Coherent islands and microstructural evolution

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Strained island growth in lattice-mismatched epitaxial systems differs from relaxed island growth. The total elastic energy of a strained island changes its chemical potential and growth rate. This effect is investigated for an ensemble of misfitting coplanar hemispherical caps interacting through surface diffusion alone. A general expression for the growth rate of strained islands is obtained by including elastic energies in the driving force for Ostwald ripening. For the first time, to our knowledge, a coherent-to-incoherent transition is shown to dramatically affect ripening kinetics. Coherent islands are shown to grow more slowly than incoherent islands of the same radius. Consequently, the growth rate of an island accelerates when it dislocates at the coherent-to-incoherent transition in agreement with recent experimental observations.

I. INTRODUCTION

Many of the physical properties of thin films depend on their microstructure which continually evolves during growth. For both the Volmer-Weber (island) and Stranski-Krastanov (layer plus island) growth modes, the last stages of microstructural evolution proceed by island coarsening (Ostwald ripening). This coarsening is driven by chemical potential differences between islands. Most treatments of two-dimensional (2D) Ostwald ripening assume that this chemical potential depends solely on surface and interfacial energies leading to an inverse radial dependence for the 2D vapor pressure. Thus small islands dissolve into larger islands and the film coarsens. For lattice-mismatched epitaxial systems, strain alters the total energy of an island. Here we demonstrate the effects of strain on Ostwald ripening in 2D. By including strain energy in the driving force for ripening, several experimentally observed deviations from conventional curvature driven ripening behavior can be explained.

The effects of strain on coarsening of precipitates in three dimensions have been observed experimentally[1,2] and described theoretically.[2–8] It has only been recently that these effects have been identified for film growth in 2D.[9] Strain in growing films can be relieved by the formation of misfit dislocations at the film-substrate interface,[10] or, in the case of island growth systems, by the formation of coherent (dislocation free) islands which elastically deform the substrate to relieve some of the mismatch.[11] Coherent islands are energetically favored over dislocated islands for islands smaller than some critical size,[12] in much the same way that pseudomorphic layer growth persists up to some critical thickness.[10] This suggests that in systems for which coherent islands may exist, all islands will initially be dislocation free. Further growth of these islands by continued deposition and/or ripening can cause a coherent-to-incoherent transition via the introduction of misfit dislocations. Recently, strained island growth in the Ge/Si(100) system was shown to significantly impact microstructural evolution.[9] Coherent islands were observed to grow more slowly than dislocated islands of the same size. Consequently, the growth rate of initially coherent islands was found to accelerate upon misfit dislocation formation.

Section II develops a model for the growth of misfitting, coplanar, diffusionally interacting spherical caps by including strain energy in the driving force for Ostwald ripening in 2D. The total elastic energy of a strained island modifies its chemical potential and growth rate. Previously obtained forms for this total elastic energy are used to explain the experimentally observed deviations from curvature-driven ripening. A discussion of these results and their relationship to other studies of two-dimensional ripening is presented prior to concluding. The aim is to understand the role that strain plays in 2D ripening.

II. STRAINED ISLAND GROWTH

The system is approximated by an ensemble of strained hemispherical caps which interact through surface diffusion alone. The principal assumptions of other mean-field, low-surface-coverage treatments of ripening apply. These treatments are based on the model of Lifshitz, Slyozov,[3] and Wagner[13] (LSW) for ripening, which was adapted to 2D by Chakraverty.[14] Following Chakraverty, the growth rate of a strained island can be written as

$$\frac{dn^x(R)}{dt} = \mathcal{F}(R)\{C_{\text{free}} - C_R^x\} . \tag{1}$$

n is the number of atoms in the island, and the superscript allows the island to be labeled either coherent or incoherent. $\mathcal{F}(R)$ is a prefactor which contains information about the rate-limiting step for island growth.[14] C_{free} is the free adatom concentration (system supersaturation), and C_R^x is the equilibrium solubility of a strained island of radius R. This equilibrium solubility can be obtained by considering the free-energy change in a growing strained island.

