

Initial Stages of Thin Film Growth in the Presence of Island-Edge Barriers

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A model of submonolayer thin film growth is studied, where the attachment of atoms to island edges is hindered by an energy barrier. A novel behavior of the density of islands, N_s , is predicted as a function of flux F and temperature T . For example, N_s scales as F^X with $X = 2i^*/(i^* + 3)$, where i^* is the critical island size, in contrast with the standard result $X = i^*/(i^* + 2)$. The theory is applicable to surfactant mediated growth and chemical vapor deposition. It explains recent experiments, which are inconsistent with the standard theory. [S0031-9007(96)02220-X]

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Thin film growth processes are of tremendous importance for the fabrication of nanostructures and electronic devices. Technological advances in device miniaturization depend largely on the degree to which one can control the growth process, the epitaxial quality of the film, and the morphology of the surface. It is therefore essential to understand the microscopic processes involved in thin film growth and especially their effect on the structure of the film.

Of particular interest are the initial stages of growth or the submonolayer regime, which is relatively easy to investigate both experimentally and theoretically. It is possible to learn from such studies about the relevant microscopic processes and their respective energy barriers. For example, when the film evolves by nucleation, growth, and coalescence of two dimensional (2D) islands, the shape and size distributions of the islands and their dependence on physical parameters, such as temperature, flux, and coverage, yield information about various diffusion processes, attachment and detachment of atoms to and from island edges, etc. [1].

The first theories of diffusion of atoms in the presence of steps assumed that step edges are perfect sinks for adatoms [2]. This assumption was later relaxed [3], and kinetic coefficients were introduced to take into account the finite energy barriers [4] associated with attachment and detachment of adatoms to and from the edges. The perfect sink assumption has been shown to yield reasonable results under many experimental conditions. It was realized, however, that it fails in several important cases. For example, a significant barrier for attachment of adatoms to steps from the terrace above leads to a kinetic instability of the flat surface and to the growth of large mounds [5]. An asymmetry in the barriers for adatom attachment from below and above the step can also lead to peculiar step bunching [6] as well as fingering [7] instabilities. Island-edge barriers may be important in surfactant mediated growth, where a surfactant atom can bind to an island edge. In order for an adatom to attach to the edge, surfactant atoms have to be removed from there. Kandel and Kaxiras explained [8,9] experimental results related to surfactant mediated growth by assuming

that the energy barrier for such a change in the atomic configuration is large [10]. Island-edge barriers may also occur in chemical vapor deposition (CVD). For example, during CVD of Si on Si using disilane, the surface is covered with hydrogen, which can bind to island edges similarly to surfactant atoms [11].

In this Letter, the effect of island-edge barriers on submonolayer growth is studied in the framework of rate equation theory [1,12,13]. In particular, the density of 2D islands on the surface, $N_s(F, T, \theta)$, is calculated as a function of flux F , temperature T , and coverage θ . It is shown that island-edge barriers have a dramatic, experimentally observable, effect on the behavior of N_s . Although finite island-edge barriers have been studied before [14,15] in the context of submonolayer growth, it is the first time their detailed effect on the dependence of the island density on flux and temperature is addressed.

The simplest scheme for the calculation of N_s is the critical island approximation, where it is assumed that islands that contain more than i^* atoms are stable, while smaller ones are not and can decay [16]. Within this scheme, N_s is the density of *stable* islands, and a detailed balance relation is assumed to hold [17] between the densities of unstable islands, N_i ($i \leq i^*$), and the average adatom density \bar{n} ,

$$\Omega N_i = (\Omega \bar{n})^i e^{\beta E_i}, \quad (1)$$

where Ω is the atomic area of the solid, $\beta = 1/k_B T$, and E_i is the binding energy of an island of i atoms.

