Simulations of low-temperature annealing of crystal surfaces

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The decay of sinusoidal grooves on solid surfaces due to surface diffusion is studied using Monte Carlo simulations of a $(2+1)$-dimensional solid-on-solid model, focusing on the decay kinetics at temperatures below the equilibrium roughening transition temperature T_R. We find that the surface relaxation initially follows an exponential decay with a characteristic time that scales as the fourth power of the grooves' wavelength. The scaling behavior breaks down after cusps and plateaus of a sufficient size develop at the top and bottom of the profile. The time needed for the surface to reach this breakdown point decreases sharply with decreasing temperature below T_R to the extent that the exponential region is too small to be observable in simulations for temperature below about $2T_R/3$. We also present simulation results that show the effect of a surface tilt on the relaxation kinetics.

I. INTRODUCTION

The decay processes of sinusoidal profiles on crystal surfaces have been investigated experimentally to measure the surface self-diffusion constant and to study the kinetics of surface relaxation.[1–4] The understanding of these kinetics is of practical importance in surface treatment and epitaxial film growth. It is known that there exists an equilibrium roughening transition temperature T_R above which the crystal surface is rough and below which it is smooth.[5] This roughening temperature depends upon the orientation of the surface. There is consensus that above T_R, the relaxation kinetics are well described by Mullins's theory[6] based on the continuum description of surface diffusion. This theory predicts that the amplitude of an initially sinusoidal profile decreases exponentially with time, with a time scale τ proportional to the fourth power of the wavelength λ^4, while the shape of the profile remains sinusoidal. These predictions are consistent with experimental observations[1,2] and computer simulations.[7–10]

However, below the roughening transition, Mullins's theory is not applicable because the surface energy has a singularity.[11] A variety of modified continuum theories[12–15] have been devised to study the kinetics in this regime. These theories generally predict nonexponential decay with a characteristic time scale $\tau\sim\lambda^{\alpha}$. The value of α ranges from 3 to 5, depending on the detailed mechanisms in the theories. Recent experiments on surface relaxation at low temperature have obtained different results. Investigations of the smoothing kinetics of the Cu(100) surface by Zuo and Wendelken[16] using time-resolved, high-resolution, low-energy, electron diffraction (HRLEED) obtained $\alpha\approx 3$ at early times and $\alpha\approx 5$ at later times. However, Grossmann and Piercy[17] obtained $\alpha\approx 4$ in a HRLEED investigation of a TiO_2 surface, except at the lowest experimental temperature (750 K), where they found $\beta=1/\alpha\approx 0.18$. The results of computer simulations at low temperature are also not conclusive.[7–10] Hampered by the slow decay kinetics, the simulations are generally unable to monitor the decay for long enough times, although some algorithms have been designed[8,9] to speed up the simulation by assuming the kinetic behavior of individual diffusing particles.

In a previous paper[7] we have reported Monte Carlo simulations of profile decays due to surface diffusion at temperatures above and below the roughening transition temperature. We used a solid-on-solid model, which is the strongly anisotropic limit of the Ising model and has been widely applied to study the roughening transition and interfacial growth phenomena.[18,19] We used Kawasaki dynamics,[20] which allows moves of randomly selected surface particles to neighboring surface sites. Individual particles move randomly with probability decided by the energy change accompanying the move. Above the roughening temperature, we found exponential decay of the profile with a characteristic decay time $\tau\sim\lambda^4$. Below the roughening temperature, we found that the decay is slower than exponential and that $\tau\sim\lambda^4$ scaling is not valid. Instead, if we insisted on a fit of the scaling form $\tau\sim\lambda^{\alpha}$, we obtained $\alpha\approx 6$. However, in a recent report of Monte Carlo simulations of virtually the same model, Searson, Li, and Sieradzki[10] found that exponential decay of the profile with a characteristic relaxation time $\tau\sim\lambda^4$ is valid not only at $T>T_R$ but also at $T<T_R$. Their results have motivated us to further investigate the model with more extensive simulations. In this paper, we report the results of these investigations, some of which have been briefly described in an earlier Comment.[21]

