Change of island density due to multi-channels of adatom diffusion

Shudun Liu [a,*], Shi-Yu Wu [a], Zhenyu Zhang [b]

[a] *Department of Physics, University of Louisville, Louisville, KY 40292, USA*
[b] *Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6032, USA*

Abstract

Recent experimental studies on surfactant-assisted thin film growth indicate that there is a strong possibility that adatoms can diffuse both on top of and under the surfactant layer. We present here a model of growth to study the effects of multi-channels of diffusion on the island density. We find that there can be four different regimes as temperature of growth increases from low to very high values. We find that there is a scaling relation of island density with deposition flux and temperature in each regime. The transition temperatures are found to be connected to the system parameters such as barriers to diffusion. © 2001 Elsevier Science B.V. All rights reserved.

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Surfactants have been increasingly used in recent years to promote the growth of smooth thin films [1–3]. The change of growth modes, for example, from three dimensions (3D) to two dimensions (2D), is often a result of the effects of these surfactants on motion of adatoms near a step or on the terrace. In the case of a submonolayer coverage of surfactant on the substrate, for example, it was found that the diffusion of adatoms on the terrace can be greatly reduced [4–6]. This results in an increased island density, which in turn favors 2D growth. At step edges, the surfactant can reduce or increase the Ehrlich–Schwoebel

barrier, thus affecting the inter-layer mass transportation. In some cases, it may create an additional barrier for attachment of adatoms at these edges. Change of island density or growth mode due to such effects of surfactants on the adatoms near step edges have been well documented [5,7–10].

For some systems, smooth 2D growth can be achieved only if the whole substrate is covered with a surfactant. The behavior of adatoms and the nucleation mechanism in such cases are not well understood. A recent scanning tunneling microscopy (STM) study of growth of Ge on Si(1 1 1) with Pb as surfactant suggests that diffusion of Ge adatoms is very fast and nucleation happens on top of the surfactant cover [11]. Camarero et al. [12], however, find that in the homoepitaxial growth on Cu(1 1 1) covered with one monolayer

* Corresponding author. Tel.: +1-502-852-0920; fax: +1-502-852-0742.
E-mail address: s0liu001@athena.louisville.edu (S. Liu).

of Pb, newly deposited Cu adatoms get buried under the Pb layer through an exchange process and then diffuses underneath the Pb. Clearly, the behavior of adatoms on a surfactant-covered surface depends on the surfactant, the substrate and adatoms. For a given system, it may also very well depend on growth conditions such as the substrate temperature and the deposition rate. Since in general the process in which an adatom exchanges with a surfactant atom to go underneath is an activated one, one can expect that in many systems there is a transition temperature below which an adatom stays on top of the surfactant and gets buried under the surfactant above this transition temperature. Thus we have the following interesting picture of nucleation of adatoms: An adatom can be in one of the two states, either on top of the surfactant layer or underneath it, with a rate to transform from one state to another. For most systems, such a transformation is likely to be an one-way process, i.e., the reverse transformation is very slow. In each state, an adatom can diffuse with a different diffusion constant. Now the question is what is the island density grown in such systems? How is the transition temperature related to the microscopic rates?

In this work, we will answer these questions through rate equation analysis of a model of nucleation and growth in which both channels of adatom diffusion are considered. The addition of the second channel of diffusion greatly enriches the picture of nucleation on surfactant-covered surfaces. We found that there are four regimes from low temperature to very high temperature. In each regime, the nucleation process is different in nature and a different scaling law of island density applies.

Rate equation theory has been used to study nucleation and growth for many years [13]. Recent advancement of experimental techniques such as STM enables accurate measurements of island morphology which in turn stimulate many new theoretical investigations on how measurable quantities such as island density and size distributions depend on microscopic processes of adatoms and growth conditions [14–16]. The nucleation model presented here involves two types of adatom populations that are correlated

through an activated process and two corresponding channels of diffusion of monomers. Our model is important and timely, in light of the increased interest in the application of surfactants to thin film growth. It is also qualitatively correct in view of the recent experimental findings [11,12]. We hope our work will stimulate further experimental investigation in this area. In this study, we will focus our attention on the dependence of island density on the deposition flux and the substrate temperature.

