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Rapid Note

Logarithmic islanding in submonolayer epitaxial growth

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Abstract. We investigate submonolayer epitaxial growth with a fixed monomer flux and irreversible aggregation of adatom islands due to an effective island diffusion, with a diffusivity for an mass k island proportional to $k^{-\mu}$. For $0 \leq \mu < 1$, there is a steady state, while for $\mu \geq 1$, continuously evolving logarithmic islanding occurs in which the island density grows extremely slowly, as $(\ln t)^{\mu/2}$. In the latter regime, the island size distribution exhibits complex, but universal, multiple-scale mass dependence which we account for theoretically.

PACS. 68.35.Fx Diffusion; interface formation – 36.40.Sx Diffusion and dynamics of clusters – 66.30.Fq Self-diffusion in metals, semimetals, and alloys

Submonolayer epitaxial thin film growth involves deposition of atoms onto a substrate and diffusion of these adatoms, leading to their aggregation into islands of ever-increasing size [1]. The resulting island morphology and mass distribution depend intimately on the microscopic hopping mechanisms of the adatoms. While this connection has long been recognized [1], its ramifications are still incompletely understood. Experimentally [2], it has been demonstrated that arbitrarily large islands diffuse due to various adatom hopping processes [3,4]. This effective island diffusivity D_k has been found to have a power-law dependence on mass k, $D_k \propto k^{-\mu}$, with μ typically in the range $(1/2, 3/2)$ [2–5]. A basic issue is to determine how this diffusivity affects the distribution of island sizes.

In this paper, we provide a comprehensive description in a minimal model for epitaxial island growth in the submonolayer regime. Simple and definitive theoretical predictions emerge which depend only on the mobility exponent μ. For $0 \leq \mu < 1$, a steady state arises in which the concentration of islands of mass k is given by $c_k \propto k^{-\tau}$, with $\tau = (3-\mu)/2$. For $\mu > 1$, the island density grows as $(\ln t)^{\mu/2}$, while the island mass distribution exhibits a complex but universal mass dependence. Our approach should apply to any epitaxial system in which the diffusivity of an island vanishes more rapidly than inversely with its mass.

A classic approach to calculate the island mass distribution is based on the Smoluchowski rate equations [6]. This method requires knowledge of the rate K_{ij} at which an island of mass i and an island of mass j aggregate to form an island of mass $i+j$. In the diffusion-controlled limit, this aggregation rate is given by the Smoluchowski formula $K_{ij} \sim (D_i + D_j)(R_i + R_j)^{d-2}$ [6]. Here R_i is the linear size of an island of mass i and d is the spatial dimensionality of the substrate. This Smoluchowski formula is applicable in $d > 2$, while in the relevant case of two dimensions, the reaction rate depends only logarithmically on the island size [6]. A crucial element in our analysis is to ignore this logarithmic dependence [7] and thus posit that the form of the reaction rate is independent of the geometrical size of islands. This allows us to treat islands as point-like throughout their evolution, a feature which further justifies the validity of a rate equation analysis and also leads to enormous simplifications in simulations.

With $D_k \propto k^{-\mu}$ and an appropriate choice of time units, the reaction rate in two dimensions becomes

$$K_{ij} = i^{-\mu} + j^{-\mu}, \tag{1}$$

and the Smoluchowski rate equations are

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j + F\,\delta_{k1}, \tag{2}$$

where F is the monomer flux. The rate equations (2) represent a mean-field approximation in which spatial fluctuations are neglected, and also a low-coverage approximation, since only binary interactions are treated.

Let us first consider the behavior in the steady state regime. To solve the rate equations in this case, we

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introduce the two generating functions

$$\mathcal{C}(z) = \sum_{k=1}^{\infty} c_k z^k, \quad \mathcal{C}_\mu(z) = \sum_{k=1}^{\infty} k^{-\mu} c_k z^k. \tag{3}$$

Multiplying equation (2) by z^k, and summing over all k, gives

$$\mathcal{C}_\mu(z)\mathcal{C}(z) - \mathcal{C}_\mu(z)N - \mathcal{C}(z)N_\mu + Fz = 0. \tag{4}$$

Here $N = \mathcal{C}(z=1) = \sum c_k$ is the total island density and $N_\mu = \mathcal{C}_\mu(z=1) = \sum k^{-\mu} c_k$.

