Stable and uniform arrays of self-assembled nanocrystalline islands

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The stability of islands against coarsening during the self-assembly process of the Stranski-Krastanow systems was explored by an energy analysis and by numerical simulation for the morphological evolution of the islands dominated by surface diffusion. The results demonstrate that the Stranski-Krastanow systems can develop islands stable against coarsening when subject to a large film-substrate interaction and a large mismatch strain. The stable systems can be adopted to grow uniform and regular island arrays by adjusting the length scale in the island formation process and by introducing a regular pattern of small amplitude on the film surface.

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The self-assembly of small crystalline islands on the surface of a heteroepitaxial film-substrate system is a remarkable phenomenon.[1–9] The process is generally observed when growing the heteroepitaxial film on the substrate under the Stranski-Krastanow (SK) mode. The film morphology is flat initially and then develops into islands on the top of a uniform layer, called the wetting layer, as the film thickness exceeds a critical value. The island size can be tailored by varying the alloy composition of the film, and the order of magnitude of the size can easily reach the nanometer scale to cause the quantum confinement effect, leading to unique electronic, magnetic, and optical properties.[8] The islands also have the advantage that they can remain coherent with the underlying film without the formation of defects in the system.[2] The capability of self-assembly, the unique material properties, and the excellent crystal quality make the nanocrystal islands an appealing building block of future semiconductor devices.

In order to realize the device applications, it is pivotal to control the island size uniformity since the size significantly affects the properties of each island due to the quantum confinement effect. This task, however, is challenging. The difficulty mainly comes from the instability of the islands against coarsening where the larger islands grow at the expense of the smaller ones, leading to a wide island size distribution.[4,5,7,10–12] Although the island-coarsening problem has been well understood and recognized as a major obstacle to the development of the self-assembly technology, how to suppress the coarsening process remains an open question.[13–16]

A possible stabilizing mechanism is the long-range interaction, also called the film-substrate interaction.[17,18] The interaction plays a significant role in the SK transition and the development of the wetting layer.[17,19] The effects of the interaction on the island stability against coarsening was first examined in Ref. 20, and it was shown that a strong interaction could result in a stable and uniform wavy surface. The result was promising for growing stable and uniform island arrays. However, the analysis focused on extremely shallow wavy profiles.[21] The more important issue of the stability of facet islands, for example, the pyramids observed in experiments,[1] has not been fully understood.

We investigated this question by carrying out energy analysis of the islands and simulation for the morphological evolution of the SK systems. The results demonstrate that the island coarsening can be stabilized by a combination of a strong film-substrate interaction and a large mismatch strain in the film. The positive effect of mismatch strain on stability, overlooked in the earlier analysis,[20] is in contrast to the common knowledge that the strain energy relaxation due to the mismatch strain favors coarsening.[13] The stable SK systems are shown to have the potential to develop uniform island arrays.

The island stability against coarsening was first examined by considering the total energy of a two-dimensional film/substrate system; see Fig. 1. The substrate and the film are elastically similar materials. The film consists of a flat wetting layer and a periodic array of facet islands. The film structure is characterized by four independent parameters: the facet angle ϕ, the average film thickness H, the normalized wetting layer thickness $\hat{h}=h/H$, and the island areal coverage $\xi=d/\lambda$ where d is the island width and λ is the island spacing.

The total energy of the SK system is controlled by the surface energy density γ of the film, the long-range film-substrate interaction, and the mismatch strain ϵ_0 between the film and the substrate. The surface energy density is anisotropic: $\gamma=\gamma_2$ on the facet, $\gamma_=\gamma_1$ on the flat wetting layer. The two quantities are normalized by a reference density γ_0, and are denoted as $\hat{\gamma}_1$ and $\hat{\gamma}_2$, respectively. The film-substrate interaction, within the continuum framework, can be modeled as a special type of film surface energy of which density g varies with the distance z between the film surface and the film-substrate interface.[14,19] The density can be ex-

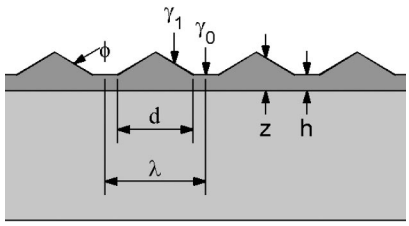

FIG. 1. A schematic diagram of an array of facet islands on a wetting layer and a substrate.

