Transition from Compact to Fractal Islands during Submonolayer Epitaxial Growth

G. S. Bales and D. C. Chrzan
Computational Materials Science Department, Sandia National Laboratories, Livermore, California 94551-0969
(Received 3 February 1995)

A linear stability analysis is applied to the study of the compact-fractal island morphological transition during epitaxial growth. The analysis includes the diffusion mediated interaction between islands within a self-consistent mean-field theory. A scaling form is derived for the length of the island edges. Results are confirmed by comparison with kinetic Monte Carlo simulations.

PACS numbers: 61.43.Hv, 82.20.Mj

Single atom high islands which form during the early stages (submonolayer) of epitaxial growth exhibit morphologies which range from ramified structures to compact polygonal shapes. For example, scanning tunneling microscopy images of Au on Ru(0001) grown at room temperature reveal fractal islands. Deposition of Co on the same substrate produces compact triangular islands [1]. Similarly, ramified islands are observed for Pt on Pt at low temperature, and compact islands are found for higher temperatures [2]. In this work the dependence of the island morphologies on externally controlled growth parameters is addressed. It is important to understand this dependence, since these islands form the template upon which all further growth proceeds [3].

The observation of ramified island growth has been understood [1] by comparison with the simplest "hit and stick" model of diffusion limited aggregation (DLA) [4]. In this model, a particle diffuses on the substrate to an island from far away and sticks at the first point of contact with the cluster. The fractal dimension for a DLA cluster is identical to that measured for islands of Au on Ru(0001) [1].

However, the growth of islands during epitaxy differs from DLA in two very important respects: (1) Atoms which diffuse to the island relax to a lower energy site, e.g., by diffusion along the edge of the island (edge diffusion). As the rate of relaxation increases relative to the rate at which atoms diffuse *to* the island, a morphological transition occurs from ramified island growth to compact island growth. For an *isolated* island this competition is well understood [5,6]. (2) The islands grow in the presence of other islands on the surface and, therefore, compete for the available diffusing monomers. The effects of this complication on the island morphology are *not* yet well understood. In fact, there is disagreement in recent literature [7–9] as to the dependence of the transition on the growth parameters.

In this paper, the morphological transition is studied by considering the shape stability of a compact island. A linear stability analysis, similar to that applied to the study of the Mullins-Sekerka instability [10], is used to study the stability of a circular island with respect to infinitesimal morphological fluctuations. In contrast to a traditional stability analysis [5,11], the environment surrounding any particular island on the surface is changing with time during the growth process, due to the presence of the other islands. In this work, therefore, the stability analysis is combined with a self-consistent mean-field theory which describes accurately average properties of the *entire* surface [12]. Based on this novel approach and the results of kinetic Monte Carlo (KMC) simulations a new scaling law is formulated, and the disagreements in the literature reconciled.

During the growth process, a competition develops between the nucleation of new islands on the substrate and the capture of monomers by already existing islands. This competition leads to a simple relation between the average distance between islands ℓ, the deposition flux F, and the monomer diffusion constant D, namely,

$$\ell \sim \left(\frac{D}{F}\right)^{\chi}, \tag{1}$$

where the exponent χ depends on the critical nucleus size [13]. The current work focuses on irreversible growth in which a dimer is stable and $\chi = 1/6$. Similarly, it is shown here that the balance of the competing effects of ramified growth and smoothing by edge diffusion also leads to a simple scaling form. Near the transition to ramified island growth the fraction n_e of deposited atoms that are at the edge of an island obeys

$$n_e \sim \left(\frac{D}{F}\right)^{-1/6} f\left[\frac{\Gamma}{D}\left(\frac{D}{F}\right)^{1/3}\right], \tag{2}$$

where Γ measures the rate at which atoms diffuse around the edge of the island and f is the scaling function.

Kinetic Monte Carlo simulations based on simple energetics provide a useful tool to investigate scaling relationships such as Eqs. (1) and (2). The current simulations are performed on a square lattice. The monomers hop on the bare substrate at a rate of $h_D = \nu e^{-\beta E_s}$, where ν is the attempt frequency, β is the reciprocal temperature, and E_s is the energy barrier to monomer diffusion on the substrate (note that $D = h_D/4$). Attachment of monomers to other monomers and existing islands is assumed irreversible. Adatoms at the edge of

an island (edge atoms) hop along the edge with a rate $h_e = \nu e^{-\beta n E_e}$, where ν is the attempt frequency and n is the number of *lateral* nearest neighbors. There is no additional barrier associated with downward interlayer diffusion.

