Study of Alloy Disorder in Quantum Dots through Multi-million Atom Simulations

G. Klimeck*, F. Oyafuso*, T. B. Boykin**, R. C. Bowen*, and P. von Allmen*

* Jet Propulsion Laboratory
4800 Oak Grove Dr. MS 169-315, Pasadena, CA, 91109, gekco@jpl.nasa.gov
** University of Alabama at Huntsville, Huntsville, AL, USA

ABSTRACT

A tight binding model which includes s, p, d, and s^* orbitals is used to examine the electronic structures of an ensemble of dome-shaped $In_{0.6}Ga_{0.4}As$ quantum dots. Given ensembles of identically sized quantum dots, variations in composition and configuration yield a linewidth broadening of less than 0.35 meV, much smaller than the total broadening determined from photoluminescence experiments. It is also found that the computed disorder-induced broadening is very sensitive to the applied boundary conditions, so that care must be taken to ensure proper convergence of the numerical results. Examination of local eigenenergies as functions of position shows similar convergence problems and indicates that an inaccurate resolution of the equilibrium atomic positions due to truncation of the simulation domain may be the source of the slow ground state convergence.

Keywords: quantum dot, boundary condition, linewidth, disorder

1 INTRODUCTION

Envelope function-based models such as **k.p** are often used to characterize the electronic structures of quantum dots. Such jellium-like models are often very useful and are not too computationally demanding. However, they suffer as the minimum feature size approaches the length scale of several nanometers or less [1], [2] and also cannot capture effects such as alloy disorder or interface interdiffusion that arise from the discreteness of the underlying medium. The two primary alternative approaches to model solids on finer length scales are tight-binding and pseudopotential methods. We have pursued the former approach for our ability to leverage previous Nanoelectronic Modeling (NEMO) developments [3]–[5], and are currently developing an atomistic nanoelectronic simulation tool (NEMO-3D) to model quantum dot structures on high performance commodity clusters (Beowulfs). Modeling of realistic structures entails simulation domains encompassing many millions of atoms. Such large-scale domains result in very large eigenproblems (dimension $\gtrsim 10^8$) which necessitate the usage of massively parallel computers. Details of the numerical implementation including performance benchmarks have been described in greater detail elsewhere [6].

Our simulation employs a nearest-neighbor tight-binding model ($sp^3d^5s^*$) with a 20 orbital basis, consisting of s, p, and d orbitals, associated with each atomic lattice site. Since this basis set is truncated (i.e. not complete) the parameters that enter the model do not correspond precisely to actual orbital overlaps. Thus, an analytical approach to determine these parameters is insufficient. Instead, a genetic algorithm package is used to determine a set of orbital couplings that reproduces a large number of physical observables of the bulk binary system, including bandgaps and effective masses at various symmetry points in the Brillouin zone. Furthermore, we assume that the dependence of the orbital couplings on bond lengths follows a power-law whose exponent is also allowed to vary in the genetic algorithm computation.

Because the basis set used consists of orthogonalized Löwdin orbitals and not the true atomic orbitals, the diagonal (self-coupling) elements are also allowed to vary with the displacement of the nearest neighbor atoms [7]. An accurate calculation of the electronic structure within the tight-binding model also necessitates an accurate representation of the positions of each atom. NEMO-3D uses a valence force field (VFF) model in which the total strain energy, expressed as a local (nearest-neighbor) functional of atomic positions, is minimized to determine the atomic positions [8], [9].

In this work, we examine the dependence of the ground state eigenenergies as a function of various buffer sizes. We shall demonstrate that the variations of eigenenergies can depend strongly on the size of simulation domain, and that proper care must therefore be taken to ensure that a solution has "converged".

