

Zn interstitial related donors in ammonia-treated ZnO powders

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ZnO powder heat treated in NH_3 atmosphere was investigated by electron paramagnetic resonance, photoluminescence, and Raman spectroscopy. We find that the treatment creates Zn interstitials (Zn_i) and complexes of Zn interstitials and nitrogen atoms substituting oxygen ($\text{Zn}_i\text{-N}_\text{O}$). A correlation between the Zn_i and an exciton at 3.366 eV (I_3) can be stated by a comparison with the PL results; furthermore, the ($\text{Zn}_i\text{-N}_\text{O}$) complex seems to be related to a recombination at 3.193 eV.

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I. INTRODUCTION

The interplay of dopants, impurities, and intrinsic defects is essential for the electrical and optical properties of ZnO, especially if one would like to achieve p -type conductivity. The recent approach for p -type doping by repeated temperature modulation growth developed by Tsukazaki *et al.* shows exemplarily that high quality crystal growth and doping with nitrogen have to be done in rather different temperature regimes.¹ However, defect creation and dopant incorporation remain to be studied systematically, if possible with methods rendering structural information on an atomistic level.

Nitrogen substituting oxygen (N_O) and N_2^- molecules have been identified in ZnO by electron paramagnetic resonance (EPR).^{2,3} Complex centers containing nitrogen and Zn interstitial ($\text{Zn}_i\text{-N}_\text{O}$) atoms were found by Aliev *et al.*,⁴ and Vlasenko and Watkins studied “pure” intrinsic defects created by low temperature, high-energy electron irradiation.⁵ Both groups used optically detected magnetic resonance. Further evidence for nitrogen-related centers comes from Raman spectroscopy, where a number of local vibrational modes (LVMs) were found to correlate to the N content of the ZnO samples.⁶

Ammonia (NH_3) is rather frequently used for doping due to its higher chemical reactivity compared to other gases such as N_2 . For NH_3 , one has to consider also the incorporation of H as a shallow donor.⁷ This can affect the nitrogen incorporation and intrinsic defect formation by changing the Fermi-level position.

In this paper, we investigate the properties of ZnO powders treated in NH_3 atmosphere at elevated temperatures. The highest amount of nitrogen was incorporated into ZnO heated in NH_3 at 650 °C for 12 h. In these materials, we previously observed by EPR the nitrogen to substitute oxygen.⁸ In samples treated at lower temperature (550 °C), we now find the EPR of Zn interstitial atoms and the ($\text{Zn}_i\text{-N}_\text{O}$) centers. This gives evidence that the O reducing effects of the NH_3 atmosphere dominate in this case. Hydrogen is observed as a shallow donor by EPR. In the Raman

spectra, also the N related LVM's show up. A correlation between the Zn interstitials (Zn_i) and the ($\text{Zn}_i\text{-N}_\text{O}$) centers on one side and the I_{3a} exciton and a recombination at 3.193 eV on the other side can be stated by comparison with photoluminescence (PL) results. This points to an important role of intrinsic defects and defect complexes for the compensation of nitrogen-doped ZnO.

II. EXPERIMENT

ZnO powders were treated with ammonia gas (5 or 60 l/h) for 12 or 20 h at 550 °C. The EPR experiments were performed on a Bruker ESP 300E spectrometer equipped with a He gas flow cryostat for measurement temperatures between 5 and 300 K. For the PL, a cw HeCd laser was used (325 nm, 10 mW) in combination with a Jobin Yvon THR 1000 monochromator and a He cryosystem. Raman spectroscopy was performed at room temperature with a LabRam microsetup system in backscattering geometry. Here, the 514 nm line of an argon laser was used. In addition to these experiments, the samples were routinely characterized by hot gas extraction in order to determine the nitrogen content by a N/O analysis (Leco TC300) and by x-ray diffraction (Siemens D5000). A maximum amount of nitrogen in the powder (0.4 m %) was found for the parameters 650 °C, 12 h, and 60 l/h. No effects of the incorporated nitrogen on the lattice constants of the wurtzite phase or the formation of secondary phases were detected.

