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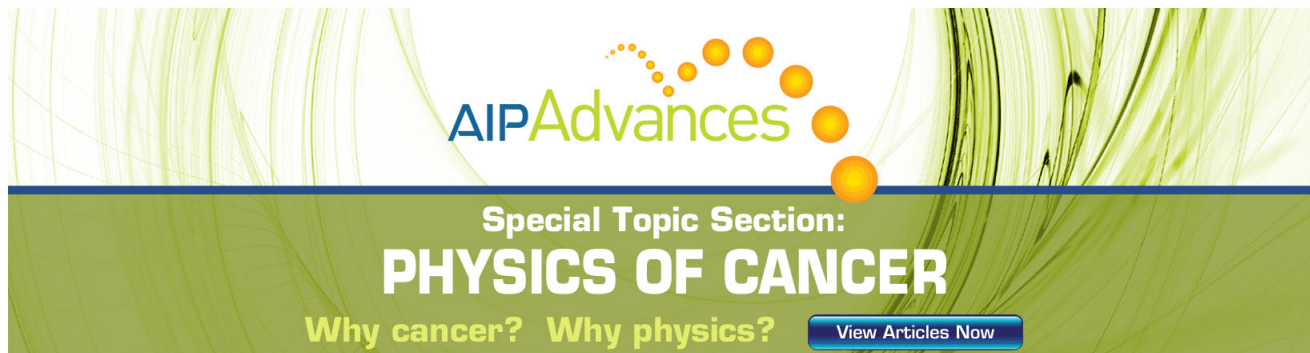
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Control of N/N₂ species ratio in NO plasma for p-type doping of ZnO

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Nitrogen-doped ZnO thin films were grown on *c*-plane sapphire (Al₂O₃) substrates via plasma-assisted molecular beam epitaxy using plasma activated nitric oxide (NO) as the oxygen source and dopant. X-ray diffraction measurements indicate that a small NO flux benefits the crystal quality of the thin films. Hall effect measurements indicate that the electron density of the ZnO films decreases gradually with decreasing NO flux, and the conduction reverses to p-type at a certain flux. Optical emission spectra indicate that the N atom content in the NO plasma increases with decreasing NO flux, and the origin of this is discussed. X-ray photoelectron spectroscopy measurements demonstrate that the number of N atom occupied O sites in the ZnO lattice increases correspondingly. © 2011 American Institute of Physics. [doi:10.1063/1.3626069]

I. INTRODUCTION

The demand for blue-ultraviolet lasers at room temperature has prompted an enormous research effort into ZnO, a wide-bandgap (3.37 eV) semiconductor material. The large exciton binding energy of 60 meV, which is much larger than the thermal energy of 26 meV at room temperature, offers the possibility to realize high efficiency short-wavelength light-emitting devices and laser diodes operating at room and even higher temperatures. Several groups have demonstrated light emitting diodes based on ZnO p-n homojunctions.¹⁻⁴ Producing a material with reliable and reproducible p-type conductivity, however, is still the hurdle to date for practical applications of ZnO due to the asymmetric doping limitation. Nitrogen (N) is thought to be the most suitable p-type dopant due to both atomic-size and electronic-structure considerations. Nevertheless, nitrogen doping is always faced with a troublesome conflict between N solubility and crystal quality. In particular, the N-N pair at the oxygen site (N_{2(O)}) was proved to be a shallow donor, which is considered as an important compensation source for acceptors in ZnO.^{5,6} Many post-treatments were reported to decrease the N_{2(O)} donors in N-doped ZnO, and significant effects were achieved. However, these routes will result in the escaping of acceptors to a certain degree, or they will introduce some unexpected impurities.⁷ Unfortunately, few reports discuss the factors influencing the N_O/N_{2(O)} ratio during the growth process.⁴ In general, N_{2(O)} in ZnO are formed via two paths. One is that N atoms on the film surface migrate and bond each other with the assistance of thermal energy, which is influenced significantly by the substrate temperature. Because of the narrow temperature scale restricted by the crystal quality and the doping level, it is diffi-

cult to increase the N_O/N_{2(O)} ratio by changing the growth temperature. The other way is that the activated N₂ molecules in precursors are introduced into the ZnO directly. Suppressing the N₂ content in precursors will be a feasible and effectual route for fabricating p-type ZnO.

