Slope Selection and Coarsening in Molecular Beam Epitaxy

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(Received 10 March 1994)

We propose a simple Langevin equation that describes the growth of pyramid-like structures on a surface under conditions typical of molecular beam epitaxy. The slope of these pyramids is selected by the crystalline symmetries of the growing film. By analogy with the problem of domain growth of systems with a conserved order parameter we show that the dynamic exponent that controls the growth of the pyramids is $z \simeq 4$. There is no mechanism that limits the size of the growing structures. This implies that the roughness exponent is $\alpha = 1$, in agreement with recent experiments.

PACS numbers: 61.50.Cj, 05.40.+j, 05.70.Ln, 68.55.Bd

Films grown by deposition processes in which surface diffusion is the dominant relaxation process reveal a surprising variety of surface morphologies [1]. The nonequilibrium growth process leads in some cases to scale invariance of the correlation functions, but in other circumstances to instabilities, which manifest themselves in pyramidal structures. A theoretical description of these scenarios is aimed at a better understanding of molecular beam epitaxy (MBE), which has become an important technique for the growth of thin films.

In this Letter we present a theory for growth under MBE conditions for systems that have potential barriers near step edges that suppress the diffusion of adatoms to a lower terrace. This effect, now commonly called the Schwoebel effect, was first studied experimentally by Ehrlich and co-workers [2] and was later investigated theoretically by Schwoebel [3]. In his seminal paper, Villain [4] illustrated the importance of this effect for MBE growth on high-symmetry surfaces and pointed out that it gives rise to instabilities, which since have been observed in experiments [5–7]. The temporal evolution of these instabilities is the subject of this Letter.

In MBE the height h describing the local position of the moving surface obeys a conservation law [4,1],

$$\partial_t h(\mathbf{r},t) = -\nabla \cdot \mathbf{j}\left[\nabla h(\mathbf{r},t)\right] + \eta(\mathbf{r},t)\ , \tag{1}$$

where η is the shot noise due to the fluctuations of the incoming particle beam, and the height is measured in a comoving frame of reference. We first recall [4,7] the form of the contribution $\mathbf{j}_s$ to the surface current due to the Schwoebel effect. Let us assume for the moment that no adatom on a vicinal surface can overcome the barrier at downward steps and therefore all adatoms remain on the terrace on which they have been deposited. If the terrace size l, is smaller than the diffusion length l_d basically all adatoms reach the step edge of the upper terrace where they are incorporated into the substrate. This results in an uphill current $j_s(m) \sim 1/m$, where $m = 1/l$ is the tilt of the vicinal surface. This is the so-called step-flow regime. If the terrace size is larger than l_d only the adatoms within a distance l_d of the upper terrace will reach that step, creating a depletion zone in its neighborhood. Only this fraction of all adatoms contributes to the current j_s. All other adatoms form islands on the terrace and the corresponding currents average to zero. Thus, the current $j_s(m) \sim l_d/l = l_d m$ has a positive derivative $j_s'(m)$ for small m and this leads to the instability discussed by Villain [4]. The crossover between the two regimes occurs when l is of the order of the diffusion length l_d.

Recently, Johnson *et al.* [7] proposed a simple analytic form for the current that interpolates between the two regimes,

$$\mathbf{j}_s(\mathbf{m}) \sim \mathbf{m}/\left[1 + (l_d\mathbf{m})^2\right]\ . \tag{2}$$

The corresponding Langevin equation for the morphological evolution of the surface in MBE growth is fundamentally different from usual equations for kinetic roughening: The growth process is similar to problems of pattern formation and coarsening [7–9]. In fact, Krug, Plischke, and Siegert [10] showed for various models that the surface current has the form (2) if Schwoebel barriers are present. However, although this form of the current is correct for early times as long as the slopes are much smaller than 1, it is too restrictive to describe the unstable three-dimensional growth of real materials in the late time regime. The arguments which led to Eq. (2) are based on currents on vicinal surfaces and there is no reason why (2) should be valid for inclinations m of order 1. We will see below that the current j_s necessarily drives the surface into a regime with $m \gg 1$. To derive a more general form it is useful to express the current (2) in terms of the angle of inclination ϑ of the surface with respect to the unstable singular surface: $j_s(\vartheta) = |\mathbf{j}_s(\vartheta)| \sim \tan\vartheta/(1 + (l_d \tan\vartheta)^2)$. From this expression it is clear that $j_s(\vartheta)$ is periodic in ϑ with period π. *In other words, the crystal that is growing has only one high-symmetry surface corresponding to* $\vartheta = 0$. Thus, we