III. RESULTS AND DISCUSSION**A. Electron paramagnetic resonance**

A representative EPR spectrum of the samples is shown in Fig. 1(a). Two groups of resonances show up. On the low field side of the spectrum, a signal with g values between $g=2.02$ and $g=2.006$ is seen; it is labeled Z. At higher magnetic fields, two superimposed signals are observed at about $g \sim 1.95$.

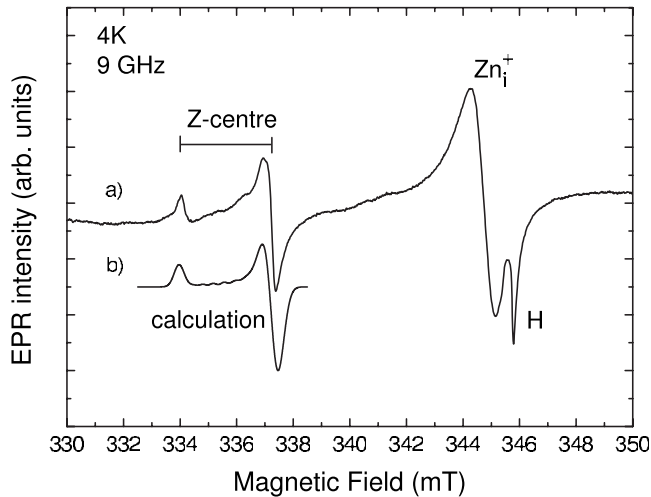


FIG. 1. Electron paramagnetic resonance (EPR) spectrum of ZnO powder annealed NH_3 for 20 h at 550°C . The resonances labeled H and Zn_i are caused by shallow donors. The line shape of the Z center is typical of a powder spectrum of an axial center. The calculated line shape using $g_{\parallel}=2.02$ and $g_{\perp}=2.006$ is shown in (b).

The line shape of the Z signal is characteristic of a powder spectrum of a center exhibiting axial symmetry with $g_{\parallel}=2.02$ and $g_{\perp}=2.006$ around the crystal c axis. Due to the random distribution of the c -axis directions of individual crystallites in the powder, their resonances occur at and in between the two extreme cases, the statistical weights of possible orientations leading to a spectrum, as shown in Fig. 1(b). The label Z is adopted from the paper of Aliev *et al.*⁴ who observed this center in nitrogen-doped ZnO. Their samples were grown in the group of Yao in Sendai by plasma assisted molecular beam epitaxy (MBE). The ordering of the g values with $g_{\parallel}>g_{\perp}$ is rather unusual and led the authors, based on the arguments given in their paper, to a defect model in which a Zn interstitial pairs with a nitrogen on an oxygen site ($\text{Zn}_i\text{-N}_\text{O}$). We would like to mention that this type of centers seems to play a rather general role in the compensation of nitrogen-doped ZnO, as Aliev *et al.* detected it in MBE grown samples. Look *et al.*⁹ gave reasons that such centers could be important in ZnO single crystals (wafers) annealed in N_2 , and we observed it after a thermal treatment of ZnO powder in NH_3 . Another candidate with $g_{\parallel}>g_{\perp}$ are N_2^- acceptors substituting for oxygen, which were observed by Garces *et al.*² Their g values, however, are $g_{\parallel}=2.0036$ and $g_{\perp}=1.9935$ and do not fit the spectra measured here.

The two resonances at $g\sim 1.95$ can be easily distinguished by their line shapes. The one at slightly lower magnetic fields has a large linewidth, whereas the signal at slightly higher magnetic fields is only a few gauss wide. Within the experimental error, the g value of the narrow line is identical to that of the shallow hydrogen donors.⁷ The field position of the broader EPR line gives evidence that it is also caused by a shallow donor. Vlasenko and Watkins assigned a very similar resonance signal to Zn interstitial atoms.⁵ This assignment is based on their detailed defect study using low temperature, high-energy electron irradiation to produce virgin intrinsic defects in ZnO. Due to the nonequilibrium situ-

ation created by the *in situ* electron irradiation at 4 K, the Zn_i became mobile at about 80 K and recombined with Zn vacancies. After heating above 200 K, the Zn_i signal was no longer detectable. In their investigation, ZnO compensated by deep Li acceptors was used. Our samples are n -type conducting with total shallow donor concentrations up to $5 \times 10^{18} \text{ cm}^{-3}$. Thus, the difference in the position of the Fermi energy might explain the different stability of the centers. At least from the experimental point of view, it seems reasonable that a ZnO crystal reacts on an oxygen reducing atmosphere such as NH_3 with the formation of Zn interstitial type of defects.

