phys. stat. sol. (c) **1**, No. 4, 731–734 (2004) / **DOI** 10.1002/pssc.200304255

Nitrogen doping in bulk and epitaxial ZnO

A. Zeuner[1], **H. Alves**[1], **J. Sann**[1], **W. Kriegseis**[1], **C. Neumann**[1], **D. M. Hofmann**[1], **B. K. Meyer**[*,1], **A. Hoffmann**[2], **U. Haboeck**[2], **M. Straßburg**[2], and **A. Kaschner**[2]

[1] I. Physics Institute, Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany
[2] Institute for Solid State Physics, Technical University Berlin, Hardenbergstr. 38, 10623 Berlin, Germany

Received 22 September 2003, revised 26 September 2003, accepted 1 December 2003
Published online 13 February 2004

PACS 61.72.Vv, 71.55.Gs, 78.47.+p, 78.55.Et

We report on the characterization of bulk and epitaxial ZnO films doped by nitrogen. The ZnO thin films were grown on GaN templates and on ZnO single crystals by vapor phase deposition using Zn and NO_2 / N_2O as precursors. Nitrogen was introduced in the epitaxial films by a mixture of ammonia in the total N_2 flow and by ion implantation into the bulk crystals. The optical properties were investigated by steady state and time resolved photoluminescence (PL). We observed a well structured donor–acceptor-pair (DAP) band with a zero phonon line (ZPL) at 3.235 eV. Time resolved PL measurements allowed to conclude on the compensation. Diffusion of Ga from the GaN templates into the ZnO layers was detected by SIMS.

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction ZnO as a wide gap semiconductor is almost exclusively n-type conducting, and it is not astonishing that p-type doping has been a challenge for many years up to nowadays. Whereas the group I elements Li and Na form shallow acceptor levels in all the other II–VI semiconductors they introduce deep acceptor states in ZnO with binding energies between 500 and 800 meV [1]. Out of the group V elements nitrogen might be the best candidate considering the success with ZnSe:N [2]. The purpose of this report is to study the optical properties of nitrogen doped ZnO and to give clear evidence about the binding energy of the nitrogen acceptor.

2 Experimental details The epitaxial films were deposited in a home-built epitaxy system by the chemical vapor deposition technique with metallic Zn and NO_2/N_2O as respective precursors. As substrates (templates) we used GaN epitaxial films which were grown by MOCVD on (0001) sapphire substrates or ZnO substrates with Zn polarity. For nitrogen doping ammonia was used. Nitrogen doping was also done by ion implantation into bulk crystals and after that an annealing procedure at 900°C was carried through. The films were investigated by different luminescence techniques and by SIMS experiments.

3 Results and discussion Nitrogen could be incorporated into ZnO in the CVD films in concentrations between 10^{17}–10^{19} cm^{-3} as shown by SIMS investigations [3]. However, the optical properties with respect to the optical activity in a neutral acceptor bound exciton recombination or in a donor–acceptor-pair recombination remained undetermined. In the spectrum of Fig. 1(a) the ZnO film is doped during the CVD growth while in (b) a nitrogen-doping by ion-implantation into a bulk ZnO crystal followed by an annealing procedure of 900°C was done. In the near-band-edge range (Fig. 1(b)) the bound exciton recombination lines are only partially resolved, they include the I_4 [4] neutral donor bound exciton line at

[*] Corresponding author: e-mail: Bruno.K.Meyer@exp1.physik.uni-giessen.de, Phone: +49 641 9933100

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

3.363 eV, and at 3.3598 eV, the bound exciton line of I_8 [4]. In the spectrum of the implanted crystal (Fig. 1(a)) the near band gap photoluminescence is dominated by the bound exciton recombination of I_9 at 3.357 eV, with lower intensity the I_6 to I_8 recombinations and at 3.367 eV the ionized donor bound exciton line. With lower intensity a DAP recombination is observed in both samples. Its zero phonon line (ZPL) peaks at 3.235 eV and it is repeated by longitudinal optical phonon replica with an energy separation of 72 meV. The intensity of the ZPL (normalized to one) relative to its replica is given in Table 1. We also compare the intensity ratios to a DAP recombination commonly found in undoped ZnO [5], its ZPL is at 3.22 eV, and with the pair recombination involving the 110 meV deep nitrogen acceptor in ZnSe [2].

