AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **102**, 113509 (2007); doi: 10.1063/1.2819367

View online: http://dx.doi.org/10.1063/1.2819367

View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v102/i11

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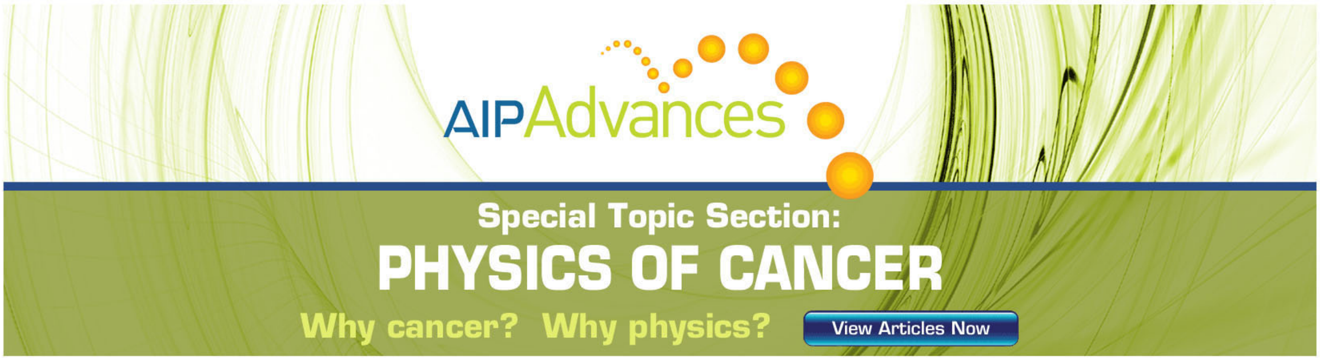

JOURNAL OF APPLIED PHYSICS **102**, 113509 (2007)

Optical and electrical properties of highly nitrogen-doped ZnO thin films grown by plasma-assisted molecular beam epitaxy

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(Received 14 September 2007; accepted 8 October 2007; published online 6 December 2007)

Nitrogen-doped ZnO thin films with different nitrogen concentrations were fabricated by plasma-assisted molecular beam epitaxy. Hall effect measurements show *p*-type conduction for samples with low doping concentration. In highly doped ZnO, the *p*-type conduction converted to high resistance or unstable *p*-type behavior. This result indicates that highly doped samples are heavily compensated. In the low temperature photoluminescence spectrum, a donor-acceptor pair (DAP) emission band shows a strong redshift and broadening with increasing nitrogen doping concentration. The large shift of the DAP emission is explained by the Coulomb-potential fluctuation model related to compensated semiconductors. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2819367]

In recent years, wide-band-gap semiconductors have been regarded as ideal materials for short-wavelength light-emitting devices. ZnO is considered a promising candidate for ultraviolet light-emitting diodes and lasers. However, one of the greatest difficulties to achieve ZnO light emission is the realization of *p*-type ZnO due to severe self-compensation in ZnO. Therefore, considerable efforts have been made to obtain *p*-type ZnO by doping group V and I elements. Nitrogen (N) is considered to be the most promising dopant for *p*-type ZnO,[1] and many groups have reported the achievement of *p*-type ZnO by N doping.[2] Most achievable *p*-type ZnOs have the maximum hole density of $10^{17}-10^{18}$ cm^{-3}.[3–5] However, in many reports, N incorporated concentration is characterized to be as high as 10^{21} cm^{-3} by secondary-ion-mass spectroscopy measurements;[6] that is to say, the doped N impurities were ionized partly to form the holes as effective acceptors. This implies the presence of compensation effect in N-doped ZnO, and this effect becomes strong with the increase of doping concentration. Theoretical calculation presented the compensation effect of N acceptors in ZnO, which probably results from the defects incorporated by N doping itself.[7] These compensation defects have significant influence on the optical and electrical properties of *p*-type ZnO. However, few investigations about the characterization of compensation defects were discussed in previous works. In fact, the study of their effect on the optical and electrical properties of ZnO is very helpful in controlling donorlike defects and, eventually, in achieving stable *p*-type conduction.

