Phys. Status Solidi B **250**, No. 10, 2102–2105 (2013) / **DOI** 10.1002/pssb.201300015

physica status solidi b
www.pss-b.com
basic solid state physics

Stable p-type ZnO films obtained by lithium–nitrogen codoping method

Shen He[1,2], Shan Chong-Xin[*,1], Liu Ji-Shan[1,2], Li Bing-Hui[1], Zhang Zhen-Zhong[1], and Shen De-Zhen[1]

[1] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 130033 Changchun, P. R. China
[2] Graduate University of Chinese Academy of Sciences, 100049 Beijing, P. R. China

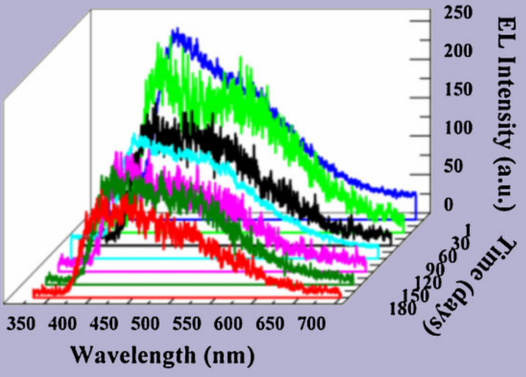
Received 31 January 2013, revised 29 March 2013, accepted 7 May 2013

Keywords doping, light-emitting devices, p–n junction, zinc oxide

---

[*] Corresponding author: e-mail shancx@ciomp.ac.cn, Phone: +86-43186176340, Fax: +86-43186176312

By employing lithium and nitrogen codoping method, p-type zinc oxide (ZnO) films have been prepared, and the p-type conduction can maintain for 207 days. ZnO p–n junctions have been constructed based on the p-type ZnO. Under the drive of continuous current, obvious emission has been observed from the p–n junctions, and the ZnO p–n junction light-emitting devices (LEDs) can still work after placing in air ambient for 180 days.



Room temperature electroluminescence spectra of the p-ZnO:(Li,N)/n-ZnO structured LEDs under continuous current recorded intermittently for 180 days.

1 Introduction Zinc oxide (ZnO) has attracted much attention in recent years for its unique properties such as wide direct bandgap, large exciton binding energy, etc. The unique properties make ZnO a promising candidate in efficient ultraviolet light-emitting devices (LEDs) and low-threshold lasers [1–3]. To realize high-performance ZnO LEDs, p–n junction is almost indispensable [4]. Therefore, it is a must to dope the intrinsic electron-dominant n-type ZnO into hole-dominant p-type one. Although numerous efforts have been paid to this issue [5–16], and p-type ZnO films have been demonstrated using various dopants such as nitrogen (N) [8], phosphorous [9], arsenic [10], antimony [11], and lithium (Li) [12], sodium [13], etc., the reproducibility of p-type ZnO is still low. Additionally, it has been reported that p-type ZnO tend to convert to n-type conduction after placing in air ambient for a short period [17, 18], that is the stability of p-type ZnO is still poor. The poor reproducibility and stability of p-type ZnO hinder the realization of high-performance ZnO-based LEDs drastically.

In this paper, we show that stable p-type ZnO films can be prepared by using a Li,N codoping method, and the p-type conduction of the ZnO:(Li,N) can persist for 207 days. A ZnO:(Li,N)/n-ZnO structure has been fabricated, and obvious emission can be detected from the p–n junctions under the drive of continuous current. The LEDs fabricated from the ZnO p–n junctions can still work after placing for over 180 days in air ambient. The above facts indicate the good stability of the p-type ZnO-based films obtained using the Li,N codoping method.

