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Olga L. Lazarenkova  
Jet Propulsion Laboratory, California Institute of Technology

Paul von Allmen  
Jet Propulsion Laboratory, California Institute of Technology

Fabiano Oyafuso  
Jet Propulsion Laboratory, California Institute of Technology

Seungwon Lee  
Jet Propulsion Laboratory, California Institute of Technology

Gerhard Klimeck  
Jet Propulsion Laboratory, California Institute of Technology; Network for Computational Nanotechnology, Electrical and Computer Engineering, Purdue University, gekco@purdue.edu

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Effect of anharmonicity of the strain energy on band offsets in semiconductor nanostructures

Olga L. Lazarenkova, Paul von Allmen, Fabiano Oyafuso, and Seungwon Lee
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Gerhard Klimeck
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California and Network for Computational Nanotechnology, School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47906

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Anharmonicity of the interatomic potential is taken into account for the quantitative simulation of the conduction and valence band offsets for strained semiconductor heterostructures. The anharmonicity leads to a weaker compressive hydrostatic strain than that obtained with the commonly used quasiharmonic approximation of the Keating model. Compared to experiment, inclusion of the anharmonicity in the simulation of strained InAs/GaAs nanostructures results in an improvement of the electron band offset computed on an atomistic level by up to 100 meV. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814810]

The accurate simulation of the electronic structure is of utmost importance for the design of nanoelectronic and optoelectronic device structures. It has been shown both theoretically, and experimentally, that the energy spectrum in semiconductor nanostructures is extremely sensitive to the built-in strain. The continuum elasticity method fails to adequately describe the strain profile in InAs/GaAs heterostructures with a 7% lattice mismatch between the constituent materials. The two-parameter valence-force-field (VFF) Keating model is a commonly used approximation for atomistic-level calculations of the equilibrium atomic positions in realistic-size nanostructures. In this letter the quasiharmonic Keating model is shown to be insufficient to describe highly strained InAs/GaAs nanostructures due to the anharmonicity of the strain energy.

The Keating model treats atoms as spring-connected points in a crystal lattice. The strain energy depends only on nearest-neighbor interactions.

\[
E = \frac{3}{8} \sum_{m} \left\{ \sum_{n} \left[ \alpha_{nn} \left( \mathbf{r}_{mn} \cdot \mathbf{r}_{mn} - d_{nn} \cdot d_{nn} \right)^{2} \right] + \sum_{k=n} \left[ \beta_{km} \left( \mathbf{r}_{mn} \cdot \mathbf{r}_{mn} - d_{kn} \cdot d_{kn} \right)^{2} \right] \right\}.
\]

The coefficient \( \alpha \) corresponds to the spring constant for the bond length distortion, while \( \beta \) corresponds to the change of the angle between the bonds (“bond-bending”). The summation is over all atoms \( m \) of the crystal and their nearest neighbors \( n \) and \( k \). \( \mathbf{r}_{mn} \) and \( d_{nm} \) are the vectors connecting the \( m \)-th atom with its \( n \)-th neighbor in the strained and unstrained material, respectively.

The Keating potential in Fig. 1 (dashed line) fails to reproduce the weakening of the realistic interatomic interaction (solid line with circles) with increasing distance between atoms and it underestimates the repulsive forces at close atomic separation. Therefore Eq. (1) can adequately describe the strain energy only at small deformations. In InAs/GaAs heterostructures, the lattice mismatch is as large as 7% and anharmonicity of the interatomic potential is expected to become important.

The anharmonicity is included directly into the VFF constants \( \alpha \) and \( \beta \) of the Keating model

\[
\alpha_{mn} = \alpha_{0}^{mn} \left[ 1 - A_{mn} \frac{(r_{mn}^2 - d_{mn}^2)}{d_{mn}^2} \right],
\]

\[
\beta_{mnk} = \beta_{0}^{mnk} \left[ 1 - B_{mnk} \left( \theta_{n}^{mnk} - \cos \theta_{0}^{mnk} \right) \right] \left( 1 - C_{mnk} \frac{(r_{mn}^2 - d_{mn}d_{mk})}{d_{mn}d_{mk}} \right),
\]