In this paper, a series of nitrogen-doped ZnO thin films were fabricated via molecular beam epitaxy using nitric oxide (NO) as a dopant. The relation between the composition of the precursors and the doping level of ZnO is discussed by changing the flux of NO. *In situ* optical emission spectra (OES) of the plasma and x-ray photoelectron spectroscopy (XPS) analyses were employed in order to determine the species ratios in the plasma and the doping level of N_O and N_{2(O)} in the ZnO thin films.

II. EXPERIMENTAL

The N-doped ZnO (ZnO:N) thin films were epitaxially grown on *c*-plane sapphire via plasma-assisted molecular beam epitaxy (P-MBE). 6N-purity Zn metal was used as the zinc source. Radio frequency (RF) plasma activated NO (5N purity), employed as the N dopant and the oxygen source, was introduced into the growth chamber through a mass flow controller. By changing the NO flux in a range of 1.2 to 0.4 SCCM (SCCM denotes cubic centimeters per minute at standard temperature and pressure), a series of samples were fabricated and labeled as S1, S2, S3, S4, and S5. The RF power was fixed at 320 W, and the substrates were maintained at 455 °C. For comparison with undoped ZnO, a reference sample, S6, without N doping was grown under the same conditions using O₂ as the oxygen source. During the growth, OES were used to value the ratios of the chemical species in the plasma under various NO fluxes.

The crystal structure of the films was characterized via x-ray diffraction (XRD) on a Bruker D8 GADDS x-ray diffractometer with a Cu K_{α1} source. The electrical properties

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were measured by an HMS7707 Hall analyzer (Lakeshore) in the Van der Pauw configuration at room temperature. Chemical bonding states were analyzed via XPS (Thermo ESCALAB 250, Al K_{α} radiation source, $h\nu = 1486.6$ eV). Because the samples were exposed to air, Ar ion etching for 1 min was carried out before the measurements. In order to investigate the local vibration modes affected by incorporating nitrogen into ZnO films, Raman spectra were recorded in backscattering geometry with an HR800 integrated Raman system (Jobin-Yvon, France) using the 488 nm line of an Ar^+ laser.

III. RESULTS AND DISCUSSION

The structure of the ZnO:N thin films was analyzed via XRD as shown in Fig. 1. For all of the samples, a broad peak corresponding to the (002) diffraction appears at 34° – 35° on the patterns. In the case of a larger NO flux, as shown by S1–S3, a (101) diffraction peak at 36.21° can be observed in addition to the (002) peak. With decreasing NO flux, the thin film turns to a c -axis preferred orientation. It should benefit from the increase of zinc atom mobility on the surface with a reduction of the oxygen amount reaching the substrate.⁸

Table I summarizes the results of Hall measurements on the ZnO:N films grown under different NO fluxes. The typical thickness of the ZnO:N thin films is about 800 nm. Without N doping, sample S6 shows n -type conduction with a background carrier density of up to $5.06 \times 10^{18} \text{ cm}^{-3}$. For the nitrogen doped samples, the background carrier density shows a decrease with different levels. When the NO flux was decreased from 1.2 to 0.8 SCCM, the electron concentration was suppressed by an order of magnitude. With a further decrease of the NO flux, the conduction (S4) is reversed to p type with a hole concentration of $1.49 \times 10^{16} \text{ cm}^{-3}$ and a Hall mobility of $1.72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This means that the concentration of acceptors overcomes the donor background in the thin films. Besides natural defects like Zn_i and V_O ,^{6,9} N–N pairs on the oxygen site ($\text{N}_{2(\text{O})}$) are proved to be double shallow donors with a low formation energy.⁶ Considering

TABLE I. Electrical properties of N-doped ZnO films grown on c -plane sapphire substrate under various NO fluxes.

