RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 60, NUMBER 16 15 OCTOBER 1999-II

Mechanisms of mound coarsening in unstable epitaxial growth

Jacques G. Amar
Department of Physics & Astronomy, University of Toledo, Toledo, Ohio 43606
(Received 19 August 1999)

Corner diffusion is shown to play a crucial role in determining the asymptotic mound coarsening exponent n in the case of unstable epitaxial growth on (001) and (111) surfaces. For the case of island-relaxation without corner diffusion the asymptotic exponent is found to satisfy $n \simeq 1/4$. However, when rapid corner-diffusion is allowed, the coarsening exponent is found to approach 1/3. An explanation for these results is presented in terms of the effects of corner diffusion on the surface current and mound morphology.
[S0163-1829(99)51440-9]

The appearance of large-scale structures (mounds), which grow and coarsen with increasing film thickness during homoepitaxial growth on singular surfaces has attracted considerable interest over the past several years. In particular, mound formation has been observed in homoepitaxial growth of materials ranging from semiconductors[1] to metals and metal alloys.[2–4] One reason for the interest has been the desire to control instabilities during the growth process in order to produce either atomically flat or nanostructured surfaces.

The origin of the mound instability in homoepitaxial growth is now understood to be the existence of diffusion bias.[5] Such a bias may be due for example to a barrier to diffusion over descending steps (Ehrlich-Schwoebel step barrier[6]) or to a short-range attraction of surface adatoms to ascending steps.[7] This bias leads to an ''uphill current'' towards ascending step edges and an increased probability for the nucleation of islands on top of existing islands and consequently to unstable, rough growth and mound formation.

However, while the origin of the mound instability is now well understood, the asymptotic mound coarsening and surface roughening behavior are not. For example, numerical integration of the simplest continuum equation for the surface height $h(\mathbf{r},t)$, which takes diffusion bias into account[8] leads to a mound coarsening exponent $n \simeq 1/4$ (where the typical mound or feature size r_c parallel to the surface scales as $r_c \sim \langle h \rangle^n$ where $\langle h \rangle$ is the average film thickness). This result is consistent with those obtained in a variety of experiments on growth on metal (001) surfaces[3,4] and Monte Carlo simulations.[9] However, in a recent experiment on epitaxial growth of Rh/Rh(111) at high temperature,[10] rapid mound formation with a significantly larger coarsening exponent ($n \simeq 0.33 \pm 0.02$) was observed. A similarly large value was also obtained[12] in simulations of metal (001) growth with a large step barrier.

Recently, a continuum analysis of mound coarsening has been presented,[11] which takes into account the symmetry of the surface as well as the topology of defects between mounds. The results indicate that for growth on (111) substrates, $n \simeq 1/3$, while for growth on (001) surfaces, in most cases the coarsening exponent $n \simeq 1/4$. However, while these results agree with existing experiments, they do not provide a clear correspondence between the mechanisms of surface relaxation and the observed behavior.

In order to understand the influence of island-relaxation mechanisms on the coarsening behavior, I have carried out kinetic Monte Carlo simulations of growth on both (001) and (111) surfaces. The simulations on (001) surfaces were carried out using a model of bcc (001) growth,[12] which takes into account downward funneling[13] due to the crystal structure. To study the dependence of the coarsening behavior on (001) surfaces on island-relaxation mechanisms, three different models were used (see Fig. 1). In all three models, atoms were deposited with deposition rate F (per site) and allowed to diffuse to nearest-neighbor sites with hopping rate D. In order to take into account the effect of an Ehrlich-Schwoebel step barrier and satisfy detailed balance, for all three models the rates for adatom motion over an ascending or descending step were assumed to be equal to the corresponding rate on a flat surface multiplied by a factor e^{-E_B/k_BT} due to the step-barrier E_B.

