Wetting Layer Thickness and Early Evolution of Epitaxially Strained Thin Films

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We propose a physical model which explains the existence of finite thickness wetting layers in epitaxially strained films. The finite wetting layer is shown to be stable due to the variation of the nonlinear elastic free energy with film thickness. We show that anisotropic surface tension gives rise to a metastable enlarged wetting layer. The perturbation amplitude needed to destabilize this wetting layer decreases with increasing lattice mismatch. We observe the development of faceted islands in unstable films.

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Epitaxial deposition of a thin film onto a substrate in cases involving lattice mismatch is central in the fabrication of semiconductor and optoelectronic devices. The lattice mismatch between the substrate and the film generates strain in the deposited film, which can cause film instability unfavorable to uniform flat film growth. The strained film can relax either by the introduction of dislocations or by the formation of dislocation-free islands on the film surface via surface diffusion. Early film growth tends to occur via the second mechanism and we shall consider only dislocation-free films. It has been observed experimentally [1,2] that dislocation-free flat films of less than a certain thickness (the critical wetting layer) are stable to surface perturbations, while thicker films are unstable. The thickness of the wetting layer is substance dependent and decreases with increasing lattice mismatch strain [2], $\varepsilon = (a_s - a_f)/a_f$, where a_s and a_f are the substrate and film lattice constants. Above the critical wetting layer, 3D dislocation-free islands form. Prediction and control of wetting layer thickness and an understanding of early thin film evolution are important for the improved fabrication of semiconductor devices.

Despite considerable efforts (see, e.g., Refs. [3–8]), the physics of the critical wetting layer is poorly understood, and the purpose of this Letter is to study its properties by considering the following two important questions: First, why is there a critical, stable wetting layer and what controls its thickness? Second, since in most cases heteroepitaxial growth is done below the roughening transition, how does anisotropic surface tension affect the thickness of the critical wetting layer? Here we attempt to answer these questions and to study early film evolution without deposition. A later paper will look at the effects of deposition and long-term growth.

We studied an elastically isotropic system under plane strain [9], which causes the system to be effectively two dimensional. The surface of the solid is at $y = h(x,t)$ and the film is in the $y > 0$ region with the film-substrate interface at $y = 0$. The system is invariant in the z direction, and all quantities are calculated for a section of unit width in the z direction.

We assume that surface diffusion is the dominant mass transport mechanism, leading to the following evolution of the surface profile [10]:

$$\frac{\partial h(x,t)}{\partial t} = K \frac{\partial^2}{\partial x^2} \frac{\delta F}{\delta h(x,t)}, \tag{1}$$

where F is the free energy of the system and K is a positive constant. The free energy is composed of elastic and surface terms:

$$F = F_{\rm el} + \int dx\, \gamma \sqrt{1 + (\partial h/\partial x)^2}, \tag{2}$$

where γ is the surface tension and $F_{\rm el}$ is the elastic free energy, which also includes any elastic contributions to the surface tension. We express $F_{\rm el}$ as $F_{\rm el} = F_{\rm el}^{(0)} + \delta F_{\rm el}$, where $F_{\rm el}^{(0)}$ is the elastic free energy of the zero strain reference state, and $\delta F_{\rm el}$ is calculated from linear elasticity theory. For each value of x, the reference state corresponds locally to a *flat* film of thickness $h(x)$, i.e., $F_{\rm el}^{(0)} = \int dx \int_{-\infty}^{h(x)} dy f_v^{(0)}(h(x), y)$, where $f_v^{(0)}(h(x), y)$ is the elastic free energy per unit volume of a flat film of thickness $h(x)$.

Because of the lateral variations in this reference state, the reference stress does not satisfy the condition of mechanical equilibrium. However, the necessary corrections vanish in the limit $a/\lambda \rightarrow 0$, where a is the length scale over which stress varies in the y direction and λ is the lateral length of typical surface structures. This is because in this limit there are no lateral variations in the reference stress. Since typical experimental islands have $\lambda \sim 100$ nm, and a is of the order of the lattice constant (see below), the corrections to the reference stress are small and have been ignored.