0031-9007/94/73(11)/1517(4)$06.00

see that if we wish to model the current for a structure with, e.g., cubic symmetry we may use

$$j_s(m) \sim \tfrac{1}{2}\tan(2\vartheta)/\left[1+(\tfrac{1}{2}l_d\tan(2\vartheta))^2\right]$$

or

$$\mathbf{j}_s(\mathbf{m}) = D_s\mathbf{m}(1-m^2)/\left[(1-m^2)^2+(l_d m)^2\right] \ . \qquad (3)$$

In the step-flow regime the current $|\mathbf{j}_s| \simeq F/m$, thus, $D_s = Fl_d^2$ [4,7]. This current is properly equal to zero on the two high-symmetry surfaces $\vartheta = 0, \pi/2$ and, moreover, is also equal to zero at the intermediate inclination $\vartheta = \pi/4$ or $m = m_0 = 1$. The generalization for other lattices is straightforward. We note that the form (3) still has the correct physical behavior: $j_s \sim m$ for $m \ll 1/l_d$ and $j_s \sim 1/m$ for $1/l_d \ll m \ll 1$. Despite these similarities (3) gives rise to a completely different behavior than the current (2) as will be shown below.

Certainly, Eq. (3) is not exact [11]. It merely gives an interpolation formula that takes into account the occurence of a zero in j_s and the requirements of the Schwoebel effect. High symmetry surfaces like the $\{110\}$ surfaces in a cubic crystal cannot be consistently described as vicinal to other surfaces [10,12]. Rather the symmetries require that the current j_s is zero for such orientations $m = m_0$. If $j'(m_0) < 0$ the homogeneous solution $m(\mathbf{r}) = m_0$ is stable and m_0 turns out to be the selected slope of the evolving surface pattern (see below). If $j'(m_0) > 0$ there has to be another zero $j(\tilde{m}_0) = 0$ with $0 < \tilde{m}_0 < m_0$ and $j'(\tilde{m}_0) < 0$ because j_s has to be a continuous function of the tilt angle ϑ. From this it is already clear that $m_0 = 1$ is not necessarily the only zero of the current $\mathbf{j}_s$. There are many processes, e.g., knock-out effects [12], which lead to downhill currents that can overcompensate the Schwoebel current for large enough slopes [9]. The selected slope is given by the smallest zero of $j_s(m)$ with $m_0 > 0$. From this point of view Eq. (3) is a minimal model: $j_s(m)$ must have at least one zero between 0 and ∞. The exact form of $j_s(m)$ does not play a role. The slope selection mechanism and the growth exponents to be described below do not depend on such details.

The total surface current $\mathbf{j}$ is the sum of $\mathbf{j}_s$ and the equilibrium surface current $\mathbf{j}_{\rm eq} = D_{\rm eq}\nabla\Delta h$, where the coefficient $D_{\rm eq}$ is proportional to the surface stiffness [13,1]. Eq. (1) is readily transformed into an equation for the tilt,

$$\partial_t\mathbf{m} = -\nabla\nabla\cdot\mathbf{j}_s(\mathbf{m}) - D_{\rm eq}\Delta\Delta\mathbf{m} + \nabla\eta \ , \qquad (4)$$

