Tight-binding approach to calculation of localised perturbations in semiconductors

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Abstract. The replacement of As by N in GaAs introduces several perturbations, including both a change in potential at the N site and also long range strain relaxation in the crystal. It can be very useful to describe this perturbation in terms of the change in the Hamiltonian, $\Delta H$, due to the introduction of N. Using plane-wave approaches, $\Delta H$ treats explicitly all atomic displacements in the structure. By contrast, a tight-binding approach allows a much simpler analysis. We illustrate the benefits of the tight-binding method by considering Ga(P,As:Bi) and GaNAs. We show that the tight-binding method provides a clear and quantitative explanation for many of the unusual electronic properties of these and related alloys, including the non-monotonic variation of electron effective mass, $m_e$, and gyromagnetic ratio, $g_e$, in GaNAs.

1. Introduction

There has been considerable interest over the last decade in the electronic structure of extreme semiconductor alloys, such as GaN$_x$As$_{1-x}$ and GaN$_x$P$_{1-x}$. It is well established that replacing a P or As atom by N introduces a defect level, which lies in the energy gap for GaP, and is a resonant state, above the conduction band edge in GaAs [1]. These localized states arise because of the large difference in size and electronegativity between N and the other group V elements. For conventional alloys such as Al$_x$Ga$_{1-x}$As, the energy gap has a close to linear variation with composition $x$, and the electronic structure can be well described using the virtual crystal approximation, which assumes that the Al and Ga atoms can each be treated like an average (Al$_x$Ga$_{1-x}$) atom. This approach fails for extreme alloys such as GaN$_x$As$_{1-x}$, where the introduction of a small amount of N leads to a very rapid reduction in energy gap, with the energy gap decreasing by ~150 meV for $x = 1\%$. Different models have been used to explain this observed reduction. The strong red shift can be modeled successfully by a band-anticrossing (BAC) interaction between the host III-V material conduction band edge (CBE) and a higher-lying band of N-related defect states which form above the CBE. This 2-level BAC model parameterizes and reproduces many of the key features of the alloy band structure, including the reduced energy gap [2], low electron mobilities [3], and a strong conduction band non-parabolicity [4]. Empirical pseudopotential calculations also describe well the key features of the band structure, and have been used to interpret the band structure in terms of the electronic states being a mixture of “perturbed host states” and N-related defect states [5].

We review here how calculations using the tight-binding model both support the BAC model and also provide useful additional insight into detail of the electronic structure of extreme alloys. We first
describe how the localized basis states used in the tight-binding method make it a particularly useful approach to study perturbations in semiconductor alloys. We then summarise how it is considerably more straightforward to derive the BAC model using localised basis states, as in the tight-binding model, compared to the plane-wave basis states which are often used in empirical pseudopotential and in \textit{ab-initio} approaches. We illustrate how the tight-binding method can quantitatively explain key experimental results for dilute nitride alloys, including the unexpectedly large and nonmonotonic variation of the electron effective mass observed in GaN.

Figure 1: (a) Schematic of periodic potential, $V_{\text{d}}(x)$ and atomic basis states, $\phi_{0i}$. (b) An impurity potential and basis state $\phi_{0i}$ are introduced, with no change in period. (c) Long-range shift in atomic sites and in basis states, $\Phi_{0i}$, with (d) resultant long-range change in potential, $V_{\text{f}}(x) - V_{\text{d}}(x)$.

2. Tight-binding description of localized states

Replacing an As atom by N in GaAs has two main effects on the periodic crystal potential, as illustrated schematically in Fig. 1 (a). Firstly there is a change in the local potential at the N site (Fig. 1(b)) and secondly there is a change in the longer range potential, due to the crystal relaxing in response to the Ga-N bond length being 20% smaller than the Ga-As bond length (Fig. 1(c)). As a result the difference $\Delta H$ between the Hamiltonian $H_0$ for the perfect crystal and the Hamiltonian $H_1$ with N present includes not just a large local perturbation at the N site but also includes a significant long-range component, due to the crystal relaxation (Fig. 1(d)). If we use plane-wave basis states, then there is a significant contribution to the difference in the wavefunctions $|\psi_{0i}\rangle$ and $|\psi_{1i}\rangle$ in the perfect and relaxed crystals due to this change in the long-range potential. However, if we work with localized basis states which are centred on the atomic sites then it is much easier to analyse the impact of $\Delta H$. We have for the unperturbed crystal in Fig. 1(a) that

$$H_0 \sum_i a^i_0 \phi_{0i} = E_{0i} \sum_i a^i_0 \phi_{0i},$$

with the energy states found by solving the determinant equation $|H_{ij}^0 - E_{ij}| = 0$, with $H_{ij}^0 = \langle \phi_{0j} | H_0 | \phi_{0i} \rangle$, and where we assume that the orbitals $|\phi_{0j}\rangle$ and $|\phi_{0i}\rangle$ are orthogonal to each other. Turning to the perturbed crystal, we have, using the modified basis states $\phi_{0i} = \phi_{D}$ and $\phi_{1i} = T\phi_{0i}$ ($i \neq 0$) from Fig. 1(c) that
with the energy states now found by solving the determinant equation $|H_{ij} - E\delta_{ij}| = 0$, where the matrix elements $H_{ij}$ involve interactions between the modified basis states, $\phi_{ij}$.

