Stability-Instability Transitions in Silicon Crystal Growth

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In order for a crystal to grow, source atoms must be incorporated into the underlying lattice. Typically, this process occurs on the surface in one of two modes: either through island nucleation or through step flow. However, a third, morphologically unstable growth mode has been predicted. Monitoring the surface of ultraflat substrates with an *in situ* scanning electron microscope, we prove that for the (111) face of silicon there is a transition from stable step flow to morphological instability and then to island nucleation.

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Crystal growth is a remarkable process. To minimize energy, source atoms arriving randomly are assembled into a perfect three-dimensional lattice. Virtually all of this takes place on the surface, either by step flow or by island nucleation. In island nucleation, atoms diffusing on the surface ("adatoms") combine into monolayer high islands, which expand and coalesce into a complete monolayer. In step flow, adatoms diffuse until they reach monolayer high steps where they become incorporated. The steps advance and the crystal grows.

Ideally, steps stay well spaced and they retain a smooth profile. But realistic models of growth predict possible morphological instabilities [1–6]. Experimentally, island growth and stable step flow are commonly observed, and wandering step profiles are sometimes obtained [7,8], but until now the transition between stability and instability had not been seen. Here we describe how to induce instability by controlling the step arrangement. Transitions are demonstrated, from stable to unstable step flow, and from step flow to island nucleation.

A schematic of a single atomic step is shown in Fig. 1. The step advances by incorporating mobile adatoms from the terrace. On average, an adatom on the lower terrace (dark sphere) travels a shorter distance to reach the bulge (short arrow) than to reach the concavity (long arrow) [9]. Assuming the step absorbs any adatom that reaches it, incorporation occurs preferentially at the bulge, which advances more quickly than the concavity, which lags. In this way, adatoms on the lower terrace destabilize the step morphology.

Bales and Zangwill (BZ) treated instability more realistically [1]. Adatom coverage satisfies a diffusion equation [10]. The coverage as a function of distance from a straight step is graphed schematically in Fig. 1 for sublimation (dotted line) and growth (solid line). The gradient is larger near the bulge. The surface flux is proportional to this gradient, therefore the bulge incorporates more material than a straight step. The underlying reason why the gradient is larger is that the distance to the central, higher coverage region is smaller [11]. In short, adatoms on the lower terrace are destabilizing.

In contrast, for an adatom on the upper terrace (light sphere), the distance to the bulge is larger. That means adatoms on the upper terrace are less likely to reach the bulge, causing it to lag. Likewise, the concavity will grow faster. An upper step stabilizes growth, in exact analogy with the way a lower step destabilizes growth.

If both terraces are the same size and steps act as perfect sinks, the stabilization exactly counters the destabilization. However, to quote BZ, if "the flux of adatoms that attach from the upper step is greatly reduced … this change is sufficient to produce a morphological instability in the terrace edge shape." BZ supposed that an Erlich-Schwoebel (ES) barrier [12,13] changed this balance, meaning that first order kinetic attachment rates differed on either side of the step.

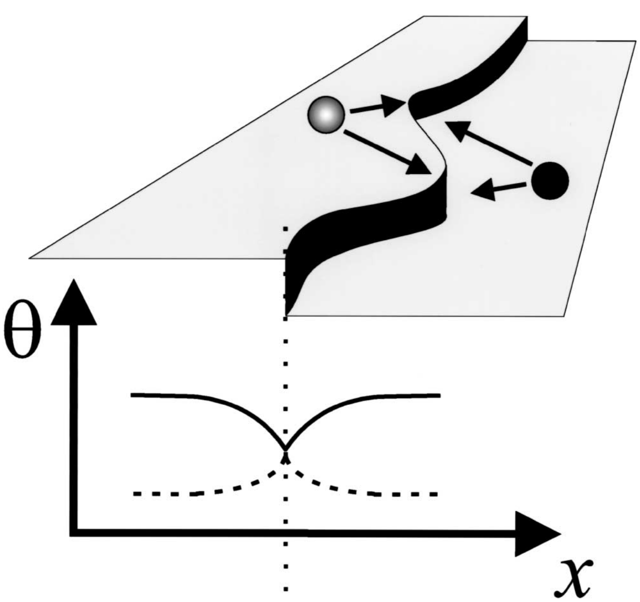

FIG. 1. Step schematic: A single step is shown with a roughly sinusoidal perturbation. The spheres represent adatoms on the surface. The graph shows the adatom coverage (θ) as a function of distance (x) perpendicular to a straight step for growth (solid line) and sublimation (dotted line).

