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An approach to enhanced acceptor concentration in ZnO:N films

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Abstract Owing to the low doping concentration of nitrogen and strong compensation of intrinsic donors, the attainment of highly conductive p-type ZnO films remains one of the largest challenges for the application of ZnO. An approach has been proposed to increase the doping concentration of nitrogen in ZnO by exposing the ZnO:N films in the ambient of nitrogen plasma periodically in this paper. Hall measurements and photoluminescence spectroscopy indicate that this approach is effective in improving the hole concentration in ZnO films. Under the optimized conditions, a p-type ZnO film with a hole concentration of 1.68×10^{18} cm^{-3} has been achieved.

Introduction

Zinc oxide (ZnO) has been considered as one of the strongest candidates in a variety of applications including light-emitting devices, laser diodes, photodetectors, transistors, etc [1–4]. However, such applications are drastically hindered by the difficulty in realizing reliable and reproducible p-type ZnO. To date, many potential acceptors have been attempted to fabricate p-type ZnO, including group I elements (Li, Na) and group V elements (N, P, As, Sb). Among these dopants, nitrogen (N) has been regarded as one of the effective p-type dopants for ZnO because it has very similar ionic radius with oxygen, and some significant progresses have been made in fabricating p-type ZnO and ZnO-based p–n homojunction light-emitting diodes employing nitrogen as dopant [5–9]. However, there is still a severe awkward situation in the doping process of ZnO using nitrogen. That is, relatively high temperature is usually necessary to obtain ZnO films with acceptably high quality that can serve as a starting point for p-type doping, however, the solubility of nitrogen in ZnO will be drastically decreased at elevated temperature [7]. The above awkward situation hinders the formation of low-resistivity p-ZnO drastically. Kawasaki and co-workers [7] have developed a repeated temperature modulation technique, in which the substrate temperature can be modulated rapidly to incorporate nitrogen at relatively low temperature and increase the structural quality of the films at high temperature. However, a complicated modification to the growth equipment is needed to realize the fast switching between low and high temperature, which is not available to most researchers. Therefore, exploring a relatively simple approach to enhance the acceptor concentration in ZnO is greatly desired. However, such approach is still lacking up to date to the best of our knowledge.

In this paper, a simple approach has been proposed to increase the acceptor concentration in ZnO films by exposing the films in the ambient of nitrogen plasma periodically. Hall measurements and photoluminescence (PL) spectroscopy show that this approach is effective in improving the acceptor concentration in ZnO.

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Experiment

The ZnO thin films studied in this paper were grown in a plasma-assisted molecular beam epitaxy (MBE) technique employing *c*-plane sapphire (Al_2O_3) as substrates. The detailed cleaning process of the substrates can be found in our previous publication [10]. In brief, after being chemically etched, the substrates were pretreated in vacuum ($\leq 1 \times 10^{-7}$ mbar) at 750 °C for 30 min to obtain a clean surface. After that, the substrates were loaded into the growth chamber. High-purity elemental zinc (99.9999%) held in a Knudsen cell was used as Zn precursor, and high-purity nitrogen (99.9999%) and oxygen (99.9999%) were used as N dopant and O source, respectively. The gaseous precursors were activated by two separate radio-frequency plasma cells (Oxford Applied Research, Model HD25) operating at 13.56 MHz. The power of the plasma cells was maintained at 350 W, the pressure in the MBE growth chamber at 2×10^{-5} mbar, and the substrate temperature at 650 °C during the growth process. Three growth modes have been performed to fabricate undoped and nitrogen-doped ZnO films in this paper.

The shutter opening and closing sequence for the three growth modes is sketched in Fig. 1. For growth mode I, the shutters of Zn and O were opened for 5 min, then closed for 5 min, as shown in Fig. 1a. Undoped ZnO films were obtained in this mode by repeating the growth cycle for 24 times. For growth mode II, the shutters of Zn, N, and O were opened for 5 min, then the O and Zn shutters were closed for 5 min, while the shutter of the N was still opened to expose the ZnO:N film in the ambient of nitrogen plasma for 5 min, as shown in Fig. 1b. The above cycle was repeated 24 times to obtain ZnO:N film. Meanwhile, in order to confirm the effect of the nitrogen plasma irradiation, another growth mode was designed and conducted. In this mode, the shutter of N was closed while that of Zn and O were opened to grow undoped ZnO film for 5 min, then the shutters of Zn and O were closed while that of N was opened for 5 min, as shown in Fig. 1c. The structural properties of the films were characterized using a Rigaku D/max-RA X-ray diffractometer (XRD) using CuKα ($\lambda = 1.54$ Å) as the irradiation source. The carrier concentration and mobility of the films were studied by Hall measurement (Lakeshore 7707) under Van der Pauw configuration. PL spectroscopy with 325 nm line of a He–Cd laser as the excitation source was used to characterize the optical properties of the films.

