Theory of conduction band structure of $\text{In}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{Sb}_{1-x}$ dilute nitride alloys

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The dependence of the optical band gap of $\text{In}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{Sb}_{1-x}$ on nitrogen content has been calculated using an sp^3s^* tight-binding Hamiltonian in large supercell calculations that explicitly include the effects of allowing a random distribution of nitrogen atoms. We calculate for InNSb that the energy levels associated with nitrogen complexes consisting of two or three atoms mostly lie above the InNSb conduction band edge (CBE). The steady reduction in the band gap of InNSb with increasing N composition is then well described using a two-level band-anticrossing model. The calculated effective mass of electrons in InNSb also smoothly decreases with composition, as predicted by the band-anticrossing model, due to the steady closure of the band gap and weak mixing with the N states. For GaNSb the situation is dramatic: the band gap and optical properties are shown to be strongly affected and highly sensitive to the distribution of the nitrogen atoms. We find that there is a wide distribution of N levels lying close to and below the CBE. The higher-lying N states push the CBE down in energy, as in GaAs, but the large number of lower-energy N states mix in strongly with the conduction band edge states, severely disrupting the band edge dispersion in GaNSb.

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I. INTRODUCTION

The electronic structure of dilute nitride alloys such as $\text{Ga}_x\text{As}_{1-x}$ and $\text{Ga}_x\text{P}_{1-x}$ has attracted considerable interest, both from a fundamental perspective, and also because of their potential device applications.¹ Replacing a small fraction of P atoms by N introduces a series of N-related defect states into the band gap of GaP, below the conduction band minimum. By contrast, when a small fraction of As atoms are replaced by N in GaAs, the energy gap initially decreases rapidly. This has been attributed to a band-anticrossing (BAC) interaction between the host matrix conduction band edge (CBE) and N-related defect levels above the CBE.² To date, most interest has focused on dilute nitride arsenide and phosphide alloys, with comparatively little analysis undertaken of the dilute nitride antimonide alloys, $\text{In}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{Sb}_{1-x}$.

InSb has the smallest energy gap of any III-V semiconductor, and it has been proposed³ and demonstrated⁴ that the addition of N to form InNSb can give a zero-gap semiconductor. GaNSb is also being considered as a potential emitter for wavelengths both at and beyond the 1.5 μm telecommunication range.⁵ We use the tight-binding method we have previously established for GaNAs (Ref. 6) and GaNP (Ref. 7) to investigate here the band structure of dilute $\text{In}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{Sb}_{1-x}$ alloys. It is well established that N-related defect states are found below the lower of the X - and L -related conduction band levels in GaAs, InAs, and GaP. We show here that this is also the case in InSb and GaSb. Because there is a large separation between these levels and the Γ conduction band minimum in InSb, we find that the N-related defect levels tend to be well above the CBE in InNSb. A comparison to the tight-binding calculations presented here shows that the two-level BAC model initially introduced to describe the band gap variation in GaNAs

gives a good description of the dependence both of the energy gap and of the conduction band dispersion on N composition in InNSb. By contrast, the lowest X - and L -related conduction band states are closer to the Γ conduction band minimum in GaSb than is the case in any of GaAs, InAs, or InSb. Our calculations show that the band structure of GaNSb is intermediate between that of GaAs and GaP. We find that N-related defect levels occur both above and below the CBE in GaSb: the large number of lower-energy N states lead to a strongly disordered band structure close to the CBE in GaNSb.

The paper is organized as follows. The sp^3s^* tight-binding Hamiltonian which we use is described in Sec. II, with the main results then presented in Sec. III. Because disorder plays such an important role, we present 1728-atom supercell calculations, investigating the lowest conduction band states both as a function of increasing N composition [$0\% < x < 1.7\%$ (3.8%) for InSb (GaSb)] and also as a function of increasing short range correlations in the N distribution. We find for InSb that such correlations have relatively little effect on the conduction band minimum, but that the assumed distribution of N atoms strongly influences the results of the GaNSb supercell calculations. We then discuss the consequences of our calculations for randomly disordered InNSb and GaNSb alloys, with the summary and conclusions of our work presented in Sec. IV.

II. DETAILS OF TIGHT-BINDING MODEL

To investigate the electronic structure of various alloy structures, we use an sp^3s^* nearest-neighbor tight-binding (TB) Hamiltonian which takes explicit account of the immediate environment. We conduct our calculations on supercells, in which all atomic positions have been relaxed to their

TABLE I. Energies (in eV) of the sp^3s^* tight-binding parameters used for bulk InSb, InN, GaSb, and GaN for $T=0$ K. For the two In-related compounds, the zero of energy is set at the valence band maximum of InSb, while the valence band maximum of InN is assumed to lie below that of InSb by 2.83 eV (Refs. 12, 16, and 17). For the two Ga-related compounds, the zero of energy is set at the valence band maximum of GaSb, with the valence band maximum of GaN set to lie below that of GaSb by 2.95 eV (Refs. 12 and 16). The different types of interaction are given using the notation of Ref. 18.

