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SURFACE FACETING AND THE EQUILIBRIUM CRYSTAL SHAPE

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We review the relationship between the thermodynamic stability of a particular surface orientation and the properties of the equilibrium crystal shape. In particular we discuss how the formation of a sharp edge in the equilibrium crystal shape when temperature or impurity pressure is changed manifests itself by reversible surface faceting. We describe some examples of this phenomenon, concentrating on our recent studies of the temperature-induced faceting on vicinal Si(111) surfaces. We briefly consider the role of surface diffusion in the interpretation of surface faceting.

1. Introduction

The reasons for the faceting of surfaces and the mechanisms by which faceting occurs are problems of long standing in materials science and surface physics [1–3]. Faceting is defined as the break-up of a surface of some arbitrary macroscopic orientation into a "hill-and-valley" structure which exposes surfaces of different orientation. Such a change in surface morphology is illustrated schematically in fig. 1. In many situations it is believed that the driving force for faceting is the possibility of lowering the surface free energy. Faceting can thus be analogous to thermodynamic phase separation: the surfaces of different orientations drawn in fig. 1 can be thought of as different thermodynamic phases (like liquid and gas). One would thus naturally hope to be able to interpret observations of faceting in terms of thermodynamic phase diagrams. The phase diagrams relevant to faceting are equilibrium crystal shapes. Faceting, however, requires a large amount of mass transport at the surface. As a consequence, faceting often occurs irreversibly when the environment of the surface is changed – for instance, by the introduction of a small density of impurities or by a change in the temperature. As we discuss in this paper, our work on Si surfaces and other recent studies show clearly that faceting can be a reversible, thermodynamic phenomenon, interpretable in terms of equilibrium crystal shapes.

Observations of faceting upon heating in a background pressure have a long history, going back at least to 1902 (for reviews of the early work on thermal faceting, see refs. [2,3]). For many years, however, detailed understanding of faceting

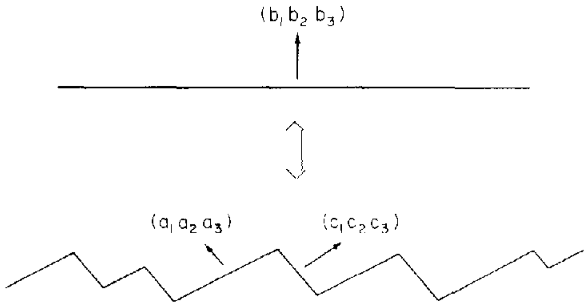

Fig. 1. Faceting will occur when the surface free energy can be reduced by decomposition of the planar surface of macroscopic orientation $(b_1b_2b_3)$ into a "hill-and-valley" structure exposing surfaces of other (often low-index) orientations. The average relative sizes of the new surfaces will be such as to conserve the net orientation. The absolute sizes of the new surfaces are determined by kinetics and can range from tens of ångströms to microns in length.

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was severely limited by the lack of controlled experimental data. Specifically, measurement and control of surface impurity concentrations were not possible, and thus, as one might expect, there were often problems with reproducibility [3]. The facets generally could not be observed unless they had reached micron sizes where optical techniques could be used, and thus comparison with the predictions of theories describing the initial stages of faceting [4] was difficult. Whether the faceting of a particular surface was driven by the possibility of lowering the surface free energy or instead by vagaries in kinetics (by anisotropic evaporation rates, for example) was often a matter of debate. With the advent of ultra-high vacuum and surface analytical techniques, more detailed measurements of faceting became possible [5]. In particular, low-energy electron diffraction (LEED) has proven to be a powerful technique for determining orientational stability. Such studies can show the occurrence of faceting at very early stages and correlate the faceting with the average surface composition. LEED has revealed that faceting can begin to occur at much lower temperatures than the older optical studies would suggest: Ni(210) has been observed to begin to facet at temperatures as low as 150 K after N adsorption [6], for example. However, LEED can provide little information about the evolution of the facet sizes or the nature of the interaction of impurity atoms with the growing facets. New progress in this area is now possible because of the recent development of surface-sensitive microscopic techniques which hold great promise for measurements of surface morphology during faceting.

The purpose of this paper is to review some of the theoretical and experimental background important in understanding faceting. In the following section we review the theory of the thermodynamics of surface stability, which leads to the introduction of the equilibrium crystal shape. In section 3 we discuss the role surface diffusion plays in the observation of faceting. In section 4 we summarize our experimental observations on a reversible faceting transition which occurs on vicinal Si(111) and discuss them in terms of a model for the temperature evolution of the Si equilibrium crystal shape.

