

Size Scaling in the Decay of Metastable Structures

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The rate of thermal decay of special fabricated structures on Si(111) has been measured for structure sizes ranging from 28 to 50 Å high. The mechanism of the decay via motion of individual steps has been observed directly using scanning tunneling microscopy. The results are consistent with size-scaling predictions of theory, and show that mass transport occurs via a mechanism in which mass is conserved locally. In addition, the theory yields a quantitative prediction of the measured rates with no adjustable parameters when previously measured equilibrium values for step-step interactions and step wandering are used. [S0031-9007(96)00789-2]

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As the size scale of fabricated structures becomes smaller and smaller, it is increasingly important to understand the mass transport governing the formation and stability of such metastable structures. Mullins described the essential physics of the decay of structures on surfaces using a continuum model that is physically appropriate for diffusion on an isotropic surface, i.e., a surface above the roughening temperature [1,2]. However, under most conditions of physical interest, the surface is well below the roughening temperature, which means that any structures on the surface are appropriately described as a series of discrete steps of the crystallographic layers of the material. Gruber and Mullins [3] and later many others [4–6] recognized the importance of steps in the decay of structures, and there is now a useful mesoscopic-scale description of surface mass transport that can be parametrized in terms of the measurable equilibrium properties of steps [4–8]. In this work, we test the validity of this mesoscopic theory by using scanning tunneling microscopy (STM) to measure the decay of specially fabricated structures on Si(111) which consist of “bunches” of steps with controlled sizes ranging from an average of 9 to 16 steps per bunch. We are able to make a quantitative comparison with theory because previous measurements of the equilibrium properties of the steps at the decay temperature provide values of the mesoscopic step parameters required for the theory: the step-step interaction coefficient and the step mobility or the alternative terrace diffusion constant [9–12].

Previous experimental studies [13–15] have used the continuum analysis of Mullins to investigate the decay of sinusoidal profiles. In this study, we have investigated the thermal relaxation of a slightly different geometry, step bunched structures. The key difference between our profiles and the previously studied sinusoids is that in our case all steps are aligned in the same direction. This provides distinct advantages for comparing experiment to theory, since we do not require a description of step and antistep annihilation events. We use direct current heating to produce these metastable structures which are ideal for use in our decay study. The dramatic changes in

surface morphology produced by the use of direct current heating on the Si(111) surface have been well documented [16–21]. For the conditions we use to obtain step bunching, the number of steps within the bunches and the distance between bunches increase with the increasing time of applied current. Thus the length of time during which direct current is applied to the sample is used to determine the size of the resulting structures produced on the surface.

The experiments were performed in a UHV system with base pressure 4×10^{-11} Torr, equipped with a homemade scanning tunneling microscope [22]. We use two methods of heating the sample, resistive heating and electron bombardment heating from a tungsten filament positioned behind the sample. The sample is $15 \times 3 \times 0.4$ mm³ in size, of nominally flat, *n*-type Si(111) with a measured equilibrium step spacing of 1300 Å.

We studied the thermal decay of three different starting surfaces prepared by applying direct current in the step-down direction, at a temperature of ~ 1260 °C, to bunch samples for 2, 1, and 0.5 min; resulting in structures with average bunch sizes of $N = 16, 12,$ and 9 steps, respectively. The voltage drop across the sample was ~ 8 V and the current used ~ 6 A. To avoid any effect of a direct current on the decay of the surface structures, we used electron bombardment heating at a temperature of 930 °C (only a small current of 0.068 A was passed through the sample for temperature measurement). For the starting surfaces which were direct current heated for 2, 1, and 0.5 min, relaxations were done for 30 and 120, 15 and 60, and 11 and 24 min, respectively. Times were chosen to produce a similar amount of relaxation on the different initial surfaces. After each relaxation, the sample was quenched and imaged at room temperature. The pressure during heating was less than 6×10^{-10} torr.