We now assume an algebraic decay of the steady state concentration, $c_k \simeq C/k^\tau$ as $k \to \infty$. For this power law to hold, the exponent τ must be greater than 1, so that $\sum k^{-\tau}$ converges; this leads to the condition $\mu < 1$ for the mobility exponent, as will be shown below. From basic Tauberian theorems [8], the asymptotic form for c_k induces the following power-law singularities in the generating functions as $z \to 1$

$$\begin{aligned} \mathcal{C}(z) &= N + C\Gamma(1-\tau)(1-z)^{\tau-1} + \dots, \\ \mathcal{C}_\mu(z) &= N_\mu + C\Gamma(1-\tau-\mu)(1-z)^{\tau+\mu-1} + \dots \end{aligned} \tag{5}$$

The leading constant factor in each line is finite and coincides with the definition given in equation (3) if the exponent of the second term is positive. Otherwise, the constant factor vanishes and the generating function has a power-law divergence as $z \to 1$. Substituting these expansions into equation (4) and matching the leading behavior in $(1-z)$ leads to the decay exponent $\tau = (3-\mu)/2$. The condition for a steady state to occur, $\tau > 1$, thus imposes an upper bound on the mobility exponent, $\mu < 1$. From matching the leading behavior in $(1-z)$, the constant C may also be determined, from which the island mass distribution in the steady-state regime $0 \le \mu < 1$ is

$$c_k \simeq \sqrt{\frac{F(1-\mu^2)\cos(\pi\mu/2)}{4\pi}}\; k^{-(3-\mu)/2}. \tag{6}$$

This mass distribution holds only up to a cutoff $K(t) \sim t^\zeta$ whose value is determined by requiring that the mass injected into the system equals Ft. Islands of mass greater than $K(t)$ have not yet had time to form. Therefore

$$M(t) = \sum_{k=1}^{\infty} k c_k(t) \sim \sum_{k=1}^{K(t)} k^{(\mu-1)/2} \sim t^{(\mu+1)\zeta/2}, \tag{7}$$

implying $\zeta(\mu) = 2/(\mu+1)$.

For $\mu \ge 1$, we shall show that the system continuously evolves, but at a logarithmic rate. When $\mu > 1$, the density of islands and the concentration of islands of size $k \ll \ln(t\sqrt{F})$, respectively, are

$$\begin{aligned} N(t) &\simeq \sqrt{F}\left[\frac{\sin(\pi/\mu)}{\pi}\;\ln(t\sqrt{F})\right]^{\mu/2}, \\ c_k(t) &\sim \sqrt{F}\,(k!)^\mu\,\Big(\ln(t\sqrt{F})\Big)^{-\mu(2k-1)/2}. \end{aligned} \tag{8}$$

In the borderline case of $\mu = 1$, nested logarithmic behavior arises with $N(t) \sim \sqrt{F\ln(t\sqrt{F})/\ln(\ln(t\sqrt{F}))}$.

Our argument leading to equations (8) is based on the physical picture that the system evolves slowly because the growth of islands by aggregation is counterbalanced by the input of monomers. These competing effects lead to nearly time-independent island concentrations over an "inner" size range, while more strongly-time-dependent behavior occurs in an "outer" range of the largest island sizes. In the inner region, this picture motivates the use of the quasi-static approximation, where the time derivative in equation (2) is initially neglected, from which relative island concentrations are obtained. The time dependent *absolute* island concentrations are then determined by the condition that the total mass in the system is proportional to t. The validity of this approach may be verified *a posteriori*, where the logarithmic dependences in equations (8) imply that the temporal derivatives in the Smoluchowski rate equations are asymptotically negligible.

