Disorder Induced Broadening in Multimillion Atom Alloyed Quantum Dot Systems

Fabiano Oyafuso, Gerhard Klimeck, R. Chris Bowen, Timothy B. Boykin, and Paul von Allmen

Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Dr., Pasadena, CA, 91109, USA

E-mail: fabiano.oyafuso@jpl.nasa.gov

Abstract

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. 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 very sensitive to the applied boundary conditions, so that care must be taken to ensure proper convergence of the numerical results.

I. Introduction

Nonatomistic methods such as **k.p** are often used to compute the electronic structure of quantum dots. However, such jellium-like models are fundamentally not well suited for the atomistic representation of nanoscale features such as impurities and interface interdiffusion.[1]. We 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 [2] and are not discussed in this work.

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, 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. 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 [3]. Clearly, an accurate calculation of the electronic structure within the tight-binding model also necessitates an accurate representation of the positions of each atom. To this end, 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 [4], [5].

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. However, even in a "perfect" system 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. Determining this variation is computationally taxing for two reasons. First, one must perform hundreds of simulations to obtain a statistically meaningful sample. Second,

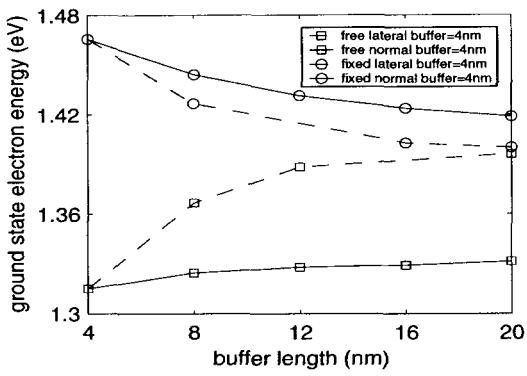

Fig. 1. Ground state electron eigenenergies obtained for fixed and free boundary condtions with the buffer length constrained to 4nm in either the lateral or vertical directions.

one must ensure that the simulation domain is sufficiently large that one has obtained convergence of the eigenenergies. That is, the influence of the boundary of the surrounding buffer and the boundary conditions themselves must be minimized. 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, roughly two orders of magnitude than previously reported experimental values for the total linewidth [6], [7].

II. SIMULATION

A. Model

The canonical model used for the QD 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, which is meant to approximate an infinite one. This particular model was selected for comparison with previously published experimental results [6], [7]. 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 [2]. Although all the QDs are of identical size, the placement of In and Ga cations varies among simulations. This variation contributes to a compositional disorder of which there are two sources. One source is configurational and arises from the constraint that the total number of In and Ga atoms in the QD be fixed. The other source is a concentrational disorder that takes into account 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 [8]. 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.

B. Convergence of ground state electron energy

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 two distinct boundary conditions for the strain, fixed and free, 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.

Fig.(1) compares the ground state electron eigenenergy for the cases of free and fixed boundary conditions as a function of buffer size in directions parallel (solid) and normal (dashed) to the base of the dome. The largest simulation employs a 20 nm buffer in the $\hat{z}$ direction, normal to the base of the dome, and encompasses nearly 3 million atoms. For variation of buffer size in the lateral (normal) direction, the buffer size in the normal (lateral) direction is fixed to 4 nm. The intent is to investigate how well such a truncated system

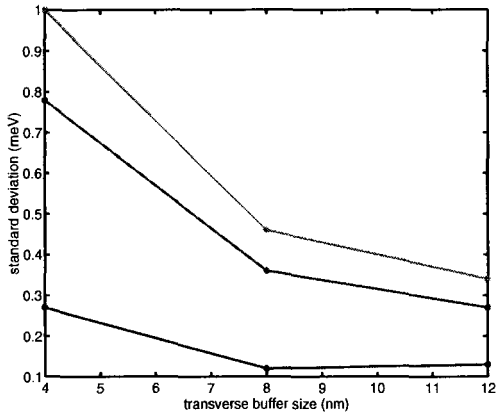

Fig. 2. Standard deviations of electron ground state (red), hole ground state (blue), and energy gap (green).

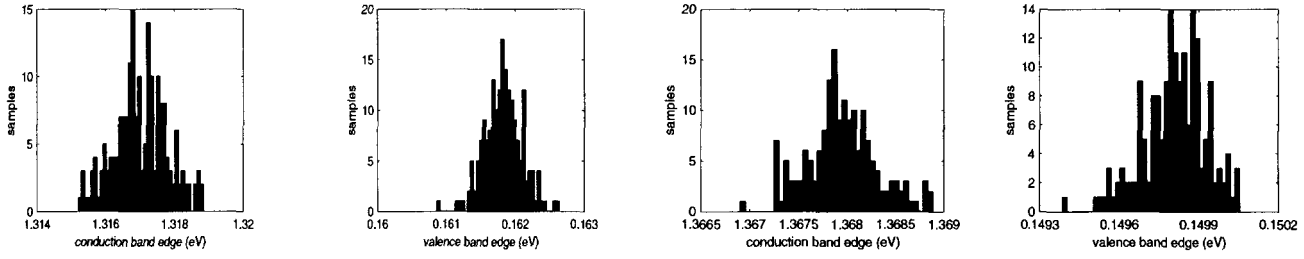

Fig. 3. Electron and hole energy distributions for a set of QD with 4 nm (top) and 8 nm (bottom) buffers.

approximates one in which the QD is embedded in an infinitely large block of GaAs. Because the QD is quite "flat", the binding energy is principally determined by confinement in the $\hat{z}$ direction. Thus, for both cases, the dependence on lateral buffer size is weak relative to the dependence on the buffer size in the z direction. 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

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

where $\Xi_d^{(000)} < 0$ [9]. 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. These results demonstrate that the simulation domain needs to extend rather far into the buffer to assure convergence.

C. 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. Our calculations for the case of fixed boundary conditions did not yield hole eigenenergies for small buffer sizes, so we consider only the case of free boundary conditions. We examine the electron and hole ground state eigenenergy distributions for three different buffer systems, 4nm, 8nm, and 12nm. Because of the computational expense it was not possible to extend the calculation for larger buffer sizes. 190 samples points were obtained for the first two systems and 93 for the larger 12nm buffer geometry. A histogram of the

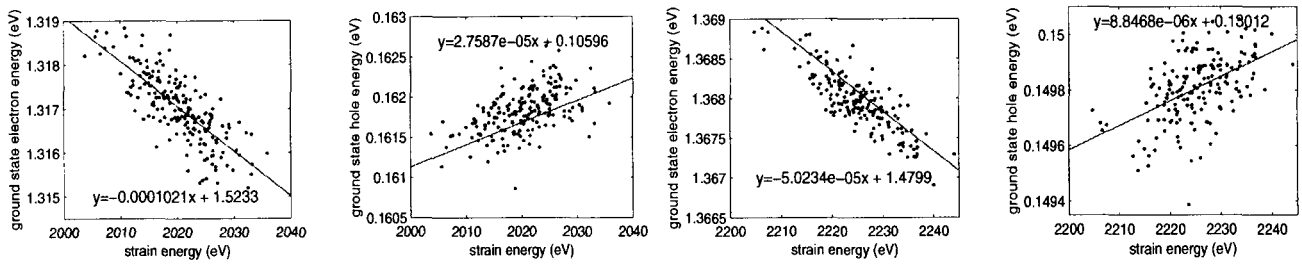

Fig. 4. Electron and hole ground state eigenenergies as a function of total strain energy of the QD for a lateral buffer size of 4nm and transverse buffer sizes of 4 nm (top two figures) and 8 nm (bottom two figures) under free boundary conditions.

distributions for the first two geometries is shown in Fig.(3), while Figure (2) 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 deviation of the hole eigenenergy, σ_v, has converged, the broadening of the electron eigenenergy, σ_c, has not, so that a larger simulation domain should be used to obtain a more accurate computation of the ground state electron broadening. One possible explanation for the observed reduction in linewidth 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. The general trend is toward less broadening as the effect of the boundary is minimized. Also, 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 [8]. 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 [8]. 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 correlation between them.

