Semiconductor nanostructure properties. Molecular Dynamic Simulations.

N I Podolska$^{1,2,3}$ and A I Zhmakin$^{1,2}$

SPb Branch of Joint Supercomputer Center of the Russian academy of sciences
Politekhnicheskaya str. 26, 194021, Saint-Petersburg, Russia

Ioffe Physical-Technical Institute of the Russian academy of sciences,
Politekhnicheskaya str. 26, 194021 Saint-Petersburg, Russia

Saint-Petersburg Academic University of the Russian academy of sciences
Khlopina str. 8/3, 194021, Saint-Petersburg, Russia

E-mail: n.i.podolska@gmail.com

Abstract. The need for research is based on the fact that development of non-planar semiconductor nanosystems and nanomaterials with controlled properties is an important scientific and industrial problem. So, final scientific and technological problem is the creation of adequate modern methods and software for growth and properties simulation and optimization of various III-V (GaAs, InAs, InP, InGaAs etc.) nanostructures (e.g. nanowires) with controlled surface morphology, crystal structure, optical, transport properties etc. Accordingly, now we are developing a specialized computer code for atomistic simulation of structural (distribution of atoms and impurities, elastic and force constants, strain distribution etc.) and thermodynamic (mixing energy, interaction energy, surface energy etc.) properties of the nanostructures. Some simulation results are shown too.

1. Introduction

Nanowires based on semiconductor materials have recently drawn much attention due to their importance for nanoscale electronics and photonics [1]-[6]. These nanowires are usually fabricated via the Vapor-Liquid-Solis (VLS) growth mechanism [7] developed long ago for micrometer scale “whiskers” [8,9]. Using modern epitaxy techniques such as MOCVD [5,7,10] or MBE [11,12], nanowires or nanowhiskers (NWs) with diameters of several tens nanometers and length up to tens microns can be obtained. The fundamental principle underlying the VLS mechanism is the catalytic effect of a liquid metal droplet (Au, for example) assisting the NW growth from a supersaturated liquid alloy [8]. The integration of NWs components into working devices requires a high degree of control that is still lacking, and many fundamental questions concerning NW nucleation and growth remain to be answered (for instance, chemical potential in the droplet, NW and droplet surface energies, solid-liquid or/and liquid-vapor interface energies etc).

The Vapor-Liquid-Solid mechanism of NWs nucleation and growth are usually investigated using continuous medium theories of crystal growth [13]-[17]. It should be noted, that many parameters (for example, chemical potentials, surface energies, interface energies etc) have not been determined experimentally or using some continuous medium theories and their effect on nanostructures growth is
not clear. Consequently, numerical simulations should be able to probe the NW nucleation and growth processes in their full atomistic detail.

2. Valence Force Field for Nanostructures

Since the high number of atoms (about thousands to hundreds of thousands) are involved in the nucleation and growth of NWs, \textit{ab initio} models become prohibitively expensive. Therefore, most of the atomistic simulations (such as molecular dynamics and Monte Carlo) are based on an empirical interatomic potential, which can be fitted to experimental and/or \textit{ab initio} data. Both molecular dynamics and Monte Carlo are important and very powerful methods for a study of atomic processes in low-dimensional (less than ten micrometers) systems. These methods allow study of kinetics of atomic processes in complex physical and chemical systems [18-40].

Strain has significant effect on the electronic and optical properties of lattice mismatched semiconductor heterostructures such as quantum dots or nanowires. In inhomogeneous systems, the strain can be conveniently computed with continuum elasticity theory, which is believed to hold down to nanometer-size systems [24]. These strains can then be used directly as input for electronic structure calculations within the effective mass or kp approximations [26, 25], which are also continuous medium theories. The strains do not, however, provide enough information for atomistic electronic structure methods such as tight-binding [27, 28] or pseudo-potentials [29, 30], which need atomic positions as input. Indeed, the atomic positions can hardly be reconstructed from the strains, whose analytic structure is very complex around, e.g., surfaces and interfaces, and which do not characterize the internal strains [31] within the unit cell (i.e., the displacement of one sublattice with respect to an other). Therefore, the atomic positions used as input for such methods are usually computed with semi-empirical force fields such as Keating’s Valence Force Field (VFF) [32], Tersoff [33], or Stillinger-Weber potentials [34].

