Theory of electronic structure evolution in GaAsN and GaPN alloys

P. R. C. Kent and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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Using the empirical pseudopotential method and large atomistically relaxed supercells, we have systematically studied the evolution of the electronic structure of $\mathrm{GaP}_{1\;\;x}\mathrm{N}_x$ and $\mathrm{GaAs}_{1\;\;x}\mathrm{N}_x$, from the dilute nitrogen impurity regime to the nascent nitride alloy. 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 and the ‘‘perturbed host states’’ with increasing nitrogen composition, we propose a new model for low-nitrogen-content $\mathrm{GaAs}_{1\;\;x}\mathrm{N}_x$ and $\mathrm{GaP}_{1\;\;x}\mathrm{N}_x$ alloys: As the nitrogen composition increases, the energy of the CS is pinned while the energy of the PHS plunges down as the nitrogen composition increases. The *impurity limit* ~PHS above CS! is characterized by strongly localized wave functions, low pressure coefficients, and sharp emission lines from the CS. The *amalgamation limit* ~PHS overtake the CS! is characterized by a coexistence of localized states ~leading to high effective mass, exciton localization, Stokes shift in emission versus absorption! overlapping delocalized PHS ~leading to asymmetrically broadened states, low temperature coefficeint, delocalized E band at higher energies!. The *alloy limit* ~PHS well below CS! may not have been reached experimentally, but is predicted to be characterized by conventional extended states. Our theory shows that these alloy systems require a polymorphous description, permitting the coexistence of many different local environments, rather than an isomorphous model that focuses on few impurity-host motifs.

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E_{CBM} 10 ~Refs. 10,9 and 24! or E_{CBM} 80 meV ~Refs. 25–27!. These levels and their associated phonon replica[28] are observed in emission after excitation into higher states. Excitation is then efficiently transferred[29,30] to the deeper pair levels via tunneling ~at low temperatures! or via thermal excitation to the mobile states, followed by hopping into the pair levels ~at higher temperatures!. The pressure coefficients of these pair levels in $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$ @35 50 meV/GPa ~Ref. 10!# are as low as those of the isolated nitrogen, while in $\mathrm{GaP}_{1\ x}\mathrm{N}_x$ they now have *positive* pressure coefficients of ; 10 30 meV/GPa,[12,13] unlike the negative, 14 meV/GPa value characteristic of the GaP CBM or the near zero value for the dilute impurity.[13,12]

~iv! *Redshift between absorption/PLE and emission is observed*. Already at a concentration of 0.05-0.1 % nitrogen in GaAs, the emission lines are redshifted with respect to absorption.[31] At higher concentrations the shift increases in energy,[32,25] in contrast with high structural quality random, direct-gap III-V alloys, where absorption and emission occur at the same energy.

As the concentration of nitrogen increases further, one observes the following.

~v! *Composition pinning of the impurity pair energy levels is seen*. The sharp emission lines from the pair levels remain initially at a fixed energy as the nitrogen composition increases both in GaP:N ~Ref. 33! and in GaAs:N @0.05-0.1 %
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behaviors. One observes *homogeneous*, bulklike characteristics, such as band-gap bowing, resonances within the con-

TABLE I. The relative anion-cation bond lengths around isolated nitrogen and nearest neighbor ~NN! nitrogen pairs in GaAs and GaP, obtained in relaxed LDA and VFF calculations. Bond lengths are expressed in fractions of the ideal bulk GaN bond length. For the nearest-neighbor ~110!-oriented pair, the 8 bonds are categorized in three symmetry distinct types: ~a! ~001! directed bonds (-4), ~b! ~110!-directed bonds (-2) sharing a common Ga atom, and ~c! the remaining ~110! directed bonds (-2).

System		Cell Size	Method	Relative bond length Bond ~a!	Bond ~b!	Bond ~c!
Ga$\underline{As}$:N	Isolated	64	LDA	1.062		
			VFF	1.045		
	NN pair	64	LDA	1.040	1.091	1.065
			VFF	1.047	1.070	1.060
Ga$\underline{P}$:N	Isolated	64	LDA	1.052		
			VFF	1.041		
	NN pair	64	LDA	1.049	1.085	1.067
			VFF	1.042	1.061	1.054

being random.[33] This was not the case. However, the cluster states in these previous works were not analyzed in detail.

