Morphological Instability in Epitaxially Strained Dislocation-Free Solid Films

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We perform the first analysis of the morphological instability of a growing epitaxially strained *dislocation-free* solid film. We derive an evolution equation for the film surface based on surface diffusion driven by a stress-dependent chemical potential. From the *time-dependent* linear stability problem we determine the conditions for which a growing film is unstable. Our results reveal that the critical film thickness for instability depends on the growth rate of the film itself, and that the instability we describe exhibits many of the observed features of the onset of the "island instability."

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It is well known that epitaxially deposited films grown layer by layer can undergo transitions to growth forms that have three-dimensional islands. Previously, it had been believed that this transition was due to the presence of elastic stress and stress-relieving interfacial dislocations. However, recent experimental work has shown that epitaxially strained thin films can undergo transitions to islandlike morphologies without the creation of misfit dislocations [1-5]. Two systems for which this transition from layer-by-layer to island growth have been observed are Ge/Si [1-3] and InGaAs/GaAs [4,5].

Motivated by these experimental results, we have developed the first theory describing the morphological development of a growing *dislocation-free* epitaxially strained planar thin film. Our work is a departure from earlier analyses in which the presence of dislocations is a prerequisite for instability [6,7]. Since the growth of a thin film is an inherently kinetic process, we feel that a dynamical description of the growth of the film as well as the development of interfacial instabilities is essential to make contact with experiment. Thus, the thermodynamic, or energy minimization, arguments that have been used previously to predict stability of films [6,8,9] have not been employed. Equally as important are the elastic states of both the film *and* the substrate; for this contrast, as we shall see, has a large influence on the development of nonplanar morphologies. Our theory incorporates the differences in lattice parameters and elastic constants between the film and the substrate and so is quite different from analyses of the stability of semi-infinite uniaxially stressed solids [10,11]. We rigorously couple the elastic state of the film to the chemical potential using the thermodynamics of elastically stressed solids [12-14], allowing for the development of a dynamic description of the morphological evolution of a growing film. In this Letter we shall develop a theory for the linear stability of both growing and static films. It may be the case that the instability we describe gives rise to island formation; future work on the nonlinear evolution of this instability will determine whether this is the case.

The model system is comprised of three phases: The solid substrate is semi-infinite and occupies $z<0$, the solid film is in the region $0<z<h(x,y,t)$, and the vapor lies in $z>h(x,y,t)$. We assume that the solid phases are single-component crystals that are free from defects such as dislocations or grain boundaries, but may contain substitutional vacancies. We assume that the interface between the film and the substrate is coherent, so that the film experiences a misfit strain due to differences in the lattice parameters of the film, a_f, and the substrate, a_s. We further assume that there is no lattice relaxation around vacancies and use isotropic linear elasticity to describe the deformations. Under the above assumptions the stress tensor is given by

$$\mathbf{T}=\lambda(\nabla\cdot\mathbf{u})\mathbf{I}+\mu[\nabla\mathbf{u}+(\nabla\mathbf{u})^T]+\eta(3\lambda+2\mu)\mathbf{I},$$

where λ and μ are the Lamé elastic constants, $\mathbf{u}$ is the displacement vector, $\mathbf{I}$ is the identity tensor, $\eta=(a_f-a_s)/a_s$ is the misfit strain in the film, and $\eta=0$ in the substrate.

We assume that the system is isothermal and take the solid phases to be in mechanical equilibrium, $\nabla\cdot\mathbf{T}=\mathbf{0}$. For simplicity, we take the pressure in the vapor to be zero. A balance of forces on the film/vapor interface then gives $\mathbf{n}\cdot\mathbf{T}=\mathbf{0}$ on $z=h(x,y,t)$, where $\mathbf{n}$ is the unit normal to the film surface. Continuity of displacements and forces at the coherent film-substrate boundary yields $\hat{\mathbf{z}}\cdot\mathbf{T}=\hat{\mathbf{z}}\cdot\mathbf{T}^S$ and $\mathbf{u}=\mathbf{u}^S$ on $z=0$, where $\hat{\mathbf{z}}$ is the unit vector in the z direction, and where $\mathbf{T}^S$ and $\mathbf{u}^S$ are the stress tensor and displacement vectors of the substrate, respectively. The equations for mechanical equilibrium along with the constitutive equations for stress yield the partial differential equations for the displacement field which are solved to determine the stress state of the film and the substrate.