2 Experimental All the films investigated in this paper were grown in a VG V80H molecular beam epitaxy technique by employing *a*-plane sapphire as a substrate. Metallic zinc and metallic lithium contained in individual

Knudsen cells were employed as the zinc precursor and lithium dopant for the growths. The temperature for the Zn and Li Knudsen cell was kept at 240 and 310 °C, respectively. Oxygen gas (6N) and nitric oxide gas (6N) activated by an Oxford Applied Research plasma cell (Model HD25) at a fixed radio-frequency power of 330 W were employed as the oxygen precursor and nitrogen dopant. The NO flow was set at 0.85 sccm. Prior to the growth, the sapphire substrate was treated by oxygen plasma at 800 °C for 15 min to produce an oxygen-terminated surface. Then a ZnO buffer layer was deposited at 800 °C for 20 min before a 2 h growth at 750 °C [19]. A thermal annealing process was performed in oxygen ambient to further improve the quality of the ZnO layer. Finally, Li,N codoped ZnO (ZnO:(Li,N)) layer was deposited onto the annealed ZnO layer to form ZnO:(Li,N)/ZnO structure. In and Ni/Au metal deposited by vacuum evaporation were used as contacts on the n-ZnO layer and the ZnO:(Li,N) layer, respectively. The electrical properties of the layers and the *I*–*V* curve of the ZnO:(Li,N)/ZnO structure were measured in a Hall measurement system (Lakeshore 7707). The capacitance–voltage (*C*–*V*) characteristics of the structure were recorded in a semiconductor parameter analyzer (Agilent B1500A). Photoluminescence (PL) measurement was performed in a JY-630 micro-Raman spectrometer employing the 325 nm line of a He-Cd laser as the excitation source. Electroluminescence (EL) measurement of the structures was carried out in a Hitachi F4500 spectrometer under the drive of a continuous current source.

3 Results and discussion

The schematic illustration of the ZnO:(Li,N)/n-ZnO structure is shown in the down-right inset of Fig. 1. The n-ZnO layer is about 500 nm in thickness and shows an electron concentration and Hall mobility of $4.0 \times 10^{16}\,\mathrm{cm}^{-3}$ and $17\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$, respectively. The ZnO:(Li,N) layer is about 100 nm in thickness. Since the direct Hall measurement on the ZnO:(Li,N) layer deposited on n-ZnO layer will be interfered by the underneath n-ZnO layer, the carrier concentration of the ZnO:(Li,N) layer in the structure cannot be given directly by a Hall measurement. To test the conduction type of the ZnO:(Li,N) layer, the *I*–*V* curve of the ZnO:(Li,N)/n-ZnO structure has been measured, as shown in Fig. 1. Although the leakage current is relatively large, the curve shows a perceptible rectifying behavior with a turn-on voltage of about 3.7 V. The linear *I*–*V* dependence for both Ni/Au electrode on the ZnO:(Li,N) layer and In electrode on the n-ZnO layer shown in the top-left inset of Fig. 1 reveals that ohmic contacts have been obtained for both electrodes. Then the rectifying behaviors observed should come from the ZnO:(Li,N)/n-ZnO interface, which suggests that the ZnO:(Li,N) layer may have p-type conduction.

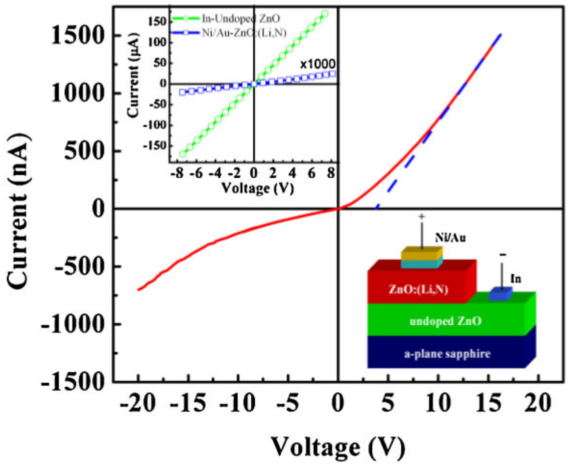


Figure 1 *I*–*V* curve of the ZnO:(Li,N)/n-ZnO structure. The insets show the schematic diagram of the structure and *I*–*V* curves of the Ni/Au contact to the ZnO:(Li,N) layer and the In contact to the ZnO layer.

