Alloyed Ge(Si)/Si(001) islands: The composition profile and the shape transformation

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Atomistic simulations combining a Monte Carlo algorithm and molecular static relaxations were carried out to predict the alloying profile in pyramid and dome shaped Ge(Si)/Si(001) islands. The results show that the composition profile is dominated by the surface segregation of Ge and segregation of Si to the substrate island interface. Within the interior of the island the composition profile is found to be uniform. An analysis of the energetics of the alloying shows that at typical growth temperatures, the lowering of the energy achievable through the formation of a nonuniform alloying profile would be too small to overcome the tendency towards randomization driven by the entropy of mixing of the system. The shape transformation from the pyramid to the dome shape is shown to be predicted accurately by the modeling.

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I. 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 three-dimensional islands. Their small size (nm in dimension) leads to quantum confinement of the electrons, resulting in electronic and optical properties which show promise for use as quantum dots in a wide range of devices ranging from semiconductor lasers to quantum computers. These properties of quantum dots are controlled by the islands' size, shape, and composition. The growth of Ge(Si) on Si(001) has been extensively studied,[2] not least 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) islands can be determined from atomic force microscopy[3] and transmission electron microscopy[4] to a high precision, experiments designed to reveal the composition and composition distribution have led to contradictory results. For islands grown at high enough temperatures (above 550 °C) and low enough growth rates (around 1.2 ML/second) so that alloying is not kinetically suppressed, all experimental methods consistently show a significant alloy formation within the islands. Generally, the Si content in the islands is higher than in the material deposited, which suggests diffusion of Si from the substrate into the islands. Experiments[5] and calculations[6,7] also show a highly nonuniform strain field within the islands. There is however a debate in the literature on the effect of this nonuniform strain field on the distribution of Ge and Si within the islands. While some experiments conclude that this nonuniformity in the strain field leads to significant nonuniform alloying[5] as in the case of In(Ga)As/GaAs(001) islands,[8] other results show large volumes of uniformly alloyed material within the islands.[9] Therefore a coherent model of the alloying profile remains elusive.

Previous approaches to modeling islands grown by strained layer epitaxy can be categorized as either atomistic or continuum modeling. Continuum techniques include the calculation of the strain field of islands using isotropic elasticity theory[10–12] and finite element modeling.[5,13–17] Rudd *et al.*[12] have predicted a nanostructure diagram, using continuum modeling of the island formation, which shows the island density, size, and shape as a function of the surface coverage. Liao *et al.*[5] have used finite element modeling to calculate the strain field from finite element analysis and used it to simulate transmission electron micrographs from which they concluded that the alloying profile inside the islands is nonuniform. Atomistic modeling has also been used to predict the strain field of alloyed strained islands in the Ge/Si system[18,19] which was then used to calculate the electronic structure of the islands. Raiteri *et al.*[7] showed that the total energy of an island can be separated into a term scaling with the surface area and another term scaling with the volume using atomistic modeling. Sonnet *et al.*[20,21] have performed Monte Carlo simulations to obtain the composition profile and stress distributions in pyramid shaped islands in the Ge/Si system and, in another study, of the GeSiC sytem.[22,23] Wagner *et al.*[24] have used a very similar technique to the one employed in this work to model the interdiffusion of Ge and Si on planar (001) surfaces.

In this paper we predict the quasiequilibrium model for the alloying profile that minimizes the total energy of an island. The paper is organized as follows. In the next section we briefly describe the computational method used in our study and simulations are carried out at different temperatures to reveal the effect of the growth temperature on the equilibrium alloying profile. In Sec. III, we analyze the composition profiles in more detail by studying the energetics of the alloying. Furthermore a simple energetic model is presented which reveals the driving forces determining the alloying profile. With the help of this model and critical comparison of the results of the atomistic simulations with experimental results from the literature, a model for the alloying profile in Ge(Si)/Si(001) islands is derived and differences between alloying of islands in the Ge/Si system and other technically important materials (e.g., InAs/GaAs) are

highlighted. In Sec. IV, the energetic model derived from the atomistic simulations in Sec. III is used to predict quantitatively the transformation from islands with shallow {105} type facets (pyramids) to islands incorporating steeper facets (domes) as observed experimentally.[4] The paper finishes with a summary in Sec. V.