III. CONCLUSION

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 the disorder-induced contribution to the broadening is small (less than 0.35 meV) compared to the empirically measured total linewidth broadening and very sensitive to the applied boundary conditions, so that care must be taken to ensure proper convergence.

IV. ACKNOWLEDGEMENT

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Video Discs for Multidimensional Computer Data Systems

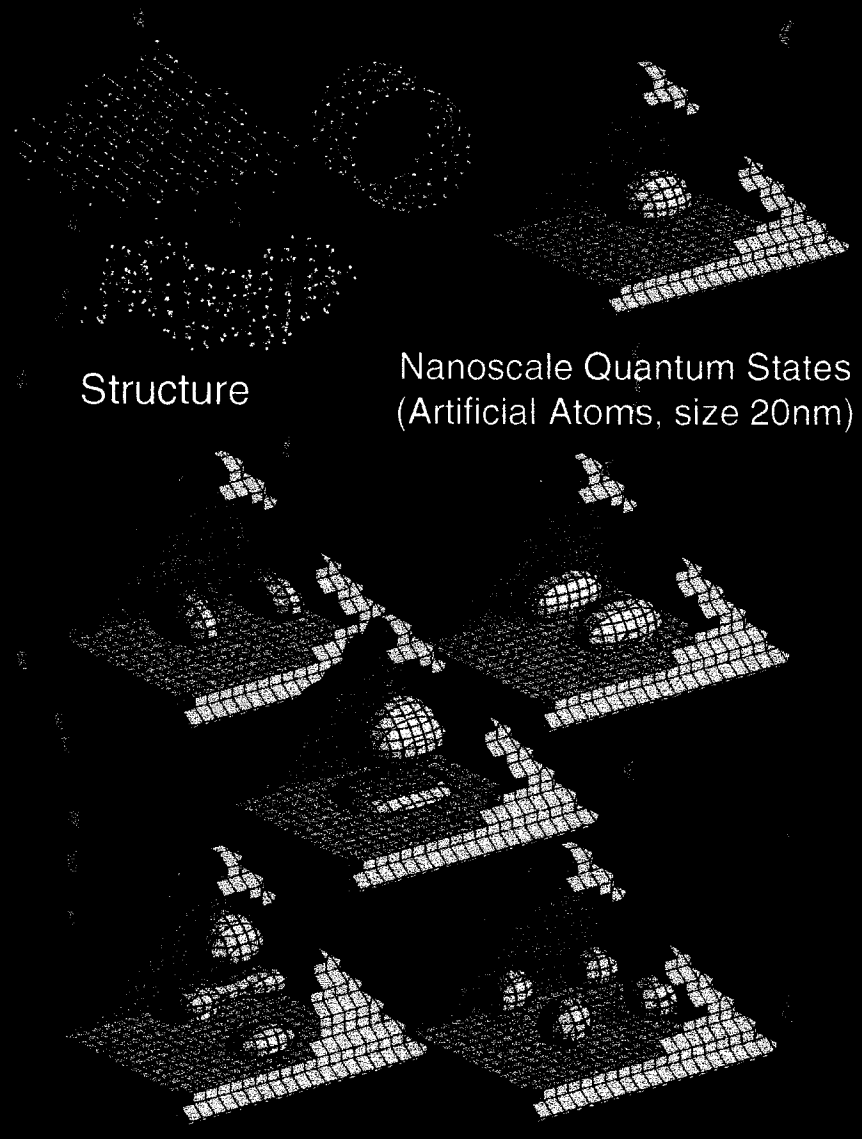
Fabiano Oyafuso, Gerhard Klimeck, R. Chris Bowen, Timothy B. Boykin*, and Paul von Allmen

Jet Propulsion Laboratory, California Institute of Technology

*University of Alabama in Huntsville

*Email: fabiano@jpl.nasa.gov

Web: http://hpc.jpl.nasa.gov/PEP/gekco/nemo3D



Parameterization:

- TB parameters determined from genetic algorithm to match experimentally measured band edges and masses.

Mechanical Strain:

- CG-based minimization of mechanical strain to determine atomic positions

Electronic Structure:

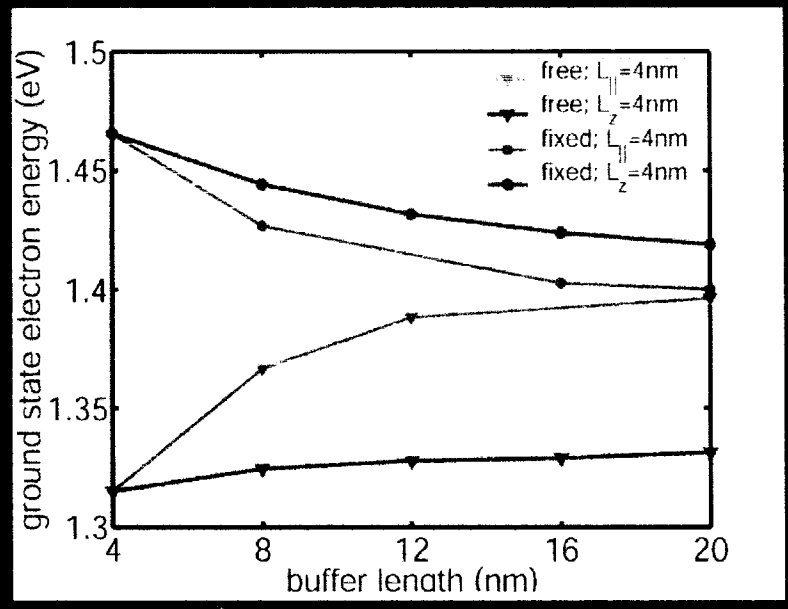
- Custom Lanczos eigenvalue solver

Numerical Simulation:

- Problem size is large: 100 GB is typical storage requirement for Hamiltonian
- Parallel implementation of both strain and electronic structure calculation is necessary!
- 1D data decomposition

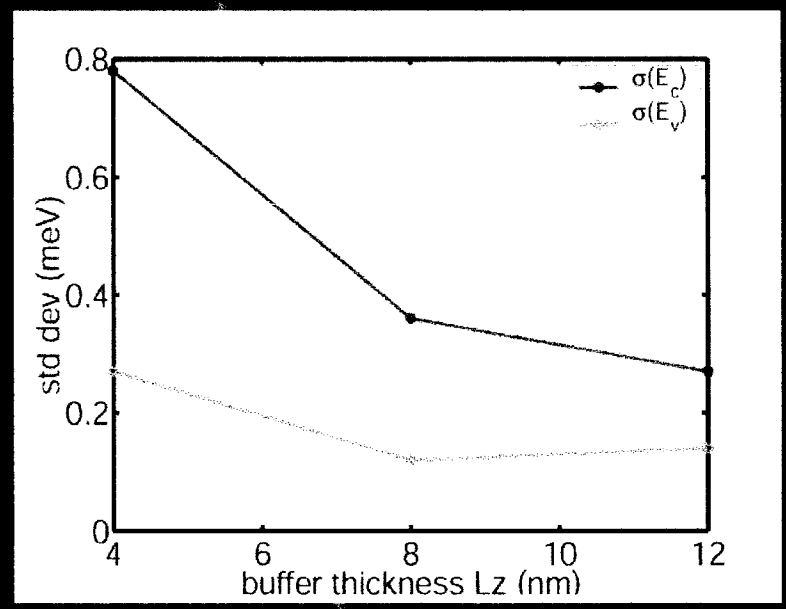
Effect on ground state electron energy:

