

## Room temperature p-n ZnO blue-violet light-emitting diodes

Z. P. Wei, Y. M. Lu, D. Z. Shen, Z. Z. Zhang, B. Yao et al.

Citation: *Appl. Phys. Lett.* **90**, 042113 (2007); doi: 10.1063/1.2435699

View online: <http://dx.doi.org/10.1063/1.2435699>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v90/i4>

Published by the [American Institute of Physics](#).

---

### Related Articles

Degradation induced decrease of the radiative quantum efficiency in organic light-emitting diodes  
*APL: Org. Electron. Photonics* **5**, 199 (2012)

Degradation induced decrease of the radiative quantum efficiency in organic light-emitting diodes  
*Appl. Phys. Lett.* **101**, 103301 (2012)

High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules  
*Appl. Phys. Lett.* **101**, 093306 (2012)

High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules  
*APL: Org. Electron. Photonics* **5**, 198 (2012)

Magnetic-field dependent differential capacitance of polymer diodes  
*Appl. Phys. Lett.* **101**, 093303 (2012)

---

### Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT



**HAVE YOU HEARD?**

Employers hiring scientists  
and engineers trust  
**physicstodayJOBS**

<http://careers.physicstoday.org/post.cfm>



## Room temperature *p-n* ZnO blue-violet light-emitting diodes

Z. P. Wei

*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dongnanhu Road, Changchun 130033, China; Graduate School of Chinese Academy of Sciences, Beijing 100039, China; and Department of Physics, Changchun University of Science and Technology, Changchun 130022, China*

Y. M. Lu,<sup>a)</sup> D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Y. Zhang, D. X. Zhao, and X. W. Fan

*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dongnanhu Road, Changchun 130033, China*

Z. K. Tang

*Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China*

(Received 26 May 2006; accepted 21 December 2006; published online 26 January 2007)

ZnO *p-n* junction light-emitting diodes (LEDs) were fabricated on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates by plasma-assisted molecular beam epitaxy. Gas mixture of N<sub>2</sub> and O<sub>2</sub> was used as the *p*-type dopant, by which the double-donor doping of N<sub>2(O)</sub> can be avoided significantly. The fabricated *p*-type ZnO layers have a higher hole density and carrier mobility. The LEDs showed a very good rectification characteristic with a low threshold voltage of 4.0 V even at a temperature above 300 K. The LEDs can even emit intensive electroluminescence in the blue-violet region at the temperature of 350 K. The blue-violet emission was attributed to the donor-acceptor pair recombination at the *p*-type layer of the LED. © 2007 American Institute of Physics. [DOI: 10.1063/1.2435699]

Since the first observation of ultraviolet lasing action at room temperature from nanostructured ZnO thin films,<sup>1,2</sup> ZnO, as a promising material for ultraviolet photoelectronic device applications, has attracted extensive attention recently. In 2004, Tsukazaki *et al.*<sup>3</sup> succeeded in the demonstration of ultraviolet-blue electroluminescence of a ZnO *p-n* junction light-emitting diode (LED) operated at room temperature. Using recently developed techniques, ZnO thin films can be fabricated with a very good quality characterized by high electron mobility and low background carrier density. However, it is still a big challenge to fabricate high quality *p*-type ZnO. There have been many reports on getting high quality *p*-type ZnO thin films. The *p*-type ZnO can be obtained by N substitution in the O site (N<sub>O</sub>), using either NO,<sup>4,5</sup> N<sub>2</sub>O,<sup>6</sup> or activated nitrogenous species generated from a N<sub>2</sub>/O<sub>2</sub> plasma as dopant sources. However, the quality of the ZnO *p*-type layers fabricated in these ways is not satisfying for practical LED applications.<sup>7-9</sup> The reason is that, on the one hand, a nitrogen atom can substitute an oxygen site to generate an acceptor site; on the other hand, a N<sub>2</sub> molecule can also occupy an oxygen site to form a shallow double-donor N<sub>2(O)</sub> site.<sup>10</sup> The electroluminescence (EL) emitted from those ZnO LEDs was green or yellowish in color, mainly due to the low-efficiency deep-level recombination. In our previous work, we reported ultraviolet-blue light emission at 200 K from a ZnO *p-n* junction diode, where the *p*-type ZnO layer was directly grown on an *a*-plane Al<sub>2</sub>O<sub>3</sub> substrate using activated NO plasma as oxygen source and acceptor dopant.<sup>8</sup> The EL emission was, however, quenched quickly when temperature was raised to above 200 K. We attributed the emission quenching to unstable *p*-type conduction at high temperature due to the compensation of the *p*-type carriers by the residual donor impu-

