Generation of nitrogen acceptors in ZnO using pulse thermal processing

Jun Xu,[1,a)] Ronald Ott,[1] Adrian S. Sabau,[1] Zhengwei Pan,[1] Faxian Xiu,[2] Jianlin Liu,[2]
Jean-Marie Erie,[3] and David P. Norton[3]

[1]*Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831, USA*
[2]*Quantum Structures Laboratory, Department of Electrical Engineering, University of California, Riverside,
California 92521, USA*
[3]*Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA*

Bipolar doping in wide bandgap semiconductors is difficult to achieve under equilibrium conditions because of the spontaneous formation of compensating defects and unfavorable energetics for dopant substitution. In this work, we explored the use of rapid pulse thermal processing for activating nitrogen dopants into acceptor states in ZnO. Low-temperature photoluminescence spectra revealed both acceptor-bound exciton (A^0X) and donor-acceptor pair emissions, which present direct evidence for acceptors generated after pulse thermal processing of nitrogen-doped ZnO. This work suggests that pulse thermal processing is potentially an effective method for *p*-type doping of ZnO. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2911725]

The need for highly efficient light emitting diodes (LEDs) attracts much interest in examining ZnO as a practical LED material. Currently, GaN and GaN-based alloys are the leading LED materials for large-scale lighting applications. In many ways, ZnO is superior to GaN. ZnO has excellent optical conversion efficiency due to a large exciton binding energy, can be easily processed into device structures, and can be synthesized into a number of interesting ZnO nanostructures. The high ZnO exciton binding energy (60 meV for ZnO, compared with 26 meV for GaN) results in a high probability for radiative recombination of excitons even at high temperature. Nanoscale *p-n* junctions of ZnO are expected to enhance the injection rate of carriers many times more than that for a planar ZnO diode,[1] leading to higher lighting efficiency. While ZnO exhibits many superior properties, the development of ZnO-based LEDs has been hindered by the difficulty of reliable *p*-type doping.

Nitrogen substitution of lattice oxygen in ZnO has been recognized as a potential method for *p*-type doping of ZnO. According to Zunger's "practical doping rules,"[2] *p*-type doping of ZnO under equilibrium conditions is difficult because spontaneous formation of compensating oxygen vacancies and Zn interstitials will overwhelm doping pathways when the pinning energy is reached. This resistance to bipolar doping is common among wide gap semiconductors.[3] Similar work by Marfaing and Lusson[4] further shows that *p*-type doping of ZnO by substituting nitrogen is limited by a balance between enriching zinc for increasing high solubility and enriching oxygen for lowering compensation donors. Despite these difficulties, many studies have reported the production of nitrogen-doped *p*-type ZnO,[5–7] rectifying junctions, and even ZnO homojunction LEDs.[8–10] In the authors' point of view, this progress has been achieved because many of these methods involve defect-complex formation and nonequilibrium doping. In this letter, we present a nonequilibrium method for producing acceptors in ZnO using pulse thermal processing (PTP).

PTP method has been used for activating dopants and regaining silicon crystal structure after ion implantation.[11]

There was no PTP application for activating dopants for ZnO. In this work, PTP utilizes high-energy thermal pulses to activate nitrogen impurities into the oxygen lattice sites during the pulse period and prevent escape via thermally induced transport because the pulse period is short.

Nitrogen-doped ZnO films were grown at the University of Florida on *n*-type silicon substrates using the pulsed laser deposition (PLD) method with growth temperatures of 400–500 °C. These temperatures are high enough for ZnO crystallization to occur while nitrogen loss via diffusion and N_2 formation is minimized. The laser frequency was 5 Hz with a laser energy density of ~1 J/cm^2. The nitrogen source was Zn_3N_2, doped into the ablation target, and N_2 background gas introduced at 120 mTorr. A detailed description of PLD experimental setup is described in Ref. 12. The thickness of all films is estimated about 400 nm.

