

## Nonclassical Smoothing of Nanoscale Surface Corrugations

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We report the first experimental observation of nonclassical morphological equilibration of a corrugated crystalline surface. Periodic rippled structures with wavelengths of 290–550 nm were made on Si(001) by sputter rippling and then annealed at 650–750 °C. In contrast to the classical exponential decay with time, the ripple amplitude  $A_\lambda(t)$  followed an inverse linear decay,  $A_\lambda(t) = A_\lambda(0)/(1 + k_\lambda t)$ , agreeing with a prediction of Ozdemir and Zangwill. We measure the activation energy for surface relaxation to be  $1.6 \pm 0.2$  eV, consistent with the fundamental energies of creation and migration on Si(001).

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Mass transport during morphological equilibration of solid surfaces can occur through surface or bulk diffusion, viscous flow, or evaporation/recondensation. The dependence of the relaxation rate on temperature and feature size are related to basic surface energy parameters, both kinetic (e.g., surface diffusivity) and thermodynamic (e.g., surface tension). The theory of continuum surface relaxation, due primarily to Mullins [1] and Herring [2], and subsequent surface annealing experiments of sinusoidally grooved surfaces supporting this theory, notably by Blakely and co-workers [3], are considered classic studies in the physics of surfaces. However, for the specific case of a crystalline surface that is near a singular orientation and below its thermodynamic roughening transition temperature  $T_R$ , the classical theory is inapplicable [4–7]. In this regime, discrete step-step interactions are expected to drive surface relaxation [8]. As a result, the amplitude of a shallow sinusoidal profile whose average orientation is a crystal facet is not necessarily expected to exhibit the classical exponential decay with time [9–11].

In this Letter, we report the first experimental observation of nonclassical annealing behavior for a corrugated surface evolving toward planarity. We studied nanometer-scale ripples on Si(001) and observed a nonexponential decay for the time evolution of the ripple amplitude during anneals over the temperature range 650–750 °C. There have been several experimental approaches to morphological relaxation [12–14]. Our work is most similar to an earlier one by Keeffe, Umbach, and Blakely (KUB) [14], who studied the annealing behavior of Si(001) at higher temperatures (800–1100 °C) using lithographic techniques to produce sinusoidal patterns with larger wavelengths (4–6  $\mu\text{m}$ ) and amplitudes ( $\sim 100$  nm) than ours. In contrast to our results, however, KUB did observe exponential amplitude decay.

The nanorippled samples used in these annealing experiments were produced by spontaneous pattern formation during low energy (750 eV)  $\text{Ar}^+$  ion bombardment at glancing angles and elevated temperatures (“sputter rippling”) [15]. We used sputter rippling to produce rippled Si(001) samples ( $p$ -type, 3–10  $\Omega$  cm, miscut  $0.1^\circ \pm 0.1^\circ$ ). Ripples ranged in wavelength from 290 to 550 nm, and in initial amplitude from 4 to 30 nm. The wave vectors of the ripples were oriented perpendicular to the [110] direction. Sample fabrication by sputter rippling in this kind of experiment is advantageous because the sample stays clean and ripples can be made very small. Samples never see any *ex situ* lithographic or other kinds of preparation after the commencement of ion beam erosion, and many microns of material over a wide area ( $\sim 1$   $\text{cm}^2$ ) are sputtered off in a clean ultrahigh vacuum environment [16,17].

Morphological evolution during annealing was monitored using a recently developed *in situ* UV spectroscopic technique (“light scattering spectroscopy,” LiSSp) that measures the spectrum of light scattered in a fixed direction [18]. Surface morphology information is contained in the measured intensity spectrum of the scattered light normalized by the incident light spectrum. This spectrum is proportional to the power spectral density (PSD) of the sample surface. The intensity of the PSD at a particular spatial frequency is proportional to the square of the real amplitude of the surface measured at that spatial frequency. The constant of proportionality was found using *ex situ* atomic force microscopy (AFM) allowing absolute amplitude vs time curves to be plotted. Details of our implementation of LiSSp, as well as sample spectral evolution, can be found in Ref. [19].

Figure 1 shows AFM micrographs representative of the observed morphological evolution. Both samples shown in

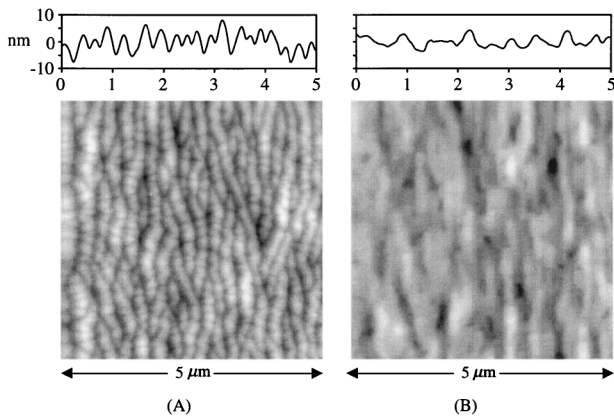


FIG. 1. Example AFM micrographs of (a) an unannealed rippled sample,  $\lambda = 360$  nm, and (b) a postannealed sample,  $\lambda = 363$  nm,  $T_{\text{anneal}} = 667$  °C, annealing time = 2145 s. The representative line scans for each micrograph are the horizontal centerlines. The gray scales are the same for each image.

