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

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The conduction band minimum formation of Ga(A_{0.5-y}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 → 0. The first process is an anticrossing with the Γ_{1e}-like extended state of Ga(A_{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(A_{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(A_{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(A_{1-x}P_x) alloys. In other words, the nitrogen impurity level is inside the band gap of Ga(A_{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(A_{1-x}P_x) alloys is strongly composition-dependent: it can be as large as ≈ 130 meV when x = 0.5 [1], i.e for GaA_{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-like state of the Ga(A_{0.5}P_{0.5}) is quite large (≈ 130 meV ) for y → 0. The impurity-like to band-like transition may thus occur 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-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 localized Γ_{1e}-like conduction state of the Ga(A_{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(A_{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$_{1-y}$P$_y$N$_y$) quantum wells 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 the standard band structure methods lead to a time scaling $n^3$. The calculations are performed at the reciprocal $\Gamma$ 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 $\psi_i$ of Ga(As$_{0.5-y}$P$_{0.5-y}$N$_{2y}$) on pure zinc-blende states $\phi_{n,k}$

$$P_{n,k} = |<\psi_i | \phi_{n,k}>|^2 ,$$

(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 $\phi_{n,k}$ is the $\Gamma_{1c}$ 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 $P_{n,k}$ projection.

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

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

(2)

where the sum is over all the atomic sites $j$ of type $\beta$. Here $F$ is a normalization factor (equal to 27). $N_{\beta}$ is the number of atoms of type $\beta$, 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 $\psi_i$ is performed in a volume $V_j = [a(x)/6]^3$ centered around atoms $j$ of type $\beta$. A large value of $Q_{\beta,i}$ indicates strong localization of the $\psi_i$ wavefunction on atoms of $\beta$ 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 $\Gamma_{1c}$ VCA state, and clearly demonstrates that $E_{\Gamma}^{(+)}$ is derived from the $\Gamma_{1c}$-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 $\approx 130$ 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 $\Gamma$ 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 striking 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 $\Gamma_{1c}$ character for very small nitrogen compositions, as consistent with its nitrogen localized nature, while its projection on the $\Gamma_{1c}$ 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 $\Gamma_{1c}$-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 2$y$ 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 $\Gamma_{1c}$ character. The latter findings demonstrates this wavefunction delocalization occurs within the nitrogen sublattice.
The energetic results of Fig. 1 and the wavefunction analysis of Fig. 2 and 3 clearly reveal the unusual mechanism of the conduction band minimum formation in Ga(AsO.5–yP0.5–yVNzV). \( E_T^-(\text{+}) \) anticrosses with \( E_T^-(\text{+}) \) state, and also interacts with other nitrogen impurity levels to generate the Bloch-like conduction band-minimum of concentrated Ga(AsO.5–yP0.5–yVNzV) 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(AsO.5–yP0.5–yVNzV) 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(AsO.5P0.5) 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 \( E_T^- \) does not interact with any \( X_{1c} \)-like delocalized state, despite the fact that the \( X_{1c} \) and \( \Gamma_{1c} \)-like states of Ga(As0.5P0.5) are very close to each other in energy [2]. This lack of interaction, as well as the anticrossing between \( E_T^- \) and \( E_T^+ \) are probably the two main reasons why the GaP1–yNy 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 \( \Gamma_{1c} \) 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(AsO.5–yP0.5–yVNzV) 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 \( \Gamma_{1c} \)-like state of Ga(As0.5P0.5). 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(AsO.5–yP0.5–yVNzV) 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(AsO.5–yP0.5–yVNzV) 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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FIG. 1. Electronic energy levels of some excited states in Ga(As$_{0.5-y}$P$_{0.5-y}$N$_y$) 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 $\Gamma$-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 $\Gamma_{1c}$ state of Ga(As$_{0.5-y}$P$_{0.5}$), as a function of the nitrogen composition.
FIG. 3. Localization parameter $Q_{d,i}$ of atoms $\beta = N$ [Eq (2)] for the $i = E^{(-)}_t$ state of $\text{Ga(As}_{0.5-y}\text{P}_{0.5-y}\text{N}_{2y})$. 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.