ZnO light-emitting diode grown by plasma-assisted metal organic chemical vapor deposition

W. Z. Xu, Z. Z. Ye,^{a)} Y. J. Zeng, L. P. Zhu, B. H. Zhao, L. Jiang, J. G. Lu, and H. P. He
*State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027,
 People's Republic of China*

S. B. Zhang
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 7 November 2005; accepted 31 March 2006; published online 24 April 2006)

We report a breakthrough in fabricating ZnO homojunction light-emitting diode by metal organic chemical vapor deposition. Using NO plasma, we are able to grow *p*-type ZnO thin films on *n*-type bulk ZnO substrates. The as-grown films on glass substrates show hole concentration of 10^{16} – 10^{17} cm⁻³ and mobility of 1–10 cm² V⁻¹ s⁻¹. Room-temperature photoluminescence spectra reveal nitrogen-related emissions. A typical ZnO homojunction shows rectifying behavior with a turn-on voltage of about 2.3 V. Electroluminescence at room temperature has been demonstrated with band-to-band emission at $I=40$ mA and defect-related emissions in the blue-yellow spectrum range. © 2006 American Institute of Physics. [DOI: 10.1063/1.2199588]

Zinc oxide is of great interest because of its large exciton binding energy (~ 60 meV), which can lead to exciton-recombination-based lasing above room temperature.¹ However, it is difficult to grow low-resistivity and reliable *p*-type ZnO—a main obstacle to the development of monolithic ZnO light-emitting diodes (LEDs) and laser diodes (LDs). Among the possible dopants for *p*-type ZnO such as group-V elements, N, P, and As, and group-I elements, Li, Na, and K, nitrogen is a promising candidate.^{2–4} Traditionally, N₂ has been used as the doping source, although the equilibrium solubility of N is expected to be low.² In order to increase the N solubility, various exotic approaches have been applied such as using NO,^{5,6} N₂O,⁶ their combination,⁷ or NH₃,⁸ as the source. It has been suggested⁹ that the use of NO may reduce the concentration of undesirable substitutional N₂ molecular donors.¹⁰ Since reactive N in electron cyclotron resonance (ECR) plasma is known to produce *p*-type ZnSe,¹¹ similar approaches have also been applied to ZnO.^{12,13}

Several groups have reported the fabrication of ZnO *p-n* junctions by various means such as pulsed laser deposition,¹⁴ excimer-laser doping,¹⁵ and sputtering.¹⁶ Recently, Tsukazaki *et al.* have demonstrated¹⁷ ZnO LED by using a highly sophisticated repeated-temperature-modulation molecular beam epitaxy (MBE) method. Metal organic chemical vapor deposition (MOCVD) has the advantage of scaling up industrial applications. So far, however, it has not been achieved *p*-type ZnO good enough for LED by using a common MOCVD method. Barnes *et al.* have reported the preparation of N-doped ZnO thin films by chemical vapor deposition using plasma-activated N₂/O₂ and N₂O/O₂ mixtures. However, *p*-type ZnO has not been achieved.¹⁸

In this letter, we report on the growth of *p*-type ZnO thin films by MOCVD using NO plasma as both the oxygen and nitrogen sources. Good *p*-type thin films have been obtained on bulk ZnO substrates. This enables the demonstration of electroluminescence (EL) from MOCVD grown monolithic

ZnO LED devices with characteristics either comparable or better than those by the state-of-the-art but complicated MBE growth.¹⁷

Nitrogen-doped ZnO thin films were grown by the plasma-assisted low-pressure MOCVD method. Diethyl zinc was used as the zinc source and N₂ as the carrier gas. NO plasma, generated by a rf power supply with 150 W operating at 13.56 MHz, was acted as the O and N sources. The substrate temperature was 300–450 °C, and the chamber pressure was 5 Pa. Zinc oxide homojunction was fabricated by growing *p*-type ZnO thin film of about 1 μm thickness on *n*-type single-crystal ZnO wafer, which was unintentionally doped with a relatively high resistivity of 200–400 Ω cm. In/Zn electrodes were used for Ohmic contact to both the *n*- and *p*-type sides of the diode. Figure 1 shows a schematic diagram of the ZnO homojunction diode. In order to determine the electrical properties of the N-doped ZnO thin films, Hall measurements were carried out on a number of thin films grown on insulating glass substrates. The optical properties of the thin films were characterized by photoluminescence (PL) measurement by using a He–Cd laser (325 nm) as the excitation source.

