Melioration of Optical and Electrical Performance of Ga-N Codoped ZnO Thin Films

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Abstract: Transparent and conducting p-type zinc oxide (ZnO) thin films doped with gallium (Ga) and nitrogen (N) simultaneously were deposited on glass substrates by spray pyrolysis technique. Phase composition analysis by X-ray diffraction confirmed the polycrystallinity of the films with pure ZnO phase. Energy dispersive X-ray analysis showed excellent incorporation of N in the ZnO matrix by means of codoping. The optical transmittance of N monodoped film was poor but got improved with Ga-N codoping and also resulted in the enhancement of optical energy gap. Hole concentration increased with codoping and consequently, lower resistivity and high stability were obtained.

Keywords: Ga-N Codoping; p-type; Spray Pyrolysis; ZnO Thin Film.

1 Introduction

ZnO is a wide bandgap semiconductor (3.37 eV) with high exciton binding energy (60 meV), and its electrical and optical properties can be fine-tuned by making alloys with other metal oxides having different bandgaps [1, 2]. ZnO possesses better piezoelectric properties and high stability in hydrogen plasma. Also, it is non-toxic, of low cost, abundant, and biocompatible. The presence of some donor defects such as zinc interstitials and oxygen vacancies leads to n-type electrical performance of ZnO, and hence, p-type doping in ZnO is a difficult task. This could be due to hindrances such as the presence of self-compensating defects, deep acceptor levels, and low solubility of acceptors. Thus, even though group I and group V elements can be used as acceptors, obtaining highly conducting and stable p-type ZnO is more difficult. In spite of great attention paid by many researchers to achieve p-type ZnO thin films using acceptor dopants like nitrogen (N), arsenic (As), and phosphorous (P) [3–5], it was found that As and P form deep acceptors and hence cannot significantly contribute to p-type conductivity [6]. Theoretical calculations of electronic band structure predicted the suitability of N as shallow acceptor in ZnO [7]. Nitrogen, having some similarity with O in terms of atomic size and nearest neighbor bond length of 1.88 Å that nearly equals the Zn-O bond length of 1.93 Å, has been attracted the interest of many researchers [8, 9]. However, the p-type conduction obtained is not stable and even disappears over time [10]. In 2001, Yamamoto and Yoshida [11] theoretically proposed that codoping ZnO by donor-acceptor pair elements can improve the acceptor solubility and can make acceptor levels shallower because donor dopants playing as reactive codopant activate the incorporation of acceptors. Previously, some authors reported the efficacy of donor-acceptor pair codoping in achieving better p-type electrical conduction in ZnO [12–18].

Deposition and characterization of undoped and doped ZnO thin films have been extensively investigated by many material researchers. Numerous techniques have been employed in depositing ZnO thin films such as atomic layer deposition [19], chemical vapor deposition [20], pulsed laser deposition [21], spray pyrolysis [22], sputtering [23], and sol-gel technique [24]. Among these, spray pyrolysis has many advantages such as simplicity, low cost, possibility of mass production, and no need of vacuum at any stage. In order to establish p-type electrical conduction in ZnO, gallium (Ga)-N codoping was tried. The samples were deposited on glass substrates by spray pyrolysis technique, and the effect of variation in Ga concentration on the various physical properties of the films was investigated. Spray pyrolysis method was adapted for its merit in doping any element in any proportion by simply adding the soluble salt of the desired dopant in the required composition into the precursor solution at the time of preparation. Moreover, it is a versatile technique for the preparation of stable p-type ZnO thin films with excellent conductivity because of lower possibility of oxygen vacancy formation during film deposition.
2 Experimental Techniques

