Chapter 5

Effect of doping on spray pyrolysed ZnO thin film

5.1 Introduction

The density of impurities in semiconductors is one of the major parameter that can control position of Fermi level. It is often possible to impart some desirable properties to semiconductor by introducing a controlled quantity of suitable impurity elements into it either during its preparation or diffusing them afterwards through thermal or other treatments. This process is called ‘doping’ and the impurities are known as ‘dopants’. Doping of impurities in wide band gap semiconductors often induces dramatic changes in electrical and optical properties. Doping of ZnO with the atoms of elements of higher valency results in replacing Zn$^{2+}$ atoms and hence improvement in the electrical conductivity. ZnO can be doped with a wide variety of atoms to meet the demands of several applications. Various dopants such as F$^{1-}$, Cu$^{1+}$, Ag$^{1+}$, Ga$^{3+}$, Al$^{3+}$, In$^{3+}$, Sn$^{4+}$ and Sb$^{5+}$ has been already tried [1-10] and efficiency of the dopant depends on its electro-negativity and ionic radius. In the present work, the technique we used for film preparation is very simple viz., CSP and it is rather easy to vary the concentrations of Zinc ion or dopant in this technique and hence to vary / control the properties of the films.

ZnO is a potential candidate for various applications in the field of opto-electronic devices in short-wavelength. In order to achieve this, high quality n- and p-type ZnO are indispensable. Interestingly, n-type doping is relatively easy compared to that for the p-type. When ZnO is doped with group III elements, [such as Al, Ga and In], the dopants substitute Zn atoms while the group VII elements [such as Cl and F] substitute O atoms; these two doping lead to n-type. P-type doping in ZnO may be possible by substituting Zn site using group-I elements (Li, Na and K) or substituting O using group-V elements (N,P and As).

The prime objective of this work was to decrease the resistance of ZnO layer deposited using CSP technique through doping. This chapter describes the effects of both ‘Ex-situ’ and ‘In-situ’ doping using different elements and the details of these two processes are given in following sections. Ex-situ doping was done through thermal diffusion using Tin and Indium while the in-situ doping was using Indium and Aluminium. Variations in
structural, electrical and optical properties of the samples due to these two are also described in detail in respective sections.

5.2 Effect of doping of ZnO thin film: A review

Benny Joseph et al. studied the variation of structural, morphological, electrical and optical properties of ZnO film prepared using CSP technique due to doping with Aluminum [11]. The films were highly transparent in visible region [97% at 550 nm] and electrically conductive [resistivity of $2.45 \times 10^{-2} \Omega \text{cm}$]. XRD studies showed that the films were polycrystalline in nature with (002) preferred orientation.

Aluminium Doped Zinc Oxide (AZO) thin films of 100 nm thickness were prepared by systematically changing the number of “Diethyl Zinc (DEZ, Zn(C$_2$H$_5$)$_2$)- Distilled-water cycles” [at 150 °C] in ‘Atomic Layer Deposition’ (ALD) method [12]. ZnO films grown without any TMA- Distilled water cycle exhibited a polycrystalline nature having (100), (002), (101), and (110) orientation. But AZO films crystallized preferentially along the (100) direction as a result of doping with Al. The lowest resistivity of $4.5 \times 10^{-3} \Omega \text{cm}$ was observed for AZO films ~100 nm thick and grown with Al doping of 3.0 at. %.

In-doped (2 mol%) ZnO films on glass substrates were deposited using the spray pyrolysis method at 500 °C [13]. Samples were annealed under N$_2$ atmosphere between 100 and 600 °C for 5 min. XRD spectra indicated that the c-axis intensity to a-axis is slightly increased with the increase in annealing temperature, along with degree of crystallinity. Average surface roughness and average grain size were almost constant with increasing annealing temperature. Electrical resistivity decreased to $4.0 \times 10^{-2} \Omega \text{cm}$ when electron mobility and carrier concentration were 3.0 cm V$^{-1}$s$^{-1}$ and $7.0 \times 10^{19}$ cm$^{-1}$ respectively at annealing temperature of 450 °C.

Effect of variation of precursors on the c-axis orientation in pure and doped ZnO films deposited using spray pyrolysis technique was also studied [14]. These authors used aluminium nitrate and aluminium chloride as precursors for aluminium doping and also the different ratios of the ZnO precursors were tried (zinc chloride, zinc acetate and the ratio of zinc chloride and acetate). Films obtained from zinc chloride and zinc chloride/zinc acetate ≥0.5 had the largest crystalline sizes of 46 nm. The preferential orientation changed by changing the deposition condition viz., the substrate temperature, precursor solution composition or by introducing aluminium.
In yet another work, the dependence of electrical and optical properties of the temperature of substrate and target had been studies for Al- and Si- doped ZnO films, prepared using R.F. sputtering [15]. The lowest resistivity was obtained for substrate temperature in the range 180-220°C, mainly due to the improvement in crystallinity.

