Effect of Annealing Atmosphere on Structural and Optical Properties of Nd:ZnO Thin Films

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Abstract

Nd doped ZnO (Nd:ZnO) thin films were deposited on glass substrate using spray pyrolysis technique. All the samples were annealed in various annealing atmospheres. The structural properties, morphology, optical properties of Nd:ZnO thin films were investigated using XRD, UV-Visible spectroscopy, photoluminescence and Raman spectroscopy. From these characterization studies, it was found that the structural and optical properties of Nd:ZnO thin films influenced with annealing atmosphere.

1. Introduction

Zinc oxide (ZnO) is an intrinsic semiconductor with wide direct band gap of 3.37 eV and large exciton binding energy 60 meV [Gottardi 2013]. Rare earth (RE) ions doped ZnO have been recently attracting increasing attention due to their several promising applications in photocatalysis, flat panel displays and optoelectronic devices [Gottardi 2013; Liu 2010]. Among the rare earth elements, Nd is one of the most widely used elements for optoelectronic applications [Chao 2009]. ZnO can act as host candidates for doping with trivalent lanthanide ions, thus allowing a better exploitation of the solar spectrum through photon conversion [Gottardi 2013].

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In general, the physical properties of the host matrix can be influenced by the incorporation of foreign elements. Doping is required to change the phase structure, physical and chemical properties of a material. Among the wide variety of deposition techniques, the spray pyrolysis [Paraguay 1999; Prasad Rao 2012] is a versatile deposition technique for large-scale production of various ZnO structure at low cost. In this paper we will study the annealing atmosphere effects on the microstructure, structural and optical properties of Nd doped ZnO (Nd:ZnO) thin films.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>Nd</td>
<td>Neodymium</td>
</tr>
<tr>
<td>PL</td>
<td>Photo luminescence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>

2. **Experimental**

The precursor solution for spray pyrolysis was prepared by dissolving appropriate amounts of zinc acetate dehydrate in the mixture of deionized water and ethanol at room temperature. In this mixture, ethanol concentration was 10 ml in 100 ml solution. A few drops of acetic acid were added to aqueous solutions to prevent the formation of hydroxides. The neodymium (III) nitrate hexahydrate was used for the neodymium (Nd) doping. The concentration of Nd was maintained at 3 at% to avoid concentration quenching at higher atomic weight percentage. The total concentration of the solution was maintained at 0.3 mol L\(^{-1}\). The glass substrates were cleaned thoroughly with acetone, isopropanol and finally with deionized water with the help of an ultrasonic bath. The nozzle was at a distance of 20 cm from the substrate during deposition. The solution flow rate was held constant at 3 ml/min. Air was used as the carrier gas at the pressure of 2 bar. When aerosol droplets arrive nearer to the substrates, a pyrolytic process occurs and highly adherent Nd:ZnO films were formed. The Nd:ZnO thin films were deposited at substrate temperature of 623 K with 500 nm thickness. The as prepared samples were annealed for 1 hour in various atmospheres (air, oxygen and nitrogen) at 673 K temperature.

Raman spectra recorded using LABRAM-HR spectrometer excited with a 325 nm He-Cd laser at room temperature. The thickness was measured using Stylus profile meter. The structural properties were studied by X-ray diffraction measurements (XRD) using Rigaku D/Max ULTIMA III diffractometer with Cu K\(_\alpha\) radiation (\(\lambda = 1.5406 \) Å). The average dimensions of crystallites were determined by the Scherer method from the broadening of the diffraction peaks. Photo luminescence (PL) measurements were performed using a He–Cd laser (325 nm) as the excitation source. The UV-Vis spectra of samples were carried out at room temperature using Shimadzu UV-1700 Spectrophotometer in the wavelength range 300 to 1100 nm. The film composition was determined using energy dispersive X-ray analysis (EDX, JEOL Model JED-2300) attached with SEM (BJEOL Model JSM-6390LV). The surface morphology profiles of the samples were recorded using Nanoscope-E instrument in contact mode with a Si\(_3\)N\(_4\) cantilever of atomic force microscope (AFM).

