Novel SiGe coherent island coarsening: Ostwald ripening, elastic interactions, and coalescence

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Real-time measurements of island coarsening during SiGe/Si (001) deposition reveal unusual kinetics. In particular, the mean island volume increases superlinearly with time, while the areal density of islands decreases at a faster-than-linear rate. Neither observation is consistent with standard considerations of Ostwald ripening. We attribute our observed kinetics to the effect of elastic interactions in the densely growing island array. Island coalescence likely plays an important role as well.

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Coherent island formation occurs to relieve strain associated with lattice mismatched heteroepitaxial growth [1-5]. Coherent islands have been shown to self-assemble to produce a narrow distribution of sizes, and to self-order spatially onto two- or three-dimensional lattices [6,7]. We have recently reported on the kinetics of self-ordering of [501]-faceted pyramidal islands ("hut clusters" [1]) in Si$_{0.8}$Ge$_{0.2}$ films on Si (001) during molecular beam epitaxy (MBE), where elastic repulsion between neighboring islands drives the spatial organization [8].

In this Letter we examine the kinetics of hut cluster coarsening during MBE growth, a process that is intimately associated with the self-ordering process. Coarsening is a competitive growth process wherein some islands grow at the expense of others in order to minimize total surface energy ("capillarity-driven coarsening"). The result is that the mean island volume increases with time, while the number of islands per unit area simultaneously decreases. Coarsening can occur via: (1) Ostwald ripening [9,10], mediated by adatom diffusion currents between islands; (2) dynamic coalescence, where islands themselves diffuse across a surface until they collide with other islands and coalesce into a single island [11]; and (3) static coalescence, where islands do not translate, but grow from supersaturation, undergoing coalescence only when neighboring islands touch [12]. We find that coarsening kinetics in dense arrays of hut clusters are much different than would be expected from capillarity-driven Ostwald ripening [9,10], even in the presence of a deposition flux. The novel kinetics observed here are attributed both to the effects of elastic interactions on Ostwald ripening, and to static coalescence. It is emphasized that only one type of island shape is present in these experiments, in contrast to previous studies [13-15].

Si$_{0.8}$Ge$_{0.2}$ films were grown on Si (001) by MBE (details may be found in [16]) at 755°C and 0.1 Å/s deposition rate. Under these conditions, an extended regime of film thickness exists, from 60 – 130 Å mass equivalent thickness, in which [501]-faceted pyramidal islands are the only island morphology present. Figure 1 shows an example of a typical hut cluster array, both as-deposited, and after annealing in situ at the growth
temperature. As-deposited (Fig. 1a), the array is quite dense, with an areal coverage, defined as the fraction of substrate surface covered by islands, of \( \theta = 0.8 \). Note that coalescence events are apparent, and that many of the islands contain holes. After annealing, the island array has coarsened further, and all islands are compact [501]-faceted pyramids, with no holes.

In order to obtain the ensemble coarsening kinetics, the island array was characterized in real-time during MBE growth and annealing, using Light Scattering Spectroscopy (LiSSp). LiSSp uses broadband illumination of the film surface, combined with spectroscopic detection of the scattered light, in a fixed scattering geometry [17]. For the lattice mismatch strain used here (0.8%), the island array is coarse enough to act as an optical diffraction grating [8,16]. From the peak in the scattered intensity we directly obtain the mean island spacing, and therefore the mean areal density, \( <N(t)> \) (number per area). Knowing the film thickness contained in the islands, we can also extract the mean island volume, \( <V(t)> \) from the LiSSp data [18,19]. Finally, knowing the island shape, the mean areal coverage, \( <\theta(t)> \), is also obtained.

