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Experimental and theoretical investigation of the conduction band edge of GaN_xP_{1-x}

M. Güngerich,[1,*] P. J. Klar,[1] W. Heimbrodt,[1] G. Weiser,[1] J. F. Geisz,[2] C. Harris,[3] A. Lindsay,[3] and E. P. O'Reilly[3]
[1]*Department of Physics and Material Sciences Center, Philipps University, Renthof 5, 35032 Marburg, Germany*
[2]*National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, USA*
[3]*Tyndall National Institute, Lee Maltings, Cork, Ireland*
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We show that a two-level band-anticrossing (BAC) model fails to describe the evolution of N-related states in GaN_xP_{1-x}. Band structure calculations prove that a two-level model describes these states in ordered GaNP supercells. Photocurrent measurements support a BAC-related blueshift of the GaP-like direct band gap in disordered GaNP, but calculations and electromodulated absorption and pressure studies show that the wide energy distribution of the lower-lying N-related states leads to the anticrossing interaction involving many N levels in disordered GaNP.

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The conduction band (CB) structure of dilute nitride III-V semiconductors has been the subject of considerable interest for more than a decade. The energy gap of the direct-gap alloys GaNAs,[1] InNAs,[2] and InNSb[3] all display a strong band-gap bowing, with the energy gap redshifting strongly when a small amount of As or Sb is replaced by N. This redshift can be modeled successfully by a band-anticrossing (BAC) interaction between the host III-V material CB edge and a higher-lying band of N-related defect states which form above the CB edge. This two-level BAC model parametrizes and reproduces many of the key features of the alloy band structure, including the reduced energy gap,[4] low electron mobilities,[5] and a strong CB nonparabolicity.[6] It is a subject of controversy which model is best suited to describe the evolution of the CB structure in GaN_xP_{1-x}. The situation here is different to the other III-N-V alloys considered above, because GaP is an indirect-gap semiconductor. The introduction of N leads also to the formation of localized defect states in GaNP, but these lie within the GaP band gap, just below the lowest *X*-like CB states, and over 0.5 eV below the GaP Γ CB minimum. N-doped GaP has been used for light-emitting diodes since the 1960s. GaAsP:N in the vicinity of the direct-to-indirect transition showed lasing.[7,8] GaP with GaNP active regions may be suitable for lasing applications on Si substrates due to their similar lattice constants. A prerequisite for this is the formation of a direct fundamental band gap in GaP by N incorporation. The debate to describe the GaPN CB minimum is mainly polarized between two opposite views. Some authors interpret the strong redshift of the absorption edge of GaNP in terms of an indirect-to-direct transition in combination with a BAC-like behavior.[9–12] Others favor a polymorphous model based on multivalley coupling as a unified theory for GaNAs and GaNP.[13] However, as shown recently by absorption studies of free-standing GaNP films, both models do not provide satisfactory agreement with experiment.[14,15] We present here a combined theoretical and experimental analysis to identify the applicability and the limitations of the BAC model in this alloy system.

A series of six GaN_xP_{1-x} epitaxial layers of about 1 μm thickness with $0 \leqslant x \leqslant 0.0286$ were grown on Zn-doped GaP substrates by metal-organic vapor-phase epitaxy. The GaNP layer was capped with a 10-nm Se-doped GaP contact layer. Nitrogen compositions of the GaNP layers were determined from double-crystal x-ray diffraction measurements in the (004) and (115) reflections. A thin layer of platinum was evaporated onto the layer surface to provide electric contact for electroabsorption (EA) as well as photocurrent (PC) measurements. Photoluminescence (PL) spectra were taken under hydrostatic pressure at 5 K up to about 10 kbar.[16]