In this paper we describe theoretically how the naturally occurring nitrogen pairs and clusters affects the electronic structure of $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ alloys as a function of nitrogen concentration. By considering both the ‘‘perturbed host states’’ and nitrogen-related ‘‘cluster states,’’ we explain, at least qualitatively, the experimental anomalies outlined above, centering on the duality of bulklike and localization phenomena in these alloys.

We begin by describing our methods in Sec. III. In Sec. IV we present our results for the isolated nitrogen impurity, whereas in Sec. V we present our results for nitrogen pairs and clusters. We identify several of the ‘‘nitrogen pair’’ lines observed in photoluminescence, and also identify the ‘‘NC’’ ~Ref. 33! triplet level recently observed in $GaP_{1-x}N_x$.[33] Interestingly, @110# chains of nitrogen atoms form particularly localized and deep ‘‘chain states.’’ In Sec. VI we consider the evolution of the conduction-band edge and nitrogen-related states with increasing nitrogen concentration. We find that ~i! unlike the suggestions of Refs. 33,39 the nitrogen cluster states inside the band gap do not interact sufficiently so as to broaden and form a conduction state made of a superposition of such nitrogen-induced states. Instead, we find the delocalized ‘‘perturbed host states’’ descend into the fundamental band gap, and overtake the cluster states one by one. ~ii! Once overtaken, the conduction-band edge exhibits *alloy fluctuations*, consisting at low energy of a broad amalgamation of Fano-resonance-like localized cluster states and, at higher energy, the delocalized perturbed host states. The low-energy side of the band edge is dominated by the just swept-in CS, while the higher-energy end consists of the more extended PHS. This localized-delocalized duality in the band edge leads to exciton localization in the tail states, the Stokes shift between absorption ~into PHS! and emission ~from CS!, an anomalous pressure dependence, and strongly modified temperature dependence of the alloy. This behavior is distinct from conventioanl isolavent III-V alloys that lack cluster states in the gap and have much weaker interband coupling within the perturbed host states.

III. METHOD

To study the role of nitrogen in GaP and GaAs we we use a supercell approach, where one or more substitutional nitrogen atoms are placed in a large supercell. We relax all atomic positions, and solve the Schrödinger equation for this periodically repeated supercell using the plane-wave pseudopotential method with high-quality empirically corrected pseudopotentials ~EPM!. Our method is nearly identical to that of Bellaiche *et al.*[58] We use improved pseudopotentials,[66,62] larger supercells for better statistics, and we analyze our results in greater detail.

To study *isolated* nitrogen we place a single nitrogen in the supercell, whereas to study *interacting* nitrogens we keep the supercell size fixed and add a varying number of nitrogens to the supercell.[58,64,64,65] By modeling nitride alloys with *many* nitrogens in a large supercell, we allow for symmetry breaking, relaxation, and multiband coupling not included in simpler models[67] using a *single* nitrogen atom in a smaller supercell. In fact, accurate modeling of the very low nitrogen concentrations where impurity physics dominates $(x_N < 0.1\%)$ requires the use of large supercells ~e.g., 13 824 atoms for 0.015%; see below! that are not accessible to current first-principles methods, such as density-functional theory. Indeed, we find that the strain field resulting from the large atomic relaxation ~reflecting ; 20% size mismatch between N and As! propagates to long distances, so small supercells are inappropriate. However, for isolated impurities the cell-size does not need to correspond to the physical concentration $x \to 0$. All that is needed in this limit is to avoid wave function overlap. Furthermore, large supercells are needed to study large impurity clusters. The atomic positions within each supercell are relaxed, at the appropriate Vegard's lattice constant, using the valence force-field method[68] and a conjugate gradient minimization of the total strain energy. The atomic positions obtained from this model, using the force-field parameters of Ref. 63 agree with bond lengths and positions obtained from our LDA calculations in 64-atom cells to within 1%. This is illustrated in Table I.

To obtain the electronic properties of each system at the relaxed positions we solve the Schrödinger equation

$$\left[\quad \frac{1}{2}\,„^{2} \quad \Big(_{a,m}\, v_{a}\text{~}\mathbf{r} \quad \mathbf{R}_{a,m}! \right] c_{i}\text{~}\mathbf{r}! \quad e_{i}\, c_{i}\text{~}\mathbf{r}!, \qquad \text{~4!}$$

where a denotes atomic species, m runs over atoms, v_{a} are the screened empirical pseudopotentials, and $\mathbf{R}_{a,m}$ are the atomic positions. Because of the local-density approximation ~LDA! error in the band gap and the need to accurately reproduce measured band gaps, combined with the use of large supercells, we have adopted an alternative approach to LDA, utilizing in Eq. ~4! the empirical pseudopotential v_{a}. We represent the wave functions, c, using a plane-wave basis set.