When comparing the resistivity of undoped ZnO thin films with Sn-doped ZnO thin films, it is found that the resistivity decreases. The decrease in resistivity may be explained as follows: since the ionic radius of tin \((r_{Sn^{4+}} = 0.38 \text{ Å})\) is smaller than that of the zinc ion \((r_{Zn^{2+}} = 0.6 \text{ Å})\), tin atoms doped into ZnO lattice act as donors by supplying two free electrons when the Sn\(^{4+}\) ions occupy Zn\(^{2+}\) ion sites. This in turn increases the free carrier concentration and hence, decreases the resistivity. The mechanism of the conduction can be described by the following equation:

\[
\text{SnO}_2\text{ZnO} \rightarrow \text{Sn}^{II}\text{Z}_n + \text{O}^{I}_o + \frac{1}{2}\text{O}_2 + 2\text{e}^l \quad (5.1)
\]

Sn\(^{4+}\) ions substituted Zn\(^{2+}\) ions in the lattice induce positive Sn\(^{II}\)\_Zn charges in the material. In order to maintain electrical neutrality, two negative electrons are induced to compensate the excess positive charges. Hence the resistivity decreases due to increasing free electrons in the film. Sn-doped ZnO (SZO) films, prepared using SILAR technique, were used as NO\(_2\) gas sensor and the results were reported [16]. Experimental results showed that the sensitivity of ZnO films increased on Sn doping.

Y. Caglar et al. [17] prepared undoped and SZO thin film using spray pyrolysis. Effect of Sn doping on structural and morphological properties of ZnO films was investigated using XRD and SEM. XRD patterns confirmed that the film had polycrystalline nature\((100),(002),(101), (102)\) and \((110). While pristine ZnO had the \((101)\) preferred orientation, Sn doped ZnO films were having \((002)\) orientation.

Nano structured pure and SZO synthesized for gas sensing application by thermal evaporation technique [18]. SEM images indicated change in the growth pattern from nano-wire [for pure ZnO] to tetra pods [for SZO]. The response towards different gases for Pure and SZO were recorded. Pure ZnO nano-wires exhibit selective response towards acetone vapour while for SZO, the response decreased. The deviation from stoichiometry and the morphology of ZnO are probably responsible for such a difference in gas response. Pure and Sn doped ZnO showed nearly same crystallite size.
M.R Vaezi et al. [19] reported the preparation of SZO films from a Zinc complex solution containing tin ions on to pyrex glass substrate using two-stage chemical deposition process. Resistance of the undoped ZnO films is high and reduces to a value 4.2x10^2 ohm cm when 2.5% Sn is incorporated. All of the ZnO films have above 80% transmittance in a rage of 400-700 nm. The optical energy gap (E_g) increases with the increase of doping amount of Sn in the films. It varied from 3.05 to 3.18 eV depending on the amount of Sn incorporated.

NO_2 gas sensor was fabricated by successive ionic layer adsorption and reaction (SILAR) technique and rapid photo thermal processing (RPP) of the SZO film [20]. Influence of variation of Sn concentration in the chemical bath and the RPP temperature on NO_2 sensitivity of thin film sensor elements was investigated in this work. Higher sensitivity was obtained at 5–10 at %, Sn concentration in the solution of ions and RPP temperature of 550–650°C. Another report was on preparation of Al or Sn doped ZnO films using spray pyrolysis [21]. These films were deposited on either indium tin oxide (ITO) coated or bare glass substrates. ZnCl_2, AlCl_3 and SnCl_2 were used as precursors. The properties of the films have been studied before and after annealing 4 h at 400°C in vacuum (10^-3 Pa). Here the lowest electrical resistivity achieved was due to doping with Sn (3x10^3 Ohm cm) and this was further lowered by 2-3 order of magnitude after the vacuum annealing (0.9 Ohm cm).

Paraguay et al. [22] prepared sprayed ZnO film and doped with different elements, Al, In, Cu, Fe and Sn. Sensitivity of the films were studied in two steps: first as a function of their temperature (435-675 K) for a fixed ethanol concentration (40 ppm) and the next case was as a function of ethanol concentration (4-100 ppm) for a fixed temperature (675 K). A better sensitivity can be observed for Sn- and Al-doped films, with a dopant/Zn ratio of 0.4 at. % and 1.8 at. %, respectively.

Bougrene et al. deposited ZnO:Sn films using spray pyrolysis technique on glass substrates and physico-chemical properties of these films were studied [23] Crystallinity and optical transmittance improved on doping. Lowest resistivity obtained was 5x10^-2 ohm cm. Olvera and Maldonado reported the deposition of high quality ZnO:Ga films using CSP technique[24]. Two different precursors were used for the deposition. Lowest resistivity obtained was 4.5x10^-3 ohm cm and the average optical transmittance in the visible region was about 85 %.
5.2.1 Summary of best results

Different group tried to deposit ZnO films using different technique. Hahn et al. deposited highly conductive polycrystalline ZnO films using MOCVD technique with resistivity of the order of 3×10⁻⁴ ohm cm. Average optical transmittance was nearly 85%[25]. Minimum resistivity of 1.4×10⁻⁴ ohm cm was obtained with Al doping [26] by Jeong et al. These films exhibited an average of 95% in the visible region. Chen et al. could get lowest resistivity of 8.54×10⁻⁵ ohm cm in films deposited using PLD technique, which showed an average optical transmittance of 88% [27]. Chemical spray pyrolysis technique generally resulted in resistive films compared to the samples from physical method like sputtering and PLD. S.Major et al. [28] reported the lowest resistivity of 8.9×10⁻⁴ Ω cm in Indium-doped spray pyrolysed ZnO thin films. H. Gómez-Pozos et al. [29] recently achieved the lowest resistivity of Al –doped spray pyrolysed ZnO thin film (4.3×10⁻³ Ω cm). They achieved this by doping the samples using ‘Aluminum 2,4 pentanediionate’ followed by high temperature vacuum annealing treatment.

