Virtual crystal description of III–V semiconductor alloys in the tight binding approach

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Abstract

We propose a simple and effective approach to construct the empirical tight-binding parameters of ternary alloys in the virtual crystal approximation. This combines a new, compact formulation of the strain parameters and a linear interpolation of the Hamiltonians of binary materials strained to the alloy equilibrium lattice parameter. We show that it is possible to obtain a perfect description of the bandgap bowing of ternary alloys in the InGaAsSb family of materials. Moreover, this approach is in good agreement with supercell calculations using the same set of parameters. This scheme opens a way for atomistic modeling of alloy-based quantum wells and quantum wires without extensive supercell calculations.

Keywords: alloys, tight-binding, virtual crystal approximation

(Some figures may appear in colour only in the online journal)
ternary alloys is quite large, with for instance an absolute gap minimum at \( x = 0.4 \) for the InAs\(_x\)Sb\(_{1-x}\) alloy. In [8] the bowing has been accounted in tight-binding by introducing bowing of diagonal energies and transfer matrix elements. This approach gives reasonable agreement with experiments, but at the expense of introducing a number of additional parameters. The observed correlation between alloy bowing and lattice mismatch of parent binaries suggests that lattice mismatch is a driving effect in bowing mechanism, which we explore in the present work.

We start from standard \( s^d\sigma\) tight-binding model which is explained in details in [6]. The wave function is written as a linear combination of localized atomic-like function which are assumed to be orthogonal [9]. The Hamiltonian in this basis is a matrix of the size \( 10 \times 2 \times n \), where \( n \) stands for basis functions \( \{s, s^\dagger, p_x, p_y, p_z, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx}\} \). 2 stands for spin index and \( n \) is the number of atoms in the system for a finite nanostructure or number of atoms in elementary cell for periodic structures. Explicit form of matrix elements of the Hamiltonian may be found in [10] or [11]. As has been shown previously [12–15], standard ETB allows for the detailed description of electronic structure of unstrained materials, but has limited use for strained materials. For a more complete description of strain we extend the procedure given in [13], as explained below.

Here we describe the strain Hamiltonian for the bulk material, but this procedure may be generalized to nanostructures as explained in [16]. The strain contribution to the tight-binding Hamiltonian has three rather distinct parts. First contribution is a scaling of the transfer matrix elements with respect to bond length [6]

\[
V_{n_1n_2|ij} = V^0_{n_1n_2|ij} \left( \frac{d_{n_1n_2}}{d^0_{n_1n_2}} \right)^n_{ij},
\]

where \( n_1 \) and \( n_2 \) are two neighboring atoms, \( ij \) encodes corresponding Slater–Koster off-diagonal parameters, \( d_{n_1n_2} \) is the relaxed interatomic distance, \( d^0_{n_1n_2} \) is the bond length in unstrained bulk binary compound and \( n_{ij} \) is the exponent of power-law scaling [6]. Here, we use an original parametrization given in table 1.

Another contribution, also considered in [6, 13], is a shift of orbital energies proportional to hydrostatic component of strain tensor:

\[
E_\beta = E^0_\beta - \alpha_\beta (E_{\text{ref}} - E_{\text{ref}})\frac{\lambda E}{3},
\]

where \( \beta \) enumerates orbitals, \( \alpha_\beta \) are parameters given in table 1. For each binary compound, we define a reference energy \( E_{\text{ref}} = E_\xi - 6E_{(1,0,0)} \), where \( E_{(1,0,0)} = h^2/(2\pi a)^2/2m_0 \) and \( a \) is the lattice constant. The introduction of the reference energy is particularly important as it avoids a change of the strain parameters when a band offset comes into play. The scaling to orbital energy used previously [6, 13] had the merit of being analytically exact in the case of a free-electron crystal where energy is purely kinetic. The choice made for the reference energy is motivated by the aim to keep, as a first approximation, the \( s^\dagger \) orbitals the same as in the free electron limit, and thus the number of adjustable parameters is reduced by maintaining \( \alpha_\beta = 2 \). \( E_{\text{ref}} \) can also be understood as the average crystal potential.

