Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Crystal Growth 301–302 (2007) 362–365
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

p-Type ZnO on sapphire by using O_2–N_2 co-activating and fabrication of ZnO LED

Z.Z. Zhang[a,*], Z.P. Wei[a], Y.M. Lu[a], D.Z. Shen[a], B. Yao[a], B.H. Li[a], D.X. Zhao[a], J.Y. Zhang[a], X.W. Fan[a], Z.K. Tang[b]

[a]*Key Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dongnanhu Road, Changchun 130033, People's Republic of China*

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

Available online 17 January 2007

Abstract

A co-activating route was employed to fabricate ZnO light-emitting diode (LED) by using molecular beam epitaxy. N_2 was used as the acceptor dopant source and O_2 was used as assistant gas for N_2 decomposing more than only oxygen source. Emission spectra of the $N_2 + O_2$ mixture plasma were monitored in situ in order to adjust growth parameters timely. Under the assistance of O_2, N atoms content in the plasma of the mixture shows a significant increase compared to the case without O_2 assistance. Electrical measurements of the as-grown p-type ZnO on sapphire show a carrier concentration of $1.2 \times 18\,cm^{-3}$ and a mobility approaching $1\,cm^2\,V^{-1}\,s^{-1}$. A ZnO LED was fabricated by depositing undoped n-type ZnO on the p-type layer. The turn-on voltage at 100 K is about 3.70 V, which approaches the bandgap of ZnO. Electroluminescence spectra show two bands: one is centered at 423 and the other centered at 523 nm, respectively.
© 2006 Elsevier B.V. All rights reserved.

PACS: 78.55.Et; 81.15.Hi; 85.60.Jb

Keywords: A3. Molecular beam epitaxy; B2. Semiconducting II–VI materials; B3. Light-emitting diodes

1. Introduction

p-Type ZnO has attracted more and more attention because it is necessary to fabricate ZnO light-emitting devices based on current injection [1–4]. Many improvements on p-type ZnO and p–n junctions were reported continually [5–10]. In these works, there is no lack of excellent electric properties and beautiful rectification curves. However, few electroluminescence (EL) results were reported [7–10]. In general, the mobility of electrons is much larger than that of holes due to the difference in effective mass. As a result, the current in the ZnO p–n junction is dominated by the electron injection from the n-layer to the p-layer [7,8]. Before resolving the problem on low-hole-mobility in ZnO, it is necessary to ensure high optical quality of p-type ZnO. Therefore, N, which has a similar atomic radius compared with O, is often selected as acceptor dopant to decrease the lattice disturbance during doping. We had reported fabricating of the ZnO p–n junction light-emitting diode (LED) on sapphire substrate by using activated NO, which means N is an appropriate candidate for ZnO p-type doping [8].

Here, another route will be introduced to fabricate p-type ZnO:N layer and p–n junction LED. Being different from the early results [8], activated N_2 is employed as the dopant, and O_2 is used to assist the N_2 decomposition as well as to act as O source. This method has ever been used in growing p-type ZnO on ZnO wafer by Look et al. [1]. Here, a ZnO LED was fabricated successfully on sapphire through this route.

2. Experiments

The samples were all grown on *c*-plane sapphire substrates by plasma-assisted molecular beam epitaxy (P-MBE). 6N zinc was evaporated as Zn source, and 5N

*Corresponding author. Tel.: +86 431 6176312; fax: +86 431 4627031.
E-mail address: zzzhang@jlmc.com.cn (Z.Z. Zhang).

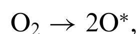
0022-0248/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2006.11.051

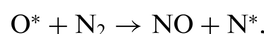
nitrogen and 5N oxygen were co-activated by a radio-frequency atom source to offer O and acceptor dopant. The growth temperature was kept at 425 °C. The chamber pressure was fixed between 1×10^{-6} and 5×10^{-5} mbar. To monitor the O_2+N_2 plasma composition, the luminescence of the plasma was introduced into a spectrometer by an optical fiber. The electrical properties of the samples were measured by a 7707 Hall analyzer (Lakeshore) in Van der Pauw configuration. EL measurement was performed.