The total supercell potential $V(\mathbf{r})$ is written as a superposition of species and strain-dependent local pseudopotentials v_{a}. The pseudopotentials are fitted to reproduce the bulk formed from *many* high-energy host bands, are denoted here $a_1(N)$. Figure 1 depicts schematically the a_1-symmetric nitrogen-perturbed states.

All states of the same symmetry representation interact under the impurity perturbation potential, DV_{tot}, which consists of the following. ~i! The difference in host-impurity screened potential DV_{chem}: A good qualitative measure of DV_{chem} is the ‘‘natural’’ band offset,[77] for example, the CBM of GaN lies ; 0.3 eV below that of GaAs and ; 0.6 eV below GaP. ~ii! The perturbation due to atomic displacement DV_{rel}: This second perturbation is expected to be substantial due to the lattice-constant mismatch between GaN and GaP ~GaAs!. The total perturbation DV_{tot} mixes *all* a_1 states ~thus, mixes G_{1c} X_{1c} L_{1c}

teractions within clusters, observed particularly for @110# clusters in GaAs:N,[10] which will be discussed in Sec. V C. Figures 3~b

a_1-symmetric states. This state appears *below* the CBM ~‘‘gap level’’! whereas in GaAs the impurity level is *above* the CBM ~‘‘resonant level’’!. Transitions to the lowest conduction state in both materials, whether delocalized or impuritylike, are dipole allowed from the valence-bnad maximum ~VBM! ~‘‘direct gap’’!. In smaller GaP supercells (<512 atoms! another band, with more L_{1c} character plunges down and becomes the conduction-band minimum. This state descends rapidly in energy with decreasing cell size, crossing the

description of nitrogen impurities @related to the zero-momentum screened potential $V(\mathbf{G}) \quad 0]$ was not recognized. Early practitioners[87,71,88] found pathologically deep nitrogen levels (; 1 eV in Ref. 87!, failing to properly align the “GaN” with the “GaP” potentials. A correct alignment explains the level order.

E. Can a two-level model capture the qualitative physics of the a_1 electron states for isolated nitrogen in dilute GaP:N or GaAs:N?

Hjalmarson *et al.*[88] noted in their tight-binding model only a single $a_1(N)$-type level and its corresponding t_2 level ~compare, however Fig. 2!. Wolford *et al.*[7] also discussed for GaAs:N the $a_1(N)$ and a_1^{G} levels. Following these works, Shan *et al.*[51] advanced a two-level model for the electron states of the $\mathrm{GaAs}_{1 \quad x}\mathrm{N}_x$ alloy, consisting of both of these turbed host states ~in the absence of gap levels! was discussed previously in detail[16−20] as these are common to conventional semiconductor alloys. There are three contribution at play for random alloys.

~i! *Volume deformation*, which represents changes in the band gaps of the *constituents* GaAs and GaN that are compressed and dilated, respectively, from their natural lattice constants to the intermediate alloy value $a(x)$. This deformation raises the band gap of GaAs and reduces the band gap of GaN.

~ii! *Charge exchange*, which represents the change in the band gap upon bringing together the constituents, already prepared at $a(x)$, without yet permitting any sublattice relaxation. This term includes charge-transfer effects that result from band mixing in an ideal, unrelaxed lattice. This term is particularly large in mixed-anion nitride alloys.

~iii! *Structural relaxation* represents the change in band gap due to sublattice relaxation at fixed $a(x)$. This term includes atomic-relaxation-induced band mixing. In mixed-anion alloys such as $\mathrm{GaP}_{1\ x}\mathrm{N}_x$, the major relaxation occurs in the *cation* sublattice; this couples primarily the cation-localized conduction states, causing the lowest to move to yet lower energies ~bowing!. In mixed-cation alloys, such as InGaN, the major relaxation occurs in the *anion* sublattice, which couples primarily the anion-localized valence bands,causing the highest to move to yet higher energies. Structural relaxation thus contributes to bowing in all alloys having common atoms; the effect is proportional to the size mismatch between the disimilar atoms. The effect is particularly strongly due to large cation displacement[58] in $\mathrm{GaP}_{1\ x}\mathrm{N}_x$ and $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$. We conclude that mixed-anion nitride alloys have a large bowing even in the absence of cluster states because of relaxation-mediated band coupling, not nitrogen-nitrogen wave-function overlap.[39]