Typical results are shown in Fig. 1 for three different temperatures and a flux chosen such that $D/F = 1 \times 10^{10}$. At low temperatures, the edge diffusion rate is very low, and the islands are ramified. At high temperatures, the islands grow while maintaining a compact structure. At intermediate temperatures, the islands assume a structure somewhere in between the two extremes. One learns two important facts from these simulations. First, this simple model displays a morphological transition between compact and fractal islands. Second, the morphological transition between compact and fractal islands is *not* abrupt, but occurs gradually as the temperature is changed.

Simulations provide the exact numerical description of the growth of a thin film (within the assumed dynamics).

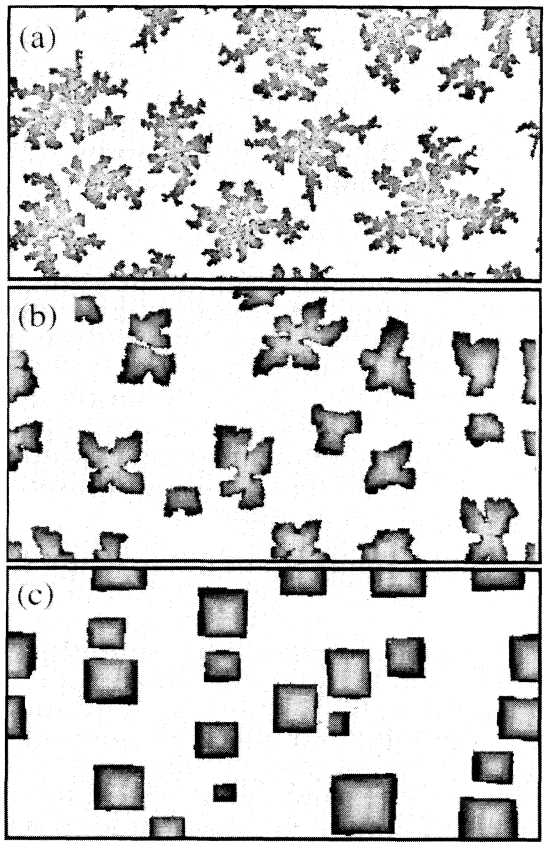

FIG. 1. Kinetic Monte Carlo simulations of irreversible island growth for $D/F = 1 \times 10^{10}$, $E_e/E_s = 1.8$ and (a) $\beta E_s = 20$, (b) $\beta E_s = 15$, and (c) $\beta E_s = 10$. The lighter shades of gray represent atoms deposited at early times, while the darker shades represent those deposited at later times.

However, in order to understand the scaling behavior, one needs an analytical description of the competition between the ramifying influence of growth, and the smoothing influence of edge diffusion. An exact theory of this competition is not yet attainable as it requires knowledge of the positions and shapes of *all* islands and monomers on the substrate. Hence, to make progress, the current work treats the shape stability of a *circular* island of radius $R(t)$ as it grows in the presence of the *average* density of diffusing monomers. The presence of the other islands is accounted for by replacing the environment surrounding the island by that of the average system. The properties of that average system are computed self-consistently from a set of couple mean-field rate equations [12].

The stability of the compact circular shape of the island is studied by examining the time dependence of small perturbations to the circular shape. The radius of the island is replaced by

$$r_e(\phi, t) = R(t) + \epsilon_m(t) e^{im\phi}, \tag{3}$$

where $R(t)$ is the unperturbed island radius, $\epsilon_m(t)$ is the amplitude of the perturbation ($\epsilon_m \ll R$), and m is a positive integer. The circular island is morphologically unstable if $\epsilon_m(t)$ increases more rapidly than $R(t)$. To first order in $\epsilon_m(t)$

$$\frac{d}{dt}\left(\frac{\epsilon_m}{R}\right) = \omega_m \frac{\epsilon_m}{R}, \tag{4}$$

where the relative stability function ω_m is determined by solving the diffusion equation for the monomers in the vicinity of the island [5,12]. It is given by

$$\omega_m = \Omega \frac{D\langle n\rangle}{\xi^2} \frac{K_1(R/\xi)}{K_0(R/\xi)} \left[\frac{\xi}{R}(m-2) + \frac{K_{m-1}(R/\xi)}{K_m(R/\xi)} - \frac{K_0(R/\xi)}{K_1(R/\xi)} \right] - \frac{\Omega}{2} Fm - \frac{\Omega\Gamma}{R^4} m^2(m^2-1). \tag{5}$$

