Electronic structures and doping of InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$

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The electronic structures of InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$ are predicted and these materials are found to be direct-band-gap semiconductors with fundamental band gaps ranging from orange through the blue-green to the ultraviolet. The deep levels associated with substitutional s- and p-bonded impurities are predicted, and, for InN we find (i) that the native defect responsible for naturally occurring n-type InN is a nitrogen vacancy (not N_{In}); (ii) that the nitrogen vacancy also produces a deep level just below the conduction-band edge, which is responsible for an observed 0.2-eV optical-absorption feature; (iii) that p-type doping should be achievable by inserting column-II impurities on In sites; (iv) that n-type conductivity should result from oxygen atoms on N sites; (v) that In_N produces s- and p-like deep levels near midgap that are responsible for an optical-absorption feature near 1 eV; (vi) that column-IV impurities on either anion or cation sites will tend to make the material semi-insulating, and (vii) that an isoelectronic electron trap should be produced by B_{In}, whereas column-V impurities on the N site should produce deep isoelectronic hole traps. Similar results hold for the alloys $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$. Some impurities undergo shallow-deep transitions in the alloys, as functions of alloy composition.

I. INTRODUCTION

High-mobility InN has recently been grown in a polycrystalline hexagonal structure.[1,2] The band gap of this material is direct and the optical absorption threshold lies in the orange portion of the visible spectrum (the band gap plus the Burstein shift is 2.05 eV). This is an exciting experimental result for at least two reasons: (i) the high mobility suggests that electronic-grade material may eventually be fabricated, and (ii) the orange color indicates that InN and alloys based on InN could be candidates for efficient semiconducting large-band-gap visible-light emitters and lasers. Until now much of the emphasis on developing large-band-gap visible solid-state light emitters has focused on II-VI compound semiconductors, materials that in many cases have proven difficult to dope both n type and (especially) p type[3] and hence do not form good diodes, much less light-emitting diodes. The origin of the II-VI compound doping problem is often ascribed to "self-compensation"—common dopants purportedly distort off site and produce accompanying vacancies which compensate them.[4] It is widely believed that such self-compensation problems do not plague III-V compound semiconductors, and so the existence of the isoanionic semiconductors InN, GaN, and AlN, all with large band gaps [2 eV (orange), 3.5 eV (ultraviolet), and 6 eV (ultraviolet), respectively], raises the possibility of fabricating alloys whose band gaps range from the orange to the ultraviolet.

Assuming that the problem of growing electronic-grade material can be solved, there will remain five major criteria that the material must meet: (i) the band gap must be the desired color (orange, blue, etc.); (ii) the band gap must be direct so that the crystal-momentum selection rule governing light emission[5] will be satisfied; (iii) the material must be crystalline and, if it is an alloy, must be relatively strain free—because large strains produce dislocations, and dislocations tend to quench luminescence (as well as trap and scatter carriers and degrade mobility);[6,7] (iv) the materials must be relatively free of deep levels in the band gap that might trap electrons or holes, leading to enhanced nonradiative transition rates and luminescence degradation; and (v) schemes for doping the material both n and p type must be found. The purpose of this paper is to provide theoretical guidance concerning these five issues, in the hope of stimulating efforts to grow electronic-grade InN and InN-based alloys.

In Sec. II we discuss the band structures of (wurtzite) InN and alloys of InN and GaN and AlN. We show that these alloys can be described by the virtual-crystal approximation, have direct band gaps that range from the orange to the ultraviolet, and should be relatively strain free because they are moderately well lattice matched. In Sec. III we discuss the deep levels associated with s- and p-bonded substitutional impurities in InN, with particular emphasis on the native defects (i.e., vacancies and antisite defects) and the dopants from columns II, IV, and VI of the Periodic Table. Section IV is devoted to a comparable discussion for the alloys. Our conclusions are summarized in Sec. V.

II. BAND STRUCTURES

The band structures are obtained using a nearest-neighbor tight-binding model of the electronic structures, based on the Slater-Koster[8] theory. The resulting Hamil-

tonian is

$$H = \begin{bmatrix} H_a & 0 & H_{1,3} & H_{1,4} \\ 0 & H_a & H_{1,4} & H_{2,4} \\ H_{1,3}^{\dagger} & H_{1,4}^{\dagger} & H_c & 0 \\ H_{1,4}^{\dagger} & H_{2,4}^{\dagger} & 0 & H_c \end{bmatrix} ,$$

where H_b is

$$\begin{array}{c|cccc} & |s,4) & |p_z,4) & |p_x,4) & |p_y,4) \\ \hline |s,1) & U(s,s) & U(s,z) & 0 & 0 \\ |p_z,1) & U(z,s) & U(z,z) & 0 & 0 \\ |p_x,1) & 0 & 0 & U(x,x) & 0 \\ |p_y,1) & 0 & 0 & 0 & U(y,y) \end{array} ,$$

$$\begin{array}{c|cccc} & |s,1) & |p_z,1) & |p_x,1) & |p_y,1) \\ \hline |s,1) & E(s,b) & 0 & 0 & 0 \\ |p_z,1) & 0 & E(p,b) & 0 & 0 \\ |p_x,1) & 0 & 0 & E(p,b) & 0 \\ |p_y,1) & 0 & 0 & 0 & E(p,b) \end{array} ,$$

for $b = a$ or c (anion site or cation site). The off-diagonal matrices are $H_{1,3} = g_1(\mathbf{k})M_{1,3}$, $H_{2,4} = g_2(\mathbf{k})M_{2,4}$, and $H_{1,4} = g_3(\mathbf{k})M_{1,4}$, where $M_{1,4}$ is

$M_{2,4}$ is

$$\begin{array}{c|cccc} & |s,4) & |p_z,4) & |p_x,4) & |p_y,4) \\ \hline |s,2) & f_0^* U'(s,s) & f_0^* U'(s,z) & -f_1^* U'(s,x) & -f_-^* U'(s,x) \\ |p_z,2) & f_0^* U'(z,s) & f_0^* (z,z) & -f_1^* U'(z,x) & -f_-^* U'(z,x) \\ |p_x,2) & -f_1^* U'(x,s) & -f_1^* U'(x,z) & f_0^* U'(x,x)+f_+^*[U'(x,x)+U'(y,y)] & f_-^*[U'(y,y)-U'(x,x)]/2 \\ |p_y,2) & -f_-^* U'(x,s) & -f_-^* U'(x,z) & f_-^*[U'(y,y)-U'(x,x)]/2 & U'(y,y)f_1^* + f_+^*[U'(x,x)+U'(y,y)]/2 \end{array} ,$$

$M_{1,3}$ is

$$\begin{array}{c|cccc} & |s,4) & |p_z,4) & |p_x,4) & |p_y,4) \\ \hline |s,2) & f_0 U'(s,s) & f_0 U'(s,z) & f_1 U'(s,x) & f_- U'(s,x) \\ |p_z,2) & f_0 U'(z,s) & f_0 U'(z,z) & f_1 U'(z,x) & f_- U'(z,x) \\ |p_x,2) & f_1 U'(x,s) & f_1 U'(x,z) & f_0 U'(x,x)+f_+[U'(x,x)+U'(y,y)] & f_-[U'(y,y)-U'(x,x)]/2 \\ |p_y,2) & f_- U'(x,s) & f_- U'(x,z) & f_-[U'(y,y)-U'(x,x)]/2 & U'(y,y)f_1 + f_+[U'(x,x)+U'(y,y)] \end{array} ,$$

and

$$g_1(\mathbf{k}) = \exp[i(-k_1 a/3 + k_2 a/3 + k_3 c/8)] ,$$

$$g_2(\mathbf{k}) = \exp[i(k_1 a/3 - k_2 a/3 + k_3 c/8)] ,$$

$$g_3(\mathbf{k}) = \exp(-i3k_3 c/8) ,$$

$$f_0(\mathbf{k}) = \exp(+ik_1 a) + 1 + \exp(-ik_2 a) ,$$

$$f_1(\mathbf{k}) = \exp(+ik_1 a) - [1 + \exp(-ik_2 a)]/2 ,$$

$$f_+(\mathbf{k}) = \tfrac{3}{4}[1 + \exp(-ik_2 a)] ,$$

and

$$f_-(\mathbf{k}) = (\tfrac{3}{4})^{1/2}[1 - \exp(-ik_2 a)] .$$

Here we have $\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3; \mathbf{b}_1$, where $\mathbf{b}_2$, and $\mathbf{b}_3$ are the reciprocal-lattice vectors divided by 2π, namely $((2/\sqrt{3})/a,0,0)$, $((1/\sqrt{3})/a,1/a,0)$, and $(0,0,1/c)$, respectively. The parameters of the Hamiltonian for AlN, GaN, and InN have been published,[9-11] and are reproduced in Table I, along with the wurtzite lattice

constants a and c, and the c/a ratio. Since the c/a ratio, to within 2.1%, is the ideal value of $(\tfrac{8}{3})^{1/2}$, we simplify the model by assuming the ideal value.