	InSb	InN	GaSb	GaN
E_s^a	-8.0157	-15.6706	-7.3207	-15.2806
E_s^c	-3.4643	-3.2094	-3.8993	-3.9494
E_p^a	0.6738	-0.6018	0.8554	-0.2303
E_p^c	2.9162	5.4418	2.9146	5.6303
E_{s*}^a	6.4530	9.3700	6.6354	9.2500
E_{s*}^c	5.9362	9.3700	5.9846	9.2500
$ss\sigma$	-1.3798	-1.5501	-1.5392	-2.0700
$s_ap_c\sigma$	1.6403	0.7974	2.1478	2.0717
$s_cp_a\sigma$	1.9875	2.5956	2.0211	3.0593
$pp\sigma$	2.2885	4.5382	2.4590	5.0530
$pp\pi$	-0.6186	-0.6592	-0.6374	-0.7150
$s_a^*p_c\sigma$	1.5444	0.4898	2.1605	1.5442
$s_c^*p_a\sigma$	1.4743	2.3295	1.8264	2.8375

equilibrium values using the GULP molecular relaxation package⁸ and a parametrized valence force field model,^{9,10} while using Végard's law to vary the unit cell basis vectors as $a(x) = xa_{\text{InN}} + (1-x)a_{\text{GaSb}}$ ($X=\text{In, Ga}$). In this model, we used the Keating⁹ bond-stretching (α) and bond-bending (β) force constants of Ref. 10 for InSb ($\alpha=29.61$ N/m and $\beta=4.77$ N/m) and GaSb ($\alpha=33.16$ N/m and $\beta=7.22$ N/m) and of Ref. 11 for InN ($\alpha=79.20$ N/m and $\beta=7.10$ N/m) and GaN ($\alpha=96.30$ N/m and $\beta=14.80$ N/m). For the N-III-Sb three-body bond-bending terms, we simply take the average of the two relevant values of β . Previous work on GaAsN has shown that the relaxed bond lengths calculated using this approach are in good agreement with those obtained from *ab initio* calculations.¹² The on-site orbital energies for each atom are determined by taking an average of

TABLE II. Calculated indices $n_{\alpha\beta}$ that describe the distance dependence of the interatomic interactions between orbital α and orbital β on neighboring atoms.

$n_{\alpha\beta}$	InSb	InN	GaSb	GaN
$ss\sigma$	3.66	2.81	3.66	2.91
$s_ap_c\sigma$	4.08	3.00	4.08	3.00
$s_cp_a\sigma$	4.09	4.58	4.09	4.58
$pp\sigma$	2.20	2.09	2.20	2.09
$pp\pi$	3.24	3.72	3.24	3.72
$s_a^*p_c\sigma$	4.20	3.00	4.20	4.00
$s_c^*p_a\sigma$	7.20	6.20	7.20	6.20

the corresponding value in each binary compound made up by the given atom and its four nearest neighbors, with a further minor adjustment due to changes in the next-nearest-neighbor shell. For the interatomic interaction energies, we take the values for the two atoms in the equivalent binary compound and adjust for lattice distortion: the interaction energies are assumed to vary as $(d_0/d)^n$, where d_0 is the equilibrium bond length in the binary compound, d is the bond length after relaxation in the alloy, and n is a scaling exponent, which can take a different value for each type of orbital combination. The effects of changes in bond angle are taken into account by using the two-center integral expressions of Slater and Koster.¹³ The scaling indices are determined by fitting the bond length dependence of the InSb, InN, GaSb, and GaN nearest-neighbor interaction parameters to a range of their respective hydrostatic deformation potentials.⁶ The self-energy and interatomic interaction parameters used in the model are taken from Vogl¹⁴ in the case of InSb and GaSb, while those for InN and GaN were derived by fitting to data from pseudopotential band structure calculations of the zincblende structures.^{12,15}

Table I lists the tight-binding parameters used for the binary compounds, while Table II shows the calculated indices $n_{\alpha\beta}$ used to describe the distance dependence of the interatomic interactions between orbitals α and β on neighboring atoms. Table III compares the band gap deformation potentials calculated using the indices in Table II with literature values for the deformation potentials.

TABLE III. Calculated band gap hydrostatic deformation potentials a_g (in eV) and absolute valence band hydrostatic deformation potential $a(\Gamma_{15v})$ (in eV), using the parameters in Table I and Table II (values with no superscript). Results from other sources (reference denoted by superscript) are given for comparison.

a_g	InSb	InN	GaSb	GaN
$\Gamma_{1c}-\Gamma_{15v}$	-6.7, -6.5 ^a	-5.8, -3.9, ^a -5.0, ^b -5.0, ^c -2.3 ^d	-7.8, -8.1 ^e	-8.7, -7.0, ^f -7.1, ^f -8.0, ^b -8.6 ^c
$L_{1c}-\Gamma_{15v}$	-2.3, -2.2 ^a	-4.1, -5.2, ^a -5.4 ^d	-2.6, -2.8 ^e	-4.5, -4.8, ^f -7.4 ^f
$X_{1c}-\Gamma_{15v}$	1.7, 1.7 ^a	-3.0, -0.9, ^a -0.1 ^d	1.8, 0.8 ^e	-0.84, 0.42, ^f -0.42 ^f
$a(\Gamma_{15v})$	0.36, 0.36 ^g	1.7, 1.7 ^b	0.48, 0.79 ^g	2.0, 2.0 ^b

^aReference 19.