K_m is a modified Bessel function of order m and Ω is the atomic area. The "diffusion length" ξ is given by

$$\xi^{-2} = \sigma\langle n\rangle + \sigma_{\mathrm{av}}(N + \langle n\rangle), \tag{6}$$

where N is the number density of islands, $\langle n\rangle$ is the average density of monomers on the surface, σ_{av} is the average "capture number" which measures the rate at which the islands capture the monomers on the surface, and σ is proportional to the rate of dimer formation [12,14]. Note that $\langle n\rangle$, N, ξ, σ, and σ_{av} are time dependent quantities which are computed numerically from the rate equations [12]. The parameter Γ represents the rate at which the islands relax toward their equilibrium shape. The continuum approximation for the edge diffusion rate j_e is

given by $j_e = -\Gamma \partial \kappa(s)/\partial s$ where $\kappa(s)$ is the local radius of curvature at a position on the edge given by the arclength s [15].

The morphological stability of the circular island is described completely by the stability function. If $\omega_m > 0$, the perturbation grows faster than the radius of the islands. If $\omega_m < 0$, the perturbation decays. The solution to the equation $\omega_m = 0$ defines a critical radius at which a circular island becomes unstable to morphological fluctuations.

It can be shown that ω_m is a function of four parameters: R, Γ/D, D/F, and the coverage $\theta = Ft$. The latter three are controlled externally. The stability function vanishes for two radii, R_1 and R_2 where $R_2 > R_1$. These roots are shown in Fig. 2 as a function of coverage for $m = 3$, the first mode to go unstable. A circular island is unstable to the perturbation if its radius is between R_1 and R_2. If $R < R_1$, edge atoms are able to sample much of the island edge and find a lower energy site. Hence the compact island is stable. If $R > R_2$, the addition of atoms to the island from on top of the island, which stabilizes the compact shape [11], becomes comparable to the addition of atoms from the bare substrate.

Also shown in Fig. 2 is the *average* radius of the islands, $\bar{R}(\theta)$. Note that $\bar{R}$ becomes greater than R_1 at about $\theta = 0.01$ monolayer for $\Gamma/D = 5 \times 10^{-6}$. Ramified islands are predicted at any higher coverage. For $\Gamma/D = 5 \times 10^{-5}$, however, $\bar{R}$ is always less than R_1 and the islands remain compact. It is useful to define a critical value for Γ when $\bar{R}(\theta)$ is equal to R_1. In other words, $\Gamma = \Gamma_c(\theta)$ when the stability function evaluated at $\bar{R}(\theta)$ is zero. One can then study the dependence of $\Gamma_c(\theta)$ on the growth parameters. In Ref. [12] it is shown that for compact islands, $\bar{R}/\xi$ is independent of the ratio D/F in the "scaling regime" (for all but very low coverage). Terms in Eq. (5) which depend on R/ξ become simple functions of the coverage θ. Furthermore, $\bar{R} \sim (D/F)^{1/6}$ and $\langle n \rangle \sim (D/F)^{-2/3}$. Neglecting the contribution from deposition on top of the islands [fourth term in Eq. (5)] and solving $\omega_m(R = \bar{R}, \Gamma = \Gamma_c) = 0$ for Γ_c gives

$$\frac{\Gamma_c}{D} \simeq \left(\frac{D}{F}\right)^{-1/3} \gamma(\theta), \tag{7}$$

where $\gamma(\theta)$ is independent of the growth parameters Γ/D and D/F. At a given coverage, if $\Gamma > \Gamma_c$ one observes only compact island shapes but if $\Gamma < \Gamma_c$ the islands have a ramified appearance.

Equation (7) is difficult to apply directly to data analysis. If Γ is close to Γ_c, it is difficult to determine by visual inspection if the island shapes have become unstable. For Γ near Γ_c the island edges are rough (as a result of kinetic roughening) and the emerging dendrites cannot be distinguished from this roughness. Instead, consider n_e defined as (number of edge atoms)/(total number of atoms in the islands) as a measure of the island morphology. This quantity is plotted in Fig. 3(a) as a function of Γ/D ($\Gamma = \Gamma_0 \nu e^{-\beta E_e}$ where $\Gamma_0 \sim 1$) [16] for four different values of D/F at a fixed coverage ($\theta = 0.2$). At low Γ/D the islands are fractal and n_e is close to 0.9. The transition to compact island shapes is continuous as one increases Γ/D.

