Anisotropic Coarsening of Periodic Grooves: Time-Resolved X-Ray Scattering

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Coarsening dynamics of mesoscopic periodic grooves (500–1500 Å) is characterized, as they self-assemble on a miscut Si(113) surface, following a temperature quench through a faceting transformation. Use of an area detector in glancing angle reflection geometry allowed for simultaneous measurements of highly anisotropic length scales. Over more than two decades of time, the length of the grooves grows as the third power of the width of the grooves. This result constitutes a direct confirmation of a recently proposed theory and the observation of anisotropic dynamic scaling behavior. [S0031-9007(97)05003-5]

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Faceting refers to the phase transformation at which an initially uniform surface decomposes into coexisting domains of different orientation [1]. Studies of faceting to date have established its close analogy to the phase separation of a binary mixture [2]. Generally, following a quench from a uniform phase into a coexistence region, domains of the low temperature phases form and subsequently coarsen in time. For binary mixtures, the mechanism of coarsening (ripening) is well known: larger domains with smaller domain wall curvature accrete material at the expense of smaller domains with larger domain wall curvature [3]. Application of this principle results in the prediction that the average domain size grows as a power law versus time with an exponent of $1/3$. In addition, the domain morphology exhibits dynamic scaling behavior, so that the distribution of domain sizes or the scattering function, when scaled to the average domain size, appears self-similar at different times. These predictions have been realized experimentally in many systems [4].

For faceted surfaces, however, the domain walls that must disappear so that coarsening may proceed are linear edges, requiring a different mechanism. Although faceting has been of considerable interest for many decades, pioneering studies of faceting kinetics have focused mainly on the early stage nucleation and growth [2,5,6]. Only recently has the subject of late stage coarsening begun to receive attention [7–9]. Of particular relevance to the present paper, it was found that when a miscut Si(113) surface was quenched from above a faceting temperature to below, quasiperiodic grooves formed and subsequently coarsened in time. The width of the grooves was observed to grow following approximately a $1/6$ power law versus time, and the scattering function from the grooves revealed a dynamic scaling behavior [8]. Another interesting observation was made on a grooved alumina surface, where a rapid increase in the aspect ratio of the grooves was noted as a function of annealing time [9].

Subsequently, Milner proposed a theory that reproduces the $1/6$ power law, and in addition predicts that the length of grooves would increase as the third power of their width [10,11], i.e., as the $1/2$ power of time. Our motivation for the present study was to directly test the theory, by quantifying the time-dependent aspect ratio of coarsening grooves on Si(113), by means of time-resolved x-ray scattering. Preliminary work by atomic force microscopy (AFM) on a quenched surface indicated an aspect ratio of approximately 50. Simultaneous measurement of the evolution of two length scales that differ by nearly 2 orders of magnitude poses a technical challenge, which was met by utilizing an area detector [12] in a glancing-angle reflection geometry, which nicely matches the instrumental resolution to the requisite length scales. The results, presented here, generally endorse the theory of Ref. [10]. The simplicity of the theory and its apparent success lead us to suspect that it will be applicable to other faceting transitions and more generally to different types of uniaxial system. Despite the prevalence of uniaxial phases in nature, the kinetics of domain formation in such systems remains largely unexplored [13].

We begin with a brief review: At nonzero temperature, steps on a crystal surface are subject to long-wavelength fluctuations. The relation between amplitude (h) and wavelength (M) of the fluctuations is determined in a statistical manner by the stiffness (Σ) of the steps [14]: $\langle h^2 \rangle \simeq M k_B T/\Sigma$. The theory asserts that a bunch of N steps on a faceted surface may itself be treated as a (macro) step possessing a stiffness that is N times larger than the stiffness of a single step ($\Sigma_N = \Sigma_1 N$) and a mobility that is N times smaller than that of a single step ($\Gamma_N = \Gamma_1/N$). Faceting proceeds via coalescence of adjacent step bunches as they thermally fluctuate and collide with each other. The rate of coalescence is controlled by the time to develop fluctuations of sufficiently large amplitude, i.e., $h \simeq L$, where L is the mean separation between step bunches. It follows that $L^2 \simeq M k_B T/\Sigma_N$.

