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F Uhlík, R Gatti and F Montalenti

L-NESS and Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca,
Via Cozzi 53, I-20125 Milano, Italy

E-mail: francesco.montalenti@unimib.it

Abstract
An efficient computational method for finding the equilibrium concentration profiles which minimize the free energy of intermixed heteroepitaxial islands of assigned shape and average composition is described. A combination of a Monte Carlo method and continuum elasticity theory solved by a finite element method is shown to provide the desired profiles allowing for a significant computational gain with respect to atomistic approaches. The role played by dimensionality (ridges versus islands) and by entropy is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last few years several experimental papers reporting Ge/Si intermixing profiles in heteroepitaxial Ge islands grown on Si(001) substrates by molecular beam epitaxy or chemical vapor deposition appeared in very high impact-factor journals [1–6] (for a review including a discussion of earlier studies, see [7] and references therein). The ability to link the experimental data to actual three-dimensional distributions of Ge and Si atoms within the islands yielded very impressive results. The main driving force for intermixing is clear: while island formation is determined by the attempt to release the strain unavoidably associated with a Ge wetting layer (WL), considerable residual elastic energy remains stored even in the presence of three-dimensional structures, particularly those close to the base of the Ge islands (see, e.g. [8]). Si injection provides a channel for the effective lowering of the lattice mismatch and thus of the stress load. While at low temperatures this process is inhibited or very slow, in the full temperature range explored in the above experiments ($T \gtrsim 500\,°C$) it is known that the kinetics of Ge/Si exchanges at the Si(001) surface is fast [9]. Theoretical estimations of the actual Si versus Ge flux arriving at islands, and of the incorporation rate of Si still require further study.

Elastic-energy minimization, however, is not the only effect which should be considered. Since sufficiently high temperatures are needed for observing Si/Ge intermixing, entropy must also be taken into account (enthalpy of mixing in Si/Ge systems is believed to be rather negligible [10, 4]). This leads to two opposite driving forces. Elastic-energy minimization will drive the system towards a strongly non-uniform Si distribution, as a direct consequence of the strongly non-uniform strain distribution within the island [8], facilitating Si incorporation at the compressed base, while leaving almost pure Ge at the relaxed top. Entropy, on the other hand, pushes the system towards uniform alloying. The most direct computational method for building a theoretical understanding of the interplay of these contributions is given by Monte Carlo (MC) simulations within a semiempirical-potential atomistic approach [11–14]. In the MC simulations, the typical Metropolis move is given by a random exchange of atomic species, acceptance being controlled by the Boltzmann statistical weight. Provided that the potential nicely reproduces the experimental elastic constants, this approach allows one to minimize the free energy of the system. The main problem, however, is that convergence is extremely slow, ruling out the possibility of considering realistically sized islands containing more than $\sim 10^4$ atoms.

In an attempt to speed up the calculation of the concentration profile minimizing the free energy, we have developed a fast, fully self-consistent method based on a combination of Monte Carlo and continuum elasticity theory,

solved by finite element methods (FEM). In [15] the method was described and applied solely to energy minimization; here we provide an extension to finite temperatures, by including entropic effects. It is worth noticing that another group has also very recently introduced an FEM-based method [16] to search for optimal concentration profiles. We believe our treatment to be simpler, also including a more direct treatment of the entropic term. Still, results seem to be fully comparable, so the two methods should be regarded as different alternatives available for fast minimization of the free energy of an island with a given shape and average composition.

2. Methodology

Our method is rather general and can be used for any functional minimization, but here we shall describe it as applied to finding the Ge concentration profile of binary Ge/Si nanoislands that minimizes the elastic energy. Also, later in the paper, minimization of a simple approximate functional for the free energy is discussed.

The profile is represented by linearly interpolated values of Ge molar fractions at vertices of a relatively coarse tetrahedral (triangular in 2D) mesh in the same way as in an FEM with linear shape functions. Typically a much finer mesh is used for solving the elastic problem [15]. We minimize the energy functional with respect to the composition profile (with a constraint of given fixed average Ge fraction) by a special version of the Monte Carlo (MC) method. Any other minimization method that does not need derivatives could be used instead but, due to the large number of unknown variables and to the constraints which must be considered, we have found that common minimization methods using searches are in our case less efficient.