- System: Dome-shaped $In_{0.6}Ga_{0.4}As$ QD 15nm radius; 5.4 nm height
- *Free BC*: no constraints on QD; strain and ground state energy are underestimated
- *Fixed BC*: QD boundary pinned; strain and ground state energy are overestimated
- Lateral extension (blue curve) of buffer does not lead to convergence
- Normal extension (red curve) of buffer converges for buffer ~ 20 nm

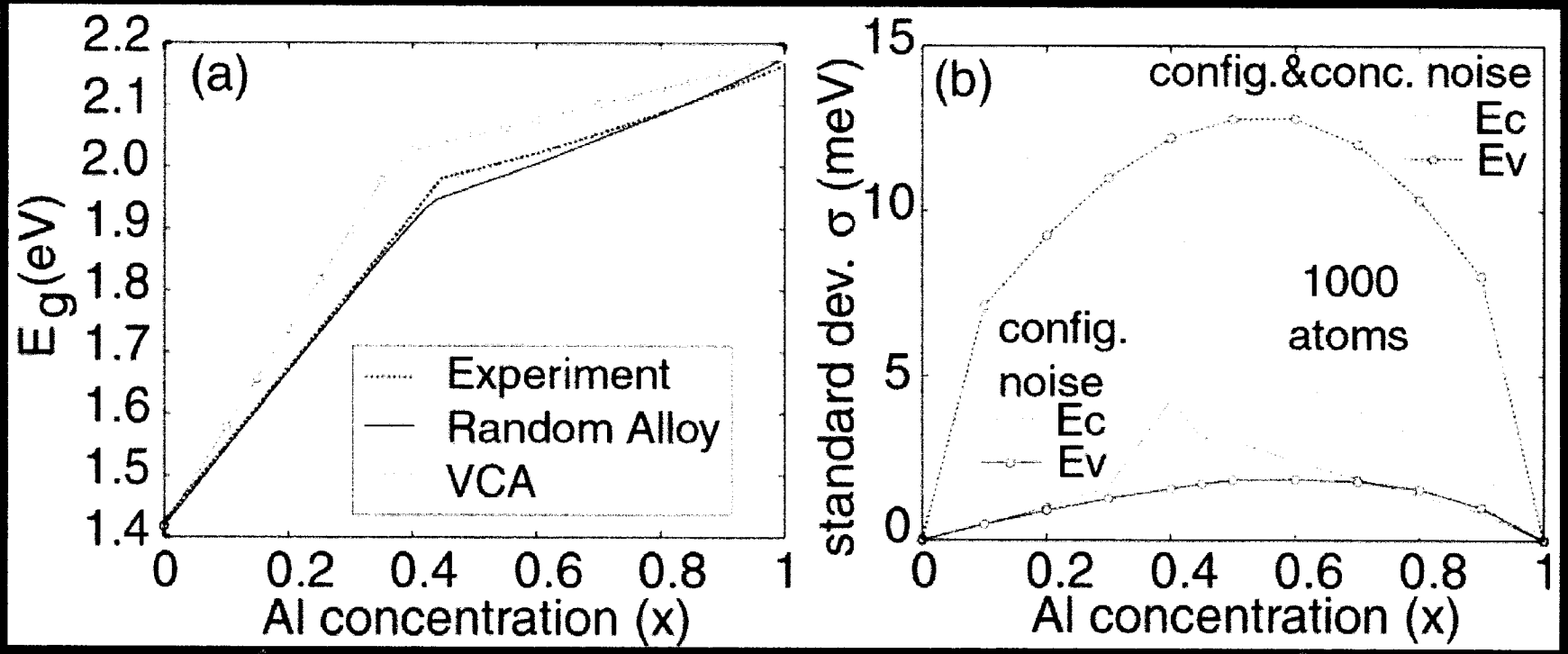


Effect on alloy disorder noise:

- Variation in ground state energy arises from configurational and compositional disorder
- Must take care to assure convergence has been attained
- Dependence on buffer size likely due to incomplete convergence of strain



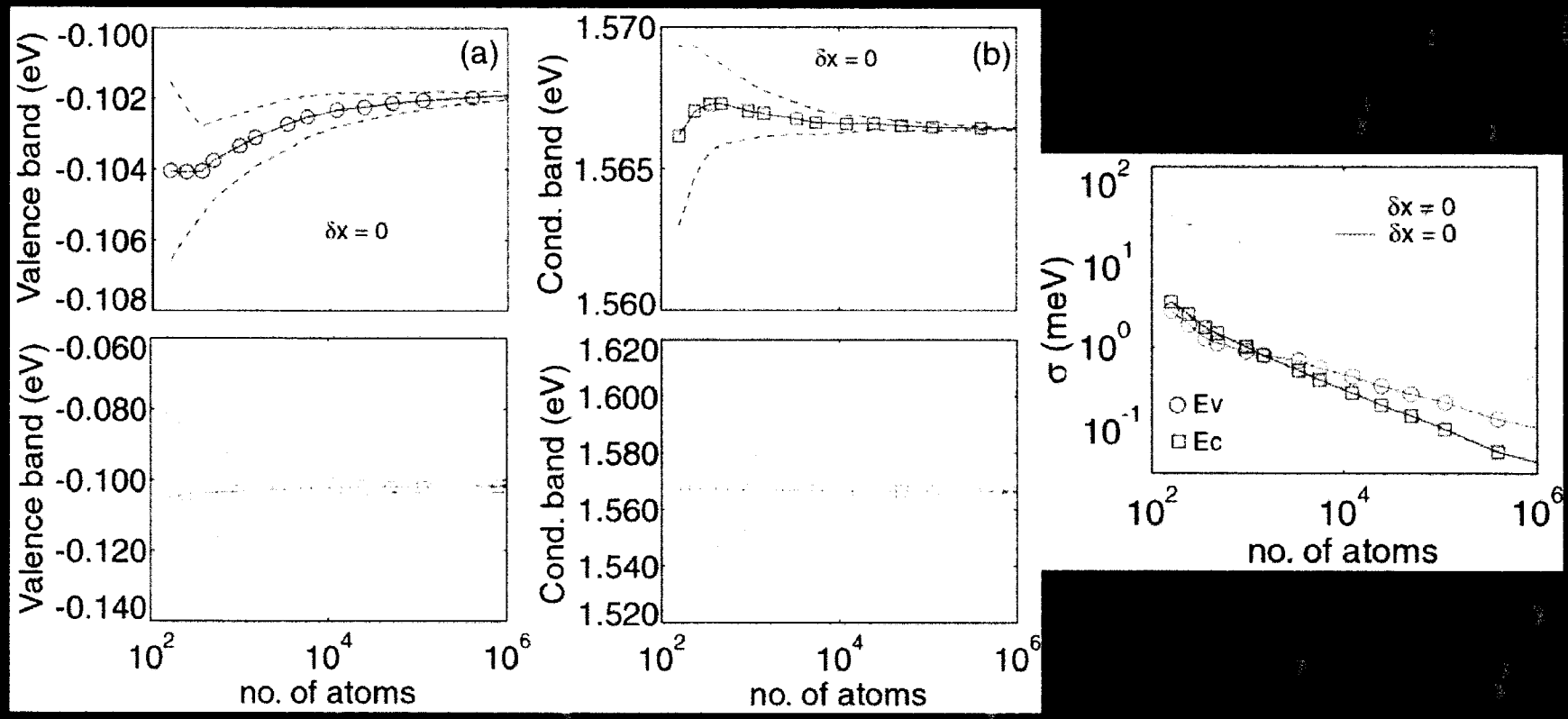
Configuration and Concentration Noise



- Concentration may vary stochastically as well.
- Concentration noise is larger than configuration noise.
- For a system containing 1000 atoms, the variation is about 10-15 meV
  - Conduction band noise shows a significant feature at the Γ-X transition (Al~0.45)
  - Valence band dependence is much smoother.