ZnO:N films were processed in the PTP facility at ORNL. The PTP facility utilizes the microflash rapid thermal processing equipment and generates high temperature pulses in a millisecond time scale. In this method, the heating pulses cover a surface area of 1.0×1.6 cm^2. The detailed description of the PTP setup has been provided in Ref. 13. In the present experiment, the profile of the thermal pulses was produced by applying a 200 A current for 2 s, followed by 900 A for 50 ms. For these conditions, the temperature as a function of time generated for the ZnO:N films was simulated using an energy transport model.[14] The heat flux and simulated temperature are shown in Fig. 1. The temperature profile has a peak temperature about 800 °C with the average pulse duration of 110 ms. Prior to thermal pulse irradiation, the sample chamber was evacuated and then backfilled with flowing nitrogen gas.

As-grown and PTP-processed ZnO:N samples were analyzed using photoluminescence (PL) spectroscopy at UC-Riverside. A 5 mW, 325 nm He–Cd laser was used for optical excitation. All spectra were measured at 8.8 K, except as noted. PL spectra were recorded for multiple spots in each sample. The optical resolution is about 0.001 eV. Further PL experimental details are available in Ref. 15.

Figure 2(a) shows PL spectra for a ZnO:N film grown at 400 °C before and after the PTP processing. Several positions on the film were examined and showed consistent PL

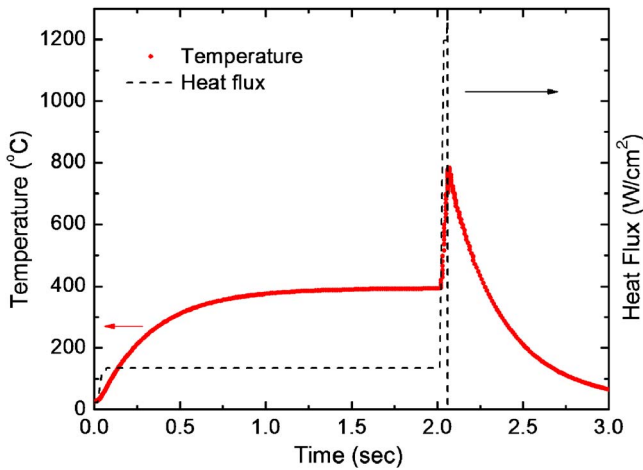a)Author to whom correspondence should be addressed. Electronic mail:
xuj2@ornl.gov.

FIG. 1. (Color online) Applied heat flux (dash) and resulting film temperature (solid) as a function of time for ZnO (400 nm) on Si wafer (0.55 mm) supported on a steel plate (1 cm). The following heat transfer coefficients are used: h_{SS}=1000 W/m^2 K for Si-steel interface and h_C=100 W/m^2 K for the film surface convection. The emissivity of ZnO was taken to be 0.9.

FIG. 3. (Color online) Temperature dependence of the DAP component. The dash lines denote the variation of the peak energy location as the temperature was increased. A least squares fit was conducted for PL spectra using four peaks, corresponding A^{0}X, DAP, their phonon replica (72 meV).

features. For the as-grown film, a dominant near band edge emission peak was observed at 3.364 ± 0.001 eV. This emission is essentially the same as the 3.363 eV emission associated with the donor-bound exciton (D^{0}X), which apparently originates from the hydrogen-bound exciton denoted by I$_4$ in the literature.[16]

The ZnO:N film was then processed using PTP with a temperature profile, as shown in Fig. 1. The low-temperature PL spectrum of the PTP-processed film significantly differs from the as-grown film by exhibiting two dominant broad peaks centered at 3.30 ± 0.005 and 3.34 ± 0.005 eV. The un-

certainty was determined using the variation of the PL peak positions with sample location and is larger than the experimental error (0.001 eV), suggesting a small inhomogeneity induced by the processing. Hereafter, this energy uncertainty will apply for all energy values reported here, unless specified otherwise. The 3.30 eV peak is close to the controversial 3.315 eV peak for N doped ZnO. Many authors[17–19] attribute this peak to a donor-acceptor pair (DAP), while Look *et al.* initially assigned this peak to acceptor-bound exciton emission (A^{0}X).[20] In the present work, the 3.30 eV emission is confirmed to be a DAP transition by the temperature-dependent PL measurement, as described later in Fig. 3. The DAP transition energy is given by