In model A, irreversible island formation was assumed with island relaxation via hopping of singly-bonded atoms along straight edges (edge-diffusion) at a rate given by $D_e = De^{-E_e/k_BT}$ [see Fig. 1(a)]. This leads to somewhat irregular islands and mounds whose edges tend to be along the (110) and $(1\bar{1}0)$ directions. Model B again corresponded to irreversible island formation but with diffusion of singly-

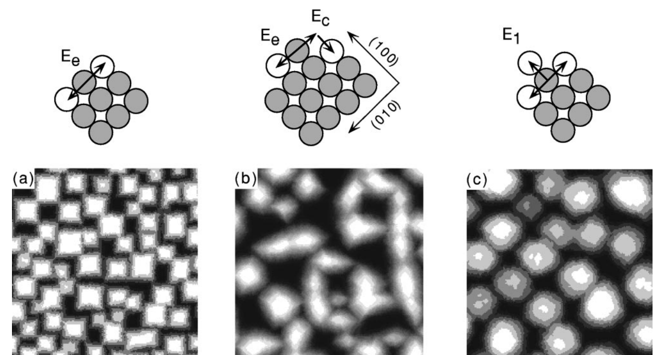

FIG. 1. Typical mound morphology (400×400 portion of lattice) after 500 layers have been deposited (moderate step barrier) along with corresponding island-relaxation mechanisms for models A, B, and C [(a), (b), and (c), respectively]. Gray scale plots in (a) and (c) correspond to slow deposition ($E_e = 0.1$ eV and $E_1 = 0.1$ eV, respectively) while (b) corresponds to fast deposition with $E_e = 0$.

 ©1999 The American Physical Society

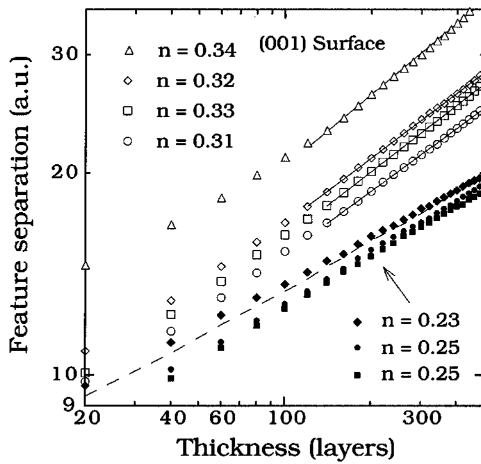

FIG. 2. Feature separation vs film thickness for models A and B. Open symbols denote corner diffusion (model B): diamonds and dashed curve (fast deposition, moderate step barrier), squares (fast deposition, large step barrier), circles (slow deposition, large step barrier). Filled symbols denote corresponding simulations without corner diffusion. Open diamonds, squares, and triangles correspond to enhanced edge diffusion ($E_e=0$) while $E_e=0.1$ eV for all others. Open triangles correspond to modification of model B with a corner-diffusion barrier larger than that for edge-diffusion ($E_c=E_B=0.07$ eV, $E_e=0$) and slow deposition.

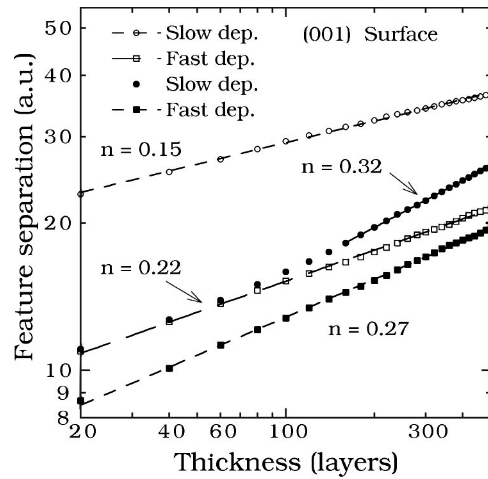

FIG. 3. Feature separation vs film thickness for reversible island growth on a (001) surface (model C, $E_1=0.1$ eV). Open symbols correspond to moderate step barrier while filled symbols correspond to large step barrier.