In this paper, nitrogen-doped ZnO thin films with different concentrations were fabricated by plasma-assisted molecular beam epitaxy (P-MBE). The study is focused on the characterization and the compensation mechanisms of the samples with heavy doping concentration by the measurements of optical and electrical properties.

N-doped ZnO thin films were fabricated by P-MBE using radial NO as O sources and N dopants. The detailed growth process was reported in our previous paper.[4] Plasma-activated NO allows varying the N concentration in ZnO via changing the NO flow rate. Usually, nitrogen concentration becomes large with the increase of the NO flow rate. The electrical properties of N-doped ZnO with different nitrogen concentrations were characterized at room temperature by the measurement of Hall effect. Table I shows the electrical properties of the as-grown samples including undoped, lightly doped, and highly doped ZnO films. When increasing the NO flow rate from 0.2 to 0.5 SCCM (SCCM denotes cubic centimeter per minute at STP), the hole concentration of samples increases from 8×10^{16} to 5×10^{17} cm^{-3}, as shown in Table I. However, when the NO flow rate is increased continuously, the corresponding increase in hole concentration is not observed. Instead, high resistivity or unstable *p*-type conductive behavior is found.

Photoluminescence (PL) spectra were carried out to study the influence on optical properties of N-doped ZnO with increasing nitrogen concentration. Figure 1 shows low temperature PL spectra made at 80 K using liquid nitrogen cryostat. He–Cd (photon energy 3.81 eV) lasers were used as excitation sources. At a high nitrogen doping concentration, a broad blue emission band that peaked around 2.98 eV is observed in Fig. 1. The emission band was seldom observed in PL spectra of ZnO. It was previously reported in electroluminescence spectra in ZnO homojunction,[8,9] in which it was attributed to the donor-acceptor pair (DAP) recombination. Meanwhile, as shown in Fig. 1, band-edge emission is quenched in highly doped films. The quenching of the band-edge emission presumably results from the increase of other competitive recombination channels and nonradiative centers by heavy nitrogen doping. To determine the effect of nitrogen doping concentration on the optical properties, a series

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TABLE I. Electrical properties of ZnO thin films with different N doped concentrations.

Sample	Growth temperature (°C)	(O_2) flow rate (SCCM)	NO flow rate (SCCM)	Type	Concentration (cm^{-3})
Undoped	500	1.0	0	*n*	⋯
Lightly doped	500	0	0.2–0.5	*p*	8×10^{16}–5×10^{17}
Highly doped	500	0	0.5–1.0	Unstable *p*-type or high	⋯

of spectra of nitrogen-doped ZnO with different concentrations was also conducted and shown in Fig. 1. All the PL spectra were investigated at the same excitation level. Undoped ZnO and lightly doped ZnO show fairly different optical properties from those of highly doped ZnO. For undoped ZnO, four emission peaks are observed at the photon energy of 3.373, 3.360, 3.315, and 3.238 eV, which are attributed to free exciton emission, exciton bound to neutral donor (D^0X), and 1LO and 2LO phonon replicas of free exciton, respectively. For the lightly doped sample, the near band emission shifts to the low energy side compared with that of undoped ZnO. The dominant emission peak located at 3.346 eV is denoted as an exciton bound to a neutral acceptor (A^0X). A pronounced DAP recombination at 3.25 eV with 1LO phonon replica is observed in the PL spectra.[10] As can be seen from the above results, only acceptor-related emissions are observed after nitrogen doping. Especially, in the case of high doping concentration, excitonic recombination disappears, and a broad and structureless DAP emission band appears and has a strong redshift of the peak by 270 meV compared to the lightly doped sample.

