Journal of Crystal Growth 311 (2009) 3577–3580

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

A facile route to arsenic-doped p-type ZnO films

S.P. Wang [a,b], C.X. Shan [a,*], B.H. Li [a], J.Y. Zhang [a], B. Yao [a], D.Z. Shen [a], X.W. Fan [a]

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

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

ARTICLE INFO

Article history:
Received 4 February 2009
Received in revised form
12 May 2009
Accepted 2 June 2009
Communicated by M. Kawasaki
Available online 6 June 2009

PACS:
61.72.Uj
72.80.Ey
73.61.Ga
78.55.Et

Keywords:
A1. Diffusion
A1. Doping
A3. Molecular beam epitaxy
B2. Semiconducting II–VI materials

ABSTRACT

Undoped zinc oxide (ZnO) films have been prepared on sapphire substrates in a molecular beam epitaxy technique, and the films were annealed in air ambient along with a GaAs wafer. Arsenic in the GaAs wafer will evaporate, and enter into the ZnO films. In this facile way, arsenic-doped p-ZnO has been obtained. Hall measurements reveal that the hole concentration and Hall mobility of the ZnO:As films obtained in this way can reach $3.7\times10^{17}\,cm^{-3}$ and $2.8\,cm^2\,V^{-1}\,S^{-1}$, respectively. X-ray photoelectron spectroscopy confirms the incorporation of arsenic into the ZnO films. The activation energy of the acceptors derived from temperature-dependent Hall measurement is about 164 meV.

1. Introduction

As a wide bandgap semiconductor, zinc oxide (ZnO) has attracted much attention in recent years for its potential applications in versatile fields, especially in the field of blue-ultraviolet light-emitting devices [1,2] and lasing diodes [3,4]. To realize such applications, high-quality p-ZnO has to be available in a reliable and reproducible manner. Up to now, various methods have been employed to prepare p-ZnO including molecular beam epitaxy (MBE) [5,6], metal-organic chemical vapor deposition [7,8], pulsed laser deposition [9], etc. Among these methods, thermal diffusion has been highlighted for its facile nature. Some groups have prepared ZnO films on GaAs (or InP) substrates, then by thermal annealing the samples, arsenic (or phosphorous) will diffuse from the substrate and enter into the ZnO films. In this way, p-ZnO or even ZnO-based p-junctions and light-emitting diodes have been obtained [10–15]. However, the diffusion method they used has three obvious shortcomings: First, the ZnO films has to be grown on GaAs (or InP) that has different crystalline structure with ZnO, which will deteriorate the crystalline quality of the ZnO films. Second, the dopants are limited by the substrates used in this method. Third, the conductive nature of the GaAs (or InP) substrate used will tamper the reliability of the Hall data of the ZnO films [16]. The above shortcomings impair the usefulness of thermal diffusion method.

In this paper, ZnO films were prepared on sapphire substrates by MBE, and then the as-grown ZnO films were annealed along with a GaAs wafer in air ambient. Because of the heat treatment, arsenic in the GaAs will evaporate and enter into the ZnO films. In this way, arsenic-doped p-ZnO films have been obtained. The above three shortcomings were avoided in our revised diffusion method, while the advantages of this method, such as simplicity and facility, were fully exploited.

2. Experiment

The ZnO thin films were grown on sapphire (α-Al_2O_3) substrates by a V80H plasma-assisted MBE. Prior to being loaded into the growth chamber, the sapphire substrates were cleaned by chemical cleaning and etching process, and then heated at about 750 °C for 30 min in a preparation chamber to remove the possible adsorbed contaminations. The precursors used for the ZnO film growth is 6N elemental Zn and radical O, note that the radical O was obtained by treating 6N O_2 in a radio-frequency plasma cell. The O_2 flow rate was fixed at 0.6 sccm and the zinc precursor

---

[*] Corresponding author. Tel.: +86 43186176312; fax: +86 43186176298.
E-mail address: phycxshan@yahoo.com.cn (C.X. Shan).

