Plasma-free nitrogen doping and homojunction light-emitting diodes based on ZnO

Y J Zeng^{1,2}, Z Z Ye^{1,3}, Y F Lu¹, W Z Xu¹, L P Zhu¹, J Y Huang¹, H P He¹
and B H Zhao¹

¹ State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

² Solid-state Physics and Magnetism Section, Department of Physics and Astronomy, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, BE-3001 Leuven, Belgium

E-mail: yezz@zju.edu.cn and huang@zju.edu.cn

Received 20 May 2008, in final form 16 June 2008

Published 25 July 2008

Online at stacks.iop.org/JPhysD/41/165104

Abstract

The authors develop a plasma-free metalorganic chemical vapour deposition method to grow N-doped p-type ZnO films. The incorporation of the N acceptor and the corresponding change in the Fermi level are well confirmed by x-ray photoelectron spectroscopy. Temperature-dependent photoluminescence reveals the acceptor-related emissions, namely, neutral acceptor-bound exciton and probably donor-acceptor pair transition. In addition, typical rectifying I - V characteristics and room-temperature electroluminescence from ZnO homojunction light-emitting diodes are demonstrated.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, with a large exciton binding energy of 60 meV, is presently receiving worldwide attention because of its advantages for blue/ultraviolet (UV) light emitters and detectors [1–3]. Nominally undoped ZnO typically exhibits n-type conductivity, which has been ascribed to various mechanisms including native defects and/or interstitial hydrogen [4–6]. The realization of p-type material, however, has been proven difficult due to its asymmetric doping limitations [7]. Fortunately, in virtue of the considerable worldwide efforts, various elements have been investigated as the p-type dopants for ZnO, such as N [8–10], P [11, 12], As [13], Sb [14] and Li [15, 16]. In particular, recent progress in ZnO homojunction light-emitting diodes (LEDs) has made the potentials of ZnO more feasible [11, 17–25].

Considering all the p-type dopants and the limited reports on ZnO homojunction LEDs, N with a similar ionic radii as O appears to be promising. Generally, due to the low solubility of N, generating activated N by a plasma-assisted process is required for effective N doping in ZnO, independently

of the adopted N sources [8, 10, 17–19, 25]. On the other hand, much less attention has been focused on plasma-free N doping in ZnO. The plasma-assisted growth, however, needs a relatively rigorous pressure condition, which is not favoured for the growth of a p-type ZnMgO barrier layer as well as mass production. In this study, we develop a plasma-free metalorganic chemical vapour deposition (MOCVD) method to grow N-doped p-type ZnO films. Room-temperature electroluminescence (EL) from the ZnO homojunction LEDs is demonstrated.

2. Experimental details

N-doped ZnO films were grown by a low-pressure plasma-free MOCVD method. c -plane (0001) sapphire and n-type bulk ZnO were used as the substrates. Diethyl zinc was used as the zinc source. A mixture of O₂ and NO was employed as both the oxygen source and the N doping source. The growth temperature was 400 °C and the chamber pressure was maintained at 20 Pa during the growth process. Hall-effect measurements were carried out in the van der Pauw configuration (Bio-Rad HL5500PC)

³ Author to whom any correspondence should be addressed.

Table 1. Electrical properties of N-doped ZnO films grown on sapphire substrates.

NO flow (sccm)	Resistivity (Ω cm)	Hall mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
10	25.9	3.83	6.25×10^{16}	40% p
13	16.3	3.27	1.16×10^{17}	p
15	43.2	1.45	9.92×10^{16}	85% p
18	96.6	0.354	1.83×10^{17}	60% p

at room temperature. The chemical states of the doped N and the position of the Fermi level with respect to the valence band maximum (VBM) were analysed by x-ray photoelectron spectroscopy (XPS Thermo ESCALAB 250, Al $K\alpha$ radiation source $h\nu = 1486.6$ eV). Temperature-dependent photoluminescence (PL) measurements were performed using an He–Cd 325 nm laser as the excitation source. ZnO p–n homojunction LEDs were fabricated by the deposition of an N-doped p-type layer on an n-type bulk ZnO substrate. Au and In–Zn alloys were used as the ohmic contact electrodes for the p side and the n side, respectively.