For convenience we work in terms of the reference elastic free energy per unit length in the x direction, $f_{\rm el}^{(0)}(h(x)) \equiv \int_{-\infty}^{h(x)} dy f_v(h(x), y)$, instead of the free energy per unit volume. As discussed below, the dependence of $f_{\rm el}^{(0)}$ on h is a nonlinear phenomenon and cannot be calculated from linear elasticity theory.

For small strains, the stress is linear in the strain, i.e., $\sigma_{ij} = s_{ij}^m + c_{ijkl} e_{kl}$, where repeated indices are summed

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over. Here e_{ij} is the strain tensor, σ_{ij} is the total stress tensor, s_{ij}^m is the stress in the zero strain reference state due to the lattice mismatch, and c_{ijkl} are the elastic coefficients of the material. According to linear elasticity theory, $\delta F_{\rm el} = \int dx \int_{-\infty}^{h(x)} dy (s_{ij}^m e_{ij} + \frac{1}{2} c_{ijkl} e_{ij} e_{kl})$. In terms of the stress tensor, we find

$$F_{\rm el} = \int dx\, f_{\rm el}^{(0)} + \int dx \int_{-\infty}^{h(x)} dy \times \left(\frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} - \frac{1}{2} S_{ijkl} s_{ij}^m s_{kl}^m \right), \quad (3)$$

where we have used the inverted Hooke's law $e_{ij} = S_{ijkl} s_{kl}$. S_{ijkl} are the compliance coefficients of the material. By combining Eqs. (2) and (3), we arrive at an expression for $\delta F / \delta h$ at the surface:

$$\frac{\delta F}{\delta h} = \left(\tilde{\gamma} \kappa + \frac{d f_{\rm el}^{(0)}}{dh} + \frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} - \frac{1}{2} S_{ijkl} s_{ij}^m s_{kl}^m \right) \Omega , \quad (4)$$

where Ω is the atomic area of the solid, κ is the surface curvature, $\tilde{\gamma}(\theta) = \gamma(\theta) + \partial^2 \gamma / \partial \theta^2$ is the surface stiffness, and θ is the angle between the normal to the surface and the y direction. Since Eq. (4) gives $\delta F / \delta h$ at the solid surface, all variables in the equation are also given at the surface. Both $d f_{\rm el}^{(0)} / dh$ and s_{ij}^m must vanish when $h \le 0$, since then the film is absent. In principle, Eq. (4) should also contain derivatives of γ with respect to h. However, we believe that the variation of surface tension with h away from a step dependence is due to elastic effects. Since we included all elastic contributions in the zero-strain elastic free energy, we modeled γ as a step function, taking the value of the substrate surface tension for $h \le 0$ and the film surface tension for $h > 0$. Thus all partial derivatives of γ with respect to surface height vanish and were omitted from Eq. (4).

Equations (1) and (4) form a complete model of film evolution. In order to solve this model, one has to evaluate $\gamma(\theta)$, S_{ijkl}, $f_{\rm el}^{(0)}$, and s_{ij}^m. The first two are material properties, while the last two are properties of the reference state, from which one can also calculate the stress tensor σ_{ij} using linear elasticity theory. Before estimating these quantities we present the results of the linear stability analysis of an isotropic flat film of thickness C. The analysis was carried out using a method similar to those used in [11] for an infinite film. The height of the perturbed film takes the form $h(x,t) = C + \delta(t) \sin kx$. We assumed that the force on the surface due to surface tension is negligible compared to the force due to mismatch stress, and that the stress σ_{ij} vanishes deep in the substrate. Using linear elasticity theory and Eq. (4) with these assumptions, we calculated $\delta F / \delta h$ to first order in the perturbation, and combined the results with the general evolution equation (1) to obtain the following equation for the evolution of $\delta(t)$:

$$\frac{d\delta}{dt} = K \left[-k^4 \tilde{\gamma}_0 - k^2 \frac{d^2 f_{\rm el}^{(0)}}{dh^2} + 2k^3 \frac{\eta^2(h)}{M} \right]_{h=C} \delta , \quad (5)$$

where $\tilde{\gamma}_0 \equiv \tilde{\gamma}(\theta = 0)$, M is the plain strain modulus derived from the elastic constants of the isotropic material, and $\eta(h)$ is s_{xx}^m at the surface of a flat film of thickness h. s_{xy}^m vanishes because the flat film is hydrostatically strained, and $s_{yy}^m = 0$ since in the reference state the force on the surface in the y direction vanishes.