To determine the origin of the large redshift of DAP recombination and the nature of the defects involved in the blue emission at 2.98 eV, the excitation density dependence of PL spectra were measured at 80 K. Figure 2 depicts PL spectra of a highly doped ZnO thin film excited by the He–Cd laser with different output powers. The excitation intensity was varied over the range from 50 W/cm^2 to 2 kW/cm^2. As shown in Fig. 2, the spectral shape changes with increasing excitation densities. At high excitation density, as indicated in curve (c), the DAP recombination and 1LO phonon replica located at 3.260 and 3.170 eV dominate the whole PL spectrum. A^0X emission is observed at 3.345 eV at its high energy side. When decreasing the excitation density corresponding to curve (b), the excitonic emission is extinguished while the DAP is favored. However, at the lowest excitation density, as indicated in curve (a), the

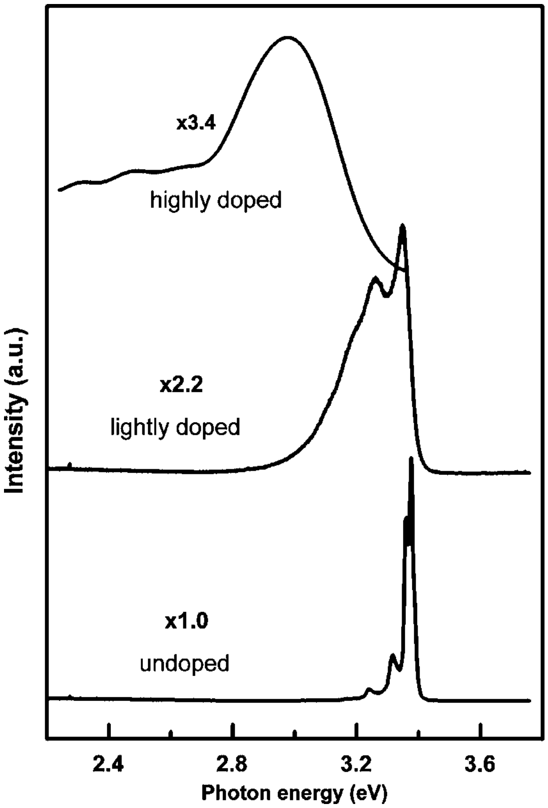

FIG. 1. Low temperature PL spectra of N-doped ZnO at different doping levels.

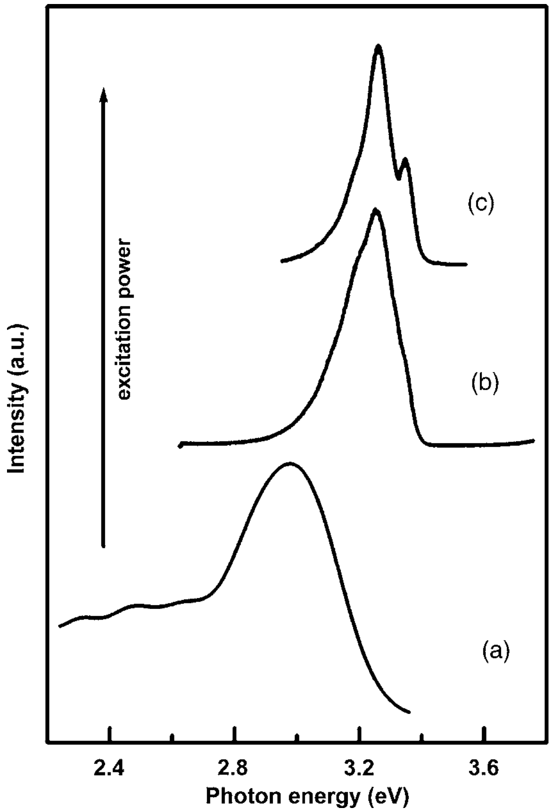

FIG. 2. Low temperature PL spectra of a highly doped sample at different excitation densities. The arrow indicates the increase of excitation power.

spectral shape changes to a structureless and broad emission band that redshifts to 2.98 eV.

