3\cdot6H_2O$ (99.9% pure) in ethanol at $450^\circ C$. Al concentration ratio in precursor solution was varied between 1 at% to 6 at% by adding appropriate parts of aluminium chloride to 0.3 M zinc acetate solution. The results obtained are discussed below:

### 4.3.5: Results and Discussions

#### 4.3.5.A: Structural Properties

Figure 4.34 shows low angle X-ray spectra of ZnO:Al films prepared by CSP technique at different doping level. All ZnO:Al films are polycrystalline in nature having hexagonal wurtzite structure with most preferred orientation along c-axis [002] direction according to ASTM data sheet [5]. The intensities of (101) and (103) planes are very weak as compared to that of the (002) peak. The intensity of (002) plane
decreases with increase in doping level, however, the intensity of (101) and (103) plane shows increasing trend. The polycrystallinity of the films was found to be increased with increase in doping level. However, the Al-doping procedure caused no additional X-ray diffraction peaks or at least Al₂O₃ content was below the detection limit. When compared with the theoretical peaks of randomly distributed crystals, the deposited films exhibit a preferred orientation.

The variation observed in the texture coefficient of [hkl] of ZnO films and measured standard deviation (σₖ) values compared with ASTM data also strengthens above inference. Figure 4.35 shows the variation of texture coefficient TC[002], TC[101] and standard deviation σₖ of [002] plane with doping level. As seen from Figure 4.35, with increase in deposition temperature TC[002] attenuates whereas TC[103] increases. This shows that the growth of ZnO film becomes increasingly preferred along the [002] plane for Al doping concentration below 3 at%.

![Figure 4.34](image)

*Figure 4.34: XRD patterns of ZnO:Al films deposited at 450°C for different doping level.*

From Figure 4.35, it is clear that standard deviation (σₖ) decreases with doping level after 3 at% Al doping level, below which it exhibits an average constant value. This could be governed by the nucleation process during film formation. If the nucleation is preferred in the initial stage of deposition, a strict improvement in preferred growth is observed.
Figure 4.35: Variation of Texture Coefficients $TC[002]$, $TC[103]$ and standard deviation $\sigma_g$ of [002] for ZnO:Al films with different doping level.

4.3.5.B: Surface Morphology

Figure 4.36 (A) and (B) shows SEM images of ZnO thin films synthesized at 450 °C with 3 at% Al doping level. The SEM images shows that films are uniform consisting of homogeneous distribution of quite small grains over the scanned area indicating that Al doping had caused marginal influence on morphology of ZnO:Al thin films. The size distribution of grains appears homogeneous. Whereas the films develop a columnar structure consisting of regularly aligned nanorods of ZnO doped with Al. SEM image shows high density of closely packed nano/submicro rods over a large area. Generally, the growth of the rods was found to occur in the vertical direction.

Figure 4.36: SEM image of the ZnO:Al (Al: 3at%) film synthesized at 450°C using CSP technique.
Figure 4.37 (A) and (B) shows AFM images (1 μm²) of ZnO thin films synthesized at 450 °C with 3 at% Al doping level. SEM and AFM scan shows randomly spaced structural features indicating the formation of vertically aligned nanorods of ZnO.

**Figure 4.37:** AFM image (1μm²) of the ZnO:Al (Al: 3at%) film synthesized at 450°C using CSP technique.

### 4.3.5.C: Optical Transmission and Absorption

Figure 4.38 shows the measured transmission curves (%T versus λ) for ZnO:Al films prepared at different doping level (1-6 at%). A sharp cutoff was observed near 370 nm wavelength in the transmission spectra. The inset graph in Figure 4.38 shows the variation of transmittance and film thickness for different Al doping. It is observed from Figure 4.38 that ZnO:Al films are highly transparent (>90%) in the spectral range 400 to 1100 nm. The thickness of the films deposited at 450°C with different Al concentration is nearly constant (230-260 nm). Figure 4.39 illustrates the variance of absorption in the range 350 to 1100 nm. It is evident that the absorption coefficient decreases with an increase in wavelength, and a sharp decrease in absorption coefficient near the band edge indicate better crystallinity of the films and lower defect density. The inset graph in Figure 4.39 shows the variation of (αhν)² vs. hν. The energy bandgap of the material from graph is x-axis intercept obtained by extrapolating the linear portion of the exponential curve. Figure 4.40 shows the dependence of bandgap energy (Eg eV) and grain size (D nm) of the Al:ZnO films synthesized at different doping level. With increase in T, grain size was found to be increased. The grain size of the films synthesized at various doping level was also
nearly constant. Bandgap energy was found to be increased from 3.280 to 3.322 eV with increase in $T_s$.

