Coarsening Dynamics of Crystalline Thin Films

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The formation of pyramid-like structures in thin-film growth on substrates with a quadratic symmetry, e.g., {001} surfaces, is shown to exhibit anisotropic scaling as there exist two length scales with *different* time dependences. Numerical results indicate that for most realizations coarsening of mounds is described by an exponent $n \simeq 1/4$. However, depending on material parameters it is shown that n may lie between 0 (logarithmic coarsening) and 1/3. In contrast, growth on substrates with triangular symmetries ({111} surfaces) is dominated by a single length $\sim t^{1/3}$.

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The formation of pyramids or mounds in growth processes such as molecular beam epitaxy has been observed in numerous experiments [1–3] and computer simulations [2–6]. This three-dimensional growth mode is caused by step-edge barriers that hinder the diffusion of adatoms across step edges. The generated surface diffusion current $\mathbf{j}$ causes the initial high-symmetry orientation of the surface to become unstable [7,2,8]. As a consequence the surface breaks up forming pyramid-like mounds, the side orientations of which correspond to stable zeros of the diffusion current [4,9]. At this level this phenomenon is theoretically well understood. Conversely, the observation that the evolving surface morphology coarsens as more and more material is deposited is poorly understood. The similarity with ordering phenomena [10] like spinodal decomposition has led to the assumption that correlation functions like the height-height correlation function

$$C(\mathbf{r},t) = L^{-2} \sum_{\mathbf{x}} \langle h(\mathbf{r}+\mathbf{x},t) h(\mathbf{x},t) \rangle \tag{1}$$

or its Fourier transform, the structure factor

$$S(\mathbf{k},t) = \langle \hat{h}(\mathbf{k},t) \hat{h}(-\mathbf{k},t) \rangle \ , \tag{2}$$

depend only on a single length scale, the pyramid size $R(t)$, which in turn, because of the scale invariance of the correlation functions, must have a power-law dependence $R(t) \sim t^n$. The surface height $h(\mathbf{r},t)$ is measured in a comoving frame of reference such that the average height is zero. $\hat{h}(\mathbf{k},t)$ is the Fourier transform of $h(\mathbf{r},t)$, and L^2 is the size of the substrate. In numerical simulations and several experiments the coarsening exponent was found to be close to $n \simeq 1/4$. However, theories that attempt to calculate this exponent are so far not very convincing.

Surprisingly, the initial assumption that there is only a single length scale and that the correlation function therefore follow simple scaling laws, was never really questioned. Only recently [11] it was found that this kind of surface dynamics is in some respects different from ordering dynamics like spinodal decomposition: The dynamical exponent z that describes the relaxation of shape fluctuations of pyramids is not equal to the inverse $1/n$ of the coarsening exponent indicating that the dynamical evolution in these two cases is governed by different length scales. In this article it will be shown that the coarsening dynamics itself depend on at least two length scales with *different time dependences*. Therefore, the standard scaling assumption for the correlation functions is invalid.

At not too high temperatures so that desorption can be neglected the evolution of the surface in molecular beam epitaxy is described by the continuity equation

$$\partial_t h = -\Delta\Delta h - \nabla \cdot \mathbf{j}(\mathbf{m}) + \eta \ , \tag{3}$$

where $\mathbf{m} = \nabla h$ is the slope of the surface profile and η represents shot noise due to fluctuations in the deposition flux. The form of the surface current $\mathbf{j}$ must be chosen such that it describes the above mentioned instability and leads to slope selection. The form $\mathbf{j} \sim \mathbf{m}(1-\mathbf{m}^2)$ has been used [3,12], however, it has stable zeros for all slopes with $|\mathbf{m}| = 1$ regardless of the direction of $\mathbf{m}$. Such an azimuthal symmetry is unrealistic for crystalline films. For substrates with a quadratic symmetry the diffusion current must have the form $j_\alpha(\mathbf{m}) = m_\alpha f_\alpha(m_x^2, m_y^2)$, $\alpha = x,\, y$, with $f_x(m_x^2, m_y^2) = f_y(m_y^2, m_x^2)$. The simplest form that describes growth on such substrates is a current with components

$$\begin{aligned} j_x &= m_x(1 - m_x^2 - b m_y^2)\,, \\ j_y &= m_y(1 - m_y^2 - b m_x^2)\,, \end{aligned} \tag{4}$$

