Tight-binding model for the x-ray absorption and emission spectra of dilute GaN$_x$As$_{1-x}$ at the nitrogen K edge

E. Nodwell,[1] M. Adamcyk,[1] A. Ballestad,[1] T. Tiedje,[1,*] S. Tixier,[1] S. E. Webster,[1] E. C. Young,[2] A. Moewes,[3] E. Z. Kurmaev,[4] and T. van Buuren[5]

[1]*Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T 1Z1*

[2]*Department of Metals and Materials Engineering, University of British Columbia, Vancouver, Canada V6T 1Z4*

[3]*Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada S7N 5E2*

[4]*Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg, GSP-170, Russia*

[5]*Lawrence Livermore National Laboratory, Livermore, California 94550, USA*

X-ray absorption and fluorescence spectra have been measured at the nitrogen K edge of dilute GaN$_x$As$_{1-x}$ alloys. The x-ray spectra are in good agreement with an sp^3s^* tight-binding model in which nitrogen is included in a supercell configuration and the disorder in the nitrogen distribution is neglected. A strong peak in the x-ray absorption spectrum is interpreted as a nitrogen resonant state in the conduction band rather than as an electron-hole exciton. The tight-binding calculation is also in good agreement with the observed nitrogen concentration dependence of the optical band gap.

The dilute nitride alloys Ga$_y$In$_{1-y}$N$_x$As$_{1-x}$ and GaN$_x$As$_{1-x}$ have attracted considerable attention recently due to the promising applications of GaInNAs quantum well structures in 1.3 and 1.55 μm semiconductor lasers.[1] Although N is isoelectronic with As, because of the large differences in the size and electronegativity of the two atoms, N behaves in many respects as an impurity rather than an alloying element.[2] For example, there is a strong resonance near the bottom of the conduction band associated with N atoms in dilute GaNAs, and N clusters are believed to form bound states in the optical band gap.[3] Furthermore low nitrogen concentrations have an anomalously large effect on the band gap. For $x<0.01$, the reduction in the band gap associated with N alloying is more than $10\times$ greater than the effect of adding a comparable amount of In. This anomalous composition dependence of the band gap can be explained remarkably well by a tight-binding model which neglects the effects of disorder.[4] On the other hand in order to explain the electronic states near the band edges observed by photoluminescence, for example, it is necessary to include the effects of the random distribution and clustering of the nitrogen.[2] In this paper we show that the tight-binding model in which the disorder is neglected also explains the x-ray emission and absorption spectra at the N K edge for dilute GaNAs alloys. These experiments are sensitive to electronic structure in the vicinity of the N atoms, deep in the conduction and valence bands.

The x-ray absorption and emission experiments were performed on GaNAs epitaxial films grown by elemental source molecular-beam epitaxy (MBE) on (100) GaAs substrates with a radio frequency plasma discharge source for activated nitrogen.[5] The output of the plasma source was baffled to block the line of sight to the discharge and suppress the ion flux. The source was operated with pure N$_2$ without a carrier gas. The films were grown at 400–450 °C with thicknesses in the 100–300 nm range, so as to be sufficiently thin to avoid strain relaxation through misfit dislocation formation

yet sufficiently thick to absorb the incident x rays. The N content was obtained by x-ray diffraction calibrated with secondary ion mass spectrometry measurements on test samples.

X-ray absorption (XAS) and emission spectroscopy (XES) measurements were carried out at the undulator beamline 8.0 of the Advanced Light Source employing a soft x-ray fluorescence endstation.[6] The N K-edge emission spectra were obtained with a 600 lines/mm diffraction grating providing an energy resolution of 0.6 eV. The absorption spectra were obtained by varying the excitation energy and measuring the total fluorescence yield by integrating the output of the XES spectrometer across the 390–397 eV N emission band.
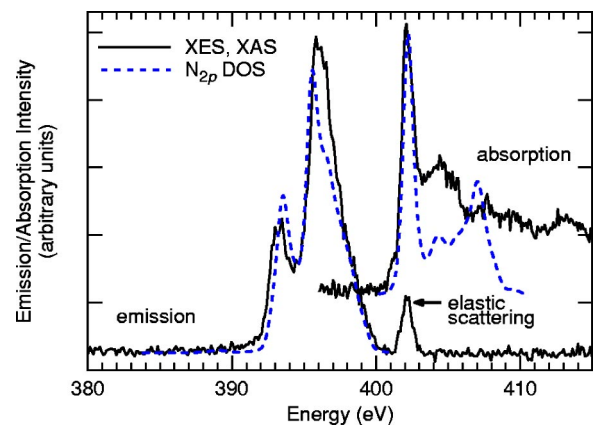

