Critical Island Size for Layer-by-Layer Growth

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We show that in epitaxial growth, there is a critical island size R_c at which a second layer nucleates on top of the island. This provides a simple perspective on the conditions for smooth versus rough growth: For island spacing L_n, if $R_c < L_n$ the islands will nucleate a second layer before coalescence, giving multilayer growth. This occurs when there is a sufficiently large diffusion barrier (the "Schwoebel barrier") at the island edge. We demonstrate that surfactants can enforce layer-by-layer growth by reducing the island spacing. The dependence upon temperature is also explained.

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Expitaxial growth has long been a central problem in surface physics and materials physics. In particular, technological applications often require controlling growth to obtain smooth abrupt interfaces. Attention has therefore focused on the conditions leading to smooth layer-by-layer growth versus rough multilayer growth.

Two recent studies of epitaxial growth have highlighted opportunities for controlling the growth mode. van der Vegt *et al.* [1] showed that surfactants can be used to control whether growth is layer by layer or multilayer. More surprisingly, Kunkel *et al.* [2] found that *either* high *or* low temperatures can lead to layer-by-layer growth.

Here we address these important observations. We show that, as a monolayer island grows, there is a critical island radius R_c at which a second layer nucleates on top of the island. If R_c is small compared with the island separation, islands will nucleate a second layer before coalescence, giving multilayer growth. We find that the crucial role of a surfactant is to reduce the spacing between islands, so that coalescence occurs before the islands ever reach the critical radius. In addition, we consider how changing temperature affects the island separation and R_c, leading to a sequence of distinct growth modes.

We begin by considering an island of monolayer height, growing under a flux of atoms. With time, adatoms accumulate on the island, although some escape across the edge. Adatoms escaping from the island or diffusing in from the terrace are incorporated into the edge of the growing island.

Eventually the island grows large enough to coalesce with neighboring islands. If this occurs while the island is still a monolayer high, the original situation of a smooth complete layer is recovered, and one has layer-by-layer growth. If the density of adatoms grows sufficiently large before coalescence, however, a new layer will nucleate on top of the island, giving multilayer growth.

To quantify this description, we need to calculate the nucleation rate on top of the island. Nucleation and growth have already been treated extensively [3–8]. The island nucleation rate on a surface can be written [7]

$$\omega = \gamma a^{-4} D \eta^{\nu}, \tag{1}$$

where ν is the number of atoms in the smallest stable island, and η is the number of adatoms per surface cell of area a^2. For $\nu = 2$, γ is of order unity.

The dimensionless adatom density η obeys the diffusion equation $d\eta/dt = D\nabla^2\eta + a^2F$, where D is the diffusion constant and F is the incident atom flux. Then assuming that there is enough diffusion to maintain a steady-state distribution as the island slowly grows,

$$\eta = \eta_0 - \frac{F}{4D} a^2 r^2, \tag{2a}$$

where r is the distance from the center of the island.

The boundary condition at the island radius R is $d\eta/dr + \eta\alpha/a = 0$. Here α is the probability per unit time that an adatom which diffuses to the island edge will cross down off the island instead of being reflected, divided by the rate for a corresponding hop on the terrace. This leads to

$$\eta_0 = \frac{F}{4D} a^2 (R^2 + R L_\alpha), \tag{2b}$$

where $L_\alpha \equiv 2a/\alpha$. If the barrier to cross the island edge (often called the "Schwoebel barrier" [9]) exceeds the barrier E_d for diffusional hopping by an amount E_e, then α varies with temperature as $\exp(-E_e/kT)$.

Now we can determine the rate Ω at which a new layer nucleates on the island:

$$\Omega = \int_0^R \omega 2\pi r \, dr$$
$$= \frac{\pi\gamma D}{\nu+1} \left(\frac{F}{4D} \right)^{\nu} a^{2\nu-4} [(R^2 + R L_\alpha)^{\nu+1} - (R L_\alpha)^{\nu+1}]. \tag{3}$$

It is convenient to focus on two limiting cases. If there is no significant extra barrier for an adatom to cross the island edge, then $\alpha \sim 1$ and so $L_\alpha \ll R$, giving *case 1*:

$$\Omega_1 = \frac{\pi\gamma D}{\nu+1} \left(\frac{F}{4D} \right)^{\nu} a^{2\nu-4} R^{2\nu+2}. \tag{4a}$$

