2003

Sintering of Metal(100) Homoepitaxial Islands: Kink Rounding Barriers, Modified Size Scaling, and Experimental Behavior

Da-Jiang Liu
Iowa State University, dajiang@fi.ameslab.gov

C. R. Stoldt
Iowa State University

Patricia A. Thiel
Iowa State University, thiel@ameslab.gov

James W. Evans
Iowa State University, evans@ameslab.gov

Sintering of Metal(100) Homoepitaxial Islands: Kink Rounding Barriers, Modified Size Scaling, and Experimental Behavior

Abstract
Near-square islands form during sub-monolayer homoepitaxial growth on metal (100) surfaces. Diffusion of these islands after deposition leads to collision of island pairs, typically corner-to-corner creating dumbbell-shaped clusters. Subsequent coalescence (or sintering) recovers a near-square equilibrium shape. This process is mediated by periphery diffusion (PD) and its study can provide detailed insight into the underlying dynamic processes and energetics. Atomistic modeling reveals that the size scaling of the characteristic relaxation time, τ, depends on the detailed energy barriers of various hopping processes that contribute to PD. Simulations without an extra kink or corner rounding barrier for PD reveals $\tau \sim L^4$, while behavior approaching $\tau \sim L^3$ is observed with a significant extra kink rounding barrier for PD. The latter is consistent with experimental observations for Ag/Ag(100) at 300 K.

Disciplines
Chemistry | Materials Science and Engineering

Comments
This is from *Morphological and Compositional Evolution of Thin Films: Proceedings of the MRS 2002 Fall Meeting* 749 (2003): pp. W2.8.1—W2.8.6, doi:10.1557/PROC-749-W2.8

Mat. Res. Soc. Symp. Proc. Vol. 749 © 2003 Materials Research Society W2.8

Sintering of Metal(100) Homoepitaxial Islands: Kink Rounding Barriers, Modified Size Scaling, and Experimental Behavior

Da-Jiang Liu[1], C. R. Stoldt[2*], P. A. Thiel[1,2], and J. W. Evans[1,3]
[1]Ames Laboratory – USDOE, [2]Department of Chemistry, [3]Department of Mathematics, Iowa State University, Ames, Iowa 50011

ABSTRACT

Near-square islands form during sub-monolayer homoepitaxial growth on metal (100) surfaces. Diffusion of these islands after deposition leads to collision of island pairs, typically corner-to-corner creating dumbbell-shaped clusters. Subsequent coalescence (or sintering) recovers a near-square equilibrium shape. This process is mediated by periphery diffusion (PD) and its study can provide detailed insight into the underlying dynamic processes and energetics. Atomistic modeling reveals that the size scaling of the characteristic relaxation time, τ, depends on the detailed energy barriers of various hopping processes that contribute to PD. Simulations *without* an extra kink or corner rounding barrier for PD reveals $\tau \sim L^4$, while behavior approaching $\tau \sim L^3$ is observed with a significant extra kink rounding barrier for PD. The latter is consistent with experimental observations for Ag/Ag(100) at 300 K.

INTRODUCTION

For submonolayer homoepitaxial systems, where the substrate is "completely wet" by the 2D islands, the natural and traditional expectation was that post-deposition coarsening of the adlayer would occur via Ostwald Ripening (OR) [1]. The remarkable discovery first made for the Ag/Ag(100) system at 300 K was that large 2D clusters or islands of 100's to 1000's of adatoms have significant diffusive mobility [2]. Furthermore, cluster diffusion and subsequent coalescence, i.e., Smoluchowski Ripening (SR) rather than OR actually dominates the coarsening process at 300 K (which occurs on the time-scale of hours) [3]. The diffusion coefficient of a cluster with linear size $\sim L$ scales like $D(s) \sim L^{-\alpha}$, with $\alpha \approx 2.2$ for L =10-20 at $T = 300$ K, and the mechanism was proposed to be periphery diffusion (PD) [4]. In fact, these and related studies have prompted much theoretical analysis of cluster diffusion (and, specifically, of the size scaling) via both atomistic [5–7] and continuum [8] models. More recently, the subsequent coalescence or sintering process through the same PD mechanism has been studied both experimentally and theoretically [9–13]. In this paper, using Ag(100) as an example, we show that one can reveal details of periphery diffusion (and specifically kink rounding) through realistic modeling of the sintering process.

