Faceting through the Propagation of Nucleation

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(Received 31 August 1995)

Experiments show that faceting of a vicinal surface can be induced by surface reconstruction, which often occurs only on sufficiently wide terraces. We study this process using a one-dimensional terracestep model that assigns a lower free energy to terraces wider than a critical width w_c . When mass is conserved locally, through surface diffusion, we find that a reconstructed terrace can nucleate the growth of another such terrace nearby. The dynamics and spatial distribution of facets arising from this model are very different from that produced by conventional thermal nucleation.

PACS numbers: 68.35.Bs, 64.60.Qb, 82.65.Dp

Surface reconstruction can often cause a vicinal surface with a single macroscopic orientation to facet into a "flat" surface, on which the reconstruction occurs, and a much more sharply inclined surface with closely spaced steps (a "step-bunched" surface) [1]. Faceting experiments on a number of different systems, such as O/Ag(110), Si(111), Pt(111), and Au(111), have found varying, but noticeable, degrees of regularity in the size and spacing of the flat facets [2–6]. It is hard to reconcile these regularities with a picture of random nucleation of the reconstructed regions.

While a number of different factors can contribute to the facet spacing in particular experiments, we argue here that there exists a rather general kinetic mechanism that can lead to regular features in the faceting process. We consider the case where the reconstruction effectively occurs only on terraces wider than some critical terrace width w_c , and assign a lower free energy (due to reconstruction) for terraces wider than w_c . When w_c is much greater than the initial terrace spacing w_i , a nucleation event is required to form the first wide terrace. The subsequent temporal and spatial behaviors of the faceting process depend crucially on the mechanism of mass transport on the surface. When mass is conserved locally, as in the case of faceting through surface diffusion, the motion of a step is directly coupled to the motion of neighboring steps. We find that a growing nucleus can induce the formation of another nucleus nearby [7]. This can lead to a propagation of nucleation events. We call this process induced nucleation. The faceted surface formed in this way will exhibit very different characteristics from the conventional thermally nucleated one. In this process, the average number of steps in a bunch, n_b , and final facet size, W_f , are mainly selected by the dynamics. Some aspects of the regularity found in recent experiments may be explained by this mechanism.

The kinetics of faceting on a vicinal surface is studied using a one-dimensional (1D) terrace-step (TS) model. Although a 1D model cannot describe the formation of the initial thermally produced 2D critical nucleus, the motion of steps after that initial nucleation event can be described by a 1D model. In most cases, once a nucleus is created, it propagates much faster in the direction parallel to the steps and quickly forms an elongated cigarlike shape. The steps which bound the lateral regions of the elongated nucleus are usually almost straight [4]. The 1D variable, the position of the *n*th step x_n in our TS model is assumed to describe the *average* (over the lateral size L_y of the elongated nucleus) position of the *n*th step.

The projected free energy [8] of a (unreconstructed) vicinal surface inclined at an average angle θ to the lowindex face on which reconstruction can occur (referred to hereafter as the flat surface) is well described by [9] $f_U(s) = f_0 + \beta s + g s^3$. Here $s \equiv \tan \theta \ge 0$ is the slope of the surface. If we take the step height to be unit length, the number density of steps is given by s and the average terrace width $w_i = 1/s$. The first term f_0 is the surface energy per unit area of the flat surface, and β is the free energy per unit length to form an isolated step. The last term gives the effective interaction between the steps. This term includes the entropic repulsion between steps (due to fluctuations along the step edge) as well as possible energetic contributions such as elastic or dipole interactions [10]. In most cases, the effective interaction between steps of the same sign is repulsive (g > 0). Hence the free energy of the vicinal surface is convex downward as shown in Fig. 1 and the surface is stable with respect to faceting.

Surface reconstruction is assumed to occur only on large $(w > w_c)$ flat terraces. The driving force for



FIG. 1. Free energies for unreconstructed surface f_U [Eq. (1)] and reconstructed surface f_R [Eq. (2)] vs slope *s*. The critical slope s_c and the slope of the surface at step bunches, s_b , are given by $s_c = \epsilon_s / \epsilon$ and $s_b = (\epsilon/2g)^{1/3}$.

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faceting arises from the physically reasonable assumption that the free energy of the reconstructed flat surface has a lower value ($-\epsilon$ per unit area) than the unreconstructed flat surface but effectively a higher energy cost (ϵ_s per unit length) for forming an isolated step [11]. Hence the free energy of a reconstructed surface with slope *s* is given by [12] $f_R(s) = (f_0 - \epsilon) + (\beta + \epsilon_s)s + gs^3$.