To see the dependence of bowing on concentration, we note that according to Eq. ~1! ~that applies only to conventional alloys! at the $x \ll 1$ dilute limit, the band-gap change $\mathrm{D}E_g(x)$ scales as $\ \ bx$, i.e., linearly with nitrogen concentration. Fitting our calculated $\mathrm{D}E_g(x)$ for the case that has no clusters ~one nitrogen per supercell! to $\mathrm{D}E_g \} x^{a}$ for $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$ gives $a\ \ 0.76$ using our EPM calculations and $a\ \ 0.76$ for the LDA data of Ref. 78. We see that bowing in cluster-free $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$ is already *anomalous* $(a\ \ 1)$, and pairs or other clusters are not needed to produce $a \ll 1$ in contrast with recent suggestions.[90] This result is due to the additional coupling between the $a_1^{GL}(1)$ CBM and the $a_1^{N}(2)$ impurity state present in $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$ but not in normal alloys, e.g., $\mathrm{GaAs}_x\mathrm{P}_{1\ x}$. In fact, when cluster states are available in the band gap below the PHS, we find *slower bowing* with $a\ \ 0.66$ ~Sec. VII B!, rather than $a\ \ 0.76$; thus clusters *reduce* bowing.

G. Does atomic relaxation make the isolated impurity level shallower?

Early calculations[87] of substitutional N in GaP first produced very deep gap levels, ;1 eV from the CBM. Phillips argued[91] that this overestimation of the binding energy is due to the neglect of atomic relaxation that will render the level *shallower*. Jaros and Brand[71] states $a_1(N)$ and perturbed host states that lead to bowing. In GaAs:N the $a_1(N)$ state is a resonance level above the CBM, whereas in GaP, with its ; 0.3 eV higher CBM, this level appears inside the band gap. Those $a_1(N)$ levels are characterized by anomalously small pressure coefficients, since they are constructed from the interference of many host bands, not just band-edge states. The lowest perturbed host state ~the CBM! is repelled downwards by the other perturbed host states *above* it @not just by $a_1(N)$ ~Refs. 51 and 54!#. This leads to strong alloy bowing and renders $\mathrm{GaP}_{1\;x}\mathrm{N}_x$ ‘‘direct gap’’ by mixing-in G character. ‘‘Cluster states’’ within the gap reduce this bowing.

V. RESULTS: NITROGEN-NITROGEN PAIRS AND HIGHER-ORDER CLUSTERS

Random statistics causes some of the substitu0e7.9(substiESUL)91.tu0e7.9niLN

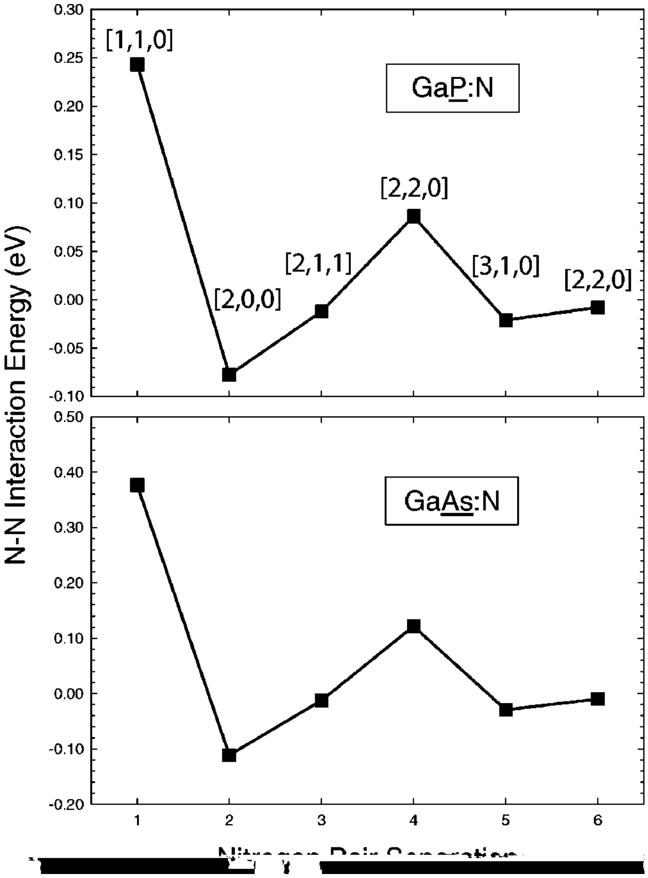

FIG. 11. N-N pair interaction energies for Ga$\underline{\text{P}}$:N calculated using the valence force field method.

