Networks of Steps on Crystal Surfaces

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Scanning tunneling microscopy observations show that steps on vicinal surfaces near (110) missing-row reconstructed surfaces of metals such as Au and Pt tend to form networks. A simple microscopic model introduced here shows that these networks are unstable (or metastable) against faceting. This leads to the formation of ridges between rounded areas and of angles in the equilibrium shape of the (110) facet.   [S0031-9007(96)00334-1]

The free energy per unit of area of a crystal surface depends rather strongly on the surface orientation. Typically, especially at low temperatures, certain orientations corresponding to high symmetry directions in the crystal lattice have low free energies and appear as large flat areas (facets) in the equilibrium crystal shape (ECS).

Orientations tilted over a small angle with respect to a facet are called vicinals and consist of steps separated by large terraces. The free energy of a vicinal is typically expressed as an expansion in the step density p ($p \ll 1$).

In this Letter we investigate the surface free energies of certain vicinals of missing-row (MR) reconstructed (110) facets of metals such as Au and Pt. We will show that these orientations are, in fact, not stable which leads to faceting, or in other words to the presence of sharp edges in the ECS [1].

Figure 1 shows a typical pattern of steps found on vicinal orientations of Au and Pt(110) surfaces [2,3] (areas of equal contrast denote terraces of the same height). Instead of an array of parallel steps, as found ordinarily on such surfaces, one sees a pattern of zigzagging steps, which repeatedly touch each other at a collection of contact points. We call this pattern a *network* of steps, since we can think of it as two arrays of roughly parallel

steps, making on average angles ϕ and $-\phi$, with the vertical direction in Fig. 1.

Why is the surface forming this pattern? The explanation [3] is related to the large energy difference between two different types of steps which can be generated on the surface: the clockwise (CW) steps and the anticlockwise (ACW) steps, illustrated in the examples of Fig. 2. Scanning tunneling microscopy (STM) observations at room temperature show that ACW steps appear very rarely on the surface and CW steps, which cost lower energy, prevail [2,3]. In Fig. 2(a) we show two possibilities for the microscopic configurations of steps: on the left side the typical crossing pattern as observed in STM experiments; on the right side two pieces of isolated steps, coming close to each other in the given example. Figure 2(b) shows the cross section of the surface along the segment AB: going from A to B one meets a CW up step and a CW down step, with a change in the reconstruction state as shown in the figure. In the configuration on the right side of Fig. 2(a), the points C and D belong to the same terrace, and therefore belong to the same reconstructed state. Only a combination of a CW and an ACW step matches this requirement [Fig. 2(c)]. The situation where four terraces meet in a single point is favored, since only
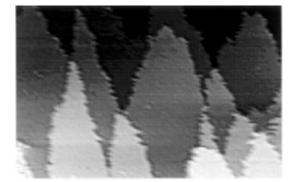

FIG. 1. STM images of vicinals of Au(110) (courtesy of M. S. Hoogeman, L. Kuipers, and J. W. M. Frenken, AMOLF Amsterdam). The area shown is of 190 nm × 120 nm at $T = 550$ K, with a miscut angle of 0.07 deg.
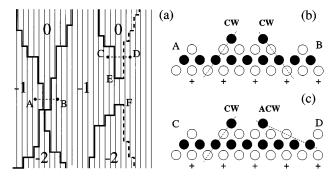

FIG. 2. (a) Top view of the surface with two possible step configurations (see text). The thin lines are the top rows of the reconstruction, while thick lines denote clockwise (solid) or anticlockwise (dashed) steps. (b), (c) Cross sections along the segments AB and CD of (a).

low energy CW steps are involved. In fact, the combination of a CW and an ACW step, as in Fig. 2(c), can also be avoided connecting, e.g., the points E and F by a domain wall between the two reconstructed phases. However, such domain walls are energetically costly and therefore the crossing (in which one could say the domain wall is reduced to a single point) is preferred.