Now one can write down the rate equation for the density of stable islands,

$$\frac{dN_s}{dt} = I - C, \quad (2)$$

where C and I are the coalescence and nucleation rates per unit area. When the coverage is small, coalescence does not occur and $C \approx 0$. Since this is the limit of interest in this work, C is completely neglected below. The nucleation rate is

$$I = \sigma \bar{n} N^* S^*. \quad (3)$$

Here σ is the capture coefficient of a critical island, $N^* = N_{i^*}$ and

$$S^* = \nu \Omega e^{-\beta(E_d + E_b^*)}. \quad (4)$$

In the equation above, E_d is the diffusion barrier and E_b^* is the additional barrier for attachment of adatoms to the edge of a critical island (the limit where the island edge is a perfect sink is obtained by taking $E_b^* = 0$). ν is the attempt frequency, assumed to be the same for all microscopic processes. Thus $S^* = D \exp(-\beta E_b^*)$, where D is the diffusion constant.

N^* can be expressed in terms of \bar{n} via Eq. (1), and thus the nucleation term, I , is a function of the average adatom density. To estimate \bar{n} , consider the density of adatoms, $n(r)$, around a typical stable island of radius R (r is the distance from the center of the island and radial symmetry is assumed). Under conditions of complete condensation, where no evaporation occurs, $n(r)$ obeys the diffusion equation

$$D \left[\frac{d^2 n(r)}{dr^2} + \frac{1}{r} \frac{dn(r)}{dr} \right] + F = 0, \quad (5)$$

where the quasistatic approximation has been used, suppressing the time derivative of the adatom density. This approximation is valid when diffusion is fast enough so that at each instance of time, $n(r)$ reaches a quasisteady state, where the flux is almost entirely compensated by the attachment of adatoms to stable islands. The relevant solution of Eq. (5) obeys the following boundary conditions:

$$\begin{aligned} \text{(i)} \quad \left. \frac{dn}{dr} \right|_{r=R} &= \frac{1}{\sqrt{\Omega}} \frac{S}{D-S} n(R), \\ \text{(ii)} \quad \left. \frac{dn}{dr} \right|_{r=L} &= 0, \end{aligned} \quad (6)$$

where $S = D \exp(-\beta E_b)$, E_b is the additional energy barrier for attachment of adatoms to the edge of a stable island, and L is half the distance between stable islands ($N_s = 1/\pi L^2$). The first boundary condition holds for large islands, and was derived by Bales and Zangwill [15].

The solution of these equations is

$$\begin{aligned} n(r) &= \frac{FL^2}{2D} \ln \frac{r}{R} + \frac{F}{4D} (R^2 - r^2) \\ &+ \frac{F\sqrt{\Omega}L^2}{2R} \frac{D-S}{DS} \left(1 - \frac{R^2}{L^2} \right). \end{aligned} \quad (7)$$

Following Stowell and co-workers [12], it is easy to obtain an expression for \bar{n} ,

$$\begin{aligned} \bar{n} &= \frac{1}{\pi(L^2 - R^2)} \int_R^L 2\pi r n(r) dr \\ &\approx \frac{F}{4\pi D} \left(-\ln \theta - \frac{3}{2} \right) \frac{1}{N_s} + \frac{F}{2S} \frac{D-S}{D} \sqrt{\frac{\Omega}{\pi\theta N_s}}, \end{aligned} \quad (8)$$

where it is assumed that the density of stable islands is already large enough so that $\theta \approx R^2/L^2$ and the contribution of \bar{n} to the coverage is negligible. Since this theory is valid only in the small coverage limit, terms that vanish when $\theta \rightarrow 0$ were omitted.

Equation (2) can now be rewritten as

$$\frac{dN_s}{d\theta} = \frac{\sigma\Omega^{i^*-2}}{F} e^{\beta E^*} S^* \bar{n}^{i^*+1}, \quad (9)$$

where the relation $\theta = F\Omega t$ was used, \bar{n} is given by Eq. (8), and $E^* = E_{i^*}$.