Figure 1 shows EA spectra for the whole series of GaNP layers in the energy range of the N localized levels and of the fundamental indirect band gap of GaP. As expected, due to the weak absorption GaP shows only very weak signals from phonon-assisted transitions at the indirect band gap, between 2.34 and 2.38 eV. The introduction of N causes the formation of multiple sharp signals which are much more intense. Going from 0.4% to 1.5% N, signals at lower energies gain intensity at the expense of those at higher energies. This becomes obvious if we concentrate, for example, on the signals at 2.32 eV and at just below 2.2 eV. For $x=0.4\%$ the amplitude of the former is about a factor of 3 larger than the

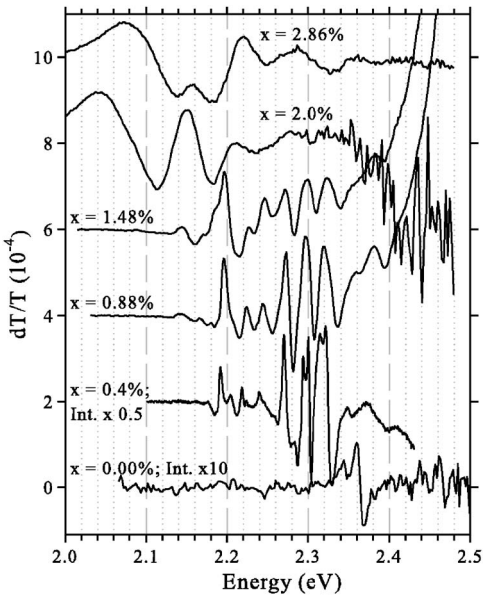

FIG. 1. EA spectra of the series of GaN_xP_{1-x} samples (20 K). dT/T denotes the relative change in transmission.

amplitude of the latter. For $x=1.5\%$ this relation is nearly inverted. An isolated N atom in GaP introduces a defect state at 2.32 eV, just below the GaP *X*-point energy. As the N composition increases, an increasing proportion of N atoms form N-N pairs, where two N atoms are in close vicinity, and also larger N clusters, containing three or more N atoms. These N pairs and clusters give defect levels at lower energies. The EA amplitude serves as a rough measure of the Γ character at a certain transition energy. Therefore, these spectra show that with increasing x direct transitions between close pair or cluster states and the valence band maximum gain probability while those from more isolated N atoms lose probability. This occurs because, first, an increase of x leads to an increased number of N atoms bound in configurations where other N atoms are close enough to interact and, second, the anticrossing interaction mixes band states of Γ character with the lowest-energy N states, as discussed further below. An increase of x causes inhomogeneous broadening but keeps the energies of the N states roughly constant up to $x=1.48\%$. This broadening reflects an increase in alloy disorder, due to interactions between the N atoms. For the two highest x (2.0% and 2.86%), only broad signals remain in the spectra. This may also be related to significant strain relaxation of the layers as observed by x-ray diffraction measurements. If there existed, as proposed by other authors,[9–11] a single N-related band gap obeying the BAC model, the EA spectra would contain a dominant signal showing a continuous redshift with increasing x. None of the spectra exhibits such a feature. The spectra rather reflect that the Γ character of transitions is distributed over a multiplicity of states due to N atoms in different configurations. In this respect GaNP differs considerably from GaNAs and other direct-gap alloys where the lowest band gap retains a significant Γ character and shows a clear redshift with increasing x. While the simple level repulsion model provides a satisfactory description for a fundamental band gap mainly formed by the host bands, it fails here when the lowest conduction levels are multiple impurity states.

Figure 2 shows PC spectra of the series up to $x=2\%$ which are normalized to the incident photon flux. The PC spectrum of GaP exhibits a strong signal at the direct band gap (2.85 eV) with a corresponding sharp excitonic feature (2.82 eV) and a weak onset of the photocurrent at 2.35 eV due to absorption across the indirect gap from the Γ valence band states to the *X* CB states. Incorporating N leads to three major changes: (i) The indirect gap feature increases in intensity but shows little change in energy. This reflects a weakening of the k selection rule with increasing N-induced disorder. (ii) Additional sharp features develop in the range of the localized N states (below 2.4 eV) which broaden with increasing x, showing again that the transition probability is distributed over a range of localized states. (iii) The maximum of the PC feature at the direct gap is blueshifted even at low x. Relating the blueshift of the PC feature to a shift of the actual GaNP CB edge at Γ is difficult because the PC signal includes contributions from both the GaNP layer and the GaP substrate. The differences in carrier-diffusion length between the two layers and the variation of the penetration depth into the heterostructure as a function of energy impede a quantification of the blueshift of the Γ CB edge of the