3. Results and discussions

In nitrogen doping for ZnSe, N_2 dimer on the Se site was regarded as a donor [11], which plays an unwelcome role in p-type ZnSe fabrication. In growth of N-doped p-type ZnO, the N–N pair on O site ($N_{2(O)}$) is also regarded as a shallow donor [12]. For samples grown by using pure N_2 as dopant, O_2 was offered by another individual rf atom source. By varying N_2 flow, we obtained n-type ZnO films with resistivity from 491 to 0.0026 Ω cm. The low-resistant n-type conductivity indicates that activated N_2 molecules offer more donor defects than acceptors.

To realize p-type conduction in ZnO:N films, it is necessary to decrease $N_{2(O)}$ concentration in ZnO. During the growth of N-doped ZnO, the probability is not large that $N_{2(O)}$ forms via migration of adsorbed N atoms on surface because of low substrate temperature. Therefore, decreasing N_2 content in the plasma of gas source is a key link in growth process. Fig. 1 shows the emission spectra of N_2, NO and O_2+N_2 mixture plasma in the radio frequency atom source. The rf power was fixed at 300 W for all the three cases. In N_2 plasma spectrum, labeled by curve *a*, ultra-violet emission from N_2 molecule (E_{N_2}) and 746-nm line from N atom (E_N) can be observed. Apparently, E_{N_2} is much stronger than E_N. It indicates that there exists considerable N_2 molecule content in N_2 plasma. Such great deal of N_2 molecules will compensate $N_{(O)}$ acceptors in ZnO. Therefore, it is not easy to obtain p-type ZnO by activating pure N_2. Curve *b* is the spectrum of activated NO, in which case we had succeeded in growing p-type ZnO [8]. For comparing conveniently, the part before 700 nm was magnified to a certain scale. The 777-nm line in spectra comes from O atom. Because the decomposing energy (6.6 eV) is smaller than that of N_2 (9.9 eV), the ratio of E_N/E_{N_2} shows a significant increase compared with pure N_2 plasma. Although NO is a good dopant, numerous advantages of N_2, such as the facilities in purifying, storage and environmental conservation, made us find a technique for fabricating p-type ZnO:N by using N_2. Introducing an assisted gas is a simple method. Compared with other gases, O_2 has enough activity and does not bring contamination into ZnO. The possible reactions could be depicted as follows:


$$O_2 \rightarrow 2O^*,$$


$$O^* + N_2 \rightarrow NO + N^*,$$

$$NO \rightarrow O^* + N^*.$$

Curve *c* is the spectrum of N_2+O_2 mixture plasma at the same power with the case of pure N_2. It is obvious that the ratio of E_N/E_{N_2}increases significantly compared with that of pure N_2 plasma. The line shape is very similar to that of NO. It means that co-activating of N_2+O_2 mixture is an appropriate route for N-doped p-type ZnO fabrication.

By changing the ratio of N_2/O_2 from 0.5 to 2, we can obtain ZnO films with different conductivity via keep other growth parameters. The electrical properties of the samples are listed in Table 1.The n-type conductivity obtained at high N_2/O_2 ratio indicates that over-high N content in gas source does not always benefit p-type doping. The detail relation between N content in the activated mixture and conductivity will be discussed elsewhere. By adjusting the chamber vacuum while the N_2/O_2 ratio of 1:2, we even obtained ZnO film with a hole concentration of $1.15\times10^{18}\,cm^{-3}$ and mobility of $0.94\,cm^2\,V^{-1}\,s^{-1}$.