Equation (5) implies that the flat film is stable at all perturbation wavelengths as long as

$$\frac{[\eta(C)]^4}{M^2} \le \tilde{\gamma}_0 \left. \frac{d^2 f_{\rm el}^{(0)}}{dh^2} \right|_{h=C} , \quad (6)$$

and the equality holds at the critical wetting layer thickness. $\tilde{\gamma}_0$ is positive if $\theta = 0$ is a surface seen in the equilibrium free crystal [12]. At a perfect facet, $\tilde{\gamma}_0 \to \infty$. Hence, as $\theta = 0$ is a facet direction for most of the materials used in epitaxial films, $\tilde{\gamma}_0$ is large and positive. Therefore, a linearly stable wetting layer of finite thickness can exist only if $d^2 f_{\rm el}^{(0)} / dh^2 > 0$. Note that η depends linearly on the lattice mismatch ε, and hence the left-hand side of (6) is proportional to ε^4, while the right-hand side of (6) is proportional to ε^2 due to the dependence of $f_{\rm el}^{(0)}$ on lattice mismatch. Therefore, if $d^2 f_{\rm el}^{(0)} / dh^2 > 0$, the thickness of the wetting layer increases with decreasing lattice mismatch and diverges in the limit $\varepsilon \to 0$.

Having recognized the importance of the elastic free energy of the reference state, $f_{\rm el}^{(0)}$, and its dependence on film thickness, we now turn to estimating it. This free energy depends strongly on the mismatch stress s_{ij}^m, and its dependence on the y coordinate. As a result of the sharp interface between the substrate and the film, we expect s_{ij}^m to behave as a step function of y with small corrections due to elastic relaxation. If we ignore these small corrections, the resulting free energy $f_{\rm el}^{(0)}$ is proportional to film thickness, and its second derivative vanishes. Hence, according to Eq. (6), the thickness of the critical wetting layer vanishes. The correction due to elastic relaxation is therefore extremely important. It turns out that this correction vanishes within linear elasticity theory. This led some investigators [6] to claim that the variation in free energy over the interface was due to nonelastic effects, e.g., film/substrate material mixing over the interface. However, we claim that this is not necessary, since nonlinear elasticity can explain the corrections to the step-function form of the free energy.

Ideally, first principles, substance-specific calculations should be performed in order to evaluate $\eta(h)$ and $f_{\rm el}^{(0)}(h)$, and we intend to carry out such calculations in the future. However, the qualitative general behavior of $f_{\rm el}^{(0)}(h)$ can be obtained from much simpler models. To demonstrate this point we carried out the calculation for two-dimensional networks of balls and springs of varying lattice-type and

spring constants. In this model the balls are connected by springs which obey Hooke's law. The natural spring length had a step variation over the interface. The film underwent a hydrostatic transformation strain so that its lattice constant became that of the substrate. The network was then allowed to relax while being constrained in the x direction and free in the y direction, so that the system boundaries in the x direction were fixed to the natural substrate length.

We calculated the mismatch stress within the film and at the film surface for films of varying thickness. However, we decided to use the step function form of mismatch stress, $\eta(h > 0) = M\varepsilon$, where $M\varepsilon$ is the mismatch stress in an infinite film, as variations in η only slightly altered the wetting layer thickness predicted from (6). We also calculated the nonlinear elastic free energy of the relaxed system per unit length in the x direction for various film thicknesses. A typical behavior of $df_{\mathrm{el}}^{(0)}/dh$ is shown in Fig. 1, where it is seen that $f_{\mathrm{el}}^{(0)}(h)$ indeed depends on the thickness h. Moreover, the model predicts that $d^2 f_{\mathrm{el}}^{(0)}/dh^2 > 0$, and therefore, according to the inequality (6) and the discussion following it, there should be a linearly stable wetting layer, whose thickness is finite and increases with decreasing lattice mismatch.

The dependence of $f_{\mathrm{el}}^{(0)}$ on h arises within our model from the elastic relaxation at the surface and its coupling to the relaxation at the interface between the substrate and the film. A similar effect should occur in real systems due to surface reconstruction, for example.