with \( \beta_{0}^{mnk} = \sqrt{\beta_{mn}^{n} \beta_{nk}^{m} \beta_{mk}^{n}} \), \( B_{mnk} = \sqrt{B_{mn}^{n} B_{mk}^{m} B_{mk}^{n}} \), and \( C_{mnk} = \sqrt{C_{mn}^{n} C_{mk}^{m} C_{nk}^{n}} \). \( \alpha_{0} \) and \( \beta_{0} \) are the actual and the unstrained angles between \( mn \) and \( mk \) bonds, respectively. In homogeneous materials all bonds are the same and the indexes \( m, n, \) and \( k \) can be dropped. \( \alpha_{0} \) and \( \beta_{0} \) are the VFF constants in the unstrained crystal. The anharmonicity corrections \( A \) and \( C \) describe the dependence of \( \alpha \) and \( \beta \) on hydrostatic strain, while \( \beta \) is responsible for the change of the bond-bending term with the angle between bonds. The details of the derivation of \( A \), \( B \), and \( C \) from the experimental phonon spectra of

FIG. 1. Schematic interatomic potential used in the Keating (dashed line) and our model (solid line). Dash-dot line plots the potential with the anharmonicity corrections to the VFF constants before the truncation. The line marked with large circles approximately traces the shape of the realistic potential.
TABLE I. Valence-force-field constants in unstrained materials and anharmonicity corrections for InAs and GaAs.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_0$(N/m)</th>
<th>$\beta_0$(N/m)</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>41.49</td>
<td>8.94</td>
<td>7.2</td>
<td>7.62</td>
<td>6.4</td>
</tr>
<tr>
<td>InAs</td>
<td>35.18</td>
<td>5.49</td>
<td>7.61</td>
<td>4.78</td>
<td>6.45</td>
</tr>
</tbody>
</table>

strained bulk materials are presented in Ref. 9. The parameters used for the simulation are listed in Table I.

The introduction of the anharmonicity corrections in the VFF model makes the form of the potential more realistic and expands the range of validity of the strain simulations. In order to ensure the convergence of the minimization of the strain energy (1) with $\alpha$ and $\beta$ given by Eqs. (2) and (3), our model interatomic potential (dash-dot line in Fig. 1) is truncated (solid line in Fig. 1).

To illustrate the effect of the anharmonicity on the strain distribution in III–V semiconductor nanostructures, the hydrostatic, $\epsilon_H=1/3(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})$, and biaxial, $\epsilon_B=1/6(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})$, components of the strain in InAs/GaAs single (SQW) and multiple quantum well and in GaAs/InAs single quantum barrier (SQB) have been computed using both the conventional Keating model and our model (Table II). Comparing the results of the two models, we note that the sharp rise of the strain energy at small interatomic distances leads to a smaller equilibrium hydrostatic compression than is obtained with the Keating model. The bond stretching is underestimated in the quasiharmonic approximation. The biaxial compression is increased in our anharmonic model, while the biaxial tension is suppressed.

The band offsets for InAs/GaAs nanostructures obtained for the strain distribution simulated within the Keating and anharmonic models are compared with the available experimental data in Table III. The local band structure was obtained within the $sp^3d^5s^*$ empirical tight-binding model where the Hamiltonian matrix elements depend on the distance between the atoms. The tight-binding parameters were fitted to reproduce the properties of the strained bulk materials. The discrepancy between the experimental and simulated energies is significantly smaller in the anharmonic model (see Table III).

The strain distribution [Figs. 2(a) and 2(b)] and the energy spectrum [Fig. 2(c)] were computed for the quantum dot crystal (QDC) reported in Ref. 5. The structure consists of three layers of regimented vertically stacked dome-shaped quantum dot arrays (with a 20 nm base diameter and a 7 nm height) on top of the 0.7 nm wetting layer, with a small (3 nm) vertical separation between the QD layers. The built-in strain distribution in such structures is very inhomogeneous. The average hydrostatic component of the strain

![Image](https://via.placeholder.com/150)

FIG. 2. Computed distribution of the hydrostatic (a) and biaxial (b) strain components, and (c) electronic band structure along the growth direction in the InAs/GaAs QDC structure taken from Ref. 5. The cross section is made near the center of the quantum dot stack. The results obtained with the Keating model are plotted with black dots. The results obtained with the anharmonic model are plotted with solid line on (a) and (b) and with gray dots on (c). The thin lines on (c) show the edges of conduction, valence, and spin-orbit split-off bands at the center of the Brillouin zone in the unstrained materials.