A. Energetics of clustering tendencies in N-N pairs

We first ask whether a pair of inifinitely separated ($m \rightarrow$ ‘) nitrogen atoms in GaAs or GaP tend to attract or repel each other. We thus estimate the strain energy of mth-neighbor N-N pairs with respect to the energy of a well-separated ($m \rightarrow$ ‘) pair by calculating the interaction energy

$$\mathrm{D}E^{(m)} \quad E\text{~}\mathrm{Ga\underline{P}{:}N}_2^{(m)}! \quad E\text{~GaP}! \quad 2E\text{~}\mathrm{Ga\underline{P}{:}N}!. \qquad \text{~8!}$$

Figure 11 shows $\mathrm{D}E^{(m)}$ from valence force field ~VFF! calculations for a large ~13 824-atom! cell, where the energies are converged. The lattice constant is taken at the Vegard value. We see that the m 2 and m 5 pairs have an attractive strain energy, whereas m 1 and m 4 are strongly repulsive. Although the VFF Hamiltonian excludes the charge-transfer terms necessary to model the rebonding around near-neighbor nitrogen atoms, this data suggests that pair formation is energetically favored clearly for at least for ~100!-oriented first neighbors.

To test these conclusions we have also performed LDA calculations with a small 64-atom cell. In GaP, we find that formation of m 2 and m 3 pairs is energetically favored ($\mathrm{D}E^{(m)}$ is negative, by 147 and 172 meV, respectively!, while m 1 pairs are unfavorable by 18 meV. In GaAs we find that only m 2 pairs are favorable. As our small LDA supercell is unable to contain the long-range lattice relaxation expected for pairs, we predict that LDA calculations in larger supercells will find pair formation increasingly favorable due to the strain relief around the impurity sites.

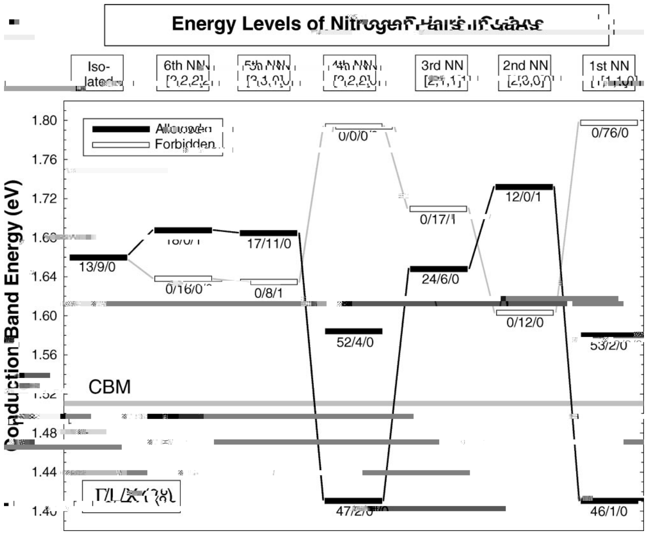

FIG. 12. The energy levels of isolated N and N-N pairs in GaAs. The legend indicates orientation ~e.g., @1,1,0#! with respect to one nitrogen at the origin. The allowed ~solid bar! or forbidden nature ~hollow bar! of transitions to the valence band is indicated and the G, *L*, *X* character of each state is shown, computed using the spectral decomposition of Ref. 70.

The attractiveness of the strain interaction for the ~100!-oriented (m 2) impurity pair is a general feature of the zinc-blende lattice ~e.g. it was found[94] for As-As pairs in cubic GaN!. Recent scanning tunneling microscopy measurements by McKay *et al.*[95] on 1.7% nitrogen in GaAs revealed that ~001!-oriented first neighbors (m 2) have a concentration that exceeds the expectations of random statistics. Both experiment and bulk calculation indicate that the distribution of other pairs is close to random statistics. Surface effects[96,97] that are important during vapor-phase growth could change this picture. We conclude that ~110!-oriented pairs are less favorable than random statistics wheras ~001! pairs are more favored, but all other pairs exist randomly.