II. ATOMISTIC MODELING OF ALLOYED ISLANDS

A. Method

We calculate the quasiequilibrium composition profile in Ge_xSi_{1-x} (with x representing the Ge content) islands using atomistic modeling. In our calculation, the island is placed directly onto a Si substrate. This is different from the islands' experimental growth, as it is known that islands form after the formation of a wetting layer. However, by the time interdiffusion between the substrate and the island takes place, the wetting layer below and in the immediate vicinity of the island is not intact anymore. The shape of the island is fixed and based on experimental data. Experiments have shown that in the Ge/Si system there are two distinct shapes that the island can assume, which are well defined in terms of the surface crystallographic planes.[4] These are {105} planes for the pyramid shaped island and {105}, {113}, and {15 3 23} planes for domes. 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. It is found experimentally that islands are coherent up to a diameter of 200 nm.[4] For their use as quantum dots, much smaller islands of about 20 nm diameter are preferred. In this work the size of the islands studied in the atomistic simulations was limited by the computational resources available. Therefore the atomistic models studied here have a diameter between 8–16 nm. We have carried out simulations for different island sizes before[25] and found that both, the strain energy and the composition profile do not strongly depend on the island size. As will be shown, this is not a significant limitation to the study, and ways to extrapolate the results obtained from smaller islands to larger systems are outlined.

In the calculations, a uniform starting composition profile is assumed and subsequently the energy of the system is minimized computationally. The system sizes and timescales involved in the formation of the composition profile are too large to employ classical molecular dynamics or ab-initio modeling, even for the relatively small islands considered here; therefore the approach used is based on a combination of atomistic total energy calculations and a metropolis Monte Carlo process that provides the mechanism for the reorganization of the alloy within the island. The assumption that the starting composition in the island is a homogeneous alloy implies that the modeling either is simulating a system in which the island 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. It is emphasized that the aim in this paper is not to model the formation process of an island but to find the quasiequilibrium alloying profile for an island with a given shape and average composition.

To obtain the quasiequilibrium alloying profile, the energy of the system is minimized by two steps: (i) while maintaining the homogeneous distribution of the island, 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.[26] The interaction between the atoms is described by the Tersoff potential,[27] and periodic boundary conditions are applied to the substrate; (ii) following this relaxation, diffusion of atoms within the island is allowed. Diffusion of atoms into the substrate is not allowed because this would result in the island dissolving and the Ge being dispersed in the Si bulk, forming a dilute alloy. In experimental growth this does not occur because of kinetic limitations (i.e., the diffusion rate in the bulk substrate is considerably lower than in the island). In this modeling, however, different diffusion rates cannot be taken into account and therefore intermixing of the island with the substrate is not allowed. To model the diffusion, one atom is randomly chosen and the atoms surrounding it, within a cut-off radius of 0.48 nm, are identified. One of these surrounding atoms, with a label [i.e., Ge or Si] 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. 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 island. Two temperatures for the Monte Carlo process were chosen (i) 900 K, which is a typical growth temperature for GeSi/Si(001),[28] and (ii) 8 K, which is well below usual growth temperatures. The aim of the simulation carried out at 8 K is to eliminate the effect of the configurational entropy on the final composition profile. More details about the simulation procedure are given elsewhere.[25,28–30]

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 that may lead to experimental results that deviate from the composition profile presented here. However, these deviations from the quasiequilibrium composition profile are expected to be small for sufficiently high growth temperatures and slow growth rates. Also, the surface of the island in this work was assumed to be bulk terminated. For several of the facets on the islands, the correct surface reconstruction is not known, which is why we have decided to assume bulk termination for all our calculations. This will result in an overestimation of the surface energies. The effect of this is discussed in Sec. IV, where we study the effect of the surface reconstruction on the shape transformation from the pyramid to the dome shape.

B. The resulting composition profile

Figure 1 shows the resulting composition profile on a section through the center of the island, for pyramid and dome shaped islands of different compositions at 900 K. General

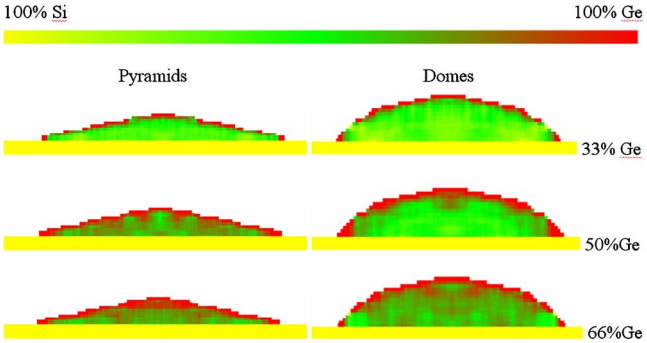

FIG. 1. (Color online) The distribution of Ge and Si in pyramid and dome shaped islands calculated at a temperature of 900 K at a concentration of 33% Ge, 50% Ge, and 66% Ge in the island. The steps on the surface of the islands represent surface steps in the atomistic model.

features of the composition profiles of both the pyramid and the domes can be summarised as follows: (i) segregation of Si takes place into certain areas close to the interface between the island and the substrate. It can be assumed that this is to alleviate strain in these areas; (ii) the surface of the islands is significantly enriched with Ge.