^bReference 20.

^cReference 21.

^dReference 22.

^eReference 24.

^fReference 12.

^gReference 16.

FIG. 1. Geometries of elementary nitrogen complexes introduced in Figs. 2 and 3 and referred to in the text and in Table IV. N atoms are indicated by the black solid points.

III. RESULTS AND DISCUSSION

The two-level BAC model explained the extreme band gap bowing observed in $\text{GaN}_x\text{As}_{1-x}$ in terms of an interaction between two levels: one at energy E_c associated with the extended CBE state ψ_{c0} of the GaAs matrix and the other at energy E_N associated with the localized N impurity states ψ_N , with the two states linked by a matrix element V_{Nc} describing the interaction between them.² The CBE energy E_- of $\text{GaN}_x\text{As}_{1-x}$ is then given by the lower eigenvalue of the determinant

$$\begin{vmatrix} E_N - E & V_{Nc} \\ V_{Nc} & E_c - E \end{vmatrix}, \quad (1)$$

with the magnitude of the interaction matrix element varying with N composition x as $x^{1/2}$, $V_{Nc} = \beta x^{1/2}$. In this model, the interaction matrix element V_{Nc} mixes N-like character into the CBE level and also mixes CBE Γ character into a higher-lying state E_+ , with the energies of the states E_- and E_+ then given by

$$E_{\pm} = \frac{E_N + E_c}{2} \pm \sqrt{\left(\frac{E_N - E_c}{2}\right)^2 + V_{Nc}^2}, \quad (2)$$

and with the alloy CBE wave function given by $\psi_- = \alpha_c \psi_{c0} + \alpha_N \psi_N$, where $\alpha_c^2 + \alpha_N^2 = 1$.

The fractional Γ character $f_{\Gamma} = \alpha_c^2$ of the E_- state provides a useful measure of how much the N-related states perturb the CBE wave function.²³ From the $\mathbf{k} \cdot \mathbf{p}$ method, the effective mass at the CBE increases with increasing energy gap and is inversely proportional to the modulus squared of the momentum matrix element linking the CBE state with the valence band zone center states. Mixing N character into the E_- state reduces this matrix element, and the alloy conduction band edge effective mass m_{alloy}^* is then inversely dependent on the magnitude of f_{Γ} .²⁵

In practice, the two-level BAC model provides only an idealized description of the CBE state in GaNAs because it ignores the distribution of N-related defect states in the alloy. It is well established that when a single N atom replaces an

As atom in GaAs, it forms a resonant defect level above the conduction band edge of GaAs.^{26,27} However, the alloy can also contain clusters of N atoms, such as N-N nearest-neighbor pairs, where a single Ga atom has two N neighbors [denoted by $N_2(110)$], as well as larger clusters, some examples of which are depicted in Fig. 1. There are in total five different types of three-atom clusters: three of these introduce a defect level below the lower energy $N_2(110)$ level, while strain relaxation in the other two cases causes the lowest cluster defect level to be above this level.²⁸ Figure 1 illustrates the three types of 3N atom clusters which give rise to the lower energy defect levels, as well as an example of one 4N atom cluster, which introduces a defect level below the three-atom cluster levels. In a random alloy, the number of such clusters markedly increases with increasing N composition, with the detail of the cluster distribution strongly influencing the alloy conduction band dispersion.^{23,28,29}

To investigate the role of N in InNSb and GaNSb alloys, we have used the TB Hamiltonian described in the previous section to calculate the band structure of a range of different 1728-atom $X_{864}\text{N}_M\text{Sb}_{864-M}$ supercells ($X=\text{Ga}, \text{In}$), with four different configurations ($i=1-4$) of N atoms considered for each nitrogen composition M . Previous work on ultralarge $\text{GaN}_x\text{As}_{1-x}$ supercells containing a statistical distribution of N atoms calculated using the TB based linear combination of isolated N states (LCINS) model²³ has shown that aside from isolated N atoms the five N complexes in Fig. 1 have the most important effect on the CBE as a function of x because of their energy relative to the isolated level and also to the CBE. Table IV lists the average number of isolated N atoms and of each of these clusters expected in a 1728-atom supercell for the different N compositions studied. It can be seen that it is impossible to exactly reproduce the average cluster composition in a single supercell calculation. The five N complexes from Fig. 1 are therefore introduced in various concentrations in each configuration. Table V lists the different $\text{In}_{864}\text{N}_M\text{Sb}_{864-M}$ supercells considered, with $M=3, 6, 10$, and 14, to investigate the evolution of band structure with N concentration x up to $x=1.62\%$. The calculations were then repeated for $\text{Ga}_{864}\text{N}_M\text{Sb}_{864-M}$ for $M=3, 6, 14$ and 32 (x

TABLE IV. Average number of isolated N atoms (N_1) and of N atoms in each of the clusters depicted in Fig. 1 expected in a 1728-atom supercell for the different N compositions studied.

