Island-corner barrier effect in two-dimensional pattern formation at surfaces

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Using rate-equation analysis, kinetic Monte Carlo simulations, and embedded-atom model calculations, we establish the crucial importance of island-corner crossing in determining the island morphology during submonolayer epitaxy. We show that compact islands can be formed only if adatoms can frequently cross island corners; conversely, without effective corner crossing the islands must be noncompact with fractional dimensionality. These conclusions provide the basis for understanding initial island morphologies in existing experiments.

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Understanding the morphological evolution of monoatomic-layer-high or, equivalently, two-dimensional (2D) islands in submonolayer epitaxial growth has been an active area of basic research in surface science. Because the shapes and the spatial and size distributions of such 2D islands often play an important role in determining the overall quality of films in the multilayer growth regime, such understanding is also technologically motivated. As emphasized recently,[1] the morphology of islands achievable in a given growth system depends critically on the substrate geometry. In both homoepitaxial and heteroepitaxial metal-on-metal growth, islands formed on substrates of triangular or hexagonal geometry are often noncompact if the growth temperature is sufficiently low, and become compact at higher temperatures.[2–9] In contrast, islands formed on substrates of square geometry are mostly compact,[10–13] with only a few exceptions in heteroepitaxial growth.[14,15]

The above observations have motivated a great deal of theoretical effort to identify the atomic diffusion processes involved in the formation of 2D growth patterns.[16–18] In the fractal growth regime, the classic ''hit-and-stick'' diffusion-limited aggregation (DLA) model[19] is frequently invoked. Within this model, the average arm thickness of the fractal islands, w, is one atom wide. A rigorous realization of the DLA model prediction with $w=1$ is still lacking. Instead, the experimentally observed[2–9] noncompact 2D islands all have wider arms, with $w \geqslant 2$. The arm thickness increases with increasing growth temperature, and the islands eventually become compact at sufficiently high temperatures. The temperature dependence of the island morphology reflects the kinetically limited nature of the growth processes. In understanding the formation of fractal patterns and the widening of their arm thicknesses, attention has been primarily focused on the rate competition between atom arrival at island edges and atom diffusion along island perimeters. The commonly accepted view[1,16–18,20–23] has been that, if the diffusion rate along steps (or equivalently, straight island edges) is slow compared to adatom diffusion on flat terraces, fractal islands can be formed at low temperatures; as edge diffusion increases at higher temperatures, islands should become compact. Conversely, if edge diffusion is faster than terrace diffusion, compact islands should always be expected.

In this Brief Report, we use rate-equation analysis, kinetic Monte Carlo (KMC) simulations, and embedded-atom model[24] (EAM) calculations to show that the ultimate rate-limiting process separating the fractal and compact growth regimes is not edge diffusion but island-corner crossing. The existence of an activation barrier V_c against atoms crossing an island corner from one edge to a neighboring edge via a corner site has been suggested in several recent studies,[1,7,8,21] and a quantitative measurement of this barrier has been reported for one model system.[25] This barrier is in general higher than the edge diffusion barrier V_e. Therefore, corner crossing may not take place even if edge diffusion is high. The central tenet of the present work is that, without frequent (either direct or effective) island-corner crossing, growth must lead to the formation of noncompact islands with fractional dimensionality. In contrast, compact islands can be formed only when frequent corner crossing is possible.[26] We derive a criterion for predicting the transition from noncompact to compact growth, and use the criterion to understand quantitatively several existing experiments.

The concept of a diffusion barrier for atoms to cross island corners is applicable to a wide variety of growth systems involving different substrates, but can most readily be illustrated using the example of island growth on a fcc (100) surface. For such systems, the three elemental atomic rate processes involved are schematically shown in Fig. 1. The first is the site-to-site hopping of an isolated adatom on a flat terrace, with an activation barrier V_t. The second is diffusion along island edges, with the barrier V_e. The third is corner crossing, with the barrier V_c. In general, we have $V_c > V_e$, because an adatom has to lower its coordination in crossing an island corner, in a manner similar to an atom moving down from an upper layer to a lower layer.[27] In the following, we use rate-equation analysis to derive a criterion that can be used to describe the separation of the noncompact growth regime from the compact regime; then we present KMC simulations to verify the criterion. Finally, we analyze earlier experimental results based on the criterion, with input parameters from experiments and our EAM calculations.

