



Thermodynamic control of germanium quantum dot growth on silicon

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Abstract

Strained epitaxial growth of Ge on Si(001) produces self-assembled, nanometer scale islands, or quantum dots. We study this growth by atomistic simulation, computing the energy of island structures to determine when and how islanding occurs. The distribution of island sizes on a surface is determined by the relation of island energy to size. Applying the calculated energy per atom to the Boltzmann–Gibbs distribution, we predict size distributions as functions of coverage and temperature. The peak populations around 86,000 atoms (35 nm wide) compare favorably with experiment. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Heteroepitaxy of germanium on silicon is an important technology in microelectronic fabrication. Under certain conditions, the Ge self-assembles into fields of small islands [1]. These islands are on the order of 30 nm wide [2], producing quantum confinement of electrons and leading to the name “quantum dots”. Such structures have

unique electronic properties and can be made into novel lasers and photodetectors [3].

During epitaxial growth, as Ge is deposited onto a Si substrate, the adatoms attempt to conform to the underlying Si lattice. A two-dimensional film forms over the surface but the 4.2% lattice mismatch between Ge and Si leads to strain. Once 3–4 monolayers (ML) of Ge are deposited [4], the growth switches to three-dimensional coherent islands that partially relieve the strain. Scanning tunneling microscopy studies have revealed that during the early stages of growth these islands are pyramids with {105} facets [4].

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We have previously shown by atomistic simulation that island formation can be explained by energetics— islands grow when, beyond a critical thickness, the energy to form an island is less than the energy to form another flat epilayer [5], as illustrated in Fig. 1. We now investigate whether there exists a minimum-energy island size. The answer determines how islands ripen with time. The energy of an island is related to its volume, surface area, and edge length. If the volume component of relaxation dominates, then the energy per atom of an island will generally decrease with size. This leads to Ostwald ripening— islands can always decrease their energy per atom by coalescing. The other possibility is that Ostwald ripening does not occur—a decrease in surface energy upon islanding produces minimum-energy islands at some ideal size.

This question is related to the issue of whether island formation is limited kinetically or thermodynamically. The key is the difference in behavior of the two mechanisms with respect to temperature [6]. For a kinetic growth mechanism, higher temperature should increase diffusion lengths and therefore produce large islands that grow far apart. Smaller islands would exchange atoms with the larger ones and eventually evaporate. Conversely, a thermodynamic mechanism will produce smaller islands at high temperature. If the change in surface energy upon island formation is negative, then the energy per atom will have a minimum value versus size and the lowest energy state for an array of islands will be a uniform ensemble at this size. At higher temperatures, however, entropy favors smaller islands since there are

more possible arrangements of the atoms into small islands than large ones.

The existence of a minimum-energy size is detected by growing Ge islands and then annealing— holding the samples at a constant temperature for a number of minutes. Many researchers have found a narrow size distribution for self-assembled Ge. For example, Liu et al. studied Ge islands on Si(001) by atomic force microscopy (AFM) [2]. They found a peak island volume around 2000 nm^3 (corresponding to a base width of 40 nm) after annealing at 825 K and concluded that the distribution matched models of thermodynamic rather than kinetic limitation. Kamins et al. also measured island size distributions by AFM and found stable configurations of roughly 2000 nm^3 pyramidal islands at $600 \text{ }^\circ\text{C}$ [7]. These results imply that the islands do have a minimum in energy per atom versus size. We now proceed to locate this minimum by atomistic simulation.

2. Methods

The simulation for these studies begins with a Si substrate 96 ML thick. The substrate spans 80 unit cells along the horizontal axes (where the Si unit cell length a_0 is 5.43 Å) with periodic boundaries at the edges. All of the atoms within this substrate are free to move during simulation and are anchored to two layers of immobile Si on the bottom face. This region of mobile substrate atoms is vital for allowing elastic interaction of the island with the substrate and with neighboring islands. The thickness of 96 ML was chosen by varying the thickness and finding that the island energy calculation converged beyond 64 ML. The substrate is covered by a 3 ML Ge wetting layer with (2×8) surface reconstruction giving an initial system size of 1,265,600 mobile atoms.

