

**Identification of a donor-related recombination channel in ZnO thin films**

Matthias Brandt,\* Holger von Wenckstern, Gabriele Benndorf, Martin Lange, Christof P. Dietrich, Christian Kranert, Chris Sturm, Rüdiger Schmidt–Grund, Holger Hochmuth, Michael Lorenz, and Marius Grundmann  
*Institut für Experimentelle Physik II, Universität Leipzig, Linnèstr. 5, 04103 Leipzig, Germany*

Markus R. Wagner, Miran Alic, Christian Nenstiel, and Axel Hoffmann

*Institute of Solid State Physics, TU Berlin, Hardenbergstr. 36, 10623 Berlin, Germany*

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An excitonic recombination line is observed in photoluminescence spectra of ZnO thin films at 3.3465 eV. The line is labeled  $I_{12}$ . Its appearance was only observed in samples grown on a MgO or heavily aluminum-doped ZnO buffer layer. The properties of the recombination mechanism were probed by photoluminescence and photoluminescence-excitation spectroscopy. The recombination was classified to be an exciton bound to a neutral donor. Both an ionized state and a two-electron satellite transition were observed and could be correlated with the central transition. The excitation channels are similar to those of the well-known  $I_6$  transition related to  $Al_{Zn}$ . The localization energy was calculated to be 29.4 meV. A donor activation energy of 90.8 meV was extrapolated using the Haynes rule for ZnO.

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**I. INTRODUCTION**

ZnO is a transparent semiconducting oxide with very promising properties for applications in optoelectronics, among them its direct band gap with a transition energy of 3.37 eV at room temperature and the high exciton binding energy of 59 meV. Doping experiments have been carried out to a great extent, especially with the aim of reliable  $p$ -type conduction. From these studies, numerous reports emerged on the luminescence properties of ZnO single crystals and thin films. The recombination spectrum at low temperatures is typically dominated by transitions due to free and bound excitons. A remarkable number of bound-exciton transitions has been reported, as compiled in Refs. 1 and 2. The chemical identity of a few impurities is known.<sup>2,3</sup> Furthermore excited states are known, as rotational transitions,<sup>2,4</sup> excitons bound to the defect in an ionized state<sup>5</sup> and recombinations with a deeper valence band (B excitons).<sup>2</sup>

In this study, we report on the observation of a neutral-donor-bound excitonic ( $D^0X$ ) recombination feature in ZnO thin films grown on a MgO or heavily aluminum-doped ZnO buffer layer which is not present in ZnO thin films directly grown on sapphire. A recombination feature at 3.345 eV was previously observed by Ohno *et al.*<sup>6</sup> in samples annealed under compressive stress, and was tentatively ascribed to an acceptor defect in the vicinity of and in interaction with a dislocation line. The intensity of the observed recombination was comparably weak, no excited states were observed, leaving the actual nature of the transition unknown. In this Brief Report, excited states of the defect in question are reported, which is identified as a donorlike recombination center for excitons. A donor with a similar thermal activation energy of about 100 meV was previously reported in ZnO thin films grown on Al-doped buffer layers.<sup>7,8</sup>

**II. EXPERIMENTAL**

All films investigated were grown by pulsed laser deposition (PLD), as described in Ref. 9. The samples were depos-

ited on  $a$ -plane sapphire substrates by ablation of sintered ceramic pellet targets. The films were investigated by photoluminescence (PL) spectroscopy and photoluminescence-excitation (PLE) spectroscopy. The PL was excited by the 325 nm line of a cw He-Cd laser and recorded at 2 K. The excitation source of the PLE experiment was a dye laser containing 2-methyl-5-*t*-butyl-*p*-quaterphenyl, pumped by the 308 nm line of a XeCl excimer laser. This allows the excitation wavelength to be tuned in the range of 345–375 nm. An intensity spectrum of the laser emission was recorded for normalization of the PLE spectra. The spectral resolution of the setup employed was better than 0.01 nm (better than 120  $\mu$ eV) and is mainly given by the width of the laser line chosen for excitation. An uncertainty in the absolute position of the spectra of 0.02 nm ( $\approx$ 240  $\mu$ eV) exists, which however does not influence the separation of adjacent peaks and their relative positions.