TABLE II. Hydrostatic ($H$) and biaxial ($B$) strain components, and the $x$ epitaxial layer in different epitaxial nanostructures computed within the Keating ($K$) and anharmonic ($A$) model. $L_x$ is the width of the $x$ layer, $L_y$ is the width of the $y$ layer (thickness of the capping layer for SQW and SQB), $\delta(\%)=100(|\epsilon|/\epsilon^e)$.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Composition</th>
<th>Structure</th>
<th>Size</th>
<th>Substr.</th>
<th>Hydrostatic strain (%)</th>
<th>Biaxial strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$</td>
<td>$y$</td>
<td>$L_x$</td>
<td>$L_y$</td>
<td>$\epsilon_{xx}$</td>
<td>$\epsilon_{yy}$</td>
</tr>
<tr>
<td>3</td>
<td>InAs</td>
<td>GaAs</td>
<td>SQW</td>
<td>2 ML</td>
<td>5 ML</td>
<td>GaAs</td>
</tr>
<tr>
<td>3</td>
<td>GaAs</td>
<td>InAs</td>
<td>SQB</td>
<td>2 ML</td>
<td>5 ML</td>
<td>InAs</td>
</tr>
<tr>
<td>4</td>
<td>InAs</td>
<td>GaAs</td>
<td>MQW</td>
<td>1 ML</td>
<td>30 nm</td>
<td>GaAs</td>
</tr>
</tbody>
</table>
TABLE III. Experimental band offsets in the conduction ($\Delta E_c$) and valence ($\Delta E_v$) bands compared with the offsets computed within the $sp^3d^2s^*$ empirical tight-binding model using the equilibrium atomic positions found within the two-parameter Keating model ($K$) and including anharmonicity corrections to the VFF constants ($A$) for 2 ML InAs/GaAs SQW and GaAs/InAs SQB 5 ML away from the surface, MQW formed by 1 ML InAs separated by 30 nm GaAs layers and InAs/GaAs QDC consisting of three vertically separated on about 3 nm layers of dome-shaped QDs with a 20 nm base and a 7 nm height on top of a 0.7 nm wetting layer. The band offsets are determined so they would be positive for potential well and negative for potential barrier. Notations: XPS—x-ray photoemission spectroscopy, CV—capacitance–voltage spectroscopy, DLTS—deep-level transient spectroscopy, hh—heavy hole, lh—light hole. $\delta_K$ and $\delta_A$ estimate the relative deviations of the simulation from the experiment.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Structure</th>
<th>Experimental</th>
<th>$\Delta E_c$(meV)</th>
<th>$\Delta E_v$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>method</td>
<td>$K$</td>
<td>$\delta_K$(%)</td>
</tr>
<tr>
<td>3</td>
<td>SQW</td>
<td>XPS</td>
<td>471.5</td>
<td>574.0</td>
</tr>
<tr>
<td>3</td>
<td>SQB</td>
<td>XPS</td>
<td>−40.7</td>
<td>−91.3</td>
</tr>
<tr>
<td>4</td>
<td>MQW</td>
<td>CV&amp;DLTS</td>
<td>475.7</td>
<td>−31.1</td>
</tr>
<tr>
<td>5</td>
<td>QDC</td>
<td>DLTS</td>
<td>242.0</td>
<td>−29.0</td>
</tr>
</tbody>
</table>

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11We used the parameter set from Ref. 10 corresponding to the commonly used positive valence band hydrostatic deformation potential $a_v$. Use of the small negative $a_v$ suggested by S.-H. Wei and A. Zunger, Phys. Rev. B 68, 5404 (1999) shifts the valence band energies up in the compressed InAs/GaAs structures, bringing the simulation closer to the experiment, while the downward shift of the valence band in stretched GaAs/InAs structures leads to the larger deviation from the experiment. For the 3% hydrostatic strain the energy shift is about 0.18 eV.