Two-dimensional pattern formation in surfactant-mediated epitaxial growth

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The effects of a surfactant on two-dimensional pattern formation in epitaxial growth are explored theoretically using a simple model, in which an adatom becomes immobile only after overcoming a large energy barrier as it exchanges positions with a surfactant atom, and subsequent growth from such a seed is further shielded. Within this model, a fractal-to-compact island shape transition can be induced by either decreasing the growth temperature or increasing the deposition flux. This and other intriguing findings are in excellent qualitative agreement with recent experiments.

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Because of stress effects, heteroepitaxial growth typically proceeds via the formation of three-dimensional (3D) islands, leading to rough films. However, it was discovered nearly a decade ago that the use of a surfactant can lead to layer-by-layer growth and drastically reduced film roughness. Since then, much effort has been devoted to the study of surfactant-mediated growth in both hetero- and homo-epitaxial systems. In these studies, it has been observed that the surfactant atoms can not only modify the 3D growth mode, but often induce the formation of fractal-like 2D islands. To date, little effort has been devoted to the understanding of the precise formation mechanisms for such fractal islands in the presence of surfactant atoms. Such understanding is vitally important because the morphology and the distribution of the 2D islands formed at submonolayer coverages can severely influence the growth mode in the multilayer regime.

Two-dimensional pattern formation is itself an important area of statistical physics. In their classic work, Witten and Sander demonstrated that a fractal island can be formed when random walkers join a seed by hit-and-stick (without any relaxation). More recently, 2D pattern formation within the context of dynamical island growth in submonolayer epitaxy has become the subject of intensive study, to a large extent advanced by the capability of the scanning tunneling microscopy (STM) in characterizing such islands. These studies have firmly established that islands can become more fractal-like if the growth temperature is decreased at a given deposition flux, or the deposition flux is increased at a given growth temperature. However, most of the earlier studies of 2D pattern formation had been focused on model homo- or hetero-epitaxial systems without surfactants. Only very recently, have the effects of Pb as a surfactant on the formation of 2D Ge islands grown on Si(111) been studied systematically by Hwang et al. They found, most surprisingly, that the fractal-to-compact transition is induced by lowering the temperature or by increasing the deposition flux. These observations are in clear contradiction with traditional expectations, and the underlying physical mechanisms for such transitions are still unclear. Michely et al. have also observed a compact to fractal transition of Pt islands on Pt(111) by decreasing the deposition flux, possibly caused by the presence of the CO impurities. In another experiment of Sb-induced growth of C60 films on NaCl(100), a compact-fractal-compact transition was observed by increasing the temperature.