The band structures of the alloys are obtained in the virtual-crystal approximation.[12] We implement the

TABLE I. Tight-binding parameters (in eV) for AlN, GaN, and InN in the notation of Ref. 12. Parameters are taken from Refs. 9, 10, and 11, respectively.

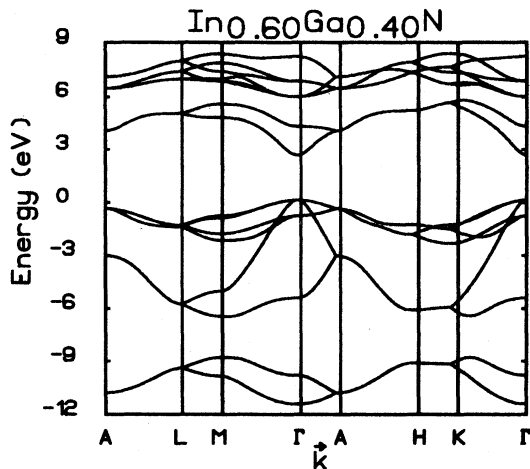|	AlN	GaN	InN
$E(s,a)$	−12.104	−13.114	−4.984
$E(p,a)$	3.581	1.269	0.565
$E(s,c)$	−0.096	−1.786	0.254
$E(p,c)$	9.419	7.131	3.895
$V(s,s)$	−10.735	−9.371	−3.841
$V(x,x)$	5.808	3.008	1.347
$V(x,y)$	8.486	6.535	3.033
$V(sa,pc)$	8.092	4.889	1.595
$V(pa,sc)$	9.755	10.867	4.000
a	3.104	3.180	3.533
c	4.963	5.166	5.693
c/a	1.599	1.635	1.611

FIG. 1. Predicted band structure of $In_{0.60}Ga_{0.40}N$. The direct energy-band gap lies in the blue-green part of the spectrum.

FIG. 3. Energies of principle conduction-band minima vs alloy composition for $In_{1-x}Al_xN$.

virtual-crystal approximation by taking weighted averages of the matrix elements. For example, in the case of $In_xGa_{1-x}N$, we average the various diagonal matrix elements E,

$$E(In_xGa_{1-x}N)=(1-x)E(GaN)+xE(InN) .$$

The off-diagonal matrix elements V, multiplied by the square of the bond length d, are also averaged this way (according to Harrison's rule[13]), with the bond length obtained from Vegard's law,[14]

$$d(In_xGa_{1-x}N)=(1-x)d(GaN)+xd(InN) .$$

Thus we assume that virtually all of the In and Ga atoms occupy cation sites, while anion sites are overwhelmingly

FIG. 2. Energies of principle conduction-band minima vs alloy composition for $In_{1-x}Ga_xN$. The symmetry points H, K, L, M, A, and Γ have the usual Brouckaert-Smoluchowski-Wigner definitions (Ref. 15).

occupied by N. The lattice mismatch, $1-d(GaN)/d$ (InN), is 9.3%; the corresponding mismatch for AlN and InN is 12.8%.[12]

The resulting predicted band structure for $In_{0.60}Ga_{0.40}N$ is given in Fig. 1. $In_xGa_{1-x}N$ is a direct-band-gap semiconductor for all compositions x, and has a band gap ranging from 2 eV for InN to 3.5 eV for GaN. The principal features of the predicted band structures of $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, namely the energies of the Γ, A, M, L, K, and H conduction-band minima,[15] are plotted as functions of alloy composition x in Figs. 2 and 3.

The principal conclusion to be drawn from these calculations is that $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ should be direct-band-gap semiconductors and hence potential light emitters for all compositions x.

III. DEEP LEVELS IN InN

A. General considerations

Every s- and p-bonded impurity produces both deep levels associated with its central-cell potential and shallow levels caused by any nonzero valence difference between the impurity and the host atom it replaces (although the "deep" levels often do not lie in the fundamental band gap as once believed, but often can be resonant with the host bands). The deep levels can be computed using the theory of Hjalmarson et al.[16] The one-electron Schrödinger equation for the deep levels E can be rewritten,

$$det[1-G_0(E)V]=0 ,$$

where $G_0(E)$ is the host Green's-function operator,

$$G_0=(E-H_0)^{-1} ,$$

and H_0 is the Hamiltonian operator that generates the band structure of the host. E is assumed to have a posi-

tive imaginary part whenever E is not in a band gap. The defect potential is $V \equiv H - H_0$, where H is the Hamiltonian of the crystal with an impurity.

If we follow established custom[16] and (i) neglect the weak long-ranged Coulomb potential responsible for shallow levels, and (ii) ignore lattice relaxation around the impurity (effects of order 0.1 eV), the defect potential V is diagonal in a basis of localized Löwdin orbitals centered at the impurity site, and the secular equation for the energy levels reduces to two[17,18] scalar equations,

$$G_{A_1}(E) = 1/V_s, \quad G_{E_2}(E) = 1/V_p .$$

Here, $G_{A_1}(E)$ and $G_{E_2}(E)$ are the host Green's functions for the s-like A_1 and p-like E_2 states,[17] respectively, and V_s and V_p are the defect potentials for the s-like and p-like states, respectively.

Using the scaling rules for the matrix elements of H_0, namely that diagonal matrix elements depend on atomic energies, whereas off-diagonal matrix elements vary inversely as the square of the bond length,[11,13,19] we find that

$$V_s = \beta_s (w_{s,imp} - w_{s,host})$$

and

$$V_p = \beta_p (w_{p,imp} - w_{p,host}) ,$$

where $w_{l,imp}$ and $w_{l,host}$ are atomic-orbital energies in the solid[19] for impurity and host, respectively. We have $\beta_s = 0.8$ and $\beta_p = 0.6$. These equations can be solved for deep levels of energy E in the fundamental band gap by computing the Green's function $G_l(E)$ and plotting E versus $[G_l(E)]^{-1} = V_l$.

B. Native defects

The first question the theory should answer is "Why is InN n type?" Tansley and Foley[1] had speculated some years ago that the n-type behavior is caused by an antisite defect: N on an In site (N_{In}), which they had suggested might be a double donor. However, we find that this defect produces both s-like and p-like[17] deep levels deep in the gap (see Fig. 4)—closer to the valence-band edge than to the conduction-band edge.

The s-like state is occupied by the two extra N electrons and is too far from the conduction-band edge to be thermally ionized—even if one makes allowances for a few-tenths-of-an-eV theoretical uncertainty in the predicted deep levels. The p-like states are far from the band edge, empty, and together can trap six electrons. (Of course, Coulombic charge-state splitting, omitted from the model, will raise these neutral-impurity levels as each additional electron is added.[20]) Thus N_{In} is a deep trap for both electrons and holes: its natural occurrence in InN cannot explain the material's n-type character.

The In_N antisite defect produces deep s-like and p-like levels near the center of the gap (Fig. 4). Six electrons occupy the lowest of the eight spin orbitals associated with this defect, making the neutral defect unquestionably a deep trap for both (two) electrons and (six) holes. Thus In_N can compensate N_{In}, but does not dope InN either n
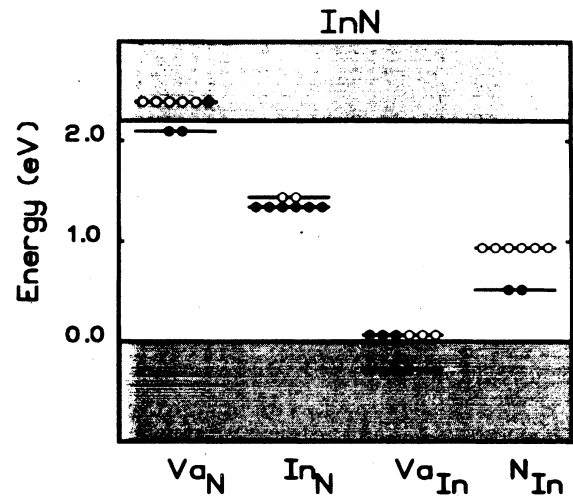

FIG. 4. Energy levels and electron occupancies of neutral native defects in InN. Holes are denoted by open circles and electrons are denoted by solid circles. For the nitrogen vacancy, $\mathcal{V}_N$, the electron in the level resonant with the conduction band decays to the band edge, where it becomes a shallow-donor electron. The energies of levels resonant with the host bands are merely schematic, are not to be taken as quantitative, and are merely to illustrate that there are resonances in the bands.

type or p type.