In typical epitaxial growth, atoms land on a substrate at a certain deposition rate and then perform thermally activated diffusive motion on the terraces. Such adatoms can randomly arrive at island edges, followed by diffusion along the edges to reach the island corners. Two time scales are important in the rate-equation analysis. One is the average time separation

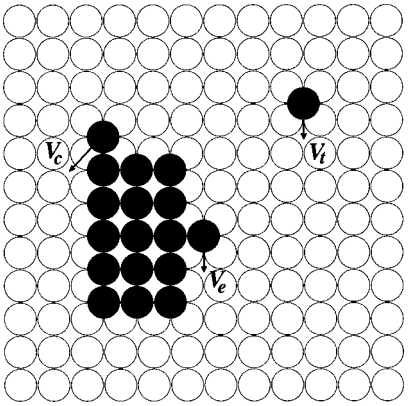

FIG. 1. Important atomic rate processes emphasized in this work: terrace diffusion (V_t), edge diffusion (V_e), and island-corner crossing (V_c).

t_a for two consecutive adatoms on the terrace to arrive at a given island edge. The other is the average time t_r for an adatom to reside at the edge before it escapes to another edge via island-corner crossing. The average residence time t_r can be approximated by the sum of the average time t_e spent by the atom at the edge before it reaches a corner, and the average time t_c for the atom at the corner site to cross around and reach a neighboring edge. Here we restrict ourselves to temperature ranges where direct adatom detachment from either a kink site or an island edge is negligible. It is natural to expect that $t_r \gg t_a$ will lead to noncompact or fractal-like islands, whereas $t_r \ll t_a$ will ensure compactness. The crossover region corresponds to $R = t_r / t_a \sim 1$.

Let *Na* denote the length of the island edge, where *a* is the surface lattice constant of the substrate and *N* the number of sites along the given edge. It can be shown that $t_e = N^2 a^2 / 6 D_e$, and $D_e = a^2 \nu_e \exp(-V_e/kT)$ is the edge diffusion coefficient, with kT the thermal energy and ν_e the attempt frequency for an atom to hop along the edge. The average time t_c is the product of the inverse of the probability for an adatom to be at either of the two corner sites and the time for the adatom to cross the corner, $t_c = (N/\nu_c)\exp(V_c/kT)$, where ν_c is the attempt frequency for corner crossing. We then have the average residence time given by

$$t_r \approx \frac{N}{\nu_c}\exp\left(\frac{V_c}{kT}\right) + \frac{N^2}{6\nu_e}\exp\left(\frac{V_e}{kT}\right). \tag{1}$$

This relation is an excellent one for any $N \geqslant 2$.

The successive arrival time t_a is given by $t_a \sim n/F$, where F is the deposition flux and n is the island density. With n given from classical nucleation theory,[28] we have

$$t_a = \left(\frac{3\theta}{\nu_t F^2 a^2}\right)^{1/3} \exp\left(\frac{V_t}{3kT}\right), \tag{2}$$

where θ is the coverage and ν_t the attempt frequency for an atom to hop on the terrace. Using $nN^2 \sim \theta$, we have for the criterion R

$$R \equiv R_c + R_e = \eta\left(\frac{\nu_t F a^2}{3\nu_c^2}\right)^{1/2} \exp\left(\frac{2V_c - V_t}{2kT}\right) + \eta\frac{1}{6}\left(\frac{F\theta\nu_t^2 a^4}{9\nu_e^3}\right)^{1/3} \exp\left(\frac{3V_e - 2V_t}{3kT}\right), \tag{3}$$

where the first term (R_c) and the second term (R_e) correspond to the contributions of corner crossing and edge diffusion, respectively, and η (≈ 1) is a parameter that weakly depends on the island geometry.