3. **Results and Discussion**

3.1. **Structure**

Fig. 1 shows XRD patterns of ZnO, as-prepared Nd:ZnO and annealed Nd:ZnO thin films. All the diffraction peaks could be indexed to wurtzite structure of pure ZnO (JCPDS, card 75-0576). The results indicate that all the as-prepared and annealed Nd:ZnO films show polycrystalline nature, a good c-axis orientation, corresponding to vertical growth with respect to the substrate [Alaoui Lamrani 2007]. All the films shown preferred orientation along (002) plane. This preferred orientation is mainly due to the minimal surface energy of the (002) plane that
corresponds to the dense packed plane of the ZnO hexagonal structure [Alaoui Lamrani 2007; Chang 2000; Cheng 2004]. The XRD results of Nd:ZnO films not shown any additional peak indicating that there are no new chemical phases related to Nd doping. The observation from Fig. 1 is that the intensity of all Nd:ZnO films decreased compared to pure ZnO films. This result indicating that the Nd doping is distorted crystallinity of ZnO. It may be due to the large mismatch in ionic radius and charge imbalance between Nd$^{3+}$ and Zn$^{2+}$ [Gottardi 2013]. The intensity of oxygen annealed Nd:ZnO films decreased compared to other atmosphere annealed samples. The particle size was calculated using Scherer method [Prasada Rao 2010] and shown in table 1. The particle size decreased with Nd doping. The pure ZnO thin film particle size is higher than Nd:ZnO thin films. We expected increment in the particle size of annealed Nd:ZnO thin films. But from the Table 1, it is observed that the particle size not varied with annealing atmosphere. It can be understand that the Nd dopants may be preventing recrystallization process during heat treatment.

![XRD of Nd:ZnO thin films with various annealing atmosphere.](image)

AFM images of Nd:ZnO films with different annealing atmosphere are shown in Fig.2. The surface morphology of the thin films was investigated by atomic force microscopy (AFM). The scanning area was $5 \mu m \times 5 \mu m$ (3-dimensional images). The values of grain size and root mean square (rms) roughness obtained from AFM are listed in Table 1. From the table, it is observed that the measured size of the particle from the AFM surface images is higher than the values calculated from XRD studies, indicating that these particles are probably an
aggregation of small crystallites on the surface of the films. Roughness of the Nd:ZnO thin films have higher value than pure ZnO thin films. From the table 1, it is observed that the roughness of Nd:ZnO thin films varied with the annealing atmosphere. The EDX analysis conform the presence of Zn, O and Nd elements in the deposited films and it is also observed that the amount of Nd in the solid film is slightly less than that in the starting solution. The average atomic percentage (at.%) of zinc, oxygen and Nd was 61.33, 36.16 and 2.51, respectively.

Fig. 2. AFM images of Nd:ZnO thin films (a) as prepared, (b) air annealed, (c) oxygen annealed and (d) nitrogen annealed.

Table 1. Variation of particle size, roughness of Nd:ZnO thin films with annealing atmosphere

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM (degree)</th>
<th>Particle Size XRD (nm)</th>
<th>Grain Size AFM (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.1671</td>
<td>49.5</td>
<td>152.2</td>
<td>28.1</td>
</tr>
<tr>
<td>Nd:ZnO (as-prepared)</td>
<td>0.1932</td>
<td>43.0</td>
<td>127.5</td>
<td>46.3</td>
</tr>
<tr>
<td>Air annealed</td>
<td>0.1932</td>
<td>43.0</td>
<td>149.4</td>
<td>38.5</td>
</tr>
<tr>
<td>Oxygen annealed</td>
<td>0.1964</td>
<td>42.3</td>
<td>141.3</td>
<td>30.7</td>
</tr>
<tr>
<td>Nitrogen annealed</td>
<td>0.1983</td>
<td>43.3</td>
<td>144.1</td>
<td>32.4</td>
</tr>
</tbody>
</table>
3.2. Optical Properties

The optical properties of Nd:ZnO thin films are determined from the transmission measurements in the wavelength range of 200–1200 nm. Fig. 3 shows the transmittance spectra of Nd:ZnO thin films. All the Nd:ZnO films are found to be transparent and it can be seen that the transmittance of the films varying with annealing atmosphere. The optical transmittance of a film is known to depend strongly on its surface morphology [Prasada Rao 2011]. The surface roughness is marginally varied with annealing atmosphere. The nitrogen annealed samples shown high transparency than other samples. It is also clear that the transmittance is improved by the nitrogen heat treatment. A slight decrease in average transmission is observed in the sample annealed in air, oxygen and is attributed to increase of surface roughness, which is evident from the AFM result. It could be observed that the transmission in the visible region decreased substantially at shorter wavelengths near the band edge for all films.

