Author(s):   P. H. Jefferson, T. D. Veal, L. F. J. Piper, B. R. Bennett, C.
F. McConville, B. N. Murdin, L. Buckle, G. W. Smith, and T. Ashley
Article Title: Band anticrossing in GaN$_x$Sb$_{1-x}$
Year of publication: 2006
Link to published version: http://dx.doi.org/ 10.1063/1.2349832
Publisher statement: None

Band anticrossing in GaN$_x$Sb$_{1-x}$

P. H. Jefferson, T. D. Veal, L. F. J. Piper, B. R. Bennett,[a] and C. F. McConville[b]
Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom

B. N. Murdin
School of Electronics and Physical Sciences, University of Surrey, Guildford GU2 5XH, United Kingdom

L. Buckle, G. W. Smith, and T. Ashley
QinetiQ Ltd., St. Andrews Road, Malvern, Worcestershire WR14 3PS, United Kingdom

Fourier transform infrared absorption measurements are presented from the dilute nitride semiconductor GaNSb with nitrogen incorporations between 0.2% and 1.0%. The divergence of transitions from the valence band to E_- and E_+ can be seen with increasing nitrogen incorporation, consistent with theoretical predictions. The GaNSb band structure has been modeled using a five-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian and a band anticrossing fitting has been obtained using a nitrogen level of 0.78 eV above the valence band maximum and a coupling parameter of 2.6 eV. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2349832]

It is well documented that the anion substitution of dilute quantities of nitrogen into III-V semiconductor compounds results in a sharp decrease in the band gap of the material from that of the host compound. A number of explanations have been suggested to describe this band gap reduction, most notably the band anticrossing model (BAC), calculations based on empirical pseudopotential methods, and interpretations based on the mixing of the Γ, L, and X character of the conduction band states.[1]

The origin of this band gap reduction is the isoelectronic nature of the nitrogen atoms in the host III-V material. Though the nitrogen atom has the same electron valence as the atom it is replacing, its physical properties (size, electronegativity, bond length, etc.) are significantly different, resulting in a considerable, highly localized perturbation to the electronic potential surrounding the atom.

According to the BAC model this localized deformation in potential results in the formation of an energy level extended in k space which may be resonant with the conduction band of the host. The interaction between the host conduction band and resonant nitrogen level results in the formation of two nonparabolic subbands (conventionally denoted E_- and E_+) given by the relation

$$E_\pm = \frac{1}{2}[E_N + E_M \pm \sqrt{(E_N - E_M)^2 + 4V_{MN}^2}], \qquad (1)$$

where V_{MN} is the matrix element describing the coupling between the host conduction band (E_M) and the resonant nitrogen level (E_N) and has the functional form $V_{MN} = C_{MN}\sqrt{x}$ where C_{MN} is the coupling parameter and x is the nitrogen concentration.[2]

Nitrogen induced band gap reduction has been observed in many alloys including GaNP,[3] GaNAs,[4] InNAs,[5] and most recently GaNSb.[6] The addition of antimony to the dilute nitride GaNAs has been shown to improve the optical and electronic properties of the material[7] and has been suggested

as a possible material for long wavelength optoelectronic devices lattice matched to GaAs.[8] To determine the dependence of the band gap of such materials as a function of nitrogen incorporation, the BAC parameters of the constituent endpoint ternaries must be known. Though these have been well investigated in GaNAs a lack of data is found for GaNSb, a fact highlighted in Vurgaftman and Meyer's review on nitrogen containing III-V materials.[9]

In this letter, Fourier transform infrared (FTIR) absorption measurements of GaNSb samples with nitrogen incorporations between 0.2% and 1.0% are presented and preliminary values for the BAC parameters E_N and V_{MN} are suggested.

The GaNSb layers were grown using plasma assisted molecular beam epitaxy on GaAs substrates. Details of the growth and structural characterization can be found elsewhere.[6,10] The optical absorption measurements were performed using a Perkin Elmer Spectrum GX FTIR spectrometer with a cadmium mercury telluride detector with a working range between 0.1 and 1.2 eV. Single field Hall measurements were conducted on the samples at both room temperature and 77 K using the standard van der Pauw configuration with In–Sn and Pt wire contacts.