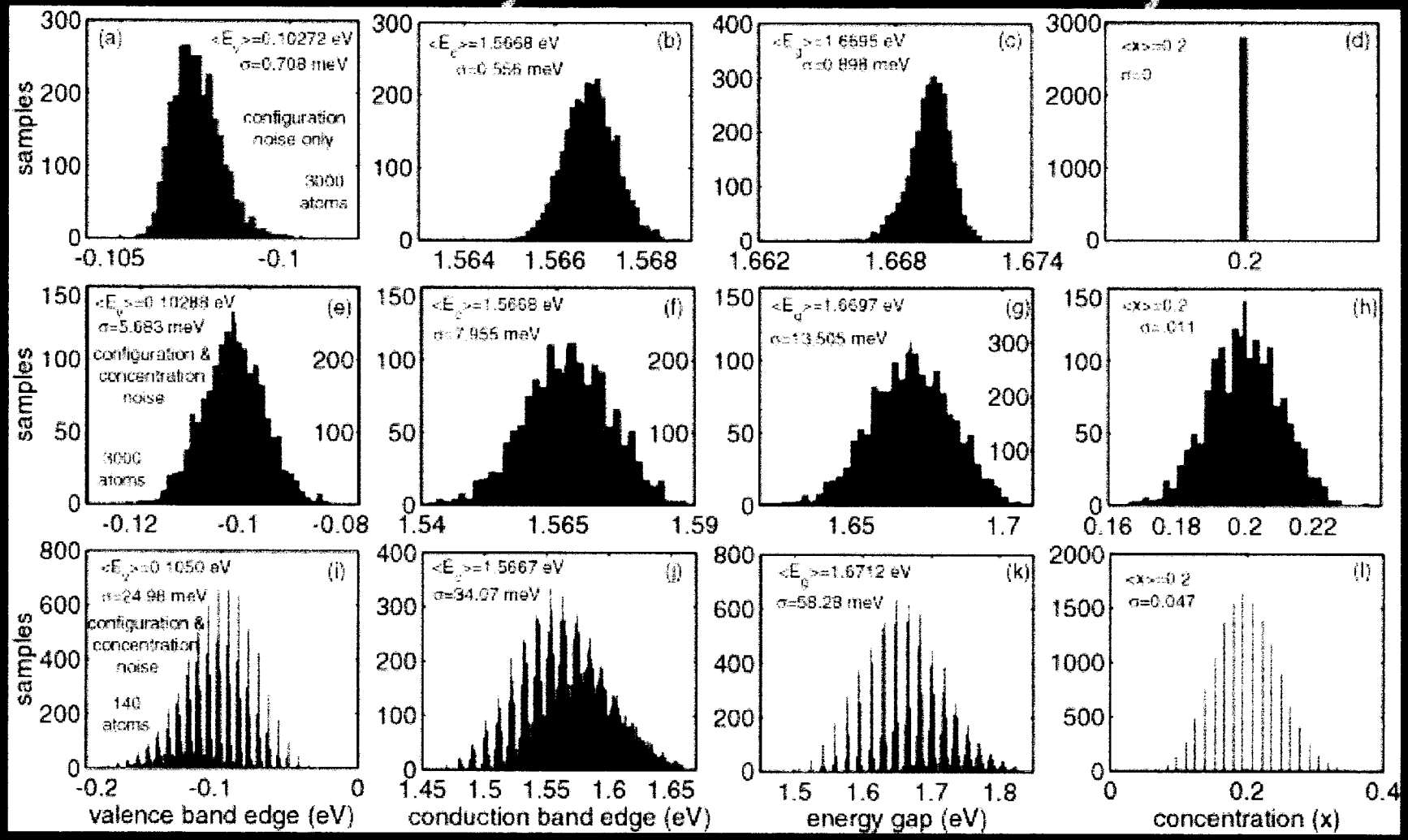
- What do the distributions look like?

Size Dependence of Bandedge Noise



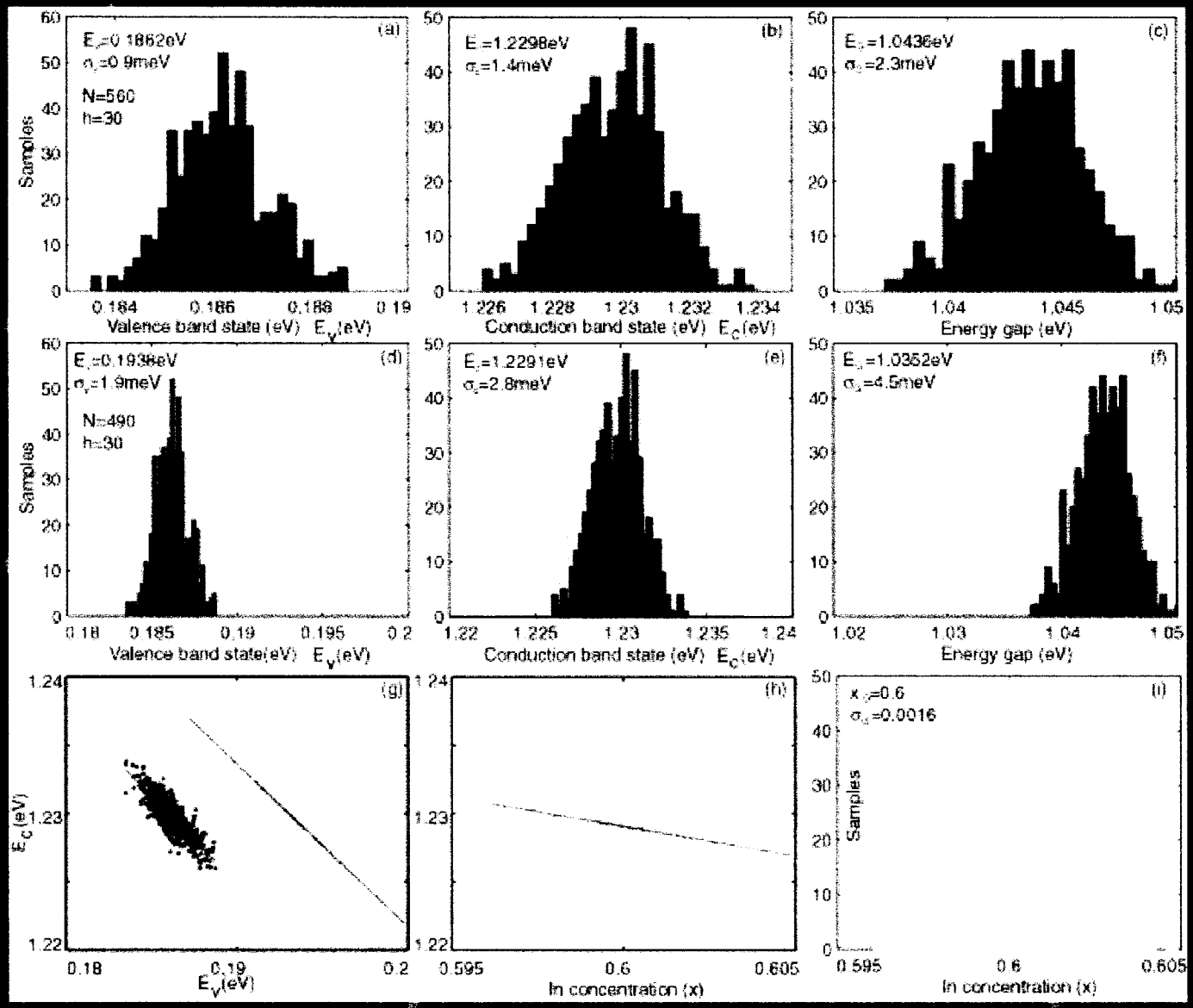
- Deviation due to configuration noise one order of magnitude smaller than concentration noise.
- 1 million atom simulations !
- Standard deviation decreases approximately as $N^{-1/2}$
- Conduction band noise < Valence band noise for configuration noise only.
- Conduction band noise > Valence band noise for the concentration noise.

