

Using Temperature to Tune Film Roughness: Nonintuitive Behavior in a Simple System

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Ag(100) homoepitaxy constitutes one of the simplest systems in which to study thin-film growth. Yet we find that the roughness variation with temperature is extraordinarily complex. Specifically, as the deposition temperature is reduced from 300 to 50 K, the roughness of 25 monolayer films first increases, then decreases, then increases again. A transition from mound formation to self-affine (semifractal) growth occurs at ~ 135 K. The underlying mechanisms are postulated. An atomistic model incorporating these mechanisms reproduces the experimental data quantitatively.

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The surface morphologies of films grown by deposition on perfect substrates can reveal surprising features. Even if the equilibrium structure is simple, deposition can drive the system into an unanticipated variety of far-from-equilibrium forms, particularly at low temperatures T where equilibration is limited [1]. Important physical properties of such films depend sensitively on these morphologies, particularly on roughness. Prominent examples are magnetic properties of thin metal films, transitions in conductivity, superconductivity, and localization in quench condensed films, and catalytic properties of bimetallic thin films [1,2]. Thus, a fundamental understanding of the atomic-scale processes that underlie film growth and their relationship to film morphology is a crucial goal, since it will enable control or “tuning” of film structure.

This goal has yet to be achieved even for simple systems. Homoepitaxy (self-growth) is at an extreme of simplicity, because thermodynamics requires that such a film grows as smoothly as possible within entropic limits, with each layer filling in sequence. Naturally, one expects to see this type of evolution at high T , where kinetic barriers—especially those to interlayer diffusion—can be overcome. Certainly, deposition at lower T can produce rougher nonequilibrium structures (“kinetic roughening”). A traditional expectation is that the roughness will increase monotonically as the deposition temperature is lowered, and the system deviates farther from equilibrium. This view was prompted in part by the “rain model” for low T deposition, where randomly deposited atoms irreversibly stick at on-top adsorption sites in a simple cubic (SC) crystal geometry [3]. This model exhibits rough growth characterized by a Poisson height distribution, behavior which persists (in an SC geometry) whenever interlayer diffusion is inoperative. A contrasting view [1] is that films should grow smoother at lower T , due to the presence of smaller islands (atoms deposited on top are closer to edges where they can hop down, but this neglects slower terrace diffusion). Neither picture is supported by our results.

In reality, metal film growth is far more complex. One example is the nonmonotonic variation of roughness with temperature observed on substrates with threefold symme-

try [4]. This behavior has been related to a transition from compact to irregular shapes of the 2D islands formed, the increase in kink sites at island edges facilitating interlayer transport. On substrates with fourfold symmetry, such as Ag(100), there is no comparable island shape transition. However, surprisingly smooth growth has been observed in metal(100) homoepitaxy at ~ 77 K [5]. More recently, roughness was observed to increase from 300 to 200 K for Ag/Ag(100) [6], but to decrease from 200 to 160 K for Cu/Cu(100) [7]. While these data for systems with fourfold symmetry have been tantalizing, they have been insufficient to provide a comprehensive picture for growth. This Letter provides the broad experimental picture that has been absent, including an assessment of behavior down to extremely low temperatures—where new surprises emerge. Atomistic growth models are applied to test our interpretation of experimental observations.

The experiments reported here detail the temperature dependence of multilayer homoepitaxy on Ag(100) between 300 and 50 K. We use an Omicron variable-temperature scanning tunneling microscope (VTSTM) in a UHV chamber with base pressure below 1×10^{-10} Torr. Films are formed by evaporation of pure Ag from an Omicron EFM3 UHV evaporator. After deposition, T remains fixed (± 5 K), and data are obtained from central portions of broad terraces in order to minimize the effect of step edges on data analysis (cf. Ref. [8]).

