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Ordering dynamics of surfaces in molecular beam epitaxy

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Abstract

The growth of thin films under conditions typical for molecular beam epitaxy is unstable, if potential barriers at step edges suppress the diffusion of adatoms to lower terraces. In these cases the dynamic evolution of the surface morphology is characterized by slope selection leading to pyramid-like structures and coarsening. The late stages of growth can be described by Langevin equations that are similar to equations that model spinodal decomposition or Ostwald ripening with the slope of the surface profile being the order parameter. It is shown that the surface evolution can be understood in terms of domain ordering, however, the orientation of the domain walls is strongly influenced by lattice anisotropies. This coupling slows down the coarsening dynamics.

1. Introduction

In the last few years it has become clear that the surface evolution of films grown by molecular beam epitaxy (MBE) is quite often characterized by the formation of pyramids, even in the case of homoepitaxial growth. In fact, theory predicts [1,2] as long as evaporation from the surface can be neglected that there are only two generic scenarios that describe the late stages of the growth process corresponding to large film thicknesses: either unstable three-dimensional growth or kinetic surface roughening described by the Edwards-Wilkinson [3] equation leading to only logarithmically rough surfaces. The three-dimensional growth mode was first predicted by Villain [4] and has been seen in several computer simulations [5–7]. The instability also has been observed in many experiments [8].

The origin of the instability lies in an asymmetry of the adatom diffusion due to step-edge barriers that were discovered by Ehrlich and Hudda [9]. These step-edge barriers suppress the diffusion of adatoms to lower terraces and consequently lead to a diffusion current of adatoms towards the upper step edge. This is a nonequilibrium effect that is present only if the adatom density on a terrace is higher than in equilibrium. Even if the diffusion towards the downward step is suppressed in the equilibrium case as well, adsorption and emission of adatoms from step edges onto the adjacent terrace are perfectly balanced so that there cannot be a net current. However, the deposition process raises the adatom density far above its equilibrium value and diffusion currents that depend on the local slope of the growing film are generated. By studying the diffusive motion of adatoms on vicinal surfaces with diffusion barriers one finds [4,10,11] that the diffusion current $j_{\rm neq}$ has the same direction as the slope and consequently tends to increase the local slope. This is the origin of the instability.

For sufficiently large slopes there are other processes that counterbalance the destabilizing effects, so that the net current in the *nonequilibrium* situation vanishes for certain slopes. If transient mobility effects of the deposited atoms [13] are negligible, the current must vanish for all slopes that correspond to other high-symmetry orientations of the growing film [11]. But transient mobility effects, such as funneling and knock-out processes [13,14], can lead to zeros of $j_{\rm neq}(m)$ for even smaller slopes m [12,15]. These effects are all temperature-, material-, and flux-dependent, thus it is very hard to predict the location of those zeros theoretically, in particular as the locations depend very sensitively on the details [7]. In this article we will not concentrate on the microscopic origins of the zeros in the surface current, but rather use stochastic differential equations to investigate the temporal evolution of the instability. Such a description is appropriate for late times corresponding to large film thicknesses, when discreteness effects are unimportant. However, it is impossible to predict the location of the zeros in the nonequilibrium diffusion current using this approach, rather they are fixed arbitrarily.

2. Surface Currents and Crystalline Symmetries

Under conditions typical for MBE, the height $h(\vec{r},t)$ that describes the position of the surface measured from some reference plane, obeys the conservation law

$$\partial_t h = D\Delta\Delta h + \nabla \cdot \vec{j}_{\rm neq} + \eta \ , \tag{1}$$

where η is white noise describing fluctuations of the deposition flux. The average deposition flux has been eliminated from Eq. (1) by the use of a comoving frame of reference. The first term on the right-hand side of Eq. (1) is also present in an equilibrium situation, where it describes surface diffusion driven by surface tension [16], however also nonequilibrium effects can contribute to this term [17]. The second term is the slope-dependent diffusion current due to step-edge barriers that was described in the previous paragraph. The form of this current must take into account the crystalline symmetries of the growing film, e.g., for $\{001\}$ surfaces the diffusion current in the $\langle 100\rangle$ directions should differ from the one in the $\langle 110\rangle$ directions. Hence, the simplest form of the surface current that is consistent with a quadratic symmetry has components

$$\vec{j}_{{\rm neq},x} = d\, m_x(1-m_x^2) \quad \text{and} \quad \vec{j}_{{\rm neq},y} = d\, m_y(1-m_y^2) \ . \tag{2}$$