where we have used the fact that $\nabla\times\mathbf{m} = 0$. For *one-dimensional* surfaces Eq. (4) is equivalent to the equation of motion of a conserved scalar order parameter in spinodal decomposition [14,15,9] as was already noted by Krug, Plischke, and Siegert [10]. Consequently, "domains" with $m = +m_0$ and $m = -m_0$ are formed and the size of the domains grows with time as $t^{1/3}$ [16], the well-known Lifshitz-Slyozov law. It is illuminating to notice the difference in the dynamical behavior resulting from the current (2): In that case the "free energy", $\mathcal{F} = -\int dm\, j_s(m) \sim -\ln(1+l_d^2m^2)$, has minima only at $m_0 = \pm\infty$. Therefore, the slope of the emerging profile does not saturate and deep grooves develop. This explains the results of earlier theories [17] and simulations [18]. Note that while true domain growth does not exist in one dimension, since an equilibrium free energy cannot have two degenerate minima, this argument does not apply here: The current $\mathbf{j}_s$ is a *nonequilibrium* contribution, which vanishes if the flux F goes to zero. Thus, its integral can have a double minimum even in $d = 1$ and this type of Lifshitz-Slyozov behavior may be observable in the step-flow regime as an instability of the step edge.

We now turn to the two-dimensional case. The equilibrium term in (4), $D_{\rm eq}\Delta\Delta\mathbf{m}$, has the usual form for ordering dynamics of a vector order parameter $\mathbf{m}$. However, the same is not true for the first term on the right hand side of (4), even if $\mathbf{j}_s = \delta\mathcal{F}/\delta\mathbf{m}$ and, of course, there is no guarantee that this current will be derivable from a free energy. In this Letter we restrict ourselves to the case where $\mathbf{j}_s$ *is* derivable from a free energy and will discuss the general case in a longer publication. We will show that the dynamical evolution of the surface can be described analogously to the theory of domain growth for a conserved order parameter. The stable solutions for the order parameter in the domain growth problem correspond to the stable surface orientations that are determined by the zeros of the current $\mathbf{j}_s$ in the present case.

Bray's theory of phase ordering [15] relates the dynamical exponent $z = d+2-y$ to the energy $E(L)$ of an elementary excitation in a system of size L^d, $E \sim L^y$. Thus, $y = d-1$ and $z = 3$ for a scalar and $y = d-2$ and $z = 4$ for a vector order parameter. The exponent y is easily determined as one only needs to solve for the steady-state solution with anti-periodic boundary conditions. For the current (3) we obtain $D_{\rm eq}\Delta\mathbf{m} + D_s\mathbf{m}f(\mathbf{m}^2) = 0$, with $\mathbf{j}_s = D_s\mathbf{m}f(\mathbf{m}^2)$. This equation is completely equivalent to that of an n-component vector order parameter with $n = 2$ (XY model). But there is an important difference between the slope $\mathbf{m}$ and the order parameter of an XY model: The slope must obey the constraint $\nabla\times\mathbf{m} = 0$ and this may slow down the dynamical evolution.

We have numerically integrated Eq. (1) for the current (3) with $\eta = 0$ since noise is known to be irrelevant for the ordering process [15,19]. To classify the growth law we determined the first zero r_0 of the order-parameter correlation function $C(\mathbf{r},t) = L^{-d}\sum_{\mathbf{x}}\langle\mathbf{m}(\mathbf{r}+\mathbf{x},t)\mathbf{m}(\mathbf{x},t)\rangle$. This function has been successfully used to determine the scaling behavior of the domain size in the XY model [19] and in the one-dimensional case [1]. Fig. 1 shows an almost perfect power law $r_0(t) \sim t^{1/z}$ with $z = 4$, that is in agreement with the renormalization group theory [15] for vector order parameters. But recent theories [20] show that the usual theories of phase ordering cannot be applied to the two-dimensional XY-model because of the long range correlations between vortices. Numerical simulations [21] indeed show deviations from the $t^{1/4}$ be-

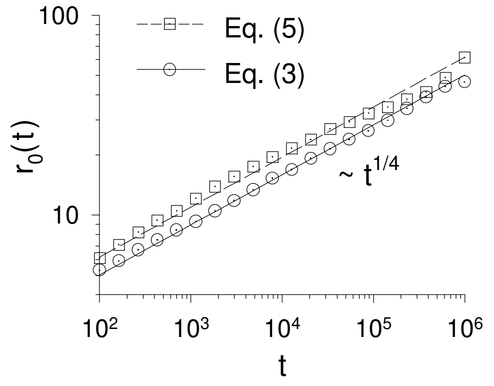


FIG. 1. Time dependence of the first zero $r_0(t)$ of the slope-slope correlation function. The lines are power law fits with an exponent $1/z = 0.25$. The system size is $L^2 = (128\Delta x)^2$ with a meshsize of $\Delta x = 2$. The parameters $l_d = 10$, $D_{\rm eq} = 1$, $D_s = 2$ have been used in both cases.

havior, which are not seen in Fig. 1. Whether this can be attributed to the effects of the constraint $\nabla \times \mathbf{m} = 0$ is unclear.