We create model Ge islands as shown in Fig. 2 to reproduce those seen experimentally [8]. The islands are square-based pyramids with $\{105\}$ facets. Fig. 3 shows how the atoms on these facets are paired into dimers according to the rebonded step model [9]. We calculate the energy of these structures with the Tersoff interatomic potential

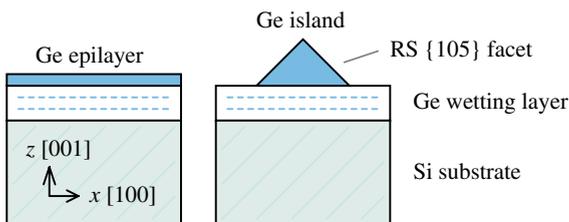


Fig. 1. Cross-section of surface structures. A Ge island grows atop a 3 ML Ge wetting layer since the energy of the island is less than the energy of another flat epilayer.

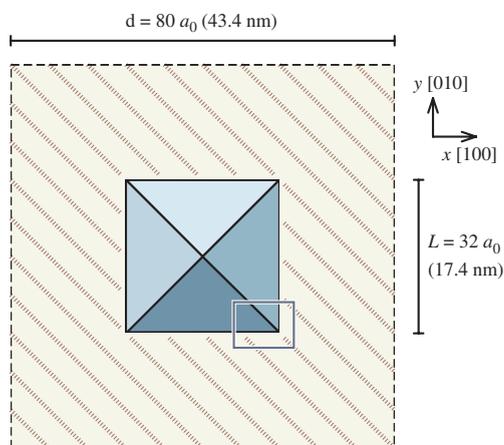


Fig. 2. Plan view of island structure with periodic boundaries along the x and y axes. The island base width is labeled L and the substrate width (equivalent to island spacing) is labeled d . Diagonal lines indicate missing dimers of the Ge (2×8) wetting layer reconstruction. Atomic structure of the highlighted area is detailed in Fig. 3.

[10]. The accuracy of this potential for modeling structure, elastic properties, and defect energies is reviewed elsewhere [11,12]. We note that the accuracy of this potential for calculating surface energies is important; data for validation is limited, but Raiteri et al. did compare energies of the rebonded step and paired dimer models of the $\{105\}$ facet. They found a change in surface energy of $4.5 \text{ meV}/\text{\AA}^2$ with the Tersoff potential, in good agreement with a value of $4.3 \text{ meV}/\text{\AA}^2$ from density functional theory [9].

Initially, atoms are set on a Si lattice and the positions of dimerized neighbors are adjusted to put them within bonding range of each other. Bond energies and forces are computed with the interatomic potential and the total crystal energy is tallied. The atom positions are then relaxed by conjugate gradient minimization [13], continuing until the net force on each atom falls below $10^{-4} \text{ eV}/\text{\AA}$. As a point of reference, each such energy minimization took 60 h of computation on a 1.0 GHz personal computer processor.

The energy per atom of an island, ε_{isl} , is calculated by comparing the minimized energy of a system with that island, E_{total} , to one without, E_{ref} . Then