Our calculations indicate that the general qualitative behavior of the mismatch stress and the elastic energy is not sensitive to the lattice structures and the values of the spring constants. While the detailed behavior close to the substrate-film interface [$\lesssim$3 ML (monolayers)] varied between different networks, it showed the same general

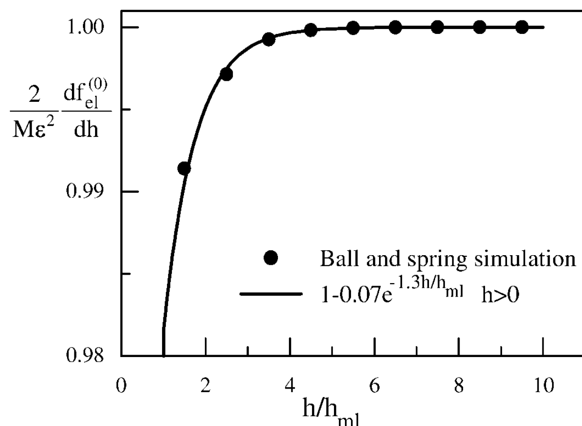

FIG. 1. Variation with film thickness of the elastic free energy of a relaxed ball and spring system, $df_{\mathrm{el}}^{(0)}/dh$, as a function of film thickness h. The free energy is normalized to the infinite film linear elastic energy density, $\frac{1}{2}M\varepsilon^2$. h_{ml} is the thickness of 1 ML.

behavior. In all systems $d^2 f_{\mathrm{el}}^{(0)}/dh^2$ showed exponential decay with a decay length of about a monolayer away from the interface. For the calculations used later in this paper we used the function $df_{\mathrm{el}}^{(0)}/dh = M\varepsilon^2[1 - 0.05\exp(-h/h_{\mathrm{ml}})]/2$ for $h > 0$ and $df_{\mathrm{el}}^{(0)}/dh = 0$ for $h \le 0$. h_{ml} is the thickness of 1 ML. The factor $M\varepsilon^2/2$ on the right-hand side ensures that the above expression becomes exact for a film of infinite thickness.

By combining this behavior of $df_{\mathrm{el}}^{(0)}/dh$ with the inequality (6), we obtained an expression for the linear stability wetting layer thickness h_c:

$$h_c/h_{\mathrm{ml}} = \max\{1, \ln[\tilde{\gamma}_0/(40M\varepsilon^2 h_{\mathrm{ml}})]\}. \quad (7)$$

Thus, the wetting layer thickness increases with decreasing lattice mismatch, as observed in experiments.

In previous works [5,6,8] on the physics of the wetting layer it was assumed that the reference state energy variation is a smooth function of h, mainly in order to avoid nonanalyticities at the interface. In contrast, our reference state energy variation behaves as a step function of the surface height with a small correction. We have shown that the nonanalytic behavior at the interface is realistic and that the smooth elastic energies in [5,6,8] are unphysical. Tersoff [3] in effect calculated $df_{\mathrm{el}}^{(0)}/dh$ via an effective atomic potential for Si/Ge under 4% lattice mismatch. However, he did not address the stability of the flat film to small perturbations. Nevertheless, since the function he obtained had $d^2 f_{\mathrm{el}}^{(0)}/dh^2 > 0$, a positive wetting layer thickness can be predicted from his results.

In order to model the early evolution of faceted islands, and to study the effect of an anisotropic form of surface tension on the wetting layer, we used the cusped form of surface tension given by Bonzel and Preuss [13], which shows faceting in a free crystal: $\gamma(\theta) = \gamma_0[1 + \beta|\sin(\pi\theta/(2\theta_0))|]$, where $\beta \approx 0.05$ and θ_0 is the angle of maximum γ. The value of γ_0 was taken as 1 J/m^2 in the substrate and about 75% of that in the film (as is the case for Si/Ge). This ensures a wetting layer of at least 1 ML. We considered a crystal which facets at 0°, ±45°, and ±90° with $\theta_0 = \pi/8$. The cusp gives rise to $\tilde{\gamma} = \infty$, and hence all faceted surfaces will have an infinite linearly stable wetting layer. However, a slight miscut of the low-index surface leads to a rounding of the cusp, which can be described by

$$\gamma(\theta) = \gamma_0\left[1 + \beta\sqrt{\sin^2\left(\frac{\pi}{2\theta_0}\theta\right) + G^{-2}}\right], \quad (8)$$

where, for example, $G = 500$ corresponds to a miscut angle, $\Delta\theta \approx 0.1°$.