N monodoped and 1–3 at% Ga-N codoped ZnO thin films were deposited on ultrasonically cleaned glass substrates of dimension 2.5 cm × 7.5 cm maintained at a temperature of 400 ± 10°C by spray pyrolysis (Holmarc HO-TH-04, Holmarc Opto-Mechatronics Pvt. Ltd., Cochin, India) technique. The starting solution of concentration 0.4 M of zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] was used as the precursor. Details of the preparation of precursor solution for the deposition of ZnO were reported elsewhere [17]. N doping was achieved by adding ammonium acetate (NH₄C₂H₃O₂) in required quantity so as to make the N:Zn ratio in the precursor as 2:1 as optimized in our previous study [8]. Gallium nitrate (Ga(NO₃) was used as the source of Ga. Doping concentration of Ga in the solution (Ga/Zn) was varied from 1 to 3 at%. All the reagents were purchased from Alfa Aesar, USA. Air was used as the carrier gas, and the carrier gas pressure was 1.5 bar. The solution flow rate and duration were 2 mL/min and 2 min, respectively. The distance between the nozzle of the atomizer and substrate was kept fixed at 15 cm, and the substrate temperature was maintained at 400 ± 10°C. (All these deposition parameters were previously optimized.)

Rigaku Miniflex 600 X-ray diffractometer (Rigaku Asia Pacific PTE LTD, Singapore) was used to obtain X-ray diffraction (XRD) pattern of the deposited films using Cu-Kα (λ = 1.5406 Å) radiation in the 2θ range between 10° and 70°. Morphology and elemental composition of the films were analyzed with JEOL Model JSM-6390 scanning electron microscope (SEM) attached with JEOL Model JED-2300 operated at 20 keV (JEOL, USA). The optical transmittance spectra were obtained on a JASCO V-650 double beam spectrophotometer (Jasco, Japan) in the 300–900 nm spectral range. The optical gap was derived from this data. Various electrical parameters of the samples were obtained from Hall effect measurements in van der Pauw geometry using the Ecopia Hall Effect Measurement System (HMS-3000 VER 3.52, USA). All the characterizations were carried out at room temperature.

3 Results and Discussion

3.1 Structural Properties

The XRD profiles of N monodoped and 1–3 at% Ga-N codoped ZnO thin films deposited by spray pyrolysis technique are shown in Figure 1. All the films are polycrystalline, and the patterns fitted well into the hexagonal wurtzite structure (JCPDS Card No. 36-1451) without disturbing the ZnO wurtzite matrix. This is attributed to the successful incorporation of Ga and N in the host lattice. N monodoped film exhibited reflections along the (100), (002), (101), (110), and (112) planes with a preferential orientation along the (100) plane. The 1 and 2 at% Ga codoped films showed extremely strong preferred orientation along (002) plane, normal to the substrate surface with diminished intensity for the reflections already present in the monodoped film. Also, new peaks corresponding to reflections from the (102) and (103) planes appeared in the XRD pattern for these films. For 3 at% doping, XRD reflection intensity along the (100) and (101) planes had become comparable with that of the (002) plane. The diffraction peak intensities for different planes are different for different Ga doping concentrations, indicating that the growth of crystallites in various planes is different and hence the growth rate is anisotropic for films doped at different levels. Films with different dopants and doping level prefer different orientations for the growth of crystallites as the thermodynamics of growth of crystallites along different planes are different. The intensity of the diffraction peak depends on the occupancy of atoms in different Wyckoff positions of a unit cell and hence the lattice. During film formation, the physical and chemical interactions between various species present in the precursor affect the thermodynamic equilibrium and energy adsorption [25]. Because of this perturbation, there will be a change in the occupancy of atoms and hence in the total scattering from each crystal plane. Thus, the dopants and doping concentration strongly influenced the texture of the ZnO thin films. Moreover, surface affinity may be different from dopant to dopant for each plane [17], which will affect the growth of planes along different orientations. Many others observed changes in preferential orientation with doping and reported similar results [26, 27].

Quantitative analysis of the crystalline quality can be obtained by computing the average crystallite size of the as-prepared films using the Scherrer formula [28]:
where $0.9$ is the value of the shape factor, $\lambda (~1.5406$ Å) is the wavelength of the X-rays used, $\beta$ is the full-width at half maximum intensity in radians, and $\theta$ is the Bragg’s angle.

