Using dual acceptor co-doping method, nitrogen and phosphorus co-doped ZnO films (NPZO) were fabricated. The doping concentration was varied from 0.25 to 1.25 at.% of N and P. The effects of N-P doping on the structural, electrical, and optical properties of NPZO films were investigated in detail using various characterization tools. A p-n junction was fabricated using p-type NPZO and n-type aluminium doped ZnO (AZO). Diode ideality factor was calculated from the slope of the forward bias lnI Vs V curve and found to be 3.16.
7.1 Introduction

Majority of the familiar and extensively used TCO thin films such as ZnO, SnO$_2$, ITO etc., show n-type conductivity, but their parallel p-type counterparts are amazingly missing for a longer period. Therefore, extensive attempts have been made for developing p-type TCOs having good applications. The most renowned case is p-type ZnO, which is intensively reported during recent years.

Usually, pure ZnO shows n-type conductivity [1]. The n-type carrier concentration in pure ZnO can be further increased using the donor dopants like B, Al, Ga and In [2]. In contrast, p-type doping of ZnO remains as a challenge [3-6]. Various approaches have been anticipated to obtain p-type ZnO, among which nitrogen doping is confirmed to be the best one [3-6]. The p-type conductivity achieved by nitrogen doping in ZnO nanostructures has gained particular importance [7]. Co-doping with suitable elements is another method to obtain good p-type conductivity in ZnO [8]. The acceptor atoms and donor atoms with a ratio of 2:1 are doped simultaneously in this technique. Co-doping method was theoretically proposed by Yamamoto and Yoshid [9]. But co-doping method may also result in self-compensation effect because of the presence of donor atoms. Another alternative method for the successful realisation of p-type ZnO is the dual acceptor co-doping method introduced by Krtschil et al [10].

It is believed that in dual acceptor co-doping method, as both the dopants hold acceptor properties, self-compensation can be restricted and also helps in nourishing better hole concentration [11-13]. In the present work this technique was adopted and simultaneous doping of group-V elements phosphorus and nitrogen in ZnO was attempted to obtain better p-type characteristics.
7.2 Experimental

The same precursor solution was prepared and all spray parameters were kept the same as in the case of nitrogen doping, which is described in the previous chapter. The dopant sources for phosphorus and nitrogen, were di-phosphorus pentoxide (Merck, extra pure, 99.9%, Germany) and ammonium acetate (Sigma-Aldrich, 99.5%, Germany) respectively. The doping concentrations of P and N were kept as the same and samples were prepared for different concentrations varying from 0.25–1.25 at. % for both nitrogen and phosphorus. The prepared precursor solution was sprayed uniformly upon ultrasonically cleaned soda lime glass substrates for 10 minutes. The deposited thin film samples were named as NPZO (0.25), NPZO (0.50), NPZO (0.75), NPZO (1.0), and NPZO (1.25). Pure ZnO sample was also prepared. The detailed analysis of the structural, morphological, electrical and optical properties of the samples was done.

7.3 Structural and morphological characterization

Figure 7.1 shows the XRD patterns of the prepared samples. Intense (002) peaks are observed in all the samples. These sharp intense peaks confirm the good crystalline nature of the samples. It is to be noted that doped samples exhibit better intensity along (002) plane than the pure one. A shift is noted in the position of (002) plane due to doping. There is a slight increase in intensity up to the doping concentration of 1 at.% of nitrogen (N) and Phosphorus (P) and then there is a decrease at 1.25 at.%.
Crystallite size was calculated for the samples using Scherrer formula. The lattice constant 'c', the average uniform strain $\varepsilon_{zz}$ and the stress developed in the sample ($\sigma_{film}$) were calculated. Table 7.1 gives information on the variation of different parameters due to doping. Variation of crystallite size and stress with doping is shown in Fig. 7.2.

**Table 7.1** Details of Structural analysis from X-ray diffraction of pure and NPZO samples

<table>
<thead>
<tr>
<th>Doping concentration (at.%)</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Strain</th>
<th>Stress(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.314</td>
<td>c=5.213</td>
<td>$1.536 \times 10^{-3}$</td>
<td>-0.696</td>
</tr>
<tr>
<td>0.25</td>
<td>28.72</td>
<td>c=5.218</td>
<td>$2.574 \times 10^{-3}$</td>
<td>-1.167</td>
</tr>
<tr>
<td>0.5</td>
<td>46.27</td>
<td>c=5.219</td>
<td>$2.689 \times 10^{-3}$</td>
<td>-1.219</td>
</tr>
<tr>
<td>0.75</td>
<td>48.60</td>
<td>c=5.220</td>
<td>$2.881 \times 10^{-3}$</td>
<td>-1.306</td>
</tr>
<tr>
<td>1.0</td>
<td>47.28</td>
<td>c=5.227</td>
<td>$4.1881 \times 10^{-3}$</td>
<td>-1.899</td>
</tr>
<tr>
<td>1.25</td>
<td>47.275</td>
<td>c=5.228</td>
<td>$4.419 \times 10^{-3}$</td>
<td>-2.004</td>
</tr>
</tbody>
</table>
Fabrication and characterisation of n-AZO/p-NPZO homo junction diode