The linear stability analysis applies in the vicinity of the compact island shapes. In this limit it is known [12] that $n_e \sim 1/\bar{R} \sim (D/F)^{-1/6}$. In addition, from Eq. (7) one expects the curves to bend upward (with decreasing Γ/D) at a value of Γ/D proportional to $(D/F)^{-1/3}$. Figure 3(b) provides a test of this behavior. When scaled as predicted by the linear stability analysis (horizontal axis) and the

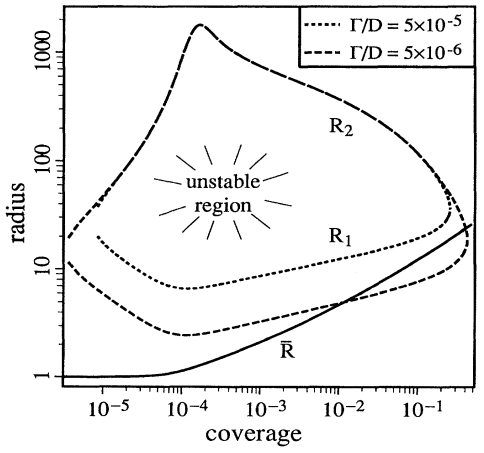

FIG. 2. Roots R_1 and R_2 and the average radius $\bar{R}$ versus coverage for $D/F = 1 \times 10^8$.

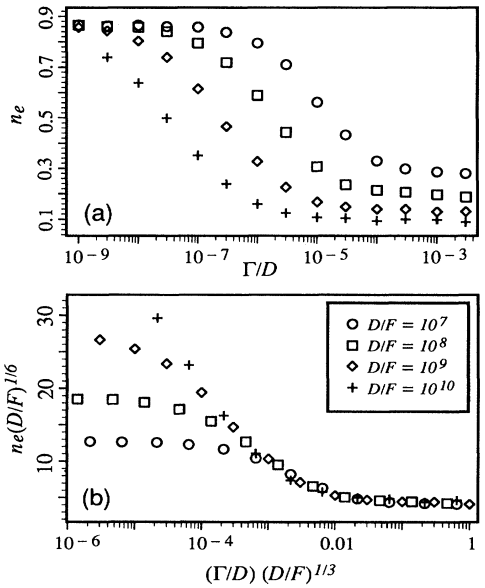

FIG. 3. Fraction of edge atoms n_e versus Γ/D.

rate theory (vertical axis), data from four different values of D/F produce a single curve near the compact island limit. This result provides proof of the validity of the simple scaling form predicted by Eq. (2).

Equation (2) may be used to measure the edge diffusion barrier from *experimental* data by locating the temperatures β_0 (as one varies the growth conditions) at which $n_e(D/F)^{1/6}$ is some constant close to (but greater than) its value in the compact island limit. Equation (2) predicts that at these temperatures $(\Gamma/D)(D/F)^{1/3} = \text{const}$. This is equivalent to

$$\ln \frac{D}{F} = 3(E_e - E_s)\beta_0 + \text{const}. \tag{8}$$

Hence, the slope of the straight line predicted by Eq. (8) gives a direct measure of the barrier to edge diffusion. This relationship has been verified with the KMC simulations. Note that application of Eq. (2) to the measurement of edge diffusion rates does not require a direct comparison with KMC simulations in contrast to the procedure outlined in Ref. [8].

It must be noted that the current formulation applies only when the experiment is in the irreversible growth limit. For example, this approximation is reasonable for Au on Ru(0001), as no Ostwald ripening was observed upon annealing, but morphological relaxation was observed [1]. In addition, the simple scaling form appears to be independent of lattice symmetry assuming that the surface diffusion is isotropic. Equation (2) is motivated by analyzing the stability of circular islands and then shown to be correct for simulations of square islands. The lattice symmetry is reflected in the absolute magnitude of the edge diffusion rate [9] which is proportional to the parameter Γ.

The theories of Pimpinelli, Villain, and Wolf [7] and Bartelt and Evans [8] predict the relation $\Gamma_c/D \sim (D/F)^{-1/3}$. However, their length scale analyses ignore the coverage dependence and cannot predict the change in morphological stability with coverage. Zhang, Chen, and Lagally predict $\Gamma_c/D \sim (D/F)^{-5/6}$ by (a) defining an edge hopping length in which the motion of an edge atom is limited only by direct collision with an incoming monomer and (b) setting that length equal to a constant [9]. Instead, the relevant edge hopping length describes the length an atom will travel to find a lower energy site (collision with the other mobile edge atoms). This length, which scales as R_1, should be compared with the circumference of the island (i.e., $R_1 = \bar{R}$) to produce the correct scaling form.