B. N-N pair energy levels and wave functions: Cluster states

Figures 12 and 13 show the calculated energy levels of N-N pairs, in GaAs and GaP, respectively ~cell size 4096 atoms!. While Fig. 14 shows isosurface plots of the lowest-energy wave function of pairs in GaP ~wave functions of nitrogen pairs in GaAs are visually similar!. Figure 14~a! shows the nitrogen localized isolated impurity level, $a_1^{\mathrm{N}}(1)$ for reference @see also Fig. 4~a!#.

Our results show that the interaction of pair nitrogens results in the formation of a series of “bonding” and “antibonding” states, as expected by the interaction of isolated impurity levels. We have classified the levels as either dipole allowed ~from the VBM! or dipole forbidden according to the computed degree of G character in the wave functions.[58] Allowed states are shown as black bars in Figs. 12 and 13. Relaxation of atomic positions, neglected in previous calculations,[87,79] can greatly change the oscillator strengths of certain transitions: for example, the unrelaxed isolated nitrogen in GaP has negligible G character ~almost forbidden!, but gains G character ~strongly allowed!

currently grown high-nitrogen-content samples[102,33,103] may be due to short chains of nitrogen atoms or similar nitrogen aggregates. Note that the @110# chain states are deeper than Ga-centered clusters for three and four nitrogen atoms ~Fig. 16! due to the large uniaxial strains along the chains.

Figure 18 shows the lowest-energy wave functions for the different cluster and chain geometries considered in GaP. Figures 18~a!–18~d! depict the wave functions of $\mathrm{Ga(P}_{4\ \ p}\mathrm{N}_p)$ clusters, showing the strong localization around the central Ga atom due to the formation of a GaN-like region. Figures 18~e!–18~h! depict the @110#-axis localization resulting from @110# nitrogen chains.

Recent photoluminescence measurements of $\mathrm{GaP}_{1\ \ x}\mathrm{N}_x$ alloys have indicated the present deeper levels in samples with $x_N > 0.43\%$.[33] The data show the presence of a new deep level ~labeled ''NC'' in Ref. 33 at 2.071 eV, which is deeper than both the calculated nitrogen pair and Ga-centered cluster levels!. Figure 16 shows that this observed center might be the three-membered @110# chain depicted in Fig. 15~c! ~which can also be thought of as two first-neighbor pairs!. This structure introduces a single gap level, calculated at ; 2.059 eV, in good agreement with the experimental data. We therefore tentatively identify the NC level[33] as an @110#-oriented triplet of C_{2v} symmetry.

D. Summary of results on nitrogen clusters

Random incorporation of N in III-V compounds leads to the formation of nitrogen pairs and higher clusters. ~001! pairs are energetically most favorable, wheras ~110! pairs are least favorable. The pairs introduce levels in the gap whose energy varies nonmonotonically with pair separation. The deepest states are the ~110!-oriented pairs. When these pairs form into ~110!-oriented chains, deeper levels result, reflecting highly-localized due to interactions along the clocse-packed ~110! chains of the zinc-blende structure. For comparison, chains of In in GaAs do not form localized levels. The levels introduced by chains are highly localized, have low pressure coefficients, and are connected to the VBM by dipole-allowed ~direct! transitions.

We offer particular clusters as tentative models for observed deep PL by Zhang *et al.*[33] and by Gil and Mariette,[101] but the complexity of the predicted pair, chain and higher cluster states for higher nitrogen concentrations precludes any definitive assignment of the many observed PL lines. The reasons that contribute to differences between our calculated energy levels and the experimental energies include a lack of electronic relaxation upon excitation, and a lack of many-body corrections to the single-particle energies. Despite this, the EPM gives a correct overall account, with the isolated impurity shallowest, pairs deeper, and ~yet unmeasured! clusters deeper still.

VI. RESULTS: ALLOY PROPERTIES

A. Why is the alloy valence band maximum split?

The foregoing discussion indicates that the introduction of a single N-N pair or N-N-N-triplet in a zinc-blende lattice lowers the global symmetry. Hence, symmetry-mandated degeneracies of the zinc-blende structure will be removed. It-292.9(Inl.6(str nitude of the splitting sharply increases due to the increased probability of cluster formation in the nascent alloy. The fluctuations in the splittings increase concomitantly ~evidenced by larger statistical spread compared to low concentrations! reflecting the strong dependence on pair, triplet, and cluster orientation within the alloy. The strong fluctuations observed here will be reflected in actual $\mathrm{GaAs}_{1\ x}\mathrm{N}_x$ samples: measured valence-band splittings will be strongly affected by the degree of clustering and short-range order within each sample. Orientational averaging over pairs is expected to broaden these features and eventually average them out.