The BAC model explains the extreme band gap bowing in GaInN$_x$As$_{1-x}$, in terms of an interaction between two levels, one at energy $E_N$ associated with the localized N impurity states $\psi_{Ni}$, and the other at energy $E_c$ associated with the extended CBE state $\psi_{c0}$ of the GaAs matrix, with the two states linked by a matrix element $V_{NC}$ describing the interaction between them [2]. The conduction band dispersion of GaInN$_x$As$_{1-x}$ is then given by the lower eigenvalue $E_c$ of the determinant

$$
\begin{vmatrix}
E_N & V_{NC} \\
V_{NC} & E_c + \frac{\hbar^2 k^2}{2m_c}
\end{vmatrix}
$$

(3)

where $m^*_c$ is an appropriately chosen band edge effective mass for the Ga(As) host material.

To investigate the resonant state $\psi_{N0}$, and its behaviour, we have developed an accurate sp$^3$s* tight-binding (TB) Hamiltonian for GaInN$_x$As$_{1-x}$ and related alloys [6]. This Hamiltonian fully accounts for the observed experimental data, and also gives results in good agreement with pseudopotential calculations [5,7]. By comparing the calculated CBE states found in large supercells $\psi_{c1}$ (defined with respect to states equivalent to the set $\phi_{1i}$) and $\psi_{c0}$ (defined with respect to states equivalent to the set $\phi_{0i}$), we can derive the nitrogen resonant state $\psi_{N0}$ associated with an isolated N atom. The calculation effectively treats the basis states $\phi_{1i}$ and $\phi_{0i}$ as equivalent. With this assumption of equivalent bases, $\psi_{c1}$ can then be calculated as a linear combination of $\psi_{c0}$ and $\psi_{N0}$, with $\psi_{N0}$ given by

$$
\psi_{N0} = \frac{\psi_{c1} - \alpha \psi_{c0}}{\sqrt{1 - \alpha^2}}
$$

(4)

where $\alpha = \langle \psi_{c1} | \psi_{c0} \rangle$, and where we have set $\langle \phi_{1i} | \phi_{0j} \rangle = \delta_{ij}$ when treating the change in basis states between Figs. 1(a) and (c). With this assumption, we find that $\psi_{N0}$ is highly localised, with over 50% of its probability density on the N site and the four neighbouring Ga atoms.

To investigate the role of disorder, we extended the tight-binding and two-level model to disordered GaN$_x$As$_{1-x}$ supercells. We find for Ga$_x$N$_{1-x}$As$_{1-M}$ supercells containing ~1000 atoms that the energy and wavefunction of the CBE state can be well represented by considering the interactions between a Linear Combination of Isolated Nitrogen resonant States and the GaAs CBE wavefunction, $\psi_{c0}$ (LCINS method). For any given Ga$_x$N$_{1-x}$As$_{1-M}$ supercell, we associate a localised resonant state $\psi_{Ni}$ with each of the $M$ nitrogen atoms ($i = 1, \ldots, M$), and a wavefunction $\psi_{c0}$ with the host matrix CBE. We then analyse the supercell conduction band states by solving the $(M+1) \times (M+1)$ matrix equation linking the $M$ defect states and the CBE state, $H_{ij} \phi = E S_{ij} \phi$, where $H_{ij} = \langle \psi_{Ni} | H | \psi_{Nj} \rangle$ and $H_{i,M+1} = \langle \psi_{N0} | H | \psi_{c0} \rangle$, $1 \leq i,j \leq M$, with $H$ the full GaNAs Hamiltonian, and $S_{ij} = \langle \psi_{Ni} | \psi_{Nj} \rangle$ a matrix reflecting that neighbouring N states can overlap each other.

3. LCINS Analysis of GaNAs band structure

The filled data points in Fig. 2 show the low temperature (a) electron effective mass $m_e$ and (b) gyromagnetic ratio $g_e$ determined by magnetophotoluminescence for a wide range of GaN$_x$As$_{1-x}$ samples [6,8]. The solid lines show the predicted variation of $m_e$ and $g_e$ in bulk GaN$_x$As$_{1-x}$ using the two-level BAC model of Eq. (3). This model significantly underestimates the measured mass, even for $x$ as low as 0.1%. The open symbols show the low temperature values of $m_e$ and $g_e$ calculated for selected compositions, $x$, using the LCINS model and including resonant defect states associated with a full random distribution of N atoms.

