Nitrogen-doped p-type ZnO films prepared from nitrogen gas radio-frequency magnetron sputtering

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Wide band gap nitrogen-doped p-type ZnO films are prepared by radio-frequency magnetron sputtering from a 99.99% purity ZnO target. The sputtering gas is Ar mixed with various flow rates of nitrogen gas. Hole concentrations increase from $1.89 \times 10^{15}$ to $2.11 \times 10^{19}$ cm$^{-3}$ as the N$_2$ flow rate decreases from 15 to 6 SCCM (SCCM denotes cubic centimeter per minute at STP), i.e., increasing N$_2$ flow rate above 6 SCCM decreases the p-type carrier concentration. Microphotoluminescence (PL) spectra peaks are in the near-UV range and change from 384 nm (3.23 eV) to 374 nm (3.32 eV) with increasing N$_2$ flow rate. The PL peaks agree with the band gap of bulk ZnO, which comes from the recombination of free excitons. Raman spectra show six peaks: 436 ($E_2$ high-frequency phonon mode for undoped ZnO film), 581 [$A_1$ (LO) mode in ZnO:N film], 275, 508, 640, and 854 cm$^{-1}$ (local vibrational modes of Raman features in N-doped ZnO film). © 2006 American Institute of Physics. [DOI: 10.1063/1.2337766]

I. INTRODUCTION

Wide band gap semiconductors such as 6H-SiC (3.0 eV, at 2 K) and GaN (3.5 eV) have received much attention in recent decades because of the increasing need for short-wavelength photonic devices and high-power high-frequency electronic devices. Breakthroughs in high quality growth of these materials have led to their wide employment in applications such as light-emitting diodes, photodetectors, and laser diode optoelectronic devices. Both ZnO and GaN are considered direct competitors for these applications since both have wide band gap, but ZnO has emerged as the preferred oxide material for optoelectronic applications because of its superior chemical and mechanical stability.

Various techniques for the growth of ZnO epitaxial layers have been employed, such as molecular beam epitaxy, pulsed laser deposition, metal-organic chemical vapor deposition, and radio-frequency (rf) magnetron sputtering. Since undoped ZnO is a n-type material by nature, it is necessary to control the concentration and conduction type of the doping carrier for ZnO’s application in semiconductor devices. Several donating dopants for n-type ZnO have been discovered, but it has proven more difficult to find suitable accepting dopants for p-type ZnO. For the latter case, efforts have been made to obtain p-type ZnO films by using acceptor dopants such as nitrogen, arsenic, and phosphorus. Both As and P are deep acceptors and make few contributions to p-type conduction, which leaves nitrogen as the relatively better choice for the acceptor dopant in p-type ZnO. Many workers have attempted to produce p-type nitrogen-doped ZnO films. For example, one recent study successfully produced p-type nitrogen-doped ZnO films using pulsed laser ZnO deposition together with electron cyclotron resonant production of an active N radical species in a N$_2$O plasma. Unfortunately, the carrier density from this study was not high enough for industrial optoelectronic applications, complicated by the fact that N$_2$O is an environmentally polluting greenhouse gas. A different study produced p-type nitrogen-doped ZnO films by the N–Al codoping method using de reactive magnetron sputtering with a N$_2$O sputtering gas and a Zn/Al target. Together with the complications of Al (a n-type dopant) contamination, the carrier density was not high enough for industrial optoelectronic applications and the greenhouse gas problem also existed in their study. In our present study, we produce high quality p-type nitrogen-doped ZnO thin films by use of rf magnetron sputtering of a ZnO target with an Ar sputtering gas mixed with variable levels of N$_2$.

II. EXPERIMENT

Power in our experimental rf magnetron sputtering system was supplied by a rf automatching box for constant operational parameters. Sputtering gases were supplied via mass-flow-controlled inlets. Prior to deposition, the chamber was evacuated to $5 \times 10^{-6}$ Torr by a turbomolecular pump. Corning glass (low expansion coefficient) was used as a substrate. Prior to use the substrate was vibrated ultrasonically first in acetone for 15 min and then again in isopropanol for
Another 15 min. The ZnO target was 3 in. in diameter, 6 mm thick, and of 99.99% purity. Tests were performed with Ar as the sputtering gas at a constant flow rate, to which N2 was added at increasing flow rates, with the exhaust port adjusted to maintain a constant chamber pressure. Deposition conditions are listed in Table I. Crystal orientation was determined by x-ray diffraction (XRD) (Rigaku, Cu Ka source). Electrical properties were measured at room temperature by the van der Pauw method (Hall effect measurement, Bio-Rad). X-ray photoelectron spectroscopy (XPS) (Fison) was used to measure atomic ratio and confirm N incorporation into the ZnO film. The optical properties were measured by microphotoluminescence (micro-PL) (Jobin Yvon) at room temperature. The pumping source was a He–Cd laser of wavelength of 325 nm. Raman measurement was performed under a micro-Raman spectrometry system (Jobin Yvon) with 532 nm yttrium aluminum garnet (YAG) laser excitation at room temperature.