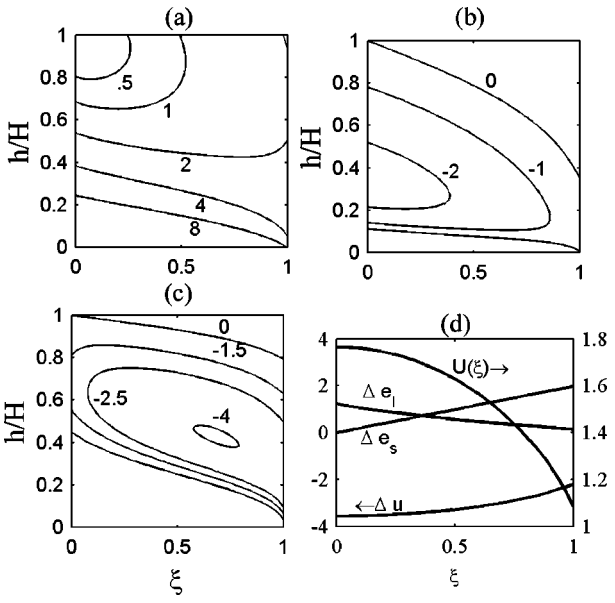

FIG. 2. The contours of the total energy Δe_{tot} for the cases where the equilibrium morphology is (a) a flat film, (b) a coarsening island array, and (c) a stable island array. (d) The variations of U, Δu, Δe_s, and Δe_I with ξ for the case in (b). The results of Δe_{tot}, Δu, Δe_s, and Δe_I are normalized by $0.01\gamma_0$. The parameters p, $\hat{\gamma}_2$, $\hat{\gamma}_1$, and ϕ are fixed to be 1, 1, 1, and 11.3°, respectively. On other hand, $\sqrt{\hat{g}_0}l/L=0.03$, 0.03, and 0.2, and $H/L=.03$, 0.15, and 0.5 in (a)–(c), respectively.

pressed as $g(z)=g_0 l^p/(z+l)^p$ where g_0 and l are material properties, and the exponent p depends on the interaction mechanism.[22,23] The mismatch strain ϵ_0, on the other hand, results in the strain energy in the system; the characteristic strain energy density of the system is given by $w_0=\mu(1+\nu)^2\epsilon_0^2/(1-\nu)$ where μ is the shear modulus, and ν is Poisson's ratio.

We calculated the variation of the total energy Δe_{tot} (per unit length in the lateral direction) with the normalized wetting layer thickness $\hat{h}$ and the island areal coverage ξ for given material properties and film thickness H. The symbol Δ denotes that the value is relative to that of the same system without islands ($\hat{h}=1$). The contributions from the surface energy Δe_s and the film-substrate interaction energy Δe_I could be calculated exactly, while the strain energy Δu was estimated by the perturbation result:[13] $\Delta u=-w_0 H(1-\hat{h})\phi U(\xi)$ where $U(\xi)$, depicted in Fig. 2(d), describes the dependence of Δu on the areal coverage ξ. Δu is negative and its magnitude increases monotonically as $\hat{h}$ and ξ decrease, meaning the strain energy favors both the transformation of wetting layer into islands and the coarsening of the islands.

