PHYSICAL REVIEW B VOLUME 62, NUMBER 19 15 NOVEMBER 2000-I

Roughening due to edge diffusion for irreversible aggregation

C. Ratsch,[1,2,*] M. C. Wheeler,[2] and M. F. Gyure[1]
[1]*HRL Laboratories LLC, 3011 Malibu Canyon Road, Malibu, California 90265*
[2]*Department of Mathematics, University of California, Los Angeles, California 90095-1555*

(Received 22 November 1999; revised manuscript received 1 March 2000)

We show that fast edge diffusion in a simple kinetic Monte Carlo simulation for epitaxial growth enhances surface roughening for a model of irreversible aggregation. The reason for this is a simple, but rather subtle effect: Faster edge diffusion makes the islands more compact, leading to a significant adatom concentration on top of islands at earlier times. As a consequence, nucleation in higher layers occurs faster, increasing the surface roughness. We also demonstrate that fast edge diffusion can effectively contribute to diffusion of small clusters, and can produce unexpected scaling results.

In many relevant technological applications it is desirable to control the quality of thin films grown by molecular beam epitaxy. For this, it is important to understand the role of individual microscopic processes and how they influence surface morphology. Kinetic Monte Carlo (KMC) computer simulations have been used with considerable success to model the essential features of homoepitaxial growth of metals as well as semiconductors. In particular, solid-on-solid (SOS) models based on a simple cubic lattice structure have helped to elucidate the basic physical mechanisms that influence the surface morphology of a growing film.

In the simplest implementation of a cubic SOS model,[1] the rate for any surface atom to move to a neighboring site is given by an Arrhenius-type rate of the form $k(T) = D\exp(-nE_N/k_BT)$, where $D = D_0\exp(-E_S/k_BT)$ is the migration rate of a free adatom, $n = 0,1,2,3,4$ is the number of nearest neighbors before the hop, E_S is a surface bond energy, E_N is a pair bond energy, and T is the temperature. The prefactor D_0 is typically assumed to be constant, and is of the order of atomic vibrations. In general, the model parameters should be interpreted as effective parameters, so that these models are mostly suited to study physical trends. However, it has also been possible with such a model to match the decay of oscillations in the specular intensity of reflection high energy electron diffraction (RHEED) signatures for GaAs(001).[2]

These simple KMC models do not take into account the direction in which an adatom is going to hop. It has been observed, however, that diffusion over a step edge is often less likely than diffusion over a terrace.[3,4] Such an Ehrlich-Schwoebel barrier can also be captured by a KMC simulation, if one also considers the local environments of the possible final sites.[5] This additional barrier implies an uphill current, which leads to instabilities and eventual mound formation, as it has been predicted analytically[6] and confirmed by both KMC simulations and continuum equations.[7]

Another important mechanism that requires knowledge of the direction of a hop and which is the focus of this study is diffusion along a step edge. For all known systems, it is more likely for an atom that is attached to a step edge to hop along the edge than to move away from the step edge. This is quite plausible because an edge atom remains partially bonded to the step edge while it moves from one edge site to the next. This has been quantified, for example, with density-functional theory calculations for metal (001) (Ref. 8) and (111) surfaces.[9]

Edge diffusion can be incorporated straightforwardly into a KMC simulation by lowering the diffusion barrier if the jump is along a step edge. Faster edge diffusion then leads to compact islands,[10] as is often observed in experiment. This effect may be exploited when attempting to validate a more macroscopic, analytic model against the results from KMC simulations.[11] In such models, the islands are considered to be square or circular, so that it is desirable to implement fast (or infinite) edge diffusion in KMC simulations to obtain similarly compact shapes.

The importance of edge diffusion has recently been studied in a context that had previously been unnoticed.[12–14] It has been shown that edge diffusion for a model with *reversible* aggregation combined with an asymmetry to move past the outer corner produces an instability. The reason is that the asymmetry at the island corner enhances diffusion toward the island, thus inducing an uphill current and the eventual formation of mounds. In fact, it is argued that this effect might be dominant compared to the additional step edge barrier for inter-layer mass transport, particularly for semiconductors.

