

## Shaping the composition profiles in heteroepitaxial quantum dots: Interplay of thermodynamic and kinetic effects

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Citation: *AIP Advances* 4, 077135 (2014); doi: 10.1063/1.4891935

View online: <http://dx.doi.org/10.1063/1.4891935>

View Table of Contents: <http://aip.scitation.org/toc/adv/4/7>

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## Shaping the composition profiles in heteroepitaxial quantum dots: Interplay of thermodynamic and kinetic effects

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(Received 9 May 2014; accepted 16 July 2014; published online 30 July 2014)

Atomistic Monte Carlo simulations, coupling thermodynamic and kinetic effects, resolve a longstanding controversy regarding the origin of composition profiles in heteroepitaxial SiGe quantum dots. It is shown that profiles with cores rich in the unstrained (Si) component derive from near-equilibrium processes and intrainland diffusion. Profiles with cores rich in the strained (Ge) component are of nonequilibrium nature, i.e., they are strain driven but kinetically limited. They are shaped by the distribution of kinetic barriers of atomic diffusion in the islands. The diffusion pathways are clearly revealed for the first time. Geometrical kinetics play a minor role. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4891935>]

One of the longstanding issues in semiconductor heteroepitaxy regards the origin and shape of composition profiles (CPs) in alloyed nanoislands. These provide a very promising route for producing quantum dots (QDs). A central question is whether intermixing in the islands and the resulting profiles can and in what extent be described by equilibrium thermodynamics and/or by non-equilibrium kinetic effects. Other important issues concern the relative contributions of elastic and entropic effects and of the various alloying mechanisms in the formation of CPs.

An extensively studied case is the heteroepitaxy of Ge on Si(100) during which nanoislands of various shapes develop and self-organize.<sup>1</sup> Experiments show the formation of CPs with either the unstrained (Si)<sup>2</sup> or the strained (Ge)<sup>3,4</sup> component enriching the core of the islands. A number of theoretical studies<sup>5–12</sup> considered thermodynamic effects (including surface, elastic and entropic contributions, and bulk interdiffusion phenomena) as the primary driving force for the formation of the CPs. On the other hand, CPs in islands grown by Molecular Beam Epitaxy (MBE)<sup>3,4,13</sup> were interpreted as arising solely from surface kinetics related to the island geometry, independent of the stress fields. While the omission of kinetic effects in the equilibrium approaches is certainly a shortcoming, the neglect of thermodynamic effects in strained heteroepitaxy is counterintuitive.

It is therefore desirable to examine the problem by coupling these two primary effects. The need to include kinetic effects in equilibrium simulation studies was earlier suggested by Hadjisavvas and Kelires.<sup>8</sup> More recently, Tu and Tersoff<sup>14</sup> studied the problem using continuum elasticity theory in two dimensions (2-D), coupling to island morphology and motion, while Niu *et al.*<sup>15</sup> considered the influence of growth modes on the CPs using a 2-D atomistic strain model.

Here, we elucidate this issue and resolve a longstanding controversy by examining the interplay and the relative contribution of these two effects in the formation of CPs in the prototypical example of Ge/Si(100) QDs, using a fully atomistic 3-D simulation approach. We show that both effects

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play a crucial role. Thermodynamics is the driving force for alloying, while kinetics controls it. Specifically, the kinetic barriers of atomic diffusion in the system determine the diffusion paths and the extent of strain-driven intermixing, and shape the profiles.

For a successful treatment of the problem, one needs to consider all possible kinetic factors, while keeping full description of thermodynamic effects. Factors that influence kinetics are geometry, temperature, and diffusion barriers. These have to be coupled to the elastic and surface energies and to the configurational entropies.

We accomplish this coupling by using a Monte Carlo (MC) method in the isobaric-isothermal ensemble, extensively used in the past for studying the equilibrium properties of semiconductor alloys and QDs,<sup>6-8,16-20</sup> and appropriately amended here to include the kinetic effects. Three types of random moves are involved in the original MC algorithm, leading to the direct minimization of the system's Gibbs free energy: atomic displacements and volume changes, which lead to geometrical relaxation, and mutual identity exchanges (flips) between atoms of different kinds, which lead to compositional equilibration and mimic atomic diffusion in the system.

