The unusual conduction band minimum formation of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys

L. Bellaiche[1], N.A. Modine[2] and E.D. Jones[2]
[1] *Physics Department,*
University of Arkansas, Fayetteville, Arkansas 72701, USA
[2] *Sandia National Laboratories, Albuquerque, NM, USA*
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The conduction band minimum formation of $Ga(As_{0.5-\delta}P_{0.5-y}N_{2y})$ is investigated for small nitrogen compositions (0.1% <2y< 1.0%), by using a pseudopotential technique. This formation is caused by two unusual processes both involving the deep-gap impurity level existing in the dilute alloy limit $y \rightarrow 0$. The first process is an anticrossing with the Γ_{1c}-like extended state of $Ga(As_{0.5}P_{0.5})$. The second process is an interaction with other impurity levels forming a subband. These two processes are expected to occur in any alloys exhibiting a deep-gap impurity level at one of its dilute limit.

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Adding a few nitrogen atoms to $Ga(As_{1-x}P_x)$ alloys considerably affects the optical properties by creating an impurity level [1], which is mainly localized around the nitrogen atoms [2,3]. This nitrogen impurity level is resonant in the conduction band of $Ga(As_{1-x}P_x)$ systems when x is smaller than 30 % [1]. For larger phosphorus composition, the impurity level is below the conduction band minimum of $Ga(As_{1-x}P_x)$ alloys. In other words, the nitrogen impurity level is *inside* the band gap of $Ga(As_{1-x}P_x)$ solid solutions for $x > 0.30$ [1]. The energetic separation between the deep-gap impurity level and the conduction band minimum of $Ga(As_{1-x}P_x)$ alloys is strongly composition-dependent: it can be as large as $\simeq$ 130 meV when $x = 0.5$ [1], i.e for $GaAs_{0.5}P_{0.5}$, and as small as 6 meV for $x = 1$, i.e. for pure GaP [3–5].

Interestingly, adding a few arsenic or phosphorus atoms to pure GaN has much milder effects on the first excited state. This state is very much like the conduction band-minimum of pure GaN. It is extended throughout all the material [2,3,6].

Consequently, two different nitrogen compositional regimes must exist in $Ga(As_{1-x-y}P_xN_y)$ solid solutions: an impurity-like region, for small y, in which the first unoccupied state is strongly localized around nitrogen atoms, and a band-like region, for larger y, in which the first excited state is a Bloch-like state. In fact, impurity and band-like regions must exist in any semiconductor alloys exhibiting an isovalent impurity level at one of their dilute alloy limits. Examples of such alloys are $Cd(S_{1-x}Te_x)$ [7–10], $Zn(S_{1-x}Te_x)$ [9,11,12], $Zn(Te_{1-x}O_x)$ [13], and $Ga(P_{1-x}Bi_x)$ [13].

Many experimental and theoretical studies were conducted from the sixties to the eighties on the impurity levels in *very dilute* II-VI and III-V semiconductor alloys [7–13]. More recently, various works investigated the properties of *concentrated* semiconductor alloys having isovalent impurity levels in their dilute alloy limits [3,6,14–16]. On the other hand, very few studies have been aimed to characterize and understand the compositional transition from the impurity region to the band-like region. A possible reason for this is that an experimental realization of such study may require the growth of many samples scanning a sufficiently dense mesh of compositions, in order to avoid the overlook of the transition. Similarly, theoretical works on the subject are very scare because of the large computational cost usually associated with the study of dilute alloys. The following questions thus remain unresolved: does the impurity-like to band-like transition occur at a specific composition as indicated in Ref. [3] or is it a smooth transition over a compositional window as proposed in Ref [17]? If it is a smooth transition, what are the quantum mechanical laws governing it? Where does the wavefunction delocalization occur, i.e. within a given sublattice or in any area of the crystal? Obviously, answering these questions is of large fundamental interest, and will greatly extend the current knowledge of semiconductor physics.