$$h\omega = E_{\text{gap}} - E_D - E_A + \frac{e^2}{4\pi\varepsilon R}, \qquad (1)$$

where E_{gap} is the ZnO band gap energy, ε is the dielectric constant, E_A and E_D are the acceptor and donor energies, respectively, R is the distance between the donor and acceptor forming the pair, and the last term in Eq. (1) represents the Coulomb interaction between the donors and acceptors. Based on the assignment of the 3.30 eV peak as the DAP transition energy, we obtained the binding energy for the N$_O$ acceptor, $E_A = E_{\text{gap}} - h\omega - E_D + \langle e^2/4\pi\varepsilon R \rangle = 3.437$ eV -3.300 eV -0.030 eV $+0.02$ eV $=127$ meV. The donor energy (E_D) was taken to be 0.030 eV which has been reported for a H donor.[21] The 0.02 eV Coulomb interaction energy is assumed to be the same as in Ref. 20. This N$_O$ binding energy is consistent within the theoretical error with the suggestion of Zeuner *et al.* of 165 ± 40 meV.[22] The 3.34 eV peak apparently is an A^{0}X emission with a 37 meV binding energy between the exciton and the N$_O$ acceptor. This is consistent with previous PL work on N-doped ZnO.[19,23] Obviously, the appearance of DAP and A^{0}X emissions suggests the generation of N$_O$-associated acceptors, which provides a direct evidence of effective acceptor activation by the PTP method.

Figure 2(b) shows the 8.8 K PL spectra for a ZnO:N PLD film grown at 500 °C before and after PTP processing. For this ZnO:N film before PTP processing, a new satellite band centered at 3.32 eV was seen in addition to the 3.36 eV
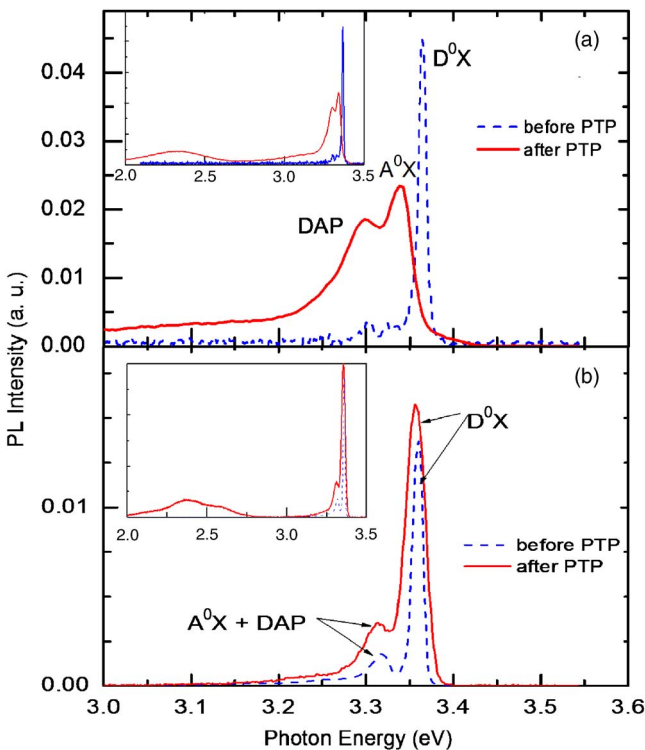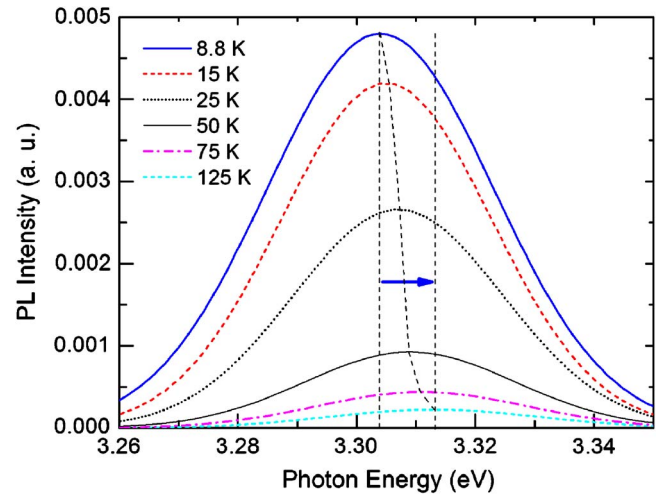