Figures 2(a)–2(c) plot the contours of Δe_{tot} in three representative cases, which differ in the characteristics of the location $(\xi_{eq},\hat{h}_{eq})$ of the minimum in Δe_{tot}. In (a) $\hat{h}_{eq}=1$, in (b) $\xi_{eq}=0$ and $\hat{h}_{eq}<1$, and in (c) $\xi_{eq}>0$ and $\hat{h}_{eq}<1$. The first case corresponds to a flat film surface at a small H where the island formation is suppressed. The second case indicates the island formation is favorable, while the islands are unstable against coarsening. The third case, contrary to the second one, is an example of a stable facet island array. The condition of the stable SK systems can be derived to be[24]

$$S=\left[\frac{U(0)\tan\phi}{p}\frac{\sqrt[p]{\hat{g}_0}l}{L}\right]^{p/(p+1)}-\hat{\gamma}_1 G>0, \tag{1}$$

where $L=\gamma_0/w_0$ is the characteristic length in the lateral direction, $\hat{g}_0=g_0/\gamma_0$, and $G=-1+\gamma_2/\gamma_1\cos\phi$.

Equation (1) indicates that the stability strength S can be increased by a strong film-substrate interaction and by a large mismatch strain. The effect of the mismatch strain on S is a significant but surprising finding. It is known that the strain energy caused by the mismatch strain favors the coarsening of islands. Why can a large mismatch strain stabilize island arrays?

The answer is revealed in Fig. 2(d), which plots the variation of the strain energy, the surface energy, and the interaction energy with the island areal coverage ξ for a case of coarsening islands. The result shows as the islands coarsen and the island areal coverage ξ approaches zero, the effect of the strain energy relaxation on the coarsening of the islands diminishes. Whether or not the coarsening can be stabilized at $\xi>0$ is determined by the competition between the surface energy and the interaction energy. In the SK system, the former favors the coarsening, and the strength is G. The latter, in contrast, causes the island array to cover the whole wetting layer since an exposed wetting layer has higher interaction energy than the island surface. The strength is proportional to the interaction density $g(h)$, which depends on the wetting layer thickness or equivalently on the volume of the film that is transformed into the islands. The transformation is controlled by the mismatch strain. A higher mismatch strain results in more transformation, a thinner wetting layer, and accordingly higher interaction strength against island coarsening.

The effects of the mismatch strain and the film-substrate interaction on the stability of self-assembled islands against coarsening in the SK systems were further examined by numerical simulation for the morphological evolution of the islands. Of particular interest was the evolution dominated by surface diffusion,[20]

$$\frac{\partial f(x,y,t)}{\partial t}=\frac{\Omega\rho_s D_s}{n_z k_B T_k}\nabla^\Gamma\cdot(\nabla^\Gamma\chi), \tag{2}$$

where $f(x,y,t)$ is the surface profile, Ω the atomic volume, ρ_s the adatom density, D_s the surface diffusivity, k_B the Boltzmann constant, T_k the temperature, ∇^Γ the surface gradient operator, and χ the surface chemical potential. The surface chemical potential χ of the SK systems can be found to be[20]

$$\chi=\mu_0+\Omega\left[w-(g+\gamma)\kappa+\frac{\partial g}{\partial z}n_z+\nabla^\Gamma\cdot\frac{\partial\gamma}{\partial\mathbf{n}}\right], \tag{3}$$

where μ_0 is the chemical potential of the film without stress, w the strain energy density, $\gamma=\gamma(\mathbf{n})$ the anisotropic surface energy density, and κ the curvature.

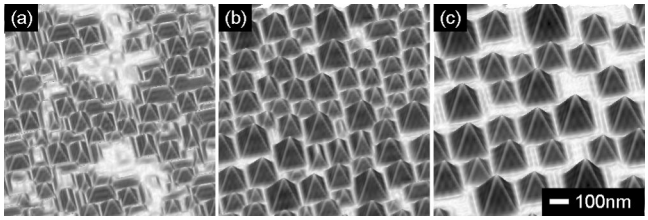

FIG. 3. The surface profiles at (a) $t/t_L=0.0695$, (b) 0.551, and (c) 2.07 during an island-coarsening process where $L=10^3$ Å, $\hat{g}_0=0.125$, and $H/L=0.05$. The tone of the colors represents the angle ϕ between the normal vector of the surface and the vertical direction. The lightest one corresponds to $\phi=0°$, and the darkest to 11°. The color scheme is also applied to Figs. 4 and 5.