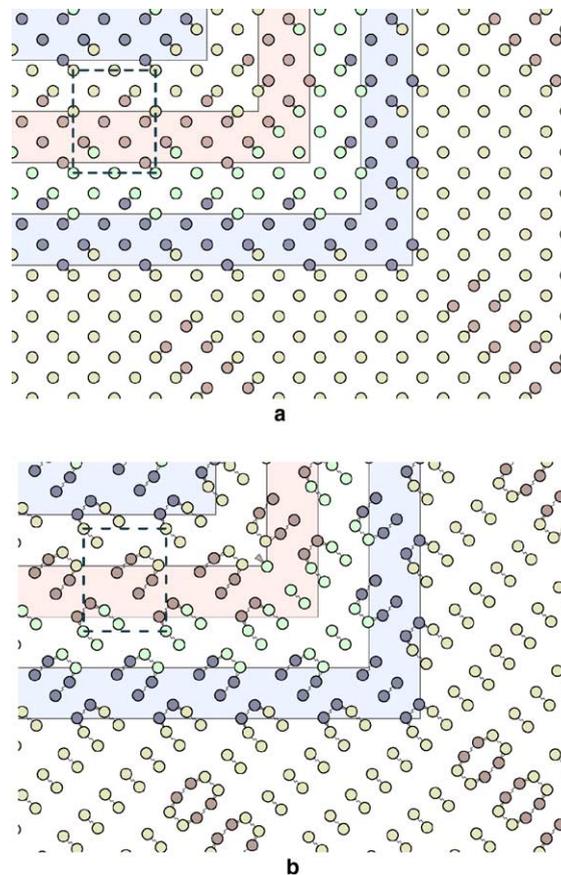


Fig. 3. Atomic structure of pyramidal Ge islands on a Ge (2×8) wetting layer. (a) Initial placement of atoms to construct island. (b) Positions after forming surface dimers, removing unpaired atoms, and relaxing stress by energy minimization. Light lines indicate step edges. Dashed rectangles mark the 2×2.5 unit mesh of the $\{105\}$ surface.

$$\varepsilon_{\text{isl}} = \frac{E_{\text{total}} - E_{\text{ref}}}{N} - \varepsilon_{\text{Ge}}, \quad (1)$$

where N is the number of atoms in the island and ε_{Ge} is the cohesive energy of bulk Ge ($-3.8506 \text{ eV}/\text{atom}$).

We presume that the wetting layer and islands are composed of pure Ge and that the substrate remains pure Si. In reality, deposited Ge may mix with the Si at growth temperatures. Experiments have found an alloy composition of $\text{Si}_{0.1}\text{Ge}_{0.9}$ for the second monolayer at 950 K [14]. We have previously modeled this intermixing and estimated that the third and fourth monolayers contain less

than 1% Si [5]. If we suppose that most of the material for islands comes from the top (third and fourth) monolayers and that the buried Si is relatively immobile, then pure Ge is a good approximation for the island composition. Alloying in the wetting layer should have only a weak influence on elastic interactions compared to the much thicker region of pure Si in the substrate. We are focused here on deposition of pure Ge, but of course if the deposited material itself were an alloy then segregation of the two components could have an important effect upon the island structure and growth energetics.

3. Energy of islands

Two important structures form the basis for comparing energies. The first is bulk Ge, defined here as 0 meV/atom. The second is biaxially strained Ge (material that is compressed to the Si lattice constant laterally and allowed to relax vertically) with a potential of +36.6 meV/atom. Any structure that has a potential higher than biaxially strained Ge will be energetically unfavorable relative to planar growth.

The energy per atom is plotted in Fig. 4(a) for a series of island base widths L and corresponding numbers of atoms, N . Germanium atoms within the volume of an island are able to relax more toward their bulk lattice constant than in a flat film, thus reducing the strain energy. However, the formation of an island creates edges between facets, thus incurring an energetic penalty. All but the smallest of these islands are energetically favorable with respect to flat, biaxially strained Ge at +36.6 meV/atom.

Each island on the surface induces a strain field in the substrate. If islands are closely spaced, then these strain fields will lead to elastic repulsion. This repulsion between islands is expected to mimic a dipole–dipole interaction, decaying inversely with the cube of the separation [15]. We examine this effect of island spacing by varying the substrate width d (equivalent to the island spacing) from $24a_0$ to $144a_0$. Fig. 5 reveals that the repulsion decays more rapidly than expected. We fit the energy per atom for each island size with