As a strained island of radius R grows, its free energy changes by

$$dG = 2\pi R\, \sigma\, dR + dG_E \ . \tag{2}$$

G_E is the total elastic energy of the strained island. σ is the appropriate combination of surface and interfacial energies apart from any elastic interactions. Noting that $dG = \Delta\mu\, dn$, the change of the chemical potential when a solute atom transfers from the dilute phase to an island can be written

$$\Delta\mu = V_m \left[\frac{\sigma}{R} + \frac{1}{2\pi R^2} \frac{dG_E}{dR} \right] . \tag{3}$$

V_m is the atomic volume of island constituents. The Gibbs-Thomson equation relates this chemical potential change $\Delta\mu$ to the ratio of the equilibrium solubility of a cluster of radius R, C_R, and the solubility over a planar surface, C_{plane},

$$\Delta\mu = kT \ln \left[\frac{C_R}{C_{\text{plane}}} \right] . \tag{4}$$

Combining (3) and (4) in the low driving force limit yields the equilibrium solubility of a strained island:

$$C_R^x = C_{\text{plane}} \left[1 + \frac{V_m}{kT} \left[\frac{\sigma}{R} + \frac{1}{2\pi R^2} \frac{dG_E^x}{dR} \right] \right] . \tag{5}$$

The relationship between the equilibrium solubility of a strained island, C_R^x, and the system supersaturation C_{free} expressed by Eq. (1) determines whether an island grows

or dissolves. Since the system supersaturation diminishes with time as the film coarsens, it is useful to express this relationship in terms of C_{plane}. An expression which relates C_{free} and C_{plane} can be found which allows elimination of C_{free} from (1). An ensemble of strained islands coarsening in a solution of known supersaturation may be described by an island size distribution function of the form

$$f(R,t) = f^C(R,t) + f^I(R,t) \ . \tag{6}$$

$f(R,t)dR$ is the number of islands with sizes between R and $R + dR$ at time t. Similarly, $f^C(R,t)dR \, (f^I(R,t)dR)$ is the number of coherent (incoherent) islands with radii between R and $R + dR$ at time t. The following assumption connects the supersaturation with this island size distribution and allows elimination of C_{free} from (1). Assume the supersaturation diminishes slowly with time, i.e.,

$$\begin{aligned} \frac{\partial C_{\text{free}}}{\partial t} &= \int_0^\infty \frac{dn}{dt} f(R,t) dR \\ &= \int_0^\infty \frac{dn^C}{dt} f^C(R,t) dR + \int_0^\infty \frac{dn^I}{dt} f^I(R,t) dR = 0 \ . \end{aligned} \tag{7}$$

From (7) an expression relating the known supersaturation to the particle size distribution can be found.

$$C^* = \frac{C_{\text{free}}}{C_{\text{plane}}} = \frac{\int_0^\infty \left\{ \sum_{x=I,C} \mathcal{F}(R) \left[1 + \frac{V_m}{kT} \left[\frac{\sigma}{R} + \frac{1}{2\pi R^2} \frac{dG_E^x}{dR} \right] \right] f^x(R,t) \right\} dR}{\int_0^\infty \left\{ \sum_{x=I,C} \mathcal{F}(R) f^x(R,t) \right\} dR} \ . \tag{8}$$

Substituting for C_{free} from (8) and C_R^x from (5) into (1) results in a growth rate equation for a strained island coarsening in an ensemble of strained islands:

$$\frac{dn^x}{dt} = \mathcal{F}(R) C_{\text{plane}} \left\{ C^* - 1 - \frac{V_m}{kT} \left[\frac{\sigma}{R} + \frac{1}{2\pi R^2} \frac{dG_E^x}{dR} \right] \right\} . \tag{9}$$

It is noted that (8) and (9) reduce to the usual expressions found in other discussions of 2D ripening in the limit $G_E \to 0$. The change in the island radius can be found from $dR/dt = V_m/(2\pi R^2)dn/dt$.

III. TOTAL ELASTIC ENERGY OF STRAINED ISLANDS

In order to extract the essential behavior of strained island growth from (9), an expression for the total elastic energy G_E must be obtained. The total elastic energy is the sum of the elastic energies of the strained island, deformed substrate, and island/substrate interface. Jesser and Kuhlmann-Wilsdorff[12] found an expression for the total elastic energy of strained (coherent and incoherent)

hemispherical islands. They minimized the sum of the strain energy of the island, substrate, and bicrystalline interface[10] to find the equilibrium interfacial strains. They showed that there is a minimum radius for the coherent-to-incoherent transition which suggests that all islands are initially coherent. Their results indicate that there is a critical radius at which dislocation introduction becomes energetically favorable, but that there is an energy barrier for this process. This energy barrier diminishes with island size facilitating the transition to incoherency. Figure 1 plots their results for total elastic energy for strained islands using materials parameters (shear moduli, Poisson's ratios, etc.) for the Ge/Si(100) system. The coherent and incoherent curves cross at the radius for which dislocation formation becomes energetically favorable. Fitting the curves of Fig. 1 reveals that the elastic energy of a coherent island varies cubically with the island radius, while that of an incoherent island varies quadratically. These functional forms of the elastic energy are used in what follows.