We consider three kinds of populations of adatoms: monomers above the surfactant layer (called A type), monomers below the surfactant layer (called B type) and islands, with n_A, n_B and N representing the corresponding densities. The diffusion rates for A and B type monomers are defined to be D_A and D_B, respectively. A monomer of A type can transform into a B type with a rate given by $1/\tau$. The reverse transformation is assumed to be very slow and will be neglected. Within the framework of rate equation theory, the evolution of the three populations can be described by the following equations:

$$dn_A/dt = F(1-\theta) - D_A n_A N - n_A/\tau \qquad (1)$$

$$dn_B/dt = n_A/\tau - D_B n_B N - D_A n_A n_B \qquad (2)$$

$$dN/dt = D_A n_A^2 + D_A n_A n_B + D_B n_B^2 \qquad (3)$$

where F is the deposition flux, and $\theta = Ft$ is the total coverage of adatoms deposited.

Eq. (1) describes the change of population of monomers of A type due to deposition, aggregation of A type monomers to existing islands, and transformation of monomers of A type into those of B type. Eq. (2) describes the change of population of monomers of B type due to transformation, aggregation, and nucleation between A and B types of monomers. Eq. (3) describes the formation of islands due to three different types of nucleation processes: The first term on the right-hand side of the equation represents nucleation among A type monomers themselves (A meets A), the second term represents nucleation between monomers of A and B types (A meets B), the last term is due to nucleation among B type monomers

(B meets B). For simplicity, we have assumed that the critical island size is 1: meeting of any two monomers of any type will form a stable island.

In writing the above equations, we have assumed that the three rates D_A, $1/\tau$ and D_B satisfy the following relation, $D_A > 1/\tau > D_B$. This should be a reasonable assumption for many systems. But our model can be easily modified if a different relation exists or if additional rates are to be considered.

Eqs. (1)–(3) can be solved numerically. We will, however, first analyze and solve them under certain approximations, and compare the approximate solutions with numerical ones later.

Under the steady-state approximation, $dn_A/dt = dn_B/dt = 0$, and assuming nucleation happens mostly at low coverages, Eq. (3) becomes

$$\begin{aligned} dN/d\theta = &\, F/((D_A N^2)(1 + 1/\alpha)^2) \\ &+ 1/((1 + \alpha)(1 + \beta + \beta/\alpha)) \\ &+ \beta/(\alpha + \alpha\beta + \beta)^2 \end{aligned} \quad (4)$$

where $\alpha = D_A \tau N$, and $\beta = D_B N^2/F$. These two density dependent parameters measure the rate of aggregation of A type monomer against its transformation into that of a B type and the effectiveness of aggregation of B monomers against deposition, respectively. There are four different regimes ranging from low to very high temperatures. In each regime, nucleation of different type dominates and a different scaling law applies. These four regimes are discussed as follows.

Regime 1 (low T): $\alpha \gg 1$, $\beta \ll 1$; *nucleation process – A meets A; scaling – $N = \theta^{1/3} F^{1/3} D_A^{-1/3}$.* In this regime, of the three kinetic processes, only diffusion of A type monomer is activated. The dominant nucleation process is monomers of A type meeting monomers of the same type: A meets A. Thus we have a very simple picture of nucleation and the standard scaling law for the island density is obtained as expected.

Regime 2 (intermediate T): $1 \ll \alpha \ll D_A N^2/F$, $\beta \ll 1$; *nucleation process – A meets B; scaling – $N = \theta^{1/2}(D_A \tau)^{-1/2}$.* In this regime, both diffusion of monomers of A type and their transformation into those of B type are activated. The B type monomers, however, are immobile at this temperature. Each transformation of a A type monomer effec-

tively results in the creation of a seed of island. As a result, island density *increases* with temperature.