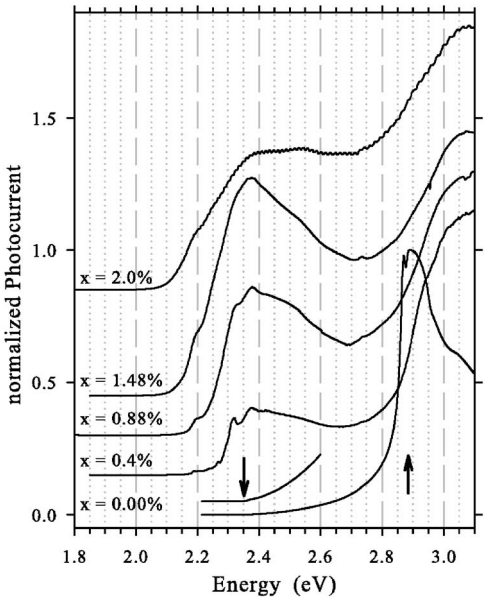

FIG. 2. Normalized and response-corrected PC spectra of the series of GaN_xP_{1-x} samples with x up to 2.0% (20 K). Arrows indicate the GaP indirect and direct band gaps.

GaNP layer. Nevertheless, the PC results in this energy range are in concordance with the observation of a blueshift in PL excitation studies.[10] This result suggests that there is indeed a BAC behavior present in GaNP although a simple two-level model is not able to describe it properly in the energy range of the localized N states. Further confirmation of the failure of the two-level BAC model is given by pressure-dependent PL spectroscopy, shown in Fig. 3. The PL band obviously involves transitions between many levels, and its shape does not change with increasing pressure in contrast to GaNAs of comparable x, where the PL shape changes as the E_- gap crosses higher-lying N cluster states.[16] The rate of the observed pressure shift of the PL features is only 1.5 meV/kbar, consistent with the one observed for localized N states in ultradilute GaP:N[17] and GaAs:N[18] and considerably lower than the shift of 9.7 meV/kbar observed for the direct gap in GaP.[19]

The two-level BAC model explains the large band gap reduction in direct-gap III-N-V alloys where the isolated N state is resonant with the CB. A BAC interaction between the bulk III-V CB edge state, ψ_{c0} at energy E_{c0}, and a higher-lying band of N resonant defect levels ψ_{N0} at energy E_N yields the III-N-V CB minimum energy E_- as the lower eigenvalue of[4]

$$H=\begin{pmatrix} E_N & V_{Nc} \\ V_{Nc} & E_{c0} \end{pmatrix}, \tag{1}$$

where the interaction V_{Nc} between the quasilocalized N states and the GaAs CB edge scales with N composition x as $V_{Nc}=\beta x^{1/2}$, with $\beta\sim 2.04$ eV in GaNAs.[20]

Turning to GaNP, the energy of the GaP Γ_{1c} CB minimum, E_{c0}, lies about 0.57 eV higher in energy than the isolated N defect state. We expect in a two-level BAC model that the lowest conduction levels in GaNP will therefore have