The purpose of this letter is to provide the answers to all the questions mentioned above, by performing a theoretical investigation. We chose the $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys as a test case since the separation between impurity level and conduction band minimum of $Ga(As_{0.5}P_{0.5})$ is quite large ($\simeq$ 130 meV) for $y \rightarrow 0$. The impurity-like to band-like transition may thus occurr at nitrogen compositions large enough to be detected by current state-of-the-art computational tools. Our main findings are that the transition from impurity–to–band-like behavior of the first unoccupied state gradually occurs for very small nitrogen compositions, namely around 0.4 %. It consists of two processes both involving the deep-gap impurity level existing at the dilute limit. The first process is an anticrossing repulsion with the delocalized Γ_{1c}-like conduction state of the $Ga(As_{0.5}P_{0.5})$ system. The second process is an interaction with the different impurity states forming a nitrogen band. These two processes lead to a delocalization of the first excited state in the nitrogen sublattice, and induce a large redshift of the band-gap of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys, when increasing the nitrogen composition.

In the present study, we model a

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random $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ system by randomly occupying the anion sites of a large supercell –typically 1000 atoms– with the alloyed elements. The atoms are then allowed to relax to their equilibrium positions by minimizing the strain energy, as predicted by the valence force field approach (VFF) [2,3,18,19]. Having obtained a relaxed random configuration of a large, periodic unit cell, we compute its band structure by using the generalized strain-dependent empirical pseudopotential approach of Ref. [20]. This new technique yields an excellent accuracy, as demonstrated by the nearly-perfect reproduction of the experimental band-gap of the complex $(Ga_{1-x}In_x)(As_{1-y}N_y)$ quaternaries as a function of the compositions and/or as a function of pressure [20]. The capability of the empirical pseudopotential approaches of treating large supercells is mainly due to the "folded spectrum method" [21], which provides a computational time scaling linearly with the number n of atoms, while standard band structure methods lead to a time scaling of n^3. The calculations are performed at the reciprocal Γ point of the large supercells.

To better understand the transition mechanism from the impurity-like regime to the band-like region, we also project the alloy wavefunction ψ_i of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ on pure zinc-blende states $\phi_{n,\mathbf{k}}$

$$P_{i,n,\vec{k}} = | < \psi_i \mid \phi_{n,\mathbf{k}} > |^2 \quad , \qquad (1)$$

where n and k denotes the band index and the first Brillouin zone vectors associated with pure zinc-blende symmetry [3]. In the present study, the selected $\phi_{n,\mathbf{k}}$ is the Γ_{1c} state of $Ga(As_{0.5}P_{0.5})$ alloys, as mimicked by the virtual crystal approximation (VCA) [22]. These projections reveal the zinc-blende character of the alloy wavefunctions. A large value of the projection indicates that the alloy wavefunction is a Bloch-like state, while a alloy state localized in the real space has a small $P_{i,n,\vec{k}}$ projection.

A direct measure of the real-space wavefunction localization can be given by calculating the atomic-type parameter $Q_{\beta,i}$ (β = Ga, As, P or N in Ga(As,P,N)) defined as:

$$Q_{\beta,i} = \frac{F}{N_\beta} \frac{1}{[a(x)]^3} \sum_{j \,\epsilon\, \beta} \int_{V_j} |\psi_i|^2 \, dV \quad , \qquad (2)$$

where the sum is over all the atomic sites j of type β. Here F is a normalization factor (equal to 27). N_β is the number of atoms of type β, which implies that $Q_{\beta,i}$ represents an *averaged* quantity over atomic-type. $a(x)$ is the lattice constant of the alloy and the integration of the square of the wave function ψ_i, is performed in a volume $V_j = [a(x)/6]^3$ centered around atoms j of type β. A large value of $Q_{\beta,i}$ indicates strong localization of the ψ_i wavefunction on atoms of β type [2,3].

Figure 1 shows the electronic energy levels of some excited states in $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ system as a function of the nitrogen composition. Two important states are denoted $E_\Gamma^{(-)}$ and $E_\Gamma^{(+)}$. Figures 2 displays the projections of $E_\Gamma^{(-)}$ and $E_\Gamma^{(+)}$ wavefunctions into the Γ_{1c} VCA state, and clearly demonstrates that $E_\Gamma^{(+)}$ is derived from the Γ_{1c}-like conduction states of $Ga(As_{0.5}P_{0.5})$ alloys [23]. The calculated direct band-gap of random $Ga(As_{0.5}P_{0.5})$ alloys is around 2.1 eV, in very good agreement with the low-temperature measurement of 2.13 eV given in Ref. [1].