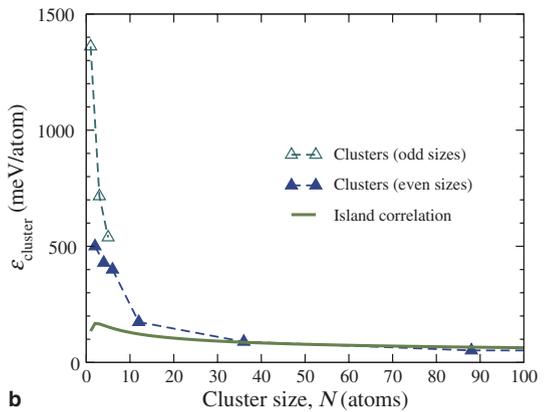
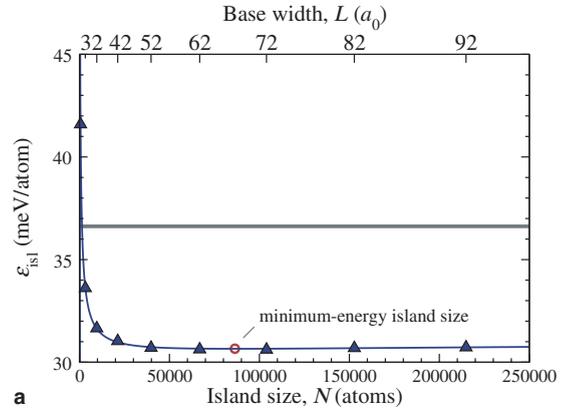


Fig. 4. Dependence of energy per atom on island size atop a 3 ML wetting layer. (a) Pyramidal islands with a minimum-energy size around 86,000 atoms. (b) Energetics of small Ge clusters.

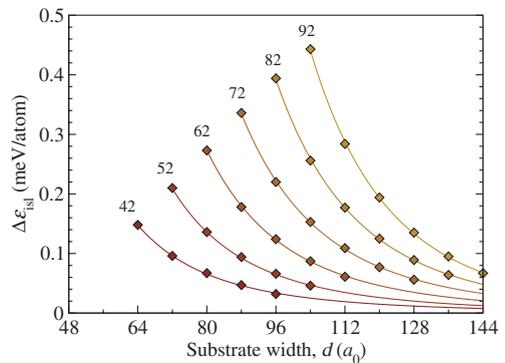


Fig. 5. Dependence of energy per atom on island spacing. For each island base width L (a_0), the energy is measured relative to that island alone on an infinite substrate.

Table 1
Parameters for elastic repulsion between islands

L (a_0)	N (atoms)	$\varepsilon_{\text{isl}}(\infty)$ (meV/atom)	κ (a_0)	γ
32	9609	31.64	34.6	3.66
42	21,258	31.01	43.2	3.65
52	39,797	30.68	52.8	4.07
62	66,820	30.59	62.8	4.38
72	103,941	30.61	69.8	4.72
82	152,750	30.69	80.1	5.17
92	214,849	30.77	90.2	5.76

$$\varepsilon_{\text{isl}}(d) = \varepsilon_{\text{isl}}(\infty) + \left(\frac{\kappa}{d}\right)^\gamma, \quad (2)$$

where $\varepsilon_{\text{isl}}(\infty)$ is the energy per atom at infinite spacing, κ is a repulsion strength parameter, and γ is the exponent of decay. As shown in Table 1, the repulsion strength increases with larger island size and the repulsion decays as rapidly as d^{-6} . The energies in Fig. 4(a) are those determined for infinitely spaced, noninteracting islands by the fit of Eq. (2).

Having found the energy per atom for noninteracting islands, we model its dependence on island size. Shchukin et al. derived an expression relating the formation energy ΔE of an island to its size [16]. We parameterize this expression in the manner of Medeiros-Ribeiro et al. [17]:

$$\Delta E(N) = CN + BN^{2/3} + AN^{1/3} \ln(a_c N^{1/3}), \quad (3)$$

where A is a positive coefficient due to edge energies, a_c is an elastic cutoff parameter, B is the change in surface energy due to island formation, and C is a coefficient of volume elastic relaxation. Dividing Eq. (3) by the number of atoms in the island gives the energy per atom:

$$\varepsilon_{\text{isl}}(N) = C + BN^{-1/3} + AN^{-2/3} \ln(a_c N^{1/3}). \quad (4)$$

Fitting to the energies in Fig. 4(a) yields the parameter values $A = 946.8$ meV/atom, $a_c = 0.770$, $B = -129.7$ meV/atom, and $C = 31.88$ meV/atom. The potential is measured relative to bulk Ge, so C is positive but still less than the potential of biaxially strained Ge. The negative value for B indicates that island formation actually decreases surface energy by 1.2 meV/Å² despite increasing surface area [18]. This supports earlier findings that {105} is a particularly stable facet for strained Ge

[19]. The surface energy term dominates edge and volume effects at moderate sizes, producing a minimum energy per atom at a size of 86,000 atoms.