5.3 Experimental details

The ZnO films for doping studies were prepared using CSP technique. Spray solution was prepared by dissolving 0.3M of the Zinc acetate in the solvent containing equal volume of isopropyl alcohol and deionised water. The typical value of pressure used for this deposition was ~5psi and the substrate temperature was kept at 450±5°C. The sample is removed easily after the deposition and cooled using post deposition treatment called ‘Zero-energy process’ (Discussed in the chapter-3, Secion-3.2.2). For further reduction of the resistance material like Aluminium, Indium and Tin were doped with different doping method (In-situ and Ex-situ doping ). The structural, optical and electrical properties of the samples was studied by X-Ray diffraction (XRD), Spectrophotometer and Photoluminescence (PL) (‘as described in chapter (4) Section (4.3.1). The carrier concentration and Hall mobility were measured using the Hall Effect instrument with magnetic field of 0.57T (Model-HMS-3000, ‘Ecopia’).

5.3.1 Ex-situ doping

In ‘ex-situ doping’, a thin layer of In/Sn was deposited over the undoped ZnO thin films using vacuum evaporation [Pressure ~ 2×10⁻⁵ mbar] method and this bilayer films were annealed in vacuum [Pressure ~ 2×10⁻⁵ mbar; Temperature-100 °C; Time- 60 min].
Different masses of In/Sn (2, 4, 6, 8 and 10 mg) were deposited over the surface of ZnO sample. These samples were annealed in vacuum for diffusing the In/Sn in to the ZnO layer. Evaporation of In/Sn and annealing did not affect thickness of the sample. The samples were named as Z-2mg-In, Z-4mg-In, Z-6mg-In, Z-8mg-In, Z-10mg-In [Indium doped samples] and Z-2mg-Sn, Z-4mg-Sn, Z-6mg-Sn, Z-8mg-Sn, Z-10mg-Sn[Tin doped samples] respectively.

5.3.2 In-situ doping

In order to reduce the resistivity further, Indium was doped by adding the required quantity of Indium nitrate in the spray solution itself and this was denoted as ‘in-situ doping’. Doping percentage of Indium was varied from 0.5 to 2.5% and the samples were named as Z-0.5In, Z-1In, Z-1.5In, Z-2In, Z-2.5In respectively. All other spray parameters are kept constant.

Next we tried the ‘In-situ doping’ of Aluminum, by adding the required quantity of aluminum 2,4 pentanedionate in the spray solution itself. Doping percentage of Aluminum was varied from 0.5 to 3.5% and the samples were named as AZ-0.5,A Z-1, AZ-1.5, AZ-2,A Z-2.5 respectively.

5.4 Results and discussion

5.4.1 Effect of Sn doping through ex-situ technique

5.4.1.1 Structural properties

X-ray diffraction patterns of undoped and doped ZnO thin films prepared at optimum parameters are exhibited in Fig 5.1 The diffraction peak corresponding to (002) orientation is located at $2\theta = 34.45^\circ$. It was observed that all the samples had the preferential orientation along (002) plane and intensity of peak corresponding to this orientation increased with Sn doping concentration. The c-axis of the grains became uniformly perpendicular to the substrate surface. No new phases were observed, even when the mass of evaporated Sn was increased up to 10 mg, indicating that incorporation of Sn neither could change the ‘wurtzite’ structure of ZnO nor resulted in the formation of SnO$_2$.

Mean crystallite size was calculated using the (002) diffraction peak using Debye-Scherrer formula, $D=\frac{9\lambda}{β\cos θ}$, [Where D is the diameter of the crystallite, λ wave length of CuKα line ($\lambda = 1.5404$ Å), β is the full width at half maximum in radians and θ is the
Bragg angle]. This result is depicted in Fig. 5.2. Bougrine et al. [23] reported that the peak intensity of the Sn doped ZnO films was higher than that of the undoped samples, and Sn doped ZnO films had (002) as the preferred orientation. However Navale et al. [18] reported that Sn doped ZnO thin films had (101) as the preferred orientation.

The crystallite size increases initially with the increase of Sn content and reached a maximum value of 38 nm and reduced afterwards (Fig. 5. 2). Probably there might be substitution of oxygen due to Sn anions in Zn sites, leading to a partial healing of the crystalline structure [23]. This can be also considered to be the ‘effect of crystallization process with doping’ [30].