Figure 2 shows the LiSSp data obtained during deposition, and for deposition followed by annealing at the deposition temperature. The island array clearly coarsens during deposition, since \( <V(t)> \) increases while \( <N(t)> \) decreases (but the islands retain their [501]-faceted shape throughout). The areal coverage increases significantly during deposition, but drops with annealing. The coarsening kinetics exhibit several unusual features of key importance here. First, for coarsening during deposition, \( <V(t)> \) increases superlinearly with time, that is, the second derivative is clearly positive. A second key observation from Fig. 2 is that, during deposition, \( d^2<N>/dt^2 \) is slightly negative, which we show later is important in elucidating coarsening mechanisms. Finally, we observe that the rate of coarsening during annealing is much slower than the coarsening during deposition.
These observations are inconsistent with elementary considerations of capillarity-driven Ostwald ripening and deposition. For deposition at constant rate, with no ripening, \( \langle V(t) \rangle \) should increase linearly with time while \( \langle N(t) \rangle \) remains constant. On the other hand, for Ostwald ripening with no deposition flux, \( \langle V(t) \rangle \) should increase no faster than \( t^{3/2} \), while \( d^2<\langle N \rangle>/dt^2 \) should be positive. To examine intermediate cases, we employ a standard mean field analysis for Ostwald ripening [13,20]. While such models cannot capture local phenomena and individual island histories, we are interested here in the generic behavior of ensemble-average quantities, for which the mean field approach is reasonable. The chemical potential for pure capillarity-driven ripening is given by \( \Delta \mu(V) = B V^{-1/3} \), where \( B \) sets the energy scale and \( V \) is an island volume (the “Gibbs-Thomson” equation). The growth rate of any class of islands of size \( V \) is, in the mean field context, given by [13]

\[
\frac{dV}{dt} = c V^{1/3} \left[ e^{\Delta \mu^*/kT} - e^{\Delta \mu(V)/kT} \right],
\]

where \( c \) is a constant, \( kT \) is as usual, and \( \Delta \mu^* \) is specified by conservation of mass:

\[
\int_0^\infty f(V,t) \dot{V} dV = \Phi
\]

In equation (2), \( \Phi \) is the deposition rate, \( f(V,t) \) is the distribution of island volumes, and \( \dot{V} \) is given by eq. (1). Finally, the evolution of \( f(V,t) \) is obtained from the flux continuity equation in size space,

\[
\frac{\partial f}{\partial t} = \frac{\partial(f \dot{V})}{\partial V},
\]

which is solved numerically [20]. From \( f(V,t) \) we directly obtain \( \langle V(t) \rangle \), \( \langle N(t) \rangle \), and \( \langle \theta(t) \rangle \) for comparison with data. The results are shown in Figure 3. For pure ripening (\( \Phi = 0 \)), \( \langle V(t) \rangle \) increases linearly, \( \langle N(t) \rangle \) decays with positive second derivative, and \( \langle \theta(t) \rangle \)
decreases, as expected (and consistent with our post-growth coarsening during annealing). For large $\Phi$, where the deposition flux is much larger than the adatom supersaturation associated with ripening, $<V(t)>$ again increases linearly with time, but $<N(t)>$ decreases only very slowly with time, again as expected. For intermediate $\Phi$, $<N(t)>$ still decays with positive curvature. Thus, capillarity-driven ripening, even in the presence of a deposition flux, cannot reproduce our essential experimental results.

We have shown previously that elastic interactions in dense arrays of hut clusters contribute significantly to the system energetics [8,21]. This should affect ripening, since during deposition, the increasing areal coverage of islands will continuously increase the elastic interaction energy of the island array. In essence, deposition combined with elastic interactions drives the system to respond by reducing the areal coverage through more rapid coarsening. The elastic interaction energy can be captured in the mean field approach through an areal-coverage-dependent term in the chemical potential:

$$\Delta \mu(V,\theta) = B[V^{-1/3} + p(\theta)]$$

In order to determine a form for $p(\theta)$, we performed finite element calculations of the elastic interaction energy as a function of areal coverage, using an axially symmetric configuration to capture the essence of the 3D situation (see inset in Fig. 4). The lateral faces of the cylindrical substrate are constrained against normal displacement to represent the symmetry constraint due to neighboring islands. The results are shown as the circles in Fig. 4. We then used a simple analytic function to represent the FEM results, $p(\theta) \propto \exp(\theta^2)-1$, for use in the mean field model. This function is shown as the solid line in Fig. 4. The mean field areal coverage is explicitly evaluated at each time step and fed back into eq. (4) and the analysis proceeds as described above.
Fig. 5 shows results of calculations for $<V(t)>$ and $<N(t)>$ using a value of $\Phi$ such that coarsening is deposition-dominated in the absence of elastic interactions (for comparison, the ripening kinetics for the same deposition rate but with no elastic interactions is also shown in the figure). The important outcome is that elastic interactions promote both superlinearity in $<V(t)>$ and decay of $<N(t)>$ with negative curvature. We also show our experimental data in Fig. 5 (open circles), scaled for comparison with calculations. A single scaling provides good generic agreement between the data and the mean field results. This should not be overinterpreted – we only seek to demonstrate that the incorporation of elastic interaction effects can reproduce the essential aspects of our experimental data.