However, if the energy barrier $E_e \gg kT$, then α becomes exponentially small, and for $L_\alpha \gg R$ one has *case 2*:

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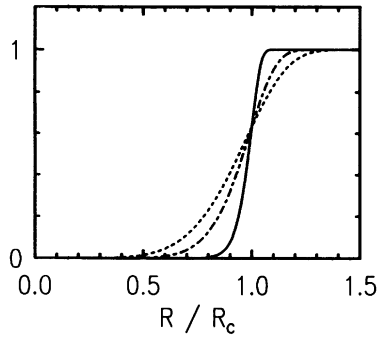

FIG. 1. The fraction f of islands on which a second layer has nucleated, versus island size R, Eq. (7). Solid, dot-dashed, and dotted lines are for $m=24$, 9, and 6. For case 2 ($m=v+4$), these correspond to $v=20$, 5, and 2. The last of these is the least abrupt onset possible.

$$\Omega_2=\pi\gamma D\left(\frac{F}{4D}\right)^{v}a^{2v-4}R^{v+2}L_a^{v}. \qquad (4b)$$

Case 1 was treated previously by Stoyanov and Markov [6]. However, as discussed below, for homoepitaxy it is generally only case 2 which leads to multilayer growth.

We now calculate the fraction f of islands which have nucleated a second layer on top. This fraction increases with time as

$$df/dt=\Omega(1-f). \qquad (5)$$

In solving Eq. (5), we prefer to focus on the island radius R instead of time t, where [10]

$$R^2=Fa^2L_n^2t. \qquad (6)$$

Here πL_n^2 is the area per island (the inverse nucleation density), so L_n is roughly half the distance between islands. Then

$$f=1-\exp[-(R/R_c)^m]. \qquad (7)$$

Equation (7) is valid in both of the limits treated above, but with different values of R_c and m. For case 1 ($L_a \ll R$), one has $m=2v+4$, and

$$R_{c1}=\left[(v+1)(2v+4)\frac{2L_n^2}{\pi\gamma}\left(\frac{4D}{F}\right)^{v-1}a^{6-2v}\right]^{1/(2v+4)}. \qquad (8a)$$

For case 2 ($L_a \gg R$), one has $m=v+4$, and

$$R_{c2}=\left[(v+4)\frac{2L_n^2}{\pi\gamma}\left(\frac{4D}{F}\right)^{v-1}L_a^{-v}a^{6-2v}\right]^{1/(v+4)}. \qquad (8b)$$

The minimum stable island size v may be as small as 2 atoms, and it is believed that $v=2$ for many systems, though for fcc metals values of v in the range 10–30 have also been suggested [7,11].

Equation (7) predicts that, as an island grows, the probability that a second layer has nucleated on top of the island will go rapidly from nearly zero for $R<R_c$ to nearly unity for $R>R_c$. This is illustrated in Fig. 1. Even in the least abrupt case, with $m=v+4$ and $v=2$, the probability of second-layer nucleation goes from 20% to 80% as R goes from $0.8R_c$ to $1.1R_c$.