There are other ways to reduce the relative flux from the upper terrace. Possibly the simplest technique is to reduce the size of the upper terrace. Depletion of the smaller "sea" of adatoms on this terrace results in smaller gradients in coverage, reducing the flux. An ES effect would simply shift the relative size of upper terrace required for stabilization.

There are also other stabilizing effects. A straight step is energetically favored—the energy savings that comes from straightening it is parametrized by the "step stiffness" [1,14]. Furthermore, atoms may diffuse along steps before attachment, or even detach from the steps, diffuse, and subsequently reattach [15]. In either process, attachment occurs preferentially at kinks and concavities, and the step profile smoothens. Overall, these effects can be expected to reduce the size of the upper terrace required for stabilization.

Experimentally, we observed steps with an ultrahigh vacuum (UHV) scanning electron microscope (SEM) [16,17]. Ultraflat substrates, which can be atomically flat on a square of over 100 μm on a side, were prepared by a standard procedure [17,18]. These substrates are particularly useful here, in part because their step spacings can be tuned, but also because growth is unstable over a wider range of fluxes for very large spacings. Smaller terraces are more stable because a bulge can easily deplete the nearby sea of adatoms, reducing its growth rate [19].

Above the 7×7-"1×1" transition temperature (~850 °C) steps retreat in an orderly fashion. When a flux of silicon is supplied, steps advance in step flow [20]. To supply a flux, a second sample was made to sublime by resistive heating. Both the source and the experimental sample were degassed by heating to high temperatures (about 1200 °C) before growth. To grow, the experimental sample was heated to the growth temperature, and then the current through the source was increased until the desired growth rate was obtained.

The best opportunity to observe instability occurs when the upper step is small and the lower step is large. For this reason, a large terrace was prepared by annealing. Later, a flux was supplied, nucleating a new island near the center of the terrace [21], as expected from nucleation theory [22]. The sample was heated causing sublimation and leaving only a small, circular island [23]. Finally, approximately equal amounts of silicon were deposited at various growth rates.

Figure 2 shows the effect of the flux rate. The starting flat terraces were approximately circular, with radii of about 35 μm. The seed islands had radii of less than about 3 μm. For low fluxes the islands remained nearly circular—the growth is stable [Fig. 2(a)]. Increasing the flux, curved step fronts appear in rapid growth directions, which correspond to the $\langle \bar{1}10 \rangle$ family of directions [Fig. 2(b)]. Slow growth facets appear, roughly perpendicular to the $\langle \bar{1}2\bar{1} \rangle$ family of directions. The approximate sixfold symmetry is even more apparent at higher fluxes,

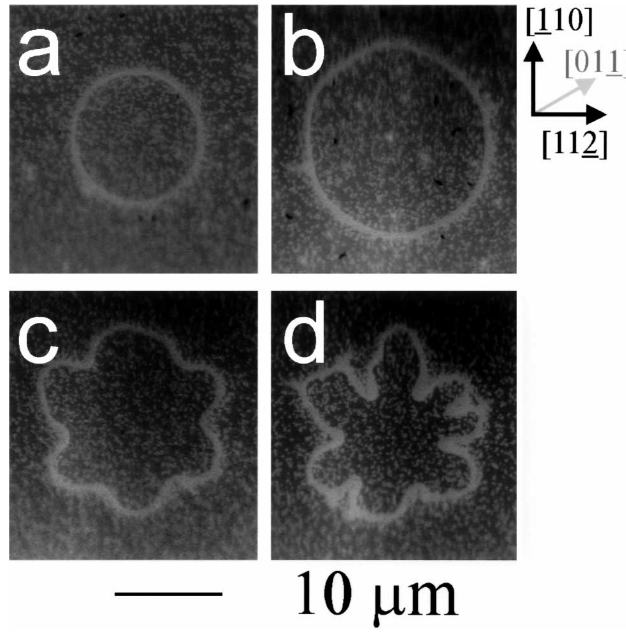

FIG. 2. Growth rate dependence of island morphology: The postgrowth island morphology is shown for initially circular islands. The substrate temperature was 930 °C with a flux of one monolayer (ML) per (a) 62 ± 6 min, (b) 13 ± 1 min, (c) 3.5 ± 0.4 min, (d) 1.6 ± 0.2 min.

for which a circular island develops a rounded sixfold star shape [Fig. 2(c)]. The smooth, star shape indicates that step length is minimized locally, but not globally. At higher fluxes the shape becomes irregular, even dendritic [Fig. 2(d)]. The growth is unstable. There is a limit to how dendritic these islands can become, because at still higher fluxes new islands are nucleated, and the proximity of new step edges stabilizes the growth. This stabilization effect has previously been described theoretically in terms of competing capture areas surrounding islands [15].

The effect of varying the lower terrace size is shown in Fig. 3. The initial terraces were approximately elliptical, except in 3(a) and 3(b) where the steps were somewhat wavy even before growth. The terraces were slightly longer vertically than horizontally. Nonetheless, it is convenient to describe their areas by effective radii given by the square root of their area divided by π, listed in the caption for Fig. 3.

For the smallest terrace no island was nucleated [Fig. 3(a)]. Steps act as sinks, depressing the coverage; therefore if the central terrace is too small, the coverage never reaches the critical level [22]. On a slightly larger terrace an island is nucleated [Fig. 3(b)]. If the terrace size is increased further, a single island is still nucleated, but it becomes more and more dendritic [Figs. 3(b)–3(d)]. The larger lower terrace is, in fact, destabilizing.

Again, there is a limit to how dendritic an island can become, because if the terrace is too large, the critical coverage for nucleation is attained in a broad area. This gives rise to structures such as Fig. 3(e). Four roughly equidistant islands have been nucleated. The inner island is

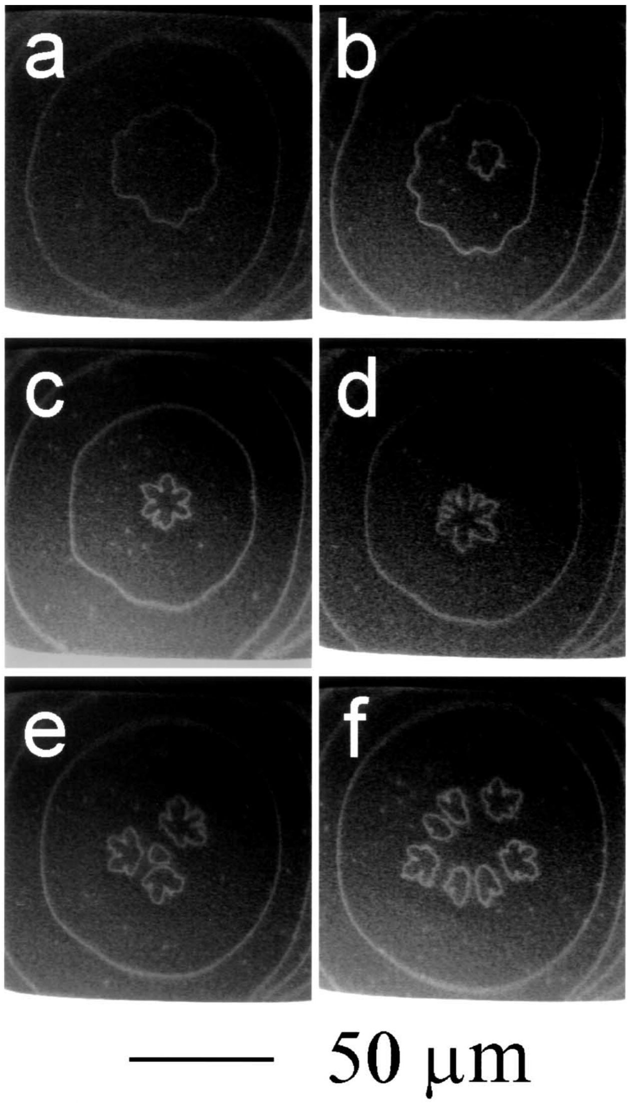

FIG. 3. Lower terrace size dependence of island morphology: The surface is shown after growth at 930 °C with a flux of one ML per 1.6 ± 0.2 min for 15 s. The effective radius of the initial terrace was (a) 24 μm, (b) 27 μm, (c) 38 μm, (d) 43 μm, (e) 46 μm, and (f) 51 μm.

circular while the outer three have "maple leaf"-like structures. The outer sides of the outer islands are dendritic because their step edges are far from any others. The inner sides are straighter, and the central island is circular because the steps of neighboring islands stabilize each other.

At very large spacing a ring of islands is observed [Fig. 3(f)]. Many islands have formed because the critical density is reached over a broad area. The island spacing decreased for increased flux, consistent with nucleation theory [22]. However, the ring is hollow—there are no islands in the center. One possible explanation is that the coverage must change from the sublimation profile to the inverted growth profile when the flux is initiated (i.e., from the dotted line to the solid line in Fig. 1). The islands may be nucleated before the steady state coverage is reached, and since the center of the terrace must change coverage the most, it may not reach critical coverage until after a delay long enough for islands to nucleate elsewhere [24].

The island geometry provides the large possible ratio of lower to upper terrace surface areas. However, changes in crystallographic direction make it unclear what might be seen on a straighter step. Also, the small size of the island makes it difficult to determine the most unstable wavelength if it is comparable to or larger than the island size. Therefore, we prepared a large, roughly circular terrace surrounded by a thinner, annular terrace following a two temperature annealing procedure [25]. When the annular terrace was wide, the growth was stable, but when the annular terrace was about 5 μm in width or thinner the instability was readily observed.

Figure 4 shows the effect of the annular terrace width. Both steps advanced; however, the imaged area was comoving with the outer step. For the wide terrace, the inner step becomes slightly more irregular, but the step motion is nominally stable. For a narrow terrace the instability is dramatic. After growth, at the same flux and for the same duration as the wider terrace, the inner step wanders with a nearly sinusoidal profile.

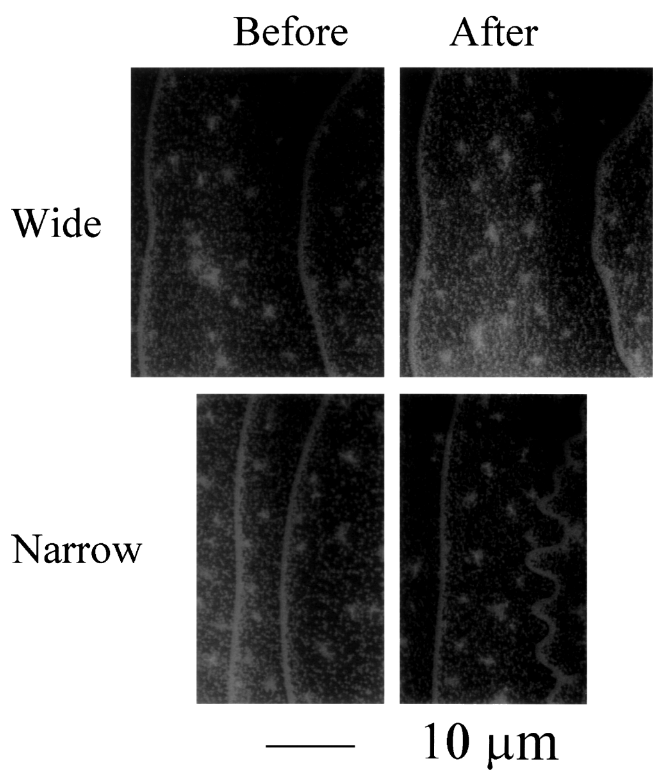

FIG. 4. Upper terrace size dependence of step morphology: Step structure before (left column) and after (right column) epitaxial growth for an initially wide annular terrace (17 μm wide, top row) and an initially narrow annular terrace (5 μm wide, bottom row). Initial inner terrace radii were 33 μm (top) and 54 μm (bottom). Growth was for 2 min 30 s with a flux of 1 ML/13 ± 1 min and a substrate temperature of 930 °C. In each image the outer step is at the left, the inner step is at the right, and the step down direction is to the right.

The wavelength of the wandering is roughly the same for the entire step, about 6 ± 1 μm [26], and, at least at early times, roughly independent of the amount of material deposited. The amplitude is highly dependent on the local step spacing prior to growth. Regions with small step spacing have much greater amplitude than larger spacings. With subsequent growth the amplitude continues to increase, becoming more and more fingerlike until ultimately the larger bulges engulf their neighbors.

To comment on the relation of the observations to BZ, although an ES barrier may exist on this surface, it is not essential here. The surface fluxes from upper and lower terraces differ even without one. The observations are in general agreement with the theory because it describes the competition of the stabilizing effects of surface tension with the destabilizing effects of incorporation from the lower step. It is clear that, unlike BZ, growth rate anisotropy is an important feature of the observed instability.

Speculating on the microscopic origin of the anisotropy, the slow growth planes may be the straightest, microscopically, and the fast growth steps may be made of slow growth segments. The rapid growth directions then correspond to the steps with the most kinks. This would be consistent with the model that incorporation occurs at kink sites, which is just the 1D analog of incorporation at steps in 2D.

To summarize, it has been shown that silicon crystal growth has a morphological instability similar to the theoretical prediction of BZ. The growth mode ranges systematically from stable step flow to unstable step flow and finally to island nucleation. Though no ES barrier is required, the instability is kinetic in origin, and kinetic anisotropy plays an essential role.

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