2. Equilibrium crystal shapes

2.1. Surface stability

In a classic paper, Herring [7] showed that only surfaces represented on the equilibrium crystal shape (ECS) are thermodynamically stable. The ECS is defined as the shape a crystal of constrained volume takes when it is in equilibrium with its vapor. The net free energy of any surface not on the ECS can be lowered by increasing the net surface area to expose a "hill-and-valley" structure of faces present on the ECS. The faces exposed on this faceted surface are thermodynamically constrained to be those adjacent to the point of contact of the plane of the macroscopic orientation with the ECS. Thus, as most recently emphasized by Wortis [8], the ECS is a phase diagram which is useful in discussing surface stability – its use is independent of the fact that equilibrium crystal shapes themselves are only very rarely directly observable (although the observations by Heyraud and Métois of the equilibrium shapes of several metals [9] have confirmed many theoretical predictions).

Given a model of surface energetics, the solution of the problem of determining the ECS was given in 1901 by Wulff [10]. A cogent consequence of his result is that the distances of the various faces appearing on the ECS from the center of the crystal are proportional to their free energies. This is illustrated schematically in fig. 2a. Using the Wulff construction it is possible to calculate the zero-temperature ECS for any crystal structure given a model for the inter-atomic interactions. The simplest models are the Kossel crystal models, where atoms are constrained to sit on a discrete lattice and the surface energy is simply determined by counting the number of bonds broken in forming the surface. Tabulations of such model crystal shapes have been made for many lattice structures [11]. There have not been many attempts to determine zero temperature crystal shapes using more realistic models of surface energies. Indeed, unless surface energy calculations are reliable enough for them to routinely predict surface reconstructions, a stage which they have not yet reached, one probably cannot expect to compute the relative surface energies of surfaces of different orientations accurately enough to predict the stable orientations at zero temperature [12]. For simple models with short-ranged interactions [13], the ECS at zero temperature is composed of only a small number of facets [14] separated by sharp edges [15]; that is, only a few surface orientations are thermodynamically stable.

2.2. Temperature dependence

What happens to the ECS at finite temperature, even for very simple models of surface energetics, is a difficult problem, for which significant progress has been made in recent years [8,16,17]. From the point of view of orientational stability, what happens to the sharp edges – the ranges of unstable orientations – when one raises the temperature from zero is of most concern. The first question to be answered is at what temperature do changes begin to occur at the sharp edges; do changes occur as soon as the temperature is nonzero or do they only begin to occur at some finite temperature? Wortis [8] classifies these two possibilities as "type-A" and "type-B" behavior, respectively, and gives heuristic arguments for when each type should occur. Both of these possibilities are realized by various models [8,16].

The next question is, how are sharp edges modified? Again there are (at least) two possibilities. The low-temperature sharp edge between facets can disappear entirely above some temperature (above zero temperature in the type-A case): below this temperature only the two facets separated by the sharp edge are stable; above this temperature the ECS between the facets is rounded, as in fig. 2b, so that *all* orientations between the facets are stable (although the surfaces with orientations on the rounded regions are technically "rough" [17]). This possibility is realized by an exact calculation using a solid-on-solid model of surface energetics [18] and by various mean-field treatments of simple Kossel crystals [8,19]. The other possibility is that the sharp edge between facets is initially only partially rounded: as in fig. 2c the range of unstable orientations might initially still include surfaces vicinal to a (low-index) facet. If this were the case, then one would expect that as one increased the temperature, the range of unstable orientations would gradually decrease and eventually vanish – for the same reasons one expects regions of phase coexistence between liquid and gas to vanish at sufficiently high temperatures.

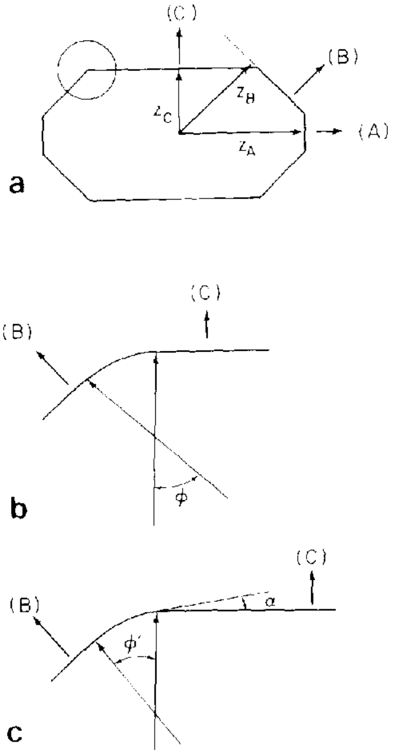

Fig. 2. Thermal evolution of the equilibrium crystal shape (ECS). (a) At low (or zero) temperatures the ECS may consist only of facets joined at sharp edges. Shown is an ECS for which only three facets, A, B and C are stable. The perpendicular distances z_A, z_B and z_C to the facets are proportional to the free energy of the facets. (b) Expanded view of the region indicated by the circle in (a), at a temperature where the edge of the ECS has rounded continuously. The full angular range of orientations, ϕ, from (C) to (B) is now stable. (c) Partial rounding of the ECS leaves a sharp edge between the (C) facet and a rounded region. Surfaces oriented within the angle ϕ' of (B) are stable. Surfaces oriented within the angle α with respect to (C) are unstable.