In this paper, we show that edge diffusion in a model for *irreversible* aggregation gives rise to an additional effect that also leads to a faster roughening of the surface. More precisely, we observe that fast edge diffusion leads to earlier nucleation in higher layers. Fast edge diffusion in effect reduces downward diffusion of adatoms to lower terraces. This manifests itself in more layers being exposed at any fixed time, as edge diffusion increases. This effect is distinct from roughening due to an ‘‘uphill current’’ induced by a diffusion bias as discussed in Ref. 13 (see below). We also find that oscillations of the step-edge density, that are presumed to be correlated to the RHEED signal,[2] disappear much more quickly, also an indication of faster roughening of the surface.

In our model, adatoms are allowed to diffuse over the surface with a diffusion constant D. Once an adatom reaches an island edge, it can diffuse along the island edge at a rate D_e, as long as it has only one nearest neighbor. It is not allowed to detach again. Once it has more than one nearest

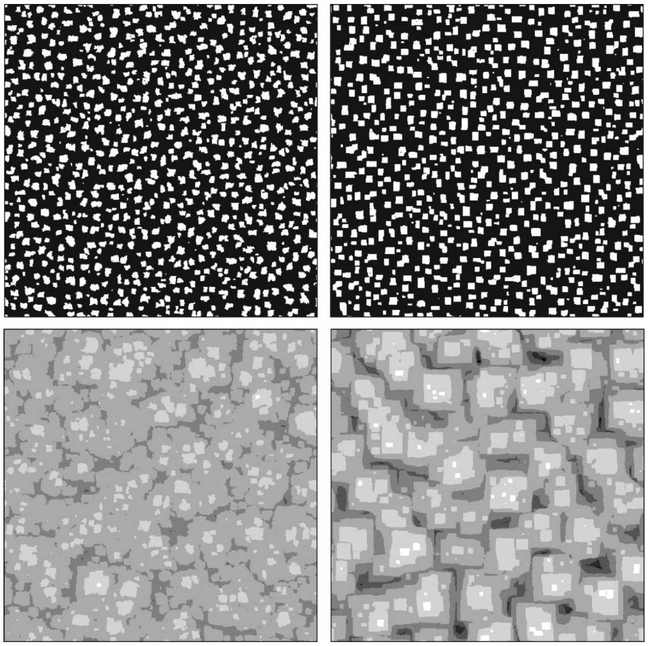

FIG. 1. Island morphologies at a coverage $\theta=0.25$ ML (upper panels) and $\theta=25$ ML (lower panels) for simulations with $D_e/D=0.001$ (left) and $D_e/D=0.1$ (right). Different gray scales correspond to different heights, with black being the lowest, and white the highest layer. At each coverage, the colors represent the same layer in each panel.

neighbor, i.e., reaches a kink (or inside corner) along the step edge, it becomes immobile. When one of these step-edge atoms reaches an outside corner, it is allowed to diffuse around the corner at the same rate D_e. Thus, in our model the rate for an atom to move can be written as $k(T)=D\exp(-mE_e/k_BT)$, where the environment-dependent parameter $m=0$ for single adatoms, $m=1$ for singly bonded step edge atoms, and $m=\infty$ for higher coordinated atoms. This implies that $D_e=D\exp(-E_e/k_BT)$. The energy E_e might be called the additional edge diffusion barrier, and diffusion for singly coordinated atoms is restricted to motion along the step edge. There is no Ehrlich-Schwoebel barrier in our model, so that downward diffusion at a step edge is treated the same as diffusion on the terrace.