Sample	NO flux (SCCM)	Resistivity ($\Omega \text{ cm}$)	Hall mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Carrier density (cm^{-3})	Carrier type
S1	1.2	4.9	0.48	3.29×10^{18}	n
S2	1.0	5	4.19	3.57×10^{17}	n
S3	0.8	37.5	0.89	2.26×10^{17}	n
S4	0.6	2.4×10^2	1.72	1.49×10^{16}	p
S5	0.4	3.2×10^2	18	1.06×10^{15}	uncertain
S6		3.8	3.29	5.06×10^{18}	n

that the oxygen amount (from activated NO) in the growth circumstance decreases gradually with decreasing NO flux, the conduction reversion does not result from the decrease of Zn_i and V_O concentrations. There should be nothing but the $\text{N}_O/\text{N}_{2(\text{O})}$ ratio leading to the conductivity reversion.

Is the deduction above a fact? Figure 2(a) shows the typical OES of the NO plasma activated by a RF atomic source. Emission lines at the ultraviolet region (represented by the 337 nm spectrum), 746 nm, and 777 nm originate from N_2 molecules (N_2^*), N atoms (N^*), and O atoms (O^*), respectively.

In order to investigate the effects of flux on the dissociation of NO, the evolution of the emission intensity ratio of N^*/N_2^* in the plasma is illustrated in Fig. 2(b). The RF power was fixed at 320 W for all of the cases. As the flux is reduced from 1.2 to 0.4 SCCM, the emission intensity of all of the species is depressed gradually, but the emission intensity ratio of N^*/N_2^* increases with decreasing gas flux. It should be noted that the chamber pressure decreases with decreasing NO flux remarkably, which affects the pressure in the atom source. According to Le Chatelier's principle, if a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts in order to counteract the imposed change, and a new equilibrium is established. Here, the reactions $\text{NO} = \text{N}^* + \text{O}^*$ and $\text{N}_2^* = 2 \text{N}^*$ are in semi-equilibrium.

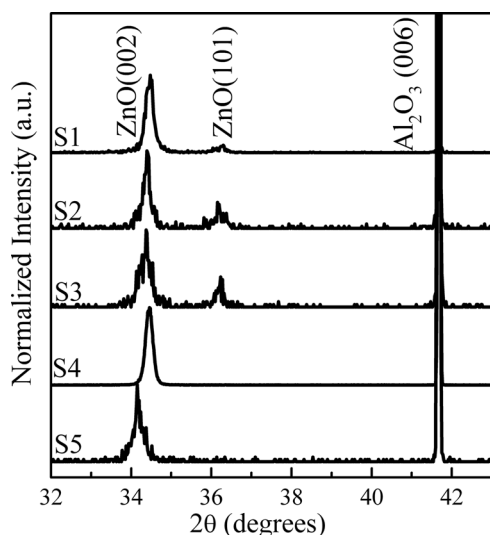


FIG. 1. The XRD spectra of the samples grown under a NO flux of 1.2 (S1), 1.0 (S2), 0.8 (S3), 0.6 (S4), and 0.4 SCCM (S5).

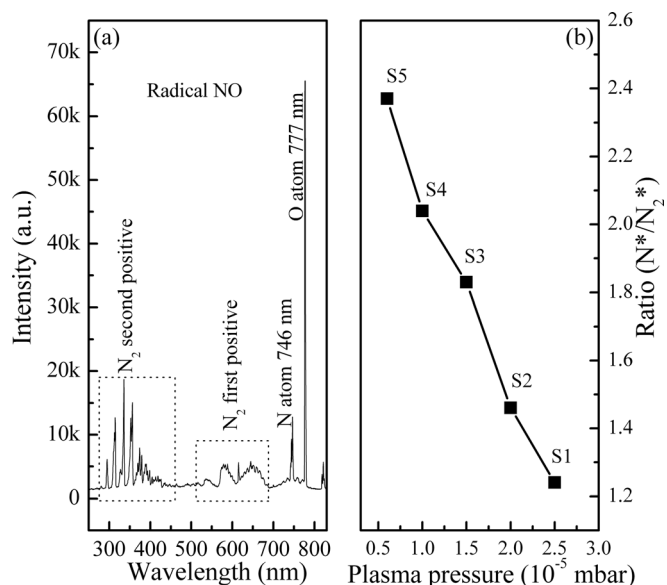


FIG. 2: (a) Optical emission spectra of the NO plasma. (b) Dependence of the emission intensity ratio N^*/N_2^* on the plasma pressure.