**Fig. 7.2** Variation of crystallite size and stress of pure and NPZO samples with doping

SEM analysis of selected samples NPZO (0.75) and NPZO (1.0), indicating better p-type conductivity was done and is shown in Fig. 7.3 (a) and (b). Nanometer-sized grains of irregular shapes are observed over the substrate surface in (a). On increasing the doping concentration to 1at.% of N and P, a change in shape and distribution of the grains is noticed. Now the film surface is composed of more uniform distribution of dense grains.

**Fig. 7.3** SEM images of (a) NPZO (0.75) and (b) NPZO (1)
7.4 Electrical characterization

Electrical properties were analyzed using Hall effect measurements. The measured values of carrier concentration, hall mobility and resistivity are tabulated in Table 7.2. Hall measurements revealed that samples NPZO (0.75), NPZO (1.0) and NPZO (1.25) exhibit p-type conduction. For p-type samples minimum value of resistivity ($\rho$) of 3.07 ohm-cm is obtained with carrier concentration (CC) of $2.012 \times 10^{18}$ cm$^{-3}$ for NPZO (0.75). For the other p-type samples, an increase in resistivity is noticed, when the N-P doping concentration is increased further above 0.75 at.%. Phonon scattering and ionized impurity scattering taking place at higher doping concentration is leading to increased resistivity beyond optimum doping concentration. A detailed study of the formation of p-type NPZO was done by Tian and Zhao [14]. P occupies the Zn site ($P_{Zn}$), whereas N occupies the O site ($N_O$) resulting in the formation of a neutral passive $P_{Zn}$-$3N_O$ complex forming a supplementary completely occupied impurity band above the valance band maximum (VBM). When additional N atoms are added into the system with the $P_{Zn}$-$3N_O$ defect complex, more energetically favoured $P_{Zn}$-$4N_O$ complex acceptors are created. As a consequence, the electrons transit from the impurity band which lowers the ionization energy and the p-conduction arises from the $P_{Zn}$-$4N_O$ acceptor complex.

Activation energy for the sample NPZO (0.75) was calculated for two different ranges of temperature. The obtained values are 0.1696 and 0.0779 eV in the temperature ranges 380 to 440K and 305 to 380K respectively. Figure 7.4 shows the Arrhenius plot drawn to calculate the thermal activation energy for electrical conduction.
Table 7.2 Electrical properties of pure and NPZO samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier concentration (\text{cm}^{-3})</th>
<th>Resistivity (\Omega\text{.cm})</th>
<th>Mobility (\text{cm}^2\text{V}^{-1}\text{s}^{-1})</th>
<th>Carrier type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>2.15 (\times) 10^{18}</td>
<td>2.079</td>
<td>1.396</td>
<td>N</td>
</tr>
<tr>
<td>NPZO (0.25)</td>
<td>3.92 (\times) 10^{18}</td>
<td>1.29</td>
<td>1.232</td>
<td>n</td>
</tr>
<tr>
<td>NPZO (0.5)</td>
<td>4.54 (\times) 10^{18}</td>
<td>1.1</td>
<td>1.29</td>
<td>n</td>
</tr>
<tr>
<td>NPZO (0.75)</td>
<td>2.012 (\times) 10^{18}</td>
<td>3.07</td>
<td>1.01</td>
<td>p</td>
</tr>
<tr>
<td>NPZO (1.0)</td>
<td>9.657 (\times) 10^{17}</td>
<td>22.46</td>
<td>0.29</td>
<td>p</td>
</tr>
<tr>
<td>NPZO (1.25)</td>
<td>4.569 (\times) 10^{17}</td>
<td>52.5</td>
<td>0.26</td>
<td>p</td>
</tr>
</tbody>
</table>

Fig. 7.4 Arrhenius plot for the determination of activation energy of NPZO (0.75)

7.5 Optical characterization

Room-temperature PL spectra of the samples recorded at an excitation wavelength of 370 nm are shown in Fig. 7.5. All samples exhibit near UV emission around 397 nm and a broad emission around 500 nm. There is also a weak emission around 466 nm, in all samples. The emission around 397 and 466 nm may be due to the transitions from various extended Zn, to valance band.
The emission around 500nm may be due to the emission from oxygen vacancy states.