Figure 2 plots the quantity in square brackets in (9) vs the island radius for Ge/Si(100) for both coherent and in-
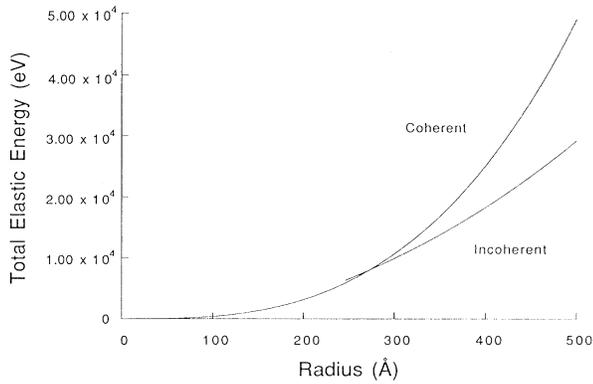
FIG. 1. Total elastic energy of the strained island plus interface plus deformed substrate according to the model discussed in the text for Ge/Si(100). The coherent and incoherent curves cross at $R_c = 272$ Å. The total energy for coherent islands is a cubic function of the island radius, while the total energy for incoherent islands is quadratic. These forms of the elastic energy for strained islands are used in the discussion of ripening in strained island systems.

coherent islands. This quantity may be reexpressed in a number of ways; it is the driving force for coarsening in strained island systems. A curve plotting σ/R for unstrained islands is displayed for comparison. For Ge/Si(100), σ is assumed to be $\gamma_{Ge} \approx 0.11$ eV/Å^2.[15] Only island radii for which both coherent and incoherent islands may exist are shown. The implications of Fig. 2 are discussed in Sec. IV.
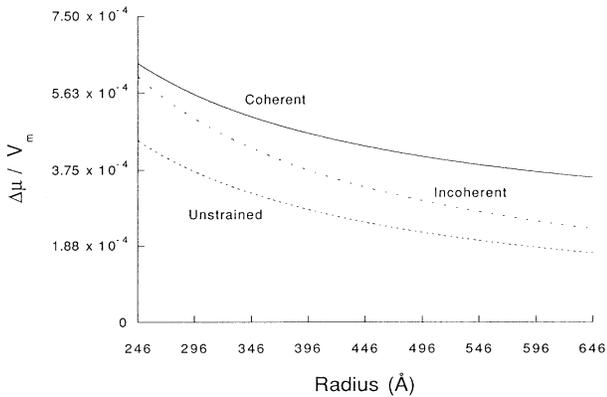

FIG. 2. The chemical potential divided by the atomic volume of island constituents [proportional to $\ln(C_R/C_{\text{plane}})$] vs the strained island radius for Ge/Si(100) for the form of elastic energy plotted in Fig. 1. Only island radii for which it is possible for dislocations to form at the island/substrate interface are displayed. A curve for σ/R for unstrained islands is plotted for comparison. The value of the surface/interface energy is assumed to be $\gamma_{Ge} \approx 0.11$ eV/Å^2. These curves demonstrate that coherent islands will grow more slowly than incoherent islands of the same radius. Consequently, an island's growth rate will accelerate subsequent to dislocation introduction at the coherent-to-incoherent transition.

IV. STRAINED ISLANDS COARSENING IN AN ENSEMBLE OF STRAINED ISLANDS

Two distinct cases are considered for the form of the total elastic energy discussed above: systems with only one type of strained island, and systems with both types of strained islands. Other functional forms of the total elastic energy are then considered. Specifically, the development of monodisperse island size distributions of coherent islands is discussed. It is shown that this is the result of the strain energy growing faster than the island volume.

The sign of the quantity in curly brackets in Eq. (9) determines whether an island grows or dissolves. Of particular importance is the critical radius for coarsening, the radius at which an island is (momentarily) in equilibrium with the supersaturation and neither grows nor dissolves. For monotonically decreasing forms of the chemical potential similar to those of Fig. 2, all islands with radii larger than this critical radius will grow, and all islands with radii smaller than the critical radius will shrink. From Fig. 2, it is evident that in systems with both types of strained islands, a unique critical radius cannot be defined. The radius at which coherent islands are in equilibrium with the supersaturation is different than the radius at which incoherent islands are in equilibrium with the supersaturation.