rities, such as the shallow double-donor N<sub>2(O)</sub>, that were thermally ionized at high temperature. Therefore, it is crucial to control the N/O atom ratio in order to fabricate *p*-type ZnO layers with stable hole-carrier conduction.

In this letter, we report fabrication of *p*-type ZnO on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates using plasma-assisted molecular beam epitaxy (P-MBE). 6N-purity Zn metal was used as the zinc source, rf plasma activated O<sub>2</sub> (5N purity) and N<sub>2</sub> (5N purity) were introduced into the growth chamber simultaneously as the oxygen and *p*-type dopant sources, respectively. The current-voltage curve of the *p-n* junction LED measured at room temperature showed a typical diode characteristic. A near-band-edge bluish electroluminescence band at around 420 nm was observed from the ZnO LED even above room temperature under a forward bias voltage with a threshold of 4.0 V, implying very stable *p*-type conduction even at high temperature.

To reduce the double-donor sites of N<sub>2(O)</sub> during N doping, the N<sub>2</sub> content in the reaction gas source should be decreased as much as possible while keeping a reasonably high ratio of the dissociated nitrogen N. Precise control of the N/O ratio is essential for growth of high quality *p*-type ZnO, especially for the dynamically controlled growth at low growth temperature.

It is noticed that the dissociation energies of N<sub>2</sub> and O<sub>2</sub> molecules are very different. The energy of dissociating a N<sub>2</sub> molecule into two N atoms is 9.60 eV.<sup>11</sup> In contrast, the dissociation energy of an O<sub>2</sub> molecule is only 5.12 eV.<sup>12</sup> Because of the high dissociation energy of N<sub>2</sub>, the dissociate rate of N<sub>2</sub> molecule to N atoms might be low for pure N<sub>2</sub> gas. Thus, it is not easy to increase the N/O ratio and decrease the N<sub>2</sub>/O ratio in the growth chamber if we separately introduce pure N<sub>2</sub> and O<sub>2</sub> gases into the growth chamber. If a gas mixture of N<sub>2</sub> and O<sub>2</sub> was used instead of pure gases, then under the assistance of plasma activation, the dissocia-

<sup>a)</sup> Author to whom correspondence should be addressed; FAX: 86-431-85682964; electronic mail: ymlu@mail.jl.cn

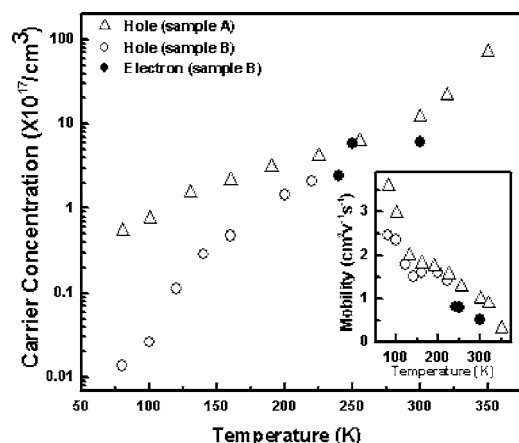


FIG. 1. Temperature dependence of the carrier concentrations and mobilities (inset) of the different samples. Triangles: data of sample A prepared using the  $N_2/O_2$  gas mixture; solid and opened circles: data of sample B prepared using NO gas.

tion reaction of the gas mixture would take place according to the following steps:



Under a given plasma activation power, reaction (1) can occur easily because of the relatively low dissociation energy of  $O_2$  (5.12 eV). With the existence of the large number of O atoms, O ions, as well as the thermal electrons produced in reaction (1),  $N_2$  can react with O atoms to produce NO and N according to reaction (2). The activation energy of reaction (2) is 318 kJ,<sup>13</sup> which can transform to 3.25 eV. NO molecules can further be dissociated with the assistance of strong collision between NO and the thermal electrons according to reaction (3) with dissociation energy of 6.6 eV.<sup>14</sup> The dissociation energy of the three reactions are lower than that of  $N_2$  (9.6 eV). The final products of the plasma activated gas mixture are dominated by the O and N atoms, and the content of  $N_2$  can be reduced significantly. Through controlling the N/O ratio, the  $p$ -type carrier density in the ZnO layer can be controlled. In the experiment, we used the following optimized growth conditions:  $N_2/O_2$  ratio=0.5, plasma power=300 W. These optimized conditions can decrease the density of intrinsic vacancy defect and increase the density of indispensable nitrogen acceptors in the  $p$ -type ZnO layers.

Figure 1 shows the electric properties of the  $p$ -ZnO layers produced using the gas mixture of  $N_2$  and  $O_2$  (sample A) and by using pure NO gas (sample B, reported in Refs. 4 and 8), which are plotted as a function of temperature. With increasing temperature, the carrier concentration of sample A and B increased, while the mobility of the two samples decreased. The carrier concentration and mobility of sample A are significantly larger than those of sample B at various temperatures. At room temperature, the hole-carrier concentration and the mobility of sample A are  $1.2 \times 10^{18} \text{ cm}^{-3}$  and  $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Most importantly, sample A keeps a stable  $p$ -type conduction at least until 350 K, while the  $p$ -type conduction of sample B is not stable at high temperature, as seen in Fig. 1; the conduction transferred from  $p$  type to  $n$  type at temperatures above 200 K because of ther-

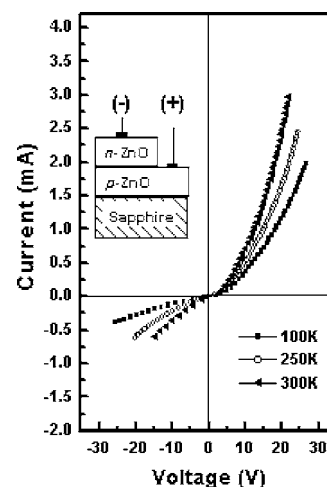


FIG. 2.  $I$ - $V$  characteristics of the ZnO LED measured in the temperature region of 100–300 K. The inset schematically shows the structure of the  $p$ - $n$  junction LED.

mal activation of the residual impurity donors [e.g.,  $N_{2(O)}$ ] in sample B.<sup>7</sup> In contrast, this  $p$ -type to  $n$ -type transition disappeared in sample A, indicating a stable  $p$ -type conduction in sample A even at high temperature. This stable  $p$ -type conduction can be attributed to the high density of net N acceptors and low density of  $N_{2(O)}$  donors, benefiting from the mixture gas technique.

A 200-nm-thick  $p$ -type ZnO layer was grown directly on the  $c$ -plane  $Al_2O_3$ , which was capped by a 200-nm-thick  $n$ -type layer that was grown using Zn and pure  $O_2$  as sources without intentional donor doping. The carrier concentration and mobility of the  $n$ -type ZnO are  $7 \times 10^{18} \text{ cm}^{-3}$  and  $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Au–Ni and In electrodes were used to form ohmic contact to the  $p$ -type and the  $n$ -type layer, respectively.<sup>8</sup> The structure of the ZnO  $p$ - $n$  junction LED is schematically shown in the inset of Fig. 2. At low temperature (100 K), the current-voltage ( $I$ - $V$ ) curve of the ZnO LED shows a good rectification characteristic with a low leak current at reversed bias voltage and a threshold voltage 4.0 V at forward bias, as seen in Fig. 2. The  $p$ - $n$  junction LED keeps a good rectifying characteristic even when increasing temperature up to 300 K.