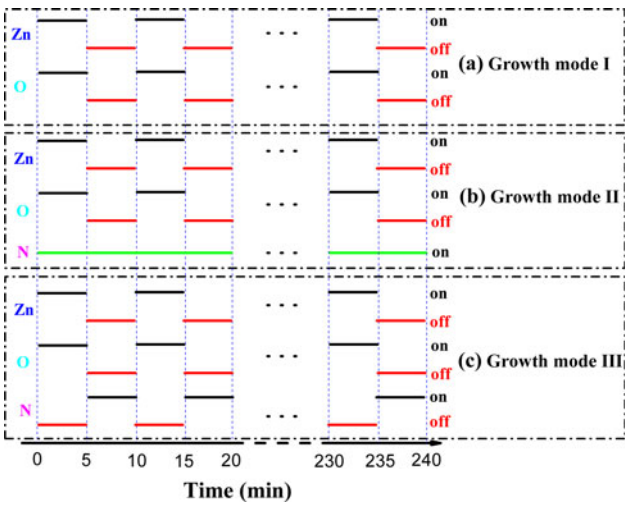

Fig. 1 Shutter control sequence for the three growth modes employed in this paper

Results and discussions

Figure 2 shows the XRD patterns of the as-grown ZnO films prepared in the above-mentioned three growth modes. Besides the peak from the Al_2O_3 substrate, only ZnO (002) diffraction peak can be observed in all the three samples, indicating that the as-grown films are of wurtzite structure with (002) preferential orientation. Meanwhile, one can see that the diffraction peak of the undoped ZnO film fabricated in modes I is located at about 34.44°, while that of the nitrogen plasma treated nitrogen-doped ZnO film fabricated in mode III shifts to 34.48°, and the diffraction peak of the nitrogen-doped and nitrogen plasma-treated ZnO film fabricated in mode II shifts to 34.50°. The obvious shift of the diffraction peak may be caused by the substitution of O by nitrogen considering that the length of Zn–N bond is shorter than that of Zn–O bond [11]. The film grown in mode II shows a larger shift may be an indication of higher doping concentration.

The electrical properties of the ZnO films are summarized in Table 1. One can see that the undoped ZnO film

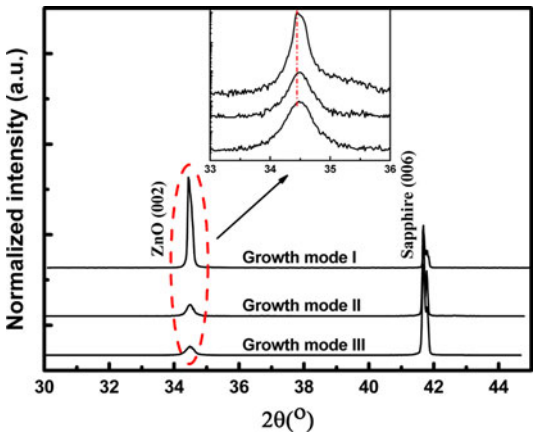

Fig. 2 XRD patterns of the as-grown ZnO films fabricated in the three growth modes

Table 1 The electrical properties of the three ZnO films fabricated in the three growth modes

Growth mode	Conduction type	Resistivity (ohm cm)	Hall mobility ($cm^2\ V^{-1}\ S^{-1}$)	Carrier concentration (cm^{-3})
Growth mode I	n	0.56	19	5.85×10^{17}
Growth mode II	p	2.5	1.98	1.68×10^{18}
Growth mode III	p	9.8	5.81	1.96×10^{17}

fabricated in growth mode I has an electron concentration of about 5.85×10^{17} cm^{-3} and a mobility of about 19 $cm^2\ V^{-1}\ S^{-1}$. The nitrogen-doped and nitrogen plasma-treated ZnO film fabricated in growth mode II behaves p-type conduction, and the hole concentration is about 1.68×10^{18} cm^{-3}. In this growth mode, the activated nitrogen atom might enter the ZnO:N film and substitute oxygen atoms to form N_O acceptors in the ambient of nitrogen plasma, which is helpful to improve the doping concentration of nitrogen [12, 13]. To test the effect of the nitrogen plasma exposure process, nitrogen plasma-treated ZnO film was fabricated in growth mode III, in which after the growth of undoped ZnO for 5 min, the ZnO film was irradiated in the ambient of nitrogen plasma for 5 min. One can see that the film grown in mode III behaves p-type conduction too, but the hole concentration is smaller by about one order of magnitude, and the resistivity is three times larger than that of the p-ZnO:N film fabricated in growth mode II, which confirms that the exposure to nitrogen plasma plays an important role in enhancing the acceptor concentration in ZnO:N films.