3. Results and discussion

Table 1 summarizes the results of Hall-effect measurements on the N-doped ZnO films grown on the sapphire substrates. The typical thickness of the N-doped ZnO layer is around 400 nm. It can be seen that stable p-type conductivity is obtained with a proper flow of NO (13 sccm (standard cubic centimetres per minute)). The optimal results include a resistivity of $16.3 \Omega \text{cm}$, a Hall mobility of $3.27 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a hole concentration of $1.16 \times 10^{17} \text{cm}^{-3}$. It is theoretically predicted that the formation energy of the N_O acceptor will decrease when NO is used as the N doping source [26]. By deliberately adjusting the NO flow, we are able to achieve stable p-type conductivity. Therefore, our experimental results support the theoretical calculation that NO would be a good p-type dopant for ZnO [26]. However, increasing or decreasing the NO flow results in the instability of the carrier type, as shown in table 1. When the NO flow is as low as 10 sccm, the concentration of the N_O acceptor is insufficient to compensate for the background donor. On the other hand, when the NO flow increases to 15 or 18 sccm, the formation of the $(\text{N}_2)_\text{O}$ donor will be energetically favoured [26], serving as the compensating centre for the N_O acceptor. It is believed that both cases become the limitation for the N acceptor doping in ZnO, which are probably responsible for the observed instability of the carrier type. The conductivity on the bulk ZnO substrates, however, is unavailable due to the possible influence of the conducting substrates.

The chemical state of the doped N in the ZnO layer grown on the bulk ZnO was analysed by XPS. Figure 1 illustrates the N 1s core level narrow scan spectrum. A peak at around 398.2 eV, attributed to Zn–N bonding [27], is observed. Additionally, the mole concentration of N is calculated to be 1.3% according to its integrated intensity and sensitivity factor. Therefore, it is confirmed that the N acceptor is introduced into the ZnO matrix, without the plasma-assisted process.

It is well known that the Fermi level of a semiconductor will shift up/down in energy due to donor/acceptor doping. In

Figure 1. An XPS narrow scan spectrum of the N 1s core level for N-doped ZnO films grown on the bulk ZnO substrate. **Figure 2.** VB XPS spectra for nominally undoped and N-doped ZnO films grown on the bulk ZnO substrate. The inset shows VB spectra near the Fermi level.

this regard, valence band (VB) XPS spectra were provided to investigate the N-acceptor doping effects. Figure 2 compares the VB XPS spectra of the nominally undoped and N-doped ZnO films grown on the bulk ZnO substrates. The features at 9.6 eV, 6.5 eV and 3.7 eV for the undoped one are known to stem from Zn 3d, mixed Zn 4s–O 2p and O 2p states, respectively [28, 29]. To better elucidate the N doping effects, the inset of figure 2 shows the VB spectra near the Fermi level. By extrapolating the leading edge of the O 2p-derived VB to its intersection with background counts near the Fermi level, the position of the Fermi level with respect to the VBM can be determined. The nominally undoped ZnO shows a Fermi level located at 2.21 eV above the VBM. Considering the band gap of 3.37 eV at room temperature, this Fermi level is near the middle of the band gap rather than the conduction band minimum (CBM). The location of the Fermi level suggests a low background electron concentration, which will favour the

Figure 3. (a) Temperature-dependent PL spectra of the N-doped ZnO film grown on the bulk ZnO substrate. (b) The UV region of the PL spectrum at 83 K.

p-type doping. The Fermi level of the N-doped ZnO shifts down towards the VBM by 650 meV in comparison with the undoped one, which offers the evidence for N-acceptor doping in view of the energy band. Furthermore, the Fermi level below the middle of the band gap, in principle, indicates a p-type behaviour, which was unavailable in the previous Hall-effect measurements.

Figure 3(a) shows temperature-dependent PL spectra of the N-doped ZnO films grown on the bulk ZnO substrates. The thickness of the N-doped layer is around 800 nm, which is much larger than the typical penetration depth of the 325 nm laser in ZnO. Thus, it is assured that the collected PL signal comes from the N-doped layer rather than the bulk ZnO substrate. The PL spectra are characterized by several resolved near-band-edge (NBE) emissions with a weak deep band, indicating a high optical quality.