2 SIMULATION

2.1 Ground state electron energy

The model used for all the simulations in this work is a dome shaped $In_{0.6}Ga_{0.4}As$ quantum dot (QD) of diameter 30 nm and height 5.4 nm embedded in a finite GaAs box. The QD itself contains roughly 2×10^5 atoms. A list of the values of the tight-binding parameters necessary for the simulation is given in Table III of reference [6]. Although all the QDs are of identical size,

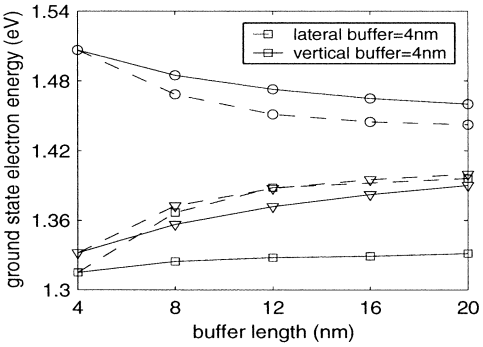

Figure 1: Ground state electron eigenenergies obtained for free, fixed, and periodic boundary conditions. For the case of unconstrained (free) boundary conditions, convergence of eigenenergies is also illustrated for the case of free boundary conditions where only the vertical buffer size is varied and the lateral buffer size is fixed at 4 nm (dashed line).

the placement of In and Ga cations varies among simulations. We make the ansatz that no correlation in species type exists between any two atomic sites. Sites on the cation sublattice are filled with a 60% (40%) probability of being In (Ga), so that it is not the case that in general exactly 60% of the cations in the QD are In atoms. The resulting broadening of the energy spectrum, then, includes not only the configurational disorder, arising from the distribution of different cations throughout the alloy subject to the constraint of a fixed overall concentration, but also a concentrational disorder that reflects the fact that a growth process never produces nanostructures with identical concentrations each time. It has been demonstrated that for bulk (periodic) systems, the concentrational disorder dominates by an order of magnitude [10]. In the following simulations, we consider three different boundary conditions, fixed, free, and periodic, that directly impact the strain calculation and therefore either indirectly or directly affect the electronic computation. In the fixed case, the surface atoms are constrained to the positions they would have if the simulation domain consisted entirely of GaAs. In the free case, the entire domain is allowed to expand without any external constraints. Finally, under periodic boundary conditions, the total strain energy is minimized with respect to both position and period. In Fig.(1), we compare the ground state electron eigenenergy for each case as a function of buffer size. Also shown is the convergence of eigenenergies for the case of free boundary conditions when only the vertical buffer size is varied and the lateral buffer size is fixed at 4 nm. The largest simulation employs a 16 nm buffer and encompasses approximately six million atoms. Because of memory constraints the buffer sizes in Fig.(1) are limited to 16 nm. The intent is to investigate how well such a truncated system approximates one in which the QD is embedded in an infinitely large block of GaAs. In the case of free boundary conditions no external constraints are imposed, so that the strain computed for the truncated system is reduced from what it should be for an infinite buffer. The shift of the conduction band edge at Γ, which depends linearly on the hydrostatic component, is given by

$$\Delta E_c = \Xi_d^{(000)} \mathrm{Tr}\{\varepsilon\} \quad (1)$$

where $\Xi_d^{(000)} < 0$ [11]. Thus, one expects a reduction in compressive strain (an increase in $\mathrm{Tr}\{\varepsilon\}$) in the QD to accompany a reduction in electron ground state energy. The situation for the fixed case, where the lattice constant on the boundary is constrained to bulk values, is inverted, since the strain effect in the QD is overestimated relative to the case of infinite buffers. Fig.(1) demonstrates that the two cases converge provided that the buffer is made sufficiently large. The periodic case lies in between the other two cases as expected, but yields eigenergies only only slightly greater than for the free case for fixed simulation domain size. Thus, we can expect that the strain computed from the periodic case closely resembles that of the free case. Finally we note that extension of the buffer in the lateral direction for the free case does not significantly alter the computed eigenenergies. This is likely due to the fact that the QD is quite "flat", so that the binding energy is principally determined by confinement in the $\hat{z}$ direction. These results demonstrate that the simulation domain needs to extend rather far into the buffer to assure convergence.