Small System Size Peculiarity

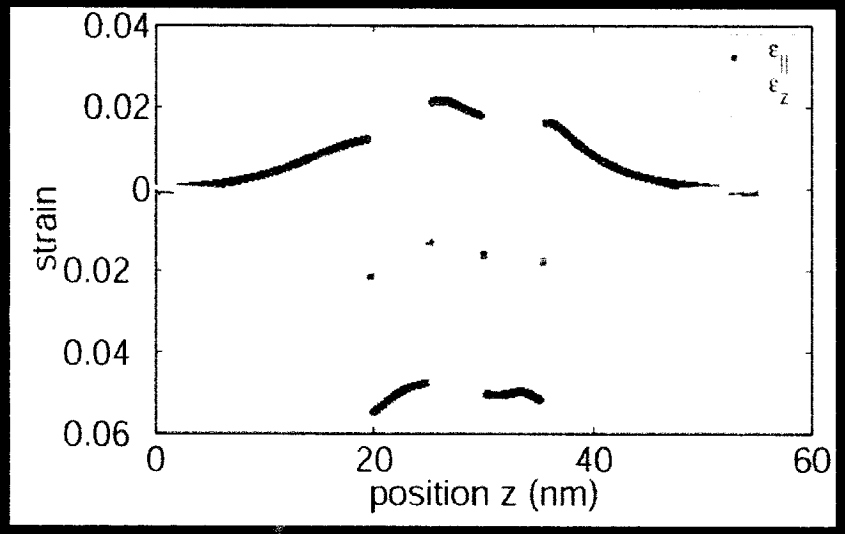


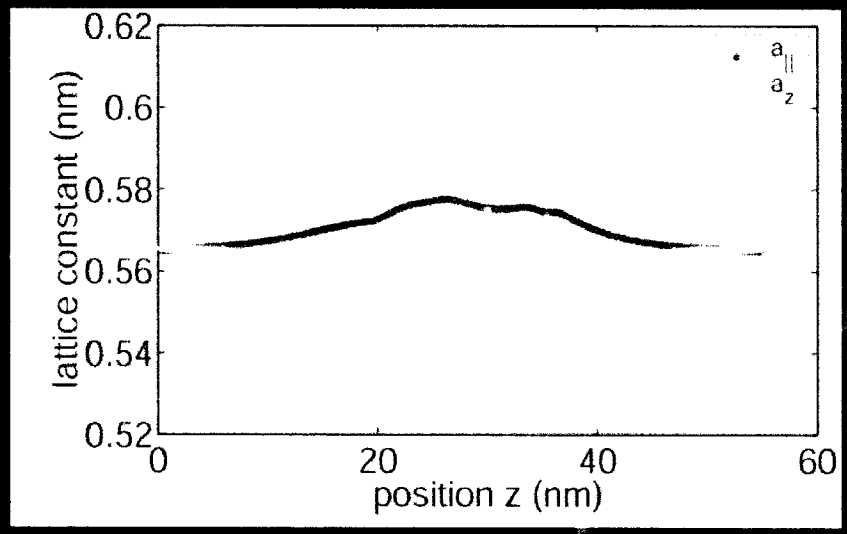
- Tiny systems (e.g. 140 atoms) only allow discrete concentrations

InAlAs Alloyed Quantum Dot Samples

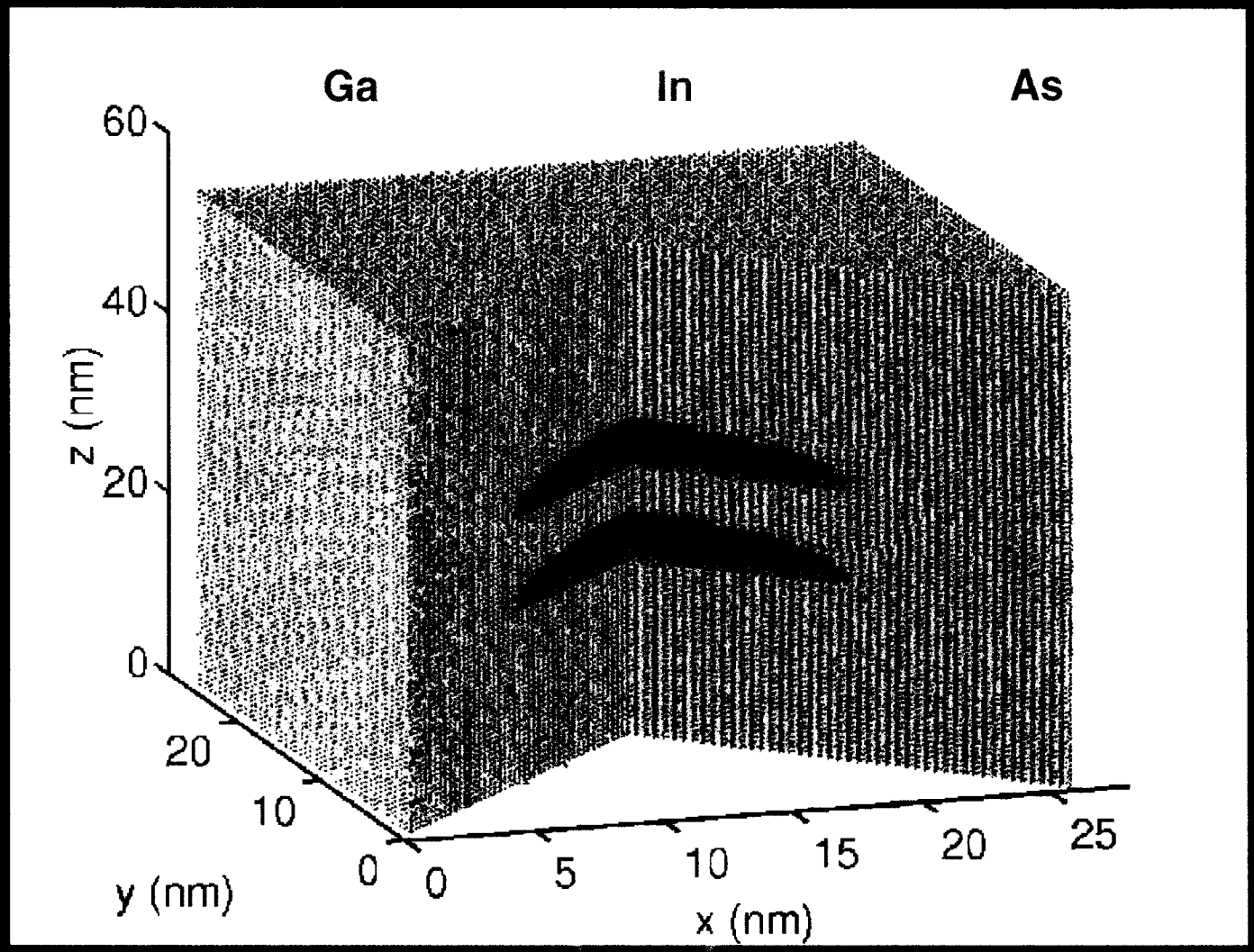


- Atomistic granularity
  σ = 2.3meV
- Cell granularity
  σ = 4.5meV
- Ec and Ev strongly correlated
- Ec and x weakly corelated