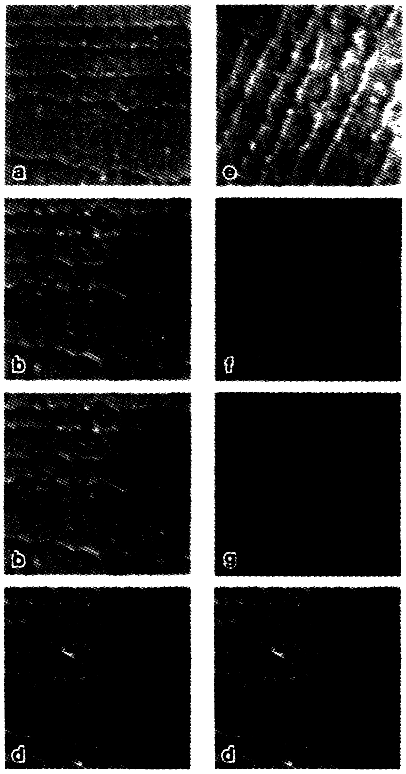

FIG. 2. LEEM images of growth of Ag on Ag(111) at $T=300$ K, without [(a)–(d)] and with [(e)–(h)] a surfactant. Each image is 1.2 μm on a side. (a) Bare Ag surface. Lines visible in image are associated with steps at the interface between Ag and the Si substrate. (b) Surface after deposition of a fraction of a monolayer of Ag, forming monolayer islands. The darker islands have atoms occupying hcp rather than fcc sites on the substrate. (c) After further deposition of Ag, small second-layer islands have nucleated on top of the largest islands. (d) Eventually, essentially all islands form second-layer islands on top. (e) Ag surface with a small fraction of a monolayer of Sb, a surfactant. (f) After deposition of roughly 0.5 monolayer of Ag, there are many closely spaced islands, so small as to be near our limit of resolution (150 Å). (g) At approximately 1 monolayer, the surface has become nearly smooth, indicating layer-by-layer growth. (h) At about 1.5 monolayers, roughness is similar to that at 0.5 monolayer.

We have observed this relatively abrupt onset of multilayer islands experimentally. Figure 2 shows low energy electron microscope (LEEM) [12] images of epitaxial growth of Ag at 300 K on step-free Ag(111). Upon deposition of a fraction of a monolayer of Ag, a number of monolayer islands appear [Fig. 2(b)]. With further growth [Fig. 2(c)] a second layer nucleates on top of the larger islands. Finally, in Fig. 2(d), the islands have all grown large enough to nucleate a second layer.

We expect layer-by-layer growth for $R_c > L_n$, and multilayer growth for $R_c < L_n$. (We neglect the statistical distribution of islands, which somewhat blurs the crossover between these two growth modes.) Qualitative arguments suggest that $R_{c1} \approx L_n$ in general [13], so for case 1 we always expect marginally layer-by-layer growth. For $\nu = 2$, we can verify this explicitly, if we are somewhat cavalier about factors of order unity. From Eq. (8a), $R_{c1} \to (L_n^2 a^2 4D/F)^{1/8}$, and it has been shown [8] that $L_n \approx (a^2 4D/F)^{1/6}$; so in this case $R_{c1} \approx L_n \approx (a^2 4D/F)^{1/6}$.

Conversely, we expect growth to be multilayer whenever case 2 holds. [Case 2 requires $L_\alpha \gg L_n \approx R_{c1}$, so from Eq. (8), $R_{c2} \ll L_n$.] For $\nu = 2$, this condition for multilayer growth reduces to $\alpha \ll (a^4 F/4D)^{1/6}$, or (assuming $\alpha \approx e^{-E_e/kT}$), $E_e > (kT/6)\ln(4D/Fa^4)$.

Recently, van der Vegt *et al.* [1] showed that such multilayer growth could be converted to layer-by-layer growth by using Sb as a surfactant. We obtain a direct picture of this process using LEEM [Figs. 2(e)–2(h)]. The presence of a little Sb dramatically increases the nucleation density over those in Figs. 2(a)–2(d). This effect was also noted in Ref. [1], and should be a common effect of surfactants [14].

In Fig. 2(c), we saw that the critical radius at this temperature and flux was ~0.2 μm. The spacing between islands in Fig. 2(f) is much smaller than this. Thus simply from the change in nucleation density, we expect layer-by-layer growth, i.e., no second-layer nucleation before the islands coalesce. Indeed, in Fig. 2(g), at one monolayer coverage the surface has grown smoother again, confirming that the growth is layer by layer. At 1.5 monolayer Ag [Fig. 2(h)], the island density is comparable to that at 0.5 monolayer, as expected for layer-by-layer growth. Our conclusion here finds further support in the recent results of Rosenfeld *et al.* [15], who showed that, by artificially increasing the island nucleation density, they could induce layer-by-layer growth even without a surfactant.

The Sb is expected to remain on the terrace, so it does not directly affect second-layer nucleation on the island. However, as suggested in Ref. [1], Sb could also act to reduce the barrier at the island edge, increasing α. While this is an intriguing possibility, the change in nucleation density is enough by itself to explain the transition from multilayer to layer-by-layer growth.

