First-layer island growth during epitaxy

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We study the growth of first-layer islands making use of a mean-field model to describe the diffusion of free adatoms on the uncovered substrate. Model parameters are determined from recent experimental results for the growth of metals. The growth law is found using the quasi-steady-state approximation and we show that this result is consistent, at short times where this approximation may be questioned, with the exact asymptotic result.

I. INTRODUCTION

Understanding the behavior of island growth is a prerequisite for determining how to control surface morphology. Theoretical studies[1] and computer experiments[2] have been based on rate equation models that only implicitly include the details of the kinetic mechanisms. More recently, the quasi-steady-state (QSS) solution of the diffusion equation[3–5] has provided the basis for different approaches to this problem. In using the diffusion equation the growth of first-layer islands presents a special problem. The diffusing adatoms that fuel the growth must move through the complex, time-varying geometry defined by the growing islands. A cell model[4] where each island occupies a circular catchment area, which no flux enters or leaves, and a mean-flux argument[3] have been used to circumvent this difficulty. The latter was used in an *ad hoc* way without considering the broader implications relative to a mean-field description at the diffusion equation level. We provide here a very basic, but serviceable, mean-field description as one of two main objectives. The use of the QSS approximation is common to the different approaches cited[3–5] based on a diffusion equation description and has been used in other directly related contexts as well.[6] The validity of this approximation at short times following first-layer nucleation has not yet been shown, so that the resulting initial island growth law is less firmly established despite agreement with rate equation predictions. Our second objective is to show that the intuitive expectation that when diffusion on the substrate is fast (compared to deposition), the reorganization of the adatom density distribution to the QSS form occurs sufficiently fast so that this approximation correctly describes initial growth. An interesting conclusion that we find is that the *initial* growth law found using the QSS, which is insensitive to the island step boundary condition, is identical to that obtained from the exact asymptotic solution of the diffusion equation only when the correct boundary condition is used with the latter.

As discussed above, the emphasis of this paper will be on providing a more rigorous theoretical foundation for existing approaches to first-layer growth based on the diffusion equation. Specifically, we seek to provide a serviceable (i.e., tractable) analytical model that includes the relevant physical processes that need to be considered. For guidance in assessing a number of necessary assumptions we will refer to experimental results for the growth of metals.[7,8] Our main objectives are addressed sequentially in Secs. II and III. The mean-field model is presented and analyzed first, in Sec. II, and in Sec. III we show that the QSS approximation predicts the correct initial growth behavior. Our main conclusions are summarized in Sec. IV.

II. MEAN-FIELD MODEL

A. Growth prior to second-layer nucleation

We assume that first-layer nucleation results in an initial distribution of dimer islands of density $N=1/\pi L^2$, where $2L$ is the average island separation. All lengths will be expressed in lattice units so that for circular islands the initial radius is $R(t=0)=R_0=1$. To describe the growth of islands by incorporation of adatoms at the island step it is necessary to find the flux into the island. In previous work this was done by assuming that each island occupied a cell of radius L, at the boundary of which the adatom flux vanished,[4] or that the island received the average value of the total flux.[3] Here we formalize the latter approach in a mean-field model. We choose the simplest possible model for two reasons. First, more elaborate models lead to corrections that are of higher order in N than the basic model[9] and the island densities we consider are very small[7,8] (L is large). Also, elaboration of the basic model involves a mathematical structure that is particularly complex in two dimensions and would not appear to lead to new physical insight.

The basic model consists of a growing circular island of radius R embedded in an effective medium that produces the same flux of adatoms at R as the actual system of distributed islands would. The adatom density $n(r)$ is described by a diffusion equation which for a QSS is

$$\nabla^2 n+(1/\tau h)-\alpha^2 n=0, \quad R\leqslant r\leqslant\infty, \tag{1}$$

where $1/\tau$ is the deposition rate (per site), h is the diffusion coefficient, and α is a parameter that characterizes the medium at given R and can be determined, if required, by a consistency argument that we discuss later. Recall that lengths are expressed in lattice units so that the diffusion coefficient $h=\nu e(-E/kT)$, here with E the surface barrier to diffusion. In the QSS the time dependence is solely through R, which enters through the boundary condition

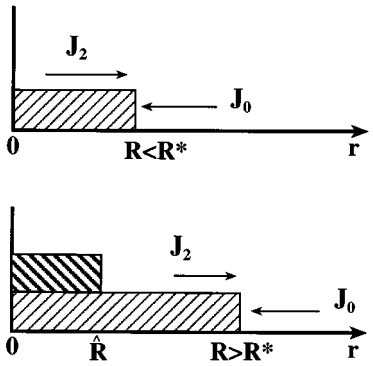

FIG. 1. Side view of first-layer island growing with radius $r=R$. When $R>R^*$ the second layer will nucleate; this changes J_2 but not J_0.

$$\frac{dn}{dr}\equiv n'=n, \quad r=R \tag{2}$$

so that

$$n=(1/\tau h\alpha^2)\left[1+\frac{K_0(\alpha r)}{K_0'(\alpha R)-K_0(\alpha R)}\right], \tag{3}$$

where K_0 is a modified Bessel function.