Figure 1 shows STM images of 25 monolayer (ML) Ag films grown on Ag(100) deposited at various T . In order to characterize the vertical morphology precisely, we discretize the continuous film height distribution obtained from STM by peak fitting using multiple Gaussian functions with a separation equal to the atomic interlayer spacing, $b = 2.04$ Å. The resulting surface roughness, W (rms width of the height distribution in units of b) versus T , is shown in Fig. 2(a). The temperature variation is remarkably complex. Specifically, the roughness of 25 ML Ag films *increases* as T is reduced from 300 to 220 K, then *decreases* as T is reduced further to 140 K, and finally *increases* again for lower T (at least down to 50 K).

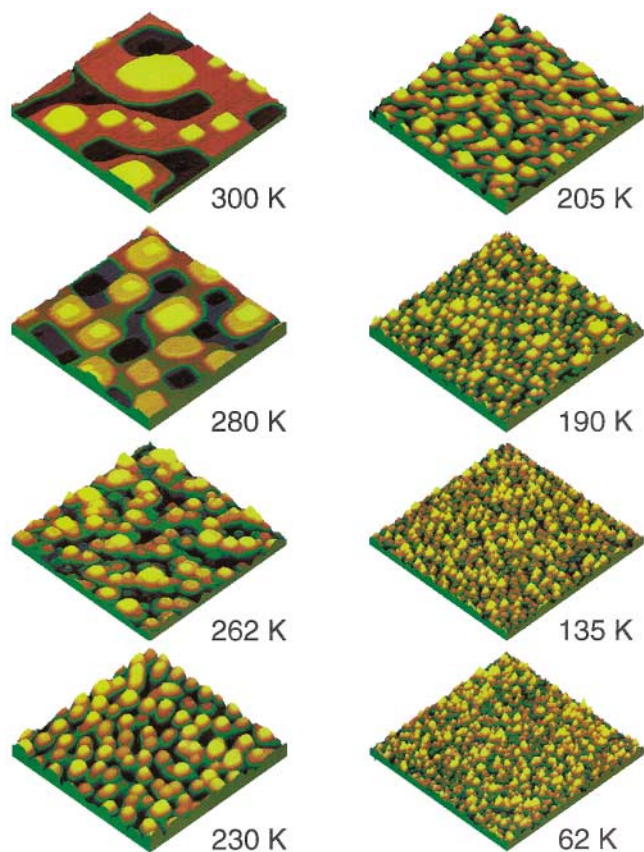


FIG. 1 (color). Differentiated $100 \times 100 \text{ nm}^2$ STM images of 25 ML Ag/Ag(100) films deposited with $F \approx 0.02 \text{ ML/s}$ at various temperatures (shown). The vertical scale is expanded.

To facilitate a more detailed characterization of film morphology, we provide further background on possible growth modes. For metal homoepitaxy, roughening is often accompanied by the development of three-dimensional mounds with a well-defined characteristic lateral size [1,3,4,7]. Although other possibilities exist [9], this behavior is usually associated with the existence of an Ehrlich-Schwoebel or step-edge barrier, which inhibits

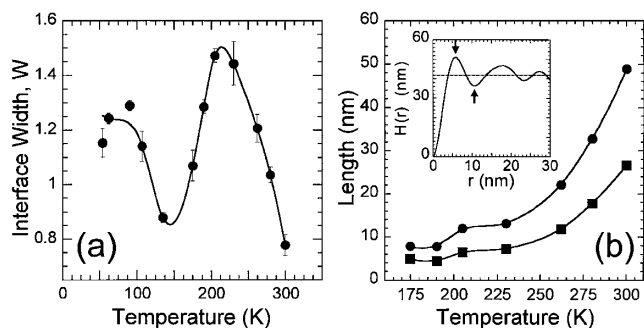


FIG. 2. Properties of 25 ML Ag/Ag(100) films deposited with $F \approx 0.02 \text{ ML/s}$ at $T \leq 300 \text{ K}$. (a) Roughness W (solid circles) in units of interlayer spacing, $b = 2.04 \text{ \AA}$. (b) Average mound separation, D_{av} (solid circles), and radius, R_{av} (solid squares). Solid curves guide the eye, and error bars indicate statistical uncertainty (excluding systematic tip effects, expected at low T). Inset: $H(\mathbf{r})$ at 230 K; arrows indicate R_{av} and D_{av} .