The absorption spectra of four GaNSb samples with nitrogen incorporations between 0.2% and 0.6% are shown in Fig. 1; the spectra are offset in the y direction for clarity. The feature seen in the region of 0.40–0.45 eV is attributed to optical transitions from the valence band to E_- states and the feature seen in the region of 0.8–0.9 eV is attributed to transitions from the valence band to E_+ states. The divergence of these features can be seen with increasing nitrogen concentration, consistent with the BAC model.

The FTIR absorption spectra were simulated using the method reported by Perlin *et al.*[11] based on the calculation of the joint density of states for each electronic transition within the defined material band structure. The band structure of GaNSb used for the absorption calculation is shown in the right section of Fig. 2. The valence bands were calculated using Pidgeon and Brown's eight-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian[12] with an experimentally determined band gap for GaSb of 0.71 eV and further band parameters taken from a review by

[a]Permanent address: Naval Research Laboratory, Washington, DC 20375-5347.
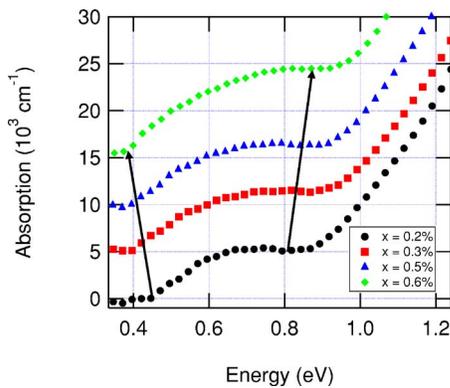[b]Corresponding author electronic mail: c.f.mcconville@warwick.ac.uk

FIG. 1. (Color online) FTIR absorption spectra of GaNSb layers with nitrogen incorporations between 0.2% and 0.6% are shown. Each spectrum is offset by 5000 cm^{-1} in the y direction. The arrows are a guide to the eye to highlight the divergence of the features attributed to transitions from the valence band to E_- and E_+.

FIG. 3. (Color online) Position of the valence band to (i) E_- (squares) and (ii) E_+ (circles) transitions together with a fitting based on the band anticrossing model (solid lines) with a nitrogen level of 0.78 eV and a C_{MN} value of 2.6 eV and a five-band $\mathbf{k} \cdot \mathbf{p}$ simulation using parameters taken from tight binding calculations by Lindsay and O'Reilly (dashed lines).

Vurgaftman *et al.*[13] The conduction bands were calculated using the BAC relation [Eq. (1)] using the nonparabolic host conduction band obtained from the $\mathbf{k} \cdot \mathbf{p}$ calculation. A nitrogen level of 0.78 eV and a coupling parameter of 2.6 eV were used for the simulation and will be discussed later.

The joint density of states and subsequently the absorption for each of the transitions from the valence band to (a) E_- and (b) E_+ states were calculated. The total absorption is a summation of each of the absorption components. The absorption (circles) of a GaNSb sample with 0.6% nitrogen can be seen in left section of Fig. 2 together with the absorption components from the light (dot dashed) and heavy (dashed) hole valence bands to (a) E_- and (b) E_+ and the total absorption (solid line).

The pronounced nature of the valence band to E_+ transition seen in the FTIR spectrum of GaNSb is a virtue of the large spin-orbit splitting of the host material. The transition from the spin-orbit band to E_- occurs at $\sim$1.4 eV, an energy far greater than that of the valence band to E_+ transition of $\sim$1.0 eV [cf. GaNAs where the valence band to E_+ occurs at $\sim$1.8 eV and is considerably masked by the spin-orbit to E_- transition beginning at $\sim$1.55 eV (Ref. 12)].