Within this quasi-static framework, equations (2) become

$$\begin{aligned} 0 &= 1 - c_1\,(N + N_\mu)\,, \\ 0 &= \frac{1}{2}\sum_{i+j=k}\left(i^{-\mu} + j^{-\mu}\right)c_i c_j - c_k\left(k^{-\mu}N + N_\mu\right). \end{aligned} \tag{9}$$

Further, by summing equations (9) over all k, the total island density in the quasi-static limit obeys

$$0 = 1 - NN_\mu. \tag{10}$$

In equations (9, 10) we have eliminated the input rate by the scale transformation $c_k \to \sqrt{F}\,c_k$, and have also scaled the time variable by $t \to t/\sqrt{F}$ so that the mass density obeys $M(t) = t$.

Equation (10) immediately gives $N_\mu = N^{-1}$, and then from the first of equations (9), $c_1 \simeq 1/N$. The remainder of equations (9) may then be solved recursively. By writing the first few of these equations, it is immediately evident that the dominant contribution to c_k is the term in the quadratic product which is proportional to $c_1 c_{k-1}$. If we keep only this contribution, the resulting recursion may be straightforwardly solved to yield

$$c_k \simeq \frac{1}{N}\prod_{j=2}^{k}(1+N^2 j^{-\mu})^{-1}\prod_{j=1}^{k-1}(1+j^{-\mu}) \equiv \frac{1}{N}\prod_{j=2}^{k}B_j\prod_{j=1}^{k-1}b_j. \tag{11}$$

Since $B_j \ll 1$ for $j^\mu \ll N^2$ and $B_j \to 1$ for $j^\mu \gg N^2$, this leads to c_k being a rapidly decreasing function of k for $k \ll N^{2/\mu} \equiv \kappa$, and then converging to a finite value defined to be ρ for $k > \kappa$ (inset to Fig. 1).

To solve for c_k, first note that for $\mu > 1$ the product $\prod_j b_j$ converges, so that it may treated as constant. We then write the product over the B_j as the exponential of a sum and take the continuum limit. This leads to

$$c_k \sim \frac{1}{N}\exp\left[-N^{2/\mu}\int_0^x \ln(1+w^{-\mu})\,dw\right], \tag{12}$$

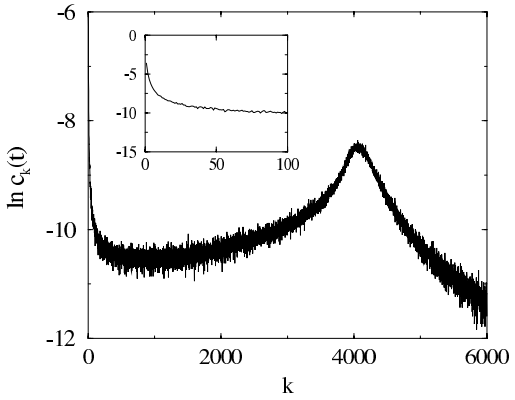

Fig. 1. Plot of $\ln c_k(t)$ *versus* k at $t \approx 22\,000$ for $\mu = 1.5$. The data is based on 5000 realizations of an initially empty system of 2000 sites with $F = 0.05$. This figure shows the existence of an inner scale $k \lesssim \kappa \approx 100$ (inset) and an outer scale for $k \approx K \approx 4000$.

where $w = j/N^{2/\mu}$ and $x = k/N^{2/\mu}$. For $\mu > 1$, the integral in equation (12) converges as $x \to \infty$ and the limiting value ρ may be determined by taking the upper limit of the integral as infinite. This gives

$$\rho \sim \frac{1}{N} \exp\left[-A_\mu N^{2/\mu}\right], \tag{13}$$

with $A_\mu = \int_0^\infty \ln(1+w^{-\mu})\, dw = \pi/\sin(\pi/\mu)$. Within the quasi-static approximation, this constancy in c_k should persist over the range, $\kappa \lesssim k \ll K$.