It is interesting to note that island density does not depend on the deposition flux in this regime. This is not totally surprising. An A type adatom has an average lifetime of τ during which it can diffuse an average distance of $(D_A \tau)^{1/2}$. If the island–island separation is larger than this distance, a newly deposited adatom will transform into a B type of monomer, thus increasing the island density. This continues until the island–island separation equals to the diffusion length of a A type of monomer. Change of deposition rate only affects when the island density becomes saturated (normally this happens at low coverage), but will have no effect on the value of the saturated island density itself. It is also worth noting that according to the standard nucleation theory, the dependence of island density on deposition flux gets weaker as critical island sizes increase. Our work shows that an observed decrease of flux dependence of island density can be due to either the increase of critical island size or transformation of adatoms into immobile ones (island seeds).

The nucleation process in this regime also corresponds to a simple model discussed previously [17]. The reverse dependence of island density on temperature has been observed in experiments [11,17]. Such a reverse dependence can also be due to effects of surfactant on the adatoms at island edges [10].

Regime 3 (high T): $1 \ll \alpha \ll D_A N^2/F\beta$, $\beta \gg 1$; *nucleation process – A meets B, scaling – $N = \theta^{1/4} F^{1/4}(D_A D_B \tau)^{-1/4}$.* In this regime, the temperature is high enough that even the slowest kinetic process considered in our model, namely, diffusion of B type monomers, is activated. This process will decrease the island density as a B type monomer is no longer an automatic seed of an island as in regime 2. It can diffuse to meet a nearby island, thus reducing the density of B type monomers, and as a result, the island density. Though the diffusion of B type monomers are activated in this regime, it, however, does not contribute to the nucleation process directly. The dominant nucleation process in this regime is still that of a A type monomer meeting a B type monomer (A meets B), which is same as in regime 2.

The reason that a B type monomer can aggregate to a nearby island but yet does not meet other B type monomers (thus to nucleate) is due to the fact that the island density is much larger than the density of monomers of either type (except at the beginning of deposition when islands are yet to form). In other words, the distance between a B type monomer and a nearby island is on the average much smaller than the average distance between two B type monomers. This is the only regime in which the island density depend on all the three microscopic processes of adatoms.

Regime 4 (very high T): $\alpha \ll 1$, $\beta \gg 1$; nucleation process – B meets B; scaling – $N = \theta^{1/3} F^{1/3} D_B^{-1/3}$. As temperature increases further, density of B type monomers becomes very large and that of A type monomers diminishes in comparison. This, plus the increased range of diffusion of B monomers in this regime, make nucleation between two B monomers much more likely than that between a A type monomer and a B type one. In the extreme case, all monomers are of B type and we go back to the simple picture of nucleation of just one kind of monomers, as in the case in regime 1. This is why the scaling law in regime 4 is of the same form as that in regime 1, except in this case, diffusion of B type monomers replaces that of A type monomers.

One can also estimate the transition temperatures between these regimes by assuming that at the transition point, the island density given by the two neighboring scaling relations are equal. This leads to the prediction of transition temperatures given by the following relations: $D_A \tau^3 F^2 = 1$ (from 1 to 2); $D_A \tau^2 F / D_B = 1$ (from 2 to 3); and $D_A^3 \tau^3 F / D_B = 1$ (from 3 to 4).

We have also solved Eqs. (1)–(3) numerically without any approximations. Rates of all three microscopic processes are assumed to be given by the Arrhenius equation. As a test, we have chosen the following parameters: E_A, E_τ, $E_B = 0.2$, 0.4, 0.6 eV as the activation energies for diffusion of A type monomer, transformation of a A type monomer into that of a B type, and diffusion of B type monomers respectively. The prefactors are chosen to be the same, and they are set at 10^{13} s^{-1}. The results of island densities as a function of temperature and deposition flux are shown in Figs. 1
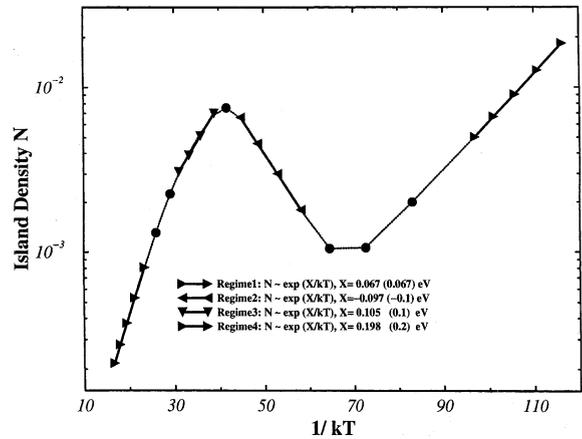