In order to determine the hole concentration in the ZnO:(Li,N) layer, *C*–*V* measurement has been carried out on the ZnO:(Li,N)/n-ZnO structure, the results of which are shown in Fig. 2. To rule out the interference of the diffusion capacitance, the capacitance of the ZnO:(Li,N)/n-ZnO structure was measured under reverse bias. As shown in the figure, the depletion layer capacitance decreases with the increase of the negative bias voltage. The net acceptor concentration, N_A–N_D, in the ZnO:(Li,N) layer can be determined from the *C*–*V* behavior using the following formula [20]:

$$N_\mathrm{A} - N_\mathrm{D} = \frac{2}{A^2 \varepsilon_\mathrm{s} q}\left[-\frac{1}{\mathrm{d}(1/C^2)/\mathrm{d}V}\right], \qquad (1)$$

where A is the effective area of the junction, ε_s is the permittivity of the semiconductor, and q is the elemental electron charge. Figure 2 also shows a plot of $1/C^2$ as a function of the bias applied on the structure. The slope is $5.7 \times 10^{20}\,\mathrm{F}^{-2}\,\mathrm{V}^{-1}$, and the net acceptor concentration calculated from Eq. (1) is about $1.7 \times 10^{15}\,\mathrm{cm}^{-3}$.

To show the stability of the p-type ZnO films, ZnO:(Li,N) films have been grown directly onto *a*-plane sapphire substrates, and the hole concentration, Hall mobility, and

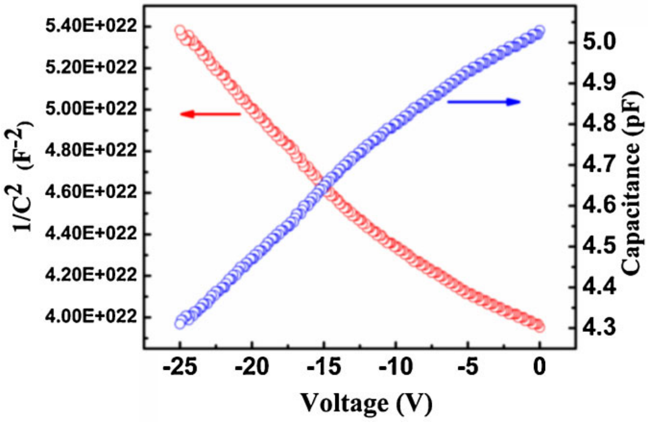


Figure 2 *C*–*V* characteristics of the ZnO:(Li,N)/n-ZnO structure and the plot of $1/C^2$ versus V for the structure.

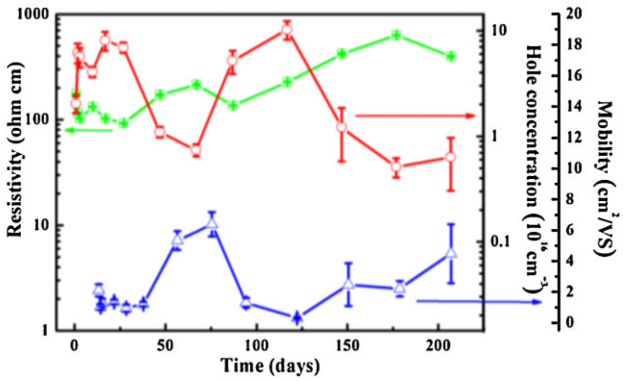


Figure 3 The hole concentration, Hall mobility, and resistivity of the ZnO:(Li,N) films as a function of time placed in air ambient.

resistivity of the films have been measured intermittently using Hall measurement system, the results of which are shown in Fig. 3. Note that the hole concentration and Hall mobility vary for different samples. One can see from the figure that although the hole concentration and Hall mobility vary greatly in the investigated 207 days, hole-dominant p-type conduction remains, indicating the good stability of the p-type ZnO obtained via the Li,N codoping method.

