Equilibrium crystal shape of silicon near (001)

J. Tersoff

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

E. Pehlke

Fritz-Haber-Institut, Faradayweg 4-6, D-1000 Berlin 33, Federal Republic of Germany

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We calculate the equilibrium shape of a silicon crystal at orientations near (001), both at $T=0$ and at elevated temperature. Comparison with recent experiments shows that several topographic features observed on Si directly reflect the equilibrium shape. In particular, our results resolve an apparent discrepancy between theory and experiment, regarding faceting between regions of single-layer and double-layer steps.

One of the oldest and most fundamental problems in surface physics is the equilibrium shape of crystals.[1-3] The manner in which surface energy determines the shape of crystals in equilibrium has been understood since the pioneering work of Wulff.[2] However, the orientation dependence of the surface free energy is generally only known for simple models, and not for real materials. Moreover, it is extremely difficult to observe equilibrium crystal shapes in practice, because of the weak driving force for shape change. Thus the formal theory of equilibrium crystal shape has not yet lead to a detailed understanding of the shape of real crystals.

Here, we calculate the equilibrium shape of a silicon crystal near the (001) orientation. Deviations from (001) orientation (or from any low-Miller-index direction) require the formation of steps, and the orientation dependence of the surface free energy is determined by the step energies. These are calculated using a realistic Hamiltonian for interacting steps,[4-6] which includes step meandering at finite temperature. Our results allow us to understand two aspects of the surface morphology, both of which are related to faceting.

First, there has been considerable controversy regarding the behavior for orientations within a few degrees of (001) towards (110). The principal issue has been whether faceting into regions of single-layer and double-layer steps occurs.[4-9] Theoretically it has been shown that faceting should not occur even at $T=0$;[6] yet Umbach, Keeffe, and Blakely have apparently observed such faceting.[8] Here, by explicitly calculating the shape along the (110) azimuth, we resolve this apparent discrepancy between theory and experiment. We also show how the faceting disappears at elevated temperature.

The second issue which we address is the geometry for orientations less than 1° from (001). In this case, faceting is predicted to occur, with the crystal forming a square pyramid with its apex along (001). This result appears to explain a fascinating "hilly" surface morphology observed on very flat Si(001) by Tromp and Reuter,[10] which we interpret as kinetically limited faceting.

Given the surface free energy as a function of orientation, the crystal shape can be constructed as described by Wulff,[2] or equivalently by using the formula[1]

$$r(\hat{n}) = r_0 \min_{\hat{m}} [\sigma(\hat{m})/(\hat{m}\cdot\hat{n})] , \tag{1}$$

where $r(\hat{n})$ is the distance from the center of the crystal to the surface in the direction $\hat{n}$. Here $\sigma(\hat{m})$ is the free energy per unit area of the surface with orientation $\hat{m}$, and r_0 specifies the overall size of the crystal.

For orientations vicinal to (001), the surface energy is determined by the formation and interaction of steps. Si(001) has attracted intense interest because of the complex behavior which results from the large and anisotropic surface stress.[4] In particular, this surface can have two different step structures for miscuts towards (110).[4-6,11] At small angles of miscut from (001), single-layer (S) steps have lower energy. However, they also have a strong repulsive interaction, so that at small step separation (large miscut), double-layer (D) steps are favored. We refer to surfaces with these two structures as the S and D phases. In such a case of multiple possible surface phases, Eq. (1) refers to the phase of lowest energy for each orientation. However, it is enlightening to plot the curve defined by Eq. (1) for each phase. Then the actual crystal shape is the region inscribed by the set of curves, and has edges wherever two curves cross.

While the orientation-dependent surface energy of Si is not accurately known, the energy for a specific model of Si [the Stillinger-Weber (SW) model] has been studied by Poon et al.[5] These model energies can be accurately reproduced with an elastic Hamiltonian, which permits the treatment of even rather complicated step structures, as well as the contribution of step meandering to the free energy.[4-6] The $T=0$ surface energy for this model is plotted versus orientation in Fig. 1(a). The corresponding crystal shape, from Eq. (1), is given in Fig. 2(a). Note that, since step interactions are included here, the facets are not planar as in simpler models.

Because the D phase has such low energy in this model for orientations $\sim 4°$ from (001), the crystal forms D facets with approximately this orientation; the S phase never occurs in equilibrium. However, we expect that this is an artifact of the SW model. (Other potentials[12] appear to give comparable artifacts for this surface.)

In order to obtain results closer to the expected behavior, we alter the parameters determined from the SW

model, by adding 50 meV/a to the energy of each double step or pair of single steps, where $a = 3.84$ Å is the surface lattice constant. (The choice of 50 meV/a is discussed below.) Since the *difference* between S and D steps is unchanged, results of previous studies[5,6] of the surface phase diagram (which considered only differences in energy) are still valid with these adjusted parameters. The resulting energy, shown in Fig. 1(b), gives the crystal shape shown in Fig. 2(b). [Note the expanded y scale in Fig. 2, which makes the tilt from (001) more visible.]

If we restrict consideration to pure S or D surface phases, as in Fig. 1(b), then at $T = 0$ the resulting crystal has S and D facets meeting at a sharp edge, as on the left side of Fig. 2(b). However, as discussed by Pehlke and Tersoff,[6] at intermediate angles the minimum-energy surface structure consists of an *ordered mixture* of S and D steps. For any given angle there is a specific periodic sequence of S and D steps which has minimum energy, and each different sequence represents a distinct phase. When several of the simplest of these mixed phases are included in the calculation, as in Fig. 1(c), the surface is seen to go through a sequence of distinct phases with increasing angle from (001).[6] The resulting crystal shape, shown on the right in Fig. 2(b), is subtly changed. The sharp edge becomes rounded; or more precisely, there is a series of closely spaced small-angle edges between successive phases, giving a quasicontinuous rounded region of
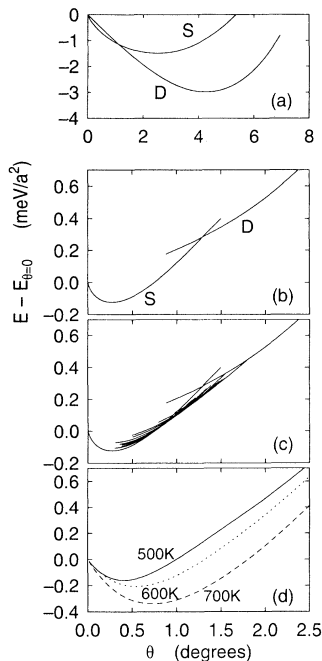
transition between the S and D facets.

We are now in a position to understand the observations of Umbach, Keeffe, and Blakely.[8] Those authors measured the spacing between steps on a curved surface (a Si grating which had been annealed to give a gentle periodic curvature), using a scanning tunneling microscope (STM). They translated the step spacing into a local tilt from (001), and plotted this tilt θ versus lateral position x. Despite considerable noise from the limited sampling, the data showed a fairly clear break at a position x_c, with the local tilt jumping from $\sim 0.7°$ for $x < x_c$ to $\sim 1.5°$ for $x > x_c$. They interpreted this jump as corresponding to an edge at $x = x_c$, reflecting faceting between S and D phases.

(Some confusion has arisen because the STM images of Umbach, Keeffe, and Blakely do not show any steps which are predominantly of double-layer height. However, as discussed by Pehlke and Tersoff,[6] at finite temperature the nominal D steps may be thought of as bound S pairs, and need not have the $T = 0$ double-layer atomic structure over most of their length. Thus the interpretation of Umbach, Keeffe, and Blakely is entirely reasonable.)

From Fig. 2(b), we can predict what such an experiment should see, if performed on an equilibrium crystal. The crystal shape inscribed by the curves in Fig. 2(b) is shown in Fig. 3, together with the local slope θ. The jump between S and D phases is not abrupt, but proceeds through a sequence of intermediate phases, with intermediate slopes. If we had included all possible intermediate phases in the calculation of Fig. 3, the plot of θ versus lateral position x would be quasicontinuous, resembling a "devil's staircase."[6]

The jump in slope, however, takes place over a region whose lateral extent is roughly 0.003 times the diameter of the crystal. If we scale the equilibrium crystal shape to a 5 μm diameter (ignoring the possible complication of finite-size effects on the shape), the local slope would vary

FIG. 1. Energy per (001)-projected area of the Si surface [relative to the energy of a flat (001) surface], for orientation at angle θ from (001) toward (110). (a) Energy for SW potential, calculated with elastic model as discussed in text. (b) Same, except with energy per D step (or per S step pair) increased by 50 meV/a. (c) Same as (b), but including also several other surface phases, consisting of various periodic ordered sequences of S and D steps. (d) Free energy for same Hamiltonian as (b) and (c), at indicated temperatures.
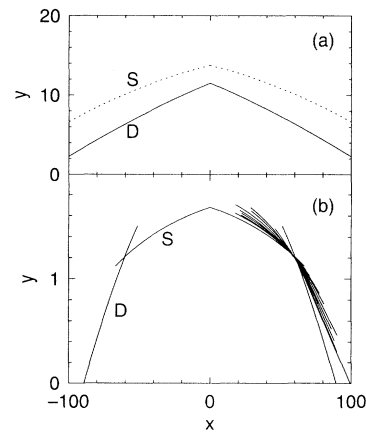

FIG. 2. Calculated equilibrium crystal shape of Si in $(1\bar{1}0)$ plane; crystal corresponds to region below all curves. Vertical direction is $\langle 001 \rangle$. Note expanded y scale; x and y units are arbitrary, since from Eq. (1), the shape is independent of size. (a) Shape calculated for energy of Fig. 1(a). (b) Shape calculated for energy of Fig. 1(b) (left) and of Fig. 1(c) (right).
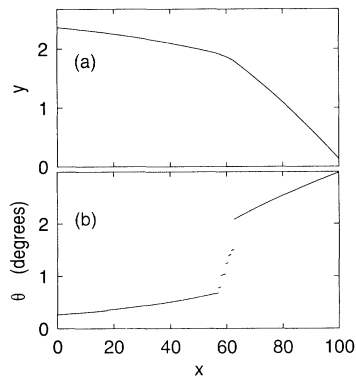
FIG. 3. (a) Crystal shape from Fig. 2(b) (right side). (b) Local orientation $\theta = \tan^{-1}(dy/dx)$ of crystal shape, vs lateral position on crystal. The x and y units are arbitrary. Distinct segments of curve correspond to distinct facets (i.e., distinct surface phases), as discussed in text.

from the S value to the D value over a lateral distance of only ~ 150 Å. But the average spacing between steps for these slopes is ~ 100 Å. Thus the local orientation cannot be measured even in principle with sufficient lateral resolution *on a small crystal* to resolve the quasicontinuous variation in orientation.

The sample studied by Umbach, Keeffe, and Blakely had a period of 2 μm, small enough to allow significant equilibration of the shape, but far too small to resolve the variation in local slope across the rounded region between the S and D phases. Thus their observations are exactly what would be expected theoretically; but because of the small sample size, these measurements cannot distinguish between simple faceting, and the more complex behavior expected[6] in the thermodynamic limit.

Umbach, Keeffe, and Blakely were aware that the inherent limitation on lateral resolution might affect the correct interpretation.[8] However, a quantitative assessment was not possible without knowing the equilibrium crystal shape. The small extent of the transition region between S and D facets is directly related to the fact that the energy of each intermediate phase is only slightly lower than the energy of a surface faceted into S and D regions, with the same average orientation. If the energies of intermediate phases were much lower, then the extent of the transition region could become comparable to the extent of the S facet, and the absence of a sharp edge between S and D facets would be easily observed.

Tong and Bennett,[9] in related work using electron diffraction, studied a sample with an effective size of 3 mm, and a characteristic radius of curvature of ~ 10 mm. They found no evidence of faceting. However, this would be expected regardless of the equilibrium shape, if, as suggested by Alerhand *et al.*,[7] equilibration of the shape is kinetically forbidden for such a macroscopically large sample.

So far, we have implicitly considered crystals to be equilibrated at $T = 0$. In practice, however, the crystal shape can equilibrate only at elevated temperatures. As the crystal is cooled, it falls out of equilibrium at some temperature T^* which depends weakly on the cooling

rate. Thus the final crystal shape, to the extent that it reflects an equilibrium property, corresponds to equilibrium at temperature T^*.

To understand the effect of temperature on the crystal shape, we calculate the surface free energy as a function of orientation, using the same elastic model (including step meandering) as previously.[6] The resulting energies are shown in Fig. 1(d), and the corresponding crystal shapes in Fig. 4. For simplicity, we show only temperatures above the critical temperature of the S-D phase transition, which occurs at $T_c \approx 490$ K with this model. [Bear in mind that the true T_c for Si(001) may be higher or lower than in this model; the results in Fig. 4 should be thought of as corresponding to $T_c + 10$ K, $T_c + 110$ K, and $T_c + 210$ K, whatever the true value of T_c may be.] Note that at these temperatures, since there is no phase transition with angle of miscut, the crystal shape is smooth except for the edge at $\theta = 0$.

In an experiment, the larger the sample and the faster the cooling rate, the higher the T^* at which the sample falls out of equilibrium. For example, the shape of the sample of Tong and Bennett discussed above certainly corresponds to a much higher T^* than does that of Umbach, Keeffe, and Blakely. Since the shape is seen in Fig. 4 to be a sensitive function of temperature, some care is required in interpreting experiments where T^* is not known.

We now turn to a second aspect of the crystal shape, the edge seen in Fig. 2 at $x = 0$. The cause of this edge is evident in Fig. 1(b)—the surface energy has a minimum, not in the (001) orientation, but at a small tilt $\theta \sim 0.3°$ from (001). Thus a (001) surface can lower its energy by faceting into regions of tilt $\pm 0.3°$. (The minimum-energy orientation depends sensitively upon the local contribution to the step energy,[13] for which no reliable calculation or measurement exists. We therefore chose this energy such that the facet angle is around $\sim 0.3°$, to accord with experimental observations,[14] giving the choice above of a 50-meV/a correction to the SW step energy.)

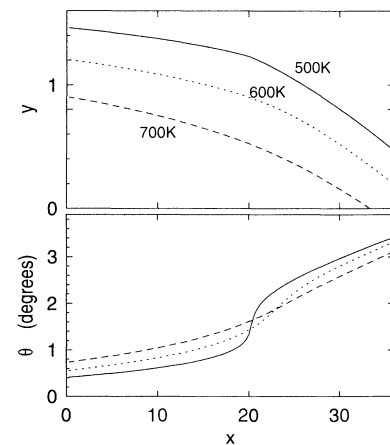The energy shown in Fig. 1(b) assumes that the surface

FIG. 4. (a) Crystal shape and (b) local orientation of this shape, as in Fig. 3, for indicated temperatures. The x and y units are arbitrary. The critical temperature at which the shape becomes smooth (except at $x = 0$) is $T_c \simeq 490$ K for this model.

has only the number of steps needed to account for the orientation. However, as noted by Alerhand et al.,[4] for orientations near (001) the surface can best lower its energy by forming extra up-and-down steps, which are even more favorable then faceting. Thus the *true* equilibrium crystal shape should be calculated including such extra steps, and (001) would then be an allowed orientation. But as discussed elsewhere,[13] the kinetics of step flow during growth or sublimation are so effective in suppressing the formation of up-and-down steps, that they apparently play no role in observed surface morphologies. We therefore do not include them here.

Even faceting tends to be kinetically suppressed on vicinal surfaces,[13] leading to a wavy-step phase,[14] though such a phase does not occur on the equilibrium crystal.[13] More recently, Tromp and Reuter[10] have observed the expected faceting on extremely flat regions of Si(001).

To calculate the shape of the equilibrium crystal very near (001), we use the same approximations[15] as in Ref. 13 to treat azimuths other than [110]. We find that the energy increases with azimuth so rapidly that, at $T=0$, the crystal facets into regions of strictly $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ azimuth. Thus the resulting shape, shown in Fig. 5(a), is a square pyramid with its apex toward $\langle 001 \rangle$, and its base edges along $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$.

If we begin with an effectively infinite Si(001) surface, and allow it to equilibrate, it should break into facets with the orientation which minimizes the energy in Fig. 1(b). This does not uniquely determine the surface morphology; but if kinetics dictate a maximally unstable wavelength for faceting, then a natural structure resembles the product of two modulations in the $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ directions, with this wavelength. Such a structure is shown in Fig. 5(b), and is quite similar to that observed by Tromp and Reuter,[10] allowing for thermal rounding of the edges. Thus we believe that in this case they are actually observing the approach towards a (locally) equilibrium shape.

In conclusion, we have calculated the equilibrium shape of Si near (001), both at $T=0$ and at elevated temperature, using the best available model for the orientation-dependent surface energy. Our results show that several recent observations of surface morphology can be understood as reflecting the equilibrium crystal
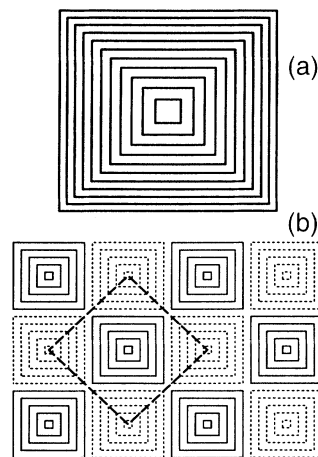

FIG. 5. (a) Topographic picture of calculated crystal shape, looking down $\langle 001 \rangle$. Horizontal and vertical correspond to $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$. Entire plot corresponds to region where S phase prevails, roughly $-60 < x < 60$ in Fig. 2(b), with contours at equal y intervals. (b) Possible surface morphology with average (001) orientation, discussed in text. Solid contours are above average level and enclose maxima, dotted contours are below and enclose minima. Dashed line indicates building block used to construct complete surface.

shape. The apparent faceting into S and D regions observed by Umbach, Keeffe, and Blakely[8] is consistent with the theoretical equilibrium crystal shape, although their effective sample size is too small to resolve the quasicontinuous nature of the "edge" expected between S and D facets in the thermodynamic limit. At higher temperature, there is no thermodynamic transition and hence no edge of any sort separating S and D regions. True faceting is, however, predicted to occur closer to (001), even at elevated temperature, explaining the novel morphology observed by Tromp and Reuter[10] on very flat Si(001).

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[15]Steps on Si(001) consist of (110) or (1$\bar{1}$0) segments. The resulting orientation dependence of the step length is enough to ensure rather flat facets with azimuths toward (110) or (1$\bar{1}$0). Thus a detailed treatment of the orientation dependence of the elastic interactions, which also favor these azimuths for facets, is not needed here.