In Sec. II we describe the solid-on-solid model and the simulation method. In Sec. III we present the results of our simulations focusing on temperatures below T_R. We will show that at $T<T_R$, the profile initially decays exponentially with a characteristic time $\tau\sim\lambda^4$. This scaling behavior ceases to be valid after a certain time when shoulders develop in the decay curves as a consequence of the formation of cusps and flat plateaus on the top and bottom of the profile, which is no longer sinusoidal. Each successive shoulder corresponds to a lowering (raising) of the flat top (bottom)

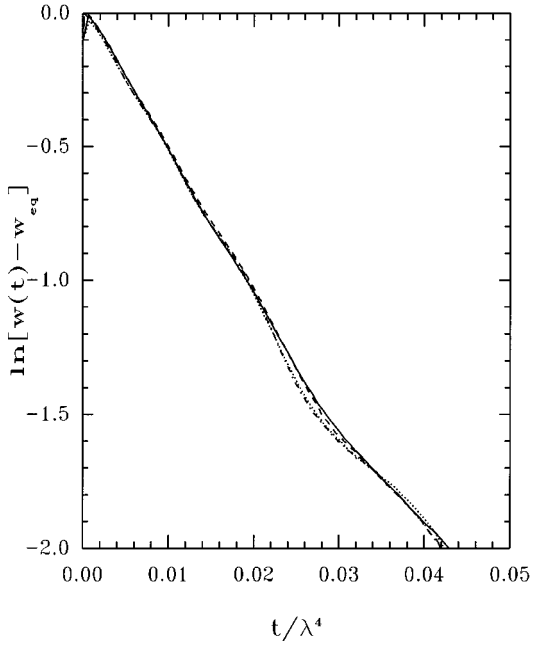

FIG. 1. $\ln[w(t)-w_{\mathrm{eq}}]$ plotted against t/λ^4 at temperature $T=0.5J/k_B$ for $\lambda=20$ (solid line), 28 (dashed line), 32 (dotted line), and 40 (dash-dotted line).

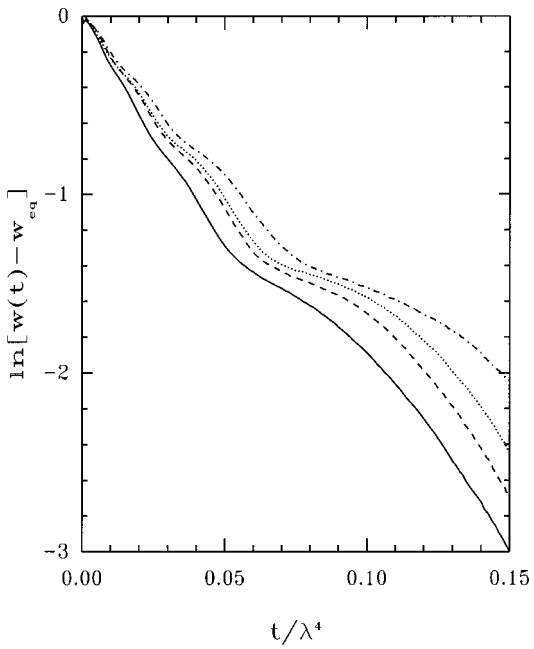

FIG. 2. $\ln[w(t)-w_{\mathrm{eq}}]$ plotted against t/λ^4 at temperature $T=0.4J/k_B$ for $\lambda=20$ (solid line), 28 (dashed line), 32 (dotted line), and 40 (dash-dotted line).

by one atomic layer. The time at which the $\tau\sim\lambda^4$ scaling breaks down decreases sharply with decreasing temperature to the extent that it is no longer observable in our simulations for T less than about two-thirds of T_R. We will also show the effects of a small tilt angle of the surface on the relaxation kinetics. In Sec. IV we discuss the implication and relevance of our results with respect to recent experiments.

II. MODEL AND SIMULATION METHODS

We use a (2+1)-dimensional solid-on-solid (SOS) model for a crystal surface. The model is on a square lattice of size $M\times N$ and has the Hamiltonian

$$H=\frac{J}{2}\sum_{\langle ij\rangle}|h_i-h_j|, \tag{1}$$

where h_i, which takes only integer values, is the height of the surface atom at site i and $\langle ij\rangle$ denotes a sum over all nearest-neighbor pairs of lattice sites. The roughening transition temperature is $T_R=0.62J/k_B$,[18] where k_B is the Boltzmann constant.