Also evident from Fig. 2 is the fact that coherent islands will always grow more slowly than incoherent islands of the same size. Consequently, the growth rate of an island will accelerate at the coherent-to-incoherent transition. At the coherent-to-incoherent transition, an island jumps vertically from the coherent to the incoherent curve, and its growth rate accelerates. This agrees with experimental observations in the Ge/Si(100) system.[9]

Systems consisting of only one type of strained island with the form of the total elastic energy discussed in Sec. III should coarsen similarly to ensembles of unstrained islands. This can be seen by examining the functional form of the quantities in square brackets in Eq. (9). For unstrained islands, only the surface term σ/R exists. For coherent islands, the elastic term contributes a constant term. For incoherent islands, the elastic term contributes a term with an inverse radial dependence. In either case, the overall radial dependence is the same as for unstrained islands. Therefore, both types of strained islands should coarsen similarly to unstrained islands for the form of elastic energy discussed in Sec. III. From Fig. 2, it is evident that coherent islands should have the smallest critical radius for coarsening for a given supersaturation. Incoherent islands should have a larger critical radius, but smaller than that of unstrained islands.

Figure 10 of Ref. 9, an experimental study of microstructural evolution in Ge/Si(100) epitaxy, displays an ensemble of coherent islands which have grown to nearly identical radii of 100 nm. It is possible to explain this monodisperse island size distribution using Ostwald ripening concepts by considering a form of the elastic energy which grows faster than the island volume, i.e.,

$G_E \alpha R^n$ with $n > 3$. In this case, the elastic term in square brackets in Eq. (9) contributes a term which increases with island size, causing the island growth to stop at a radius determined by the system supersaturation. This will allow all of the smaller islands to "catch up" producing the monodisperse island size distribution. Similar behavior was reported by Schmelzer, Pascova, and Gutzow,[2] who investigated precipitation in 3D. Their monodisperse precipitate size distributions were attributed to an elastic energy which grew faster than the precipitate volume.

V. DISCUSSION AND SUMMARY

This paper has demonstrated a number of consequences for the late stages of microstructural evolution (Ostwald ripening) in film growth systems for which strained islands may exist. It is instructive to note the relationship of these results to other studies of ripening in two dimensions. Contrary to the case for three dimensions, where effects attributed to elasticity have been well known for some time, such effects have only recently been identified in 2D. This is at least partially due to the difficulty of characterizing films with the spatial resolution necessary to observe the effects presented here. However, there have been several studies of microstructural evolution in film growth[16-18] which were sensitive to islands with radii greater than about 0.1 μm. Islands in this size range are usually all incoherent, so elastic effects would be difficult to notice. The primary effect elasticity would have on dislocated islands in this size range would be to slow growth rates of individual islands

and to shift the critical radius for coarsening to larger radii as described by Eq. (9). The one instance in which elastic effects were identified for islands in this size range was for Ge grown on Si(100) at a temperature higher than normal for this heteroepitaxial system.[9] This observation was discussed in Sec. IV.

In summary, the total elastic energy of the strained island plus interface plus deformed substrate was shown to affect the equilibrium solubility of strained islands. This elastic effect on the equilibrium solubility was expressed in a growth rate equation for isolated, diffusionally interacting coplanar hemispherical caps. For a model of the elastic energy in strained island systems originally presented by Jesser and Kuhlmann-Wilsdorff, it was shown that the total elastic energy in strained island growth is a cubic function of island radius for coherent islands, and a quadratic function of island radius for incoherent islands. However, the experimental observation of monodisperse island size distributions suggests that the total elastic energy may grow faster than the island volume for coherent Ge islands grown on Si(100).

For systems with only one type of strained island, the microstructural evolution may be quantitatively different but qualitatively similar to relaxed island evolution for the model of elastic energy discussed in Sec. III. For systems with both types of strained islands, coherent and incoherent, it is no longer possible to define a unique critical radius for coarsening. Some experimentally observed consequences of strained island growth predicted here are that coherent islands of a given radius will grow more slowly than incoherent islands of the same radius. Consequently, the growth rate at an initially coherent island will accelerate at the coherent-to-incoherent transition.

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