Raman spectroscopy measurements were carried out on the samples excited by the 532 nm line of a frequency-doubled Nd:YAG laser. The response signal was dispersed using a 1 m focal length double monochromator with 2400 L/mm gratings and detected by a liquid-nitrogen-cooled charge-coupled-device detector. All samples were measured in  $z(xy)\bar{z}$  backscattering geometry. The accuracy of the spectral position in the Raman measurement was better than 0.1  $cm^{-1}$ .

Three samples were included in the study. Sample A contains an approximately 160-nm-thick highly aluminum-doped ZnO layer; the aluminum concentration was around 1 wt %. Sample B contains a roughly 10-nm-thick MgO buffer layer. On top of the respective buffer layers, a  $\approx$ 1- $\mu$ m-thick nominally undoped ZnO layer was deposited. Sample C was grown without a buffer layer. In all samples discussed, the crystallographic  $c$  axis is parallel to the sample  $z$  axis, as determined by x-ray-diffraction investigations.

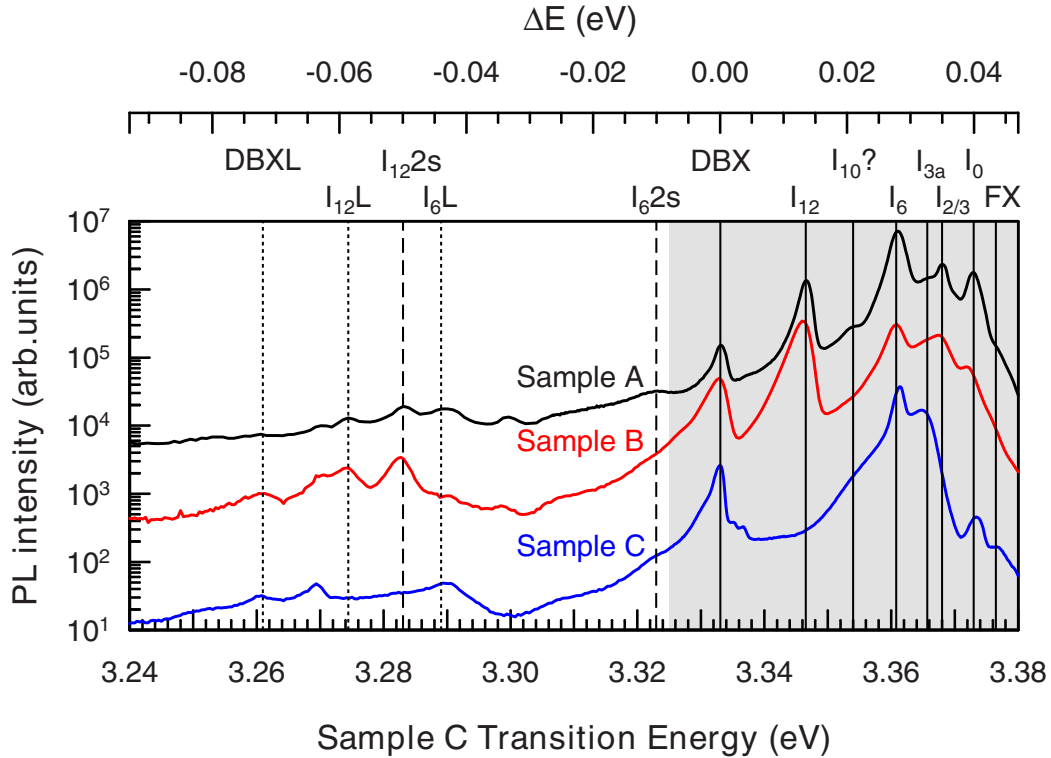


FIG. 1. (Color online) 2 K PL of ZnO thin films, from top to bottom samples A, B, and C. The lines are shifted for clarity, as described in the text. The upper axis gives the spectral shift with respect to the DBX line and the lower axis gives the absolute transition energy scale for sample C. The labels of the vertical lines are: FX: free A exciton, DBX: exciton bound to an extended structural defect (Ref. 2),  $I_n$ : donor-bound excitons as labeled in Ref. 2 (apart from the new  $I_{12}$  line),  $I_n 2s$ :  $s$ -orbital-like two-electron satellite transitions, taken from, or calculated following Ref. 2, and  $I_n L$  first phonon replica.

