Scanning Microscopy Vol. 12, No. 1, 1998 (Pages 107-111) 0891-7035/98$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

RELAXATION OF SURFACE CORRUGATIONS BELOW THE ROUGHENING TEMPERATURE

M.V. Ramana Murty* and B.H. Cooper

Laboratory of Atomic and Solid State Physics, Cornell University, NY 14853

(Received for publication May 20, 1996 and in revised form December 19, 1996)

Abstract

We have studied the evolution of sinusoidal profiles and the motion of parallel like steps below the roughening temperature using Monte Carlo simulations on a solid-on-solid model. The two step separation follows $l \sim t^{0.20 \pm 0.02}$ and is consistent with a theory of their separation driven by the entropic repulsion, i.e., the cubic term G_3 in the projected surface free energy. For sinusoidal profiles on a surface with the average orientation corresponding to a facet, we find that the wave-length scaling exponent n depends on the temperature below T_R for the range of wavelengths studied (L = 10-40 lattice units). Close to the roughening temperature, the amplitude in sinusoidal profiles of wavelength 10-40 lattice units decays with t/L^4 scaling approximately. Well below T_R, the amplitude decay in sinusoidal profiles over the same range of wavelengths follows $h/h_0 \sim (1 + \lambda t/L^5)^{-1}$. We discuss possible causes for deviations from perfect wavelength scaling in the evolution of amplitude in sinusoidal profiles.

Key Words: Surface diffusion, surface free energy, roughening transition, sinusoidal profile decay, wavelength scaling.

*Address for correspondence:
M.V. Ramana Murty
Department of Physics
Cornell University
Ithaca, NY 14853

Telephone number: (607) 255 3326
FAX number: (607) 255 6428
E mail: murty@msc.cornell.edu

Introduction

Relaxation of a rough surface towards equilibrium during growth, etching or annealing can significantly effect the properties of thin films and patterns being fabricated. Mass transport can occur through several mechanisms including surface and bulk diffusion and evaporation-condensation. At the typical length scales (nm-μm) and temperatures involved, surface diffusion often dominates the smoothing process due to lower activation barriers. Above the roughening temperature (T_R) of the surface, the Herring-Mullins theory provides a good description of mass transport driven by surface diffusion (Mullins, 1963). The description is less clear below the roughening temperature due to the existence of a cusp (a non-analytic point) in the projected surface free energy at low index orientations. This has led to the development of several analytical models (Hager and Spohn, 1995; Ozdemir and Zangwill, 1990; Rettori and Villain, 1988; Straley and Kolomeisky, unpublished) and Monte Carlo simulation studies (Erlebacher and Aziz, 1996; Jiang and Ebner, 1996; Murty and Cooper, 1996; Searson *et al*., 1995; Selke and Duxbury, 1995) of sinusoidal profile evolution below T_R. We have performed Monte Carlo simulations on a solid-on-solid (SOS) model to study profile evolution below T_R. For sinusoidal profiles on a surface with the average orientation corresponding to a facet, we find that the wavelength scaling exponent n depends on the temperature below T_R for the range of wavelengths studied (L = 10-40 lattice units), with n increasing from 4 to 5 as the temperature is dropped from T_R to 0.54 T_R. Deviations from perfect wave-length scaling in the evolution of amplitude are observed and possible causes are discussed.

Solid-on-Solid Model

The simulations were performed on a square lattice with the Hamiltonian

$$H = \frac{\varepsilon}{2} \sum_{ij} | h_i - h_j | \qquad (1)$$

where i and j are nearest neighbors. Here, h_i is the height at site i and ε is the bond energy. The roughening temperature of this model is $T_R = 0.62\, \varepsilon/k_B$ (Shugard *et al*., 1978). Below T_R, the projected surface free energy G can be expanded in terms

of the slope h_x as (Tsao, 1993):

$$G = G_0 + G_1 |h_x| + (1/3) G_3 |h_x|^3 + ... \quad (2)$$

The coefficient of the linear term G_1 represents the step free energy and the cubic term G_3 arises from the entropy reduction of steps due to the condition of no overhangs.