Unless specified otherwise, edge diffusion is not allowed for very small islands (dimers and trimers), and we therefore refer to this model as the *frozen dimer* model. As we explain in more detail later, this was done to preclude the model from effectively having cluster diffusion, which leads to spurious scaling behavior of the island density. All the results shown here have been obtained with $D/F=10^6$, where F is the deposition rate. We have also studied other values of D/F, and found essentially the same results. Data typically represents an average of at least five independent runs on a lattice of size 500×500.

In Fig. 1 we show the surface morphology at two different coverages for simulations with small and very fast edge diffusion. It is evident that at submonolayer coverages the number of islands, and the number of exposed layers is nearly the same, while at higher coverages the number of exposed layers increases significantly with increasing edge diffusion. This can be seen more quantitatively in Fig. 2, where we show the evolution of the roughness for different values of edge diffusion. The roughness w is defined by the surface width, $w^2=\langle(h_i-\langle h\rangle)^2\rangle$, where the index i specifies the lattice site. We clearly see that for increasing edge diffusion, the surface roughness increases. This is quite surprising, as one might naively expect that fast edge diffusion has a smoothing effect.

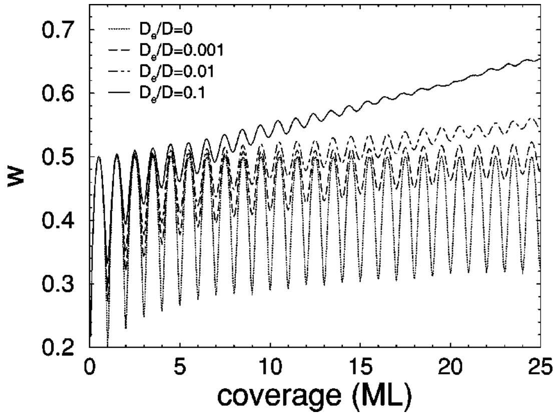

FIG. 2. Surface roughness w for different edge diffusion rates. The data represents the average over five runs on a lattice of size 500×500.

The explanation for this behavior is the following: When edge diffusion increases, the step edges straighten, and islands become more compact. As a result, it is less likely for atoms that are deposited on top of islands to diffuse downwards; there are fewer edge sites available for an atom to hop down, and atoms are on average farther away from step edges. Thus, the adatom concentration, and therefore the nucleation rate on top of islands, increases, leading to nucleation in higher layers at earlier times.[15] This can be seen in Fig. 3, where we plot the adatom density on top of the second (a) and 23rd (b) layer. At early times, the adatom density is essentially the same for growth with different values of edge diffusion. But at higher coverages, the adatom concentration is smeared out. We find a nonzero adatom concentra-

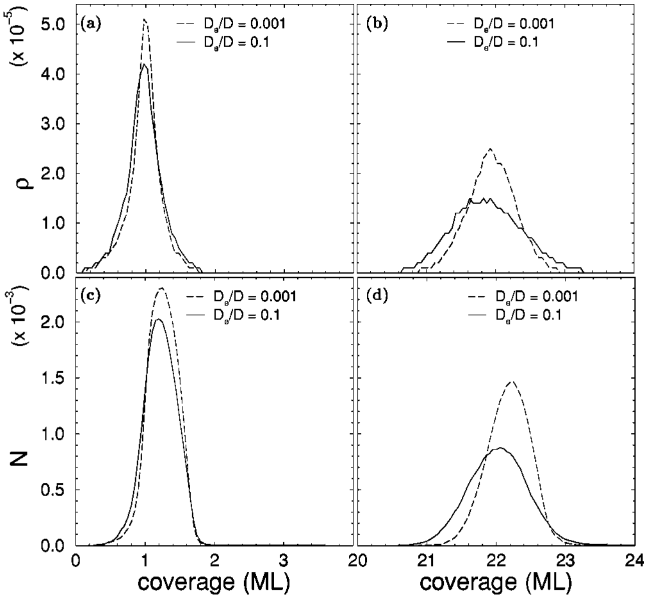

FIG. 3. Adatom density ρ (top) and island density N (bottom) on the second layer [(a) and (c)] and on the 23rd layer [(b) and (d)].