### III. RESULTS

#### A. Structural properties

Raman measurements were employed in order to determine the strain in the thin films. The phonon frequencies of the  $E_2^{(2)}$  mode were determined to be 437.5, 437.1, and 438.1  $\text{cm}^{-1}$  for samples A, B, and C, respectively. Values of 437–444  $\text{cm}^{-1}$  for this mode are reported in the literature, as obtained by measurements on single-crystal material (Refs. 10–12, and references therein). For PLD-grown thin films on sapphire, a value of 438.0  $\text{cm}^{-1}$  was reported,<sup>13</sup> which corresponds very well to the value obtained for sample C. A definite statement on the strain state of the films cannot be given, however from the lower phonon frequency of the films A and B, it is evident that their lattice must be expanded with respect to sample C. The relative strain with respect to sample C was calculated. The biaxial in-plane strain is expressed by the uniaxial out-of-plane strain and the poisson ratio. From the shift of the  $E_2^{(2)}$  frequency and following the approach given in Ref. 14, the out-of-plane strain  $\epsilon_{zz}$  (along the  $c$  axis) was calculated from the shift in the  $E_2^{(2)}$  mode. Values of  $-1.3 \times 10^{-3}$  and  $-2.2 \times 10^{-3}$  with respect to sample C were obtained for samples A and B, respectively.

#### B. Photoluminescence

The photoluminescence spectra of all three thin films are depicted in Fig. 1. The lines have been shifted in vertical

direction for better visibility. The upper energy scale is displayed with respect to a prominent luminescence feature label DBX typically occurring at 3.333 eV. Therefore, a shift toward higher energies of 1.4 meV for sample A and 1.9 meV for sample B was necessary. All remaining peak positions are well aligned after the horizontal shift. The decrease in the fundamental band gap of samples A and B is consistent with the expansion of the lattice found from Raman spectroscopy. From the values obtained in the Raman experiment and following Ref. 14, the strain-induced shift of the band gap with respect to sample C was calculated to be  $-1.0$  and  $-1.7$  meV for samples A and B, respectively, which is in good agreement with the experimental values.

The spectra are subdivided into two regions: region D (3.325–3.38 eV, highlighted by a gray background in Fig. 1 containing the free-exciton and donor-bound-exciton luminescence) and region R [3.24–3.325 eV, with a white background in Fig. 1 containing the first phonon replica and two-electron satellite (TES) transitions]. The free-exciton recombination is comparatively weak in all of the films and is best visible for sample C, denoted as FX in Fig. 1. Numerous donor-bound excitons are found and were labeled following Ref. 2. All samples show  $I_0$  and  $I_6$  lines, corresponding to excitons bound to ionized and neutral aluminum donors,<sup>5</sup> respectively. The  $I_{3a}$  line, corresponding to excitons bound to Zn on interstitial site<sup>3</sup> was also observed. Likewise, a feature marked as DBX was resolved, corresponding to an exciton bound to an extended defect.<sup>2</sup> In region D, two ad-

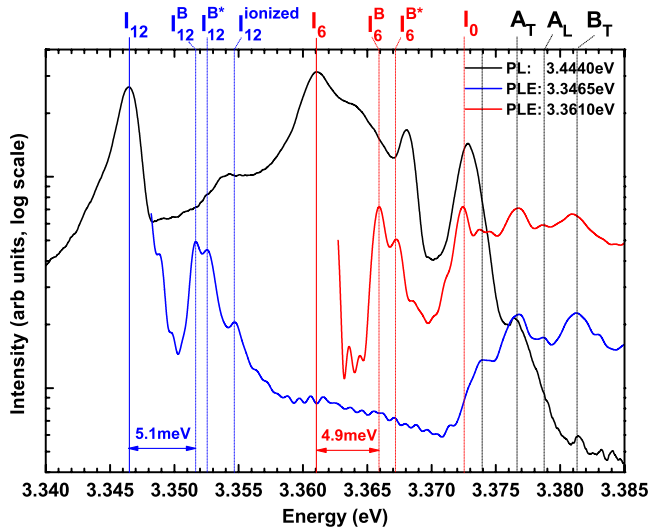


FIG. 2. (Color online) PL and PLE spectra obtained from sample A, detection was carried out at the  $I_{12}$  and the  $I_6$  peak position.

