Low-Energy Electron-Microscopy Investigations of Orientational Phase Separation on Vicinal Si(111) Surfaces

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We have used low-energy electron microscopy to investigate in real time the thermodynamically driven faceting of stepped Si(111) surfaces into (7×7) reconstructed (111) facets and "step bunches." Our data are inconsistent with the thermodynamic expectation that an isolated linear facet should grow without limit: Instead we find that the width of the (7×7) reconstructed (111) facets quickly reaches a constant maximum size. We discuss the possibility that elastic relaxations caused by the facet edges are responsible for the finite facet width.

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One of the most striking predictions of the thermodynamics of solid surfaces is the possibility that surfaces of arbitrary orientation can be thermodynamically unstable with respect to the breakup, or faceting, into surfaces of different orientation [1]. While this possibility is clear in principle, there can be severe kinetic limitations which serve to hinder the creation of facets in practice. In particular, thermodynamic arguments suggest that without kinetic restrictions facets grow to infinite size, which, obviously, is not observed. A natural question is: What determines the finite size of observed facets? For solid surfaces which are not in equilibrium with the vapor phase, e.g., in vacuum, faceting must occur through surface self-diffusion, i.e., by diffusion driven by gradients in surface curvature [2]. While it is clear that such diffusion must occur via the motion of steps, many of the basic physical mechanisms governing the creation of facets are very poorly understood. Long ago, Mullins [2] proposed a model for the growth of linear facets based on classic theories of surface self-diffusion. In this paper, we present low-energy electron-microscope (LEEM) images of the faceting of vicinal (stepped) Si(111) surfaces; these unique measurements allow us to test directly the predictions of the classic theories.

From thermodynamic considerations one would expect that, once nucleated, facets would continue to grow indefinitely: For the case appropriate to Si(111), when facets grow only through atoms diffusing across the surface, Mullins [2] showed that at late times the facet width should grow as $t^{1/4}$. As discussed below, this prediction seems inconsistent with our experimental data: We find that facet growth becomes immeasurably slow once the facets reach a fixed, well-defined size. We consider two explanations of this behavior. First we examine certain simplifying assumptions made by the classical theory: In particular, we correctly treat the orientational dependence of the surface free energy (following Ref. [3]). We find that the modified theory reproduces the long-time behavior predicted by Mullins. The rather gross conflict with experiment remains. We thus consider an alternative explanation for the restricted facet growth. As has been previously noted [4], the faceting of vicinal Si(111) is driven by the (1×1)-to-(7×7) reconstructive transition. We propose that the facet size is limited not by kinetic effects, but rather by the balance between the free energy cost of the (7×7) reconstruction just above the (1×1)-to-(7×7) transition and the energy gain of elastic relaxations caused by faceting, which causes the surface to become unstable with respect to the formation of facets of a particular size. The facet size expected from these arguments is of the same order of magnitude as we observe.

LEEM is a recently developed technique which allows *real-time* surface imaging with 1 Å vertical and 100 Å lateral resolution [5]. The particular instrument used in these experiments has been described elsewhere [6]. The specimen and immersion lens are contained in an ion-pumped stainless-steel bell jar with a base pressure below 1×10^{-10} torr. The specimen was heated by electron bombardment from a tungsten filament located behind it. The known vicinal Si(111) phase diagram [4] was used for determining the (7×7)-to-(1×1) transition temperature, and further changes in temperature were determined using infrared and disappearing filament pyrometers. LEEM images of the surface in the vicinity of the (7×7)-to-(1×1) transition allowed some estimate of the stability of the temperature. For all of the data presented here, the temperature could be held constant to within 1° for tens of minutes.

The silicon specimens used were cut and polished along orientations slightly away from [111] toward $[\bar{2}11]$ by angles ranging from 0.8° to 4.0°. The doping of the specimens was *n* type with resistivity between 10 and 50 Ω cm. The specimen was cleaned by heating to approximately 1200 °C, as discussed elsewhere [7].