The third contribution is a splitting of the on-site energies of degenerate orbitals according to strain symmetry [16, 12–15]. The simplest approach for this contribution is to use a correction proportional to the strain tensor [13, 16]. The strain tensor here is an input parameter for the TB approximation which is set from the standard elasticity theory for VCA alloy or can be extracted from atomistic calculations, e.g. following [16]. Using the method of invariants, it can be shown that the \( p \)-orbital same-atom block in the tight-binding Hamiltonian (the basis functions are \( p_x, p_y, p_z \)) has the form:

\[
\delta H = \begin{pmatrix}
\lambda(\sqrt{3} \delta_1 - \varepsilon_2)
& \lambda(\sqrt{3} \delta_1 + \varepsilon_2)
& \lambda(\sqrt{3} \delta_1 + \varepsilon_2)

\lambda(\sqrt{3} \delta_1 + \varepsilon_2)
& \lambda(\sqrt{3} \delta_1 - \varepsilon_2)
& \lambda(\sqrt{3} \delta_1 - \varepsilon_2)

\lambda(\sqrt{3} \delta_1 - \varepsilon_2)
& \lambda(\sqrt{3} \delta_1 + \varepsilon_2)
& 2\lambda \varepsilon_2
\end{pmatrix},
\]

where we defined \( \varepsilon_1 = \sqrt{3}(\varepsilon_{xx} - \varepsilon_{yy}) \), \( \varepsilon_2 = 2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy} \), \( \varepsilon_{ij} \) are components of strain tensor and \( \mathbf{u} \) is the internal strain vector [17]. Following [13] we also assume \( \xi = \pm \lambda_\xi \), with ‘+' for anion and ‘–’ for cation. To make the parametrization space more compact, we assume that the parameters on anion and cation are connected as:

\[
\lambda_{\beta \gamma} = \frac{1}{2}(E_{p\beta} - E_{\text{ref}})\eta_{0,0}
\]

\[
\lambda_{\beta \gamma} = -\frac{8}{3}(E_{p\beta} - E_{\text{ref}})\eta_{1,1}.
\]

Here \( \beta \) is either anion or cation and parameters \( \eta_{0,0}, \eta_{1,1} \) are similar to parameters introduced in [13]. Note that in principle, a completely similar splitting holds for the \( f_\Gamma \) representation of \( d \) orbitals. However, for deformation potentials at

\begin{table}[h]
\centering
\caption{Strain parameters used in calculations.}
\begin{tabular}{|c|c|c|c|}
\hline
  & InAs & GaAs & GaSb & InSb \\
\hline
\( \alpha_\beta \) & 0.5603 & 0.0000 & 2.3379 & 3.7257 \\
\hline
\( \alpha'_\beta \) & 1.9539 & 1.6257 & 1.6791 & 1.9344 \\
\hline
\( \alpha''_\beta \) & 1.7005 & 2.4531 & 2.1356 & 1.7868 \\
\hline
\( \alpha_\gamma \) & 0.5603 & 0.0000 & 2.3378 & 3.7257 \\
\hline
\( \alpha'_\gamma \) & 1.9539 & 1.6257 & 1.6791 & 1.9344 \\
\hline
\( \alpha''_\gamma \) & 1.7005 & 2.4531 & 2.1356 & 1.7868 \\
\hline
\hline
\( n_{\alpha\alpha} \) & 5.4002 & 4.5619 & 4.5148 & 2.6840 \\
\hline
\( n_{\beta\beta} \) & 4.4014 & 3.0363 & 6.1992 & 5.1288 \\
\hline
\( n_{\alpha\beta} \) & 6.8053 & 3.1594 & 5.8953 & 3.9353 \\
\hline
\( n_{\text{e\epsilon}} \) & 5.8401 & 3.2676 & 4.8067 & 2.5400 \\
\hline
\( n_{\alpha\text{pet}} \) & 6.8116 & 6.9229 & 5.4202 & 3.0409 \\
\hline
\( n_{\beta\text{pet}} \) & 6.9787 & 6.2602 & 3.5118 & 7.1611 \\
\hline
\( n_{\text{pet\pet}} \) & 6.0189 & 7.0824 & 2.2676 & 4.5794 \\
\hline
\( n_{\text{e\epsilon}\text{dd}} \) & 2.7559 & 3.5344 & 5.1031 & 2.6183 \\
\hline
\( n_{\text{e\epsilon}\text{dd}} \) & 6.0212 & 7.3976 & 4.9576 & 2.9027 \\
\hline
\hline
\( \sigma_{001} \) & 0.0952 & 0.1476 & 0.1130 & 0.1993 \\
\hline
\( \sigma_{11} \) & 0.1456 & 0.1588 & 0.1236 & 0.1000 \\
\hline
\end{tabular}
\end{table}
Table 2. Bulk ETB parameters used in present calculations.