To further investigate the composition profile, the average compositions of shells of one atom layer thickness parallel to the island surface, and of layers of one atom layer thickness parallel to the Si substrate, were determined. For the composition in layers parallel to the Si substrate, the Ge rich island surface was removed before averaging, to reveal the composition inside the island without the influence of the surface segregation.

The analysis of the compositions of the shells parallel to the island surface [Figs. 2(a) and 2(c)] indicates that, in the case of the dome shaped islands, the Ge content in the outer shells is significantly higher than the average Ge content. However, away from the island surface, the composition of the shells is approximately constant. A similar trend is observed for the pyramid shaped islands, except for a slight increase of Ge content with shell number.

The analysis of the Ge composition of the layers parallel to the Si substrate [Figs. 2(b) and 2(d)] shows that for both pyramids and domes, the layers close to the Si substrate are rich in Si whereas the layers further away from the substrate contain an increasing amount of Ge.

To study the effect that the configurational entropy of mixing has on the composition profile, a simulation of a dome shaped island with an average Ge content of 50% was carried out at 8 K. Experimentally, mainly for kinetic reasons, growth is carried out at much higher temperatures. In the algorithm used in this paper, however, diffusion is driven only by energy minimization and does not directly depend on

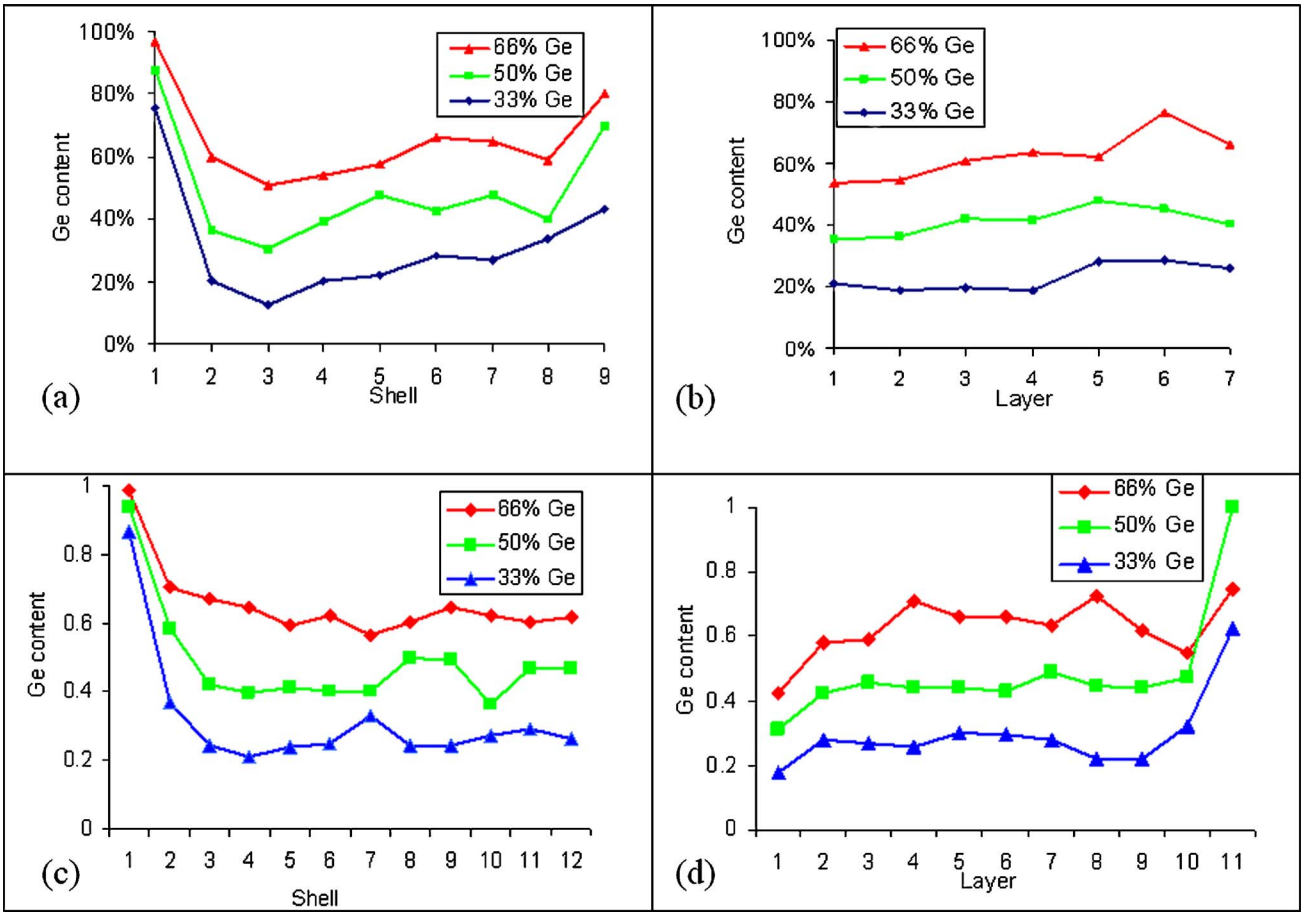

FIG. 2. (Color online) (a) and (c) show the composition in shells parallel to the island surface for pyramids and domes respectively. (b) and (d) show the composition in layers parallel to the substrate–island interface for pyramids and domes, respectively.

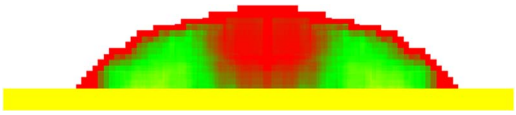

FIG. 3. (Color online) The composition profile on a cutting plane through the center of a dome shaped island with an average Ge content of 50% at a temperature of 8 K.

the temperature. In the Monte Carlo step, however, the temperature determines the probability of accepting higher energy steps, which is related to the entropy of mixing in the experiment, as outlined in Sec. II A. At low temperatures, the influence of the entropy of mixing is very small and the composition profile can be assumed to be driven only by the enthalpy (i.e., strain and surface energy). Therefore, by combining the results of a low temperature simulation and a high temperature simulations the effect of the temperature on the quasi-equilibrium composition profile can be obtained. Figure 3 shows the composition for the island at 8 K. As for the case of the simulation at 900 K, Ge segregates to the surface of the island forming a highly Ge rich surface layer. However, inside the island, the composition profile at 8 K is very different from the high temperature profiles. Whereas for the high temperature case the composition away from the island surface was approximately uniform, the composition profile is found to be highly nonuniform at 8 K. In the center of the island there is a Ge-rich area which extends from the top of the island almost down to the island-substrate interface. Away from the island center, the Si content increases, being highest halfway between the center of the island and the edge of the island. Towards the island surface, the Ge content increases.