the figure had the same wavelength; however, the sample in Fig. 1(a) was not annealed while the one shown in Fig. 1(b) was annealed for a prolonged period of time. Figure 2 illustrates our key result—the ripple amplitude does not decay in the classical exponential manner at any time. Instead, for a ripple with wavelength  $\lambda$ , the time evolution of the amplitude,  $A_\lambda(t)$ , for all cases followed the inverse linear form:

$$A_\lambda(t) = A_\lambda(0)/(1 + k_\lambda t). \quad (1)$$

The parameter  $k_\lambda$  contains all the temperature and scale dependence. The form of Eq. (1) is predicted by a nonclassical model for the amplitude decay of perfect sinusoids presented by Ozdemir and Zangwill (OZ) [4], who built on earlier work by Rettori and Villain (RV) [5] (we herein collectively refer to this model as RV-OZ). The salient points of the RV-OZ model are summarized as follows.

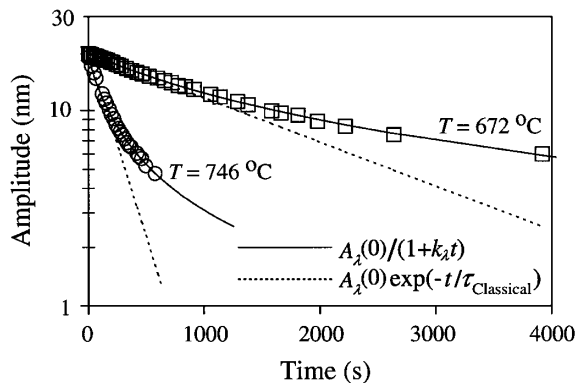


FIG. 2. Typical amplitude decay behavior (data: squares, circles) during an *in situ* anneal, illustrating the nonclassical decay behavior (classical: dashed lines) and the good fit to the RV-OZ form, Eq. (1) (solid lines). For these samples,  $\lambda = 565$  nm,  $T = 672$  °C (squares),  $\lambda = 485$  nm,  $T = 746$  °C (circles).

Consider a one-dimensional model for a decaying sinusoidal profile. In general, the local change in height  $h(x, t)$  at a point  $x$  on a surface is proportional to the divergence in the local flux of diffusing species  $j(x, t)$  at that point, a result simply due to mass conservation. That is,

$$\partial h(x, t)/\partial t \propto -\nabla \cdot j(x, t). \quad (2)$$

The local flux of the diffusing species on a surface during relaxation depends on the width of the terrace upon which the adatoms sit,  $l(x)$ , and also the local chemical potential difference between atoms on the steps bounding that terrace,  $\Delta\mu_0(x)$ . When the mass transport rate is limited by diffusion across the terrace,

$$j = (D_S C_0/k_B T)\Delta\mu_0/l, \quad (3)$$

where  $D_S$  is the surface diffusivity, and  $C_0$  is the equilibrium concentration of adatoms on an infinitely wide terrace [20]. When the rate is limited by step traversal,

$$j = (ak_P C_0/k_B T)\Delta\mu_0, \quad (4)$$

where  $k_P$  is the rate constant for hopping down a step onto the next lowest terrace [21], and  $a$  is the in-plane lattice constant. The connection between the continuum and the discrete is through the approximation that  $l(x) \propto 1/|\partial h(x)/\partial x|$ . With this approximation and the appropriate form for  $\Delta\mu_0$  (discussed below), a sinusoid with amplitude evolution given by Eq. (1) is found to be an approximate solution of Eq. (2) using either Eq. (3) or (4) [4].

How the time-dependent behavior of the amplitude of a surface feature is related to a characteristic length scale of the overall surface morphology has been the subject of most theoretical studies of surface relaxation. RV-OZ show that the time decay of the amplitude of the infinite sinusoid obeys the following scaling behavior, derivable from careful consideration of the discrete forms the surface diffusive flux. In general, the amplitude  $A_\lambda(t)$  of a sinusoid with wavelength  $\lambda$  can be expressed as a universal amplitude decay function,

$$A_\lambda(t) = A(t/\lambda^n), \quad (5)$$

such as Eq. (1). The value of the scaling exponent,  $n$ , depends on the microscopic surface kinetics; for diffusion-limited kinetics [Eq. (3)],  $n = 5$ , and for step traversal-limited kinetics [Eq. (4)],  $n = 4$ . In the classical model, only diffusion limited kinetics are applicable and  $A(t/\lambda^n)$  is a decaying exponential with  $n = 4$ .

To find the full temperature dependence of Eq. (1), the form of  $\Delta\mu_0$  first needs to be clarified. Classically and above  $T_R$ , the chemical potential gradient is connected to the local morphology by a Gibbs-Thomson effect. In this case,  $\Delta\mu_0$  is proportional to the local curvature  $\kappa$  and the local surface energy,  $\gamma$ . Instead of continuum surface tension as a driving force for surface area reduction, the forces that drive relaxation are primarily due to step-step interactions. For discrete surfaces, the chemical potential of

an atom at a step is proportional to the difference in the inverse cubes of the neighboring terrace lengths, a form expected when steps communicate only through elastic or entropic interactions [4,5]. The constant of proportionality  $G_3(T)$  describes the temperature dependence of the step-step interactions. If steps interact elastically, then  $G_3$  is temperature independent; if the steps repel each other entropically then to first order,  $G_3 \propto (k_B T)^2$  [10]. It follows that  $\Delta\mu_0(x)$  in Eqs. (3) and (4) has the temperature dependence of  $G_3$ .

The full temperature dependence of  $j(x)$  is found by multiplying the temperature dependence of  $\Delta\mu_0(x)$  by that of  $D_S$  or  $k_P$  and that of  $C_0$ . The latter three quantities are all thermally activated. Thus, we can write either product,  $D_S C_0$  or  $k_P C_0$ , in a form proportional to  $\exp(-\varepsilon/k_B T)$ , where  $\varepsilon$  is an activation energy associated with the relaxation process. For diffusion-limited kinetics,  $\varepsilon = E_M + E_F$ . The migration energy  $E_M$  appears because the diffusivity  $D_S$  is thermally activated; the formation energy  $E_F$  appears because the equilibrium concentration of mobile species  $C_0$  is also thermally activated. For step traversal-limited kinetics,  $\varepsilon = E_P + E_F$ , where  $E_P$  is the step traversal barrier. Combining the temperature dependencies of  $D_S$ ,  $k_P$ , and  $C_0$  with that of  $G_3$  leads to the following temperature dependence for  $j(x)$ :

$$j(x) \propto \exp(-\varepsilon/k_B T) (k_B T)^m, \quad (6)$$

with  $m = \pm 1$ .

Equations (1), (2), (5), and (6) can be combined so as to conclude that the full temperature and wavelength scaling dependencies of  $k_\lambda$  are of the form  $k_\lambda \propto \exp(-\varepsilon/k_B T) (k_B T)^m \lambda^{-n}$ . In fact, assuming the wavelength scaling behavior of Eq. (5), the particular form of  $A_\lambda(t)$  need not be known in order to find an activation energy for relaxation. The following data collapse strategy should be all that is required; it is essentially a three-parameter fit. Look for the best overlap of the amplitude relaxation curves,  $A_\lambda(t)$  vs  $t \exp(-\varepsilon/k_B T) (k_B T)^m \lambda^{-n}$ , while varying the constrained set of parameters  $\{\varepsilon; m = \pm 1; n = 4, 5\}$ . The activation energy,  $\varepsilon$ , gives the sum of the formation energy and the rate limiting barrier to transport. The step-step interaction exponent,  $m$ , tells us whether steps interact entropically ( $m = -1$ ) or elastically ( $m = 1$ ). The scaling exponent tells us whether relaxation kinetics are diffusion-limited ( $n = 5$ ) or step traversal-limited ( $n = 4$ ).

Figure 3 shows the best data collapses of the amplitude decay for five samples annealed between 650 and 750 °C [22]. We find a slight preference for step traversal-limited kinetics ( $n = 4$ ), and we cannot distinguish entropic ( $m = -1$ ) and elastic interactions ( $m = +1$ ). In Fig. 3, data collapse for  $m = -1$  is shown, for which the best collapse is obtained for  $\varepsilon = 1.7$  eV. The only effect of replacing  $m = -1$  with  $m = +1$  for both  $n = 4$  or  $n = 5$  is that we obtain just as good a fit but with the value of  $\varepsilon$  reduced by 0.2 eV. Based on these results, we ascribe

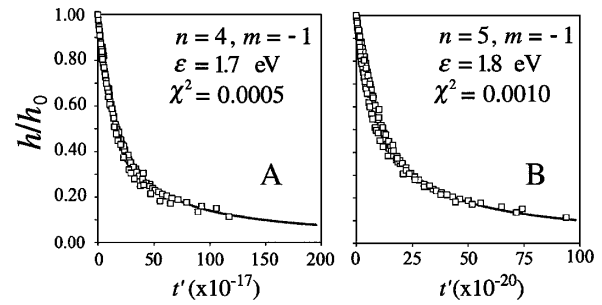


FIG. 3. Best data collapses for relaxation data assuming step traversal-limited kinetics [(a):  $n = 4$ ] and diffusion-limited kinetics [(b):  $n = 5$ ]. The scaled time,  $t' = [t/(1 \text{ s})] \cdot [k_B T/(1 \text{ eV})]^m \exp(-\varepsilon/k_B T) [\lambda/(1 \text{ nm})]^{-n}$ , as discussed in the text. Data are shown as open squares. The best fit to Eq. (1) is shown as a solid line and the associated  $\chi^2$  deviations from the data collapse are reported.

an activation energy of  $\varepsilon = 1.6 \pm 0.2$  eV with  $n = 4$  or 5 to the relaxation mechanism on Si(001) in this temperature range.

As discussed, one interprets the activation energy found in this type of experiment as a sum of the creation energy of the mobile surface species and the rate limiting barrier to transport. “Hot” and “atom tracking” STM measurements have found that the migration energy of dimers on Si(001) is  $E_M = 1.1 \pm 0.1$  eV [23]. Our own set of sputter induced rippling experiments suggests that in this temperature regime dimers are in fact the predominant species effecting transport, and we measured a migration energy of  $E_M = 1.2 \pm 0.1$  eV [15]. Recently, Tromp *et al.* measured the formation energy of dimers on the Si(001) surface at temperatures in the range 750 to 1050 °C, and found that  $E_F = 0.35 \pm 0.05$  eV [24,25]. As our results do not unequivocally distinguish between diffusion-limited and step traversal-limited kinetics, let us consider both possibilities. If transport is diffusion-limited, then our best fit activation energy is 1.7 eV which we interpret as  $E_F + E_M$ . The independently measured values of  $E_F$  and  $E_M$  sum to about 1.5 eV, which is within experimental error of our value. If transport is step traversal-limited, then our best-fit activation energy is 1.6 eV which we interpret as  $E_F + E_P$ . The proximity of this value to the sum of the independently measured values of  $E_F$  and  $E_M$  would then suggest that the barriers for step traversal and terrace migration in this system are similar [26].

The RV-OZ model of surface relaxation is applicable to surfaces with simple step-step interactions and perfect sinusoidal morphologies. Despite the possible complexities in the step-step interactions associated with the  $1 \times 2$  and  $2 \times 1$  reconstructions of the Si(001) surface and the obvious irregularities of our sputter ripples, we find that RV-OZ works well to describe the annealing behavior.

It has been suggested that “crossing steps,” at the extrema of the terraces play an important role during annealing of Si(001) [27]. One can, in fact, construct a rippled surface comprised entirely of very high amplitude crossing

steps. The direction of the ripple wave vector,  $[1\bar{1}0]$ , and the small miscut of our samples,  $0.1^\circ \pm 0.1^\circ$ , are such that our ripples should be comprised of alternating  $S_A$  and  $S_B$  steps running along  $[110]$  with relatively few steps crossing adjacent peaks and valleys. The sides of the ripples should have steps of opposite sign, fulfilling the basic morphological requirement of the RV-OZ model. We note that the RV-OZ model neglects step-step interactions across the uppermost and lowermost terraces as well as the overall reduction in surface energy when steps are annihilated. Other models address this issue by analyzing the relaxation along the slopes and along the extremal terraces separately [28]. However, no model except for RV-OZ has predicted a form for the amplitude decay consistent with our data. It may be that a detailed description of the activity at extremal terraces during relaxation is simply not important for this material system under our experimental conditions.

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- [17] TEM reveals there are stacking fault defects that penetrate  $<10$  nm from the surface. However, if all of the observable defects evaporated into interstitials, there would be at most  $10^{15}$  cm $^{-2}$  interstitials thereby generated. If all these excess interstitials diffused to the surface and filled in the troughs, it would only account for at most 5% of the typical measured amplitude decrease.
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- [20] Note that Eq. (3) contains an implicit assumption of being near equilibrium—it allows  $C_0$  to be written in a thermally activated form.
- [21] For Si(001) there appears to be two pathways for step traversal. One is conventional attachment and detachment from the step edge. The other is direct permeation without attachment, as discussed in [12]. Whichever has the lower barrier will be relevant for Eq. (4).
- [22] Data were collected for  $\{\lambda, T\} = \{485 \text{ nm}, 746^\circ\text{C}\}$ ,  $\{425 \text{ nm}, 687^\circ\text{C}\}$ ,  $\{565 \text{ nm}, 672^\circ\text{C}\}$ ,  $\{363 \text{ nm}, 667^\circ\text{C}\}$ ,  $\{405 \text{ nm}, 651^\circ\text{C}\}$ .
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