The typical PL spectrum of the ZnO:(Li,N) films measured at 11 K is illustrated in Fig. 4, in which four peaks at 3.362, 3.351, 3.309, and 3.234 eV can be observed. According to their position, the peak at 3.362 eV can be attributed to the emission from excitons bound to neutral donors (D^0X), the one at 3.351 eV from excitons bound to neutral acceptors (A^0X) [21]. The origin of the emission at 3.310 eV is controversial, some researchers demonstrated that it is related with stacking faults [22], while others assigned it to donor–acceptor pairs (DAP) emission in ZnO [21, 23]. The peak at 3.234 eV comes from the phonon replica of DAP emission (DAP-1LO) [21]. The dominant acceptor-related emission consolidates the p-type conduction of the ZnO:(Li,N) films.

To test the applicability of the ZnO:(Li,N)/ZnO p–n junction in LEDs, the EL spectra of the structure are measured at room temperature under the injection of continuous current, as shown in Fig. 5. When the injection current is 7 mA, obvious emission can be detected, and the spectrum can be well fitted using two Gaussian lineshapes at around 415 and 500 nm, as shown in the inset of Fig. 5. We note that the emission at around 500 nm comes from the deep-level emission of ZnO. As for the emission at 415 nm, it has been frequently observed in ZnO p–n junctions, and can be attributed to the emission from DAP in ZnO [5, 24]. It is noteworthy that after being placed in air ambient for over 180 days, emission can still be detected from the LEDs, and the spectra of which under the same injection current are shown in Fig. 5. One can see that the spectra of the device after 180 days degrade little compared with that of the as-grown one besides that its intensity decreases slightly. The above facts confirm the good stability of the p-type ZnO films obtained using the Li,N codoping method.

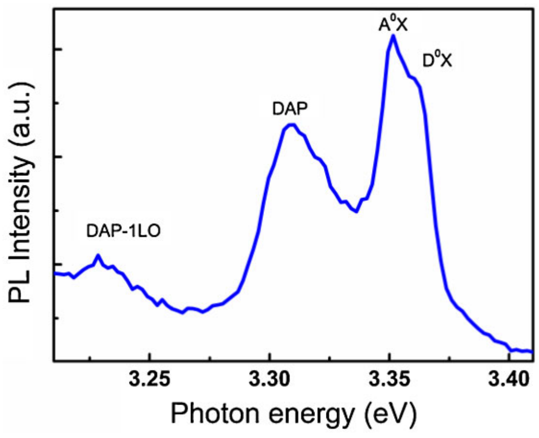


Figure 4 PL spectrum of the ZnO:(Li,N) film at 11 K.

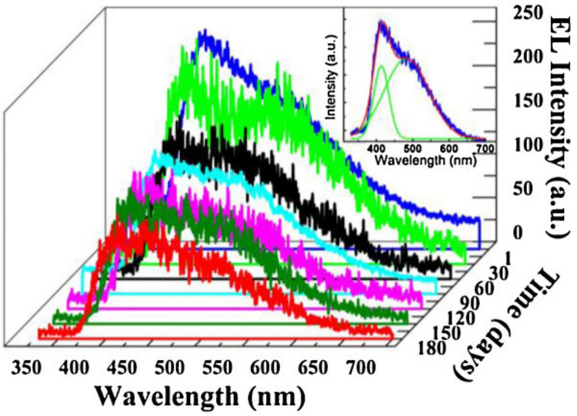


Figure 5 Room temperature EL spectra of the p-ZnO:(Li,N)/n-ZnO structured LEDs under an injection current of 7 mA recorded intermittently for 180 days, and the inset shows the spectrum of the as-grown structure, which can be well fitted using two Gaussian curves.