To determine the island growth law we do not need to know α, which we will see later depends strongly on R. Consistency requires that the net flux into the island step at $r=R$ from the substrate is equal to the net loss per island as described by the medium, which is given by $J_0=\bar{n}(h\alpha^2/N)(1-N\pi R^2)$, with $\bar{n}$ the density at infinity $\bar{n}=(1/\tau h\alpha^2)$, which follows from Eq. (3). Note that J_0 is independent of the step boundary condition Eq. (2). Then

$$\pi\dot{R}^2=2\pi R[J_0+J_2], \tag{4}$$

where J_2 is the net flux into R from the second layer (Fig. 1). For $R<R^*$, where R^* is the radius at which second-layer nucleation occurs, the QSS applied to the island surface (second layer) gives $J_2=(d/dr)[A-r^2/4h\tau]=R/2h\tau$, where the second-layer boundary condition is reflected in the dependence of the constant A on R, but J_2 will not depend on this. Collecting the above results, we find the known growth law

$$R^2=R_0^2+L^2(t/\tau), \tag{5}$$

where $R(t=0)\equiv R_0$.

Previously the total first-layer coverage has been equated to the island coverage,[3] with the free adatom contribution neglected. A calculation of the latter will provide a good illustration of representative values of α, which are found by equating J_0 to the net flux into R from the substrate $2\pi Rhn'|_R$, leading to

$$(2R/\alpha^2)_\alpha\left[\frac{\alpha K_1(\alpha R)}{K_1(\alpha R)+K_0(\alpha R)}\right]=(L^2-R^2). \tag{6}$$

For growth on Pt(111) (Ref. 7) at 425 K, experimental values are $L=97$, $R^*=53$, and $h\tau=10^{12}$. When $R=1$ we find $\alpha=5.8\times10^{-3}$ and for $R=50$, $\alpha=2.0\times10^{-2}$. The fractional coverage due to free adatoms is then

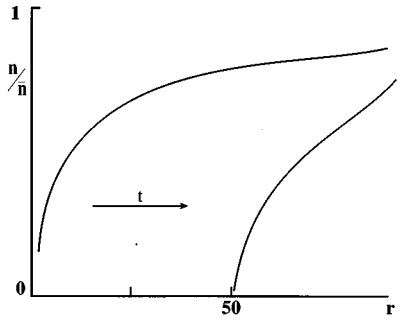

FIG. 2. First-layer adatom density ratio $n/\bar{n}$ from Eq. (3) for the growth conditions described below Eq. (6). Upper curve, $R_0=1$; lower curve, $R_0=50$.

$$\Theta_a(R)=(1/\tau h\alpha^2)[(R^2/L^2)+(1/\tau h\alpha^2)]^{-1} \tag{7}$$

and we find that this is negligible in both cases. In Fig. 2 we show $n/\bar{n}$ over the range $R\leqslant r\leqslant L$ for the limiting cases of $R=1$ and 50 using the values of α calculated above. The enhanced depletion at the island step in the latter case, due to the greater capture surface, is of particular interest.

In concluding this section we first note that, as seen in the above example, N is typically very small so that further elaboration of the mean-field model is impractical. The dependence of α on R given by Eq. (6), characteristic of two-dimensional systems with circular geometry, does not offer any specific insights other than the qualitative confirmation of the expected increase of α with R. A more transparent algebraic relationship can be found in one dimension, but as this is not of immediate interest we do not include these results here.

B. Post-second-layer nucleation growth

Following second-layer nucleation the adatom density $\hat{n}(r)$ in that layer is no longer defined over $0\leqslant r\leqslant R$, but rather $\hat{R}\leqslant r\leqslant R$, where $\hat{R}$ is the radius of the second-layer island. Accordingly, the QSS solution changes from $\hat{n}=A-(r^2/4h\tau)$ to $\hat{n}=A+B\ln r-(r^2/4h\tau)$, introducing a second nonzero constant of integration B. This then changes $J_2=h\hat{n}'|_R$, which from Eq. (4) results in a changed growth law. An artifact of the QSS is that the step boundary condition at R does not influence the growth law until second-layer nucleation occurs. To determine J_2 we find B from the boundary conditions $\hat{n}'|_R=\hat{n}|_{\hat{R}}$, $\hat{n}'|_R=(-s/h)\hat{n}|_R$, where $s/h=e-(E_B/kT)$ with E_B the *added* barrier to hopping down at the step

$$Bh=(1/2\tau)\left[\frac{R+(s/h)\hat{R}+(s/2h)(R^2-\hat{R}^2)}{(s/h)\ln R/\hat{R}+(1/R)+(s/h)(1/\hat{R})}\right]. \tag{8}$$

This is too complicated an expression to derive an analytical result for the growth law, but it does provide a basis for assessing the effectiveness of the barrier to limiting interlayer transport. Previously[4] we estimated the barrier for both growth on Pt(111) and Ag(111) using the experimental results cited earlier.[7,8] In both cases $s/h\cong10^{-3}$ so that $J_2=(R/2\tau)-Bh/R\cong0\ll J_0$, where J_0 is unchanged from

the value found earlier. The growth law for R then follows the schedule for the case where there is no interlayer transport

$$R^2 = L^2[1 - e(-t/\tau)] + R^{*2} e(-t/\tau), \tag{9}$$

where $t = 0$ now corresponds to $R = R^*$.