which leads to a buildup of pyramids with selected slopes $m_0 = (\pm 1, \pm 1)/\sqrt{1+b}$ for $-1 < b < 1$. Terms of higher than third order in the slope have been neglected in (4) as such terms only modify the edge profile of the pyramids and do not influence the ordering dynamics. Most of the results presented below do not depend on the specific form of the functions f_α as long as $f_\alpha(0,0) > 0$ and $f_\alpha(m_0^2, m_0^2) = 0$ [13]. Terms that depend on derivatives of the slope, in particular a term proportional to $\nabla(\mathbf{m}^2)$ [14,7], have been neglected as well. Recently, it has been shown [15] that, at least in one dimension, such a term does not change the growth law. Triangular symmetries applicable to {111} substrates are discussed further below.

Coarsening in phase-ordering dynamics, e.g., spinodal decomposition or Ostwald ripening, is a deterministic process, i.e., noise is irrelevant [16]. In the same spirit the focus of this work is on the deterministic aspects of the dynamics described by Eq. (3) with $\eta = 0$. Effects of the noise are discussed at the end of the article. The important differences between the problem studied here and phase-ordering dynamics described by the Cahn-Hilliard equation [17] become apparent, when the domain configurations are plotted as in Fig. 1. A domain in this context is an area of constant slope corresponding to one of the four values $(\pm 1, \pm 1)$ (we will concentrate on the case $b = 0$ first and discuss the relevance of the parameter b further below). The analogous case in phase-ordering dynamics is described by a four-state clock model [18]. However, in that case domain walls do not have any particular orientation, whereas here domain walls are intersections of planes of constant slopes and therefore form *straight* lines. Furthermore, there are two types of domain walls: Domain walls at which only one component of the slope changes are aligned along the x- and y-axes. These are the edges of the pyramids, see Fig. 1b. Domain walls at which both components of the slope change run at 45° with respect to the principal axes. These latter domain walls form roof tops as illustrated in Fig. 1c. Domain walls in systems that phase order give rise to a power-law tail in the structure-factor called Porod's law [19]. On scales $\xi \ll x \ll R(t)$ the height function close to an edge of a pyramid running in the y-direction has the form $h(x,y) = |x| + y$. Here, ξ is the width of such a domain wall [$\xi = \sqrt{2}$ for (4) and $b = 0$]. Hence, the slope $\mathbf{m} = (\mathrm{sign}(x), 1)$ leads to a singular contribution in the slope-slope correlation function [20], $C_{\mathbf{m},\mathrm{sing}} = -2|x|\rho_{\mathrm{pe}}$, where ρ_{pe} is the density of these domain walls [21]. More generally, domain walls that make an angle ψ with the y-axis yield a contribution $S_{\mathbf{m}} = 4k^{-3}\delta(\varphi - \psi)\rho_\psi(t)$ to the slope structure factor, where $\rho_\psi(t)$ is again the density of the domain walls and φ the azimuthal angle such that $\mathbf{k} = (k\cos\varphi, k\sin\varphi)$. Consequently, the structure factor (2) for crystalline films with a quadratic anisotropy has a highly anisotropic tail: for $1/R(t) \ll k \ll 1/\xi$

$$S(\mathbf{k},t) = \frac{4}{k^5}\sum_{\nu=0}^{3}\left[\rho_{\mathrm{pe}}(t)\delta\left(\varphi - \frac{\pi}{2}\nu\right) + 2\rho_{\mathrm{rt}}(t)\delta\left(\varphi - \frac{\pi}{4} - \frac{\pi}{2}\nu\right)\right], \quad (5)$$

where the additional factor 2 in front of the density $\rho_{\mathrm{rt}}(t)$ of domain walls at 45° directions (roof tops) comes from the fact that both components of the slope change at such a domain wall. Eq. (5) is one of the central results of this article: It shows that the structure factor depends on two different length scales $1/\rho_{\mathrm{pe}}$ and $1/\rho_{\mathrm{rt}}$, specifying the average separation of pyramid edges and roof tops, respectively. While for $\rho_{\mathrm{pe}} \gg \rho_{\mathrm{rt}}$ the former is directly related to the average pyramid size $R(t)$, no obvious relation exists between ρ_{rt} and $R(t)$. In fact, *there is no reason why* $1/\rho_{\mathrm{pe}}$ *and* $1/\rho_{\mathrm{rt}}$ *should have the same time-dependence or follow the same power law.* Therefore, the structure factor does not obey a scaling law $S(\mathbf{k},t) = R^4(t)s(kR(t))$, not even in a modified anisotropic form [22]. Hence, all theoretical approaches that assume such a dependence on a single length scale are unfounded.