ATOMISTIC MODELING OF PERIPHERY DIFFUSION

For simplicity, our atomistic model of PD assumes that configuration energies can be determined by counting nearest-neighbor (NN) bonds with strength ϕ. The four key elementary

*Current Address: Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309

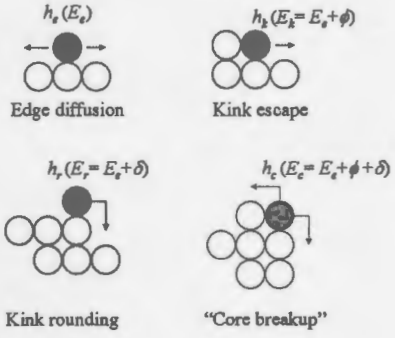

Figure 1: Bird's eye view of key periphery diffusion (PD) processes and the associated barriers assuming NN interactions ϕ: straight edge diffusion (barrier E_e); kink escape (barrier $E_e + \phi$); kink rounding (barrier $E_e + \delta$); core breakup (barrier $E_e + \phi + \delta$). Copyright ©2002 American Institute of Physics.

PD processes shown in Fig. 1 are [9–12]: diffusion along close-packed edges with "low" barrier E_e; escape from kinks along step edges with barrier $E_k = E_e + \phi$; diffusion around kinks with barrier $E_r = E_e + \delta$; "core breakup" with barrier $E_c = E_e + \phi + \delta$. The third and fourth processes actually involve two hops, the first (slow) step to a diagonal NN site to the cluster, and the second "fast" step back to a NN site, but we combine these into a single effective hop.

The activation energy for back-to-equilibrium shape relaxation through PD in this model is typically $E_{act} = E_e + \phi + \delta$. This can be understood in two ways: one is by observing that "core breakup" with barrier E_c is the rate limiting process; the other is by noting that the diffusion barrier of an edge atom with a single bond is E_e, the population of such atoms is $\sim \exp[-\phi/(k_B T)]$, and there is an extra barrier δ for the atom to cross a kink or corner.

From the overall relaxation rate of clusters, one can estimate E_{act} for PD. Comparing kinetic Monte Carlo (KMC) simulations of the above atomistic model with STM experiments of the relaxation of worm-like structures for Ag/Ag(100) shows $E_{act} = 0.68$ eV [11]. Various calculations using density functional theory and embedded atom method estimate that $E_e =$ 0.26-0.27 eV [14, 15]. The binding energy ϕ can be estimated from the step formation energy β along the closed pack direction and theoretical calculation gives $\phi = 2\beta a = 0.20$-0.27 eV where a is the lattice constant [14, 16]. Thus, we conclude that there is a significant kink rounding barrier δ in the range of 0.14-0.22 eV.

However, the effectiveness of this type of estimation depends on the accuracies of each parameter involved, which are often hard to gauge. For example, a recent experiment by Hoogeman *et al.* [17] claims that the activation energy for kink escape is 0.6±0.1 eV, which should be equal to $E_e + \phi$. If one takes the upper bound of this estimate, and compares to the total activation energy of PD, one would conclude that $\delta = 0$.

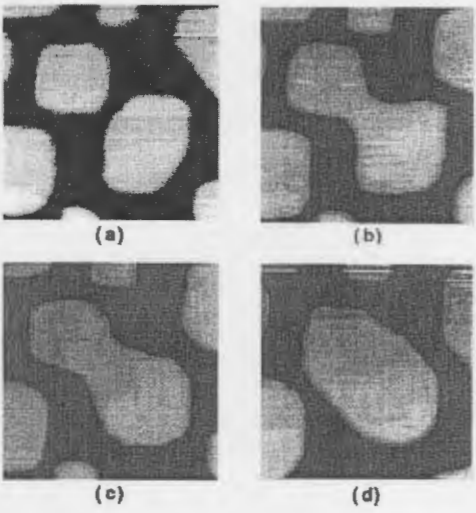

Figure 2: Experimental STM images (50×50 nm^2) of dumbbell formation and relaxation after corner-to-corner collision of Ag islands on Ag(100) at 300 K. Image times are: (a) 0 min; (b) 46 min (<10 min after collision); (c) 91 min; and (d) 271 min.