M	N_1	$N_2(110)$	$N_3(C)$	$N_3(B)$	$N_3(A)$	$N_4(A+1)$
3	2.87	0.12	2.6×10^{-3}	6.6×10^{-4}	4.5×10^{-4}	1.2×10^{-5}
6	5.48	0.48	2.1×10^{-2}	5.1×10^{-3}	3.6×10^{-3}	1.9×10^{-4}
10	8.51	1.29	0.096	2.4×10^{-2}	1.6×10^{-2}	1.5×10^{-3}
14	10.90	2.46	0.264	0.066	0.045	5.6×10^{-3}
32	14.30	11.0	3.16	0.79	0.53	0.156

TABLE V. Numbers of different types of N complexes present in each of the $\text{In}_{864}\text{N}_M\text{Sb}_{864-M}$ and $\text{Ga}_{864}\text{N}_M\text{Sb}_{864-M}$ supercells considered in this work. N_1 refers to isolated N atoms with no N second nearest neighbors. $N_2(110)$ refers to a (1,1,0) first neighbor N-N pair [depicted in Fig. 1(a)], $N_3(C)$ refers to a 3N triplet with reflective symmetry only (C_s symmetry) [Fig. 1(b)], $N_3(B)$ refers to a 3N (1,1,0) oriented triplet chain [Fig. 1(c)], $N_3(A)$ refers to a 3N In(Ga) centered triplet [Fig. 1(d)], and $N_4(A+1)$ refers to a 4N [$N_3(A)$ -related] quadruplet [Fig. 1(e)]. The italic number in square brackets next to each N-type indicate its concentration in the given exemplar relative to the average number (see Table IV). For example, $1N_3(C)^{[140]}$ means that the concentration of the $N_3(C)$ cluster in the $[M=6, i=4]$ supercell is 140 times the concentration expected for the same cluster in case of random atom distribution.

M	$i=1$	2	3	4
3	$3N_1^{[1.0]}$ (5,3,0) ^a	$3N_1^{[1.0]}$ (4,4,2) ^a	$3N_1^{[1.0]}$ (2,2,0) ^a	$1N_1^{[0.3]}$ $1N_2(110)^{[17]}$
6	$6N_1^{[1.1]}$ (4,0,0) ^a	$6N_1^{[1.1]}$ (2,1,1) ^a	$4N_1^{[0.7]}$ $1N_2(110)^{[4.2]}$	$3N_1^{[0.5]}$ $1N_3(C)^{[140]}$
10	$10N_1^{[1.2]}$ (2,2,0) ^a	$8N_1^{[0.9]}$ $1N_2(110)^{[1.6]}$	$6N_1^{[0.7]}$ $2N_2(110)^{[3.1]}$	$7N_1^{[0.8]}$ $1N_3(C)^{[37]}$
14	$14N_1^{[1.3]}$ (2,1,1) ^a	$9N_1^{[0.8]}$ $1N_2(110)^{[0.8]}$ $1N_3(C)^{[11]}$	$9N_1^{[0.8]}$ $1N_2(110)^{[0.8]}$ $1N_3(B)^{[45]}$	$7N_1^{[0.6]}$ $2N_2(110)^{[1.6]}$ $1N_3(A)^{[68]}$
32	$17N_1^{[1.2]}$ $3N_2(110)^{[0.5]}$ $3N_3(C)^{[2.8]}$	$17N_1^{[1.2]}$ $3N_2(110)^{[0.5]}$ $2N_3(C)^{[1.9]}$ $N_3(B)^{[3.8]}$	$16N_1^{[1.1]}$ $2N_2(110)^{[0.4]}$ $2N_3(C)^{[1.9]}$ $1N_3(B)^{[3.8]}$ $1N_3(A)^{[5.7]}$	$17N_1^{[1.2]}$ $1N_2(110)^{[0.2]}$ $1N_3(C)^{[0.9]}$ $1N_3(B)^{[3.8]}$ $1N_3(A)^{[5.7]}$ $1N_4(A+1)^{[26]}$

^aMinimum displacement between N atoms.

=3.70%), with the same four i arrangements of N atoms used for InNSb also used for GaNSb for $M=3, 6$, and 14. For each value of M , the label $i=1$ refers to the supercell with the smallest number of N clusters included in the calculation: only isolated N atoms and second and/or further neighbor pairs are included for $i=1$ in all cases other than for $M=32$. We define an isolated N atom (denoted N_1) as one where there are no N atoms occupying any one of its (1,1,0) second neighbor sites; i.e., all 12 of its second nearest neighbors are host group-V atoms. The energy of an isolated N atom can be perturbed by other N atoms which are close by, but which are not immediate second neighbors. To monitor the effect of these more distant interactions, we also note in Table V the minimum separation between N atoms in each structure where only isolated N atoms are included. Increasing numbers of larger N clusters are included with increasing i , through to $i=4$ having the greatest number of larger N clusters. The clusters include the $N_2(110)$ clusters depicted in Fig. 1(a) and, depending on M , an increasing number of 3N clusters [depicted in Figs. 1(b)–1(d)] and (for $M=32$, $x=3.70\%$ only) a 4N cluster of the type depicted in Fig. 1(e). Our calculations are set up so that the random alloy distribu-

tion lies closest to that assumed for $i=1$ and $i=2$. Table V summarizes the specifications of the supercell configurations considered in this work, the band structures of which are presented in Figs. 2 and 3.