Another possible mechanism for coarsening, relevant to our situation, is static island coalescence. In the high areal coverage regime, coalescence events during deposition should occur frequently, even in the presence of elastic interactions. Several features in Fig. 1 are consistent with coalescence. From simple considerations, partial coalescence to form a single ridge-shape hut cluster is likely when two pyramids of similar size coalesce. Several such structures are visible in Fig. 1. When two islands of much different size coalesce, a compact pyramid may result if adatom mobility is sufficient to allow the smaller island to be "adsorbed" onto the larger, which is akin to a liquid-like coalescence process. Elastic repulsion between islands in very close proximity to one another may promote formation of locally steeper facets between the islands. However, with continued deposition, and because the islands are constrained on all sides by other islands, coalescence eventually must occur, leaving behind the small "holes" observed in Fig. 1. Holes thus represent a signature of coalescence in progress, or recently completed. During post-deposition annealing, coalescence is far less frequent, and islands tend towards compact pyramids with no holes.

The kinetics of coarsening due to liquid-like coalescence during deposition (with no Ostwald ripening) have been derived by Family and Meakin (FM), and by Beysens et al [22, 12]. Using statistical self-similarity arguments, Family showed that for 3D islands
growing in a 2D diffusion field, \( \langle V(t) \rangle \propto t^2 \). We have fit our \( \langle V(t) \rangle \) data to the form \( \langle V \rangle = \langle V_0 \rangle + A(t-t_0)^y \) by enforcing a range of time exponents \( y \) (from \( y = 1.5 \rightarrow 4 \)) and minimizing the least-square error. The result indicates that \( y = 3 \) provides a good fit and that fits with \( y < 2 \) are unlikely. Unfortunately, the time-dependent areal density, \( \langle N(t) \rangle \), resulting from coalescence cannot be determined from self-similarity arguments [22], so we cannot discriminate with confidence whether coalescence could be solely responsible for the island coarsening kinetics we observed during deposition. Pinto et al. have invoked the FM coalescence model to explain the island size distributions they observe during SiGe growth, although their analysis is complicated by the presence of both coherent and dislocated islands [15].

We have also considered whether dynamic coalescence or interdiffusion from the substrate could produce the observed coarsening kinetics, but reject these mechanisms on physical grounds.

In summary, using real-time light scattering we have observed novel coarsening kinetics during deposition and formation of SiGe hut clusters at high areal coverage. Ostwald ripening is enhanced by elastic repulsion energy between the islands, coupled with deposition that forces the islands closer together, thereby continuously driving up the system energy. Copious island coalescence likely also contributes to the coarsening kinetics.

Our gratitude to Peter Voorhees, Jerry Tersoff, and Corbett Bataille for useful discussions, John Hunter for technical assistance, and Bonnie McKenzie for SEM. L.B.F. acknowledges the MRSEC program at Brown University funded by the National Science Foundation under award DMR-9632524. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.
References

11. Smoluchowski
18. The wetting layer thickness has been verified by cross-section TEM, see [19].


**Figure Captions**

Figure 1. Plan-view scanning electron micrographs of Si$_{0.8}$Ge$_{0.2}$/Si(001) hut cluster arrays grown by MBE at 755°C. (a) as-deposited (1000 seconds deposition time, 100 Å thick); (b) annealed for 40 minutes at the growth temperature, also 100 Å thick.

Figure 2. LiSSp data obtained during growth of the films shown in Fig. 1. Square symbols are for continuous deposition, while diamonds are for deposition followed by annealing. In (a), the curves have been offset for clarity.

Figure 3. Mean field model results, comparing effect of increasing deposition flux, $\Phi$. Note that $<N(t)>$ always has positive second derivative, unlike the data shown in Fig. 2(b) for continuous deposition. $<V(t)>$, $<N(t)>$, and $<\theta(t)>$ have all been normalized by their initial values.

Figure 4. Results of finite element calculations of excess elastic interaction energy as a function of areal coverage (circles). Also shown is an analytic representation of the FEM results (line). The numbers are normalized by the value at $\theta=1$.

Figure 5. Results of the mean field model incorporating elastic interactions at large $\Phi$ (solid line). Also shown for reference is $p(\theta) = 0$, i.e., no elastic interactions, but the same deposition rate. The open circles are the data of Figure 2, scaled for comparison with the calculations.
Figure 2
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Figure 3
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