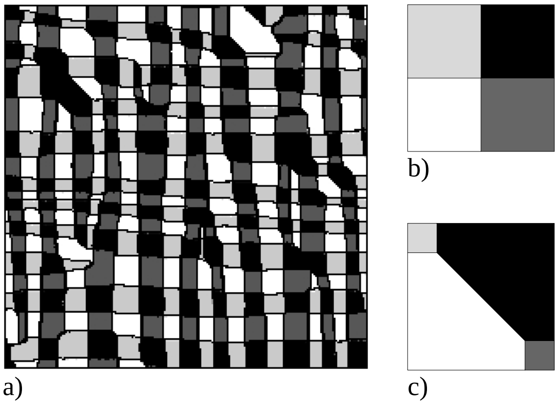

FIG. 1. a) Domain wall structure obtained from a numerical solution of Eqs. (3), (4); b, c) types of domain walls: b) pyramid edges, c) roof top. The greyscales correspond to average slopes in the following way: white $\equiv (+1,+1)$, black $\equiv (-1,-1)$, light grey $\equiv (+1,-1)$, dark grey $\equiv (-1,+1)$.

The result that the structure factor is nonzero only for $k_x = 0$ or $k_y = 0$ ($\langle 100\rangle$ directions) and $|k_x| = |k_y|$ ($\langle 110\rangle$ directions) as indicated by the delta functions in (5) is a consequence of the assumption that the singular part of $C(\mathbf{r},t)$ dominates the contributions to the tail of $S(\mathbf{k},t)$. In directions other than these high symmetry directions no singularities exist and $S(\mathbf{k},t)$ decays exponentially. Furthermore, although fluctuations of the domain wall directions are finite [11], such fluctuations remove the delta singularities and replace them by a sharply peaked function of finite width. Nevertheless, the prediction that $S(\mathbf{k},t) \sim k^{-5}$ in directions normal to the domain walls, and that $S(\mathbf{k},t)$ decays faster for all other directions is confirmed in numerical simulations [23] and it should also be possible to observe this behaviour experimentally.

Length scales that show the anisotropic scaling of the structure factor in a numerical solution of Eqs. (3,4) can be defined as inverses of moments of the structure factor

$$k_{\mathrm{pe}}(t) = \sum\nolimits_{k_x} k_x S((k_x,0),t) \Big/ \sum\nolimits_{k_x} S((k_x,0),t)\ , \quad (6)$$

$$k_{\mathrm{rt}}(t) = \sum\nolimits_{k} \sqrt{2}kS((k,k),t) \Big/ \sum\nolimits_{k} S((k,k),t) \quad (7)$$

in the two directions in question. Figure 2 shows clearly that the scaling behaviour of $S(\mathbf{k},t)$ depends on the direction of $\mathbf{k}$: whereas $1/k_{\mathrm{rt}}(t)$ is well described by a power law $\sim t^{1/3}$, $1/k_{\mathrm{pe}}(t)$ grows more slowly. In fact, in a numerical simulation coarsening stops as soon as the average distance $1/k_{\mathrm{rt}}$ between two roof tops is of the same order as the system size. *At the same time the average pyramid size can be several orders of magnitude smaller.* The coarsening

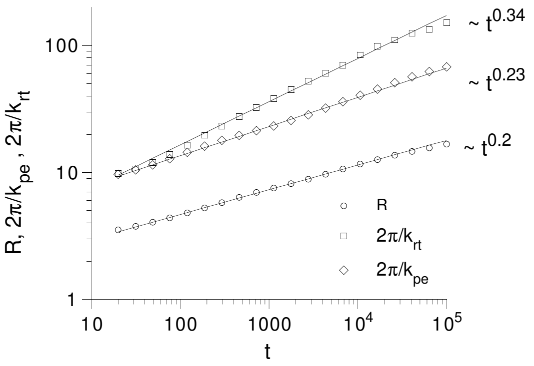

FIG. 2. Time dependence of the length scales $1/k_{\mathrm{pe}}(t)$ and $1/k_{\mathrm{rt}}(t)$ as defined in Eqs. (6), (7). The average pyramid size $R(t)$ measured as the first zero of the correlation function $C(\mathbf{r}, t)$ in the $\langle 110 \rangle$ directions is plotted as well.