One of the powerful methods for modelling structural and thermodynamic properties of III-V semiconductor solid solutions (including both bulk and nanostructures) is Valence Force Field [19-24] and Keating potential as an empirical interatomic potential (See Figure 1, for example). Since the Keating’s VFF model only accounts for elastic relaxation (no kinetic of dislocations), the comparison between the atomic positions obtained by the simulation and the positions obtained by an experimental method like TEM can suggest the presence or absence of dislocations in a system [22-24]. The strain distribution of differently shaped quantum dots, quantum dots and disks in nanowires, heterostructures in nanowires and others can also be simulated by using VFF too.

The popularity of VFF models for studying the thermodynamic properties of semiconductor alloys is due to a few reasons. First, even in the approximate form, the VFF approach has been proved to provide quantitatively accurate estimates for the mixing energies of conventional III-V compounds [25,26] and III-N compounds [19-24, 38-40]. Second, the VFF models invoke a limited number of parameters, most of which can be found directly from the experimental data on binary constituents of the alloy. Third, even with large atomic clusters, the VFF simulations can be now routinely performed on personal computers. Forth, Keating’s VFF model provides a good balance between accuracy and efficiency.

3. Valence Force Field Simulations

Sometimes ago, we have derived a statistical model of ternary A\textsubscript{III}B\textsubscript{V} alloys by using a new methodology, based on numerical calculations of their configuration partition function [38-40]. This statistical model allows calculating chemical potentials, mixing energy, mixing enthalpy, mixing entropy, phase diagrams etc. To find the mean mixing energy and the density of states in an alloy, the VFF simulations have been carried out with the Keating potential. The use of multiple computation runs (\(N_{exp}\)) is found to improve the representative statistics of the VFF computations, which is necessary for an accurate prediction of the mixing energy dispersion. The computational runs were
performed for the same solid composition, differing in the random group-III atomic distributions in the cation sublattice and/or group-V atomic distributions in the anion sublattice.

![Graph](image)

**Figure 1.** (a) Interaction energy as a function of GaP mole fraction in GaPSb. (b) Mixing energy and mixing enthalpy as functions of AlN mole fraction in AlInN. Number of atoms \( N_a = 5832 \) and 13824 and number of computation runs \( N_{exp} = 50 \).

Thus, this developed earlier optimized VFF method and this new methodology can be applied also to nanostructures, and not only to bulk materials. To do this, the boundary conditions for surface atoms of a modeling structure should be changed from periodic boundary conditions on free surface condition because it is no longer necessary to reduce the contribution of the surface atoms. In other aspects the simulation method is the same. The initial atomic positions are chosen to match those of a virtual crystal with the lattice constant dependent on the alloy composition via the Vegard law (the so-called "strained" modeling crystal). Both anions and cations are then allowed to relax lowering the distortion energy of the domain determined from the interatomic potential. The relaxation is allowed until the total distortion energy was converged with a relative accuracy of \( 10^{-5} \). After minimizing the distortion energy we get the so-called "relaxed" modeling crystal.