The surface is initially created with a one-dimensional sinusoidal profile with a wavelength of λ, i.e.,

$$h(m,n)=\mathrm{Int}[h_0\sin(2\pi m/\lambda)], \tag{2}$$

where $h(m,n)$ is the height at site (m,n) of the lattice and $\mathrm{Int}[x]$ is a function that rounds x to the nearest smaller (in absolute value) integer. The size of the system is $N=32$ and M is an integral multiple of λ, ranging from $M=240$ to 256; wavelengths from 4 to 40 have been studied with initial amplitudes $h_0=5$. Periodic boundary conditions are employed in both directions. In the scaling regime there are strong deviations from scaling for wavelengths that are too short; these have all but disappeared for $\lambda\geqslant 20$. Results reported here, with the exception of the profiles in Fig. 4, are averages over 40–50 individual runs. The relaxation of the surface is modeled with Kawasaki dynamics in which the atom atop a randomly picked column or site of the two-dimensional SOS lattice is moved to the top of a randomly picked nearest- or next-nearest-neighbor column with probability

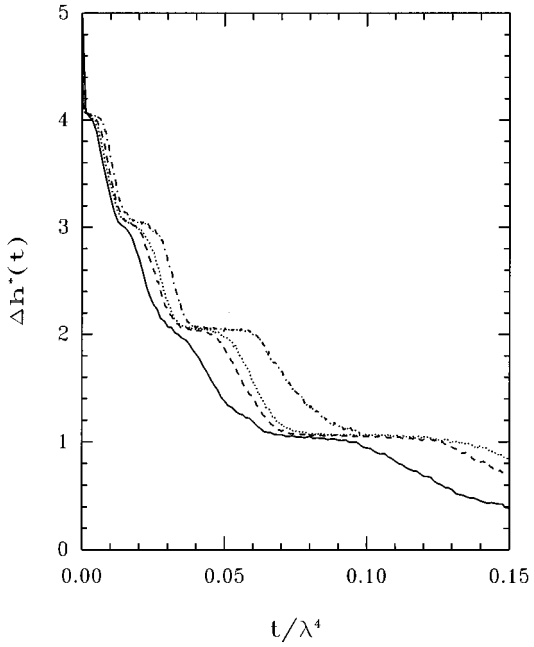

FIG. 3. $\Delta h^*(t)\equiv\Delta h(t)/2$ plotted against t/λ^4 for $\lambda=20$ (solid line), 28 (dashed line), 32 (dotted line), and 40 (dash-dotted line) for $T=0.4J/k_B$. The curves are the averages of 40–50 individual runs; in addition, Δh is averaged along rows parallel to the grooves.