0022-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2009.06.002

temperature at 250 ± 0.1 °C during the growth process. The background pressure in the chamber was less than 1×10^{-9} mbar, and the pressure was maintained at 1×10^{-5} mbar during growth. To realize acceptor doping of ZnO, the as-grown ZnO films were annealed in air ambient in a tube furnace along with a GaAs wafer. In this way, unexpected elements, such as Ga, were excluded from the ZnO films.

Electrical characteristics of the ZnO films were studied using a Hall measurement system (LakeShore 7707). A Rigaku D/max-RA X-ray diffractometer (XRD) with the CuKα line of 1.54 Å as the radiation source was used to characterize the structure of the films. The morphology of the films was observed by a field emission scanning electron microscope (SEM, Hitachi S-4800). The composition of the films was characterized by an X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with AlKα ($h\nu = 1486.6$ eV) line as the irradiation source. Photoluminescence (PL) spectra were recorded in a JY-630 micro-Raman spectrometer using the 325 nm line of a He–Cd laser as the excitation source.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-grown ZnO film. The film exhibits a prominent ZnO (0 0 0 2) diffraction peak locates at 34.48° besides the diffraction from the sapphire substrate, indicating that the film has preferential orientation with *c*-axis perpendicular to the substrate surface. The above XRD data reveal that the as-grown ZnO film has acceptably good crystallization properties, which can serve as a platform for further thermal diffusion doping procedure.

The carrier density and mobility of the ZnO films annealed at different temperature along with GaAs wafers are shown in Fig. 2. The carrier density is in the order of 10^{18} cm^{-3} when the annealing temperature is below 545 °C, while it decreases to about 4.7×10^{17} cm^{-3} when the sample was annealed at 555 °C. It is noteworthy that the sample shows n-type conduction when annealed at 525, 545, and 555 °C, while it converts to p-type when annealed at 565 °C. However, the film returns to n-type conduction when further increase the annealing temperature to 575 °C. The above facts mean that p-ZnO can be realized by annealing the as-grown n-ZnO in air along with GaAs wafer by proper optimizing the annealing conditions.

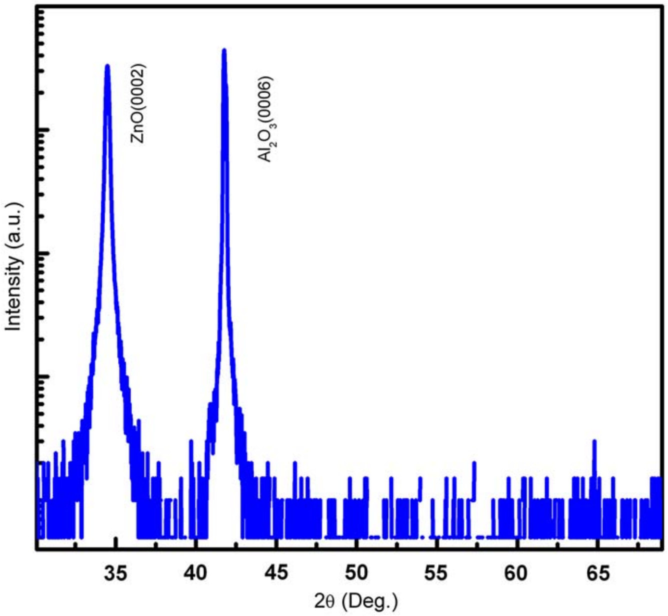

Fig. 1. (Color online) XRD pattern of the as-grown ZnO film.