Another intrinsic defect expected to be formed is the oxygen vacancy (V_O). It is not in a paramagnetic charge state in n -type ZnO but gives rise to a deep emission band at 2.45 eV (see below).

For the appearance of the shallow H donors, the overall trend is that NH_3 treatment decreases the concentration. On the one hand, the temperatures used here are known to reduce the concentration of these donors; on the other hand, the NH_3 atmosphere is likely to increase the total H concentration during the annealing, which may also create new H donors.^{10,11}

The EPR results described above differ from the findings of our previous study on ZnO powders treated with NH_3 at higher temperatures (650 and 700°C).⁸ Under these conditions, we observed EPR signals of nitrogen acceptors (N_0). Such behavior is comparable to the annealing effects reported by Garces *et al.* for single crystals.² They observed that the formation of paramagnetic N_0 centers required annealing temperatures higher than 550°C (N_2 ambient). Under the experimental conditions chosen by Garces *et al.*, the concentration of shallow donors decreased upon annealing at temperatures below 550°C . The effect of the NH_3 gas in our investigation seems to be the preferential creation of Zn interstitial atoms; i.e., NH_3 is more aggressive to ZnO than N_2 .

B. Photoluminescence

Discussing the PL results, three spectral ranges have to be considered: (1) Below 2.9 eV: where the broad, mostly unstructured recombinations related to deep centers are located, (2) between 2.9 and 3.35 eV: Region of the donor-acceptor pair (DAP) recombinations with their phonon replica, and (3) above 3.35 eV: recombination of bound excitons.

Comparing the ZnO samples treated with NH_3 to the untreated ones (Fig. 2), we find that the recombinations in range (1) are much more intense after the treatment. The maximum emission intensity of this “green” band is found at the 2.45 eV band, and it has a full width at half maximum of about 300 meV. These are features typical of the emission related to the oxygen vacancy defects (V_O).¹² Thus, not unexpected, the thermal NH_3 treatment reduces the oxygen concentration in the samples.

In the DAP range (2), we find several recombinations (Fig. 3). We have labeled the recombinations A, B, C, and E and their LO phonon replica in Fig. 3 [D is not used here to avoid confusion with the donor bound excitons (D^0X)]. It should be mentioned that the spectra are similar to those

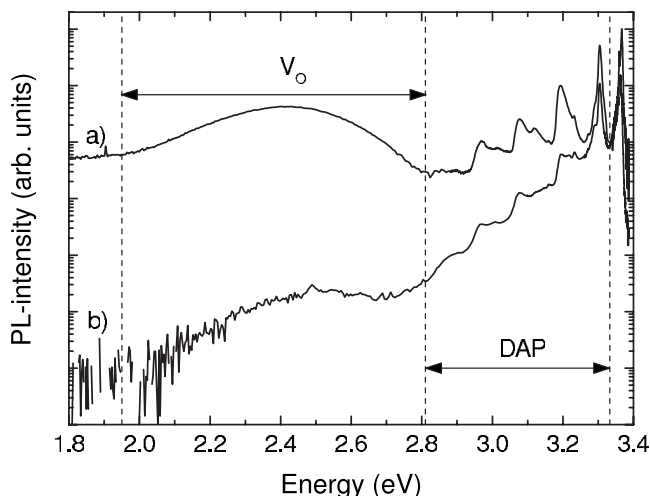


FIG. 2. Overview photo-luminescence spectrum of (a) the NH₃ treated powder annealed at 550 °C for 20 h. The dashed vertical lines indicate the spectral ranges of the deep emission bands (1) the donor-acceptor pair recombinations (DAP) (2), and above 3.35 eV exciton range (3), as described in the text. One can see the strong increase of the intensity of the broad oxygen vacancy (V_O) related PL band in range (1); (b) the ZnO reference powder.