ditional features are observed in samples A and B only: a line labeled as  $I_{2/3}$  with unknown origin and a prominent line not labeled so far at 3.3465 eV, from now on referred to as the  $I_{12}$  line. None of these transitions is present in sample C. Further, in sample A, a shoulder at the position of the  $I_{10}$  line was observed. In Ref. 5, this line is assigned to be a ( $D^0X$ ) transition, with an ionized donor-bound transition ( $D^+X$ ) at 3.363 eV labeled  $I_*$ . No distinct feature can be seen at this position in the present study, however, the peak would have to be rather small and would be most likely masked by the intense  $I_6$  transition nearby.

In region R, the phonon replica of the DBX line were observed, along with replica of the  $I_6$  and the  $I_{12}$  line. No spectral feature is present where replicas of  $I_{2/3}$  and  $I_{3a}$  lines are expected. All phonon replicas are denoted with an additional L added to the label of the original transition. Further, a two-electron satellite transition is observed, related to the  $I_6$  line. Additional features appear at 3.269 and 3.283 eV. The feature observed at 3.283 eV is exclusively found in samples showing the  $I_{12}$  line. We attribute this transition to be a  $2s$  TES of the  $I_{12}$  line, as its intensity scales with that of the  $I_{12}$  line. Following the calculations in Ref. 2, such a transition would be expected at 3.274 eV, the same position at which the phonon replica of the  $I_{12}$  line occurs. However, the approximation which was used in Ref. 2 only holds for small donor binding energies, being a possible explanation of the discrepancy. Already for the  $I_{10}$  transition, a slight blueshift of the experimental TES positions compared to the theoretical predictions is visible in Fig. 17 of Ref. 2.

### C. Photoluminescence excitation

The results of the photoluminescence-excitation experiment are depicted in Fig. 2. The excitation channels of  $I_6$  and  $I_{12}$  are shown. Both show resonant excitation channels via the free A and B excitons. For the  $I_6$  line, a resonant excitation was found at the position of the  $I_0$  line, consistent with

the attribution of that peak to a ( $D^+X$ ) transition of the  $Al_{Zn}$  defect. Two further excitation channels are seen for both recombination lines, located 6.2 and 4.9 meV above the  $I_6$  and 6 and 5.1 meV above the  $I_{12}$  recombination line. We conclude that these excitation channels stem from the same mechanisms for both recombination lines, namely, the excitation of the bound B exciton ( $\Delta E \approx 4.9$  meV) and most likely a rotator state of the bound B exciton ( $\Delta E \approx 6.1$  meV). Both excitation channels were found for the luminescence of bound excitons in ZnO in a previous study,<sup>4</sup> denoted therein as  $I_{6aB}^2$  and  $I_{6aB}^3$ . For the  $I_{12}$  line, another excitation channel is present at 3.3545 eV, roughly at the position of the  $I_{10}$  line. Following Ref. 5 and assuming  $I_{12}$  being a ( $D^0X$ ) recombination line, a binding energy of 90.8 meV was calculated, resulting in an expected position of the corresponding ( $D^+X$ ) transition at 3.3535 eV, identical with the excitation channel near the  $I_{10}$  line. We therefore conclude that the feature observed at 3.3545 eV is not the  $I_{10}$  line reported in the literature, being most likely a ( $D^0X$ ) transition<sup>2</sup> but the ( $D^+X$ ) transition corresponding to  $I_{12}$ . A weak excitation of the  $I_6$  line via the  $I_{3a}$  line is observed, however in this case, the most likely mechanism of the excitation is a charge transfer, as both luminescence lines are known to be related to excitons bound to different defects.

