Critical aspects of alloying and stress relaxation in Ge/Si(100) islands

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(Received 19 May 2005; published 12 August 2005)

We report Monte Carlo simulations of alloying and stress relaxation in Ge/Si(100) dome and pyramidal islands. In both cases, the simulated composition profiles consist of inhomogeneous Si-rich cores and outer Ge-rich shells. Comparison to experimentally deduced profiles gives us the opportunity to discuss some of the most controversial aspects of the problem. We propose that, in addition to surface events and kinetically driven alloying, volume diffusion and stress-driven intermixing need to be considered for a global interpretation of experimental results.

DOI: 10.1103/PhysRevB.72.075334 PACS number(s): 68.55.−a, 68.35.Bs, 68.35.Dv, 68.35.Fx

Despite the intense investigations in recent years, the issue of intermixing/alloying in self-assembled strained semiconductor islands is far from being well understood. Some of the most controversial aspects of the problem include the specific mechanisms of alloying, the relative contributions of thermodynamics and kinetics to intermixing, and its effect on the stress state of the islands.

Because it is a simple, two-element heteroepitaxial system, Ge/Si(100) has been the model case for such investigations. Recently, some experimental studies have been able to report quantitative island composition profiles.[1–4] However, the results and the conclusions drawn from these studies are highly controversial. Malachias *et al.*[1] analyzed dome islands grown at 600 °C by chemical vapor deposition (CVD), using anomalous x-ray diffraction (AXRD) and selective etching. They found that the domes consist of a Si-rich core covered by a Ge-rich outer shell. Subsequent work by the same groups[2] analyzed, in addition, dome islands grown by molecular beam epitaxy (MBE) at 700 °C, using AXRD. They again reached the same conclusion.

On the other hand, Schülli *et al.*[4] who analyzed dome islands grown at 600 °C by MBE, also using AXRD, found no evidence for a Si-rich core. The extracted vertical variation of Ge content was rapid at the bottom, with an abrupt jump from ~10% to ~80%, very different than in Refs. 1 and 2. Even more striking was the profile suggested by Denker *et al.*,[3] which was extracted from small pyramidal islands grown by MBE at 560 °C using selective etching. Instead of a Si-rich core, they found Si-enriched corners with the center remaining rich in Ge. However, larger pyramids and domes, in the *same sample*, were heavily enriched with Si, even in the core.

These vastly different results unavoidably open up the discussion about the very fundamental processes occuring during alloying. The possibility for a variety of diffusion paths cannot be excluded, because these results would otherwise be hard to reconcile. At present, it is unclear whether these experimental profiles are a result of thermodynamics or kinetics, or both, and in what degree the different experimental growth techniques influence the profiles.

The authors of Ref. 3 explained their profile using a purely kinetic model of random surface diffusion of Ge and Si atoms during growth, excluding any strain-driven intermixing and any volume diffusion events at the basal interface in the center of an island. On the other hand, the authors of Refs. 1 and 2 interpreted their profiles as a result of thermodynamics, i.e., as arising from strain-energy minimization, but they also excluded any volume diffusion events.

The scope of this paper is to shed some light into this fuzzy picture, and to discuss some of the critical aspects of stress relaxation and alloying in Ge/Si(100) islands, such as the relevance of surface and volume diffusion events. We report the results of Monte Carlo (MC) simulations and the comparison of the simulated profiles with experimental ones. The MC profiles consist of a Si-rich core, though inhomogeneous, and an outer Ge-rich shell. We thus show that some of the reported experimental strain and composition profiles[1,2] are compatible with quasiequilibrium conditions, and that volume exchange diffusion events are possible. The other profiles[3] cannot just be explained by a pure kinetic model, but in addition strain-driven intermixing needs to be considered. We also present simulated stress maps for alloyed islands.

The extent of atomic diffusion is a crucial factor in this problem. Often, it is argued that only surface diffusion is significant,[1,3,5] but there are unambigious experimental indications that diffusion involves several subsurface layers. Nakajima *et al.* convincingly showed that in the Ge/Si(100) system diffusion readily takes place down to at least the fourth subsurface layer, even at submonolayer Ge coverages and low T's.[6] This happens because of the substantial subsurface stress field due to the reconstruction[7] which enhances diffusion by lowering the barriers. Calculations have shown[8] that the diffusion barriers in the subsurface region are significantly lower (~1 eV) than the bulk values (~4 eV). This mechanism alloys the WL and the island at the initial stages of growth. Similarly, stress-enhanced diffusion is expected to operate when high stress builds up in the islands.[9]

We are thus led to simulate the diffusion processes in the islands by a *quasiequilibrium* MC approach, which assumes that at high enough temperatures diffusion in the island, the WL, and few monolayers (ML) in the substrate is fast due to strain. Details of the method have been previously published.[10,11] Here, we briefly describe the central points.