bonded atoms around corners at a rate $D_c=D_e$ equal to that for edge-diffusion as shown in Fig. 1(b). This leads to compact square islands and mounds whose edges are along the (100) and (010) directions and which tend to form short "chains" of coalescing mounds in the (110) and $(1\bar{1}0)$ directions (see Fig. 1). Finally, in model C, reversible island formation was studied using a model in which the (in-plane) hopping rate (either away from or along an edge) for an adatom with one lateral in-plane bond is given by $D_1=De^{-E_1/k_BT}$ while atoms with two or more bonds are assumed to be effectively "frozen." As shown in Fig. 1(c) this also leads to compact islands and mounds with edges along the (100) and (010) directions.

In order to study the coarsening behavior over a wide range of deposition conditions, and ensure that asymptotic behavior was observed, simulations were carried out using both moderate ($E_B=0.07$ eV) and large ($E_B=0.6$ eV) step-barriers while the substrate was assumed to be at room temperature ($T=298$ K). In addition, two different deposition rates were used—a "fast" deposition rate corresponding to $D/F=5\times10^3$, and a "slow" deposition rate corresponding to $D/F=10^5$. To eliminate finite-size effects all simulations were carried out using very large system sizes (1024×1024). As in previous studies,[3,12] the average mound size or feature separation was estimated as proportional to the position r_c of the first zero crossing of the circularly averaged height-height correlation function. From the dependence of the feature separation r_c on film thickness $\langle h\rangle$, the mound coarsening exponent n (where $r_c\sim\langle h\rangle^n$) was obtained.

Figure 2 shows simulation results for the case of irreversible island growth with rapid edge-diffusion both for the case *without* corner diffusion (filled symbols, model A) and *with* corner diffusion (open symbols, model B). As can be seen, in the absence of corner diffusion, $n\simeq1/4$ regardless of the deposition rate or step-barrier strength. However, in the presence of corner diffusion a much larger value ($n\simeq1/3$) is observed. These results indicate that corner diffusion plays a key role in determining the asymptotic coarsening behavior.

Also shown in Fig. 2 are results (dashed line) for growth with a moderate step barrier and less rapid edge-and-corner diffusion ($E_e=0.1$ eV) for which the late-time coarsening exponent is only slightly higher than 1/4. A comparison of these results to the corresponding results with a larger step barrier (open squares) as well as to those with the same step barrier but with enhanced edge-and-corner diffusion (open diamonds) indicates that less corner diffusion is needed in the case of a large step barrier than for a moderate step barrier in order to observe a large coarsening exponent. Thus, the strength of the step barrier also plays an important role in determining the observed coarsening behavior. Also included in Fig. 2 are results for a modification of model B corresponding to a corner-diffusion barrier which is comparable to the step barrier but larger than the edge-diffusion barrier. In this case, the combined effects of rapid edge diffusion and moderate corner diffusion again lead to a large effective rate of corner diffusion, so that rapid mound coarsening with $n\simeq1/3$ is observed.

Figure 3 shows results for the case of *reversible* island formation (model C). As indicated by Fig. 1(c), for the case of slow deposition and a moderate step barrier the resulting mounds are quite large and regular. In addition, due to the absence of corner diffusion, the effective coarsening exponent is less than or equal to 1/4. However, for the case of slow deposition with a *large* step barrier, a large coarsening exponent $n\simeq1/3$ is again obtained while the surface morphology becomes similar to that shown in Fig. 1(b).

These results may be explained in terms of the presence of an *effective* corner diffusion. For a large step barrier, atoms that detach from an island are reflected by nearby descending steps and are likely to reattach at nearby island edges. As a result, an atom detaching from a corner is likely to reattach at a nearby edge leading to an *effective* corner

diffusion. In contrast, for a moderate step barrier, atoms detaching from an island are likely to descend at nearby step-edges and so do not contribute to corner diffusion.

