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Evolution of Electron States with Composition in GaAsN Alloys

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We present a theory of the evolution of the electronic structure of GaAsN alloys, from the dilute impurity limit to the fully formed alloy. Using large scale empirical pseudopotential calculations, we show how substitutional nitrogen forms Perturbed Host States (PHS) inside the conduction band whereas small nitrogen aggregates form localized Cluster States (CS) in the band gap. By following the evolution of these states with increasing nitrogen composition we develop a model that explains many of the experimentally observed phenomena, including high effective masses, Stokes shift in emission versus absorption, and anomalous pressure dependence.

Introduction GaAsN is a special class of semiconductor alloy: due to the difference in the properties of the host and impurity atoms, bound states (or "cluster states", CS) are created near the fundamental gap, leading to discontinuous or rapidly changing optical properties with increasing nitrogen composition. The change in the electronic structure with nitrogen composition has been popularly described theoretically by approaches [1, 2] that ignore the evolution of the CS with nitrogen composition and the (statistical) fluctuations in nitrogen content present in even perfectly random samples. However, recent photoluminescence (PL) [3], pressure [4], and theoretical [5, 6] evidence demonstrate that fluctuations in nitrogen content, including the random formation of pairs, triplets and clusters of nitrogen atoms, must be explicitly included for accurate modeling and understanding of these materials.

We present fully atomistic pseudopotential calculations of the evolution of the GaAsN conduction band edge (of primary importance in PL and absorption, and applications) for purely random alloys, and calculations of the energy levels induced by prototype clusters of several nitrogen atoms. Combining these results we present a description of the conduction band edge structure of current grown material that explains many of the experimentally observed phenomena, including enhanced effective mass [7, 8], Stokes shift between emission and absorption, and anomalous pressure dependence [1].

Methodology To study the role of nitrogen in GaAs we use a supercell approach, where substitutional nitrogen atoms are placed in a large supercell. We relax all atomic positions using a valence force field method, and solve the Schrödinger equation for this periodically-repeated supercell using the plane-wave pseudopotential method with high-quality empirical pseudopotentials (EPM). Our method [5, 6] is nearly identical to that of Bellaiche et al. [9], except that we use improved pseudopotentials [10], larger supercells for better statistics, and we analyze our results in greater detail.

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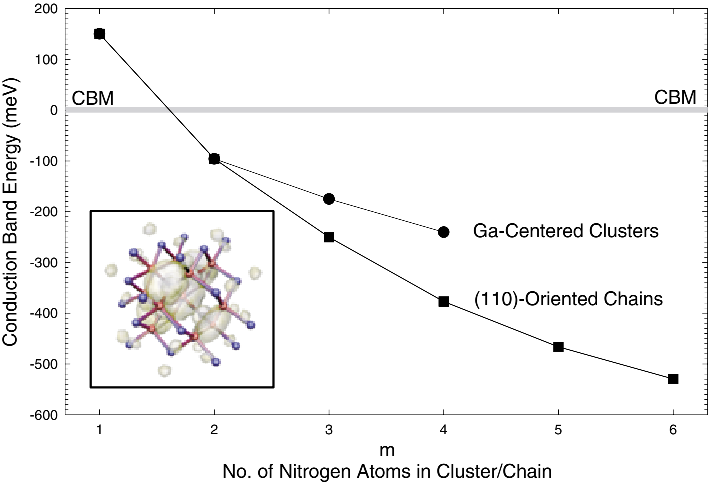

Fig. 1 (colour). Energy levels of Ga-centered nitrogen clusters and (110) directed nitrogen chains in GaAs, calculated in 4096 atom cells. Inset: wave function isosurface of cluster state at an GaN_4 cluster, showing strong nitrogen localization

Properties of Single Nitrogen Impurities and Small Nitrogen Clusters in GaAs The fundamental physics of dilute nitride impurities in GaAs is characterized by the formation of nitrogen localized near band gap CS. Historically, only the $a_1(N)$ level, resonant 150–180 meV above the conduction band minimum (CBM) has been identified [11], but small clusters of nitrogen atoms are expected to create other levels. The CS result from the differences in atomic size and orbital energies between the nitrogen and arsenic atom it substitutes. Our empirical pseudopotential calculated $a_1(N)$ level is at $E_c + 150$ meV and $E_c + 180$ meV for 4096 and 13824 atom cells, respectively, in close agreement with experiment.