To better assign the NBE PL peaks, the UV region of the PL spectrum at 83 K is illustrated in figure 3(b). The peaks at 3.368 eV, 3.356 eV and 3.311 eV are tentatively assigned to free exciton (FX), neutral donor-bound exciton ($D^{\circ}X$) [30] and neutral acceptor-bound exciton ($A^{\circ}X$) [8], respectively. The 3.236 eV emission might be donor-acceptor pair transition (DAP) or the longitudinal-optical phonon replica of $A^{\circ}X$. As evident in figure 3(a), the intensity of $D^{\circ}X$ as well as of $A^{\circ}X$ decreases significantly with the increased temperature and is eventually buried by the FX emission at around 150 K, showing the typical characteristics of the bound exciton. The observations of obvious acceptor-related transitions, such as $A^{\circ}X$ and probably DAP, indicate the presence of an acceptor state in the N-doped layer, which is probably associated with

Figure 4. I - V characteristics of the ZnO p-n homojunction, consisting of an N-doped p-type layer and an n-type bulk ZnO substrate.

Figure 5. A room-temperature EL spectrum of ZnO homojunction LEDs.

the N_O acceptor. In addition, an acceptor energy level located at 170–200 meV above the VBM is obtained, assuming that the 3.236 eV emission is a DAP transition [8]. This value agrees fairly well with those reported for N-doped ZnO, such as 165 meV [31] and 180 meV [32].

Finally, ZnO homojunction LEDs were fabricated by the deposition of a N-doped p-type layer on an n-type bulk ZnO substrate. Au and In-Zn alloys were used as the ohmic contact electrodes for the p side and the n side, respectively, showing linear I - V characteristics indicative of good ohmic behaviour (data not shown). Figure 4 shows the I - V characteristics of the ZnO homojunction. The device exhibits rectification for the repeated measurements, which is consistent with the formation of a p-n homojunction at the interface. Note that the quasi-linear I - V characteristics at the larger forward bias might be associated with the series resistance of the bulk ZnO substrate.

Figure 5 demonstrates a room-temperature EL spectrum of ZnO homojunction LEDs. At a current of 20 mA, a UV peak centred at 379 nm dominates the EL spectrum, which could be ascribed to exciton-related emission. It is believed that the UV emission comes from the electron injection from n-type bulk ZnO to the p-type layer, because the electron mobility of the bulk ZnO ($\sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is much larger than the hole mobility of the p-type layer. In addition, the intensity ratio of the exciton emission to the deep band is higher than the previous reports on ZnO homojunction

[17, 18, 21–24], including that grown by a complicated plasma-assisted process.

4. Conclusion

In summary, we have developed a plasma-free MOCVD method to grow reproducible N-doped p-type ZnO films. The incorporated N acceptor, as identified by XPS, will effectively lower the Fermi level towards the VBM and is responsible for p-type conductivity. The observations of obvious acceptor-related PL transitions, such as A[°]X and probably DAP, indicate the presence of an acceptor state in the N-doped ZnO. In addition, typical rectifying *I*–*V* characteristics and room-temperature EL from the ZnO LEDs are demonstrated, which is comparable to or even better than those grown by a complicated plasma-assisted process. Our results suggest that the plasma-free N doping would be a promising way to produce stable p-type ZnO.

Acknowledgments

This work was supported by the National Basic Research Program of China under Grant No 2006CB604906 and the National Natural Science Foundation of China under Contract Nos 50532060 and 90601003.

