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. Analytical and numerical results indicate that for most realizations coarsening of mounds is described by an exponent $n = 1/(3\sqrt{2})$. However, depending on material parameters, $n$ 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 scale $\sim t^{1/3}$.

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to one of the four values ($\pm 1, \pm 1$). The analogous case in phase ordering dynamics is described by a four-state clock model \cite{13}. 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. Domain walls at which both components of the slope change run at $45^\circ$ with respect to the principal axes. These latter domain walls form roof tops as illustrated in Fig. 1. Domain walls in systems that phase order give rise to a power-law tail in the structure-factor corresponding to 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 $\equiv (-1, +1)$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{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 $\equiv (-1, +1)$.}
\end{figure}

Consequently, the structure factor (2) for crystalline films comes from the fact that both components of the slope
\[\phi \equiv \sum_{k \neq 0} \left[ \rho_{100}(t) \delta \left( \varphi - \frac{\pi}{2} \right) + 2 \rho_{110}(t) \delta \left( \varphi - \frac{\pi}{4} \right) \right], \tag{5}\]

where the additional factor 2 in front of the density $\rho_{110}(t)$ of domain walls at $45^\circ$ directions (roof tops) comes from the fact that both components of the slope change at such a domain wall. Eq. (3) is one of the central results of this article: It shows that the structure factor depends on two different length scales $1/\rho_{100}$ and $1/\rho_{110}$, specifying the average separation of edges of pyramids and roof tops, respectively. Whereas for $\rho_{100} \gg \rho_{110}$ the former is directly related to the average pyramid size $R(t)$, no obvious relation exists between $\rho_{110}$ and $R(t)$. In fact, there is no reason why $1/\rho_{100}$ and $1/\rho_{110}$ should have the same time-dependence or follow the same power law. Therefore, the structure factor does not obey a scaling law $S(k, t) \sim R^2(t) \cdot k R(t)$, even in a modified anisotropic form \cite{16}. Hence, all theoretical approaches that assume such a dependence on a single length scale, are unfounded.

The result that the structure factor is nonzero only along the (100) and (110) directions as indicated by the delta functions in (3) is a consequence of the assumption that the singular part of $C(r, t)$ dominates the contributions to the tail of $S(k, t)$. For directions other than these high symmetry directions no singularities exist and one should expect an exponential decay. Furthermore, although fluctuations of the domain wall directions are finite \cite{10}, such fluctuations will remove the delta singularities and replace them by a sharply peaked function with finite width. Nevertheless, the prediction that $S(k, t) \sim k^{-5}$ in directions normal to the domain walls, and that $S(k, t)$ decays faster for all other directions is confirmed in numerical simulations \cite{19} and it should also be possible to observe this behaviour experimentally.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Time dependence of the length scales $1/k_{100}(t)$ and $1/k_{110}(t)$ as defined in Eqs. (6), (7). The average pyramid size $R(t)$ measured as the first zero of the correlation function $C(r, t)$ in the (110) directions is plotted as well.}
\end{figure}

Length scales that show the anisotropic scaling of the structure factor in a numerical solution of Eqs. (3) can be defined as inverses of moments of the structure factor
\[k_{100}(t) = \sum_{k_x} k_x S((k_x, 0), t) / \sum_{k_x} S((k_x, 0), t), \tag{6}\]
\[k_{110}(t) = \sum_k \sqrt{2k} S((k, k), t) / \sum_k S((k, k), t) \tag{7}\]
in the two directions in question. Fig. 2 shows clearly that the scaling behaviour of $S(k, t)$ depends on the direction of $k$: whereas $1/k_{110}(t)$ is well described by a power law $\sim t^{1/3}$, $1/k_{100}(t)$ grows more slowly. In fact,
in a numerical simulation coarsening stops as soon as the average distance $1/k_{(110)}$ 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 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. 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 Ref. 4, the theory of Bray and Rutenberg[20] can no longer be used to calculate the growth law. In the limit where the average roof-top distance $D \sim 1/\rho_{(110)}$ is much larger than $1/\rho_{(100)} \sim R$ there exists a simple geometric relation between the two length scales: Coarsening proceeds by elimination of finger-like domain configurations, two of which are indicated by arrows in Fig. 3b. Such fingers are always terminated by roof tops of length $\sqrt{2}R/(t)$ at either end. If such a finger disappears within a time interval $\Delta t$, the roof top density changes by $\Delta(1/D) = -2\sqrt{2}R/L^2$, where $L$ is some unit of length. In the same time the average density of pyramid edges changes by $\Delta(1/R) = -2D/L^2$. It follows that $D\Delta(1/D) = \sqrt{2}R\Delta(1/R)$ or $D(t)^{1/\sqrt{2}} \sim R(t)$. Using the result $D \sim t^{1/3}$ (see below) one finds $R \sim t^n$ with $n = 1/(3\sqrt{2}) \simeq 0.2357$, hardly distinguishable from $1/4$ in a numerical simulation.