of pyramids is enslaved to dynamics of roof tops. A configuration without any roof tops does not coarsen, i.e., it is a metastable state [23]. Roof tops represent defects in such perfect pyramid lattices and coarsening proceeds by eliminating such defects. However, because of the more complicated scaling behaviour indicated in (5) the theory of Bray and Rutenberg [24] can no longer be used to calculate the growth law.

During the temporal evolution of the surface morphology shown in Fig. 1 many more pyramids than roof tops are formed. The reason lies in the value $b = 0$ that was used in that simulation. The parameter b describes how the x-component of the current depends on the y-component of the slope. Such transverse currents are typical for, e.g., edge diffusion, the importance of which for growth morphologies has been emphasized by Bartelt and Evans [25] and was recently confirmed in an experiment [26]. It is possible to assign a "surface tension" σ to domain walls by integrating over the domain wall profile,

$$\sigma = \int_{-\infty}^{\infty} dr_\perp \left[\left(\frac{\partial m_x}{\partial r_\perp} \right)^2 + \left(\frac{\partial m_y}{\partial r_\perp} \right)^2 \right] , \qquad (8)$$

where the coordinate $r_\perp$ runs perpendicular to the domain wall and the domains are assumed to extend to infinity on both sides of the wall. Using the steady-state solutions for the domain wall profiles that correspond to Eqs. (3), (4), it is found that $\sigma_{\mathrm{pe}} = 4/[3\sqrt{2}(1 + b)]$ for pyramid edges and $\sigma_{\mathrm{rt}} = 4/[3\sqrt{1 + b}]$ for roof tops. Therefore, for $b = 0$ the formation of roof tops is suppressed. To understand the coarsening mechanism it is instructive to study perturbations to a perfect lattice of pyramids (see Figs. 3a-e). The movement of domain walls necessarily involves the nucleation of roof tops, see Figs. 3b and 3c. Such a perturbation does not cost anything, if $\sqrt{2}\sigma_{\mathrm{rt}} = \sigma_{\mathrm{pe}}$, or, if $b = -3/4$. For this value of the parameter b edge-like domain walls can transform without cost into roof-top-like domain walls and coarsening is no longer enslaved to the dynamics of the roof tops.

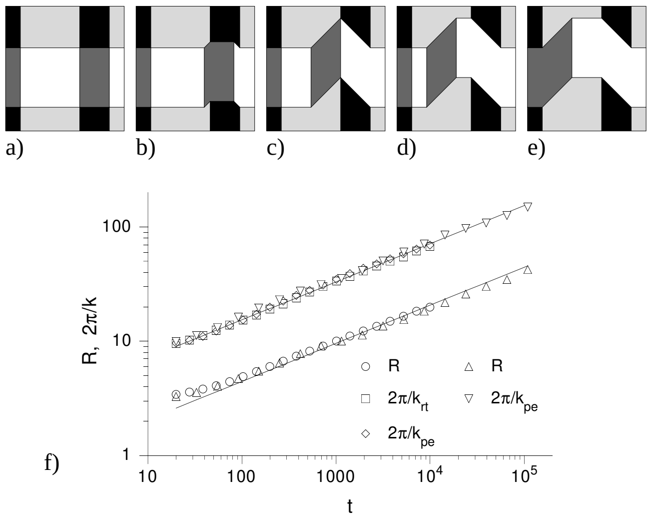

FIG. 3. Domain wall motion for films with a quadratic anisotropy: a-e) schematics of domain wall motions through the introduction of roof tops, f) coarsening dynamics for the special degenerate case $b = -3/4$. Data for triangular anisotropies (triangles) are included as well. The straight lines correspond to power laws $\sim t^{1/3}$.

This is convincingly confirmed by numerical solutions of Eq. (3) with a current (4) and $b = -3/4$. As seen in Fig. 3f coarsening is much faster as all length scales increase as $t^{1/3}$, i.e., *the coarsening of the pyramid size* $R(t)$ *depends on the parameter* b that in turn is determined by microscopic processes like edge diffusion.