Figure 1 shows a series of bright-field LEEM images of

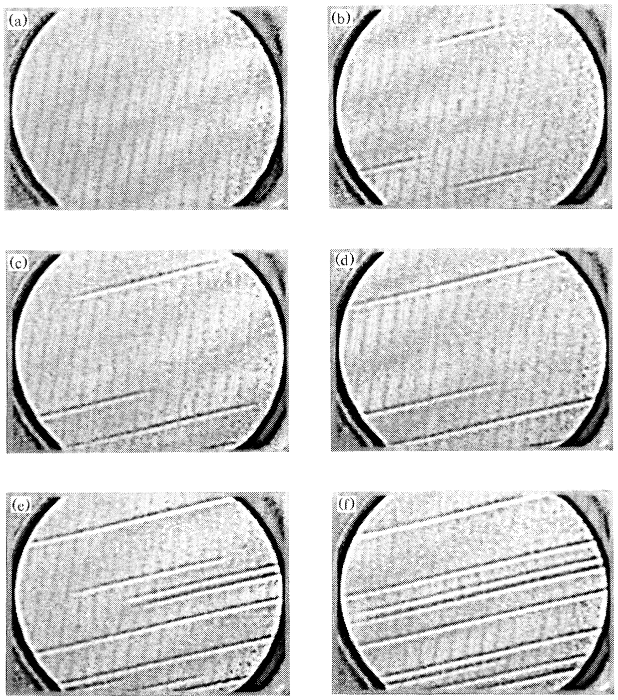

FIG. 1. LEEM images of a vicinal Si(111) surface misoriented by 4° towards the $[\bar{2}11]$ direction, as it is quenched through the (7×7)-to-(1×1) transition. The bright regions are (7×7) reconstructed facets. The temperature of (a) is 851 °C; the temperature of (b)–(f) is 848 °C. (a)–(d) are separated by 7.5 s each; (d)–(f) are separated by 37.5 s. The horizontal dimension is ≈ 4 μm.

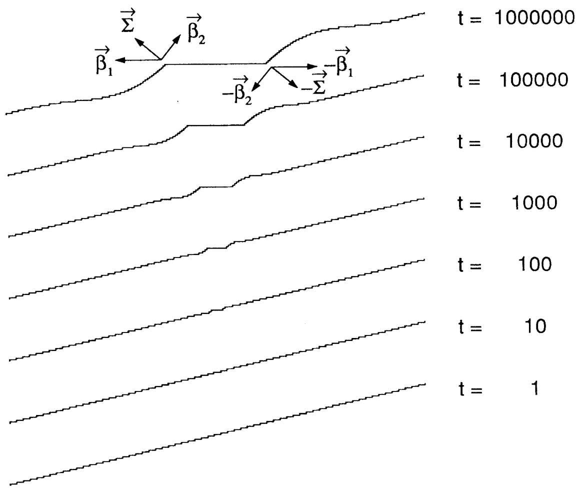

FIG. 2. Results of a model calculation of the evolution of surface profiles during the type of faceting measured experimentally. (This particular evolution is for a simple one-dimensional model of step motion described briefly in the text.) The forces created by the mismatch in surface stresses, β_1 and β_2, at the facet boundaries are shown on the final profile. These forces $\pm\boldsymbol{\Sigma}\approx\pm(\boldsymbol{\beta}_1+\boldsymbol{\beta}_2)$ create a mechanical instability; subsequent relaxations lower the surface energy, and could in principle stabilize facets of a particular width.

a surface misoriented by 4° toward $[\bar{2}11]$, as the surface is quenched by 3 °C below the (1×1)-to-(7×7) transition temperature. These images were acquired at an out-of-phase condition for the specular beam for steps of height equal to the Si(111) interlayer spacing, at which one expects optimum contrast for steps of this height. The image in Fig. 1(a), taken before the quench, appears featureless. This is consistent with the LEED observation that above the transition temperature the surface contains a uniform density of steps of 49-Å average spacing, which is below the predicted 150-Å resolution of the microscope at these conditions [8]. After the temperature is lowered, regions of high reflected intensity become resolvable, as seen in Fig. 1(b).