We work with a fixed system composition, i.e., we assume that a given amount of Ge atoms is deposited on Si(100) and

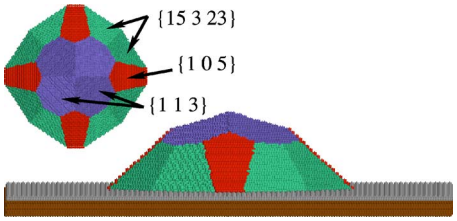

FIG. 1. (Color online) Schematic of a multifaceted dome island used in the simulations. Different facets are shown by arrows.

this material forms the WL and the island. The formation of the composition profile is driven by free-energy minimization. Individual contributions include the surface energy, the strain energy, the alloy mixing energy, and the configurational entropy. Energy lowering is achieved by redistributing the atoms in the system. Equilibration is achieved within the isobaric-isothermal (N,P,T) ensemble, supplemented by identity flips in the form of Si-Ge exchanges, keeping the composition constant.[7] We constrain the two randomly chosen flipped atoms to be nearest neighbors, in order to realistically simulate Si-Ge exchange diffusion events. The Metropolis algorithm is used.

For the interactions, we use the well established interatomic potentials of Stillinger-Weber[12] (SW) for multicomponent systems, which treat strain, heteronuclear bonding, and the energetics of the reconstructed Si(100):Ge surface reasonably accurately.[13] The stress state of the islands is analyzed using the tool of atomic level hydrostatic stresses.[9,10,14] The stress field is mapped site by site, and average values over a region can also be inferred. Positive (negative) sign indicates compressive (tensile) stress.

The simulational cells consist of coherent islands on top of the WL and the Si(100) substrate. We study both pyramids and domes. The pyramids have a square base and {105} facets, aspect ratio ~0.1, and contact angle ~11°. Their size is ~90 Å. The total amount of Ge corresponds to 3.7 ML. The domes are multifaceted, bounded by {113}, {105}, and {15 3 23} planes, and have an aspect ratio 0.2 and size 120 Å. The amount of Ge is equivalent to 4.8 ML. A characteristic model dome structure is sketched in Fig. 1. The width of the WL is fixed at 3 ML. We limit the identity switches, and thus the extent of diffusion, down to 6 ML in the substrate, to conform with experimental observations. The substrate contains 10 ML of Si atoms, with the bottom layer kept fixed. Epitaxial strain is imposed by constraining the lateral cell dimensions to the Si lattice constant. Periodic boundary conditions are imposed in the lateral directions.

We begin with the analysis of the stress field in nonalloyed Ge islands.[9,10,15,16] This corresponds to experimental situations where intermixing is either negligible (relatively low growth temperatures) or it is not yet initiated (the stress is below a critical compressive value[9]).

The stress pattern of a typical nonalloyed dome island is analyzed in Fig. 2. In the upper panel, the x dependence of the stress in the island base layer and the top substrate Si layer is plotted. In the lower panel, a stress map of the whole structure is portrayed. Stresses are overwhelmingly compressive in the interior of the island, but at the edges become tensile. Compression fades as we move upwards to the top.

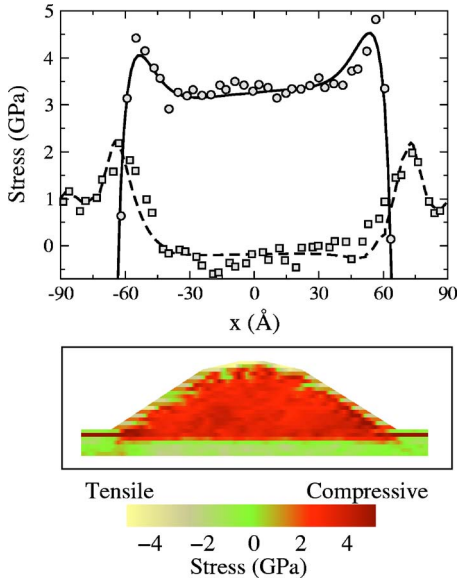

FIG. 2. (Color online) Top panel: Variation of hydrostatic stress in the base layer of a nonalloyed dome (circles, solid line), and in the top substrate layer (squares, dashed line), along a line passing through the island base center. Bottom panel: Stress map of the dome island. A thin slice cut through its center is shown.