Recently, the existence of the kink rounding barrier for PD has been shown independently by Pierre-Louis *et al.* [18] and Ramana Murty and Cooper [19] to create instability during growth. There are efforts [20, 21] to use this instability to account for experimentally observed step meandering during growth on vicinal surfaces. However, it is difficult to separate effects from the the Bales-Zangwill instability [22] due to the Erhlich-Schwoebel barrier, and the instability due to δ. The kink rounding barrier is also shown to play a critical role in multilayer mound formation at low temperature where islands become irregular [23].

Since sintering involves only diffusion of atoms along the step edge, it is not entangled with interlayer diffusion, making it ideal for studying the effect of the kink rounding barrier.

SIZE SCALING OF THE RELAXATION RATE

The "typical" experimental case of sintering involves corner-to-corner collision of two islands for Ag/Ag(100) at 300 K forming dumbbell-shaped clusters. See Fig. 2. One of the distinctive features of cluster dynamics is that the characteristic rate has a size scaling relationship, with the scaling exponent depends on the mechanism. It is instructive to look at the Mullins-type continuum theory for relaxation via PD. Here, the cluster perimeter is described by a continuous curve. Let V_n denote its normal velocity, J_{PD} the mass current around the perimeter, μ the chemical potential of step edge atoms, σ_{PD} the mobility of step edge atoms, $\tilde{\beta}$ the step edge

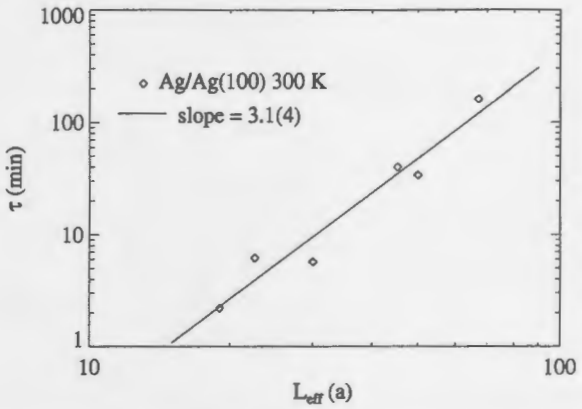

Figure 3: Relaxation time τ versus effective length L_{eff} of dumbbell relaxation. L_{eff} is defined as $\sqrt{A_{\text{av}}}$ where $A_{\text{av}} = (A_1 + A_2)/2$ is the average area of the two clusters that form the dumbbell, with area A_1 and A_2 respectively. τ is defined as the time for the neck width to increase from $L_{\text{eff}}/2$ to L_{eff}. The solid line is a fit to the power relationship $\tau \sim L^n$, which gives $n = 3.1 \pm 0.4$.

stiffness, and κ the step edge curvature. Then, one has

$$V_n \propto -\nabla \cdot \mathrm{J}_{\mathrm{PD}}, \text{ with } \mathrm{J}_{\mathrm{PD}} \propto -\sigma_{\mathrm{PD}} \nabla \mu \text{ and } \mu \propto \tilde{\beta}\kappa, \tag{1}$$

the first equation imposing mass conservation, and ∇ denoting the derivative along the perimeter. Since σ_{PD} and $\tilde{\beta}$ depend only on step-edge orientation, it is straightforward to show that this continuum formulation produces exactly the scaling relation for the relaxation time $\tau \propto L^4$.

Detailed simulation studies of the atomistic model for PD described reveal that the value of the exponent for dumbbell relaxation equals the classic value of $n = 4$, the continuum model prediction, in the *absence* of a kink rounding barrier ($\delta = 0$). In fact, when anisotropy in $\tilde{\beta}$ is incorporated, the continuum formulation reproduces remarkably well results of atomistic simulations for relaxation of dumbbells when $\delta = 0$, even for small L [12]. However, n decreases toward 3 upon increasing δ, crossover occurring when the "kink Ehrlich-Schwoebel length" $L_\tau = \exp[\delta/(k_B T)]$ increases above L [12].