The calculated and experimental data are in remarkable agreement with each other, confirming that hybridisation between the CB edge and nitrogen cluster states causes the observed enhancement of
effective mass values. The mass $m_e$ initially increases with composition $x$, as the band edge passes between $x = 0.1$ and $0.2\%$ through N-N pair states, where a Ga atom has two N neighbours. For $x > 0.2\%$, we might expect a decrease in $m_e^*$ towards the 2-level BAC value, as the CBE $E_\text{c}$ level passes through the N pair states. However, the density of other low-energy N-related states starts to increase markedly with increasing $x$. These combined interactions lead to a further reduction in the $\Gamma$ character at the band edge, consistent with the additional, sudden increase in $m_e$ observed experimentally in Fig. 2 in this concentration range. Similar effects are also observed in the theoretical and experimental data for $g_\epsilon$. These results highlight the advantages of using a tight-binding approach with localised basis states to analyse the effects of localised perturbations in semiconductors.

![Figure 2: Dependence (a) of the electron mass $m_e$ and (b) gyromagnetic ratio $g_\epsilon$ on nitrogen effective concentration in GaN$_x$As$_{1-x}$. Solid symbols: experiment; open square symbols: full tight-binding-based theory. The dashed lines show the calculated values of $m_e$ and $g_\epsilon$ based on the BAC model of Eq. (3) [From ref. 6].](image)

4. Band structure of GaAsBi and GaPBi

It has been proposed that replacing arsenic by bismuth (Bi) could introduce a similar BAC effect to that in GaNAs [9]. Bi is much larger than As, and is also less electronegative. In this case the resonant defect level should therefore lie in the valence band and the anticrossing interaction should occur between the Bi defect level and the valence band edge (VBE). The energy gap of GaAs$_{1-x}$Bi$_x$ is observed both theoretically [10] and experimentally [11] to decrease quite rapidly with increasing Bi composition, but it has not yet been confirmed as to whether this reduction is due to an anticrossing interaction [9] or is better explained using more conventional alloy models. To address this question, it is useful to first consider GaPBi, because Bi is sufficiently different to P that it introduces defect states just above the VBE in GaP [12]. Because these states are in the energy gap, it is then much easier to identify and follow the interaction between the VBE and these levels as a function of increasing Bi composition. Our calculations show clearly for GaPBi that there is an anticrossing interaction between the Bi defect states and the GaP VBE.

Full tight-binding calculations were carried out on 1000-atom supercells to compare the valence band structure of GaY and of GaY$_{1-x}$Bi$_x$ (Y = P, As) as a function of Bi composition $x$ for Bi compositions ranging from 0.2\% (1 Bi atom) to 7\% (35 Bi atoms), with the Bi atoms placed at random on the group V sites. We first analyse the electronic structure of GaP$_{1-x}$Bi$_x$, where it is easier to follow the evolution of the Bi energy states.

When we replace a single P atom by Bi in a Ga$_{500}$P$_{500}$ supercell, we calculate that this gives a four-fold degenerate defect level above the GaP VBE. These four levels have the same symmetry as the
heavy- and light-hole states at the valence band maximum. Even in a 1000 atom supercell, these defect levels interact with the host matrix VBE states. We calculate that the isolated Bi impurity states are 0.052 eV above the GaP VBE, with each impurity state 62% localised on the Bi atom.

Having established the character of the isolated Bi impurity states, we now investigate how the Bi levels evolve as we increase the number \( L \) of Bi atoms in a \( \text{Ga}_{500}\text{P}_{500},\text{L}_{2},\text{Bi}_{L} \) supercell. In order to trace the evolution of the highest valence states, we use the \( sp^3s^* \) Hamiltonian to calculate exactly the energy states and wavefunctions at the zone centre of the \( \text{Ga}_{500}\text{P}_{500},\text{L}_{2},\text{Bi}_{L} \) supercell. Figure 3 shows the calculated \( \text{Ga}_{500}\text{P}_{500},\text{L}_{2},\text{Bi}_{L} \) supercell energy spectrum projected onto the unperturbed GaP VBE heavy-hole and light-hole wavefunctions, \( \psi_{\alpha,i} \):

\[
G_\alpha(E) = \sum_{i=1}^N |\alpha, i|^2 \langle \alpha | \hat{T} | E - v_i \rangle
\]

where \( |\alpha, i|^2 \) is the amplitude of the \( i^{th} \) eigenstate, of energy \( E_i \), projected onto the \( \alpha^{th} \) valence band zone centre state (\( \alpha = 1, \ldots, 4 \)).