In this Letter, we use a novel model to explore the effects of a monolayer of surfactant atoms on 2D pattern formation in epitaxial growth. The model contains a minimum number of key assumptions, each based on sound physical grounds. First, an adatom needs to overcome a rate-limiting potential energy barrier in order to exchange positions with a surfactant atom and become immobile. Second, for other adatoms to join such a seed and form a stable island, they still need to overcome a repulsive potential energy barrier surrounding the seed. Third, only islands formed inside the surfactant layer are stable. Our study of this simple model leads to various intriguing findings on both the morphology and the distribution of the 2D islands formed under surfactant action. Most notably, a fractal-to-compact island transition can be induced by either decreasing the growth temperature or increasing the deposition flux. We also obtain the characteristic dependences of the island density as a function of temperature (T), flux (F), and coverage (θ), and rationalize our findings based on a simple physical picture emphasizing the shielding effect on the incoming adatoms by the surfactant atoms surrounding the islands. Our findings are in excellent qualitative agreement with the observations of Ge growth on Pb-covered Si(111), and may find different degrees of applicability in other surfactant-induced growth systems as well.
We start with an ideally flat substrate of material A, covered with a complete surfactant layer of material S. Atoms of a different type, B, are deposited onto the surfactant layer at a given deposition rate. We consider the case where the coverage of S is sufficiently high, such that the adatom islands, once formed, are always surrounded by the surfactant atoms. As our first study, we consider a simple model that catches the essential physics involved in the shape transitions but with a minimum number of input parameters (hereafter referred as the first model). Three elementary rate processes are emphasized in this model: diffusion (dif) of a B-type atom on top of the surfactant layer; a B-type adatom diving (d) from above to below the surfactant layer (via place exchange with an S-type atom); and the aided diving (ad) of a subsequent B atom to join the first one. We denote the activation barriers for these three processes by $V_{\text{dif}}$, $V_{\text{d}}$, and $V_{\text{ad}}$, respectively, and the corresponding rates by $R_{\text{dif}}$, $R_{\text{d}}$, and $R_{\text{ad}}$, with $R = \nu \exp(-V/kT)$. The three barriers satisfy the inequality chain $V_{\text{dif}} \ll V_{\text{ad}} < V_{\text{d}}$. $V_{\text{dif}}$ is the smallest because adatom diffusion is often significantly enhanced due to the passivation of the surface by the surfactant layer [10]. $V_{\text{d}}$ is the largest, making it the rate-limiting process for eventual formation of a stable island. The first inequality reflects the fact that there exists an effective repulsive wall surrounding the seed atom or an island formed underneath the surfactant layer. The existence of such a repulsive potential to the incoming adatoms due to the presence of the surfactant atoms surrounding an island has been proposed previously [17,10], and its effect on the island density has been explored very recently [18]. An isolated adatom can hop with the rate $R_{\text{dif}}$, or exchange down with the rate $R_{\text{d}}$. Here for simplicity, the in-plane mobility of the B atoms underneath the surfactant layer is taken to be negligible. We also ignore the reverse exchange process in which a B-type atom resurfaces to the top of the surfactant layer, corresponding to the case where a B atom strongly favors the underneath site. On the other hand, islands formed on top of the surfactant layer can still disassociate, and are therefore unstable. When a B atom hops to a site which has $n_d$ static B-type nearest neighbors, it remains stuck there until it exchanges down with the rate $n_d R_{\text{ad}}$. Because the activation barrier for this process must be in between $V_{\text{ad}}/n_d$ and $V_{\text{ad}}$, for simplicity we choose the rate $n_d R_{\text{ad}}$ to take into account the effect of the $n_d$ neighboring static atoms without introducing another parameter at this stage. Using the definition of classical nucleation theory [19], we actually have two critical island sizes: $i^* = \infty$ and $i^* = 0$ for the upper layer and the lower layer, respectively. In contrast to the earlier irreversible "hit-and-stick" [7] or the "hit-stick-relax" model [1], the stable islands in the present study consist only of down-exchanged atoms. Overall, the current model is consistent with the fact that the binding energy between A and B is typically much larger than that between A and S. [20] Later we will show that considerations going beyond this first model do not change the main qualitative features of the present study.

We primarily use kinetic Monte Carlo (KMC) simulations to study this model; later we also briefly describe the main results from rate equation analysis. The KMC simulations were carried out on a square $200 \times 200$ lattice, though simulations using a lattice of triangular geometry yield qualitatively similar conclusions. We take a small diffusion barrier $V_{\text{dif}} = 0.59$ eV, reflecting the fast adatom diffusion on top of the surfactant layer. The barriers of the exchange (diving) and the aided exchange processes are taken as $V_d = 0.90$ eV and $V_{\text{ad}} = 0.82$ eV, respectively. The attempt frequency is uniquely chosen to be $\nu = 4.1671 \times 10^{10}/T$, with $T$ given in degree K.

The temperature dependence of the island shapes obtained at $F = 0.005$ ML/s and $\theta = 0.1$ ML is shown in Fig. 1. At 300 K, the islands are typically compact (Fig. 1a); at 340 K, the islands are typically fractal-like. The transition from compact to fractal patterns takes place approximately at 315 K. Fig. 1b shows the pattern at 310 K, just below the transition temperature; the islands are still compact, though there are some ramified structures in the outer part of the islands. Fig 1c is the pattern at 320 K, just above the transition; here the islands are predominantly fractal-like.