Each Monte Carlo step consists of picking a site at random and moving an atom to an adjacent site with probability

$$p = (1/4) \exp(-\Delta E/k_B T), \quad \text{for } \Delta E > 0 \quad (3)$$

and $p = (1/4)$ for $\Delta E < 0$;

where ΔE is the difference in binding energy between the present site and the new (adjacent) site. Thus, the barrier for edge diffusion at a step is the same as the barrier for terrace diffusion for an adatom and smaller than the barrier for detachment from a step. There is no additional barrier at the edge of a step and we expect diffusion-limited kinetics. Time is measured in units of Monte Carlo steps per site. The evolution of unidirectional sinusoidal corrugations and the separation of two parallel like steps was followed as a function of time. We note that the simulation cell must be sufficiently wide in the direction perpendicular to the corrugation to allow for several collisions between steps. A large number of collisions between steps is necessary to represent the entropic repulsion and the distribution of island shapes at the extrema of sinusoidal profiles by averages in continuum theory. It is noted that the wavelength scaling exponent and the time evolution of the amplitude in sinusoidal profiles in our study differ significantly from a previous study using the same kinetics but employing small simulation cells (Jiang and Ebner, 1996).

Evolution of Corrugated Surfaces

According to analytic theory, the amplitude of a sinusoidal profile should follow an exponential law $h/h_0 = \exp(-\alpha t/L^4)$ above T_R (Mullins, 1963). Below T_R, there are conflicting predictions for the time evolution and the wavelength scaling exponent for a unidirectional sinusoidal profile. A power law decay $h/h_0 \sim (1 + \lambda t/L^5)^{-1}$ is predicted in Ozdemir and Zangwill (1990), whereas, a linear decay $h \sim h_0 - \beta t/L^3$ is predicted in Hager and Spohn (1995) and Straley and Kolomeisky (unpublished). It is noted that these analytic expressions were derived in the limit of small slopes whereas the initial (maximum) slope of the sinusoidal profiles in our simulations exceeds 45°. This was necessary due to computing limitations. Figure 1 shows the evolution of the amplitude h of sinusoidal corrugations at $T = 0.8\ T_R$ and $0.54\ T_R$ for wavelengths of L = 10-40 lattice units. The initial height (h_0) and width (W) were 4 and 1000 lattice units, respectively. Periodic boundary conditions were employed in the transverse directions. The amplitude h represents an average over one or two rows at the extrema of the starting sinusoidal profile. The data shown is averaged over several periods and includes at least 5000 columns. Below the roughening temperature, the time evolution of the amplitude shows a shift from the exponential law toward a power law as the temperature is lowered. At $T = 0.8\ T_R$, the functional form of amplitude decay is intermediate between the two, and the wavelength scaling exponent is $n = 4.1 \pm 0.1$, in agreement with the previously reported value of 4.0±0.1 (Searson *et al*., 1995). At $T = 0.54\ T_R$, the amplitude decay follows a power law $h/h_0 \sim (1+\lambda t/L^n)^{-1}$ with the wavelength scaling exponent $n \sim 5$. The parameters α and λ were chosen to give a good fit to the initial 25% of the amplitude decay. A power law function was found to give a better fit to the amplitude decay at $T = 0.54\ T_R$ compared to an exponential function. The amplitude evolution at $T = 0.54\ T_R$ agrees with the analytically predicted form of Ozdemir and Zangwill (1990) for profile evolution below T_R. It is noted that λ is proportional to the initial height h_0 in the analytic theory of Ozdemir and Zangwill (1990). The plateaus in the decay function (marked by horizontal lines in Fig. 1c) correspond to integer heights h. The plateaus would be less prominent for higher values of the initial amplitude h_0.