Fig.5.1 XRD pattern of pristine and Sn doped [using Ex-situ method] ZnO thin films

Fig.5.2 Variation of crystallite size of Sn doped ZnO film with doping percentage
5.4.1.2 Optical properties

Optical absorption spectra were recorded in the wavelength region 200 -1200 nm. In order to determine the optical band gap, $(\alpha h\nu)^2$ against $h\nu$ graph was plotted (Fig. 5.3) as described earlier. The band gap of the pristine sample was 3.28 eV and remained almost the same for the doped samples too.

Fig. 5.3 $(\alpha h\nu)^2$ versus $h\nu$ graph for the Sn doped ZnO thin films

Fig.5.4 Transmission spectra of ZnO (Sn doped and pristine) thin films
Fig. 5.4 makes it clear that the percentage of transmission decreased with increasing the doping concentration. The sample ZnO-6mg-Sn attained transmission above 80%. In fact the ‘metal to oxygen ratio’ decided the transmission [31, 32]. If the sample is metal rich, it will have low transmission. Here it is quite clear that as doping percentage increased, the (Zn+Sn)/O ratio is also increased, leading to the reduction in optical transmission.

5.4.1.3 Electrical resistivity measurement

Electrical Resistivity measurements were carried out using two – probe method. The pristine sample had a resistivity of $2.8 \times 10^{-2} \, \Omega \text{ cm}$. When the doping percentage increased the resistivity decreased and ZnO-10mg-Sn had the lowest resistivity of $8 \times 10^{-3} \, \Omega \text{ cm}$. As pointed out in the many works [33,34] the main factor affecting the resistivity of sprayed ZnO thin films is zinc interstitial and /or oxygen vacancies and quantity of dopant diffused into the ZnO lattice. The decrease in the resistivity must be due to the donor action of tin, through replacement of Zn atoms and / or occupying the interstitial position.

![Graph showing variation of electrical resistivity](image)

**Fig. 5.5** Variation of electrical resistivity of Sn doped ZnO with doping percentage.

**5.4.2 Effect of ex-situ doping using Indium Diffusion**

**5.4.2.1 Structural properties**

Fig. 5.6 shows XRD pattern of the ZnO thin films doped with different indium concentrations. It was found that all the films had preferential orientation along (002) plane.
Zn can be easily substituted by In without any lattice distortion due to the similarity in their atomic sizes (Atomic radii of Zn and In atoms are $r_{Zn}^{2+}=0.074$ nm and $r_{In}^{3+}=0.080$ nm respectively). Hence one could state that, due to indium diffusion, oxygen concentration was also not varying much in the sample. Again, the doped samples maintained the (002) orientation, indicating that the c-axis of the grains became uniformly perpendicular to the substrate surface. In the case of indium doping also no new phases were observed, even when mass of evaporated In was increased up to 10 mg, indicating that incorporation of indium neither could change ‘wurtzite’ structure of ZnO nor resulted in the formation of $In_2O_3$ or $In_2S_3$.

![Fig.5.6 XRD pattern of pristine and In doped [Ex-situ method] samples](image)

When indium is incorporated into the ZnO thin films through ex-situ method, the crystallite size increased as the mass of the dopant increased from 2 mg to 6 mg. However when the mass of indium diffused was above 6 mg, reduction in the crystallite size was observed. Similar variation of crystallite size was observed in the case of tin diffusion and here the optimum mass was 8 mg.
Table 5.1 Variation of lattice parameters, strain, stress as a function of Ex-situ doping

<table>
<thead>
<tr>
<th>sample name</th>
<th>lattice parameters</th>
<th>Strain %</th>
<th>Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-In</td>
<td>3.24 8.22</td>
<td>1.60</td>
<td>-8.11 0.40</td>
</tr>
<tr>
<td>Z-2mg-In</td>
<td>3.26 8.22</td>
<td>1.60</td>
<td>0.25 -1.72</td>
</tr>
<tr>
<td>Z-4mg-In</td>
<td>3.29 8.18</td>
<td>1.69</td>
<td>-8.25 1.72</td>
</tr>
<tr>
<td>Z-6mg-In</td>
<td>3.33 8.13</td>
<td>1.63</td>
<td>-8.26 1.72</td>
</tr>
<tr>
<td>Z-8mg-In</td>
<td>3.25 8.18</td>
<td>1.59</td>
<td>-8.35 1.72</td>
</tr>
<tr>
<td>Z-10mg-In</td>
<td>3.23 8.16</td>
<td>1.59</td>
<td>-8.75 3.44</td>
</tr>
</tbody>
</table>

5.4.2.2 Optical properties

Optical absorption spectra were in the wavelength region 200 -1200 nm. In order to determine the optical band gap, $(\alpha h\nu)^2$ against $h\nu$ graph was plotted (Fig. 5.7). Pristine sample has band gap of 3.22 eV; however in the case of Indium doping, the band gap increased with doping percentage. Transmittance decreased at high doping level and this may be due to the increase in scattering of photon by crystal defects created by doping or probably due to the increase in the metal to oxygen ratio $(Zn+In)/O$ [35].