III. ANALYSIS OF THE ENERGETICS OF ISLAND FORMATION

To understand the cause of the composition profile found in these simulations, and the large difference between the simulations at 900 K and 8 K, the energetics driving the formation of the composition profile need to be revealed by analyzing the different contributions to the total 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 occurs only 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 caused by the formation of the island. Likewise, any shape transition from an island with smaller to larger surface area occurs only when the increase in the surface energy due to the shape change is outweighed by a decrease in the strain energy. It is therefore useful to separate the total energy it takes to form an island (formation energy) into two terms: one that scales with the surface area of the island (surface energy) and another that scales with the volume (strain energy).

A. The surface energy

After the molecular static relaxation, the total energy (E_{total}) of the island system is calculated. The total energy comprises the formation energy ($E_{formation}$) of the island system plus the cohesive energy ($E_{cohesive}$) of pure Si and Ge. From this the formation energy is

$$E_{formation} = E_{total} - (N_{Si}E_{cohesive}^{Si} + N_{Ge}E_{cohesive}^{Ge}), \quad (1)$$

where N_{Si} and N_{Ge} are the number of Si and Ge atoms respectively and $E_{cohesive}^{Si}$ and $E_{cohesive}^{Si}$ are the energies of a Si atom and a Ge atom respectively in an unstrained bulk slab ($E_{cohesive}^{Si}$=−4.63 eV and $E_{cohesive}^{Ge}$=−3.85 eV).

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 contributing to the surface energy (1) the formation energy of atoms on the island surface (i.e., atoms with less than four nearest neighbors) ($E_{surf\text{-}I}$) 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 ($E_{surf\text{-}II}=E_{formation}-E_{strain}$). The total formation energy of the island is the sum of the surface and the strain energy (volume term):

$$E_{formation} = E_{strain} + E_{surf\text{-}I} + E_{surf\text{-}II}. \quad (2)$$

B. The strain energy—link to continuum simulations

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

$$E_{strain} = \tfrac{1}{2} * \sigma_{ij} * \varepsilon_{ij}. \quad (3)$$

Pryor *et al.*[31] have shown that a quantity related to the strain tensor in the surroundings of a four-fold coordinated atom can be calculated from the atomistic model using the following equation:

$$\varepsilon'_{ij} = R_{ij} * R_{ij}^{0-1} - I, \quad (4)$$

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

$$\varepsilon_{ij} = \frac{\varepsilon'_{ij} + \varepsilon'_{ji}}{2}.$$

The stress tensor σ_{ij} in the vicinity of an atom α is given by[32]

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

where $(i,j)=(x,y,z)$, m_α and p_α are the mass and the momentum respectively 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 atom β, and Ω_0 is the average atomic volume. In this work, molecular statics is used and therefore p_α=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.

