# Intermixing during Ripening in Ge-Si Incoherent Epitaxial Nanocrystals

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**ABSTRACT:** Ostwald ripening is an interesting phenomenon that takes place in a variety of systems in nature, including nanostructured materials. A large number of nanoscale systems are formed by a mixture, which has to be considered for a realistic description of its evolution upon equilibrium. Here, a thermodynamic-based model is used to explain the intermixing contribution to Ostwald ripening phenomenon in a two-components system  $(A_xB_{1-x})$ . By considering the mixing entropy



on the general growth rate equation of particles, ripening is maximized for an alloy with x = 0.5. As an example, Ge–Si incoherently strained epitaxial islands were analyzed. A selective chemical etching was used to reveal the complex effect of intermixing in islands' final composition profile. Alloying was found to take place primarily through surface diffusion, as revealed by the etching experiments.

# INTRODUCTION

Ostwald ripening (OR) is defined as the coarsening of larger clusters at the expense of smaller ones and is driven by chemical potential minimization through mass transport.<sup>1,2</sup> This wellknown phenomenon usually occurs in solid and liquid solutions. OR is a spontaneous process that can be observed in a variety of systems in nature, from water recrystallization during ice cream refreezing to ceramics.<sup>3</sup> In particular, OR phenomena have been extensively studied in a variety of nanostructured systems. To date, the size distribution of superparamagnetic clusters formed by magnetite embedded within silica was found to be dependent on coarsening.<sup>4</sup> By engineering the amorphization and recrystallization of a single-crystal substrate, the size of ion-implanted nanocrystalline precipitates can be controlled, as a consequence of OR as well.<sup>5</sup> In colloidal nanoparticles,<sup>6,7</sup> the understanding of particles' coarsening through OR is critical to predict and engineer size distribution, shell thickness of core-shell geometries, and composition of alloyed nanoparticles.<sup>6-10</sup> Self-assembled nanocrystals' growth mechanism and evolution are also strongly influenced by OR,<sup>11</sup> which can affect different morphologies ranging from nanowires<sup>12</sup> to quantum rings<sup>13,14</sup> and three-dimensional epitaxial islands.<sup>15–18</sup>

In Ge–Si:Si(001) epitaxial nanocrystals, a binary system, ripening results from a surface-driven process, which depends on kinetics and thermodynamics. OR has been often observed in the late growth stages of Ge–Si islands as a direct consequence of chemical potential reduction.<sup>17–19</sup> Recently, the role of the wetting layer diffusion on Ge–Si hut clusters was investigated in a careful real-time scanning tunneling microscopy experiment.<sup>20</sup> It was observed that the growth rate of the huts decreases with annealing time and OR can be suppressed for high Ge supersaturation, while a critical nucleus size is less than the smallest facet of the hut. This situation can only take place when there are no

lower chemical potential islands that reduce the Ge supersaturation. Lang et al.<sup>21</sup> showed that the addition of Si to Ge–Si incoherently strained islands causes an unexpected island shrinkage, which is claimed to modify the wetting layer composition and to lead to an unstable critical thickness for island formation. As a consequence, the islands dissolve by diffusion. Thus, adatom diffusion was shown to play an important role during material deposition and island evolution upon postgrowth annealing. To date, there is a good understanding of the chemical composition of the postgrown islands, which have been determined by using complementary analytical techniques, such as X-ray diffraction using synchrotron radiation,<sup>22,23</sup> a selective wet chemical etching.<sup>26,27</sup> However, the influence of intermixing during ripening (at constant material volume) and its effect on islands' growth, dissolution, and final composition are still unclear.

Here, we explain the role of intermixing during ripening for a binary mixture  $(A_xB_{1-x})$ . Classical OR takes cluster size into account, but does not include intermixing effects. By combining a thermodynamic-based model with a controlled set of experiments for Ge–Si epitaxial nanocrystals (a binary model system), we show the importance of alloying through the islands' approach to equilibrium throughout the OR process. The composition profile of the incoherently strained islands was found to be a direct result of the dome-shaped islands' coalescence, which takes place during Ge deposition, combined with OR, which occurs when the island + wetting layer system is at constant volume (postgrown annealing). We found that ripening is maximized when the islands are formed by a Ge<sub>0.5</sub>Si<sub>0.5</sub> alloy

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instead of pure Ge, and intermixing can alter the Gibbs—Thomson effect. A selective chemical etching<sup>24,25,28</sup> revealed domeshaped islands' footprint after material surface diffusion to superdomes throughout the wetting layer, which plays a key role during islands' intermixing. Our model is general and can be expanded to *any* nanoscale binary system with similar dimensions.

## EXPERIMENTAL SECTION

Nanocrystals' Growth. The epitaxial Ge-Si nanocrystals were grown by chemical vapor deposition on 150 mm diameter Si(001) slightly doped (p-type) substrates by the deposition of pure Ge at 6 ML/min in a H<sub>2</sub> environment  $[P(GeH_4) = 2.5 \times$  $10^{-4}$  Torr] in a 10 Torr ambient at 600 °C. The layers were deposited in a commercially available, load-locked, lamp-heated reactor with the wafer supported by a SiC-coated, graphite plate with moderate thermal mass. After baking a wafer at a nominal temperature of 1150 °C in a H<sub>2</sub> ambient to clean the surface, a Si buffer layer was grown at about 1080 °C, using SiH<sub>2</sub>Cl<sub>2</sub> as the Si source gas. The temperature was then reduced to the nominal 600 °C Ge deposition temperature. The Ge source gas was GeH<sub>4</sub> diluted in H2.18 The reference sample was quenched to room temperature after the deposition of 12 equiv-ML of Ge (sample as-grown A). The other three samples were annealed in situ at the growth temperature for 10, 30, and 120 min (samples B, C, and D, respectively) under a H<sub>2</sub> constant flux of 10 Torr. The reproducibility of film thickness from run to run as determined by Rutherford backscattering analysis was better than 5%.

**Nanocrystals' Characterization.** The island size and shape distributions were studied by tapping-mode, atomic force microscopy (AFM) using a Digital Instruments Nanoscope microscope, with 512 × 512 pixels in each image. The atomic force micrographs show the height, diameter, and basic shape of the islands. Islands' diameter were computed by scanning areas of  $10 \times 10 \ \mu\text{m}^2$ . X-ray diffraction measurements were performed using a conventional Cu K $\alpha$  source ( $\lambda = 1.5406$  Å and receiving slit =  $1/2^\circ$ ).  $\omega - 2\theta$  scans at the symmetric (004) reflection were used to determine the lattice spacing distribution within the nanocrystals.

**Selective Wet Chemical Etching.** The selective chemical etching experiments were performed using a solution of  $1NH_4OH:1H_2O_2$ , which was prepared with room temperature reagents and used after 1 h, to allow for its stabilization. At room temperature, this etching attacks preferentially Ge richer alloys, forming GeO<sub>2</sub>, which is soluble in water. The solution was calibrated by measuring the amount of material removed in a series of Ge<sub>x</sub>Si<sub>1-x</sub> alloyed thin films with x = 0.34, 0.60, 0.74, 0.90, and 1.00. Combined with AFM measurements, the etching experiments allowed us to infer the chemical composition within the incoherent nanocrystals of samples as-grown A and annealed B.

## RESULTS AND DISCUSSION

Representative AFM images of all samples are shown in Figure 1a–d. Sample as-grown A shows a uniform array of dome-shaped islands ( $9 \times 10^9$  cm<sup>-2</sup>) and a small but significant population of superdomes (incoherent nanocrystals) with well-defined facets. A population of pyramidal-shaped islands is also observed (see Figure 1e), which is in equilibrium with the dome-shaped islands and presents a distinct and nonoverlapping size distribution, as reported in detail elsewhere.<sup>18,29</sup> These pyramids can transform into the faceted, dome-shaped islands as they become larger. The annealed samples (B–D) exhibit a higher



Figure 1. Representative atomic force microscopy images of chemical vapor deposition grown Si-Ge:Si(001) epitaxial nanocrystals after depositing 12 equiv-ML of pure Ge at 600 °C [(a) sample A] and after in situ annealing for 10 min [(b) sample B], 30 min [(c) sample C], and 120 min [(d) sample D] under a hydrogen flux. Arrows in (b) point to the footprints left by domes that were consumed during the Ostwald ripening process. The AFM images shown in (a)-(d) correspond to an area of  $1 \times 1 \,\mu\text{m}^2$ , and the scale bar to 100 nm. High contrast 250  $\times$ 250 nm<sup>2</sup> AFM images highlighting four pyramids present in sample A (e), and the domes' footprint in sample B, together with residual pyramids left after surface diffusion takes place (f)-(h). The scale bar refers to 100 nm. (i) Conventional X-ray diffraction  $\omega - 2\theta$  measurements of all samples at (004) reflection after subtracting the wetting layer signal. Note that by increasing the annealing time, the lattice spacing decreases due to the introduction of dislocations within the superdomes and consequent island's relaxation. (j) Superdomes' mean diameter  $\langle d \rangle$  for samples A–D as a function of annealing time *t*. The gray solid line refers to the  $t^{1/4}$  dependence of the island size expected by Ostwald ripening phenomenon.

population of superdomes and a nonconstant density of domes. In the vicinity of the superdomes, the density of domes is lower, and domes' footprints [highlighted by arrows in Figure 1b and by dashed circles in f-h] are observed, indicating the occurrence of OR phenomenon by surface diffusion. Additional evidence of OR process during postgrowth annealing is the presence of residual pyramids in samples B–D [Figure 1f–h], resulting from the domes' dissolution. These stable nanocrystals correspond to a Ge–Si alloy and are formed at domes trenches, usually with 2- or 4-fold symmetry.<sup>18</sup> A trench is also observed around all superdomes, as a result of strain relief by dislocation introduction.<sup>24,30</sup> The conventional X-ray diffraction measurements presented in Figure 1i show a broader lattice spacing distribution by increasing annealing time, confirming island's relaxation by dislocation introduction within the superdomes. Simultaneously, the average lattice spacing decreases with annealing ( $\omega$  increases), as a direct consequence of Si incorporation (with smaller lattice constant than Ge) within the islands by diffusion.<sup>25</sup> The graph in Figure 1j shows the mean diameter of the superdomes  $\langle d \rangle$  as a function of annealing time *t* for all samples. The solid line shows the  $t^{1/4}$  dependence of the island size expected for OR phenomenon.<sup>2</sup>

For the growth parameters used, low supersaturation conditions cannot be easily achieved. By depositing the same amount of Ge for 960 s, no OR was observed and no depletion was found around SDs (not shown), in contrast to annealed sample B. Besides, the domes' density was found to be constant, confirming that significant ripening only occurs when there is no Ge deposition, that is, during in situ after growth annealing. Therefore, the set of Ge–Si samples presented here (A–D) constitutes an ideal system to study the effect of intermixing in binary mixtures during ripening. The postgrowth annealing under H<sub>2</sub> allows for enough surface diffusion so that the system can slowly approach the equilibrium. Simultaneous mass transport was only possible because the postgrowth annealing occurred under H<sub>2</sub> flux instead of ultrahigh vacuum conditions.<sup>25</sup>

Thermodynamic Model for Ripening in Binary Mixtures. In the thermodynamic regime (at constant pressure and temperature), a system will evolve until it approaches the equilibrium, which can be well described by the general Gibbs free energy (GFE) equation (G = E - TS). This equation takes into account all system's internal energy terms (kinetic + potential + chemical, represented here by E) minus the entropic term TS, which will be maximum at the equilibrium. In a binary system like the Ge–Si nanocrystals investigated here, a fraction of the Gibbs free energy is associated with mixture formation ( $G_M$ ). By neglecting edge (line) and surface effects due to superdomes' large size (surface/ volume ratio  $\sim 2 \times 10^{-6}/$ atoms),  $G_M$  for a superdome on a lattice-mismatched Si(001) substrate can be written as a sum of the elastic and the chemical energies, and the mixing entropy  $TS_M$  contribution:<sup>39</sup>

$$G_{\rm M} = E_{\rm el} + E_{\rm chem} - TS_{\rm M} \tag{1}$$

For incoherently strained islands, the elastic energy term  $(E_{el})$  depends on the number of dislocations present within one island and cannot be easily estimated. Here, we overestimate this term by assuming that the superdomes are coherently strained. Thus,  $E_{el}$  can be written as:

$$E_{\rm el} = 2\gamma \varepsilon^2 \left(\frac{1+\nu}{1-\nu}\right) \tag{2}$$

where  $\gamma$  is the Young modulus,  $\varepsilon$  is the elastic in-plane strain, and  $\nu$  is the Poisson ratio.<sup>31,32</sup> Assuming Vegard's law, the upper value of  $E_{\rm el}$  can be described as a function of the Ge content x within the islands as:

$$E_{\rm el} = ANx^2 \tag{3}$$

where *N* is the number of atoms comprising one island, and *A*, related to bulk strain, is equal to 32.0 meV/at for a coherently strained island. Thus,  $E_{\rm el}$  will be maximum for a pure Ge island (x = 1.0) on a Si(001) substrate (with in plane strain = 4.2%).

The chemical energy term  $(E_{chem})$  is associated with the charge transfer that occurs during the formation of a chemical bond. For Ge and Si, the chemical energy values are:  $E^{SiSi} = 301.0 \pm 21.0 \text{ kJ/mol}$ ,  $E^{GeGe} = 263.6 \pm 71 \text{ kJ/mol}$ ,  $E^{SiGe} = 301.0 \pm 21.0 \text{ kJ/mol}$ , and  $(E^{SiSi} + E^{GeGe})/2 = 295.2 \pm 17.1 \text{ kJ/mol}.^{33}$  The values of  $E^{SiGe}$  and  $(E^{SiSi} + E^{GeGe})/2$  are approximately the same, confirming that a Ge–Si alloy is quasi-ideal.<sup>31</sup> For a Ge<sub>x</sub>Si<sub>1-x</sub> alloy, the chemical energy depends on the volume of the island and on the Ge content *x* as:

$$E_{\rm chem} = CNx(1-x) \tag{4}$$

where *C*, the interaction parameter, is obtained from ab initio calculations<sup>34</sup> performed for a Ge<sub>x</sub>Si<sub>1-x</sub> crystal alloy and is equal to 45.0 meV/atom.<sup>31,35-37</sup> Thus, the maximum value of  $E_{\text{chem}}$  (11.3 meV/at) occurs for a Ge<sub>0.5</sub>Si<sub>0.5</sub> alloy.

Combining eqs 3 and 4, eq 1 can be written as a function of *x*:

$$G_{\rm M} = ANx^2 + CNx(1-x) + NkT[x \ln x + (1-x) \ln(1-x)]$$
(5)

where k is the Boltzmann constant and T is the growth temperature.<sup>31,36</sup>

For a binary system, the chemical potential  $\mu$  is also a thermodynamic variable, defined as:

$$\mu = \left(\frac{\partial G_{\rm M}}{\partial N}\right)_{T,V} \tag{6}$$

Substituting eq 5 into eq 6, one can write  $\mu$  as a function of the Ge concentration for one island:

$$\mu = Ax^{2} + Cx(1-x) + kT[x \ln x + (1-x)\ln(1-x)]$$
(7)

The well-known equation that describes islands' growth rate during OR process is usually written as:<sup>2,18</sup>

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\beta(T)}{r} \left(\frac{1}{r_{\rm c}} - \frac{1}{r}\right) \tag{8}$$

where *r* is the island radius at an instant of time *t*,  $\beta$  is a function of temperature *T*, and *r*<sub>c</sub> is the critical radius above which the island grows and bellow which it dissolves, as defined by classical OR phenomenon. *r*<sub>c</sub> follows a power law in time that does not depend on the system's initial conditions. By combining eqs 7 and 8, one can describe the island growth rate as a function of its chemical potential at an instant of time *t*,<sup>17</sup> where volume is constant, plus a composition-dependent term derived from the entropic contribution to the system's overall energy. Thus, the growth rate for binary mixtures, such as Ge–Si alloyed islands, can be described as a function of the Ge concentration *x* as:

$$\frac{dr}{dt} = \frac{\beta(T)}{r} \left( \langle \mu \rangle - Ax^2 - Cx(1-x) - kT[x \ln x + (1-x)\ln(1-x)] \right)$$
(9)

where  $\langle \mu \rangle$  is defined as the average chemical potential over an ensemble of islands, that is, the chemical potential of an island with critical radius ( $r_c$ ), which corresponds to a metastable condition.<sup>2,17</sup>



**Figure 2.** Contribution of each energetic term to islands' growth rate equation (dr/dt) during Ostwald ripening phenomenon in an  $A_xB_{1-x}$  binary system. The entropic term (red) is the primary contribution to the total energy for alloys with Ge content up to 0.9 in fraction (indicated by the black dashed line) and will be maximum for an alloy formed by Ge<sub>0.5</sub>Si<sub>0.5</sub>. The entropic term was calculated for 600 °C, the growth temperature for all samples.

The contribution of each energetic term to dr/dt is shown in Figure 2. The entropic term (solid red line) is the primary contribution for  $G_{\rm M}$  and has to be taken into account when considering any binary system. In fact, this entropic term  $(TS_{\rm M})$ will determine the island final composition profile and how fast it grows throughout OR. Taking into account all energetic terms to the chemical potential minimization, dr/dt is expected to have a maximum value for x = 0.5, which corresponds to an alloyed island formed by  $Ge_{0.5}Si_{0.5}$ . Therefore, according to the model proposed here, the Ge chemical concentration x will influence the OR process more from the entropic standpoint (composition dependent) than the internal energy term's minimization.<sup>38,39</sup> Thus, alloying is an important effect during the ripening process in mixtures, including the incoherently strained islands analyzed here.

Superdomes' Formation: Coalescence, Intermixing, and Ripening. To determine how the superdomes are formed, samples A and B were submitted to a selective wet chemical etching (room temperature  $NH_4OH:H_2O_2$ ), which attacks preferentially Ge richer alloys.<sup>24</sup> The etching calibration is shown in Figure 3a. Figure 3b and c displays AFM images of samples asgrown A and annealed B after 128 min of etching. As revealed by the selective chemical etching, the superdomes in sample A are formed by the coalescence of a few domes (Figure 3b). When two or more domes are close enough to each other, coalescence takes place rather than diffusive growth. This process occurs when the volume of the system is not constant, while the number of particles (i.e., Ge atoms) is increasing with time. Static coalescence, when the immobile domes' perimeter lines grow together, strongly depends on islands' density<sup>2</sup> and has been reported as the primary factor for the formation of superdomes at relatively low growth temperatures.<sup>30,40</sup> In contrast, the chemical etching revealed a unique profile for the superdomes in annealed sample B (Figure 3c). Upon annealing under H<sub>2</sub>, these superdomes grow at the expanse of the surrounding domes, resulting in a nonuniform Si-rich shell<sup>41</sup> and a Ge-rich core that was removed by the selective etching. The surface diffusion of Ge and Si atoms, combined with intermixing, ends in the profile shown in Figure 3c. The growth of the incoherent islands during the ripening process depends primarily on its original size and composition. During OR, the superdomes consume the small islands in their surroundings by surface diffusion through the



Figure 3. (a) NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> selective chemical etching calibration. The solution was calibrated by measuring the amount of alloy removed in a series of  $\text{Ge}_x\text{Si}_{1-x}$  alloyed thin films with x = 0.34, 0.60, 0.74, 0.90,and 1.00. Note that the etching preferentially attacks Ge-rich alloys. Atomic force microscopy images (AFM) of samples (b) as-grown A and (c) annealed B after 128 min of exposure to the selective wet chemical etch. The boxes (squared area on the top of each image) show the region corresponding to a superdome after Ge-Si alloy complete removal by the etching. In both cases, the superdomes were initially formed by the coalescence of a few domes that were close enough to each other during Ge deposition (two domes for sample A and three domes for sample B), as revealed by the AFM images. For sample annealed B, significant ripening occurs through surface diffusion during annealing, resulting in a unique profile. The dashed circle in (c) delimits Ostwald ripening domain for the superdome shown. (d) Ostwald ripening radius of capture as a function of superdome diameter for sample annealed B, showing a linear dependence. The AFM images correspond to an area of  $2.0 \times 1.5 \,\mu m^2$ .

wetting layer, resulting in a region poor in dome-shaped islands, as pointed out by the dashed circle in Figure 3c. This region corresponds to the radius of capture of OR, which delimits the



Figure 4. Atomic force microscopy (AFM) images of representative superdomes from samples (a) as-grown A and (b) annealed B after exposure to the NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> calibrated selective wet chemical etching. The material preserved after the etching is a Si-rich alloy. (c,d) Sequence of line scans taken after successive etching steps showing very distinct composition profiles for samples A and B (line scans are shown in gray). While the superdomes in A are uniquely formed by the coalescence of dome-shaped islands during Ge deposition, superdomes in B result from coalescence combined with ripening by surface diffusion. The color scale represents the Ge fraction for the Ge<sub>x</sub>Si<sub>1-x</sub> alloy constituting the superdomes shown in (a) and (b). Ge average content is 0.65 and 0.54 in fraction for samples A and B, respectively. The AFM images correspond to an area of  $500 \times 500 \text{ nm}^2$ .

vicinity within which ripening will take place; it depends linearly on the superdome diameter, as shown in Figure 3d. The diameter and height growth of the superdomes are, therefore, interconnected.

The images on the boxes of Figure 3b and c correspond to superdomes after complete Ge-Si alloy removal. The profiles are similar, proving that in both cases the superdomes are originally formed by the static coalescence of a few domes during Ge deposition (two domes for sample A and three domes for sample B). Generally, coalescence and OR do not occur simultaneously; the first process refers to an early stage of growth, while ripening happens in a late growth stage. Coalescence is caused by additional arriving material, which occurs during Ge deposition. The dark area, a 1 nm deep trench region, corresponds to a Ge-Si alloy that composed the wetting layer underneath the superdome<sup>42</sup> plus the top layer of the substrate, which has a modified composition due to stress-enhanced diffusion. This region was removed by the chemical etching. This result indicates that during the Ge deposition and annealing, intermixing takes place not only within the islands but also at the wetting layer subsurface<sup>25</sup> corresponding to an area occupied by a superdome.

**Chemical Composition of Nanocrystals.** To determine the composition profile of the superdomes in samples as-grown A and annealed B, successive selective (calibrated) etching steps were performed on the same representative island of each sample. By using this technique,<sup>43</sup> we were able to elucidate how intermixing process and surface diffusion from the wetting layer modify superdomes' final composition profile and to determine its average Ge final content. Figure 4 shows one



Figure 5. Average Ge content as a function of superdome volume for annealed sample B determined by the calibrated  $NH_4OH:H_2O_2$  selective chemical etching shown in Figure 3. To minimize the total energy, ripening occurs privileging the formation of alloyed islands with Ge content equal to 0.5 in fraction, independent of superdome size.

representative superdome for each sample, together with a sequence of line scans (in gray) on the same islands taken after each selective etching step. Therefore, each line scan corresponds to  $Ge_xSi_{1-x}$  alloyed layers that were preserved after the etching attacks. Besides the distinct composition profiles, the superdomes also presented different average Ge content, as revealed by the selective etching experiments. Assuming a cylindrical symmetry for the composition profiles shown in Figure 4c and d, the average Ge fraction for the superdomes in samples A and B was 0.65 and 0.54, respectively. Sample as-grown A is composed of a Ge-rich shell and three Si-rich cores with well-defined boundaries (Figure 4a), resulting from domes' coalescence, which has been shown to be the dominant pathway for dislocation nucleation for relatively low growth temperatures.<sup>30</sup> The introduction of dislocations in the superdomes allows for more Ge incorporation within the incoherent island.

Conversely to sample A, the superdome in sample annealed B results from the original coalescence of dome-shaped islands combined with the OR process. During ripening, the diameter of this superdome expanded over 80% as compared to A, while its height increased only by 30% (see Figure 4c and d for comparison). When Si and Ge surface diffusion takes place through the wetting layer during annealing,<sup>25</sup> the Si atoms preferentially accommodate at the island shell, close to superdome's base. In opposition, Ge atoms diffuse to the superdomes' top, as a direct consequence of higher diffusion length or strain relief. The footprints left by the domes that participate in the OR process can be seen in the AFM image of sample B (Figure 4b). These results demonstrate that the domes surrounding a superdome are consumed if their size is smaller than the critical size  $(r_{\rm c})$  corresponding to the superdome and if they are within the OR radius of capture. Although both Si and Ge atoms participate in OR process, superdome's final composition profile is determined by the intermixing that occurs within the island to maximize the entropic term of dr/dt and minimize the overall energy, as previously discussed.

Figure 5 shows the average Ge content for sample annealed B as a function of superdomes' volume. Independent of its size, the average Ge content is approximately 0.5 in fraction. The superdomes with x > 0.5 have not reached the equilibrium yet (10 min of annealing is not enough time). To lower the system overall energy, Ostwald ripening takes place, privileging a certain composition profile that corresponds to a Ge<sub>0.5</sub>Si<sub>0.5</sub> alloy.



Figure 6. Schematic of superdomes' formation and intermixing process during Ostwald ripening phenomenon in incoherently strained Ge-Si epitaxial islands. (1) Dome-shaped islands are initially formed by Stranski-Krastanov growth method to relieve elastic energy. A Ge-rich shell and a Si-rich core are usually observed. The wetting layer is formed by a Ge–Si alloy. (2) Depending on the distance between the domes, the coalescence of a few domes during Ge deposition leads to superdomes' formation, preserving the Si-rich core and Ge-rich shell of the original domes (represented by dashed lines). (3) During annealing, the domes close to a superdome dissolved by surface diffusion and the material is incorporated into the larger island, as a result of Ostwald ripening phenomenon. (4) Simultaneously, Ge atoms preferentially incorporate at the superdome top, and intermixing takes place to minimize the overall energy of the system. The resulting superdome chemical composition profile (Si-rich shell and Ge-rich top) is a snapshot of the system's approach to equilibrium.

This experimental result is in agreement with our thermodynamicbased model, which predicts that x = 0.5 island corresponds to the minimum energy due to entropy maximization.

Figure 6 summarizes the superdomes' formation by coalescence and its approach to equilibrium through intermixing during OR. Dome-shaped islands with a Ge-rich shell and a Sirich core are initially formed during Ge deposition to relieve strain (1).44 Depending on the density of these coherently strained islands, they coalesce, forming superdomes (2). These dislocated islands are composed of a Ge-rich shell surrounding the Si core of the original domes. During postgrowth annealing under hydrogen, the OR process takes place (3) together with surface diffusion and island intermixing. Dome-shaped islands that are surrounding the superdomes are consumed if their size is smaller than the critical radius  $r_{\rm c}$  and if they are within the OR radius of capture, resulting in island's growth. Surface diffusion through the wetting layer is the primary mechanism for domes' dissolution, as observed in our selective etching experiments. As a consequence, it is expected that the wetting layer composition is constantly changing during ripening. In fact, independent X-ray diffraction<sup>40</sup> and in situ scanning tunneling microscopy<sup>20</sup> experiments were used to inspect the wetting layer modifications during annealing, as predicted by Monte Carlo

calculations.<sup>42</sup> During annealing, a significant amount of Ge  $(1-3 \text{ ML})^{39,40}$  is transferred between the wetting layer and the nanocrystals. Simultaneously, intermixing happens within the superdome (4). The unique final composition profile of the annealed islands corresponds to a Si-rich outside ring and a Gerich top with an average Ge content close to 0.5 in fraction, which maximizes entropy. More intermixing (i.e., more annealing time) would lead to an alloyed island with Ge average content of 0.5 in fraction, which minimizes the overall energy.

### CONCLUSIONS

Summarizing, we have presented the contribution of intermixing to Ostwald ripening phenomenon in a two-components system  $(A_x B_{1-x})$ . By considering the mixing entropy term  $(TS_M)$ to the particles' growth rate general equation (dr/dt), it was found that ripening preferentially occurs in alloyed particles and is highest when entropy is maximized (A<sub>0.5</sub>B<sub>0.5</sub>). Our thermodynamic-based model explains the experimental results observed in Ge-Si incoherent epitaxial islands, a quasi-ideal mixture system. The Ge-Si superdomes are initially formed by the coalescence of a few dome-shaped islands during Ge deposition. Throughout in situ annealing under hydrogen, ripening takes place through Ge and Si surface diffusion, leading to superdomes growth and a modified composition profile, revealed by successive selective etching steps on the same superdome islands. This change in composition occurs as a direct consequence of alloying, which happens to boost the mixing entropy and minimize the system's overall energy. Our model is general and can be applied to any nanoscale mixture system with similar conditions and can be used to tune its final chemical composition.

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