Room temperature single field Hall analysis of the samples revealed degenerate *p*-type carrier concentrations of

$(3-6) \times 10^{18}$ cm^{-3}. The cause of the high carrier concentrations seen in the samples investigated is thought to be due the high level of native acceptor defects found in GaSb (Ref. 14) enhanced by a large dislocation density due to the lattice mismatched growth of the nitride layer on the GaAs substrate and by the incorporation of nitrogen. A band gap narrowing resulting from the high carrier concentrations was incorporated into the band structure with a 35 meV increase in the valence band with respect to the conduction band and nitrogen level.[15]

In addition to a small narrowing of the band gap, localized deformations in potential surrounding the high quantity of native acceptor defects act to smear both the conduction band (in our case E_-) and valence band edges. The valence band edge is unaffected by this as the perturbed part of the valence band is found above the Fermi level.[16,17] For the E_- level, however, the formation of tail states into the band gap results in a nonzero absorption below the expected valence band to E_- transition. As the E_+ level is predominantly nitrogenlike at the Γ point,[2] the position of the valence band to E_+ transition remains unaffected by this and acts as a good reference point to determine the BAC band parameters.

The position of the transitions to E_- and E_+ were estimated from the FTIR spectra for samples with nitrogen incorporations between 0.2% and 1.0%. The errors were estimated to be ±20 meV for valence band to E_+ transitions and ±0.03% in the nitrogen incorporation. Determination of the accuracy of the valence band to E_- transitions is not possible without further investigation into the effects of the high carrier concentration and has been conservatively estimated at ±50 meV for illustrative purposes. A least squares fitting of the positive root of Eq. (1) to the E_+ transition data was used to determine the value for the coupling parameter for GaNSb. Figure 3 shows the experimentally determined transitions to E_- (squares) and E_+ (circles) together with a BAC model fitting (solid lines) and a five-band $\mathbf{k} \cdot \mathbf{p}$ simulation (dashed lines).

The BAC fit was calculated using a coupling parameter of 2.6±0.1 eV, from the least squares fit and a nitrogen level of 0.78 eV above the valence band maximum, from tight binding calculations by Lindsay and O'Reilly.[18] The $\mathbf{k} \cdot \mathbf{p}$ simulation used a 5×5 Hamiltonian with the valence band elements the same as those used in Ref. 12. Conduction band and nitrogen level elements of $E_M - \alpha x$ and $E_N - \gamma x$, respec-
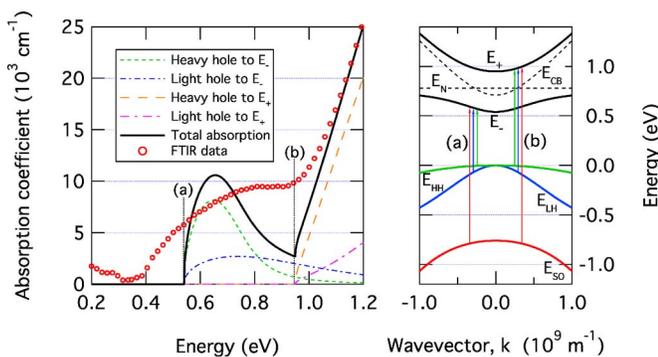

FIG. 2. (Color online) Right: band structure of GaNSb used for the absorption simulation. The valence bands were calculated using Pidgeon and Brown's eight-band $\mathbf{k} \cdot \mathbf{p}$ method and the conduction bands using the band anticrossing model with C_{MN}=2.6 eV and E_N=0.78 eV. Left: FTIR absorption spectrum (circles) of GaN$_x$Sb$_{1-x}$/GaAs with x=0.006 together with the constituent components [dashed and dot-dashed lines representing heavy and light hole bands to (a) E_- and (b) E_+ bands, respectively] and the sum total (solid line) of the absorption simulation.
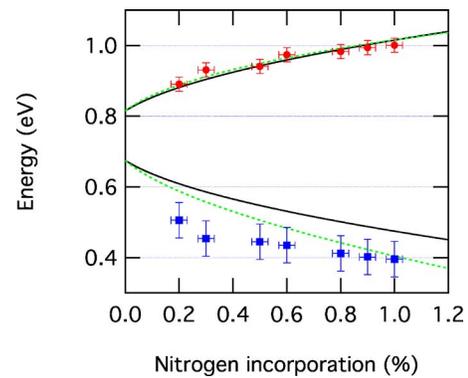
tively, were used coupled by the term $\beta\sqrt{x}$. The values of α, β, γ, and E_N were taken from the tight binding calculations of Lindsay and O'Reilly and were 2.34, 2.80, 2.30, and 0.78 eV, respectively.[18]