III. RESULTS AND DISCUSSION

The thickness of produced films is monitored with Surfcoater α-step system produced by Kosaka Laboratory Ltd. company. The thickness of ZnO films is 2.1 μm. The Hall effect measurement system is HL5500PC manufactured by Bio-Rad. The van der Pauw arrangement for Hall effect measurement uses four contact electrode at the four corners of a square sample (5 × 5 mm²). An In ball is used for Ohmic contact between the measuring probe and the produced film. The results for Hall measurement of produced ZnO films are listed in Table II. The ZnO films are found to be p type. As can be seen, the carrier concentration decreases and film resistivity increases with increasing N2 flow rate. The electrical characteristics of the undoped ZnO film (produced with Ar sputtering gas only) for resistivity, carrier concentration, and mobility are 1.55 Ω cm, −1.60 × 10¹⁸ cm⁻³, and 2.53 cm²/V s, respectively. The undoped ZnO film is n type but is converted to p type as small amounts of the acceptor-type N dopant become entrapped in the ZnO layer during deposition. Since our final film is confirmed as p type and since N2 is a n-type dopant, it is reasonable to assume that even if there is N2 (molecular) contamination, then the N:N2 ratio must be high.

XPS is used to confirm and quantify N doping of the ZnO films. Figure 1 shows the N/Zn atomic ratio as a function of nitrogen flow rate. The inset table shows the XPS measurements (1s orbit, typical XPS center=397 eV) for the three different N2 inflow rates. It can be seen that the amount of atomic N (i.e., the normalized area under the curve) decreases as the N2 flow rate increases. From these data we arrive at the N/Zn atomic ratio values shown in Fig. 1, showing that the N/Zn atomic ratio decreases with increasing N2 flow rate. This trend is the same as that for carrier densities of the nitrogen-doped ZnO films (Table II). However, this trend seems counterintuitive. During normal film deposition, dopant/film concentration tends to increase as the dopant/ambient-environment concentration increases. Thus one would expect a similar relation between the N/film concentration relative to the N2/sputtering-gas concentration. The cause of our observation of the inverse relation is unknown, but we presently attribute it to limited ionization of the N2 gas at higher flow rates. In other words, N2 itself is not the dopant (N2 is actually a n-type dopant). Our system obtains the p-type N dopant by ionizing the molecular N2 gas as a side effect of sputtering. It appears that the functional amount of N (atomic) in the sputtering gas decreases as the N2 flow rate in the sputtering gas increases. It may be that the ratio of N₂(molecular):N(atomic) is a critical factor, but further investigation of this will be a topic of a later paper. For the present, our experimental data clearly confirm incorporation of N into the ZnO film and production of good quality p-type ZnO. By the simplest model for this process, incorporation of N into the ZnO film involves substituting a N for an O at one of the ZnO crystal lattice sites, the substituted N functioning as a p-type acceptor in the ZnO:N film.

The highest value of N incorporated into the ZnO film is found for the N2 flow rate to be 6 SCCM (SCCM denotes cubic centimeter per minute at STP), producing a film with resistivity, carrier concentration, and mobility values of 3.21 Ω cm, 2.11 × 10¹⁹ cm⁻³, and 9.22 × 10⁻² cm²/V s, respectively, as shown in Table II.

![FIG. 1. N/Zn atomic ratio as a function of nitrogen flow rate. The inset shows the measuring parameters of XPS for N atom (1s orbit).](image-url)
Crystal orientation of the p-type ZnO films is studied via XRD spectroscopy with Cu Kα for x-ray source, as shown in Fig. 2. The small figure inset in Fig. 2 shows that the undoped ZnO film produced by our method under a sputtering gas of pure Ar has a ZnO (002) crystal orientation peak of 34.33°.21 The main plots in Fig. 2 also show XRD spectra peaks of ZnO (002) crystal orientation for all our deposited films. This confirms that the proposed methodology produces ZnO:N films that are consistently oriented along the c axis. However, the XRD spectra plots with N2 gas flow show two smaller peaks that are in all our N-doped films. One peak belongs to the (222) crystal orientation of zinc nitride. The other indicates zinc nitride (431) and ZnO (102), which have very nearly the same XRD diffraction angle.21,22 It therefore follows that the produced ZnO:N films are polycrystalline structures with a preferred orientation in the c axis. Scherrer’s formula [Eq. (1)] could be used to calculate the grain size from XRD pattern.

\[
t = \frac{0.9\lambda}{B \cos \theta},
\]

where \(t\) is the grain size, \(\lambda\) is the wavelength of measured x-ray (1.54 Å), \(B\) is termed as the full width at half maximum, and \(\theta\) is the half diffraction angle of crystal orientation peak. The values of grain size are listed in Table III. The undoped ZnO film has the maximum grain size in the ZnO (002) crystal orientation (24.6 nm) and no grain size in the zinc nitride (222) crystal orientation. The grain size decreases in the ZnO (002) crystal orientation and increases in the zinc nitride (222) crystal orientation because N is incorporated into the ZnO film.