Figure 3 shows the size dependence of the relaxation rate from experiments that suggest that $\tau \sim L^n$, with $n \approx 3$ deviating from the Mullins' value [9, 10], although the uncertainty is large. The deviation of the size scaling exponent n from the "conventional" value 4 suggests that $L \leq L_\tau$, which gives a lower bound to the kink rounding barrier 0.11 eV.

To gain some simple understanding of the size-scaling [12] of τ in dumbbell relaxation, consider the removal of a complete "outer layer" of $\sim L$ atoms towards the neck by transferring them around kink sites a distance $\sim L$ away. As indicated in Fig. 4, this overall process is essentially a "random walk" between configurations with different numbers of transferred atoms. However, the energy decreases upon transfer of the last atom biasing the walk, so this configuration is an (imperfect) adsorbing state for the "walk". Thus, based on Einstein's relation

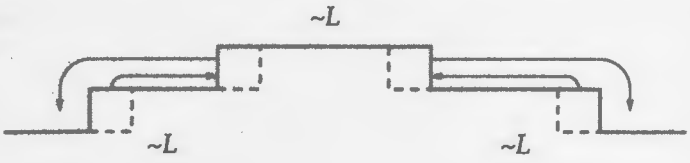

Figure 4: Schematic of adatom mass transfer from an outer terrace of a non-equilibrium nanostructure during shape relaxation via periphery diffusion. Typical terrace lengths are $\sim L$ sites. Atoms are transferred reversibly between this outer terrace and the kinks on the lower terrace, as the system undergoes a "random walk" in configuration space. However, complete removal of the outer terrace lowers the energy, thus biasing evolution in this direction.

for random walks, the time to transfer $\sim L$ atoms scales like the square of the number of transferred atoms, i.e., $\tau_{\text{layer}} \sim L^2\tau_0$, where τ_0 is the typical time to transfer a single atom. Detailed analysis shows that $\tau_0 \sim (L_r + L)\tau_k$, where $\tau_k = 1/h_k$. The overall relaxation process requires transfer of $\sim L$ layers so that [12]

$$\tau \sim L\tau_{\text{layer}} \sim L^3(L_r + L)\tau_k. \tag{2}$$

This expression reveals the behavior $\tau \sim L^4$ for $L \gg L_r$, and $\tau \sim L^3$ for $L \ll L_r$.

We briefly mention that relaxation of rectangular clusters formed by side-to-side collision of square islands is distinct from the above case. For L below the characteristic length $L_c = \exp[\phi/(2k_BT)]$, which gives the separation of kinks on a close-packed step edge, the rate limiting process for relaxation is nucleation of new step edges [12,24,25]. In contrast, relaxation of the dumbbell shape does not requires formation of new step edges. For relaxation of rectangular islands with $L \ll L_c$, one finds that $n \approx 2$ for $\delta = 0$ [12,25], with lower values for $\delta > 0$ [12]. The same processes control cluster diffusion. For $\delta = 0$, the size scaling exponent $\alpha = 3$ when $L \gg L_c$, and $\alpha = 1$ for $L \ll L_c$. The experimental value $\alpha \approx 2.2$ presumably reflects crossover from the classic value of $n = 4$ to this lower value. Existence of the kink rounding barrier δ can further lower the scaling exponent, however, it is only secondary to the effect of ϕ, while its main effect is to reduce the overall mobility.

In general, two length scales, L_c (related to the binding energy ϕ) and L_r (related to the kink rounding barrier δ), are important in determining the size scaling of dynamical processes. In addition, they are reflected in the azimuthal angle dependence of the step formation energy $\beta(\theta)$ and PD mobility $\sigma_{\text{PD}}(\theta)$. The exact relation for $\beta(\theta)$ is well known [12] and, from phenomenological arguments, we propose that $\sigma_{\text{PD}}(\theta) \approx \sigma_{\text{PD}}(0)/(1 + |\sin\theta|L_r/a)$ for our model.