The intriguing temperature dependence described above can be understood by considering the shielding effect of the adatoms stuck around the edge of a nucleation seed or an island of down-exchanged atoms in the sublayer. At high temperatures, such surrounding adatoms can easily dive into the sublayer at their initial points of sticking; once they manage to exchange into the sublayer, their mobility is severely limited, making the whole situation very similar to the classic hit-and-stick diffusion limited aggregation [6]. On the other hand, at lower temperatures, such stuck adatoms and the surfactant atoms surrounding them effectively block incoming adatoms from reaching a seed atom or an island in the sublayer. Therefore, these incoming adatoms have a chance to leave their initial points of sticking, and after some random walking can restick at different points of the same island. Such processes effectively lead to relaxation around the edge of an island, resulting in more compact island morphology [11].

Figure 2 shows an interesting nonmonotonous dependence of the island density with the temperature. The minimum in island density is located right at the temperature at which the compact-to-fractal transition in island morphology has been observed. We note that the temperature dependence shown here is similar to that obtained previously by Meyer and Belz [21], but the two cases differ in physical origins. In their case, islands formed either by nucleation of two mobile adatoms or by meeting of one mobile and one trapped adatom are both stable, and the minimum in the island density as a func-
tion of the temperature is associated with the transition from the nucleation-dominant to exchange-prominent region. In our case, islands formed on top of the surfactant layer are unstable, and the rate-limiting process for the nucleation of a stable island is the diving of an adatom into the sublayer. Therefore, our system is always in the exchange-prominent region. Nevertheless, when the temperature is low, a stable seed atom in the surfactant layer may not necessarily grow into a stable island because of the effective shielding of the incoming adatoms. But those seeds which manage to grow into islands will grow even faster as their sizes increase. The decrease in island density with temperature is caused by the increased mobility of the adatoms in searching for such islands. On the other hand, after the transition temperature, the shielding effect is very weak, and every seed atom is likely to grow into a stable island. The island density increase with temperature reflects the enhanced rate in creating such seeds.

Figure 3 displays the island patterns obtained at different deposition rates. Here the growth temperature is fixed at $T = 300$ K and the coverage is again at 0.1 ML. Fig. 3a is an ideal fractal pattern at the flux of 0.0001 ML/s. Fig. 3b is still a fractal pattern at the flux of 0.001 ML/s, though there are islands that are more compact. In Fig. 3c the flux is 0.0025 ML/s and the island shape already becomes compact. In Fig. 3d the islands are ideal compact patterns, obtained at the flux of 0.028 ML/s. Because the shielding effect increases with flux, the flux-induced fractal to compact transition is also driven by the shielding effect, but here the transition is from strong shielding to weak shielding when the flux increases.

Figure 4 shows the flux dependence of the stable island density, $N_s$, obtained at $T = 300$ K and $\theta = 0.1$ ML. The curve can be divided into three regimes: the low-flux fractal regime, where the dependence is very weak; the intermediate flux regime, where a scaling law can be well defined ($N_s \sim F^\beta$ with $\beta = 0.40$); and the high-flux compact regime, where the island density has saturated. When the maximal saturation island density (obtained at different coverages) is plotted as a function of flux, a much larger scaling exponent is obtained ($\beta = 0.7$).

We have also carried out a limited rate equation analysis of the above model. In this approach, we introduce the island perimeter $L_d$ and parameterize the area of an island by $S_d = pL_d^q$, where $p$ is a constant and $q$ is the dimension of the islands [13]. For compact islands we have $q = 2$ and for fractal patterns $1 < q < 2$. In the low-coverage limit, we have the following rate equations:

$$\frac{d}{dt} n_a = F \theta(t_0 - t) - \alpha_d n_a - \alpha_b n_a N_s (L_d - n_b) \quad (1)$$

$$\frac{d}{dt} (N_s n_b) = -\alpha_e n_b N_s + \alpha_e n_a N_s (L_d - n_b) \quad (2)$$

