

Energetics of non-uniformly alloyed Ge(Si)/Si(001) Quantum Dots

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ABSTRACT

The non-uniform composition profile in Ge(Si)/Si(001) quantum dots is calculated using atomistic modeling. A Ge rich surface is found on the quantum dots. The difference between the surface Ge content and the average Ge content away from the surface is found to be around 40% regardless of the quantum dot shape, size or average composition. An energetic analysis of the atomistic models reveals that a lower surface energy of Ge in the case of uniformly alloyed quantum dots is responsible for the Ge enrichment of the surface. For the case of the non-uniformly alloyed quantum dots the surface energy of Ge and Si is found to be approximately equal. It is therefore concluded that the segregation of Ge is induced by the lower surface energy of Ge but limited by the build up of strain between the Ge rich surface and the rest of the QD.

An extension of the energetic model to large Ge/Si islands shows that the surface energy term contributes significantly more than the strain energy to the total formation energy.

Keywords: quantum dots, energetics, non-uniform, alloying, segregation

1 INTRODUCTION

During the layered growth of lattice-mismatched semiconductors, a strain-induced transition from planar growth to 3D island growth (Stranski-Krastanow growth [1]) can occur leading to the formation of quantum dots (QDs). Their small size (nm in dimension) leads to quantum confinement of the electrons, resulting in electronic and optical properties which show promise for use in a wide range of devices ranging from semiconductor lasers to quantum computers. These properties of the QDs are controlled by their size, shape and composition. The growth of Ge(Si) on Si(001) has been extensively studied (e.g. [2, 3]) because of its importance as a model system for the growth of other, more complicated, lattice mismatched semiconductors.

Whereas the shape and size of Ge(Si)/Si(001) QDs can be determined from AFM [4] and TEM [2] to a high precision, an accurate measurement of the composition and composition distribution remains unsolved. All methods consistently show a significant non-uniformity in the composition profile [5, 6] but although several details of the composition profile have been resolved, a coherent model

of the alloying profile, taking into account all different driving forces, remains elusive.

For a complete understanding of the QD formation process it is necessary to take into account the non-uniformity of the composition profile. In this paper an atomistic modeling approach is presented that accounts for the non-uniformity of the composition profile. The atomistic model forms the basis for an analysis of the energetics of the QD.

2 THE QUANTUM DOT MODEL

To obtain an accurate representation of the energetics of a non-uniformly alloyed QD, the atomistic model has to resemble the shape, size and non-uniform composition profile of a real QD as closely as possible. In the case of Ge/Si quantum dots, there are two distinct shapes the QD can assume which are well defined in terms of the crystallographic planes which they contain [2].

Initially, quantum dots grow having a pyramid shape with facets along {105} crystallographic planes. At a certain critical size, islands transform to a more complicated domes shape with steeper facets.

The size of coherent Ge/Si islands (i.e. not containing dislocations) has been found to vary strongly depending on the average composition of the island. Coherent islands with diameters between 20nm and 200nm are possible. For their use as QDs, smaller islands are preferred. In this work the size of the QDs studied in the atomistic simulations was limited by the computational resources available. Therefore the atomistic models studied here have a diameter between 8-16nm. However, ways to extrapolate the results obtained from smaller QDs to larger systems are outlined further down in this paper.

The aim in this work is to calculate the quasi-equilibrium composition profile in $\text{Ge}_x\text{Si}_{1-x}$ (with x representing the Ge content) QDs. It is important to point out that the present simulation does not account for kinetic effects on the composition profile such as the anisotropic surface diffusion due to surface reconstruction and the difference in the diffusion lengths of Ge and Si, effects which may lead to experimental results which deviate from the composition profile presented here. However, these deviations from the quasi-equilibrium composition profile are expected to be small for sufficiently high growth temperatures and slow growth rates.

In the calculations, a uniform starting composition profile is assumed and subsequently the energy of the system is minimized computationally. The system sizes and time-scales involved in the formation of the composition profile are too large to employ classical molecular dynamics or ab-initio modeling; therefore the approach used here is based on a combination of atomistic total energy calculations and a Metropolis Monte – Carlo process which provides the mechanism for the reorganization of the alloy within the QD. Experimentally, QDs larger than those studied here are commonly found. However, the computation time the system takes to equilibrate increases considerably with the system size and it is therefore not possible to treat larger sizes. It turns out that this is only a small limitation since the composition profile is not very sensitive to the system size. The starting composition in the QD is assumed to be a homogeneous alloy. This assumption implies that the modeling either is simulating a system in which the QD grows with a composition as deposited, and then undergoes diffusion/segregation post-growth, or is simply a starting model as a basis for energy minimization.