For very low nitrogen compositions, $E_\Gamma^{(-)}$ is the deep-gap impurity level. Interpolating to $y \to 0$ our two smallest nitrogen compositions calculations – corresponding to the insertion of one nitrogen atom inside a 1728 or 1000 atoms supercell – leads to an energetic position of $E_\Gamma^{(-)}$ lower by 115 meV from the conduction band minimum of $Ga(As_{0.5}P_{0.5})$ alloys. This quantitative value is in rather good agreement with the experimental finding of $\simeq$ 130 meV [1], and further demonstrates the accuracy of our simulations.

Increasing slightly the nitrogen composition by inserting more and more nitrogen atoms inside our 1000 atoms supercells naturally results to an interaction between impurity deep-gap states, and thus leads to the formation of a nitrogen subband within the band-gap of $Ga(As_{0.5}P_{0.5})$ alloys. Consequently, new nitrogen-localized states appear at the reciprocal Γ point of our supercells, as also shown in Figure 1.

Adding nitrogen atoms to the $Ga(As_{0.5}P_{0.5})$ alloy has a double effect on $E_\Gamma^{(-)}$. First of all, $E_\Gamma^{(-)}$ strongly interacts with $E_\Gamma^{(+)}$, as demonstrated by the drastic decrease (respectively, increase) of the electronic energy level of $E_\Gamma^{(-)}$ (respectively, $E_\Gamma^{(+)}$) seen in Figure 1. This is particularly strinking for very small nitrogen compositions, typically ranging between 0 and 0.2 %. Secondly, $E_\Gamma^{(-)}$ is further pushed down for larger nitrogen composition. This second push is due to the other nitrogen impurity levels forming the nitrogen band. Figure 2 indicates that the energetic changes are associated with a rather unusual modification of the alloy wavefunctions. As a matter of fact, the $E_\Gamma^{(-)}$ wavefunction has almost no Γ_{1c} character for very small nitrogen compositions, as consistent with its nitrogen localized nature, while its projection on the Γ_{1c} VCA state of $Ga(As_{0.5}P_{0.5})$ is as large as 42 % for only 1 % of nitrogen composition! Inversely, $E_\Gamma^{(+)}$ progressively loses its Γ_{1c}-character when the nitrogen composition increases. Figure 3 shows that the nitrogen-averaged type localization parameter of $E_\Gamma^{(-)}$ (see Eq (2)) drastically decreases when the nitrogen composition increases. On the other hand, we find that the *product* between the nitrogen $2y$ composition and this localization parameter is independent of the nitrogen composition. The former finding indicates a real-space delocalization of $E_\Gamma^{(-)}$ which is consistent with its nitrogen-induced gain of Γ_{1c} character. The latter findings demonstrates this wavefunction delocalization occurs within the nitrogen sublattice.

The energetic results of Fig. 1 and the wavefunctions analysis of Fig. 2 and 3 clearly reveal the unusual mechanism of the conduction band minimum formation in $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$. $E_\Gamma^{(-)}$ anticrosses with $E_\Gamma^{(+)}$ state, and also interacts with other nitrogen impurity levels to generate the Bloch-like conduction band-minimum of *concentrated* $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys. This conduction band-minimum is delocalized within the nitrogen sublattice. It originates from the deep-gap impurity level existing at the *dilute* nitrogen composition limit, as proposed by Yaguchi *et al* [17]! The transition of the lowest excited state from impurity-like to Bloch-like behavior occurs over a nitrogen compositional window that we estimate to be centered around 0.4 % (see Fig. 2). Another direct consequence of these two unusual processes is that the band-gap of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys drastically decreases when increasing the nitrogen composition. For instance, incorporating only 1 % of nitrogen leads to a band-gap of 1.8 eV, i.e. around 300 meV smaller than the band-gap of $Ga(As_{0.5}P_{0.5})$ alloys! Nitrogen-induced anticrossing between different electronic levels have already been discovered in anion-mixed nitride alloys [24–27]. However, we believe that it is the first time that it is demonstrated that such anticrossing participates to the formation of the conduction band minimum from a deep-gap impurity level. It is worth noting that we find that $E_\Gamma^{(-)}$ does not interact with any X_{1c}-like delocalized state, despite the fact that the X_{1c} and Γ_{1c}-like states of $Ga(As_{0.5}P_{0.5})$ are very close to each other in energy [2]. This lack of interaction, as well as the anticrossing between $E_\Gamma^{(-)}$ and $E_\Gamma^{(+)}$ are probably the two main reasons why the $GaP_{1-y}N_y$ alloy is predicted to have a *direct* band-gap for very small nitrogen compositions –around 3% [3,14]–, despite the fact that pure GaP exhibits a X_{1c} state lower by 0.5 eV from the Γ_{1c} level energy [2]!