2.2 Linewidth broadening

We now consider the issue of linewidth broadening. That is, given an ensemble of quantum dots with identical alloy composition, we explore the fundamental limits of linewidth broadening that arise solely as a result of variations in configurations of cations in the quantum dots and ignore any additional contributions such as size variation, strain-induced spatial perturbations on a QD due to neighboring QDs, and many-body effects. Ideally one would use periodic boundary conditions. However, it was demonstrated in the previous section that the results obtained from using unconstrained boundary conditions with small buffers in the lateral direction did not produce significantly different results. Since the "periodic" case is computionally more expensive due to the additional relaxation of the period, free boundary conditions have been applied. We examine the electron and hole ground state eigenenergy distributions for buffer sizes up to 12nm. Because of the computational expense it was not possible to extend the calculation for

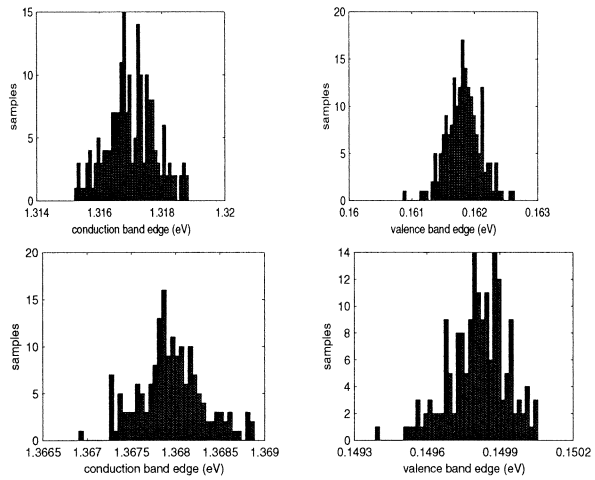

Figure 2: Electron and hole energy distributions for a set of QD with 4 nm (top) and 8 nm (bottom) buffers.

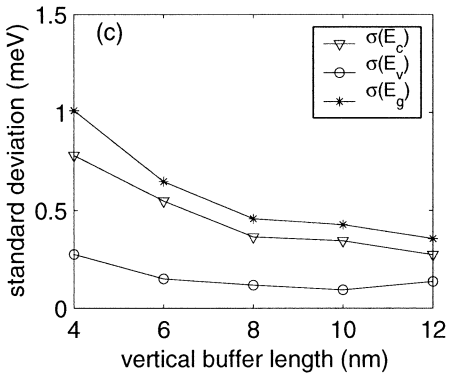

Figure 3: Standard deviations of electron ground state, hole ground state, and energy gap as a function of buffer length.

larger buffer sizes, and since the electron eigenenergies have not yet completely converged for this buffer size, we do not expect the variance to have completely converged either. 190 samples points were obtained for the buffer sizes less then 10 nm, and 100 and 93 for the larger 10 nm and 12nm buffer geometries, respectively. A histogram of the distributions for the 4 nm and 8 nm buffers is shown in Fig.(2), while Fig.(3) demonstrates the behavior of the standard deviation of the eigenenergies obtained from these ensembles as a function of buffer size. First we note that while the standard deviations of both the hole and electron eigenenergies, σ_v and σ_c, have not yet converged, so that a larger simulation domain should be used to obtain a more accurate computation of the ground state electron broadening. However, the general trend shows a reduction in broadening as the effect of the boundary is minimized. One likely reason for this is that as eigenstates are pushed up (down) closer to the bulk GaAs conduction (valence) band edges, they become more delocalized and therefore less sensitive to local perturbations within the quantum dot. Most importantly, one sees that the contribution to the linewidth broadening for an interband transition from alloy disorder is quite small (less than 0.35 meV), compared to the overall broadening as measured from experiment. That σ_c appears to be much greater than σ_v differs from an earlier finding for bulk unstrained $Al_xGa_{1-x}As$ in which the electron broadening was found to be only slightly larger than that of holes [10]. This difference might be due to the fact that both light and heavy holes are broadened in the bulk unstrained case, while the confinement of a QD splits the heavy hole/light hole degeneracy. Finally, note that the sum of electron and hole standard deviations is still (roughly) equal to the standard deviation of the energy gap, which indicates that the electron and hole eigenenergies are strongly correlated. This result is not unexpected since the concentrational broadening has previously been identified to be the most dominant effect in bulk unstrained systems [10]. If concentrational broadening is the dominant effect in QDs, then a variation in overall concentration will affect both electron and hole eigenenergies in a systematic manner and therefore lead to a correlation between them.