To obtain this quasi-equilibrium profile, the energy of the system is minimized by two steps: (i) while maintaining the homogeneous distribution of the QD, and the pure Si of the substrate, the top two atom layers of the substrate and the total contents of the island are relaxed using a conjugate gradient type algorithm implemented in the OXON package [8]. The interaction between the atoms is described by the Tersoff potential [9], and periodic boundary conditions are applied to the substrate. (ii) following this relaxation, diffusion of atoms within the QD is allowed. Diffusion of atoms into the substrate is not allowed because this would result in the QD dissolving and Ge being dispersed in the Si bulk forming a dilute alloy. In experimental growth this does not occur because of kinetic limitations. To model the diffusion, an atom is randomly chosen and the atoms surrounding it, within a cut-off radius of 0.48nm, are identified. One of these surrounding atoms, with a label different from the first atom, is then chosen at random, and the labels of this atom and the first atom are exchanged. The energy of the new configuration is calculated, and a Metropolis Monte-Carlo process is employed to decide which configuration to accept. The temperature for the Monte Carlo process was set at 900K, a typical growth temperature for GeSi/Si(001) [6,10]. This process is continued to convergence: it was found that, for the system described, the process converges after about 3*N steps where N corresponds to the number of atoms in the QD.

Figure 1 shows the resulting composition profile for a dome shaped QD on a plane cutting through the centre of the QD. The results indicate that for both, pyramids and domes, Ge has migrated to the top and to the surface of the QD whereas Si has diffused to the bottom. The result is in good agreement with a measurement using X-ray diffraction by Malachia et al. [5] who also found a Ge rich surface layer

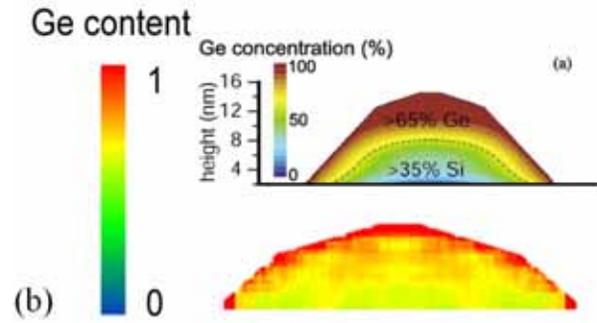


Figure 1: The composition profile of a dome shaped Ge/Si QD (a) measured experimentally by Malachias et al. [5] and (b) as resulting from the modeling in this work.

and a Si rich core of the QDs.

To understand the driving forces leading to this composition profile and to gain a better insight into the mechanisms governing QD formation it is necessary to calculate the strain and surface energy of the atomistic QD model.

3 THE STRAIN AND THE SURFACE ENERGY

Island formation on a substrate occurs because the islands relieve the strain between the substrate material and the deposited material more effectively than continued planar growth would. However, the transition from planar growth to island formation only occurs when the decrease in the strain energy due to island formation is larger than the increase in the surface energy due to the larger surface of the island. Likewise, any shape transition to an island shape with steeper facets only occurs when the increase in the surface energy due to the shape change is outweighed by a decrease in the strain energy. It would therefore be useful to split the total energy it takes to form a QD (formation energy) into two energy terms: one energy term that scales with the surface area of the island (surface energy) and another energy term that scales with the volume (strain energy).