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![Fig. 5.7 $(\alpha h\nu)^2$ versus $h\nu$ graph of In doped [through Ex-situ method] samples](image-url)
5.4.2.3 Photoluminescence measurement

The luminescence of ZnO films typically has ‘near band edge emission’ and ‘blue-green emission’. Owing to these properties, ZnO can be used to make devices for UV or blue emission. Since these films find great application in the areas of optics and opto electronics, it is important to investigate the optical properties of ZnO films. Researchers have considered that the UV emission could be due to the excitonic transition. But still controversy exists in the explanation of the origin of blue-green emission.

Ortiz et al. reported the PL spectra of undoped and TbCl$_3$ doped ZnO films. The undoped film had emission at 510 nm, while doped sample exhibited the emission at 550 nm [36,37]. However the exact origin of the blue green emission (510 nm) was not given. This emission was assumed to be due to the transition within a self activated center formed by doubly ionized zinc vacancy and ionized zinc interstitial. Another detailed experimental evidence was given to explain the origin of blue green emission in ZnO phosphor powder [38]. It was suggested that the green emission was due to the recombination of electron in
the singly occupied oxygen vacancies (V$_{o}^+$) with photo excited holes in the valence band. Hur et al. discussed the variation in the PL emissions of ZnO due to different annealing conditions in air and found that the concentration of antisite oxygen increased when ZnO ceramics were in O-rich conditions [39]. It was also seen that, as the concentration of O-antisite increased, intensity of green emission also increased. Hence in this report, it was proposed that the green emission resulted from the transition from conduction band to the acceptor level of antisite oxygen. However band edge emission intensity reduced when ZnO was in O-rich condition. In an interesting paper, Lin et al. tried to explain the origin of blue-green emission, in undoped ZnO films [40]. In these samples, two emissions were observed with energies 3.18 eV and 2.38 eV. It was concluded that the green emission was corresponding to the local levels composed by oxygen antisites and the transition was from the conduction band to deep acceptor level of oxygen antisites (O$_{Zn}$).

The PL emission centered at ~510 nm [Blue-Green Emission (BGE)] is the characteristic emission of ZnO thin films. This emission is extremely broad and this might be due to phonon-assisted transition [41]. But the exact reason for this emission is not clearly understood. Ratheesh kumar et al. [35] concluded that this was due to the transition from conduction band to the acceptor level corresponding to the oxygen antisite [O$_{Zn}$].

![Fig.5.9 Photoluminescence spectra of Indium doped sample [Ex-situ doping]](image)
5.4.2.4 Electrical resistivity measurement

The undoped ZnO sample has resistivity of $2.4 \times 10^{-2}$ Ω cm. But in the case of samples which were doped using the ‘ex-situ method’, the resistivity decreased (Fig. 5.10) and the lowest resistivity of $8 \times 10^{-3}$ Ω cm was obtained for the sample Z-8 mg-In. Resistivity slightly increased as the mass of indium evaporated increased beyond 8 mg.

![Electrical Resistivity of Ex-situ doped Indium in ZnO thin films.](image)

Reason for the variation of resistivity can be explained using the results from XRD and PL analysis of doped samples. Here we find that there is no change in grain orientation due to ‘Ex-situ’ doping process as revealed by the analysis using XRD technique (Fig. 5.6). After the ex-situ doping of indium its (Zn+In/O) metal to oxygen ratio increased. Metal to oxygen ratio increases density of free carriers for conduction hence the reduction in resistivity. When the metal to oxygen ratio increased, the band edge emission also decreased [39]

5.4.3 Studies on samples doped with Indium through in-situ doping

5.4.3.1 Structural analysis

Fig.5.11 shows XRD pattern of pristine and in-situ doped samples with different Indium concentration. Pristine sample had only peak corresponding to (002) orientation [$2θ=34.42^\circ$]. But for the doped samples, another peak corresponding to the orientation of (101) also developed right from the Z-0.5-In onwards. On increasing the doping percentage further, the intensity of peak corresponding to the plane (002) decreased and that of (101)
increased. Finally for the sample Z-2.5-In, the (101) peak was the prominent one. Similar behaviour has been reported in many other works [35, 22].

Variation of crystalline size of the doped films, with doping concentration of indium, is shown in the Fig. 5.12. In the case of in-situ doping, the crystallite size decreased from 30 nm to 20 nm when the doping concentration of Indium increased.

Fig 5.11 XRD pattern of pristine and In doped [In-situ] ZnO thin films

Fig. 5.12 Crystallite Size of Indium doped ZnO thin films, through in-situ method.
Table 5.2 Lattice parameters of In-situ doped In-ZnO thin films.