downward diffusion at step edges [10]. In many systems [3], an alternative to mounding is observed known as self-affine (semifractal) growth, which is characterized by a continuous spectrum of lateral lengths. A single system usually exhibits just one of these two types of behavior, and distinction between them is provided by examination of the height-height correlation function, $H(\mathbf{r})$, i.e., the mean-square height difference for two points on the film surface versus their lateral separation \mathbf{r} [3].

Thus, we next examine $H(\mathbf{r})$ vs \mathbf{r} for the STM data shown in Fig. 1. Behavior at 230 K is plotted in the inset of Fig. 2(b). The presence of oscillations indicates formation of somewhat ordered arrays of mounds. The first maximum (minimum) corresponds roughly to the average mound radius, R_{av} (separation or diameter, D_{av}). Figure 2(b) shows that R_{av} and D_{av} ($\approx 2R_{\text{av}}$) decrease rapidly with decreasing T to about 205 K, after which they remain roughly constant. Oscillations in $H(\mathbf{r})$ are apparent down to 175 K, but are gone by 135 K, suggesting a transition to self-affine growth. This claim is supported by examining the roughness exponent α determined from the roughness W_L for a range of short STM scans of length L , and using $W_L \sim L^\alpha$ [3]. We find that $\alpha \approx 1$ for $T > 135 \text{ K}$ (reflecting “regular” mounded morphologies), with α decreasing to < 0.5 below 135 K (reflecting self-affine morphologies). See Table I. Hence, two independent analyses of the film morphology support a transition from mound formation to self-affine growth in the range of 175–135 K. We also find that the average step density (or mean local slope) and the slope of mound sides increase monotonically with decreasing T (Table I), observations which we shall exploit below in interpreting low T growth.

The discussion of the possible atomic processes responsible for the observed growth characteristics is split into the two temperature regimes for mounding and self-affine growth, respectively.

Mounding regime at higher T .—We propose that the film structure at 175 K and above is determined by three main processes: (i) intralayer terrace diffusion (with barrier E_d) leading to the irreversible formation [8] of near-square islands in each layer, (ii) downward interlayer diffusion inhibited by a small step-edge barrier (of magnitude E_{se}), and (iii) “downward funneling” (DF) [11] or deflection of deposited atoms from step edges and other microprotrusions to lower fourfold hollow (4FH) adsorption sites. See Fig. 3(a). (DF results from the high kinetic energy acquired by atoms on approaching the surface.) Villain noted that the Ehrlich-Schwoebel barrier

TABLE I. Variation of the roughness exponent α , the average local slope ϕ_{av} , and the slope of mound sides ϕ_{md} (in degrees) with T for 25 ML Ag/Ag(100) films.

T	54 K	135 K	175 K	230 K	280 K
α	0.50	0.93	1.05	1.07	...
ϕ_{av}	14.0	10.6	10.4	8.4	2.7
ϕ_{md}	16.0	12.0	12.2	9.6	3.2

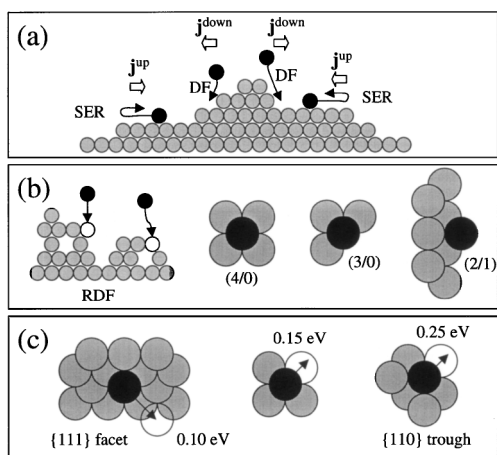


FIG. 3. Schematics: (a) mound formation—step-edge reflection (SER), downward funneling (DF), and associated lateral mass currents; (b) restricted downward funneling (RDF) with a top view of some trap sites (No. supports/No. in-layer atoms); and (c) low-barrier downward hops.