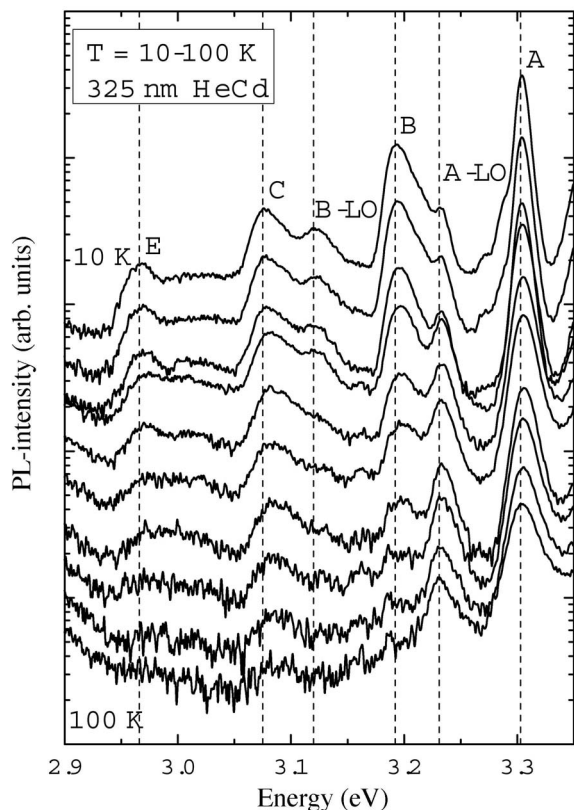


FIG. 3. Temperature dependent photoluminescence spectra of NH₃ treated ZnO powder annealed at 550 °C for 20 h. Shown is the donor acceptor pair range. From the top to the bottom spectrum the measurement temperature was varied from 10 to 100 K in steps of 10 K. The recombinations A–E show differing intensity ratios with increasing temperature. It can be taken as evidence for a different origin.

observed earlier in powder treated at 650 °C in NH₃ (Ref. 8) and the metal organic vapor phase epitaxy films of Rommeluère *et al.*¹³ However, the various recombinations are better resolved in the samples described here. The A line has been attributed to the presence of N acceptors.¹³ Also in contention are N acceptor bound excitons,^{14,15} DAP,^{16,17} free to bound, and free exciton LO.^{18,19} The A-line intensity does not change noticeably by the NH₃ treatments of the powder [see Fig. 5(c)]. In line with the previous investigations, it may be taken as a hint that N_O acceptors are formed by the treatments. However, here, they are not observed in EPR due to the higher shallow donor concentrations (Zn_i and H), which causes the acceptors to be in the diamagnetic charge state.

Remarkable is that the PL lines A, B, C, and E show up with an equal spacing of about 110 meV. It may suggest that they have a common origin; furthermore, 110 meV is about the activation energy in the discussions for the N acceptors.¹³ Earlier, Studenikin *et al.*²⁰ observed in the same spectral range PL lines with a periodicity of 108 meV. They suggested a two-photon process as an explanation. In addition to the usual LO phonon coupling, which causes the replica to be separated 72 meV below the zero phonon lines, a process involving two transverse optical (TO) phonons should become allowed due to the limited crystalline quality of the powder (two times $E_{TO\perp c} = 50.8$ meV would approximately account for the observed spacing). The conservation of momentum requires that two TO phonons with oppositely directed moments are emitted or excited in the process.

Arguments opposing those suggestions come from the temperature dependence of the luminescence and from Raman spectroscopy. In Fig. 3, the PL spectra are shown from 10 K (upper spectrum) to 100 K (lowest spectrum) in steps of 10 K. The intensity of the A line and its LO replica behaves differently from the intensity of the B line. At temperatures above 70 K, only the A line and the A-LO remain visible; B and B-LO have already vanished. Line C can still be noticed at this temperature while the E line is also gone.

