Thermodynamic Self-Limiting Growth of Heteroepitaxial Islands Induced by Nonlinear Elastic Effect

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ABSTRACT: We investigate nonlinear elastic effect (NLEF) on the growth of heteroepitaxial islands, a topic of both scientific and technological significance for their applications as quantum dots. We show that the NLEF induces a thermodynamic self-limiting growth mechanism that hinders the strain relaxation of coherent island beyond a maximum size, which is in contrast to indefinite strain relaxation with increasing island size in the linear elastic regime. This self-limiting growth effect shows a strong dependence on the island facet angle, which applies also to islands inside pits patterned in a substrate surface with an additional dependence on the pit inclination angle. Consequently, primary islands nucleate and grow first in the pits and then secondary islands nucleate at the rim around the pits after the primary islands reach the self-limited maximum size. Our theory sheds new lights on understanding the heteroepitaxial island growth and explains a number of past and recent experimental observations.

KEYWORDS: Quantum dots, nonlinear elastic effect, self-limiting growth, nanopatterned substrate

Since first discovered in 1990,¹ heteroepitaxially grown self-assembled 3D islands have drawn continued attention due to fundamental interest in understanding their complex growth behavior and their potential applications as quantum dots in nano electronic and optoelectronic devices.²−⁵ Growth of such islands is a strain-mediated and thermally activated nucleation process, characterized by random island positions and broad size distribution.⁶−⁸ However, by manipulating the strain field on the surface prior to growth, island nucleation can be directed and growth can be controlled to achieve highly ordered island arrays with significantly improved size uniformity. The most successful examples include using multilayer growth with buried islands⁹,¹⁰ and patterned substrates with surface ridges, grooves, mesas and metal patterns,¹¹−¹⁶ and most recently pits.¹⁷−²⁴ Despite extensive experimental and theoretical studies, however, fundamental understanding of nucleation and growth of strained islands, especially on patterned substrates is far from complete.

Our basic understanding has so far relied mostly on theoretical analyses based on continuum linear elastic theory.²⁵−³² Island formation is triggered by a competition between surface energy and strain energy: the former increases with island volume in the power of 2/3 and the latter decreases with island volume in the power of 1, so that strain relaxation always wins beyond a critical island size, as shown in Figure 1. The linear-elastic theory has enjoyed tremendous success in explaining many experimental observations as well as guiding new experiments.⁶−⁸ However, they are in principle limited to islands with shallow facet angles (shallow-angle approximation²⁵−³²) and relatively small size or nonlinear elastic effects should kick in. For example, within the linear elastic regime

Figure 1. Reduced island total energy in the linear (Eₗ) and nonlinear elastic regime (Eₙ) along with island surface energy (Eₙ), linear strain relaxation energy (Eₗ), and nonlinear strain relaxation energy (Eₙₗₗ) as a function of reduced island volume. Eₗ and Vₗ is the island nucleation barrier and critical size in linear elastic regime. γ₇f, γ₇w, and γ₇wp are the surface energy density of the island facet, the wetting layer on flat surface, and inclined pit surface, respectively.
thermodynamically the strain relaxation energy decreases continuously with the increasing island size so that island would continue to grow indefinitely, whereas experimentally island sizes are limited before dislocation formation. For this reason, kinetic self-limiting growth mechanisms have been incorporated to explain the experiments. Furthermore, recent experiments have shown an intriguing behavior of island growth on a pit-patterned substrate. The pit inclination angle is strongly on both island facet angle and pit inclination angle, leading to complex growth behavior that are all consistent with experimental observations.

In this Letter, we develop a theoretical model that goes beyond linear elasticity by including nonlinear elastic effects in calculating strain energy. We show that nonlinear strain relaxation gives rise to a thermodynamic self-limiting growth mechanism, which is unknown before. It may trigger dislocation formation within a coherent island beyond a maximum size that decreases with the increasing island facet angle, that is, the steeper the island, the sooner the dislocation forms. Furthermore, the island growing in a pit depends strongly on both island facet angle and pit inclination angle, leading to complex growth behavior that are all consistent with experimental observations.