Temperature is another powerful factor controlling growth. At sufficiently high temperature (or high step density), atoms diffuse to steps without nucleating islands, giving step-flow growth. Below the step-flow regime, growth is typically layer by layer at high temperature, and multilayer at low temperature.

We can now understand this progression in terms of three competing length scales. These are the step separation L_s, the island separation L_n, and the length L_α which characterizes the diffusion barrier at the island edge. Step flow occurs if $L_n > L_s$ [16], and L_s is fixed by the angle θ of surface miscut ($L_s = h/\tan\theta$, where h is the step height). However, L_n is a rapidly increasing function of the temperature T, because the diffusion constant D reflects thermally activated hopping. Thus there is always some temperature T_s where $L_s \approx L_n$. Above T_s, $L_n > L_s$ and growth is by step flow. Below T_s, $L_n < L_s$ and growth is by island growth and coalescence.

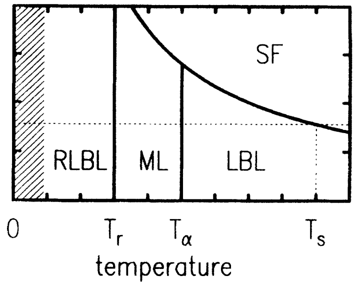

FIG. 3. Example of a possible "phase diagram" for growth. SF, LBL, ML, and RLBL, respectively, denote regimes of step-flow, layer-by-layer, multilayer, and reentrant layer-by-layer growth. Boundary lines indicate smooth crossover between regimes, not abrupt transitions. T_s corresponds to the onset of step flow at a given angle of miscut (a given step density) denoted by the dotted line. (The boundary shown for step flow represents a formal extrapolation [17]. If the y axis were restricted to a physically reasonable range of θ, the step-flow boundary would appear nearly vertical.) Crosshatching on left is a reminder that at very low T, our assumption of a nearly steady-state adatom distribution may be inapplicable.

Island growth is layer by layer if $L_\alpha \ll L_n$ (so case 1 applies), and multilayer for $L_\alpha \gg L_n$ (case 2), as discussed above. Since L_n is an increasing function of T, while L_α is a decreasing function of T, there is always a temperature T_α where $L_\alpha \approx L_n$. Unless preempted by step flow, growth is layer by layer for $T > T_\alpha$, and multilayer for $T < T_\alpha$.

It is helpful to draw a "phase diagram" to picture the behavior expected. Such a diagram is shown in Fig. 3. We stress that the temperatures discussed above do not correspond to true abrupt transitions, but rather to crossovers between regimes of behavior. These "transition temperatures" depend on the flux F as well as the material parameters.

While this simple picture is consistent with most observations, Kunkel *et al.* [2] recently reported "reentrant" layer-by-layer growth of Pt on Pt(111). They found that as the temperature was lowered, there was a transition from layer-by-layer to multilayer growth, but then there was an unexpected second transition at still lower temperature, back to layer-by-layer growth. The low-temperature islands have a dendritic shape [2], and the layer-by-layer growth has been attributed to a reduced diffusion barrier associated with the island shape [2,18].

While the actual low-temperature island shape is complex, we can explicitly understand the growth in two limits of the shape. If the island shape is essentially compact, but the edge is rough, then the shape of the edge gives adatoms more chances to escape, purely from the geometry. Thus on a coarse scale the rough edge has the same effect as a reduced barrier (larger a), so this geometric effect is not easily distinguished from the proposed [2] barrier reduction. Alternatively, we can consider a shape consisting of dendritic arms of characteristic width $2W$, with W remaining roughly constant as the island grows. In this case the maximum distance to diffuse to the island edge is W rather than R, and R enters explicitly only via Eq. (6). Repeating the nucleation calculation, we find that Eq. (7) still applies, but for this dendritic case (case 3) we have $m=2$ independent of ν, and

$$R_{c3}=L_n\left[\frac{\pi\gamma}{2}\left(\frac{F}{2D}\right)^{\nu-1}a^{2\nu-6}L_a^{\nu}W^{\nu+2}\right]^{-1/2}, \qquad (8c)$$

where R refers to the overall island size, and is implicitly defined by (6).

