Coarsening of Self-Assembled Ge Quantum Dots on Si(001)

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The size distribution of self-assembled heteroepitaxial islands is critical to their application as quantum dots in novel devices. *In situ*, real time UHV transmission electron microscopy studies of Ge island growth on Si(001) show that island coarsening occurs even during growth. With increasing volume, a shape transition from pyramids to domes gives rise to an abrupt change in chemical potential. This leads to a bifurcation in the size distribution and ultimately to a narrow size range. Simulations of coarsening in the presence of a shape transition are in good agreement with experimental results. [S0031-9007(97)05174-0]

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Strain-induced self-assembly of islands in heteroepitaxial systems is a promising route to the utilization of nanoscale particles as quantum dots in optoelectronic devices. Critical to the success of such applications is that the island size distribution be carefully controlled; in general a well defined size with little dispersion is desirable. The growth of Ge "quantum dots" on Si(001) has been studied by many groups [1–7]. However, the kinetic and thermodynamic factors determining quantum dot self-assembly are not yet well characterized or understood.

One of the most remarkable observations is a bimodal distribution of island sizes under certain growth conditions [5–7]. In a beautiful scanning tunneling microscopy study [7] it was shown that the two peaks in the island size distribution correspond to two different shapes. Islands at small volume are pyramidal, exhibiting four {105} facets; at greater volume the islands have a "dome" shape with additional, larger angle facets. Pyramids and domes are coherently strained (dislocation-free), although after prolonged growth dislocated islands appear [3,6] and a trimodal distribution may even be seen [6]. The origin of the bimodal size distribution is not well understood. One explanation [7] is that pyramids and domes correspond to two minimum-energy configurations of strained islands, with an activated transition from pyramid to dome. As an island makes this transition it would need to increase its volume by some 100 000 atoms in a fraction of a second.

Here we present an alternative model. We observe extensive Ostwald ripening during growth of Ge islands [8], indicating that the histories of individual islands are intimately coupled to the evolution of the ensemble. The key idea is that the chemical potential of an island undergoes an abrupt change as the equilibrium shape changes from pyramid to dome. This occurs at the well defined volume at which the dome energy becomes lower than the pyramid energy. Significantly, there is no need for a minimum-energy configuration: we show that the dependence of chemical potential on a shape is sufficient to explain the bifurcation of the size distribution. We also find that the shape transition can lead to a dramatic narrowing of the size distribution, so that the narrow distributions which are often observed can be explained without the need to invoke complex mechanisms for self-limiting island growth [7,9–11]. Shape changes have been observed during coarsening not only of islands on surfaces, but also of precipitates in solids [12]. We believe that our results apply equally well to such systems, as the basic ingredient—dependence of chemical potential on shape—appears to be universal.

Our experiments were carried out in a 300 kV Hitachi H9000 transmission electron microscope (TEM) with a base pressure of 2×10^{-10} Torr. This microscope has been modified to allow *in situ* deposition of Ge using digermane gas introduced to the specimen area through a capillary tube [4]. Deposition was onto a 100 μm thick Si(100) substrate which had been chemically thinned from one side to <100 nm and flash cleaned at 1200 °C prior to growth.

At substrate temperatures around 650 °C and digermane pressures of 1×10^{-6} Torr, initial growth of Ge on Si(100) (after completion of the wetting layer) was in the form of small strained islands. We imaged these using dark-field strain contrast in a $(\mathbf{g}, 3\mathbf{g})$ diffracting condition. Video recordings made during growth enabled us to track the development of individual islands from nucleation onwards, and a particle counting program was used to measure the distribution of island sizes from photographic plates. Since the strain field around each island is responsible for the image contrast, the island shape and size could not be determined directly. Instead, the size was estimated as the major axis of the approximately elliptical strain contrast. This is likely to be an overestimate [13] but does not change the nature of our conclusions. The smallest islands (less than 10 nm in diameter) had weak strain contrast and were not detected by the counting program.