The standard Metropolis Monte Carlo involves an ergodic Markov chain whose stationary distribution ρ is taken to be the Boltzmann distribution [17]. In the simplest form a trial move from state o to state n is selected uniformly at random and accepted with probability $\min(1, \rho_n/\rho_o) = \min(1, \exp(-(E_n - E_o)/(kT)))$, where E is energy, T thermodynamic temperature and k the Boltzmann constant. If the fraction of accepted moves is too low, the method becomes inefficient. An important extension that tries to overcome this limitation is the configuration-bias MC [17], known in many different particular forms as preferential sampling, force-bias MC, smart MC and others. The Markov chain is generated by making trial moves from state o to state n according to probabilities α_{on} and accepting them with probability $\min(1, \alpha_{no}\rho_n/(\alpha_{on}\rho_o))$. The stationarity is guaranteed even for $\alpha_{on} \neq \alpha_{no}$.

The MC procedure can be an efficient way to explore a many-dimensional configurational space. In our case we use it for minimization of a many-dimensional function E by taking the limit $T \rightarrow 0+$ as in the simulated annealing method (SA) [18]. If the temperature is decreased slowly enough, it can be shown that the probability that SA finds the global minimum goes to 1. However, the known lower bounds on the annealing temperature schedule are rather impractical. In our case we always observed the existence of only a single

minimum, allowing us to simply keep $T = 0$ and take only down-hill steps. For more a complicated energy landscape with several local minima one can always revert back to SA.

An essential ingredient of any MC is the generation of trial moves. Here we use a simple exchange of a certain amount of Ge between two vertices satisfying necessary constraints. For the molar fraction x it must always hold that $x \geqslant 0$ and $x \leqslant 1$. Also, as the tetrahedra of the mesh are not all the same, different vertices have different geometrical weights with which they contribute to the overall concentration profile. The weight of a particular vertex can be easily calculated by taking the volume integral of a profile that is zero everywhere except for the given node, where it is equal to 1. We also need to satisfy the constraint of a constant overall average Ge molar fraction. Due to linearity of shape functions, all these constraints can be easily fulfilled and they only limit the possible values of the Ge exchange to some eventually smaller, but single, interval of permissible values. From this interval we could uniformly select a random value (that determines the new values of Ge molar fractions at both vertices chosen for an exchange). This is a possible method, but it would be quite inefficient, especially near the minimum, as most of the trial moves would be rejected for driving the solution away from the minimum. It is beneficial to bias the moves so that more likely accepted moves are generated. By a suitable choice of the bias function α the performance can be increased by orders of magnitude. In our method we find and update a suitable bias function during the simulation. It would be possible to make the whole scheme a valid MC scheme sampling the desired distribution π at any $T > 0$, but, as we only need to minimize our energy functional, we describe a simplified version only. We start with a uniform bias function α for all vertices and update this function by the addition of a suitable kernel function (e.g., a Gaussian) centered at the value achieved in the last step of the Markov chain. The kernel width and the kernel weight (with which it is mixed with the old bias function) should be positive, but otherwise can be rather arbitrary and we use them as empirical tuning parameters. Not to threaten the ergodicity, we keep the kernel width larger than the desired final accuracy of the solution. The bias function remains strictly positive everywhere upon updates and evolves during the simulation to a kernel centered about the value at minimum. As we need to effectively generate samples from α, we approximate it conveniently (and in the spirit of the overall FEM procedure) as a piecewise linear function.