Neither antisite defect can explain the observed n-type character of InN.

The theory for In_N does provide a simple and natural explanation for the optical absorption data of Tansley and Foley:[2] They find a deep level in n-type InN, with p-like character lying ~ 1 eV below the conduction-band edge, which they attribute to an In_N antisite defect. Our theory (Fig. 4) does seem to be in excellent agreement with their data.

The In-site vacancy Va_{In} (Fig. 4) produces s-like and p-like levels near the valence-band maximum, with the s-like level doubly occupied and the p-like neutral vacancy level containing three electrons and three holes. The theory, taken literally, places the p-like level in the gap, where it can trap both electrons and holes, and the s-like level in the valence band. (It is conceivable that the p-like level actually lies below the valence-band maximum, in which case the In vacancy would be a triple shallow acceptor, because the holes would bubble up to the valence-band edge.) Clearly, the In vacancy cannot account for the observed n-type character of InN either.

The N vacancy can (Fig. 4). (Tansley and Foley have also speculated that the N vacancy might be the defect responsible for the natural n-type character of InN.[21]) N produces an s-like level (containing two electrons) near the conduction-band edge and a p-like level (containing one electron) above the conduction-band edge. Since the p-like level is resonant, its electron is autoionized, decays to the conduction-band edge, and dopes InN n type (one electron per vacancy). It is also possible that the s-like deep states lie a bit higher than predicted (not in the gap) and are resonant with the conduction band, donating

their electrons to the conduction band. In this second case the N vacancy would be a triple donor. Thus we conclude that the N vacancy is most likely responsible for the n-type behavior of InN, and is most likely a single donor (but possibly donates three electrons to the conduction band). Moreover, the nitrogen vacancy, if it is a simple donor with its s-like deep level in the gap just below the conduction-band edge, provides a natural explanation of the 0.2-eV feature in the Tansley-Foley optical absorption data.[22] Thus we propose that the N vacancy both dopes InN n type and produces a deep level 0.2 eV below the conduction-band minimum which has been detected in the optical absorption.

Another defect possibly responsible for the n-type character of InN is oxygen on a N site, which is not a native defect, but is nevertheless likely to be present in significant concentrations (Fig. 5).

C. Dopants

1. p type

Since InN occurs n type naturally, the central question concerning doping is whether it can be doped p type. If, as we predict, InN is naturally n type because of N vacancies, then p-type material must be relatively free of these vacancies or contain a sufficiently large number of acceptors to compensate them.

The best candidate for an acceptor is a column-II impurity on an In site (Fig. 6). Such an impurity will be a shallow acceptor in the classic sense. There is a problem with ordinary acceptors in InN, however, because this large-band-gap semiconductor should have a moderately small dielectric constant, estimated to be $\epsilon = 8.3$,[22] and a rather large (calculated) valence-band effective mass, $m^* = 1.6$,[22] causing the acceptor's effective-mass-theory binding energy to be rather large, ~ 0.3 eV. Thus unless these crude estimates of m^*/ϵ^2 are too large by a factor

FIG. 6. Energy levels and occupancies of neutral impurities from columns I, II, and III on the cation site and B on the In site in InN, GaN, and AlN. Holes are denoted by open circles. All column-II impurities on the III site are predicted to yield shallow acceptors. Column-I impurities are predicted to yield double acceptors. Isoelectronic impurities on the III site are predicted to be inert, except for B_{In} in InN only, which is predicted to be a trap.

of 3 or more, the shallow-impurity binding energy is large enough to inhibit thermal ionization of holes at room temperature. Ultimately, the fact that the shallow-acceptor binding energy is so large, not the purported difficulty of incorporating shallow acceptors, may be the reason InN cannot be fabricated sufficiently p type.

Column-IV impurities on the N site will very likely not produce shallow acceptors, but instead will produce both s-like (except perhaps for C) and p-like deep levels in the fundamental band gap—with one hole and five electrons in the upper (p-like) level and two electrons in the s-like level (Fig. 7)—except for Pb, which has its s-like and p-like levels reversed. Thus neutral column-IV impurities on N sites are deep traps for both electrons (one) and
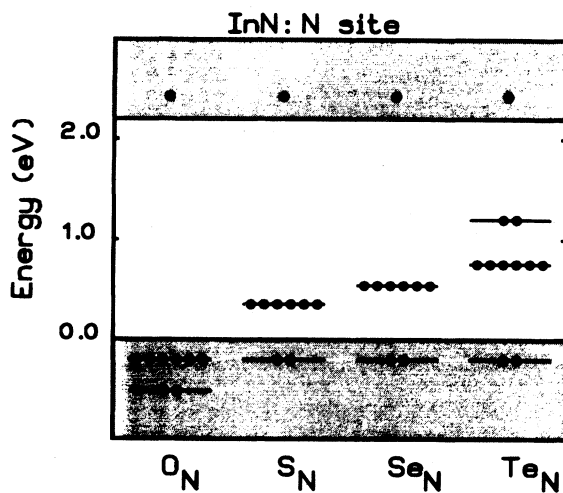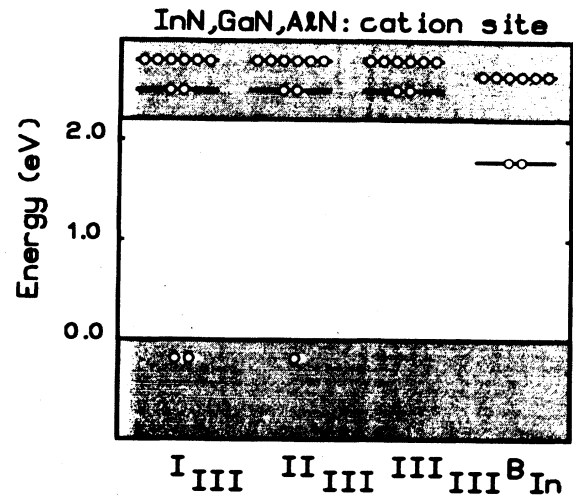

FIG. 5. Energy levels and occupancies of neutral column-VI impurities on the N site in InN. Electrons are denoted by solid circles. All column-VI impurities on the N site are predicted to be donors. The extra donor electron is denoted by a solid circle in the conduction band.
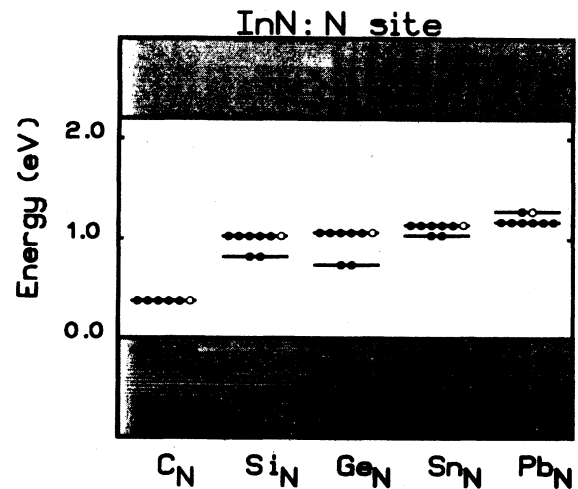

FIG. 7. Energy levels and occupancies of neutral column-IV impurities on the N site in InN.

holes (five).

We also note that the In vacancy, if its p-like level actually lies below the valence-band maximum, could dope InN p type (see Fig. 4).

2. n-type

For n-type doping, the best candidate, other than the N vacancy, is oxygen or some other chalcogen on a N site. Oxygen produces no deep levels in the fundamental band gap, and so is a classic shallow donor (Fig. 5). Neutral S, Se, and Te, in addition to producing the shallow donor, each also yield a p-like fully occupied deep level in the gap, which is driven up from the valence band because the s atomic-orbital energies of S, Se, and Te are higher than that of N.[23]

Column-IV impurities on the In site are not good candidates for donors, since they are predicted to have s-like deep levels in the gap, and so, when neutral, could either trap electrons or holes (Fig. 8). The predicted s-like levels for Pb and possibly Sn are close enough to the conduction-band edge that, allowing for a small uncertainty in the theory, these levels could lie resonant with the conduction band, and so could conceivably lead to shallow-donor behavior.

