Enhanced Nucleation and Enrichment of Strained-Alloy Quantum Dots

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An epitaxial strained layer is metastable against nucleation of three-dimensional "islands." For an alloy, I show that these islands nucleate at a substantially different composition than the alloy layer. This stress-induced segregation drastically increases the nucleation rate. For planar-layer electronic devices, these effects exacerbate the roughening problem. However, the same effects enhance the promise of "self-assembled quantum dots." Possible "self-capping" of quantum dots is also discussed. [S0031-9007(98)07308-6]

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Many electronic devices incorporate strained layers, formed by growing a semiconductor on a substrate having a different lattice constant. Prominent examples include SiGe on Si and InGaAs on GaAs. A crucial factor limiting such applications is the nucleation of three-dimensional "islands" on the planar layer [1]. All strained layers are metastable [1] (or unstable [2]) against such island formation, because it allows partial elastic relaxation of the strain. Islanding can occur even for layers too thin to form dislocations [1,3].

In most electronic devices such island formation is highly undesirable, because it leads to rough interfaces and easier introduction of dislocations [1]. Thus understanding and suppressing the nucleation of islands is an important step in the robust integration of strained layers into electronic devices. Such islands have also received great attention because of their potential applications as self-assembled "quantum dots," when islands of a small-band-gap semiconductor are buried in a larger-band-gap matrix [4–6]. There, too, understanding and controlling the nucleation is crucial.

Here I show that when islands nucleate on a strained *alloy*, they do not in general have the same composition as the alloy. Instead, there is segregation of the larger-misfit component to the island. This segregation has two important consequences. First, it dramatically lowers the nucleation barrier. Thus an island nucleates from an alloy with strain ε much more readily than from a pure material of the same strain. Second, because the island nucleates and grows with an enriched composition, the behavior of any electronic devices incorporating the island will be strongly affected.

These effects are potentially beneficial for typical quantum dot applications. For example, islands nucleated from InGaAs on GaAs(001) will nucleate at a smaller size and higher In fraction, enhancing quantum confinement effects. This is important because even nominally pure films often form alloys by intermixing with the substrate during the deposition process [7,8].

For growth of traditional planar devices, however, these effects are deleterious. The reduced nucleation barrier makes it harder to suppress stress-induced roughening. And once such roughening occurs, it will entail alloy decomposition which cannot be erased by subsequent planarization.

After nucleation, further island growth is complicated by kinetic factors. For such standard systems as SiGe on Si and InGaAs on GaAs, differences in surface diffusivity can further increase the compositional enrichment of the islands. There may even be a sort of "self-capping" of islands, forming quantum dots with, e.g., an In-rich core and Ga-rich outer shell as the alloy film is depleted.

Experimental measurements of local composition are quite difficult, but recently there has been some evidence of the importance of alloying and decomposition. Deposited material may intermix with the substrate during the film deposition process [7,8]. And intermixing between islands and the surrounding surface has been seen during annealing [9].

The analysis here begins with a calculation of the free energy of formation of an alloy island from a planar alloy layer. The island is characterized by two variables, its composition and size. The next step is to identify the saddle point of the corresponding two-dimensional energy surface. This gives the nucleation barrier, as well as the composition and size of the critical nucleus. Finally, subsequent growth of the island is discussed, in order to address the expected composition of quantum dots.

The island is assumed to have a fixed shape as it grows, e.g., a faceted pyramid, with no dislocations. Also, the island is treated as having uniform composition, rather than allowing the composition to vary across the volume of the island. This may be viewed as a variational treatment, giving an upper bound on the island nucleation barrier. Thus including internal island inhomogeneity would only strengthen the conclusions of this analysis.