However, this quasi-static approximation is inadequate in the outer region $k \gg \kappa$, because the temporal decay of the densities becomes important in this size range. We therefore separately account for the distribution of these "raw" (evolving) islands and then perform a matched asymptotic expansion [9], to join the inner ($k \ll K$) quasi-static solution of "ripe" islands to the outer solution of raw islands in the overlap region $\kappa \ll k \ll K$. We shall see that $\kappa \sim \ln t$ and $K \sim t/(\ln t)^{\mu/2}$, so that the matched asymptotic expansion is valid.

In the outer region, the maximal reactivity of large islands is with monomers and the asymptotically dominant terms in the rate equations are [10]

$$\frac{dc_k}{dt} = c_1\,(c_{k-1} - c_k)\,. \tag{14}$$

Since these raw islands are large, we employ the continuum limit of equation (14),

$$\left(\frac{\partial}{\partial T} + \frac{\partial}{\partial k} - \frac{1}{2}\,\frac{\partial^2}{\partial k^2}\right) c_k(T) = 0, \tag{15}$$

where $T = \int_0^t dt'\, c_1(t')$. If we neglect the diffusive term, the solution of the resulting wave equation is $c_k(T) = f(T-k)$, with $f(x)$ arbitrary. Matching with the inner solution, we get

$$c_k(T) = \rho(T-k), \tag{16}$$

where T has to be determined self-consistently. Thus the density of relatively large islands, with k of the order of T, equals the density of the smallest islands; this is the mechanism that leads to the peak in $c_k(t)$ (Fig. 1). The above formula also provides the estimate $k = K \approx T$ for the cutoff size beyond which the island density vanishes.

To close the solution, we need to determine the time dependence of the total island density N and hence the absolute island concentrations. To accomplish this, we use the sum rules for the mass and island densities, $\sum k c_k = M \equiv t$ and $\sum c_k = N$. These imply

$$t = \int_0^T du\,(T-u)\rho(u), \quad N = \int_0^T du\,\rho(u). \tag{17}$$

In both integrals, the subdominant contribution due to small islands has been neglected; further, the second term in the first integral is negligible. The second sum rule also gives $\dfrac{dN}{dT} = \rho(T)$. Combining this with equation (13), we find

$$\rho(T) \sim \frac{(\ln T)^{\mu/2-1}}{T} \tag{18}$$

and we also obtain equation (8). The raw island size distribution, obtained by combining equations (16, 18), is,

$$c_k(T) \sim \frac{[\ln(T-k)]^{\mu/2-1}}{T-k}, \tag{19}$$

which is singular at $k = K = T$. Near the mass cutoff, $T - k \sim \sqrt{T}$, this singularity is smoothed out by the diffusive term in equation (15). Thus instead of the singularity, the density of raw islands reaches a peak value of the order of $t^{-1/2}$ and then rapidly vanishes.

To check our prediction for c_k, we simulated the mean field limit of submonolayer epitaxial growth. In the simulation, a point island of mass k moves equiprobably to any site with a probability proportional to $k^{-\mu}$, as mandated by the power-law mass-dependent island diffusivity. There is also irreversible aggregation whenever two islands meet, as well as a steady monomer flux entering the system. We observe that $N(t)$ grows extremely slowly with time and that $c_k(t)$ has a complex mass dependence where $c_k(t)$ first decreases extremely quickly with k, then increases at a slower rate over a substantial range in k, and finally exhibits a peak when $k \approx K$, in agreement with our theory (Fig. 1).

In the borderline case $\mu = 1$, subtler nested logarithmic behavior arises, as reflected by the additional singularity in equation (8) as $\mu \to 1$. In this case, the contribution of the next leading term $c_2 c_{k-2}$ in the rate equations (Eqs. (9)) is relevant and we find that for $k \ll N^2$, c_k has similar qualitative behavior as in the case $\mu > 1$, but the analog of equation (13) is now $\rho \sim \exp\left[-N^2 \ln N^2\right]$. Paralleling the analysis of the case $\mu > 1$, the total island concentration and the concentration of islands of mass $k \ll N^2$ are (compare with Eqs. (8))

$$\begin{aligned} N(t) &\sim \sqrt{\ln t/\ln(\ln t)}, \\ c_k &\sim (k+1)!\,[\ln t/\ln(\ln t)]^{-(2k-1)/2}\,. \end{aligned} \tag{20}$$

Over the intermediate-mass range $\kappa \lesssim k \ll K$, the density is approximately constant, $c_k(T) \simeq \rho(T)$, with

$$\rho(T) \sim T^{-1}(\ln T)^{-1}[\ln(\ln T)]^{-1}. \quad (21)$$

Finally, the raw island density given by equations (16, 21) holds up to a mass cutoff which is now $K(t) \sim t\sqrt{\ln(\ln t)/\ln t}$.