In summary, we used the strain-dependent empirical pseudopotential technique of Ref. [20] to investigate the conduction band minimum formation of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ as a function of the nitrogen composition. Our calculations reveal that this formation is very unusual, and consists of a double interaction both involving the deep-gap impurity level existing in the dilute alloy limit. First of all, an anticrossing with the Γ_{1c}-like state of $Ga(As_{0.5}P_{0.5})$. Secondly, an interaction with other nitrogen states leading to the formation of a nitrogen band. As a result, the conduction band minimum of concentrated $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys originates from a strongly localized impurity level existing at the dilute limit, and its wavefunction is delocalized within the nitrogen sublattice. Another consequence of this double interaction is that the band-gap of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ strongly decreases when increasing the nitrogen composition. Similar features are expected to occur in any semiconductor alloys exhibiting an isovalent deep-gap impurity level at one of its dilute limit.

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[23] Figure 2 indicates that $E_\Gamma^{(+)}$ in $GaAs_{0.5}P_{0.5}$ alloy do not converge to 100% of Γ_{1c} character. This is due to the fact that the virtual crystal model wavefunctions do not exactly correspond to the wavefunctions of a real GaAsP alloy. This is the reason why we use the wording Γ_{1c}-*like* in the text.
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FIG. 1. Electronic energy levels of some excited states in $Ga(As_{0.5-y}P_{0.5-y}N_{2y}$ alloys as a function of the nitrogen composition. Two important states are denoted $E_\Gamma^{(-)}$ and $E_\Gamma^{(+)}$ (see text). All the impurity states folding into the Γ-point are shown by means of open symbols. The origin of the energy is chosen to be at the top of the valence band.