Layer-by-layer growth requires $R_{c3}>L_n$. This could happen if the real or effective barrier is reduced as discussed above, giving a small L_a. However, another possibility arises simply from the geometry. If the characteristic width W shrinks sufficiently rapidly with decreasing T, then R_{c3} can become larger than L_n at low T, giving precisely the sort of reentrant layer-by-layer growth seen by Kunkel *et al.* [2].

Unfortunately, it is difficult to generalize about the dependence of W (or of the real or effective barrier) on T in this dendritic regime. Nevertheless, we can denote by T_r the temperature at which $R_{c3}\approx L_n$, marking the onset of reentrant layer-by-layer growth. If $T_r<T_a$, as shown in Fig. 3, then one has the complex behavior reported by Kunkel *et al.* [2]. However, if $T_r>T_a$ (or if $T_r>T_s$), multilayer growth never occurs.

In conclusion, we have shown that as an island grows, there is a critical radius at which a second layer nucleates on top of the island. Whether growth is layer by layer or multilayer depends primarily upon whether the separation between islands is large or small compared to this radius. We have directly shown that a surfactant reduces the island separation, leading to layer-by-layer growth. For homoepitaxy, though, the growth mode is controlled primarily by the island-edge diffusion barrier. This picture also provides a natural explanation for the effect of temperature upon growth, in terms of competing length scales with different dependences on temperature.

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[10] Our assumption of a steady-state adatom density at each R implies that even atoms landing on the island eventually diffuse across the edge and are incorporated into the island. Thus the flux over the entire area πL_n^2 contributes to island growth. The steady-state assumption may break down for very large barriers, but then $R_{c2}\ll L_n$, so Eq. (6) is still rather accurate at the point where second-layer growth begins. However, once a second layer nucleates, it traps many or most atoms landing on the island. Then growth of the first layer slows and Eq. (6) no longer holds.

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[13] Essentially, L_n is the nearness of adatom "sinks" needed to keep the density η below the threshold for significant further nucleation [7,8]. Similarly, if island edges act as sinks for adatoms on top of the island (case 1), then R_{c1} is the nearness required for the sink to prevent further nucleation. Thus L_n and R_{c1} are determined by roughly the same condition, and so $R_{c1}\approx L_n$. (We assume throughout that the initial island nucleation takes place at the same temperature and flux as subsequent growth.)

[14] Just as a surfactant coats the surface and lowers the surface energy, in small quantities we expect the surfactant to segregate at steps, lowering the step energy and so reducing the barrier to nucleation. The net result is a much higher nucleation density, with smaller islands at a given coverage. The surfactant could also increase the nucleation density by reducing the adatom mobility; see S. Oppo, V. Fiorentini, and M. Scheffler, Phys. Rev. Lett. **71**, 2437 (1993).

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[16] This is a sufficient condition for step-flow growth. Since step flow is not a central concern here, we do not further pursue the necessary conditions.

[17] Roughly speaking, $L_n \sim L_{n0}e^{-E_n/kT}$ [7], where E_n is related to the island energy and diffusion barrier. The step-flow condition $L_n>L_s=h/\tan\theta$ then translates (for $\theta \ll 1$) to $\ln\theta > E_n/kT+\ln(h/L_{n0})$.

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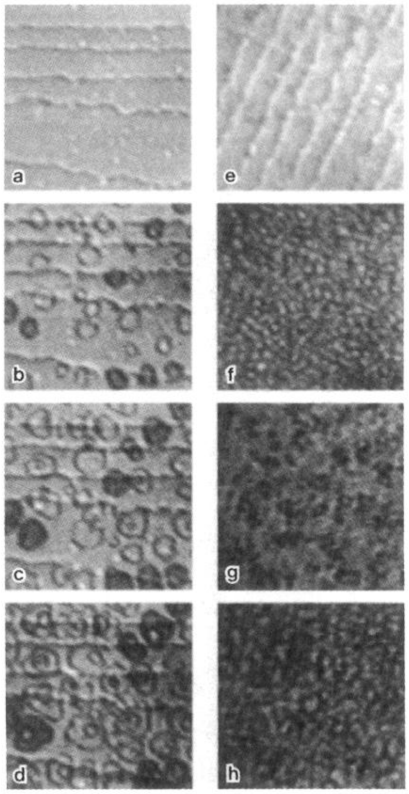

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