We consider only the mass transport mechanism of surface diffusion along the film/vapor surface. The surface flux of atoms, $\mathbf{J}_S$, is taken to be proportional to the surface gradient of the diffusion potential [14-16],

$$\mathbf{J}_S=-\frac{D_S\nu}{kT}\nabla_S M_{1v}\quad\text{on } z=h(x,y,t),$$

where D_s is the surface diffusivity of atoms, v is the surface density of lattice sites, k is the Boltzmann constant, T is the absolute temperature, and $\boldsymbol{\nabla}_S M_{1v}$ is the surface gradient of the diffusion potential. Using the thermodynamics of stressed solids [12–14] with a reference state for the film of zero strain, and under the additional assumptions of isotropic surface energy, zero surface stress, and an ideal solution of vacancies, the gradient of the diffusion potential on the film/vapor surface can be written as

$$\boldsymbol{\nabla}_S M_{1v} = \Omega \boldsymbol{\nabla}_S (\sigma' \kappa' + \mathcal{E}) \text{ on } z = h(x,y,t)\,,$$

where Ω is the volume of a lattice site and σ' is the surface energy of the film in the reference state. The quantity $\kappa' = \boldsymbol{\nabla}'_S \cdot \mathbf{n}'$ is the curvature of the surface in the reference state which can be written in terms of the actual interface position, h, and the displacements at the surface [17]. The quantity $\mathcal{E} = \frac{1}{2} \mathsf{T} \cdot \mathsf{S} \cdot \mathsf{T}$ is the strain energy density of the film at the surface, where S is the isotropic elastic compliance tensor.

The motion of an interface $\mathbf{r} = [x, y, h(x,y,t)]$ in the presence of a volume flux of atoms $\mathbf{V}$ from above is given by the accumulation of atoms due to surface diffusion [16] and the aggregation of atoms incident upon the surface:

$$\frac{\partial \mathbf{r}}{\partial t} = -\Omega (\boldsymbol{\nabla}_S \cdot \mathbf{J}_S)\mathbf{n} + (\mathbf{V} \cdot \mathbf{n})\mathbf{n}\,. \tag{1}$$

After Mullins [16], the z component of Eq. (1) gives the general nonlinear surface evolution equation,

$$\frac{\partial h}{\partial t} = \frac{\mathcal{D}}{(1 + h_x^2 + h_y^2)^{1/2}} \nabla_S^2 (\sigma' \kappa' + \mathcal{E}) + \frac{V}{1 + h_x^2 + h_y^2}\,, \tag{2}$$

where $\mathcal{D} = D_S v \Omega^2 / kT$, V is the z component of $\mathbf{V}$, and subscripts on h imply partial derivatives with respect to the subscripted variables. Equation (2) is reminiscent of the evolution equation of Srolovitz [10] who analyzed the stability of a uniaxially stressed semi-infinite solid. However, it differs because the $\mathcal{E}$ term accounts for the presence of a film with a different elastic state than the substrate. Further, Eq. (2) includes the effect of film growth, and the curvature term κ' is given in a thermodynamically rigorous form and thus includes the (minor) corrections from the displacement field in going from actual to reference states.