A p–n junction LED was fabricated by directly covering an undoped n-type ZnO film on the p-type layer by masking an area for electrode. The LED structure is sketched in Fig. 2(a). The electron concentration and mobility of the n-type layer are at $10^{18}\,cm^{-3}$ order and $40\,cm^2\,V^{-1}\,s^{-1}$, respectively. Indium and Ni–Au electrodes were used to obtain Ohmic contacts to the n- and p-type layers, respectively. The *I–V* curve measured at about 100 K is shown in Fig. 2(b). As seen, the LED shows a clear rectification effect. The turn on voltage is about 3.7 V, which approaches the band gap of ZnO.

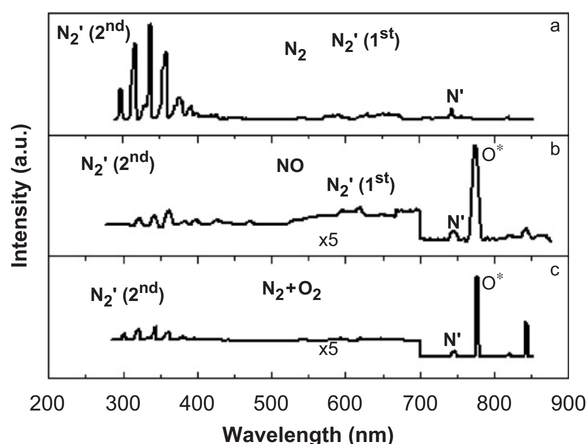


Fig. 1. Emission spectra of plasmas for activated N_2, NO and N_2+O_2 mixture.

Table 1
Electrical properties of ZnO films grown by using activated N_2+O_2 mixture, respectively

N_2/O_2 (sccm)	0.3:0.15	0.2:0.2	0.15:0.3
Conduction type	n	p	p
Carrier concentration (cm^{-3})	2.1E14	3.0E14	1.3E16
Mobility ($cm^2\,V^{-1}\,s^{-1}$)	7.8	8.3	0.44
Resistivity (Ω cm)	3930	2610	1170

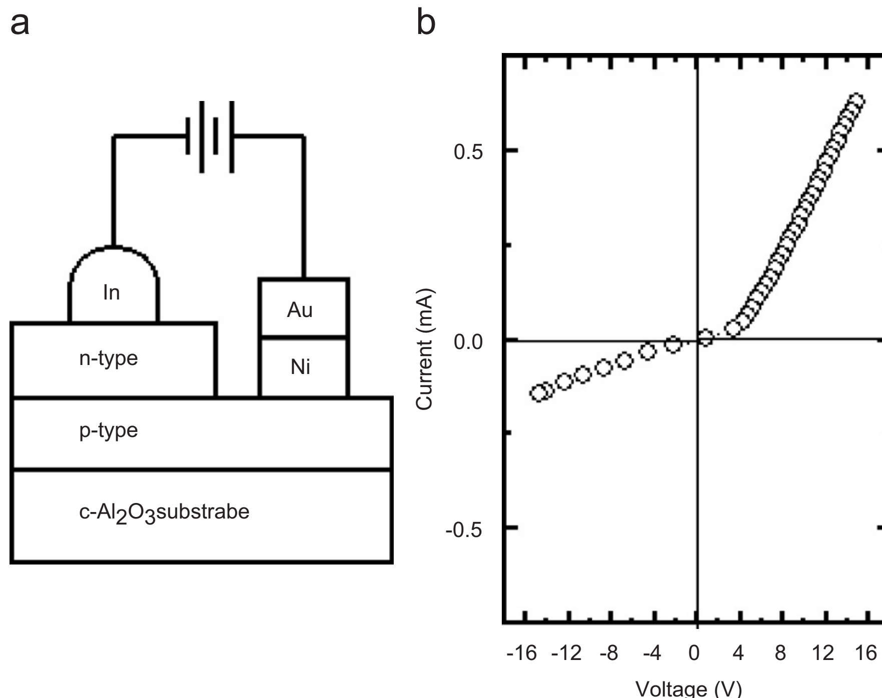


Fig. 2. (a) The ZnO LED structure sketch and (b) *I–V* curve of the LED measured at 100 K.