The free energy of formation for an island of composition c and volume V is then

$$E(c,V) = E_{\mathrm{surf}}(c,V) + E_{\mathrm{mix}}(c,V) + E_{\mathrm{strain}}(c,V) - (V/V_a)[c\mu_A + (1-c)\mu_B]. \tag{1}$$

Here c refers to the atomic fraction of component A of an AB alloy, and V_a is the volume per atom. Assuming that the surface energy is independent of composition [10], the first term in (1) may be written $E_{\mathrm{surf}}(c, V) = \Gamma V^{2/3}$, where Γ is fixed by the actual surface energies and the island shape [1]. (I use the term "shape" to refer to the scale-free shape, independent of size.) The next term is the free energy of mixing $g(c)$ for the *unstrained* alloy at composition c, $E_{\mathrm{mix}}(c, V) = Vg(c)$. Then there is the elastic energy of the island, $E_{\mathrm{strain}}(c, V) = V(1 - \alpha)M\varepsilon^2$. Here α is the fractional elastic relaxation of the island relative to a planar layer, and is a function only of the shape (which is assumed constant); M is an elastic constant; and ε is the misfit strain for a planar layer of composition c, $\varepsilon = c\varepsilon_A + (1 - c)\varepsilon_B$, where $\varepsilon_A = (1 - a_A/a_0)$ and $\varepsilon_B = (1 - a_B/a_0)$, a_0 and a_A being the lattice constants of the substrate and of pure material a_A, respectively.

Finally, we need the chemical potential of the reservoir, i.e., the planar film of composition $\bar{c}$:

$$\mu_A V_a^{-1} = g(\bar{c}) + \bar{c}_B g'(\bar{c}) + M\bar{\varepsilon}^2 + 2M\bar{c}_B\bar{\varepsilon}(\varepsilon_A - \varepsilon_B),$$

$$\mu_B V_a^{-1} = g(\bar{c}) - \bar{c}_A g'(\bar{c}) + M\bar{\varepsilon}^2 - 2M\bar{c}_A\bar{\varepsilon}(\varepsilon_A - \varepsilon_B),$$

where V_a is the volume per atom, $g' = dg/dc$, and $\bar{\varepsilon} = \bar{c}\varepsilon_A + (1 - \bar{c})\varepsilon_B$ is the strain of the planar layer. Note that the island nucleus forms as a thermal fluctuation, so it presumably takes material from a wide area, with negligible perturbation of the local film composition and thickness. In converting between volume and atom number, the atomic size difference (a correction of order $\bar{\varepsilon}$) is neglected.

The island free energy per unit volume is thus

$$\begin{aligned} E(c, V)V^{-1} = {} & \Gamma V^{-1/3} + g(c) - g(\bar{c}) + (\bar{c} - c)g'(\bar{c}) \\ & + M(1 - \alpha)[c\varepsilon_A + (1 - c)\varepsilon_B]^2 - M\bar{\varepsilon}^2 \\ & + 2M\bar{\varepsilon}(\varepsilon_A - \varepsilon_B)(\bar{c} - c). \end{aligned} \tag{2}$$

Note that this has a unique minimum with respect to composition c, independent of the island volume. Thus to find the nucleation barrier we can simply take the minimum of E with respect to c and the maximum with respect to V.

Let us begin by considering two simple limits. If the composition is assumed fixed (no decomposition, $c = \bar{c}$), Eq. (2) simplifies to

$$E(V) \rightarrow \Gamma V^{2/3} - \alpha V M\bar{\varepsilon}^2, \tag{3}$$

which has been studied previously [1]. Taking fixed $c = \bar{c}$ is a good approximation if $g'' \gg kT$, and, of course, is exact for a nonalloyed system. The energy barrier for island nucleation is then

$$E_b = \frac{4}{27}\Gamma^3\alpha^{-2}(M\bar{\varepsilon}^2)^{-2}, \tag{4}$$

where $M\bar{\varepsilon}^2$ is simply the strain energy density of the planar film.

The other simple limit is $g \approx 0$. Then the free energy of mixing is negligible, and the composition is determined entirely by the minimization of strain energy. In that case, regardless of island volume, the minimum free energy occurs at composition

$$c = \bar{c}(1 - \alpha)^{-1} + \frac{\varepsilon_B}{\varepsilon_A - \varepsilon_B}\frac{\alpha}{1 - \alpha} \tag{5}$$

subject to the constraint that $0 \le c \le 1$. For $\alpha\varepsilon_B/(\varepsilon_B - \varepsilon_A) < \bar{c} < 1 + \alpha\varepsilon_A/(\varepsilon_B - \varepsilon_A)$, the island composition c is determined by Eq. (5) (rather than by the constraint $0 \le c \le 1$). In that range, maximizing the energy with respect to volume gives the nucleation barrier

$$E_b = \frac{4}{27}\Gamma^3(1 - \alpha)^2\alpha^{-2}(M\bar{\varepsilon}^2)^{-2}. \tag{6}$$

