phys. stat. sol. (c) **0**, No. 4, 1149–1152 (2003) / **DOI** 10.1002/pssc.200303020

Disorder induced broadening in multimillion atom alloyed quantum dot systems

Fabiano Oyafuso[*, 1], **Gerhard Klimeck**[1], **R. Chris Bowen**[1], **Tim Boykin**[2], and **Paul von Allmen**[1]

[1] Jet Propulsion Laboratory, 4800 Oak Grove Dr. MS 169-315, Pasadena, CA, 91109, USA

[2] Deptartment of Electrical and Computer Engineering, University of Alabama in Huntsville, Huntsville, Alabama, 35899, USA

Received 30 September 2002, accepted 2 December 2002
Published online 23 June 2003

PACS 73.21.La

Disorder-induced broadening of the conduction and valence band eigenenergies is calculated for an ensemble of dome-shaped $In_{0.6}Ga_{0.4}As$ quantum dots of diameter 30 nm using an $sp^3d^5s^*$ tight binding model. An assumption is made that there is no alloy clustering, so that neighboring cations are uncorrelated. For this case, it is found that the contribution to the broadening from alloy disorder is small (less than 0.35 meV) relative to the total broadening determined from photoluminescence experiments and sensitive to the applied boundary conditions, so that care must be taken to ensure proper convergence of the numerical results.

1 Introduction It is well known that the linewidth of any ensemble of quantum dots (QDs) is inhomogeneously broadened by the distribution in QD sizes and strain profile. The best photoluminescence (PL) measurements for ensembles of QDs have found linewidths on the order of 20 meV for self-assembled InGaAs QDs grown on GaAs substrates [1–3]. Single QD measurements on AlGaAs/GaAs QDs, by contrast, can exhibit very narrow linewidths (~0.9 meV) [4]. However, even in a "perfect" ensemble in which all QDs have the same size and experience identical externally-induced strain, QDs composed of alloyed materials will still exhibit variations in linewidth that arise from differences in the spatial distribution of the constituent cations and anions. In this work we shall examine the magnitude of the broadening of the ground state eigenenergies induced by alloy disorder through the use of an atomistic tight-binding model. We find that for a typical dome-shaped $In_{0.6}Ga_{0.4}As$ QD of diameter 30 nm, the broadening induced by the disorder is less than 0.35 meV.

2 Simulation The "standard" method for computing electronic structure of quantum dots is $\boldsymbol{k}\cdot\boldsymbol{p}$. However, this jellium-like model is fundamentally not well suited for the atomistic representation of nanoscale features [5]. It has been demonstrated that the envelope function approximation central to $\boldsymbol{k}\cdot\boldsymbol{p}$ degrades as the minimum feature size approaches the length of several monolayers or less [6]. Two principal approaches, tight-binding and pseudopotential methods, are typically used to model solids on finer length scales. We have pursued the tight-binding approach for our ability to leverage previous Nanoelectronic Modeling (NEMO) developments [7–9]. Our simulation employs a nearest-neighbor empirical tight-binding method ($sp^3d^5s^*$) with a 20 orbital basis, consisting of s, p, and d orbitals associated with each atomic lattice site. Since the basis set that is used is not complete in a mathematical sense,

[*] Corresponding author: e-mail: fabiano@jpl.nasa.gov, Phone: 818.393.2537, Fax: 818.393.4802

 1610-1634/03/00007-1149 $ 17.50+.50/0

the parameters that enter the model are determined by a fit to experimental data, and 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 [10–12]. These orbital couplings must also depend on bond lengths to account for the shifts in atomic positions in strained systems. A power-law scaling is assumed (whose exponent is also determined with the genetic algorithm) to account for strain-induced shifts. 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 [13]. To compute the positions of each atom a valence force field (VFF) model is used in which the total strain energy, expressed as a local (nearest-neighbor) functional of atomic positions, is minimized [14, 15]. Modeling of realistic structures entails simulation domains encompassing many millions of atoms and results in very large eigenproblems (dimension $\sim 10^8$), which necessitate the usage of massively parallel computers. Details of the numerical implementation including performance benchmarks on Beowulf commodity clusters have been described in greater detail elsewhere [10].