An interesting feature, found also by Sonnet and Kelires[10] and Yu and Madhukar[15] in pyramidal islands, is a highly compressed region near, but not at, the island edges. In conjunction with the well known[9,15,16] formation of a compressive corral in the WL and in the substrate at the island periphery—see the variation in the top substrate layer—this feature bears significance for the discussion on alloying that follows. Outside the corral, stresses in the substrate below the island are tensile.

At the initial stages of growth, stress in the island and the compressive corral is low.[9] When stress sufficiently builds up, in a manner exemplified in the pattern of Fig. 2, strain-driven intermixing and alloying is activated. (Possible kinetic mechanisms are discussed below.) To simulate the effect, MC switching-exchange moves, initiating at the interface, are performed over the runs, yielding at the ergodic limit average site occupancies. These denote the local compositions, and thus the composition profiles are mapped.

Characteristic composition profiles of a pyramid and a dome, calculated at 900 K, are shown in Fig. 3. It is clear that in both cases the profile is partitioned into two distinct regions: An inner region enriched with Si and an outer Ge-rich shell, which covers the islands from the base up to the top. The Si-rich area (Si fraction more than 40%) is not homogeneous, but there are clusters of sites with higher Ge probabilities dispersed in this core. It is also evident that the highly compressed regions near the island edges are now enriched with Si. This is because sites under compression (tension) tend to be occupied by the smaller (larger) species in the system.[7] Such subtle features were also observed in simulations of pyramids using the Tersoff potential.[10] On the other hand, the formation of the Ge-rich outer shell can mainly be attributed to the lower surface energy of Ge,[10] but also to the tensile conditions prevailing at the edges.

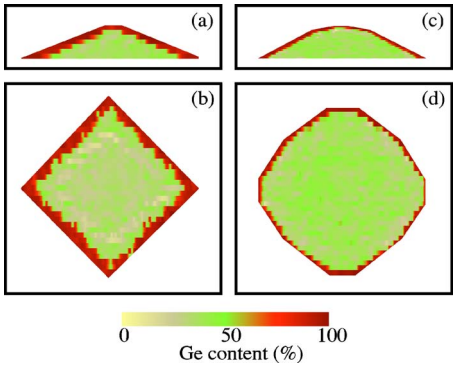

FIG. 3. (Color online) Composition profiles in a pyramidal (left) and a dome island (right). Panels (a), (c) portray thin slice cuts through the center of the islands. Panels (b), (d) show the base layers.

It is striking that these MC composition profiles, simulated under quasiequilibrium conditions, are similar in general lines to the experimental profiles in Refs. 1 and 2. We may interpret this similarity as implying that the latter profiles are formed under conditions of strain-enhanced diffusion, including Si-Ge volume exchanges at the central basal region of the island. This mechanism readily explains the formation of a Si-rich core. Indeed, there is no reason to exclude such events, either at the initial stages of growth or at later stages when high stress accumulates in the island.

Exchanges are also expected between the Si-enriched corral in the WL and the compressed regions in the island *near the edges*. These should also be considered as volume diffusion events. In the simulations, we see volume events both at the center and near the edges. True surface events, i.e., Si atoms diffusing on the terrace and attaching to the edges, intruding then into the island, may contribute to alloying. However, they should not be so favorable because the edges are under tension,[10,15] and there is a barrier to cross over them. Indeed, we see very few surface Si-Ge exchanges at the edges.

An alternative explanation for the generation of the Si-rich core was given in Ref. 1. It says that stress relief is achieved by Si-Ge alloying of the island edges through the compressive corral by means of *surface diffusion*.[2] The alloyed regions are continuously buried under newly deposited Ge, as the edges move radially outward, giving rise to the Si-rich core. This is a plausible scenario, but there are some difficulties with it. (a) Edges are under tension. Diffusion through them is limited. Instead, volume exchanges with the compressed near-edge region are more likely. (b) Even in this case, volume exchanges with central regions are also likely, since the stress difference between the two regions is small (see Fig. 2). (c) Then, the notion of buried alloyed regions at the edges is redundant to explain the Si-rich core. (d) The strain-driven surface diffusion model cannot explain the crosslike shape of the profile in Ref. 3.