To confirm the enhancement of the acceptor concentration, PL spectroscopy was employed, and the spectra of the three samples taken at 80 K are shown in Fig. 3. The PL spectrum of the undoped ZnO film grown in mode I can be well fitted by five Gaussian peaks. The dominant peak is located at 3.362 eV, and the position of which is in good accordance with the neutral donor-bound excitons (D^0X) of ZnO (3.363 eV) [14]. The dominant D^0X indicates that there exist many donors in the undoped ZnO film. The peak at 3.370 eV can be attributed to the free exciton (FE) emission of ZnO, and there are also three peaks at 3.310, 3.238, and 3.166 eV, which can be assigned to the first, the second, and the third longitudinal optical (LO) phonon replicas of the FE considering that their energy difference (72 meV) is in sharp accordance with the phonon energy of ZnO (72 meV) [15–17]. The PL spectrum of the N-plasma-treated ZnO film grown in mode III is dominated by a peak at 3.325 eV, and it can be attributed to the transition from the free electron in the conduction band to the acceptor levels (FA) [18, 19].

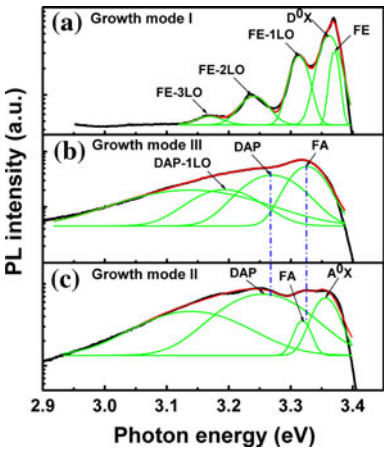

Fig. 3 The 80 K PL spectra of the three ZnO films fabricated in the three growth modes, in which the spectra has been fitted by Gaussian lineshapes

A peak at 3.267 eV and a weak broad line centered at 3.195 eV are also observed in the spectrum, which can be assigned to donor–acceptor pair (DAP) emission and its phonon replica, respectively [20, 21]. The appearance of acceptor-related emission (FA) indicates that nitrogen has entered into the ZnO film to form acceptors in the irradiation process of nitrogen plasma. In the PL spectrum of the p-ZnO:N film grown in mode II, the DAP peak dominates the spectrum, as shown in Fig. 3c. Another noteworthy phenomenon is that there is an obvious redshift in the DAP emission of the sample grown in mode II compared with that in mode III. A similar redshift has been observed in p-ZnSe:N by increasing nitrogen concentration, and it has been considered as an indication of the enhanced acceptor concentration [22–24]. Meanwhile, an emission peak at 3.355 eV is also observed in the spectrum, which can be attributed to the acceptor-bound excitons (A^0X) in the ZnO film according to its position [25, 26]. The appearance of A^0X further indicates that there are many N_O acceptors in the p-ZnO:N film grown in mode II. One can see from the PL data that acceptor-related emissions (A^0X and DAP) have been enhanced in the film grown in mode II compared with that in mode III, which confirms that the acceptor concentration has been enhanced after this periodical exposure to nitrogen plasma.

Conclusions

Undoped ZnO and N-doped p-ZnO films have been grown on sapphire substrates by plasma-assisted MBE in three growth modes. The N-doped p-ZnO film in the growth mode II shows a p-type conduction with the hole concentration of 1.68×10^{18} cm^{-3} and the mobility of 1.98 $cm^2\ V^{-1}\ S^{-1}$. The relatively high hole concentration is a result of the

enhanced acceptor concentration in the ZnO:N film under the irradiation of nitrogen plasma. PL data confirm that the concentration of N_O acceptor has been increased in the nitrogen plasma irradiated N-doped ZnO film. The results reported in this paper provide a simple route to enhanced acceptor concentration in nitrogen-doped ZnO, thus may lay a solid ground for the future application of ZnO in opto-electronic devices.