causes diffusing atoms to be reflected from descending step edges, enhancing their probability of capture at ascending step edges. This produces a lateral mass current in the uphill direction (\mathbf{j}^{up}) resulting in a growth instability (mounding) [10]. DF produces stabilizing downhill current (\mathbf{j}^{down}) which for sufficiently large slopes of mound sides can counterbalance the uphill current (i.e., $\mathbf{j}^{\text{up}} + \mathbf{j}^{\text{down}} \approx \mathbf{0}$), resulting in selection of these mound slopes [11]. See again Fig. 3(a).

At 300 K, for films up to ~ 25 ML terrace diffusion is highly active producing large lateral structures. Intralayer diffusion is also efficient, and allows atoms deposited in higher layers to readily reach lower layers perpetuating smooth growth. Only for thicker films would mounds become well developed.

As the deposition temperature is reduced from 300 to about 200 K, the main effect on roughness comes from increasing inhibition of interlayer diffusion due to the presence of the small step-edge barrier. Atoms become less likely to reach lower layers and, as a result, mounds become more pronounced even by 25 ML. This is reflected in an increase in W , which peaks between 230 and 205 K [Fig. 2(a)], where the mounds are still nearly square with broad, flat summits (see Fig. 1). At least at 230 K (and below), DF significantly influences mound morphology, inhibiting the growth of mound slopes already by 25 ML.

As temperature is reduced, a strong inhibition of terrace diffusion also occurs, leading to a significant decrease in feature size [see Figs. 1 and 2(b)], and a corresponding increase in step density. Below about 200 K, we propose that this increase in step-edge density becomes the determining effect: It leads to an enhancement of the effect of the DF mechanism. DF acts to smooth the surface, as evidenced by the decrease in W below 230 K [Fig. 2(a)], and ultimately to induce a transition out of the mounding regime.

To test our understanding of the evolution of film structure in the mounding regime, we employ kinetic Monte

Carlo simulations of an atomistic model for homoepitaxial growth with an fcc(100) crystal geometry that incorporates the elements described above. This generic model has been presented previously [11], although at that time detailed experimental data for Ag/Ag(100) did not exist for comparison. From previous Arrhenius analyses of submonolayer island separation [8], and from *ab initio* theory [12], we know $E_d \approx 0.38\text{--}0.45$ eV. Interestingly, a consistent estimate of $E_d \approx 0.45$ eV follows from an Arrhenius analysis [3,11] of the mound separation data in Fig. 2(b). Here, we use $E_d = 0.40$ eV. We estimate the step-edge barrier to be 30 ± 5 meV from a fit to the value of W at 230 K reported above. All attempt frequencies were set to the value 10^{13} s^{-1} (cf. Ref. [8]). Hence, there remain no adjustable parameters in the model.

As shown in Fig. 4(a), this kinetic model reproduces very well the experimental W 's between 300 and 135 K. It also reproduces the monotonic increase in slope with decreasing T , and a transition out of the mounding regime for lower T , trends seen in previous generic simulations [11]. Despite this success, we emphasize our simplifying assumptions: the step-edge barrier is assumed uniform; isolated islands are square with [110] step edges, and do not restructure upon “collision” due to growth. In reality, open [100] step edges are present, and E_{se} is likely lower for [100] than [110] edges [13], so our $E_{\text{se}} \approx 30$ meV is an effective value.