Figure 1(a) shows a three-dimensional STM image of the structures created by heating with direct current for 2 min. Figures 1(b) and 1(c) show the surface after subsequent relaxations of 30 and 120 min. There are two things to note in these images. First, even after 120 min,

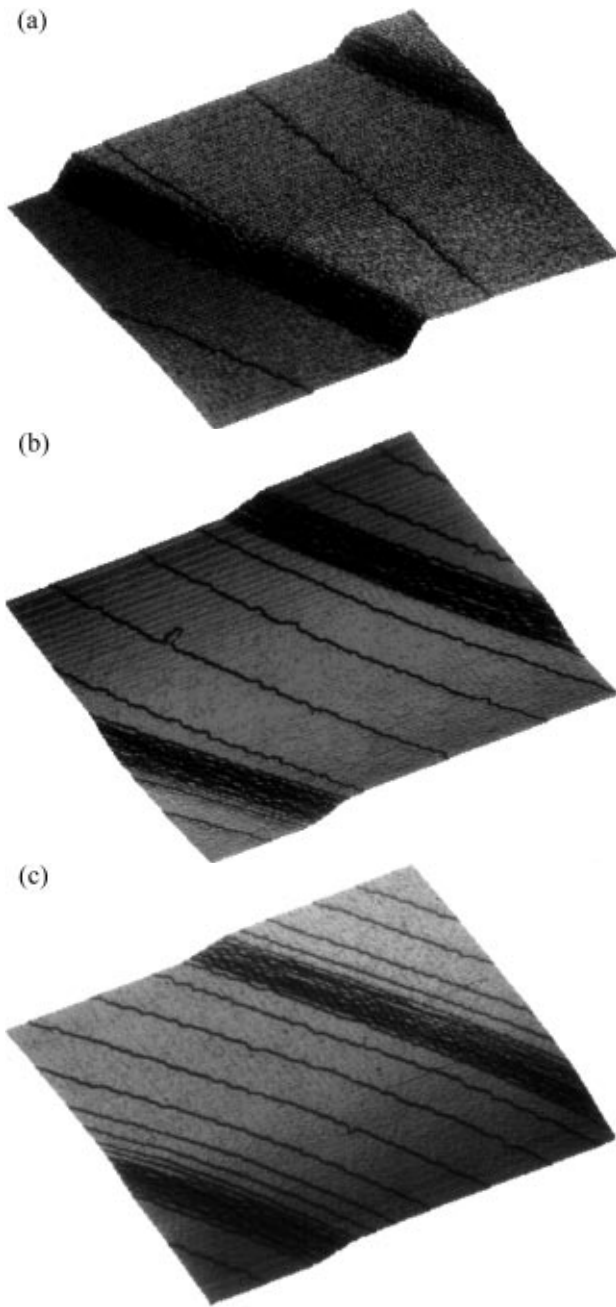


FIG. 1. $50000 \text{ \AA} \times 50000 \text{ \AA}$ STM images of surfaces with an average bunch size of 16 steps, a bunch-bunch separation of 22300 \AA , and an initial step-step separation within the bunches of $\sim 1.24 \text{ \AA}$. Individual steps are a single interplanar spacing, 3.14 \AA , high. The starting surface (a) was prepared by heating with DC in the step-down direction for 2 min. This was followed by relaxations under indirect heating for (b) 30 min and (c) 120 min.

the bunches have spread out by only a small amount. We are still in an early stage of the relaxation. The second thing to note is the presence of the crossing steps [21] (e.g., single height steps that cross the large terraces with extremely shallow slope) on the surface. The relaxation measure which we found to be the most useful under these conditions is the maximum slope of the bunches. For each

heating preparation, the maximum slope of the bunches was measured for 11 to 22 bunches on the surfaces. The slopes were then averaged and plotted as a function of time as shown in Fig. 2. The error bars on each point represent the standard deviation of the mean. The initial slope (and thus the step-step distance) of the bunches is different for each of the starting surfaces. The step-step spacing within the bunches decreases as the number of steps within the bunches increases, which is important because the thermal relaxation of the surface is driven by the repulsive step-step interaction. Thus, comparison of the relaxation curves for the different starting surfaces requires setting the zero of time for the experimental data so that all curves have the same slope at $t = 0$.