5.4.3.2 Optical studies

Optical absorption and transmission spectra were recorded in the wavelength region of 350–1200 nm. Optical band gap of the samples is determined using the following equation,

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

(5.2)

Where \(h \nu\) is the photon energy, \(E_g\) is the optical band gap and \(A\) is the constant. In order to determine the optical band gap, \((\alpha h \nu)^2\) vs. \(h \nu\) graph was plotted (Fig.5.13). No significant variation in the band gap was observed. In the case of samples which had undergone in-situ doping, optical transmission was above 80% in the visible region (Fig.5.14)

![Graph showing (\(\alpha h \nu\))^2 versus \(h \nu\) for In doped films](image)

Fig.5.13 \((\alpha h \nu)^2\) versus \(h \nu\) graph for the In doped films [in-situ method]
Fig. 5.14 Transmission spectra of In-ZnO thin films [in-situ doped]

5.4.3.3 Photoluminescence Measurements

Interestingly the BGE is not present in the case of samples doped through the in-situ process and it is this set of samples which exhibits the lowest resistivity after doping. In-situ doping results in a clear variation of grain orientation from (002) to (101); more than that, just by introducing 1% of indium itself, the resistivity comes to the lowest value of $2 \times 10^{-3}$ ohm.cm. Similar observation had been reported by several groups in connection with indium doping in ZnO [42, 40, 22].

Fig. 5.15 PL Spectra of In-situ doping of Indium
5.4.3.4 Electrical resistivity measurement

In the case of in-situ doping also resistivity of the samples decreased on increasing the doping concentration up to 1% of indium and it was $2 \times 10^{-3}$ Ω cm. This is probably one of the lowest reported resistivity values obtained for Indium doped spray pyrolysed ZnO thin films; it is to be specifically noted here that the samples prepared in our lab are having area of 30 cm$^2$. Moreover the resistivity is uniform over ~80% of the area of the sample (Fig.5.17). In the case of doping of sprayed ZnO samples using indium, Benouis et al. recently reported that 2% doping resulted in the resistivity of $6 \times 10^{-3}$ Ω cm [43] while Kenji Yoshino et al.[44] reported the lowest resistivity of $4 \times 10^{-2}$ Ω cm could be achieved in Indium doped samples by annealing in vacuum at 450°C.

Fig.5.16 Electrical resistivity of ZnO thin film in In-situ doping of Indium

Fig.5.17 Surface mapping of sheet resistance of sample over an area of 30 cm$^2$ (Z-1%In) The blue region indicates resistance in the range, 34 Ω to 37 Ω / square while the red region indicates the resistance in the range, 37 Ω to 40 Ω / square. Maximum variation ~15%].

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5.4.4 In-situ doping of Aluminum

5.4.4.1 Structural Analysis

Fig. 5.18 depicts XRD patterns of AZO having different doping percentages. All the AZO samples are having (002) peak (angle 34.42°) as the prominent one. Intensity of (002) plane increases up to 2.5% of doping and decreased on further increase in doping percentage. However, no extra phases, corresponding to either aluminum or aluminum oxide, were detected.

![XRD pattern of AZO at different doping percentages](image)

Table 5.3 preferentially oriented planes and grain size variations of AZO at different doping percentages:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Plane</th>
<th>FWHM</th>
<th>Crystalite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>(002)</td>
<td>0.26</td>
<td>31.9</td>
</tr>
<tr>
<td>AZO-0.5</td>
<td>(002)</td>
<td>0.30</td>
<td>27.6</td>
</tr>
<tr>
<td>AZO-1</td>
<td>(002)</td>
<td>0.22</td>
<td>37.8</td>
</tr>
<tr>
<td>AZO-2</td>
<td>(002)</td>
<td>0.22</td>
<td>37.1</td>
</tr>
<tr>
<td>AZO-2.5</td>
<td>(002)</td>
<td>0.23</td>
<td>36.3</td>
</tr>
<tr>
<td>AZO-3</td>
<td>(002)</td>
<td>0.34</td>
<td>24.7</td>
</tr>
</tbody>
</table>

Fig.5.18 XRD pattern of ZnO at different Aluminium concentration.
When the doping percentage of aluminium increased from 0.5 % to 2.5 %, the grain size also increased from 27 nm to 36 nm and further increasing of doping percentage resulted in decrease of crystallite size

SEM analysis (Fig 5.19) clearly shows that there is a change in the surface morphology of ZnO films due to the presence of Aluminium. Pristine film has hexagonal grains on the surface. But as the doping percentage of Al increased, the structure becomes ‘triangular shaped’ and this resembles the AZOI thin film samples deposited using a dc-magnetron sputtering [45].

![SEM micrograph of films with different doping percentage Of AZO](image)

Fig.5.19 SEM micrograph of films with different doping percentage Of AZO

**5.4.4.2 Optical studies**

Optical absorption and transmission spectra were recorded in the wavelength region of 300–1100 nm. In order to determine the optical band gap, \((\alpha h\nu)^2 vs h\nu\) graph” was plotted. Plot of \((\alpha h\nu)^2 vs h\nu\) is linear over a wide range of photon energies, indicating direct band to band transition. Values of the band gaps are given in the table 5.4 which shows that it increased from 3.25 eV to 3.30 eV after the doping. Fig. 5.20 shows that all the films have transmission above 80%.
Fig. 5.20 Transmission spectra of pristine and AZO samples.

In the case of a transparent conducting oxide film, optical transmission as well as electrical conductivity has to be as large as possible for the application in the optoelectronic devices. ‘Figure of merit’ is given by the expression, $\Phi_{TC} = T/R_s$ where $R_s$ is the sheet resistance of the film and $T$ is the optical transmittance [31].