This relation for energy per atom versus size adequately describes the energetics for islands containing thousands of atoms, but as the number of atoms is reduced to mere dozens the concepts of surface area and edge length become imprecise. Therefore, we separately calculate the energy for smaller clusters. The energetics of these clusters is important since their low total energy (energy per atom multiplied by the number of atoms) makes them accessible at growth temperatures. The clusters are simulated on the same substrate as the pyramidal islands. Dimers are laid into vacant sites of the (2×8) reconstructed surface, with odd-sized clusters formed by removing an atom from a terminal dimer. Larger clusters are modeled by constructing pyramidal islands with base widths reduced to $6a_0$ (88 atoms), $4a_0$ (36 atoms), and $2a_0$ (12 atoms). The resulting energies are plotted in Fig. 4(b). Deviation from the correlation for pyramidal islands is apparent for clusters smaller than thirty atoms.

4. Island size distributions

We now turn our attention to how the energetics of island formation determine the distribution of island sizes. At zero temperature, the deposited Ge material will form the lowest energy structure, an array of islands with a uniform size of 86,000 atoms. However, at growth temperatures, entropy will favor smaller islands with higher energy since there are more possible arrangements of the atoms into various smaller islands than larger uniform ones.

Shchukin et al. investigated the role of entropy in submonolayer heteroepitaxy [6]. They developed a finite-temperature thermodynamic theory of island formation, but the analysis was restricted to monolayer-high islands since calculating the energy of larger islands was not analytically tractable. With the energy relation derived above, we can now adapt their theory to the self-assembly of pyramidal Ge islands.

The areal concentration P of islands of size N is expected to obey the Gibbs–Boltzmann distribution:

$$P(N) = \exp\left(\frac{N[\mu_{\text{ensemble}} - \varepsilon_{\text{isl}}(N)]}{k_{\text{B}}T}\right), \quad (5)$$

where μ_{ensemble} is the chemical potential of the entire array of islands, T is the growth or anneal temperature, and k_{B} is the Boltzmann constant. Eq. (5) is constrained by conservation of mass—the total amount of Ge in all the islands must sum to the amount of Ge coverage, q , beyond the critical thickness so that

$$q = \sum_{N=1}^{\infty} NP(N). \quad (6)$$

We determine the size distribution for a given anneal temperature and coverage by beginning with an estimate for $\varepsilon_{\text{ensemble}}$ equal to the minimum energy per atom, ε_{isl} (86,000). The resulting concentration for each island size is computed from the cluster and island energy relations. Then Eq. (6) is evaluated and compared to the given coverage, adjusting $\varepsilon_{\text{ensemble}}$ to achieve the appropriate value for q .

For coverages between 4 ML and 8 ML of Ge at 500 °C, Fig. 6(a) shows that the island sizes are mostly between 75,000 and 90,000 atoms. Increasing coverage changes the overall number of islands while keeping the relative distribution constant. A few small islands with sizes below 2500 atoms are present; these are adatoms, dimers, and small clusters. The total areal densities of islands at each coverage are $90 \mu\text{m}^{-2}$ at 4 ML, $260 \mu\text{m}^{-2}$ at 6 ML, and $420 \mu\text{m}^{-2}$ at 8 ML. These values agree favorably with the experimental measurement of $210 \mu\text{m}^{-2}$ by Liu et al. for 6 ML of Ge annealed at 550 °C [2].

We also calculate the size distribution for 6 ML of Ge annealed at various temperatures. Fig. 6(b) shows the results for typical growth temperatures of 400 °C and 600 °C. A slight broadening of the distribution and a shift to lower sizes occurs at the higher temperature. Experimentally, Liu et al. measured island size distributions by AFM and found a peak size between 1500 and 2000 nm^3 for annealing at 825 K [2], in good agreement with our simulations.