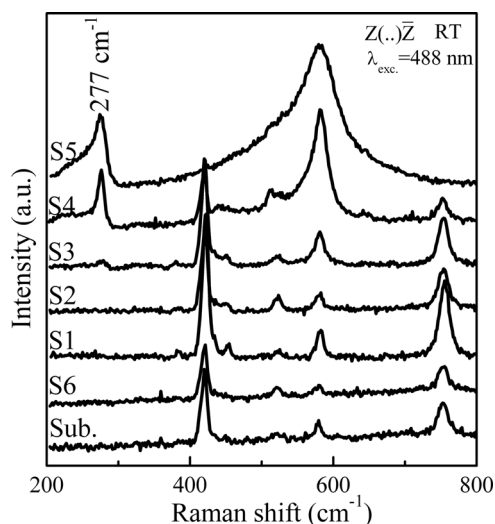


FIG. 3. Room temperature Raman backscattering spectra from ZnO:N films grown at different NO fluxes, nominally undoped ZnO, and the substrate: 1.2 (S1), 1.0 (S2), 0.8 (S3), 0.6 (S4), 0.4 SCCM (S5), undoped ZnO film (S6), and the *c*-Al₂O₃ substrate (Sub.).

When the system pressure is decreased, the two reactions will shift to the dissociation direction in order to counteract the pressure decrease. Thus, lower NO gas flux generates a higher N^*/N_2^* ratio in NO plasma. When the NO flux decreases to 0.6 SCCM, the ZnO:N film transforms into p-type conduction, suggesting a higher N^*/N_2^* ratio in the precursor plasma. As the NO flux decreases further, the film shows not a stronger p-type conduction, but an uncertain one. Given that the concentration of intrinsic donor defects such as Zn_i and V_O increases with a decreasing amount of oxygen, this uncertain conduction is not difficult to explain.

Raman spectroscopy is a convenient technique for studying nondestructively phonon scattering processes in materials. A vibration mode related to hetero-atoms at 277 cm^{-1} has been observed in the Raman spectra of ZnO:N films,^{10–14} as shown in Fig. 3. The spectra of the substrate (*c*-Al₂O₃) and the undoped ZnO film are also measured for comparison.

Of particular interest is the strengthening of the peaks at 277 cm^{-1} with decreasing NO flux. Kaschner *et al.*¹⁰ have reported a Raman peak at 275 cm^{-1} and attributed it to vibrating nitrogen-related complexes. However, there is an argument against this opinion. Based on theoretical and experimental study, Wang *et al.*¹¹ attributed the 275 cm^{-1} peak to the vibration of Zn atoms, the first nearest neighbor O atoms of which are replaced partially by N atoms. Moreover, a 275 cm^{-1} peak has also been found in Fe-, Sb-, Al-, Ga-, Li-,¹² and P-doped ZnO films.¹³ Researchers have observed this mode even in undoped ZnO films grown on *r*-plane sapphire.¹² So, the 275 cm^{-1} mode could represent not the dopant-related local vibration but a wurtzite-ZnO silent mode aroused by the breakdown of the translational crystal symmetry induced by defects and impurities.¹⁴ In any case, the 275–277 cm^{-1} Raman peak reflects the doping level by hetero-atoms to a certain degree. Here, the intensity of the 277 cm^{-1} peak plays a semi-quantification graduation for the N_O in the ZnO lattice. As indicated by the Hall measurement and Raman results, nitrogen was doped into the ZnO thin