Thus we predict that the best dopants for InN are column-II impurities on the In site for p-type doping, and either a vacancy or oxygen on the N site for n-type doping. Column-IV dopants on either or both sites will tend to produce semi-insulating material.

D. Isoelectronic impurities

Isoelectronic impurities, namely impurities from the same column of the Periodic Table as the host atom they replace, are normally thought of as electronically inert. Rather spectacular counterexamples to this thinking are the N isoelectronic traps in $GaAs_xP_{1-x}$ and $Al_{1-x}Ga_xAs$ alloys, electron traps which play major roles in localizing electrons and enhancing the intensity of recombination radiation.

Isoelectronic impurities (unlike heteroelectronic donors and acceptors) can often trap one carrier without repelling a carrier of opposite sign, as in the case of N_P in GaP, which traps an electron—and the electron is subsequently able to capture a hole and to form an impurity-bound exciton.

In InN, according to the theory, neutral B on an In site produces such an isoelectronic trap, an s-like level slightly below the conduction-band edge (Fig. 6). (The p-like level of B is predicted to be resonant with the conduction band.) The remaining In-site isoelectronic traps are electronically inert, according to the theory, with their deep levels all being resonant.

On the N site, the Bi and Sb isoelectronic impurities produce both s-like and p-like deep levels in the band gap (fully occupied by electrons for the neutral defect) and hence are deep hole traps (Fig. 9). Similarly, As and P on the N site have (full) p-like deep levels in the gap, while their (full) s-like levels lie just below the valence-band maximum. They too are deep hole traps.

One of the interesting features of these isoelectronic traps is that they bind one carrier in a localized orbital, and so can bind an exciton by binding one carrier which binds the second through the electron-hole interaction. For example, B_{In} can bind an electron which, in turn, can bind a hole. Similarly, Bi_N, Sb_N, and As_N, or P_N, can bind a hole which can attract an electron. By localizing an exciton this way, an isoelectronic trap can enhance the intensity of the recombination luminescence, because the recombination rate for a localized state is generally much larger than for a delocalized state.

E. Other deep levels

Impurities two or more columns of the Periodic Table distant from the host atom they replace tend to be rather insoluble; nevertheless, their solubilities are not zero, and we include their predicted deep levels here for completeness.
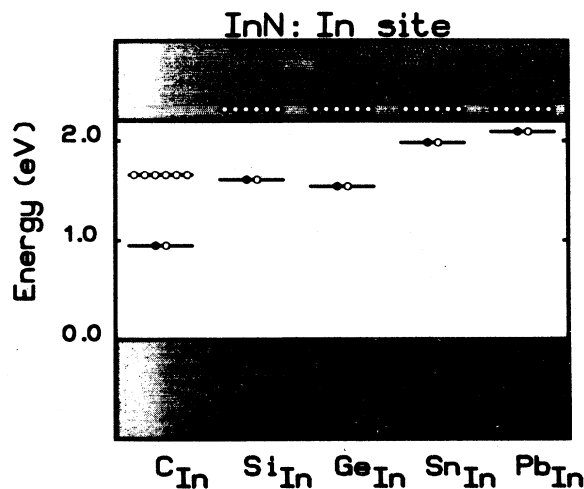

FIG. 8. Energy levels and occupancies of neutral column-IV impurities on the In site in InN.
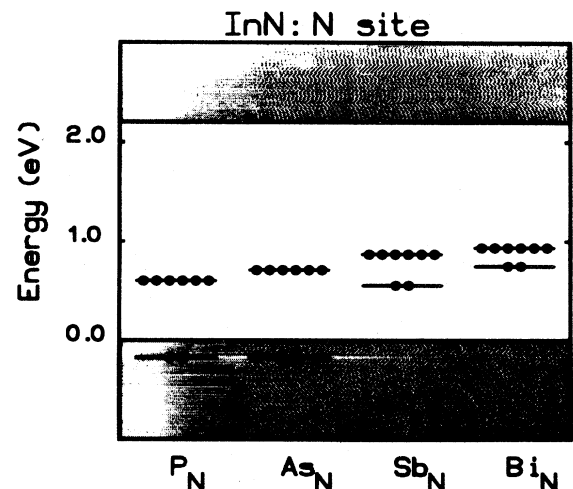

FIG. 9. Energy levels and occupancies of neutral isoelectronic impurities on the N site in InN.
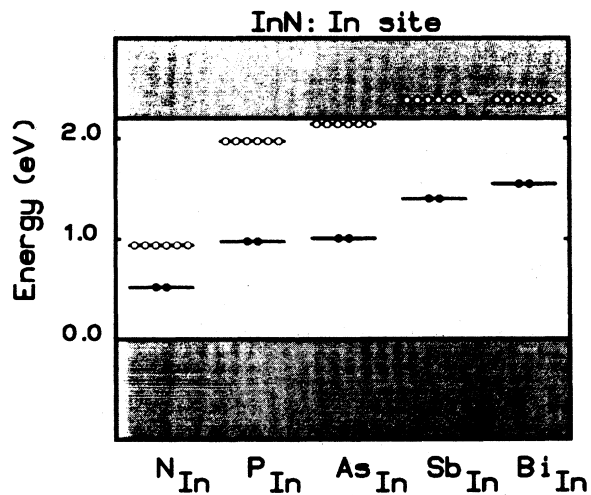
FIG. 10. Energy levels and occupancies of neutral column-V impurities on the In site in InN.
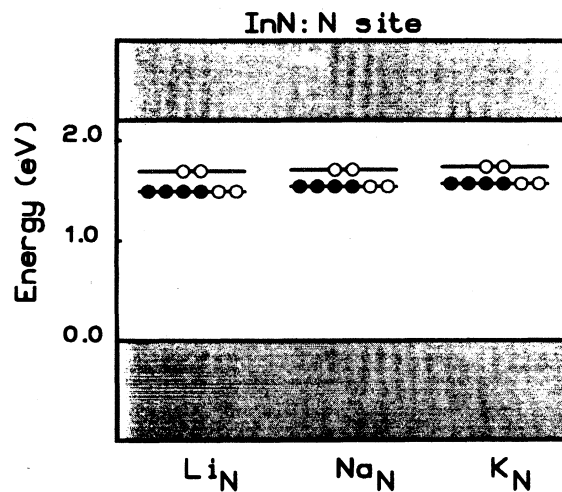

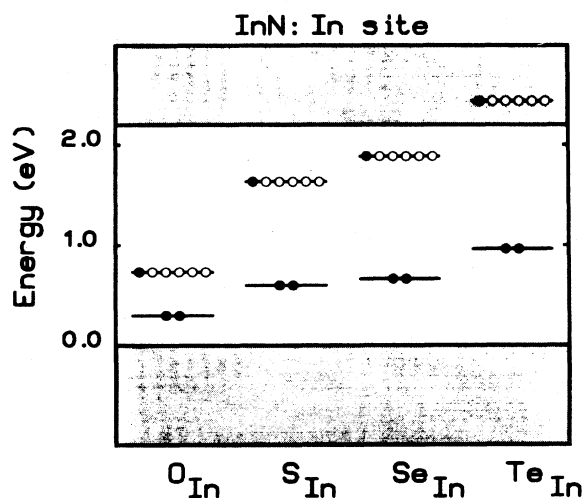FIG. 13. Energy levels and occupancies of neutral column-I impurities on the N site in InN.

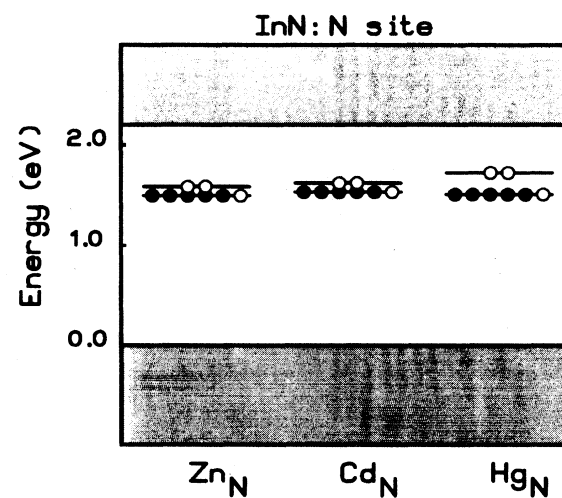FIG. 11. Energy levels and occupancies of neutral column-VI impurities on the In site in InN.