2.3 Local bandstructure

We next examine the effect of the deformation of the primitive cells under strain on the local electron and hole band structure within the GaAs buffer. At each cation (Ga) site, we define a "local" eigenenergy obtained by computing the band minima at Γ of a bulk solid constructed from the single primitive cell formed by the cation and its four neighboring As anions. In essence, these local eigenenergies define for each cation a spatially dependent band edge that depends only on the relative position of its surrounding As atoms. Thus, these local eigenvalues reflect local strain conditions. Fig.(4) shows local eigenvalues of the buffer material for our canonical problem with buffer sizes of 4nm, 8nm, and 12nm under the assumption of free boundary condtions. Here, larger dot size corresponds to larger buffer size. In each case, local eigenvalues are computed about each cation contained within a narrow tube aligned along a lateral (x) direction that passes close to axes of maximal symmetry. The tube extends from the edge of the enclosing buffer up to the QD, and it was verified that the behavior of the eigenvalues in buffer at the other end was symmetric, due to the reflection symmetry of the system. The finite thickness of the tube accounts for the spreading of the local eigenvalues as one moves from

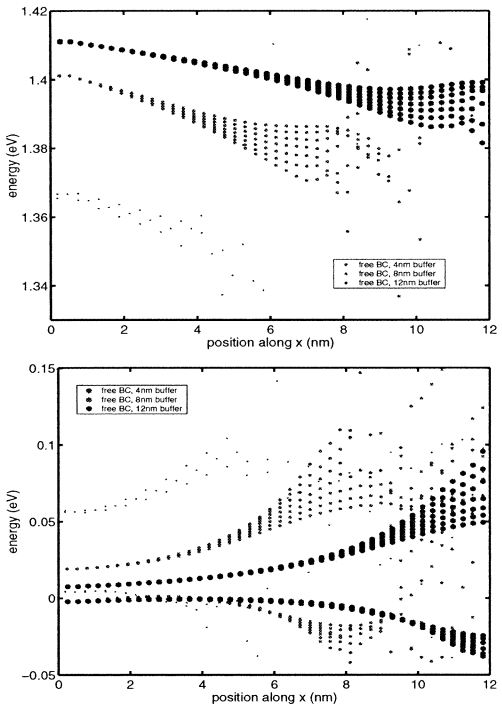

Figure 4: Local electron and hole eigenenergies of the GaAs buffer along a lateral axis of the QD for buffer sizes of 4nm, 8nm, and 12 nm. Larger dot size corresponds to larger buffer size. Free boundary conditions are assumed.

the edge of the simulation domain toward the quantum dot. Note that a buffer of 4 nm is not sufficient to characterize the QD, since the local eigenenergies at the boundary of the simulation domain are not close to the bulk eigenvalue of 1.424 eV. However, convergence toward this bulk value is evident as the buffer size is increased. One sees that the electron eigenvalues are pushed down from their bulk values, since for very small buffers under free boundary conditions, GaAs unit cells on the surface should stretch out biaxially to match the larger $In_{0.6}Ga_{0.4}As$ lattice constant.

The convergence of hole eigenenergies demonstrates behavior similar to that seen for electrons, except that light hole and heavy hole splitting of roughly 10 meV is evident even for the largest buffer size. The loss of degeneracy arises from the symmetry breaking due to strain. Furthermore, even for the largest buffer size, the local eigenergies "flatten out" and saturate to an asymptotic value that differs from unstrained GaAs. This suggests that the inaccurate characterization of the strain may be the principal limitation on the accuracy of the "global" eigenvalues.

3 CONCLUSION

The convergence of electron and hole ground states of a dome-shaped $In_{0.6}Ga_{0.4}As$ quantum dot has been explored within an $sp^3d^5s^*$ tight binding model. It has been demonstrated that within this model, one must include a barrier region many times the size of the embedded quantum dot. The inadequate convergence of the local bandstructure is a direct reflection of the lack of convergence of the strain, and may be the principal cause for the slow convergence of the "global" ground state eigenenergies.

4 ACKNOWLEDGEMENT

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