Equation (2) was solved by the simulation scheme described in Ref. 20. The scheme was modified by including the minimums of the surface energy density $\gamma(\mathbf{n})$ in the directions of {105}, {102}, and {113} in order to capture qualitatively the island morphology observed in experiments.[25] The minimums in $\gamma(\mathbf{n})$ were limited to shallow ones in the simulation because the numerical method lacked the capability to produce perfect facets. This prevented us from comparing the simulation results with the stability condition in Eq. (1) quantitatively. Nevertheless, the simulation results reveal, from the kinetic point of view, an insightful picture of the effects of the mismatch stain and the film-substrate interaction on the stability of islands during the self-assembly process. The agreement between the island shapes in the simulation and in the experimental results is also notable, as shown in Figs. 3–5.

The initial surface $f(x,y,0)$ in our simulation was taken to be an almost flat profile with some random roughness.[20] The film-substrate interaction is assumed to be dominated by the quantum confinement mechanism; in other words, $p=1$. The simulation results were normalized by the characteristic time $t_L=k_BT_kL^4/\rho_sD_s\Omega^2\gamma_0$.

Figure 3 depicts the morphological evolution of the case where $L=10^3$ Å, $\hat{g}_0=0.125$, $H/L=0.05$, and $l=4$ Å.[26] The evolution started with the island formation process during which the pyramid islands emerged and covered most of the film surface; see Fig. 3(a). Followed by the formation process was the coarsening of the islands, characterized by the growth of larger islands at the expense of smaller ones and by a gradual decease of island areal coverage; see Figs. 3(b) and 3(c).

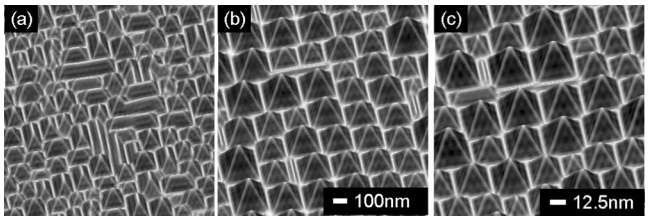

FIG. 4. The morphological evolution of islands stable against coarsening. (a), (b) The surface profiles at $t/t_L=0.2$ and 58.2 for the case where $L=10^3$ Å, $\hat{g}_0=1$, and $H/L=0.11$. (c) The profile at $t/t_L=28.4$ for the case where $L=125$ Å, $\hat{g}_0=0.125$, and $H/L=0.085$.

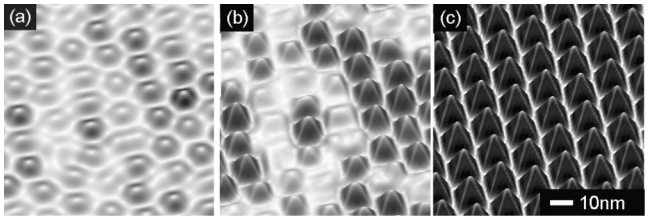

FIG. 5. The surface profiles at (a) $t/t_L=1.34$, (b) 1.46, and (c) 12.0 during the morphological evolution of the stable SK system in the two-step approach where $L=62.5$ Å, $\hat{g}_0=0.125$, and $H/L=0.08$. The initial surface contains a hexagonal pattern and some random roughness. The contrast of (a) is increased to enhance the visual effect.