To apply our results to real submonolayer epitaxial systems, note that in the submonolayer regime, the coverage must be small, that is, $M \equiv Ft \ll 1$ [12]. On the other hand, the asymptotic predictions of our theory apply when $t\sqrt{F} \gg 1$. Consequently, our results should be valid in the time range $F^{-1/2} \ll t \ll F^{-1}$. Since the (dimensionless) flux F is small in epitaxy experiments, the time range over which our theory will apply is correspondingly large. A further connection with experimental results is to determine the island density at the end of the submonolayer regime, $t_{max} \sim F^{-1}$. Our theory predicts that this island density attains the value

$$N_{max} \sim F^{1/2}[\ln(1/F)]^{\mu/2}. \quad (22)$$

Various investigations found that N_{max} varies as F^{χ}, with flux exponent typically in the range $1/3 \leq \chi \leq 1/2$ [11,13]. In fact, for the class of models where only islands of up to a given size diffuse and larger islands are immobile, the flux exponent depends on this cutoff [13]. Fortunately, the generic situation of power law mass-dependent island diffusivity is simpler, and the flux exponent is independent of the mobility exponent, although the subdominant logarithmic factor does depend on the mobility exponent. This leads to a corresponding μ dependence for the *effective* flux exponent $\chi_{eff} = \frac{1}{2}\left[1 - \mu\frac{\ln(\ln(1/F))}{\ln(1/F)}\right]$, a feature which may be useful for interpreting experimental and numerical data.

Finally, our approach can be applied to *any* mass-dependent island diffusivity which decays faster than its inverse mass. For this general situation, the analog of equation (11) is $c_k \sim N^{-1}\prod^{k}(1+D_j)(1+N^2D_j)^{-1}$. For example, if the diffusivity decays exponentially in island mass, $D_k \sim e^{-2ak}$, a case investigated numerically in reference [14], we obtain $N(t) \sim \exp(\sqrt{a\ln t})$. This unusual growth – faster than any power of logarithm but slower than any power law – would be difficult to deduce by numerical methods alone. Correspondingly, the maximum island density is

$$N_{max} \sim \sqrt{F}\exp\left[\sqrt{\frac{a}{2}\ln(1/F)}\right], \quad (23)$$

so again $\chi = 1/2$. Numerically, the exponent χ was found to be a decreasing function of a [14].

In summary, we determined the kinetics of islanding in submonolayer epitaxial growth, for which adatom hopping induces a power-law mass-dependent island diffusion, with $D_k \propto k^{-\mu}$. For mobility exponent $0 \leq \mu < 1$, a steady state island concentration arises. For $\mu \geq 1$, logarithmic time dependence arises in which the total island density $N(t) \propto (\ln t)^{\mu/2}$. Such a logarithmic dependence, a feature which generally signals marginal behavior, occurs in the entire regime $1 \leq \mu < \infty$. The island mass distribution exhibits a rich dependence, with a precipitous decay in a "boundary layer" $k \ll \kappa$ (with $\kappa \sim \ln t$); a gradual growth in the main part of the mass distribution $\kappa < k < K$ (with $K \sim t(\ln t)^{-\mu/2}$); followed by an internal layer $|k - K| \sim \sqrt{t}$ where the density of islands reaches a peak and then sharply vanishes. Our analysis also suggests that for all epitaxial systems with the diffusivity of an island decaying more rapidly than its inverse mass, N_{max} is universally proportional to $F^{1/2}$ times a subdominant model-dependent factor, as in equations (22) or (23).

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