As shown in Fig. 1, two free energy curves cross at a critical slope $s_c \equiv \epsilon_s/\epsilon$. The thick curve in the figure, given by

 $f(s) = f_U(s) - (1 - s/s_c) \epsilon \Theta(s_c - s),$ (1)

with the unit step function Θ , represents the free energy of a hypothetical system in which *all* terraces are reconstructed (unreconstructed) when the average slope s is less than (greater than) s_c . In a real system there would be a distribution of terrace widths around the average slope s, and near s_c we expect to find both reconstructed and unreconstructed terraces. This would remove the cusp at s_c and produce a smoothly varying curve in this region. Still, because reconstruction is possible, the free energy of the combined system loses overall convexity just as the uniform terrace model illustrates, and faceting will take place. Thus "phase separation" will occur between the two "phases" whose properties are determined by the usual tie bar construction as indicated by the dashed line in Fig. 1. In particular, the slope of the step bunches coexisting with the reconstructed flat surface is given by $s_b \equiv (\epsilon/2g)^{1/3}$ as shown in Fig. 1.

However, Fig. 1 does not describe the spatial distribution of terraces and step bunches. The key factor in determining the sizes of the final facets is how far the facet nuclei are from each other when they form (or, how often they are created when facets grow slowly compared to the creation of a nuclei). This requires a study of the *dynamics* of step motion as influenced by the attachment or detachment kinetics of atoms at the step edges. This in turn can be related to the chemical potential at the step edge [13]. The chemical potential ξ_n of step n (which separates the n - 1 and the *n*th terrace) is defined as the difference in the total surface free energy before and after an atom is removed from step n:

$$\xi_n = [F(w_n) + F(w_{n-1})] - [F(w'_n) + F(w'_{n-1})]$$

= $L_y[\{w_n f(w_n) - (w_n - \delta)f(w_n - \delta)\}$
+ $\{w_{n-1}f(w_{n-1}) - (w_{n-1} + \delta)f(w_{n-1} + \delta)\}]$

$$\approx \partial_{w}(wf(w))|_{w_{n}} - \partial_{w}(wf(w))|_{w_{n-1}}.$$
 (2)

Here w_n (w'_n) is the average distance between step n and n + 1 before (after) an atom is removed from the step, $L_y = 1/\delta$ is the length of a step edge (i.e., the lateral size of the facet), and $F(w_n) \equiv L_y w_n f(w_n)$ is the surface free energy of the *n*th terrace [14]. When we assume that the reconstruction effectively occurs only when a given terrace is wider than some w_c , $f(w_n)$ can be accurately approximated as in Eq. (1):

 $f(w_n) = f_U(w_n) - (1 - w_c/w_n) \epsilon \Theta(w_n - w_c).$ (3) Thus the chemical potential ξ_n of step *n* is given by

$$\xi_n = \frac{2g}{w_{n-1}^3} - \frac{2g}{w_n^3} + \epsilon \left[\Theta(w_{n-1} - w_c) - \Theta(w_n - w_c)\right].$$
(4)

We now assume that the velocity of a step is proportional to the change in free energy produced by its motion [13]. When the mass movement is nonlocal (case I), atoms at step edges effectively exchange with the reservoir (vapor) and steps move according to the chemical potential difference between the step and the reservoir:

$$\partial_t x_n = D_{\text{res}}[\xi_n - \xi_{\text{res}}], \qquad (5)$$

where D_{res} is an effective step-reservoir exchange coefficient. The chemical potential of the reservoir ξ_{res} is set to be zero when there is no overall motion of steps. However, when the mass movement is local (case II), as in mass movement through surface diffusion, we expect the current between step *n* and step *n* + 1 to be proportional to $\xi_n - \xi_{n+1}$:

$$\partial_t x_n = D_s[(\xi_n - \xi_{n+1}) + (\xi_n - \xi_{n-1})], \qquad (6)$$

where D_s is some effective surface diffusion coefficient [15].

Let us consider the case where only one (thermally nucleated) terrace is larger than w_c at time t = 0 as shown in Fig. 2(a). The surface profiles at t > 0 are obtained by (numerically) integrating the differential equations (5) and (6) with ξ_n given by Eq. (4). For case I, as shown in Fig. 2(b), the nucleated facet continues to grow indefinitely. The width of the facet increases as $t^{1/2}$ [16,17]: $w_0(t) \approx w_0(t = 0) + 2[2D_{res}\epsilon(w_i - w_b)]^{1/2}t^{1/2}$, where $w_b = 1/s_b = (2g/\epsilon)^{1/3}$ is the equilibrium step spacing in the step bunches.

On the other hand, for case II, the facet does not continue to grow indefinitely, in contrast to what simple



FIG. 2. Surface profiles at different times. (a) At t = 0, there is only one terrace which is wider than w_c (in the middle). The other terraces are uniform with width $w_i < w_c$. (b) Surface profiles at t > 0 in case I. (c) Surface profiles at t > 0 in case II. A growing flat facet induces a new nucleus for another flat facet. Here $w_b/w_i = 1/20$ and $w_c/w_i = 3$.

thermodynamic consideration would predict [4]. Rather, it grows only to a certain size and stays there [Fig. 2(c)]. This is because the local mass conservation causes a growing facet to *induce* a new nucleus which "collides" with the original facet as it grows.

To understand this process, we first consider the motion of steps in the initial stages of faceting near the original reconstructed terrace. Let the origin be the middle of this "zeroth" terrace as shown in Fig. 2(a). We assume the system is in the nucleation regime with $w_i < w_c$, and consider the simplest case, which arises when the spacing between steps in a bunch w_b is much less than w_i . From Fig. 1, this implies $\epsilon \gg 2g/w_i^3$ and means that step repulsions play an important role in the dynamics only when the spacing approaches w_b .

At t = 0, all terraces except the zeroth one are smaller than the critical width $(w_n = w_i < w_c \text{ for } n \ge 1)$. ξ_n , given by Eq. (4), is zero for $n \ge 2$ and is approximately ϵ at step 1 ($\xi_1 = \epsilon + 2g/w_0^3 - 2g/w_1^3 \approx \epsilon$). Since $\xi_1 \gg$ ξ_2 , atoms move from step 1 to step 2, allowing the facet to grow. Thus step 1 moves right and step 2 moves left, i.e., w_1 decreases and w_2 increases. Because this movement also produces an increased repulsive interaction between step 1 and 2, ξ_2 increases a little and becomes higher than ξ_3 . Although some atoms at step 2 can then move to step 3, the net motion of step 2 is still to the left as long as $\xi_1 - \xi_2 > \xi_2 - \xi_3$: more atoms come from step 1 than go to step 3. However, as time goes on (and ξ_2 continues to increase, while ξ_1 decreases), $\xi_1 - \xi_2$ eventually becomes smaller than $\xi_2 - \xi_3$. Both step 1 and step 2 now move to the *right* and w_2 now *decreases*. This occurs when the repulsive interaction between step 1 and 2 becomes large enough to drive step 2 to the right; the spacing between the two steps is then of order w_b . Since the ξ 's are rapidly varying functions of w for such spacings, a quasisteady state is quickly established in which both steps 1 and 2 move right with the same velocity [18] as the facet continues to expand.

Figure 3(a) shows x_n , the position of step *n*, as a function of time, t. We define the collision time t_1 as the time at which step 2 first begins to move to the right. The spacing between steps 1 and 2 is then of order w_b , the thermodynamically determined bunch spacing. Since $w_b \ll w_i$, it follows from Eqs. (5) and (7) that the value x_3 barely changes for $t < t_1$. If we ignore this small change, we have the following zeroth order picture. Step 1 moves right with a constant velocity, V_1 , and step 2 moves left with another constant velocity until they collide at $t = t_1$. The system then quickly achieves a quasisteady state where both steps 1 and 2 move right with the same constant velocity, V_2 . Now atoms from both steps 1 and 2 effectively contribute to the motion of step 3, which moves left until it collides with step 2 (at $t = t_2$). For $t > t_2$, steps 1, 2, and 3 move right with the velocity, V_3 , while step 4 moves left, and so on. It is straightforward to show that the velocity of steps $1, \ldots, n$ for $t_{n-1} < t < t_n$ is given by [17]

$$V_n = 6(2n + 1)D_s \epsilon / n(n^3 + 2n^2 + 2n + 1), \quad (7)$$

in the zeroth order picture. Since $V_n \sim n^{-3}$ for large *n*, we expect $t_n - t_{n-1} \sim 1/V_n \sim n^3$ and, therefore, $t_n \sim n^4$. On the other hand, the width of the zeroth terrace at $t = t_n$ is proportional to *n* since there are *n* steps in the step bunch. Thus in the absence of other nucleation events, we have $w_0(t_n) \sim n \sim t_n^{1/4}$, in agreement with the classic continuum treatment of Mullins [16]. A detailed calculation shows that

$$w_0(t) = \frac{4}{3} (72D_s \epsilon)^{1/4} (\tilde{w})^{3/4} t^{1/4}, \qquad (8)$$

for large t where $\tilde{w} \equiv w_i - w_b$.

Figure 3(b) shows the widths of the first four terraces as a function of time. As explained, for $t < t_1$, w_1 decreases while w_0 (not shown) and w_2 increase. For $t_{n-1} < t < t_n$, w_n decreases while w_{n+1} increases. Hence w_n has its maximum w_n^{\max} at $t = t_{n-1}$. In the zeroth order picture, w_n^{\max} and t_n satisfy the following equations [17]

$$w_n^{\max} = w_i + \frac{2n-1}{3n-2} \left[\sum_{k=1}^{n-1} \tilde{w} \, \frac{k}{2k+1} + \sum_{k=2}^{n-1} (w_k^{\max} - w_i) \, \frac{1}{4k^2 - 1} \right],$$

$$t_n = t_{n-1} + w_n^{\max} / V_n (1 + n^2 / (2n+1)).$$
(9)

For large *n*, w_n^{\max} increases *linearly* with *n* [$w_n^{\max} \approx (\tilde{w}/3)n$] and t_n increases as n^4 ($t_n \approx \tilde{w}n^4/18D_s\epsilon$). Note that there is a large time interval $\Delta t_n^{\max} \sim (w_n^{\max})^3$ around t_{n-1} where terrace *n* is larger than any of its neighbors.

One important physical implication of this observation is that new nuclei for reconstruction can be *induced* by a growing nucleus. Since w_n^{\max} increases with *n*, for any given critical terrace width w_c there is an integer *n* such that $w_n^{\max} > w_c$. Let n_b be the smallest *n* such that $w_n^{\max} > w_c$. Once w_{n_b} gets larger than w_c , reconstruction can occur. As w_{n_b} continues to grow it will induce another nucleus at $2n_b$. Then w_{2n_b} will induce w_{3n_b} and so on [see Fig. 2(c)]. All flat facet sizes (W_f) [all step bunch sizes (W_b)] are essentially the same and given by $W_f \approx n_b \tilde{w} [W_b \approx (n_b - 1)w_b]$, since the nuclei are separated by the same number of steps, n_b . The velocity of the nucleation front is *linear* in *t* because it always takes the same amount of time to induce a nucleus. This propagation is much faster than the conventional faceting through surface diffusion ($\sim t^{1/4}$) or through evaporation or condensation ($\sim t^{1/2}$) [16].

In real materials, this kinetic facet size selection would not be sharp due to thermal fluctuations. However, in the zeroth order approximation, aside from the original facet,



FIG. 3. The step positions and the terrace widths as a function of time. Here $w_b/w_i = 1/20$. Recall that $w_n = x_{n+1} - x_n$ when comparing (a) and (b).

only one terrace is larger than w_i at a given time. As n and hence w_n^{max} increase, there is an increasing long interval Δt_n^{max} where terrace n is larger than any others due to the induced nucleation mechanism. A thermal fluctuation leading to a width $w > w_c$ is more likely to occur on such a wide terrace. Thus even when thermal fluctuations contribute to achieving a width $w_n > w_c$, this is most likely to happen on that largest terrace and probably when w_n^{max} is close to w_c .

This simple zeroth order picture breaks down if the inequality $\epsilon \gg 2g/w_i^3$ (or $w_i \gg w_b$) is not satisfied. Then we can solve the set of equations (7) numerically. We then find the effects of mass conservation spread out more evenly as w_b/w_i increases, producing slower variation in adjacent terrace widths. Since there are many large terraces on which thermal nucleation may occur, nucleation sites and times are less precisely determined in this case. This is the limit where the continuum theory of Hibino, Homma, and Ogino [7] most likely applies.

To understand the role of thermal fluctuations in the nucleation process we have begun to study a 2D TS kink model that builds in the idea of a critical nucleation width. The preliminary results of a Monte Carlo simulation show the propagation of nucleation for large kink energy and large ϵ [17]. As ϵ decreases, the propagation of nucleation is less clear but still the final faceted surface shows more regularity than would be expected from random thermal nucleation without local mass conservation.

For quantitative comparison with experiments, more studies are needed, including, in particular, a detailed analysis of a 2D model. However, many of the qualitative predictions of the present 1D model of induced nucleation, such as the regularity in spacing and size of the final terraces, may have already been observed in some recent experiments.

We are grateful to N. Bartelt, D.-J. Liu, J.E. Reutt-Robey, and E. Williams for helpful discussions.

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