Figure 2 shows schematically the expected evolution of surface profiles perpendicular to the step edges during this faceting. We identify these regions as (7×7) reconstructed facets, since their appearance coincides with that of the seventh-order and integer-order (111) facet beams in the LEED pattern. When first observed, the facets are compact in all directions. Subsequent facet growth is quite anisotropic, being fastest along directions perpendicular to the misorientation direction (i.e., parallel to the step edges). Broadening of the facets along the misorientation direction, which forces a decrease in the step separation in the neighboring groups of steps, becomes noticeable only if the temperature is further lowered by several °C. The rate at which facets nucleate is sufficiently small that a given facet tends to propagate all the way across the 4-μm field of view without encountering another growing facet. The propagation speed is approximately 1000 ± 200 Å/s. Occasionally two facets grow in opposite directions in close proximity and "pin" each other, apparently due to the trapping of intervening steps [7]. Once formed, step bunches were never observed to coalesce: The sizes of the isolated facets largely determines the sizes of the facets on the completely faceted, low-T surface. This indicates that the migration of atoms across existing facets is very small.

To try to analyze the growth of these facets quantitatively, we examined profiles of intensity across the facets. The profiles (see the inset in Fig. 3) are similar to what one would expect for the surface topography postulated by Mullins (see Fig. 2) [2]. We will discuss elsewhere [7] how the surface contrast of our instrument is related to surface topography. In this Letter, we simply take the width of a facet, L, to be the distance between adjacent minima and maxima in intensity. Figure 3 shows the long-time dependence of the width. For our data analysis, time $t=0$ was chosen for a given facet as the last time before features due to the facet became observable. This dependence verifies the impression given by Fig. 1: After an initial very rapid increase, the size quick-

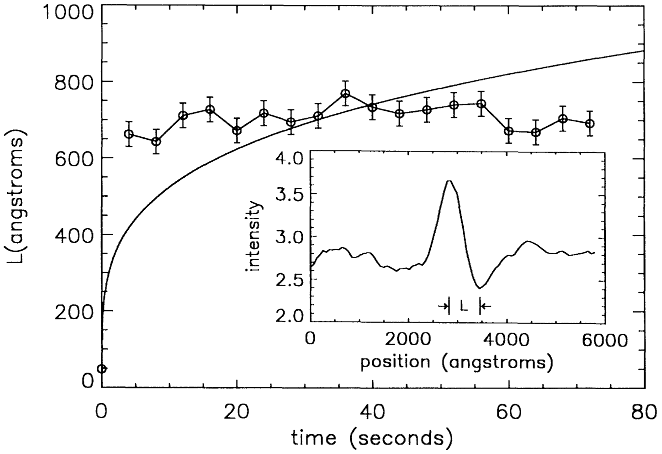

FIG. 3. The measured time dependence of the facet width (circles) compared to a fit by the $t^{1/4}$ prediction of Mullins [2]. The fit was performed with a fixed zero of time, and the amplitude as the only adjustable parameter. The jagged line is a guide for the eye. Inset: A profile of the scattered intensity across the center of the uppermost facet in Fig. 1(c).

ly saturates. The saturation size, 700 ± 100 Å, is the same for all isolated facets. This saturation is startling because thermodynamic arguments suggest that the facets should have no special size: Once the facets form, the thermodynamic driving force causing their formation should increase their size indefinitely (i.e., until facets begin to collide with each other). Figure 3 also shows the inconsistency of this time dependence with a fit by the $t^{1/4}$ behavior predicted for facets growing by surface diffusion. Independent of the proportionality constant of the fit, the $t^{1/4}$ behavior would require an increase in size by a factor of 2 between 5 and 80 s. The measured width is clearly constant in this time regime. Another telling indication of saturation of the facet sizes is the parallel facet edges. If the isolated facets were growing, the shape of the facets edges would *not* be parallel: Regions of the facets which had existed for longer periods of time would be broader.

One possible explanation of the conflict between our measurements and Mullins' theory of facet growth by surface diffusion is that certain simplifying assumptions significantly affect the growth exponent. For example, Mullins assumes an isotropic surface free energy and isotropic diffusion constants. These assumptions have been shown to yield results which are inconsistent with microscopic models of crystal growth based on the attachment of atoms at individual steps [3]. To see if these assumptions do indeed affect the power law, we have constructed a simple model of faceting, based on that proposed by Noziéres [3]. As discussed elsewhere [7], this model, in which the dependence of the free energy on step density is properly treated, and in which individual steps move with a velocity proportional to the free-energy gradient, reproduces Mullins $t^{1/4}$ law (even when the steps have moved distances only of the order of twice the initial terrace width). An overview of the results is shown in Fig. 2, which shows the time dependence of a surface profile in the model.

Since there thus seems to be no obvious *kinetic* mechanism for the saturated facet width, we turn to the possibility of an *energetic* mechanism: that *isolated* facets of a particular size are stable because they minimize the local surface free energy due to effects of surface elasticity. There has been much concern about how elastic forces influence surface morphology [9,10]. As pointed out by Marchenko [11], surface faceting creates force densities on the surface which must be balanced by elastic relaxations (see Fig. 2). Marchenko showed that these elastic relaxations cause a preference for facets of a particular size on the completely faceted surface. [The arguments are similar to those suggested by Alerhand *et al.* [9] for the spontaneous breakup of Si(100) into stress domains.] To apply these arguments to our case, we first expect [9,11] the elastic relaxations of the surface to lower the energy (per unit length parallel to the step edges) by an amount $E_{\text{el}} = -g\ln(L/a)$, with $g=(1-\sigma^2)\Sigma^2/\pi Y$, where Σ is the difference between surface stresses of the reconstructed and unreconstructed stepped regions of the surface (see Fig. 2), Y and σ are Young's modulus and Poisson's ratio for Si, respectively, a is on the order of the (7×7) unit-cell lattice constant perpendicular to the step edges (i.e., ~47 Å), and L is the width of the facet. This elastic relaxation *favors* faceting [just as it favors the spontaneous breakup of Si(100) into stress domains]. Above the (7×7)-to-(1×1) phase transition, faceting is opposed by the free-energy cost of forming the (7×7) reconstruction: The total free energy per unit length along the facet is $F_{\text{tot}}(T,L) = L\Delta f(T) + E_{\text{el}}(L) + \epsilon$, where $\Delta f(T)$ is the free-energy cost (per unit area) of converting the unreconstructed stepped surface into (7×7) reconstructed (111) facets, and ϵ is the energy cost (per unit length) for forming the edges of the facets (i.e., the phase boundaries between unreconstructed and reconstructed regions) [12]. Clearly, $\Delta f(T)$ decreases with increasing temperature, and vanishes at the thermodynamic faceting transition. The inclusion of the elastic term causes the surface to become unstable to the formation of isolated facets of finite size *above* the temperature at which Δf vanishes. Simultaneously minimizing F_{tot} with respect to L and setting F_{tot} equal to 0 yields $L_{\min} = a\exp(1+\epsilon/g)$. The temperature of the instability is determined by $\Delta f(T) = g/L_{\min}$. Our observation of $L_{\min} \approx 700$ Å suggests that $\epsilon \sim 1.7g$. To estimate the order of magnitude of g we suppose that Σ is roughly the difference between the surface stresses of the (7×7) reconstructed surface (measured by Martinez, Augustyniak, and Golovchenko [13] to be 0.185 eV/Å^2) and the stress of the (2×2) adatom-covered Si(111) surface (estimated by Vanderbilt [14] to be 0.14 eV/Å^2). Thus $g \sim 0.0006$ eV/Å, which would require that ϵ be ~0.0010 eV/Å, or ~330 K per width of the (7×7) unit cell, which seems reasonable given the transition temperature of ~ 1100 K.

In summary, have observed the growth of isolated reconstructed facets on vicinal Si(111). We find that these facets grow to a well-defined size which largely determines the size of the facets on the completely faceted low-temperature surface. However, the existence of a well-defined size of an isolated facet conflicts with simple pictures of facet growth. To explain the saturation in facet width, we have tentatively proposed that elastic relaxations of the surface caused by the faceting play a role [15].

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[a] Also with the Institute of Physical Science and Technology.

[1] C. Herring, Phys. Rev. **82**, 87 (1951).

[2] W. W. Mullins, Philos. Mag. **6**, 1313 (1961).

[3] P. Nozières, J. Phys. (Paris) **48**, 1605 (1987).

[4] R. J. Phaneuf, E. D. Williams, and N. C. Bartelt, Phys. Rev. B **38**, 1984 (1988).

[5] E. Bauer and W. Telieps, Sc. Micr. Suppl. **1**, 99 (1987).

[6] L. H. Veneklasen, Ultramicroscopy **36**, 76 (1991).

[7] R. J. Phaneuf, N. C. Bartelt, W. Święch, E. D. Williams, and E. Bauer (to be published).

[8] J. Chmelík, L. H. Veneklasen, and G. Marx, Optik (Stuttgart) **83**, 155 (1989).

[9] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[10] F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

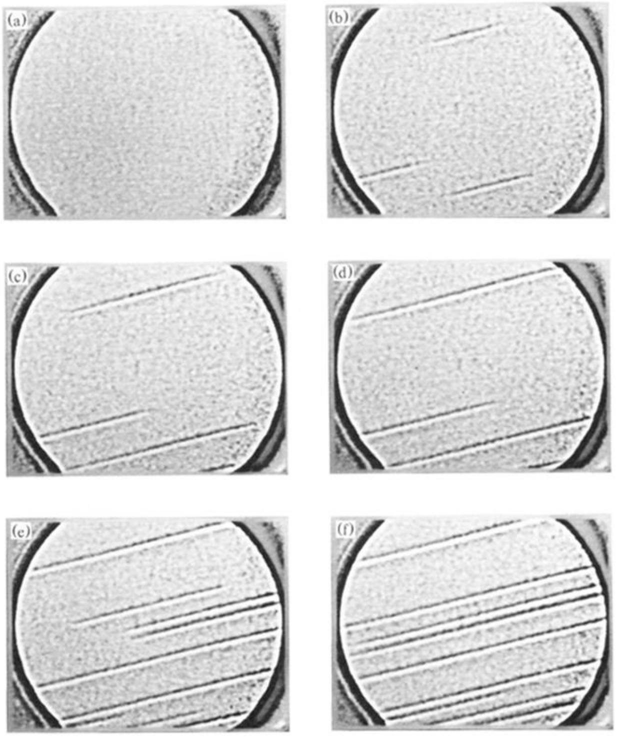
[11] V. I. Marchenko, Zh. Eksp. Teor. Fiz. **81**, 1141 (1981) [Sov. Phys. JETP **54**, 605 (1981)]. Note Marchenko determines the lowest-energy size of facets on a surface completely covered by facets: This size will in general be different from the size of an isolated facet at the onset of faceting given in the text.

[12] More precisely, if $f_{1\times1}(s,T)$ is the free energy per unit area [projected onto the (111) plane] of the unreconstructed stepped surface as a function of surface slope s, and $f_{7\times7}(T)$ is the free energy per unit area of the reconstructed surface, then $\Delta f = f_{7\times7} - f_{1\times1} - s\,\partial f_{1\times1}/\partial s$.

[13] R. E. Martinez, W. M. Augustyniak, and J. Golovchenko, Phys. Rev. Lett. **64**, 1035 (1990).

[14] D. Vanderbilt, Phys. Rev. Lett. **59**, 1456 (1987).

[15] The same argument would predict an equilibrium size of (7×7) domains on singular (111) surfaces at temperatures near the (1×1)-to-(7×7) transition. This is consistent with the observations on Si(111) surfaces with widely spaced steps of N. Oskabe, Y. Tanishiro, K. Yagi, and G. Honjo, Surf. Sci. **109**, 353 (1981).



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