As discussed in section 4 we have observed this type of behavior on vicinal Si(111) surfaces. It is unclear what types of surface energetics is needed to have a sharp edge between a facet and rounded regions. Such a sharp edge has been observed to occur in a mean-field approximation of the thermal evolution of the ECS for simple cubic Kossel crystals model with nearest and next-nearest neighbor interactions [19]. The possibility of finding this behavior in terrace-step-kink models of vicinal surfaces has been addressed in detail by Jayaprakash et al. [20]. In contradiction to the mean-field results, they find that for short-ranged interactions between steps there does not exist a sharp edge between facets and rounded regions in the ECS. However, they propose that long-ranged (dipolar) attractive interactions between steps could lead to such sharp edges.

With increase in temperature, one also expects the sizes of facets (linear regions) on the ECS to decrease until each disappears into a continuously rounded region at a roughening temperature [9]. This roughening transition is of considerable theoretical interest [17]. From the point of view of orientational stability, roughening transitions can be important because when a surface becomes rough, a continuous range of neighboring orientations are stable. Also, the rounding shown in figs. 2b and 2b might have developed from the roughening of high-index surfaces.

2.3. The effect of impurity adsorption

The evolution of the equilibrium crystal shape as a function of impurity adsorption can be expected to be generically much different from the temperature evolution. This is because the effect of increasing temperature is simply to make the surface free energy and the ECS more isotropic, while impurity adsorption, by, for example, favoring different types of binding sites and thus faces of different orientation, can drastically change the surface anisotropy, causing facets different from those of the clean surface to be stable. It is thus not surprising that impurity adsorption is often observed to induce faceting [2].

To show explicitly how preferential adsorption can alter the ECS, fig. 3a shows an example of how an ECS might develop when in equilibrium with an impurity atmosphere. Surfaces of macroscopic orientations (A), (B), and (C) are assumed to be stable when clean, as shown by the outermost shape. As the impurity pressure (or chemical potential) increases we suppose that there is preferential adsorption on the facets of orientation (A). Because the surface impurity concentration is the negative of the derivative of the surface free energy with respect to the impurity chemical potential [2], this lowers the relative free energy of surfaces of orientation (A) with respect to surfaces of orientation (B) and (C), which are assumed to have comparatively little adsorption. This causes the relative sizes of the facets on the ECS to change, as shown by the sequence of dashed equilibrium crystal shapes in fig. 3a. Eventually, the preferential adsorption on A will have the effect of making surfaces of orientation (B) unstable with respect to faceting to surfaces of orientation

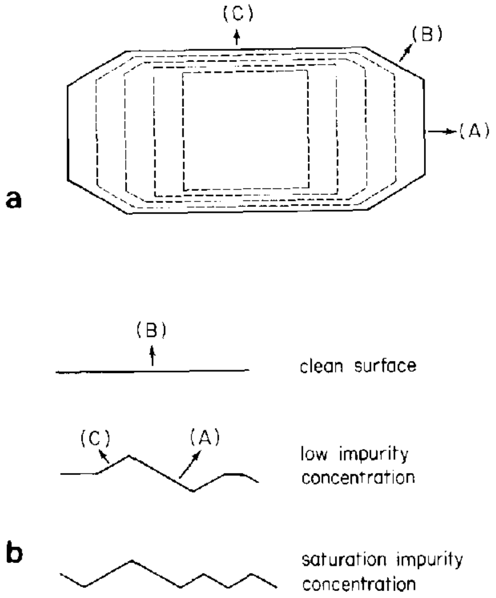

Fig. 3. Example of impurity-induced faceting: (a) The solid lines indicate the profile of an ECS in the absence of impurities. Three surface orientations, (A), (B), and (C), are stable when clean. The dashed lines indicate how the equilibrium shape might change when the crystal is exposed to an impurity atmosphere; we envision that there is preferential adsorption on facets of orientation (A) which lowers their relative free energy with respect to facets of orientation (B) and (C). Facets of orientation (B) and (C) are assumed to have small adsorption which does not significantly affect their relative free energies. Because of the lowering of the free energy of facets of orientation (A), eventually the ECS will contain only (A) and (C) facets. (b) The evolution as a function of impurity concentration of a surface orientation (B) as the (B) facet disappears from the equilibrium crystal shape. There is an intermediate range of concentrations where all three facets coexist.

(A) and (C), as shown by the innermost equilibrium shapes of fig. 3a.