### 4. Some Simulation Results

As an example, some surface energy numerical calculations will be shown here. Surface energy \( E_{surf} \) quantifies the disruption of intermolecular bonds that occurs when a surface is created. In the physics of solids, surfaces must be intrinsically less energetically favourable than the bulk of a material (the molecules on the surface have more energy compared with the molecules in the bulk of the material), otherwise there would be a driving force for surfaces to be created, removing the bulk of the material. The surface energy may be calculated as the excess energy at the surface of a material compared to the bulk \( E_{surf} = (E_{PBC} - E_{FBC})/S_{free} \), where \( E_{PBC} \) is the energy of the modelling crystals with the periodic boundary conditions (PBC), \( E_{FBC} \) is the energy of the modelling crystals with the free surface boundary conditions (FBC), and \( S_{free} \) is the free surface area (here is the surface area of the cubic of side \( L \)). Table 1 shows the values of free surface area of cubic crystals with a different number of atoms. It must be remembered that \textit{ab initio} calculations and simulations can be held only for crystals with atoms of less than 1000 whereas a III-V cubic crystal with a side of less than 10 nm composed of about 32000 atoms.

Figure 2 shows that \( (E_{PBC} - E_{FBC}) \) and free surface area are functions of number of atoms in the cubic modelling crystals, i.e. the surface energy will be a function of the free surface area. This means that the surface energy calculated for the modelling crystals with various sizes of crystals (number of atoms and/or free surface area) can vary greatly.
Figure 2. Excess energy at the surface of a material (cubic GaAs crystals, in this case) compared to the bulk and surface area as functions of number of atoms in modelling crystals.

We can see in Figure 3 surface energy as a function of number of atoms and/or free surface area, computed for zinc-blend InAs (111) by Valence Force Field (see Section 3). It can be seen that the surface energy of the “strained” crystals (see Figure 3a) does not vary with the free surface area of the crystals and is \(0.47 \pm 0.01\) J/m\(^2\). In the case of the “relaxed” crystals (Figure 3b) surface energy is a function of the free surface area. A similar behavior of the surface energy is also observed for other materials, such as GaAs (111) (see Figure 4).

Figure 3. Surface energy as functions of free surface area and number of atoms in modelling crystals (blue circles) as well as average surface energy \(<E>\) with standard deviation SD (red dashed line). Green downward triangles (\(\nabla\)) are \textit{ab initio} simulations and theoretical calculations and yellow upward triangles (\(\Delta\)) are experimental results [41-43].

In Figure 3 and Figure 4 it can be seen a good agreement simulations with experiments and other calculations [41-43] for small number of atoms. However, apparently small number of atoms of
modelling crystals is not enough to estimate surface energy of real nanosystems, especially of systems like nanoneedls, quantum dots etc (in this case we can not apply periodic boundary conditions). So, firstly, necessary to consider information about the free surface area and geometry of the system, for which the data obtained experimentally and/or calculated; secondly, the need to develop new methods for calculating (theoretical and numerical) of the surface energy of different materials and systems.

Figure 4. Surface energy as functions of free surface area and number of atoms in modelling crystals: blue circles (o) in the case of “relaxed” GaAs modelling crystals and red diamonds (◊) in case of the “strained” modelling crystals. Average surface energy \( \langle E \rangle \) (dark red dashed line) with standard deviation SD. Green downward triangles (∇) are \textit{ab initio} simulations and theoretical calculations and yellow upward triangles (Δ) are experimental results [41-43].

5. Conclusions
Accordingly, now we are developing a computer program for simulation of structural (distribution of atoms and impurities, elastic constants, strain distribution, etc.) and thermodynamic (surface energy, elastic energy, mixing energy, mixing enthalpy, mixing entropy, etc.) properties of new and practically important nanomaterials - low-dimensional nanostructures (e.g. nanowires, nanoneedles etc.) based on III-V, II-VI and IV semiconductors.

Numerical (operational) parameters of simulations and software packages can significantly affect simulation results (quality of energy relaxation). Small number of atoms of modelling crystals is not enough to estimate surface energy of real nanosystems, especially of systems like nanoneedls, quantum dots etc (in this case we can not apply periodic boundary conditions). To compare simulations, calculations and experimental results correctly one should know additional information (free surface area, geometry, simulation parameters etc.)

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