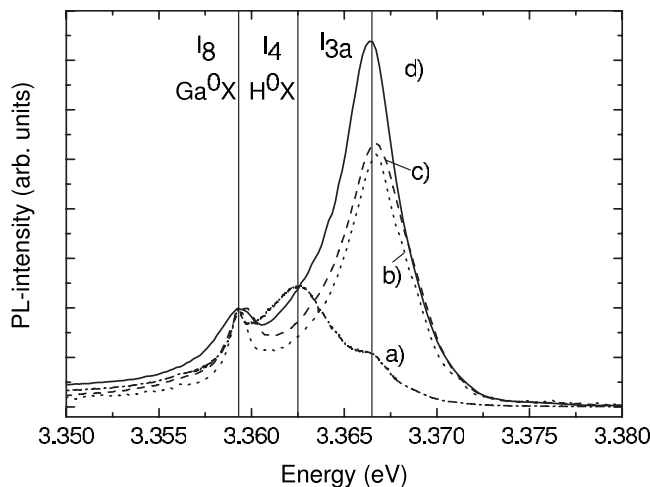


FIG. 4. The donor bound exciton recombinations in the NH₃ treated ZnO samples: (a) reference sample; [(b) and (c)] from the samples with 0.38% and 0.44% nitrogen content, respectively; and (d) 0.11%.

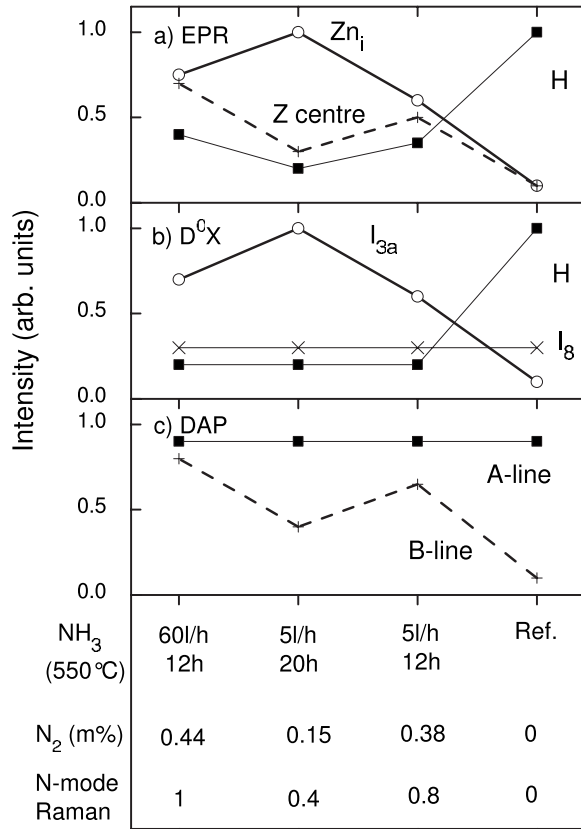


FIG. 5. (a) Intensity variations of the EPR and [(b) and (c)] photoluminescence signals after annealing the ZnO powder at 550 °C in NH_3 . The total N_2 concentration of the powder was measured by hot gas extraction; also, the relative intensities of the nitrogen-related Raman modes are given (see Fig. 6, right side).

Although the observed intensity variations are too small to allow an Arrhenius type of analysis to obtain certain thermal activation energies, the temperature dependent PL shows that lines A and B are of different origins.

This follows also from the comparison of the different NH_3 treatments (Fig. 5). As mentioned before, the A-line intensity is almost unaffected by the annealing time and NH_3 flow, but a rather strong dependence is found for the B line at 3.194 eV [Fig. 5(c)]. It follows the intensity dependence observed for the Z center [see Fig. 5(a)]. Inspecting the line shape of the recombinations in more detail, one can see that it is nonsymmetrical. The PL line shapes extend to higher energies, which might be typical of free to bound transitions, meaning the carrier concentration to be quite high which is in line with the EPR experiments. On the other hand, the rapid decrease with temperature (Fig. 3) is more indicative of a DAP recombination. One might estimate a binding energy E_{bin} from the energy position of the B line (E_B) using $E_{\text{bin}} = E_{\text{gap}} - E_B$. With $E_{\text{gap}} = 3.437$ eV, one obtains $E_{\text{bin}} \sim 0.240$ eV for the case of a free to bound transition or about $E_{\text{bin}} \sim 200$ meV for a DAP recombination.