We now examine the morphological instability of a two-dimensional film for the case of (i) a static film of thickness h_0 and (ii) a film growing at speed V. Both cases are considered simultaneously by taking the basic-state film thickness to be $\bar{h} = h_0 + Vt$. The basic-state displacement fields correspond to uniform relaxation strain in the film in the z direction: $\bar{u}_3 = Ez$, $\bar{u}_1 = \bar{u}_2 = 0$, and $\bar{u}_i^S = 0$, for $i = 1$–3, where $E = \eta(3\lambda + 2\mu)/(\lambda + 2\mu)$, and where the subscripts denote the Cartesian components of the displacement vectors. We perturb the basic-state solution, substitute into the governing equations, linearize in the disturbance quantities, and use normal modes proportional to $\exp(ia_x x + ia_y y)$. The solutions to the resulting differential equations for the displacement fields can be substituted into Eq. (2) to obtain an ordinary differential equation for the normal-mode amplitude $\tilde{h}(t)$ of the perturbation to the planar surface:

$$\frac{d\tilde{h}}{dt} = \sigma[a, \bar{h}(t), \ldots]\tilde{h}(t)\,, \tag{3}$$

where

$$\sigma = \mathcal{D}\{a^3 \mathcal{E}_0 F(a\bar{h}) - a^4 \sigma' [1 - \kappa_0 G(a\bar{h})]\}\,, \tag{4}$$

$$\kappa_0 = \frac{\eta(3\lambda + 2\mu)}{\lambda + \mu}, \quad \mathcal{E}_0 = \frac{2\eta^2 \mu (3\lambda + 2\mu)^2}{(\lambda + \mu)(\lambda + 2\mu)}\,,$$

$$F(x) = \frac{b_1 + x b_2 + b_3 \sinh x \cosh x + 2b_1 \sinh^2 x}{b_4 + x^2 b_2 + 2b_1 \sinh x \cosh x + b_3 \sinh^2 x}\,,$$

$$G(x) = \frac{b_5 + 2b_1 \sinh x \cosh x + b_3 \sinh^2 x}{b_4 + x^2 b_2 + 2b_1 \sinh x \cosh x + b_3 \sinh^2 x}\,,$$

$$b_1 = \rho(\Lambda + 2)(\Lambda^S + 2)\,,$$

$$b_2 = (\Lambda + 1)[(\Lambda^S + 1) + 2\rho - \rho^2(\Lambda^S + 3)]\,,$$

$$b_3 = (\Lambda^S + 1)(\Lambda + 3) + 2\rho + \rho^2(\Lambda^S + 3)(\Lambda + 1)\,,$$

$$b_4 = (\Lambda + 2)^2(\Lambda^S + 1)/(\Lambda + 1)\,,$$

$$b_5 = (\Lambda + 2)[\rho + (\Lambda^S + 1)]\,,$$

and where $a = (a_x^2 + a_y^2)^{1/2}$, $\rho = \mu/\mu^S$, $\Lambda = \lambda/\mu$, and $\Lambda^S = \lambda^S/\mu^S$. The linear stability results also have important length and time scales given by $l \equiv \sigma'/\mathcal{E}_0$ and $\tau \equiv l^4/\mathcal{D}\sigma'$, respectively.

Equation (3) can be solved using normal modes in time when the basic state is static ($V = 0$). In this case, the normal-mode amplitude is given by

$$\tilde{h}(t) = \tilde{h}_0 e^{\sigma t}\,,$$

and the growth rate σ is identically given by (4) with $\bar{h} = h_0$. One can plot the growth rate σ versus the disturbance wave number a for fixed film thickness h_0. The curve intersects the origin at zero slope, rises to a positive maximum with increasing wave number, and then decreases monotonically, crossing the $\sigma = 0$ axis at a_c. Modes with wave numbers smaller than a_c grow; those having larger wave numbers decay. For thin enough films the instability is thus characterized by long waves since $a_c \bar{h} \ll 1$. A long-wave instability is consistent with observations of film instability involving perturbations with wavelengths much longer than the thickness of the film [2].