FIG. 14. Energy levels and occupancies of neutral column-II impurities on the N site in InN.
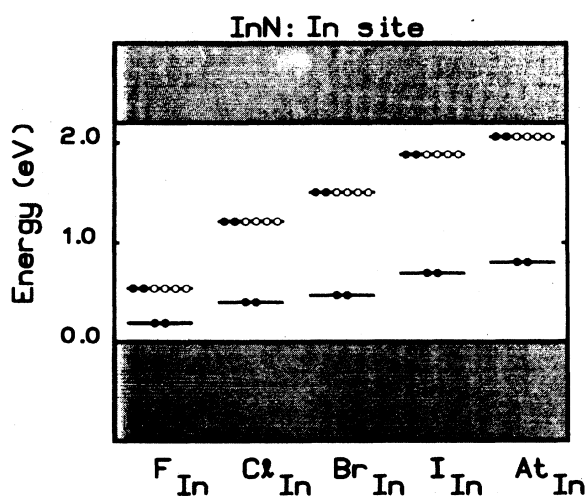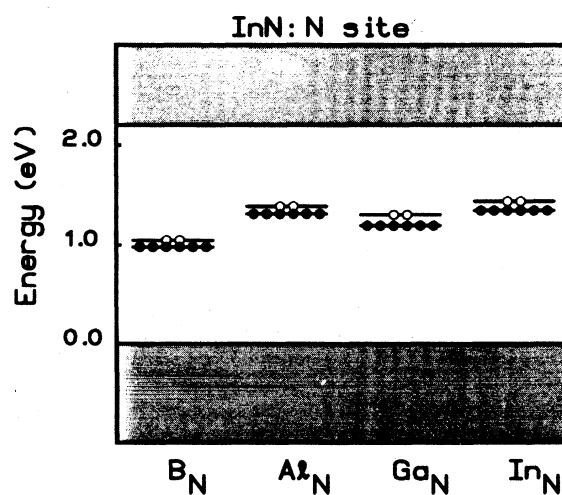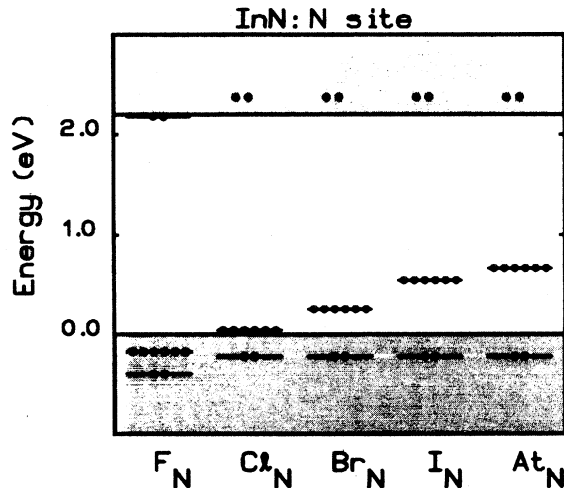

FIG. 12. Energy levels and occupancies of neutral column-VII impurities on the In site in InN.

FIG. 15. Energy levels and occupancies of neutral column-III impurities on the N site in InN.

FIG. 16. Energy levels and occupancies of neutral column-VII impurities on the N site in InN.

On the In site column-I and -II impurities are double acceptors and single acceptors, respectively, with their s and p deep levels in the conduction band (see Fig. 6). The column-V impurities produce deep traps: doubly occupied deep s levels in the gap and empty p levels that are in the gap for P_{In} and As_{In} but in the conduction band for Sb_{In} and Bi_{In} (Fig. 10). The column-VI impurities (Fig. 11) produce doubly occupied s levels deep in the gap plus singly occupied p levels that are deep in the gap, except for Te (which should produce a shallow donor!). The halogens on the In site should produce deep s and p levels in the gap (Fig. 12).

On the N site, columns-I, -II, and -III impurities all produce s-like and p-like deep levels in the gap of InN, all at about the same energy (Figs. 13–15). Column-VII impurities (Fig. 16) are all double donors, except possibly for F, which the theory predicts to be inert (which, within the theoretical uncertainty, may also be a double donor).

IV. DEEP LEVELS IN $In_x Ga_{1-x}N$ AND $In_x Al_{1-x}N$

A. Doping anomalies

The deep levels in the alloys $In_x Ga_{1-x}N$ and $In_x Al_{1-x}N$ are similar to those in InN. As functions of alloy composition they vary in energy rather smoothly. In many cases, deep levels that lie in the fundamental band gap for InN move out of the gap as a function of alloy composition and lie resonant with the host bands of GaN or AlN. When this happens, the character of the impurity changes (e.g., from a deep trap to a shallow donor) and a "doping anomaly" occurs.

There are two common types of doping anomaly: (i) false valences, and (ii) deep-shallow transitions.

False valences occur when, as a function of alloy composition, a deep level completely crosses the fundamental band gap. False valences do not occur in $In_x Ga_{1-x}N$ or $In_x Al_{1-x}N$, but, to understand the concept of a false valence, suppose that the s-like level of Si on a cation site (Fig. 8) were to descend from the conduction band of

GaN through the gap to the valence band of InN (it does not). Then the hole in the deep level would bubble up to the valence-band maximum, and neutral Si would become a single acceptor rather than a deep trap for both electrons and holes, and would have a false valence of -1 instead of its normal valence $(+1)$ with respect to the column-III cation. The reason false valences do not occur in $In_x Ga_{1-x}N$ or $In_x Al_{1-x}N$ is that the vacancies have both s-like and p-like levels in or very near the fundamental band gap (Fig. 4). Since the vacancies correspond to infinite defect potentials,[24] they separate the impurity levels that originate from the conduction band with finite defect potentials from those that come from the valence band—and, if the vacancy levels lie in the gap for all alloy compositions, prevent impurity levels from crossing the gap.

Deep-shallow transitions occur when a deep level in the gap moves out of the gap (as a function of x). Consider, as an example, a column-IV impurity such as Si on a cation site in $In_x Ga_{1-x}N$. In InN, neutral Si on an In site produces an s-like deep level in the gap occupied by one electron and one hole (Fig. 8). Therefore neutral Si_{In} is a deep electron and hole trap in InN, but in GaN or AlN, Si on a cation site produces an s-like level degenerate with the conduction band (Figs. 17 and 18). The electron that occupied this level in InN is autoionized in GaN or AlN and falls to the conduction-band edge (where the long-ranged Coulomb potential omitted in this paper traps the electron in a shallow-donor state). As a result cation-site Si in GaN or AlN is a shallow-donor impurity: its ground state has the extra electron in a shallow level (whereas in InN this extra electron occupies a deep level). For some intermediate alloy composition between InN and GaN, the deep level of Si_{In} in InN passes through the conduction-band edge, and the Si impurity changes its character from a deep trap to a shallow donor (Fig. 19).

The predicted dependences on alloy composition x of substitutional deep levels in $In_x Ga_{1-x}N$ are displayed in Figs. 19–22.
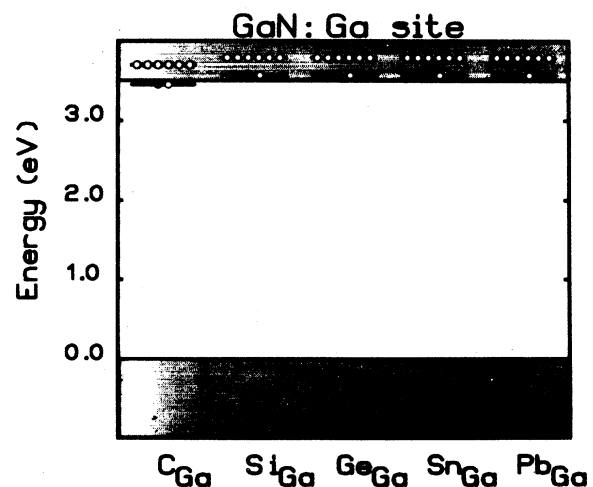

FIG. 17. Energy levels and electron occupancies of neutral column-IV impurities on the Ga site in GaN.
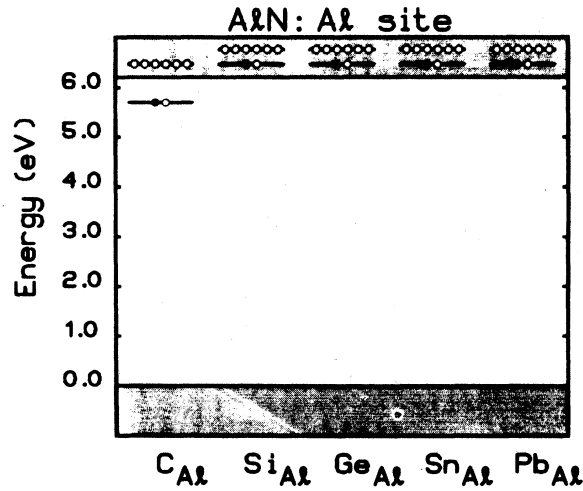
FIG. 18. Energy levels and electron occupancies of neutral column-IV impurities on the Al site in AlN.