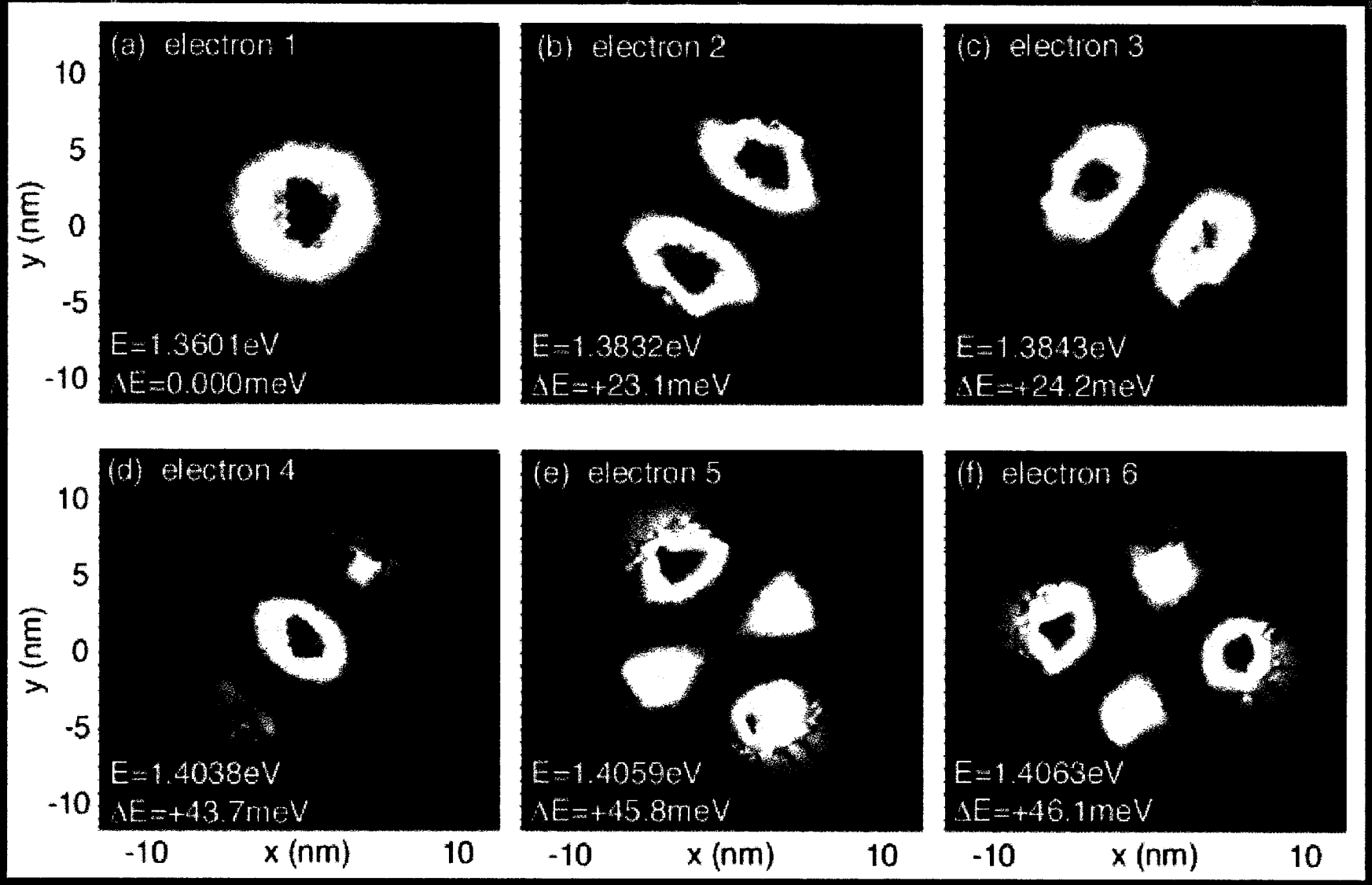


- Examine strain along major symmetry axis (z) for primitive cells centered about As atoms
- Tensile bi-axial strain outside QD ($\varepsilon_{||}>0$) due to stretching of GaAs to match InAs. Compressive strain in QD.
- Lattice constants follows same trends.

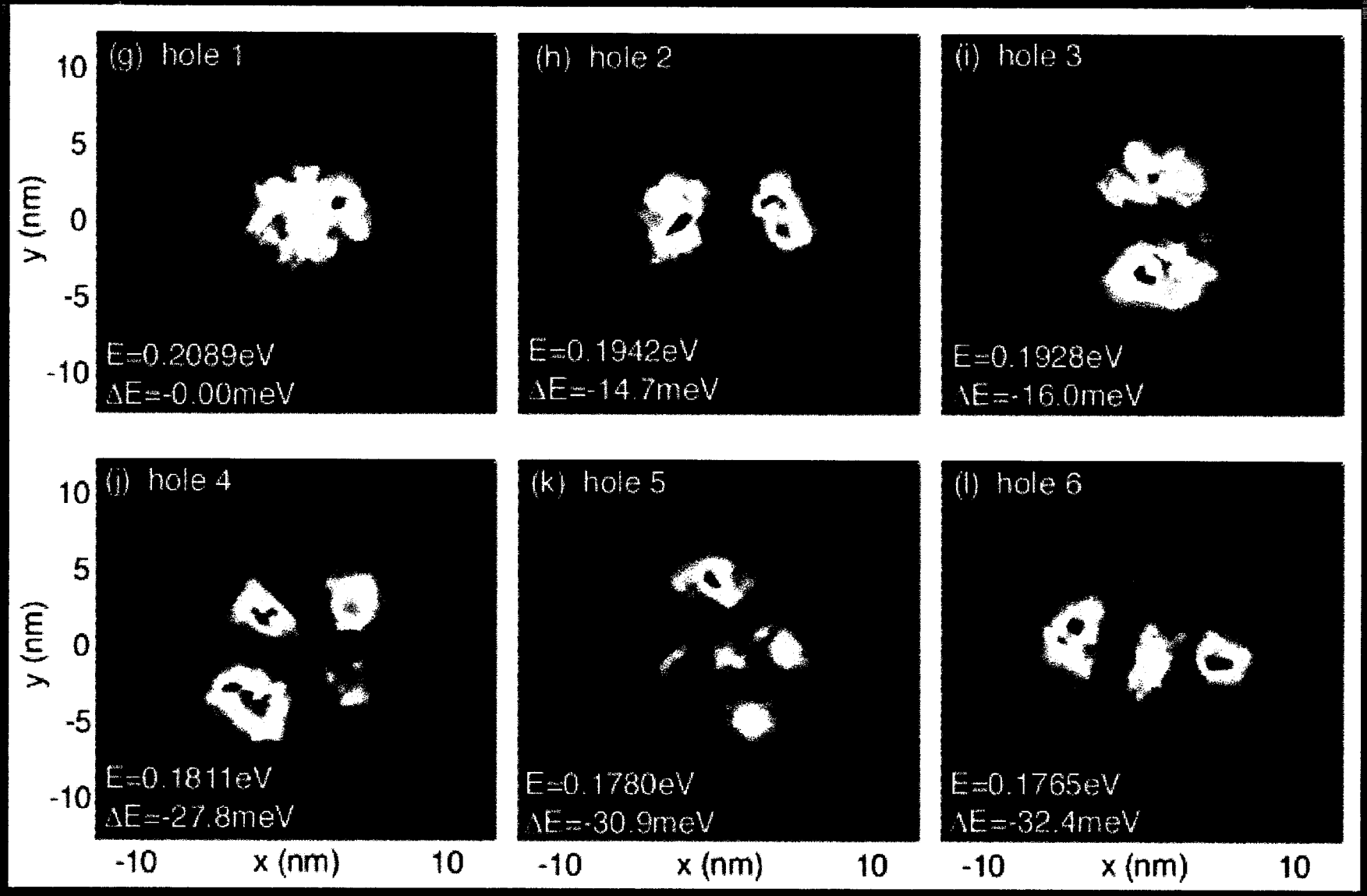


- Cutaway of simulation domain
- Coupled InAs QDs: Diameter = 18 nm; QD separation = 5 nm