The continuous change of the spectral shape with increasing N doping concentration and decreasing excitation densities is thought to be related to the high compensation in a highly doping level. A theory of high compensation semiconductor was discussed by Shklovskii and Efros,[11] which was successfully applied to explain the compensation in ZnSe:N[12] and GaAs:Li.[13] In a highly compensated *p*-type semiconductor, it is assumed that the concentration of acceptors (N_A) is higher than the concentration of compensating donors (N_D). According to the electric neutrality condition in a compensation semiconductor, the hole concentrations (p) should satisfy $p = N_A - N_D$. Assuming that the concentration of the charged impurities (N_A^-, N_D^+) is sufficiently large, that is to say, the compensation ratio is sufficiently high. Thus, the high density of the charged donors and acceptors will create a strong electrical field, which will lead to Coulomb-potential fluctuations in the band gap at different positions. They lead to spatially separate potential wells as well as to respective fluctuations of the absolute impurity level energies. Thus, the acceptor and donor levels form a series of energy "valley" and "hill" structures, respectively, by potential fluctuation modulation. The amplitude γ of potential fluctuations depends on the concentration of charged impurities $N_t (N_t = N_A^- + N_D^+)$ and hole concentration p, as indicated in the following:

$$\gamma = \frac{e^2}{4\pi\varepsilon\varepsilon_0} \frac{N_t^{2/3}}{p^{1/3}}. \tag{1}$$

The recombination of DAP $[E(h\nu)]$ is described by[11]

$$E(h\nu) = E_g - (E_D + E_A) - 2\gamma, \tag{2}$$

where E_g is the band gap of ZnO, and E_D and E_A are the donor and acceptor binding energies, respectively. As seen from Eq. (1), the amplitude γ of potential fluctuations increases with the increase of the charged impurity concentration N_t, as well as increases with the decrease of the concentration of uncompensated free carriers p. According to Eq. (2), the PL band will shift to the low energy side in a highly compensated sample. This is indeed observed, as shown in Fig. 1.

For varying excitation density corresponding to Fig. 2, at the lowest excitation density, only a few charged donors and acceptors are occupied by photoexcited carriers, which relax quickly to the lowest donor and the highest acceptor states, as shown in Fig. 3. Figure 3 shows the schematic diagram of the fluctuating band structure in a highly doped ZnO according to the theory above[11] at low excitation density. Then, DAP recombination processes take place between the lowest donors and the highest acceptors, corresponding to the valleys in the donor band and the hills in the acceptor band, which results largely in a recombination energy redshift. Due to the effect of the Coulomb potential, a considerable broad emission band is observed. At high excitation densities, enough high concentrations of photoexcited electrons and holes neutralize most charged donors and acceptors, resulting in the strong screening effect vanished fluctuations. The structured DAP emission can be observed, as shown in curve (c) of Fig. 2.

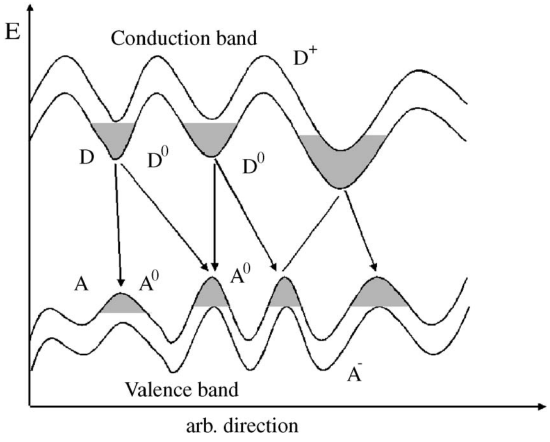

FIG. 3. Schematic diagram of fluctuating band structure in real space of a strongly doped and highly compensated ZnO. The arrows indicate the recombination of donors and acceptors at low excitation density.