Figures 2 and 3 show, respectively, the calculated conduction band structure of the different InNSb and GaNSb supercells considered. We also include for comparison at the bottom left of each figure the band structure of the host binary compounds InSb and GaSb. The right hand panel for each value of i and M shows the band dispersion calculated along the k_z direction between the supercell zone center and Brillouin zone edge. The left hand panel shows how the host Γ_{1c} state, ψ_{c0} , is distributed over the alloy states j at the Γ point, with

$$f_{\Gamma}(j) = |\langle \psi_j | \psi_{c0} \rangle|^2. \quad (3)$$

We consider first the influence of isolated N atoms on the band dispersion in the ultradilute alloys. Figure 2 ($M=3$, $i=1$) shows that the inclusion of three isolated N atoms into a 1728-atom supercell ($x=0.35\%$) introduces three N-related levels centered around 0.75 eV above the valence band maximum and therefore lying ~ 0.55 eV above the CBE. This is twice the energy separation of ~ 0.25 – 0.30 eV between the isolated N level and the CBE in GaNAs. There is a small 30 meV reduction in the CBE energy E_- of the alloy compared to that of InSb [Fig. 4(a)]. The CBE is only slightly perturbed from that of InSb, retaining over 95% host Γ_{1c} character [Fig. 4(b)]. The calculated effective mass is slightly lower than that of InSb due to the reduction in energy gap more than compensating for the reduced CBE Γ_{1c} character [Fig. 4(c)]. The three levels centered at ~ 0.75 eV originate from a combination of three highly localized s -like impurity states, each associated with one of the N atoms. One of these levels [identified with E_+ in Eq. (2)] is shifted upward to a slightly higher energy and has around 5% Γ_{1c} character. This level is made up of a symmetric combination of the s -like impurity states centered on each N atom, which interact with the host Γ_{1c} state to give the E_+ state.

Turning to GaNSb [Fig. 3 ($M=3$, $i=1$)], we again see that the introduction of a small number of isolated N atoms leads to the formation of localized defect levels in GaSb, similar to those in GaNAs and InNSb, and which have a similar though more dramatic effect on the CBE. The key change is in the relative positioning of the N levels and the CBE in GaNSb. The isolated N level is calculated to be almost degenerate with and to have a large interaction matrix element with the GaSb CBE. This can be clearly seen in Fig. 3 ($M=3$, $i=1$), where two closely spaced N levels are found at 0.77 eV, while the symmetric combination of localized N states strongly interacts with the host CBE to give approximately equal f_{Γ} character on the alloy CBE state (E_-) and on the E_+ level. We therefore find a strong redshift in the CBE energy, with $\sim 50\%$ drop in f_{Γ} and an almost 50% enhancement in the band edge mass (Fig. 4). Here, in contrast to InSb, the reduction in f_{Γ} is then the dominant factor contributing to the change in effective mass.

We next consider the dependence of the band structure on the density of isolated N levels. Moving down the $i=1$ series in Fig. 2, we see classical BAC behavior as the number of

FIG. 2. Calculated band structure of $\text{In}_{864}\text{Sb}_{864}$ and 16 $\text{In}_{864}\text{N}_M\text{Sb}_{864-M}$ supercells of various N concentrations (M) and distributions (i), as defined in Table V. The band dispersion is calculated for $T=0$ K along the k_z direction with levels relating to various types of N complex states (defined in the text). The left hand side of each band structure shows the distribution of fractional InSb Γ_{1c} character (f_Γ) across the states at $k=0$. L refers to InSb L_{1c} levels, which, in these supercells, are folded back at the Γ point. E_- is the CBE and E_+ is identified with E_+ in Eq. (2).

“isolated” N atoms in the InNSb supercells increases from 3 to 14. An increasing number of N levels appear in the region of 0.75 eV, which is consistent with the number of isolated N atoms. These levels also broaden out over a 100 meV range due to medium-range interactions between the increasing density of isolated N atoms. One of the N levels in each case has a small amount of Γ_{1c} character and is split off from

the main group to a higher energy. This E_+ state shifts upward to higher energy and its f_Γ character increases as the interaction V_{Nc} increases with x . We also observe a steady reduction in both the CBE energy and its Γ_{1c} character with x , while the conduction band effective mass close to the Γ point becomes steadily lighter as the conduction band shifts down toward the valence band.

FIG. 3. Calculated band structure of $\text{Ga}_{864}\text{Sb}_{864}$ and 16 $\text{Ga}_{864}\text{N}_M\text{Sb}_{864-M}$ supercells of various N concentrations (M) and distributions (i), as defined in Table V. The band dispersion is calculated for $T=0$ K along the k_z direction with levels relating to various types of N complex states (defined in the text). The left hand side of each band structure shows the distribution of fractional GaSb Γ_{1c} character (f_Γ) across the states at $k=0$. L refers to GaSb L_{1c} levels, which, in these supercells, are folded back at the Γ point. E_- is the CBE and E_+ is identified with E_+ in Eq. (2).