References

- [1] Look D C 2001 *Mater. Sci. Eng. B* **80** 383
- [2] Pearton S J, Norton D P, Ip K, Heo Y W and Steiner T 2005 *Prog. Mater. Sci.* **50** 293
- [3] Özgür Ü, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S J and Morkocd H 2005 *J. Appl. Phys.* **98** 041301
- [4] Van de Walle C G 2000 *Phys. Rev. Lett.* **85** 1012
- [5] Cox S F J *et al* 2001 *Phys. Rev. Lett.* **86** 2601
- [6] Kohan A F, Ceder G, Morgan D and Van de Walle C G 2000 *Phys. Rev. B* **61** 15019
- [7] Zhang S B, Wei S H and Zunger A 2001 *Phys. Rev. B* **63** 075205
- [8] Look D C, Reynolds D C, Litton C W, Jones R L, Eason D B and Cantwell G 2002 *Appl. Phys. Lett.* **81** 1830
- [9] Rommeluere J F, Svob L, Jomard F, Mimila-Arroyo J, Lusson A, Sallet V and Marfaing Y 2003 *Appl. Phys. Lett.* **83** 287
- [10] Zeng Y J, Ye Z Z, Xu W Z, Liu B, Che Y, Zhu L P and Zhao B H 2007 *Mater. Lett.* **61** 41
- [11] Lim J H, Kang C K, Kim K K, Park I K, Hwang D K and Park S J 2006 *Adv. Mater.* **18** 2720
- [12] Heo Y W, Kwon Y W, Li Y, Pearton S J and Norton D P 2004 *Appl. Phys. Lett.* **84** 3474
- [13] Vaithianathan V, Lee B T and Kim S S 2005 *Appl. Phys. Lett.* **86** 062101
- [14] Guo W, Allenic A, Chen Y B, Pan X Q, Che Y, Hu Z D and Liu B 2007 *Appl. Phys. Lett.* **90** 242108
- [15] Zeng Y J, Ye Z Z, Xu W Z, Li D Y, Lu J G, Zhu L P and Zhao B H 2006 *Appl. Phys. Lett.* **88** 062107
- [16] Zeng Y J, Ye Z Z, Lu J G, Xu W Z, Zhu L P, Zhao B H and Limpijumnong S 2006 *Appl. Phys. Lett.* **89** 042106
- [17] Tsukazaki A *et al* 2005 *Nature Mater.* **4** 42
- [18] Xu W Z, Ye Z Z, Zeng Y J, Zhu L P, Zhao B H, Jiang L, Lu J G, He H P and Zhang S B 2006 *Appl. Phys. Lett.* **88** 173506
- [19] Nause J, Pan M, Rengarajan V, Nemeth W, Ganesan S, Payne A, Li N and Ferguson I 2005 *Proc. SPIE* **5941** 59410D
- [20] Ryu Y, Lee T S, Lubguban J A, White H W, Kim B J, Park Y S and Youn C J 2006 *Appl. Phys. Lett.* **88** 241108
- [21] Wang H T, Kang B S, Chen J J, Anderson T, Jang S, Ren F, Kim H S, Li Y J, Norton D P and Pearton S J 2006 *Appl. Phys. Lett.* **88** 102107
- [22] Liu W *et al* 2006 *Appl. Phys. Lett.* **88** 092101
- [23] Sun J C, Zhao J Z, Liang H W, Bian J M, Hu L Z, Zhang H Q, Liang X P, Liu W F and Du G T 2007 *Appl. Phys. Lett.* **90** 121128
- [24] Adekore B T, Pierce J M, Davis R F, Barlage D W and Muth J F 2007 *J. Appl. Phys.* **102** 024908
- [25] Wei Z P, Lu Y M, Shen D Z, Zhang Z Z, Yao B, Li B H, Zhang J Y, Zhao D X, Fan X W and Tang Z K 2007 *Appl. Phys. Lett.* **90** 042113
- [26] Yan Y F, Zhang S B and Pantelides S T 2001 *Phys. Rev. Lett.* **86** 5723
- [27] Maki H, Sakaguchi I, Ohashi N, Sekiguchi S, Haneda H, Tanaka J and Ichinose N 2003 *Japan. J. Appl. Phys.* **42** 75
- [28] Girard R T, Tjernberg O, Chiaia G, Soderholm S, Karlsson U O, Wigren C, Nylen H and Lindau I 1997 *Surf. Sci.* **373** 409
- [29] Perkins C L, Lee S H, Li X N, Asher S E and Coutts T J 2005 *J. Appl. Phys.* **97** 034907
- [30] Meyer B K *et al* 2004 *Phys. Status Solidi b* **241** 231
- [31] Zeuner A, Alves H, Hofmann D M, Meyer B K, Hoffmann A, Haboeck U, Strassburg M and Dworzak M 2002 *Phys. Status Solidi b* **234** R7
- [32] Zeng Y J, Ye Z Z, Lu Y F, Lu J G, Xu W Z, Zhu L P and Zhao B H 2007 *J. Phys. D: Appl. Phys.* **40** 1807