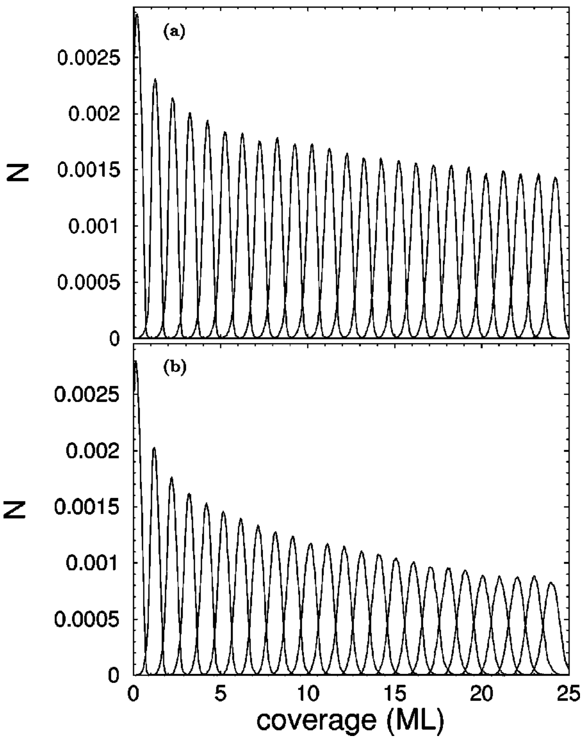

FIG. 4. Island densities N on each layer with $D_e/D = 0.001$ (a) and $D_e/D = 0.1$ (b). There are 25 curves in each plot, corresponding to the 25 layers. The order of the peaks corresponds to the order of the layers.

tion on top of the 23rd layer at an earlier time when edge diffusion is faster. This leads to earlier nucleation, and a correspondingly faster roughening of the surface.

This is also evident from Figs. 3(c) and 3(d), where we show the island densities on top of the second and 23rd layer. Clearly, islands start to nucleate earlier at higher coverages when the edge diffusion is high. Additionally, higher layers are exposed for a longer time when the edge diffusion is faster, corresponding to a rougher surface. It is important to note that this effect behaves rather differently than the uphill current discussed in Ref. 13. In the limit of very fast edge diffusion, the uphill current as discussed in Ref. 13 vanishes because there are fewer (no) corners that produce an asymmetry. At the same time, the effect of second layer nucleation is the largest in this limit. Moving away from this limit of infinite edge diffusion (i.e., decreasing edge diffusion), increases the uphill current due to a diffusion bias. But we observe that decreasing edge diffusion leads to smoother surfaces, in contrast to what would be predicted by the diffusion bias alone.

Interestingly, the enhanced nucleation at higher coverages occurs despite the fact that the magnitude of the adatom concentration is lower. All that matters is that nucleation starts sooner. In fact, we find (cf. Fig. 4) that the number of islands per layer decreases faster for fast edge diffusion, a result of the reduced magnitude of the adatom concentration. Thus, fast edge diffusion also leads to faster coarsening. This has a dramatic effect on the step-edge density, which is computed by counting all the nearest neighbor sites on the lattice at which there is a height discontinuity, independent of the magnitude of the height difference. With small edge diffusion, we can clearly see in Fig. 5 oscillations of the step-edge density for at least 25 layers, while the oscillations disappear after just 6-8 layers for $D_e/D = 1/10$. The degradation of the quality of the oscillations changes smoothly with increasing D_e. Interestingly, the magnitude of the average step-edge density is slightly reduced for faster edge diffusion, despite the fact that more layers are exposed and the surface is rougher. Thus it is apparent that step-edge density and roughness do not behave the same way. Step edges with many kinks increase the step edge density (by definition), while they reduce the adatom concentration on top of islands, resulting in a decrease of the roughness.