DISCUSSION AND CONCLUSION

We have conducted detailed simulations of a realistic but bare-bones atomistic model for corner-to-corner coalescence or sintering of near-square 2D clusters through periphery diffusion. Deviations from the continuum model prediction, which has been observed in experiments, are

revealed and explained. Specifically, an extra kink rounding barrier δ gives rise to the deviation from the continuum model in the case of dumbbell relaxation (and for other geometries where relaxation does not involve formation of new step edges).

ACKNOWLEDGMENTS

This work was supported by NSF Grants EEC-0085604 and CHE-0078596, and was performed at Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

REFERENCES

[1] M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, Surf. Sci. Rep. **16**, 377 (1992).
[2] J.-M. Wen, S.-L. Chang, J. W. Burnett, J. W. Evans, and P. A. Thiel, Phys. Rev. Lett. **73**, 2591 (1994).
[3] J.-M. Wen, J. W. Evans, M. C. Bartelt, J. W. Burnett, and P. A. Thiel, Phys. Rev. Lett. **76**, 652 (1996).
[4] W. W. Pai, A. K. Swan, Z. Zhang, and J. F. Wendelken, Phys. Rev. Lett. **79**, 3210 (1997).
[5] D. S. Sholl and R. T. Skodje, Phys. Rev. Lett. **75**, 3158 (1995).
[6] G. Mills, T. R. Mattsson, L. Møllnitz, and H. Metiu, J. Chem. Phys. **111**, 8639 (1999).
[7] S. Pal and K. A. Fichthorn, Phys. Rev. B **60**, 7804 (1999).
[8] S. V. Khare, N. C. Bartelt, and T. L. Einstein, Phys. Rev. Lett. **75**, 2148 (1995).
[9] C. R. Stoldt, A. M. Cadilhe, C. J. Jenks, J.-M. Wen, J. W. Evans, and P. A. Thiel, Phys. Rev. Lett. **81**, 2950 (1998).
[10] A. M. Cadilhe, C. R. Stoldt, C. J. Jenks, P. A.Thiel, and J. W. Evans, Phys. Rev. B **61**, 4910 (2000).
[11] W. W. Pai, J. F. Wendelken, C. R. Stoldt, P. A. Thiel, J. W. Evans, and D.-J. Liu, Phys. Rev. Lett. **86**, 3088 (2001).
[12] D.-J. Liu and J. W. Evans, Phys. Rev. B **66**, 165407 (2002).
[13] M. Eßer, K. Morgenstern, G. Rosenfeld, and G. Comsa, Surf. Sci. **402-404**, 341 (1998).
[14] B. D. Yu and M. Scheffler, Phys. Rev. B **55**, 13916 (1997).
[15] U. Kürpick and T. S. Rahman, Phys. Rev. B **57**, 2482 (1998).
[16] R. C. Nelson, T. L. Einstein, S. V. Khare, and P. J. Rous, Surf. Sci. **295**, 462 (1993).
[17] M. S. Hoogeman, L. Kuipers, D. C. Schlößer, and J. W. M. Frenken, Surf. Sci. **447**, 25 (2000).
[18] O. Pierre-Louis, M. R. D'Orsogna, and T. L. Einstein, Phys. Rev. Lett. **82**, 3661 (1999).
[19] M. V. R. Murty and B. H. Cooper, Phys. Rev. Lett. **83**, 352 (1999).
[20] H. Emmerich, Phys. Rev. B **65**, 233406 (2002).
[21] J. Kallunki, J. Krug, and M. Kotrla, Phys. Rev. B **65**, 205411 (2002).
[22] G. S. Bales and A. Zangwill, Phys. Rev. B **41**, 5500 (1990).
[23] K. J. Caspersen, A. R. Layson, C. R. Stoldt, V. Fournee, P. A. Thiel, and J. W. Evans, Phys. Rev. B **65**, 193407 (2002).
[24] P. Jensen, N. Combe, H. Larralde, J. L. Barrat, C. Misbah, and A. Pimpinelli, Eur. Phys. J. B **11**, 497 (1999).
[25] N. Combe and H. Larralde, Phys. Rev. B **62**, 16074 (2000).