FIG. 2. (Color online) Low-temperature PL spectra for a ZnO:N film before (dash) and after (solid) PTP. The ZnO films were grown using pulsed laser deposition at (a) 400 °C and (b) 500 °C. The insets correspond to a wider spectral range.

peak, different from the film grown at 400 °C. The more intense 3.36 eV peak is attributed to the donor-bound exciton (D[0]X), the same as for the film grown at 400 °C. The 3.32 eV peak is probably due to a mixture of both A[0]X and DAP emissions. The appearance of a PL peak at 3.32 eV may suggest that some of the mixed nitrogen dopants have already resulted in oxygen site substitution. The low intensity of the 3.32 eV peak is due to the typical low solubility of nitrogen. After PTP, the satellite peak is slightly shifted to 3.31 eV and the relative intensity is enhanced, as shown Fig. 2(b) (solid). This intensity remains low compared to the intensity of the D[0]X peak, very different from the 400 °C grown film in which A[0]X and DAP features become dominant and D[0]X peak is not detectable. The difference implies that the 500 °C grown sample has a lower concentration of initial dopants due to greater thermal diffusion. For the film grown at lower temperature, more of the nitrogen dopants remain within the film and can be effectively converted to *p*-type carriers using PTP.

A weak and broad peak was also observed at approximately 2.3 eV after PTP processing for both the 400 and 500 °C samples, as shown in the insets of Fig. 2. This peak position suggests formation of oxygen vacancies[24] induced during PTP processing, but the relatively weak intensity suggests these species are not dominant.

Temperature-dependent PL spectra of PTP-processed ZnO:N films were recorded for temperatures ranging from 8.7 to 125 K. Since each spectrum was a superposition of multiple peaks, a least squares fitting was performed using four peaks, corresponding to A[0]X, DAP, and their phonon replicas. After fitting, the DAP components were plotted in Fig. 3. The peak energy position of the DAP emission shifted to higher values with increasing temperature. This blueshift is interpreted as increased donor concentration at higher temperatures, leading to reduced distance between the donor and acceptor. This is consistent with prediction by Eq. (1) and previous observations.[25] The blueshift supports the assignment of the 3.30 eV peak as DAP and confirms that acceptors in ZnO can be generated using short thermal pulses.

It is noted that our Hall effect measurement does not indicate *p*-type conductivity for the sample before or after PTP processing. This likely reflects the propensity of ZnO to form donor defects that are difficult to be completely eliminated by annealing.[3] An unlikely possibility is creation of two nitrogen dopants occupying an oxygen vacancy site $(N_2)_O$, as predicted by theoretical calculations.[26] Formation of this structure is unlikely because it requires two nitrogen dopants to merge at the same site within the short PTP pulse width. Additionally, there is no PL data of $(N_2)_O$ reported in the literature.

For nitrogen doping of ZnO under *equilibrium* conditions, few dopants occupy the oxygen lattice sites, due to the low solubility and high pinning energy. A *nonequilibrium* method can activate nitrogen impurities into the acceptor state due to the rapid heating characteristic of PTP. This short heating pulse allows the nitrogen dopants to substitute for the lattice oxygen's. This may also assist in driving out any residual hydrogen that introduces donor states and/or passivates acceptor states. If the temperature remains high, as during conventional annealing, these dopants have enough energy and time to diffuse out of the solid. However, the rapid drop in film temperature in the PTP method captures nitrogen acceptors in a metastable state. While some donor defects may be generated during this period, the concentration seems to be small.

