Formation of p-type MgZnO by nitrogen doping

Applied Physics

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

Letters

Δ

Citation: Appl. Phys. Lett. **89**, 102104 (2006); doi: 10.1063/1.2345846 View online: http://dx.doi.org/10.1063/1.2345846 View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v89/i10 Published by the American Institute of Physics.

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/ Journal Information: http://apl.aip.org/about/about_the_journal Top downloads: http://apl.aip.org/features/most_downloaded Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT



Formation of *p*-type MgZnO by nitrogen doping

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

B. Yao,^{a)} Z. Z. Zhang, Y. M. Lu, D. Z. Shen, B. H. Li, X. H. Wang, 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 & Technology, Clear Water Bay, Kowloon, Hong Kong, China

(Received 15 May 2006; accepted 5 July 2006; published online 5 September 2006)

A wurtzite N-doped MgZnO film with 20 at. % Mg (MgZnO:N) was grown by plasma-assisted molecular beam epitaxy on *c*-plane sapphire using radical NO as oxygen source and nitrogen dopant. The as-grown MgZnO:N film behaves *n*-type conduction at room temperature, but transforms into *p*-type conduction after annealed for 1 h at 600 °C in an O₂ flow. The *p*-type MgZnO:N has a hole concentration of 6.1×10^{17} cm⁻³ and a mobility of 6.42 cm²/V s. X-ray photoelectron spectroscopy measurement indicates that substitution of N for O site is in forms of N atom (N)_O and N molecule (N₂)_O for the as-grown MgZnO:N, but almost only in a form of (N)_O for the annealed MgZnO:N. The mechanism of the conduction-type transition induced by annealing is discussed in the present work. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345846]

Due to a wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, ZnO is considered as a candidate material for preparation of short wavelength optoelectronic devices, such as blue-ultraviolet lightemitting diodes (LEDs) and laser diodes (LDs) with low thresholds.^{1,2} However, this material has largely failed to live up to its potential, because LED and LD require both high quality *n*-type and *p*-type ZnO, and it has been proven to be very difficult to produce a stable *p*-type ZnO with high conductivity and mobility. Recently, investigations on p-type ZnO and ZnO based LEDs have proceeded at a more rapid pace. Many research groups have reported obtaining *p*-type ZnO by single doping of I or V group elements, such as Li, N, P, etc., and by codoping of III-V groups, such as Al-N etc.³⁻⁶ ZnO p-n homojunction LEDs have also been produced by using N-doped p-type ZnO recently, which emit blue or yellow light.⁷⁻⁹ However, the dominant emissions do not come from near-band-edge recombination but is related to defects with deep levels. To obtain strong near-band-edge violet emission and even high effective UV laser, it is necessary to prepare LED and LD with active layers of ZnO superlattice or quantum well, which need high quality *p*-type ZnO and *p*-type ZnO alloy barrier materials. Since band gap of $Mg_xZn_{1-x}O$ alloy with wurtzite structure is larger than that of ZnO and can be tuned by changing Mg concentration,^{10,11} it is considered as candidate barrier material of ZnO based heterostructure. However, research progress about p-type MgZnO is limited. Only phosphor doping and N-Al codoping *p*-type MgZnO have been reported.^{12,13}

^{a)}Author to whom correspondence should be addressed; electronic mail: yaobin196226@yahoo.com.cn

In the present work, p-type N-doped MgZnO (MgZnO:N) was obtained via plasma-assisted molecular beam epitaxy (PAMBE) followed by postannealing process. The mechanisms of formation as well as electrical property of the p-type (MgZnO:N) were investigated.

A MgZnO:N film was grown by PAMBE on *c*-plane sapphire (Al₂O₃) at 425 °C. NO gas (99.99%) was used as O source and N dopant and activated during the growth process by an Oxford Applied Research Model HD25 rf (13.56 MHz) atomic source. The film thickness is measured by ellipsometer to be about 200 nm. The crystal structure of sample was characterized by x-ray diffraction (XRD) with Cu $K\alpha_1$ radiation (λ =0.154 06 nm). The electrical properties of the samples were measured in Van der Pauw configuration by a Hall analyzer (Lakeshore7707) at room temperature.

Figure 1 shows XRD pattern of the as-grown MgZnO:N



FIG. 1. XRD of as-grown MgZnO:N film deposited on *c*-plane Al_2O_3 sub-strate at 425 °C. The inset shows its Mg_{1s} peak of XPS.

^{© 2006} American Institute of Physics

TABLE I. Electrical parameters of MgZnO, and as-grown and annealed MgZnO:N.