FIG. 1. (Color online) N K-edge absorption and emission spectra for a GaN$_{0.02}$As$_{0.98}$ sample. The energy scales for the absorption and emission spectra are aligned with the aid of the elastic peak associated with diffuse scatter in the x-ray emission spectrum. The dashed lines are the smoothed N $2p$ densities of states as discussed in the text. The model curves are smoothed with Lorentzian and Gaussian broadening functions with FWHM's of 0.143 and 0.6 eV, respectively, to simulate the core hole lifetime (Ref. 10) and experimental resolution.

Figure 1 shows N *K*-edge absorption and emission spectra for a GaN$_x$As$_{1-x}$ sample with $x = 0.02$. The absorption spectrum is similar to the results of Lordi.[7] The N emission spectrum is similar to the results of Strocov,[8] except that the resolution is somewhat higher in our experiments (0.6 eV vs ~1.4 eV). The absorption and emission spectra are offset for clarity but their energy scales are aligned by matching the elastic peak in the XES spectrometer with the corresponding energy in the x-ray absorption spectrum. The elastic peak is caused by diffuse x-ray scattering from the surface of the film. In the x-ray emission spectrum shown, the excitation energy was set at the peak in the absorption spectrum to maximize the signal. Similar absorption and emission spectra were obtained for seven different samples with N concentrations ranging from 0.5% to 2% with intensity scaling approximately proportional to the N concentration. The relative height, position, and shape of the two peaks at 393 and 396 eV do not differ for the different N concentrations. A weak N signal was observed with a N concentration as low as 0.02% but the spectrum could not be resolved due to low signal levels. This XES signal is likely dominated by surface adsorbed N$_2$ since the measured signal did not scale linearly with N content. At 402 eV, the x-ray penetration depth in GaAs is 129 nm at normal incidence[9] or 92 nm at 45°. Therefore residual adsorbed nitrogen could contribute a significant fraction of the total N fluorescence signal for the lowest doped sample. The fact that the emission signal scaled with the measured N content for the higher N content samples indicates that the contribution of the adsorbed N can be neglected in the emission spectrum in Fig. 1. The surface N could be removed by heating the samples, although this was not done.

Emission spectra were excited with various photon energies in the vicinity of the absorption edge including at the small shoulder at 401.2 eV, the main peak at 402 eV, and the secondary features at 404 eV and 407.5 eV. No differences were observed in the emission spectra indicative of resonant inelastic-scattering phenomena, contrary to earlier work on GaNAs and GaN (Refs. 8 and 11). The absorption and emission spectra were measured on samples before and after rapid thermal annealing at 850 °C for 60 s. Annealing is known to improve the electronic properties. We were unable to detect any differences in the absorption or emission spectra after annealing. Similar to the emission spectra, no change in the shape of the absorption spectra was observed at lower N content, although the intensity and signal to noise ratio were smaller.

The N $K\alpha$ emission is caused by $2p \rightarrow 1s$ dipole transitions and is therefore sensitive to the occupied N $2p$ states. As the final state contains a hole in the valence band but no core hole, one can expect that the spectra reflect the partial density of states for the ground-state configuration owing to the final state rule.[12]

The x-ray fluorescence and absorption measurements are compared with a tight-binding calculation of the electronic structure of GaN$_x$As$_{1-x}$. The tight-binding technique was used for these calculations as it is known to give excellent agreement with the valence-band structure in covalent semiconductors. The lower part of the conduction band also

TABLE I. Parameters used in the tight-binding model.

Orbital energies ε (eV)

	s	p	s^*
Ga	-6.943	0.000	4.660
As	-10.356	-1.589	4.037
N	-17.465	-4.262	-1.400

Overlap coefficients $\eta_{ll'm}^{1,2}$

	Nearest neighbor	Next-nearest neighbor
s-s-σ	-1.786	0.588
s-s^*-σ	-0.494	-0.637
s^*-s^*-σ	0.606	-0.532
s-p-σ	-1.418	0.407
s^*-p-σ	0.046	-1.201
p-p-σ	2.915	0.671
p-p-π	-0.659	-0.276

Atom size factor C

N		0.875

agrees with the calculations when second neighbor interactions are included, and it is relatively easy to compute large supercells with this technique. The tight-binding band structure was calculated for various size supercells. Typical calculations were carried out with a $3 \times 3 \times 3$ supercell of conventional zincblende unit cells for a total of 216 atoms. Substitution of N into a single As site is thus equivalent to a N atom concentration of $x = 0.009$. A so-called sp^3s^* Hamiltonian is used, which accounts for the partially filled s and p orbitals ($4s$, $4p$ in the case of Ga and As; $2s$, $2p$ for N), as well as the next-highest orbital, an empty s orbital ($5s$ and $3s$, respectively). Spin-orbit effects are neglected. With this combination of orbitals an excellent fit can be obtained to the valence band of GaAs and GaN as well as the bottom of the conduction band. We parametrized both nearest-neighbor and next-nearest-neighbor overlap integrals. However in order to keep the number of parameters small, we employ Harrison's[13] original suggestion for universal overlap matrix elements, with the modification of a prefactor for atom size for nitrogen, following Ref. 4, because of its small size. In this scheme the overlap matrix element is

$$V_{ll'm}^{1,2} = C \eta_{ll'm}^{1,2} \frac{\hbar}{md^2}, \tag{1}$$

where C is the prefactor for atom size, non-unity only for bonds involving a nitrogen atom; the coefficient η is dependent only on the orbitals participating in the bond and their symmetry, and not on the atom species. The parameters shown in Table I were obtained from a best fit to a pseudopotential determination of the band structure of GaAs from Ref. 14. The fits to the band structure were obtained through an iterative thermal annealing algorithm and match the pseudopotential valence-band structure to within 0.2 eV. Ini-
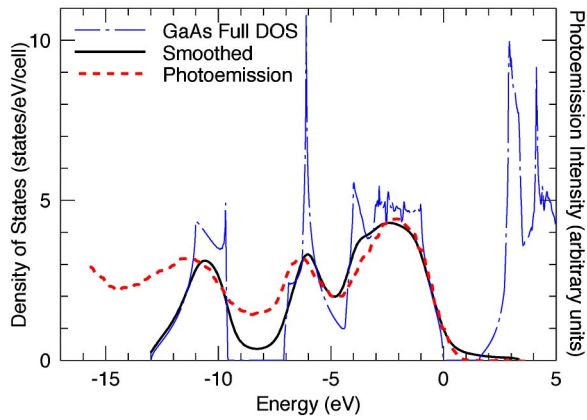
FIG. 2. (Color online) GaAs density of states calculated from the tight-binding model (thin, dashed). The solid line is the valence-band density of states smoothed using Lorentzian and Gaussian broadening functions with FWHM's of 0.6 and 0.55 eV, respectively. The heavy dashed line is an experimental photoemission spectrum for GaAs from Ref. 16.

FIG. 3. (Color online) (a) N $2s$ and N $3s$ partial densities of states calculated from the tight-binding model with the parameters in Table I. The bottom two panels are the N $2p$ partial densities of states for N on (b) a Ga site and (c) an As site. The solid curves are smoothed versions obtained by convolving the density of states with Lorentzian and Gaussian broadening functions as in Fig. 1.

tial values for the nitrogen levels were obtained by a fit to the band structure of wurzite GaN.[15] The N p and $s*$ ($2p$ and $3s$) levels were further tuned as discussed below.

The total density of states is shown in Fig. 2 for the best fit to the GaAs band structure. Also plotted in this figure is the density of states obtained by smoothing the calculated valence-band density of states with Lorentzian and Gaussian functions with full widths at half maximum (FWHM) of 0.6 and 0.55 eV, respectively, along with a GaAs valence-band x-ray photoemission spectrum.[16] Note the good agreement between the calculated density of states and the x-ray photoemission spectrum. In comparing the XES spectrum for Ga-NAs with the photoemission spectrum of GaAs, notice that the lower peak in the photoemission is absent in the XES spectrum and the energy positions of the two upper peaks are somewhat different in the two different experimental spectra.

The partial density of states from the tight-binding calculation is shown in Fig. 3 for N on Ga and As sites. We also show the N $2s$ and $3s$ partial densities of states. The N $2p$ partial density of states shown in Fig. 3(c) is replotted in Fig. 1 and shows excellent agreement with the experimental XES data. The smoothed N $2p$ partial density of states in Fig. 3(c) was found to be insensitive to N concentration for N concentrations between 0.8% and 3%.

There are a number of notable features in the calculated partial densities of states. There is almost no N $2p$ character to the lower part of the valence band for N on the As site, in agreement with the experimental XES data. For N on both the As and Ga sites the majority of the weight for the N $2s$ orbital is in a bound state below the bottom of the valence band. This shows up in the calculation as a δ-function-like vertical line near -16 eV. This bound state should be observable by photoemission spectroscopy although there may be interference from the Ga $3d$ orbital which is in the same energy range. For N on the Ga site the tight-binding calculation predicts that there are bound states in the gap between the two parts of the valence band and in the optical band gap. These results show that the partial density of states (and XES
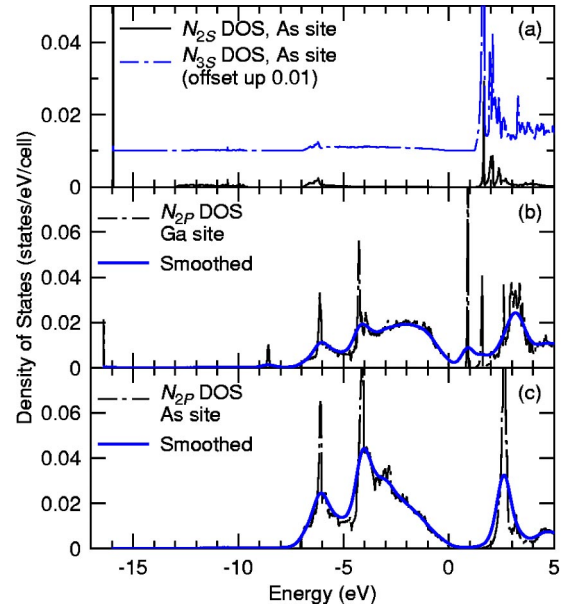
spectrum) is sensitive to the N site. The bottom of the conduction band has s symmetry as expected. About 1 eV above the bottom of the conduction band for N on the As site there is a strong peak in the density of states with $2p$ symmetry. The position of this peak is in good agreement with the strong peak observed in the x-ray absorption spectrum, as shown in Fig. 1. The weak low-energy shoulder at 401.2 eV in the experimental x-ray absorption spectrum may be due to absorption into the s states at the bottom of the conduction band located on neighboring atoms, for which the dipole selection rule does not apply.

The shape of the N $2p$ density of states in the valence band is sensitive to the energy of the N $2p$ orbital. In Figs. 1 and 3 the N $2p$ energy has been optimized to give a best fit to the experimental XES spectrum. On the other hand the position of the peak in the N $2p$ density of states near the bottom of the conduction band for N on an As site is relatively insensitive to the energy of the N $2p$ orbital. Decreasing the energy of the N orbitals by 1 eV to mimic the effect of the N $1s$ core hole in the final state of the XAS only slightly modified the intensity of the peak in the N $2p$ density of states and had little effect on its energy position (shifted down 0.12 eV). The agreement between the experiment and the model suggests that the large peak in the N K-edge absorption is due to a N-related resonance in the lower part of the conduction band and is not an excitonic bound state.

The energy for the N $3s$ orbital was obtained from experimental data for the concentration dependence of the optical band gap as shown in Fig. 4. Experimental data from Ref. 17, as well as photoluminescence measurements on our GaN_xAs_{1-x} samples in a narrower concentration range, are
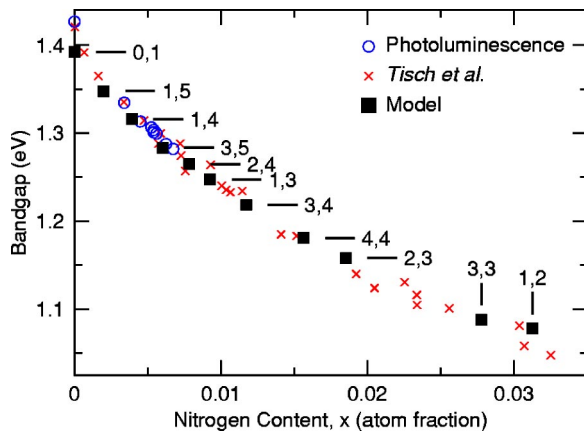
FIG. 4. (Color online) Band-gap dependence on nitrogen concentration, showing the agreement between photoluminescence data measured on our samples, published optical data by Tisch *et al.* (Ref. 17), and the tight-binding model. For the model points, the number of nitrogen atoms and the size of supercell are indicated (e.g., "1,3" indicates 1 nitrogen atom in a supercell of $3 \times 3 \times 3$ conventional unit cells).