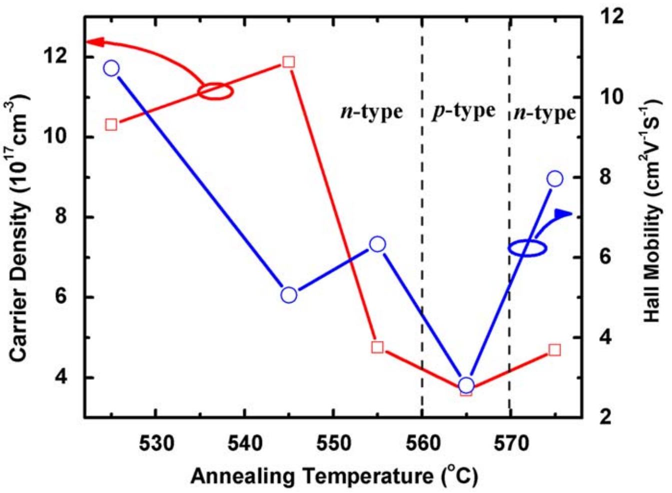

Fig. 2. (Color online) Hall mobility, carrier concentration of the ZnO films annealed at different temperature.

Table 1
Electrical properties of the as-grown samples, the samples annealed with and without GaAs wafer at 565 °C.

Sample	Hall mobility (cm^2 V^{-1} S^{-1})	Carrier density (cm^{-3})	Conduction type
As-grown	33.3	1.1×10^{18}	n
Annealed without GaAs	15.5	9.4×10^{17}	n
Annealed with GaAs	2.8	3.7×10^{17}	p

Note that some groups have claimed that by annealing ZnO films in air, the electron concentration will be decreased, and even p-type conduction can be realized [11,17]. To clarify the origin of the p-type conduction obtained in our experiment, another ZnO film was also annealed under the same conditions as the sample annealed at 565 °C except that no GaAs wafer was loaded, the electrical data of which are shown in Table 1. The as-grown ZnO film shows typical n-type conduction with an electron concentration of 1.1×10^{18} cm^{-3}. After the sample was annealed without GaAs, the conduction keeps n-type; while with GaAs, the annealed ZnO films shows p-type conduction with a hole concentration of 3.7×10^{17} cm^{-3}. One can conclude from the above phenomenon that the p-type conduction was resulted from the incorporation of arsenic from the GaAs wafer.

The above conclusion was confirmed by XPS measurement. The XPS spectrum of the ZnO film annealed at 565 °C along with GaAs wafer is shown in Fig. 3. There appears a peak at 44.8 eV, which is characteristic of As–O bonding, while the characteristic peaks of As–Zn bonding located at 40–41 eV and those of isolate As at 41–42 eV are absent [9]. The above facts reveal that arsenic has been incorporated into the ZnO films, and maybe the arsenic atoms occupy Zn sites. This conclusion is consistent with the popular proposal that the acceptors in arsenic-doped ZnO come from the complex formed by the arsenic occupying Zn site and its bonding with two Zn vacancies [15,18].

Fig. 4 shows the 80 K PL spectra of the ZnO films annealed at different temperature. Note that the spectra have been normalized according to the height of their near-band-edge (NBE) emissions. Sharp NBE emissions and weak shoulders at about 3.313 eV can be seen in all the spectra. The shoulder is frequently observed in ZnO, and usually attributed to the recombination between electrons in

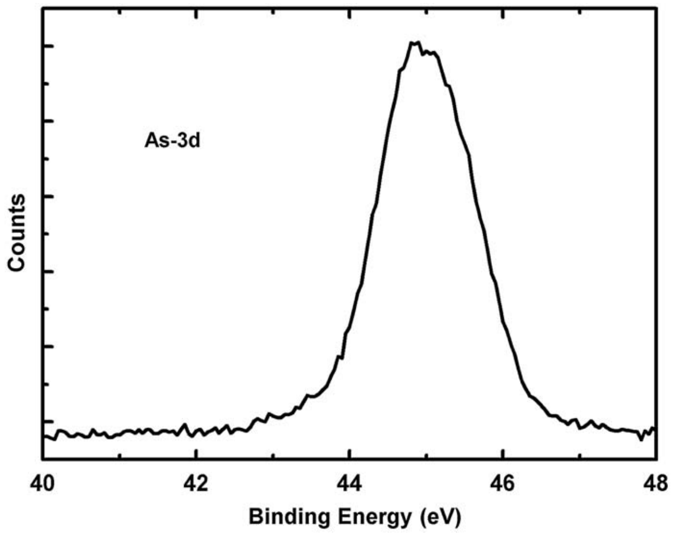

Fig. 3. XPS spectrum of the p-ZnO: As by annealing the as-grown ZnO film at 565 °C with GaAs, revealing the incorporation of As into the ZnO film.