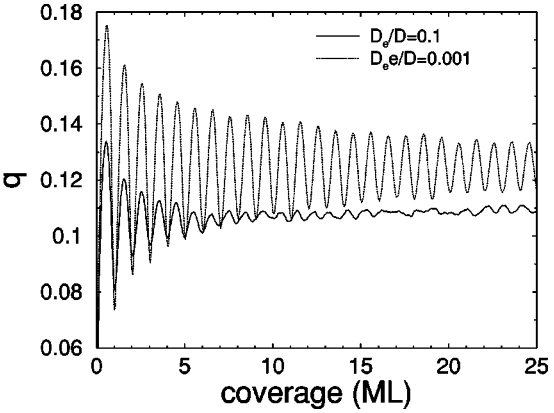

FIG. 5. Step edge density q with $D_e/D = 0.001$ and $D_e/D = 0.1$.

In the remainder of this paper, we discuss a ‘‘technical detail’’ of KMC simulations with edge diffusion that needs to be considered. More precisely, we find that fast edge diffusion for very small clusters (i.e., dimers and trimers) leads effectively to diffusion of these small clusters. This has been demonstrated to be important for Cu(100) (Ref. 16) and Al(111).[17,18] Consider, for example, a dimer: the two atoms diffuse around each other, leading to overall migration of the cluster. As a result, dimers that formed can disappear by diffusing into and merging with other islands. In Fig. 6 we see that for each D/F, the number of islands decreases with increasing ratio of D_e/D.

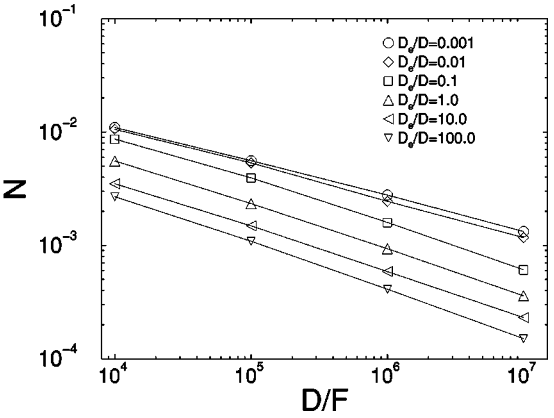

FIG. 6. Log-log plot of the island density N as a function of D/F for different values of D_e/D, for a model where motion of dimers and trimers is not frozen. The data represent the average over (at least) five runs on a lattice of size 500×500 for each point. N is measured at a coverage of $\theta = 0.15$ ML. The scaling exponents obtained are (for increasing D_e/D) $\chi = 0.31, 0.32, 0.38, 0.39, 0.40, 0.42$.

This has unexpected consequences for certain scaling results. For negligible edge diffusion, we do recover the well-known scaling result $N \sim D/F^{-\chi}$ (Ref. 19), where $\chi = 1/3$ for irreversible aggregation. However, as is evident from Fig. 6, the exponent χ increases as a function of D_e/D, even for irreversible aggregation. This is in agreement with KMC simulations that explicitly have included mobility of small clusters,[20] and with analytical results that derived $\chi = 2/5$ for a model of irreversible aggregation that includes dimer diffusion.[21] For very small edge diffusion (top curve), we find that $\chi = 0.31$, while for very large edge diffusion, $\chi = 0.42$. Thus, our results explain the dependence of χ on edge diffusion. It was also observed in Ref. 10, but the unusual result of $\chi \sim 0.4$ was not explained in that paper.

It is therefore clear that caution must be exercised in including edge diffusion for models with irreversible aggregation to guarantee compactness of the resulting islands. One way to avoid this problem is the approach we call the *frozen dimer* model, where edge diffusion is allowed only for atoms with one nearest neighbor as long as the island contains more than three atoms. In that case, a core of four atoms will very rapidly arrange itself such that each atom has two nearest neighbors, inhibiting any further movement of the island. We have verified that the frozen dimer code indeed reproduces $\chi \simeq 1/3$ for all values for edge diffusion (data not shown here).