### IV. CONCLUSION AND SUMMARY

A recombination feature named the  $I_{12}$  transition has been observed in ZnO thin films grown on a highly aluminum-doped ZnO or a MgO buffer layer. It is not present in otherwise equivalent films directly grown on sapphire. Raman measurements on the films indicate an expansion of the lattice of samples A and B with respect to sample C, which might be responsible for the formation of the defect. The microscopic nature of the defect remains unclear, however, in accordance to Ref. 6, we suggest that a distorted lattice is necessary to form this defect. In contrast to the assignment in that work, which tentatively assigns this to an acceptor in the vicinity of a dislocation line, we give clear evidence that this defect is a donor, and the spectral feature corresponds to a ( $D^0X$ ) transition. A  $2s$  TES transition of the defect is observed in PL spectra at 3.283 eV in close correlation with theoretical data given in Ref. 2, and an excitation channel assigned to the corresponding ( $D^+X$ ) transition was found, in perfect agreement with an empirical relationship published in Ref. 5. The donor binding energy was calculated following this relationship to be 90.8 meV. The existence of a donor with a thermal activation energy of about 100 meV was previously reported in ZnO thin films grown on Al-doped buffer layers.<sup>7,8</sup>

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\*m\_brandt@uni-leipzig.de

- <sup>1</sup>D. C. Reynolds, C. W. Litton, and T. C. Collins, *Phys. Rev.* **140**, A1726 (1965).
- <sup>2</sup>B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak *et al.*, *Phys. Status Solidi B* **241**, 231 (2004).
- <sup>3</sup>J. Sann, J. Stehr, A. Hofstaetter, D. M. Hofmann, A. Neumann, M. Lerch, U. Haboeck, A. Hoffmann, and C. Thomsen, *Phys. Rev. B* **76**, 195203 (2007).
- <sup>4</sup>J. Gutowski, N. Presser, and I. Broser, *Phys. Rev. B* **38**, 9746 (1988).
- <sup>5</sup>B. K. Meyer, J. Sann, S. Lautenschläger, M. R. Wagner, and A. Hoffmann, *Phys. Rev. B* **76**, 184120 (2007).
- <sup>6</sup>Y. Ohno, H. Koizumi, T. Taishi, I. Yonenaga, K. Fujii, H. Goto, and T. Yao, *J. Appl. Phys.* **104**, 073515 (2008).
- <sup>7</sup>F. D. Auret, W. E. Meyer, P. J. J. van Rensburg, M. Hayes, J. M. Nel, H. von Wenckstern, H. Hochmuth, G. Biehne, M. Lorenz, and M. Grundmann, *J. Phys.: Conf. Ser.* **100**, 042038 (2008).
- <sup>8</sup>F. D. Auret, W. Meyer, P. Janse van Rensburg, M. Hayes, J. Nel, H. von Wenckstern, H. Schmidt, G. Biehne, H. Hochmuth, M. Lorenz *et al.*, *Physica B* **401-402**, 378 (2007).
- <sup>9</sup>M. Lorenz, *Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells*, Springer Series in Materials Science (Springer, Berlin, 2007), Vol. 104, Chap. 7, pp. 303–357.
- <sup>10</sup>T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.* **142**, 570 (1966).
- <sup>11</sup>R. H. Callender, S. S. Sussman, M. Selders, and R. K. Chang, *Phys. Rev. B* **7**, 3788 (1973).
- <sup>12</sup>B. H. Bairamov, A. Heinrich, G. Irmer, V. V. Toporov, and E. Ziegler, *Phys. Status Solidi B* **119**, 227 (1983).
- <sup>13</sup>N. Ashkenov, B. N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashev, A. Kasic, M. Schubert, M. Grundmann *et al.*, *J. Appl. Phys.* **93**, 126 (2003).
- <sup>14</sup>M. R. Wagner, T. P. Bartel, R. Kirste, A. Hoffmann, J. Sann, S. Lautenschläger, B. K. Meyer, and C. Kisielowski, *Phys. Rev. B* **79**, 035307 (2009).