![Fig. 7.5 PL spectra of pure and NPZO samples](image)

**Fig. 7.5 PL spectra of pure and NPZO samples**

Figure 7.6 shows the transmission spectra of the samples, an average transmission of 90% is shown by all the samples in the visible region. The \((hv)\) Vs \((\alpha hv)^2\) plot is presented in Fig. 7.7. The intercepts of this plot on the energy axis give the energy band gap of the material. The band gap decreases from 3.289 to 3.274 eV as doping concentration increases. Band gap values of NPZO samples are presented in Table 7.3. The theoretically proposed coupling mechanism between p-states of phosphorus and nitrogen and d-states of zinc may result in the formation of a defect band just above the valence band maximum (VBM). This proposed p-d coupling exchange interaction plays the major role in the lowering of band gap. [17]
Fabrication and characterisation of n-AZO/p-NPZO homo junction diode

Fig. 7.6 Transmission spectra of pure and NPZO samples

Fig 7.7 Band gap trend of NPZO samples

Table 7.3 Band gap values of NPZO samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPZO(0.25)</td>
<td>3.289</td>
</tr>
<tr>
<td>NPZO(0.5)</td>
<td>3.284</td>
</tr>
<tr>
<td>NPZO(0.75)</td>
<td>3.281</td>
</tr>
<tr>
<td>NPZO(1.0)</td>
<td>3.279</td>
</tr>
<tr>
<td>NPZO(1.25)</td>
<td>3.274</td>
</tr>
</tbody>
</table>
7.6 Thickness dependence of electrical properties of NPZO (0.75) samples

Better p-type conductivity is exhibited by the sample NPZO (0.75). The variation of electrical and optical properties of this sample with thickness was also studied. For this purpose NPZO (0.75) samples were prepared by changing the spray duration from 5 minutes to 20 minutes in equal step size.

Table 7.4 shows the variation of electrical properties of NPZO (0.75) samples with thickness. Surface roughness values obtained from ellipsometry measurements are also indicated. All samples are found to be exhibiting p-type conduction. Observed minimum resistivity of 2.32 Ω.cm is exhibited by the sample prepared for spray duration of 15 minutes.

Table 7.4 Variation of electrical properties and surface roughness values of NPZO (0.75) samples with thickness

<table>
<thead>
<tr>
<th>Spray Time (minute)</th>
<th>C.C (cm⁻³)</th>
<th>ρ (Ω.cm)</th>
<th>Mobility (cm²V⁻¹ s⁻¹)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.558 x 10¹⁸</td>
<td>4.007</td>
<td>1.01</td>
<td>350</td>
<td>25.47</td>
</tr>
<tr>
<td>10</td>
<td>2.012 x 10¹⁸</td>
<td>3.07</td>
<td>0.55</td>
<td>500</td>
<td>39.16</td>
</tr>
<tr>
<td>15</td>
<td>4.882 x 10¹⁸</td>
<td>2.32</td>
<td>0.335</td>
<td>665</td>
<td>46.53</td>
</tr>
<tr>
<td>20</td>
<td>5.486 x 10¹⁸</td>
<td>3.39</td>
<td></td>
<td>800</td>
<td>28</td>
</tr>
</tbody>
</table>

7.7 Thickness dependence of the optical properties of NPZO (0.75) samples

Transmission spectra (Fig.7.8) reveals an average transmission of 90% for the samples prepared for spray duration of 5 and 10 minutes and the percentage transmission is reduced to an average value of 85% in the other two samples in the visible region. From the absorption spectra (fig.7.9) it is seen that all samples display minimum absorption in the visible region.
Fabrication and characterisation of n-AZO/p-NPZO homo junction diode

**Fig. 7.8** Transmission spectra of NPZO (0.75) samples

**Fig. 7.9** Absorption spectra of NPZO (0.75) samples

Figure of merit was also calculated for the NPZO (0.75) samples using Haacke’s formula, and calculated values are presented in Table 7.5. Larger value of figure of merit is obtained for the sample prepared for the spray duration of 15 minutes and having a thickness 665nm.
Table 7.5 Variation of figure of merit of NPZO (0.75) samples with spray duration