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band Gap(eV)</th>
<th>Figure of merit($\Omega^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>3.25</td>
<td>9.4×10^{-1}</td>
</tr>
<tr>
<td>AZO-0.5</td>
<td>3.28</td>
<td>4.1×10^{-4}</td>
</tr>
<tr>
<td>AZO-1</td>
<td>3.29</td>
<td>6.0×10^{-4}</td>
</tr>
<tr>
<td>AZO-2</td>
<td>3.31</td>
<td>1.2</td>
</tr>
<tr>
<td>AZO-2.5</td>
<td>3.30</td>
<td>2.4</td>
</tr>
<tr>
<td>AZO-3</td>
<td>3.30</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 5.4 Variation of Band gap and figure of merit in AZO-I thin film with different doping concentration

This parameter was calculated for all the samples at wavelength $\lambda=540$ nm and it is given in the table. 5.4. The highest value of $\Phi_{TC}$ [2.4 $\Omega^{-1}$] was obtained for AZO films doped with 2.5% of aluminum. AZO-2.5 samples have highest transmittance in the whole visible
region. The transmittance of AZO is better than SZO and IZO. Hence from the studies, it was observed that the film could be used as transparent conducting electrode for device like solar cells, flat panel displays etc.

5.4.4.3 Photoluminescence measurements

PL spectra, at room temperature, were recorded in the range of 350–625 nm. All the AZO-I samples showed two emission peaks centred at 377 nm and 520 nm (Fig. 5.21), in which the peak at 377 nm was corresponding to the NBE while the one at ~520 nm was corresponding to the characteristic BGE.

Fig. 5.21 Photoluminescence spectra of pristine, AZO samples with different doping concentration.

As stated earlier, PL emission centred at ~ 520 nm [BGE] is characteristic emission of ZnO thin films. This emission was extremely broad and might be due to phonon-assisted transition. Bylander put forward a model, suggesting that the emission was due to electronic transition from interstitial Zn to Zn vacancy [46]. It was also seen that the intensity of NBE emission increased considerably after the hydrogen treatment. Lin et al. tried to explain the origin of BGE, in undoped ZnO thin film [47]. In these samples, two emissions were observed with energies 3.18 eV and 2.38 eV.

PL properties depend on the growth conditions, including growth temperature and ambience. In our case, the growth temperature is kept constant and hence the film properties depend on the ambient condition. In CSP technique there is strong possibility of O-rich
condition and oxygen is incorporated in the sample from the atmosphere. PL spectra of these samples also have both UV [NBE] and blue-green emission [BGE]. In the case of ZnO, donors are oxygen vacancy \([V_o]\) and Zinc interstitial \([Z_{ni}]\). When the sample is kept in the oxygen atmosphere [which usually happens in CSP technique] the oxygen concentration increases. In this condition, quantity of oxygen diffusing into the sample increases reducing oxygen vacancies. Hence the Oxygen antisite \((O_{zn})\) in the oxygen rich condition is easily formed from the interstitial oxygen \((Oi)\) and zinc vacancies \((V_{zn})\). More over Oxygen antisite has relatively low formation energy \([48]\).

In CSP method, as air is used as the carrier gas, there is every chance for the enhancement of concentration of oxygen antisite in ZnO film. This condition results in the increase of BGE intensity which is due to the transition from the conduction band to antisite oxygen \((O_{zn})\). However intensity of the BGE decreased with the increase in the doping percentage of aluminium. When the Aluminium was doped in the film, it was assumed that some of aluminium atoms occupied the zinc lattice site, reducing the probability of oxygen occupying the zinc site. Hence the density of oxygen antisite would be less in the film. This might be the reason for the decrease in the intensity of BGE due to doping. Resistivity of the film decreased with aluminium doping at lower concentration, which proved the occupancy of Aluminium at zinc site. After reaching the optimum percentage of doping, intensity of this peak started increasing. It is also worth mentioning here that the resistivity became minimum at the optimum doping percentage.

5.4.4.4 Electrical studies

Electrical measurements were done employing ‘two probe technique’ and for this two electrical contacts using silver paint [in the form of two end contacts having distance of 1cm between them] were used. In this study, the sheet resistivity is calculated by the following equation

\[
\rho = R_s d.\]

Where \(\rho\) is the resistivity, \(R_s\) is the sheet resistance \((\Omega/sq)\) and \(d\) is the sample thickness (nm). The undoped ZnO sample had resistivity of \(2.4 \times 10^{-2} \Omega\) cm. After doping, resistivity of the sample decreased and Fig. 5.22 shows that the lowest resistivity of \(1.5 \times 10^{-3} \Omega\) cm is obtained for AZO-2.5 sample. Four probe measurements were also in good agreement with the electrical resistivity values measured using two probe method \((1.2 \times 10^{-3} \Omega\) cm).
After doping, resistivity of the AZO thin films decreased due to the gradual replacement of Zn$^{2+}$ ions by Al$^{3+}$ ions, releasing a free electron to the conduction band for every Al ion incorporated into the lattice. In order to verify this, Hall measurement was conducted on the doped samples. This clearly proved that carrier concentration in doped samples was increasing as doping concentration increased. In addition to this, the Hall measurement has also indicated that the mobility of carriers was increasing up to the optimum doping concentration (Table 5.5). Hence the increase of carrier concentration and mobility resulted in the decrease of resistivity of the doped samples. However carrier concentration and Hall mobility are increasing only up to the doping percentage of 2.5% after which both start decreasing. Enhancement of concentration of aluminium atoms in the film beyond the optimum value [2.5%] may be resulting in the action of these dopant atoms as ‘scattering centres’ [49], leading to the lower carrier mobility.