Using these equations, we have calculated the strain energy from the atomistic models for both pyramid and dome

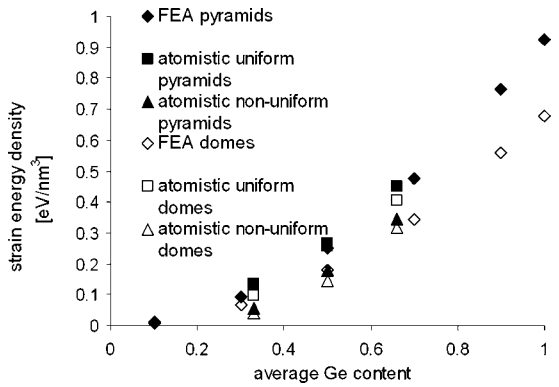

FIG. 4. The strain energy density for a range of compositions calculated for pyramids and domes, using finite element analysis (FEA), and from the atomistic models with uniform and nonuniform composition profiles (before and after compositional equilibration).

shaped island for three different average compositions, and before and after compositional equilibration (i.e., uniform and nonuniform composition profile). In the calculations before compositional equilibration (uniform composition profile), the island model was relaxed using a conjugate gradient type relaxation. Figure 4 shows that nonuniform alloying reduced the strain in the island by between 20 and 50 percent compared to uniformly alloyed islands for simulations at 900 K. This decrease in the strain energy due to nonuniform alloying is partly due to the surface segregation of Ge which leaves the rest of the island depleted of Ge and therefore significantly less strained. This effect is expected to be less important in large islands due to their lower surface to volume ratio.

In the literature, finite element analysis has been shown to be an accurate way to treat the strain field of the islands.[5] To test the validity of our atomistic modeling, in addition to calculating the strain field directly from the atomistic models, we have also used finite element analysis to calculate the strain of the islands. The resulting strain energy from the finite element calculations is compared to the strain energy from the atomistic calculations (before and after compositional equilibration) in Fig. 4. We find excellent agreement between the results from finite element calculations and the atomistic calculations.

C. Energetics of the alloying profile

An analysis of the surface and the volume energy terms, as outlined in the previous sections, can be used to understand the main features of the composition distributions observed in domes and pyramids. The energies calculated are shown in Table I and their effect on the composition profile is analyzed in more detail below.

1. Ge enrichment on the surface

The analysis of the formation energy of a Ge and a Si atom on the surface of a uniformly alloyed island before the Monte Carlo process ($E_{surf\text{-}I}$ in Table I) reveals that the surface energy of a Ge atom is about 0.5 eV lower than that of a Si atom. Away from the surface, a Ge atom would contribute to the strain between the island and the substrate. It is therefore energetically beneficial for a Ge atom to exchange places with any Si atom that is at the surface. This leads to Ge enrichment of the island surface during the Monte-Carlo process, and explains why, after the equilibrium composition distribution is reached, the Ge content of the surface of the islands is much greater than the average composition (see Table I). After the equilibrium composition is reached, Table I shows that the formation energies of Ge and Si atoms on the surface are equal to within 0.04 eV for the islands. Consequently, there is then no incentive for more Ge to segregate to the surface. The reason for this is that while Ge segregating to the surface reduces the surface energy, it also causes a buildup of strain between the surface layer and the rest of the island and therefore results in an increase of the strain energy of the system. This buildup of strain prevents the surface

TABLE I. The values for the different terms of the total formation energy calculated from the atomistic simulations before and after compositional equilibration.