Figure 2 shows the separation *l* with time t of two like steps that were initially together, i.e., formed a double step. Screw periodic boundary conditions were employed in the direction perpendicular to the steps. The surface was 500 lattice units wide in the direction parallel to the steps and 60 lattice units in the orthogonal transverse direction. The data shown is averaged over eight such simulations. At $T = 0.8\ T_R$, this width of 500 lattice units is sufficient to provide several collisions between steps for separations up to eight lattice units. The average position of steps was determined by counting the number of atoms at each level. This introduces an error due to the presence of adatoms and vacancies. However, the fluctuations in their populations are small and should not influence the results discussed here. The step separation at $T = 0.8\ T_R$ follows $l \sim t^{0.20 \pm 0.02}$. The driving force for the step separation comes from the entropic repulsion between steps (cubic term G_3; Rettori and Villain, 1988). A larger separation between steps allows them to wander more and reduce their free energy. The results in Figure 2 agree with the expectation of $l \sim t^{1/5}$ for diffusion-limited kinetics (Bartelt *et al*., 1994; Hager and Spohn, 1995; Ozdemir and Zangwill, 1990; Rettori and Villain, 1988). Experimental studies of the evolution of step bunches on Si(111) have shown $l \sim t^{\beta}$ with $\beta \sim 0.2$-0.3 and are consistent with either diffusion-limited or interface-limited kinetics (Fu *et al*, 1996).

The two step separation in Figure 2 is driven by entropic repulsion alone and hence follows $l \sim t^{1/5}$ even close to the roughening temperature. For sinusoidal profiles, the wavelength scaling exponent is seen to shift gradually from 4

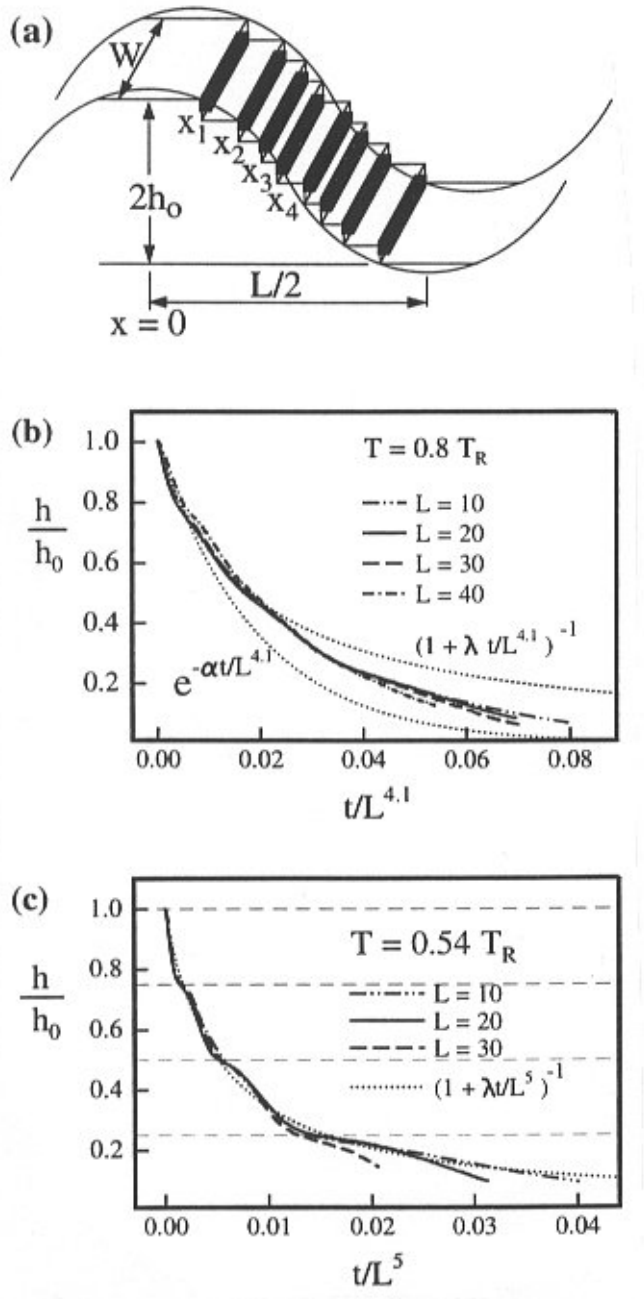

Figure 1. (**a**). A discretized sinusoidal profile with initial amplitude h_0, width W and wavelength L. Evolution of amplitude h with scaled time at (**b**) $T = 0.8\ T_R$ and (**c**) $T = 0.54\ T_R$. The horizontal dashed lines correspond to integer values of the amplitude h.