It is clear from Eq. (3) that large values of V_c and V_e are likely to result in $R \gg 1$ at low temperatures, leading to fractal growth. More importantly, even at temperatures where $R_e \ll 1$ (corresponding to high edge diffusion), the existence of the island-corner barrier V_c can still lead to $R \sim R_c \gg 1$ and the formation of noncompact islands. Only when both $R_c \ll 1$ and $R_e \ll 1$ can the system reach the compact growth regime. Therefore, with $V_c > V_e$ valid for most systems, the island-corner crossing is *the ultimate* rate-limiting process[16] dividing the noncompact and compact growth regimes, in contrast to conventional wisdom.[1,17,18,20–22]

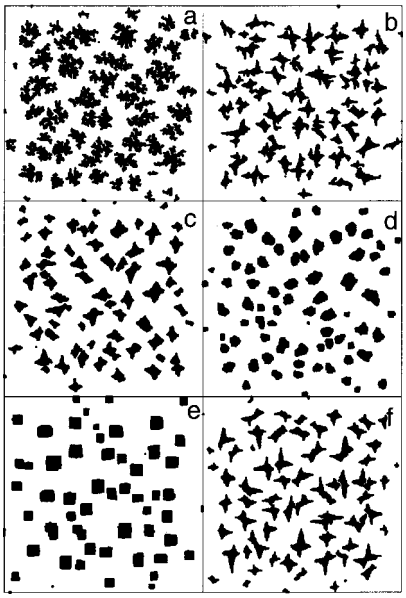

FIG. 2. KMC simulations of two-dimensional islands grown on a square lattice at temperatures (a) 50, (b) 100, (c) 200, (d) 300, and (e) and (f) 500 K. The only difference between (e) and (f) is the higher corner barrier for the latter case.

Prior to our derivation of Eq. (3), we had performed extensive KMC simulations to study the effect of island-corner barriers on the noncompact-compact transition in island morphology.[16,29] One representative set of results is illustrated in Fig. 2 using the example of growth on a square lattice with periodic boundary conditions. The size of the substrate used in the simulations is 300×300, and the coverage is 0.11 monolayer (ML). The barriers against terrace and edge diffusion are chosen to be $V_t = 0.15$ eV, and $V_e = 0.215$ eV, respectively. The barrier against corner crossing V_c is 0.32 eV in Figs. 2(a)–2(e) and 0.80 eV in Fig. 2(f). The corresponding diffusion rate is $q_i = \nu_i \exp(-V_i/kT)$, where $i = c$, e, or t, and $\nu_i \equiv \nu = 4.1671 \times 10^{10} T$, with T given in K. In order to compare the island shapes more closely, we en-

sure comparable island densities at different growth temperatures by choosing different deposition rates, namely, $F = 1.3\times10^{-12}$, 4×10^{-4}, 0.28, 41, and 410 ML s^{-1} for $T = 50$, 100, 200, 300, and 500 K, respectively. In these simulations, we have also recorded the numbers of events for both edge diffusion and corner crossing, given by $(I_e, I_c) = (1.6\times10^3, 0)$, $(5.0\times10^5, 1)$, $(2.8\times10^7, 2.0\times10^3)$, $(4.2\times10^7, 2.2\times10^4)$, $(2.6\times10^7, 1.7\times10^5)$, and $(2.2\times10^8, 290)$ for Figs. 2(a)–Fig. 2(f), respectively. The fractal islands shown in Fig. 2(a), for the case of slow edge diffusion, are very similar to those obtained within the classic hit-and-stick diffusion-limited aggregation model.[19] By increasing the growth temperature to 100 K, edge diffusion becomes rapid, while island corner crossing is still rare. In this case, we find fractal-like structures with larger arms, as shown in Fig. 2(b). Upon further increase of temperature, the island growth goes through a crossover regime, as shown in Figs. 2(c) and 2(d), and reaches the compact growth regime shown in Fig. 2(e), where both edge diffusion and island-corner crossing become rapid.