This current has four zeros at $\vec{m} = (\pm 1, \pm 1)$ that correspond to stable solutions of the equation of motion (1). Thus planes with these orientations are expected to dominate the morphology of the surface, i.e., one expects four-sided pyramids to form. For $\{111\}$ surfaces the appropriate current is not described by (2): For Pt on Pt(111) it was found that the growing pyramids have a three-fold symmetry [18]. Thus, in this case the correct form of the current is

$$\begin{aligned} \vec{j}_{\mathrm{neq},x} &= d\,(1+2m_x)[m_x(1-m_x)-m_y^2]\;, \\ \vec{j}_{\mathrm{neq},y} &= d\,m_y[1-2m_x-2(m_x^2+m_y^2)]\;, \end{aligned} \tag{3}$$

and the stable solutions of Eq. (1) correspond to the orientations $\vec{m} = (1,0)$ and $\vec{m} = (-1/2, \pm\sqrt{3}/2)$.

3. Ordering Dynamics

The equation of motion (1) with diffusion currents (2) or (3) can be integrated numerically using the Euler method, see, e.g., Ref. [12]. The surface morphologies that are obtained in such a numerical integration are shown in Fig. 1. The quadratic, resp. triangular symmetry of the pyramids is clearly visible. The three-dimensional views illustrate the slope-selection mechanism: the sides of the pyramids are almost planar.

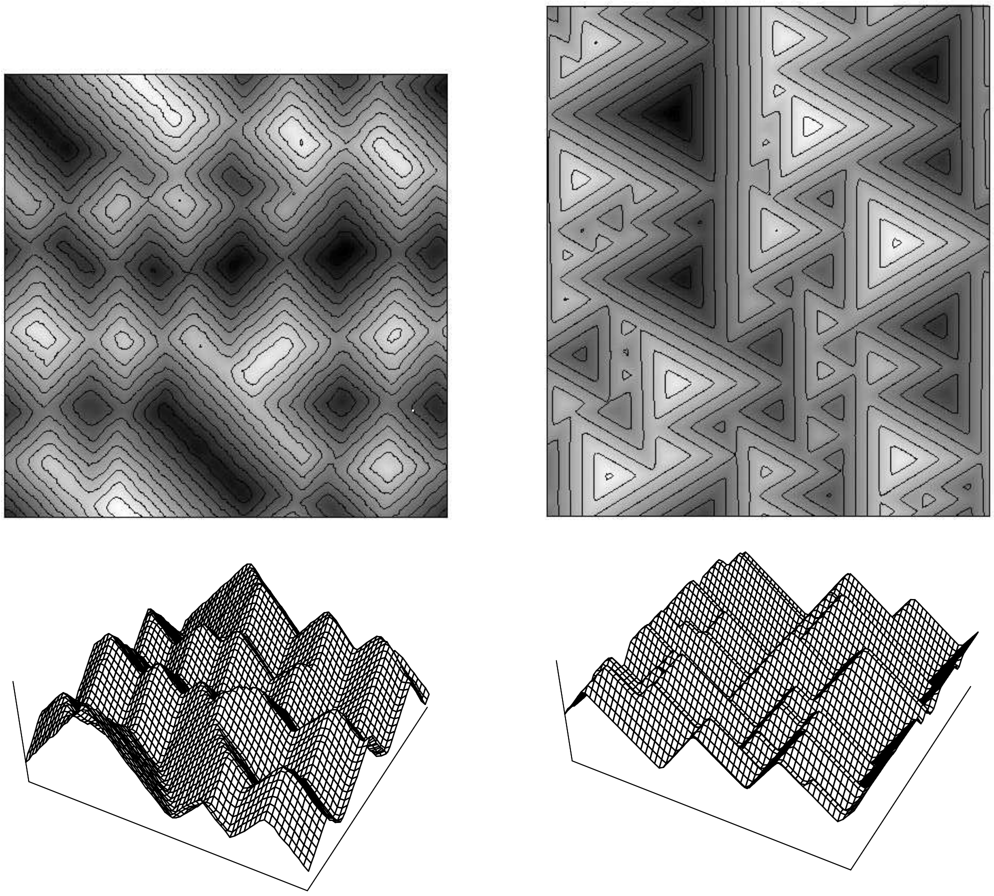

Fig. 1. Evolution of the surface morphology as obtained from a numerical integration of Eq. (1) for quadratic symmetry (left) corresponding to the current (2) and triangular symmetry (right) corresponding to Eq. (3). Contourplots and three-dimension views of the same surface configurations are shown.