	Pyramid			Dome		
Average Ge content	33%	50%	66%	33%	50%	66%
			Before compositional equilibration			
$E^{Ge}_{surf\text{-}I}$ [eV]	1.31	1.42	1.45	1.11	1.19	1.23
$E^{Si}_{surf\text{-}I}$[eV]	1.86	1.90	1.97	1.59	1.60	1.69
$E_{surf\text{-}II}$[eV]	−0.06	−0.08	−0.12	−0.03	−0.07	−0.1
E_{strain} [eV]	0.0028	0.0057	0.0095	0.0021	0.0054	0.0086
			After compositional equilibration			
x_{surf}	61%	76%	90%	63%	80%	89%
x_{bulk}	20%	37%	55%	24%	41%	60%
$E^{Ge}_{surf\text{-}I}$ [eV]	1.50	1.48	1.49	1.29	1.24	1.26
$E^{Si}_{surf\text{-}I}$[eV]	1.53	1.50	1.41	1.27	1.28	1.29
$E_{surf\text{-}II}$[eV]	0.1	0.05	0.05	−0.05	0.05	−0.07
E_{strain} [eV]	0.0012	0.0038	0.0073	0.0009	0.0031	0.0067

composition reaching 100% in small islands. In fact Table I shows that, independently of the island shape, a difference of Ge of more than 40% between the surface and the bulk of the island is not favorable. An *ab initio* treatment the strain dependence of the surface energy in pyramid shaped islands by Shklyaev *et al.*[33] shows the importance of the relationship between strain and surface energy for the balance between the different energy terms controlling island formation.

2. Si segregation to the bottom of the island

Figures 2(b) and 2(d) indicate that, near the bottom of the islands, the Si content of the layers parallel to the substrate is higher than the average Si content in the island. The increased Si content near the bottom of the islands is expected, since this allows for a graded composition profile from the pure Si substrate to the alloyed island. In experimental studies, the graded composition profile may be even more pronounced and would be expected to reach down into the substrate due to intermixing of the materials in the island and the substrate. However, especially for the simulation at low temperature, there is a significant variation of the composition even within one layer, as can be seen from Fig. 3. The highest Si content in the island is found in a region about half way between the island edge and the island center. From this region towards the center and the island surface the Si content decreases. This finding for the simulation carried out at 8 K agrees with experimental finding of strain driven island growth in other materials system like InAs/GaAs,[34] and is discussed in Sec. III.

3. The composition profile in the island center

Away from the island-substrate interface and the island surface, the composition distribution is found to be approximately uniform in the case of the simulations at 900 K. This indicates that the composition distribution in the center does not follow the strain energy distribution, as the strain energy distribution is known to be highly nonuniform.[5] However, in the case of the low temperature simulation the composition distribution is non-uniform throughout the island. The difference in the composition profile in the high temperature case and the low temperature case can be understood by considering the probability of accepting an MC step that leads to a higher energy of the system. The probability P of accepting such a step depends on the difference in the energies of the current configuration (E_{old}) and the energy of the proposed configuration (E_{new}) and on the temperature T:

$$P = \exp\left(-\frac{E_{new} - E_{old}}{kT}\right),$$

with k being the Boltzmann constant. The acceptance of higher energy steps in the MC simulations with a certain probability corresponds to the configuration entropy of mixing in experiments[24] which can be interpreted in our case as a driving force towards uniform (random) alloying. The average strain energy per atom for a uniformly alloyed dome shaped island with 66% Ge content is 0.0086 eV (Table I). If this value is assumed to be the upper limit for the energy difference between an unfavorable (higher energy) MC step,

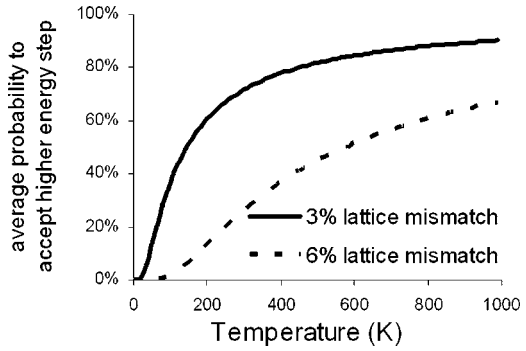

FIG. 5. The average probability to accept an unfavorable step if the energy difference equals the average strain energy is shown as a function of temperature for two different lattice mismatches.

then Fig. 5 (solid line) shows the probability of accepting such a higher energy step as a function of temperature. At 900 K the probability of accepting such a higher energy step in the MC simulation is around 90%, whereas at the low temperature the probability of accepting a higher energy step is close to zero. The situation changes, when the strain energy goes up. The dotted line in Fig. 5 shows the case for a lattice mismatch of 6%, assuming that the strain energy scales with the square of the lattice mismatch. In this case the probability is only between 50% and 65% for growth temperatures between 600 K and 900 K. Therefore, at higher mismatches, the likelihood of the formation of a nonuniform composition profile is considerably higher.

