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Chemical Thermodynamics of the Size and Shape of Strained Ge Nanocrystals Grown on Si(001)

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Introduction

The ability to create architectonic materials, for which the electronic, magnetic, optical, and/or mechanical properties are designed for a specific task by assembling an "unnatural" structure from chemically different components, is currently most advanced in the area of semiconductor heteroepitaxy. Those practicing this art have usually chosen to deposit films of one semiconductor onto another with atomic structures and lattice constants as nearly identical as possible to avoid complications caused by introducing strain in the resulting system. However, the feasibility of growing an overlayer on a substrate with a significantly different lattice constant greatly expands the space of materials properties to explore and also introduces a new parameter, the lattice misfit

$$\epsilon = (a_O - a_S)/a_S \tag{1}$$

where a_O and a_S are the lattice constants of the overlayer material and substrate, respectively, which can in principle be tuned to yield an entirely new range of structures and properties. Epitaxial films grown under stress initially store energy by elastically adopting the in-plane lattice parameter of the underlying substrate to remain flat. Eventually, a portion of the stored strain energy is released, either through introducing crystal defects into the overlayer by a plastic relaxation[1,2] or by roughening of the surface of the film.[3,4]

The deposition of Ge onto Si(001), for which $\epsilon = 0.042$, has been described as a classic Stranski−Krastanow (SK) process.[5] The SK model presumes that a uniformly strained film (the wetting layer) grows pseudomorphically on the substrate to a certain thickness, with further deposition leading to the growth of three-dimensional islands on top of the uniform film. Interest in this system increased dramatically after two reports appeared in 1990 in which island formation occurred when 3−8 equivalent monolayers (eq-ML) of Ge was deposited on nominally 500 °C Si(001) substrates. Although these are among the most well-known and often cited studies of SK growth, the results reported by the two groups were remarkably different. Using transmission electron microscopy (TEM), Eaglesham and Cerullo[6] observed "dome-shaped" nanocrystals of Ge as large as 140 nm in diameter and 50 nm high that were "coherently strained" on the substrate (i.e., any relaxation was totally elastic since the islands contained no defects). Larger islands contained crystal defects, dislocations, that were presumably caused by a plastic relaxation of the islands as they grew beyond some critical size. Even though their experimental growth conditions were nominally the same, Mo et al.[7] reported entirely different nanocrystal shapes, primarily rectangular-based "huts" bounded by {105} facets, from their scanning tunneling microscopy (STM) studies.

The behavior of Ge on Si(001) is considerably more complex than that of the idealized SK model.[5] At temperatures of 550 and 600 °C, experiments from this laboratory[8−10] have revealed three distinct island shapes, which we will give the descriptive names pyramids, domes, and superdomes (see Figures 1 and 2). As can be seen in the atomic resolution STM images of Figure 3, the pyramids are a special case of a hut with a square base and four equal-area {105} facets, whereas the domes are actually-

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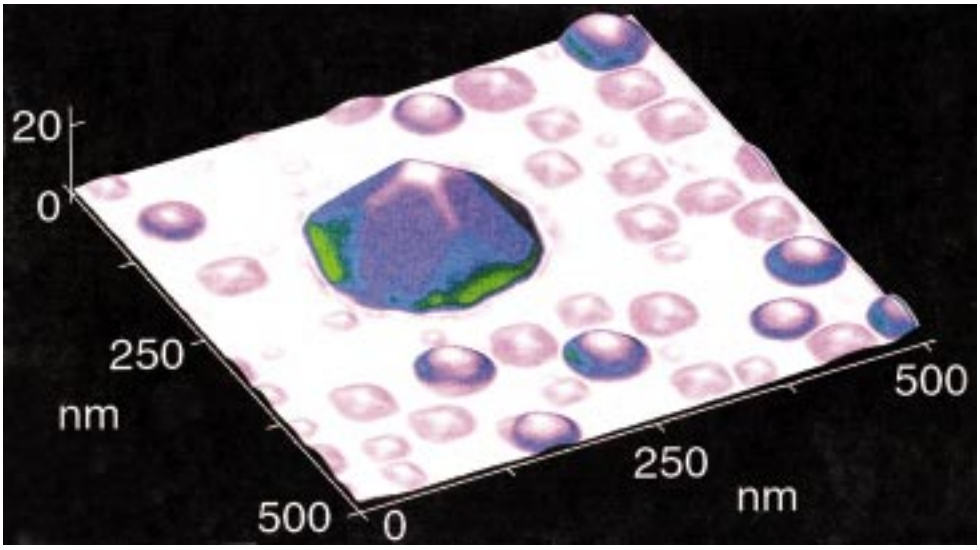

FIGURE 1. An AFM topograph showing the three different types of Ge islands observed on Si(001) at a temperature of 550 °C: pyramids, domes, and a single superdome. This particular example is a 500 nm × 500 nm image for a 13 eq-ML Ge overlayer deposited by CVD at 550 °C and annealed for 30 s. The color scale corresponds to the angle between a given area and the substrate surface plane: white is the (001) plane, with magenta corresponding to {105} facets, blue to {311} and {518} facets, and green to {111} and other steep facets (on the lower edge of the superdome).

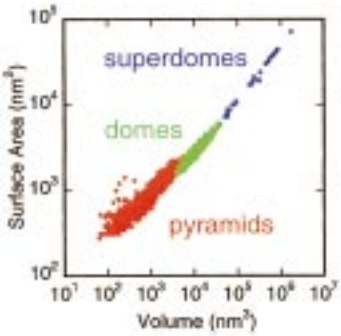

FIGURE 2. A log−log scatter plot of the total facet area of every Ge pyramid (red), dome (green), and superdome (blue) versus the volume of that island, obtained by integrating over the islands in several AFM topographs of the same sample shown in Figure 1. Each island family forms a distinct cluster in the plot, although for this case the resolution of the images was not sufficient to clearly separate the pyramid and dome distributions. All three shape ensembles have a slope of 2/3, but each shape has a different characteristic "*y*-intercept" or vertical offset.

multifaceted structures dominated by {311} and {518} facets but also exhibiting small but distinct {105} and (001) facets as well. The superdomes, the largest islands that have been given several different names by other researchers, are very similar in shape to the domes but have in addition {111} and other steep facets at the boundary with the substrate. There are transitions between the different island shapes with changes in Ge coverage and substrate temperature, and the superdomes also contain one or more dislocations.[6,8] In the temperature range cited above, the rectangular-based huts of Mo et al.[7] are metastable with respect to square-based pyramids, which in turn can survive long annealing cycles even in the presence of larger islands.[10]

All Ge islands on Si(001) are only metastable with respect to alloying with the substrate, as observed recently by Kamins et al.[11] The rate of diffusion of Si into the Ge islands is quite rapid at 650 °C, approximately 20 times faster than at 600 °C, which corresponds to an activation energy for the alloy formation of about 4.2 eV. Alloying must be considered carefully when the growth and annealing of Ge islands are examined, since even a small change in the composition of an island can have a dramatic effect on its strain energy and thus its characteristic volume, which scales as ϵ^{-6}.[12] Thus, the data from experiments that have been performed at substrate temperatures ≥650 °C are significantly complicated by the fact that the composition of the islands is changing appreciably during deposition and annealing, which has not been considered in the interpretation of previous results. The true equilibrium state after very long annealing is essentially a Si substrate with a dilute concentration of Ge that has diffused throughout the sample, so any discussion of the stability of strained nanocrystals must be qualified by the temperature and time scale of the observations.

To utilize lattice-mismatched heteroepitaxy as a potential technology for the "self-assembly" and "self-organization" of oriented and coherent nanocrystals on a substrate, it is necessary to control the shape, the average size, and the size distribution of the islands, since these factors will determine the properties of an island ensemble. Two very different views of the growth and evolution of Ge nanocrystals on Si have emerged that have considerably different consequences for the rational design of strained nanocrystal arrays. One model[12,13] is that the island sizes and distributions are dominated by the kinetic process of Ostwald ripening,[14] whereas the other states that the islands are essentially in thermodynamic (or at least metastable) equilibrium with each other.[9,15−17] If island evolution is essentially a kinetic process, the

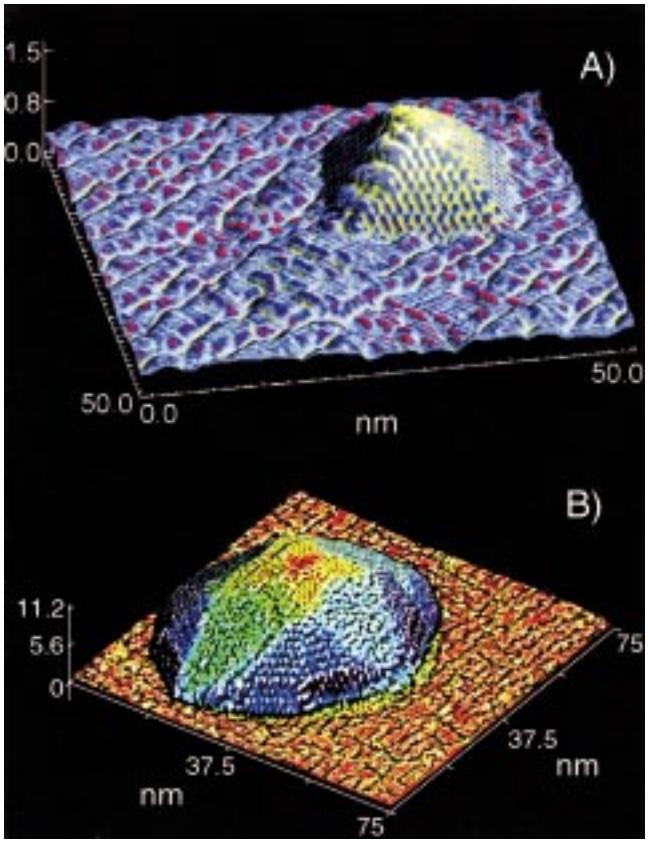

FIGURE 3. (A) An atomic-resolution 50 nm × 50 nm STM topograph of a Ge pyramid grown by PVD on a 600 °C Si(001) substrate. This is one of the smallest 3D structures found (it contains ~2000 Ge atoms) out of over 10^6 islands measured. We have never observed a 2D Ge platelet or monolayer island large enough to act as a precursor for such a structure. The color palette is keyed to the Laplacian at each point on the topograph to reveal the local curvature. (B) An atomic-resolution 75 nm × 75 nm STM topograph of a Ge dome grown by PVD on a 600 °C Si(001) substrate. The color palette is keyed to the local surface angle with respect to the horizontal plane to distinguish the different crystal facets.

attempts by researchers to grow stable and uniform nanostructures on surfaces by chemical self-assembly may be impossible, whereas if the islands are at least quasi-equilibrium structures, then they should be stable for some significant amount of time.

The next section highlights a small subset of experimental observations from this laboratory that have been reported in more detail in separate publications.[8−11,18,19] The following section describes Ostwald ripening and some of the observations regarding Ge on Si(001) that relate to kinetic models. The rest of this Account is devoted to the exposition of a simple equilibrium model to better understand the size distributions of the nanocrystals. In this chemical thermodynamic treatment, the Ge islands are regarded as giant molecules adsorbed on the substrate surface. This model is consistent with both the observed nanocrystal size distributions and the long-term stability of mixed populations of pyramids and domes with respect to annealing at 550 °C.

Summary of Experimental Observations

We have performed a wide variety of experiments aimed at understanding the growth behavior and the stability of strained nanocrystal islands. These include deposition of Ge overlayers by physical vapor deposition (PVD) in ultrahigh vacuum (UHV) followed by in situ analysis with atomic-resolution STM and growth by chemical vapor deposition (CVD) using GeH_4 in an H_2 ambient followed by ex situ imaging with atomic force microscopy (AFM). When the results of these two types of experiments are compared for approximately the same substrate temperature, growth rate, and amount deposited, the island shapes, sizes, and populations are quite similar (within the limits of the differences in resolution between STM and AFM). The similarities are remarkable given that the background pressures during Ge overlayer growth differed by 11 orders of magnitude and the CVD samples were exposed to air before measurement. This observation favors an equilibrium interpretation for nanocrystal growth, as the Ge atom deposition kinetics differ significantly for the two growth techniques. Another important observation is that the shape transition from pyramids to domes is reversible, as shown by etching of Ge domes back to pyramids by HCl gas at the same temperature at which they were originally grown.[18] A high-resolution STM image of a sample with both pyramids and domes grown by PVD at 600 °C is shown in Figure 4, and the corresponding histogram of island volumes for this sample is in Figure 5.

Ostwald ripening is best characterized for a mass-conserving system, where the total amount of deposited material is held constant for a sequence of annealing times. We have deposited 8 eq-ML of Ge on Si(001) substrates at 550 °C by CVD.[10] Immediately after a Ge overlayer was deposited, each sample was annealed at the growth temperature for a different time inside the growth chamber in H_2 and then cooled rapidly to room temperature. Analysis of similarly grown and annealed series of samples by Rutherford back-scattering (RBS) has shown that the amount of Ge deposited by CVD is highly reproducible and does not change during annealing. These samples were also examined ex situ using AFM to quantitatively determine the size and shape distributions of the nanocrystals. The analysis of an annealing sequence allowed us to investigate the temporal evolution of the various nanocrystal morphologies and ascertain their long-time stability. The results of one such experiment[10] are illustrated in Figure 6, which shows the average volumes of the pyramids and domes annealed at 550 °C as a function of time, along with the total integrated volume of all the islands on the surface. Note that the absolute values of the integrated volumes are only approximate because of the resolution of the AFM topographs and are not to be compared quantitatively with the total equivalent thickness measured by RBS.

Here we see that, initially, the average size and the relative populations of the pyramids and domes evolved rapidly, but after 10 min of annealing, the system stabi-

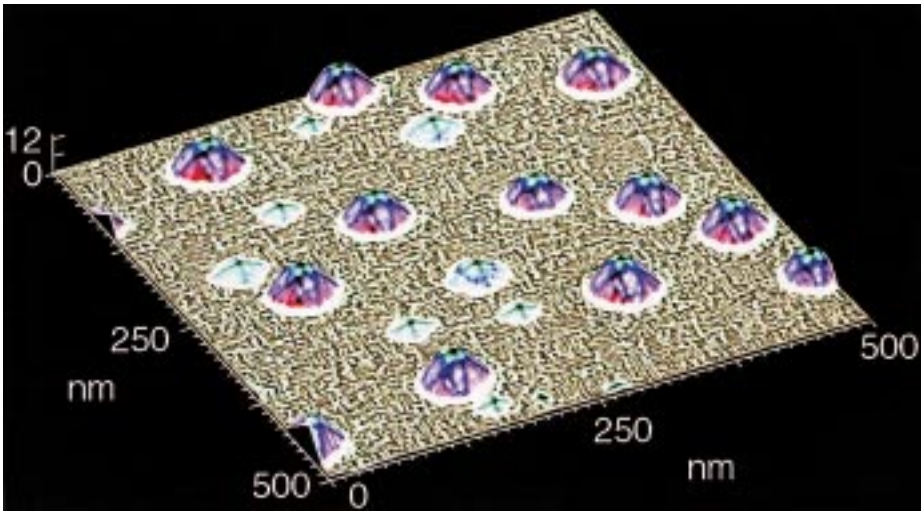

FIGURE 4. A high-resolution 500 nm × 500 nm STM topograph of Ge pyramids and domes grown by PVD on a 600 °C Si(001) substrate. In this image, the different facets are keyed to different colors and the edges of the facts are enhanced by including a component of the local Laplacian in the image. The domes display a complex network of edges that separate the various facets of the structure.

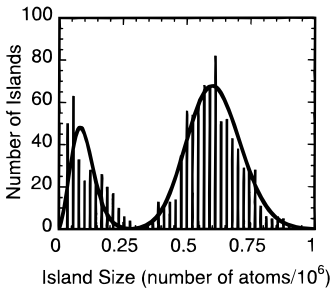

FIGURE 5. The histograms are the experimentally measured volume distributions of the pyramids and domes measured from high-resolution STM topographs of the same sample as Figure 4. The solid lines are the fits to the experimental data using eq 11.

lized and thereafter pyramids and domes coexisted with each other on the surface up to the maximum observation time of 80 min. This is an excellent indication that the two types of islands are stable with respect to each other. The temporal profile of the coarsening of the island distribution corresponded to the increase in the total integrated island volume, which shows that Ge was still being incorporated into the islands during the initial stage of the annealing process. This coarsening during growth can be explained in terms of interisland repulsions causing the island population to shift toward domes during growth because they contain more atoms per unit surface area than pyramids.[19]

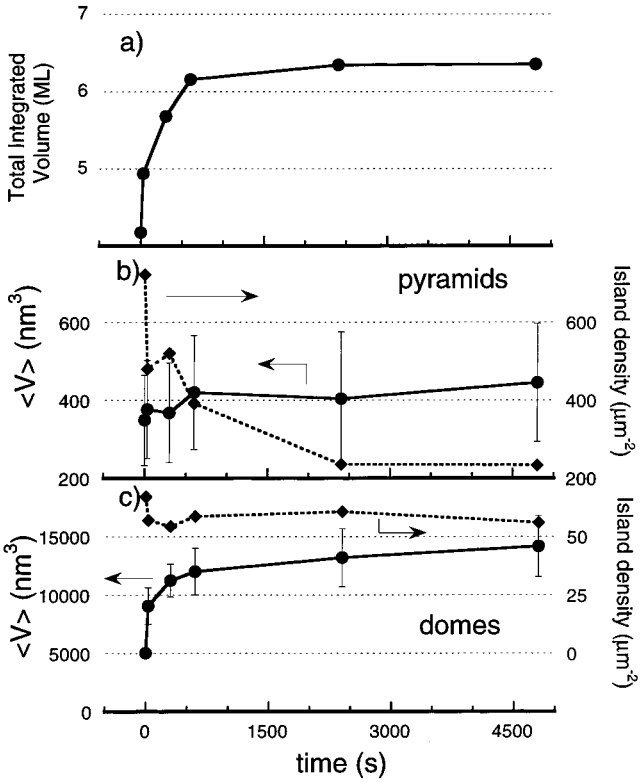

FIGURE 6. (a) Total integrated volume, (b) average volume and island density for pyramids, and (c) average volume and island density for domes as a function of annealing time for 8 eq-ML of Ge deposited by CVD on 550 °C Si(001) substrates.

Kinetic Models of Island Growth

Ostwald ripening[14] is the coarsening of a particle size distribution driven by the Gibbs–Thomson effect.[20,21] Lifshitz and Slyozov[22] and later Wagner[23] developed an analytical mean-field theory (LSW theory) for particle evolution in a (3D) solution, which was later extended to islands on surfaces by Chakraverty.[24] These Ostwald ripening models incorporate a driving force that depends on the inverse of the radius of curvature of an island. Atoms detach more readily from smaller islands, which have a higher "vapor pressure", and condense more readily on larger islands. For a constant amount of material in islands, larger islands grow at the expense of smaller islands, and the size distribution broadens with time as the number density of islands on the surface decreases.

Analytical expressions for the time-dependent island size distributions provide explicit predictions about both the spatial and temporal evolution of the islands.[14] For LSW theory, the average and the standard deviation of the island volume both increase linearly with time t, while the

number density of islands on the surface decreases as t^{-1}. For Chakraverty theory, the average and standard deviation of the island volume increase as $t^{3/4}$ while the island density decreases as $t^{-3/4}$. Investigators often fit an experimentally obtained island radius distribution with an LSW or Chakraverty distribution[25] or plot the average island radius raised to some power versus time[26] to determine if Ostwald ripening has occurred and to determine the mechanism involved.

The most convincing experimental evidence and theoretical justification for the applicability of the Ostwald ripening model to Ge on Si(001) appeared in the recent paper of Ross et al.[13] Using an elegant real-time TEM procedure, they observed that as additional Ge was added to a Si surface populated with islands, many of the smaller islands in the distribution actually shrunk and eventually disappeared. This experimental observation was compared with calculated behavior expected for a system in which both pyramids and domes evolve by Ostwald ripening, with the free energy curve for the domes crossing that of the pyramids to become the lower free energy structure at larger island volume. The qualitative agreement between the simulation and the experimental data was reasonable, but the experimental data also displayed an apparent limiting size for the islands, which could be interpreted in terms of an equilibrium state of the system.

Several researchers have noted that the size distribution of Ge islands on Si(001) is narrower and more symmetric than expected for an Ostwald ripened distribution, and this has led to several suggestions for modified kinetic models for strained nanocrystal growth. Drucker[27] has proposed that the incipient creation of a defect in an island may create a barrier to further material incorporation, thus decreasing the growth rate of larger islands and causing a narrowing of the size distribution. Jesson et al.[28] have suggested that narrowing of the distribution results from an energy barrier to add atoms to the facets of the islands, while Chen and Washburn[29] and Goldfarb et al.[30] have both postulated a size-dependent barrier for the attachment of atoms to the boundary of an island. Kamins and Williams[31] have shown that, for an LSW model modified to include a kinetic barrier to atom attachment, the distribution of island sizes can collapse to a single island volume in the absence of noise. Priester and Lannoo[32] have presented a model in which a narrow equilibrium distribution of 2D monolayer islands transforms into 3D structures, thus initiating the uniform ensemble of nanocrystals. Each of these mechanisms should have a significant effect on island size distributions and temporal evolution, which in turn may act as signatures for their presence.

Chemical Thermodynamic Model

Since Ge on Si has $\epsilon = 0.042$, the most important energetic issues that influence the island size distributions are the effects of crystallinity and strain. The elastically strained Ge islands are compressed at the interface to nearly match the lattice constant of Si, but near the top of the islands the relaxation to the lattice constant of Ge may be nearly complete.[33] The Si substrate is somewhat deformed, especially near the edges of an island.[34−36] These forces make the energy of the islands a nonlinear function of volume.[36] Shchukin et al.[15,16] presented an energetic model for lattice-mismatched heteroepitaxy, which for some systems can display a minimum in the energy of island ensembles that would act to stabilize the distribution at a particular island size. The detailed STM measurements of Ge island sizes of Medeiros-Ribeiro et al.[9] were consistent with Boltzmann distributions, in agreement with the energetic model[15] broadened by finite temperature effects. This report also showed that the pyramids and domes each had distinct and nonoverlapping size distributions that were presumably in equilibrium with each other. The model used by Priester and Lannoo[32] to determine the size distribution of their postulated precursor 2D islands (which are not observed experimentally[37,38]) also utilized a size-dependent free energy with a minimum and a Boltzmann-like distribution, but these authors did not consider such a possibility for the 3D nanocrystals.

Here we present a modified and more detailed analysis of the equilibrium distribution[9] of nanocrystal sizes. First, consider the general case of two islands in equilibrium with each other

$$\mathbf{I_X}(m) \leftrightarrow \mathbf{I_Y}(n) \tag{2}$$

where $\mathbf{I_X}(m)$ is an island with shape **X** containing m atoms and similarly for $\mathbf{I_Y}(n)$. The first issue that we notice about this chemical equation is that it is not balanced, and thus any thermodynamic expression based on eq 2 will violate conservation of mass. To balance this chemical equation, we can either multiply the left-hand side by n and the right-hand side by m to produce an equation involving $m \times n$ atoms, or more simply rewrite eq 2 in the following form:

$$m^{-1}\mathbf{I_X}(m) \leftrightarrow n^{-1}\mathbf{I_Y}(n) \tag{3}$$

to express the reaction in terms of a single atom, which is possible because the "reactant" and "product" species contain only Ge. Now we express the difference in the standard free energies of the islands implied by the chemical reaction of eq 3:

$$\Delta F^\circ = n^{-1}F^\circ_{\mathbf{Y}}(n) - m^{-1}F^\circ_{\mathbf{X}}(m) \tag{4}$$

where $F^\circ_{\mathbf{X}}(m)$ is the standard (or internal) free energy of formation of $\mathbf{I_X}(m)$. Note that the "normalized" values of the standard free energies in eq 4 are necessary to maintain mass conservation, which acts as a thermodynamic constraint on the system. The change in the total free energy for a system with ensembles of islands $\mathbf{I_X}(m)$ and $\mathbf{I_Y}(n)$ is

$$\Delta F = \Delta F^\circ + k_B T \ln[\omega_{\mathbf{Y}}(n)^{1/n}/\omega_{\mathbf{X}}(m)^{1/m}] \tag{5}$$

where k_B is Boltzmann's constant (since we are considering the reaction on a per atom instead of a per mole basis) and $\omega_{\mathbf{X}}(m)$ is the population or number density of islands

$\mathbf{I_X}(m)$ on the surface. Equation 5 includes both the internal free energies of the islands and the entropy of mixing for the island ensembles on the surface.[20,21] At equilibrium, $\Delta F = 0$ and eq 5 provides an explicit relationship between $\Delta F°$ and the equilibrium constant

$$K_{\mathbf{X,Y}}(m,n) = \omega_{\mathbf{Y}}(n)^{1/n}/\omega_{\mathbf{X}}(m)^{1/m} \tag{6}$$

for the two island shapes and/or sizes.

If we choose the standard state to be that of an isolated island (or more exactly one island per unit area of surface under consideration), then we can use an equation similar to the one derived by Shchukin et al.[15] to determine the size-dependent standard free energies of the islands:

$$F°_{\mathbf{X}}(m) = C_{\mathbf{X}}m + B_{\mathbf{X}}m^{2/3} + A_{\mathbf{X}}m^{1/3} \tag{7}$$

The Shchukin et al.[15] expression for the energy of a strained nanocrystal on a lattice-mismatched substrate explicitly includes the bulk strain inside the island, the island facet and interface energies, and the elastic interaction of the edges, where $F°_{\mathbf{X}}(m)$ is actually the difference between the free energy of the elastically strained (and defect-free) nanocrystal that contains m atoms and the free energy of those m atoms if they formed a single strained monolayer (2D island) on top of the Ge wetting layer. $A_{\mathbf{X}}$ is a positive coefficient determined by the magnitude of the edge energy (the logarithmic term from ref 15 has been dropped, since it has a relatively minor effect on eq 7 and we want as few fitting parameters as possible), $B_{\mathbf{X}}$ is determined primarily by the nanocrystal facet and interface energies, and $C_{\mathbf{X}}$ is a negative coefficient determined by the bulk energy of the atoms in a strained nanocrystal with respect to those in a pseudomorphic 2D island on top of the wetting layer. The coefficient $B_{\mathbf{X}}$ contains two competing contributions, and the net facet and interface contribution to the free energy of a strained nanocrystal can be either positive or negative.[16,17]

The properly "normalized" free energy required for computing $\Delta F°$ in eq 4 is

$$m^{-1}F^0_{\mathbf{X}}(m) = C_{\mathbf{X}} + B_{\mathbf{X}}m^{-1/3} + A_{\mathbf{X}}m^{-2/3} \tag{8}$$

A local minimum for eq 8 is assured if $B_{\mathbf{X}}$ is negative. The size of the shape **X** nanocrystal with the lowest internal free energy per atom can be found by minimizing eq 8 to yield

$$m_0 = -(2A_{\mathbf{X}}/B_{\mathbf{X}})^3 \tag{9}$$

To make m_0 as small as possible to utilize the strained nanocrystals as quantum dots, the facet energy ($B_{\mathbf{X}}$) must be negative and large in magnitude and the edge energy ($A_{\mathbf{X}}$) must be small.

Equilibrium Size and Shape Distributions and the Free Energy Surface

We choose the sample grown by PVD displayed in Figure 4, which contained only domes and pyramids, to illustrate the equilibrium size distributions within each shape. If we substitute eq 7 into eq 5, and compare the number density of an arbitrary nanocrystal size m to m_0, the nanocrystal of the same shape with the lowest internal free energy, we obtain

$$m^{-1}\ln[\omega_{\mathbf{X}}(m)] - m_0^{-1}\ln[\omega_{\mathbf{X}}(m_0)] = -(k_BT)^{-1}(B_{\mathbf{X}}m^{-1/3} + A_{\mathbf{X}}m^{-2/3} - B_{\mathbf{X}}m_0^{-1/3} - A_{\mathbf{X}}m_0^{-2/3}) \tag{10}$$

We see that the size distribution for a particular shape is independent of the bulk energy $C_{\mathbf{X}}$ of the strained nanocrystals. Substituting eq 9 into eq 10 yields

$$m^{-1}\ln[\omega_{\mathbf{X}}(m)] - m_0^{-1}\ln[\omega_{\mathbf{X}}(m_0)] = -(k_BT)^{-1}(B_{\mathbf{X}}m^{-1/3} + A_{\mathbf{X}}m^{-2/3} + B_{\mathbf{X}}^2/4A_{\mathbf{X}}) \tag{11}$$

Figure 5 shows a comparison of the measured island size distributions with those calculated for pyramids and domes using eq 5 after finding the facet and edge energy parameters by fitting the experimental data to eq 11. Note that only two fitting parameters are required for each nanocrystal shape. Here the entropy of mixing is viewed as the factor that broadens the size distribution, whereas the earlier procedure[9] to find the parameters in eq 8 from the nanocrystal size distributions considered the size fluctuations of the nanocrystals to be the origin of the entropy of the ensemble. The details are somewhat different, but the end results are very similar.

Having obtained the free energy parameters that determine the size distributions for each shape, one can find the free energy difference between the shapes. For this purpose, we return to the more general form of eq 4. In principle, one can determine the energy difference between two shapes by comparing the relative populations of any size island from each shape. However, to simplify the issue, we specifically choose m_0 to be the size of the lowest internal free energy pyramid (shape **X**) and n_0 to be the size of the lowest internal free energy dome (shape **Y**). With this choice, eq 5 becomes

$$n_0^{-1}\ln[\omega_{\mathbf{Y}}(n_0)] - m_0^{-1}\ln[\omega_{\mathbf{X}}(m_0)] = -(k_BT)^{-1}(C_{\mathbf{Y}} - C_{\mathbf{X}} + B_{\mathbf{Y}}^2/4A_{\mathbf{Y}} - B_{\mathbf{X}}^2/4A_{\mathbf{X}}) \tag{12}$$

which yields the value for $C_{\mathbf{Y}} - C_{\mathbf{X}}$. Without further information, it is not possible to determine explicit values for $C_{\mathbf{Y}}$ and $C_{\mathbf{X}}$, but in principle either can be chosen as the zero of the free energy scale of the system. The difference in the lowest internal free energy for islands of two different shapes will be denoted

$$\Delta F°_{\mathbf{XY}}(m_0,n_0) = C_{\mathbf{Y}} - C_{\mathbf{X}} + B_{\mathbf{Y}}^2/4A_{\mathbf{Y}} - B_{\mathbf{X}}^2/4A_{\mathbf{X}} \tag{13}$$

We have also deduced the existence of an activation barrier along the reaction coordinate for the shape change, because the base widths of the smallest domes are 20% smaller than those of the largest pyramids.[9] This barrier is assumed to be equal to the energy required to remove from a pyramid the amount of Ge, estimated to be at least 30 000 atoms, necessary to yield an intermediate structure

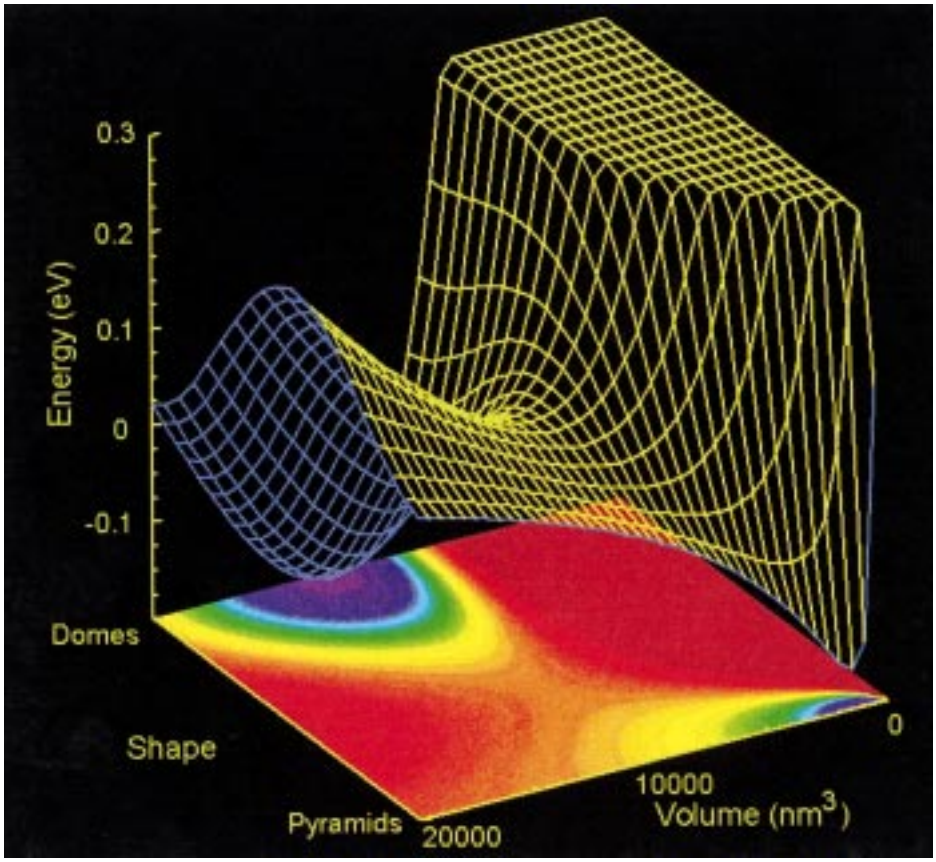

FIGURE 7. A representation of the internal free energy per atom as a function of size and shape for Ge nanocrystals on Si(001). The volume dependence for the pyramids and domes is plotted using eq 8 from parameters found by least-squares fits to the experimental data in Figure 6. The shape axis is the reaction coordinate Γ taking a pyramid ($\Gamma = 0$) to a dome ($\Gamma = \pi$). The functional form for the plot along the shape axis is $E_a \sin^2[\Gamma]$ added to the linear interpolation between the two energies of the limiting shapes at each volume. The saddle point in this free energy surface represents the transition state of the shape change.

with the same base area as a dome. Figure 7 is a qualitative representation of the internal free energy per atom for the pyramids and domes. The volume dependence of the free energy is plotted along one axis using eq 7 with the parameters determined from a least-squares fit to the island distributions. The shape dependence is plotted along a reaction coordinate Γ that takes the nanocrystals from pyramids ($\Gamma = 0$) to domes ($\Gamma = \pi$) through an intermediate transition structure. The functional form for the activation barrier is arbitrarily chosen to be $E_a \sin^2[\Gamma]$, where E_a is the energy of the transition structure estimated from the number of atoms that need to be moved to change the shape of the nanocrystal.

We can now use this model to understand the shape transition. The 2D Ge islands on top of the wetting layer act as a reservoir, and the nanocrystal ensemble is an open system that can exchange energy and atoms with this reservoir. The pyramids nucleate and grow to a maximum volume that is smaller than that for which the domes are more stable than the pyramids plus a fourth Ge monolayer on the wetting layer. After a particular pyramid has reached this maximum size, additional Ge atoms are deposited or diffuse nearby from 2D islands until the pyramid plus these reservoir atoms can form a dome, and the transition from pyramid to dome occurs relatively abruptly, as observed for a few islands in the real-time TEM studies of Ross et al.[13]

The annealing experiments at 550 °C reveal an initial rapid coarsening of the island distributions followed by long periods where the island distributions change very little (see Figure 6).[10] These observations are explained by a process of continued growth of the islands caused by transfer of Ge from an overgrown wetting layer followed by a regime where the islands are stable with respect to each other. In the cases of low substrate temperatures and/or high fluxes, the wetting layer may initially be thicker than its equilibrium value or it may contain a large number of essentially 2D islands. For the annealing experiments performed at 550 °C (Figure 6), we observed that the island evolution, particularly the increase in the average volume of the domes, was accompanied by a simultaneous increase in the total integrated island volume, indicating transfer of material from the wetting layer to the islands. As initially deposited, the Ge is in a metastable state with an overgrown wetting layer while the islands are primarily pyramids. As annealing transfers atoms from the wetting layer to the islands, the amount of Ge stored in islands increases. After the total amount of Ge stored in the islands stabilizes, the island shape and size evolution stops. Thereafter, a mixed population of pyramids and domes in close proximity to each other is

stable for long times at an annealing temperature of 550 °C. This is an excellent indication that both pyramids and domes are stable structures and that they can coexist with each other in equilibrium. At very long annealing times or higher temperatures, alloying with Si becomes important, which decreases ϵ and shifts the equilibrium for each island shape to larger volumes.[11]

The major issue that must still be addressed using an equilibrium model is how to explain the coarsening observed during growth of Ge on Si(001) by Ross et al.[13] and others. In this paper, a qualitative appeal to Le Chatelier's principle will have to suffice, but a more quantitative treatment has appeared elsewhere.[19] The strain fields induced in the Si substrate by the Ge islands lead to an interisland repulsive energy, as mentioned earlier. This repulsive energy increases with increasing Ge coverage because of the increase in the density of islands. Thus, as the population of islands increases, a smaller number of larger islands are favored over a large population of small islands because this will reduce the repulsive energy. The larger islands literally squeeze many of the smaller ones out of existence as Ge is deposited onto the surface because the larger islands store Ge atoms more efficiently. This coarsening looks like Ostwald ripening, but in fact the entire island population is in (or near) equilibrium during the entire process, and the statistical evolution of the island population stops when the Ge available for continued island growth is exhausted.

Conclusions

Ge on Si(001) is not the simple SK model system that many researchers have assumed. There are several competing factors that confuse what should be the straightforward issue of whether the islands that form during Ge deposition are kinetic or equilibrium structures. One of these factors is that the wetting layer may be overgrown during deposition, so that growth of islands can continue after deposition is halted by drawing atoms from the wetting layer.[10] Another is the fact that, with annealing, Si can diffuse into the islands to alloy with the Ge and thus shift the equilibrium distributions to larger volumes.[11] Also, it is always true that any chemical process occurring at a finite rate will be influenced by kinetics. Thus, there is no simple answer to the question of what is the dominant mechanism governing the growth of Ge islands, and any answer must be qualified by stating the history of the sample.

Perhaps because of these complications, there has been a significant debate about the relative importance of the kinetic process of Ostwald ripening and thermodynamic equilibria in the formation and growth of the various shapes and sizes of strained Ge nanocrystals on Si(001). This disagreement can only be resolved through the quantitative comparison of accurate and statistically reliable experimental data with detailed theoretical treatments of the possible mechanisms for island growth. There are several detailed mathematical models available for Ostwald ripening that predict the temporal and spatial behavior of an epitaxial island ensemble depending on various assumptions about the rate-limiting kinetic steps in the growth of islands, and it is at least possible to make quantitative comparisons of these models to experimental data.

We have adopted the viewpoint that strained nanocrystals on a substrate are essentially giant adsorbed molecules or *n*-mers containing up to 500 000 or more atoms, and have examined how the familiar concept of an equilibrium constant can be applied to understand the size distributions of the different island shapes. We have demonstrated that an equilibrium model is consistent with the observed size distributions of pyramids and domes, as measured using quantitative STM, given the size-dependent free energy expression of Shchukin et al.[15] We have also shown that, after a short-time transient, a mixed population of pyramids and domes is stable with time during long-term annealing, again indicating that both island shapes are thermodynamically stable structures.

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