where $n_a$ is the density of the movable active atoms, $n_b$ is the number of edge atoms per stable island, $\alpha_d$ and $\alpha_e$ can be taken as $R_d$ and $R_{ae}$, and $\alpha_b$ is the capture constant. We have introduced the step function $\theta(t_0 - t)$ to reflect the fact that the STM imaging was typically some time after the deposition time $t_0$. Letting $N_s$ be the total number of active atoms, one has $N_s = n_a + N_s n_b$. When the flux is low or the temperature is high, very few adatoms remain active at the end of deposition. The island patterns can then be determined mainly by the $t < t_0$ region. In such situations, a steady-state approximation can be made for $N_s$, similar to what has been done previously [10, 11, 12]. Then a scaling law of island density can be derived: $N_s \sim F^{s0} \theta^{as}$, where $n_F = 0$, as suggested in the low-flux regime shown in Fig. 4; and $n_\theta = (q - 1)/(2q - 1)$. The constant $q$ can be easily determined from the island shapes only in the limit of very low flux or very high temperature. In the compact and intermediate regimes, both the $t < t_0$ and $t > t_0$ regions should be considered. It is then more involved to obtain a simple analytical scaling law [13].

The temperature- or flux-induced fractal-compact transition in the island shapes predicted within the present model provides, on a qualitative level, the theoretical basis for the transitions observed in Pb-induced growth of Ge on Si(111) [12]. Because there are only three parameters in our first model, the agreement in the main features between theory and experiment should be viewed excellent. In particular, the shielding effect emphasized in the present model plays the essential role in causing the shape transition.

We have expanded the range of applicability of our simple model to various more realistic growth systems in several aspects, such as KMC simulations on a triangular lattice and variations of the three basic model parameters. We have also considered physical effects beyond the first model, including the binding energy of the adatoms in an island formed above the surfactant layer, detachment of the adatoms trapped around the edge of a stable island, and the possibility of simultaneous exchange of multi-adatoms [11, 12]. These lattice and parameter variations, as well as the improvement beyond the first model, do not change the central qualitative findings of the present work, namely, the counter-intuitive fractal-compact transition caused by the temperature or the flux. Of course, one should expect that, on a quantitative level, the island density will depend differently on the temperature, flux, and the coverage $\theta$. We should also note that the fractal-compact transitions predicted here are expected to be observable even if the stable islands are formed on top of the surface but surrounded by a sufficiently high coverage of impurity atoms, as long as those
impurity atoms can effectively hinder the growth of the stable islands by shielding. Furthermore, the phenomena are not limited to heteroepitaxial growth only: Even in surfactant-induced homoepitaxy, similar phenomena are likely to occur if the shielding effect associated with the impurity or surfactant atoms is sufficiently effective.

In summary, we have theoretically explored the effects of a monolayer of surfactant atoms on two-dimensional pattern formation in epitaxial growth by using a simple but physically sensible model. We find that a fractal-to-compact island transition can be induced by either decreasing the growth temperature or increasing the deposition flux. Furthermore, the flux and temperature dependence of the island density on the fractal side is very different from that on the compact side. The counterintuitive predictions on the island morphological evolution can be rationalized based on the shielding effects. Our findings on the shape transitions are in excellent qualitative agreement with recent observations, while the predicted nonmonotonic temperature dependence of the island density is yet to be confirmed in future experimental studies.

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FIG. 1. Island shapes obtained on a 200 × 200 lattice with a constant deposition flux of 0.005 ML/s and a constant coverage of 0.1 ML, but at four different temperatures: (a) 300 K; (b) 310 K; (c) 320 K; and (d) 340 K. The compact-to-fractal transition takes place approximately at 315 K.

FIG. 2. Island density as a function of temperature, with the flux fixed at 0.005 ML/s and the coverage fixed at 0.1 ML. The temperature at which the density is a minimum is the same temperature for island shape transition.

FIG. 3. Flux dependence of the island shapes obtained on a 200 × 200 lattice at a constant temperature of 300 K and a constant coverage of 0.1 ML, but with four different fluxes: (a) 0.0001 ML/s; (b) 0.001 ML/s; (c) 0.0025 ML/s; and (d) 0.028 ML/s. The shape transition takes place between 0.001 ML/s and 0.0025 ML/s.

FIG. 4. Island density as a function of flux. The temperature is fixed at 300 K and the coverage fixed at 0.1 ML. There exists an approximate scaling law in the intermediate flux region.