The principal deep levels for substitutional defects in GaN and AlN are given in Figs. 17 and 18 and 23–30. The variation with alloy composition x of deep levels in $In_xAl_{1-x}N$ is given in Figs. 31–34. In many cases, the qualitative level structure for a specific impurity on a given site is the same for all alloy compositions of $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ (e.g., for oxygen on an anion site), and no deep levels cross either the valence-band or conduction-band edge as alloy composition is varied. In such cases, the qualitative doping character of the defect does not change, although its quantitative energy levels do, according to Figs. 19–22 and 31–34. Here we focus
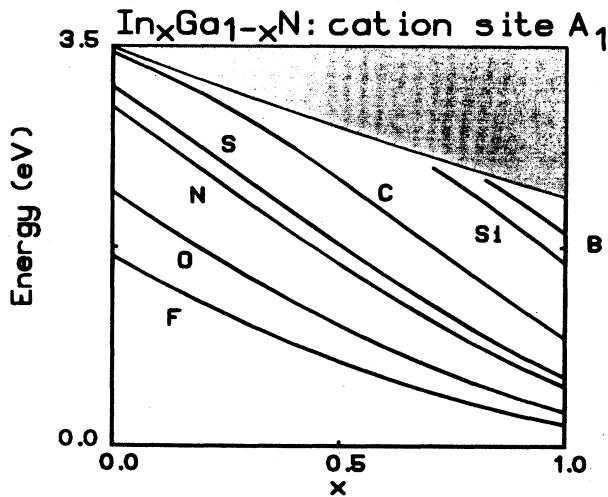
FIG. 19. A_1 (s-like) defect levels vs alloy composition x for impurities on the cation site in $In_{1-x}Ga_xN$. Levels for impurities from columns V, VI, and VII are completely filled, levels for impurities from column IV have one electron and one hole, and levels for isoelectronic impurities are unoccupied by electrons. Other impurities are acceptors.
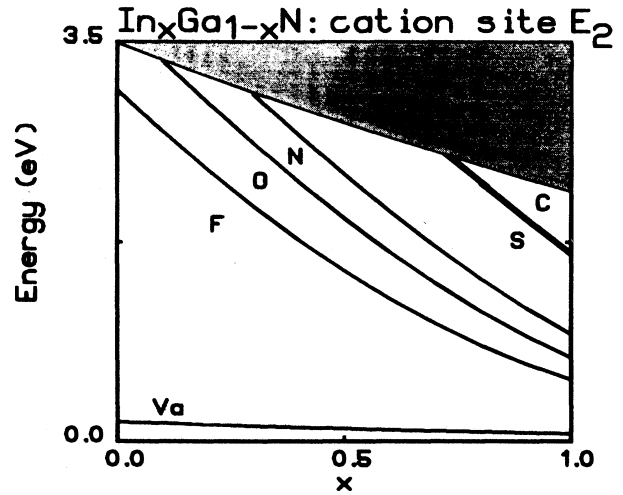

FIG. 20. E_2 (p-like) defect levels for impurities on the cation site in $In_{1-x}Ga_xN$. Only levels for impurities from columns VI and VII are partially filled by electrons; other impurity levels are unoccupied.

on those defects whose qualitative characters do change with alloy composition, defects that undergo deep-shallow transitions.

B. Native defects

The antisite defects, N on a cation site and a cation on a N site, have the same qualitative level structures in GaN and AlN, but a different one in InN (Figs. 4, 23, and 27). In InN the (neutral) N_{In} defect has both a filled (doubly occupied) s-like level and an empty p-like deep level in the gap. The p-like level is in the conduction band for GaN and AlN. Thus N_{In} is a deep trap for both electrons
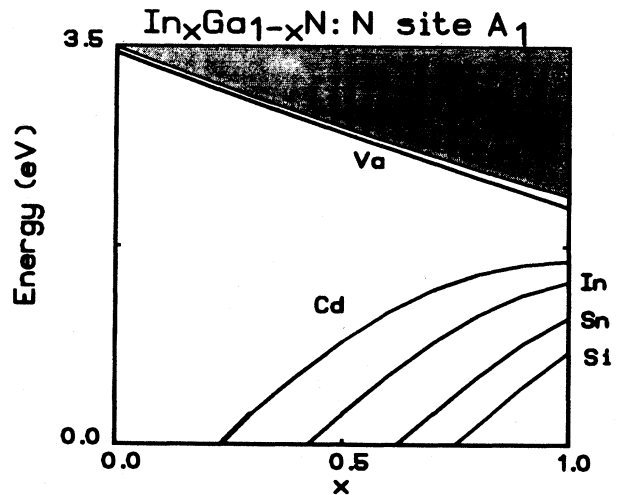

FIG. 21. A_1 (s-like) defect levels for impurities on the N site in $In_{1-x}Ga_xN$. All the levels shown are occupied by two electrons.
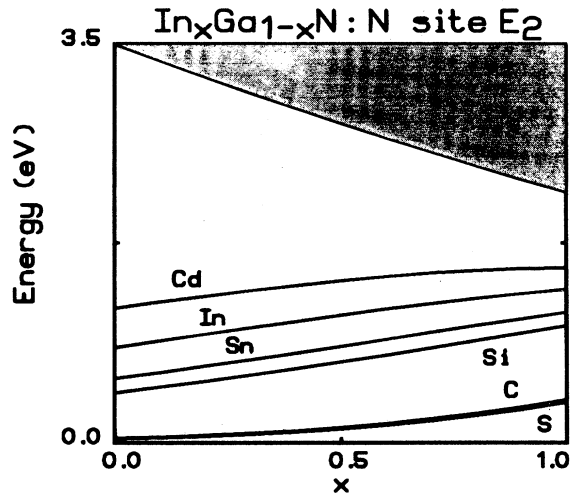
FIG. 22. E_2 (p-like) defect levels for impurities on the N site in $In_{1-x}Ga_xN$. Levels due to impurities which have fewer valence electrons than N, such as Si, are partially occupied by electrons and trap both electrons and holes. Impurities which have more valence electrons than N, such as O, are donors: their levels are completely occupied by electrons and have extra electron in the conduction band.

and holes, whereas neutral N_{Ga} in GaN and N_{Al} are deep-hole traps.

The cation-vacancy p-like level is barely in the gap for InN and GaN, and deep in the gap for AlN (Figs. 4, 23, and 27), whereas the s-like level is resonant with the valence band for InN and GaN, but in the gap for AlN. This vacancy, when neutral, can trap either electrons or holes.

The N vacancy is a shallow donor in InN and GaN (Figs. 4 and 23), with its p-like level in the conduction band and its s-like deep level doubly occupied in the gap. In AlN the p-like level lies in the gap (Fig. 27), making the neutral N vacancy a deep electron trap.
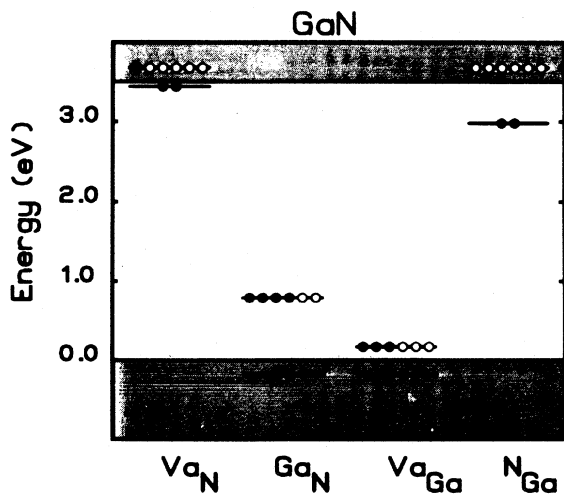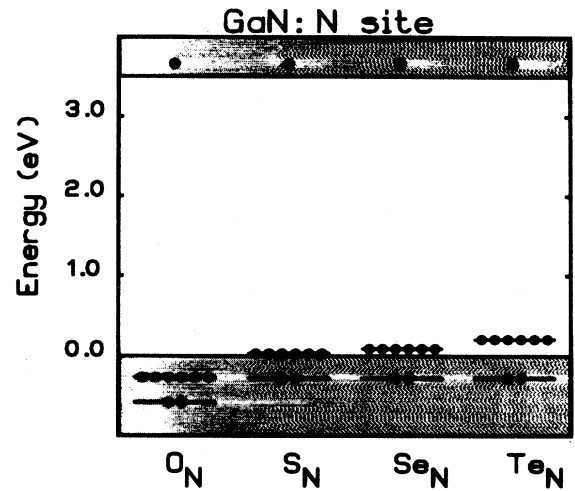