Note that although obvious emission has been realized reproducibly from ZnO p–n junctions, the emission is dominated by DAP emission, which means that the most noteworthy character of ZnO, the large exciton binding energy, has not been fulfilled yet. To realize excitonic emission of ZnO, p-$\mathrm{Mg_{0.25}Zn_{0.75}O}$:(Li,N)/n-ZnO heterostructures have been fabricated experimentally by using the above-mentioned Li,N codoping method. In these structures, electrons will be confined into the n-ZnO layer by the conduction band offset at the $\mathrm{Mg_{0.25}Zn_{0.75}O}$/ZnO interface, while holes can enter from the p-$\mathrm{Mg_{0.25}Zn_{0.75}O}$ into the n-ZnO easily, then electrons and holes will recombine radiatively in the n-ZnO layer, and near-band-edge emission from ZnO has been realized. The p-$\mathrm{Mg_{0.25}Zn_{0.75}O}$:(Li,N)/n-ZnO heterostructured LED can work continuously for 6.8 h under the injection of 20 mA continuous current, which has been published in our previous publication [20]. This is the first report on ZnO-based p–n junction LEDs that can work continuously to the best of our knowledge. The above facts confirm again the good stability of the p-type ZnO-based films obtained via the Li,N codoping method.

The reason for the stable p-type ZnO via Li,N codoping method is not clear yet. It is anticipated that when Li is incorporated into ZnO films, both interstitial Li (Li_i) and Li substituted Zn (Li_{Zn}) will be formed, and Li_i is a donor, while Li_{Zn} is an acceptor in ZnO [25–27]. While in Li,N codoped ZnO films, the Li_i may be passivated by N, thus Li_{Zn} act as effective acceptors in the films [14, 28], and the activation energy for the Li_{Zn} acceptors is about 90 meV [14, 29]. Furthermore, it has been reported that Li can be easily bonded with N [30], and the Li–N bond in ZnO:(Li,N) films has been confirmed by X-ray photoelectron spectroscopy [14, 28]. The bonding will decrease the movement of the dopants in ZnO, thus may help to improve the stability of the p-type ZnO films. Nevertheless, obviously the actual mechanism needs further investigations.

4 Conclusions In summary, p-type ZnO films have been prepared by using Li,N codoping method, and the p-type conduction can maintain for 207 days. ZnO-based p–n junction LEDs have been fabricated based on the p-type films. Obvious emission can be observed from the ZnO p–n junction structured LEDs under the injection of continuous current. The LEDs can still work after placing in air ambient for over 180 days, confirming the good stability of the p-type ZnO films obtained via the Li,N codoping method. The results reported in this paper provide a route for stable p-type ZnO films, thus may lay a ground for a variety of ZnO-based optoelectronic devices. We note that although p-type ZnO films have been realized, the hole concentration and Hall mobility of the films are still low, and the performance of the LEDs is still far below expectation. Thus, there is still a long way to go for efficient p-type ZnO and high-performance ZnO-based LEDs.

Acknowledgements This work is supported by the National Basic Research Program of China (2011CB302005), the Natural Science Foundation of China (11074248, 11104265, 61177040, and 11134009), and the Science and Technology Developing Project of Jilin Province (20111801).

References

[1] L. Beaur, T. Bretagnon, B. Gil, T. Guillet, D. Tainoff, M. Teisseire, and J. M. Chauveau, Phys. Status Solidi C **9**, 1320 (2012).

[2] H. Zhu, C. X. Shan, B. Yao, B. H. Li, J. Y. Zhang, Z. Z. Zhang, D. X. Zhao, D. Z. Shen, X. W. Fan, Y. M. Lu, and Z. K. Tang, Adv. Mater. **21**, 1613 (2009).

[3] E. S. P. Leong and S. F. Yu, Adv. Mater. **18**, 1685 (2006).

[4] K. Ding and C. Z. Ning, Light Sci. Appl. **1**, e20 (2012).

[5] 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, Nature Mater. **4**, 42 (2005).

[6] 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).

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

[8] K. Nakahara, S. Akasaka, H. Yuji, K. Tamura, T. Fujii, Y. Nishimoto, D. Takamizu, A. Sasaki, T. Tanabe, H. Takasu, H. Amaike, T. Onuma, S. F. Chichibu, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, Appl. Phys. Lett. **97**, 013501 (2010).