Island growth on the surface will induce strained film thickness variation, and consequently the surface stress variation. In the linear elastic theory, the surface stress is proportional to the film thickness as well as the bulk strain in the film, that is, \( \sigma(x,y) = Y \varepsilon_c h(x,y) \), where \( Y \) is the elastic modulus of the film, \( h(x,y) \) is the film thickness function, \( \varepsilon_c \) is the bulk strain in the film due to lattice mismatch, which is assumed to be constant (not varying along z-direction). However, as the island facets becomes steeper and the island size becomes larger, the top part of the island feels less constraint from the substrate and becomes partially relaxed, that is, the strain in the film (island) decreases along z direction. Such strain variation with z will inducing a nonlinear, higher-order dependence of surface stress on film thickness. In the simplest possible form, we assume the strain decreases linearly along z-direction as \( \varepsilon(z) = \varepsilon_0 (1 - \tau z) \) and then the surface stress is expressed as

\[
\sigma(x,y) = \sigma_0 h(x,y) - \frac{\tau_0 h^2(x,y)}{2}
\]

where \( \sigma_0 = Y \varepsilon_0 \) is the bulk stress in the film due to lattice mismatch, \( h(x,y) \) is the film thickness depending on position, and \( \tau_0 \) is nonlinear coefficient. Alternatively, the nonlinear elastic effect can simply be included by extending the linear stress–strain relationship \( [\sigma(x,y) = Y \varepsilon_c h(x,y)] \) to the second order as \( \sigma(x,y) \sim C_1 h(x,y) + C_2 h^2(x,y) \), which is equivalent to eq 1, while the physical origin of the second-order term is shown to come from nonuniform strain distribution within the island.

The first and second term in eq 1 represents the linear and nonlinear strain relaxation energy, respectively. For a faceted island formation, the strain relaxation energy can be calculated using the elastic Green’s function method

\[
E_{\text{el}} = -\frac{1}{2} \int dr \chi(r) f(r) f(r')
\]

where \( \chi \) is the elastic Green’s function, \( r = (x,y) \) is the surface position, \( f(r) \) is the force monopole density on the island surface defined by \( f_i(r) = \partial \sigma_i(r) \) where \( i = x, y \). In the linear elastic regime, \( f(r) \) is a constant for a given facet; adding the nonlinear elastic effect, \( f(r) \) becomes thickness dependent and it is smaller at the apex region of the island.

The island total energy on a surface [see Figure 1 (upper inset)] can be obtained by integrating eq 2 and adding surface energy, which gives

\[
E_{\text{tot}} = \alpha V^{2/3} - \beta V + \eta V^{4/3}
\]

where \( \alpha = (\sec \theta - \gamma_f/\gamma_w)(6 \cot \theta)^{2/3}, \beta = 9 \tan \theta/2 \) and \( \eta = 6^{4/3} \tan^{4/3} \theta, \gamma_f \) and \( \gamma_w \) are the surface energy density of the island facet and the wetting layer [Figure 1 (upper inset)], respectively, and \( \theta \) is the island facet angle. To obtain eq 3, we use \( \gamma_f/\gamma_w \) as energy unit, \( \gamma_f/\gamma_w \) as volume unit, while \( c = \sigma_0(1 - \tau z) \).
− ν^2)/πY is the scaled elastic energy density, ν is Poisson ratio, Y is the Young's modulus, V = L^3 tan θ/6 is the island volume, L is the island base length, and τ is the scaled nonlinear coefficient. In the calculation below, we use γ_s/γ_f = 1 for simplicity, that is, we neglect surface energy anisotropy, which will not alter the general conclusion we obtain.