Figure 4.38: Spectral dependence of transmittance for ZnO:Al films synthesized at different doping level. The inset shows variation of film thickness and transmittance at different doping level.

Figure 4.39: Spectral dependence of absorptance for ZnO:Al films synthesized at different doping level. The inset is plot of $(ahv)^2$ vs. $hv$ of ZnO:Al films synthesized at different doping level.
Figure 4.40: Variation of bandgap energy (Eg eV) and grain size (D nm) with Al doping level.

4.3.5.D: Electrical Properties

The variation observed in electrical conductivity (\(\sigma\)), mobility of charge carriers (\(\mu\)) and carrier concentration (\(n\)) of the deposited ZnO:Al films with Al doping level is shown in figure 4.41. It was found that the conductivity increases with increase in Al doping level and becomes maximum (5.3 \(\times\) 10\(^3\) \(\Omega^{-1}\text{-cm}^{-1}\)) at 3 at% Al doping level, above which it decreases. The early increase in conductivity can be attributed to the increase in carrier concentration due to Al doping and increase in mobility of the charge carriers. Also, it was found that the carrier concentration and mobility of charge carriers, decreases for higher Al doping level > 3 at%. The early increase in conductivity can be attributed to the presence of interstitial Al atoms contributing to increased carrier concentration. As compared to undoped ZnO films the carrier concentration for ZnO:Al films increased substantially. The maximum value of carrier concentration 8.81 \(\times\) 10\(^{20}\)/cm\(^3\) was observed at 3 at% Al doping level at which the carrier mobility 37.4 cm\(^2\text{-V}^{-1}\text{-S}^{-1}\) was also maximum. The comparative analysis of figure 4.40 and 4.41 is indicative of the Burstein Moss shift, which results in the increase in bandgap energy due to increase of carrier concentration.

The comparative analysis of figure 4.40 and 4.41 relating carrier concentration with bandgap energy supports the Burstein Moss shift. The band gap energy increases due to increase in carrier concentration. This is combined effect of, (Al\(^{3+}\)) occupying
an interstitial position contributing to three free electrons and Al atoms replacing regular zinc sites in the ZnO lattice produces only one free electron. The increase in mobility with concentration is indicative of the fact that instead of occupying interstitial sites Al prefers to replace the regular Zn sites during the film formation. This reduces grain boundary scattering. It is a well known fact that excellent transparent and conductive coatings with high value of figure of merit should have the maximum carrier mobility value [12]. The increase in the mobility of a such polycrystalline semiconductor may be due to the improvement in the crystallinity of ZnO:Al film, which reduces scattering of charge carriers from grain boundaries [13]. The lower mobilities at higher Al doping level are limited by not only the grain boundary scattering but also by ionized impurity scattering. Although aluminium atom (Al\textsuperscript{3+}) occupying an interstitial position contribute three free electrons to charge carrier, it has targeted effect on charge mobility because interstitial aluminium atom not only produce conduction electron but also ionized impurity scattering centers.

**Figure 4.41:** Plot shows variation of mobility ($\mu$), conductivity ($\sigma$) and charge carrier concentration ($n$) in ZnO:Al films synthesized at different doping level.

It can be observed from figure 4.42 that bandgap varies linearly with $n^{2/3}$, supporting the Burstein-Moss model which can explain the results for ZnO:Al thin films. This indicates though the dopant concentration $D_c$ is different in precursor solution but actual doping incurred in the deposited material may be less than the desired doping.
Figure 4.42: Plot of energy gap (eV) versus $\eta^{2/3}$ for ZnO:Al films deposited at different $D_c$.

Figure 4.43 shows the variation of sheet resistance ($R_s$) in $\Omega/cm^2$ and figure of merit ($\Phi_{TC}$) with $T_s$, for ZnO:Al thin films. From figure 4.43 it is observed that $R_s$ decreases with increase in Al doping level up to 3 at%. With further increase in Al doping level $R_s$ increases. With increase in Al doping level, $\Phi_{TC}$ increases up to Al content 3 at% after which it decreases. The highest figure of merit obtained is $6.5 \times 10^2 \Omega^{-1}$ for Al doping level 3 at% with the minimum sheet resistance 8.14 $\Omega/cm^2$.