To include the kinetic effects and for a more realistic description of the diffusion processes under nonequilibrium conditions, we use kinetic barriers in the exchange flips, which depend on the location of the event. This might be at the surface and subsurface layers, on the terraces and island facets, and in the bulk. The probability of accepting an exchange trial move in the Metropolis algorithm is given by  $P_{acc} \sim \exp\{-(\Delta U + E_b)/k_B T\}$ , where  $\Delta U$  is the energy change due to the move and  $E_b$  is the kinetic barrier for the flip. The two randomly chosen identity-exchanged atoms are constrained to be nearest neighbors ( $NN$ ), as for diffusion by the concerted-exchange mechanism.<sup>21,22</sup> This approach allows for a self-consistent treatment of the extent of diffusion and local equilibration in the growing island, avoiding the rather arbitrary assumptions of certain diffusion lengths, and unravels the details of the diffusion paths in the system. The anisotropic nature of diffusion on the reconstructed terraces and facets is naturally taken care of. In the absence of kinetic barriers, and with unlimited diffusion, full compositional equilibration is achieved.

Values for the kinetic barriers are taken from various first principles calculations.<sup>22-26</sup> These range, on average, from few tenths of an eV for events on the (100) surface to  $\sim 2$  eV for diffusion down to the sixth subsurface layer.<sup>25</sup> The effect of the reconstruction stress field is taken into account in the estimation of barriers. Nominal values of barriers used<sup>27</sup> are 0.1, 0.2, 1.0, 1.5, and 2.2 eV for exchanges on the surface (dimers), 1st to 2nd, 2nd to 3rd, 3rd to 4th, and 4th to 5th layer, respectively. Deeper events are considered as bulk events with a barrier of  $\sim 4$  eV. Such a distribution of barriers suggests that diffusion in surface and near-surface layers is rapid, establishing local equilibrium, while deeper layers are inaccessible to diffusion when buried during growth, with local configurations frozen in.<sup>15,16,28</sup> The concept of local/facet equilibrium was recently employed<sup>16</sup> to explain the observed atomic ordering in SiGe dome islands.<sup>29,30</sup>

The simulations are run in a parallel-processing mode, which speeds considerably the algorithm.<sup>31</sup> The energy is calculated using well-established interatomic potentials for Si/Ge.<sup>32</sup> The accuracy of these potential models in treating the energetics of the highly stressed environments involved in reconstructed surfaces and island facets has been extensively tested by our group over the years.<sup>6-8,16-20</sup>

We use simulational cells consisting of coherent Ge islands on top of a wetting layer (WL) with three monolayers and a Si(100) substrate, as in Stranski-Krastanov (SK) growth. We study faceted islands with the appropriate facet reconstructions.<sup>16</sup> Namely, shallow pyramids with  $\{105\}$  facets and  $11^\circ$  contact angles  $\theta$ , steeper pyramids with  $\{101\}$  and  $\{111\}$  facets ( $\theta = 36^\circ$  and  $45^\circ$ , respectively), and domes with  $\{105\}$ ,  $\{113\}$ , and  $\{15\ 3\ 23\}$  facets ( $\theta = 11^\circ$ ,  $25^\circ$ , and  $36^\circ$ , respectively). The base size of the islands ranges from 20 to 60 nm. The largest island (dome) contains  $\sim 850,000$  atoms.

We begin with the equilibrium state of the alloyed Ge islands. This may not be the usual state, since surface diffusion is the dominant alloying mechanism<sup>4,14</sup> at typical growth conditions, but it may occur at high growth or annealing  $T$ 's, or at any other conditions at which substantial intrasland diffusion and redistribution of the alloy species can take place.<sup>33,34</sup> Fig. 1 shows the equilibrium CPs of the four representative types of QDs at 900 K. The composition in the islands was kept constant during equilibration. The particular Si content was extracted from the non-equilibrium intermixing processes, to be discussed below.

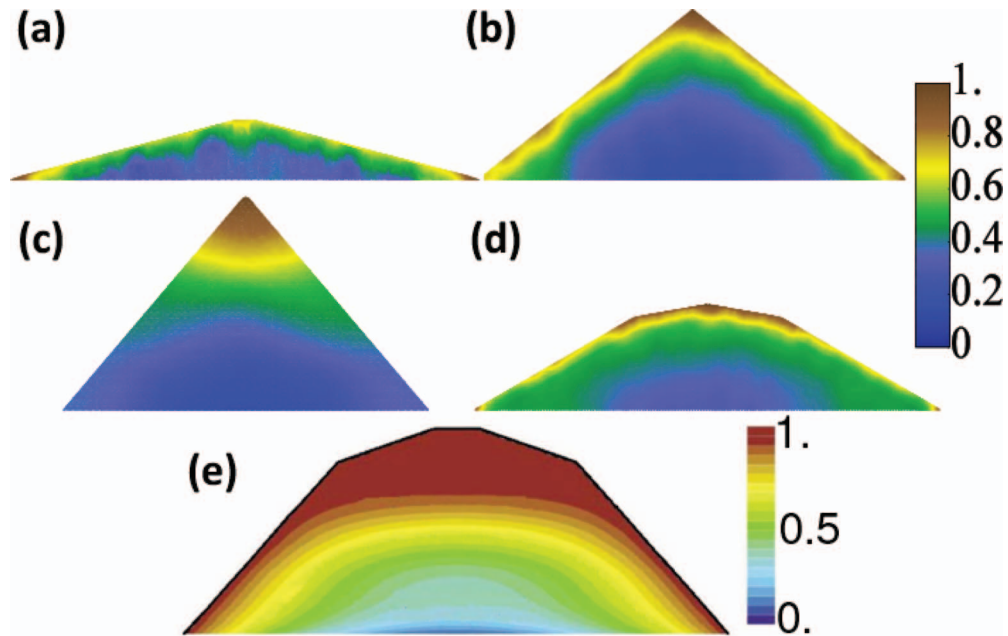


FIG. 1. Cross-sectional maps of equilibrium CPs of (a)  $\text{Si}_{0.35}\text{Ge}_{0.65}$  shallow angle pyramid with  $\{105\}$  facets (20 nm), (b)  $\text{Si}_{0.37}\text{Ge}_{0.63}$  steep angle pyramid with  $\{101\}$  facets (30 nm), (c)  $\text{Si}_{0.32}\text{Ge}_{0.68}$  steep angle pyramid with  $\{111\}$  facets (30 nm), and (d)  $\text{Si}_{0.35}\text{Ge}_{0.65}$  multifaceted dome with  $\{105\}$ ,  $\{113\}$ , and  $\{15\ 3\ 23\}$  facets (60 nm). Atom-projected Ge composition is merged into a continuous mesh by averaging over spheres of 3 Å in radius. (e) Experimental CVD dome profile (recreated from Ref. 2.)

The main and profound characteristic of all these CPs is the accumulation of the unstrained component (Si) in the core of the islands, while the strained component (Ge) segregates to the top and the corners of the base. The shape and inhomogeneous nature of the dome CP in Fig. 1(d) is in excellent agreement with experimental CPs in domes, seen in Fig. 1(e), produced by chemical vapor deposition (CVD) at 873 K.<sup>2,10</sup> This can be explained by noting that CVD is suggested to operate at near-equilibrium conditions,<sup>30</sup> in contrast to MBE which is a nonequilibrium method. This is the first equilibrium calculation to accurately reproduce these experimental dome CPs. Previous finite element,<sup>11</sup> MC/continuum elasticity,<sup>12</sup> and MC strain model 2-D equilibrium calculations<sup>15</sup> do not predict a Si-rich core in dome and shallow pyramid CPs. Instead these profiles<sup>11,12</sup> are characterized by accumulation of Ge in the middle and top and of Si in the base corners, and rather resemble the kinetically limited CPs to be discussed below. The origin of this discrepancy is not clear. It probably indicates inability of these methods to reach the equilibrium state due to insufficient minimization of Gibbs free energy. For consistency and a check, we also carried out some 2-D simulations for domes and pyramids, using the above compositions as well as compositions used in these previous works. The results are qualitatively very similar to the 3-D ones, showing Si-rich cores.

The equilibrium CPs can be understood by noting that stress fields can trigger site-specific composition selectivity in alloyed systems.<sup>16,17,28,35</sup> Figure 2 shows stress maps of atom-projected local stresses<sup>17</sup> in nonalloyed (pure Ge) islands of the type and size shown in Fig. 1, calculated at 900 K. The resemblance of the stress profiles to the composition profiles is obvious. In the interior, sites under large compressive stress, which in some areas exceed 3-4 GPa and correspond to a compression of more than 0.5 eV/atom, are occupied by Si atoms in the alloyed state, leading to the formation of Si-rich cores. This may take place, for example, when CVD annealing conditions favor intrasland diffusion and atom redistribution within the island,<sup>33</sup> especially close to the substrate where strain is large, and equilibration is achieved. Ge prefers to accumulate in less compressed

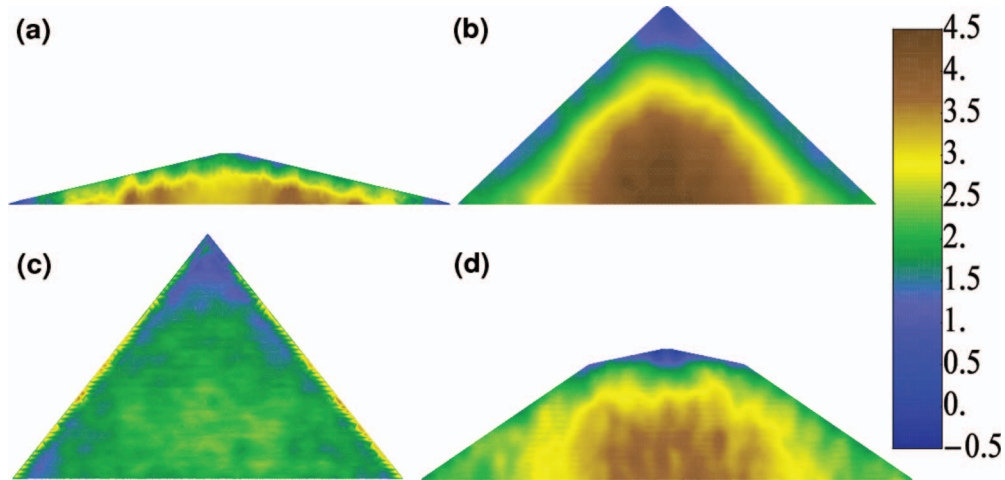


FIG. 2. Cross-sectional views of stress maps at 900 K of (a)  $\text{Si}_{0.35}\text{Ge}_{0.65}$  shallow angle pyramid with  $\{105\}$  facets, (b)  $\text{Si}_{0.37}\text{Ge}_{0.63}$  steep angle pyramid with  $\{101\}$  facets, (c)  $\text{Si}_{0.32}\text{Ge}_{0.68}$  steep angle pyramid with  $\{111\}$  facets, and (d)  $\text{Si}_{0.35}\text{Ge}_{0.65}$  multifaceted dome with  $\{105\}$ ,  $\{113\}$ , and  $\{15\ 3\ 23\}$  facets. The islands are nonalloyed. Atom-projected stresses are merged into a continuous mesh by averaging over spheres of 3 Å in radius.

areas, such as at the top and the corners, and on the reconstructed facets due to the lower surface energy of Ge.<sup>16,17</sup>

We now discuss the formation of nonequilibrium CPs. Driven mainly by strain, Si atoms from the substrate and the WL intrude into the growing island, but now their motion and distribution is kinetically limited by the diffusion barriers in their path. We first consider pyramidal islands. These are usually formed by faceted growth (FG) in a typical SK process, in which growth proceeds in the facet normal direction.<sup>15,36</sup> An alternative mode, the layer-by-layer growth (LG), in which growth proceeds in the substrate-surface normal direction, is believed to operate at the initial pre-pyramidal, non-faceted stages of growth.<sup>15,37</sup>

We therefore consider small pyramidal islands, initially nonalloyed, growing with FG at the early stages of growth. Local equilibration, whose depth is self-consistently controlled by the distribution of diffusion barriers both laterally and normally to the facets, redistributes Si and Ge atoms in the near surface region. Further growth buries and freezes these local configurations, while the newly formed facets and layers below are again locally equilibrated. The kinetic barriers used<sup>27</sup> are those of the reconstructed SiGe(100) surface, down to the sixth subsurface layer.<sup>23–25</sup> This is exact for the terraces around the islands and a very good approximation for the  $\{105\}$  facets,<sup>24</sup> which are vicinal to and dimer-reconstructed as the  $\{100\}$  surface. For the other facets, where the exact values of barriers are not known, this procedure is approximate but sufficient to give qualitative results and trends.

The kinetically-limited CPs of the three pyramidal islands under study are shown in Fig. 3(a)-(c). They are distinctly different from the equilibrium CPs. They exhibit cores rich in the strained component ( $x_{\text{Ge}} > 0.8$ ), while Si enriches the corners. A characteristic V-like shape appears, more evident in the  $\{111\}$ -facet case, Fig. 3(c). In Fig. 3(e), we demonstrate that by removing alloy material with  $x_{\text{Ge}} > 0.65$  from the shallow pyramid one unravels the unique rosette (crosslike) shape seen in pyramidal SiGe islands grown by MBE after selective etching,<sup>3,4</sup> shown in Fig. 3(f). The formation energy<sup>38</sup> of the crosslike CP is calculated to be -0.41 eV/atom, compared to -0.52 eV/atom for the equilibrium CP in Fig. 1(a), as expected. Both are lower in energy than the nonalloyed case (-0.37 eV/atom).

The close similarity of the simulational and experimental etched profiles confirms that this class of CPs, rich in the strained component, are thermodynamically driven but kinetically controlled and limited. The shape of the CPs arises because of the particular distribution of kinetic barriers that determine the diffusion paths. The highly compressed areas in the island, especially the core, attract Si atoms. Incorporation from underneath the island can not occur due to the high bulk diffusion

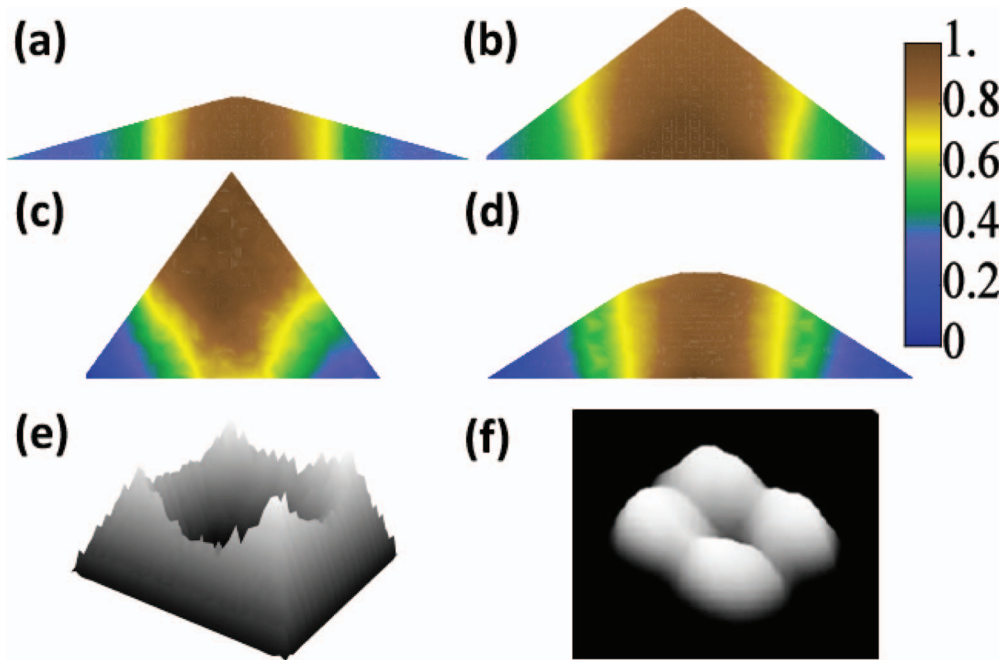


FIG. 3. Cross-sectional views of nonequilibrium CPs of the four representative types of QDs at 1200 K, panels (a)-(d). Atom-projected Ge composition is merged into a continuous mesh by averaging over spheres of 3 Å in radius. Panels (e) and (f) show selectively etched simulational and experimental (recreated from Ref. 3) profiles, respectively.

barriers ( $\sim 4$  eV). Thus, approach to the island may only occur through surface diffusion of Si atoms reaching the terraces from the alloyed WL.

To make this transparent, we monitored the diffusion paths of Si atoms reaching and intruding into the  $\{105\}$ -faceted pyramidal island, by recording all successful atom-identity  $NV$  switching events associated with each atom. Fig. 4(a) shows some characteristic paths. They illustrate Si atoms diffusing on the terrace, approaching the island either near the corners or the middle of the base edges, and climbing up the facets. They reach not too high before entering into the island (not shown).

A careful analysis of the diffusion paths, by counting all Si atoms on the terrace reaching the island periphery one by one, shows that the Si atoms attracted by the middle of the base edges are actually a bit more numerous ( $\sim 55\%$  of the total), than those reaching the corners.<sup>39</sup> This phenomenon is strain driven. We compute a higher strain energy at the middle of the base edges than in the corners. This was also found in Ref. 3. Therefore, the interpretation<sup>3</sup> that Si enrichment at the corners arises because Si atoms reach them from two sides, and are thus more numerous, does not seem to hold. The obvious question then is why more Si atoms are incorporated in the corners than in the middle basal areas.

To understand this, let us visualize the distribution of barriers in the two regions. A schematic of the island with atomic sites categorized as “surface” or “bulk”, according to the respective barriers and on whether they are accessible to diffusion or not, is shown in Fig. 4(b). This distribution indicates that the diffusion length in the interior may extend to several nanometers *parallel* to the facets, within the thin subsurface layer with low barriers, but it is limited to  $\sim 6$  monolayers ( $\sim 1$  nm) *normal* to the facets. Thus, Si atoms can not reach the core of the island. One also realizes that in the bottom of the island, at the corners, where two inclined facets meet at an angle, there are fewer “bulklike” atomic layers compared to the middle edge regions, where a single facet meets the terrace. Since the diffusion barriers are lower in near-surface layers, this makes the corners more accessible to intermixing.

In addition, many Si atoms that approach at the middle edge areas, move on the facets up to a certain height, and then diffuse toward the corners by exchanges within the first 4 MLs, parallel

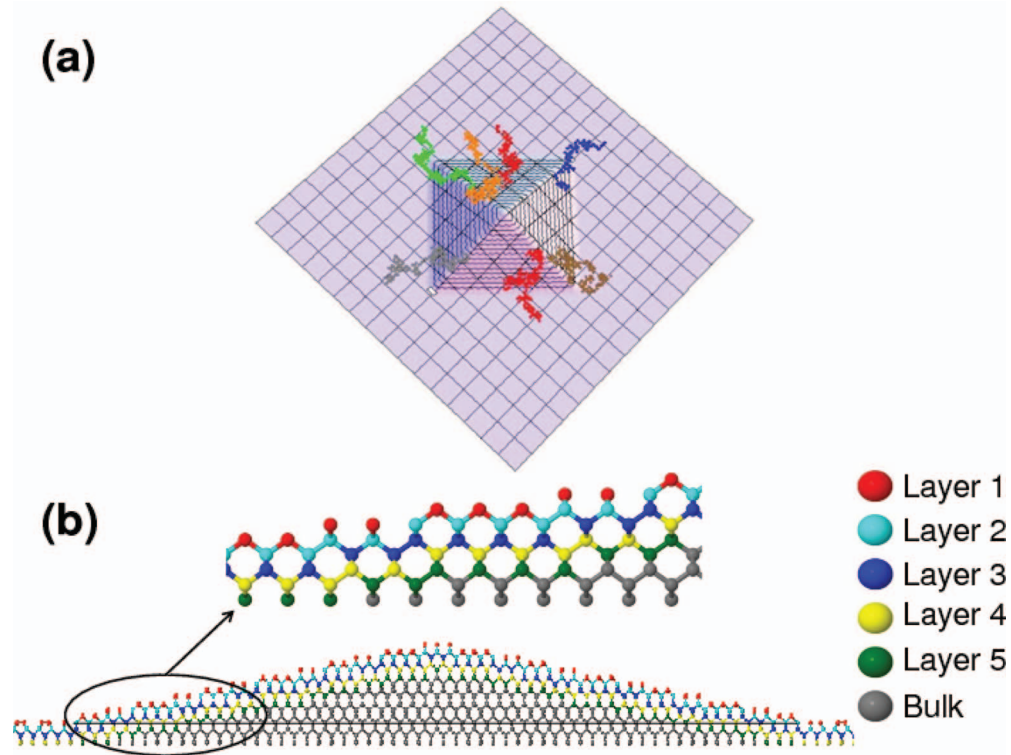


FIG. 4. (a) Characteristic paths of Si atoms diffusing on the terrace and climbing up the facets of the  $\{105\}$  shallow pyramid. (b) Schematic of the island with sites colored according to their accessibility to diffusion. The cross section plane applies to both the diagonal and the normal to the edge direction.

to the facets, while Ge atoms tend to move upwards to the more relaxed regions. Note that it is preferable for the Si atoms to climb up the facets, enter, and then diffuse downwards, than entering directly at the base (facet/terrace edge) and move parallel to the substrate. The latter path is blocked by high barriers.

We conclude that the origin of CPs in pyramidal islands is not due to geometrical kinetics,<sup>3</sup> but instead due to diffusion barrier kinetics which favor and facilitate the easier incorporation of Si atoms in the corner regions. The continuous sequence of the two processes, i.e., local equilibration of the intermixed material under the facets, and freezing of configurations under further growth, leads to the observed V-like shapes.

The kinetically limited dome profile is shown in Fig. 3(d). Despite being approximate, it possesses similar characteristics to the other FG profiles, with the strained component (Ge) enriching the core. A more accurate picture will emerge when barrier values for the various dome facets become available. Also, note that domes and large pyramids are often surrounded by trenches that further facilitate the diffusion of Si from the substrate to the surface.<sup>7,14</sup> This will not alter the CPs since incorporation and diffusion within the islands will follow the same paths described above.

Finally, we comment on the proposition by Niu *et al.*<sup>15</sup> that the CVD dome profiles,<sup>2,10</sup> as the one shown in Fig. 1(e), may originate from non-equilibrium LG which yields structures with cores rich in the unstrained component. This could be an alternative mechanism, but there are problems with it. LG is suggested to operate for shallow mounds (prepyramids),<sup>15,37</sup> which transform into faceted pyramids and further grow via FG, and finally transform into larger domes. The argument is that the composition of the final faceted QD should be affected by LG and contain remnants of the early stages of growth. However, the size of such a Si-rich core would be much smaller than the observed ones, given that the QDs grow substantially larger with FG beyond the prepyramid phase. Also, FG would reverse the CP shape as the island grows, burying the initial one, and the two shapes would actually co-exist. This has not been observed. Thus, most likely the CVD CPs

are indeed close to equilibrium. On the other hand, CPs with cores rich in the strained component can not be described by equilibrium methods, as interpreted in Refs. 11 and 12, but are clearly of nonequilibrium nature.

In conclusion, our atomistic MC simulations, coupling thermodynamic and kinetic effects, have elucidated the origin of CPs in SiGe nanoislands. CPs with cores rich in the unstrained component derive from near-equilibrium processes and enhanced intrainland diffusion. CPs with cores rich in the strained component are of nonequilibrium nature due to barrier kinetics, which determine the diffusion paths and intermixing in the islands. The concepts described here are general and we anticipate that similar processes operate in all alloy heteroepitaxial QD structures. We are currently extending our investigations to nanostructures grown on patterned substrates and curved surfaces.

## ACKNOWLEDGMENTS

This work is supported by the Strategic Infrastructure Project NEW INFRASTRUCTURE/ΣTPATH/0308/04 of DESMI 2008, which is co-financed by the European Regional Development Fund, the European Social Fund, the Cohesion Fund, and the Research Promotion Foundation of the Republic of Cyprus. We acknowledge computation time provided by the Cy-Tera facility of the Cyprus Institute under the project CyTera (NEW INFRASTRUCTURE/ΣTPATH/0308/31).

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- <sup>31</sup> Parallelization is achieved by dividing the computational cell into a system of grids, each assigned to a different processor. Local Monte-Carlo sampling is performed by each processor in the bulk of its assigned domain, thus avoiding the need of communication with neighboring processors. Detailed balance is preserved by randomly shifting the system of grids after each local Monte-Carlo sampling. The communication required during a shift of the grids is limited to receiving a boundary and sending another to the neighboring processors.
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- <sup>38</sup> The formation energy of an island with a given CP is defined as the total energy of the system (substrate, WL, and island) relative to the sum of the cohesive energies (chemical potentials) of its constituents, all calculated at 900 K. The constituent cohesive energies equal the sum of the respective chemical potentials (cohesive energies per atom) of the bulk materials (crystalline Si and Ge) times the number of atoms in the constituent.
- <sup>39</sup> The extent of the corner regions is extracted from the dimensions of the Si-rich ( $x_{Ge} < 0.35$ ) areas in Fig. 3(a).