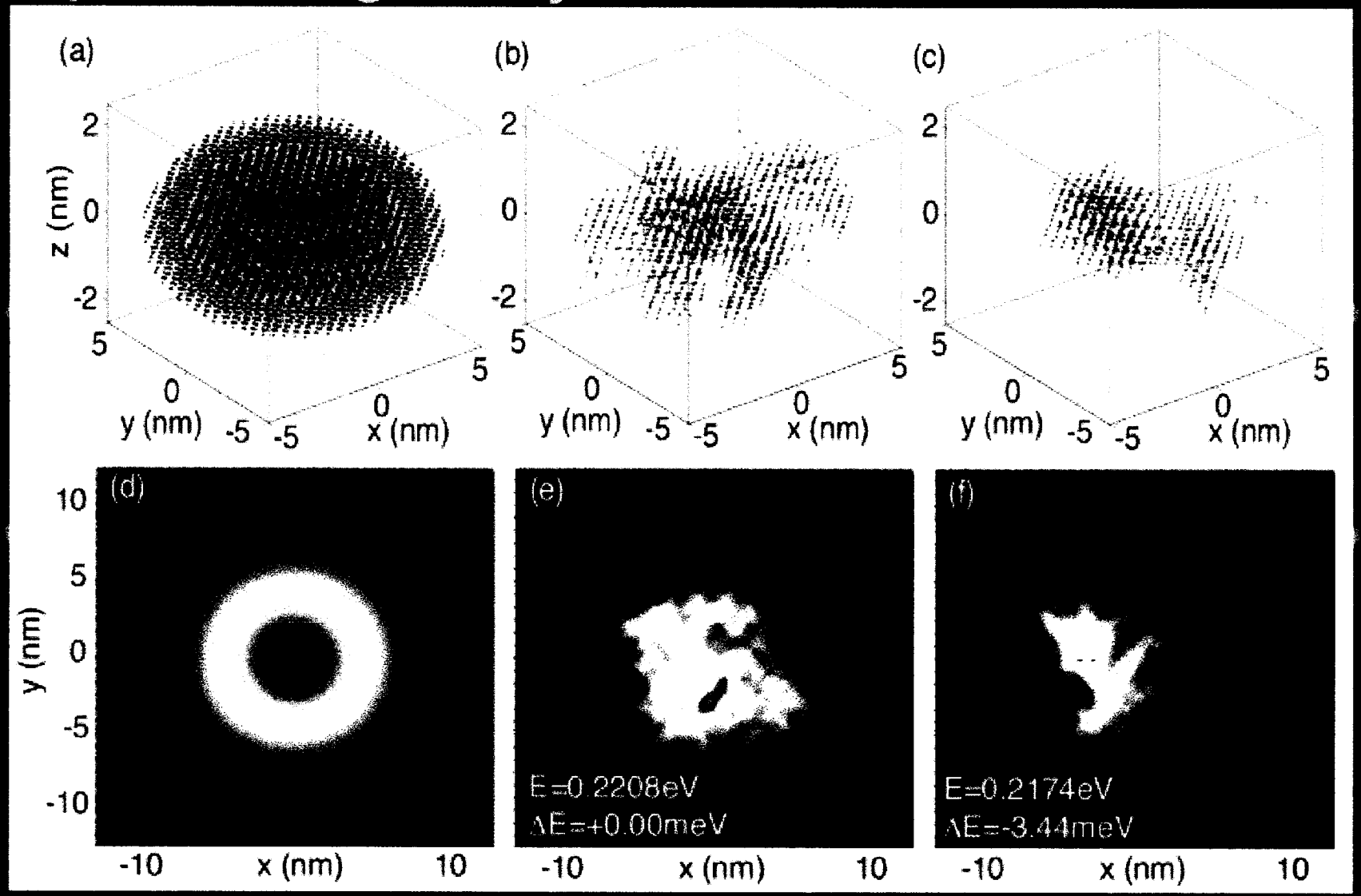
Spatial inequivalency in the electron states