We present here a theoretical estimate of the total free energy of the network. First, we calculate the free energy of a single isolated step under an angle ϕ with the y axis (see Fig. 3). We introduce δ_x and δ_y, the energies per unit of length of step segments along the x and y axes, denoting the directions perpendicular ([001]) and parallel ([1$\bar{1}$0]) to the MRs. Only step segments in the $\pm x$ directions and the $+y$ direction are allowed (i.e., we forbid anticlockwise step segments), which will have length $2a$ and $a/\sqrt{2}$, respectively. In this approximation the step free energy becomes identical to the surface free energy of
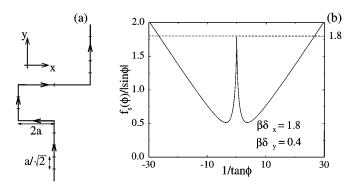

FIG. 3. (a) Example of microscopic configuration of a step. (b) Step free energy per unit of projected length onto the x direction.

a one dimensional solid-on-solid model (see, for instance, Ref. [4]). In the present case we find a step free energy per unit of length of the following form:

$$f_s(\phi) = \frac{\ln z(\phi)}{2\beta} |\sin\phi| + \left[\delta_y + \frac{\sqrt{2}}{\beta} \ln\left(\frac{2\cosh(2\beta\delta_x) - [z(\phi) + 1/z(\phi)]}{2\sinh(2\beta\delta_x)}\right)\right]\cos\phi, \tag{1}$$

where $\beta = 1/(k_B T)$ and

$$z(\phi) = \frac{\cosh(2\beta\delta_x)t(\phi) + \sqrt{1 + \sinh^2(2\beta\delta_x)\,t^2(\phi)}}{1 + t(\phi)}, \tag{2}$$

with $t(\phi) = |\tan\phi|/2\sqrt{2}$. The limiting value for the free energy of a step running perpendicular to the MRs is simply $f_s(\pi/2) = \delta_x$: such steps are perfectly straight.

It is convenient to consider $f_s(\phi)/|\sin\phi|$, the step free energy per unit of projected length along the x direction. This quantity is shown in Fig. 3(b): it has a local maximum with a cusp at $\phi = \pi/2$. For steps slightly inclined with respect to this orientation it decreases, since such steps have a larger entropy. Obviously $f_s(\phi)/|\sin\phi|$ diverges for $\phi \to 0$. The function reaches its minimum at an angle ϕ_0 satisfying

$$t(\phi_0) = \frac{\sqrt{[\cosh(2\beta\delta_x) - e^{-\beta\delta_y/\sqrt{2}}\sinh(2\beta\delta_x)]^2 - 1}}{e^{-\beta\delta_y/\sqrt{2}}\sinh(2\beta\delta_x)}. \tag{3}$$

Note that the quantity under the square root may become negative; this happens at temperatures above the roughening temperature (at small values of $\beta\delta_x$ and $\beta\delta_y$) when the solid-on-solid approximation for the step free energy $f_s(\phi)$ is not positive definite and the simple theory considered here breaks down. Equation (3) gives an explicit relationship between the angle ϕ_0, the step energies per unit length δ_x and δ_y and temperature. This relationship may be used to determine the parameters δ_x and δ_y from measured values of ϕ_0 at different temperatures.

To calculate the total free energy as a function of the orientation we use the simple geometric construction of

Fig. 4; we suppose that a miscut along the [1$\bar{1}$0] direction is generated by a pattern of crossing steps forming angles ϕ_1 and ϕ_2 with the y axis. The parameters p and q are fixed and denote the tangents of the tilting angles of the surface along the [1$\bar{1}$0] and [001] directions. The dashed inclined lines indicate hypothetical parallel isolated steps that would generate the same macroscopic orientation as the network; $1/q$ and $1/p$ are the average distances between these steps along the x and the y direction. To each pair of crossing steps we associate an interaction free energy ϵ, which keeps account of both short and long range interactions between them.

The free energy per unit of projected area reads

$$\tilde{f}(p,q,\phi_1,\phi_2) = f_0 + \frac{1}{2A}[l_1 f_s(\phi_1) + l_2 f_s(\phi_2) + \epsilon], \tag{4}$$

where f_0 is the free energy per unit area of the (110) facet, while l_1 and l_2 are the lengths of the two sides
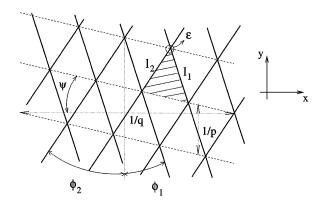

FIG. 4. Schematic view of the network of crossing steps.

of the dashed triangle, of area A, shown in Fig. 4. The following relations hold: $2A = l_1 l_2 \sin(\phi_1 - \phi_2)$, $l_1 = \cos\psi / [p \cos(\phi_1 - \psi)]$, and $l_2 = \cos\psi / [p \cos(\phi_2 - \psi)]$, where ψ is the angle shown in Fig. 4 ($q = p \tan\psi$).

The actual free energy can be found by minimizing the free energy (4) with respect to ϕ_1 and ϕ_2; using the preceding relations for A, l_1, and l_2 one can show that, to lowest orders in p and q and for $\psi < \pi/2 - \phi_0$, this amounts to minimizing $f_s(\phi)/|\sin\phi|$. Therefore the minimum of (4) is at $\phi_1 \approx -\phi_2 = \phi_0 + O(p, q)$, where ϕ_0 is the angle given by (3). Substituting this back into (4) and expanding to lowest orders in p and q we find

$$f(p, q) = f_0 + \frac{f_s(\phi_0)}{\sin\phi_0} p + \frac{\epsilon}{2}\left(\frac{p^2}{\tan\phi_0} - \tan\phi_0 q^2\right).$$

(5)

The term linear in p represents the contribution of noninteracting steps. The interaction terms are quadratic in the step densities, differently from usual step-step interactions which lead to terms cubic in the step densities [5]. The origin of the quadratic term can be understood easily: the number of step crossings per unit area is simply proportional to the product of the densities, $p \pm q \tan\phi_0$, of the two types of steps. ϵ is the interaction free energy of two crossing steps and depends obviously on the angles ϕ_1 and ϕ_2; however, to lowest order $\phi_1 = -\phi_2 = \phi_0$, so the angle dependence of ϵ can be neglected. In addition, there are long range interactions between parallel steps, but they will only contribute to terms of cubic or higher order in the step density expansion of the free energy [5].

For $\psi > \pi/2 - \phi_0$ the expression (4) is minimized by a single array of steps (so $\phi_1 = \phi$ and $l_2 = 0$) and the free energy takes the usual form [5]

$$f(p, q) = f_0 + f_s(\phi)\sqrt{p^2 + q^2} + O((p^2 + q^2)^{3/2}).$$

(6)

Notice that the expression (5) for the free energy of the step network is a nonconvex function of p and q. This leads to instabilities and to the disappearance of certain ranges of orientations from the equilibrium crystal shape. Our results imply that the network is unstable irrespective of the sign of ϵ. *A priori* either sign could be expected: the increase in horizontal kink length at a step crossing compared to an ordinary kink yields a positive contribution to ϵ, whereas for $\phi_0 < 45°$ the elastic interaction between crossing steps usually is negative [6]. The two possibilities for ϵ give rise to two different types of faceting, which we discuss separately.

(1) $\epsilon > 0$.—In this case the instability is along the q direction, as a function of the parameter p the free energy is stable. The instability can be understood as follows: a positive amount of free energy is associated with each pair of crossing steps, therefore the total free energy can be reduced by decreasing the density of crossings. By applying the Maxwell construction to Eqs. (5) and (6) one finds that the system separates into two orientations of
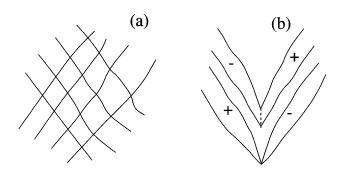

FIG. 5. (a) The network of crossing steps, and (b) a combination of two step arrays of different orientation, after the phase separation, predicted by (5) for $\epsilon > 0$, has occurred. The $+$ and $-$ indicate the opposite reconstruction phases induced by the clockwise steps.

slopes $(p, p \tan\phi_0)$ and $(p, -p \tan\phi_0)$ joining at a ridge, as depicted in Fig. 5(b).

We recall that two clockwise steps ending in a common point [as the steps shown in Fig. 5(b)] induce a different reconstruction order in either the lower or the upper terrace: they must be accompanied by a boundary separating two different reconstruction phases. It suffices having boundaries every other couple of steps, as shown in the figure. Furthermore, as in the case of crossings, the domain boundary can be avoided by having four steps joining in the same lattice point. This too is schematically illustrated in Fig. 5(b).

The *equilibrium shape of the* (110) *facet* can be found by applying the Wulff construction to the step free energy as a function of the orientation [1]. The result is shown in Fig. 6. Because of the instability of steps of orientations close to $\phi = \pi/2$, the facet shape shows sharp cusps. A typical arrangement of steps around this facet is sketched in Fig. 6(b). Notice the vertical ridges extending from the cusps.

There is no contradiction between the instability described here, and the observation of networks of steps in the STM experiments. Crystals hardly ever assume equi-
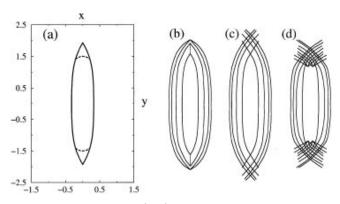

FIG. 6. Top view of the (110) facet calculated from the model for the same parameters as in Fig. 3: (a) $\epsilon > 0$ (solid line) and truncation of this shape by edges for $\epsilon < 0$ (dashed lines). Arrangement of the surrounding steps for $\epsilon > 0$ in the stable phase (b), in the metastable phase (c), and for $\epsilon < 0$ (d).

librium shapes. In many cases, though, unstable surfaces will facet after a certain amount of time; in the present case this may be extremely long. In fact, once the network has been formed, the process of disentangling it into stable orientations as the ones shown in Fig. 5(b) may require the investment of a large amount of free energy to go through very unfavorable states, and it may be difficult to observe it experimentally without a careful long annealing of the surface. For describing the surface free energy and the shape of the metastable surface one can use Eq. (5) again. A typical arrangement of steps around the (110) facet in this situation is shown in Fig. 6(c). In this case the shape profile along the y axis of the crystal for vicinal orientations is expected to be of the type $z(y) \sim (y - y_0)^2$, due to the term proportional to p^2 in the surface free energy. A free energy expansion with a term cubic in the step density would produce a shape profile with an exponent 3/2, the so-called Pokrovski-Talapov exponent (see, for instance, [1]).

Thermodynamically the metastability encountered here is highly unusual. In, e.g., a homogeneous gas-liquid system a free energy that is a concave function of density always leads to instability due to spinodal decomposition. In our system this is impeded by topological constraints on the steps, requiring concerted mass transportation over relatively large distances for the decomposition of a network into stable surfaces. Therefore even a nonconvex free energy can be metastable.

(2) $\epsilon < 0$.—In this case orientations with a large density of step crossings are favored, which will give rise to ridges connecting the (110) facet either to other facets, into which one then could say the crossing steps condense, or to rounded areas, in case the entropic repulsion between steps is strong enough to restore a convex free energy for larger values of p. In either case the vicinal orientations are really unstable, as there is no free energy barrier against the contraction of the network to a state of higher step density. The same phenomena, occurring in a simple model giving rise to a negative crossing energy, are described in Ref. [7]. In Fig. 6(a) the dashed lines show the truncation of the equilibrium shape of the (110) facet by ridges connecting the facet to rounded areas, and Fig. 6(d) shows the expected arrangement of steps around the truncated facet. Notice that in this case there are ridges between rounded regions covered by networks of steps and regions covered by noncrossing step arrays.

In conclusion, we studied the typical pattern of steps observed in STM experiments on Au(110) and Pt(110) surfaces. The free energy of vicinal orientations was calculated from a simple, yet quite realistic, model. In this model step segments under positive and negative angles with the y axis cannot be simply joined together, because this would give rise to a mismatch in the reconstruction order. As a consequence of this, sloped surfaces show a tendency to form networks of crossing steps, which can avoid the reconstruction mismatch. However, these networks turn out to be unstable (or at least metastable) with respect to faceting. This leads to a cusped equilibrium shape for the (110) facet and to the formation of ridges in the equilibrium crystal shape between rounded parts of the crystal and, in the case of negative free energies for step crossings, between the (110) facet and the surrounding region. The model produces detailed predictions for the equilibrium shape of the (110) facet, as well as for the preferred step directions as a function of microscopic step energies and temperature. These predictions could be checked experimentally by studying equilibrium crystal shapes and average orientations of steps in networks.

Small gold crystallites in thermal equilibrium with their vapor were studied by Heyraud and Métois [8], but the range of temperatures investigated ($T = 1000\,°C$) is above the roughening temperature of the (110) facet: only the (111) and (100) facets were observed. We hope that our work will stimulate new experimental investigation of the equilibrium shapes of MR reconstructed surfaces at lower temperatures, below the roughening temperature of the (110) facet.

In this Letter we restricted ourselves to the range of vicinal orientations around the (110) facet. In a recent paper Vilfan [9] discussed the influence of long range interactions, which become important for a higher density of steps. However, he does not take into account the instabilities arising from the quadratic terms in the expressions for the surface free energy.

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