We note that a change of the exponent χ due to edge diffusion might have important consequences for the interpretation of many experimental results. One can measure island densities as a function of temperature (for example, by counting the islands in a scanning tunneling image); if the temperature is low enough, growth is irreversible, and from nucleation theory and the exponent χ one then obtains the diffusion constant D.[22–24] Clearly, if edge diffusion changes χ, this analysis changes as well, so that one has to be very cautious in determining diffusion parameters by using nucleation theory.

In conclusion, we have shown that edge diffusion during irreversible growth leads to surface roughening, even when atoms are bound irreversibly to an island. In addition to its obvious significance for simple KMC models, we believe that this behavior might open interesting possibilities to control the quality and smoothness of a growing film. For example, a surfactant that sticks to step edges and reduces the diffusion of adatoms along the step edge might prolong the layer-by-layer growth regime. One might also be able in an experiment to adjust the relative importance of edge diffusion to surface diffusion by changing the temperature, so that smoother step edges extend the layer-by-layer growth regime.

We acknowledge helpful discussions with R.E. Caflisch, W. Barvosa-Carter, and R.S. Ross. This work was supported by the NSF and DARPA through cooperative agreement DMS-9615854 as part of the Virtual Integrated Prototyping Initiative.

---

*Corresponding author: Electronic address: cratsch@math.ucla.edu

[1] S. Clarke and D. D. Vvedensky, J. Appl. Phys. **63**, 2272 (1988).

[2] T. Shitara, D. D. Vvedensky, M. R. Wilby, J. Zhang, J. H. Neave, and B. A. Joyce, Phys. Rev. B **46**, 6615 (1992).

[3] G. Ehrlich and F. G. Hudda, J. Chem. Phys. **44**, 1039 (1966).

[4] R. L. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).

[5] P. Šmilauer and D. D. Vvedensky, Phys. Rev. B **47**, 4119 (1993).

[6] J. Villain, J. Phys. I **1**, 19 (1991).

[7] M. D. Johnson, C. Orme, A. W. Hunt, D. Graff, J. Sudijono, L. M. Sander, and B. G. Orr, Phys. Rev. Lett. **72**, 4246 (1994).

[8] B. D. Yu and M. Scheffler, Phys. Rev. Lett. **77**, 1095 (1996).

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

[10] G. S. Bales and D. C. Chrzan, Phys. Rev. B **50**, 6057 (1994).

[11] C. Ratsch, M. F. Gyure, S. Chen, M. Kang, and D. D. Vvedensky, Phys. Rev. B **61**, R10 598 (2000).

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

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

[14] S. Das Sarma, P. Punyindu, and Z. Toroczkai, cond-mat/9908013 (unpublished).

[15] We note that there is already a speculation about this mechanism in Ref. 13.

[16] Z.-P. Shi, Z. Zhang, A. K. Swan, and J. F. Wendelken, Phys. Rev. Lett. **76**, 4927 (1996).

[17] P. J. Feibelman, Phys. Rev. Lett. **58**, 2766 (1987).

[18] A. Bogicevic, P. Hyldgaard, G. Wahnström, and B. I. Lundqvist, Phys. Rev. Lett. **81**, 172 (1998).

[19] J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).

[20] L. Kuipers and R. E. Palmer, Phys. Rev. B **53**, R7646 (1996).

[21] J. Villain, A. Pimpinelli, L. Tang, and D. E. Wolf, J. Phys. I **2**, 2107 (1992).

[22] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).

[23] J. A. Stroscio, D. T. Pierce, and R. A. Dragoset, Phys. Rev. Lett. **70**, 3615 (1993).

[24] H. Brune, K. Bromann, H. Röder, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. Nørskov, Phys. Rev. B **52**, R14 380 (1995).