Dislocation density ($\delta$), defined as the length of dislocation lines per unit volume of the crystal [29] for the deposited films, was evaluated using the formula given below [30]:

$$\delta = \frac{1}{D^2}. \quad (2)$$

Average crystallite size and dislocation density evaluated for the most intense diffraction peak are presented in Table 1. All the films are nanocrystalline, and 1 at% Ga codoping resulted in an increase in crystallinity, whereas for higher doping concentration, crystallinity monotonously deteriorated. Defects and disorders introduced by doping might be the reason for the deterioration in crystallinity.

As the deposited samples assumed hexagonal wurtzite structure, lattice parameters ($a$ and $c$) and unit cell volume ($V$) can be evaluated using the following equations [31], and the results are presented in Table 1.

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (3)$$

$$V = \frac{\sqrt{3}}{2} a^2 c. \quad (4)$$

It was clear that the lattice parameters got elongated compared to bulk ZnO (JCPDS Card No. 36-1451), and hence, the unit cell expanded implying that the films are under stress arising from crystallite deficiency, defects, impurities, etc., or from growth parameters and also because of the incorporation of dopants in the lattice. The internal relaxation parameter ($u$) measuring the displacement of each atom with respect to the next along the $c$-axis and the bond length ($b$) were calculated using the equations given below [32], and the results are tabulated in Table 1. The results show that there is a deviation in the $u$ values for the samples under study from the ideal value of 0.375 for wurtzite crystal. Because of the strain experienced, bond length also increased from the ideal value 1.93 Å of Zn-O bond.

$$u = \frac{1}{3} \left( \frac{a^2}{c^2} \right) + \frac{1}{4}$$

and

$$b = cu. \quad (6)$$

### 3.2 Morphological and Compositional Analysis

The SEM images of the N monodoped and Ga-N codoped ZnO thin films are shown in Figure 2. The micrographs revealed the polycrystalline nature of the films and confirmed the uniform distribution of the grains over the substrate. Also, the grains are well connected. The energy dispersive X-ray (EDX) spectra shown in Figure 3 confirmed the presence of N in the monodoped film and Ga and N in the codoped films along with Zn and O. There is also no trace of any other impurity.

### 3.3 Optical Properties

Figure 4 shows the optical transmittance spectra of the samples measured over the 300–900 nm spectral range. The average transmittance in the near infrared-visible spectral region for the N monodoped film is below 70%, while for the codoped films, it was above 80%. With increase in Ga concentration, optical transmittance slightly decreased. The enhancement of average optical transmission for 1 at% Ga doped film could be due to the better crystallinity with textured growth normal to the substrate surface. Moreover, the film possessed smoother surface compared to monodoped film as evident from the higher amplitude of interference fringes present in the transmittance spectra. Thus, the observed variation in

### Table 1: Average crystallite size ($D$), dislocation density ($\delta$), lattice parameters ($a$ and $c$), unit cell volume ($V$), internal relaxation parameter ($u$), and bond length ($b$) of 0–3 at% Ga-N codoped ZnO thin films.

<table>
<thead>
<tr>
<th>Ga concentration (at%)</th>
<th>$D$ (nm)</th>
<th>$\delta$ ($\times 10^{15}$ m$^{-2}$)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ ($\times 10^{-30}$ m$^3$)</th>
<th>$u$</th>
<th>$b$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.91</td>
<td>2.28</td>
<td>3.2507</td>
<td>5.2364</td>
<td>47.92</td>
<td>0.378</td>
<td>1.979</td>
</tr>
<tr>
<td>1</td>
<td>24.97</td>
<td>1.60</td>
<td>3.2531</td>
<td>5.2403</td>
<td>48.03</td>
<td>0.378</td>
<td>1.980</td>
</tr>
<tr>
<td>2</td>
<td>20.89</td>
<td>2.29</td>
<td>3.2577</td>
<td>5.2428</td>
<td>48.18</td>
<td>0.380</td>
<td>1.982</td>
</tr>
<tr>
<td>3</td>
<td>16.34</td>
<td>3.75</td>
<td>3.2621</td>
<td>5.2456</td>
<td>48.34</td>
<td>0.379</td>
<td>1.988</td>
</tr>
</tbody>
</table>
optical transmittance might be the result of scattering of photons at the surface of the film itself. In the near ultraviolet region, all the films exhibited sharp absorption and got blue-shifted with increase in Ga concentration indicating bandgap broadening. Thickness of the deposited films was electronically calculated using the PARAV software [33], and the results are presented in Table 2.