The PL in the exciton range (3) in our powder samples is not as well resolved as in single crystals. Nevertheless, two bound exciton recombinations can clearly be seen (Fig. 4). At energies corresponding to the donor bound excitons commonly labeled I_8 and I_{3a} , we find peak maxima; in between,

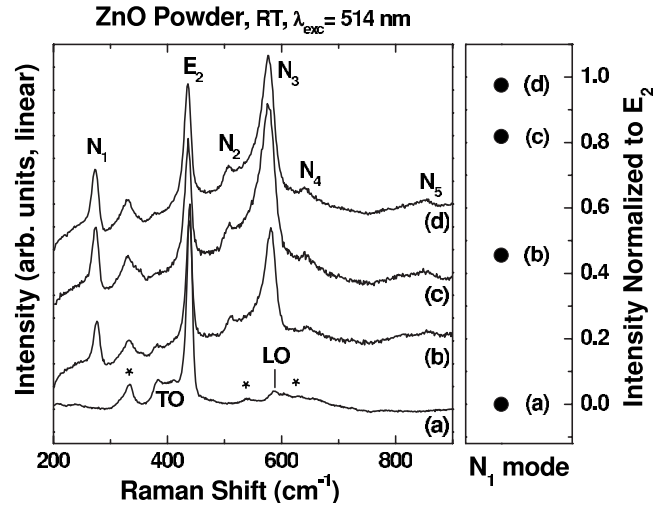


FIG. 6. On the left: Raman spectra of (a) the native ZnO powder and [(b)–(d)] samples with increasing nitrogen concentration. Peaks labeled N_1 – N_5 are nitrogen-related vibrational modes; multiphonon scattering features are indicated with an asterisk. On the right: average intensity of the N_1 mode for the different samples.

at 3.3625 eV (I_4), the line shape gives evidence that also H donor bound excitons participate in the recombination. The intensity of the I_8 line is not changed significantly as a result of our annealing treatments. This is to be expected because it was previously assigned to residual Ga_{Zn} impurities.¹¹ For I_{3a} at 3.3665 eV, we find a correlation to the Zn interstitials (Fig. 5). Using the free exciton energy of 3.3760 eV, a localization energy for the I_{3a} exciton of about $E_{\text{loc}} = 10$ meV results. Applying the Haynes rule with the parameters as given in Ref. 11 ($E_{\text{loc}} = 0.36E_D - 3.8$ meV), we can estimate a donor binding energy of about 37 meV.

From our experimental results, it would be natural to assign a binding energy in the 37 ± 5 meV range to the zinc interstitials observed in EPR, which have a g value typical of shallow donors (the binding energy estimated from the effective mass theory is about 40 meV). Such an assignment would also be consistent with the interpretation of the electrical data on high-energy electron irradiated ZnO by Look *et al.*²¹ In this sense, we would assign the Z centers to the defects causing the B line in the PL experiments (Fig. 5). The Z centers are deeper with a binding energy of roughly $E_B \sim 240$ meV; consequently, the g values are close to $g = 2.00$.

C. Raman spectroscopy

In order to get a deeper insight on the lattice dynamics of the samples, which is here important for the interpretation of the PL results, Raman spectroscopy was used. Figure 6 displays a spectrum of the untreated ZnO powder [curve (a)], which is the source material to produce the nitrogen-doped samples [curves (b)–(d)]. The predominant line in the case of the nominally undoped powder is the E_2 (high) mode, with a frequency between 436 and 438 cm^{-1} . On the low-energy side of this vibration, a broad band is located around 400 cm^{-1} , with maxima at 380 and 411 cm^{-1} originating from the TO phonons. The weak structure at 585 cm^{-1}

belongs to the LO modes. Both the TO and LO lines appear as broad bands due to the random orientation of the c axes because of the arbitrary distribution of the crystallites. Owing to the angular dispersion, they cover the whole frequency range between the modes having pure A_1 and E_1 symmetries,²² respectively. Some lines arising from multiphonon scattering,²³ particularly the prominent feature at 330 cm^{-1} , are labeled with an asterisk. Comparing the data of the reference sample to the ammonia treated samples, we can see that the intrinsic phonon properties of the samples are not affected significantly, and, especially, no new mode appears at two times the TO frequency.