These structures coarsen in time: small pyramids disappear, whereas larger pyramids grow. The coarsening process can be understood in the following way: The nonequilibrium currents (2) and (3) can be written as the derivative of a pseudo-potential,

$$V(\vec{m}) = d \sum_{\alpha=x,y} \left[-\tfrac{1}{2}m_\alpha^2 + \tfrac{1}{4}m_\alpha^4\right] \tag{4}$$

for the quadratic symmetry and

$$V(\vec{m}) = d\left[-\tfrac{1}{2}(m_x^2+m_y^2) - \tfrac{1}{3}(m_x^3 - 3m_x m_y^2) + \tfrac{1}{2}(m_x^2+m_y^2)^2\right] \tag{5}$$

for the triangular symmetry, so that $j_{\mathrm{neq},\alpha} = -\partial V/\partial m_\alpha$. Thus, the equation of motion (1) can be cast into the form

$$\partial_t \vec{m} = \nabla\left[\nabla\cdot\frac{\partial\mathcal{F}}{\partial\vec{m}}\right] + \nabla\eta \tag{6}$$

with $\vec{m} = \nabla h$ and the pseudo free energy

$$\mathcal{F} = \int d^2x \, \left\{\tfrac{1}{2}D[(\nabla m_x)^2 + (\nabla m_y)^2] + V(\vec{m})\right\} \ . \tag{7}$$

Eq. (7) has the usual form of a Ginzburg-Landau-type free energy that is commonly used to describe ordering phenomena [19]. It must be emphasized that $\mathcal{F}$ does not have the physical meaning of a free energy, instead it was obtained by integrating the *nonequilibrium* currents (2), (3). However, equation (6) is very similar to the Cahn-Hilliard equation [20]

$$\partial_t \vec{M} = (\nabla\cdot\nabla)\,\frac{\partial\mathcal{F}}{\partial\vec{M}} + \nabla\cdot\vec{\eta} \tag{8}$$

that describes ordering phenomena like spinodal decomposition with a conserved order parameter $\vec{M}$: For the potential (4) [with $\vec{m}$ replaced by $\vec{M}$] Eq. (8) describes conserved ordering dynamics of a four-state clock model for the special case, where the free energy breaks up into the free energy of two uncoupled Ising models. Eq. (8) in connection with Eq. (5) applies to conserved ordering dynamics of a three-state clock model. The growth law that is obtained from Eq. (8) does not to depend on the number of degenerate minima of the free energy [21] *as long as there is only a discrete set of minima.* Therefore, the size R of the growing domains increases like $R(t) \sim t^{1/3}$, the same power law that is found for Ising-like symmetries. This behavior is commonly known as the Lifshitz-Slyozov-Wagner (LSW) law [22].

The analogy with ordering phenomena described by the Cahn-Hilliard equation (8) explains the coarsening mechanism of the pyramids: The surface orders into orientations that correspond to the minima of the pseudo-potentials (4) and (5), respectively. The system coarsens since it relaxes towards the minimum of the "free energy" (7) thereby eliminating the "domain" boundaries between areas that correspond to different surface orientations. However, it was found [11] that the slight differences between (6) and (8) do lead to a change in the growth law: The size of the pyramids increases as $R(t) \sim t^{1/4}$.

The question remains whether this growth law depends on the crystalline symmetries of the growing film. Fig. 2 compares the temporal evolution of the pyramid size for the surface currents (2) and (3). Although there appears to be a slight difference in the growth law, within the numerical accuracy the pyramid size $R(t)$ does not depend on the crystalline symmetries of the film: both results are consistent with a power law $R(t) \sim t^{1/4}$.