The NLEF induces a strain term that increases with island volume in the power of 4/3 (keeping only the first order of τ term), which reduces the strain relaxation energy from the linear term and gives rise to a minimum of total energy at V_m as shown in Figure 1b. Interestingly, this implies a thermodynamic self-limiting effect induced by nonlinear elastic term to hinder the island growth beyond V_m, because the island energy would increase with further growth, different from the previous works on interrupted coarsening due to kinetic limited growth rate, surface energy anisotropy, nonlinear stress field, or strain stabilization of 2D islands in linear regime. Consequently, beyond this “maximum” size, the coherent island becomes more prone to injection of dislocations. Note that previous studies of the dislocation injection are based on comparison between the dislocation formation energy and island-induced strain relaxation within the linear regime; here, we show that the dislocation formation may kick in sooner due to the nonlinear elastic strain relaxation within the island.

Different from metal island, semiconductor strained island is usually faceted, and the specific facet is often stabilized by strain, such as (10S) facet of Ge. Below we will use Ge/Si(001) as a prototype system to do some quantitative analysis and the facets involved including (105) for “pyramid”, (113) for “dome”, and (111) for “barn” island, where the facet angles (with respect to the substrate (001) surface) are 11.3, 25.2, and 54.7, respectively. Figure 2a shows the total energy E_m versus the island size V at these three island facet angles. We can see that at small θ = 11.3 (pyramid), E_m first increases with increasing V, reaches the maximum at critical size V_c (see inset), and then decreases as V further increases until it reaches the minimum at V_m and then increases again. At intermediate θ = 25.2 (dome), the shape of E_m − V curve is similar to that of pyramid, while it crosses with pyramid energy line twice. This indicates that beyond certain size, pyramid would transform into dome. At even larger θ = 54.7, E_m increases monotonically with island size and the critical size V_c going to infinity, which implies that large facet angle island (barn) would never form under such condition.

The general dependence of V_c and V_m on θ is shown in Figure 2b with the three typical θ values indicated. One can see that V_c increases with increasing θ. This is because when island size is small, surface energy plays the dominant role, formation of steeper island (large θ) forms with larger surface area for a given volume, leading to a larger critical size. This is consistent with the experimental observation that “pyramid” with shallow facet angle form first, followed later by “dome” with steeper facet angle or upon annealing. On the other hand, V_m decreases quickly as θ increases, indicating that steeper island has a smaller V_m. This is because steeper island has a larger height, maximizing the nonlinear effect. For large enough θ, E_m has no extremum and V_c goes to infinity.

V_m being smaller for larger θ seemed to contradict our intuition, because in experiments dome is always larger than pyramid. However, in the experiment the pyramid actually cannot reach its maximum size before transforming to dome or elongated to nanowire, while dome will reach its V_m without shape transition. This is also consistent with the experimental observation that dislocations usually form in the dome (presumably after it reaches V_m) but not in the pyramid without reaching V_m.

Figure 2b also shows that when NLEF is strong (large τ), the growth of too steep an island (large θ, for example, barn island with (111) facet) is forbidden. This finding is consistent with the experimental observations that barn island cannot be found in pure Ge growth on Si substrate, while it appears in SiGe alloy island growth where NLEF should be smaller due to the larger island size and smaller bulk strain in the island comparing...
to the pure Ge island. Figure 2c shows the dependence of $E_m$ on $\tau$. One sees that $V_c$ does not vary much with $\tau$ because $\tau$ is a higher-order term, which only plays a role when $V$ becomes large, so we can expect that the nonlinear elastic effect or nonuniform strain distribution would not affect the island nucleation behavior, such as, the nucleationless island formation.\(^6\) In contrast, $V_m$ decreases sharply with increasing $\tau$. This is further shown in Figure 2d where $V_c$ and $V_m$ are directly plotted as a function of $\tau$. The strong dependence of $V_m$ on $\tau$ indicates that the self-limiting effect depends strongly on island facet angle, so does the dislocation location within the island.