Figure 1 shows a series of images taken from a typical growth sequence, and the size histograms derived at each time. We find that all nucleation events occur within a few seconds. After nucleation a coarsening process takes place: some islands continue to grow while others shrink and disappear. This reduction in the number of

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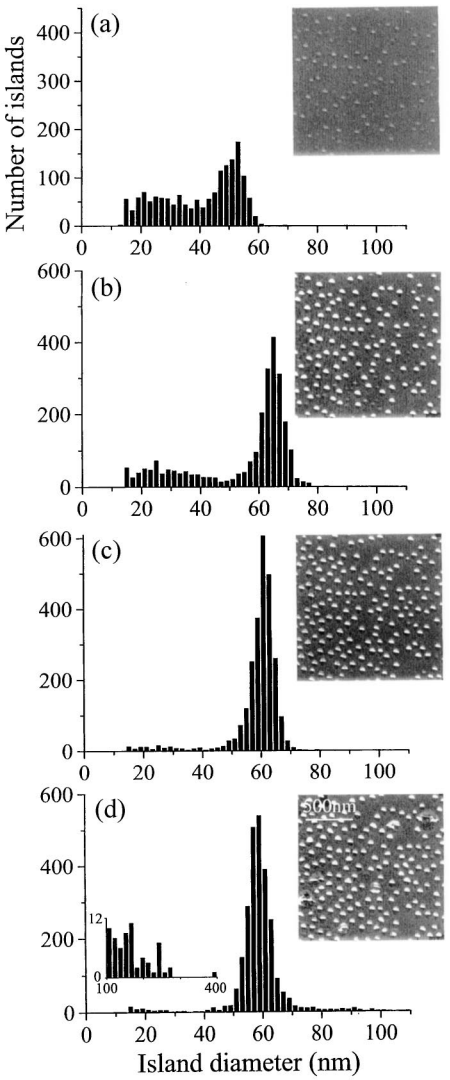

FIG. 1. Images (inset) and histograms obtained during Ge deposition from 2×10^{-7} Torr digermane at a substrate temperature of 640 °C. Images were obtained (a) 21 sec, (b) 51 sec, (c) 98 sec, (d) 180 sec after "nucleation" (i.e., the time at which distinct strain contrast is first seen). Nucleation occurred after a dose of approximately 50 L digermane. The flux remains on during this sequence. The low contrast from the smallest islands is responsible for the cutoff at about 15 nm diameter. In (d) the inset histogram shows the very large islands making up the tail of the distribution.

islands occurred even though the flux remained on, and resulted in the development of a bimodal size distribution (Fig. 1) similar to that seen after growth interruption [5–7]. The larger islands had a rather narrow size distribution (FWHM = 15%) centered around 60 nm. We did not observe coalescence of the strained islands; coarsening presumably occurred by detachment and diffusion of adatoms on the surface.

To obtain detailed information about individual island behavior, we examined the evolution of every island within a 0.5 μm $\times$ 0.5 μm area of the specimen [Fig. 2(a)]. About 60 islands nucleated initially in this area but within 25 sec only 20 remained. A histogram [Fig. 2(b)] shows the same bimodal distribution observed in Fig. 1, but from the individual trajectories it can now be seen that the upper branch of the histogram consists of islands increasing in size at the expense of islands in the lower branch, which are shrinking.

At longer times after nucleation, the island density decreased further while the average size increased, due both to further coarsening and to the continuing flux. The first dislocations appeared as the largest islands grew above 75 nm diameter, and dislocated islands then grew rapidly at the expense of nearby strained islands, attaining very large sizes [Fig. 1(d)].

Similar growth kinetics were observed for digermane pressures in the range $8 \times 10^{-8} - 4 \times 10^{-6}$ Torr at substrate temperatures of 650 $\pm$ 30 °C. Furthermore, if the digermane flux was turned off immediately after nucleation, the coarsening was very similar to the process we have described with the flux on.

Standard models of coarsening invariably give a *unimodal* distribution of sizes [14], and the bimodal distribution observed here and elsewhere [5–7] appears to not be well understood. We believe that the bimodal distribution results from a novel type of coarsening, reflecting the existence of distinct island shapes at different sizes.

In general, the equilibrium shape of a strained island depends on its size. Except at high temperatures, islands are expected to be faceted, with higher-angle facets introduced at increasing volume.

The role of island shape transformations in driving a multimodal size distribution has already been recognized. Medeiros-Ribeiro *et al.* [7] concluded that each peak in the size distribution corresponds to a stable or metastable energy-optimal size for each shape, following a suggestion of Shchukin *et al.* [9]. However, we observe that the peak positions move continuously over time, which is inconsistent with this model. Furthermore, our simulations show that a shape transition leads to a multimodal distribution, even without minima in the energy-volume curve. We illustrate this with an explicit mean-field calculation of the coarsening. Mean-field theory has been shown to give an accurate description of the overall island distribution, even if it does not capture local correlations [15]. For concreteness, we use an approximate formula for the energy of a shallow pyramidal island [16] and we take the surface energy as the same for every allowed facet. Then, with an appropriate scaling of the length and energy, the island energy is described by the dimensionless formula

$$E = V^{2/3}\alpha^{4/3} - V\alpha\,, \tag{1}$$

where α is the ratio of the facet angle to an arbitrary reference angle, and V is the volume in scaled units. The dimensionless chemical potential (per volume rather than per atom) is then

$$\mu = \frac{\partial E}{\partial V} = \frac{2}{3}\,\alpha^{4/3}V^{-1/3} - \alpha\,. \tag{2}$$

We emphasize that this is not intended as a realistic

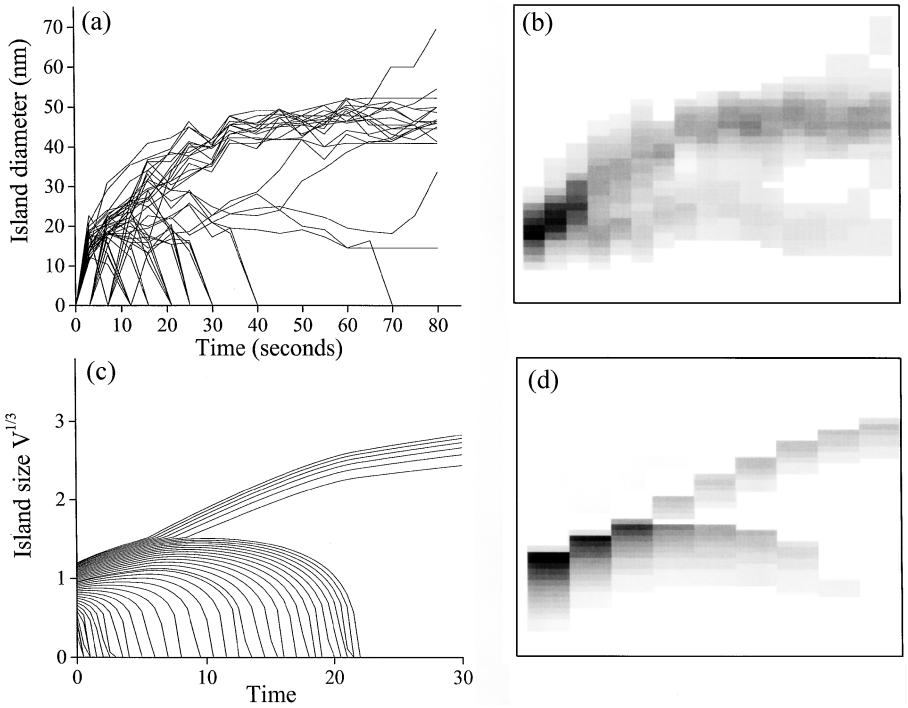

FIG. 2. (a) The evolution of every island within an area of 0.25 μm^2. Growth conditions were 5×10^{-7} Torr digermane and 650 °C. The island showing rapid growth near the end of the sequence has probably formed a dislocation. (b) The same data plotted as a grey scale histogram to show the two branches of island size. (c) Simulation showing the fate of islands with different initial sizes. (d) Histogram of the size distribution in the simulation as a function of time. The model does not include dislocated islands and therefore at large times it predicts a higher growth rate in strained islands than is observed experimentally.

model for the system, but is rather the simplest model which incorporates the essential shape transition so as to illustrate the qualitative effect at play here.

Suppose there are two or more types of islands distinguished by different angles α, and that at any given volume the island assumes the shape with the lowest energy. This is based on the well known idea that higher aspect ratio islands relieve strain more effectively than flatter islands. Figure 3 shows the energy for two island types. The chemical potential is the slope of whichever curve is *lower*, so it is discontinuous at V1, the point where the curves cross. Even a more detailed model with multifaceted domes exhibits such a discontinuous transition [17].

Consider now a standard case where coarsening is limited by attachment of adatoms to the island perimeter. With an appropriate scaling of the units of time, island evolution is governed by the dimensionless equation

$$dV/d\tau = V^{1/3}\alpha^{-1/3}(\bar{\mu} - \mu). \qquad (3)$$

The mean-field chemical potential $\bar{\mu}$ is determined by the constraint that the rate of volume change integrated over all islands must equal the total flux incident on the surface.

Beginning with island sizes uniformly distributed between zero and V_0, to mimic the early stages of nucleation, we integrate (3), recalculating $\bar{\mu}$ at each time step, to obtain the evolution of the islands. (The choice of V_0 and the total flux are somewhat arbitrary.) Results are compared with experimental data in Fig. 2.

It can be seen that this simulation reproduces the essential features of the experimental data. At small times, coarsening proceeds among a population of islands which all have the same shape leading to a unimodal distribution. However, as some islands exceed V1 they assume a shape with higher facet angles. The chemical potential is thus lowered, allowing these islands to grow rapidly at the expense of the smaller islands. A bimodal distribution is therefore predicted for a specific range

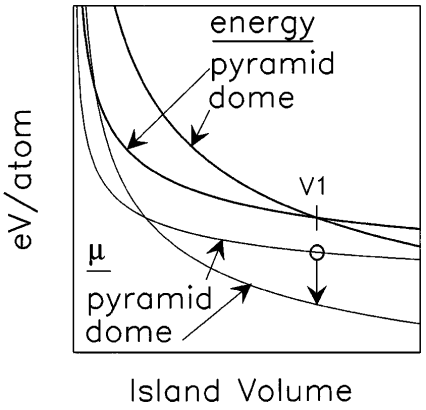

FIG. 3. Energy per atom and chemical potential (μ) of islands with two types of facets with values of α in the ratio 1:2, calculated from Eqs. (1) and (2). The shape transition occurs at volume V1, where the energy curves cross, at which point there is a discontinuity in μ.

of times, with the smaller peak consisting of islands which are shrinking. A significant feature is that the peak position for the smaller islands varies with time [Fig. 2(d)]; there is no preferred size.

The distribution of smaller islands is relatively broad, depending on details of the original nucleation, whereas the larger islands have a comparatively narrow distribution. The model thus generates a narrow distribution without any mechanism for limiting island growth (as in [7,9–11]). Narrow and even bimodal distributions have been observed in other semiconductor systems [11,18] and we believe that it would be worth looking for shape transitions in these systems.

We can extend this model qualitatively to include the appearance of dislocated islands. As the population of strained islands coarsens, dislocations will be introduced into the largest domes, allowing them to grow at the expense of unrelaxed domes (as in the model of Drucker [19]). The transition between dislocated and unrelaxed domes is analogous to that between domes and pyramids, and a trimodal distribution could result (cf. [6]). On the basis of our model we expect the average diameter of unrelaxed domes to reach a maximum and then decrease as dislocated islands appear [20], in the same way that we have seen for the population of pyramids.

In conclusion, we have used *in situ*, video UHV TEM to observe the evolution of individual Ge islands grown on Si(001) by chemical vapor deposition. We observe significant coarsening during growth, indicating that the adatom supersaturation is small even in an overpressure of Ge from the external flux. The island size distribution becomes bimodal after some time. We describe a model in which a change in island shape with increasing volume gives rise to a discontinuous change in the island chemical potential. Numerical simulations show that the bifurcation and further evolution of the island size distribution can be fully explained by the effect of this discontinuity on the coarsening process.

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[20] Figure 2(c) shows the largest islands growing steadily, whereas experimentally these islands appear to reach a maximum size. This discrepancy occurs because the model does not include the transition to dislocated islands. With dislocated islands included, the dome size would reach an apparent maximum and then decrease.