Because N and Σ_N increase linearly with L, this relationship between amplitude and wavelength of the colliding step bunches yields $L^3 \simeq Mk_BT\ell_0/\Sigma_1$, where ℓ_0 is the mean step separation. The theory furthermore takes the characteristic time for a collision between two step bunches to be $\tau \simeq k_BTM^2/\Gamma_N\Sigma_N \simeq L^6\Sigma_1/k_BT\ell_0^2\Gamma_1$, assuming that step fluctuations are determined by adatom attachment and detachment [11]. As a consequence, L will increase as a $1/6$ power of time in the coarsening process of the step bunches. M increases more rapidly, with a coarsening exponent of $1/2$. The step-free facets bounded by step bunches should become increasingly elongated along the step edge direction with increasing time.

Experiments were performed at beam line X20C at the National Synchrotron Light Source [15]. X rays with a wavelength of $\lambda = 1.4$ Å were selected by W/Si multilayers with a relative bandpass of $\sim 10^{-2}$. The scattering geometry is illustrated in Fig. 1(a). A CCD area detector [12] was mounted 0.92 m downstream of the sample. X rays scattered into the detector correspond to a plane in reciprocal space defined by $Q_z = k\sin(2\theta_i - \delta_x)$, $Q_y = k\delta_y$, and $Q_x = \sin\theta_i k\delta_x$, where δ_x and δ_y are horizontal and vertical angular displacements of the scattered x rays from specular reflection, $\theta_i = 0.56°$ is the incident angle,

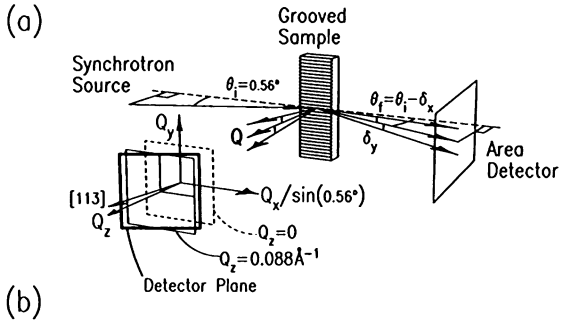

FIG. 1. (a) Scattering geometry. Q_z is along the surface normal. An area detector subtends a plane in reciprocal space. Centered at the specular reflection $Q_z^o = 2k\sin\theta_i = 0.088$ Å^{-1}, this plane is nearly parallel to Q_yQ_z with a small component along Q_x: $Q - Q_z^o = (\sin\theta_i k\delta_x, k\delta_y, \cos\theta_i k\delta_x)$. Since the scattered intensity from the structure of (b) is independent of Q_z within the range of Q_z sampled, we may consider the horizontal ($k\delta_x$) and vertical ($k\delta_y$) axes of the detector plane to represent $Q_x/\sin\theta_i$ and Q_y, respectively. (b) AFM image of a grooved sample with 500 Å periodicity. One side of each groove is the (113) facet, and the other side is a bunch of 11 steps.

and $k = 2\pi/\lambda$. However, for shallow structures such as shown in Fig. 1(b) and for the values of Q_z studied here, the scattering intensity depends only weakly on Q_z, so that our measurements accurately reflected the variation versus Q_x. It follows that the resolution in Q_x is finer than in the Q_y direction by a factor of $\sin\theta_i = 10^{-2}$. This choice of scattering geometry is particularly suitable for our studies, where strong anisotropy in length scales is expected. The sample was a Si(113) wafer with its surface miscut by 2.1° towards (001) so that steps are separated on average by $\ell_0 = 45$ Å. The equilibrium morphology of this surface has been studied extensively [15]. Faceting occurs at 1220 K, whereupon the steps self-assemble into a grooved superstructure. An example of a faceted surface is shown in Fig. 1(b). One side of each groove is a step-free (113) facet, and the other side is a step bunch. The sample was oriented so that the grooves were horizontal, as indicated in Fig. 1(a).

After annealing the sample at 1530 K for 60 s, we cooled the surface to 1250 K, where the surface is known to have a uniformly stepped morphology. The scattering from such a surface is a single peak with a resolution-limited width corresponding to specular reflection. The peak width corresponds to 1.9×10^{-5} Å^{-1} in the Q_x direction and 1.4×10^{-3} Å^{-1} in the Q_y direction. The line shape is well described by a Gaussian. We then quenched the surface to 1195 K and collected the scattered intensity every 4 s with an exposure time of 1 s. Examples are displayed in Fig. 2 for times 10, 100, 1000, and 10 000 s after the quench.