Equation (9) can be solved numerically starting from some initial condition $N_s(F, T, \theta_i) = N_s^{(i)}$ ($\theta_i \neq 0$ since the quasistatic approximation does not hold when $\theta = 0$). But it is useful to consider two limiting cases where the problem can be solved analytically. These limits occur when one of the two terms in expression (8) for \bar{n} is small and can be neglected. More quantitatively, the ratio of the two terms is

$$G(F, T, \theta) = \frac{2\sqrt{\pi\Omega}}{\sqrt{\theta}(-\ln\theta - 3/2)} (e^{\beta E_b} - 1)\sqrt{N_s}. \quad (10)$$

If G is much smaller than 1 (limit I) for $\theta > \theta_i$, the second term on the right-hand side of Eq. (8) can be neglected. This is the perfect sink limit $S \rightarrow D$ ($E_b \rightarrow 0$), and in this case standard results [1] are expected to hold. In limit II, on the other hand, $G \gg 1$ for $\theta > \theta_i$, and the second term in (8) dominates; this is the case where $\exp(\beta E_b) \gg 1$, and the island-edge barrier is most important. In limit I, attachment of adatoms to island edges is infinitely fast and the kinetics is diffusion limited, whereas in limit II diffusion is fast, and the kinetics of adatoms is limited by the slow attachment to island edges. In both limits, Eq. (9) can be written in the form

$$\frac{d(N_s \Omega)^\Gamma}{d\theta} = \Gamma \sigma H(\theta) e^{\beta \mathcal{E}} \left(\frac{\Omega F}{\nu} \right)^{i^*}. \quad (11)$$

Taking for simplicity $E_b^* = E_b$, one gets in limit I

$$\Gamma = i^* + 2, \quad \mathcal{E} = E^* + i^* E_d,$$

and

$$H(\theta) = \left(\frac{-\ln\theta - 3/2}{4\pi} \right)^{i^*+1} \quad (12)$$

while in limit II

$$\Gamma = \frac{i^* + 3}{2}, \quad \mathcal{E} = E^* + i^* (E_d + E_b),$$

and

$$H(\theta) = \left(\frac{1}{\sqrt{4\pi\theta}} \right)^{i^*+1}. \quad (13)$$

The solution of Eq. (11) is

$$(N_s \Omega)^\Gamma - (N_s^{(i)} \Omega)^\Gamma = \Gamma \sigma e^{\beta \mathcal{E}} \left(\frac{\Omega F}{\nu} \right)^{i^*} \int_{\theta_i}^\theta H(\theta') d\theta'. \quad (14)$$

Assuming $N_s^{(i)} \ll N_s(\theta)$, the second term on the left-hand side of (14) can be neglected and N_s takes the form

$$N_s(F, T, \theta) = \left[\Gamma \sigma \int_{\theta_i}^\theta H(\theta') d\theta' \right]^{1/\Gamma} e^{\beta \mathcal{E}/\Gamma} \left(\frac{\Omega F}{\nu} \right)^{i^*/\Gamma}. \quad (15)$$

Therefore, in limit I

$$N_s \sim e^{\beta(E^* + i^* E_d)/(i^* + 2)} F^{i^*/(i^* + 2)}, \quad (16)$$

while in limit II

$$N_s \sim e^{2\beta[E^* + i^*(E_d + E_b)]/(i^* + 3)} F^{2i^*/(i^* + 3)}. \quad (17)$$

The coverage dependence of N_s also differs in the two limits. However, it is known [13,18] that the methods that have been used in this work are not suitable for an accurate calculation of this dependence. For this reason, only the flux and temperature dependence of N_s are emphasized in Eqs. (16) and (17).

As expected (see above), in limit I the result [Eq. (16)] coincides with the standard result calculated under the assumption that island edges are perfect sinks for adatoms. Equation (17) clearly shows that in limit II, when island-edge barriers are important, the behavior of N_s as a function of F and T is strikingly different [19]. The most unambiguous information about the importance of island-edge barriers in a specific experimental system can be obtained from the functional dependence of the island density on flux. It is a simple power law, $N_s \sim F^X$, with an exponent X that depends only on the critical island size i^* . While in limit I the exponent is in the range $1/3 \leq X_I \leq 1$, in limit II it can be larger than 1 ($1/2 \leq X_{II} \leq 2$). For a given value of i^* , X_{II} is significantly larger than X_I , a difference that can be detected experimentally. If one has some information about i^* , a measurement of $N_s(F)$ can indicate which of the two limits is more appropriate for the experimental system in question. Furthermore, if there is no *a priori* knowledge of i^* , one can still identify the relevant limit (and thus evaluate i^*) if $X < 1/2$ or $X > 1$. The former case is possible only in limit I, and the latter only in limit II. Once the proper limit has been identified and i^* evaluated, the temperature dependence of N_s can be used to estimate energy barriers; in particular, one can evaluate \mathcal{E} .