The samples were also measured by micro-PL spectroscopy in order to determine the direct band of the ZnO, a parameter of particular interest to our study since ZnO is a primary candidate for use in a variety of light-emitting applications. The spectra are shown in Figs. 3(a)–3(d) for the films produced without N2 flowing in chamber and under N2 flow rates of 6, 10, and 15 SCCM, respectively. PL measurements were obtained at room temperature. The undoped ZnO film has near-ultraviolet PL peak’s wavelengths of 382 nm (3.25 eV), in agreement with the band gap of bulk ZnO,24,25 which comes from the recombination of free excitons. The PL peaks for the various N2 gas flows are seen to be 384 nm (3.23 eV), 379 nm (3.27 eV), and 374 nm (3.32 eV) for N2 flow rates of 6, 10, and 15 SCCM, respectively. These peaks locate at the near-UV emission band. The peak at the N2 flow rate of 6 SCCM is the highest. If we assign this peak a relative value of 1, then the peak intensities for the 10 and 15 SCCM N2 flow rates become, respectively, 0.58 and 0.25. As shown in Fig. 1, the nitrogen-doping concentration decreases as the N2 flow rate increases. Notably, the peak wavelength becomes shorter with decreasing doping concentration and increasing nitrogen flow rate, while at the same time the peak intensity decreases.28 These factors can be of use to designers of optoelectronic devices optimized for specialized applications.

As a former study, ZnO has a hexagonal wurtzite structure and belongs to the C₆₆ symmetry group and, therefore, there are the Raman-active phonon modes E₁ (low), E₂ (high), A₁ (TO), A₁ (LO), E₁ (TO), and E₁ (LO). The B₁ modes are silent. The E₂ modes and the A₁ (LO) mode are expected to observe in unpolarized Raman spectra according to the well-known selection rules.26

The N-doped p-type ZnO samples then were measured by micro-Raman spectroscopy, with results as shown in Fig. 4. Six peaks appear in the Raman spectra: 275, 436, 508, 581, 640, and 854 cm⁻¹. The peak at 436 cm⁻¹ is attributed to the E₂ (high) phonon mode of undoped ZnO. The 581 cm⁻¹ peak was already found in ZnO:N films and interpreted as the A₁ (LO) mode.27 The other four peaks (275, 508, 640, and 854 cm⁻¹) may be considered local vibrational

### Table III. Grain size of ZnO:N films prepared by rf magnetron sputtering with various ratios of N₂/Ar sputtering gas.

<table>
<thead>
<tr>
<th>N₂ (SCCM)</th>
<th>ZnO (002) (nm)</th>
<th>Zinc nitride (222) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.6</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>12.2</td>
<td>29.3</td>
</tr>
<tr>
<td>10</td>
<td>13.9</td>
<td>24.6</td>
</tr>
<tr>
<td>15</td>
<td>11.5</td>
<td>34.1</td>
</tr>
</tbody>
</table>
modes of Raman features because their intensities are related to nitrogen concentration in ZnO:N films according to a former study.

IV. CONCLUSION

This study has produced the high quality p-type doping of ZnO by rf magnetron sputtering with an Ar sputtering gas mixed with various flow levels of N2. The ZnO:N films were confirmed as p type by Hall measurement. N/Zn atomic ratios were investigated by x-ray photoelectron spectroscopy and found to decrease with increasing N2 flow rate. The observed microphotoluminescence spectra peaks were in the near-UV range and changed from 3.23 eV (384 nm) to 3.32 eV (374 nm) as the N2 flow rate increased. The PL peaks agree with the band gap of bulk ZnO, which comes from the recombination of free excitons. Six peaks were observed in the micro-Raman spectra: the peak at 436 cm\textsuperscript{−1} is attributed to the E\textsubscript{2} frequency phonon mode of ZnO; the 581 cm\textsuperscript{−1} peak is interpreted as the A\textsubscript{1} (LO) mode in ZnO:N films; the other four peaks, 275, 508, 640, and 854 cm\textsuperscript{−1}, are local vibrational modes of Raman features in ZnO:N films.

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