Fig. 3a allows one to describe completely the evolution of the morphology of a surface of orientation (B) as a function of impurity pressure. However, small amounts of (chemisorbed) impurities are rarely in equilibrium with the gas (or bulk) phase, and so one is often interested in the dependence of the surface morphology on total surface impurity *concentration*, rather than the pressure. Fig. 3b shows the expected dependence on concentration for surfaces of macroscopic orientation (B). As the impurity concentration is increased above the concentration the facets of orientation (B) have when they disappear from the ECS, facets of orientation (A) form on which the impurity is concentrated. To preserve the net orientation, facets of orientation (C) must also form, although they contain only small amounts of impurity. The new facets increase in size as the amount of impurity increases (by the analog of a lever rule) until no facets of (B) orientation exist on the surface. Notice that if the surface were in equilibrium with an impurity atmosphere the intermediate region where facets (A), (B), and (C) coexist would be in general impossible. In fact, as the number of facets which one expects to meet at one point on the ECS is limited, the number of facets which can coexist on a clean surface, or a surface in equilibrium with an impurity atmosphere, are constrained by a phase rule. The observation of more than this number in equilibrium, as in the intermediate surface in fig. 3b, can allow one to deduce the presence of a fixed concentration of impurities [12].

That the ECS in general contains facets of different impurity concentration illustrates Cahn's [21] discussion of how sharp edges on an ECS in the presence of impurities can be interpreted in terms of changes in surface composition (or structure): the impurity concentration generally will vary discontinuously across sharp edges. The ECS can be thought of as the inner envelope of crystal shapes with varying surface concentrations.

The example of fig. 3 is only meant to be an illustration of the changes that can occur in the presence of impurities. Much more complex sequences can be envisioned. The impurity adsorption can occur through a series of structural phases. Changes in the nature of the chemical bonding can also occur due to thermal annealing. Thus a full description of the ECS in the presence of impurities can involve many parameters. The forms of the ECS at zero temperature for simple lattice-gas models of adsorption on Kossel crystals have been computed by Shi [22]. Understanding of the ECS with impurities has practical importance as the initial stages of epitaxial growth can be described as impurity adsorption. The possible resulting changes in the ECS will determine the nature of the epitaxial interface. Experimental studies of orientational stability therefore should accompany attempts to develop new epitaxial systems. Such studies should encompass both the range of initial orientations [23] and surface compositional phases [11,24,25].

3. Surface diffusion and reversibility in faceting

Given the huge number of surfaces which have come under the scrutiny of surface science, what types of conclusions can be drawn about surface stability, in particular about the temperature dependence of stable surfaces? Surface scientists frequently work on surfaces of arbitrary orientation. Particular favorites for study are vicinal surfaces, i.e. those cut a few degrees away from a low-index orientation. When clean, these surfaces generally appear to be stable over a temperature range from 90 to 300 K to near the melting temperature (see table 1). From this we might try to draw the general conclusion that even at quite low temperatures no sharp edge separates clean low-index surfaces from the vicinal surfaces. However, caution is quite obviously warranted in drawing such a conclusion, because the ECS is only relevant if the kinetics are such as to allow equilibrium to be established. Mass transport sufficient to allow orientational changes on the scale of microns can only be achieved by equilibration with a substantial vapor pressure or when surface diffusion is large (typically at T greater than half the melting temperature [42]). Thus surfaces that appear stable at room temperature might actually be below their faceting temperature, but simply may not have

Table 1
Electron diffraction studies under UHV conditions of the stability of vicinal surfaces (additional studies can be found in ref. [26])

Material	Terrace plane	Condition	Structure	Ref.
UO_2	(111)	Clean, $T < 600\,^\circ C$	Monatomic steps	[27,28]
		Clean, $700\,^\circ C < T < 900\,^\circ C$	Faceted	
Cu	(100)	Clean	Monatomic steps	[29]
		Adsorbed N or S	Monatomic steps	
		Adsorbed O, $T \cong 200\,^\circ C$	(410) facets	
		Adsorbed C, $T \cong 800\,^\circ C$	(210) + (310) facets	
Ge	(111)	Clean, cleaved	Monatomic steps	[30]
		Clean, $T \cong 300\,^\circ C$	Monatomic steps	
		Adsorbed O	Monatomic steps	
		0.2 ML Ag, $T \cong 400\,^\circ C$	(544) + (111) facets	[31]
		> 0.7 ML Ag, $T \cong 400\,^\circ C$	(211) facets	
Pt	(110)	Clean	Diatomic steps	[32]
	(111), (100)	Clean	Monatomic steps	[33–35]
		Heated in O_2	Depends on orientation	[32,33]
		Adsorbed C, heated	Depends on orientation	[32]
W	(110)	Clean	Monatomic steps	[36,37]
Ni	(111)	Clean, $T \geq 350\,^\circ C$	Monatomic steps	[38,39]
		$\cong 0.1$ ML C, $T \leq 350\,^\circ C$	Multi-atomic steps	
Fe	(100)	Clean	Diatomic steps	[40]
		Adsorbed N	Monatomic steps	
		Surface nitride	Faceted	
Si	(100)	Clean	Diatomic steps	[41]
		Adsorbed As	Four-level steps	
	(111)	See text		[52–54]

sufficient atomic freedom of motion to allow orientation rearrangement.