As an alternative unambiguous proof that the compactness of the islands shown in Fig. 2(e) is indeed induced by frequent corner crossing rather than fast edge diffusion, we present in Fig. 2(f) island morphologies obtained with identical growth parameters as those for Fig. 2(e), but with a much higher corner barrier, which has effectively reduced the corner crossing events by three orders of magnitude. A comparison between Figs. 2(e) and 2(f) clearly shows that, even though edge diffusion is very frequent in both cases [in fact more frequent in Fig. 2(f)], the islands *cannot* develop compact shapes if island-corner crossing does not occur often enough relative to atom arrival at the edges.

We have also used the parameters employed in these simulations to confirm quantitatively the validity of the crossover criterion, Eq. (3). For parameters corresponding to Figs. 2(a)–2(f), we obtain $(R, R_e, R_c) = (2.3\times10^{12}, 1.3\times10^2, 2.3\times10^{12})$, $(1.3\times10^4, 0.11, 1.3\times10^4)$, $(1.9, 5.2\times10^{-3}, 1.9)$, $(0.014, 4.9\times10^{-4}, 0.014)$, $(9.0\times10^{-4}, 1.5\times10^{-4}, 7.5\times10^{-4})$, and $(16, 6.9\times10^{-5}, 16)$, respectively. Based on these values, we should expect noncompact islands in Figs. 2(a), 2(b), and 2(f); compact islands in Figs. 2(d) and 2(e); and crossover behavior in Fig. 2(c). These theoretical predictions are in complete agreement with the simulation results.

To illustrate the dynamical evolution of fractal islands such as those shown in Fig. 2(f) at larger coverages, we show in Fig. 3 the growth of a single island starting from a 2×2 square-shaped seed placed at the center of a square lattice of 300×300. As in the classic DLA model,[19] atoms are randomly released from the boundary of the lattice, and move toward the seed by random walking. Here we take the extreme case where (a) edge diffusion is infinitely fast, namely, every atom reaching an edge of the island must have joined a kink site, if such a kink site exists along that edge, before the release of a new atom; and (b) corner crossing is infinitely slow, namely, no atom is able to cross an island corner. Three different stages of the island morphology are displayed with different colors. The red zone corresponds to the island at size $M = 100$, which is very similar to a typical

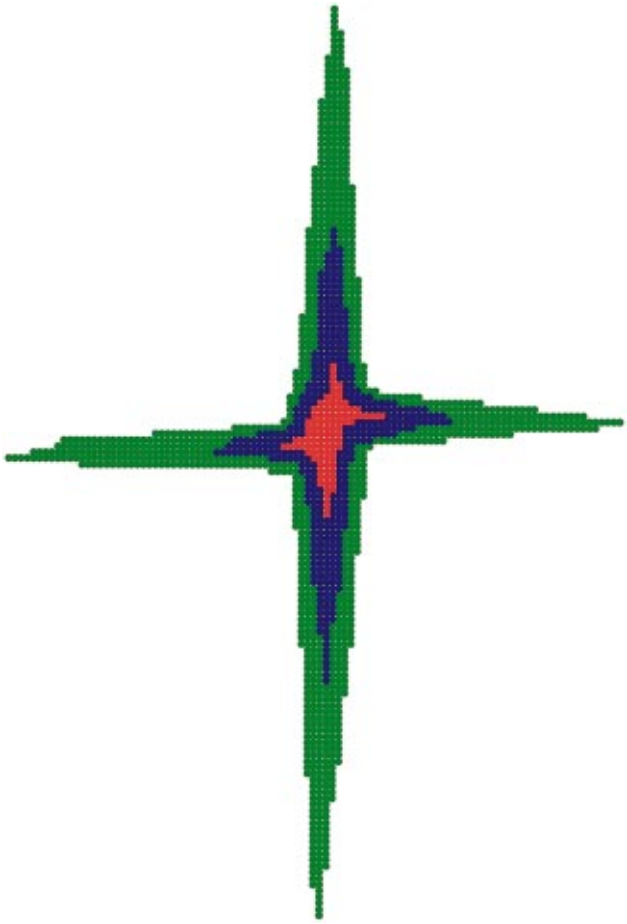

FIG. 3. (Color) Island morphology at three different growth stages. The numbers of atoms contained are 100, 400, and 1000 in the red, blue, and green zones, respectively. The island is noncompact and dendritic, with a fractal dimension of ~1.45.