shown. Comparable concentrations were obtained with the tight-binding model using supercells varying in size from $2 \times 2 \times 2$ to $5 \times 5 \times 5$ conventional unit cells, containing between 1 and 4 nitrogen atoms. Nitrogen atoms were placed maximally separated at anion sites along [111]. In the tight-binding fit the only adjusted parameter was the energy of the N $3s$ orbital, with all other parameters obtained from the fit to the GaAs band structure and the XES spectrum as discussed above and listed in Table I. The agreement with the experimental data is excellent. A similar result was reported earlier in Ref. 4. The circles are photoluminescence measurements from GaNAs samples prepared in a similar way to the sample in Fig. 4. The tight-binding model is conceptually similar to the band anticrossing model in which one takes into account the effect of nitrogen by adding an additional orbital which couples to the bulk GaAs bands while neglecting disorder.[18,19] The energy of the N $3s$ orbital has only a small effect on the N $2p$ density of states in the valence band.

To summarize, we present soft x-ray absorption and emission measurements at the N K edge on MBE grown GaN_xAs_{1-x} with N content x from 0.5% to 2.2%. An excellent fit to the experimental data is obtained with a tight-binding model in which the random N distribution is simulated with an ordered distribution using a supercell approach. No changes in the shape of the spectra were observed as a function of N content or thermal annealing. The excellent agreement between the model and the experiments is remarkable given that the randomness in the N distribution is neglected. In our model the large peak in the N K-edge absorption is due to a N $2p$ resonance near the bottom of the conduction band and is not excitonic in origin.

*Also at Department of Electrical and Computer Engineering, University of British Columbia.

[1] E. Tournié, M.-A. Pinault, M. Laügt, J.-M. Chauveau, A. Trampert, and K.H. Ploog, Appl. Phys. Lett. **82**, 1845 (2003).

[2] P.R.C. Kent and A. Zunger, Phys. Rev. Lett. **86**, 2613 (2001).

[3] Y. Zhang, A. Mascarenhas, H.P. Xin, and C.W. Tu, Phys. Rev. B **61**, 7479 (2000).

[4] A. Lindsay and E.P. O'Reilly, Solid State Commun. **112**, 443 (1999); **118**, 313 (2001).

[5] M. Adamcyk, J.H. Schmid, T. Tiedje, A. Koveshnikov, A. Chahboun, V. Fink, and K.L. Kavanagh, Appl. Phys. Lett. **80**, 4357 (2002).

[6] J.J. Jia, T.A. Callcott, J. Yurkas, A.W. Ellis, F.J. Himpsel, M.G. Samant, J. Stöhr, D.L. Ederer, J.A. Carlisle, E.A. Hudson, L.J. Terminello, D.K. Shuh, and R.C.C. Perera, Rev. Sci. Instrum. **66**, 1394 (1995).

[7] V. Lordi, V. Gambin, S. Friedrich, T. Funk, T. Takizawa, K. Uno, and J.S. Harris, Phys. Rev. Lett. **90**, 145505 (2003).

[8] V.N. Strocov, P.O. Nilsson, A. Augustsson, T. Schmitt, D. Debowska-Nilsson, R. Claessen, A.Yu. Egorov, V.M. Ustinov, and Zh.I. Alferov, Phys. Status Solidi B **233**, R1 (2002).

[9] See URL: www-cxro.lbl.gov/optical_constants/

[10] M. Coville and T.D. Thomas, Phys. Rev. A **43**, 6053 (1991).

[11] S. Eisebitt, J. Lüning, J.-E. Rubensson, and W. Eberhardt, Phys. Status Solidi B **215**, 803 (1999).

[12] U. von Barth and G. Grossmann, Phys. Rev. B **25**, 5150 (1982).

[13] W.A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1980).

[14] J.R. Chelikowsky and M.L. Cohen, Phys. Rev. B **14**, 556 (1976).

[15] A. Rubio, J.L. Corkill, M.L. Cohen, E.L. Shirley, and S.G. Louie, Phys. Rev. B **48**, 11 810 (1993).

[16] L. Ley, R.A. Pollak, F.R. McFeely, S.P. Kowalczyk, and D.A. Shirley, Phys. Rev. B **9**, 600 (1974).

[17] U. Tisch, E. Finkman, and J. Salzman, Appl. Phys. Lett. **81**, 463 (2002).

[18] 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).

[19] N. Shtinkov, P. Desjardins, and R.A. Masut, Phys. Rev. B **67**, 081202(R) (2003).