The cutoff wave number a_c is a function of the static-film thickness h_0, as shown in Fig. 1 for different values of film stiffness $\rho = \mu/\mu^S$. When $\rho \neq 0$, the static film is absolutely unstable for all film thicknesses. When the substrate and the film have identical elastic constants ($\rho = 1$), perturbations cannot distinguish the substrate/film

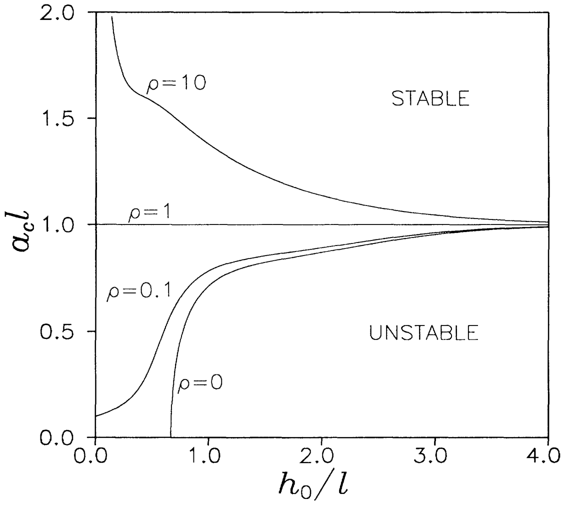

FIG. 1. Linear stability results for a static film (no deposition) for different film stiffnesses ρ. A film of a given thickness h_0 is unstable to perturbations with wave number less than a_c. The length scale l is defined below Eq. (4). The stiffness of the film ρ is given by the ratio of shear moduli for the film and substrate. The Poisson ratios for both the film and the substrate are taken to be $\frac{1}{3}$ ($\Lambda=\Lambda^S=2$). For $\rho=0$ (rigid substrate) there exists a critical film thickness below which the film is stable.

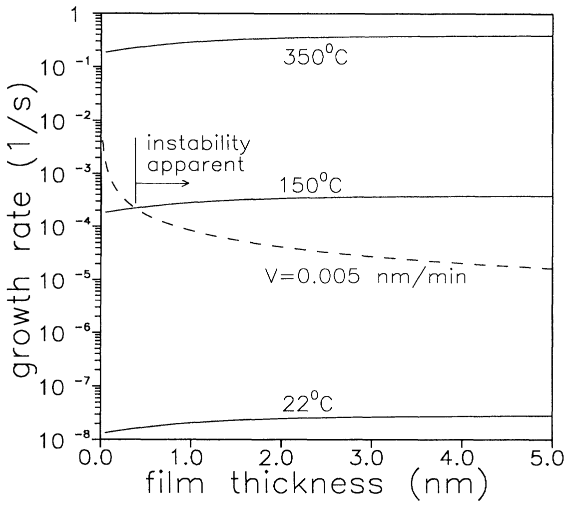

FIG. 2. Linear stability results for a growing film (Ge on Si substrate). Solid curves correspond to the maximum perturbation growth rate at different temperatures. The dashed curve represents the effective growth rate of the planar film, $V/\bar{h}$. Perturbations grow relative to the film when the perturbation growth rate (solid curves) is larger than $V/\bar{h}$ (dashed curve). The material parameters [21] used are (in cgs units) $\eta=0.0418$, $\sigma'=1927$, $D_S=8.45\times10^{-6}\exp[(-0.83\ \mathrm{eV})/kT]$, $\mu=0.568\times10^{12}$, $\lambda=0.371\times10^{12}$, $\mu^S=0.682\times10^{12}$, $\lambda^S=0.525\times10^{12}$, $\nu=1.5\times10^{15}$, and $\Omega=1.7\times10^{-23}$.

interface; hence the stability results are independent of the film thickness and correspond to those of an infinitely thick film. Thus, in this limit of identical elastic constants we can recover the stability results for an elastically stressed semi-infinite solid [10] if we (1) neglect the correction to the curvature in going from the actual state to the reference state, and (2) assume a particular form for the unspecified elastic constant [10], $M=4\mu(\lambda+\mu)/(\lambda+2\mu)$.