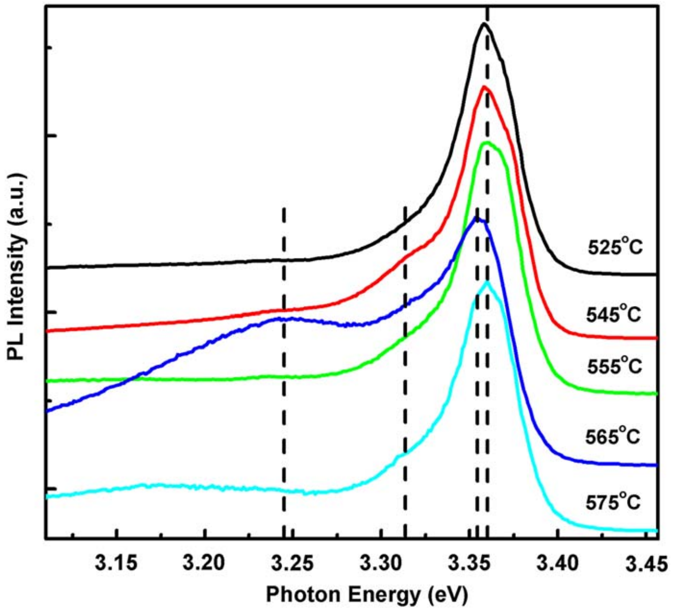

Fig. 4. (Color online) PL spectra of films annealed at different temperature.

conduction band and acceptor-related levels (labeled as FA) [19–22]. A noteworthy phenomenon is that the NBE emission of the samples annealed at 565 °C is located at 3.353 eV, while those of all the other four samples are at 3.360 eV. It is generally accepted that the peak at 3.353 eV is from the emission of excitons bound to neutral acceptors (labeled as A^0X) [19,22], while the one at 3.360 eV is from neutral donor bound excitons emission in ZnO (labeled as D^0X) [20–24]. Furthermore, there appears an emission at 3.244 eV for the ZnO film annealed at 565 °C, which can be attributed to the donor–acceptor pair recombination in ZnO (labeled as DAP) [6,22]. The significant enhanced acceptor-related emissions (A^0X and DAP) and the decreased donor-related emission (D^0X) of the sample annealed at 565 °C compare with that of other samples verify the Hall data that p-ZnO has been obtained for the sample annealed at 565 °C.

Fig. 5 exhibits the PL spectra of the as-grown ZnO, the samples annealed at 565 °C with and without GaAs wafer. It can be seen that the spectra of the as-grown ZnO film has a similar shape with that of the sample annealed without GaAs. They both have a characteristic peak at 3.360 eV (D^0X), as well as a shoulder at 3.372 eV which is typically attributed to free exciton (FX_A) emission in ZnO [22–25]. However, the spectra of the ZnO film annealed with GaAs shows characteristic peaks of p-ZnO at 3.244 eV (DAP), 3.313 eV (FA) and 3.353 eV (A^0X). The PL spectroscopy validates that p-ZnO film has been realized by this facile thermal annealing method.