The composition profile found in InGaAs/GaAs islands, described by Liu *et al.*[35] as an "inverted pyramid" and by Migliorato *et al.*[8] as a "trumpet shaped" composition profile, is very similar to the one found here in the low temperature simulations. The average mismatch in the InGaAs system is on the order of 6%, depending on concentration of Ga in island. This mismatch corresponds to the curve for the larger mismatch in Fig. 5. The significantly lower probability of accepting higher energy steps at 6% mismatch may be the reason why the trumpet shaped composition profile is found in InGaAs/GaAs islands but not in GeSi/Si islands. A very detailed systematic study of the composition profile of GeSi/Si(001) islands has been carried out by Smith *et al.*[9] using energy dispersive x-ray spectroscopy and electron energy-loss spectroscopy. They found that, for a range of growth temperatures, while there is significant Si diffusion into the islands, the composition varies only close the substrate–island interface. Away from the substrate–island interface it remains approximately constant. In the technique used by Smith *et al.* to study the composition profile, one would not expect to detect the high Ge concentration at the surface of the islands, as the islands are viewed side-on and the composition measured is an average through the diameter of the island. The uniform alloying found in the island center resembles the composition profile that was found in this work for the simulations at 900 K. Malachias *et al.*[36] used grazing incidence anomalous x-ray scattering data to obtain three-dimensional maps of the composition profile. In their study, they found a significantly higher Ge concentration near the island surface than inside the island. Our findings

are in good agreement with these results. There is however a significant body of literature predicting a highly nonuniform alloying profile inside the islands.[5] These results are mainly based on the comparison of plan-view transmission electron micrographs with image simulations. However, the composition in these measurements is not measured directly but inferred from the strain field in the island. As the results in this paper show, a nonuniform strain field may not be enough to drive a nonuniform alloying profile in the case of GeSi/Si(001) islands. We therefore suggest that experiments which do not clearly separate between strain and composition should not be used for the measurement of the composition profile in these systems.

IV. THE SHAPE TRANSFORMATION

It is found experimentally[4] that there is a critical size of island below which the domes exist, and above which the pyramids exist. The energetic model derived from the atomistic simulations above can be used to predict this critical size as a function of island composition.

For the purpose of calculating the critical size for the shape transformation, the faceted dome shape is approximated here by a spherical cap shape. The critical volume V_c, where the energies per atom of pyramid and dome shape are equal, is then given by

$$V_c = \frac{E_{surf}^{dome} * A_{dome} - E_{surf}^{pyramid} * A_{pyramid}}{E_{strain}^{pyramid} - E_{strain}^{dome}},$$

where E_{surf}^{dome} and $E_{surf}^{pyramid}$ denote the surface energies dome and pyramid, E_{strain}^{dome} and $E_{strain}^{pyramid}$ the strain energy per unit volume for the dome/pyramid, and $A_{pyramid}$ and A_{dome} the additional surface area of the dome/pyramid when compared to a planar surface. The critical pyramid side length $a_P^{critical}$ (which is the parameter that is accessible to experimental measurements) is

$$a_P^{critical} = \frac{30 * (F * E_{surf}^{dome} - 0.0198 * E_{surf}^{pyramid})}{E_{strain}^{pyramid} - E_{strain}^{dome}},$$

$$\text{with } F = \frac{1}{5}\sqrt[3]{\frac{5\pi}{(3d^2+1)^2}}, \quad (5)$$

and $1/d$ is the height to width ratio of the dome shape. The height to width ratio of the pyramid shape is 1/10 ({105} type facets are assumed).[4] Both the strain and the surface energy depend on the composition of the island. A set of polynomials was chosen to fit the data obtained from the atomistic simulations (cf. Table I) in units of eV/atom.

$$E_{strain}^{pyramid} = 0.022 * x_{bulk}^{\ 2},$$

$$E_{strain}^{dome} = 0.019 * x_{bulk}^{\ 2},$$

$$E_{surface}^{pyramid} = -0.517 * x_{surface} + 1.928,$$

$$E_{surface}^{dome} = -0.307 * x_{surface} + 1.547. \quad (6)$$

A further polynomial was chosen to fit the dependence of the surface composition on the bulk composition shown in Table I,

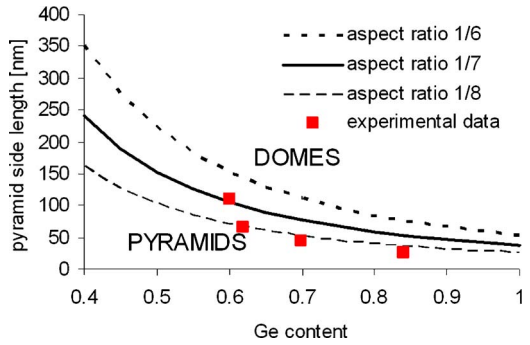

FIG. 6. (Color online) The critical pyramid side length for different aspect ratios of the dome shape and a comparison with experimental data (Ref. 39 and 40).

