Shape Oscillations in Growth of Small Crystals

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The equilibrium shape of a large crystal is uniquely determined by the anisotropic surface energy. In sharp contrast, we show here that the equilibrium shape of a *small* crystal is *not unique*, for temperatures below the roughening temperature. Instead, the degree of facetting is an oscillatory function of crystal size. Using low-energy electron microscopy, we observe oscillations in the shape of silver crystallites as they grow; we demonstrate theoretically that such oscillations with size occur even in thermodynamic equilibrium.

One of the most fundamental problems in surface physics is the equilibrium shape of a crystal, which gives a direct picture of the dependence of surface energy on orientation [1]. Crystal shape has been understood in principle since the work of Wulff [2], and further fundamental contributions have been made by Herring and others [1,3]. However, all of this theoretical work addresses the thermodynamic limit of *large* crystals. In contrast, experimental observations of shape are restricted to very *small* crystals, since for larger crystals the shape approaches equilibrium at an intractibly slow rate.

Here we show that small crystals differ from large ones in a fascinating and unanticipated way. The equilibrium shape of small crystals is *not unique* at temperatures below the roughening temperature T_R. Instead, the shape is an *oscillatory function of the number of atoms*. The oscillations in shape reflect oscillations in the chemical potential as the crystal grows, with each cycle corresponding to completion of another layer on the flat facets. Thus the nonunique shape is directly connected to the fact that the canonical and grand canonical ensembles are not equivalent for small systems.

We have directly observed shape oscillations in the growth of small silver crystallites on Si(111), using low-energy electron microscopy (LEEM) [4]. With growth, the rounded corners of the crystal fill in and become sharper, until a step or two-dimensional (2D) island nucleates on the facet. The corners then become rounded again, and remain so until the 2D island grows to a complete layer. At that point the cycle begins again.

We begin with a very schematic discussion of the shape of small crystals, which permits us to qualitatively understand the experimental observations. A more detailed analysis, which shows that such oscillations are a fundamental feature of the equilibrium shape of small crystals, is given below.

Crystal shape generally evolves with temperature as sketched in Fig. 1. The $T = 0$ shape has smooth facets, here assumed to be flat, which meet at sharp corners as in Fig. 1(a). Above a temperature T_0 (which may be zero), the corners become rounded as in Fig. 1(b). The rounded corners, though macroscopically smooth, are thermally

"rough" on an atomic scale [1]. With increasing T, the rough regions grow at the expense of the flat facets, until at the roughening temperature T_R the facets shrink to nothing and the entire surface is rough, as in Fig. 1(c).

Even in the equilibrium case of arbitrarily slow growth, we must distinguish two limiting regimes. At low temperature, evaporation and vapor pressure are negligible. The crystal in effect has a fixed number N of atoms, and the shape equilibrates via surface diffusion. At high temperature, in contrast, evaporation is rapid; to maintain a steady state the crystal must be in equilibrium with a vapor, which fixes the chemical potential μ. Thus the low- and high-temperature regimes correspond to the canonical (constant N) and grand canonical (constant μ) ensembles. For a sufficiently large crystal, these are equivalent, but for the small crystals of interest here the distinction becomes crucial. In our experiment, and in molecular beam epitaxy in general, we are clearly in the low-temperature regime.

Now consider the growth of a crystal containing both rough and smooth regions, as in Fig. 1(b). A sufficiently large crystal will always have 2D islands on the facets, due to entropy. A small crystal will not, so atoms added to the flat facets must initiate 2D islands. Because of the energy cost of the step at the island's edge, 2D island formation is energetically unfavorable, especially for small islands (which have a large edge-to-area ratio). In contrast, atoms added to the rough region incur no such penalty. (Thermal roughness corresponds in effect to the
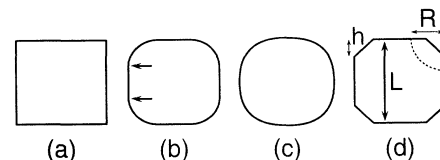

FIG. 1. Schematic of crystal shape in three temperature regimes: (a) $T < T_0$; (b) $T_0 < T < T_R$; (c) $T > T_R$. Arrows show boundary of one flat facet. Approximation used for shape (b) in calculation is shown in (d), along with assumed shape of 2D island (dotted line).

absence of any formation energy for steps.) Thus in a small crystal, atoms added to the crystal will at first go exclusively to the rough region.