To perform a calculation we now only need to specify the geometry of an island and the overall Ge molar fraction; create a mesh for local molar fractions; prescribe the energy functional and set up its evaluation. The evaluation of E was performed with a commercially available program package COMSOL [19] using its structural mechanics module running in a script mode on a pseudo-terminal under the UNIX programming environment. This was called by our MC program whenever a new value of the energy functional was needed. An example of the concentration profile evolution and convergence is shown in figure 1. From a practical point of view a single energy evaluation by COMSOL for a good quality FEM mesh with a system consisting of an
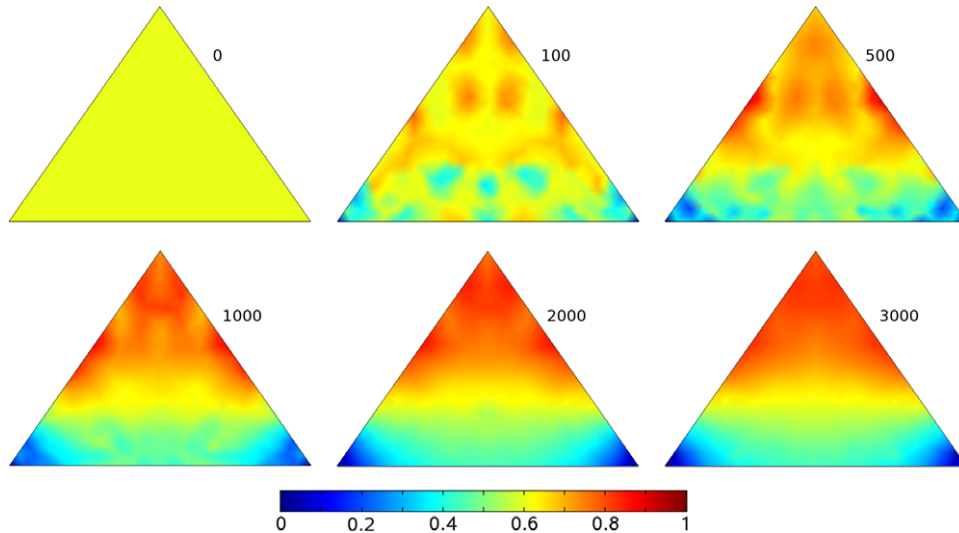
Figure 1. Convergence of the Ge concentration profile during MC minimization for a triangle with aspect ratio of $\sqrt{2}/2$ and 60% of Ge. The MC step corresponding to each configuration is indicated.

island and substrate takes about 15–30 s and, for a satisfactory convergence of the composition profile with mesh points, about 10000 evaluations were needed (starting from the uniform distribution). This performance can be improved. If the island plus substrate geometry has some symmetry, the calculation can be sped up by using only the minimum symmetry non-equivalent part. For a typical case of an island with the shape of a regular pyramid or which is dome-like [20, 21], this immediately gives a factor near to 8 as for the number of mesh points. Further acceleration can be achieved by less accurate evaluation of the energy functional, by using coarser FEM meshes when far from the minimum, or using a previous FEM solution as the initial guess for the calculation of E after an exchange (a relatively small change of the problem). Another problem is the choice of the mesh points for the representation of the concentration profile. This affects not only the accuracy of the solution, but also the efficiency, as it is useless to make the mesh too fine where a coarser mesh would give almost the same results. A possible solution is to build the mesh adaptively. This is shown in the following section together with some basic results for model Ge/Si islands and ridges and considering a simple free energy functional applied to more realistically shaped islands.

3. Applications

The smallest Ge/Si nanoislands grown on the Si(001) substrate usually have shapes of (105) pyramids (height to base aspect ratio: 0.1). At later stages of the growth they undergo a transformation to steeper (0.2 aspect ratio) domes [20–22]. The simplest way to study their compositional profiles is to choose the elastic energy as the functional to be minimized. Since the energy release occurs not only via the bending of island surfaces but also through the substrate deformation (where the magnitude of the effect can be rather small but occurring in a large volume), it is necessary to compute the elastic field both

in the island and in the substrate. In order to account accurately for both contributions, we take the substrate large enough to contain any elastic field modulation and we impose periodic boundary conditions in the lateral directions, a fixed boundary condition at the substrate bottom and leave free all other surfaces. The anisotropic experimental material constants for pure Si and Ge [23] are mixed according to Vegard's law and the initial strain ϵ is taken to be $\epsilon_{ij} = \epsilon_m x(r) \delta_{ij}$, where $x(r)$ is the molar fraction of Ge, $\epsilon_m = 0.0399$ is the lattice mismatch and δ is the Kronecker delta. The comparison of concentration profiles minimizing the total elastic energy for (105) pyramids and infinite (105) ridges (effectively pyramids in 2D) for average Ge content 40, 60 and 80% are shown in figure 2. We show only the (010) cross sections and it is necessary to keep in mind that while in the case of a ridge it immediately shows the whole system, in the case of a pyramid, the information is incomplete. In the case of a pyramid there is also a geometrical factor implying that the higher the cross section, the less of volume is represented. The most relevant feature is that in all cases Ge prefers to stay at the top where it can more easily relieve the strain due to the lattice mismatch. In contrast Si is preferentially located near the bottom edges where the most of the compressive stress is relieved. This general view is compatible with many experimental results including selective etching [5] of Ge and x-ray scattering [4]. For a higher Ge content a whole Ge rich region is obtained than can be fully etched out, revealing the peculiar profiles shown in [24].

