Kinetics of Faceting Driven by Attractive Step-Step Interactions on Vicinal Si(113)

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We have studied the far-from-equilibrium kinetics of faceting caused by short-ranged attractive step-step interactions on vicinal Si(113), using scanning tunneling microscopy. We show that a network of step bunches coarsens via both zipping up of the neighboring step bunches and irreversible binding events which alter the local topological configuration. A step-network model which incorporates the irreversible step-bunch-binding events yields quantitative understanding of the experimental results.

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On crystal surfaces with arbitrary orientation, breakups of surfaces into regions of two or more different orientations, or faceting, occur due to the orientational dependence of the surface free energy. Though the thermodynamic arguments for faceting have long been well established [1], the kinetics of faceting is a long-standing problem for surface physics. Mullins [2] pioneered the study of the kinetics of facet growth, developing a one-dimensional mathematical formulation in terms of a continuum model. However, more detailed and quantitative understanding of faceting kinetics requires exploration of the step dynamics, since the surface mass transport depends on the nature of steps below the roughening temperature. Vicinal Si(113) surfaces are appropriate for investigating such step dynamics during faceting. Song and Mochrie [3] have first observed that faceting occurs on vicinal Si(113) surfaces by x-ray scattering, and then theoretical works [4–6] have shown that the observed orientational phase diagram for equilibrium surface morphology is characteristic of vicinal surfaces with short-range attractive step-step interactions and long-range repulsive step-step interactions. Recently, similar morphological features involving attractive step-step interactions have been found on a TaC surface [7]. As for the kinetics of the faceting on vicinal Si(113) surfaces, it has been observed that the characteristic length of hill and valley structure increases as $t^{1/6}$ [8–10], different from the facet growth as $t^{1/4}$ under surface diffusion, which is expected from the continuum model [2].

In this Letter, we study the far-from-equilibrium kinetics of faceting due to attractive step-step interactions, using a variable temperature scanning tunneling microscope (STM). Measurements were performed after a temperature drop to far below the transition temperature, establishing far-from-equilibrium conditions for the subsequent kinetic processes. We analyze the observed time evolution of surface morphology in terms of the continuum step model. Under these conditions, we find that facet growth results from coarsening of a network of step bunches via zipping up of neighboring step bunches and irreversible step-binding events which alter the local topological configuration. We extend the continuum step model to study the two-dimensional pattern evolution of a step network, and demonstrate that the step-network model reproduces not only the time scaling behavior but also real time evolution of surface morphology.

We have studied the Si(113) surface misoriented by 1.7° toward a low symmetry azimuth which is rotated by 33° to $[\bar{3}\bar{3}2]$ from $[\bar{1}10]$. The experiments were performed in an ultrahigh vacuum chamber with a base pressure of 3.0×10^{-8} Pa, equipped with a variable temperature STM. We observed morphological changes in the course of annealing at 600 °C, which is lower than the faceting temperature of ~720 °C for this surface from an initially uniformly stepped surface formed at 1000 °C.

Figure 1 shows wide area STM images of the surface annealed at 600 °C for various annealing periods and quenched to room temperature. In these STM images, we observe networks of step bunches and coarsening with increasing annealing time. In Fig. 1(d), we show the

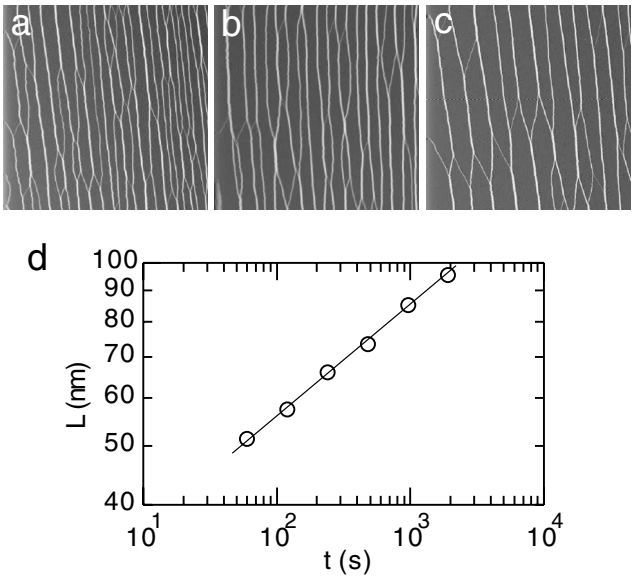

FIG. 1. 1300 nm × 1300 nm STM images of Si(113) surfaces taken at room temperature after annealing at 600 °C for (a) 1 min, (b) 8 min, and (c) 32 min. (d) Time dependence of the average terrace width.

measured time dependence of the average terrace width L, showing a power law dependence, i.e., $L(t) \sim t^{\phi}$. From the data, the exponent ϕ is determined to be 0.18 ± 0.02, in agreement with $t^{1/6}$ previously observed by the x-ray scattering measurement of Song *et al.* [8,9].