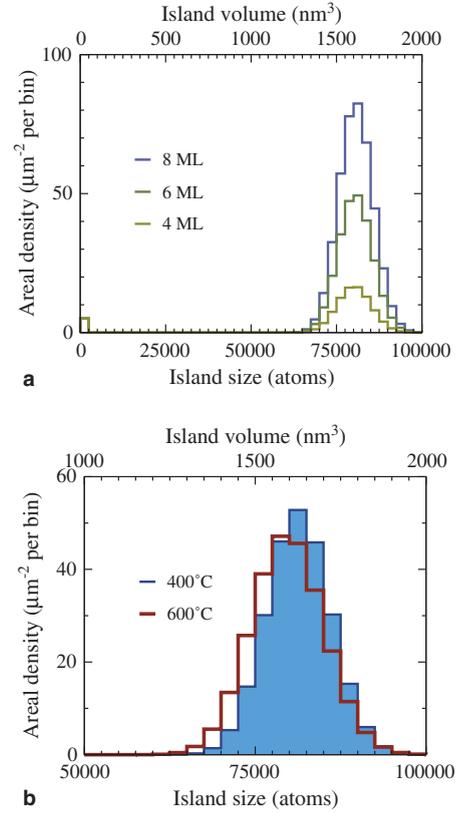


Fig. 6. Effects of coverage and anneal temperature on island size distribution.

The solution of Eq. (5) yields a lower energy per atom for the ensemble at 500 °C as compared to zero temperature. The entropic contribution to the free energy is found to be -0.016 meV/atom for 6 ML coverage at this temperature. The difference is small enough that it does not impact our comparison of islanding to planar growth [5].

Up to this point, we have neglected island–island interactions in predicting size distributions. But as the total density increases, the islands will grow close enough that such interactions become important. At 8 ML coverage, the total density corresponds to an average island spacing of $90a_0$. If coverage were increased further, the interisland spacing would enter the region of strong elastic repulsion as illustrated in Fig. 7. Recalling Eq. (2), the repulsion energy varies with $\frac{E}{d}$ to the power

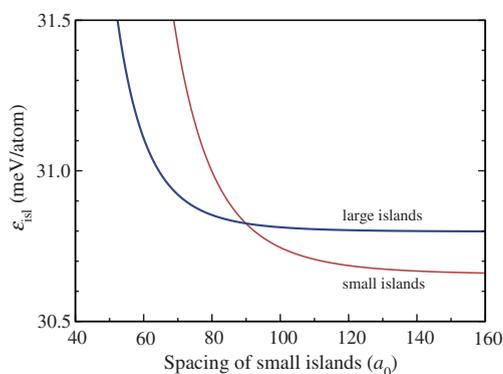


Fig. 7. Effect of spacing on different island sizes. Small islands (86,000 atoms) have the lowest energy at infinite spacing, but upon crowding an equivalent Ge coverage arranged in large islands (344,000 atoms) relieves elastic repulsion more efficiently.

of $\gamma \approx 6$. Such high coverages favor the formation of larger islands since, for a given coverage, the separation d between islands scales as $N^{1/2}$ while the elastic repulsion parameter κ scales as $N^{1/3}$. Then, $\frac{\kappa}{d}$ scales as $N^{-1/6}$ and the repulsion contribution to the energy per atom scales as $\frac{1}{N}$. Thus, larger islands encounter less repulsion and become favorable at higher coverages.

These calculations of island–island interaction are confined to scenarios of identically sized islands in lateral alignment. Due to the computational burden of modeling larger systems with multiple islands, we have not examined more varied arrangements. Such calculations would shed light on the driving force for self-organization of self-assembled islands and are fit for future study. Another interesting extension of this work would be examination of quantum dot superlattices—structures with alternating layers of self-assembled Ge islands and Si buffers. Buried islands should strongly influence the growth of additional islands on the surface by producing strain in the buffer layers.

5. Summary

Based on experimental support for the thermodynamic model of island formation, we have

calculated size distributions for islands at equilibrium. Rising temperatures drive the distributions toward smaller sizes as entropy increases. The effect of coverage is a nearly linear increase in total areal density until island–island repulsion finally drives the distribution toward larger sizes. We applied the effects of entropy and elastic repulsion to predict equilibrium island sizes around 35 nm and a maximum areal density of $420 \mu\text{m}^{-2}$ occurring at 8 ML Ge coverage.

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