Since the steps remain relatively straight, we used a quasi-one-dimensional model to analyze the data. We considered two different classes of relaxation mechanisms. The first involves physical mechanisms for mass transport in which the adatom density on the terraces is not locally conserved. This case is physically relevant in instances in which there is a rapid exchange of adatoms across step edges (or across widely separated transverse regions of the same terrace in a two-dimensional (2D) model). For this class we consider mass transport in which diffusion on the terraces is fast, and the rate-limiting factor is the rate of attachment or detachment of adatoms to or from the step edges. In this case, the concentration, and thus the chemical potential of all terraces, assumes a constant value determined by μ_0 , the chemical potential of an adatom on a terrace (in the absence of deposition or evaporation). The resulting equation for the velocity of a given step n is [4,23]

$$\frac{\partial x_n}{\partial t} = \frac{2\Gamma h^3 g}{kT} \left(\frac{1}{l_{n-1}^3} - \frac{1}{l_n^3} \right), \quad (1)$$

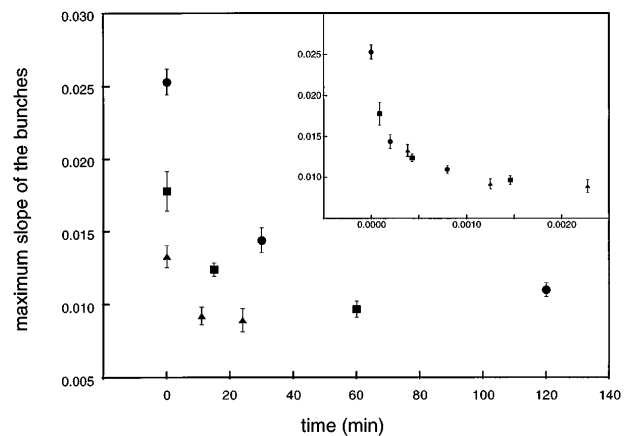


FIG. 2. Plot of the maximum slope of the bunches versus time for the three experimental data sets. Each data point is an average of approximately 11–22 measurements, and the error bars represent the standard deviation of the mean. The inset shows the maximum slope versus the scaled time, t/N^α , with the best fit value of $\alpha = 4.3$.

where x_n is the position of step n , Γ is the step mobility [24], g is the step-step interaction constant [12], and l_n is the width of terrace n .

In the second class of relaxation mechanisms, we assume there is local conservation of adatoms. Specifically, the flux onto any terrace from the two adjacent steps is required to be zero. Within this conserved class, we consider two different physical mechanisms, attachment/detachment limited and diffusion limited. The fast diffusion in the attachment/detachment limited case [4,6,11] results in a well defined and spatially uniform chemical potential on each terrace, with a value determined by the chemical potential of the adjacent steps and the step kinetic coefficients at these step edges. The equation for the step velocity in this case is [6,23]

$$\frac{\partial x_n}{\partial t} = \frac{\Gamma h^3 g}{2kT} \left(\frac{1}{l_{n+1}^3} - \frac{3}{l_n^3} + \frac{3}{l_{n-1}^3} - \frac{1}{l_{n-2}^3} \right). \quad (2)$$

The second conserved mechanism assumes that the attachment/detachment events at the step edges occur rapidly, while diffusion on the terraces is the rate-limiting factor. We make the simple assumption that the net flux of adatoms is proportional to a constant concentration gradient across the terraces with the slope determined by the ‘‘step chemical potential’’ at the adjacent steps. The equation for the step velocity in this case is [6,7,23,25]

$$\frac{\partial x_n}{\partial t} = \frac{D_s c_{eq0} a^2}{k_b T} \left(\frac{\mu_n - \mu_{n-1}}{l_{n-1}} + \frac{\mu_n - \mu_{n+1}}{l_n} \right), \quad (3)$$

where $\mu_n = 2ga^2 h^3 (1/l_{n-1}^3 - 1/l_n^3) + \mu_0$ is the chemical potential of the step edge n relative to the equilibrium value of the chemical potential, D_s is the diffusion constant, and c_{eq0} is the equilibrium adatom concentration on the terraces.

In the continuum limit, appropriate for large N , we expect that the rate of relaxation of the slope of the bunches satisfies the following scaling relationship:

$$S(N, t) \approx \left(\frac{t + t_0}{N^\alpha} \right)^\beta, \quad (4)$$

where $S(N, t)$ is the maximum slope of the bunches, N is the number of steps in the bunches, t is the time, α is the size-scaling exponent, and β is the time-scaling exponent. From numerical solutions of Eqs. (1)-(3), we find that the same relation holds approximately even for moderate N . For our initial ‘‘sawtooth’’ geometry, the size-scaling exponent α is found to be close to 2 for the model assuming local nonconservation of adatoms, and is close to 4 for models requiring local adatom conservation. The time-scaling exponent is $-1/4$ for the two attachment/detachment limited mechanisms, and $-1/5$ for the diffusion limited mechanism. It is assumed in obtaining these results that surfaces with different bunch sizes are subject to the same initial driving force (i.e., have the same ini-

tial slope), and that the initial slope is independent of the period (the distance between one end of a bunch and the corresponding end of an adjacent bunch).

To investigate if the size-scaling relation exists in the experimental data, we iteratively scaled the time axis of the data as $(t + t_0)/N^\alpha$ by varying the values of α and the time shifts for data sets two and three [26]. The result, shown by the collapse of the data points onto a single curve in the inset to Fig 2, for the best fit value of $\alpha = 4.3 \pm 0.5$, confirms the predicted size scaling and shows that the physical mechanism of decay falls in the conserved class. The error bar on α was obtained by varying α about the best value of 4.3 and finding the values at which two experimental data points moved outside their error bars from the scaled curves. In an independent fitting procedure, we tested the specific power law functional form predicted by Eq. (4). The result (not shown in figures) showed that the relaxation of the slope follows a power law with the exponent close to -0.23 (-0.2 to -0.3 give reasonable fits). A fit by an exponential form, in contrast, gave poor results with a substantially larger reduced χ^2 . We cannot distinguish between the conserved mechanisms that are attachment/detachment limited and diffusion limited, for which the time-scaling exponents are $-1/4$ and $-1/5$, respectively [23]. These power-law results for the relaxations are also in agreement with the results of Ozdemir and Zangwill [6]. They found that the individual terrace widths for shape preserving solutions evolve as $t^{1/4}$ and $t^{1/5}$ for attachment/detachment limited and diffusion limited mechanisms, respectively.

To make a quantitative comparison of the three theoretical classes of relaxation mechanisms with the experimental results, we need values of the step-step interaction coefficient g , the step mobility Γ , and the diffusion coefficient for atoms on the terraces $D_s c_{eq0}$. The value of the step-step interaction coefficient at 900 °C has been found experimentally to be $g = 0.015 \text{ eV}/\text{\AA}^2$, with an uncertainty of approximately 30% [9,12,24]. The kinetic parameters have been determined by direct observations of the equilibrium fluctuations of the steps [7,10,11]. The result has been alternatively interpreted as due to step attachment/detachment limited kinetics with a step mobility of $\Gamma = 5.5 \times 10^7 \text{ \AA}^3/\text{s}$ [11], and as due to diffusion limited kinetics with a diffusion constant of $D_s c_{eq0} = 1 \times 10^8 \text{ s}^{-1}$ [10]. These parameters were used in the numerical solutions of Eq. (1)–(3) to predict the rate of decay. The resulting calculated relaxation curves were then scaled in the same way as the experimental data to produce the curves shown in Fig. 3. The agreement of the predictions of both conserved cases with the observed rate is well within the uncertainties. As in the case of the analysis of the step fluctuations, the data do not allow the two cases to be distinguished. However, it is clear that, by using physically meaningful parameters, it is possible to make quantitative predictions of the rate of decay using the mesoscale theory.

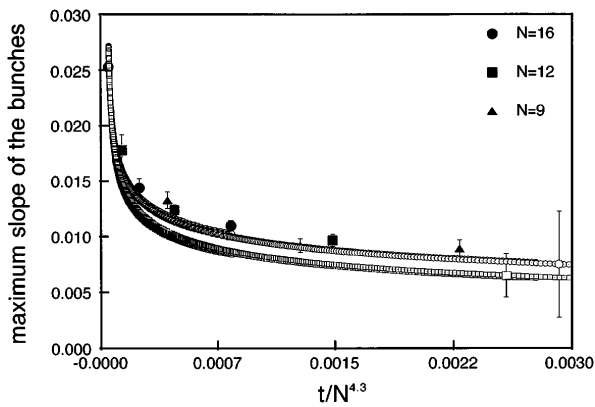


FIG. 3. Plot of scaled slope versus time for the experimental data and the results of the numerical solutions. The three experimental data sets are plotted using different symbols, ● for $N = 16$, ■ for $N = 12$, and ▲ for $N = 9$, and the error bars represent the standard deviation of the mean. The closely spaced points are the results of numerical solutions for the two conserved relaxation mechanisms. The hollow squares with dots in the centers denote results for the attachment/detachment limited mechanism, and the hollow circles with dots in the centers denote results for the diffusion limited mechanism. The error bar shown for each mechanism was obtained from the numerical solution results, assuming an error in g of 30%, an error in Γ of 50%, and an order of magnitude variation in $D_s c_{eq}$. The error bar in each case is representative of the larger percentage variations in slope for the times shown in the figure.

Finally, we consider the recent results of Keefe *et al.* who have studied the decay of large sinusoidal profiles on the Si(100) surface [15]. They found a scaling relation in which the amplitude of the sinusoids depends on the wavelength to the inverse fourth power. This result seems to be in agreement with our size-scaling result. However, this may only be fortuitous, since the geometry of Keefe *et al.* contains antisteps for which an adequate theoretical formalism is not yet available. Keefe *et al.* also found good agreement between the experimentally measured decay of the amplitude and the exponential form predicted by Mullins [2] using a continuum approach. Initially this may seem surprising, since it is known that the Si(001) surface is not rough at the temperature of the measured decay, and that the step fluctuations obey a wavelength-squared behavior similar to that observed on Si(111) [27]. However, the results of a numerical solution of Eq. (2) for an initial sinusoidal profile [23], show that an exponential form will be observed over part of the decay range (as has also been shown for tilted sinusoids with no antisteps [8]). The application of this model to Si(100) is complicated by the fact that the step-step interactions on Si(100) are more complex than on Si(111) due to the anisotropy of the surface reconstruction [28]. In addition, as discussed by Keefe *et al.* [15], the presence of crossing steps at the extrema of the sinusoids further clouds comparison with quasi-one-dimensional theoretical predictions of the decay.

In summary, we have used direct current heating to create metastable structures of a controlled size on the Si(111) surface. We have investigated their thermal relaxation to test the applicability of a step-based theory of mass transport. In agreement with theoretical predictions, we have found a size-scaling relation in which the decay of the slope of the bunches scales as $tN^{-\alpha}$, where N is the number of steps in the bunches. The scaling exponent α is found to be 4.3 ± 0.5 , consistent with decay mechanisms which require local adatom conservation. We have shown that the rate of decay can be predicted with no adjustable parameters using the mesoscopic theory of mass transport and the parameters determined from the measurement of the equilibrium surface properties. These results show that the theory may be extended to arbitrary quasi-one-dimensional geometries with confidence, and set the stage for studies of more complex geometries.

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