The spectra of the samples treated with NH_3 exhibit five peaks denoted as N_1 – N_5 aside from the mentioned ZnO features. They are located around 275, 510, 582, 643, and 856 cm^{-1} and characterize the incorporation of nitrogen in ZnO. What might be the origin of these bands was controversially discussed: nitrogen-related local vibrational modes,²⁴ host-lattice defects,²⁴ a combination of local vibrational modes and disorder activated scattering,^{25,26} or even a fingerprint of the silent B_1 modes.²⁷ Supported by Refs. 25 and 26, we emphasize that, in our opinion, the occurrence of these lines indicates the incorporation of nitrogen in ZnO. For example, if we compare the intensity of the N_1 mode at 275 cm^{-1} (right hand side of Fig. 6) to the nitrogen content as measured by hot gas extraction (bottom of Fig. 5), we find a good correlation for the two samples with the high nitrogen content. Only the sample treated with 5l NH_3 for 20 h shows a N_1 mode which diverges from a linear relation between the N_1 mode intensity and the hot gas extraction data.

These results show that the intensities of the N_1 – N_5 modes correlate to the total N content of the samples. In addition to Kaschner *et al.*,⁶ who related the Raman mode intensity to the secondary ion mass data, we find here that it also holds true for the relation to the hot gas extraction. The Z center shows a similar dependence on the NH_3 treatment

(Fig. 5). In addition to the results of Aliev *et al.*,⁴ it gives further evidence that a nitrogen atom is part of the atomistic structure of the Z center. As mentioned before, these complexes seem to be rather important for the compensation mechanisms in ZnO, but care must be taken; the concentration of the Z centers is in the order of $5 \times 10^{17}\text{ cm}^{-3}$ (EPR), while the total nitrogen content is typically 2 orders of magnitude higher. Thus, also other complex centers are likely to be formed.

Recently, arguments coming from theoretical considerations also favor that complexes of nitrogen and Zn interstitials (like Z centers) are probable candidates to explain the n -type conductivity of nitrogen-doped ZnO.⁹

IV. SUMMARY

In summary, we have investigated ZnO powders heat treated in ammonia atmosphere and find evidence that Zn interstitials (Zn_i) and complexes of Zn interstitials and nitrogen atoms substituting oxygen ($\text{Zn}_i\text{-N}_\text{O}$) are formed. The investigations suggest a correlation between the interstitials and a bound exciton at 3.366 eV, while the defect complex seems to be related to a recombination at 3.193 eV. The results support the evidence of earlier investigations that such centers play an important role in the compensation of nitrogen-doped ZnO. The experimental results give a hint that models of complex defects may be able to explain the nitrogen-related Raman modes; however, detailed calculations have to be awaited.

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¹A. Tsukazaki *et al.*, Nat. Mater. **4**, 42 (2005).

²N. Y. Garces, Lijun Wang, N. C. Giles, L. E. Halliburton, G. Cantwell, and D. B. Eaton, J. Appl. Phys. **94**, 519 (2003).

³W. E. Carlos, E. R. Glaser, and D. C. Look, Physica B **308-310**, 976 (2001).

⁴G. N. Aliev, S. J. Bingham, D. Wolverson, J. J. Davie, H. Makino, H. J. Ko, and T. Yao, Phys. Rev. B **70**, 115206 (2004).

⁵L. S. Vlasenko and G. D. Watkins, Phys. Rev. B **72**, 035203 (2005).

⁶A. Kaschner, U. Habocek, M. Strassburg, G. Kaczmarczyk, A. Hoffmann, C. Thomsen, A. Zeuner, H. R. Alvez, D. M. Hofmann, and B. K. Meyer, Appl. Phys. Lett. **80**, 1909 (2002).