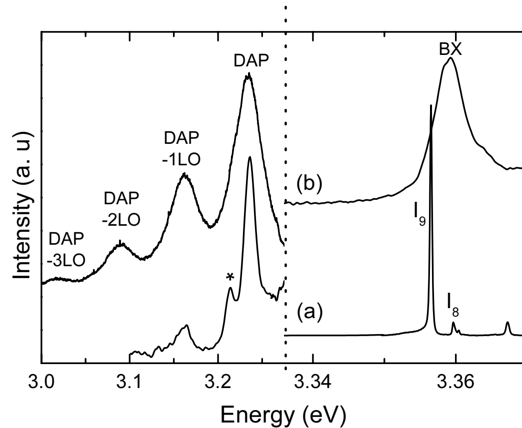

Fig. 1 Photoluminescence spectra at 4.2 K of a ZnO bulk crystal nitrogen implanted and thermaly annealed at 900 °C (a) and a nitrogen doped ZnO film by thermal decomposition of ammonia (b).

Table 1 Intensity of the zero phonon line (normalized to one) and replica of the donor acceptor pair recombination in undoped ZnO, in ZnO:N epitaxial films, and in ZnSe:N.

Transition intensity	ZnO undoped	ZnO:N	ZnSe:N [2]
ZPL	1	1	1
ZPL–1LO	0.15	0.54	0.50
ZPL–2LO	0.069	0.23	0.18
ZPL–3LO	-	0.084	0.05
ZPL–4LO	-	0.0236	-

The similarities between nitrogen doped ZnO and ZnSe:N are obvious. The acceptor binding energy can be estimated from the peak position of the ZPL by Eq. (1):

$$E_A = [E_g - E_D] - [E(D^o,A^o) - \alpha\, N_D^{\ 1/3}]. \quad (1)$$

For E_g we take 3.4360 eV, for E_D the shallow donor binding energy we take 52 meV the effective-mass-estimate, and for $\alpha = 3\times10^{-5}$ meVcm [5]. In order to calculate the acceptor binding energy an estimate for N_D is needed. We can assess this parameter by time-resolved experiments. The DAP transition showed a distribution of lifetimes typical for a donor acceptor pair transition (see Fig. 2). From the analysis of the luminescence transients a concentration of 2×10^{17} cm^{-3} was deduced [6]. We thus obtain for E_A = (165±10) meV. The implanted sample showed the same DAP transition (see Fig. 1(a)) in addition to the DAP transition (marked by a star) already present in the unimplanted crystal. Note that for this residual acceptor a binding energy of 195 meV was estimated consistent with the energy separation as shown in Fig. 1(b).

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

The excitonic transitions of I_4 and I_8 which are attributed to neutral donor bound exciton recombinations (also I_9) [7] are still dominating in the emission spectra and indicate that the films are still n-type conducting (what they are from Hall-effect measurements). I_4 is attributed to the shallow hydrogen donor [8] and I_8 to Ga [9]. Whereas hydrogen may come from ammonia, the source for the contamination with Ga was not obvious. We therefore performed SIMS measurements and looked for the depth profile of the respective elements starting from GaN/ZnO interface (see Fig. 3).

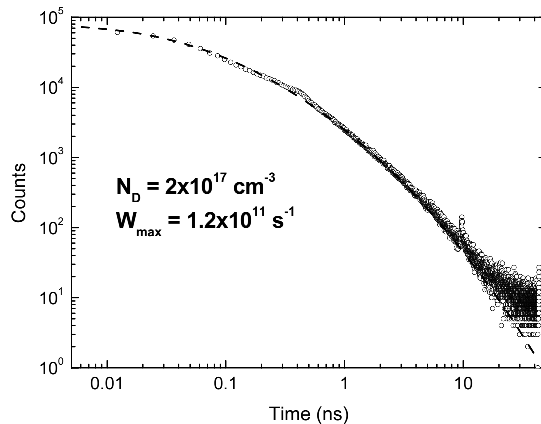

Fig. 2 Photoluminescence transient measured on the donor–acceptor-pair recombination band in nitrogen doped ZnO epitaxial films.

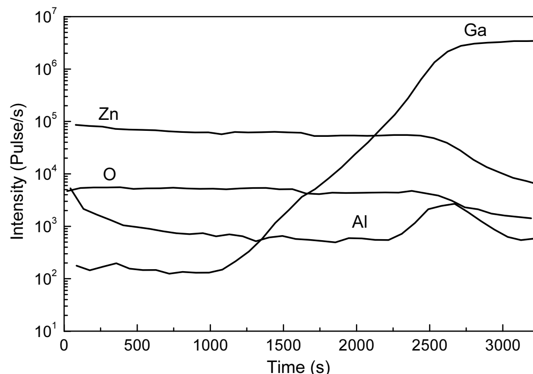

Fig. 3 Depth profile of Zn, O, Al, and Ga in a CVD grown ZnO film on GaN template as measured by secondary ion mass spectroscopy.