According to the Tauc relation [34], absorption coefficient (α) varies with the incident photon energy (hv) as

$$\alpha = \frac{B}{hv} (hv - E_g)^n,$$

where $B$ and $n$ are constants independent of photon energy, $E_g$ is the optical energy gap, and $n$ is equal to 1/2 for direct gap materials and 2 for indirect transitions. As ZnO is a direct bandgap material, $E_g$ can be calculated as the intercept on the x-axis by extrapolating the linear portion of $(\alpha hv)^2$ versus $(hv)$ plots for the films as shown in Figure 5. The calculated values of energy gap are presented in Table 2. For the monodoped film, the energy gap value was estimated to be 3.25 eV, while for the codoped films, energy gap increased monotonously with increase in Ga concentration. This bandgap broadening with codoping was ascribed to the increase in carrier concentration as evident from the Hall measurement results (Table 3).

$$Figure 2: The SEM images of 0–3 at% Ga-N codoped ZnO thin films.$$

However, some researchers observed a decrease in bandgap energy with increase in hole concentration obtained by donor-acceptor pair codoping in ZnO thin film [12]. When the upper levels of the valence band are filled with holes, the energy needed to make transitions to the conduction band becomes equal to that of the electrons at the lower levels in the valence band, and hence, the effective bandgap blue-shifts. Moreover, the monotonous increase in optical energy gap at higher doping concentration may further attribute to the degraded crystallinity.

### 3.4 Electrical Properties

Results of Hall measurement are presented in Table 3. In order to investigate the stability of these films, we performed the same measurement after 30 days. The details are also presented in the same table. All the samples were p-type in nature. While N monodoped film was highly resistive, codoping resulted in comparatively lower resistivity. The decrease in resistivity with codoping was attributed
to the increased carrier concentration and mobility. The increase in hole concentration with Ga-N codoping is attributed to the better incorporation of N as acceptors at oxygen lattice sites (N\(_{ox}\)) in the host ZnO lattice. Because of the lower acceptor solubility and the comparatively deeper level of acceptors in the ZnO, the lesser number of holes will be donated by N, and a part will be used for the compensation of electrons provided by native defects such as zinc interstitials and oxygen vacancies, leading to poor electrical performance of N monodoped film. Moreover, increase in the Madelung energy with p-type doping makes the N doped film unstable. Bian et al. [13] reported a maximum hole concentration of 2.04 \times 10^{18} \text{ cm}^{-3} and a resistivity of 1.7 \times 10^{-2} \text{ \Omega cm} with In-N codoping, while Lu et al. [12] obtained a hole concentration of 2.27 \times 10^{17} \text{ cm}^{-3} with resistivity 57.3 \text{ \Omega cm}.

The p-type electrical conduction can be established in ZnO only when a single N atom occupies an oxygen site (N\(_{ox}\)), which is difficult at some extent as its formation
energy is rather high. On the other hand, the formation energy of a doubly shallow donor \((\text{N}_2)_O\) is comparatively smaller, and hence, there is a great possibility of formation in the case of N doping. Moreover, because of the larger ionization energy, a single N atom occupied at O site cannot possibly donate holes to the valence band in many times. In the case of donor-acceptor pair codoping, \(\text{N}_O\) substitutes oxygen sites to donate free holes to the structure by changing the chemical state of N. By some ab initio theoretical calculations, Yamamoto and Yoshida [11] suggested that simultaneous doping of acceptors and reactive donor codopant into ZnO can ensure better solubility of acceptors, whereas Yan et al. [35] suggested a modification of band structure by codoping giving shallow acceptor levels leading to better \(p\)-type electrical conductivity. Thus, by Ga-N codoping, reactive donor dopants strongly interact with N to form some complex structures in the host lattice, which results to the formation of reactive \(\text{N}_O\) defects leading to better solubility of N as acceptors with the formation of shallow acceptor level within the forbidden gap. Thus, Ga-N codoping succeeds in providing \(p\)-type electrical conduction in ZnO thin film with increased hole concentration via ensuring better solubility and shallow acceptor levels in ZnO. From Table 3, it was seen that mobility decreased at higher Ga concentration, which might be related to the increased scattering of carriers by ionized impurities, grain boundaries, etc.