island shown in Fig. 2(f). The blue zone corresponds to $\Delta M = 400$, showing clearly the existence of a fingering instability as a result of the island-corner barrier effect. Such a fingering instability is further amplified in subsequent growth, as indicated by the green zone of area $\Delta M' = 1000$. The lack of compactness of the cross-shaped island is quite apparent. A quantitative measure of its fractional dimensionality is given by the scaling law $M \sim L^{\delta}$, where L is the branch length from tip to tip, and $\delta \approx 1.45$, obtained by averaging over 20 islands from independent simulations. This finding once again proves how the lack of island-corner crossing prevents an island from acquiring a compact shape, something that is also physically and intuitively quite reasonable.

Before considering specific systems, we first discuss our results in connection with different classes of growth systems. Recent theoretical and experimental studies have shown that, in general, $V_c > V_e \gg V_t$ for fcc (111) and hcp (0001) surfaces, and $V_c \approx V_t \gg V_e$ for fcc (100) surfaces.[8,23,30] Therefore, we can conclude from Eq. (3) that the temperature range for fractal-like growth on fcc (111) or hcp (0001) surfaces is much wider than it is on fcc (100) surfaces. It should be noted that, although Eq. (3) does not exclude the existence of the fractal-like growth regime on fcc (100) surfaces,

the small difference between V_c and V_t makes it improbable, because corner crossing will be frequent at temperatures at which terrace diffusion is rapid enough to form sizable islands.

We now apply the crossover criterion Eq. (3) to island growth on fcc (111) and fcc (100) surfaces. For Pt(111) homoepitaxy, using $F=10^{-4}$ ML s^{-1}, $\theta=0.1$ ML, $\nu_t=\nu_e=\nu_c=10^{12}$ s^{-1}, and the diffusion barriers $V_t=0.25$, $V_e=0.6$, and $V_c=0.7$ eV,[7,8] we expect a morphological crossover at around 360 K, in good agreement with the experimental value of 400 K.[4,7] For the fcc (100) systems Cu/Cu, Ag/Ag, and Ni/Ni, our EAM calculations give $(V_t,V_e,V_c)=(0.505,0.265,0.555)$, (0.478,0.260,0.519), and (0.632, 0.337,0.681), respectively (all in eV). Taking $\nu_t=\nu_e=\nu_c=10^{12}$ s^{-1}, $F=10^{-4}$ ML s^{-1}, $\theta=0.1$ ML, and $T=300$ K, we have $R\sim 7.0\times 10^{-4}$ (Cu), 2.9×10^{-4} (Ag), and 7.8×10^{-3} (Ni), indicating that only compact islands can be obtained in these systems at such typical growth conditions. This conclusion again agrees with existing experiments.[10,11,13]

In summary, we have demonstrated the physically reasonable result that island-corner crossing is the ultimate rate-limiting process separating fractal and compact growth regimes in submonolayer epitaxy, in disagreement with conventional wisdom. Without effective island-corner crossing, growth must lead to the formation of noncompact islands with fractional dimensionality. Conversely, compact islands can be formed only when frequent corner crossing is activated. We have derived a criterion for predicting the crossover transition of island morphologies from the noncompact to the compact growth regime, and have successfully applied this criterion to explain quantitatively several existing experiments. The power of this crossover criterion will be best realized in future studies, when state-of-the-art first-principles calculations and advanced experimental probes can yield quantitatively accurate values for the key parameters appearing in Eq. (3). With such quantitative information and the criterion, the crossover transition from fractal to compact growth can be reliably predicted for essentially any given growth system.

We recently became aware of two very recent related papers addressing how island-corner crossing induces step meandering and 3D growth instabilities.[31,32]

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