FIG. 24. Energy levels and electron occupancies of neutral column-VI impurities on the N site in GaN.
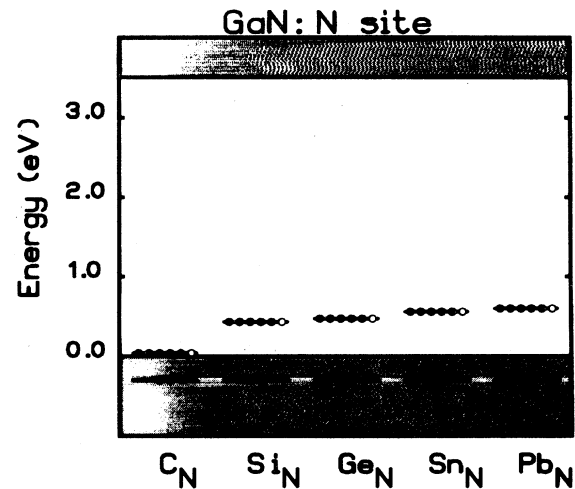

FIG. 25. Energy levels and electron occupancies of neutral column-IV impurities on the N site in GaN.

FIG. 23. Energy levels and electron occupancies of neutral native defects in GaN.
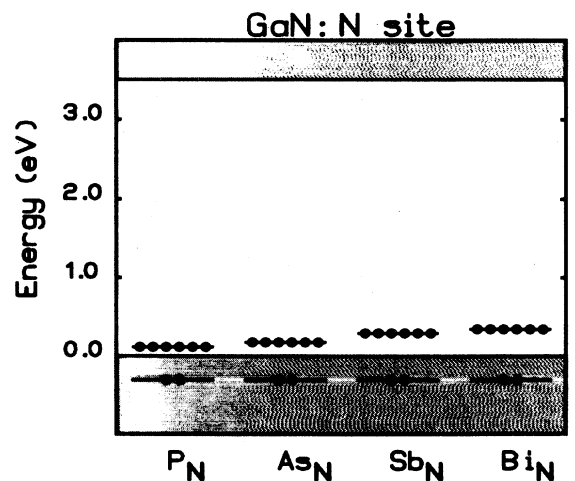

FIG. 26. Energy levels and electron occupancies of neutral isoelectronic impurities on the N site in GaN.
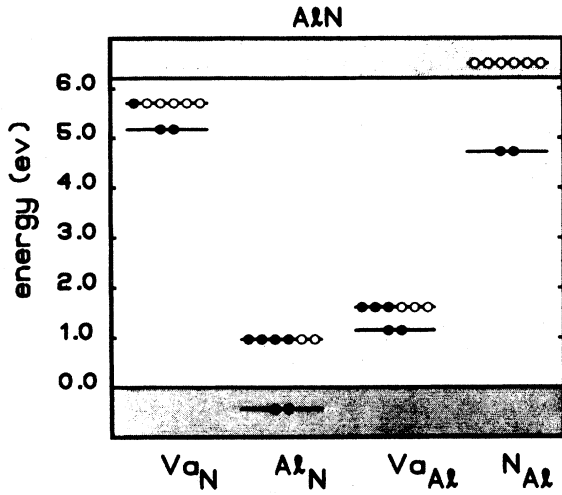
FIG. 27. Energy levels and electron occupancies of neutral native defects in AlN.
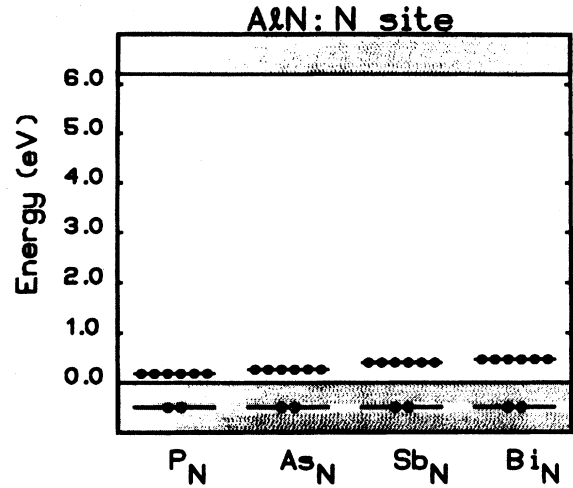

FIG. 30. Energy levels and electron occupancies of neutral isoelectronic impurities on the N site in AlN.
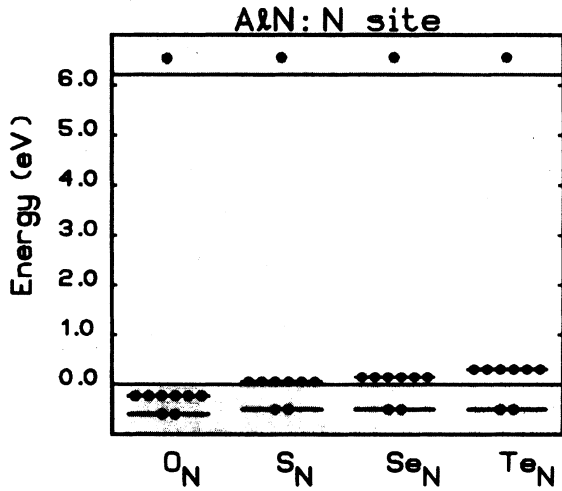

FIG. 28. Energy levels and electron occupancies of neutral column-VI impurities on the N site in AlN.
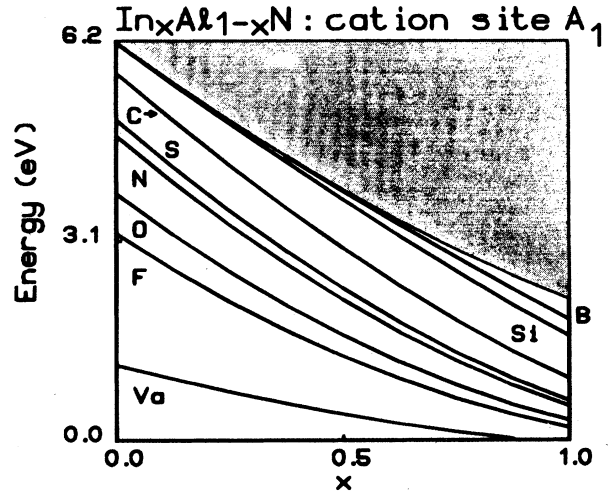

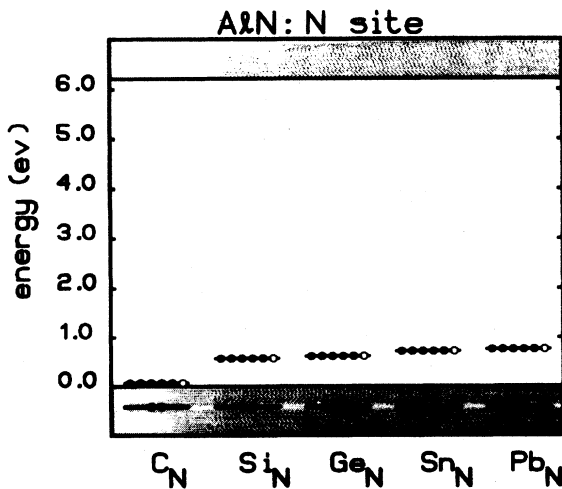FIG. 31. A_1 (s-like) defect levels for impurities on the cation site in $In_{1-x}Al_xN$.

