Shape Transition of Germanium Nanocrystals on a Silicon (001) Surface from Pyramids to Domes

Gilberto Medeiros-Ribeiro, Alexander M. Bratkovski,
Theodore I. Kamins, Douglas A. A. Ohlberg, R. Stanley Williams*

Chemical vapor deposition of germanium onto the silicon (001) surface at atmospheric pressure and 600 degrees Celsius has previously been shown to produce distinct families of smaller (up to 6 nanometers high) and larger (all approximately 15 nanometers high) nanocrystals. Under ultrahigh-vacuum conditions, physical vapor deposition at approximately the same substrate temperature and growth rate produced a similar bimodal size distribution. In situ scanning tunneling microscopy revealed that the smaller square-based pyramids transform abruptly during growth to significantly larger multifaceted domes, and that few structures with intermediate size and shape remain. Both nanocrystal shapes have size-dependent energy minima that result from the interplay between strain relaxation at the facets and stress concentration at the edges. A thermodynamic model similar to a phase transition accounts for this abrupt morphology change.

The deposition of Ge onto Si(001) has been described (*1*, *2*) as a classic Stranski-Krastanow process (*3*), for which a uniformly strained Ge film (the wetting layer) grows pseudomorphically to a thickness of about three monolayers, followed by a transition to the growth of three-dimensional (3D) nanocrystals on top of the uniform film. Interest in this particular system, for which Ge has a 4% larger lattice constant than Si, increased dramatically with the reports in 1990 by Eaglesham and Cerullo (*1*) that the nanocrystals were free of dislocations up to some maximum size and by Mo *et al.* (*2*) that there was an intermediate phase of metastable clusters that formed before the appearance of micrometer-sized Ge crystallites. However, the nanocrystal shapes reported by the two groups were entirely different; in the former, they were rounded domes, and in the latter, they were mainly elongated "huts" bounded by (105) planes. Tomitori *et al.* (*4*) systematically determined the phase diagram of the nanocrystals for Ge depositions of 1 to 8 equivalent monolayers (1 eq-ML = 6.3 × 10^{14} atoms/cm^2); substrate temperatures of 300°, 400°, and 500°C; and typical deposition rates of 1 to 5 eq-ML/min. Their diagram revealed that different structures dominated for different deposition conditions, but that huts and domes could coexist for deposits of more than 6 eq-ML and a substrate temperature of 500°C.

This behavior is considerably more complex than that of the idealized Stranski-Krastanow model, which is primarily an empirical classification of one commonly observed growth mode out of many. The details of whether deposited material on a flat surface will form planar films, rough surfaces, or islands with particular orientations, shapes, and size distributions are still matters of significant research and debate (*5*). In particular, the fact that both thermodynamic and kinetic effects may be important in any particular system can cause considerable confusion and lack of reproducibility among research groups. The substrate preparation, temperature of the substrate, rate of material deposition, chemical form of the depositing species, and ambient conditions can all affect the growth of films and lead to dramatically different morphologies for the same combination of materials.

Kinetic limitations, in the form of low surface diffusivities or high deposition rates, can roughen a film that is energetically favored to be flat or lead to the formation of many small islands for a system in which the thermodynamically stable configuration is a single large crystallite sitting on the substrate (*5*). In the latter case, the islands are only metastable; as the growth proceeds, the smallest ones dissolve as the relatively larger ones grow. This process is known as Ostwald ripening or coarsening because both the average island size and the width of the size distribution increase with time as the number density decreases. If coarsening dominates for nanocrystal islands, the attempts by many researchers to grow stable and uniform nanostructures on surfaces by chemical self-assembly may be futile. This study was initiated to determine if any of the observed types of Ge nanocrystals on Si(001) are actually stable or if they are simply transient structures that form and eventually disappear.

Recently, Kamins *et al.* (*6*) examined the growth of Ge nanocrystals on Si(001) by chemical vapor deposition (CVD) at substrate temperatures of 550° and 600°C, Ge coverages up to 20 eq-ML, and various gas pressures and flow rates. Atomic force

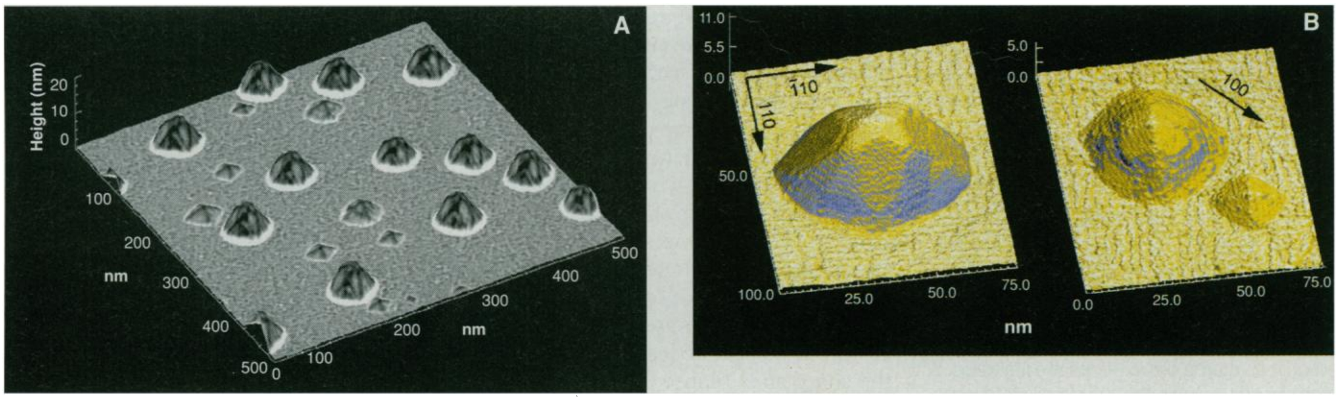

Fig. 1. (**A**) STM topograph [surface height $h(x, y)$ as a function of position] of strained Ge nanocrystals on Si(001), showing both pyramids and domes. The gray scale is proportional to the local surface curvature as determined by the Laplacian $\nabla^2 h(x, y)$: positive curvature is white, flat areas are gray, and negative curvature is black. This visualization mode emphasizes the nanocrystal edges, which appear black and clearly frame the gray facets of the nanocrystals, showing that edges contain a significant fraction of the atoms on the surface of the nanocrystals. (**B**) Higher magnification images of the nanocrystals: (left) a mature dome and (right) a nanocrystal entering the transition stage and a small pyramid.

Hewlett-Packard Laboratories, 3500 Deer Creek Road, Mail Stop 26U, Palo Alto, CA 94304–1392, USA.

*To whom correspondence should be addressed. E-mail: stan-williams@hpl.hp.com

microscope topographs of their surfaces revealed a bimodal population of nanocrystal sizes, with a significant discontinuity in the height distributions separating shorter and taller nanocrystals. A scatter plot of the diameters of the nanocrystals versus their heights for Ge coverages from 5.5 to 11 eq-ML revealed two distinct families of nanocrystals: The smaller grew with a constant aspect ratio up to a maximum height of 6 nm, and the larger formed a relatively narrow height distribution, with an average of 15 nm and a standard deviation <1 nm that was relatively independent of Ge deposition as long as both types of crystallites were present. Transmission electron microscope images showed that both types of nanocrystals were free of dislocations (6).

We investigated these nanocrystal families with higher spatial resolution and without air exposure by depositing Ge onto Si(001) using physical vapor deposition (PVD) in ultrahigh vacuum (7) and examining the nanocrystals that formed in situ with a scanning tunneling microscope (STM) to measure the surface height $h(x, y)$ quantitatively with a lateral resolution of 1.25 nm or better (Fig. 1A). Depositing the Ge onto Si(001) at approximately the same substrate temperature, deposition rate, and amounts as for the CVD studies, we obtained bimodal height distributions similar to those in (6), even though the background pressures in the two experiments differed by ~11 orders of magnitude. With the resolution of the STM, we determined that the smaller nanocrystals were square-based pyramids and the larger nanocrystals were multifaceted domes (Fig. 1B). We did not observe the elongated hut clusters (2) for the growth conditions used.

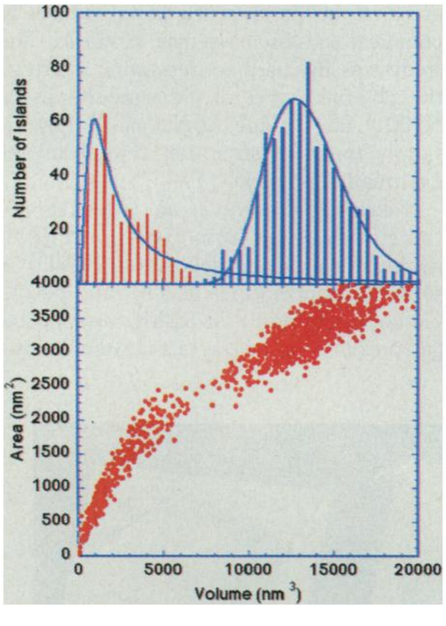

Fig. 2. Histogram of over 1000 nanocrystal volumes determined from topographs (lateral resolution of 2.4 nm) for a surface covered with 10 eq-ML Ge (top) and the corresponding scatter plot of the surface area of the nanocrystals as a function of their volume (bottom). The solid lines superimposed on the volume distributions are fits to Eq. 3. The scatter plot reveals the two families of nanocrystal shapes. The spread in the scatter plot data is mainly caused by digital noise in the measurements of the volume and the surface area resulting from the finite pixel density. The bulk density of Ge is 44.3 atoms/nm^3.

Figure 2 shows the volume histogram for over 1000 nanocrystals grown at 600°C with 10 eq-ML of Ge and the scatter plot of the nanocrystal surface area versus volume, which is an energetically relevant measure of size and shape (8). The scatter plot reveals two distinct nanocrystal shapes. There is a significant gap of nearly 2000 nm^3 in the measured volume distribution between the largest pyramid and smallest dome, which corresponds to ~90,000 Ge atoms. Examination of ~1000 nanocrystals revealed only two to four that are intermediate in size and shape between the pyramids and domes (for an example, see Fig. 1B). This gap has been reproducibly observed over many different samples and preparation procedures. Both the pyramids and domes have maximum sizes and distribution widths that are nearly independent of the amount of Ge deposited as long as both coexist (6), which indicates that in these cases, neither experiences Ostwald ripening because their free energies have local minima with respect to nanocrystal size; both are stable over some regime of surface coverage.

Tersoff and Tromp (9) predicted that a square-based pyramid should be unstable with respect to ripening and spontaneous elongation to form huts. However, at growth temperatures above 550°C, Ge (105) pyramids transformed only into domes at larger volumes. Tersoff and LeGoues (10) stated that in some cases, one could expect the formation of a series of pyramids or prisms with increasingly steep facets as the volume of the nanocrystal increased. The major dome facets we observed in our STM topographs are (113) and (102) planes, which form angles of 25.2° and 26.6°, respectively, with the (001) substrate plane, compared to 10.9° for the (105) pyramid facet. The dome shape appears to be a compromise between two nearly degenerate pyramids rotated 45° with respect to each other and with the sharp apex blunted. The dome may be more stable than a (113) or (102) pyramid with the same volume because it has less oblique, and thus lower energy, edges.

Shchukin *et al.* (11) derived an expression for the energy of a strained nanocrystal on a lattice-mismatched substrate that explicitly includes the bulk strain, the facet and interface energies, and the elastic interaction of the edges (12); we parameterized the equation in the following form

$$\Delta E(n) = Cn + Bn^{2/3} + An^{1/3}\ln(a_c/n^{1/3}) \qquad (1)$$

where ΔE is the difference between the energy of the partially relaxed (and defect free) nanocrystal that contains n atoms and the energy of those n atoms if they formed a single monolayer patch (2D island) on top of the 3 eq-ML Ge wetting layer; A is a positive coefficient determined by the magnitude of the edge energy; a_c is an elastic cutoff parameter; B is determined by the nanocrystal facet and interface energies; and C 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 contains two contributions: one (a positive facet energy) from the higher number of broken bonds on the nanocrystal facets compared with those on the wetting layer with the same area as the base of the nanocrystal, and the other (a negative contribution) that comes from the fact that the Ge atoms in a strained nanocrystal facet can relax more than those in a pseudomorphic film. Thus, the net facet contribution to the energy of a nanocrystal can be either positive or negative, depending on the specific case (11). The pyramids and domes are each described by their own set of parameters for Eq. 1, and for the domes, the parameters represent averages over many facets and edges.

However, we want to understand the behavior of an ensemble of nanocrystals on a surface, not a single nanocrystal. If N is the area density of the atoms deposited onto the wetting layer to form an ensemble of nanocrystals, then the difference in the area density of the energy between that ensemble and a uniform 2D film formed from those atoms (11) is

$$\begin{aligned}\Delta\mathcal{E}(n) &= (N/n)\Delta E(n)\\ &= N[C + Bn^{-1/3} + An^{-2/3}\ln(a_c/n^{1/3})] \qquad (2)\end{aligned}$$

where $\Delta\mathcal{E}(n)$ is the energy difference per unit area and N/n is the area density of nanocrystals, each with n atoms. Conservation of mass acts as a thermodynamic constraint on the ensemble that would be ignored when minimizing the mechanical energy of a single strained nanocrystal on a surface. A local minimum for Eq. 2 is assured if B is negative (11), that is, when the relaxation energy is greater than the facet broken bond energy. The ensemble with the most stable nanocrystals of size n_0 can be found by minimizing Eq. 2 with respect to n. Thus, the interplay between the facet ($\sim -n^{-1/3}$) and edge ($\sim +n^{-2/3}$) relaxation energies averaged over the atoms determines the characteristic size n_0 (if there is one).

If surface diffusion is fast compared with the incident flux of Ge, then the ensemble of nanocrystals may be close to equilibrium, and the distribution of nanocrystal sizes would have an approximately Boltzmann form:

$$\Omega(n) = \frac{n_0}{n}\Omega(n_0)\exp\left[\frac{\frac{\Delta E(n)}{n} - \frac{\Delta E(n_0)}{n_0}}{k_B T}\right] \quad (3)$$

where $\Omega(n)$ is the probability density of finding a nanocrystal with n atoms, $\Delta E(n_0)/n_0$ is the minimum per-atom energy of the nanocrystals from Eq. 2, k_B is the Boltzmann constant, and T is the substrate temperature during deposition. We performed least-squares fits of the observed pyramid and dome volume distributions for Eq. 2 substituted into Eq. 3 (Fig. 2).

We used the above fits to determine the volume dependence of the pyramid and dome free energies. We expect kinetic factors, especially the nucleation density of pyramids, to play a role in determining the nanocrystal size distributions, so the resulting fitting parameters are only qualitatively correct (*13*). We have also inferred 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. This barrier is assumed to be equal to the energy required to remove from a pyramid the number of atoms necessary to yield an intermediate prism structure with the same base area as a dome (Fig. 1B), which is estimated to be at least 30,000 atoms for the largest pyramids. Figure 3 is a qualitative representation of the energy for the pyramids and domes. The volume dependence is plotted along one axis using Eq. 2 with the parameters determined from the least-squares fit. The shape dependence is plotted along a reaction coordinate θ that takes the nanocrystals from pyramids to domes through some intermediate structure. The functional form for the activation barrier is chosen to be $E_a \sin^2\theta$, 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, and θ is the parameter that determines the shape of the nanocrystal. The zero of the energy scale is the energy of the atoms in a 2D island on top of the wetting layer.

We can now use this model to understand the observed shape transition. The 2D Ge islands on top of the wetting layer act as a reservoir; the nanocrystal ensemble is an open system that can exchange energy and atoms with these islands. The pyramids nucleate and grow to a maximum volume that is smaller than the volume 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 the maximum size, additional Ge atoms that are deposited or diffuse nearby form 2D islands until the pyramid plus these reservoir atoms can form a dome, and the transition from pyramid to dome occurs relatively abruptly.

The process is conceptually similar to a structural phase transition, for instance, when a solid transforms into a different crystal structure under applied pressure (*14*). It is possible to exceed the phase transition pressure because the movement of all the atoms required to form the new crystal imposes a significant activation energy barrier to the transition. A fluctuation in the system allows the transition to take place, and then it occurs quickly. Similarly, in the present case, Ge atoms are continually diffusing back and forth between a critical-size pyramid and the surrounding 2D islands, and a large enough fluctuation in the number of atoms arriving at the pyramid can cause a shape transition to a larger volume dome.

Note added in proof: A phase diagram based on Eq. 2 has recently been presented (*15*).

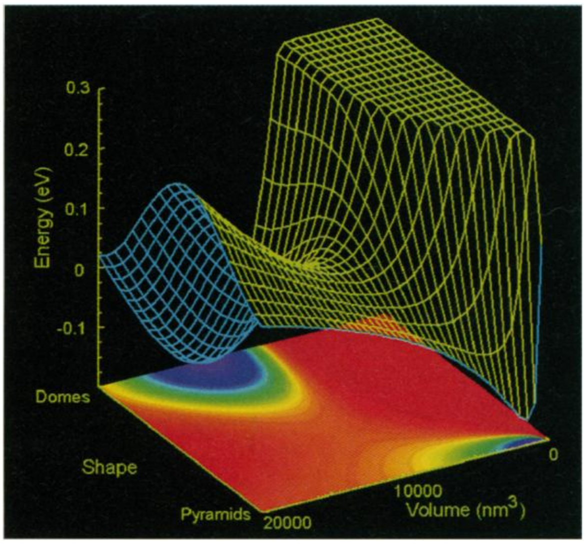

Fig. 3. A model free-energy surface for Ge nanocrystals on Si(001), plotted with reference to a pseudomorphic 2D island on top of the wetting layer. The size axis for the pyramids and domes is plotted using Eq. 2, with the parameters determined from fitting the size distributions to a Boltzmann distribution. The shape axis is a reaction coordinate that includes an activation energy barrier to account for the rearrangement of atoms to change the size of the base of the pyramid to that of an equal-volume dome. The saddle point in this energy surface, which represents the transition state of the shape change, occurs at a volume that is between those of the largest pyramid and the smallest dome.

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8. To obtain quantitative size and shape information on a statistically significant number of nanocrystals, we wrote a program, based on existing code [R. Mirim, thesis, University of California, Santa Barbara (1996)], to analyze the topographs. This program locates the (*x*, *y*) position of the nanocrystals, measures their height and base width along two orthogonal axes, and integrates to find their surface area and volume.
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