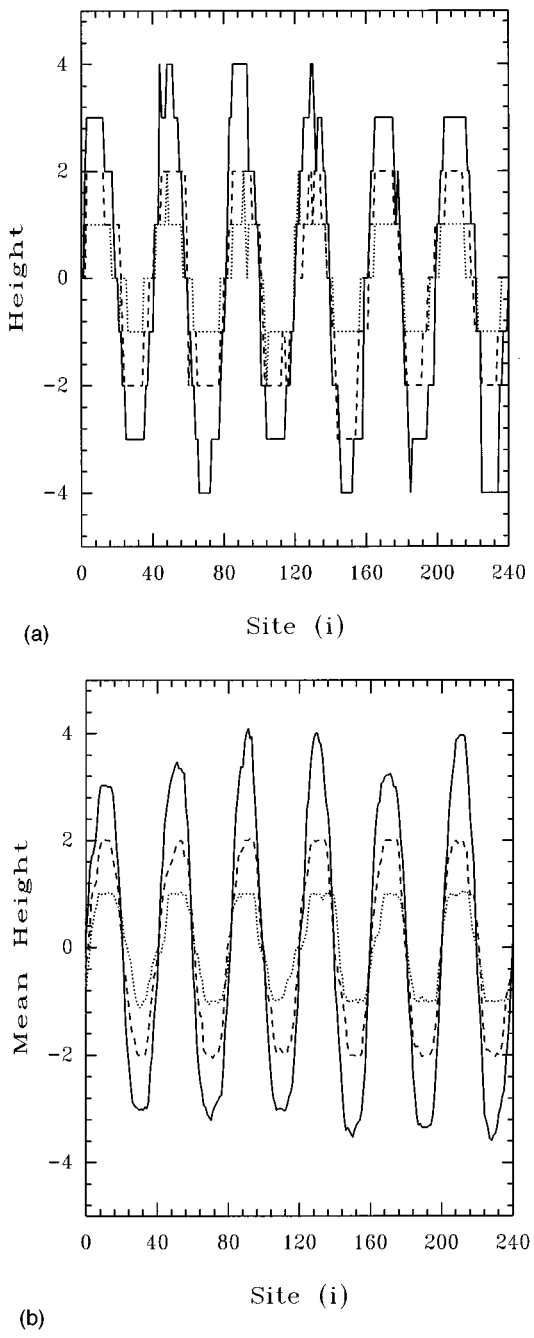

FIG. 4. Surface profiles shown at $t=20\,000$ (solid line), 100 000 (dashed line), and 200 000 (dotted line) time steps for $\lambda=40$ and $T=0.4J/k_B$; in (a) the profile is a particular cross section of one system, while in (b) the profile of a single system has been averaged over the direction parallel to the grooves.

$$P=\begin{cases}\exp(-\Delta E/k_BT) & \text{if } \Delta E>0\\ 1 & \text{if } \Delta E<0,\end{cases} \tag{3}$$

where ΔE is the change of the total energy of the system due to the move. This procedure, defined as a Monte Carlo trial, is repeated. The time t is measured in units of Monte Carlo trials per lattice site.

The normalized width of the surface $w(t)$ is calculated as

$$w(t)=\frac{1}{w_0}\sqrt{\langle h^2(t)\rangle-\langle h(t)\rangle^2}, \tag{4}$$

where

$$\langle h(t)\rangle=\frac{1}{MN}\sum_i h_i(t) \tag{5}$$

is the mean height of the surface and

$$\langle h^2(t)\rangle=\frac{1}{MN}\sum_i h_i^2(t) \tag{6}$$

is the mean-squared height; w_0 is the initial value of the surface width $w_0=\sqrt{\langle h^2(0)\rangle}$. Also monitored in the simulation is the difference Δh between the maximum and minimum heights, i.e.,

$$\Delta h(t)=h_{\max}(t)-h_{\min}(t), \tag{7}$$

where $h_{\max}$ and $h_{\min}$ are the maximum and minimum heights obtained by averaging the height of the surface along rows of sites parallel to the grooves and over a number of distinct runs.

We have also done some simulations for a tilted surface in which the initial configuration has sinusoidal grooves superimposed on a surface with evenly spaced terraces along the same direction as that along which the grooves vary. Periodic boundary conditions in the direction of m are imposed by changing the height of a particle that moves across the edge of the system in this direction in an appropriate manner. The initial terrace width is always commensurate with the size M of the system.

III. RESULTS

At temperatures above the roughening transition temperature T_R, we find the width of the surface decays exponentially with a characteristic time $\tau\sim\lambda^4$. This is the same as reported in our previous paper[7] and is consistent with other simulations. In the remainder of this paper, we will therefore focus on the results for temperatures below T_R.

Figure 1 displays $\ln[w(t)-w_{\rm eq}]$ as a function of t/λ^4 at temperature $T=0.5J/k_B$ with $\lambda=20$, 28, 32, and 40; $w_{\rm eq}$ is the equilibrium width at the given temperature, normalized by the initial width. This temperature has been used in the simulations of Searson, Li, and Sieradzki.[10] They found exponential decay with a scaling of $\tau\sim\lambda^4$. This is consistent with the data in Fig. 1 up to a certain point, beyond which shoulders start to appear in the decay curves and the scaling behavior no longer holds. The deviation from scaling is much more obvious in Fig. 2, where the same quantities are plotted at temperature $T=0.4J/k_B$. At this lower temperature, the scaling breaks down at an earlier stage of the decay and successive shoulders appear in the decay curve. Each