Fig. 1. Semi-log plot of island densities as a function of temperature at a fixed deposition rate of $F = 0.01$ s^{-1}. The barriers to diffusion on top, to exchange down, to diffusion below were chosen to be 0.2, 0.4, 0.6 eV, respectively. All solid symbols (solid circles, upper, left, down and right triangles) are data points obtained from the full solution of rate equations. Four regimes ranging from low to very high growth temperatures are identified. In each regime, the data points (triangles) are fitted to the form shown in the figure. The slopes obtained from the fitting are compared with the exponents (shown in parentheses) given by the scaling laws. The solid circles mark the transitions between regimes. The dotted line, which simply connects all the data points, is to guide the eyes.

and 2 respectively. We did not test the coverage dependence of island density as it is known [15,18] that the point-island model used here is not suitable to study such dependence accurately. In general, island density saturates after a few percentage of coverage of adatoms and stays as a constant until coalescence occurs at high coverages. In Figs. 1 and 2, all island density data is taken at a fixed adatom coverage of 0.2 ML. We tested the data taken at 0.1 ML coverage and found that they gave the same dependence of island density on the flux and temperature.

Four regimes are identified in Fig. 1. Numerical solutions of the rate equations (1)–(3) are fitted according to the predicted scaling law in each regime. The scaling exponents obtained are then compared with those predicted by the scaling laws. As shown in Figs. 1 and 2, the agreements between scaling laws and full rate solutions are nearly perfect. This validates both the scaling laws as well as the approximations made in deriving them.
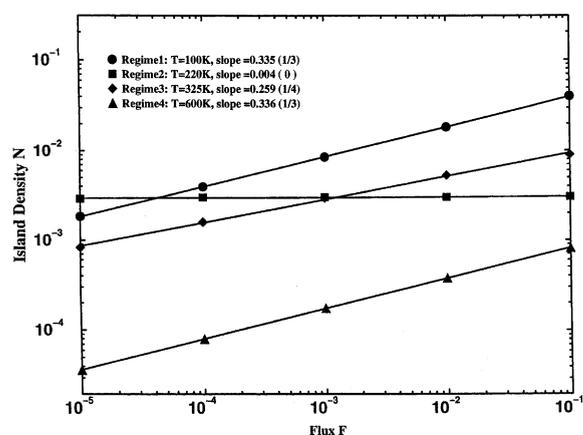
Fig. 2. Log–log plot of island densities as a function of deposition fluxes at four temperatures representative of the four scaling regimes. The barriers to diffusion on top layer, to exchange down, to diffusion below were chosen to be 0.2, 0.4, 0.6 eV, respectively. The data points (solid symbols) are obtained from full solution of rate equations. In each regime, the data points are fitted as a power law. The slopes obtained from the fitting are compared with the exponents (shown in parentheses) given by the scaling laws.

For the parameters chosen, the predicted transition temperatures based on the previously described criteria, are $T = 168$ K (from 1 to 2), $T = 269$ K (from 2 to 3) and $T = 404$ K (from 3 to 4). As it can be seen in Fig. 1, these values are also in close agreement with full solutions of rate equations. It should be noted that the transition temperatures depend mainly on the activation energies and the scaling exponents. It has a very weak dependence on the prefactor, deposition flux and coverage. Even a change of a factor of 10 in those quantities, for example, will only shift the transition temperatures by a few degrees.

In summary, we have presented a model of nucleation and growth at surfaces involving two types of monomers with two channels of diffusion. Four regimes from low to very high temperatures are identified. Island density in each regime is predicted to scale with deposition flux and rates of microscopic processes with different scaling exponents. Our model is simple but quite general. Many experimental growth conditions can be classified into one or more of the above defined regimes, depending on temperature, the deposition flux and the three kinetic rates. Our model can also be generalized to include more microscopic processes.

Acknowledgements

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