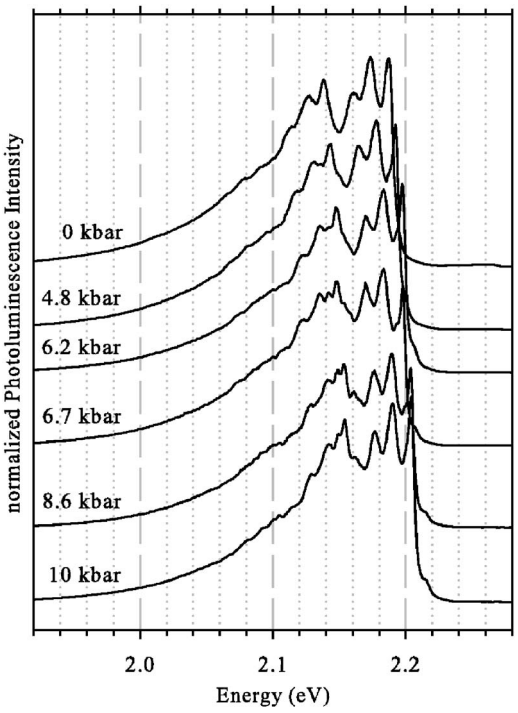

FIG. 3. Normalized PL spectra of a $GaN_{0.003}P_{0.997}$ at different hydrostatic pressures (5 K, UV excitation).

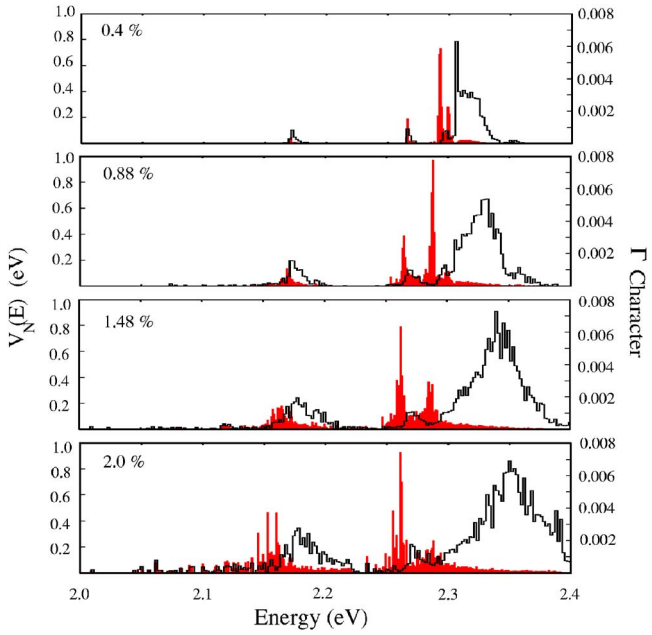

FIG. 4. (Color online) Black open histograms: calculated N-state energies weighted by the square of their interaction with the Γ CB minimum. Red (gray) filled histograms: $G_\Gamma(E)$, the projection of the N-state spectrum onto the unperturbed GaP Γ state.

predominantly N character ψ_{N0}, with just a small admixture of the GaP host Γ state ψ_{c0}. We have carried out a systematic theoretical investigation to identify the applicability of the BAC model to describe the CB structure of GaNP. Full details of the calculations are presented in Ref. 21. We present here a summary of the results relevant to the interpretation of the experimental data. We have first used a sp^3s^* tight-binding (TB) Hamiltonian to explicitly evaluate the evolution of the lowest CB state

$$\psi_- = \alpha_N \psi_{N0} + \alpha_c \psi_{c0} \tag{2}$$

in ordered $Ga_MN_1P_{M-1}$ supercells[21] with $32 \leqslant M \leqslant 864$ (composition $0.12\% \leqslant x \leqslant 3.1\%$), following a similar approach to that which we used previously for ordered GaNAs supercells.[22] We can extract a single, N-related level below the GaP CB edge for each of these ordered supercells and find that the evolution of the band structure is well described by the BAC interaction between this N-related state and the GaP Γ CB minimum. The TB calculations for these ordered structures show a clear redshift of the lowest CB state and a general upward shift of the higher-lying Γ states, consistent with the two-level BAC model.