Why does rapid corner diffusion lead to enhanced mound coarsening? A qualitative explanation may be obtained by considering the effects of corner diffusion on the surface current which may be expanded in the form $j_x = m_x(a - cm_x^2 - bm_y^2)$ (Ref. 11) where $j_x > 0$ corresponds to an ''uphill'' mass current in the x-direction, $m_x(m_y)$ corresponds to the surface slope in the (100) [(010)] direction, and the last term with coefficient b corresponds to a cross current. In the presence of a sufficiently large step barrier, one expects[14,15] that rapid edge and corner diffusion will lead to a *positive* cross current ($b<0$) since adatoms attaching to ascending step edges will tend to migrate uphill (in the x direction) by diffusing around corners to an inside kink site with two nearest-neighbor bonds. In contrast, in the *absence* of corner diffusion or for a *weak* step barrier no such cross current will be observed. In simulations of growth on a vicinal surface using the same parameters as in the coarsening simulations, I have verified that for the case of rapid corner diffusion or effective corner diffusion there is a positive cross-current, while in the absence of rapid corner diffusion the cross-current is either negligible or negative. Thus, the sign of the cross current appears to determine the coarsening behavior.

Why does a positive cross current lead to enhanced mound coarsening? A simple kinetic explanation is as follows. When two mounds begin to coalesce the region between them has a significant slope in *both* the (100) and (010) directions. A positive cross-current tends to favor such regions so that mound coalescence is enhanced as in Fig. 1(b). On the other hand, a negative cross current tends to suppress such regions so that mound coalescence is suppressed as in Fig. 1(c).

In order to study the effects of surface symmetry on the asymptotic coarsening behavior, I have also carried out simulations of growth on a (111) surface for which it has been argued[11] that in general $n \simeq 1/3$. In my simulations a simple solid-on-solid model of irreversible growth on a triangular lattice was used, with ''knockout''[17] of atoms at a step-edge by freshly deposited atoms in order to mimic downward funneling. By independently varying the parameters for edge and corner diffusion along A and B step edges[18] the island and mound morphology were varied from hexagonal to triangular.

Figure 4 shows results for the case of triangular mounds corresponding to rapid corner diffusion around A step edges and slow corner diffusion around B step edges. The asymmetry in corner diffusion leads to the formation of triangular islands and mounds as in experiment[10] with A edges favored and B edges suppressed. For the case of rapid edge diffusion and a large step barrier, a large coarsening exponent ($n \simeq 1/3$) is observed. This is consistent with the rapid edge and corner diffusion along A edges in this case. However, in the case of slow edge diffusion, due to the suppression of mass transport along the A edges,[16] the mounds are significantly smaller and a lower coarsening exponent ($n \simeq 1/4$) is observed.

Similar results have been obtained for the case of hexagonal mounds. For the case of rapid edge and corner diffusion the mound edges are smooth and a large coarsening exponent

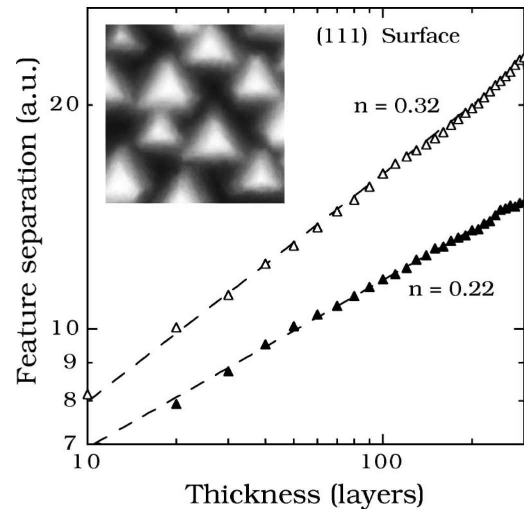

FIG. 4. Feature separation vs film thickness for deposition on a (111) surface with a large step barrier and $D/F = 10^3$. Fast island-relaxation rates correspond to $D_e/F = 10^4$ while slow rates correspond to $D_e/F = 0$. Open triangles correspond to fast edge diffusion while filled triangles correspond to slow edge diffusion.