In accordance with the experiment, we may perform some quantitative estimation of the nonlinear coefficient. As discussed above, the NLEF comes from the partial relaxation in the island along $z$-direction. Usually the height of the “dome” shape coherent island is about $10–30$ nm\(^3\),\(^5\),\(^4\) if we assume the strain $\epsilon(z)$ relaxes to half of the bulk strain in the island at $30$ nm, the nonlinear coefficient $\tau_n$ in eq 1 is $1/60$ nm\(^{-1}\) and the reduced nonlinear coefficient $\tau = \tau_n(\gamma/\epsilon)$. For Ge/Si(001) island, $\gamma = 6100$ meV/nm\(^2\), $\epsilon = 270$ meV/nm\(^2\), so we have $\tau \approx 0.38$. Experiments showed that the size of Ge dome island ranges from $10^4$ to $2 \times 10^4$ nm\(^2\); if we assume these are approximately their thermodynamic self-limited size, from Figure 2d we estimate that the $r$ ranges from $0.35$ to $0.42$. Nevertheless, we also plot $r$ over a larger range in Figure 2 just to reveal some general behavior.

Now, we consider the island grown inside a pit, as shown in Figure 1 (lower inset). The solution of eqs 1 and 2 is similar as eq 3 and becomes

$$E_{\text{in}}^p = \alpha' V^{2/3} - \beta' V + \eta' V^{4/3}$$

where $\alpha' = (\sec \phi - \gamma_{\text{wp}} \sec \phi/\gamma_i) [6/(\tan \phi + \tan \phi)]^{2/3}$, $\beta' = 9(\tan \phi + \tan \phi)/2$ and $\eta' = 6^{4/3} ((\tan \phi + \tan \phi))^{5/3}$, $\gamma_{\text{wp}}$ is the surface energy density of the inclined pit surface, $\phi$ is the pit inclination angle, and the island size in the pit is $V = L^3(\tan \phi + \tan \phi)/6$, where $L$ is the length of the boundary formed between island facet and inclined pit surface; we use the same reduced energy and volume units as for eq 3. Apparently, eq 4 reduces to eq 3 for $\eta = 0$.

The qualitative behavior becomes more complex due to the additional freedom, $\phi$. Figure 3a shows the total energy of island in the pit $E_m^p$ as a function of island size $V$ at different $\phi$. One sees that for small $\phi$ (smaller than $\theta$), $E_m^p$ also has a maximum at critical size $V_c$. The inset of Figure 3a shows the enlarged plot for small island size $V$, and one can see that as $\phi$ increases, the critical size and energy barrier for island nucleation in the pit becomes smaller, same as the linear elastic analysis.\(^3\)\(^0\) For large $\phi$, $E_m^p$ decreases from the beginning, that is, the nucleation energy barrier reduces to zero. This is because when $\phi \geq \theta$, $\alpha'$ becomes negative and the surface energy does not increase when island forms in the pit. When $\phi < \theta$, that is, $\alpha' > 0$, the behavior of $E_m^p$ is similar to $E_m$ only with different dependence on $\theta$, $\phi$, and $\tau$.

Figure 3b shows the maximum island size $V_m$ as a function of $\phi$ for different $\theta$. For small $\theta$, $V_m$ decreases quickly with $\phi$ for small $\phi$ and slows down as $\phi$ becomes larger; while for large $\theta$, $V_m$ does not change too much with $\phi$. Especially, when $\theta$ is too large, at small $\phi$ $V_m$ goes to infinity and an island cannot form, whereas at larger $\phi$ $V_m$ becomes finite and $V_m$ appears so an island can form and grow. These results indicate that a pit can greatly enhance the nucleation of an island inside the pit, especially for large pit inclination angle.

The total energy of the island in the pit shows similar dependence on the nonlinear coefficient $\tau$ as that of island on flat surface, that is, $V_m$ decreases with increasing $\tau$; however, the maximum island size $V_m$ becomes smaller because of the pitting effect, as shown in Figure 3c in comparison with Figure 2c. Figure 3d shows the dependence of $V_m$ on $\tau$ for different $\phi$; $V_m$ decreases quickly at small $\tau$, and slows down when $\tau$ becomes larger. For comparison, we also showed results without pit $(\phi = 0)$, $V_m$ becomes smaller as $\phi$ increases.