The EL spectra of the ZnO LED recorded at temperatures ranging from 250 to 350 K are shown in Fig. 3(a). The

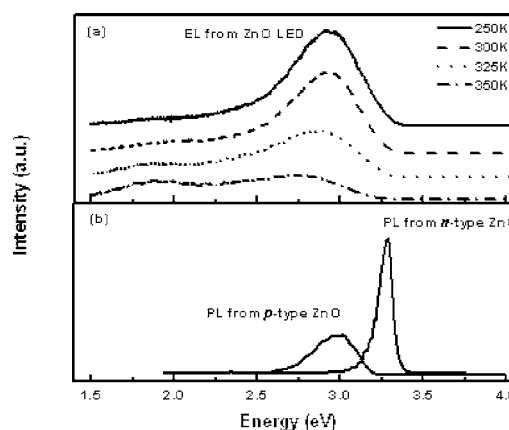


FIG. 3. (a) EL spectra measured at 250–350 K under a fixed forward-biased voltage of 20 V. (b) PL spectra of undoped  $n$ -type and  $N$ -doped  $p$ -type ZnO layers at 300 K.



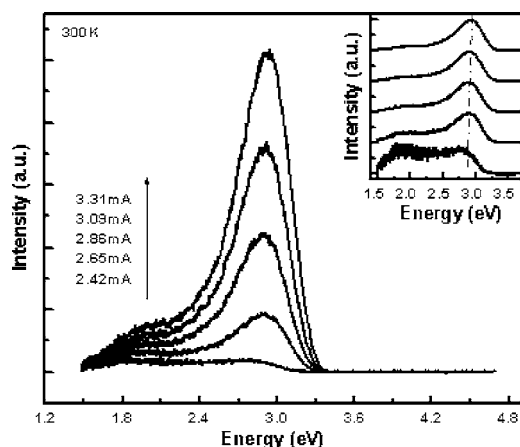


FIG. 4. EL spectra of the ZnO LED measured at room temperature under various injection currents. The inset shows the normalized EL spectra in which blueshift of the emission peak is clearly seen.

forward-biased voltage was fixed at 20 V. To investigate the origin of the EL band, photoluminescence (PL) spectra of the *p*-type and *n*-type ZnO layers excited using the 325 nm line of a He-Cd laser were also measured at room temperature, shown in Fig. 3(b). The PL peak of the *n*-type side of the LED located at 3.29 eV comes from the exciton relative emission, while this emission cannot be measured from the *p*-type side. The PL peak of *p*-type side is located at 3.0 eV, which is due to the recombination of donor-acceptor pairs.<sup>15–17</sup> At 250 K, the EL spectrum is dominated by the emission band in the blue-violet region (423 nm) with a weak emission band in the red region (650 nm). Note that the blue-violet EL band is very similar to the PL spectrum of the *p*-type ZnO layer. With increasing temperature from 250 to 350 K, the blue-violet emission band slightly shifted from 420 to 446 nm, accompanied with decrease in emission intensity, and the whole spectrum was gradually dominated by the red emission band. Because mobility of the hole carriers in the *p*-type side is much smaller than that of electron carriers in the *n*-type side, electron injection from the *n*-type side to the *p*-type side is more efficient than the injection of holes from the *p* side to the *n* side. Thus, the EL of the ZnO LED mainly resulted from the combination of holes in the *p*-type side with the electrons injected from the *n*-type side. That is why the EL spectrum is so similar to the PL spectrum of the *p*-type ZnO layer.

Figure 4 shows the EL spectra measured at room temperature under various forward injection currents of 2.42, 2.65, 2.86, 3.09, and 3.31 mA. Under the injection current of 2.42 mA, the emission band is located at 2.83 eV with a full width at half maximum of 500 meV. With increasing injection current, the emission band shifted to the higher energy side. The inset shows the normalized EL spectra, from which we can see the peak energy of the emission band shifting from 2.83 to 2.95 eV when the injection current changed from 2.42 to 3.31 mA. The blueshift of the emission band with the injection current suggests that the EL mechanism originated from the donor-acceptor pair recombination in the *p*-type ZnO layer.