Which experimental systems are suitable for such a study? Homoepitaxial growth experiments of semiconductors and metals with and without surfactants may be good candidates. For example, consider the experiments of Voigtländer and Zinner [20] on submonolayer growth of Si/Si(111) with Sb as a surfactant. In this case, the additional island-edge barrier E_b corresponds to $E_{ex} - E_d$, where E_{ex} is the barrier for exchange of an adatom with a surfactant atom at the edge of a stable island, and E_d is the barrier for diffusion *on top* of the surfactant layer. Limit II corresponds to the model proposed by Kandel and Kaxiras [8,9] to describe surfactant mediated film growth; they assumed that surfactant atoms passivate island edges. Limit I is associated with the more standard approach to the same problem [21], where no island-edge passivation is taken into account. An experimental value of $X > 1$ would therefore indicate that the model of Kandel and Kaxiras is adequate for this system. A value of $X < 1/2$, on the other hand, would favor the standard

approach to surfactant mediated epitaxy. Intermediate results would be inconclusive.

It is instructive to use experimental numbers in Eq. (10) for the function G , and estimate what E_b should be in order for the system to be in limit II. For example, at $T = 900$ K Voigtländer and Zinner measured an island density of $N_s \approx 10^{11} \text{ cm}^{-2}$ in the case of Sb mediated growth (see Fig. 3 of Ref. [20]). The coverage was 0.15 bilayers, and since $\Omega \approx 10^{-15} \text{ cm}^2$, the estimate of G is $G \approx 0.23[\exp(\beta E_b) - 1]$. Therefore, for $E_b = 0.4 \text{ eV}$ $G \approx 39$, and the system should be in limit II. Limit I would be clearly observed only if $E_b < 0.1 \text{ eV}$.

Another work of relevance here is the experiment of Andersohn *et al.* [22], who measured the exponent X for homoepitaxial growth of silicon with molecular beam epitaxy (MBE) and CVD using disilane (Si_2H_6). They concluded that in MBE $X \approx 0.75$, which corresponds to $i^* = 5-7$ assuming that the standard limit I applies. In CVD, on the other hand, they obtained $X \approx 1.25$. As they emphasize, standard rate equation theory cannot explain this result, since it always predicts $X < 1$. In the framework of the present work, the result $X = 1.25$ is a natural consequence of a significant island-edge barrier (limit II) and corresponds to $i^* = 5$. In fact, since during CVD with disilane, hydrogen is always present on the surface of the growing film, it is possible that hydrogen atoms bind to island edges and have to be displaced before a silicon atom can attach to the island. In this sense, hydrogen acts as a surfactant in this system [11], and the present interpretation of the experimental result favors the mechanism of Kandel and Kaxiras over the standard surfactant mediated growth mechanism in this particular case.

Here again it is possible to use the experimental numbers in Eq. (10). The CVD experiments at $T = 800$ K show that for different values of the flux, the island density at coverage of 0.15 bilayers changes between 10^{11} and 10^{12} cm^{-2} (see Fig. 4 of Ref. [22]). Taking the smaller of the two values with $E_b = 0.4 \text{ eV}$, one gets $G \approx 75$, and the system should exhibit a limit II behavior. Thus, the analyses of both experiments show that the values of the additional barrier, E_b , need not be ridiculously large for the system to be in limit II.

It should be emphasized that the CVD experiments interpreted above are not a reliable test of the theory due to the complexity of the processes involved in CVD. Hopefully, this work will stimulate experiments on simpler systems that will enrich our understanding of the role of surfactants in thin film growth.

In summary, this paper shows that island-edge barriers have a profound effect on the density of 2D islands during submonolayer epitaxy, and as a result on the morphology of the growing surface. The novel behavior of the island density, predicted in this case, has been shown to be relevant for experimental systems, including surfactant mediated epitaxy and chemical vapor deposition.

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