So in this range of composition, the nucleation barrier is reduced by a factor of $(1 - \alpha)^2$ from what it would be without alloy decomposition. For $\bar{c}$ outside this range, c is saturated at 0 or 1, and the barrier can be obtained by substituting $c = 0$ or $c = 1$ into Eq. (2). In that case the nucleation barrier is still reduced by alloy decomposition, but by less than a factor of $(1 - \alpha)^2$.

For typical island shapes, α is in the range 0.2–0.6 [11], so alloy decomposition can reduce the nucleation barrier by 30%–85%. The nucleation rate R varies with barrier E_b as $R \sim R_0 e^{-E_b/k_BT}$, and the prefactor R_0 is typically large enough that nucleation occurs on a laboratory time scale while $E_b \gg k_BT$. Therefore a 30%–85% reduction in energy barrier corresponds to an increase in the nucleation rate by many orders of magnitude.

Besides lowering the energy barrier for nucleation of surface roughness, these results have an interesting implication for the morphology. In a simple linearized theory [1], nucleating an island or a pit is completely equivalent energetically, and a full numerical treatment [3] shows that pit nucleation is actually favored. However, allowing alloy decomposition gives a very different picture. In the absence of bulk diffusion, a pit can be formed only by removing material of composition $\bar{c}$. Thus the nucleation barrier for islands can be lower than that for pits, because only islands benefit from alloy decomposition.

Let us now focus on island nucleation in the important special case of an AB alloy film on a substrate of B. This includes such widely studied and technologically important systems as $\mathrm{Si}_{1-c}\mathrm{Ge}_c$ on Si and $\mathrm{In}_c\mathrm{Ga}_{1-c}\mathrm{As}$ on GaAs. Here the composition c refers to the fraction of the misfitting component A, so $\varepsilon_B = 0$, $\bar{\varepsilon} = \bar{c}\varepsilon_A$, and $\Delta\varepsilon = \varepsilon_A$. Then Eq. (2) becomes

$$\begin{aligned} E(c, V)V^{-1} = {} & \Gamma V^{-1/3} + g(c) - g(\bar{c}) + (\bar{c} - c)g'(\bar{c}) \\ & + M\varepsilon_A^2[(c - \bar{c})^2 - \alpha c^2]. \end{aligned} \tag{7}$$

The fixed-composition case above is unaffected, but the $g \approx 0$ case simplifies—the composition in this case is enriched from $\bar{c}$ to $c = \bar{c}(1 - \alpha)^{-1}$ (or $c = 1$ for $\bar{c} \ge 1 - \alpha$). For $\bar{c} \le 1 - \alpha$, the barrier is reduced by a factor of $(1 - \alpha)^2$ to

$$E_b = \frac{4}{27}\Gamma^3(1 - \alpha)^2\alpha^{-2}(\bar{c}^2 M\varepsilon_A^2)^{-2}. \tag{8}$$

For $\bar{c} \geq 1 - \alpha$, we instead have $c = 1$ and

$$E_b = \frac{4}{27}\,\Gamma^3 (M\varepsilon_A^2)^{-2}[(1 - \alpha) + \bar{c}^2 - 2\bar{c}]^{-2}. \qquad (9)$$

This dependence of the island composition and nucleation barrier on film composition $\bar{c}$ is shown in Fig. 1.

It is unrealistic to expect in general that $g \approx 0$. The enthalpy of mixing varies from system to system, and may often be negligible (as for SiGe). But the entropy of mixing is always present, and will prevent the island from ever attaining a pure composition $c = 0$ or 1, if the film is an alloy. We therefore take

$$g(c) = V_a^{-1} k_B T[c\ln(c) + (1 - c)\ln(1 - c)] \qquad (10)$$

at temperature T, as for a random alloy with negligible enthalpy of mixing.