According to Eq. (7), anisotropic surface tension greatly enlarges the linearly stable wetting layer thickness. Does this conclusion survive beyond linear stability analysis? When a linearly stable flat film is perturbed strongly so

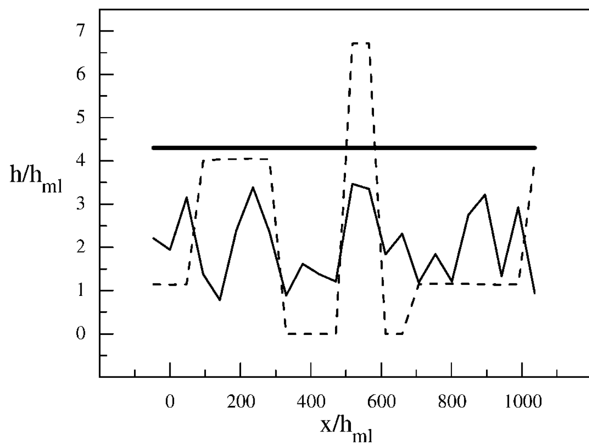

FIG. 2. Evolution of a randomly perturbed film, in which perturbations were larger than the critical perturbation amplitude. Lattice mismatch in this film is 4%. The initial film surface is shown as a thin solid line. The dashed line shows the film surface at a later time. The linear wetting layer thickness is shown as a thick solid line.

that the surface orientation in some regions is far from the $\theta = 0$ direction, the local surface stiffness in these regions is much smaller than the $\theta = 0$ stiffness. This tends to destabilize the linearly stable film. Indeed, we carried out Monte Carlo simulations which showed that films thinner than the linear wetting layer were unstable to random perturbations greater than a certain critical amplitude (see Fig. 2). The linear elastic energy was calculated by the method used by Spencer and Meiron [14]. Hence films thinner than the linear wetting layer thickness are *metastable*. When large perturbations were applied, faceted islands developed in the film, which underwent Ostwald ripening at later stages of the evolution.

The critical perturbation amplitude was found to be proportional to ε^{-2}. It was largely independent of film thickness for $h < h_c$ as long as perturbations did not penetrate the substrate, when it became much larger. It was also largely independent of cusp smoothness G, unlike the linear wetting layer thickness which depended strongly on G. The size of the critical perturbation amplitude in monolayers is plotted as a function of lattice mismatch in Fig. 3. The linear wetting layer thickness for $G = 500$, $M = 1.5 \times 10^{11}$ N/m^2, and $h_{\rm ml} = 5$ Å is also shown for comparison. When the lattice mismatch is small, the critical perturbation amplitude is much larger than a monolayer. Hence, in practice, flat films thinner than the linear critical thickness are stable at small lattice mismatch. On the other hand, for large mismatch a perturbation smaller than a monolayer is sufficient in order to destabilize the linearly stable wetting layer. Therefore, in practice, the wetting layer will be a single monolayer at large lattice mismatch. Our predictions cannot be compared with current experiments involving the wetting layer and lattice mismatch variation [2], since they were carried out with

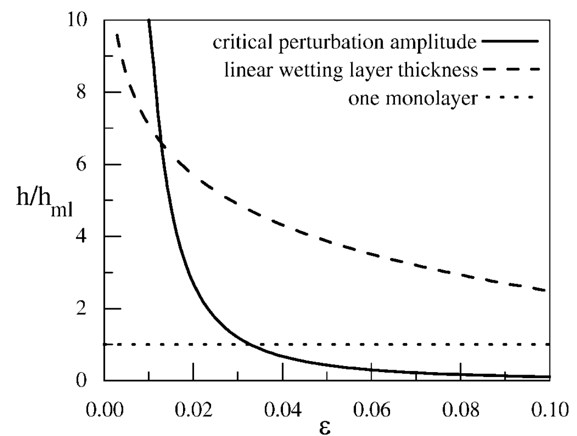

FIG. 3. Variation of critical perturbation amplitude with lattice mismatch.

deposition flux. We hope this work will encourage such experiments to be performed, and we are currently adding deposition to our model.

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