In the case of heteroepitaxial growth, under conditions where the deposited material does not wet the substrate but forms islands or droplets on the substrate, it is found that the size of the droplets grows proportional to $t^{1/4}$ as well [23]. However, in contrast to the surface ordering dynamics discussed in this article, the growth of heteroepitaxial islands can in fact be described by the LSW theory: The order parameter is the density of the deposited material. It is large within the droplets and small between islands, where one finds a dilute gas of adatoms. The coarsening mechanism is the same as described by the original LSW theory, i.e., coarsening is driven by curvature and surface tension effects due to the Gibbs-Thompson relation [24]. However, the current of adatoms does not enter the islands through the surface of the islands, but only through the contact line with the substrate. Dimensional analysis [25] then shows that the droplet radius grows proportional to $t^{1/4}$. This kind of theory does not apply to pyramid-like homoepitaxial growth: It is not possible to define a scalar order parameter that corresponds to the density of the deposited material, since this density is the same everywhere. In contrast, the proper order parameter, the slope of the film, is a two-component vector and the same kind of arguments no longer apply. Furthermore, the driving mechanism of the coarsening dynamics is unclear: we do not have a Gibbs-Thompson relation in this case.

The fundamental differences between domain and surface growth become clear, if the domain structures are studied. The different grayscales in Fig. 3 indicate the areas that correspond to different directions of the slope $\vec{m}$ of the surface and the magnetization $\vec{M}$

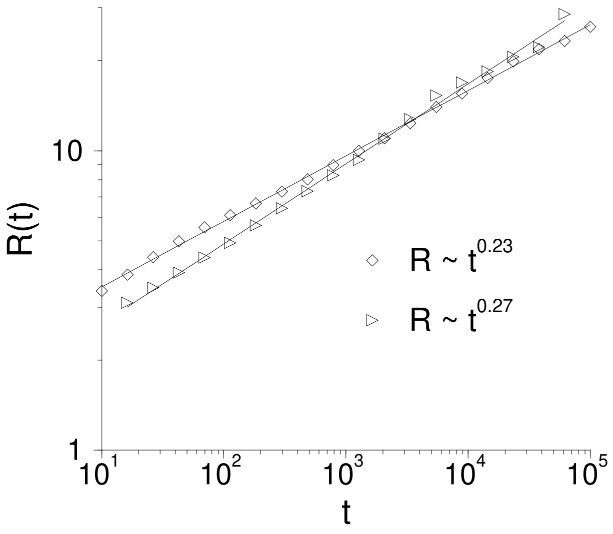

Fig. 2. Comparison of the growth law for threefold (triangles) and fourfold (diamonds) symmetries. In both cases the pyramid size shows a power-law behavior that is consistent with $R(t) \sim t^{1/4}$.