Finally, as a definitive test of our claim that DF produces the decrease in W below 220 K, we have repeated these simulations with the same parameters, but for a SC crystal geometry with on-top adsorption sites where DF does not occur. The results reveal a monotonic increase in W for 25 ML films as T decreases below 300 K (achieving a Poisson value of $W = 5b$ for low T).

Self-affine growth regime at lower T .—Below 135 K, W increases again. Such a phenomenon has not been observed previously. Why does this occur? A key point is that the surface becomes increasingly irregular and local slopes become steeper at lower T (see Table I). Molecular dynamics simulations of metal(100) homoepitaxy [14] indicate that in such situations, DF can break down,

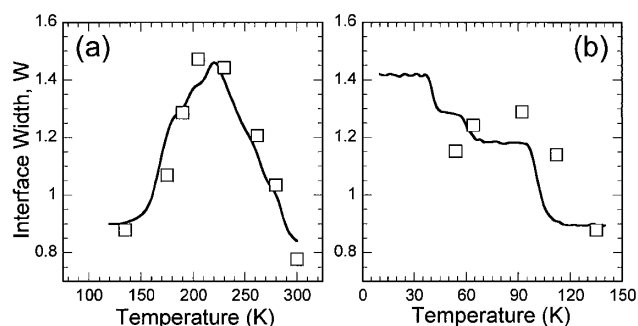


FIG. 4. Monte Carlo simulation results for the following: (a) mound formation up to 300 K (solid curve); (b) RDF with low barrier hops up to 135 K (solid curve). Experimental data are open squares.

deposited atoms becoming captured on the sides of microprotrusions rather than reaching lower 4FH sites, leading to formation of overhangs and internal defects [Fig. 3(b)].

We have attempted to model growth in this regime, by starting from a “restricted downward funneling” (RDF) model, which should apply at 0 K. In RDF, deposited atoms funnel downward, but can get stuck when they reach sites which do not contain complete quartets of four supporting atoms. These “trap sites” contain at least three supporting atoms in the layer beneath, or two such atoms beneath and at least one in-layer neighbor, or one atom beneath and at least two in-layer neighbors [Fig. 3(b)]. For a 25 ML film, $W^{\text{RDF}} = 1.41b$ [solid line in Fig. 4(b) below 40 K] and the film has a significant density of internal voids versus $W^{\text{DF}} = 0.74b$ and no voids for standard DF.

The next challenge is to extend this model to describe the T dependence of W in the range up to 135 K where terrace diffusion is inoperative. The key point here is that on the irregular structures formed during film growth at low T , there are many other thermally activated interlayer hopping processes, with low barriers, E_{act} , which can be operative and affect film morphology. For example, consider a “micropyramid” with sides corresponding to $\{111\}$ microfacets. Atoms on such facets are thermally mobile even down to 40 K [1], which can lead to a novel downward transport pathway. We thus augmented the RDF model by incorporating various interlayer hopping processes for atoms with low coordination number m as follows: Hopping is instantaneous for $m < 3$, $E_{\text{act}} = 0.10$ eV for $m = 3$ (or 0.15 eV for three supporting atoms), and $E_{\text{act}} = 0.25$ eV for interlayer hops with $m = 4$ and 5. See Fig. 3(c). Attempt frequencies are set to 10^{12} s^{-1} . These choices are motivated by the known attempt frequency and terrace diffusion barrier (0.10 eV) for Ag/Ag(111) [1], and by semiempirical studies of other activation barriers. As T increases from 0 K, these processes turn on in sequence according to the hierarchy of energetic barriers, leading to the stepwise variation in W for a 25 ML film shown in Fig. 4(b). Consequently, our model recovers the general experimental trend between 135 and 50 K.

Thus, a picture emerges that idealized DF provides a reasonable description of deposition dynamics at temperatures above 100 K, because either the film morphology is locally smooth enough to make breakdown rare, or when breakdown occurs, low barrier interlayer diffusion processes are active which can bring deposited atoms to lower 4FH sites.