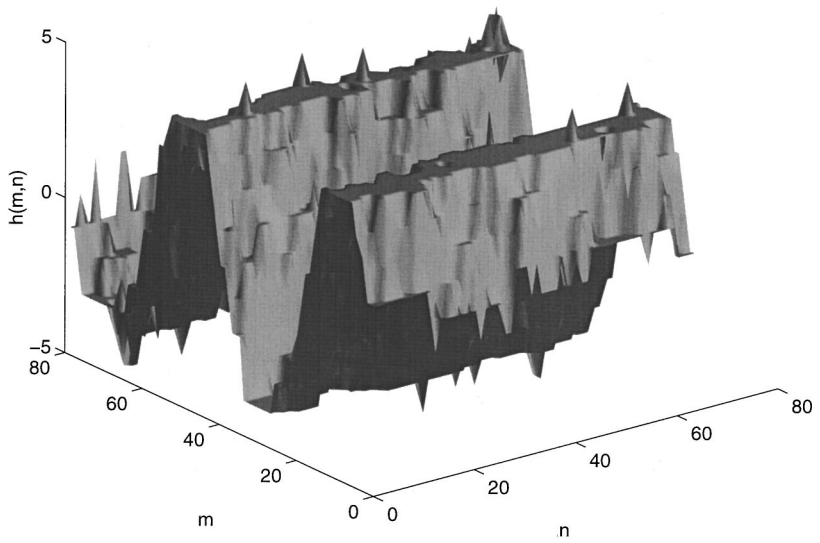

FIG. 5. Surface with $\lambda = 40$, shown at $t = 20\,000$ time steps and $T = 0.4J/k_B$. This system measures 80×64 sites.

shoulder corresponds to lowering (raising) the flat top (bottom) of each groove by one atomic layer, as evidenced in Fig. 3, where $\Delta h^*(t) \equiv \Delta h(t)/2$ is plotted against t/λ^4 for $\lambda = 20$, 28, 32, and 40, at the same temperature $T = 0.4J/k_B$; Δh^* is a simple measure of the amplitude of the surface profile, normalized so that its value decreases by unity as the amplitude of the profile decreases by the same amount. Notice that the plateaus on the curves in Fig. 3 occur roughly at successive integer values, consistent with lowering (raising) the flat top (bottom) by one atomic layer. These curves tend to be less smooth than those for the width in Fig. 2 because in any given system the width changes relatively smoothly in comparison with the height difference from the top layer to the bottom one, which must change abruptly by integral amounts. The averaging we have done smooths this behavior somewhat, but not completely. The overall time dependence of the curves in Fig. 3 seems to follow a hyperbolic behavior, i.e, $\Delta h^*(t) \propto 1/t$, which has been predicted in Ref. 14. However, this conclusion is not unambiguous because of the existence of the plateaus in the curves.

In Fig. 4(a) we show typical cross sections of surface profiles at times $t = 20\,000$, $100\,000$, and $200\,000$ for $T = 0.4J/k_B$ and $\lambda = 40$. It is evident that, as time increases, flat plateaus and cusps develop at the peaks and valleys of the profile and the average size of the cusps increases with time. Such cusps have been observed[12] in experiments at temperatures sufficiently far below T_R. Notice that the profiles consist mostly of steps of integral height in units of the spacing between atomic layers. The plateaus are not perfectly flat as a consequence of atomic-size defects, as clearly displayed in Fig. 5, which is a three-dimensional picture of a typical surface profile during decay. The concentration of defects is temperature dependent, being considerably larger at higher temperatures (but still below T_R); therefore, the system is able to sense that the equilibrium configuration of the surface is globally flat only when the size of the cusps is sufficiently large. At this point the scaling behavior breaks down. The time it takes to reach this point decreases sharply with decreasing temperature, as indicated by Fig. 6, which shows $\ln(w - w_{\rm eq})$ against T/T_R, the width being evaluated at the time that scaling breaks down. The breakdown is identified by comparing the decay curves for $\lambda = 20$ with those for $\lambda = 32$. The figure is at best qualitative because identification of the breakdown point depends quite a bit on the amount of scatter in the results for the width. Finally, Fig. 4(b) displays the surface profiles averaged over the direction parallel to the grooves. Because the position of the edges of the terraces fluctuates, the averaged profiles are much smoother than the unaveraged ones.

In most experimental situations, surfaces are not exactly at a perfect crystal orientation, meaning the surface is not precisely a low-index face such as a (001) face. Rather they normally deviate from such an orientation by a small angle. To explore the effect of that on the decay kinetics, we have done simulations in which the surface is tilted in the direction perpendicular to the grooves by a small angle. Figure 7 shows $\ln[w(t) - w_{\rm eq}]$ at $\lambda = 32$ and $T = 0.4J/k_B$ for three different tilt angles corresponding to average terrace widths of

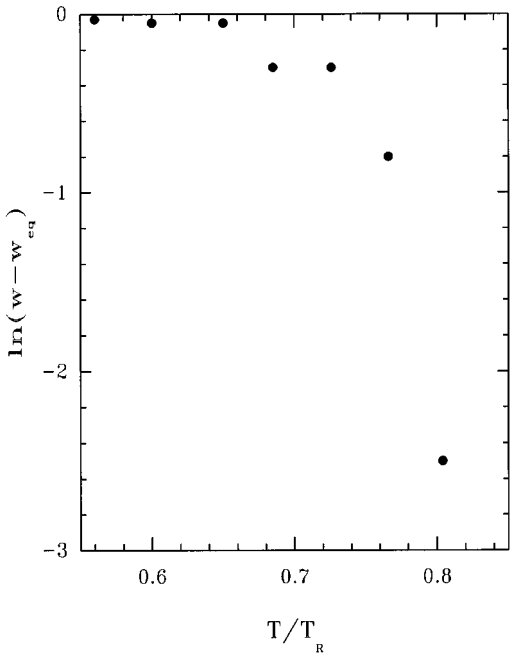

FIG. 6. Value of $\ln(w - w_{\rm eq})$ at which scaling breaks down, shown as a function of T/T_R.

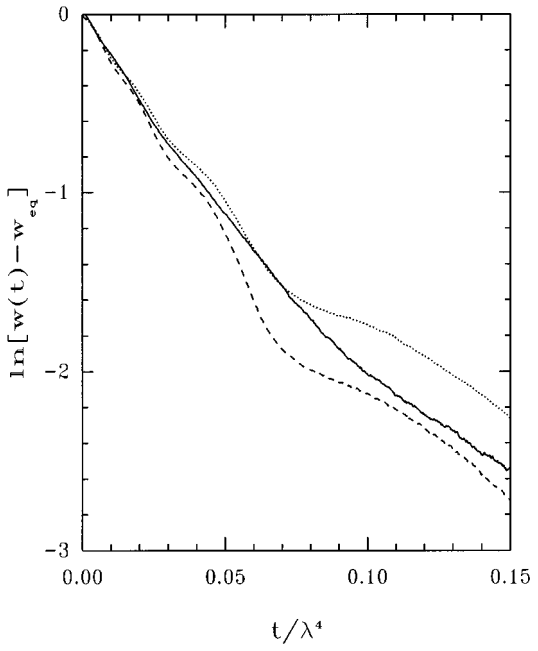

FIG. 7. $\ln[w(t)-w_{\mathrm{eq}}]$ plotted against t/λ^4 for tilt angles 14° (solid line), 3.6° (dashed line), and 0.9° (dotted line), corresponding to mean terrace widths of 4, 16, and 64 lattice spacings.

4, 16, and 64 lattice spacings. Because these surfaces require a very long time to reach a global equilibrium, w_{eq} here is not the true equilibrium width but rather the minimum value of the width observed during the decay. What typically happens is that the width reaches a minimum as the grooves decay and then very slowly increases as the surface makes its way toward global equilibrium. Although this slow relaxation introduces some ambiguity into the later stages of the grooves' decay, one may see from the plot that the decay is close to being exponential when the mean terrace width is much smaller than λ. That is expected because the roughening temperature of a tilted surface is zero. On the other hand, when the terrace width is larger than λ, the decay curve is very similar to the ones for an untilted surface at the same temperature; the system is unable to sense the tilt in this case.

IV. DISCUSSION

It clearly emerges from our simulations that at temperature below the roughening transition, the surface relaxation initially follows an exponential decay with a characteristic time scale $\tau\sim\lambda^4$, consistent with recent simulations of Searson, Li, and Sieradzki.[10] This scaling behavior, however, breaks down after the cusps on the peaks and valleys of the profile develop up to a certain size so that the system is able to recognize that the equilibrium configuration of the surface is globally flat. At this point flat shoulders start to appear in the width decay curve; each shoulder corresponds to raising (lowering) the cusps at the top (bottom) of the profile by an interlayer spacing. The time needed to reach the breakdown point decreases sharply with decreasing temperature.

In a recent experiment on a $TiO_2(110)$ surface by Grossmann and Piercy, it was observed that $\beta=1/\alpha=0.23-0.25$ at temperatures 800–875 K. This result is consistent with the initial decay observed in our simulations. At $T=750$ K, their data actually show sort of a flat shoulder (see Fig. 2 of Ref. 17) and they obtained an effective exponent of $\beta=0.18$. This exponent is consistent with our previous estimate[7] of $\alpha=6$. It would certainly be interesting to see more experiments at lower temperatures or for longer times at the higher temperatures.

Recently a paper by Selke and Duxbury[22] has come to our attention. Their simulations of a SOS model with evaporation-condensation dynamics also show plateaus in the decay curves at temperatures below T_R; see Figs. 5 and 6 of Ref. 22. These results, in addition to our results, suggest that the layer-by-layer kinetics is a very general behavior for surfaces below T_R.

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[1] P. S. Maiya and J. M. Blakely, J. Appl. Phys. **38**, 698 (1967); J. M. Blakely and H. Mykura, Acta Metall. **9**, 23 (1961).
[2] H. P. Bonzel and E. E. Latta, Surf. Sci. **76**, 275 (1978).
[3] H. P. Bonzel, E. Press, and B. Steffen, Appl. Phys. A **35**, 1 (1984).
[4] Z. L. Liau and H. J. Zeiger, J. Appl. Phys. **7**, 2434 (1990).
[5] W. K. Burton, N. Cabrera, and F. C. Franck, Philos. Trans. R. Soc. London Ser. A **243**, 299 (1951).
[6] W. W. Mullins, J. Appl. Phys. **28**, 333 (1957); **30**, 77 (1959).
[7] Z. Jiang and C. Ebner, Phys. Rev. B **40**, 316 (1989).
[8] W. Selke and T. Bieker, Surf. Sci. **281**, 163 (1993); W. Selke and J. Oitmaa, *ibid.* **198**, L346 (1988).
[9] M. A. Dubson and G. Jeffers, Phys. Rev. B **49**, 8347 (1994).
[10] P. C. Searson, R. Li, and K. Sieradzki, Phys. Rev. Lett. **74**, 1395 (1995).
[11] M. Wortis, in *Fundamental Problems in Statistical Mechanics VI*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1985), p. 87.
[12] K. Yamashita, H. P. Bonzel, and H. Ibach, Appl. Phys. **25**, 231 (1981).
[13] F. Lancon and J. Villain, in *Kinetics of Ordering and Growth at Surfaces*, edited by M. G. Lagally (Plenum, New York, 1990), p. 369; J. Villain, Europhys. Lett. **2**, 531 (1986); A. Rettori and J. Villain, J. Phys. (Paris) **49**, 257 (1988).
[14] M. Ozdemir and A. Zangwill, Phys. Rev. B **42**, 5013 (1990).

[15] J. Hager and H. Spohn, Surf. Sci. **324**, 365 (1995); H. Spohn, J. Phys. (Paris) **3**, 69 (1993).
[16] J. K. Zuo and J. F. Wendelken, Phys. Rev. Lett. **70**, 1662 (1993).
[17] B. Grossmann and P. Piercy, Phys. Rev. Lett. **74**, 4487 (1995).
[18] J. D. Weeks, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1979), p. 293, and references therein.
[19] Z. Jiang and C. Ebner, Phys. Rev. B **40**, 4833 (1989); Z. Jiang, Ph.D. thesis, The Ohio State University, 1990 (unpublished).
[20] K. Kawasaki and T. Ohta, Prog. Theor. Phys. **27**, 147 (1982); **28**, 5496 (1983).
[21] Z. Jiang and C. Ebner, Phys. Rev. Lett. **75**, 4153 (1995).
[22] W. Selke and P. M. Duxbury, Acta Phys. Slovaca **44**, 215 (1994).