In conclusion, evidence of a band anticrossing interaction has been observed in the dilute nitride GaN_xSb_{1-x} from FTIR absorption with $x \leq 1.0\%$. Simulations of the absorption, based on a joint density of states method, have indicated a prominent valence band to E_+ transition, confirmed by the absorption spectra. The BAC parameter C_{MN} was estimated to be 2.6 eV from fitting the composition dependence of the valence band to E_+ transition, using a nitrogen level of 0.78 eV from tight binding calculations. Finally, five-band $\mathbf{k} \cdot \mathbf{p}$ simulations based on the work of Lindsay and O'Reilly were shown to agree well with the E_+ and E_- positions.

[1]*Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, New York, 2005).

[2]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).

[3]J. N. Baillargeon, P. J. Pearah, K. Y. Cheng, G. E. Hofler, and K. C. Hsieh, J. Vac. Sci. Technol. B **10**, 829 (1992).

[4]M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).

[5]T. D. Veal, L. F. J. Piper, P. H. Jefferson, I. Mahboob, C. F. McConville, M. Merrick, T. J. C. Hosea, B. N. Murdin, and M. Hopkinson, Appl. Phys. Lett. **87**, 182114 (2005).

[6]T. D. Veal, L. F. J. Piper, S. Jollands, B. R. Bennett, P. H. Jefferson, P. A. Thomas, C. F. McConville, B. N. Murdin, L. Buckle, G. W. Smith, and T. Ashley, Appl. Phys. Lett. **87**, 132101 (2005).

[7]H. B. Yuen, S. R. Bank, M. A. Wistey, J. S. Harris, Jr., M.-J. Seong, S. Yoon, R. Kudrawiec, and J. Misiewicz, J. Appl. Phys. **97**, 113510 (2005).

[8]J.-C. Harmand, A. Caliman, E. V. K. Rao, L. Largeau, J. Ramos, R. Teissier, L. Travers, G. Ungaro, B. Theys, and I. F. L. Dias, Semicond. Sci. Technol. **17**, 778 (2002).

[9]I. Vurgaftman and J. R. Meyer, J. Appl. Phys. **94**, 3675 (2003).

[10]L. Buckle, B. R. Bennett, S. Jollands, T. D. Veal, N. R. Wilson, B. N. Murdin, C. F. McConville, and T. Ashley, J. Cryst. Growth **278**, 188 (2005).

[11]P. Perlin, P. Wisniewski, C. Skierbiszewski, Y. Suski, E. Kaminska, S. G. Subramanya, E. R. Weber, D. E. Mars, and W. Walukiewicz, Appl. Phys. Lett. **76**, 1279 (2000).

[12]C. R. Pidgeon and R. N. Brown, Phys. Rev. **146**, 575 (1966).

[13]I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).

[14]P. S. Dutta, H. L. Bhat, and V. Kumar, J. Appl. Phys. **81**, 5821 (1997).

[15]S. C. Jain, J. M. McGregor, and D. J. Roulston, J. Appl. Phys. **68**, 3747 (1990).

[16]J. I. Pankove, Phys. Rev. **140**, A2059 (1965).

[17]J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).

[18]A. Lindsay and E. P. O'Reilly (private communication), GaNSb band parameters for five-band $\mathbf{k} \cdot \mathbf{p}$, model from tight-binding calculations.