To consider the role of small nitrogen aggregates formed during growth, we have considered a number of prototypical clusters: pairs, triplets, clusters of multiple nitrogens around a single gallium, and directed chains of nitrogen atoms [6]. In Fig. 1[2]), we show the calculated energy levels for a Ga-centered tetrahedron with its four vertices occupied by $As_{4-p}N_p$, with $0 \le p \le 4$. Note that $p = 1$ corresponds to an isolated impurity, and $p = 2$ to a first nearest neighbor N–N pair. We see that the levels become deeper as p increases, consistent with the fact that on an absolute scale the CBM of GaN is ~0.5 eV below that of GaAs. The induced CS are highly nitrogen localized, evidenced by the wave function isosurface (inset). We also considered, in Fig. 1, extended [110]-oriented chains of increasing length, motivated by the comparatively deep nature of even a [110]-oriented pair ($p = 2$, above). Consisting of 3, 4, 5 etc. nitrogen atoms we observed that each additional atom in the chain produced successively deeper levels. In general we find that an increased local concentration of nitrogen atoms, of any orientation, induces deep, dipole allowed levels. Small nitrogen aggregates therefore can contribute to below bandgap PL even at low impurity concentrations.

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[2]) Colour figure is published online (www.physica-status-solidi.com).

Evolution of GaAsN Alloy Properties Nitrogen introduces two types of states in the dilute limit: (i) The Perturbed Host states (PHS) residing within the continuum such as $a_1(X_{1c})$, $a_1(L_{1c})$, and $a_1(\Gamma_{1c})$, and (ii) the Cluster States (CS) residing inside (or near) the band gap, e.g. the pair and higher cluster states (Fig. 1). We next address the question of how the PHS and CS evolve as the nitrogen composition increases.

We perform calculations as a function of nitrogen concentration, by randomly distributing up to 20 nitrogen atoms onto the anion sites of GaAs in a 1000 atom supercell, and 13824 atom supercells for convergence checks. We relax the atomic positions and calculate the electronic structure, repeating this for 15 randomly selected configurations at each composition to establish a statistically representative sample. The ensuing energy levels are then collected and analyzed for their degree of localization, by computing for each level ψ_i the distance $R_\alpha^{(i)}$ from the α-th nitrogen site at which 20% of the wave function is enclosed. Through this measure we have classified each level as either "localized" or "quasi-localized". This polymorphous approach describes the evolution of alloy states in an unbiased manner as alloy fluctuations are fully retained: specific CS and PHS are not assumed (e.g. as in isomorphous models [1]).

Figure 2 depicts the spectral dependence of the average localization $\sum_\alpha 1/R_\alpha^{(i)}$ for localized and quasi-localized levels of GaAsN. Panel a shows the resonant localized single-impurity $a_1(N)$ state, located within the conduction band, and selected pair, triplet and quadruplet ($GaAs(N_3)$ and $Ga(N_4)$) cluster states, appearing inside the band gap. These wave functions are highly localized. Panel b shows the more extended per-

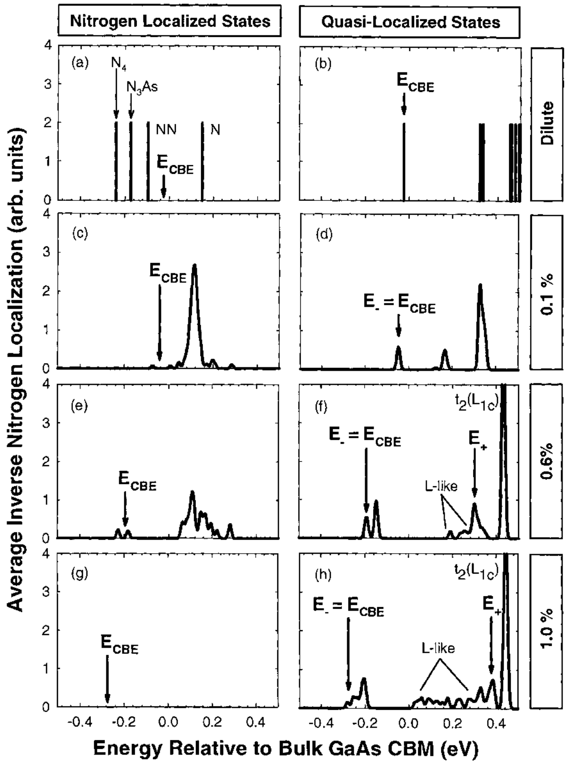

Fig. 2. Spectral dependence of average nitrogen localization for: left panel: nitrogen localized "cluster states" and right panel: quasi-localized "perturbed host states" of GaAsN for selected nitrogen compositions. The vertical arrows show the position of the alloy conduction band edge E_{CBE}