Qualitatively, the same behavior is observed in the $i=1$ series in Fig. 3 for GaNSb, where we consider isolated N atoms only for $M=3-14$. The E_- (E_+) level moves to lower (higher) energy with increasing x . The N band shows similar broadening to the InNSb case. The calculated band edge mass starts to decrease beyond $M=3$ due to the continued reduction of the energy gap and due to f_Γ remaining approxi-

mately constant at ~ 0.5 with increasing x (Fig. 4). There is one noteworthy difference compared to InNSb, namely, that the calculated E_+ state starts to break up dramatically with increasing M , as it is pushed up in energy into the region of L -related host states, with which it strongly hybridizes. We conclude that the two-level BAC model therefore effectively describes the band dispersion in dilute XNSb ($X=\text{In, Ga}$) al-

FIG. 4. (Color online) Variation of the E_- (a) energy (relative to host CBE), (b) fractional Γ_1 character, and (c) effective mass in the $\text{In}_{864}\text{N}_{M_i}\text{Sb}_{864-M_i}$ (continuous line) and $\text{Ga}_{864}\text{N}_{M_i}\text{Sb}_{864-M_i}$ (dashed line) band structures of Figs. 2 and 3. Red squares (Ref. 30) correspond to experimental data.

loys containing only isolated N atoms. From the band structure calculations, we can extract the value of the BAC coupling matrix element $V_{Nc} = \beta x^{1/2}$ to describe the interaction between the host CBE and the higher-lying N level. We calculate $\beta = 2.0$ eV for InNSb , similar to that obtained in full TB calculations on GaNaS , and $\beta = 2.4$ eV for GaNSb . We estimate, based on the calculations in Fig. 2 and further calculations, that the incorporation of N in $\text{InN}_x\text{Sb}_{1-x}$ will lead to a zero-gap semiconductor for $x \gtrsim 2.7\%$ at $T = 0$ K.

Having established that a BAC model can be used to describe the band structure when we include only isolated N atoms, we now turn to consider the effects of N correlations on the band structure at the lowest N concentration considered here, $M=3$ ($x=0.34\%$). Comparing Fig. 2 ($M=3, i=1$) to Fig. 2 ($M=3, i=2$), we calculate that for distances between N atoms greater than (2,2,0) the N atoms are effectively independent of one another: little difference can be seen between the two band structures, and in particular the three N levels at ~ 0.75 eV are very similar in both panels. This is also the case for the equivalent GaNSb structures [Fig. 3 ($M=3, i=1$) and Fig. 3 ($M=3, i=2$)]. Figures 2 and 3 ($M=3, i=3$) show the calculated band structure when we include in the supercell a $N_2(220)$ pair, where two N atoms are placed on opposite corners of one side of the FCC unit cell of Fig. 1. We see that the interaction between the two N atoms starts to perturb the distribution of N-related defect levels, with the introduction of two new defect levels, which can be described as a symmetric [$N_2^+(220)$] and an antisymmetric [$N_2^-(220)$] combination of the isolated N defect levels. Finally, we see from $M=3, i=4$ the effect of introducing an isolated N atom and a N-N pair [$N_2(110)$, Fig. 1(a)] into the supercell. The $N_2(110)$ pair introduces two defect levels,

with even (+) and odd (−) symmetries, which are related to the levels in Fig. 2 ($M=3, i=4$) at 0.54 and 0.84 eV, respectively, and at 0.50 and 0.85 eV, respectively, in Fig. 3 ($M=3, i=4$). For InNSb , the introduction of this N-N pair has little influence on the band dispersion near the CBE, with little observed change in energy gap or CBE effective mass. The concentration of N-N pairs in supercell ($M=3, i=4$) is around an order of magnitude greater than what would be expected in a random alloy with $x=0.34\%$ so that the two-level BAC model should remain appropriate to describe the CBE in this case. By contrast, the introduction of a $N_2(110)$ pair strongly modifies the band structure of GaNSb near to the conduction band minimum. There is now significant Γ character on two of the lower-lying conduction levels in Fig. 3 ($M=3, i=4$), the lower of which has also strong $N_2^+(110)$ character. As a result the CBE cannot be fitted to a two-level BAC model in this case. Statistically, we would expect far fewer $N_2(110)$ pairs in a random GaNSb alloy for $x=0.34\%$, but given that the pair states determine the lowest conduction levels in Fig. 3 ($M=3, i=3,4$), they will still strongly modify the band structure and must be explicitly included in any model of the electronic properties of this alloy.

In a random alloy, the number and average size of N clusters increases with increasing N composition x . Considering the $i=4$ series, which contains the highest proportion of N clusters at each x , we observe in Figs. 2 and 3 an increasing number of new levels appearing below the isolated N level due to the introduction of larger N clusters with increasing N concentration (increasing x). We see in Fig. 2 that because of the large energy separation between the isolated N-related levels and the CBE, the lower energy states associated with the N clusters do not in general have a significant effect on the InNSb CBE. Figure 4(a) shows that the CBE energy smoothly decreases with increasing N composition x for the different structures considered in Fig. 2. This is also true for the fractional Γ character f_Γ and for the CBE effective mass [Figs. 4(a) and 4(b)]. Of the 16 structures considered, there are only two cases where a N-related defect level has a significant influence on the CBE energy and its f_Γ character, namely, $M=6$ and $M=14$ (both $i=4$), where the $N_3^+(C)$ level at about 0.42 eV and the $N_3^+(A)$ level at 0.26 eV, respectively, strongly mix with the CBE state, reducing its Γ character, and pushing the CBE to lower energy compared to the other structures considered. For both cases, the number of N_3 clusters in the 1728-atom supercell is at least an order of magnitude greater than would be expected in a random alloy. We therefore expect these states to have a much weaker effect near the conduction band minimum in a random alloy. The two-level BAC model should therefore provide a good description of the variation with composition x of the CBE energy and the band edge effective mass in $\text{InN}_x\text{Sb}_{1-x}$.