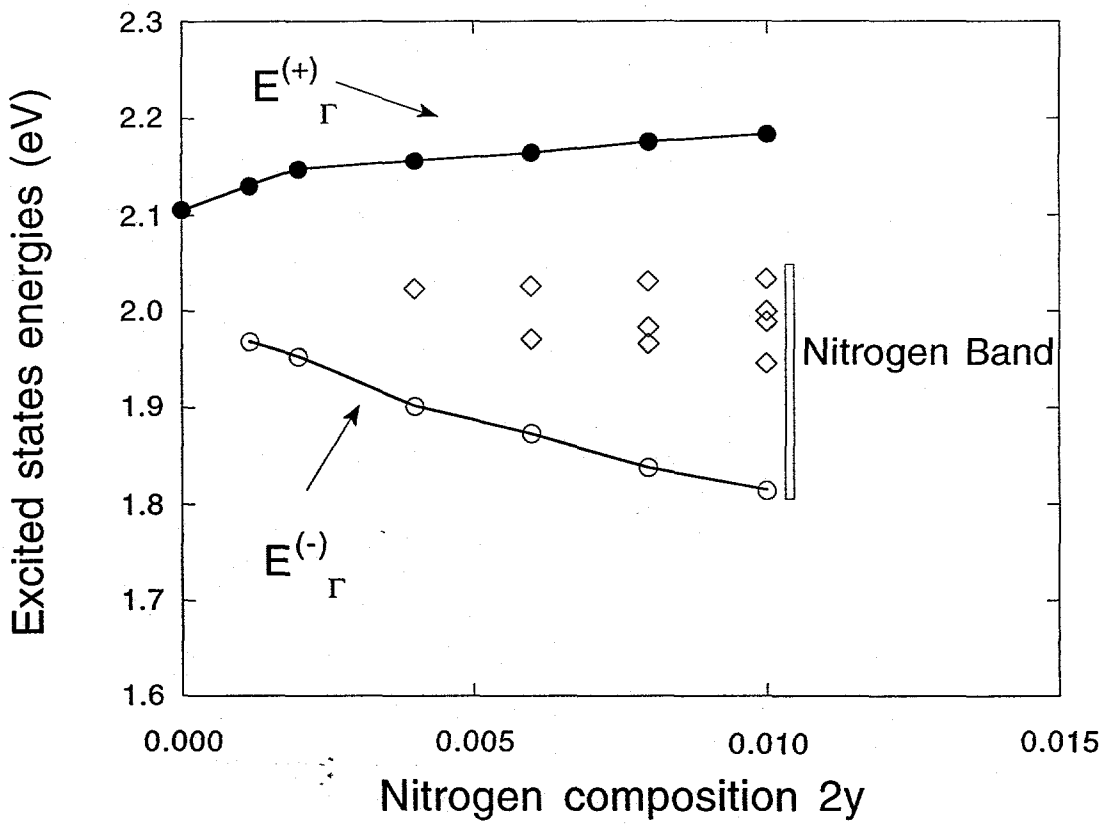

FIG. 2. Projection of the alloy wavefunctions $E_\Gamma^{(-)}$ and $E_\Gamma^{(+)}$ in $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$ alloys onto the VCA Γ_{1c} state of $Ga(As_{0.5-y}P_{0.5})$, as a function of the nitrogen composition.

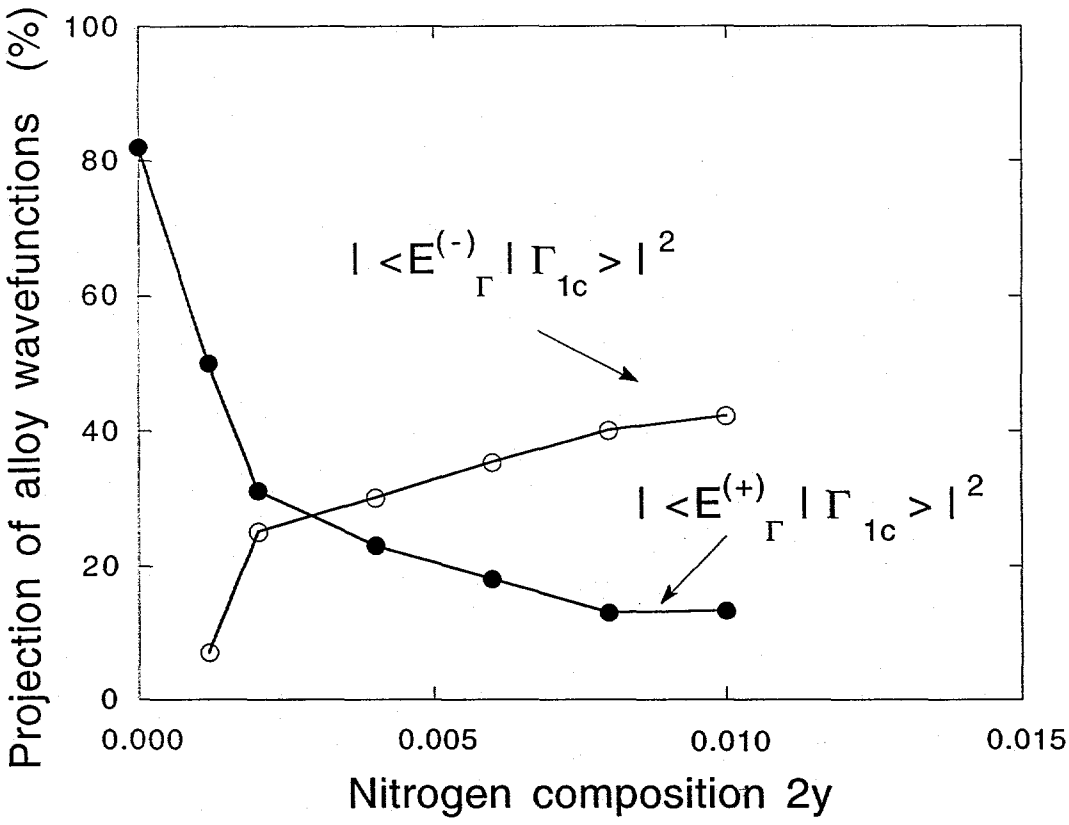

FIG. 3. Localization parameter $Q_{\beta,i}$ of atoms β =N [Eq (2)] for the $i = E_{\Gamma}^{(-)}$ state of $Ga(As_{0.5-y}P_{0.5-y}N_{2y})$. The localization parameters of the other atoms (e.g., Ga, As and P) have values ranging between 1 and 2, and are nearly independent of the composition