Including this free energy of mixing in Eq. (7), the case of island nucleation from an AB alloy on substrate of B gives

$$\frac{E(c,V)}{E_0} = \left(\frac{V}{V_0}\right)^{2/3} + \frac{V}{V_0}[(c - \bar{c})^2 - \alpha c^2] + \frac{k_B T}{E_a}\,\frac{V}{V_0}\left[c\ln\frac{c}{\bar{c}} + (1 - c)\ln\frac{1 - c}{1 - \bar{c}}\right], \qquad (11)$$

where $E_0 = V_0 M\varepsilon_A^2$, $E_a = V_a M\varepsilon_A^2$, and $V_0 = (E_0/\Gamma)^{3/2}$. Besides the overall energy scale E_0 and size scale V_0, the behavior is controlled by three dimensionless parameters: α, $\bar{c}$, and $k_B T/E_a$. Given these, the composition and nucleation barrier may be determined by minimizing Eq. (11) with respect to c and then maximizing with respect to V.

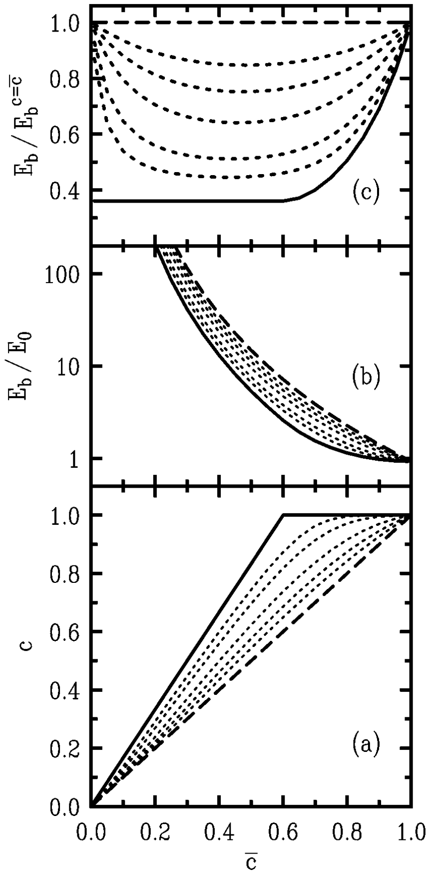

FIG. 1. Island nucleation from a planar alloy of composition $\bar{c}$, for AB alloy on B substrate with $\alpha = 0.4$. (a) Composition of nucleated island. (b) Energy barrier for nucleation. (c) Energy barrier for nucleation *relative to* the value for fixed composition $c = \bar{c}$, to show fractional reduction of nucleation barrier due to alloy segregation. Dotted lines are results for Eq. (11) for a series of temperatures $k_B T/E_a = 0.1$, 0.2, 0.5, 1, and 2. Dashed line is the limit $k_B T \gg E_a$, equivalent to fixed composition $c = \bar{c}$. Solid line is the $k_B T \ll E_a$ limit, equivalent to $g = 0$.

The resulting behavior is summarized in Fig. 1. The high-temperature limit $k_B T \gg E_a$ is equivalent to the case of fixed composition $c = \bar{c}$ discussed above. Similarly, the limit of $k_B T \ll E_a$ is equivalent to the $g \approx 0$ case above. Varying T gives a family of curves which interpolate smoothly between these extremes.

The variation of the nucleation barrier E_b with temperature in Fig. 1b is obscured by the log scale, which is needed due to the strong dependence on $\bar{c}$. To better show the role of g, Fig. 1c gives the barrier *relative to* the case of no alloy decomposition, $c = \bar{c}$. Note that both the enhancement of composition and the reduction of nucleation barrier are maximal for intermediate $\bar{c}$, and both effects disappear in the limits $\bar{c} \to 1$ and $\bar{c} \to 0$.

For SiGe on Si, $E_a \approx 30$ meV, so at typical growth temperatures, $k_B T/E_a \sim 2$. In contrast, for InGaAs on GaAs E_a is roughly 8 times larger—it has twice the misfit, and V_a in this case is the volume *per cation*. Thus the typical reduced temperature is closer to $k_B T/E_a \sim 0.25$. From Fig. 1, one sees that both the composition enhancement and barrier reduction will generally be much larger for InGaAs than for SiGe, assuming similar α.