On the other hand, the kinetic model in Ref. 3 seems to explain the crosslike shape of the profile in small pyramids, but it does not account for the profiles in larger pyramids and domes, grown in the same sample, with the same method, at the same T. The model is proposed to hold during growth. Then, since larger pyramids obviously develop from smaller ones, and domes are well known to develop from pyramids through facet transformations,[17] and diffusion within the islands is assumed to be limited, one would expect to see larger pyramids and domes with frozen-in Ge-rich cores. This is not seen in the experiment. The model does not account for the dome profiles in Refs. 1 and 2, either.

Therefore, a pure kinetic model is inadequate for a global description. Instead, the profiles in Ref. 3 can be explained by also considering strain-driven alloying, in addition to kinetics. In smaller pyramids, under limited diffusion (MBE growth, 560 °C), the most compressed areas, near the edges, tend to be alloyed. Coupled to kinetic and geometrical factors, which are significant and dominant under conditions of low diffusivity, this favors Si enrichment at the corners. However, when pyramids grow larger or transform into domes, high stress builds up in the interior. Now, strain-enhanced diffusion overwhelms kinetic contributions, and the crosslike shape disappears. Volume diffusion events, both near the edges and at the center, are triggered leading to extensive intermixing. On the other hand, strain-enhanced diffusion sets in from the outset at near equilibrium conditions. This requires high T's to activate volume events, as in Ref. 2 (MBE growth, 700 °C). Alternatively, CVD growth may provide such conditions, at even lower T's, as in Ref. 1.

Of course, we must emphasize that the above discussion about the interplay of strain-driven and kinetic effects is not directly based on the results of our quasiequilibrium simulations, but it is instigated by the comparison of the simulated profiles to the experimental ones. For a more complete description, which can clarify the relative importance of each contribution, one needs to consider a simulational model where both thermodynamics and kinetics are simultaneously taken into account. We are currently in the process of devel-

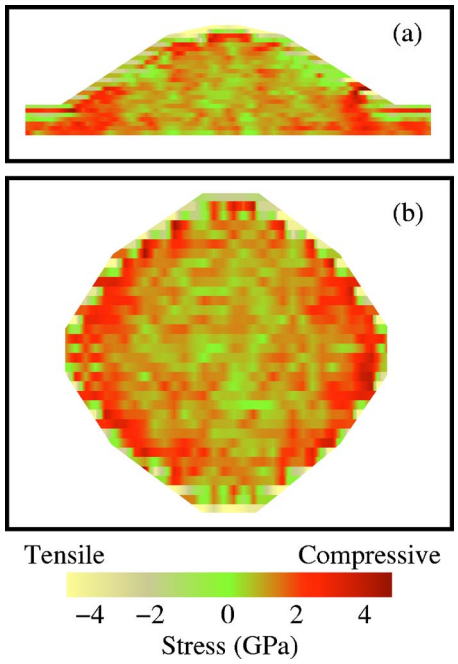

FIG. 4. (Color online) Stress maps of an alloyed dome. (a) The whole cell. (b) The dome base layer.

oping such a model, by including kinetic barriers to the diffusion events.

We now discuss the stress state of the alloyed domes. Figure 4 shows the stress map of the dome shown also in Fig. 2 before alloying. Comparison of the two maps reveals that much of the compression in the island is relieved, especially in the core, but elastic energy still is stored in the compressive ring near the edges, and in the corral below. Thus, further annealing would alloy these regions. The map is very similar to the stress maps of alloyed islands reported in Ref. 2. This is another indication that in these experiments near-equilibrium conditions might have been achieved.

Finally, we comment on the effect which misfit dislocations might have on alloying. It is well known that dislocations induce large strain and stress fields near the core and along the dislocation lines.[18] This might drive site-specific segregation of species, as some areas are under compression while other areas are under tension. Such segregation has been recently reported for thin SiGe alloy films.[19] We have preliminary results suggesting that, in addition, dislocation core energies are significantly changed due to segregation.[20] We are also examining such effects in dislocated islands. In particular, an interesting subject which needs investigation is the effect of segregation around dislocations on nanoisland shape transformations.[21,22] It is possible that segregation might change the energetics of this process.

In summary, our MC simulations provided stress and composition maps in Ge/Si(100) islands, whose comparison to experimental profiles, generated with different methods and deposition conditions, allowed us to discuss some of the most controversial issues in this subject. We proposed that, in addition to surface diffusion, volume exchange events may play a role in shaping up the composition profiles, and that stress-driven intermixing is needed for the global interpretation of experimental results.

This work was supported by a grant from the EU and the Ministry of National Education and Religious Affairs of Greece through the action "ΕΠΕΑΕΚ" (programme "ΗΡΑΚΛΕΙΤΟΣ").

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