In conclusion, it was demonstrated that nitrogen impurities can be activated into acceptor states using a nonequilibrium method, PTP. The observation of A[0]X and DAP emission after PTP processing of ZnO:N films provides direct evidence for nitrogen acceptors. This work suggests that PTP is potentially an effective method for *p*-type doping of ZnO.

[1]G. D. Smit, S. Rogge, and T. M. Klapwijk, Appl. Phys. Lett. **81**, 3852 (2002).
[2]A. Zunger, Appl. Phys. Lett. **83**, 57 (2003).
[3]U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).
[4]Y. Marfaing and A. Lusson, Superlattices Microstruct. **38**, 385 (2005).
[5]D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[6]A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nat. Mater. **4**, 42 (2005).
[7]D. C. Look, Semicond. Sci. Technol. **20**, S55 (2005) and related references thereafter.
[8]Y. R. Ryu, T. S. Lee, J. A. Lubguban, H. W. White, Y. S. Park, and C. J. Young, Appl. Phys. Lett. **87**, 153504 (2005).
[9]J. H. Lim, C. K. Kang, K. K. Kim, I. K. Park, D. K. Hwang, and S. J. Park, Adv. Mater. (Weinheim, Ger.) **18**, 2720 (2006).
[10]Z. P. Wei, Y. M. Lu, D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Y. Zhang, D. X. Zhao, X. W. Fan, and Z. K. Tang, Appl. Phys. Lett. **90**, 042113 (2007).
[11]D. M. Camm, J. C. Gelpey, T. Thrum, G. C. Stuart, and S. McCoy, JOM **58**, 32 (2006).
[12]D. P. Norton, Y. W. Heo, M. P. Ivill, K. Ip, S. J. Pearton, M. F. Chisholm, and T. Steiner, Mater. Today **7**, p. 34 (2004).
[13]R. D. Ott, P. Kadolkar, C. A. Blue, A. C. Cole, and G. B. Thompson, JOM **56**, 45 (2004).
[14]A. S. Sabau, P. B. Kadolkar, R. B. Dinwiddie, R. D. Ott, and C. A. Blue, Metall. Mater. Trans. A **38**, 788 (2007).
[15]F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, Appl. Phys. Lett. **87**, 252102 (2005).
[16]B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forseter, F. Bertram, J. Christen, A. Hoffmann, M. Strassburg, M. Dworzak, U. Haboeck, and A. V. Rodina, Phys. Status Solidi B **241**, 231 (2004).
[17]K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger, and S. Niki, Appl. Phys. Lett. **79**, 4139 (2001).
[18]J. Lu, Y. Zhang, Z. Ye, L. Wang, B. Zhao, and J. Huang, Mater. Lett. **57**, 3311 (2003).
[19]L. J. Wang and N. C. Giles, Appl. Phys. Lett. **84**, 3049 (2004).
[20]D. C. Look and B. Claflin, Phys. Status Solidi B **241**, 624 (2004).
[21]C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[22]A. Zuener, H. Alves, D. M. Hofmann, B. K. Meyer, A. Hofmann, U. Haboeck, M. Strassburg, and M. Dworzak, Phys. Status Solidi B **234**, R7 (2002).
[23]S. J. Jiao, Y. M. Lu, D. Z. Lu, D. Z. Shen, Z. Z. Zhang, B. H. Li, Zh. H. Zheng, B. Yao, J. Y. Zhang, D. X. Zhao, and X. W. Fan, J. Lumin. **122/123**, 368 (2007).
[24]K. Vanheusden, W. L. Warrant, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, J. Appl. Phys. **79**, 7983 (1996).
[25]K. Thonke, T. Gruber, N. Teofilov, R. Schonfelder, A. Waag, and R. Sauer, Physica B **308**, 945 (2001).
[26]H. Park, S. B. Zhang, and S. H. Wei, Phys. Rev. B **66**, 073202 (2002).