($n \simeq 1/3$) is observed, while in the absence of corner diffusion the mound edges are rough and a smaller exponent ($n \simeq 1/4$) is observed. These results disagree with the prediction[11] that $n \simeq 1/3$ in general on (111) surfaces and again indicate the critical role of corner-diffusion in determining the coarsening behavior.

The dependence of the mound coarsening behavior on surface relaxation mechanisms may also be explained by considering the rate of coalescence of two mounds of lateral size L due to mass transfer from the ''outside'' region to the ''inside'' via diffusion of adatoms along the ridges (mound edges) between them. The mound coalescence time τ_L is given by the volume that must be ''filled in'' (which is of order L^3) divided by the total rate at which mass is transferred. For the case of reversible island formation without a large step barrier, a quasi-equilibrium argument for the rate of mass transfer based on the curvature dependence of the chemical potential leads to $n = 1/4$.[16] However, in the case of island relaxation without detachment or for a large step-barrier, such a quasi-equilibrium assumption no longer holds. In particular, for the case of rapid edge and corner diffusion, the outside edges of individual mounds are quite smooth so that edge adatoms may carry out a one-dimensional random walk along mound edges from the outside to the region between the mounds. Assuming an edge-adatom density ρ, which is independent of the mound size this implies a rate of mass transfer in each layer dM_1/dt, which is proportional to the number of edge-adatoms ρL divided by the time $t_1 \sim L^2$ for diffusion over a distance L, i.e., $dM_1/dt \sim 1/L$. Since there are of order L layers in each mound this leads to a total rate of mass transfer which is independent of mound size and a coalescence time $\tau_L \sim L^3$, which implies $n = 1/3$. In contrast, for the case of irreversible island formation without corner diffusion [Fig. 1(a)] the mound edges are quite ''rough'' so that mass transfer via edge diffusion is suppressed. In this case, an analysis that takes into account deposition-induced fluctuations again leads to $n = 1/4$.[16]

I now consider the applicability of these results to recent experiments.[3,4,10] For the case of growth on metal (001) surfaces one expects that corner diffusion will be relatively slow[19] since it requires either a next-nearest-neighbor hop, or a two-step process involving single-bond detachment and reattachment, or a complicated substitution process. Furthermore, in the presence of significant one-bond detachment[4] there will only be a significant amount of *effective* corner diffusion if the step-barrier is sufficiently large. This implies that for growth on (001) surfaces, $n \simeq 1/4$ is most likely to be observed. However, on (111) surfaces the barriers for edge and corner diffusion are likely to be comparable[20] since both processes involve the ''breaking'' of one nearest-neighbor bond while the other is unchanged. Furthermore the (111) geometry implies that each edge adatom has two nearest-neighbor bonds so that edge adatoms are unlikely to detach at high temperatures.[10,20] Thus, at high temperatures both rapid edge and corner diffusion may occur leading to a large coarsening exponent as observed for Rh/Rh(111) at 725 K.[10]

In conclusion, corner diffusion has been shown to play a crucial role in determining the island and mound morphology and asymptotic coarsening behavior in unstable epitaxial growth on both (001) and (111) surfaces. Depending on the strength of the step barrier and the rate of corner diffusion, either ''slow'' ($n \simeq 1/4$) or rapid ($n \simeq 1/3$) mound coarsening may be observed. Further work will be needed to study the crossover behavior and detailed dependence on deposition rate, step barrier, and corner diffusion.

I would like to thank T.L. Einstein and L. Anthony for comments on the manuscript.