The clustering-induced splitting D_{CS} at the valence-band maximum results from lifting of the cubic symmetry of GaAs by the nitrogen clusters in the film. This source of splitting should be distinguished from the film/substrate mismatch strain effects D_e, proportional to the misfit strain $e_\perp$

$(a_{\mathrm{GaAs}} \quad a_{\mathrm{GaAs}_{1\ x}\mathrm{N}_x}$

functions, the primary interaction could be between CS and PHS. To decide between these possibilities one needs to know the localization of the relevant wave functions. Since the CS are manifestly nonhydrogenic centers ~i.e., their wave function mixes bands throughout the Brillouin zone!, we can not estimate their spatial extent of the wave function from simple effective-mass formulas involving a single band, but a full calculation is needed. This is our next task.

We perform calculations as a function of nitrogen concentration, by randomly distributing up to 20 nitrogen atoms onto the anion sites of GaP and GaAs of a 1000-atom supercell ~i.e., x_{N} 4%). 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 c_i the distance $R_a^{(i)}$ from the ath nitrogen site at which 20% of the wave function is enclosed. Through this measure we have classified each level as either ''localized'' or ''quasilocalized'' for ~CS! and PHS, respectively.

1. *Evolution of alloy states in GaP$_{1-x}$N$_x$*

Figure 19 depicts the spectral dependence of the average localization ($_a$(1/$R_a^{(i)}$) for localized and quasilocalized levels of GaP$_1$ $_x$N$_x$. Panel ~a! shows the localized single-impurity a_1(N) state, selected pair, and triplet and quadruplet @GaP(N$_3$) and Ga(N$_4$)] cluster states, appearing inside the band gap. These wave functions are highly localized. Pannel b shows the more extended perturbed X, L, and G host states, and the edge of the conduction band, denoted by the bold arrow ''E_{CBE}.'' As the nitrogen concentration increases, Figs. 19~d,f,h,j! show that the edge E_{CBE} of the conduction-band minimum ~vertical heavy arrow! moves rapidly to lower energies, due to anticrossing and repulsion with higher-energy members of the PHS. At the same time, the energy of the CS are pinned and remain fixed, as these highly localized states do not strongly interact with each other. Indeed the wave function of the CS do not change with composition. 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 @Fig. 20~b!# from both semilocalized ~Fano-resonance-like! states ~shown in red isosurfaces! and more delocalized parts ~shown as green isosurfaces!. As we will see below, this duality in the amalgamated state can lead to unusual physical effects. For higher nitrogen concentrations exceeding x_c @Fig. 19~g!#, the CS are well inside the conduction band, and the states near the edge are more extended @Fig. 20~c!#.

as x_{N}

2. *Evolution of alloy states in GaAs$_{1-x}$N$_x$*

Figure 21 shows the evolution of the GaAs$_1$ $_x$N$_x$ states as a function of composition. We see that as the conduction band edge ~CBE, also called ''E ''! plunges *down in energy*

ized states $(\mathtt{G},L)$ are mixed into the localized states. For GaP$_{1\ \ x}$N$_{x}$, the band gap pressure coefficient is no longer weak $(\ ;0)$ as in the isolated impurity case, but is strongly positive. In GaAs$_{1\ \ x}$N$_{x}$ we observe in this composition range the development of a broad E band that shifts up with composition while the $t_2(L_{1c})$ states is fixed.

~c! *The high concentration $x\ \ \ x_c$ limit*: While electronic structure calculations can be made in this concentration limit, in practice, actual limitations in nitrogen solubility in III-V compounds prohibit one from getting stable homogeneous samples. The properties of experimental samples in this limit are critically determined by the degree of clustering or phase decomposition. It is interesting to consider what the electronic properties in this regime would be. Assuming a continued random distribution of nitrogen, our calculations pre-

GaP, GaAs, InP, and InAs. Conversely, since the electron mass of InAs is exceedingly light $(0.02 m_e)$, only a very large host material conduction-band barrier could lead to localization in InAs-dilute alloys. Thus alloys with InAs tend to have only extended states.

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