FIG. 29. Energy levels and electron occupancies of neutral column-IV impurities on the N site in AlN.
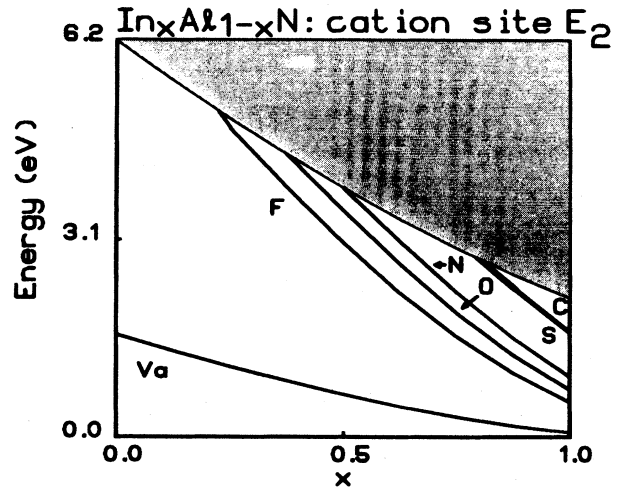

FIG. 32. E_2 (p-like) defect levels for impurities on the cation site in $In_{1-x}Al_xN$.
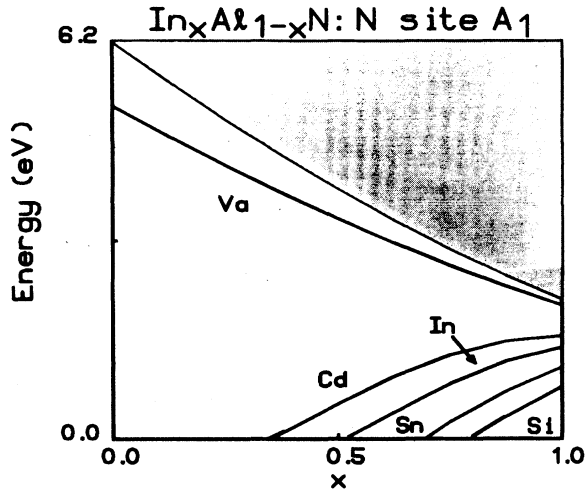
$In_xAl_{1-x}N$: N site A_1

FIG. 33. A_1 (s-like) defect levels for impurities on the N site in $In_{1-x}Al_xN$.

C. Donors and acceptors

Column-II impurities on cation sites are ordinary acceptors in InN, GaN, and AlN (Fig. 6). Column-I impurities are double acceptors.

Column-VI impurities on anion sites are ordinary donors, but S, Se, and Te each have a fully occupied deep p-like level deep in the gap for InN, and barely in the gap for GaN and AlN. (This level is in the valence band for oxygen.) See Figs. 5, 24, and 28.

Column-IV impurities on a N site each produce a deep electron and hole trap due to a p-like deep level in the gap (occupied by one hole and five electrons for the neutral defect) in InN, GaN, and AlN (Figs. 7, 25, and 29). The filled s-like deep level is also in the gap for InN (except for C), but not for GaN or AlN (See Figs. 7, 25, and 29).
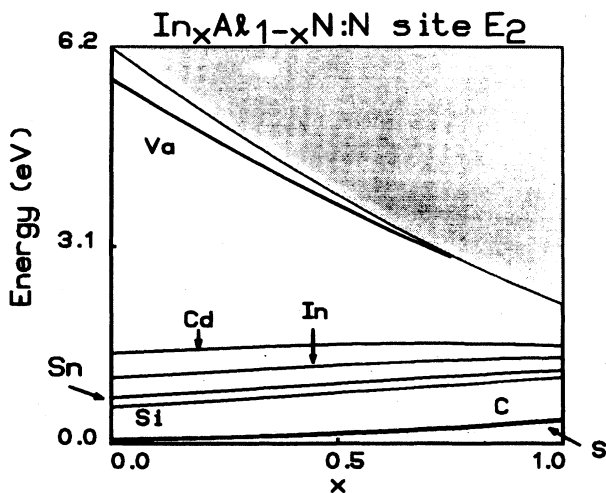
$In_xAl_{1-x}N$: N site E_2

FIG. 34. E_2 (p-like) defect levels for impurities on the N site in $In_{1-x}Al_xN$.

Column-IV impurities (except C) on the Ga site in GaN and the Al site in AlN produce shallow donors (Figs. 17 and 18). In InN (Fig. 8) they produce s-like deep levels in the gap. Indeed, the p-like deep level of C_{III} even lies well in the gap of InN, while the s-like levels of neutral carbon are predicted to be deep electron and hole traps for alloys of InN, GaN, and AlN.

D. Isoelectronic defects

The isoelectronic defect B on a cation site produces an s-like deep level in the gap of InN, but this level is in the conduction band of GaN and AlN (Fig. 6). Thus with decreasing x in $In_xGa_{1-x}N$ or $Al_xGa_{1-x}N$, B undergoes a deep-inert transition (Figs. 19 and 31). (The isoelectronic impurity has no long-ranged Coulomb potential and hence no shallow levels; thus it becomes inert rather than shallow when its deep levels are all resonant with host bands.) The other column-III isoelectronic defects are inert in InN, GaN, and AlN.

Column-V impurities on the N site (except N) all produce occupied p-like levels in the gap and are hole traps in InN, GaN, and AlN (Figs. 9, 26, and 30). In addition, Bi and Sb in InN have occupied s-like levels in the gap for InN. (These levels descend into the valence bands of GaN and AlN.)

V. SUMMARY

We have predicted the electronic structures of InN, $In_xGa_{1-x}N$, and $In_xAl_{1-x}N$, and find that these materials exhibit direct band gaps ranging from orange to ultraviolet. We find that the N vacancy, not the antisite defect N_{In}, is primarily responsible for InN's n-type character as grown. We propose that the nitrogen vacancy is also responsible for the 0.2-eV absorption feature and we confirm the Tansley-Foley suggestion that In_N is responsible for the absorption attributed to the midgap defect level. We predict that column-II impurities on cation sites should produce p-type behavior, while column-IV impurities should yield semi-insulating properties. B on an In site in InN should produce an isoelectronic electron trap, while column-V impurities on the N site should yield hole traps. However, the shallow-acceptor binding energy may be too large to permit thermal ionization of large numbers of holes, and it may be difficult to prepare these materials with high concentrations of positive carriers. Various deep-shallow and deep-inert transitions occur in the $In_xGa_{1-x}N$ alloy system. We conclude that $In_{0.40}Ga_{0.60}N$ and $In_{0.85}Al_{0.15}N$, if these materials can be successfully grown, should produce blue-green luminescence, and should be dopable, both n type and p type— although the shallow-acceptor binding energy may be so large as to limit the number of holes in the valence band.

ACKNOWLEDGMENTS

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[12]The virtual-crystal approximation can be given a modicum of justification because the Onodera-Toyozawa ratios for $In_xGa_{1-x}N$ [Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **24**, 341 (1968)], namely the ratios of In-Ga diagonal on-site matrix-element differences to valence- (conduction-) band width are 0.22 (0.98) and 0.04 (0.08) for s and p orbitals, respectively. These values place $In_xGa_{1-x}As$ in the "amalgamated" limit for the valence band and marginally for the conduction band. The values are somewhat higher than the corresponding values for $Al_{1-x}Ga_xAs$, 0.07 (0.16) and 0.005 (0.008), a material for which the virtual-crystal approximation is known to be a good model for the electronic structure; however, the theory agrees with the band-gap data of Osamura *et al.* [K. Osamura, S. Naka, and Y. Murakami, J. Appl. Phys. **46**, 3432 (1975)] to within 0.3 eV. (These data were taken at 77 K, while our theory describes the material at 4 K.) Thus we conclude that this approximation will provide an adequate "zeroth-order" description of all the InN alloys.

Similar values for $In_xAl_{1-x}N$ are 0.94 (0.10) and) 0.40 (1.66) for the valence (conduction) band for s and p states, respectively. These parameters vary with composition and are in the "amalgamated" regime for Al-rich alloys.

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[17]A substitutional defect in a wurtzite material has two spin-degenerate s-like (A_1) states, two spin-degenerate p_z-like states (A_1), and four spin-degenerate p_x-like and p_y-like states (E_2). We approximate the ratio between the repeat distance in the z axis c and the lattice constant in the x-y plane a to be $c/a=(\frac{8}{3})^{1/2}$. In this approximation the small splitting between the p-like A_1 and E_2 states vanishes.

[18]The Green's functions are defined by

$$G_l(E)=\sum_{n,\mathbf{k}}\int d^3k\frac{|\langle l',\mathbf{k},n|l',\mathbf{k},n\rangle|^2}{E-E_n(\mathbf{k})},$$

where $E_n(\mathbf{k})$ is the nth eigenvalue at wavevector $\mathbf{k}$ and $|l,\mathbf{k},n\rangle$ is the nth eigenvector at $\mathbf{k}$ with $l=s$ or p for the A_1 or E_2 symmetry, respectively.

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