3.1 The Strain Energy

The strain energy density (strain energy per volume) is given by the strain tensor ϵ_{ij} and the stress tensor σ_{ij} :

$$E_{strain} = \frac{\sigma_{ij} * \epsilon_{ij}}{2} \quad (1)$$

Prior et al. [11] have shown that a quantity related to the strain tensor in the surrounding of a four-fold coordinated atom can be calculated from an atomistic model using the following equation:

$$\varepsilon'_{ij} = R_{ij} * R_{ij}^{0-1} - I \quad (2)$$

where R_{ij} are the components of a matrix made up of the vectors between the four nearest neighbour atoms and I is the identity matrix. The actual strain tensor is symmetric and is therefore defined as:

$$\varepsilon_{ij} = 0.5 * (\varepsilon'_{ij} + \varepsilon'_{ji}). \quad (3)$$

The stress tensor σ_{ij} in the vicinity of an atom α is given by [12]:

$$\sigma_{ij}(\alpha) = 1/\Omega_0 \left[\frac{p_i^\alpha p_j^\alpha}{m_\alpha} + \frac{1}{4} \sum_{\beta} (r_j^{\alpha\beta} f_i^{\alpha\beta} + r_i^{\alpha\beta} f_j^{\alpha\beta}) \right] \quad (4)$$

where $(i,j)=(x,y,z)$, m_α and p_α are the mass and the

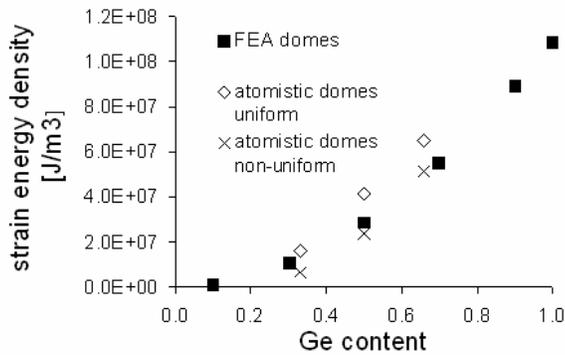
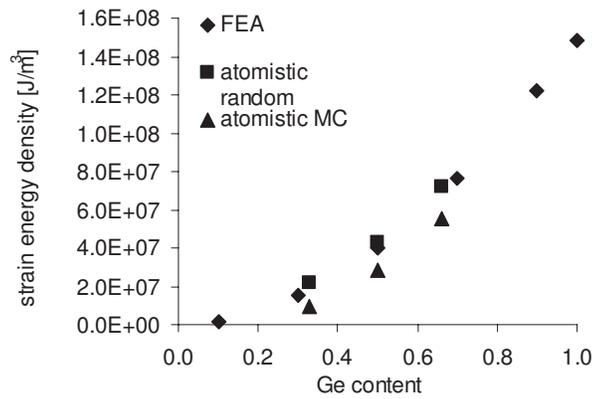


Figure 2: The strain energy density (strain energy/volume) obtained from atomistic calculations and finite element analysis (FEA) for (a) pyramids and (b) domes.

momentum of atom α , $r^{\alpha\beta}$ is the distance from atom α to atom β , $f^{\alpha\beta}$ is the force on atom α due to β , and Ω_0 is the average atomic volume. In this work, molecular statics is used and therefore $p_\alpha=0$. The expression for the stress is then reduced to the sum of the forces between the atoms

multiplied by the distance and divided by the volume. The forces between the atoms are obtained from the molecular static relaxation.

We have calculated the strain energy from atomistic models of pyramid and dome shaped QD at three different average compositions and for a uniform and a non-uniform alloying profile. The non-uniform alloying profiles were obtained using the method outlined above. We have also compared the strain energy calculated from atomistic calculations with finite element calculation for uniformly alloyed QDs. These results are shown in figure 2. We find excellent agreement between the results from finite element calculations and the atomistic calculations for uniformly alloyed QDs. This underlines the validity of our calculations of the strain energy from atomistic models as finite element calculations have been shown previously to be able to treat accurately the strain in QDs [13]. We also find that non-uniform alloying reduced the strain in the QD by between 20 and 50 percent compared to uniformly alloyed QDs. However, this decrease in the strain energy due to non-uniform alloyed is partly due to the surface segregation of Ge which leaves the rest of the QD depleted of Ge and therefore significantly less strained. This effect is expected to be less important in large QDs due to their lower surface to volume ratio.

3.2 The Surface Energy

After the molecular static relaxation the total energy (E_{total}) of the QD system is calculated. The total energy comprises of the formation energy ($E_{formation}$) of the QD system plus the cohesive energy ($E_{cohesive}$). From this the formation energy is obtained by:

$$E_{formation} = E_{total} - (N_{Si} E_{cohesive}^{Si} + N_{Ge} E_{cohesive}^{Ge}) \quad (5)$$

where N_{Si} and N_{Ge} is the number of Si and Ge atoms respectively and $E_{cohesive}^{Si} = -4.63\text{eV}$ and $E_{cohesive}^{Ge} = -3.85\text{eV}$. As shown above, the strain energy in the QD can be calculated independently of the total energy. For the calculation of the surface energy of the system the fact that the approach used here to calculate the total energy also allows the calculation of the energy for each individual atom.