| InAs | GaAs | GaSb | InSb |
|------|------|------|------|
| α | 6.0580 | 5.6500 | 6.0959 | 6.4794 |
| VBO | 0.4000 | 0.0000 | 0.7600 | 1.0500 |
| $E_p^*$ | −6.4738 | −5.9820 | −6.0022 | −6.1516 |
| $E_s^*$ | 16.8502 | 19.4477 | 16.4645 | 14.7582 |
| $E_d^*$ | −0.1418 | −0.3803 | −0.6905 | −0.3634 |
| $E_s^{p*}$ | 16.8393 | 19.4548 | 16.4745 | 14.8015 |
| $E_d^{p*}$ | 2.4784 | 3.3087 | 2.3961 | 2.1150 |
| $E_d$ | 11.3833 | 13.2015 | 11.1422 | 9.8811 |
| $E_p$ | 5.2829 | 6.3801 | 5.7961 | 5.5198 |
| $E_d$ | 11.3991 | 13.2055 | 11.1469 | 9.9511 |

$s\sigma$ $−1.5096$ $−1.6874$ $−1.4707$ $−1.2228$
$s_d\sigma$ $−2.0155$ $−2.1059$ $−1.8137$ $−1.6619$
$s_d\sigma$ $−1.1496$ $−1.5212$ $−1.2303$ $−1.3929$
$s_s^*\sigma$ $−3.3608$ $−3.7170$ $−3.0680$ $−2.8985$
$s_q\sigma$ $2.2807$ $2.8846$ $2.3357$ $2.0406$
$s_p\sigma$ $2.6040$ $2.8902$ $2.5600$ $2.3639$
$s_p\sigma$ $1.9930$ $2.5294$ $2.0586$ $1.6962$
$s_p\sigma$ $2.0708$ $2.3883$ $2.2985$ $1.9879$
$s_d\sigma$ $−2.8945$ $−2.8716$ $−2.6114$ $−2.3737$
$s_d\sigma$ $−2.3175$ $−2.2801$ $−2.3460$ $−2.1767$
$s_d\sigma$ $−0.6393$ $−0.6568$ $−0.6274$ $−0.5548$
$s_d^*\sigma$ $−0.5949$ $−0.6113$ $−0.5925$ $−0.4875$
$p\sigma$ $3.6327$ $4.4048$ $3.8153$ $3.4603$
$p\pi$ $−0.9522$ $−1.4471$ $−1.4133$ $−1.1630$
$p_d\sigma$ $−1.1156$ $−1.6035$ $−1.2955$ $−1.3928$
$p_d\sigma$ $−1.3426$ $−1.6260$ $−1.8115$ $−1.4145$
$p_d\pi$ $1.2101$ $1.8423$ $1.6714$ $1.1921$
$p_d\pi$ $1.5282$ $2.1421$ $1.8909$ $1.7536$
$dd\sigma$ $−0.8381$ $−1.0885$ $−0.9200$ $−0.6688$
$dd\pi$ $1.9105$ $2.1560$ $1.8697$ $1.4601$
$dd\delta$ $−1.3348$ $−1.8607$ $−1.6545$ $−1.4373$

Δ/$\lambda$ 0.1558 0.1745 0.3841 0.3810
Δ/$\lambda$ 0.1143 0.0408 0.0410 0.1275

The $p$- and $d$-orbitals effects can be renormalized into each other, so for simplicity, we set to zero the $d$-orbital splitting.

We further reduce the parameter space by setting coefficients $m_{n\delta}$ for the nearly free-electron states $s^*$ and $d$ to the free electron value $n = 2$ and by imposing regularity in the chemical dependencies. In comparison with other strain parameterizations, our approach has relatively small number of parameters. Still, the determination of strain parameters for the InGaAsSb family represents a challenging task, because of the small number of available well documented deformation potentials. We also carefully checked the stability of the parameters by using genetic algorithm. Numerical experiments show that a few sets of parameters which precisely fit the basic deformation potentials are possible and the strain bulk properties of binaries do not allow to choose between them. To compensate for the ambiguity, we added the target band gap bowing of the alloys into parametrization procedure. We also assume that the valence band bowing contribute 30% to the band gap bowing. The strain parameters and the bowing are numerically fitted to reproduce the recommended values of deformation potentials in the center of Brillouin zone and bowings given in [18]. For completeness, the bulk ETB parameters are listed in table 2. They are a slightly re-worked version of those in [6]. In the table we give valence band offset separately, it should be added to diagonal energies. Note that in case of a significant modification of these bulk parameters, strain parameters themselves should also be revised.