![Transmittance spectra of Nd:ZnO thin films with various annealing atmosphere](image)

3.3. Raman studies

At room temperature, the Raman spectra of the Nd:ZnO thin films are shown in Fig. 4. Four major Raman bands are observed, one located at about 436.5 cm$^{-1}$ and the others centred at about 98.5, 331 and 574 cm$^{-1}$. Each vibration mode corresponds to a band in the Raman spectrum and the intensity of them depends on scattering cross section of these modes [Zhang 2009]. The non-polar phonon modes are observed at 98.5 cm$^{-1}$ and band at 438.5 cm$^{-1}$. They are associated with the vibration of the heavy Zn sublattice and oxygen atoms, respectively. It indicating that the Nd:ZnO thin films has perfect crystal quality [Zhang 2009]. The Raman band located at 331 cm$^{-1}$ is optical phonon overtone and it may be due to multi phonon scattering. The Raman band observed at about 574 cm$^{-1}$ correspond to asymmetric polar longitudinal-optical phonon mode, which can appear only when the c-axis of wurtzite ZnO is parallel to the sample surface [Panda 2009; Zhang 2009]. In the Raman spectra, a marginal red shift is observed for the 438.5 cm$^{-1}$ mode and other modes in air, oxygen annealed samples. According to previous reports, the shift is
probably due to the optical phonon confinement, defect or impurity in the Nd:ZnO thin films, laser irradiation heating, and the tensile strain effect [Panda 2009; Zhang 2009]. In this study, optical phonon confinement and laser irradiation heating effects are negligible. We strongly believe that the shift is due to strain/stress, which can occur due to impurity doping. It is evident from the XRD results.

![Raman Spectra of the Nd:ZnO thin films with various annealing atmosphere](image)

**Fig. 4.** Raman Spectra of the Nd:ZnO thin films with various annealing atmosphere

### 3.4. PL studies

PL is powerful and non-destructive optical tool to study the optical properties of Nd:ZnO thin films. Fig. 5 represent the room temperature photoluminescence spectra of Nd:ZnO thin films with various annealing atmosphere. Fig. 5 shows a strong broad peak which covers entire UV to visible region. The as-prepared Nd:ZnO thin films shown strong emission peak at 408 nm. Other weak emission peaks are observed at 436, 470, 547 nm. These observed emission peaks can be compared with previous reports. According to previous reports, the UV emission originates from the exciton recombination corresponding to the near-band edge (NBE) exciton emission of the wide band gap ZnO [Lin 2013; Meng 2007; Samanta 2005]. The violet emission is probably due to radiative defects related to the interface traps existing at the grain boundaries and emitted from the radiative transition between this level and the valence band [Jin 2000]. The green-yellow emission is induced from the recombination of a photogenerated hole with an electron that belongs to a singly ionized defect, such as oxygen vacancy or oxygen interstitial [Li 2010; Lin 2013; Liu 2011]. From the Fig.5, it is observed that the intensity drastically increased for annealed Nd:ZnO thin films. The deep level emission intensity increased for all the samples, irrespective of annealing atmosphere. It indicates that the density of deep level defects in Nd:ZnO increased during heat treatment. Other possible reason for this is the slight substitution of Nd ions into Zn site. It may occur due to recrystallization process during heat treatment.
4. Conclusion

The Nd:ZnO thin films were deposited by spray pyrolysis. The structural and optical properties of the Nd:ZnO thin films have been found to be influenced by the annealing atmosphere. From the XRD studies, it was found that the annealing atmosphere effect negligible on particle size. All the Nd:ZnO films shown polycrystalline nature with hexagonal wurtzite structure. All the samples had shown 80% transparency in the visible region. From AFM studies, it was found that the roughness of Nd:ZnO films varied with the annealing atmosphere. From the Raman studies, it was found that the polar and non-polar modes of Nd:ZnO influenced by annealing atmosphere. The room temperature PL spectra reveal the good optical properties of Nd:ZnO films. PL study was confirmed that broad visible emission in Nd:ZnO thin films due to Nd doping into ZnO host. It was found that the PL emission of Nd:ZnO thin films strongly influenced by annealing atmosphere.

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