The time scale in the degenerate case $b = -3/4$ is set by the time it takes to get from configuration 3c to configuration 3e. This is a diffusion process as the changes indicated in 3d do not affect the lengths of the domain walls. This behaviour and the time dependence $\sim t^{1/3}$ suggest an approach similar to the Lifshitz-Slyozov-Wagner theory [27]. Assuming that the magnitude of the slope is slightly less than the asymptotic value, i.e., $|m_{x,y}(\mathbf{r}, t)| = m_0 - \epsilon_{x,y}(\mathbf{r}, t)$ with $\epsilon_{x,y} \ll m_0$ it can be shown that there exists a diffusion current from the small domains to the larger domains that leads to a coarsening law $\sim t^{1/3}$. However, the same theory also predicts that the average deviation $\langle \overline{\epsilon}(t) \rangle$ should decrease as $t^{-1/3}$. This latter behaviour is not confirmed in numerical solutions of Eq. (3) for the current (4) with $b = -3/4$ [23]. This problem requires further investigation.

In the nondegenerate case with $b > -3/4$ the configurations 3b and 3c are highly suppressed as they correspond to activated processes. Hence, coarsening proceeds by eliminating roof tops that were nucleated in the initial stages of the instability. Consequently, the roof-top distance becomes much larger than the pyramid size R.

Although coarsening exponents close to 1/3 were found in a numerical simulation [6], the situation that the surface tensions obey the relation $\sqrt{2}\sigma_{\mathrm{rt}} = \sigma_{\mathrm{pe}}$ exactly is unlikely to be realized in nature. The fact that many experiments measured a coarsening exponent close to $1/4$ indicates that typically pyramid coarsening is enslaved to the dynamics of roof tops. However, this is no longer correct for thin films with a triangular lattice anisotropy, i.e., for (111) substrates. In that case there is only one type of domain wall; thus one expects fast coarsening in any case. The appropriate form of the surface current in that case was given in Ref. [18]. Results of a numerical solutions of Eq. (3) are included in Fig. 3f (triangles). They indeed show that the pyramid size $R(t) \sim t^{1/3}$. The author is aware of a single experiment that studied coarsening on a (111) substrate [28]. The results of that experiment are in perfect agreement with the theory presented here. Nevertheless, it must be emphasized that even in those cases where coarsening is $\sim t^{1/3}$ the correlation functions (1) and (2) do not obey a simple scaling law. The result (5) that the structure factor scales differently in directions perpendicular to the domain walls than in all other directions remains valid.

This result (5) that establishes the existence of several length scales is very general and does not depend on the specific form of the surface current. Instead, it follows from the constraints imposed by the crystalline anisotropies of the growing film, which in turn severely restrict the possible domain configurations. Consequently, the correlation functions do not obey a simple scaling law and the method by which the characteristic length scales are measured becomes important: Whereas the average roof-top distance could be separated from the average pyramid size using moments of the structure factor in different directions (6), (7), this cannot be accomplished in real space, e.g., the height-height correlation function (1) in directions parallel to the pyramid edges changes its functional form with time and does not permit the determination of any length scale.

As mentioned in the introduction, most experiments measured a coarsening exponent for the pyramid size on substrates with quadratic symmetries of $n \lesssim 1/4$ indicating that real systems are nondegenerate, i.e., they correspond to $b > -3/4$ in Eq. (4). In these cases the roof-top distance $D \sim t^{1/3}$ becomes much larger than the pyramid size R. However, if the late stages of the coarsening process are studied on scales smaller than D, the pyramid size coarsens only logarithmically as is typical for activated processes and as has in fact been predicted for this kind of systems [29]. The measurement of the coarsening behaviour in these cases is severely complicated by a wide cross-over regime [23] where almost any value between $n = 0$ and $n \lesssim 1/4$ can be observed. The interpretation is further complicated when effects of the noise $\eta \neq 0$ are included: For some time such stochastic fluctuations provide a mechanism to overcome the activation barriers that suppress the formation of roof tops. However, the activation barriers are proportional to the pyramid size. Hence, in the asymptotic regime, where the pyramid size is sufficiently large, stochastic effects become unimportant. This is in agreement with arguments presented by Shore *et al.* [29]. For deposition on $\{111\}$ substrates noise is clearly irrelevant.

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