Figure 1 also shows that, when $\rho<1$, the range of unstable wave numbers is smaller than that for $\rho=1$, reflecting the stabilizing effect that a stiffer substrate has on the film. This stabilizing influence is consistent with the observation that deformation of the substrate plays a role in the formation of coherent, dislocation-free islands [1,5]. For the case of a perfectly rigid substrate, $\rho=0$, instability is predicted only for film thicknesses exceeding a critical value [18] h_c given by

$$h_c=l\frac{(\lambda+2\mu)(1-E)}{2(\lambda+\mu)}\,. \tag{5}$$

This critical thickness gives the onset of morphological instability for a static film *without dislocation generation* and is not to be confused with the thickness for the onset of dislocations [19,20], although it is of the same order of magnitude in most cases.

For a growing film, $V\neq0$, the basic state varies with time and thus normal modes in time cannot be used to solve (3). However, (3) can be integrated directly to give the time evolution of the perturbation amplitude:

$$\tilde{h}(t)=\tilde{h}_0\exp\left[\int_0^t\sigma(s)ds\right]. \tag{6}$$

For a time-dependent basic state there is also no single way to measure stability as with the normal-mode growth rate of the static problem. We define the *relative growth rate* Σ as the growth rate of perturbations *relative* to the growing basic state:

$$\Sigma=\left[\frac{\tilde{h}}{\bar{h}}\right]^{-1}\frac{d}{dt}\left[\frac{\tilde{h}}{\bar{h}}\right]=\sigma-\frac{V}{\bar{h}(t)}\,. \tag{7}$$

Thus, a perturbation growing more slowly than the basic state has $\Sigma<0$ and the amplitude of the perturbation shrinks relative to the film thickness.

Figure 2 shows the stability results for a growing film. The growth rates of the perturbations are very sensitive to temperature, as can be expected from the exponential character of the surface diffusion coefficient (the growth rate is also very sensitive to the misfit scaling like η^8). When the basic state is growing faster than the perturbations, perturbations appear to shrink relative to the film. Thus, at 150 °C we predict that films become unstable at a thickness of about 0.4 nm. At 350 °C the growth rate of the perturbations exceeds that of the basic state even at very small film thicknesses, predicting that the film becomes unstable almost immediately. Experimentally [3], the transition from layer-by-layer to island growth at

350 °C and $V = 0.005$ nm/min occurs at 3 monolayers (ML) (0.4 nm) for these growth conditions. The discrepancy between theory and experiment may be due to the omission in our model of inherently thin-film effects such as the molecular interaction of the film with the substrate (bonding) and/or anisotropic elasticity. Tersoff [9] has shown in a molecular-bond-energy calculation for the static film that a molecular interaction with the substrate can stabilize the film for thicknesses up to 3 ML (0.4 nm). Including such effects in this model might give the observed critical thickness. In effect, the film would become unstable when the film thickness exceeds the interaction range of the substrate. At 22 °C the basic-state growth rate is larger than the growth rate of the perturbations, even for very thick films. This is consistent with the experiments of Asai, Ueba, and Tatsuyama [3] who observe that at room temperature (and at a slightly lower growth speed of 0.001 nm/min) films grow layer by layer up to *at least* 6 ML (0.8 nm). The instability is postponed to greater thicknesses at lower temperatures because of the "kinetic stabilization" of the growing film.

These results suggest experiments to determine whether there is a correspondence between the temperature and deposition-rate dependence of the critical thickness for instability, as given by our theory, and the critical film thickness for the formation of islands. Good agreement might be expected when substrate interactions are not important.

We have analyzed the morphological stability of a growing, epitaxially strained dislocation-free solid film. From the time-dependent linear stability analysis we have determined the conditions for which the instability will occur. We find that (1) the wavelength of the instability is long compared to the film thickness, (2) the instability is driven by the lattice mismatch, (3) substrate stiffness is stabilizing, (4) lower temperatures suppress the instability, and (5) the growing film has an *apparent* critical thickness due to a kinetic stabilization. The instability that we describe has many features in common with the island instability and may describe the onset of island formation.

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