In order to obtain a better insight into this behavior, we show the corresponding maps of the elastic-energy density in figure 3 for all the six cases considered. The situation for uniform distribution of Ge for a pyramid and a ridge with 40% of Ge is also shown for a comparison. In the case of pyramids, most of the energy due to the intermixing is relieved at the bottom edges and the tip at a small expanse at the bottom of an island near the center. While for pyramids the tip is fully relaxed, this is not possible for ridges
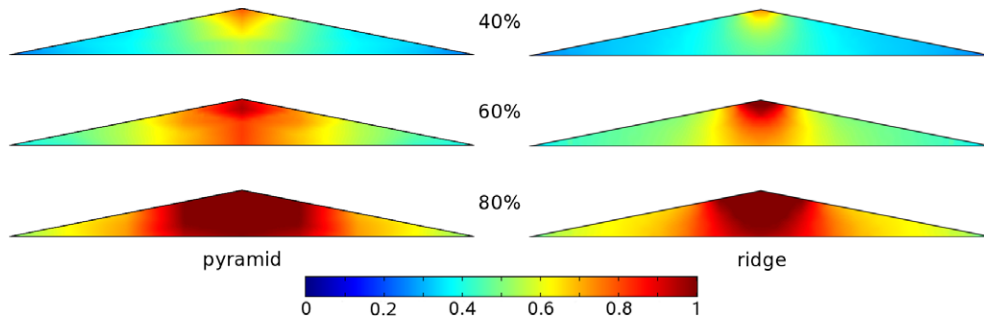
Figure 2. Minimum elastic-energy concentration profiles for (105) pyramids (left column) and ridges (right) with 40, 60 and 80% of Ge.
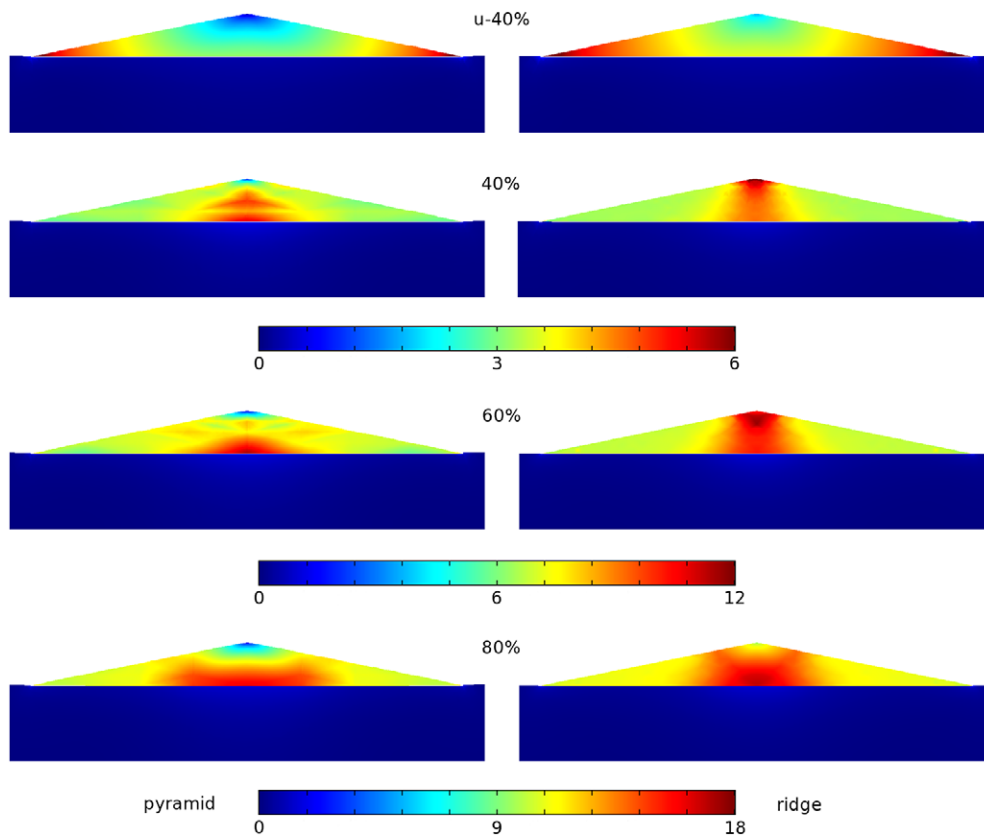