Another situation where much caution is needed in the interpretation of the observation of faceting in terms of thermodynamics is when considerable sublimation is taking place from the surface. Surfaces with slow sublimation rates can be preferentially exposed during sublimation [3]. That sublimation is responsible for the observation of faceting can be established [43], for example, by comparing surfaces under conditions where they are in equilibrium with the gas phase to the more usual situations where they are not. Recent low-energy microscopic work on Si(100) [44] shows dramatically how delicately the morphology of a surface which facets during sublimation can depend on surface impurities and other defects.

The introduction of impurities to vicinal surfaces, as seen in table 1, is commonly observed to induce faceting. This also might lead one to suspect that the pressure of impurities often induces sharp edges in the ECS, making vicinal surfaces unstable. However, the same caution about the role of mass transport in the observation of faceting should also be invoked here, although perhaps not so obviously. If a surface has been quenched below a temperature where it becomes thermodynamically unstable, then if it is exposed to a small amount of an impurity which greatly increases its surface self-diffusion rate, it might be able to relax to its equilibrium (impurity-free) faceted structure. This would be a distinctly different process from that caused by impurity-induced changes in the ECS. One might hope to be able to experimentally distinguish the two cases: if the faceting were induced by a change in surface kinetics, faceting might be able to proceed to completion in the presence of very small quantities of impurity, and be independent of the nature of the impurity.

Reversibility is the crucial observation needed to confidently interpret changes in surface stability in terms of thermodynamics, that is, in terms of the evolution of the ECS. In the next section we discuss in detail our observations of reversible thermal faceting on vicinal Si(111) surfaces. Another example of reversible thermal faceting has been reported for surfaces vicinal to Cu(110). Using X-ray diffraction, Ocko and Mochrie [45] have observed that the vicinal surfaces are stable at 900 K, but reversibly facet to the (110) and some other undetermined orientation at 520 K. The transition has not yet been measured directly, however, and there are questions about the role of impurities.

In the case of a surface which is faceted because the presence of an impurity has created a sharp corner on the ECS, removal of the impurity should reverse the faceting. An example of this type of reversibility has been demonstrated by Eizenberg and Blakely [46] for surfaces vicinal to the (111) face of a Ni crystal, into which large amounts of carbon has been dissolved. They observed that the vicinal surfaces are stable at temperatures above approximately 350 °C. Upon cooling, the surfaces facet to the (111) and to (113) or (110), depending on the direction of the misorientation. Simultaneously, a marked increase in the surface carbon concentration is observed. The carbon apparently diffuses into the bulk at high temperature and returns to the surface at low temperature, causing corresponding changes in the surface free energy. This is an unusual example of reversible changes in the ECS which warrants further investigation.

Regardless of whether faceting begins to occur because of changes in the ECS or because of changes in the surface kinetics, the ultimate size of the facets is dependent on kinetics. Many of the same philosophical issues which arise in discussions of the kinetics of phase separation, such as the existence of metastable states and of spinodal decomposition [47], also arise in discussions of the kinetics of faceting. From a more practical viewpoint, however, measurement of morphology changes, including faceting, on a micron scale has been an important technique for determining surface self-diffusion parameters of solid surfaces at high temperatures [42,48].

The analysis of these measurements has been of necessity based on a continuum, macroscopic description of surfaces [48]; descriptions of the diffusion process during faceting on atomic length scales are to date largely schematic. One plausible picture has surface atoms breaking free from a kink at a step-edge, diffusing across a low-index terrace as adatoms, and crossing a second step [3]. The result of this process would be a steady increase in size of the low-index facet, while the size of the evolving complex (not simply oriented) region decreases but its step density increases. In this type of self-diffusion, involving significant mass transport, how the adatoms are created and trapped at steps, or other strongly binding defects, is important. Intrinsic diffusion associated with motion of single atoms across defect-free terraces is observed to be much faster than mass transfer diffusion [48]. Thus characterization of steps as they move to form facets is necessary to provide the elementary information needed to understand the kinetics of faceting. The experimental power needed to make such observations has only been recently achieved in the development of low-energy electron microscopy (LEEM) [49] and, to a more limited extent, by reflection electron microscopy (REM) [50] and scanning tunneling microscopy (STM) [51].

4. LEED studies of vicinal Si(111)

We have studied in detail an example of reversible thermal faceting for surfaces vicinal to Si(111) [52–54]. In the following we discuss the observations and relate them to the previous discussion of ECS and surface diffusion.

The Si(111) surface reconstructs to a rather complex surface structure with a (7 × 7) periodicity [55]. This reconstruction disorders at approximately 850 °C leaving a (1 × 1) diffraction pattern, reflective of the subsurface structure [56]. Surfaces vicinal to the (111) are stable above the disordering temperature [52–54]. LEED shows that they contain a periodic array of steps of height equal to one (111) interplanar spacing and with a separation consistent with the net angle of misorientation. However, upon cooling through the temperature at which the (7 × 7) reconstruction appears, changes in the step structure occur. These changes depend on the direction of misorientation. For surfaces misoriented toward the $[2\bar{1}\bar{1}]$ direction, the step period triples. For surfaces misoriented toward either the $[\bar{2}11]$ or the $[1\bar{1}0]$ directions, the surface facets to the (111) orientation plus a second orientation which contains a higher density of steps than the original surface. Notably, the orientation of this second surface changes continuously with decreasing temperature: its angle α with respect to the (111) increases. The changes in the surface morphology are illustrated schematically in fig. 4. The value of α is a unique function of the temperature, and the transition is totally reversible. This suggests that the observed transition is thermodynamic. If this is the case, the functional dependence of α on T should be independent of the net misorientation of the sample. This proves to be the case, as illustrated in fig. 5. As the net angle of misorientation is increased the temperature at which the (7 × 7) reconstruction and the faceting simultaneously begin decreases dramatically. However, for initial misorientations from 1° (not shown) to 12°, the phase separation of the surface into (111) facets and surfaces of misorientation α falls on the same phase diagram.

We can discuss this orientational phase separation in the language of the ECS introduced in section 2. Specifically, we find it profitable to use the concepts developed to discuss impurity-induced faceting. However, in this case the (7 × 7) reconstruction will serve the role of the impurity. The measurements show that all vicinal surfaces are stable above approximately 850 °C. Thus at these temperatures the ECS must be continuously rounded near the (111) facet. Once the (7 × 7) reconstruction appears, however, the vicinal surfaces are no longer stable. This indicates the formation of a sharp edge on the ECS. That the orientation of the new surface changes continuously with decreasing temperature suggests that the sharp edge exists not between two facets, but between the facet (the (111)) and a rounded region

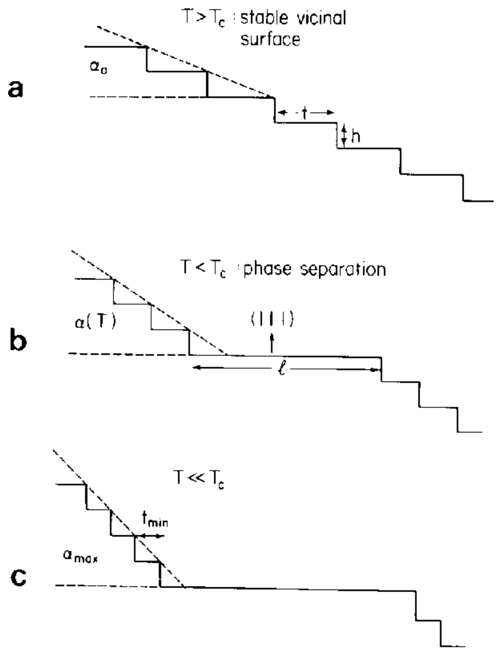

Fig. 4. (a) At high temperature, the Si(111) vicinal surface represents a single, uniform phase. Initial terrace widths t are typically tens of angstroms, as determined by the net angle of miscut α_0, and the step-height h, which is one interplanar spacing (~ 3.1 Å). (b) Below the (7×7) reconstruction temperature T_c (~ 850 °C) the steps group together to form a new surface of misorientation angle $\alpha(T)$. A facet of (111) orientation with (7×7) reconstruction forms simultaneously. The width of the (111) facet, l, is larger than the experimentally resolvable width of 500 Å. (c) Well below the transition, the step separation reaches a minimum distance, t_{min} ~ 10 Å. No further changes occur, possibly because surface diffusion is too slow at these temperatures (≤ 600 °C).

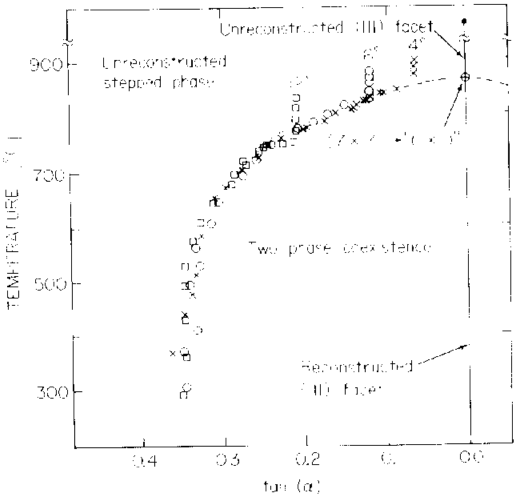

Fig. 5. Measured values of the orientation $\alpha(T)$ of the surface formed by the groups of steps illustrated in fig. 4 during the phase separation. The results for three different net angles of misorientation are shown. The data form a phase boundary, below which the separation into a reconstructed (111) facet and the highly stepped surface occurs. The data shown here were measured on cooling. Hysteresis observed for the 12° sample on warming is shown as solid dots.

of the ECS. The temperature dependence of the ECS can be described by a picture of intersecting crystal shapes as illustrated in fig. 6a. The solid curve represents the ECS near the (111) facet when the (7 × 7) reconstruction is disordered. The dashed curve shows the ECS when the (7 × 7) is present. At temperatures above the disordering temperature, the free energy of the disordered surface must be lower. Therefore the (7 × 7) ECS is shown at a larger distance from the crystal center at $T > T_c$ in the figure. At the transition temperature, the reconstructed and the disordered surfaces must have the same free energy. Therefore the two curves are shown intersecting at $T = T_c$ in the figure. Finally, as the temperature decreases below T_c, the free energy of the reconstructed surface will drop below that the disordered surface. The inner envelope of the intersecting shapes then will be the new ECS, exactly as in the case of impurity-induced faceting. As shown in the figure, this results in a sharp edge between the (111) facet and a rounded region of the ECS. The corresponding phase diagram shown in the left column of the figure is in qualitative agreement with the observations.

The description of reconstruction-induced faceting can be generalized: we might expect to see similar behavior on any surface which undergoes a reversible (first-order) reconstructive transi-

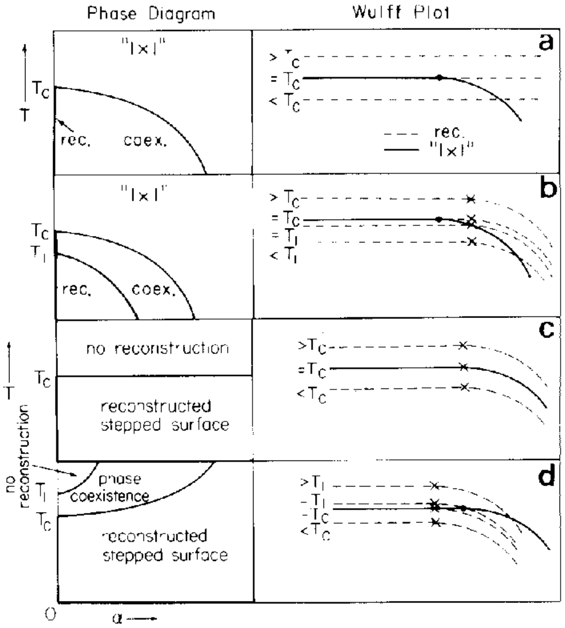

Fig. 6. Wulff plots illustrating the effect of a reconstructive transition on the equilibrium crystal shape, and corresponding temperature–orientation phase diagrams. The solid curve represent the crystal shape with an unreconstructed ("(1 × 1)") facet, and the dashed curves with a reconstructed facet. As temperature decreases, the relative free energy of the reconstructed facet decreases. Below the transition temperature, the two shapes intersect, giving a net equilibrium shape that is the inner envelope of the two. The phase diagram shows regions where all orientations are allowed for the unreconstructed crystal ("(1 × 1)"), regions of phase separation (coex.), and regions where the reconstruction (rec.) is allowed for certain values of α. The relative size of the reconstructed and unreconstructed facets depends on the free energy to create a step on the reconstructed (111) face, compared to its unreconstructed counterpart. Panel (a) shows the behavior for extremely large energy to create steps on the (7 × 7) terrace. Panel (b) represents a smaller such energy. Panel (c) shows the case when the step energy is the same for both. Panel (d) depicts what would occur in the unlikely event that steps were more favorable in the reconstructed phase. Solid circles show the continuous edge on the unreconstructed crystal shape. Crosses show the intersection of the facet and the rounded part of the crystal shape for the reconstructed phase.

tion. Such transitions are in fact quite common on semiconductor surfaces as shown by Olshanetsky and Mashanov [57,58]. However, we would not expect all of these surfaces to display phase diagrams identical to that found here. This can be understood by placing the description of the observed phase diagram in terms of surface energetics. The observation that the steps move closer together when the (7×7) reconstruction appears indicates a repulsive interaction between the step edges and the reconstruction. This conclusion is implicit in the picture of the intersecting ECSs shown in fig. 6. Specifically, the relative sizes of the reconstructed and unreconstructed facets is determined by the relative free energy cost of steps on those facets. Thus, on other surfaces it is possible to imagine different types of orientational phase diagrams that might occur if the relative interaction-energy between steps and facets were different. A series of such diagrams is illustrated in fig. 6, for a reconstruction-step interaction that changes from strongly repulsive to neutral to strongly attractive. Our observation that surfaces vicinal to Si(111), but misoriented toward the $[2\bar{1}\bar{1}]$, do not undergo phase separation when the (7×7) appears may be an illustration of the case where the step-reconstruction interaction is neutral. Evidence for a strong difference between the nature of the interaction of the reconstruction with the step edges for the two orientations has been provided by the observations of Telieps and Bauer [59] of the nucleated growth of the (7×7) reconstruction at steps. They show that the (7×7) domains are triangular and appear with an edge preferentially aligned with the top edges of steps misoriented toward the $[\bar{2}11]$ direction, and with a truncated apex aligned with steps misdirected toward the $[2\bar{1}\bar{1}]$ direction.

Before concluding this discussion of vicinal Si(111), it is desirable to discuss the kinetics of the faceting. From fig. 4, it can be seen that the transition proceeds by the grouping of the steps into bunches with smaller separating terrace widths than on the high-temperature surfaces. The initial high-temperature step separations for the surfaces we have studied range from approximately 180 Å for the 1° misoriented surface to 15 Å for the 12° misoriented surface. The final low-temperature step separation is approximately $t_{\text{min}} = 10$ Å, regardless of the initial angle of miscut. It seems reasonable to assume that following some initial nucleation of the groups of steps, the number of steps in any given group remains constant throughout the transition. Thus changes in orientation of the stepped regions would be accomplished by motion of the steps within one group. This motion would take place by atoms breaking away from kinks at the step edges and diffusing across the terraces as discussed in the previous section. The distances which atoms would need to travel to accomplish the phase separation would be comparable to the facet size.

One would hope to be able to determine the parameters governing Si surface diffusion by measuring the kinetics of the phase separation [60]. To be complete, such an analysis requires knowledge of the length of the facets, l, formed in the phase separation. Fairly simple geometrical considerations can be used to illustrate how sensitively dependent the results of any analysis will be on

Table 2
Mass transport required to achieve different facet sizes as a function of angle of misorientation; model 1 assumes a constant number, $n = 10$, of steps in the step groups; model 2 assumes a constant size of $l = 1000$ Å for the (111) facet; the number of atoms moved per facet is calculated for unit width ($W = 3.84$ Å) of the facet perpendicular to the direction of faceting; the net distance over which mass transport must occur is approximately equal to 1/2 of the facet length, l plus 1/2 of the length of the stepped region, nt_{min} (see fig. 4)

Miscut angle (deg)	Initial terrace width (Å)	Model 1			Model 2		
		n	l (Å)	Atoms moved	n	l (Å)	Atoms moved
1	180	10	1700	130	5	1000	120
6	30	10	200	20	50	1000	1200
12	15	10	50	10	200	1000	4800

the value of the facet size. Given a facet width and the net angle of misorientation, the number of steps n in a group can be determined. If n remains constant, the number of atoms that move per facet formed is roughly $nlhW\rho_{Si}/8$, where h is the height of the steps, W is the width of the facet and ρ_{Si} is the number of density of Si. The strong dependence of this quantity on the morphology of the facets is illustrated in table 2. We have chosen two simple models to show extremes of possible behavior as a function of miscut angle. In model 1, the number of steps per group n is assumed to be constant with a value of 10. In model 2, the facet width is fixed at a value $l = 1000$ Å. By simply comparing the results of the two models for a misorientation angle of 6°, it is clear that no accurate analysis of the kinetics is possible without prior knowledge of the facet sizes.

Our LEED results can only place a lower limit of 500 Å on the facet size for all initial misorientations (1°–12°) measured [54]. REM measurements [61] suggest that the facets are much larger, perhaps microns in size. Recent STM results [62], however show facet sizes of approximately 1000 Å at room temperature. The LEEM observations of Telieps and Bauer [59] indicate that the phase separation does not occur when the original step separation is much greater than 200 Å. A combination of room-temperature measurements of the structure using STM, and of the kinetics using LEED, as a function of the angle of misorientation could yield definitive values for the Si surface self-diffusion coefficients [60].

5. Conclusions

In this paper we have described how faceting (or orientational instability) of macroscopic surfaces can be interpreted in terms of the evolution of a sharp edge in the equilibrium crystal shape. These changes are much more dramatic than those associated with the disappearance of a facet in the equilibrium crystal shape (surface "roughening") which has been the subject of many recent studies [17]. Faceting is easily detected using LEED. However, because constraints on surface diffusion greatly limit the occurrence of morphology changes, care must be taken in interpreting the onset of such changes in terms of the thermodynamic description afforded by the equilibrium crystal shape. The reversible faceting we observe on vicinal Si(111) surfaces is an example where a thermodynamic description seems to be valid. A direct measurement [9] of the ECS of Si would provide valuable input about the use of the thermodynamic description for such macroscopic surfaces.

The faceting of vicinal Si(111) is a particularly interesting example because it is possible to identify the formation of the surface reconstruction as the causal agent for the appearance of a sharp edge in the equilibrium crystal shape of Si. The role of the reconstruction in this case is analogous to that of the impurity in impurity-induced faceting, as both abruptly alter the relative free energies of the surface orientations.

Further study is needed to fill the biggest gap in our understanding of surface morphology changes, which is the description at an atomic level of the kinetic phenomena which determine when and to what extent surface morphology changes can occur.

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