### Table 2: Film thickness \((t)\) and energy gap \((E_g)\) of Ga-N codoped ZnO thin films.

<table>
<thead>
<tr>
<th>Ga concentration (at%)</th>
<th>(t) (μm)</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.352</td>
<td>3.25</td>
</tr>
<tr>
<td>1</td>
<td>0.388</td>
<td>3.29</td>
</tr>
<tr>
<td>2</td>
<td>0.379</td>
<td>3.36</td>
</tr>
<tr>
<td>3</td>
<td>0.408</td>
<td>3.38</td>
</tr>
</tbody>
</table>

### Figure 5: Plot of \((\alpha h\nu)^2\) versus \(h\nu\) for spray pyrolyzed thin films of 0–3 at% Ga-N codoped ZnO for bandgap energy \((E_g)\) determination.

### Table 3: Carrier type, concentration \((p)\), mobility \((\mu)\), and resistivity \((\rho)\) obtained from Hall effect measurement for the thin films of N monodoped and Ga-N codoped ZnO.

<table>
<thead>
<tr>
<th>Measurement time</th>
<th>Ga concentration (at%)</th>
<th>Type</th>
<th>(n) (cm(^{-3}))</th>
<th>(\mu) (cm(^2)/Vs)</th>
<th>(\rho) (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>0</td>
<td>(p)</td>
<td>(1.01 \times 10^{16})</td>
<td>6.96</td>
<td>(8.85 \times 10^1)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(p)</td>
<td>(1.04 \times 10^{19})</td>
<td>13.21</td>
<td>(4.54 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>(p)</td>
<td>(3.82 \times 10^{19})</td>
<td>4.34</td>
<td>(3.97 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>(p)</td>
<td>(4.27 \times 10^{19})</td>
<td>1.53</td>
<td>(9.55 \times 10^{-2})</td>
</tr>
<tr>
<td>After 30 days</td>
<td>0</td>
<td>(p)</td>
<td>(8.43 \times 10^{14})</td>
<td>6.38</td>
<td>(1.22 \times 10^2)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(p)</td>
<td>(0.96 \times 10^{16})</td>
<td>13.64</td>
<td>(4.76 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>(p)</td>
<td>(3.41 \times 10^{19})</td>
<td>3.59</td>
<td>(5.21 \times 10^{-2})</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>(p)</td>
<td>(4.19 \times 10^{19})</td>
<td>1.48</td>
<td>(9.94 \times 10^{-2})</td>
</tr>
</tbody>
</table>

### 4 Conclusions

The effect of Ga-N codoping on the optoelectronic properties of ZnO thin films was investigated. N monodoped and Ga-N codoped films were \(p\)-type in nature, but codoping enhanced the hole concentration by successfully incorporating N as acceptors in the ZnO lattice. Thus, we obtained lower resistivity with Ga-N codoping. XRD analysis revealed the monophasic and polycrystalline nature of the films and EDX spectra confirmed the better incorporation of N with codoping. Optical transmission in the visible and near infrared region was improved with codoping compared with the monodoped one, which could be due to the better crystallinity as well as smoother surface of the films. Optical energy gap blue-shifted with codoping.
because of the increase in hole concentration. Thus, Ga-N codoped $p$-type ZnO thin film will suit for a large number of short wavelength optoelectronic applications.

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References