The surface energy is generally defined as the energy increase of a system due to the creation of a surface. Here we consider two terms to contribute to the surface energy (1) the formation energy of atoms on the QD surface i.e. atoms with less than four nearest neighbors (E_{surf-I}) and (2) the effect that the creation of the surface has on fully coordinated atoms given by the formation energy of the atom minus the strain energy ($E_{surf-II}$).

4 ANALYSIS OF THE ENERGETICS

Adding up the surface term and the strain term, the total formation energy of the QD is given by:

$$E_{\text{formation}} = E_{\text{strain}} + E_{\text{surf-I}} + E_{\text{surf-II}} \quad (6)$$

Each of these energy terms has been calculated per atom. It is interesting to compare the magnitude of the strain energy and the surface energy for QDs of different sizes (Figure 3). The ratio of the total surface energy to the total strain energy changes because the surface to volume ratio changes. From this analysis it can be seen that only for very large islands the strain energy dominates. For the island sizes (<50nm) which are generally used as QDs the surface energy far exceeds the strain energy.

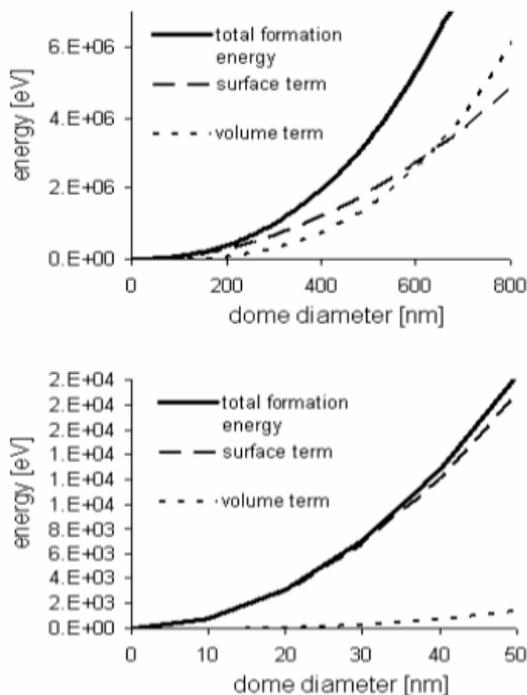


Figure 3: The magnitudes of the surface term, the volume (strain) term and the total formation energy are shown for QDs of different sizes.

This separation of the total formation energy into a bulk term and a surface term can also be useful when analyzing the composition profiles formed after equilibration (e.g. figure 1). It was found that the outer layer of the QDs is extremely Ge rich. The average surface formation energy of a Ge atom on the surface of a uniformly alloyed QD is about 0.5 eV lower than that of a Si atom. On the other hand a Ge atom which is not on the surface but inside the QD contributes to the strain energy and therefore raises the total energy of the QD. It is therefore beneficial for a Ge atom in a uniformly alloyed QD to migrate to the surface. In the non-uniformly alloyed QD the situation has changed. Here the surface formation energies of Si and Ge are found

to be approximately equal and therefore there is no more incentive for more Ge to segregate to the surface. The surface Ge content is however below 100% for QDs with an average Ge content of 50% and 33%. Significantly, the difference between the Ge content inside the QD and on the surface is about 40% for all possible compositions. This is because the strain between the surface layer and inside of the QD builds up with increasing segregation of Ge to the surface. The strain between the surface layer and the rest of the QD therefore limits the surface segregation of Ge.

5 CONCLUSIONS

It was shown that it is possible to model an equilibrium composition profile in agreement with experimental results. A method to analyze the energetics of the alloyed QD by splitting the energy into a term scaling with the surface area and another term scaling with the volume was presented and the analysis revealed the importance of the surface term for the formation energy of the QD. Any model for the non-uniform alloying profile therefore has to take the surface energy term and surface segregation into account.

An energetic model, splitting the formation energy into a surface and a volume term, may also be employed to predict the critical pyramid size for the shape transformation.

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