The simple two-level BAC model breaks down when we use the TB method to calculate the electronic structure of large (1000-atom) disordered GaN_xP_{1-x} supercells containing a random distribution of N atoms. For a given x, the energy of the lowest CB state now depends explicitly on the relative positions and interactions between the N atoms. The Γ character can be distributed over several lower-lying N levels in the disordered supercells, with the Γ distribution also varying significantly between different supercell calculations.

We need to choose significantly larger supercells to minimize the effects of different random distributions of N atoms. We model the effects of the random N distribution by placing $L=5000$ nitrogen atoms at random on the group-V sites in a $Ga_MN_LP_{M-L}$ supercell with $2M$ total atoms and with composition $x=L/M$. We follow the same approach we have used previously for GaNAs,[23] using a TB Hamiltonian to calculate the energies ϵ_l and wave functions ψ_{Nl} ($l=1,\ldots,L$) due to the interactions between the random distribution of nitrogen atoms considered. The strength of the interaction between the GaP Γ host CB state ψ_c and the lth N-related level is then given by $V_{Nl}=\langle\psi_{Nl}|H|\psi_c\rangle$, with the alloy CB energy levels E_i and wave functions ϕ_i found by diagonalizing the $(L+1)\times(L+1)$ Hamiltonian $H_{ij}\phi_i=E_i\phi_i$, where $H_{ll}=\epsilon_l$, $l=1,\ldots,L$; $H_{L+1,L+1}=E_{c0}$, $H_{l,L+1}=H_{L+1,l}=V_{Nl}$, and $H_{ij}=0$ otherwise.

The black open histograms in Fig. 4 display the calculated evolution with N concentration of the interaction $V_N(E)$ between the GaP Γ CB state and the N defect states ϵ_l close to the GaN_xP_{1-x} CB edge, where $V_N(E)$ is given by

$$V_N(E) = \Sigma_l |V_{Nl}|^2 T(E-\epsilon_l), \tag{3}$$

with $T(x)$ a top-hat function of width 2 meV and unit area. For low N composition, most of the interaction arises from states close to the isolated N defect level ($E_N=2.306$ eV). A feature due to N-N (110) pairs is observed about 2.180 eV, as well as other calculated features at 2.282 eV and 2.298 eV due to N-N (220) and (221) pairs, respectively. These calculated energies correlate well with the main peaks in the PL spectra of GaNP samples with very low x (0.05%).[24]

The red (gray) filled histograms in Fig. 4 show $G_\Gamma(E)=\Sigma_i|\langle\phi_i|\psi_c\rangle|^2\delta(E-E_i)$, the projection of the N-related band-edge states onto the GaP Γ CB edge state. The evolution of these states closely matches the evolution of the EA (see Fig.

1) and PL spectra (see Ref. 24). Because the GaP Γ state is interacting with a distribution of N levels, we do not find a single N-related level undergoing a strong redshift. Instead, many levels each experience a small redshift, and the overall distribution of Γ-related states both broadens and shifts towards lower energy with increasing x, as also observed experimentally.

In conclusion, we have shown that a simple two-level band-anticrossing model is not suitable to describe the electronic structure of the lowest CB levels in P-rich GaN_xP_{1-x} with x up to a few percent. The Γ character of transitions in the energy range of the N localized states is distributed over many levels which do not exhibit a significant redshift with increasing x. The redshift observed in PL and EA measurements is interpreted in terms of increasing contributions of N atoms bound in close pairs or cluster configurations. TB supercell calculations indicate that the BAC model gives a good description of the band gap for ordered structures. In contrast, when the N atoms are distributed statistically in a disordered alloy, different configurations have to be taken into account. The evolution of the lowest CB states in GaNP can be described in terms of a BAC interaction, but because the GaP Γ level lies above the distribution of N states with which it is interacting, we must include explicitly the distribution of N levels, rather than assuming that they are all at the same energy. The resulting distribution of Γ character in energy suggests that GaNP, even with x of a few percent, is not suitable as an active laser material. The extended BAC model, which we use here to describe GaNP CB states, was previously justified in studies of GaNAs, where it provided a quantitative explanation of the anomalously large electron effective mass and its nonmonotonic variation with composition. It therefore provides a unified description of the conduction band structure of GaNAs and GaNP, despite the major differences in their observed behavior.