As more atoms are added the corners fill in, until eventually the atoms have nowhere to go but to the facets. Subsequent atoms must form a 2D island on the facet. The island then acts as a reservoir, pinning the chemical potential near its large-crystal value, and absorbing the extra atoms from the corners, which become rounded again. Once the 2D island grows to cover the facet, additional atoms have nowhere to go but the rough region, and the cycle begins again. (However, once enough atoms have been added to form a complete layer on one facet, they will leave the rough region to do so, completing the cycle, even if the corners are not yet sharp.)

We have directly observed this cycle in LEEM images of growth of Ag crystals. Small epitaxial single crystals were grown at ~500 K by atom deposition on a Si(111) substrate. A time-ordered sequence of images is shown in Fig. 2. Only the facet parallel to the substrate surface is visible, because only the specularly reflected (0,0) low-energy electron diffraction (LEED) beam at normal incidence was used to form the image.

In Fig. 2(a) the crystal is completely facetted, with sharp corners. A 2D island (indicated by the arrow) then nucleates at the upper edge, and spreads across the facet, Figs. 2(b)–2(d), and the corners of the crystal become rounded. With the island gone, the rounded corners gradually become sharp again, Figs. 2(e)–2(h), at which point a new 2D island nucleates, Fig. 2(i), and the cycle repeats. In several cases we recorded multiple cycles of this oscillation in real-time video LEEM. To show the sharpening more clearly, Figs. 2(i)–2(l) give three images of a similar but larger crystal, grown at a lower Ag deposition rate.

We do not expect that our Ag crystallites are fully in equilibrium. But we have confirmed that the shape of the crystallite, whether sharp or rounded, is stable in time when growth is interrupted. This constitutes strong evidence that the nonunique shape is characteristic of equilibrium, and not an artifact of growth kinetics (a rich subject in its own right [5]). Nevertheless, given the unexpected nature of our observations, it is essential to demonstrate that such shape oscillations are a natural feature of thermodynamic equilibrium for small crystals. We illustrate this by explicitly calculating the shape of a small crystal as a function of the number of atoms. The necessary and sufficient conditions for shape oscillations are discussed further below.

For simplicity, we consider a crystal which at $T=0$ is a cube. To make the geometry tractible, we model the thermally rounded corners as flat (111)-oriented facets (though still thermally rough). One facet of this corner-truncated cube is shown in Fig. 1(d). The distance between cube faces is L, and the length of edge removed by truncation at each corner is h.
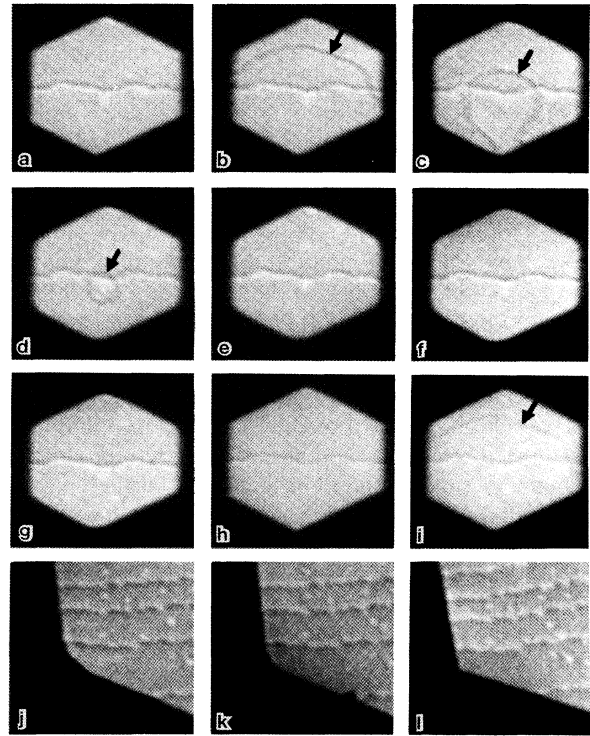