All of the data presented above are for 25 ML films. How would our observations depend upon film thickness? The qualitative variation of W vs T should remain the same up to at least 100 ML, as is, in fact, predicted by our simulation models. However, since the film roughens at different rates for different T , such features as the temperature for maximum roughness shift (higher with θ). There is much current interest [1,15,16] in characterizing kinetic roughening, usually described by the relation $W \sim \theta^\beta$, the coarsening of lateral mound dimensions described by D_{av} (or $R_{\text{av}}) \sim \theta^n$, and the relationship between these.

Our results will be reported in detail elsewhere. But here we note that at 230 K, where initial mound formation is most pronounced (and 25 ML films are roughest), analysis of growth up to 100 ML reveals that roughening occurs much more quickly than coarsening (n is slightly below 0.2, whereas β is roughly 0.4 or higher initially). This behavior is consistent with our simultaneous observation of slow slope selection during growth (at 230 K), and recent theoretical analyses of such growth regimes [16].

In summary, we have shown that the simple system, Ag/Ag(100), exhibits the most complex variation of W vs T yet observed in any metal homoepitaxial system. Atomistic simulations support the following characterization of the deposition and diffusion processes controlling observed behavior: a small step-edge barrier leads to mound formation at the higher temperatures; downward funneling at step edges triggers smoother growth and ultimately a transition to self-affine morphologies at lower T (where step edges are more prevalent); and, finally, the breakdown of funneling on small steep microprotrusions leads to rougher growth at very low T .

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- [1] *Morphological Organization in Epitaxial Growth and Removal*, edited by Z. Zhang and M. G. Lagally (World Scientific, Singapore, 1998).
 - [2] Special issue on *Magnetism on a Microscopic Scale* [MRS Bull. **20**, No. 10 (1995)]; K.L. Ekinici and J.M. Valles, Phys. Rev. B **58**, 7347 (1998).
 - [3] A.-L. Barabasi and H.E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).
 - [4] R. Kunkel *et al.*, Phys. Rev. Lett. **65**, 733 (1990); F. Tsui *et al.*, *ibid.* **76**, 3164 (1996).
 - [5] W.F. Egelhoff and I. Jacob, Phys. Rev. Lett. **62**, 921 (1989).
 - [6] W.C. Elliot *et al.*, Phys. Rev. B **54**, 17938 (1996).
 - [7] H.-J. Ernst *et al.*, Phys. Rev. Lett. **72**, 112 (1994).
 - [8] C.-M. Zhang *et al.*, Surf. Sci. **406**, 178 (1998).
 - [9] M. V.R. Murty and B.H. Cooper, Phys. Rev. Lett. **83**, 352 (1999); J.G. Amar and F. Family, *ibid.* **77**, 4584 (1996).
 - [10] J. Villain, J. Phys. I (France) **1**, 19 (1991).
 - [11] M.C. Bartelt and J.W. Evans, Phys. Rev. Lett. **75**, 4250 (1995); Surf. Sci. **423**, 189 (1999).
 - [12] B.D. Yu and M. Scheffler, Phys. Rev. Lett. **77**, 1095 (1996).
 - [13] U. Kurpick and T.S. Rahman, Phys. Rev. B **57**, 2482 (1998).
 - [14] C.L. Kelchner and A.E. DePristo, Surf. Sci. **393**, 72 (1997).
 - [15] M. Siegert, Phys. Rev. Lett. **81**, 5481 (1998); L.-H. Tang, P. Smilauer, and D.D. Vvedensky, Eur. Phys. J. B **2**, 409 (1998); J.G. Amar, Phys. Rev. B **60**, R11317 (1999).
 - [16] L. Golubovic, Phys. Rev. Lett. **78**, 90 (1997); P. Politi and A. Torcini, J. Phys. A **33**, L77 (2000).