[9] Y. W. Heo, S. J. Park, K. Ip, S. J. Pearton, and D. P. Norton, Appl. Phys. Lett. **83**, 1128 (2003).

[10] J. C. Fan, C. Y. Zhu, S. Fung, Y. C. Zhong, K. S. Wong, Z. Xie, G. Brauer, W. Anwand, W. Skorupa, C. K. To, B. Yang, C. D. Beling, and C. C. Ling, J. Appl. Phys. **106**, 073709 (2009).

[11] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, Appl. Phys. Lett. **87**, 252102 (2005).

[12] Y. J. Zeng, Z. Z. Ye, W. Z. Xu, D. Y. Li, J. G. Lu, L. P. Zhu, and B. H. Zhao, Appl. Phys. Lett. **88**, 062107 (2006).

[13] S. S. Lin, J. G. Lu, Z. Z. Ye, H. P. He, X. Q. Gu, L. X. Chen, J. Y. Huang, and B. H. Zhao, Solid State Commun. **148**, 25 (2008).

[14] F. Sun, C. X. Shan, B. H. Li, Z. Z. Zhang, D. Z. Shen, Z. Y. Zhang, and D. Fan, Opt. Lett. **36**, 499 (2011).

[15] S. Chu, G. P. Wang, W. H. Zhou, Y. Q. Lin, L. Chernyak, J. Z. Zhao, J. Y. Kong, L. Lin, J. J. Ren, and J. L. Liu, Nature Nanotechnol. **6**, 506 (2011).

[16] J. C. Sun, J. Z. Zhao, H. W. Liang, J. M. Bian, L. Z. Hu, H. Q. Zhang, X. P. Liang, W. F. Liu, and G. T. Du, Appl. Phys. Lett. **90**, 121128 (2007).

[17] L. G. Wang and A. Zunger, Phys. Rev. Lett. **90**, 256401 (2003).

[18] T. M. Barnes, K. Olson, and C. A. Wolden, Appl. Phys. Lett. **86**, 112112 (2005).

[19] J. S. Liu, C. X. Shan, S. P. Wang, F. Sun, B. Yao, and D. Z. Shen, J. Cryst. Growth **312**, 2861 (2010).

[20] J. S. Liu, C. X. Shan, H. Shen, B. H. Li, Z. Z. Zhang, L. Liu, L. G. Zhang, and D. Z. Shen, Appl. Phys. Lett. **101**, 011106 (2012).

[21] C. X. Shan, Z. Liu, and S. K. Hark, Appl. Phys. Lett. **92**, 073103 (2008).

[22] M. Schirra, R. Schneider, A. Reiser, G. M. Prinz, M. Feneberg, J. Biskupek, U. Kaiser, C. E. Krill, K. Thonke, and R. Sauer, Phys. Rev. B **77**, 125215 (2008).

[23] Y. Kashiwaba, K. Haga, H. Watanabe, B. P. Zhang, Y. Segawa, and K. Matsushita, Phys. Status Solidi C **1**, 912 (2004).

[24] 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).

[25] Z. Zhang, K. E. Knutsen, T. Merz, A. Yu Kuznetsov, B. G. Svensson, and L. J. Brillson, J. Phys. D, Appl. Phys. **45**, 375301 (2012).

[26] J. S. Lee, S. N. Cha, J. M. Kim, H. W. Nam, S. H. Lee, W. B. Ko, K. L. Wang, J. G. Park, and J. P. Hong, Adv. Mater. **23**, 4183 (2011).

[27] S. Y. Tsai, M. H. Hon, and Y. M. Lu, J. Phys. Chem. C **115**, 10252 (2011).

[28] B. Y. Zhang, B. Yao, Y. F. Li, Z. Z. Zhang, B. H. Li, C. X. Shan, D. X. Zhao, and D. Z. Shen, Appl. Phys. Lett. **97**, 222101 (2010).

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

[30] E. Döneges, in: Handbook of Preparative Inorganic Chemistry, 2nd edition, Vol. 1, edited by G. Brauer (Academic Press, New York, 1963), p. 984.