The canonical model used for the simulations in this work is a dome-shaped $In_{0.6}Ga_{0.4}As$ QD of diameter 30 nm and height 5.4 nm containing roughly 2×10^5 atoms embedded in a finite GaAs box, which is meant to approximate an infinite one. This particular model was selected for comparison with previously published experimental results [2, 3]. A list of the values of the tight-binding parameters necessary for the simulation is given in Table III of reference [10]. Although all the QDs are of identical size, the placement of In and Ga cations varies among simulations and leads to a configurational disorder. Another source of disorder is concentrational and stems from the fact that a growth process will never produce nanostructures with exactly the same concentration each time. It was found previously for bulk materials that this concentrational broadening is the dominant contributor to the overall compositional disorder [16]. To include both sources in our model, we make the ansatz that within the QD no correlation exists in species type between any two atomic sites. Thus, sites on the cation sublattice are filled with a 60% (40%) probability of being In (Ga) without guarantee that the overall concentration will exactly equal the local probabilities.

To investigate linewidth broadening, we use a "direct sampling method" in which we sample a small but statistically significant number of representative configurations of materially identical quantum dots. Determining the resulting variation in eigenenergies is computationally taxing for two reasons. First, one must ensure that the simulation domain is sufficiently large that the influence of the boundary of the surrounding buffer and of the boundary conditions themselves is minimized. Second, one must perform hundreds of simulations to obtain a statistically meaningful sample.

3 Simulation Results Prior to delving into a discussion of the broadening, we first need to ensure that the eigenenergies we obtain are independent of the extent of the surrounding buffer and of the constraints placed on the boundary. The electronic calculation is strongly dependent on the atomic configuration determined from the VFF model. We consider three distinct boundary conditions for the strain: fixed, free, and periodic. 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, the periodic case is periodic in all three dimensions with vanishing supercell wavevector. Figure 1 compares 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 where only the vertical buffer size is varied and the lateral buffer size is fixed at 4 nm. Memory constraints limit the largest simulation to one with a 16 nm buffer encompassing approximately six million atoms. 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

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

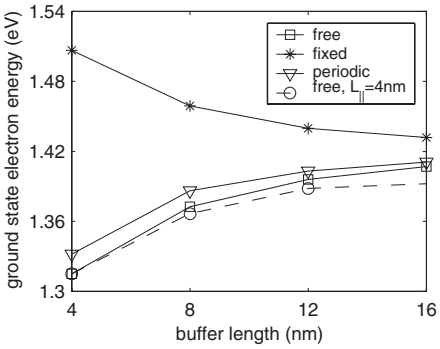

Fig. 1 Ground state electron eigenenergies obtained for free, fixed, and periodic boundary conditions. For unconstrained (free) boundary conditions, convergence of eigenenergies is also illustrated for the case where only the vertical buffer size is varied and the lateral buffer size is fixed at 4 nm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

where $\Xi_d^{(000)} < 0$ [17]. 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. Figure 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 eigenenergies only slightly greater than that of the free case for a given 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 vertical direction. These results, however, demonstrate that the simulation domain needs to extend rather far into the buffer to assure convergence.

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, alloy clustering, 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 12 nm. Because of the computational expense it was not possible to extend the calculation for 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 12 nm buffer geometries, respectively. Figure 2 shows histograms of the distributions for the 4 nm buffer and demonstrates the behavior of the standard deviation of the eigenenergies obtained from these ensembles as a function of buffer size. First we note that the standard deviations of

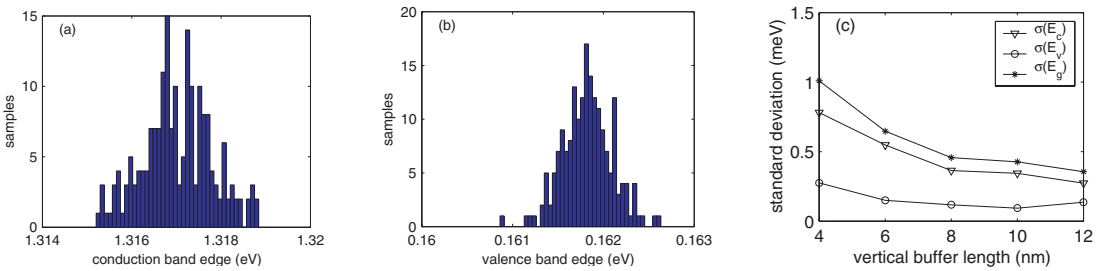

Fig. 2 (online colour at: www.interscience.wiley.com) a) Electron and b) hole energy distributions for a set of QDs with 4 nm buffers. c) Standard deviations of electron ground state, hole ground state, and energy gap.