In conclusion, a high density of double-donor doping of  $N_{2(O)}$  sides exists in those *p*-type ZnO layers fabricated using pure  $N_2$  gas as the *p*-type dopant. Because of the high dissociation energy of nitrogen molecules, the dissociation rate of  $N_2$  is very low in pure nitrogen gas even with the assis-

tance of plasma activation. The incompletely dissociated  $N_2$  molecules can occupy the oxygen sites in the ZnO lattice, leading to the double-donor doping of  $N_{2(O)}$  defects. Instead of using pure  $N_2$  gas, we used a gas mixture of  $N_2$  and  $O_2$  as the *p*-type doping source, so that the content of  $N_2$  molecules in the plasma activated gas product can be decreased significantly. The electric properties of the *p*-type ZnO layers prepared using the gas-mixture technique were improved obviously, characterized by high density and high mobility of the hole carriers. We fabricated ZnO *p-n* junction LEDs on *c*-plane  $Al_2O_3$  substrates using P-MBE technique. The LEDs showed a very good rectification characteristic even at a temperature above 300 K. The threshold voltage for the light emission was as low as 4.0 V at 300 K. The LED can even emit intensive EL in the blue-violet region at the temperature of 350 K. The blue-violet emission was attributed to the donor-acceptor pair recombination at the *p*-type layer of the LED.

This work is supported by the “863” High Technology Research Program in China, under Grant No. 2001AA311120, the Key Project of National Natural Science Foundation of China under Grant No. 60336020, the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos. 60278031, 60376009, 50402016, 60506014, and 60501025, the State Natural Science Foundation—Outstanding Oversea Chinese Young Scholar Foundation, No. 60429403, and the Direct Allocation Grant of Research Grants Committee of Hong Kong, No. DAG04/05.SC24.

- <sup>1</sup>Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
- <sup>2</sup>D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **73**, 1038 (1998).
- <sup>3</sup>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).
- <sup>4</sup>Xin-Li Guo, Hitoshi Tabata, and Tomoji Kawai, J. Cryst. Growth **223**, 135 (2001).
- <sup>5</sup>H. W. Liang, Y. M. Lu, D. Z. Shen, Y. C. Liu, J. F. Yan, C. X. Shan, B. H. Li, Z. Z. Zhang, J. Y. Zhang, and X. W. Fan, Phys. Status Solidi A **202**, 1060 (2005).
- <sup>6</sup>D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
- <sup>7</sup>A. Tsukazaki, M. Kubota, A. Ohtomo, T. Onuma, K. Ohtani, H. Ohno, S. F. Chichibu, and M. Kawasaki, Jpn. J. Appl. Phys., Part 2 **44**, L643 (2005).
- <sup>8</sup>S. J. Jiao, Z. Z. Zhang, Y. M. Lu, D. Z. Shen, B. Yao, J. Y. Zhang, B. H. Li, D. X. Zhao, X. W. Fan, and Z. K. Tang, Appl. Phys. Lett. **88**, 031911 (2006).
- <sup>9</sup>W. Liu, S. L. Gu, J. D. Ye, S. M. Zhu, S. M. Liu, X. Zhou, R. Zhang, Y. Hang, and C. L. Zhang, Appl. Phys. Lett. **88**, 092101 (2006).
- <sup>10</sup>Eun-Cheol Lee, Y. S. Kim, Y. G. Jin, and K. J. Chang, Phys. Rev. B **64**, 085120 (2001).
- <sup>11</sup>K. Ohkawa, T. Karasawa, and T. Mitsuyu, J. Cryst. Growth **111**, 759 (1991).
- <sup>12</sup>P. Brix and G. Herzberg, Can. J. Phys. **32**, 110 (1954).
- <sup>13</sup>J. V. Michael and K. P. Lim, J. Chem. Phys. **97**, 3228 (1992).
- <sup>14</sup>T. A. Cleland and D. W. Hess, J. Electrochem. Soc. **136**, 3103 (1989).
- <sup>15</sup>A. Zeuner, H. Alves, D. M. Hofmann, B. K. Meyer, A. Hoffmann, U. Haboeck, M. Strassburg, and M. Dworzak, Phys. Status Solidi B **234**, R7 (2002).
- <sup>16</sup>S. J. Jiao, Y. M. 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).
- <sup>17</sup>K. Tamura, T. Makino, A. Tsukazaki, M. Sumiya, S. Fuke, T. Furumochi, M. Lippmaa, C. H. Chia, Y. Segawa, H. Koinuma, and M. Kawasaki, Solid State Commun. **127**, 265 (2003).