FIG. 2. LEEM images of a Ag crystallite growing on Si(111). Ag(111) facet parallel to surface is visible as a hexagon; substrate, other facets, and rounded regions of crystallite appear dark. (a)–(i) Time-ordered sequence of images showing full cycle. Each field of view is 1 μm across. Horizontal line present in all images is step at Ag-Si interface. 2D island (indicated by arrow) forms at the top in (b), and covers all of facet except small hole by (d); and corners become rounded. With further growth (e)–(h), corners become sharper, until new 2D island nucleates (i). (j)–(l) Similar sequence for larger crystallite, where sharpening of corner is more clearly resolved. Horizontal lines are steps at Ag-Si interface.

The crystal shape in the thermodynamic limit is given by [1]

$$r(\hat{n}) = r_0 \min_{\hat{m}} \left[\frac{\sigma(\hat{m})}{\hat{m} \cdot \hat{n}} \right] , \qquad (1)$$

where $\sigma(\hat{m})$ is the free energy per unit area of the surface with orientation $\hat{m}$, and r_0 specifies the overall size of the crystal. The shape assumed here is fully characterized by the dimensionless ratio h/L, the value of which in the thermodynamic limit we denote η. Solving Eq. (1) for η gives

$$\eta = \frac{3}{2} \left[1 - \frac{\sigma_r}{\sqrt{3}\sigma_0} \right] , \qquad (2)$$

where σ_0 and σ_r are, respectively, the free energy per unit area of the flat (001) and rough (111) regions. [We can

safely neglect the small difference between energy and free energy for the (001) facets, so σ_0 is also used below to denote the energy.]

To treat the small crystal, we make two observations regarding thermal fluctuations. First, we note that thermal fluctuations of the rough region of the crystal have very short correlation length, much shorter than the dimension of the crystal. Thus the rough corner region can still be accurately described by the "macroscopic" free energy σ_r. Second, fluctuations of the facet involve very long length scales; they consist either of large 2D islands or small islands which are far apart and so have large positional entropy. For a sufficiently small facet, such fluctuations cannot occur. While an island will eventually form on the facet, this does not correspond to a thermal fluctuation, and must be treated explicitly.

Describing the rough region by a macroscopic free energy, and explicitly including the possibility of a 2D island on a facet, which may grow to a complete layer, we have

$$N = N_c + N_i + N_l \, ,$$
$$E = E_c + E_i + E_l \, , \tag{3a}$$

where

$$N_c = (L^3 - 4h^3/3)/\Omega \, ,$$
$$E_c = N_c\varepsilon + \sigma_0(6L^2 - 8\eta h^2) \, , \tag{3b}$$

$$N_i = \pi R^2/4A \, ,$$
$$E_i = N_i\varepsilon + \lambda\pi R/2 \, , \tag{3c}$$

$$N_l = vL^2/A \, ,$$
$$E_l = N_l\varepsilon + 4\sigma_0 vL\,\Omega/A \, . \tag{3d}$$

Here N is the total number of atoms and E the total free energy of the crystal. N_c refers to the number of atoms in the crystal without any islands or extra layers on the facets, and E_c to its energy. L and h are defined above and in Fig. 1(d). [The last term in Eq. (3b) is the surface energy, where we have eliminated explicit reference to σ_r by using Eq. (2).] N_i and E_i are the contributions from the island, and N_l and E_l are those from v complete layers added to the facet. Ω is the volume and ε the energy per bulk atom. R is the 2D island radius, as in Fig. 1(d), and λ the free energy per length of the step defining the island edge. (We have assumed that the island forms a quarter circle at the corner of the facet; the energy of the extra surface area from the two straight sides can be absorbed into the value of λ.) The extra surface area created by adding v layers gives the last term in Eq. (3d). In Eqs. (3c) and (3d) we have omitted additional small terms which occur when $h \neq 0$, but which have no significant effect on our discussion.