During the temporal evolution of the surface morphology shown in Fig. 3a 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 effects like edge diffusion, the importance of which for growth morphologies has been emphasized by Bartelt and Evans [21] and was recently confirmed in an experiment [22]. It is possible to assign a “surface tension” $\sigma$ to domain walls by integrating over the domain wall profile,

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

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 $\sigma_{pe} = 4/[3\sqrt{2}(1 + b)]$ for pyramid edges and $\sigma_{rt} = 4/[3\sqrt{1 + b}]$ 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 Fig. 3b-e). The movement of domain walls necessarily involves the nucleation of roof tops, see Fig. 3a, c. Such a perturbation does not cost anything, if $\sqrt{2}\sigma_{rt} = \sigma_{pe}$, 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. This is convincingly confirmed by numerical solutions of Eq. (3) with a current (4) and $b = -3/4$. As seen in Fig. 3a the 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 for the elimination of roof tops is set by the time it takes to get from configuration a to configuration b. This is a simple diffusion process as the changes indicated in Fig. 3b do not change the lengths of the domain walls. This behaviour and the time dependence $\sim t^{1/3}$ suggest that an approach similar to the Lifshitz-Slyozov-Wagner theory[23] can be used here. Assuming that the magnitude of the slope is slightly less than the asymptotic value, i.e., $|m_{x,y}(r,t)| = m_0 - \epsilon_{x,y}(r,t)$ 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 $\langle \epsilon(t) \rangle$ should decrease as $t^{-1/3}$. This latter behaviour is not confirmed in numerical solutions of Eq. (3) for triangular symmetries or quadratic symmetries with $b = -3/4$[23]. This problem requires further investigation.

In the nondegenerate case with $b > -3/4$ the configurations b, c 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[2], the situation that the surface tensions obey the relation $\sqrt{2}\sigma_{rt} = \sigma_{pe}$ exactly is...
unlikely to be realized in nature. The fact that many experiments measured a coarsening exponent close to 1/4 instead indicates that typically the pyramid coarsening is enslaved to the dynamics of the roof tops in which case the theoretical value of the exponent is $1/(3\sqrt{2})$ as explained above. 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. [4]. Results of a numerical solutions of Eq. (3) are included in Fig. 3 (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 [24]. 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 [6] that the structure factor scales differently in directions perpendicular to the domain walls than in all other directions is still valid.

Most of the results derived in this article do not depend on the specific form of the surface current, e.g., the anisotropic tail of the structure factor [3] and the growth exponents follow from the constraints imposed by the crystalline anisotropies of the growing film, which in turn severely restrict the possible domain configurations. Only the results for $\sigma_{PE}$ and $\sigma_{T}$ are specific to the form of the surface current [4]. Because of the existence of several length scales and the fact that the correlation functions do not obey a simple scaling law, 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 [3], [7], this cannot be accomplished in real space, e.g., the height-height correlation function [4] in the (100) directions 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 $D$ becomes much larger than the pyramid size $R$ and $R \sim t^{1/(3\sqrt{2})}$ whereas $D \sim t^{1/3}$. 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 these kind of systems [24]. The measurement of the coarsening behaviour in these cases is severely complicated by a wide cross-over regime 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 $\eta \neq 0$ is 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. [25]. For deposition on (111) substrates noise is clearly irrelevant.

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