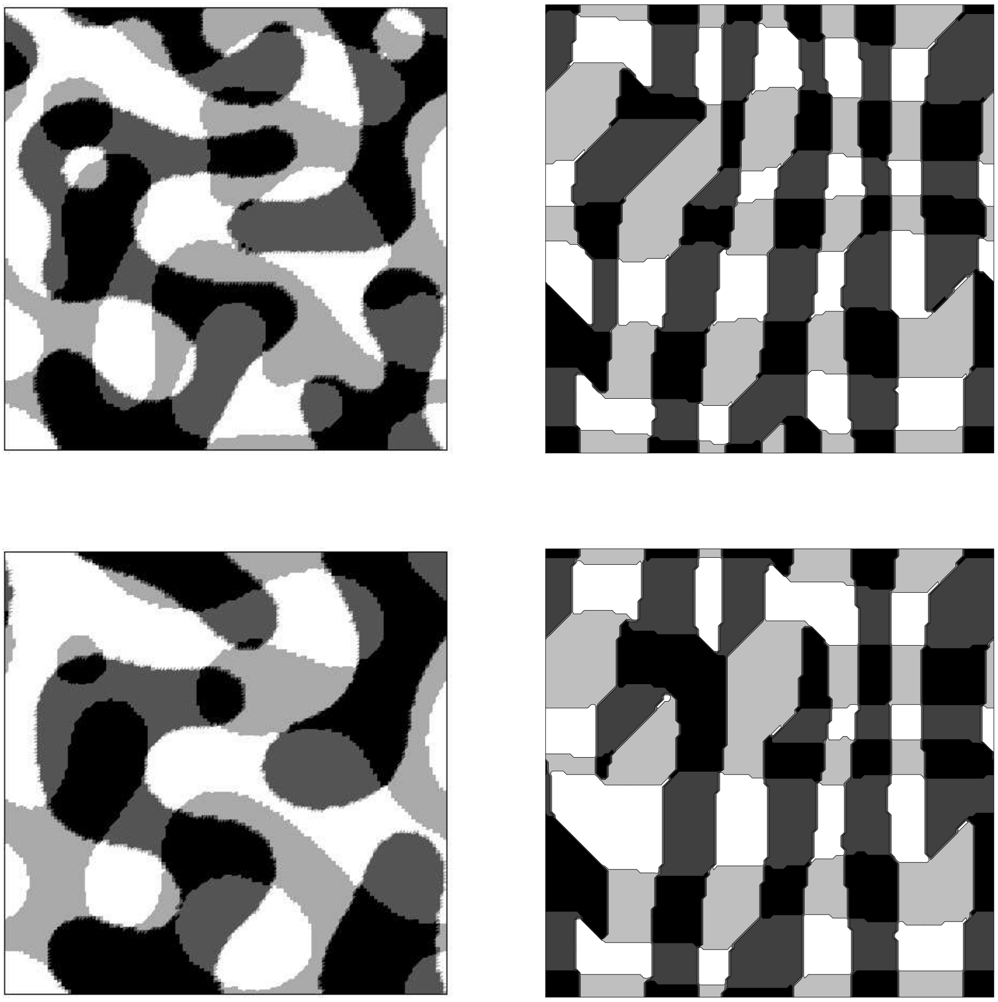

Fig. 3. Domain structure for surface ordering [right, eq. (6)] and for the conserved four-state clock model [left, eq. (8)]. The white and black domains correspond to orientations of $\vec{m}$, $\vec{M}$ = $(1, 1)$ and (-1,-1), whereas the light and dark gray domains correspond to (1,-1) and (-1,1). The lower configurations correspond to later times.

of a four-state clock model. In the latter case the domain walls are round in general and not oriented in any particular way. In the case of surface growth the domain walls have to form straight lines because these are intersections of planes with orientations that correspond to the zeros of the surface currents (2) and (3). Most of the walls are light walls oriented along the principal axes of the underlying lattice that have a smaller energy (7) than the heavy walls that form a 45° angle with respect to the principal axes. Already these observations indicate that the growth mechanism must be different in the two cases. The dominant growth mode in the case of the four-state clock model described by the Cahn-Hilliard equation (8) is the diffusion of small droplets[1] from a small [e.g., (1,1)] domain through another domain [$(-1,-1)$, $(-1,1)$, or (1,-1)] to a larger domain of the same kind. This is not possible in the case of pyramid-like growth

[1] These can be single atoms as, e.g., in the case of an alloy.

on surfaces: There cannot be a droplet of the $(1,1)$ phase within a $(-1,-1)$ domain because this would violate the constraint $\nabla \times \vec{m} = 0$ and such a configuration does not correspond to a surface profile. Instead, the entities that diffuse from a small domain to a larger domain must have the form of a kink or slab that has the length of the domain itself. Since the size of these diffusing kinks increases linearly with the average size of the pyramids $R(t)$, the growth velocity is reduced by one power of R compared to the LSW-type growth. Therefore the size of the pyramids increases only as $t^{1/4}$.

4. Summary

Because of an adatom density that is much larger than the equilibrium adatom density slope-dependent diffusion currents are generated that dominated the evolution of surface morphology in an MBE experiment. In the presence of step-edge barriers that suppress the inter-layer diffusion the surface evolution is unstable and leads to the formation of pyramids on the surface. The zeros of the diffusion current determine the selected slopes of the side planes. The areas of constant slope can be interpreted as domains that are limited by domain walls. Coarsening proceeds through the elimination of domain boundaries. Since the locations of the zeros of the surface current depend strongly on the lattice symmetries, the domain walls are oriented predominantly along the principal axes of the lattice, in contrast to the conserved ordering dynamics of the corresponding clock models for which such dependencies do not exist. Due to this coupling the coarsening exponent is $n = 1/4$, smaller than the LSW exponent of $1/3$.

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