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. However, we should also note that in previous work with sp^3s^* basis sets [10], we have found that a simplified unit cell oriented clustering model can increase the broadening by a factor of 2 relative to the linewidth obtained from the model of uncorrelated cation species used in this work. 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 [16]. 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 [16]. If also true for 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.

4 Conclusions The broadening of the conduction and valence band eigenenergies induced by disorder has been examined for ensembles of dome-shaped $In_{0.6}Ga_{0.4}As$ quantum dots of diameter 30 nm using an $sp^3d^5s^*$ tight binding model. It has been demonstrated that under the assumption of no alloy clustering, the disorder-induced contribution to the broadening is small (less than 0.35 meV) compared to the empirically measured total linewidth broadening and sensitive to the applied boundary conditions, so that care must be taken to ensure proper convergence.

Acknowledgements The work described in this publication was carried out at the Jet Propulsion Laboratory, California Institute of Technology. The Beowulf cluster on which our calculations were performed was provided by funding from the NASA Offices of Earth Science, Aeronautics, and Space Science. Another Beowulf cluster that was used in this work has been provided by Purdue University in a collaboration between JPL and the Network for Computational Nanotechnology (NCN) funded by grant EEC-0228390.

References

[1] K. Nishi, H. Saito, S. Sugou, and J. S. Lee, Appl. Phys Lett, **74**, 1111 (1999).
[2] C. Lobo, R. Leon, S. Fafard, and P. G. Piva, Appl. Phys. Lett. **72**, 2850 (1998).
[3] R. Leon, S. Marcinkevicius, X. Z. Liao, J. Zou, D. J. H Cockayne, and S. Fafard, Phys. Rev. B **60**, R8517 (1999).
[4] Y. Nagamune, H. Watabe, M. Nishioka, and Y. Arakawa, Appl. Phys. Lett. **67**, 2850 (1995).
[5] H. Fu, Lin-Wang, and A. Zunger, Phys. Rev. B **57**, 9971 (1998).
[6] T. G. Dargam, R. B. Capaz, and B. Koiller, Phys. Rev. B **56,** 9625 (1997).
[7] R. C. Bowen, W. R. Frensley, G. Klimeck, and R. Lake, Phys. Rev. B **52**, 2754 (1995).
[8] G. Klimeck, R. Lake, R. C. Bowen, W. Frensley, and T. Moise, Appl. Phys. Lett. **67**, 2539 (1995).
[9] R. C. Bowen, G. Klimeck, R. Lake, W. R. Frensley, and T. Moise, J. Appl. Phys. **81**, 3207 (1997).
[10] G. Klimeck, et al., accepted for publication in Computer Modeling in Engineering Science (2002).
[11] G. Klimeck, R. C. Bowen, and T. Boykin, Phys. Rev. B **63**, 195310 (2001).
[12] G. Klimeck, R. C. Bowen, and T. Boykin, T. Cwik, Superlattices Microstruct. **27**, 519 (2000).
[13] T. Boykin, G. Klimeck, R. C. Bowen, F. Oyafuso, accepted for publication in Phys. Rev. B (2002).
[14] P. Keating, Phys. Rev. **145**, 637 (1966).
[15] C. Pryor, J. Kim, L. W. Wang, A. J. Williamson, and A. Zunger, J. Appl. Phys. **83**, 2548 (1998).
[16] F. Oyafuso, G. Klimeck, R. C. Bowen, T. Boykin, accepted for publication in J. Comp. Electronics (2002).
[17] P. Bhattacharya, Indium Gallium Arsenide, Vol. 8 (INSPEC, London, 1993).