Figure 3. Elastic-energy density in meV/atom for (105) pyramids (left column) and ridges (right). The topmost left and right panels display the simple case, of a uniform distribution, for a 40% Ge concentration. In all the others, the distribution providing elastic-energy minimization is shown, for 40 (two panels below the uniform case), 60 and 80% average Ge content. Clearly, the FEM calculation yields volumetric energy densities. The conversion in energy/atom is however more suitable for possible comparisons with atomistic approaches.

(effectively 2D pyramids) as there is always a constant non-zero stress component along the [010] direction. This effect is enhanced, with respect to the uniform-concentration case, by the accumulation of Ge close to the apex.

In figure 4 we show how the mesh can be automatically iteratively adapted to speed up the calculations by refining the mesh only where it is needed. For simplicity we show a 2D case only. The refinement proceeds in several iterations, starting with an arbitrarily coarse mesh and minimizing the chosen energy functional. The mesh is then incrementally refined where needed so that all elements are eliminated that have an area larger than some predetermined limit (that

controls the minimum required spatial resolution), have too small angle (that removes elements near to being degenerate), or where the solution between the two previous iterations changes by more than the convergence limit imposed on the accuracy of the solution. The mesh adaptation shown in figure 4 is based on the Delaunay triangulation refinement algorithm [25].

As a final example we consider a simple functional for the free energy. We want to minimize the Gibbs free energy $G = H - TS$, where H is the enthalpy and S is the entropy at constant pressure, temperature and total Ge content with respect to the Ge concentration profile. The two main
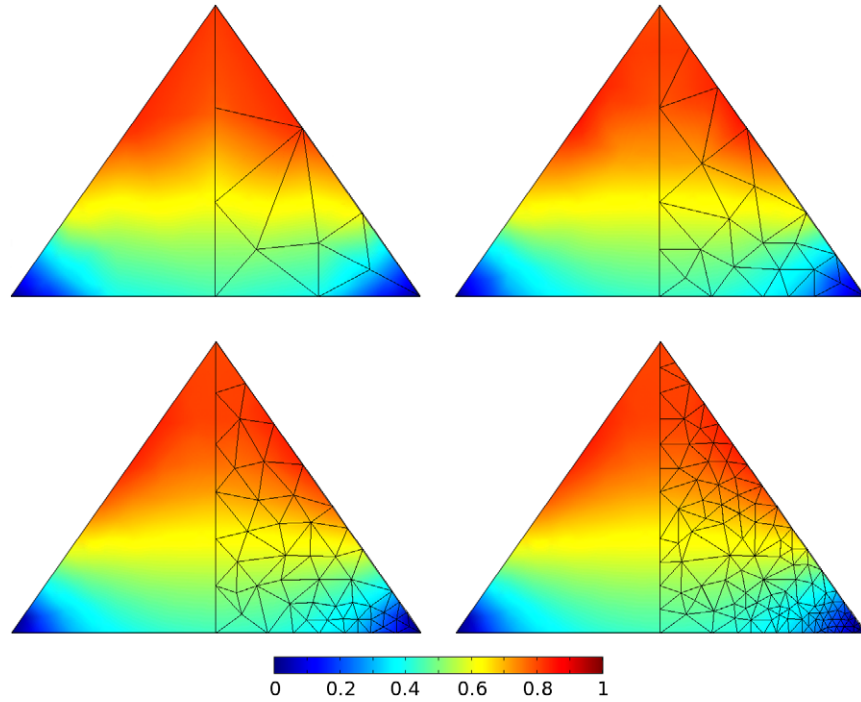
Figure 4. Four steps of mesh adaptation for 2D pyramids with minimum elastic energy and 60% of Ge.