In conclusion, the compact-fractal island morphological transition has been studied within a self-consistent mean-field theory and KMC simulations. The scaling behavior of the smooth transition is discussed, and a new scaling form for the length of an islands edge is obtained and verified by KMC simulations.

We thank M. S. Daw, J. C. Hamilton, and R. Q. Hwang for a critical reading of the manuscript. Support for this work has been provided by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences under Contract No. DE–AC04–94AL85000.

[1] R. Q. Hwang, J. Schröder, C. Günther, and R. J. Behm, Phys. Rev. Lett. **67**, 3279 (1991).
[2] M. Bott, T. Michely, and G. Comsa, Surf. Sci. **272**, 161 (1992).
[3] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990); P. Šmilauer, M. R. Wilby, and D. D. Vvedensky, Phys. Rev. B **47**, 4119 (1993).
[4] T. A. Witten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[5] M. Avignon and B. K. Chakraverty, Proc. R. Soc. London A **310**, 277 (1969).
[6] S. R. Coriell and R. L. Parker, J. Appl. Phys. **37**, 1548 (1966).
[7] A. Pimpinelli, J. Villain, and D. E. Wolf, J. Phys I (France) **3**, 447 (1993).
[8] M. C. Bartelt and J. W. Evans, Surf. Sci. **314**, L835 (1994).
[9] Z. Zhang, X. Chen, and M. G. Lagally, Phys. Rev. Lett. **73**, 1829 (1994).
[10] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **34**, 323 (1963).
[11] G. S. Bales and A. Zangwill, Phys. Rev. B **41**, 5500 (1990).
[12] G. S. Bales and D. C. Chrzan, Phys. Rev. B **50**, 6057 (1994).
[13] S. Stoyanov and D. Kashchiev, in *Current Topics in Materials Science,* edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, pp. 69–141.
[14] J. A. Venables, Philos. Mag. **27**, 697 (1973).
[15] W. W. Mullins, J. Appl. Phys. **28**, 333 (1957).
[16] The parameter Γ defined for circular islands is proportional to the edge diffusion rate. For the square islands observed in the simulations Γ is assumed proportional to the rate at which atoms hop along the island edge in the fast direction.

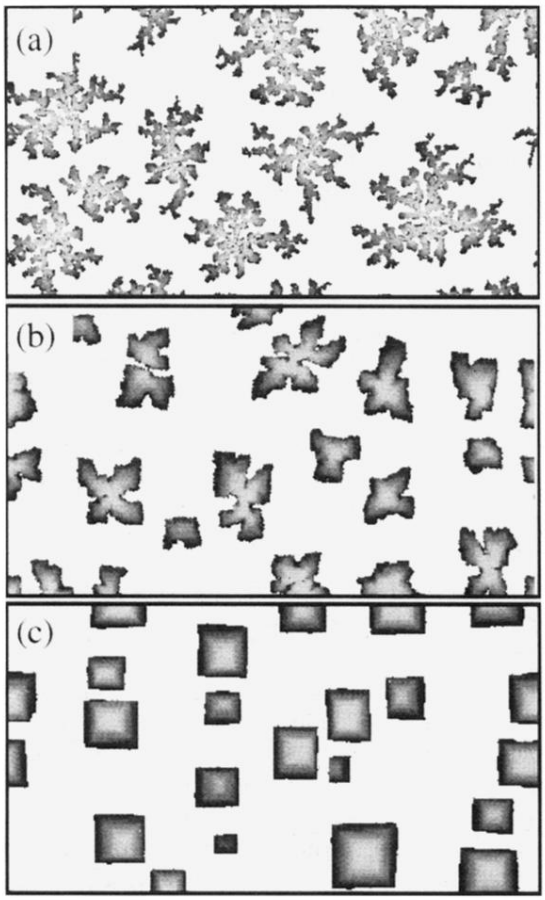

FIG. 1. Kinetic Monte Carlo simulations of irreversible island growth for $D/F = 1 \times 10^{10}$, $E_e/E_s = 1.8$ and (a) $\beta E_s = 20$, (b) $\beta E_s = 15$, and (c) $\beta E_s = 10$. The lighter shades of gray represent atoms deposited at early times, while the darker shades represent those deposited at later times.