Sample	Resistivity (Ω cm)	Hall mobility (cm ² /V s)	Carrier concentration (cm ⁻³)	Conduction type
MgZnO (as grown)	2.31	3.07	9.4×10^{17}	п
MgZnO (annealed)	7.44	3.70	2.3×10^{17}	п
MgZnO:N (as grown)	1.90	1.10	3.0×10^{18}	п
MgZnO:N (annealed)	1.60	6.42	6.1×10^{17}	р

film. Besides (006) diffraction peak of the Al₂O₃, only (002) diffraction peak is observed at 34.60°, indicating that the as-grown MgZnO:N is of single wurtzite structure with (002) preferential orientation. As shown in the inset of Fig. 1, a Mg_{1s} peak was detected by x-ray photoelectron spectrum (XPS) measurement, indicating existence of Mg in the film. The XPS calculation shows that about 20 at. % Zn is replaced by Mg in the as-grown MgZnO:N.

The Hall measurements indicate that both as-grown undoped MgZnO and MgZnO:N films behave *n*-type conductivity in the present work. Their electrical parameters are listed in Table I. In order to obtain *p*-type MgZnO, the asgrown MgZnO:N and MgZnO were annealed for 1 h at 600 °C in an O₂ flow, based on our previous research works about preparation of *p*-type ZnO.¹⁴ It was found that the annealed MgZnO:N transformed into *p*-type conduction, while the annealed MgZnO still behaved *n*-type conductivity. These results indicate that both N doping and postannealing are necessary for obtaining *p*-type MgZnO.

As mentioned above, the MgZnO behaves n-type conductivity, implying that it has many native donor defects, such as O vacancies (V_0) and Zn interstitial (Zn_i) . In order to compensate these donor defects and obtain *p*-type MgZnO, NO was used to produce MgZnO:N by PAMBE in the present work. Unfortunately, the as-grown MgZnO:N does not show *p*-type but *n*-type conductivity; furthermore, as shown in Table I, its resistivity decreases and electron concentration increases by comparison with the MgZnO. It is well known that nitrogen occupies two chemical environments in N-doped ZnO.¹⁵ One is formed by substitution of N atom for O sublattice to act as an acceptor, denoted by N_O, and the other by substitution of N molecule for O site to act as double donors, denoted by $(N_2)_{\rm O}.$ In order to understand chemical environments of nitrogen in the MgZnO:N and give the mechanism of the conduction-type transition induced by annealing, XPSs were recorded for the as-grown MgZnO:N and annealed MgZnO:N, as shown in Fig. 2. Curve a presents XPS of the as-grown MgZnO:N, which reveals three peaks, located at 396.1, 400.0, and 404.3 eV, respectively. Since the 400.0 eV is close to N_{1s} binding energy of C–N bond,¹⁶ the peak is assigned to radiation of N_{1s} in C-N bond. In the present work, formation of the C-N bond is due to chemical reaction between N in the MgZnO:N and C or CO₂ absorbed on the surface of the MgZnO:N film. Many research works have indicated that the 396.1 and 404.3 eV peaks are characterization radiation of N_{1s} of $(N)_O$ and $(N_2)_0$ in N-doped ZnO, respectively.¹⁵ In the present work, N doping was performed in the growth process of the MgZnO film, so the N should be incorporated into the entire film. Therefore, the appearance of the 396.1 and 404.3 eV



FIG. 2. N_{1s} peaks of XPS of as-grown (a) and annealed (b) MgZnO:N films.

peaks implies that there are $(N)_0$ and $(N_2)_0$ defects in the whole as-grown MgZnO:N.

The ratio of hole to electron concentrations, which originate from $(N)_0$ and $(N_2)_0$, respectively, was estimated by calculating the ratio of I_N to $2I_{N_2}$, where I_N and I_{N_2} represent integrated areas of the N_{1s} peaks of $(N)_O$ and $(N_2)_O$, respectively. The ratio is 0.4 for the as-grown MgZnO:N, indicating that electron concentration originated from (N₂)_O is larger than hole concentration that comes from $(N)_{O}$. Assuming that electron concentration of the native defects is not affected by N doping, the hole concentration of $(N)_{O}$ and electron concentration of (N₂)_O in the as-grown MgZnO:N can be calculated to be 1.37×10^{18} and 3.42×10^{18} cm⁻³, respectively, by using the data in Table I and the ratio of $I_N/2I_{N_2}$. Therefore, the *n*-type conductivity of the as-grown MgZnO:N with high net electron concentration is attributed to that electron concentration of the $(N_2)_0$ is not only larger than the hole concentration of (N)₀, but also much larger than electron concentration of the native donor defects.