<table>
<thead>
<tr>
<th>Spray duration(minute)</th>
<th>Figure of merit(Ω⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7.6 x 10⁻⁶</td>
</tr>
<tr>
<td>10</td>
<td>8.6 x 10⁻⁶</td>
</tr>
<tr>
<td>15</td>
<td>8.8 x 10⁻⁶</td>
</tr>
<tr>
<td>20</td>
<td>6.2 x 10⁻⁶</td>
</tr>
</tbody>
</table>

7.8 Fabrication of p-n junction diode

The transparent conducting oxide (TCO) based electronics has become a new class of materials for realizing active and passive components with better performance efficiency. Wide band gap TCO materials are of immense interest in this respect. They have the ability to combine the high or low conductivities with better visual transparency. TCOs can be grown efficiently as thin films and find a variety of applications including solar cells, transistors etc[18-23]. The p-n junction, which is the basic structure of solar cell, light-emitting diode, and diode laser, is seen in all types of transistors.

Using p-type NPZO and n-type ZnO:Al (AZO), a p–n junction was fabricated. The n-type ZnO: (Al-2 at. %) thin film was first grown on ITO coated glass substrate by spray pyrolysis at 450°C. The p-type ZnO (N-P-0.75 at. %) thin layer was grown at 425°C on the top of the n-type ZnO: (Al) layer through a shadow mask. The schematic representation of the diode and the Current-Voltage characteristics of the junction thus fabricated are shown in Fig.7.10.

The maximum forward to reverse current ratio is about 19 at 0.57 V. The turn on voltage is low and can be enhanced by decreasing the carrier concentration in the aluminium doped zinc oxide thin films. The diode ideality
Fabrication and characterisation of n-AZO/p-NPZO homo junction diode

The ideality factor was determined from the slope of the forward bias $\ln I$ vs. $V$ curve [24] using the equation given by

$$\text{Ideality Factor} (n) = \left( \frac{q}{kT} \right) \times \frac{dV}{d \ln I}$$

Where $k$ is the Boltzmann constant and $dV/d\ln I$ is the inverse slope of $\ln I$ vs. $V$ curve, which is shown in Fig. 7.12. The obtained value of ideality factor is 3.16. According to Sah-Noyce Shockley theory [25], in a p-n junction, the ideality factor is in between 1 and 2. The high value of the ideality factor obtained here may be due to the factors like the surface effect, charge carrier tunnelling between states in the band gap, the high injection condition that may happen even at comparatively low forward bias, inhomogenity of barrier height etc [24]

ZnO:Al thin films are degenerately doped when used as transparent electrodes. This results in the shifting of fermi level to near the conduction band and lead to the dropping of the turn on voltage of the developed device. Compared to aluminium doped zinc oxide thin films, undoped ZnO have lower carrier concentration. Use of un doped zinc oxide may improve the characteristics of the zinc oxide homo junction. Improving the interface between the p-type zinc oxide and the n-type zinc oxide would also enhance the features of the device.
Fig. 7.10 Structure of p–n junction and Current - Voltage characteristics of the junction

Fig 7.11. In I Vs. V plot for determining the ideality factor
7.9 Conclusion

Adopting the dual acceptor co doping method, nitrogen- phosphorus co doped ZnO thin films were fabricated at different doping concentrations of N and P. All samples indicated preferential growth along (002) plane. NPZO (0.75), NPZO (1) and NPZO (1.25) were found to be possessing p-type conductivity. Resistivity of 3.07 ohm-cm was exhibited by sample NPZO (0.75), with carrier concentration $2.012 \times 10^{18}$ cm$^{-3}$ and hole mobility 1.01 cm$^2$ V$^{-1}$ s$^{-1}$. Activation energy was calculated for this sample and the obtained values are 0.1696 and 0.0779 eV in the temperature ranges 380 to 440K and 305 to 380K respectively. Transmission studies revealed an average transmission of 90% for all NPZO samples, in the visible region. Thickness dependent variation of properties were studied on the selected p-type conducting sample NPZO (0.75). Lowest resistivity of 2.32 ohm-cm was obtained for the sample, prepared for a spray duration of 15 minutes. A p-n junction was fabricated using AZO (Al 2 at.%) and NPZO (N-P 0.75at.%), with maximum forward to reverse current ratio of about 19 at .57 V. Ideality factor of the diode was found to be 3.16. This larger value of ideality factor may be credited to the presence of interface defect states and higher carrier concentration in n-type ZnO.

7.10 References


Fabrication and characterisation of n-AZO/p-NPZO homo junction diode


*****