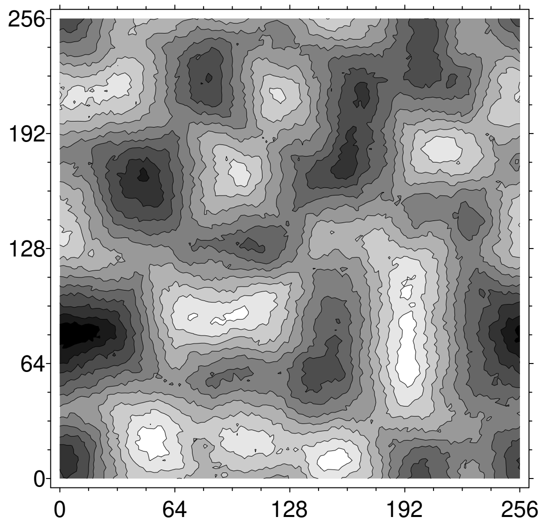
The current (3) is a simplification in the sense that it neglects in-plane anisotropies: For cubic symmetry $\mathbf{j}_s$ only has to be periodic with a period of $\pi/2$ for rotations around the [100] and [010] axes, whereas (3) has this symmetry for all axes lying in the xy-plane. Thus the above results are valid only on timescales for which such anisotropies in the diffusion current can be neglected. In the more general case we consider a current with components $j_{s,x} = m_x f(m_x^2)$ and $j_{s,y} = m_y f(m_y^2)$ with the same function f defined above. The corresponding "free energy" is simply $\mathcal{F} = -\int dm_x\, j_{s,x} - \int dm_y\, j_{s,y}$. Thus, it has minima at $\mathbf{m} = (\pm 1, \pm 1)$ instead of $\mathbf{m} = (\pm 1, 0)$ and $\mathbf{m} = (0, \pm 1)$ as required. This is easily repaired by a coordinate transformation. The current with components

$$\begin{aligned} j_{s,x} &= D_s\big[(m_x + m_y) f((m_x + m_y)^2) \\ &\quad +(m_x - m_y) f((m_x - m_y)^2)\big]\ , \\ j_{s,y} &= D_s\big[(m_x + m_y) f((m_x + m_y)^2) \\ &\quad -(m_x - m_y) f((m_x - m_y)^2)\big] \end{aligned} \tag{5}$$

has all the required symmetries and still has the correct physical properties. Since this free energy has only four discrete minima we expect "domain growth" as in spinodal decomposition, i.e., $z = 3$ and a Lifshitz-Slyozov law $r_0(t) \sim t^{1/3}$.

We have numerically integrated Eq. (1) with periodic boundary conditions using the current (5) with $f(x) = (1-x)/[(1-x)^2 + l_d^2 x]$ both with and without noise, for a number of values of l_d. Our result for the first zero $r_0(t)$ of the slope-slope correlation function for the current (5) is included in Fig. 1. In Fig. 2 we show topographic maps of the surface at an early stage of the domain growth and at the final time. The square shape of the domains is clearly seen. The orientation of each of the facets is one of the four available {110} facets. Fig. 3 shows the actual surface configuration, which corresponds to the time

(a)



(b)

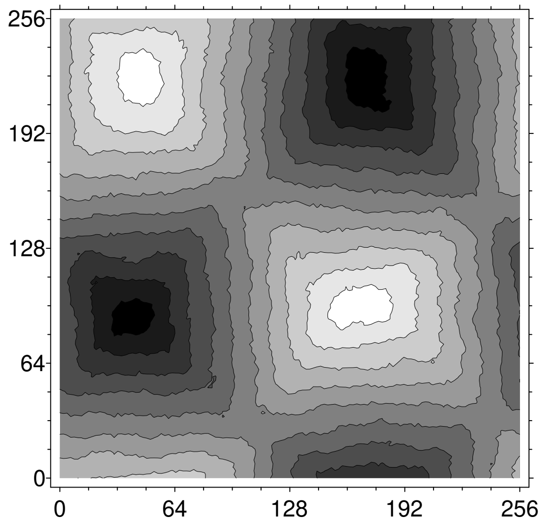


FIG. 2. Contour plots of the height $h(\mathbf{r}, t)$ for the current (5) at a) $t = 4.65 \cdot 10^4$ and b) $t = 10^6$. Same parameters as in Fig. 1, and $\langle \eta^2 \rangle = 1$.