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*Electronic address: Martin.Guengerich@physik.uni-marburg.de

[1] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).
[2] H. Naoi, Y. Naoi, and S. Sakai, Solid-State Electron. **41**, 319 (1997).
[3] B. N. Murdin, A. R. Adams, P. Murzyn, C. R. Pidgeon, I. V. Bradley, J.-P. R. Wells, Y. H. Matsuda, N. Miura, T. Burke, and A. D. Johnson, Appl. Phys. Lett. **81**, 256 (2002).
[4] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).
[5] S. Fahy and E. P. O'Reilly, Appl. Phys. Lett. **83**, 3731 (2003).
[6] J. Endicott, A. Patanè, J. Ibáñez, L. Eaves, M. Bissiri, M. Hopkinson, R. Airey, and G. Hill, Phys. Rev. Lett. **91**, 126802 (2003).
[7] N. Holonyak, Jr., D. R. Scifres, R. D. Burnham, M. G. Craford, W. O. Groves, and A. H. Herzog, Appl. Phys. Lett. **19**, 254 (1971).
[8] N. Holonyak, Jr., D. R. Scifres, M. G. Craford, W. O. Groves, and D. L. Keune, Appl. Phys. Lett. **19**, 256 (1971).
[9] W. Shan, W. Walukiewicz, K. M. Yu, J. Wu, J. W. Ager III, E. E. Haller, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **76**, 3251 (2000).
[10] I. A. Buyanova, M. Izadifard, A. Kasic, H. Arwin, W. M. Chen, H. P. Xin, Y. G. Hong, and C. W. Tu, Phys. Rev. B **70**, 085209 (2004).
[11] I. A. Buyanova, M. Izadifard, W. M. Chen, H. P. Xin, and C. W. Tu, Phys. Rev. B **69**, 201303(R) (2004).
[12] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, Y. G. Hong, H. P. Xin, and C. W. Tu, Phys. Rev. B **65**, 241303(R) (2002).
[13] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).
[14] Y. Zhang, B. Fluegel, M. C. Hanna, J. F. Geisz, L.-W. Wang, and A. Mascarenhas, Phys. Status Solidi B **240**, 396 (2003).
[15] B. Fluegel, Y. Zhang, J. F. Geisz, and A. Mascarenhas, Phys. Rev. B **72**, 073203 (2005).
[16] P. J. Klar, H. Grüning, W. Heimbrodt, J. Koch, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, Appl. Phys. Lett. **76**, 3439 (2000).
[17] B. Gil, M. Baj, J. Camassel, H. Mathieu, C. Benoit à la Guillaume, N. Mestres, and J. Pascual, Phys. Rev. B **29**, 3398 (1984).
[18] X. Liu, M.-E. Pistol, L. Samuelson, S. Schwetlick, and W. Seifert, Appl. Phys. Lett. **56**, 1451 (1990).
[19] S. Ves, K. Strössner, C. K. Kim, and M. Cardona, Solid State Commun. **55**, 327 (1985).
[20] A. Lindsay and E. P. O'Reilly, Solid State Commun. **112**, 443 (1999).
[21] C. Harris, A. Lindsay, and E. P. O'Reilly (unpublished).
[22] A. Lindsay and E. P. O'Reilly, Solid State Commun. **118**, 313 (2001).
[23] A. Lindsay and E. P. O'Reilly, Phys. Rev. Lett. **93**, 196402 (2004).
[24] M. Felici, A. Polimeni, A. Miriametro, M. Capizzi, H. P. Xin, and C. W. Tu, Phys. Rev. B **71**, 045209 (2005).