As described above, the compensation impurities play an important role for electrical and optical properties in highly doped samples. To understand the origin of compensation defects in highly doped ZnO, x-ray photoelectron spectroscopy (XPS) was employed to identify the chemical state of N atoms in lightly and highly doped ZnO. Theory predicts[7,14] that N can be incorporated into ZnO by at least two different states. N atom substitution in the oxygen site of ZnO (N_O) is a desired acceptor, and $(N_2)_O$ is a N_2 molecule occupying a position on the oxygen sublattice as a shallow double donor. Figures 4(a) and 4(b) present the XPS results of the lightly and highly N-doped ZnO thin films, respectively, corresponding to Table I. Two peaks with maximum values at about 398 and 406 eV are observed in both XPS spectra of ZnO thin films, which correspond to the N1*s* core level. The peak at about 398 eV is usually attributed to the signal of the N–Zn bond,[15] while the peak at 406 eV is considered to be the signal of $(N_2)_O$.[16] The N–Zn bond dominates in the whole spectrum for the lightly doped sample, which confirms that the nitrogen mainly forms a N_O state in ZnO. With increasing N doping concentration, a strong N–Zn bond is still observed, but its intensity tends to saturate and the peak intensity at the high energy side (406 eV) improves signifi-

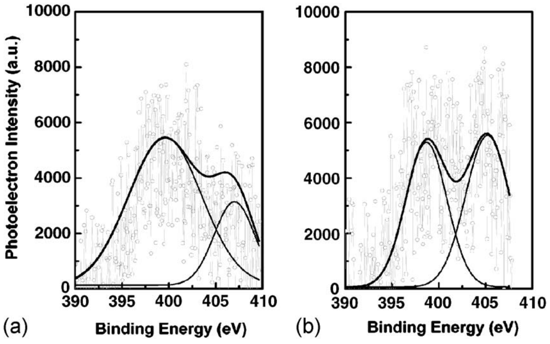

FIG. 4. [(a) and (b)] X-ray photoelectron spectroscopy of lightly doped and highly N-doped ZnO thin films, respectively.

cantly. Meanwhile, the electrical properties of the highly nitrogen-doped ZnO thin film become unstable *p*-type or high resistance by Hall measurement, as shown in Table I. From XPS results, it can be seen that the presence of $(N_2)_O$ donor defects is responsible for the degradation of *p*-type conduction with increasing nitrogen doping concentration. Lee *et al.*[7] predicted by first-principles pseudopotential calculations that $(N_2)_O$ molecules are one of the dominant compensating species when an active N_2 plasma is used as dopants. In the case of NO plasma as nitrogen dopants, the formation probability of $(N_2)_O$ molecules is improved significantly with increasing NO flow rate, and it is similar to the active N_2 plasma. In this case, N_O acceptors are compensated partly by the $(N_2)_O$ donors, resulting in the degradation of *p*-type conduction for highly doped ZnO.

In conclusion, optical and electrical properties of N-doped ZnO thin films with different doping concentrations were investigated. For a highly doped sample, a broad and structureless DAP emission band located at 2.98 eV is observed in a low temperature PL spectrum. With increasing excitation density, the DAP emission band experiences a blueshift, developing into a well-resolved DAP structure at 3.26 eV. This change of spectral shape and large shift of emission is attributed to the Coulomb-potential fluctuations arising from the presence of electrical field, which is induced by high density of ionized impurities in highly doped ZnO. The characteristic of the large redshift of the DAP band is a powerful evidence for a strong compensation. The XPS result indicates the presence of donor defects $(N_2)_O$, except for the effective acceptor (N_O) in highly doped ZnO. These results suggested that highly N doped samples are highly compensated, and $(N_2)_O$ is a main compensation mechanism.

This work is supported by the Key Project of National Natural Science Foundation of China under Grant Nos. 60336020 and 50532050, the "973" program under Grant No. 2006CB604906, the Innovation Project of Chinese Academy of Sciences, and the National Natural Science Foundation of China under Grant Nos. 60429403, 60506014, 50402016, 60576040, and 10674133.

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