turbed X, L, and Γ host states, and the edge of the conduction band, denoted by the arrow "E_{CBE}" (also called "E_-" [1]). As the nitrogen concentration increases, Figs. 2d, f, h show that the edge E_{CBE} of the conduction band minimum (vertical arrow) moves rapidly to lower energies, due to anti-crossing and repulsion with higher energy members of the PHS. At the same time, the energy of the CS is pinned and remains fixed, as these highly localized states do not strongly interact with each other. Indeed, the wave functions of the CS do not change with composition. At the same time, the $t_2(L_{1c})$ band appears constant in energy, at $E_c + 0.4$ eV, while the upper edge of the PHS (also called "E_+" [1]) appears for $x \sim 0.6\%$ and moves up in energy as x_N increases. This broad band represents mostly delocalized or weakly localized a_1 perturbed host states.

As the edge of the PHS moves rapidly to lower energies ("optical bowing") this broad band of states sweeps past the discrete CS one-by-one. At a critical composition x_c (which depends on the degree of randomness in the samples), the deepest CS is overtaken by the moving PHS. Near x_c, the conduction band minimum is an "amalgamated state" formed from both semi-localized (Fano-resonance like) states and more delocalized states of comparable energy. The duality of semi-localized and delocalized states at the conduction band edge is responsible for many of the anomalous optical properties of dilute nitride alloys, discussed below and elsewhere [5, 6].

Conduction Band Edge Structure By considering our calculated random alloy results in combination with our results for small impurity clusters in the dilute, the current experimental data and conduction band edge structure may be interpreted as follows:

(i) The conduction band edge is formed from the delocalized PHS and some localized CS.

(ii) The low energy side of the band edge is dominated by the low energy CS, while the higher energy end consists of the more extended PHS, resulting in a Stokes shift between emission (from CS) and absorption (into PHS), exciton localization and long exciton lifetimes [12].

(iii) The effective mass at the bottom of the conduction band is enhanced as heavy, non-Γ, character is mixed in.

(iv) The pressure coefficient of the alloy is strongly reduced from the bulk [1], due to the weaker pressure dependence of the localized CS at the band edge, which couple only weakly with the extended PHS [6].

(v) The long, low energy PL tail results from low energy below gap CS, due to clusters of nitrogen atoms. These states are populated in PL by sufficiently mobile excitons finding the low energy CS. The tail CS may be due to [110]-oriented chains, or other energetically unfavorable clusters locked-in during growth. Sufficient concentrations (cross-section) of these states may also be detected in absorption. Optimized annealing of GaAsN samples will therefore give an overall blue-shift of PL and narrowing of the peak, as low-energy but unfavorable clusters are removed.

Conclusion We have presented a polymorphous theory of the evolution of the electronic structure of GaAsN alloys with nitrogen composition. Current GaAsN samples exhibit substantial alloy fluctuations resulting in many below gap cluster states, as evidenced by our calculations and broad PL seen experimentally.

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References

[1] W. Shan et al., Phys. Rev. Lett. **82**, 1221 (1999).
[2] A. Lindsay and E. P. O'Reilly, Solid State Commun. **112**, 443 (1999).
[3] Y. Zhang et al., Phys. Rev. B **63**, 085205 (2001).
[4] M. S. Tsang et al., Appl. Phys. Lett **78**, 3595 (2001).
[5] P. R. C. Kent and A. Zunger, Phys. Rev. Lett. **86**, 2613 (2001).
[6] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).
[7] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **61**, 7479 (2000).
[8] P. N. Hai et al., Appl. Phys. Lett. **77**, 1843 (2000).
[9] L. Bellaiche, S.-H. Wei, and A. Zunger, Phys. Rev. B **56**, 10233 (1997).
[10] T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. B **60**, R11245 (1999).
[11] D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson, in: Proc. 17th Internat. Conf. Physics of Semiconductors, Springer-Verlag, New York 1984 (p. 627).
[12] I. A. Buyanova et al., Appl. Phys. Lett. **75**, 3781 (1999).