The characteristics of the morphological evolution change drastically when the film-substrate interaction $\hat{g}_0$ is increased and/or the length L is reduced. The effect of a higher $\hat{g}_0$ is presented in Figs. 4(a,b) where $\hat{g}_0=1$, $H/L=0.11$, and the other material parameters are identical to those in Fig. 3. Instead of island coarsening, the film in this case underwent island formation and coalesce process, and more importantly, the morphological evolution reached a steady state. The result confirms that a higher $\hat{g}_0$ enhances the stability of islands against coarsening. The effects of a smaller L on the morphological evolution were found to be similar to those of higher $\hat{g}_0$, characterized by island formation, island coalescence, and a steady state stable against coarsening. The steady state of the case where $L=125$ Å, $\hat{g}_0=0.125$, and $H/L=0.085$ is depicted in Fig. 4(c) as an example.

The significance of the ratio $\hat{g}l/L$ in the stability of islands against coarsening, as indicated in Eq. (1), was examined by simulating a series of cases where the ratio $\hat{g}l/L$ was the same as that employed in Fig. 4 while L varied from 10^3 to 62.5 Å. All of the simulation reached steady states. Simulation was also carried out for the cases where $\hat{g}l/L$ was as small as that adopted in Fig. 3, and the coarsening of islands was found in all of the cases.

Figure 4 indicates that the stability against island coarsening, though resulting in a steady state, does not lead to islands of uniform size. The variation of island size came from two causes. First, the initial surface was a ''randomly'' rough profile without any regular pattern, and second, the length scale in the island formation process differed from that in the steady state, as suggested in Figs. 4(a) and 4(b).

The two causes were demonstrated in simulation by showing that solving only one of the issues would not yield a uniform island array, but solving both would. For example, the first issue could be eliminated by including a regular pattern on the initial surface profile. The pattern, however, disappeared either in the initial island formation process or in the later island coalescence process, irrespective of the length scale of the pattern. Similarly, the second issue could be resolved in the simulation by using two steps with different $\gamma(\mathbf{n})$ to handle the formation of islands and the steady state.[20] The approach enabled the length scale in the former to match that in the latter, but it did not produce a uniform island array.

We then examined the situation when the two-step approach and a regular pattern on the initial surface were both adopted. The simulation result for the case where $L = 62.5$ Å, $\hat{g}_0 = 0.125$, and $H/L = 0.08$ is plotted in Fig. 5. The result indicates that a simple pattern on a stable SK system could motivate homogeneous formation of islands and consequently a uniform island array stable against coarsening during the two-step approach even though a significant amount of random roughness was present in the initial surface profile.

A question raised naturally by the results in this paper is how to increase the strength of the interaction in order to grow stable and uniform island arrays on the SK systems. One possible scheme of strong interaction is to enhance the quantum confinement mechanism.[22] The mechanism can cause the interaction strength $g_0 l$ to be as high as 6.5×10^{-10} J/m for a good conductor like Ag.[22] This value is large enough to stabilize shallow islands with $\phi = 11°$ and $\gamma_2/\gamma_1 = 0.99$ even when the mismatch strain ϵ_m is only 0.2%, assuming $E = 100$ GPa, $\nu = 1/3$, $\hat{\gamma}_1 = 1$, and $\gamma_0 = 1\,\mathrm{J/m^2}$. The quantum confinement mechanism is much weaker in semiconductor materials; however, the problem may be overcome by doping the film heavily. For example, $g_0 l$ can be 5.7×10^{-12} J/m in the SiGe/Si systems when introducing one atomic percent of donors in the film. The interaction strength can stabilize the pyramid island array if L is less than 250 Å, assuming $\gamma_2/\gamma_1 = 0.99$ and $\hat{\gamma}_1 = 1$, which roughly corresponds to SiGe films with more than 50% of Ge in atomic concentration.

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[23] The case where $p = 1$ corresponds to the quantum confinement mechanism and $p = 2$ to dispersion force (Ref. 22).
[24] The result is also valid for the three-dimensional case of pyramid island arrays when $U(0)$ is replaced by the value of the pyramid islands.
[25] The orientations of the minimums in $\gamma(\underline{\mathbf{n}})$ followed the facet orientations reported in Ref. 6.
[26] The surface energy density $\gamma(\mathbf{n})$ and l were fixed in our simulation except mentioned otherwise.