contributions to G are believed [4] to be the elastic energy and the entropy of mixing, hence for the change of G (with respect to a hypothetical standard state of an unstressed solid with separated Si and Ge) we can write

$$\Delta G = \int_{I+S} W(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} + Tk \int_{I} \rho(\boldsymbol{r})(x(\boldsymbol{r}) \log x(\boldsymbol{r}) \\ + (1-x(\boldsymbol{r})) \log(1-x(\boldsymbol{r})))\, \mathrm{d}\boldsymbol{r},$$

where $W(\boldsymbol{r})$ is the elastic-energy density, k is the Boltzmann constant, $\rho(\boldsymbol{r})$ is local density of atoms and $x(\boldsymbol{r})$ is the molar fraction of Ge atoms (the formula is symmetrical with respect to the exchange of atom types). This is the generalization of a simpler formula (used, e.g., in [4]) valid for uniform distribution $x(\boldsymbol{r})$. The results for a dome shaped island with 60% of Ge using the 3D experimental geometry and several different values of temperature are shown in figure 5. For $T \rightarrow +\infty$ the minimum of free energy would go to the maximum entropy distribution that is uniform. For a finite temperature the enthalpic term allows for some compromise. The usual experimental temperature at which intermixed Ge/Si nanoislands are grown is above $500\,^{\circ}$C. The experimentally observed Ge profile is fairly inhomogeneous and resembles our profiles below 100 K [4, 5]. This suggests, that the observed concentration profile is rather far from thermodynamic equilibrium and is the likely result of a competition between kinetic and thermodynamic effects. As pointed out in [4], the entropy of mixing is larger than any other contribution to G, being roughly up to $kT \log 2$ per atom for a 50% Ge island. This is much larger than the elastic-energy contribution, reaching at most a few tens of meV/atom. Although the free energy could be lowered by increased intermixing, these high entropy states are not accessible in
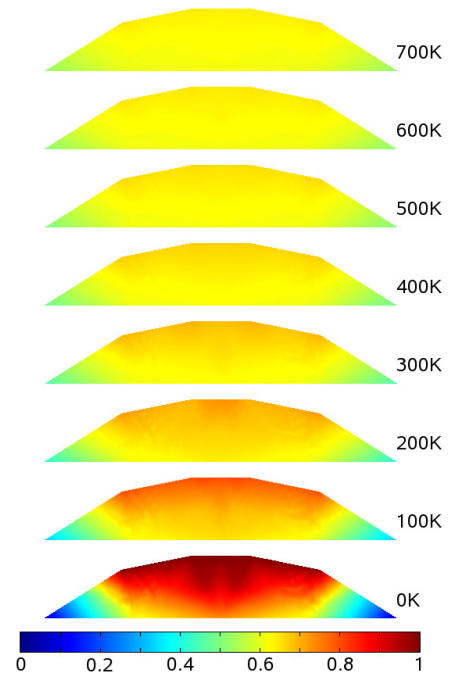

Figure 5. Minimum free energy concentration profiles for domes with 60% of Ge and the indicated temperatures.

experimental times due to the very slow (vanishing) bulk diffusion [7]. In this respect, our model has the same limitations of the above recalled atomistic MC approaches, or of [16]. By allowing for Si/Ge exchanges within the whole island one overestimates the entropic contribution. A full understanding of island formation and evolution including intermixing, ideally requires a kinetic model. While we feel

that some important atomic-scale information is still missing (for example, barriers for Si/Ge exchanges at the various exposed facets of the islands have never been explored) for developing such a model, a very interesting attempt to tackle the whole complexity of the problem was recently presented by Tu and Tersoff [26]. While keeping the comparison between theory and experiments at a qualitative level, due to an approximated evaluation of the strain fields and to a simplified kinetic scheme, these authors were able to capture impressively some of the key observed phenomenology.

4. Conclusions

In this paper we presented a very fast method for finding the concentration profile minimizing the free energy of lattice-mismatched heteroepitaxial islands. Since during the iterative MC procedure the elastic problem is solved at each step, the method is fully self-consistent. We applied our method to SiGe/Si islands in 2D and 3D, and showed the role played by entropy at finite temperatures. We wish to stress that a full understanding of island formation and evolution including intermixing, ideally requires a kinetic model allowing the system to explore only the available configurational phase space. In this respect, any thermodynamic treatment such as the one here presented, where bulk diffusion is tacitly assumed, is expected to overestimate the role of entropy. In fact, the highly non-uniform concentration profiles found here and in [15] at $T = 0$ K (elastic-energy minimization only) seem to recover the experimental data much better. We find this result very interesting, since it reveals that in SiGe/Si systems the availability of fast diffusion channels at surfaces only provides an efficient elastic-energy minimization channel, while strongly frustrating entropy maximization.

Acknowledgments

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