The focus thus far has been on nucleation. However, for quantum-dot applications a crucial issue is the composition of the island at its final size, which is generally much larger than the critical nucleus. As shown above, the optimum composition is the same at any size. However, kinetic factors may lead to growth at a somewhat different composition. Consider growth of SiGe islands on Si(001). If the growth is limited by surface diffusion, then since Ge diffuses much more quickly than Si [12], the island will be Ge enriched even beyond the prediction of Fig. 1. This is true for InGaAs on GaAs(001) also [13]. However, there are a host of other kinetic issues, involving strain effects on diffusion [14] and incorporation [15,16], which complicate the problem.

For quantum-dot applications, typically the alloy film is only a few atomic layers thick. For island *nucleation*, we could safely treat this film as an infinite reservoir. But if island growth takes place after the incident flux is turned off, then the islands grow at the expense of the film, and the compositional enrichment of the islands leaves behind a compositionally depleted film. For example,

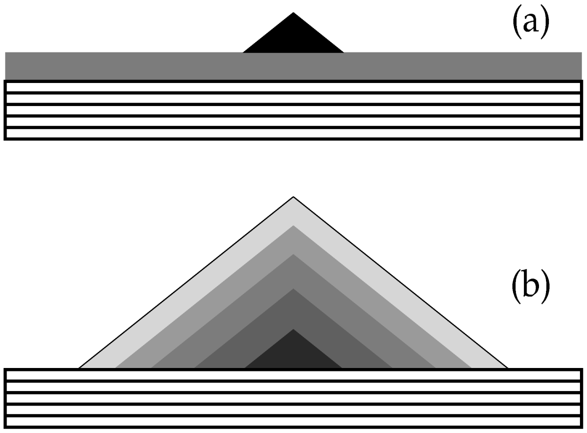

FIG. 2. Schematic illustration of "self-capping" of quantum dot, for, e.g., In$_c$Ga$_{1-c}$As on GaAs. Darker shade of gray indicates higher composition c. Substrate is indicated by white with horizontal lines. (a) Initial nucleation of In-enriched island on strained alloy film on substrate. (b) Later stage, when island has consumed alloy film, which becomes progressively In depleted during growth process.

for InGaAs on GaAs, as the island grows In rich, the film is progressively depleted of In. If bulk diffusion is negligible, the island grows only by adding material to its surface. Then the island will have an In-enriched core, but as it grows from the progressively In-depleted reservoir, the outermost layers of the island become progressively less In rich. This is illustrated schematically in Fig. 2.

Thus the island may be to some extent self-capping, with electrons confined to a more In-rich central region of the island. In this case the electronic properties would be radically affected, since the "effective" quantum dot is both smaller and more In rich than measurements of total size or average composition would suggest. At the same time, fabrication may be more robust—the electronically important region is confined to the core, and so will be less affected by subsequent capping with GaAs or other passivating layers.

Note that this effect is distinct from surface segregation, and takes place simultaneously. Thus the profile in Fig. 2 could also include a highly enriched layer of atomic thickness at the surface. However, this would presumably float away during subsequent capping. The possibility of maintaining an enriched core despite surface segregation in the opposite direction depends to some extent on a kinetic competition between surface segregation and island growth. For other systems, such as SiGe on Ge, the surface segregation could even enhance the self-capping effect.

So far, the discussion has been restricted to coherent islands, i.e., islands having no dislocations. If the islands grow sufficiently large, however, they will eventually form strain-relieving misfit dislocations. At high misfit or low temperature, islands may even nucleate with dislocations from the outset [17]. Roughly speaking, such dislocated islands may be described by Eq. (2) above, but with α approaching 1, and a much larger value of Γ (reflecting the formation energy of the dislocations) [3]. Thus one may anticipate particularly strong alloy enrichment for such dislocated islands.

In conclusion, alloy decomposition is a ubiquitous and important effect in nucleation and growth of strained islands. It can alter the properties of self-assembled quantum dots, and exacerbates the problem of strain-induced roughening of planar layers in electronic devices.

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