[1] M.D. Johnson, C. Orme, A.W. Hunt, D. Graff, J. Sudijono, L.M. Sander, and B.G. Orr, Phys. Rev. Lett. **72**, 116 (1994); J.E. Van Nostrand, S. Jay Chey, M.-A. Hasan, D.G. Cahill, and J.E. Greene, *ibid.* **74**, 1127 (1995); J.E. Van Nostrand, S. Jay Chey, and D.G. Cahill, Phys. Rev. B **57**, 12 536 (1998).

[2] H.-J. Ernst, F. Fabre, R. Folkerts, and J. Lapujoulade, Phys. Rev. Lett. **72**, 112 (1994); W.C. Elliott, P.F. Miceli, T. Tse, and P.W. Stephens, Phys. Rev. B **54**, 17 938 (1996); B.W. Karr, D.G. Cahill, and J.E. Greene, Appl. Phys. Lett. **70**, 1703 (1997).

[3] J.A. Stroscio, D.T. Pierce, M. Stiles, A. Zangwill, and L.M. Sander, Phys. Rev. Lett. **75**, 4246 (1995); K. Thürmer, R. Koch, M. Weber, and K.H. Rieder, *ibid.* **75**, 1767 (1995); J. Alvarez, E. Lundgren, X. Torrelles, and S. Ferrer, Phys. Rev. B **57**, 6325 (1998).

[4] L.C. Jorritsma, M. Bijnagte, G. Rosenfeld, and B. Poelsema, Phys. Rev. Lett. **78**, 911 (1997); J.-K. Zuo and J.F. Wendelken, *ibid.* **78**, 2791 (1997).

[5] J. Villain, J. Phys. I **1**, 19 (1991); J. Krug, M. Plischke, and M. Siegert, Phys. Rev. Lett. **70**, 3271 (1993).

[6] G. Ehrlich and F. Hudda, J. Chem. Phys. **44**, 1039 (1966); R.L. Schwoebel, J. Appl. Phys. **40**, 614 (1969).

[7] S.C. Wang and G. Ehrlich, Phys. Rev. Lett. **75**, 2964 (1995); J.G. Amar and F. Family, *ibid.* **77**, 4584 (1996).

[8] M. Siegert and M. Plischke, Phys. Rev. Lett. **73**, 1517 (1994).

[9] P. Smilauer and D.D. Vvedensky, Phys. Rev. B **52**, 14 263 (1995); K. Thürmer, P. Koch, P. Schilbe, and K.H. Rieder, Surf. Sci. **395**, 12 (1998).

[10] F. Tsui, J. Wellman, C. Uher, and R. Clarke, Phys. Rev. Lett. **76**, 3164 (1996).

[11] M. Siegert, Phys. Rev. Lett. **81**, 5481 (1998).

[12] J.G. Amar and F. Family, Phys. Rev. B **54**, 14 742 (1996).

[13] J.W. Evans, D.E. Sanders, P.A. Thiel, and A.E. DePristo, Phys. Rev. B **41**, 5410 (1990).

[14] M.V. Ramana Murty and B.H. Cooper, Phys. Rev. Lett. **83**, 352 (1999).

[15] O. Pierre-Louis, M.R. D'Orsogna, and T.L. Einstein, Phys. Rev. Lett. **82**, 3661 (1999).

[16] L.-H. Tang, P. Smilauer, and D.D. Vvedensky, Eur. Phys. J. B **2**, 409 (1998).

[17] D.D. Vvedensky, A. Zangwill, C.N. Luse, and M.R. Wilby, Phys. Rev. E **48**, 852 (1993).

[18] T. Michely, M. Hohage, M. Bott, and G. Comsa, Phys. Rev. Lett. **70**, 3943 (1993).

[19] P. Stoltze, J. Phys.: Condens. Matter **6**, 9495 (1994).

[20] A. Bogicevic, J. Strömquist, and B.I. Lundqvist, Phys. Rev. Lett. **81**, 637 (1998).