$t = 4.65 \times 10^4$. For the time regime we have been able to integrate the Langevin equation (see Fig. 1) we obtain a growth law $r_0(t) \sim t^{1/4}$, i.e., the same as for the current (3), although we expected Lifshitz-Slyozov-like behavior. To study this problem further we also integrated Eq. (4) using the current (5) with $f = 1 - x$. If the two operators in front of $\mathbf{j}_s$ in Eq. (4) are exchanged the equations for the two components of the order parameter are completely decoupled and the problem is equivalent to spinodal decomposition for which $z = 3$ is obtained [22]. In the present case the two components *are coupled through the dynamics* and we again obtain $z = 4$ [9]. We are forced to conclude that the constraint $\nabla \times \mathbf{m} = 0$ is indeed relevant and leads to a slower growth in comparison with the corresponding domain growth problem. Liu and Metiu [23] have integrated an equation similar to Eq. (4) but in a different context. Their result is in agreement with ours.

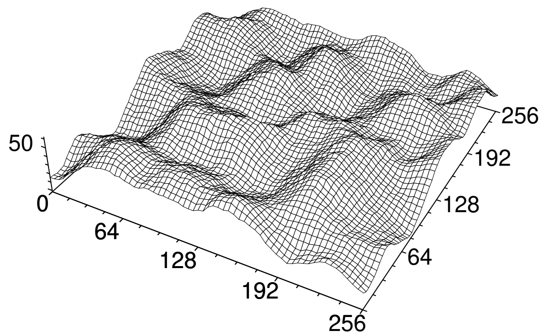


FIG. 3. Surface plot corresponding to Fig. 2a.

An important result of these calculations is that there is no wavelength-selection in this form of the theory: In an infinite system the pyramids would continue to grow, whereas in a finite system the profile saturates when only a single pyramid remains. Instead, our theory predicts a selection of the slope, which corresponds to the order parameter in the domain growth problem. Therefore, the height and the base of the pyramids grow in the same way. Thus, we conclude that the exponent α that characterizes the roughness of the surface is $\alpha = 1$. This is consistent with recent experimental results [6]. The exponent $\beta = \alpha/z$ describing the growth of the pyramids is equal to $1/z$. These results follow directly from the fact that there is only *one* lengthscale and therefore only *one* exponent z in the theory of domain growth in contrast to the conventional theories of surface roughening, which contain two independent exponents, α and z. We emphasize, however, that these latter theories do not apply in the case of instabilities, since the surfaces are no longer self-affine and the usual scaling laws for kinetic surface roughening are not valid [18,1]. In our case the exponents α and β are only effective exponents; they do not describe the scaling of, e.g., the height-height correlation functions. Furthermore, the hyperscaling relation $z = 2\alpha + d$ is not necessarily valid as has already been shown for instabilities in one dimension [1]. We emphasize that our theory quite naturally limits the surface roughness to $\alpha = 1$ even in the case of an instability. In $d = 1$ this roughness is in fact smaller than the one obtained for models *without* an instability [1,24,25], which are no longer consistent with the solid-on-solid assumption.

We predict, on the basis of our simulations that an exponent $\beta = \alpha/z \simeq 1/4$ will be found. In [6] the unstable homoepitaxial growth of Cu was studied at two different temperatures and the exponent β was determined to be $\beta = 0.26$ or 0.56, at least in partial agreement with our prediction. More experimental and theoretical work will be needed to clarify this situation further.

We thank Joachim Krug and Dietrich Wolf for helpful conversations. This research was supported by the Deutsche Forschungsgemeinschaft under SFB166 and by the NSERC of Canada.

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