Hall measurement shows that the as-grown N-doped ZnO films on the glass substrates are *p*-type with hole concentration of 10^{16} – 10^{17} cm⁻³ and mobility of 1–10 cm² V⁻¹ s⁻¹. The lowest resistivity being recorded for these films was 20 Ω cm. Figure 2 shows a typical PL spectrum at $T=298$ K. Compared with the near-band-edge emission peak at 377 nm (or 3.29 eV) of bulk ZnO in Fig. 2, the emission peak for the N-doped ZnO thin film broadens with

FIG. 1. A schematic sketch of our monolithic ZnO LED. No geometrical optimization has been performed to enhance luminescence yield.

^{a)} Author to whom correspondence should be addressed; electronic mail: yezz@zju.edu.cn

FIG. 2. Photoluminescence spectra at $T=298$ K for bulk ZnO and nitrogen-doped ZnO thin films on glass substrates. Note that the spectrum in the latter case has been multiplied by a factor of 10.

the central peak redshifted to 389 nm (3.19 eV), alongside with two pronounced shoulders, one at the original 377 nm and the other at 398 nm (3.11 eV). These changes can be understood in terms a mixture of free exciton emission and nitrogen-related emissions such as donor-acceptor-pair (DAP) or electron-acceptor (e, A^0) transitions.^{19,20} The PL spectra of N-doped ZnO thin films confirm that nitrogen serves as relatively shallow acceptor in ZnO. Besides the near-band-edge emission, a much weaker, green-band emission at around 550 nm (2.25 eV) was also observed, which is generally attributed^{21,22} to radiative recombination at defects such as oxygen vacancies.

The Hall data and PL spectrum of the p -type ZnO thin films grown on glass substrates indicate that they have reasonably good electrical and optical properties. We expect that the p -type ZnO films grown on single-crystal ZnO wafers, under similar deposition conditions, should have even better physical properties than their counterparts on amorphous glass substrates. It should also be noted that our NO-plasma doping method have good repeatability, and that our MOCVD growth is considerably simpler than any MBE methods, especially than the repeated-temperature-modulation MBE previously reported.¹⁷

Figure 3(a) shows the I - V characteristics of a typical ZnO p - n junction on single-crystal ZnO substrate at $T=298$ K. It can be seen from the figure that the ZnO homo-junction has a rectifying behavior with a turn-on voltage of about 2.3 V, which is a little lower than that has been anticipated. The reduction of the turn-on voltage might be attributed both to the high defect concentration in the interface and to the low carrier concentration in the n -type side of the junction, as reported previously.^{15,23} The I - V characteristics of the In/Zn electrodes on the n - and p -type ZnO are shown in Fig. 3(b), respectively. They are reasonably linear, indicating a good Ohmic contact at both ends of the device.

Figure 4 shows the room-temperature EL spectra of the ZnO LED. At a forward current of 20 mA, we started to detect a weak luminescence in the region between yellow and blue (430–600 nm or 2.88–2.07 eV). As the current increases to 40 mA, besides the emissions at the visible region, which intensify as expected, an ultraviolet emission at around 375 nm (3.31 eV) was also detected. It coincides

(a)

(b)

FIG. 3. I - V characteristics of (a) the ZnO LED and (b) Ohmic contacts on both ends of the device by using the In/Zn alloy.

with the near-band-edge 377 nm peak seen in the PL in Fig. 2, suggesting band-to-band transition. At this current, the visible emission can be clearly seen in a dark background by naked eyes. We speculate that they are originated from defects such as the oxygen vacancies, which also have been detected in the PL spectrum. But the intensity ratio of the near-band-edge emission to the visible in the EL spectrum is much lower than that in the PL spectrum, due possibly both to reabsorption of the ultraviolet light by the p -type ZnO layer¹⁷ and to the differences in excited state density between the PL and the EL, as well as to the fact that the structure of the device has not yet been optimized. Even so, this intensity ratio is significantly better than those of the p - i - n junctions and metal-insulator-semiconductor (MIS) junctions demonstrated previously.^{17,24} The performance of our ZnO LEDs should be further improved by using transparent electrodes and double heterostructures such as ZnMgO/ZnO/ZnMgO or ZnO/ZnCdO/ZnO.