This conclusion is supported by the available experimental data. There have been relatively little data reported concerning the dependence of the energy gap on N composition x in $\text{InN}_x\text{Sb}_{1-x}$. Part of the difficulty in determining the band gap is that both InSb and $\text{InN}_x\text{Sb}_{1-x}$ tend to have a large intrinsic electron concentration⁴ so that the Moss-Burstein shift then makes it difficult to determine the fundamental

energy gap. We estimated above that the incorporation of N into InNSb will lead to a zero-gap semiconductor for $x > \sim 2.7\%$ at $T=0$ K. A zero-gap band structure has been reported for $\text{InN}_x\text{Sb}_{1-x}$ with $x=6\%$, with the conduction band minimum estimated to be ~ 255 meV below the valence band maximum at room temperature at this composition. These numbers are consistent with our analysis here. The conduction band dispersion has also been measured by cyclotron resonance in pulsed magnetic fields up to 150 T, allowing the dispersion to be probed over a wide energy range.³¹ These results directly demonstrated the band anticrossing, with the measured results in good quantitative agreement with theoretical calculations for a value of $x < 1\%$. Overall, we conclude that the two-level BAC model is therefore appropriate to describe the conduction band dispersion in $\text{InN}_x\text{Sb}_{1-x}$.

By contrast, Figs. 3 and 4 show that the two-level BAC model of Eq. (1) is not appropriate to describe the band dispersion in GaNSb. We saw in Fig. 3 ($M=3, i=1$) that the isolated N defect level is almost degenerate with the GaSb CBE energy at $T=0$ K. Because the N cluster state levels lie below the GaSb CBE energy, we find that the specific distribution of N levels then strongly influences the calculated CBE energy and effective mass for the $\text{GaN}_x\text{Sb}_{1-x}$ supercell structures considered in Fig. 3. The GaNSb results presented in Figs. 3 and 4 include the case of $x=3.70\%$ to investigate the band structure for a GaNSb alloy whose energy gap is close to that of InSb. This higher N composition leads to an increased number of larger N clusters in a random alloy. We find that there is strong hybridization between the host band states and pair and/or cluster defect levels lying close to the band edge over the full range of x considered here. For each composition, the calculated energy gap and its f_Γ character strongly depend on the assumed distribution of N atoms.

The square red data points in Fig. 4(a) compare the measured room temperature change in the energy gap of a series of $\text{GaN}_x\text{Sb}_{1-x}$ epilayers³⁰ with the calculated variation of the CBE energy in our tight-binding calculations. The valence band edge E_v approximately shifts upward as $E_v = E_{v0} + 0.13x$ eV in our calculations. The experimental energy gaps have consequently been shifted by $0.13x$ eV to compare to the calculated variation in the CBE energy. The calculated and measured shifts are of comparable magnitude over the limited composition range for which there are experimental data available. The strong hybridization between N cluster levels and the conduction band edge will have significant consequences for the electronic and optical properties of GaNSb. We estimate below that there will be an order of magnitude more N resonant states close to the CBE in GaNSb compared to GaNAs. The N cluster states contribute to the observed inhomogeneous broadening of the absorption spectrum in GaNAs (Ref. 32) and also contribute to the strong carrier localization effects observed at low temperature in microphotoluminescence experiments.³³ These effects should be even more dramatic in the case of GaNSb. In addition, the N resonant states severely limit the electron mobility in GaNAs,³⁴ giving an intrinsic electron mobility of order $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The high density of N clusters in GaNSb should have an even stronger effect on the mobility. It has been proposed that the low electron mobility and high

electron mass could make GaNAs particularly suited as the multiplication region in avalanche photodiodes operating at telecommunication wavelengths.³⁵ This should also be the case for GaNSb. Overall, we conclude that defect levels associated with N clusters will play a dominant role in determining the lowest conduction band structure of GaNSb, leading to strong inhomogeneous broadening of the band edge, and a low electron mobility.^{23,29,34}

The calculations presented here and previous work on GaNAs show that there are two main factors which determine the extent of hybridization between the host band states and pair and/or cluster defect levels that lie close to the band edge:

- (a) the energy levels of some basic key N clusters and where they lie in relation to the initial CBE energy and
- (b) the rate at which the CBE moves down in energy with x .