We see in the left hand panel of Fig. 3 for a single Bi atom in the supercell (\( x = 0.2\%\)) that the amplitude of the unperturbed GaP valence band edge states, \( \psi_{\alpha,0} \), is distributed over two levels, \( E \) and \( E_v \), as expected from the BAC model of Eq. (3). Because of the \( T_\alpha \) symmetry around the isolated Bi atom, the four \( E \)-related levels are degenerate and so cannot be distinguished for \( M = 1 \) (\( x = 0.2\%\)). We calculate for the isolated Bi impurity that the band anticrossing interaction \( V_{MD} \) between the Bi defect levels \( E_{Bi} \) and the VBE \( E_v \) is of magnitude \( V_{MD} = \beta x^3 \), with \( \beta = 1.67 \) eV. The calculated magnitude of the interaction parameter \( \beta \) in \( \text{GaP}_{1,0},\text{Bi}_{x} \) is then comparable to that which we have calculated previously for \( \text{GaP}_{1,0},\text{N}_{x} \) (\( \beta = 1.74 \) eV) and for \( \text{GaAs}_{1,4},\text{N}_{x} \) (\( \beta = 2.00 \) eV) [6].

![Fractional Γ Character [HH/LH]](image)

When we consider a single Bi atom in a \( \text{Ga}_{500}\text{As}_{500},\text{Bi}_{1} \) supercell (\( x = 0.2\%\)), we find that the HH and LH Γ character remains predominantly on the highest valence states in this case, with a small fraction of the Γ character (< 3%) also associated with an energy state 0.25 eV below the GaAs valence band maximum. Using Eq. (4), we identify that the states which mix with the GaAs VBE states are localised Bi resonant defect levels, with very similar character to the localised defect states found in GaPBi. The Bi state is calculated to be 65% localised on the Bi atom in the \( \text{Ga}_{500}\text{As}_{500},\text{Bi}_{1} \) supercell, compared to being 62% localized in the equivalent GaPBi supercell. We calculate by evaluating \( V_{MD} = \langle \psi_{\text{Bi}} | H | \psi_{\alpha,0} \rangle \) that the band anticrossing interaction \( V_{MD} \) between the Bi resonant defect level \( E_{Bi} \) and the valence band edge \( E_v \) is of magnitude \( V_{MD} = \beta x^3 \), with \( \beta = 1.22 \) eV. The calculated magnitude of the interaction parameter \( \beta \) in \( \text{GaAs}_{1,4},\text{Bi}_{x} \) is then smaller than the value in GaPBi, reflecting that there is less difference in electronegativity and size between a Bi and As atom than there is between Bi and P.

Figure 3: Calculated evolution of fractional Γ character \( G_\alpha(E) \) (defined in Eq. (5)) for a series of \( \text{Ga}_{500}\text{P}_{500},\text{L}_{2},\text{Bi}_{L} \) supercells. The BAC interaction can be clearly observed between Bi defect states in the energy gap and the valence band edge for \( x \leq 1\% \). States due to Bi pairs and Bi clusters are also observed at higher Bi composition.
In addition to the BAC interaction pushing the VBE upwards, the conduction band edge energy is calculated to shift down by about 40 meV per % of Bi replacing As, but the fractional Γ character, $f_\Gamma = |<\psi_c|\psi_{c0}>|^2$ at the CBE remains close to 1. The evolution of the conduction band states is then best described using a conventional alloy model, including band gap bowing.

In summary, our calculations confirm that the highest valence band states in Ga(P,As)Bi can be described using a BAC model. The reduction in energy gap with composition in GaNAs is due predominantly to the conduction band BAC interaction, with most of the energy gap difference giving rise to a large conduction band offset and virtually zero valence band offset between GaAs and GaNAs. By contrast, the conduction band edge energy also varies with composition in GaAsBi, so that the reduction in energy gap with increasing Bi composition then contributes to approximately equal conduction and valence band offsets between GaAsBi and GaAs.

5. Conclusions
In summary, we have described how a well parameterised tight-binding method can be particularly suited to investigating the effects of localised perturbations in the electronic structure of semiconductor alloys. We illustrated the method by considering two examples. We first reviewed how tight-binding calculations provide a clear and quantitative explanation for many of the unusual electronic properties of GaNAs, including the non-monotonic variation of electron effective mass, $m_e$, and gyromagnetic ratio, $g_e$, in this alloy. We then presented for the first time an analysis which shows that the highest valence band states in Ga(P,As)Bi can be described using a BAC model, but that the conduction band edge energy also varies with composition in GaAsBi, so that the reduction in energy gap with increasing Bi composition then contributes to approximately equal conduction and valence band offsets between GaAsBi and GaAs.

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