In conclusion, nitrogen-doped ZnO thin films have been grown on bulk ZnO substrate by MOCVD using NO plasma. The films exhibit p -type conductivity, allowing for the real-

FIG. 4. Room-temperature electroluminescence spectra of the LED as a function of the injected current.

ization of ZnO homojunction LED. The I - V curve of the homojunction has a turn-on voltage of about 2.3 V. Room-temperature electroluminescence has been demonstrated with a spectrum composed of both ultraviolet band-to-band emission and subband bluish-greenish emissions.

This work was supported by the National Natural Science Foundation of China under Grant Nos. 50532060, 50572095 and 60340460439.

¹M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. King, E. Weber, R. Russo, and P. Yang, *Science* **292**, 1897 (2001).

²C. H. Park, S. B. Zhang, and S. H. Wei, *Phys. Rev. B* **66**, 073202 (2002).

³S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, *J. Vac. Sci.*

Technol. B **22**, 932 (2004).

⁴E. C. Lee and K. J. Chang, *Phys. Rev. B* **70**, 115210 (2004).

⁵X. Li, Y. Yan, T. A. Gessert, C. L. Perkins, D. Young, C. DeHart, M. Young, and T. J. Coutts, *J. Vac. Sci. Technol. A* **21**, 1342 (2003).

⁶H. Matsui, H. Saeki, T. Kawai, H. Tabata, and B. Mizobuchi, *J. Appl. Phys.* **95**, 5882 (2004).

⁷W. Z. Xu, Z. Z. Ye, T. Zhou, B. H. Zhao, L. P. Zhu, and J. Y. Huang, *J. Cryst. Growth* **265**, 133 (2004).

⁸Z. Z. Ye, J. G. Lu, H. H. Chen, Y. Z. Zhang, L. Wang, B. H. Zhao, and J. Y. Huang, *J. Cryst. Growth* **253**, 258 (2003).

⁹Y. Yan, S. B. Zhang, and S. T. Pantelides, *Phys. Rev. Lett.* **86**, 5723 (2001).

¹⁰S. Limpijumnong, X. N. Li, S. H. Wei, and S. B. Zhang, *Appl. Phys. Lett.* **86**, 211910 (2005).

¹¹H. Tsukamoto, M. Nagai, E. Katoh, K. Tamamura, A. Ishibashi, and M. Ikeda, *Appl. Phys. Lett.* **70**, 1453 (1997).

¹²M. Joseph, H. Tabata, and T. Kawai, *Jpn. J. Appl. Phys., Part 2* **38**, L1205 (1999).

¹³D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).

¹⁴Y. R. Ryu, W. J. Kim, and H. W. White, *J. Cryst. Growth* **219**, 419 (2000).

¹⁵T. Aoki, Y. Hatanaka, and D. C. Look, *Appl. Phys. Lett.* **76**, 3257 (2000).

¹⁶F. Zhuge, L. P. Zhu, Z. Z. Ye, D. W. Ma, J. G. Lu, J. Y. Huang, F. Z. Wang, Z. G. Ji, and S. B. Zhang, *Appl. Phys. Lett.* **87**, 092103 (2005).

¹⁷A. 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).

¹⁸T. M. Barnes, J. Leaf, S. Hand, C. Fry, and C. A. Wolden, *J. Appl. Phys.* **96**, 7036 (2004).

¹⁹B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworak, U. Haboeck, and A. V. Rodina, *Phys. Status Solidi B* **241**, 231 (2004).

²⁰L. Wang and N. C. Giles, *Appl. Phys. Lett.* **84**, 3049 (2004).

²¹K. Vanhausden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, *J. Appl. Phys.* **79**, 7983 (1996).

²²S. B. Zhang, S. H. Wei, and A. Zunger, *Phys. Rev. B* **63**, 075205 (2001).

²³K. H. Bang, D. K. Hwang, M. C. Park, Y. D. Ko, I. Yun, and J. M. Myoung, *Appl. Surf. Sci.* **210**, 177 (2003).

²⁴X. L. Guo, J. H. Choi, H. Tabata, and T. Kawai, *Jpn. J. Appl. Phys., Part 2* **40**, L177 (2001).