In GaNAs for example, which has properties intermediate between those of InNSb and GaNSb, the CBE passes through the $N_2^+(110)$ level at low temperatures at $x \sim 0.2\%$. We estimate a concentration x_2 of $N_2(110)$ pairs at this composition of $x_2 \approx 2 \times 10^{-3}\%$ using the approximation for a random alloy that $x_2 \approx 6x^2$. We calculate that the CBE then passes through the $N_3^+(C)$ level at $x \sim 0.8\%$, for which composition $x_3(C) \approx 1 \times 10^{-3}\%$ [where we assume the concentration of $N_3(C)$ clusters, $x_3(C)$, varies as $24x^3$], and passes through the $N_3^+(B)$ level at $x \sim 2\%$, where $x_3(B) \approx 5 \times 10^{-3}\%$ [using $x_3(B) \approx 6x^3$], before finally passing through the $N_3^+(A)$ level at $x \sim 4\%$, where $x_3(A) \approx 0.03\%$ [using $x_3(A) \approx 4x^3$]. These different N cluster levels then lead to a well-defined nonmonotonic variation of the measured low temperature CBE mass with increasing N composition in $\text{GaN}_x\text{As}_{1-x}$. For InNSb, we calculate that the $N_2^+(110)$ level lies ~ 0.3 eV above the host CBE, and therefore has little influence on the CBE mass for any x . Of the states which were key to determine the band edge mass in GaNAs, we calculate that only the $N_3^+(A)$ level initially lies below the InSb CBE in the band gap, shifting into the conduction band at $x \sim 0.3\%$. At this composition, the concentration of $N_3(A)$ clusters is only $x_3 \approx 1 \times 10^{-5}\%$ in a random alloy. This is about 2 orders of magnitude smaller than the concentration of $N_2(110)$ pairs in GaNAs at a similar x . Hence, we conclude that the band dispersion of InNSb should be well described by a two-level BAC model, with N cluster states having little effect on the observed band structure at the conduction band minimum.

By contrast, if we use the two-level BAC parameters derived from Fig. 3 ($i=1$) then the GaNSb CBE passes through the $N_2^+(110)$, $N_3^+(C)$, $N_3^+(B)$, and $N_3^+(A)$ levels at $x \sim 1.2\%$, 2.2% , 3.3% , and 4.4% , respectively. At these compositions, we calculate $x_2 \approx 0.09\%$, $x_3(C) \approx 0.03\%$, $x_3(B) \approx 0.02\%$, and $x_3(A) \approx 0.03\%$. These concentrations are generally an order of magnitude larger than the corresponding ones in GaNAs. We conclude therefore that the CBE character of GaNSb will be dominated by the presence of N-related defect levels. These will mix strongly with the GaSb host Γ conduction band states and should give a broad series of optically active defect-related transitions. We conclude that the electronic properties of GaNSb will be intermediate between those of GaNAs, where a small number of N-related cluster states are

approximately degenerate with the CBE, and GaNP, where the electronic properties are dominated by an increasing density of N-related defect states below the conduction band minimum.

Finally, we note the effect that nitrogen has on the upper valence bands of InNSb and GaNSb. We see from Figs. 2 and 3 that the heavy-hole valence band remains largely unaffected by N for both InNSb and GaNSb. However, it is evident from Fig. 2 and Fig. 3 (for $M=32$) that the light-hole (LH) valence band is significantly affected by the introduction of N. Because InSb is a narrow band gap semiconductor, the effect of reducing the band gap through the introduction of nitrogen is both to modify the LH band edge effective mass and also to increase significantly the nonparabolicity of the LH band. This change in LH dispersion is expected to modify the energy dependence of loss mechanisms such as Auger recombination³⁶ and so must be taken into account in models of InNSb-based materials and devices. This can be achieved by extending the standard eight-band $\mathbf{k}\cdot\mathbf{p}$ model to a ten-band $\mathbf{k}\cdot\mathbf{p}$ model that includes the coupling between the nitrogen levels and the conduction band edge.^{6,37} For GaNSb, high concentrations of nitrogen also significantly modify the LH band dispersion. However, it is more difficult to model this effect with a modified $\mathbf{k}\cdot\mathbf{p}$ model due to the strong dependence of the conduction band structure on the assumed N distribution.

IV. CONCLUSION

In summary, the electronic structure of various $\text{InN}_x\text{Sb}_{1-x}$ and $\text{GaN}_x\text{Sb}_{1-x}$ alloys ($x \leq 3.7\%$) has been presented and

discussed in detail. We find that N-related defect levels will generally lie well above the conduction band minimum in InNSb, with the band dispersion of InNSb then well described by a two-level band-anticrossing model. We estimate that the incorporation of N in an ideal InNSb alloy should allow a zero-gap III-V semiconductor for $x \geq 2.7\%$ at low temperature. By contrast, the calculated electronic structure of $\text{GaN}_x\text{Sb}_{1-x}$ supercells strongly depends on the assumed distribution of N atoms within the supercell, with N-related defect levels strongly perturbing the lowest conduction band states and energy gap. This should lead to strong inhomogeneous broadening and localization effects due to N-related defect levels close to the conduction band minimum in GaNSb. Overall, we find that details of the lowest conduction band states in dilute nitride alloys are dominated by the relative energy of the N-related defect levels and the host matrix conduction band edge. We conclude that the distribution of N states has an increasingly large effect as the states shift down in energy relative to the host matrix CBE on going from InSb to GaAs to GaSb and finally to GaP.

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