We see that the ZnO films are contaminated especially by Ga which shows a continuous transition from the GaN template into the ZnO film. A crude estimate assuming equal sensitivity factors for Ga in GaN and ZnO would imply concentrations of mid 10^{17} cm^{-3}. With such high concentrations p-type doping will probably be impossible.

In order to avoid the Ga contamination from the GaN template we deposited ZnO on Zn-face ZnO bulk crystals. The photoluminescence spectrum of such a film is shown in Fig. 4(b). We can observe the donor acceptor pair transition and the pronounced phonon replica but the bound exciton recombination of I_6 to I_8 are still dominating. The substrate luminescence not shown in Fig. 4, had as main transition the I_6 recombination. It might be that the incorporation of Ga giving rise to I_8 is caused by a memory effect in the reactor.

A surprising fact is that changing the oxygen precursor from NO_2 to N_2O the bound exciton spectrum of N-doped films is distinct different (see Fig. 4(a)). We observe two transitions at 3.37 eV (unknown origin) and at 3.358 eV. The 3.358 eV line is just in the middle between the I_8 and I_9 recombinations, and

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

it is not clear whether it is due to a neutral acceptor or donor bound exciton recombination. The structure and position of the DAP transition is more or less uninfluenced.

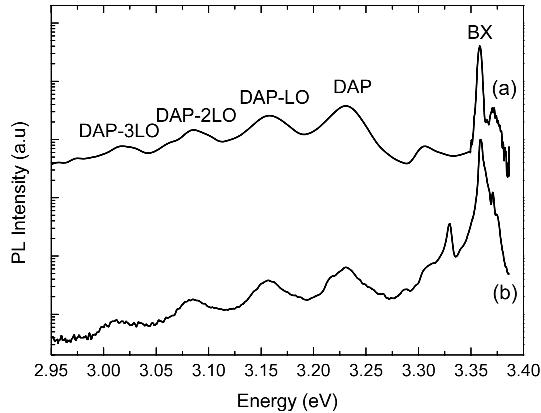

Fig. 4 Photoluminescence spectra of a nitrogen doped ZnO film on GaN template with N_2O as oxygen precursor (a) and of a ZnO:N epitaxial film deposited on the ZnO substrate (b).

4 Conclusions To summarize, the donor acceptor pair transition at 3.23 eV is consistently found in ZnO films grown in the presence of ammonia i) on GaN templates (heteroepitaxy), ii) on ZnO substrates (homoepitaxy) and iii) independent which oxygen precursor source N_2O or NO_2 is used. It is also introduced by nitrogen implantation into bulk crystals followed by a subsequent anneal at 900°C in N_2 atmospheres. In the films on GaN templates compensation by diffusion of Ga into ZnO prohibits p-type activity. With a binding energy of 165 meV a shallow acceptor level is present in ZnO which may open the route towards bi-polar doping if the residual, compensating donor concentration can be suppressed to an acceptable level.

Acknowledgements This work was supported by the BMBF (contract number 01 BM151).

References

[1] R. T. Cox, D. Block, A. Hervé, R. Picard, and C. Santier, Solid State Commun. **25**, 77 (1978); see also F. H. Leiter, Thesis, Gießen, 2002.
[2] J. Qiu, J. M. De Puydt, H. Cheng, and M. A. Haase, Appl. Phys. Lett. **59**, 2992 (1991).
[3] A. Kaschner, U. Haboek, Martin Strassburg, Mathias Strassburg, G. Kaczmarczyk, A. Hoffmann, C. Thomsen, A. Zeuner, H. R. Alves, D. M. Hoffmann, and B. K. Meyer, Appl. Phys. Lett. **80**, 1090 (2002).
[4] C. Klingshirn, phys. stat. sol. (b) **71**, 547 (1975);
J. Gutowski, N. Presser, and I. Broser, Phys. Rev. B **38**, 9746 (1988).
[5] K. Thonke, Th. Gruber, N. Teofilov, R. Schönfelder, A. Waag, and R. Sauer, Physica B **308–310**, 945 (2001).
[6] A. Zeuner, H. R. Alves, D. M. Hofmann, B. K. Meyer, A. Hoffmann, U. Haboeck, M. Straßburg, and M. Dworzak, phys. stat. sol. (b) **234**, R7 (2002).
[7] H. Alves, D. Pfisterer, A. Zeuner, T. Riemann, J. Christen, D. M. Hofmann, and B. K. Meyer, Opt. Mater. **23**, 33 (2003).
[8] D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, and B. K. Meyer, Phys. Rev. Lett. **88**, 045504 (2002).
[9] H. J. Ko, Y. F. Chen, S. K. Hong, H. Wenisch, and T. Yao, Appl. Phys. Lett. **77**, 3761 (2000).

© 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim