Annealing of Ge nanocrystals on Si(001) at 550 °C: Metastability of huts and the stability of pyramids and domes

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We performed a series of annealing experiments for Ge nanocrystals on Si(001) at 550 °C in order to clarify some issues related to island stability and coarsening. We determined the nanocrystal shape and size distributions for 8 Ge equivalent monolayers as a function of annealing time for up to 80 min after terminating the depositions. Elongated islands or ''huts'' disappear within 30 s, leaving only equiaxial islands, the ''pyramids'' and ''domes.'' During the first 10 min of annealing, the nanocrystals grow further by drawing additional Ge from the wetting layer. Thereafter, the pyramid and dome size distributions are stable.
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Germanium nanocrystals grown on Si(001) have been intensively examined as a model system for the formation of low-dimensional crystallites through self-assembly since the first reports on small coherent islands appeared.[1–3] Nevertheless, the mechanisms involved in Ge nanocrystal appearance and growth are still controversial: a variety of nanocrystal morphologies has been experimentally observed and several models for their formation and evolution have been reported.[4–12] A significant debate that has arisen is whether the various nanocrystal shapes and sizes are (locally) energetically stable[5,13,14] or are metastable configurations on a monotonic kinetic pathway[12,15,16] that leads to very large islands (essentially an Ostwald ripening process[17]). As experience has shown, the Ge on Si(001) system is extremely complex, so a simple experimental differentiation between kinetically produced and equilibrium morphologies has been difficult to obtain. Sorting out the details in this system, for which there are several simultaneously competing processes, will require a large amount of systematic experimental work to compare to the various models.

We report here a series of experiments aimed at understanding the stability of various Ge nanocrystal sizes and shapes on Si(001). Ostwald ripening in particular can be most easily characterized for a mass-conserving system, where the total amount of deposited material is held constant for a sequence of annealing times. We deposited Ge on 550 °C Si(001) substrates by chemical vapor deposition (CVD) using GeH_4 in an H_2 ambient.[4] One set of samples was prepared with an equivalent Ge thickness of 8 monolayers (1 eq ML $= 6.27 \times 10^{14}$ Ge atoms cm^{-2}) deposited at 5 eq ML/min. Immediately after each Ge layer was deposited, it was annealed at 550 °C for a different time (from 0 to 4800 s) 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 backscattering has shown that the amount of Ge deposited by CVD is highly reproducible and does not change during annealing.

We examined the samples *ex situ* using atomic force microscopy (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 stability. The advantages of this procedure are (a) the CVD growth process produces extremely reproducible results, so that the starting surfaces for each annealing period are statistically indistinguishable; (b) the measurements are performed at several locations on a wafer to determine the uniformity of the deposition and annealing processes; and (c) many thousands of nanocrystals on each sample are measured to obtain statistically reliable size and shape distributions. The chief disadvantage is that exposure of the samples to air may distort the island shapes, but comparison with data from *in situ* scanning tunneling microscopy of nanocrystals grown in ultrahigh vacuum by physical vapor deposition (PVD) (Ref. 5) showed that this was not a significant issue.

Figure 1 shows 0.5 μm × 0.5 μm regions from atomic-force micrographs of 8 eq ML Ge films after annealing times of 0 s, 30 s, and 4800 s. The unannealed sample [Fig. 1(a)] displayed three distinct nanocrystal morphologies: huts (elongated islands bounded by {105} facets as reported by Mo *et al.* and others[2,8–10]), pyramids (square-based islands also bounded by {105} facets), and domes (structures with a large number of facets[5] that look rounded at lower resolution[1,4]). There were also some nanocrystals with irregular bases that do not belong to these geometrically well defined categories but are primarily bounded by {105} facets. The surface morphology changed significantly after only 30 s of annealing [Fig. 1(b)]: the island density was significantly lower, there were very few huts or irregular islands, and the average size of the domes was slightly larger, observations that are nominally consistent with Ostwald ripening.[17] However, by 600 s of annealing at 550 °C (not shown), the surface reached a stable configuration, since there were no significant additional changes in the island density or size and shape distributions even up to 4800 s [Fig. 1(c)]. Over the entire annealing period from 600 s to 4800 s, there were only pyramids and domes, which coexisted with each other in close proximity on the surface.

We can distinguish among the different shapes by measuring the axial lengths of the nanocrystals along the [100] (parallel to the scan direction) and [010] axes. Figure 2 displays a time sequence of scatter plots of these lengths measured over a 3 μm^2 area. In these plots, pyramids and domes (or any equiaxial island) cluster along the 45° line intersect-

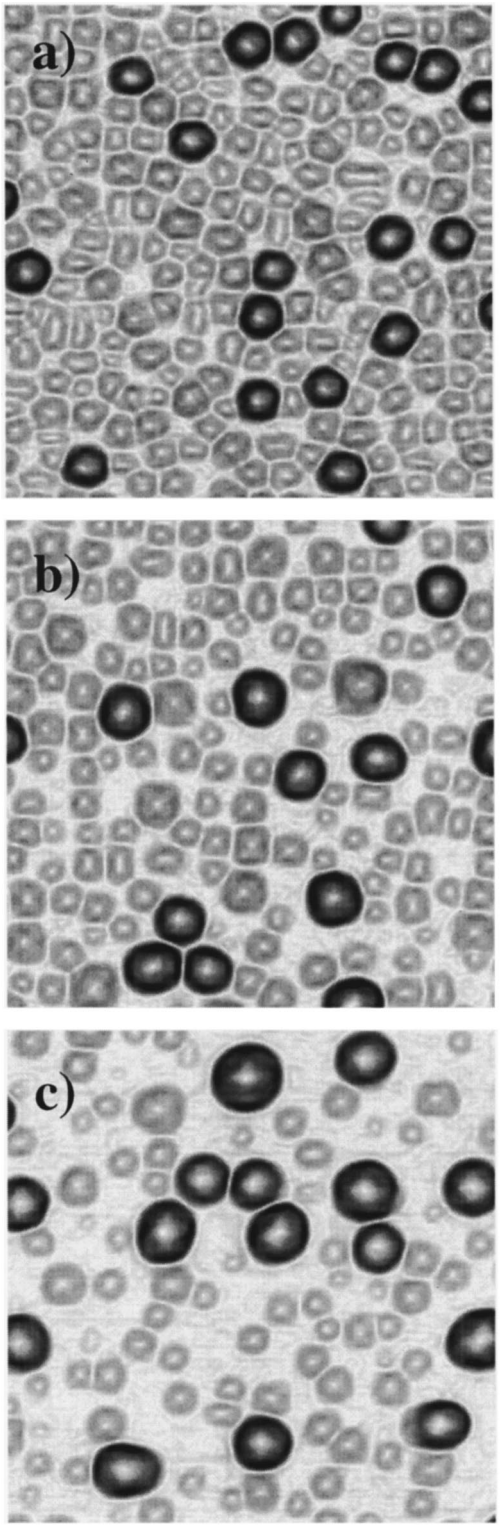

FIG. 1. 0.5 μm $\times$ 0.5 μm regions from 1 μm $\times$ 1 μm atomic-force micrograph scans of 8 eq ML Ge films after annealing times of (a) 0 s, (b) 30 s, and (c) 4800 s. The scan direction is [100]. The gray scale in the images was determined by calculating the projection of the local surface normal onto the growth plane. Darker regions correspond to steeper facets, which assists the visualization of the various facets and nanocrystal shapes present on these samples. Tip artifacts are minimal, since we observe equivalent facets and shapes that are independent of scan direction.

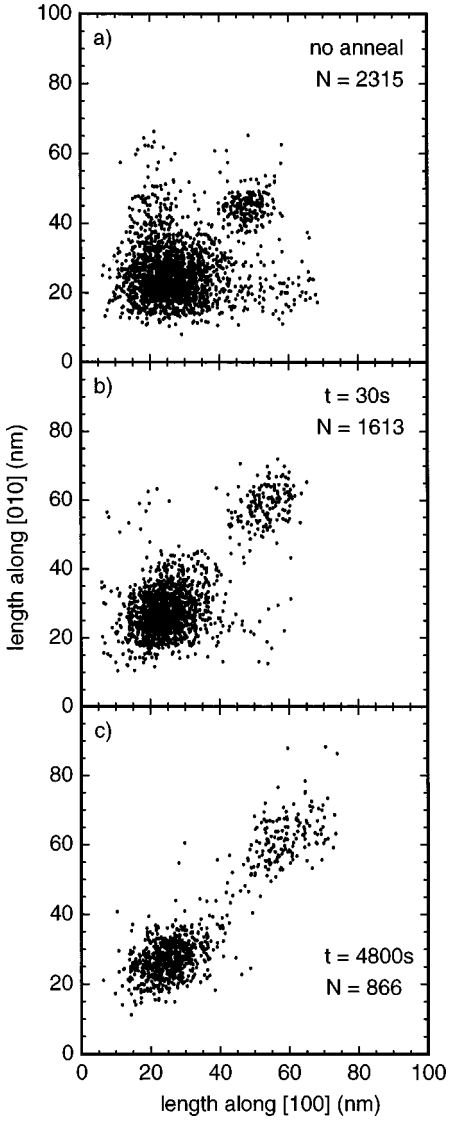

FIG. 2. Scatter plot of the base dimensions of islands found in a 3 μm^2 area. Deviations from a line at 45° intersecting the origin of these plots correspond to islands with asymmetric bases. Plots (a), (b), and (c) correspond to the samples displayed in Figs. 1(a), 1(b), and 1(c), respectively.

ing the origin, whereas any systematic deviations from this line correspond to families of islands with elongated bases, such as huts. For the unannealed sample [Fig. 2(a)], the scatter plot shows the loci of the three dominant island morphologies, although intermediate and irregularly shaped islands cause significant broadening of the distributions. After annealing for only 30 s, the extinction of the huts and irregular islands was revealed by their collapse onto and the narrowing of the pyramid distribution, which is the opposite of the behavior expected for a ripening process. With few exceptions, the nanocrystals clustered around two loci centered on the 45° line. Within the experimental uncertainties, the lateral dimensions of the pyramids did not change during the entire annealing experiment, and thus no coarsening model describes this family of nanocrystals. For the domes, there was an increase in the median length from 45 nm to 60 nm in the first 30 s, and then a further increase of only 5 nm for annealing up to 4800 s, which may or may not be related to a standard ripening process.

The fact that the growth and annealing experiments took place in an H_2 atmosphere could suggest that the stability of a given morphology or size was dictated by the surfactant action of H_2.[18] However, since the CVD of Ge on Si at 600 °C under 10 Torr H_2 (Refs. 4 and 7) and PVD at 10^{-10} Torr (Ref. 5) seldom if ever produce elongated huts, the metastability of the huts with respect to the pyramids is most likely an intrinsic property of the strained Ge nanocrystals at temperatures $\geqslant$550 °C. This observation demonstrates that the model for a shape transition for strained nanocrystals on a lattice-mismatched substrate proposed by Tersoff and Tromp[15] does not generally apply to the Ge on Si(001) system, but it is consistent with later models proposed by Tersoff and LeGoues[16] and by Shchukin *et al.*[13]

Tersoff and Tromp[15] showed that with the assumption of a constant island height, continued growth of an island should lead to a situation in which the island elongated to maintain a smaller lattice strain along the shorter axis of the nanocrystal, and this was used as an argument to demonstrate that Ge huts were more stable than pyramids. Tersoff and LeGoues[16] demonstrated that for islands that can grow in height, the stable configuration was a square-based pyramid and further proposed that as an island grew, it should adopt increasingly steeper facets. Shchukin *et al.*[13] further predicted that for some epitaxial systems, there could be a minimum in the free energy of the pyramids that would lead to stable island sizes. Thus, the significant difference in these last two models is that Tersoff and LeGoues[16] predicted that pyramids should grow continuously by a process of Ostwald ripening, whereas Shchukin *et al.*[13] predicted that pyramids could be energetically stable species that would have a definite size. Our experimental results indicate that the model of Shchukin *et al.*[13] is a more accurate description of Ge on Si(001).

Figure 3 further quantifies the annealing results, with Fig. 3(a) showing the evolution of the total integrated volume of all the islands as a function of annealing time. During the first 600 s of annealing, the integrated island volume increased by the equivalent of almost two Ge monolayers, and then remained constant. The various theories for Ostwald ripening of islands on a surface,[17] which explicitly assume conservation of mass, predict that both the mean island volume and the standard deviation of the volume distribution should increase linearly or slightly sublinearly with time. Figures 3(b) and 3(c) show the evolution of the mean island volume (left axis) and the island density (right axis) with annealing time for pyramids (including huts) and domes, respectively. The standard deviation of the volume distributions is represented by the error bars. The mean volume increased and the area density decreased for both the pyramids and domes through the first 600 s of annealing, but after 600 s the distributions were essentially stable up to 4800 s. The standard deviation of the distributions also did not change significantly after the first 600 s.

Most of the apparent Ge nanocrystal coarsening on Si(001) at 550 °C occurred during an annealing regime in which the total amount of material in the islands was still increasing. The integrated volume of the pyramids and domes approached its steady-state value exponentially, with a time constant of about 100 s. This increase in the total nanocrystal volume could be the result of a decrease in the wetting layer thickness if the initial uniform Ge coverage was thicker than the equilibrium value for the wetting layer (estimated at 3 ML) because of the high growth rate.[19,20] During annealing, the nanocrystals grew either by obtaining additional Ge from a metastable wetting layer, or (less likely) by alloying with Si, as has been observed for annealing at 650 °C.[21] There was also substantial redistribution of Ge among the islands, as shown by the decrease in the density of islands during the first 600 s of annealing. However, this decrease may have been driven by repulsion between the islands[13,14] causing a shift to more domes, since they have a much larger volume to (001) interface area ratio than pyramids,[5] as the net amount of Ge in the islands increased. After the net mass transfer to the islands ceased, so did the shape and size evolution. The fact that pyramids and domes coexisted together in close proximity [Fig. 1(c)] without changing significantly for 4200 s of annealing reveals that both are energetically stable structures over some range of total Ge coverage and substrate temperature, as suggested previously.[5]

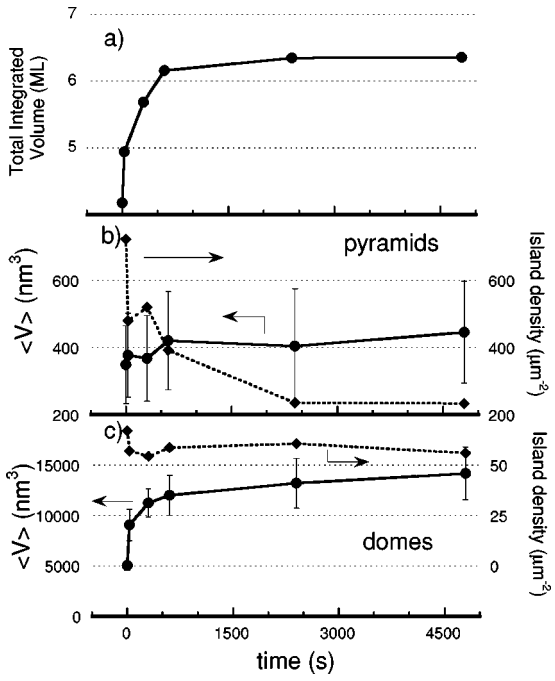

FIG. 3. Evolution of total integrated volume (a) in islands, and mean volume and area densities of pyramids (b) and domes (c) as a function of annealing time. The error bars on the mean volume data correspond to the standard deviation of the volume distributions. The total amount of Ge in these samples remained constant.

Following the example of Mo *et al.*,[2] most researchers in this field do not distinguish between rectangular and square-based islands, but call all Ge islands on Si(001) defined by {105} facets huts. We carefully discriminate between the elongated huts and square-based pyramids for more than simple semantic reasons, because as shown here the huts are metastable structures whereas the pyramids are stable with respect to annealing for long times, even in the presence of much larger domes. Thus, the distinction is important, especially since there is a general recognition that huts are metastable structures. Calling all {105} faceted islands huts then leads to the misconception that pyramids are also only metastable.

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