Now we proceed to analyze how island may nucleate on pit-patterned substrates. First of all, at any pit inclination angle $\phi$, island grown in the pit has a smaller nucleation energy barrier and critical size or no barrier compared with island grown on a flat surface, including at the rim of a pit. This means that island prefers to first nucleate and grow in the pit. In the experiments,\(^2\)\(^1\),\(^2\)\(^3\) island can be found in all the pits; for the pit with larger $\phi$ when additional islands form at the rim of pit, the islands in the pit are bigger, implying that they nucleate and grow first.

Furthermore, our results suggest that on pit-patterned substrates primary islands first nucleate in the pits and grow. When they reach the maximum size $V_m$ whose growth slows down or stops, secondary islands may then nucleate at the rim. For pits with small inclination angle $\phi$, islands grown in them have a very large maximum size, so that islands may never reach the maximum size and hence no secondary islands appear. Also, the pits may be too small, so that primary islands in the pits may grow to a large size to impede the nucleation of secondary islands at the rim next to them due to the repulsive elastic interaction between islands.\(^2\)\(^6\),\(^3\)\(^1\) For pits with large $\phi$, the maximum island size becomes smaller and islands in the pits can easily reach $V_{\text{in}}$ so that secondary islands are more likely to nucleate at the rim. Indeed, experiments found islands nucleate at the rim for larger $\phi$; the larger the $\phi$ is, the smaller the island size in the pit will be, and no island is expected at the rim if the pit size and/or inclination angle is very small. All these theoretical predictions are perfectly consistent with experimental observations.\(^2\)\(^1\),\(^2\)\(^3\)

According to the discussion above, the maximum island size $V_m$ is the key physical quantity in determining whether secondary islands can nucleate at the rim, and it depends on pit inclination angle, island facet angle, and nonlinear strain relaxation. Thus, it is important to get a complete picture of how $V_m$ varies with these parameters. Figure 4 shows a 3D plot of $V_m$ as a function of $\phi$ and $\theta$. In general, for a given $\phi$, $V_m$ decreases as $\theta$ increases; for a given $\theta$, $V_m$ decreases as $\phi$ increases; however if $\theta$ is too large, an island may not nucleate and grow at small $\phi$ (black region in Figure 4). The nonlinear coefficient $\tau$ does not significantly affect the contour of $V_m(\phi, \theta)$; however, it affects the scale of $V_m$ and the range of black region where the island does not form.

In conclusion, we have developed a theoretical model to elaborate the NLEF on strained island growth on flat and pit-patterned substrates beyond the conventional linear elastic theory, which significantly advances our fundamental understanding of the strain island growth. We predict that the NLEF introduces a thermodynamic self-limiting effect on the growth of coherent islands, which depends on the island facet angle and pit inclination angle. In pit-patterned substrates, primary islands first nucleate and grow in the pit, then secondary islands may nucleate at the rim. Such a trend becomes stronger for larger and steeper pits. These findings explain several outstanding past and recent experimental observations.
Figure 4. Maximum island size $V_m$ of island grown in the pit as a function of island facet angle $\theta$ and pit inclination angle $\varphi$ for (a) $\tau = 0.4$ and (b) $\tau = 0.6$. The black region means $V_m$ does not exist, that is, the total energy increases monotonically with island size.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work at Xi’an Jiaotong University was supported by NSFC (Grant 11404252) and the Startup Funding from FIST, Xi’an Jiaotong University (H.H.). The work at University of Electronic Science and Technology of China was supported by the Startup Funding from UESTC(X.B.). The work at Utah was supported by DOE-BES (Grant DE-FG02-04ER46148) (F.L.).

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DOI: 10.1021/acs.nanolett.6b01525
Nano Lett. 2016, 16, 3919–3924
(43) It can be shown $\tau$ is proportional to $\tau_0$ but independent of $\theta$, and $\tau = 2(4 \ln 2 - 1)\tau_0/3$ in 2D but its analytical form in 3D is unknown.
(44) Note that our expression of the linear term has a small difference from ref 25, because we use the exact volume expression instead of $V = L^3 \tan \theta/8$. Also, the units for energy and volume that we use are not the critical size and energy barrier in the linear regime, because we need to examine the dependence on $\theta$ so the reduced units cannot depend on $\theta$.