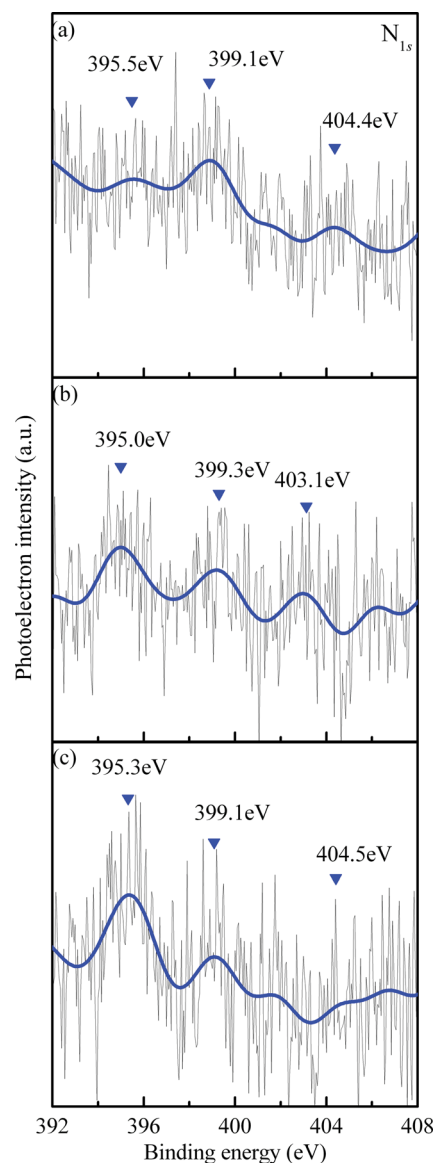


FIG. 4. (Color online) N_{1s} peaks of the ZnO:N films prepared at NO fluxes of (a) 1.0 (sample S2), (b) 0.8 (sample S3), and (c) 0.6 SCCM (sample S4).

films, and the doping level shows a changing trend with a varying NO flux.

The N_{1s} XPS spectra for samples S2, S3, and S4 are illustrated in Fig. 4. Each N_{1s} spectrum could be fitted by three Gaussian curves. The binding energy components located at around 399.1 eV could be attributed to C–N bonds. The C–N pairs are considered as donors in ZnO.¹⁵ The source of carbon in C–N bonds might be contamination and adsorption.

The lower binding energy components are located at about 395.5 eV, with integrated areas (in arbitrary units) of 6 [Fig. 4(a)], 63 [Fig. 4(b)], and 99 [Fig. 4(c)] for samples S2, S3, and S4, respectively. Compared with the N_{1s} (398.8 eV) of free amine, the main 1s peaks have a large chemical shift and present the formation of N–Zn bonds.^{16–18} This result confirmed the nitrogen substitution at the oxygen site (N_O) of ZnO, acting as an acceptor.

Using standard XPS sensitivity factors, the content of N_O has been estimated as 0.05, 0.34, and 0.57 at. % for the three samples, respectively, according to the formula

$$C_N = \frac{I_N/S_N}{\sum_i I_i/S_i},$$

where I_N and S_N are the integrated peak area and sensitivity factor of the respective N 1s peak, and I_i and S_i are the intensities and sensitivity factors for zinc, oxygen, and nitrogen. It is obvious that sample S4 contains the most N_O acceptors.

Furthermore, as shown in Fig. 4, the N_{1s} peak of N_{2(O)} appearing at about 403.1–404.5 eV (Refs. 18–20) became weaker in sample S4, in comparison with the other two. This is to be expected. The evolution of both N_O and N_{2(O)} contents are highly consistent with the observations in Hall-effect measurements. Compared with the strong N_{1s} peak of N_{2(O)} in the p-type ZnO:N produced using a post-annealing process in some previous reports,^{20,21} the fabrication of p-type ZnO:N accomplished through adjusting the N/N₂ species ratio in precursors can depress the N_{2(O)} doping efficiently and expediently.

IV. CONCLUSION

In summary, ZnO:N thin films have been deposited on *c*-plane sapphire (Al₂O₃) via P-MBE. Oxygen and nitrogen dopants were offered by the RF plasma activated NO. N_O was proved to be introduced into the films by Raman and XRD measurements. Along with the decrease of chamber pressure caused by reducing the NO flux, both the N/N₂ species ratio in the precursors and the N_O/N_{2(O)} ratio in the films increased significantly; this was supported by the OES and XPS characterizations. It was attributed to the fact that the equilibrium between N atoms and N₂ molecules shifts to the decomposition side at low pressure. Correspondingly, the n-type conduction of the thin films degraded gradually and turned to p-type at a NO flux of 0.6 SCCM. In conclusion, decreasing the plasma pressure accelerates the decomposition of NO, which is helpful for increasing the N_O acceptor density and suppressing the N_{2(O)} donors. This points out a clear direction for the fabrication of p-type ZnO using nitrogen in precursors in a controlled process.

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