III. VALIDITY OF THE QSS APPROXIMATION AT SHORT TIMES

At the onset of first-layer nucleation the free adatom density on the substrate will be uniform and equal to the critical value for nucleation. Because diffusion is relatively fast compared to typical deposition times, the expectation that the adatom density will quickly reorganize to a QSS distribution provides the motivation for the use of this approximation in describing the slower process of island growth[3–5] as well as other diffusion-controlled processes[6] including the thermal oxidation of silicon.[10] The results already obtained in Sec. II A allow us to validate this expectation by exploiting the almost identical structure of Eq. (1) and its solution and the exact equations describing island growth at short times. This leads to an interesting conclusion regarding the step boundary conditions, which as we saw earlier play no role in the initial growth determined in the QSS approximation.

The island densities typical of metal deposition[4] are sufficiently small so that at the very short times we are concerned with the freshly nucleated islands can be considered as isolated. The free adatom density will respond to the islands presence by changing from its initial constant value and eventually the changing density fields about each island will begin to overlap and influence each other and the islands can no longer be considered as isolated. The *initial* growth can then be described by determining the flux to the island, directly from the substrate and through interlayer transport, obtained from the asymptotic solution of the time-dependent diffusion equation. On the substrate

$$\dot{n} = h\nabla^2 n + 1/\tau, \quad R \leqslant r \leqslant \infty, \tag{10}$$

subject to $n(r,0) = n_0$ and a boundary condition at $r = R$ for which we again take Eq. (2). Laplace transforming we obtain

$$\tilde{n} = p^{-1}(n_0 + 1/p\tau)\left[1 + \frac{K_0(qr)}{qK_0'(qR) - K_0(qR)}\right], \tag{11}$$

where p is the Laplace variable and $q = (p/h)^{1/2}$. This is virtually identical to Eq. (3); the required asymptotic analysis is simpler here since we are interested in $t \ll 1$ or large p. It follows from the properties of K_0 that $\tilde{n}' = 0$ at $r \ll L$, confirming our earlier assertion that at short times the islands can be considered as isolated. Differentiating Eq. (11), expanding for large p, and inverting we find

$$n'(R,t) = n_0[1 + 2(ht/\pi)^{1/2} + O(t)]. \tag{12}$$

Repeating this procedure for $\hat{n}$ we find

$$\hat{n}'(R,t) = O(t/\tau) \tag{13}$$

[note that $\hat{n}(r,0) = 0$ and that the homogeneous solution will contain $I_0(qr)$ rather than $K_0(qr)$ since $\hat{n}$ is defined over $0 \leqslant r \leqslant R$]. To lowest order we then have $\dot{R} = hn'(R,t)$ or

$$R = R_0 + n_0[ht + \tfrac{4}{3}(ht/\pi)^{3/2} + O(t^2)]. \tag{14}$$

The critical density can be estimated[4] as $n_0 = O(L^2/h\tau)$ so that to lowest order, i.e., for initial growth, the QSS prediction is qualitatively identical to the exact asymptotic result Eq. (14).

It is interesting to note that although the QSS is insensitive to the step boundary condition at short times, it leads to a growth law consistent with the exact asymptotic result, which explicitly depends on the boundary condition. If we had used the ''absorbing'' boundary[11] condition $n(R,t) = 0$, the second term in the square brackets in Eq. (11) becomes changed to $-K_0(qr)/K_0(qR)$ and $n'(R,t) = O(1/t^{1/2})$, which results in an initial growth law inconsistent with the QSS. Although the absorbing boundary condition is useful in some applications, the inconsistency illustrated above provides another example in which it leads to an incorrect qualitative behavior.[12]

IV. SUMMARY

We have obtained results for first-layer island growth based on a mean-field model for the free adatom diffusion on the substrate used together with the QSS approximation. For deposition on metals, making use of recent experimental results to establish the values of the model parameters, we have shown that the growth changes from perfect layer to nondiffusive behavior following second-layer nucleation. This crossover indicates that prior to nucleation the barrier to hopping down cannot alone prevent interlayer transport, but when it is coupled with an effective sink (the island) it becomes able to accomplish this. This suggests that delaying the onset of second-layer nucleation by lowering the barrier to interlayer transport would be an effective surfactant mechanism,[13] but a definitive answer to this important question will require consideration of other possibilities[3,14] and the final answer is still unclear. The mean-field model introduced here offers a distinct improvement over the cell model[4] and should also provide a more systematic basis for further study of growth than the related *ad hoc* approach used previously.[3]

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