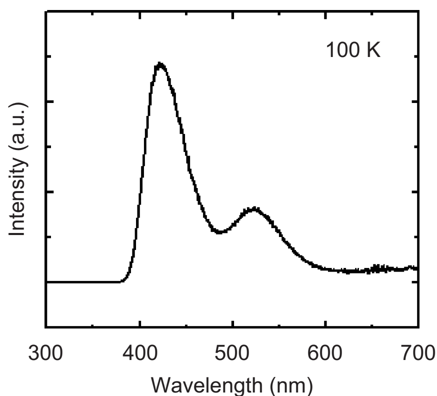


Fig. 3. Electroluminescence spectrum of the ZnO LED measured at 100 K.

Fig. 3 is the EL spectrum measured at about 100 K. A violet emission located at 423 nm and a green band centered at 523 nm could be observed. The UV luminescence of ZnO is absent here. According to our early results and other reports [7,8], the violet band was attributed to donor–acceptor pair emission. For the green band, it was attributed to emissions relative to intrinsic defects in ZnO, such as O vacancy, etc [13,14]. The detail origins of luminescence will be discussed elsewhere.

4. Conclusion

In summary, p-type ZnO on sapphire was fabricated by plasma-assisted P-MBE. Co-activated N_2+O_2 mixture was used as acceptor dopant and O source. Assistance of O facilitates decomposition of N_2 molecules significantly. Homo-junction ZnO LED was also fabricated, which has clear rectification effect. The EL spectrum includes two bands, a violet emission at 423 nm and a green emission at 523 nm.

Acknowledgments

This work is supported by the Key Project of National Natural Science Foundation of China under Grant No 60336020, the National Natural Science Foundation of China under Grant No 60429403, No 60376009, No 60506014, No 50402016 and No 60501025, the Innovation Project of Chinese Academy of Sciences.

References

[1] D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, Appl. Phys. Lett. 81 (2002) 1830.
[2] 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, X.W. Fan, Phys. Stat. Sol.(a) 202 (2005) 1060.
[3] Y.R. Ryu, T.S. Lee, H.W. White, Appl. Phys. Lett. 83 (2003) 87.
[4] B. Claflin, D.C. Look, S.J. Park, G. Cantwell, J. Crystal Growth 287 (2006) 16.
[5] J.G. Lu, L.P. Zhu, Z.Z. Ye, F. Zhuge, B.H. Zhao, J.Y. Huang, L. Wang, J. Yuan, J. Crystal Growth 283 (2005) 413.
[6] Y.R. Ryu, T.S. Lee, J.H. Leem, et al., Appl. Phys. Lett. 83 (2003) 4032.
[7] A. Tsukazaki, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki, Nat. Mater. 4 (2005) 42.
[8] 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, Z.K. Tang, Appl. Phys. Lett. 88 (2006) 031911.

[9] J. Nause, M. Pan, V. Rengarajan, W. Nemeth, S. Ganesan, A. Payne, N. Li, I. Ferguson, Proc. SPIE 5941 (2005) 59410D.
[10] Y. Ryu, T.S. Lee, J.A. Lubguban, H.W. White, B.J. Kim, Y.S. Park, C.J. Youn, Appl. Phys. Lett. 88 (2006) 241108.
[11] S. Gundel, W. Faschinger, Phys. Rev. B 65 (2001) 035208.
[12] E.-C. Lee, Y.S. Kim, Y.G. Jin, K.J. Chang, Phys. Rev. B. 64 (2001) 085120.
[13] K. Vanhausden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. 79 (1996) 7983.
[14] Y.W. Heo, D.P. Nortona, S.J. Pearton, J. Appl. Phys. 98 (2005) 073502.