The crystal shape at a given N is determined by minimizing the free energy E with respect to h, R, and v, for fixed N. The resulting values of h and R are oscillatory with increasing N, where each cycle corresponds to adding a layer to the facet ($v \rightarrow v+1$). As an illustration, we treat the special case $\eta = 0$, which arises at $T = T_0$. This case is convenient because E_c is then independent of h, and because the large-crystal equilibrium shape is simply a cube ($h = 0$). We also assume a large step energy, $\lambda \gg \sigma_0\Omega/A$, to guarantee (as seen below) that the island never becomes large enough for the assumption of circular shape to break down; however, these specific choices for η and λ are not required to obtain shape oscillations.

The resulting dependence of crystal properties on N is shown in Fig. 3. Beginning with the perfectly facetted cubic crystal of $N_0 = L^3/\Omega$ atoms, as atoms are added they initially must form an island. However, when the number of atoms added becomes greater than $N_x = 16\sigma_0^2 L^2\Omega^2/\pi\lambda^2 A^3$, it is energetically favorable to draw enough atoms from the corners to complete the layer. This eliminates the island energy E_i, at the cost of additional surface energy E_l. (Since $\eta = 0$, E_c is constant.) The corners are left rounded, despite the fact that the large-crystal shape has sharp corners. Any further atoms which are added then go to fill the corners, until the crystal is again fully facetted for $N = N_0 + L^2/A$, and the cycle begins again. Since either R or h is zero at all times, the dependence of h or R upon N can be read directly from Eq. (3) for N_i or N_c.

We also show in Fig. 3 the chemical potential $\mu \equiv dE/dN$ vs N. Here, μ varies dramatically with N. In particular, there is nominally a divergence of μ each time the crystal becomes fully facetted ($h \rightarrow 0$); but because
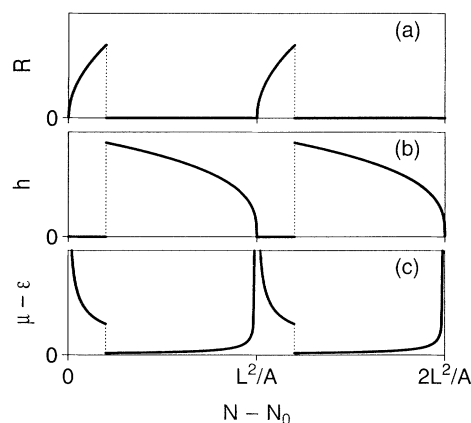

FIG. 3. Calculated variation of island size R and corner rounding h [cf. Fig. 1(d)], and of chemical potential μ, vs number of atoms N. Vertical scales are arbitrary. For $\eta = 0$ case treated here, $\mu - \varepsilon = 0$ throughout range where $R = 0$; to illustrate more typical behavior, μ is shown for small nonzero η.

of the discreteness of N, μ never actually becomes larger than an adatom energy. The close relation between μ and h has also been noted by Xiao and Rosenberger [6], in the somewhat different context of growth from a vapor.

A particularly intriguing feature of Fig. 3 is that, in equilibrium, there is a discontinuity in all quantities (μ, R, and h) at a critical value of N_i. Since this transition involves the motion (presumably by surface diffusion) of a large number of atoms from the corner to the facet, it cannot take place instantaneously. Thus in any experiment at a finite growth rate, as in Fig. 2, this transition will inevitably be smeared out as the island, though unstable, requires some time to cover the facet.

We stress that none of the approximations made here affects the basic conclusion, that the shape of a small crystal is an oscillatory function of N *even in equilibrium.* Including a more accurate shape than that of Fig. 1(d) would alter the detailed functional form of Eq. (3), but not its general features. Solving Eq. (3) for a value of η other than zero, or for a smaller value of λ, would simply shift the transition point in Fig. 3, and perhaps allow coexistence of nonzero R and h.