Figure 4.43: Plot shows variation of sheet resistance ($R_s$) and figure of merit ($\Phi_{TC}$) of ZnO films synthesized at different doping level.
4.4: CONCLUSIONS

The undoped ZnO and ZnO:Al thin films are successfully prepared by spray pyrolytic deposition of metal-organic solution of zinc acetate \((\text{Zn(CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})\) in ethanol on soda lime glass substrate. The variations in structural and optoelectronic properties of undoped ZnO thin films have been studied as a function of substrate temperature, solution flow rate and molarity of precursor solution. The optimized process parameters for undoped ZnO films are \(T_s = 450\, ^\circ\text{C}\), \(S_f = 2.5\, \text{ml/min}\), \(S_c = 0.3\, \text{M}\), \(A_f = 15\, \text{lpm}\) and \(V = 50\, \text{ml}\). ZnO:Al films deposited at different substrate and impurity doping level were also investigated for structural and optoelectronic properties. The investigation shows that structural and optoelectronic properties are very sensitive to the impurity doping level. The formation of nanocrystalline and nanostructured ZnO and ZnO:Al film is confirmed from X-ray diffraction, SEM and AFM measurements. The UV-VIS-NIR spectroscopic measurement and electrical measurement by Hall effect (Van der Pauw geometry) technique reveals that the films synthesized at optimized conditions have excellent optoelectronic properties with transmittance > 90\%, sheet resistance of the order of \(10^2\, \text{\Omega}\cdot\text{cm}^2\) for undoped and \(10\, \text{\Omega}\cdot\text{cm}^2\) for ZnO:Al thin films. The ZnO based films consisting of high figure of merit can be repeatedly synthesized using CSP technique. Hall measurements for ZnO:Al indicates that the Al incorporation in the sprayed ZnO film decreases sheet resistance and increases optical transparency as compatible to those of undoped ZnO film. From structural properties, it is shown that growth mechanism (preferred growth) of ZnO thin film is predominantly controlled by substrate temperature \((T_s)\), solution flow rate \((S_f)\) and molar concentration \((S_c)\) of the precursor solution. However, preferred growth is less significantly dependent on doping level. The optical and electrical properties are quite sensitive to aluminium doping. The electrical resistivity and optical transmittance of the best undoped ZnO film with a thickness of about 280 nm, deposited under optimized condition were found to be \(1.52 \times 10^2\, \text{\Omega}\cdot\text{cm}\) and 96\%, respectively. The highest value of \(\Phi_{TC} = 12.3\times 10^4\, \text{\Omega}^{-1}\) was obtained for 0.3 M concentration of precursor solution and at \(450\, ^\circ\text{C}\), for which \(R_s = 555\, \text{\Omega}\cdot\text{cm}^2\). A sharp decrease in the transmission in the ultra-violet and near infrared regions is related to the increase in carrier concentration. The corresponding values of carrier concentration and carrier mobility are \(4.15 \times 10^{19}\, \text{cm}^{-3}\) and 9.89 \(\text{cm}^2\, \text{V}^{-1}\, \text{S}^{-1}\) respectively. The ZnO:Al films deposited under optimized
conditions are far superior to undoped ZnO films based on the structural and optoelectronic properties. These films are well suited for TCO applications and in photovoltaic devices.

The typical process parameters for the synthesis of transparent and conducting ZnO: Al films are listed in Table 4.3.

**Table 4.3: Typical process parameters for the synthesis of ZnO: Al films**

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>450 °C</td>
</tr>
<tr>
<td>Solution Flow Rate</td>
<td>2.5 ml/min</td>
</tr>
<tr>
<td>Concentration of precursor solution</td>
<td>0.3 M</td>
</tr>
<tr>
<td>Air flow rate</td>
<td>15 lpm</td>
</tr>
<tr>
<td>Volume of Precursor</td>
<td>50 ml</td>
</tr>
<tr>
<td>Substrate to nozzle distance</td>
<td>30 cm</td>
</tr>
<tr>
<td>Nozzle diameter</td>
<td>0.3 mm</td>
</tr>
<tr>
<td>Dopant level</td>
<td>3 at%</td>
</tr>
</tbody>
</table>

The typical opto-electronic properties of as deposited transparent conducting ZnO: Al films are shown in Table 4.4.

**Table 4.4: Opto-electronic properties of as deposited ZnO: Al films**

<table>
<thead>
<tr>
<th>Opto-electronic Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmittance (400 - 1100 nm)</td>
<td>94%</td>
</tr>
<tr>
<td>Resistivity</td>
<td>$1.89 \times 10^{-4} , \Omega \cdot \text{cm}$</td>
</tr>
<tr>
<td>Figure of Merit</td>
<td>$6.5 \times 10^{-2} , (\Omega^{-1})$</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>233 nm</td>
</tr>
<tr>
<td>Carrier Concentration</td>
<td>$8.81 \times 10^{20} , \text{cm}^{-3}$</td>
</tr>
<tr>
<td>Mobility</td>
<td>37.4 cm$^2$/ V-s</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.321 eV</td>
</tr>
</tbody>
</table>
REFERENCES: