Penetration of electronic perturbations of dilute nitrogen impurities deep into the conduction band of GaP$_{1-x}$N$_x$

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The electronic structure consequences of the perturbations caused by dilute nitrogen impurities in GaP are studied by means of supercell calculations using a fully atomistic empirical pseudopotential method. We find that numerous localized states are introduced by a single N atom and N clusters, not only close to the band edge but also throughout the GaP conduction band, up to ~1 eV above the conduction band edge. These localized states suggest an alternative interpretation for a previously puzzling observation of splitting of photoluminescence excitation intensity at the GaP Γ_{1c} energy into two features, one blueshifting and the other staying pinned in energy with increasing N concentration.

Significant efforts have recently been made to understand the nature of the perturbations induced by nitrogen alloying of GaP, as observed by photoluminescence[1–6] (PL), its excitation[7–9] (PLE), ballistic electron emission,[10] resonant Raman scattering,[11] and ellipsometry[12,13] spectra. While initial efforts have focused on the spectral region near the indirect, X_{1c} absorption/emission threshold (2.35 eV), more recent studies[7–9,13] have revealed significant spectral changes not only at such low energies (LE) but also at high energies (HE), up to and exceeding the direct gap threshold Γ_{1c} at 2.85 eV. For example, a splitting of PLE intensity at the GaP Γ_{1c} energy into two features, one being blueshifted[12] and the other being *pinned*,[7] has been observed with increasing N concentration. The existence of both LE and HE nitrogen-induced perturbations already at very low concentrations, $x \lesssim 0.5\%$, raises the question of the nature of the coupling[3,4,14,15] between nitrogen impurity states and the host crystal states: Viewing the effect of nitrogen as an "impurity band"[3,14] (IB) formed by N impurity levels initially located below the host conduction band minimum (CBM), and gradually broadening with increased nitrogen concentration until this band touches the host CBM addresses, by construction, only the LE spectral region. Yet, profound spectral changes were seen at high energies even for low N concentration,[7–9,13] which remain unexplained by such a model. The clear evidence that application of pressure,[16] which raises the conduction band minimum, exposes *narrow* impurity levels, rules out the IB model. Furthermore, the observation[17,18] of an *increase* of the electron effective mass with N concentration for GaAs$_{1-x}$N$_x$, even after the alleged merging with the conduction band, also contrasts with expectations[19] of the IB model. The "band anticrossing" (BAC) model[4] views the effect of nitrogen as a coupling between a single impurity state $a_1(N)$, initially in the gap, with the host conduction band states. The model assumes that there is *only one* N state (the one in the GaP gap), and it predicts that both the N state and the host conduction states shift with composition. Yet, spectroscopic evidence shows *multiple* N-related peaks both at LE and HE, some of which being *pinned in energy* as the composition changes. Furthermore, the BAC model does not account for the observed

cluster states, which control the emission spectra and transport.[1–3,5,6] Finally, neither BAC nor IB can explain the recently observed splitting of PLE intensity at Γ_{1c} energy into two spectral features,[7,12] with one of them being blueshifted and the other being pinned as N concentration increases. It is becoming evident that simple models[3,4,14] do not account for the main spectroscopic features of this system.

We have taken a different approach:[15,20,21] instead of postulating *a priori* an energy-level model,[3,4,14] we first solve quantum mechanically for the detailed electronic structure, using a fully atomistic approach and permitting isolated nitrogen as well as various nitrogen clusters to interact and perturb all host states over a broad energy range. We then distill *a posteriori* from the numerical results a simple energy level model. We find multiple spectral changes not only at the LE region, but also at the HE region. Many of these ensuing states have no counterpart in any of the previous IB or BAC models. We find new localized states introduced by single N and N clusters throughout the GaP conduction band. These states suggest a new interpretation for a previously puzzling observation[7,12] of the split Γ_{1c}. We also point at the existence of L character just below the valence band maximum, and the coexistence of dominant cluster states at the conduction band edge.

We model the substitutional GaP$_{1-x}$N$_x$ alloy systems within a supercell approach, using a large cubic $6 \times 6 \times 6$ (1728 atom) supercell. To simulate *isolated* N we place a single N atom in it ($x = 0.12\%$), whereas to simulate isolated *pairs* we add one more N atom at different neighbor positions with respect to the first N atom, creating first-neighbor pairs (NN1), second-neighbor pairs (NN2), etc., up to the fourth-neighbor (NN4) position. Finally, to study diluted *alloys* we take 6, 11, and 30 nitrogen atoms and distribute them randomly over the anion sites of the same 1728 atom cell, considering 12 different randomly generated atomic realizations for each N concentration x. This simulates random alloys with x equal to 0.69%, 1.27%, and 3.51%. In all cases the electronic structures of these GaP$_{1-x}$N$_x$ alloy models are calculated fully atomistically by means of the empirical pseudopotential method,[15,20,21] using the same computational

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parameters as in Ref. 15. The atomic site positions are fully relaxed with the valence force field method (VFF)[22] with VFF parameters from Ref. 20. As shown in Ref. 15, VFF reproduces to within 1% the first-principles local-density approximation (LDA) calculated atomic positions and bond lengths in $GaP_{1-x}N_x$ alloy. The pseudopotential is made of a superposition of screened atomic pseudopotentials of Ga, P, and N situated on the corresponding atomic sites. The screened atomic potentials are empirically adjusted to closely reproduce the bulk band structures, effective masses, and deformation potentials, and they include explicitly local environment[23] and local strain[24] dependencies. The electronic Hamiltonian is diagonalized in a plane-wave basis set via the folded spectrum method.[25] The calculated electronic states are analyzed by evaluating their Γ, L, and X character using the "majority representation" projections.[26] Those projections are calculated by expanding the explicit wave function of a given electronic state in a complete set of Bloch wave functions and then calculating the sum over bands of the projections at a given bulk wave vector (e.g., Γ, L, or X). The Γ character of a conduction band state determines the dipole matrix element squared for optical transitions to that state from the Γ-like $GaP_{1-x}N_x$ valence band maximum (VBM), and is particularly relevant in PL/PLE data interpretations.

Single nitrogen and nitrogen pairs. Previous IB (Refs. 3 and 14) and BAC (Ref. 4) models assumed that the sole fingerprint of an isolated nitrogen impurity is the appearance of a N-localized electronic state $a_1(N)$ below the GaP conduction band. To check this assumption, Fig. 1 considers, over a broad energy range, the percentage of Γ, L, and X character for the electronic states of GaP with a *single* N atom [Fig. 1(a)] or a *single* N-N pair at different separation [Fig. 1(b)–1(e)]. The hostlike states ["perturbed host states" (PHS), solid lines in Fig 1] and cluster states (CS, symbols in Fig. 1) vecto0 TD aecto0

spectroscopy[11] is likely to come from the $e(X_{1c})$ PHS. The cluster states couple very weakly to the $e(X_{1c})$, but strongly to the a_1 PHS. The most clear indication of this behavior in our calculated results can be found in the X intensity curve

host states in Fig. 3(b) [viz., Fig. 1(a)], and identifies the main cluster states due to *isolated* nitrogens as well as *isolated* nitrogen pairs [viz., Figs. 1(b)–1(e) and 3(d)]. The levels of $GaP_{1-x}N_x$ are described as a mixture of PHS and CS [Fig. 3(c)].

We divide our discussion into three energy regimes: (i) low-energy states, i.e., near and below the host X_{1c} CBM; (ii) intermediate-energy states, between X_{1c} and Γ_{1c}; and (iii) high-energy states, in the vicinity of the direct band edge Γ_{1c}.

(i) Low-energy states (up to X_{1c}). *(a)* Γ *character*. Figure 2(a) shows that at LE we have alloy states with strong Γ character. This Γ mixing leads to a *positive* conduction band edge pressure coefficient,[4] even though in pure GaP with its X_{1c}-like band edge the pressure coefficient is negative. We see that these LE states red-shift, broaden, and *increase* their intensity as the nitrogen concentration increases. Furthermore, the Γ-like alloy LE peak [Fig. 2(a)] exhibits clear spectral structure, due to amalgamation of cluster states being overtaken by the down shifting conduction band edge.[15]

(b) non-Γ-character. The intensity of the L and X character [Fig. 2(b) and 2(c)] in this LE region is much stronger than that of the Γ character there, similar to the LE cluster states in Fig. 1. This behavior can be understood (Fig. 3) by attributing the broadening and buildup (with increasing N concentration) of the L and X intensity in this region to the growing number of cluster states, which dominate the LE region. These cluster states hybridize with LE PHS, especially with the a_1 one, which is redshifted due to repulsion from the higher energy a_1 PHS.[15] The stationary peak at X_{1c} energy observed in the resonant Raman scattering