However, the *magnitude* of the oscillations depends sensitively upon the conditions. We have focused on the case of a fully facetted crystal, both because of its simplicity and to make direct connection with our experiment. However, at temperatures closer to T_R, where the crystal is more rounded, the added atoms will have only a slight effect on the shape before enough atoms have accumulated to form a full layer on a facet. The more rounded the crystal, the weaker the shape oscillations. As $T \rightarrow T_R$, the size of the facets approaches zero, and so the amplitude of the shape oscillations approaches zero. Also, the larger the crystal, the less the shape will be affected by the number of atoms corresponding to a layer on the facet, since this number scales as the $\frac{2}{3}$ power of the crystal size. As the crystal size becomes infinite, the relative shape oscillations go to zero.

Previous crystal-shape experiments [1] have typically been at temperatures near T_R, where the crystals are only weakly facetted, so only negligible shape oscillations could be expected. Moreover, the crystals studied were generally somewhat larger than here. In any case, in static electron-microscope pictures the oscillations would appear only as tiny shape differences between crystals, which are difficult to compare since they also differ in size and orientation. In contrast, by observing the growth of a single crystal over time, at a temperature where it is almost fully facetted, we are far more sensitive to small variations in shape, while the variations are much larger than at higher temperatures where the crystal is rounder.

The central remaining question is, what are the necessary and sufficient conditions for shape oscillations. For $\eta > 0$ ($T_0 < T < T_R$), if the crystal is so small that there are no thermal fluctuations on the facet, there clearly must be shape oscillations. But consider a larger crystal. There will then be thermally induced islands (and holes), but no thermally induced steps crossing the facet. As atoms are added, they may go to the rough region, go to the terrace (by changing the island distribution), or nucleate a step across the terrace. If there is a sufficiently high cost in free energy to change the island distribution, then the situation becomes just as for a small crystal, with the thermal islands playing no role except in determining the surface free energy σ_0. While a treatment of the thermal distribution of islands and its dependence on the number of atoms is beyond the scope of this paper, it thus appears likely that shape oscillations may occur even for large crystals in equilibrium, though these oscillations must be far too small to detect.

[1] For a review of equilibrium crystal shape and thermal effects, see M. Wortis, in *Chemistry and Physics of Solid Surfaces VII,* edited by R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1988), p. 367.

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[5] See, for example, M. Ozdemir and A. Zangwill, Phys. Rev. B **45**, 3718 (1992); R. F. Xiao, I. I. D. Alexander, and F. Rosenberger, Phys. Rev. A **43**, 2977 (1991); F. Liu and N. Goldenfeld, Physica (Amsterdam) **47D**, 124 (1991).

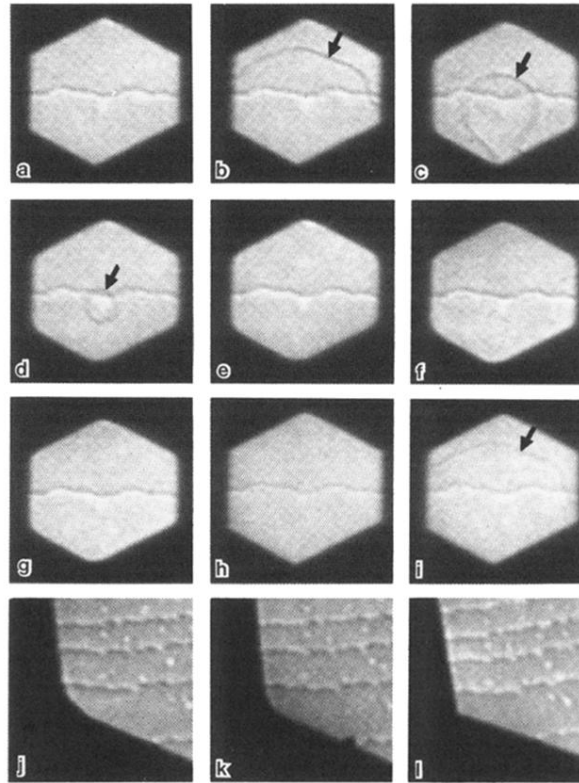[6] R. F. Xiao and F. Rosenberger, J. Cryst. Growth **114**, 536 (1991).

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