Curve b in Fig. 2 presents XPS of the annealed MgZnO:N, which shows that the 404.3 eV peak almost disappears, while the N_{1s} peak of $(N)_O$ located at 396.1 eV becomes dominant. These results imply that the (N₂)_O defects are few in the annealed MgZnO:N and the electron concentration originated from the $(N_2)_0$ can be ignored. Hall measurement performed in the present work indicates that electron concentration from native donor defects is about $2.3 \times 10^{17} \mbox{ cm}^{-3}$ for undoped MgZnO annealed at the same conditions as the annealed MgZnO:N. Supposing that the electron concentration of the native donor defects is not affected by N doping and that the hole concentration of the (N)_O in the annealed MgZnO:N is the same as that in the as-grown MgZnO:N, the net carrier concentration of the annealed MgZnO:N is equal to difference between hole concentration of $(N)_{O}$ and electron concentration of the native donor defects since electron concentration of (N2)O can be ignored. It is calculated to be about 1.14×10^{18} cm⁻³. Hole is the dominant carrier, implying that the annealed MgZnO:N should show *p*-type conductivity, in agreement with the present Hall measurement result. Based on above discussion, it can be concluded that the conduction-type transition induced by annealing is attributed to almost disappearance of $(N_2)_0$ defects in the annealed MgZnO:N, which leads to that the electron concentration of $(N_2)_O$ can be ignored and the hole concentration of the $(N)_O$ becomes much larger than electron concentration of the native donor defects in the annealed MgZnO:N.

It should be noted that the calculated net hole concentration of 1.14×10^{18} cm⁻³ is larger than the measured hole concentration of 6.1×10^{17} cm⁻³ for the annealed MgZnO:N. That may be due to the supposition that the hole concentration of the (N)_O in the as-grown MgZnO:N is the same as in the annealed MgZnO:N. In fact, the amount of (N)_O decreases after annealing, so that the hole concentration of (N)_O in the annealed MgZnO:N is smaller than in the as-grown MgZnO:N.

In summary, the as-grown MgZnO:N produced by PAMBE is *n*-type conductor; it transforms into *p*-type conductor with a resistivity of 1.60 Ω cm, a carrier concentration of 6.1×10^{17} cm⁻³, and a mobility of $6.42 \text{ cm}^2/\text{V}$ s, after annealed at 600 °C in an O₂ flow. There are two chemical environments of (N)_O acceptor and (N₂)_O double donors in the as-grown MgZnO:N. After annealing, the (N₂)_O donors almost disappear and the (N)_O acceptor becomes dominant in the MgZnO:N. Therefore, the conduction property transition of the MgZnO:N from *n*-type to *p*-type is mainly attributed to a great decrease of the (N₂)_O after annealing.

The authors would like to thank financial support of the program of CAS Hundred Talents, Key Projects of the National Natural Science Foundation of China (Grant Nos. 60336020 and 50532050), the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos. 60278031, 60376009, 50402016, 60506014, 60501025, and State Natural Science

Foundation—Outstanding Oversea Chinese Young Scholar Foundation No. 60429403.

- ¹Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
- ²H. Cao, J. Y. Wu, H. C. Ong, J. Y. Dai, and R. P. H. Chang, Appl. Phys. Lett. **73**, 572 (1998).
- ³D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
- ⁴H. 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).
- ⁵Kyoung-Kook Kim, Hyun-Sik Kim, Dae-Kue Hwang, Jae-Hong Lim, and Seong-Ju Park, Appl. Phys. Lett. **83**, 63 (2003).
- ⁶T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys., Part 2 38, L166 (1999).
- ¹A. Tsukazaki, 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).
- ⁸S. 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. **81**, 1830 (2006).
- ⁹W. 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).
- ¹⁰A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, and H. Koinuma, Appl. Phys. Lett. **72**, 2466 (1998).
- ¹¹S. Choopun, R. D. Vispute, W. Yang, R. P. Sharma, T. Venkatesan, and H. Shen, Appl. Phys. Lett. **80**, 1529 (2002).
- ¹²Y. W. Heo, Y. W. Kwon, Y. Li, S. J. Pearton, and D. P. Norton, Appl. Phys. Lett. 84, 3474 (2004).
- ¹³X. Zhang, X. M. Li, T. L. Chen, C. Y. Zhang, and W. D. Yu, Appl. Phys. Lett. 87, 092101 (2005).
- ¹⁴B. Yao, D. Z. Shen, Z. Z. Zhang, X. H. Wang, Z. P. Wei, B. H. Li, Y. M. Lu, X. W. Fan, L. X. Guan, G. Z. Xing, C. X. Cong, and Y. P. Xie, J. Appl. Phys. **99**, 123510 (2006).
- ¹⁵Craig L. Perkins, Se-Hee Lee, Xiaonan Li, Sally E. Asher, and Timothy J. Coutts, J. Appl. Phys. **97**, 034907 (2005).
- ¹⁶Sadananda Sahu, Stefan Kavecky, L'ubica Illesova, Jana Madejova, Imre Bertoti, and Janos Szepvolgyi, J. Eur. Ceram. Soc. 18, 1037 (1998).