To see how a network of step bunches coarsens, we have monitored the evolution of a step configuration while annealing the sample at 600 °C. An example of a sequence of STM images is shown in Fig. 2. After annealing the surface for 530 s, step bunches have already grown and formed a network. We could not directly observe the process of formation of such a random network of step bunches from regularly arranged single steps in the very early stage, because of the sample drifting following the stepwise temperature change. At such a low temperature, a step bunch neither fluctuates largely nor debunches by thermal excitation. Distinct changes in the step configuration are recognized only in the vicinity of points where two step bunches merge. One case is that the merger points propagate along the step direction just like zipping up (one of them is indicated by a large arrow in Fig. 2). Another distinctive feature is that the neighboring step bunches are mediated to approach with each other by a crossing step trapped between them, as shown by the small arrow in Fig. 2. In Fig. 3, we show the measured distance l between the step bunches which are connected by a crossing step (see inset of Fig. 3) as a function of time. When the distance between the step bunches decreases down to ~30 nm, the two step bunches suddenly contact each other, and the topological configuration of the network changes. The mechanism of this behavior has not been investigated in detail, because such rare events are difficult to capture in high resolution (small area, small time step) imaging. However, it does appear that the onset of this topological change is associated with thermal fluctuations of the step bunches since this kind of change in step-bunch topology was not observed at lower temperatures.

The basic theory of the motion of continuous steps was well established for various physical situations [11–13]. Previously, we have quantitatively explained the local zipping move, applying the theory to a ramified step configuration by allowing for the effect of the short-range attractive step-step interaction in the boundary condition [14]. In order to treat the coarsening of network structures of step bunches, the surface morphology is represented by a network of strings where each string is connected with two other strings at the both ends. Assuming attachment/detachment limited kinetics here, we describe the time evolution of the configuration of a step bunch as

$$\frac{\partial x_i(y)}{\partial t} = \frac{\Gamma_n \tilde{\beta}_n}{kT} \frac{\partial^2 x_i}{\partial y^2}, \tag{1}$$

where $x_i(y)$ is the position of the ith step bunch at point y along the step direction, n is the size of the step bunch,

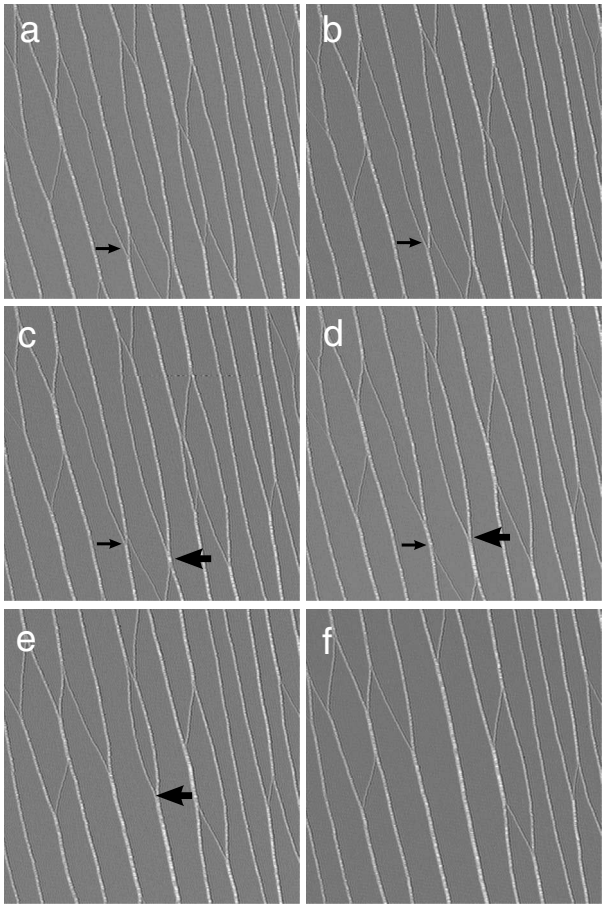

FIG. 2. The time evolution of surface morphology during faceting at 600 °C. The images correspond to (a) 530 s, (b) 610 s, (c) 650 s, (d) 690 s, (e) 930 s, and (f) 1085 s, after starting to anneal at 600 °C.

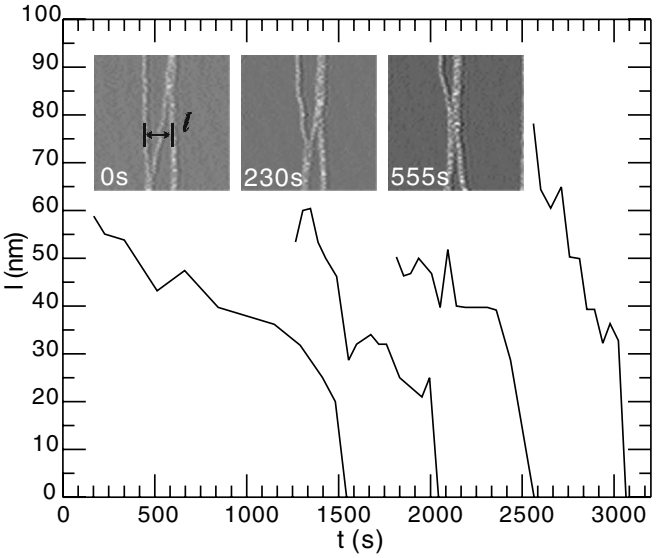

FIG. 3. The time dependence of the distance l between the step bunches which are mediated to approach with each other by the crossing step. The inset shows an example of crossing-step-mediated approaching of step bunches.

and Γ_n and $\tilde{\beta}_n$ are the mobility and the stiffness of the step bunch, respectively. In this model, the shape of a step bunch evolves so that the local curvature may decrease. Since the attractive step-step interaction is short ranged, we are able to incorporate its effect in the boundary condition of Eq. (1). Here we assume that a step bunch always contacts with the neighboring step bunches at an angle which minimizes the local surface free energy. The contact angle θ, which is determined by a competition between the energy gained by the attractive interaction and the energy lost by increasing the length of the step bunch, is given by

$$\cos\theta = \frac{nh}{\tilde{\beta}_n \tan\phi}\left(\frac{\gamma_{\text{bunch}}}{\cos\phi} - \gamma_{113}\right), \qquad (2)$$

where γ_{113} and γ_{bunch} are the free energy of (113) facets and step bunches per unit area, respectively, ϕ is the angle between the (113) facet and the step bunch, and h is the height of the single steps. Both the mobility and the stiffness of the step bunch appearing in Eqs. (1) and (2) in general depend on the bunch size n. Here we assume that $\tilde{\beta}_n = n\tilde{\beta}_1$, and that $\Gamma_n = \Gamma_1/n$; therefore the factor of n cancels in Eqs. (1) and (2) and the behavior of each step bunch is independent of its bunch size. Previously, Song and co-workers assumed these relationships [9], and we confirmed the linear dependence of the step stiffness on bunch size using STM [15]. Yamamoto [16] has predicted these dependences of the stiffness and the mobility for a group of steps on rough surfaces in the harmonically interacting step picture [17].

As shown in Fig. 2, the approach of step bunches through zipping leads to a change in topological configuration of the step network when the bunches become sufficiently close. In particular, the reconnection in the network configuration from an H-shaped connection with a crossing step to an X-shaped connection, as shown in the inset of Fig. 3, plays an important role in the coarsening of the network, since it triggers another zipping move. Our equations of step motion, which describe the curvature driven step motion, reproduce the initial slow decrease in distance l shown in Fig. 3. However, the final rapid decrease leading to the contact of step bunches is not reproduced, because they contain no term representing a strong bunch-bunch interaction. Instead, by the use of Eqs. (1) and (2), the H-shaped configuration eventually ceases to change as the distance l decreases to a certain value, since the step curvatures become very small during the relaxation. To incorporate the irreversible binding that leads to step-bunch merging, we introduce a characteristic length l_c as an empirical parameter. When the distance l between the step bunches in an H-shaped configuration decreases down to l_c, we mechanically change the H-shaped configuration to an X-shaped one as experimentally observed. To examine this model, we propagate the configuration extracted from the STM image in Fig. 2(a) forward in time, numerically integrating Eq. (1) while allowing the alteration of the topological configuration of the network. In the numerical integration, we use a rescaled time: $\tau = t(\Gamma_1\tilde{\beta}_1/kT)$, thus only θ and l_c are parameters for the simulation. Here we set parameters estimated from the experimental results: $\theta = 30°$ and $l_c = 35$ nm. Figure 4 shows the result of the numerical simulation. One can see that the simulation qualitatively reproduces the observed time evolution of the step configuration shown in Fig. 2. From comparison between the time scales in the simulation and the experiment, we estimate that $\Gamma_1\tilde{\beta}_1/kT = 90 \pm 20$ nm^2/s.

To quantify the scaling properties in our kinetic model, we performed larger scale simulations, employing the experimental step configuration extracted from the 1300 nm $\times$ 1300 nm STM images of a surface quenched from 1000 °C to room temperature as initial configurations. On each surface, a fine random network of step bunches (mainly, single, double, and triple steps), which is formed by random coalescence of thermally fluctuating steps in the earlier stage of faceting, is frozen. The resulting calculated time dependence of average terrace width is shown in Fig. 5. Here we set l_c and θ to 35 nm and 30°, respectively, and the result is averaged over nine individual calculations with different initial configurations. The result is consistent with the power law dependence on time, though the range of the data is too narrow because of the simulation in a finite system size. The obtained

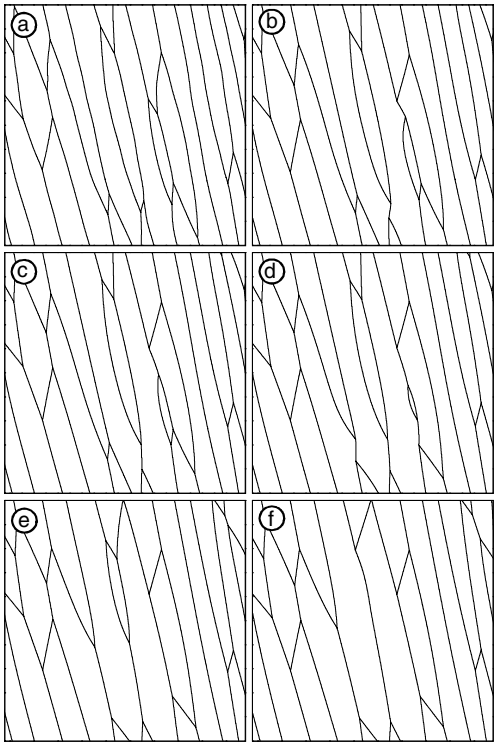

FIG. 4. Sequence of configurations generated in the simulation. (a) starting configuration created from the experimental data in Fig. 2(a). The configurations correspond to (b) $\tau = 7000$, (c) $\tau = 11\,000$, (d) $\tau = 14\,000$, (e) $\tau = 36\,000$, and (f) $\tau = 50\,000$, where τ is the rescaled time, $t(\Gamma_1\tilde{\beta}_1/kT)$.

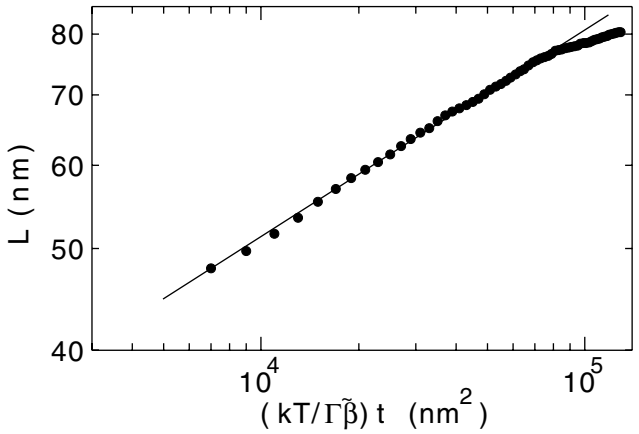

FIG. 5. The time dependence of the average terrace width obtained by the simulation for $l_c = 35$ nm and $\theta = 30°$.

exponent is 0.18 ± 0.02, which is consistent with the time dependence as $t^{1/6}$. A comparison in amplitude of the power law fit between the simulation and the experiment [Fig. 1(d)] yields $\Gamma_1 \tilde{\beta}_1/kT = 100 \pm 20$ nm^2/s, which is consistent with the value estimated from the simulation in Fig. 4. Though the fate of the surface morphology depends on the parameter l_c, we confirmed that the exponent is independent of l_c in the range of 25–50 nm. For the exponent of $1/6$, Mochrie and co-workers [9] have also proposed a model in which step bunching occurs via collisions of thermally fluctuating step bunches. Though their model is appropriate for higher temperatures at which thermal fluctuations are crucial, our model considers faceting at lower temperatures where binding of step bunches following a collision is irreversible.

In summary, we have studied the step dynamics in faceting caused by the short-range attractive step-step interactions in a regime far from equilibrium. In the late stage of the faceting, the two-dimensional network of step bunches coarsens via zipping of the neighboring step bunches and irreversible binding events that alter the network topology. For coarsening of the step network, we have constructed a phenomenological model based on the continuum step model, incorporating the irreversible binding events as a distinct change in junction topology occurring when bunch separations become smaller than a critical distance. The numerical calculation reproduces the qualitative two-dimensional pattern evolution and the quantitative time scaling behavior. The essential physics of the complex two-dimensional evolution of morphology is captured by only three important parameters: the product of the step stiffness and the step mobility, the step contact angle, and a critical distance for irreversible binding.

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