We construct the tight-binding parameters of the alloy $\text{A}_x\text{B}_1-x\text{C}$ from the tight-binding parameters of binary materials AC and BC using the following procedure: first, the lattice constant of the alloy is found as a linear interpolation between binaries (Vegard’s law). Then we use our description of strain (see above) to construct the parameters of materials AC and BC strained to the lattice constant of the alloy. Next, the tight-binding parameters of the alloy are taken as linear interpolation of the strained binary materials.

To compare with experimental data, we use the values from [19]. As can be seen from figure 1, the comparison is almost perfect. The bandgap bowings are very well reproduced, and
we further checked that the change of the top of valence band and bottom of conduction band separately agree with available experimental data. Also, we observe reasonable behavior of basic properties of alloys in VCA like effective masses and deformation potentials. For completeness, we also give in table 3 effective masses of electron and deformation potentials of ternary alloys as a function of composition for the InGaAsSb family of materials in the present paper. Despite its obvious usefulness, the virtual crystal approximation is known to differ appreciably from reality: EXAFS studies [20–22] have revealed in the early 80’s that in ternary alloys, individual bond lengths keep a value very close to that in corresponding unstrained binary bulk material. It is therefore of utmost interest to compare our VCA approach with a virtual crystal, the bandgaps, computed with the same set of ETB parameters, are in close agreement. For a more detailed and accurate comparison, the unfolding procedure [1–5] is necessary, which goes far beyond the scope of the present paper.

In conclusion, we propose a VCA description of ternary alloys from the InGaAsSb family of materials in the spds ETB model. The method is based on a new parametrization of strain coefficients in the binary materials and a simple yet original interpolation scheme. The present parametrization gives an accurate fit of available experimental data for the basic properties of ternary alloys, and also nicely reproduces results of random alloy simulations. Combination of VCA and tight-binding allows for the accurate modeling of nano-sized heterostructures where atomistic details and/or full-band description is necessary.

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Table 3. Some material parameters computed using strain parameters from table 1 and ETB unstrained hamiltonian parameters from table 2.

| Alloy | $E_g$ (eV) | $m_e$ (m_e) | $\alpha_c$ | $\alpha_s$ | $b$ | $d$ |
|-------|------------|------------|------------|------------|-----|-----|
| InAs  | 0.417      | 0.0235     | −5.08      | 1.00       | −1.80 | −4.25 |
| GaAs  | 1.519      | 0.066      | −7.17      | 1.16       | −2.00 | −5.82 |
| GaSb  | 0.811      | 0.0402     | −7.50      | 0.80       | −2.00 | −5.09 |
| InSb  | 0.234      | 0.0132     | −6.94      | 0.36       | −2.00 | −5.18 |
| In$_{0.53}$Ga$_{0.47}$As | 1.207 | 0.0519 | −6.62 | 1.22 | −1.35 | −5.22 |
| In$_{0.2}$Ga$_{0.8}$As | 0.814 | 0.037 | −5.88 | 1.23 | −0.13 | −5.00 |
| InAs$_{0.4}$Sb$_{0.6}$ | 0.1239 | 0.0069 | −6.04 | 0.40 | −0.54 | −4.86 |

For this relaxed structure we extract a microscopic strain tensor using the approach explicated in [16]: for each atom we take coordinate of its neighbors. From bond lengths of binary materials, we also know their ‘nominal’ (unstrained) positions. The tetrahedron of four neighbors is defined by three vectors. The microscopic strain tensor is calculated as the polar decomposition $T = (1 + \varepsilon)R$ of the matrix $T$ which connects ‘real’ (strained) tetrahedron of the neighbors with ‘nominal’ one. The position of central atom inside this tetrahedron gives the internal strain vector $\varepsilon$. Using relaxed atomic positions and microscopic strain tensor, we construct the matrix of ETB Hamiltonian and find few eigenvalues near the band gap using the original implementation of thick-restarted Lanczos iterations [24]. From these energies we estimate the bandgap of alloy. Its value depends on particular distribution of atoms within the considered random supercell. To estimate the error in random alloy bandgap, we compute this value for a set of five supercell realizations and compare the obtained bandgap with the VCA calculation. The results for all four ternary alloys as a function of composition $x$ are presented in figure 3. Dashed lines show the VCA bandgap as a function of alloy composition and dots show the bandgap of random alloys. As can be seen, despite the fact that the latter has a complicated strain distribution and cannot be easily mapped to a virtual crystal, the bandgaps, computed with the same set of ETB parameters, are in close agreement. For a more detailed and accurate comparison, the unfolding procedure [1–5] is necessary, which goes far beyond the scope of the present paper.

Figure 3. Band gap of random alloys (symbols) as a function of composition for the 10$x$ × 10$x$ × 10$x$ supercell, compared with VCA (dashed lines).
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