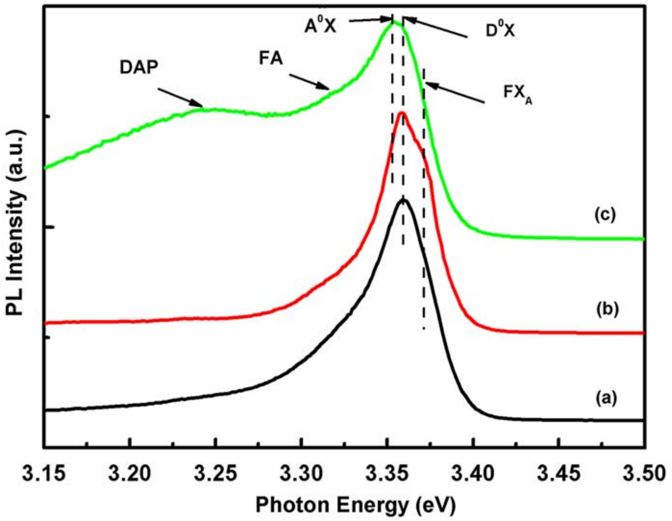

Fig. 5. PL spectra of the as-grown sample (a) and the samples annealed at 565 °C without (b) and with GaAs wafer (c).

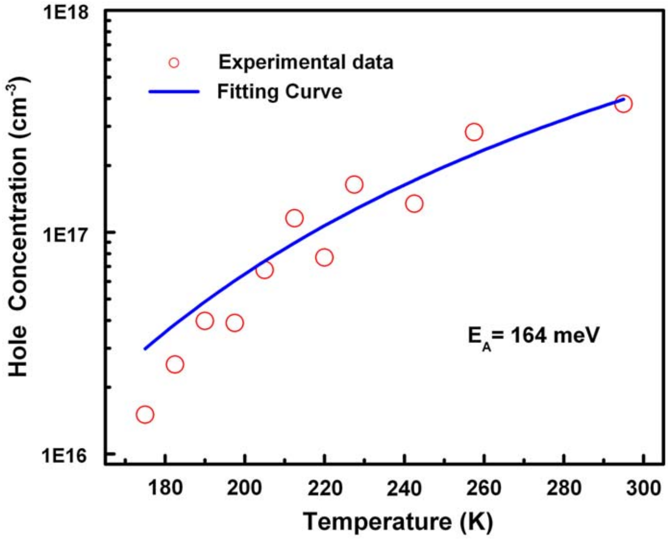

Fig. 6. Temperature-dependent carrier concentration of the p-ZnO films, in which the scattered symbols are experimental data, while the curve is the fitting result.

Temperature-dependent hole concentration of the obtained p-ZnO has been measured to derive the activation energy of the acceptors. As show in Fig. 6, the carrier concentration decreases with temperature, and the activation energy of E_A can be derived from the following relationship [20]:

$$n_p = C\exp(-E_A/kT) \times T^{3/4} \tag{1}$$

here C is a fitting constant and n_p the carrier concentration. By best fitting the data, E_A yields a value of about 164 meV. The value is in acceptable agreement with the activation energy of arsenic acceptors in ZnO reported in literature (146 meV [15] and 150 meV [18]).

4. Conclusions

Arsenic-doped p-ZnO film was prepared by a simple thermal diffusion process. Hall measurement exhibits a hole concentration of $3.7\times 10^{17}\,\mathrm{cm}^{-3}$ and a Hall mobility of $2.8\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{S}^{-1}$. PL spectroscopy confirms the formation of p-ZnO. XPS reveals that the p-type conduction was resulted from arsenic incorporation. It is speculated that the method employed in this paper can be extended to other dopants, such as phosphorous, by replacing GaAs with InP or other wafers with similar properties. The facility and simplicity nature of this method promises a possible feasible route to p-ZnO.

Acknowledgements

This work is supported by the Key Project of the NNSFC under Grant no. 50532050, the “973” program under Grant nos. 2008CB317105 and 2006CB604906, the Knowledge Innovation Program of the Chinese Academy of Sciences (KJCX3.SYW.W01), the NNSFC under Grant nos. 10674133, 10774132, 60776011.

Reference

[1] 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.

[2] 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.