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References

1. Tang ZK, Wong GKL, Yu P, Kawasaki M, Ohtomo A, Koinuma H, Segawa Y (1998) Appl Phys Lett 72:3270
2. Bagnall DM, Chen YF, Zhu Z, Yao T, Koyama S, Shen MY, Goto T (1997) Appl Phys Lett 70:2230
3. Cao H, Wu JY, Ong HC, Dai JY, Chang RPH (1998) Appl Phys Lett 73:572
4. Uedono A, Koida T, Tsukazaki A, Kawasaki M, Chen ZQ, Chichibu SF, Koinuma H (2003) J Appl Phys 93:2481
5. Look DC, Reynolds DC, Litton CW, Jones RL, Eason DB, Cantwell G (2002) Appl Phys Lett 81:1830
6. Liang HW, Lu YM, Shen DZ, Liu YC, Yan JF, Shan CX, Li BH, Zhang ZZ, Zhang JY, Fan XW (2005) Phys Stat Sol A 202:1060
7. Tsukazaki A, Onuma T, Ohtani M, Makino T, Sumiya M, Ohtani K, Chichibu SF, Fuke S, Segawa Y, Ohno H, Koinuma H, Kawasaki M (2005) Nat Mater 4:42
8. Jiao SJ, Zhang ZZ, Lu YM, Shen DZ, Yao B, Zhang JY, Li BH, Zhao DX, Fan XW, Tang ZK (2006) Appl Phys Lett 88:031911
9. Wei ZP, Lu YM, Shen DZ, Zhang ZZ, Yao B, Li BH, Zhang JY, Zhao DX, Fan XW, Tang ZK (2007) Appl Phys Lett 90:042113
10. Li L, Shan CX, Li BH, Yao B, Zhang JY, Zhao DX, Zhang ZZ, Shen DZ, Fan XW, Lu YM (2008) J Phys D Appl Phys 41:245402
11. Yao B, Shen DZ, Zhang ZZ, Wang XH, Wei ZP, Li BH, Lu YM, Fan XW, Gan LX, Xing GZ, Cong CX, Xie YP (2006) J Appl Phys 99:123510
12. Xiao ZY, Liu YC, Zhang JY, Zhao DX, Lu YM, Shen DZ, Fan XW (2005) Semicond Sci Technol 20:796
13. Matsui H, Saeki H, Kawai T, Tabata H, Mizobuchi B (2004) J Appl Phys 95:5882
14. Meyer BK, Alves H, Hofmann DM, Kriegseis W, Forseter D, Bertram F, Christen J, Hoffmann A, Strassburg M, Dworzak M, Haboeck U, Rodina AV (2004) Phys Stat Sol B 241:231
15. Ko HJ, Chen YF, Yao T, Miyajima K, Yamamoto A, Goto T (2000) Appl Phys Lett 77:537
16. Meng XQ, Shen DZ, Zhang JY, Zhao DX, Dong L, Lu YM, Liu YC, Fan XW (2005) Nanotechnology 16:609
17. Liang WY, Yoffe AD (1968) Phys Rev Lett 20:59
18. Sun JW, Lu YM, Liu YC, Shen DZ, Zhang ZZ, Yao B, Li BH, Zhang JY, Zhao DX, Fan XW (2007) J Appl Phys 102:043522
19. Ryu YR, Lee TS, White HW (2003) Appl Phys Lett 83:87
20. Wang LJ, Giles NC (2004) Appl Phys Lett 84:3049
21. Xiong G, Ucer KB, Williams RT, Lee J, Bhattacharyya D, Metson J, Evans P (2005) J Appl Phys 97:043528
22. Tamura K, Makino T, Tsukazaki A, Sumiya M, Fuke S, Furumochi T, Lippmaa M, Chia CH, Segawa Y, Koinuma H, Kawasaki M (2003) Solid State Commun 127:265
23. Qiu J, DePuydt JM, Cheng H, Haase MA (1991) Appl Phys Lett 59:2992
24. Yang Z, Bowers KA, Ren J, Lansari Y, Cook JW Jr, Schetzina JF (1992) Appl Phys Lett 61:2671
25. Shan CX, Liu Z, Hark SK (2008) Appl Phys Lett 92:073103
26. Teke A, Özgür Ü, Doğan S, Gu X, Morkoc H, Nemeth B, Nause J, Everitt HO (2004) Phys Rev B 70:195207