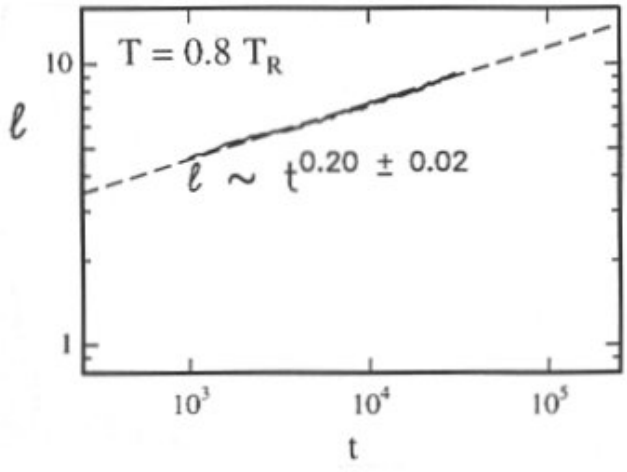

Figure 2. The separation *l* in lattice units of two like steps with time at $T = 0.8\ T_R$. Time is measured in number of Monte Carlo steps per site (MCS). The two steps were together, i.e., formed a double step, at t = 0. The variation in *l* is shown from t = 1000 MCS after the evolution has reached a steady state. The analytically expected form is $l \sim t^{1/5}$ (Bartelt *et al*., 1994; Hager and Spohn, 1995; Ozdemir and Zangwill, 1990; Rettori and Villain, 1988).

to 5 as the temperature is lowered from T_R to $0.54\ T_R$. In addition, we do not see perfect wavelength scaling toward the end of sinusoidal profile decay at the $T = 0.54\ T_R$. The evolution of sinusoidal profiles below T_R occurs through both entropic repulsion and line tension as pictured in Figures 3a, 3b, 3c and 3d (Murty and Cooper, 1996; Rettori and Villain, 1988; Selke and Duxbury, 1995). Initially, the steps A and A' at the extrema are driven towards each other by entropic repulsion from steps B and B' respectively (Fig. 3a). There is no interaction between steps A and A'. This continues until the two steps touch each other as in Figure 3b. The contact between the steps leads to the formation of islands which now decay through both enropic repulsion and line tension. After the islands have evaporated, the process repeats with the steps B and B', and so on. A theory of sinusoidal profile evolution based on entropic repulsion alone yields a power law decay with t/L^5 scaling Ozdemir and Zangwill (1990). Evolution of a unidirectional sinusoidal profile dominated by line tension is predicted to yield a linear decay with approximately t/L^3 scaling (Hager and Spohn, 1995; Straley and Kolomeisky, unpublished). The observation of t/L^5 scaling at $T = 0.54\ T_R$ suggests that the island decay in Figures 3c and 3d is dominated by entropic repulsion. One source for an enhanced entropic repulsion between the islands and the penultimate step is as follows. At low temperatures, there is less step wandering due to a lower excitation probability of kinks. As a result, the points of contact of the steps at the extrema are far apart resulting in islands with highly non-equilibrium shapes (Figs. 3b and 3c). These islands will try to

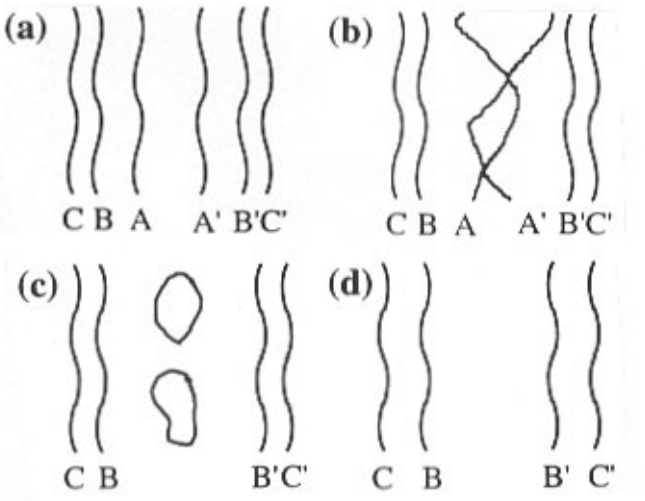

Figure 3. A schematic of the decay of sinusoidal profiles. (**a**). The two steps at the extrema A and A' move toward each other due to repulsion from steps B and B', respectively. (**b**). The two steps A and A' at the time of contact. (**c**). This leads to the formation of islands and their subsequent decay. (**d**). The two steps A and A' have vanished and the process repeats with steps B and B', and so on.

attain equilibrium shape (approximately square with rounded corners at low temperatures in this SOS model) as they evolve. This is aided by fast edge diffusion which pushes the long straight edge of the island closer to the penultimate step resulting in an enhanced entropic repulsion.

The wavelength scaling at $T = 0.54\ T_R$ is not as good (Fig. 2c) toward the end ($h/h_0 < 0.25$) when only one pair of steps is left. On one hand, this may be due to a finite size effect arising from an insufficient number of collisions between the (last pair of) steps over the width W. On the other hand, this behaviour of the amplitude decay appears similar to the amplitude evolution in bidirectional sinusoidal corrugations below T_R (Murty and Cooper, 1996). Here, the amplitude evolution at $T = 0.54\ T_R$ was observed to change from a power law decay to a linear decay with a corresponding shift in the wavelength scaling exponent from 5 toward 3 as the wavelength of the corrugation was increased. It was proposed that this may result from the increase in the relative importance of the line tension contribution to the step chemical potential compared to the entropic repulsion with increasing wavelength (Murty and Cooper, 1996). It is conceivable that a similar transition to linear decay with t/L^3 scaling (Hager and Spohn, 1995; Straley and Kolomeisky, unpublished) will occur for unidirectional sinusoidal profiles (of initial height h_0) for wave-lengths much longer than those considered in this study.

Conclusion

In conclusion, we have studied the evolution of sinusoidal profiles and the motion of parallel like steps below the roughening temperature using Monte Carlo simulations on a solid-on-solid model. The two step separation follows $l \sim t^{0.20 \pm 0.02}$ and is consistent with a theory of their separation driven by the entropic repulsion, i.e., the cubic term G_3 in the projected surface free energy (Rettori and Villain, 1988). For sinusoidal profiles on a surface with the average orientation corresponding to a facet, we find that the wavelength scaling exponent n depends on the temperature below T_R for the range of wavelengths studied (L = 10-40 lattice units). Close to the roughening temperature, the amplitude in sinusoidal profiles decays with t/L^4 scaling approximately. Well below T_R, the amplitude decay in sinusoidal profiles follows $h/h_0 \sim (1 + \lambda t/L^5)^{-1}$. This is in agreement with an analytic theory which treats only the entropic repulsion between steps (Ozdemir and Zangwill, 1990). We have discussed possible causes for deviations from perfect wavelength scaling in the evolution of amplitude in sinusoidal profiles below T_R.

Acknowledgements

We acknowledge several useful discussions with Jim Sethna, Eugene Kolomeisky, Mike Aziz and Jonah Erlebacher. This work was supported primarily by the MRSEC Program of the NSF under Award Number DMR-9632275 with partial support from the NSF under grant GER 9022961.

References

Bartelt NC, Einstein TL, Williams ED (1994) Measuring surface mass diffusion coefficients by observing step fluctuations. Surf. Sci. **312**, 411-421.

Erlebacher J, Aziz MJ (1997) Morphological equilibration of rippled and dimpled crystal surfaces: The role of terrace width fluctuations. Surf. Sci. **374**, 427-442.

Fu ES, Johnson MD, Liu DJ, Weeks JD, Williams ED (1996) Size scaling in the decay of metastable structures. Phys. Rev. Lett. **77**, 1091-1094.

Hager J, Spohn H (1995) Self-similar morphology and dynamics of periodic surface profiles below the roughening transition. Surf. Sci. **324**, 365-372.

Jiang Z, Ebner C (1996) Simulations of low-temperature annealing of crystal surfaces. Phys. Rev. **53**, 11146-11151.

Mullins WW (1963) Solid surface morphologies governed by capillarity. In: Metal Surfaces: Structure, Energetics and Kinetics. Gjostein NA, Robertson WD (eds.). Am. Soc. Metals (ASM), Metals Park, Ohio. pp. 17-66.

Murty MVR, Cooper BH (1996) Dynamics of surface profile evolution through surface diffusion. Phys. Rev. **54**, 10377-10380.

Ozdemir M, Zangwill A (1990) Morphological equilibration of a corrugated crystalline surface. Phys. Rev. **42**, 5013-5024.

Rettori A, Villain J (1988) Flattening of grooves on a crystal surface: A method of investigation of surface roughness. J. Phys. (France) **49**, 257-267.

Searson PC, Li R, Sieradzki K (1995) Surface diffusion in the solid-on-solid model. Phys. Rev. Lett. **74**, 1395-1398.

Selke W, Duxbury PM (1995) Equilibration of crystal surfaces. Phys. Rev. **52**, 17468-17479.

Shugard WJ, Weeks JD, Gilmer GH (1978) Monte Carlo test of theories for the planar model, the F model, and related systems. Phys. Rev. Lett. **41**, 1399-1402.

Tsao JY (1993) Materials Fundamentals of Molecular Beam Epitaxy. Academic Press, Boston. Chapter 6, and references therein.

Discussion with Reviewers

A. Zangwill: The analytic theory involves "real" time not "Monte Carlo" time (see, e.g., Kang and Weinberg, 1989). The relationship is not obviously linear and so might affect the result presented here.

Authors: For the atom dynamics in the SOS model, we have **assumed** that the energy of the transition state between any two neighboring sites i and j is ε_d higher than the higher of the two states i and j. This leads to the jump probabilities mentioned in eq. (3). The time corresponding to one Monte Carlo step per site is $\{\nu \exp(-\varepsilon_d/k_BT)\}^{-1}$ where ν is the attempt frequency. Hence, the time scale in the Figures 1 and 2 is indeed linear and corresponds to "real time". We have performed kinetic Monte Carlo simulations and they yield the same results as discussed in this paper.

M.J. Aziz and J. Erlebacher: Can you offer a reason for the disagreement between the results of your simulation and those of kinetic Monte Carlo simulations of the same physical process (Erlebacher and Aziz, 1996) in which h is found to be a function of t/L^{α} with $3.4 < \alpha < 4.0$ rather than $\alpha = 5$?

Authors: Erlebacher and Aziz (1996) found a different wavelength scaling exponent for sinusoidal profile decay below the roughening temperature. They employed the same SOS model discussed in this paper but with different dynamics. An important difference was in the activation barriers for hopping for an atom attached to a step with one bond. In their model, the activation barrier for the atom to detach from the step ($= \varepsilon + \varepsilon_d$) was the same as the barrier for diffusion along the step. In our model {see eq. (3) and reply to Prof. Zangwill above}, the detachment barrier is $\varepsilon + \varepsilon_d$ whereas the edge diffusion barrier is ε_d. For any given configuration, the driving force (chemical potential gradient) for decay might be expected to be the same for both models as the thermodynamic parameters (step free energy and step-step interaction energy) are the same. The difference must, therefore, arise from the different dynamics. At present, we do not understand why the two models should give different wavelength scaling laws. It is noted that analytic theories frequently use only one diffusion constant, namely, the terrace diffusion constant of an adatom. The fast edge diffusion in our model follows the assumptions of analytic theory more closely.

Additional References

Kang HC, Weinberg WH (1989) Dynamic Monte Carlo with a proper energy barrier: Surface diffusion and two-dimensional domain ordering. J. Chem. Phys. **90**, 2824-2830.