[3] E.S.P. Leong, S.F. Yu, S.P. Lau, Appl. Phys. Lett. 89 (2006) 221109.

[4] Y.R. Ryu, J.A. Lubguban, T.S. Lee, H.W. White, T.S. Jeong, C.J. Youn, B.J. Kim, Appl. Phys. Lett. 90 (2007) 131115.

[5] F.X. Xiu, Z. Yang, L.J. Mandalapu, D.T. Zhao, J.L. Liu, W.P. Beyermann, Appl. Phys. Lett. 87 (2005) 152101.

[6] 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. Status Solidi A 202 (2005) 1060.

[7] W.Z. Xu, Z.Z. Ye, T. Zhou, B.H. Zhao, L.P. Zhu, J.Y. Huang, J. Cryst. Growth 265 (2004) 133.

[8] S. Gangil, A. Nakamura, Y. Ichikawa, K. Yamamoto, J. Ishihara, T. Aoki, J. Temmyo, J. Cryst. Growth 298 (2007) 486.

[9] N. Xu, Y. Xu, L. Li, Y. Shen, T. Zhang, J. Wu, J. Sun, Z. Ying, J. Vac. Sci. Technol. A 24 (2006) 517.

[10] H.F. Liu, S.J. Chua, G.X. Hu, H. Gong, N. Xiang, J. Appl. Phys. 102 (2007) 063507.

[11] P. Wang, N. Chen, Z. Yin, F. Yang, C. Peng, R. Dai, Y. Bai, J. Appl. Phys. 100 (2006) 043704.

[12] K.H. Bang, D.K. Hwang, M.C. Park, Y.D. Ko, I. Yun, J.M. Myoung, Appl. Surf. Sci. 210 (2003) 177.

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

[14] J.Y. Zhang, P.J. Li, H. Sun, X. Shen, T.S. Deng, K.T. Zhu, Q.F. Zhang, J.L. Wu, Appl. Phys. Lett. 93 (2008) 021116.

[15] H.S. Kang, G.H. Kim, D.L. Kim, H.W. Chang, B.D. Ahn, S.Y. Lee, Appl. Phys. Lett. 89 (2006) 181103.

[16] O. Maksimov, B.Z. Liu, J. Cryst. Growth 310 (2008) 3149.

[17] J.C. Sun, H.W. Liang, J.Z. Zhao, Q.J. Feng, J.M. Bian, Z.W. Zhao, H.Q. Zhang, Y.M. Luo, L.Z. Hu, G.T. Du, Appl. Surf. Sci. 254 (2008) 7482.

[18] S. Limpijumnong, S.B. Zhang, S.H. Wei, C.H. Park, Phys. Rev. Lett. 92 (2004) 155504.

[19] D.K. Hwang, H.S. Kim, J.H. Lim, J.Y. Oh, J.H. Yang, S.J. Park, K.K. Kim, D.C. Look, Y.S. Park, Appl. Phys. Lett. 86 (2005) 151917.

[20] Y.R. Ryu, T.S. Lee, H.W. White, Appl. Phys. Lett. 83 (2003) 87.

[21] J.W. Sun, Y.M. Lu, Y.C. Liu, D.Z. Shen, Z.Z. Zhang, B. Yao, B.H. Li, J.Y. Zhang, D.X. Zhao, X.W. Fan, J. Appl. Phys. 102 (2007) 043522.

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

[23] S.C. Su, Y.M. Lu, Z.Z. Zhang, B.H. Li, D.Z. Shen, B. Yao, D.X. Zhao, X.W. Fan, Physica B 403 (2008) 2590.

[24] A.B.M.A. Ashrafi, N.T. Binh, B.P. Zhang, Y. Segawa, J. Appl. Phys. 95 (2004) 7738.

[25] C.X. Shan, Z. Liu, Z.Z. Zhang, D.Z. Shen, S.K. Hark, J. Phys. Chem. B 110 (2006) 11176.