In addition to the central peak which corresponds to specular reflection, two vertically displaced peaks are observed. They may be identified as the first order diffraction peaks from the periodic grooves. With increasing time they grow in intensity, narrow in width, and move in towards the center. The vertical position of the peaks is related to the groove periodicity via $\epsilon_y = 2\pi/L$, so that the growth of L versus time is evident from these data. Equally evident is the dramatic decrease in the horizontal width of the groove peaks, which arises from the increasing extent of ordering along the grooves. Especially striking is the change in the shape of the peaks. Beginning elongated along Q_x at early times, the peaks evolve to appear nearly circular in shape at late times. In fact, because of the resolution effects described above, the length of the grooves in the x direction is much larger than the period in the y direction, even at the earliest times.

Closer examination reveals that the two first-order peaks evolve slightly differently. In particular, it may be seen that at late times the horizontal width of the lower peak (at negative Q_y) seems broader than that on the upper side (positive Q_y). We observe no difference in the vertical width or in the vertical position of the two. In reference to the scattering geometry shown in Fig. 1(a), the facet side of the grooves is oriented towards the positive Q_y direction, and the step-bunch side towards the negative Q_y direction. Apparently, the peak on the step-bunch side is broader.

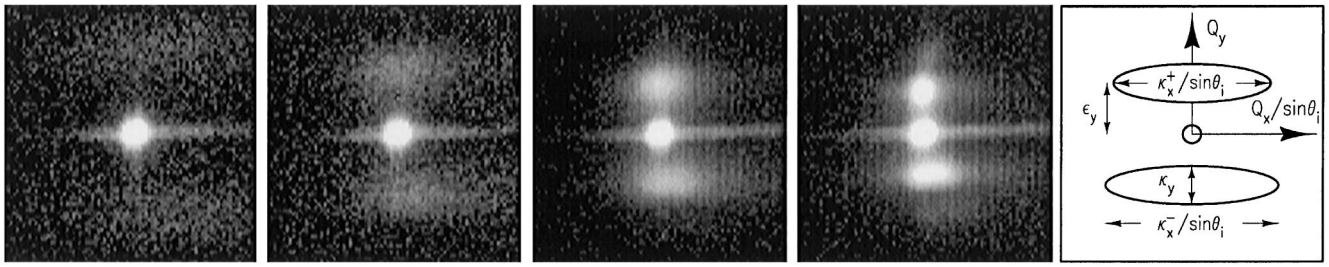

FIG. 2. Diffraction patterns from a grooved sample after quench. 10, 100, 1000, and 10 000 s. Intensity is displayed in logarithmic scale. Each frame displays a detector area of 8×8 mm^2. Projected in the $Q_x Q_y$ plane, it corresponds to a reciprocal area of 3.5×10^{-4} Å by 3.5×10^{-2} Å. The peaks are fit to 2D Gaussian with the fitting parameters as defined in the schematic.

The source of broadening along Q_x on the facet side is the finite length of the grooves. By contrast, on the negative Q_y side, step fluctuations within the step bunches may contribute to a broader peak width, in addition to the finite length of the grooves. We do not at present understand this behavior quantitatively. Instead, we will focus on the peak on the facet side, which is unaffected by these fluctuations.

We have also fit the groove peaks to 2D Gaussian line shape, examples of which are shown in Fig. 3. The results for the position (ϵ_y) and the deconvoluted full widths at half maximum ($\kappa_x^{\pm}$ and κ_y) are shown in Fig. 4. The width of the specular peak remains resolution limited at all times. The position and the width in the Q_y direction reproduce the findings of Ref. [8]. Evolution of the horizontal width proceeds at a much faster rate, as shown in Fig. 4. Beginning at 4×10^{-4} Å^{-1} at the earliest times measured, the two peaks evolve to 2×10^{-5} Å^{-1} and 4×10^{-5} Å^{-1}, respectively. The behavior of each appears consistent with a power law versus time. The best fit for times less than 2000 s yields $\kappa_x^+ = 0.00077 t^{-0.44}$ Å^{-1} for the peak on the facet side and $\kappa_x^- = 0.00066 t^{-0.35}$ Å^{-1} for the peak on the step-bunch side. The exponents 0.44 and 0.35 for $\kappa_x^{\pm}$ are unquestionably different from 0.16 for ϵ_y and κ_y. The width of the peak on the facet side follows a power law up to 4000 s, at which time it reaches our resolution limit. The measured exponent of 0.44 is close to the predicted exponent of $1/2$, given the uncertainties at early times (due to counting statistics) and at very late times (due to instrumental resolution.) The dashed line in Fig. 4 indicates the expected $1/2$ power law. Relating κ_x^+ to the finite length of grooves via $M = 5.9/\kappa_x^+$ [10], we find that at 1195 K the groove length increases from 1.4 to 16.5 μm for times between 4 and 1000 s, while L increases from 450 to 960 Å. The anisotropy ratio M/L of the shape of the coarsening grooves changes from 32 at 4 s to 172 at 1000 s.

We plot in Fig. 5 the ratios ϵ_y/κ_y and ϵ_y^3/κ_x^+. For times between 4 and 1000 s, we measure constant ratios $\epsilon_y/\kappa_y = 2.0$ and $\epsilon_y^3/\kappa_x^+ = 0.0069$ Å^{-2}. Constant ϵ_y/κ_y signifies dynamic scaling along the Q_y direction [8]. Constant ϵ_y^3/κ_x^+ indicates that M is proportional to L^3, in agreement with Milner's predictions [10]. We may define the coarsening regime to correspond to times from ~4 to 1000 s, in which the growth of grooves is governed by simple scaling relations. This is the principal result of this Letter, namely, that the scaling relations, predicted by a model of thermally fluctuating step bunches, are

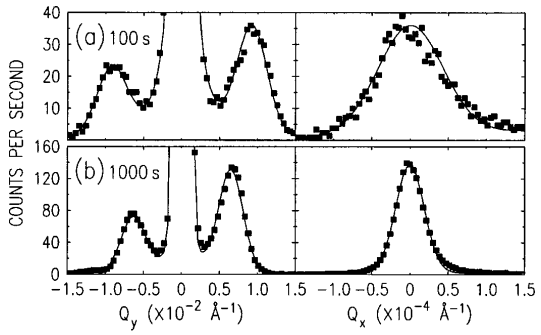

FIG. 3. Line profiles of data obtained at (a) 100 s and (b) 1000 s.

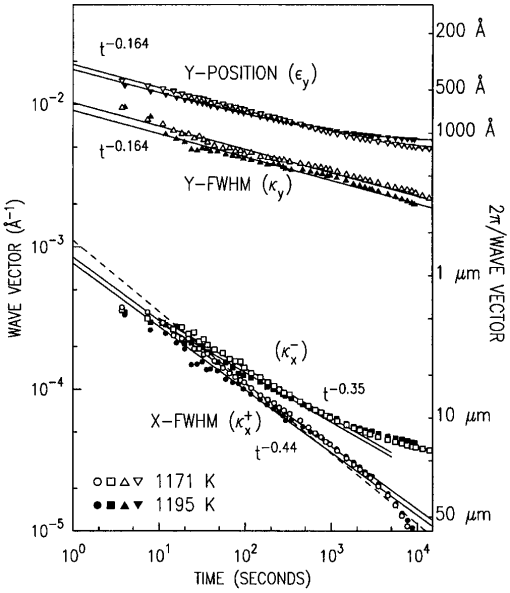

FIG. 4. Power law evolution of the position and width of the first-order groove peaks. Results for two temperatures are displayed. Resolution corresponds to 30 μm in the x direction and 4500 Å in the y direction.

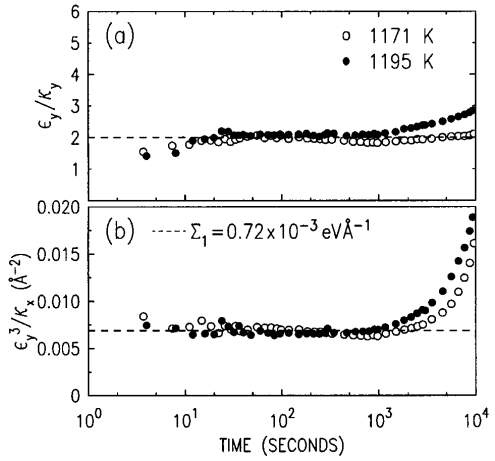

FIG. 5. Scaling relations are demonstrated in the coarsening regime. (a) Best fit to a constant yields $\epsilon_y/\kappa_y = 2.0$. (b) $\epsilon_y^3/\kappa_x^+ = 0.0069$ Å^{-2}. This quantity is proportional to M/L^3, from which the single-step stiffness Σ_1 can be deduced.

observed to hold for steps on Si(113). To our knowledge, anisotropic dynamic scaling has not previously been observed. In view of the simplicity of the model, we anticipate that this behavior may be generic to different uniaxial systems that undergo phase separation and coarsening. Beyond 1000 s, an ordering regime follows in which the equilibrium grooved morphology is approached [16], as evidenced by the approach to a limiting groove size and the continually decreasing scattering peak widths.

The theoretically constant ratio M/L^3 may be estimated as $\Sigma_1/k_BT\ell_0$ [14]. It follows that the single-step stiffness is estimated to be of the order of $\Sigma_1 \simeq 0.72$ meV Å^{-1} for $k_BT = 100$ meV. For comparison, we note that at the same temperature the stiffness of S_B steps on Si(001) is approximately 1 meV Å^{-1}, and that of S_A steps is 7 meV Å^{-1} [17]. For steps on Si(111), several values of the stiffness have been reported within the range 30–68 meV Å^{-1} [11].

Previous to this Letter, the dynamics of step fluctuations on Si(001) and Si(111) have been studied by electron microscopy [11,17], yielding vivid real space images and such quantities as Σ_1 and Γ_1. Here, we have used an area detector in glancing-angle reflection geometry to demonstrate that x-ray scattering may provide complementary information concerning the collective behavior of steps undergoing a phase transformation. Specifically, after quenching a miscut Si(113) surface from above to below its faceting point, we characterized *in situ* and in real time the two-dimensional scattering function of the evolving morphology. The width of the scattering along the groove direction evolves as a power law versus time with an exponent close to 1/2, and the width of the scattering across the grooves and the peak wave vector of the scattering both evolve with an exponent of 1/6. Such is a clear realization of a simple model of groove coarsening, which focuses on the thermal fluctuations of step bunches and takes the collision between adjacent step bunches as the rate-limiting mechanism.

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[1] C. Herring, Phys. Rev. **82**, 87 (1951); C. Rottman and M. Wortis, Phys. Rep. **103**, 59 (1984).
[2] R. J. Phaneuf *et al.*, Phys. Rev. Lett. **67**, 2986 (1991); **71**, 2284 (1993).
[3] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, New York, 1983), Vol. 8.
[4] For example, N. C. Wong and C. M. Knobler, J. Chem. Phys. **69**, 725 (1978); M. Seul, N. Y. Morgan, and C. Sire, Phys. Rev. Lett. **73**, 2284 (1994).
[5] W. W. Mullins, Philos. Mag. **6**, 1313 (1961).
[6] J. S. Ozcomert *et al.*, Phys. Rev. Lett. **72**, 258 (1994).
[7] F. Liu and H. Metiu, Phys. Rev. B **48**, 5808 (1993); J. Stewart and N. Goldenfeld, Phys. Rev. B **46**, 6505 (1992); M. Papoular, Europhys. Lett. **33**, 211 (1996).
[8] S. Song, S. G. J. Mochrie, and G. B. Stephenson, Phys. Rev. Lett. **74**, 5240 (1995).
[9] J. R. Heffelfinger, M. W. Bench, and C. B. Carter, Surf. Sci. Lett. **343**, L1161 (1995); **370**, L168 (1997).
[10] S. Song *et al.*, Surf. Sci. **372**, 37 (1997).
[11] N. C. Bartelt *et al.*, Phys. Rev. B **48**, 15 453 (1993); C. Alfonso *et al.*, Surf. Sci. **262**, 371 (1992).
[12] M. W. Tate *et al.*, J. Appl. Cryst. **28**, 196 (1995).
[13] M. Seul and D. Andelman, Science **267**, 476 (1995); G. Gonnella, E. Orlandini, and J. M. Yeomans, Phys. Rev. Lett. **78**, 1695 (1997).
[14] A. Pimpinelli *et al.*, Surf. Sci. **295**, 143 (1993).
[15] S. G. J. Mochrie *et al.*, Physica (Amsterdam) **221B**, 105 (1996).
[16] V. I. Marchenko, Zh. Eksp. Teor. Fiz. **81**, 1141 (1981) [Sov. Phys. JETP **54**, 605 (1981)].
[17] N. C. Bartelt, R. M. Tromp, and E. D. Williams, Phys. Rev. Lett. **73**, 1656 (1994).