⁷D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt, and P. G. Baranov, Phys. Rev. Lett. **88**, 045504 (2002).

⁸D. Pfisterer, J. Sann, D. M. Hofmann, M. Plana, A. Neumann, M. Lerch, and B. K. Meyer, Phys. Status Solidi B **243**, R1 (2006).

⁹D. C. Look, G. C. Farlow, Pakpoom Reunchan, Sukit Limpijum-nong, S. B. Zhang, and K. Nordlund, Phys. Rev. Lett. **95**, 225502 (2005).

¹⁰N. H. Nickel and K. Fleischer, Phys. Rev. Lett. **90**, 197402 (2003).

¹¹B. K. Meyer *et al.*, Phys. Status Solidi B **241**, 231 (2004).

¹²F. Leiter, H. Alvez, D. Pfisterer, N. G. Romanov, D. M. Hofmann, and B. K. Meyer, Physica B **340-342**, 201 (2003); D. M. Hofmann, D. Pfisterer, J. Sann, R. Tena-Zaera, V. Munoz-Sanjose, T. Frank, and G. Pensl, Appl. Phys. A: Mater. Sci. Process. **88**, 147 (2007). Note: The energy position of the oxygen vacancy related PL band differs from that given in Ref. 5. One reason is that we used above band gap excitation by the 325 nm line of a HeCd laser, while in Ref. 5 below band gap excitation was used. The below band gap excitation was possible due to an excitation involving the Li acceptors.

¹³J. F. Rommeluère, L. Svob, F. Jomard, J. Mimila-Arroyo, A. Lusson, V. Sallet, and Y. Marfaing, Appl. Phys. Lett. **83**, 287 (2003).

- ¹⁴J. G. Ma and Y. C. Liu, *J. Vac. Sci. Technol. B* **22**, 94 (2004).
- ¹⁵D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).
- ¹⁶B. P. Zhang, N. T. Binh, Y. Segawa, K. Wakatsuki, N. Usami, *Appl. Phys. Lett.* **83**, 1635 (2006).
- ¹⁷V. V. Ursaki, I. M. Tiginyanu, V. V. Zalamai, V. M. Masalov, E. N. Samarov, G. A. Emelchenko, and F. Briones, *J. Appl. Phys.* **96**, 1001 (2004).
- ¹⁸H. J. Ko, Y. F. Chen, T. Yao, K. Miyajima, A. Yamamoto, and T. Goto, *Appl. Phys. Lett.* **77**, 537 (2000).
- ¹⁹Jiansheng Jie, Guanzhong Wang, Yiming Chen, Xinhai Han, Qingtao Wang, and Bo Xu, *Appl. Phys. Lett.* **86**, 31909 (2005).
- ²⁰S. A. Studenikin, M. Cocivera, W. Kellner, and H. Pascher, *J. Lumin.* **91**, 223 (2000).
- ²¹D. C. Look, J. W. Hemsky, and J. R. Sizelove, *Phys. Rev. Lett.* **82**, 2552 (1999).
- ²²C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, *Phys. Rev.* **181**, 1351 (1969).
- ²³J. M. Calleja and M. Cardona, *Phys. Rev. B* **16**, 3753 (1977).
- ²⁴C. Bundesmann, N. Ashkenov, M. Schubert, D. Spemann, T. Butz, E. M. Kaidashev, M. Lorenz, and M. Grundmann, *Appl. Phys. Lett.* **83**, 1974 (2003).
- ²⁵F. Reuss, C. Kirchner, Th. Gruber, R. Kling, S. Maschek, W. Limmer, A. Waag, and P. Ziemann, *J. Appl. Phys.* **95**, 3385 (2004).
- ²⁶J. Yu, H. Xing, Q. Zhao, H. Mao, Y. Shen, J. Wang, Z. Lai, and Z. Zhu, *Solid State Commun.* **138**, 502 (2006).
- ²⁷F. J. Manjón, B. Marí, J. Serrano, and A. H. Romero, *J. Appl. Phys.* **97**, 053516 (2005).