$$x_{surface} = 0.889 * x_{bulk}^{\ 4} - 2.191 * x_{bulk}^{\ 3} + 1.073 * x_{bulk}^{\ 2} + 0.812 * x_{bulk} + 0.413. \quad (7)$$

Combining Eqs. (5)–(7) the critical pyramid side length can be calculated. The results are shown in Fig. 6. It is seen that the critical pyramid size is strongly dependent on the aspect ratio assumed for the dome shape. We note (i) that there is excellent agreement with the experimental values; (ii) the trend of decreasing critical size with increasing Ge content is reproduced well. Higher quantitative accuracy could be achieved by taking into account effects of the surface reconstruction on the island energy, but the corresponding surface energies are not known. An estimate for the uncertainty introduced by the effect of the surface reconstruction can be obtained by taking values for the surface energy as calculated by Stekolnikov *et al.*[37] for the {001} type surface. The result is shown in Fig. 7.

The shape transformation from pyramids to domes can be understood qualitatively when one considers that islands containing only shallow facets (i.e., the pyramids) relieve the strain energy less efficiently than islands with steeper facets (i.e., domes). This is illustrated in Fig. 4. However, the surface added to a planar layer by the creation of an island with shallow facets is less than the surface added to an island with steeper facets. Therefore, for small islands with a larger sur-

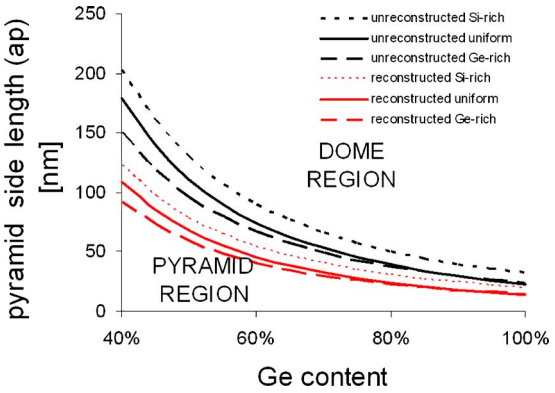

FIG. 7. (Color online) The dependence of the critical pyramid size on the surface composition and the surface reconstruction [values for the {001} surface from Stekolnikov *et al.* (Ref. 37)].

face to volume ratio, shallow facets are preferred, and for larger islands steeper facets, which relieve the strain more effectively, occur.

An important effect for the use of Ge/Si islands as quantum dots is the reverse shape transformation from the dome shape to the pyramid shape. Figure 7 shows that the critical pyramid side length for an island having a Si-covered surface is about 30% larger than for an island with a Ge-rich surface. This is due to the different surface energies of Si and Ge. Therefore, an island that grows originally with a Ge-rich surface and a composition profile as described above may initially transform from the pyramid shape to the dome shape. However, unless its volume is significantly larger than the critical volume it will transform back into a pyramid when it is capped by Si. This has been observed experimentally[38] when Si is deposited on the islands to cap them and agrees with the fact that capped islands usually have much shallower facets than uncapped islands.

V. SUMMARY

The alloying of Ge(Si)/Si(001) islands of different shapes has been treated by atomistic simulations and the resulting energetics analyzed. The composition profiles evolving during the atomistic simulations were shown to agree with experimental measurements. Significantly, different alloying behavior was observed near the interfaces and surfaces and inside the islands. While the alloying near the surfaces and interfaces was found to be highly nonuniform, with Ge segregating to the surface and Si segregating to the region close to the substrate–island interface, there is a significant volume inside the island where the alloy composition is constant. This result is unexpected, because the alloy composition has generally been assumed to follow the highly nonuniform strain field within the island. However, a calculation of the strain energies in the islands has revealed that, at the growth temperature the strain energy per atom is significantly lower than the thermal energy, and therefore the alloying within the intern of the island is random and uniform for entropic reasons.

Based on a simple energetic model that separates the total formation energy of the island into a surface and a volume part, the critical size for an island bound by {105} type facets has been calculated, and the shape transformation from pyramids to domes has been predicted as a function of the average island composition. The predicted critical size for this was found to be in excellent agreement with the experimental data. It was shown that the surface composition is crucial in determining the point of the shape transformation. It was also shown that for energetic reasons a spontaneous change in the surface composition induced by e.g., capping of an island with Si, will result in a reverse shape transformation of domes to pyramids, which explains the fact that in capped samples generally only pyramid shaped islands are observed.

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