Nitrogen pairs, triplets, and clusters in GaAs and GaP

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The electronic and atomic structure of substitutional nitrogen pairs, triplets, and clusters in GaP and GaAs is studied using the multiband empirical pseudopotential method with atomistically relaxed supercells. A single nitrogen impurity creates a localized $a_1(N)$ gap state in GaP, but in GaAs, the state is resonant above the conduction-band minimum. We show how the interaction of multiple a_1 impurity levels, for more than one nitrogen, results in a nonmonotonic relationship between energy level and impurity separation. We assign the lowest (NN1) line in GaP to a [2,2,0] oriented pair, the second (NN2) line to a triplet of nitrogen atoms, and identify the origin of a deeper observed level as an [1,1,0] oriented triplet. We also demonstrate that small nitrogen clusters readily create very deep levels in both GaP and GaAs. © *2001 American Institute of Physics.*
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Although when inserted as a *single* substitution many isovalent impurities in semiconductors (GaAs:Al, GaAs:P) do not perturb the host crystal sufficiently to create band-gap levels, small *aggregates* of such impurities may conspire to create deep levels. This is the case for nitrogen pairs in GaAs (Refs. 1–3) and GaP (Refs. 4–9) and is predicted[10] to be the case for Al_4 in GaAs. Although random statistics suggests that in a dilute alloy the number of N–N pairs can be a small fraction of the total nitrogen concentration, such pairs dominate the emission spectra of *nitrogen-dilute* GaP (Refs. 4 and 6–8). Indeed, because nitrogen pairs form rather deep gap levels, and because photogenerated carriers are transferred efficiently from higher-energy levels of the substitutional centers to such deeper pair states,[11] experimental and theoretical studies of these strongly luminescing dilute impurities have held the fascination of the semiconductor defect community since their discovery in 1966 by Hopfield, Thomas, and Lynch.[5] This classic subject has recently become the focus of intense renewed interest,[1,3,12–16] as GaAsN alloys, evolving from nitrogen pairs in GaAs, have emerged as electro-optic materials.[16] In this letter, we study theoretically nitrogen pairs and higher aggregates in GaP and GaAs, using large (4096 and 13824 atom) atomistically relaxed supercells and the multiband pseudopotential plane-wave approach.[17] This method offers a ''theoretical laboratory'' that can answer questions pertaining to the electronic structure of complex defects such as nitrogen aggregates in GaP and GaAs, without using the effective-mass approximation.

Modeling the low nitrogen concentrations at which the pair spectra are observed [$x<0.5\%$ (Refs. 9 and 18)] requires the use of large supercells, which is beyond the capability of current first-principles calculations. We, therefore, adopt an alternative approach: To determine the electronic structure we use screened empirical pseudopotentials[19] adjusted to reproduce the *experimental* band gaps, electron and hole masses, the valence- and conduction-band pressure coefficients, and the calculated band offsets.[19] The atomic positions within the alloy supercell are obtained from a valence force field model (see Ref. 19, and references therein), which reproduces the local density approximation bond lengths and interatomic positions in small supercells to within 1%–2%. Using this method, described in detail in Ref. 19, we investigate *isolated* nitrogen, and nitrogen pairs, triplets, and higher clusters using large supercells.

Figure 1 gives the calculated energy levels for first to sixth nearest-neighbor N–N pairs and isolated N in GaP, while Fig. 2 gives the corresponding results for GaAs, calculated using 4096 atom cells and checked for convergence using 13 824 atom cells. We compute the Γ, L,X projections of each state, shown numerically in Figs. 1 and 2, which are not very sensitive to binding energy. Solid (empty) levels denote dipole-allowed (forbidden) transitions from the valence-band maximum (VBM). This is correlated with the amount of Γ character in the wave function. Our analysis provides answers to the following questions:

(i) *Are the energy levels associated with the mth pair a monotonic function of the N–N separation in the pair?* The discoverers of the pair spectra in III–Vs (Ref. 4) made the reasonable assumption that the shallowest level, closest to the conduction-band minimum (CBM), corresponds to the most widely separated N–N pair, whereas progressively deeper levels correspond to systematically closer spaced N–N pairs. This view has also been echoed by the tight-binding calculations of Shen, Shan, and Dow,[20] the effective-mass analysis of Benoit *á* la Guillaume,[21] as well as contemporary analysis of experiments.[22,23] Our results (Figs. 1 and 2) clearly indicate a nonmonotonic behavior of level position with pair separation, with the first and fourth nearest-neighbor pairs, corresponding to *planar* [1,1,0] and [2,2,0] N–N vectors, being clearly the deepest. The reason is that the (110) direction in zinc-blende is connected via atomic zigzag chains, which leads to strong coupling *through* the chains. The nonmonotonicity results from the interference between the different conduction-band valleys (Γ,X,L) and the nitrogen impurity potential. Γ-only models such as those derived from the simple effective-mass theory[25] produce, by necessity, a monotonic relationship. In contrast, models that include inter valley ($\Gamma-X-L$) coupling[24] can produce a

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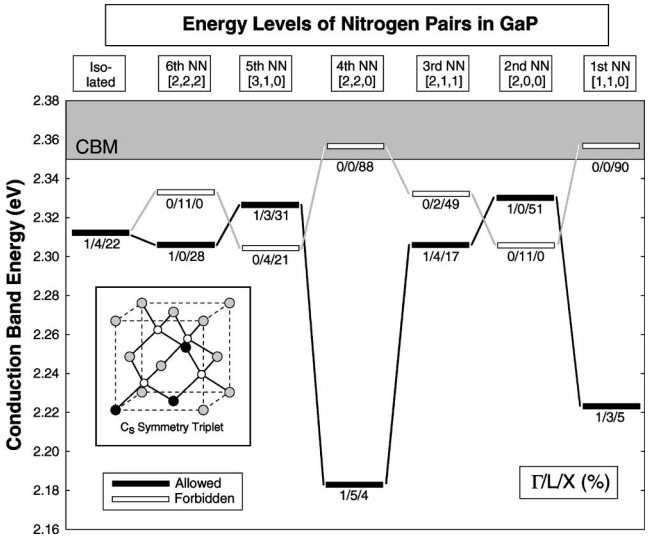

FIG. 1. Energy levels of isolated N and N–N pairs in GaP and, inset, the geometry of the nitrogen triplet assigned to the NN2 photoluminescence line, calculated using 4096 atom cells.

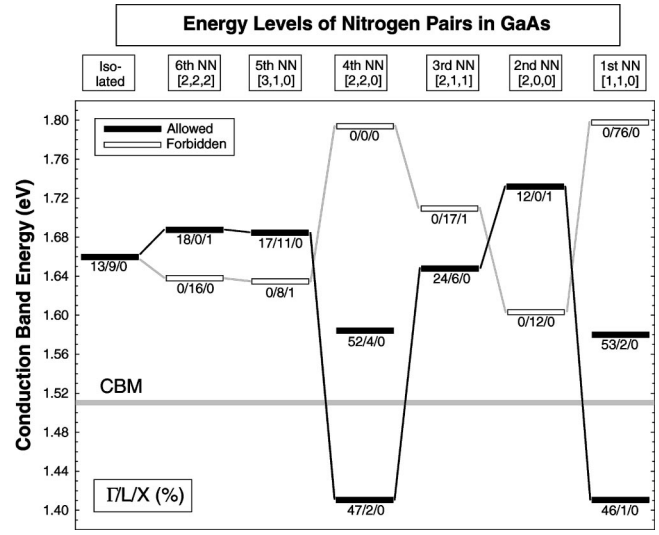

FIG. 2. Energy levels of isolated N and N–N pairs in GaAs, calculated using 4096 atom cells.

nonmonotonic behavior. In our calculations we find that multiband-coupling *alone* produces a nonmonotonic ordering, even for similarly oriented pairs, e.g., pairs oriented on the [1,1,0] axis: In GaP, for unrelaxed supercells we find NN4 [2,2,0] to be *deeper* than NN1 [1,1,0], while for relaxed pairs along the [1,1,0] axis we find, from deepest to shallowest level, NN4 [2,2,0], NN1 [1,1,0], then NN9 [3,3,0], and more distantly spaced pairs.

(ii) *Are all of the assigned PL lines due to nitrogen pairs?* When first discovered,[4,5] it was proposed that the sharp "NN" lines observed in PL were due to pairs of nitrogen atoms at increasing separation. This assignment has remained contentious to the present day. Uniaxial pressure measurements of GaP:N (Ref. 8) find that, except for NN1, NN3, and NN4, the stress-induced splittings cannot be assigned to mth nearest-neighbor pairs as originally proposed, suggesting the other lines are due to other small aggregates of nitrogen atoms (triplets, clusters, etc.), despite the low nitrogen concentration. In particular, the NN2 PL line of GaP:N displays several anomalies: (1) the amplitude in PL is significantly smaller than for NN1 or NN3,[4–6] (2) the hydrostatic pressure coefficient for the level is larger than for NN1 or NN3,[7] and (3) the local symmetry is C_s,[8] while a second nearest-neighbor pair would display D_{2d} symmetry. In our calculations, we find the second nearest-neighbor pair levels to be both forbidden and high in energy (Figs. 1 and 2), i.e., in agreement with Ref. 7, a second nearest-neighbor pair cannot explain the experimental observation of the NN2 line. We considered several symmetry-compatible triplet and cluster geometries.[26] Our calculations find a planar triplet with symmetry compatible with the NN2 line (inset to Fig. 1) has an allowed level 11 meV above the [2, 2, 0] pair level (Fig. 1), compared with ~6 meV measured experimentally,[7,13] and a calculated pressure coefficient of 26 meV/GPa, in excellent agreement with 21 meV/GPa (Ref. 7) found experimentally.

For other triplet geometries[26] in GaP we find yet deeper levels, the deepest (295 meV below the CBM) occurring for a triplet with atoms oriented along the [1,1,0] axis. This energy level is in excellent agreement with the "NC" level recently observed at 2.071 eV by PL in GaPN samples with $x_N \geqslant 0.43\%$.[13] We, therefore, identify the "NC" level[13] as an [1, 1, 0] oriented triplet of C_{2v} symmetry. Similarly, we find that multiple nitrogen atoms centered around a single gallium atom, i.e. $Ga(N_mP_{4-m})$ "clusters," result in successively deeper levels, at 38, 128, 196, and 214 meV below the GaP CBM, for $m=1$, 2, 3, and 4, and at 68, 147, 213 meV below the GaAs CBM, for $m=2,3,4$, respectively. These results indicate that in GaP:N *all* nitrogen aggregates create deep levels, while in GaAs:N gap levels are created beyond a critical local nitrogen concentration of $\sim 2-3$ nearest-neighbor nitrogen atoms, depending on orientation. Furthermore, the comparative ease with which deep levels are created by small nitrogen aggregates suggests that in higher nitrogen concentration alloys, e.g., 1% nitrogen, the presence of deep levels below the conduction-band edge is inevitable.

(iii) *Comparison with experiment.* One measures experimentally the ground-state energy of the impurity-bound exciton, as well as the hole binding energy. The electron energy level in the gap, with respect to the bulk free exciton, is thus at $E^{(i)}_{\mathrm{IBE}} - E^{(i)}_{\mathrm{HBE}}$ for the ith level. Adding the bulk exciton binding energy Δ_{BE} to this value then yields the electron level $\Delta^{(i)} = E^{(i)}_{\mathrm{IBE}} - E^{(i)}_{\mathrm{HBE}} + \Delta_{\mathrm{BE}}$ with respect to the CBM. Using Cohen's data for GaP:N,[6] and $\Delta_{\mathrm{BE}} = 22$ meV, we find: (1) the NN1 line is the 4th neighbor [2,2,0] pair: its binding energy is $\Delta^{(1)} = 142$ meV, in reasonable agreement with our deepest calculated level, 167 meV below the CBM for a [2,2,0], fourth nearest-neighbor pair ($x_{\mathrm{N}} = 0.05\%$), (2) the NN2 line is calculated as a triplet 126 meV below the CBM, in agreement with $\Delta^{(2)} = 135$ meV, (3) the NN3 line is the third nearest-neighbor [2,1,0] pair, and calculated to be 44 meV below the CBM, in similar agreement with the experimental level, $\Delta^{(2)} = 63$ meV, (4) the NN3 line should be the first neighbor pair [1,1,0], however, our calculated energy lies *below* the NN3 line, i.e., it is too deep. Our calculation places NN4 above NN1, which on the basis of experimentally determined NN symmetries,[26] must both be [1,1,0] oriented. We, therefore, assign NN4 to the [1,1,0] first neighbor pair. Our method, when excitonic effects are included, predicts for the isolated center ~60 meV compared with the

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TABLE I. Dipole allowed (A, nonzero Γ character) or forbidden (F, zero Γ character) nature of the lowest impurity level of the nitrogen pairs and isolated impurity in GaP and GaAs, for unrelaxed and relaxed geometries. The configurations are given in energetic order, from deepest to shallowest, calculated using the EPM and atomistically relaxed geometries. Results are compared with the predictions of the unrelaxed model calculations of Refs. 12 and 24.

	Unrelaxed		Relaxed
Configuration	Model	EPM	EPM
	GaP		
[2,2,0]	A	A	A
[1,1,0]	F	F	A
[2,0,0]	A	F	F
[3,3,0]	F	F	A
Isolated	A	F	A
	GaAs		
[1,1,0]	F	A	A
[2,2,0]	A	A	A
[2,0,0]	A	F	F
[3,3,0]	F	A	A
Isolated	A	A	A

measured ~36 meV.[6,7] Our model thus predicts the overall trends for isolated impurities and clusters.

(iv) *Does a model considering nitrogen pairs at the unrelaxed sites of the host lattice preserve the essential physical picture of the relaxed description*? Many previous models (e.g., those of Refs. 24, 12, and 21), have assumed that the nitrogen atoms take up the unrelaxed lattice sites of the unperturbed host crystal. However, there is a significant mismatch in the atomic sizes (18.9% and 22.5% lattice constant mismatch for GaP/GaN and GaAs/GaN, respectively), indicative of lattice relaxation. A significant outcome of such *unrelaxed* model calculations (see Ref. 12) is that the lowest levels of the odd-index pairs (e.g., first, third, and fifth neighbor, located at [1,1,0], [2,1,1], and [3,1,0] respectively) are dipole forbidden from the VBM, while the lowest states of the even-index pairs (second, fourth, and sixth pairs situated at [2,0,0], [2,2,0], and [2,2,2], respectively), are dipole allowed from the VBM. The distinction is important as it dictates the assignment of the measured spectroscopic transitions. Table I summarizes whether a transition is forbidden (F, denoting zero Γ character by symmetry), or allowed (A, finite Γ character) for both relaxed and unrelaxed pseudopotential calculations. Comparing the relaxed and unrelaxed EPM calculations, we see that relaxation can change the character of the state, e.g. the lowest levels of the [1,1,0] and [3,3,0] oriented pairs are strongly allowed in the relaxed model, but are forbidden in the unrelaxed model. Thus, neglect of relaxation[12,21,24] is unjustified here. Inspection of the wave-function character before and after relaxation shows a significant spectral redistribution. For example, the lowest level of the unrelaxed [1,1,0] pair in GaP has 77% X character, while upon relaxation this changes to 5%, the rest being distributed throughout the Brillouin zone.

Table I also gives us the opportunity to contrast the qualitative feature of the *one-band* unrelaxed model[12] with our *multiband* unrelaxed model (first two columns in Table I). We see that there are important failures of the one-band model, e.g., the [2,0,0] pair is *allowed* in the one-band model, but forbidden in the multiband model, and the [1,1,0] pair in GaAs is allowed *only* in the multiband model. Also, in GaP (but not in GaAs) the unrelaxed nitrogen does not have a strong enough perturbation to change the indirect CBM to direct; only relaxation converts the level to allowed. We conclude that although simplified models with adjustable parameters may be fit to reproduce the experimental *range* of N–N pair energy levels, our results clearly show the importance of both relaxation and multiband coupling in determining the *nature* and the precise *ordering* of the levels.

In summary, we find that nitrogen pairs in GaP and GaAs result in a rich series of energy levels that are nonmonotonic with pair separation. Larger aggregates of nitrogen atoms readily create very deep levels. Our calculations also show that multiband coupling, atomistic relaxation, and impurity orientation are critical to the impurity level spacing and impurity state character, explaining the wide variance in the predicted photoluminescence lines of these materials.

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