Table 5.5 Hall co-efficient, mobility and carrier concentration of AZO samples with different percentage of doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Carrier concentration (cm$^{-3}$)</th>
<th>Sheet carrier concentration (cm$^{-2}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Hall Co efficient (cm$^3$/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO-1</td>
<td>-1.326E+19</td>
<td>-1.326E+15</td>
<td>1.601E+01</td>
<td>-4.707E-01</td>
</tr>
<tr>
<td>AZO-2</td>
<td>-1.473E+19</td>
<td>-1.473E+15</td>
<td>1.622E+01</td>
<td>-4.239E-01</td>
</tr>
<tr>
<td>AZO-2.5</td>
<td>-1.866E+19</td>
<td>-1.866E+15</td>
<td>1.655E+01</td>
<td>-3.346E-01</td>
</tr>
<tr>
<td>AZO-3</td>
<td>-1.625E+19</td>
<td>-1.625E+15</td>
<td>1.191E+01</td>
<td>-3.840E-01</td>
</tr>
</tbody>
</table>
Fig. 5.22 Variation of electrical resistivity of AZO thin film with doping percentage.

Fig. 5.23 Surface mapping of sheet resistance of AZO-2.5 sample over an area of 30 cm² (Z-2.5%Al). The blue region indicates resistance in the range, 30Ω to 33 Ω / square while the navy blue region indicates the resistance in the range, 33Ω to 36 Ω / square.
5.4.4.5 Annealing Effect

In order to reduce the resistivity of doped film further, the film having the lowest resistivity [Z-2.5Al] was annealed at 450°C for 2 hours at pressure of 2×10⁻⁵ mbar, with heating and cooling rate as 5°C/min. Crystallinity improved after the annealing. Electrical resistivity also reduced drastically by one order, to 6×10⁻⁴ Ω cm. The reason for the reduction of resistivity may be attributed to desorption of oxygen leading to the annihilation of the oxygen acceptor state in the sample [41].

Fig.5.24 Transmission spectra of AZO and AZO- annealed samples.

Fig.5.24 shows that the transmission spectrum of AZO film before and after vacuum annealing. Transmission in the NIR region considerably decreased after the vacuum annealing. This is probably due to the free carrier absorption, a phenomenon that is common in all transparent conductors with higher carrier concentration [51]. The absorption in NIR region is usually not seen in ZnO films and this makes it difficult to do ‘laser scribing’ using IR lasers. This results hints that this will become possible provided we fully optimise the NIR absorption.

5.5 Conclusions

Large area Zinc oxide thin films having good opto-electronic properties can be prepared using CSP technique through optimisation of deposition parameters and proper
doping. In the present work, ZnO films were doped with tin through thermal diffusion. Successive annealing 100 °C in vacuum resulted in diffusion of the whole tin in to the sample. There is small variation of band gap after the doping. Resistivity of the sample reduced from $28 \times 10^{-3} \, \Omega \, \text{cm}$ to $8 \times 10^{-3} \, \Omega \, \text{cm}$. Transmittance of the sample decreased when the doping percentage increased.

Doping using Indium was carried out in two ways such as in-situ as well as ex-situ method. In-situ doping using Indium is an excellent method for enhancing the conductivity of the sample. Incorporation of 1% Indium through in-situ method resulted in giving the lowest resistivity of $2 \times 10^{-3} \, \Omega \, \text{cm}$ and $>80\%$ transmission in visible region. PL analysis also supported the results from electrical characterisation studies of the samples.

Aluminum was doped by adding the required quantity of aluminum 2,4 pentanedionate in the spray solution itself [In-situ method]. Doping percentage of Aluminum was varied from 0.5 to 3.5%. Samples doped with aluminium in the range 2 to 2.5 % had lowest resistivity of $1.5 \times 10^{-3} \, \Omega \, \text{cm}$ [having large area- 30cm$^2$]. Annealing of these samples in vacuum further lowered the resistivity [$6 \times 10^{-4} \, \Omega \, \text{cm}$], with optical transmittance [in visible region] remaining in the range 85 to 90%.

Transmission in the NIR region decreases after the vacuum annealing; this is common in all other transparent conductors [like ITO] with higher carrier concentration. Room temperature PL revealed that the intensity of the blue-green emission (520 nm) decreased in these samples. Lowest intensity for the PL emission was also obtained for the sample having the optimum doping. The ‘zero-energy process’ was found to be very useful to large area samples too and hence suited for photovoltaic device applications.

References
Chapter 5

Effect of doping ..... 