Spatial inequivalency in the hole states

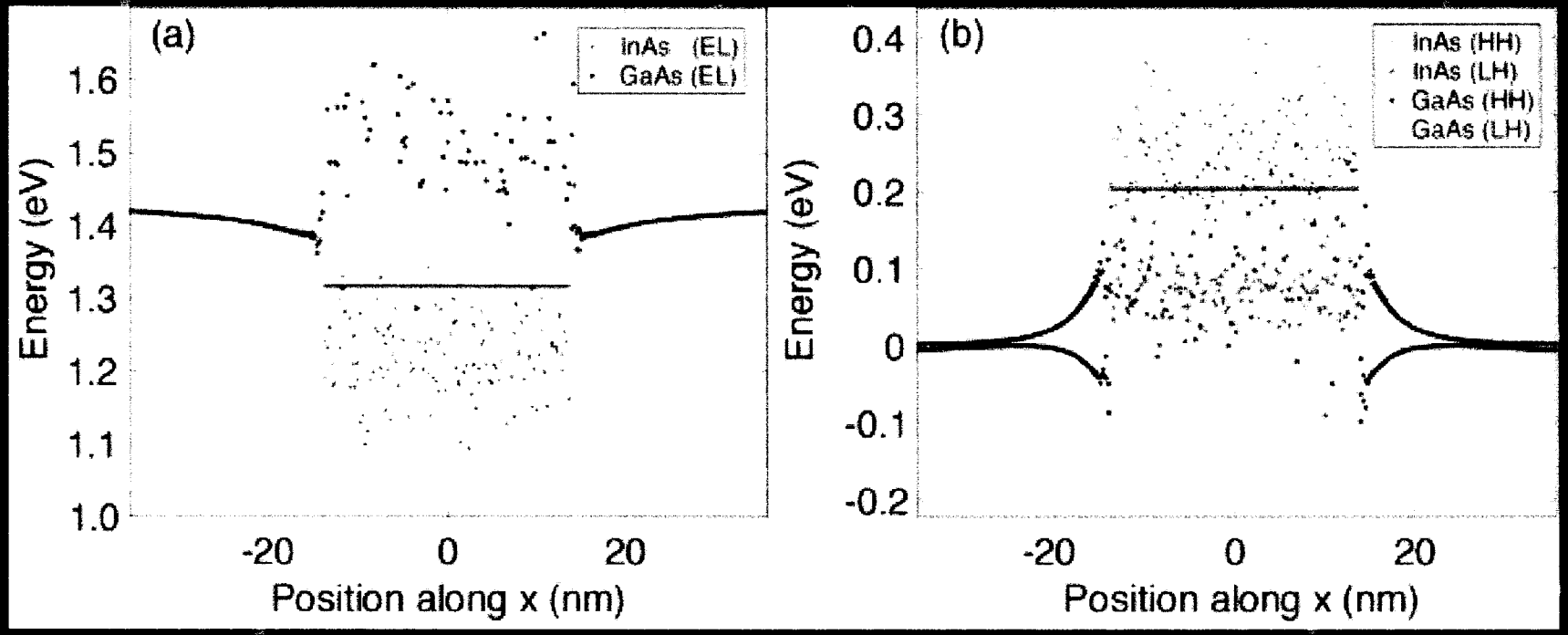


Spatial irregularity in the hole ground state



VCA / no Disorder | Disorder Sample 1 | Disorder Sample 2

Local Deformations in an Annealed QD



In-As bonds compressed in x-y

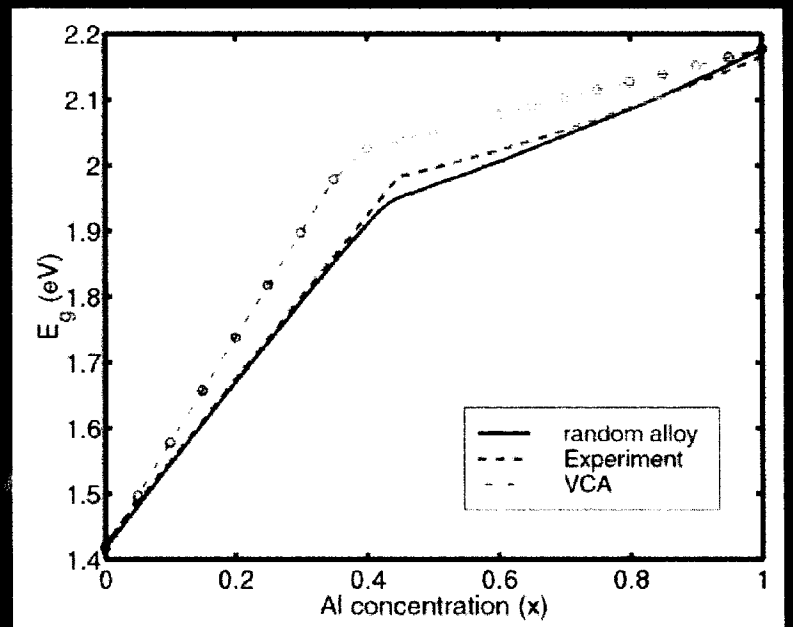
-> Ec raised from bulk value of ~0.58eV to ~1.2eV

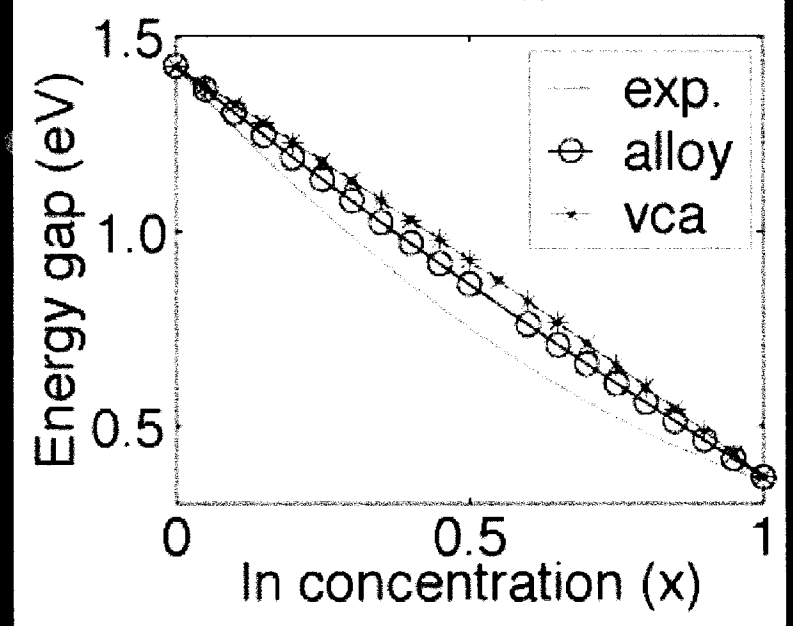
-> Ev HH raised from bulk value of ~0.22eV to ~0.3eV

Ga-As bonds compressed in x-y and stretched in z inside dot

-> Ec raised from bulk value of ~1.42eV to ~1.55eV

-> Ev raised from bulk value of 0eV to ~0.1eV





Problem:

- VCA provides generally a linear bandgap if interpolated from the binaries GaAs, AlAs, and InAs.

Approach:

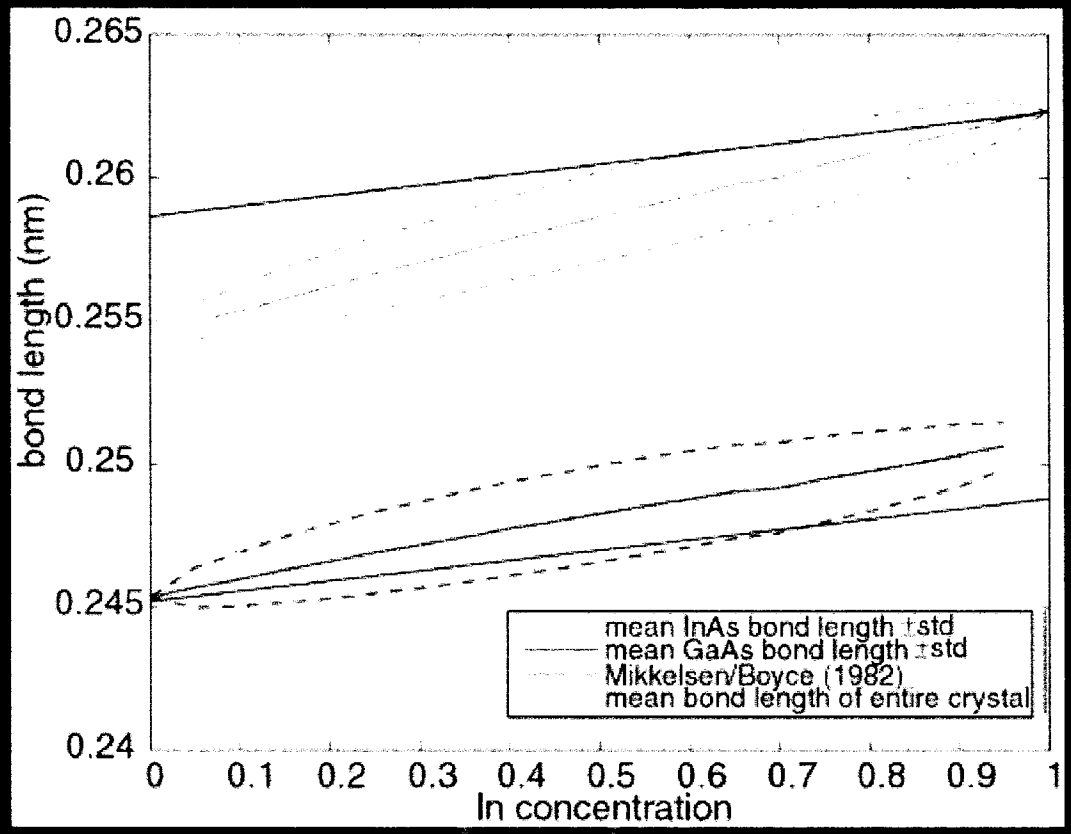
- sp3s* tight binding model
- Perform 3-D alloy simulation of the bandedges.
- Represent each individual atom in the chunk of material
- 3-D random alloy simulation matches experimental data well.

AlGaAs:

- VCA derived from pure GaAs and AlAs results in an wrong bandgap.
- 3-D simulation gives the correct bowing.

InGaAs:

- Improved bowing versus the VCA.
- Still a problem with over estimating the band gap
  -> parameterization dependent



InGaAs bond length distribution:

- VCA on the bond length is incorrect
- Locally, InAs and GaAs (mostly) maintain their bond length character

Bulk Semiconductors are described by:

- Conduction and valence bands, bandgaps (direct, indirect), effective masses
- 10-30 physically measurable quantities

Tight Binding Models are described by:

- Orbital interaction energies.
- 15-30 theoretical parameters

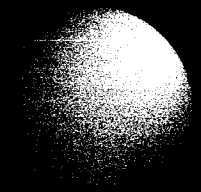
Analytical approach:

- Exact diagonalization at Γ for $sp^3d^5s^*$
- Formulas developed by Tim Boykin at UAH (subcontract) for effective masses and bandgaps from interaction energies

Numerical approach:

- Use a genetic algorithm to do fitting.

- Match experimental data in various electron transport areas of the Brillouin zone:
  - Effective masses of electrons at Γ, X and L
  - Effective masses of holes at Γ
  - Band edges at Γ, X and L



15-30 theoretical interaction energies