Morphological Stability of Alloy Thin Films

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Misfit stresses are known to produce a morphological instability in dislocation-free thin films. We examine the linear stability of a planar, alloy thin film, growing by a deposition flux from the vapor. The stability of the film surface is influenced by stresses generated by both compositional inhomogeneity and lattice mismatch between the film and substrate. Under certain conditions, tensile misfit strain can completely stabilize the growing film, whereas the same magnitude of compressive strain is destabilizing. We compare our results with previous theoretical and experimental work.

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For many years, it was thought that the only mechanism for strain relaxation in lattice-mismatched thin films was the development of dislocations along the substrate-film interface [1]. An alternate mechanism for elastic strain relief in heteroepitaxial films has been demonstrated, both theoretically [2–7] and experimentally [7–12]. In this case, the elastic stress induces the surface of the film to undergo a morphological instability, which can lead to the formation of islands [7,9,10], nonplanar surfaces [8,11,12], or, in some cases, the formation of deep, cusplike morphologies [12–15]. Such morphologies can provide sources for stress-relieving dislocations.

These theories for the destabilization of a planar, stationary interface all predict that, in the absence of substrate-film molecular interactions and gravity [3,6], a planar thin film is always unstable to the development of nonplanar morphologies. The wavelength of the instability with zero growth rate λ_c is set by the competition between the stabilizing influence of surface energy and the destabilizing influence of misfit-induced elastic strain energy. This wavelength is independent of the sign of the misfit ϵ between the film and substrate $\lambda_c \sim \epsilon^{-2}$.

Growing thin films, however, are not necessarily unstable. Both Spencer, Voorhees, and Davis [5] and Snyder, Mansfield, and Orr [7] have suggested that the growing planar surface can be kinetically stabilized, if the growth rate of the film exceeds the growth rate of the instability. A sufficiently thick film, however, will always exhibit a surface instability. Tersoff and LeGoues [16] have shown that a sufficiently anisotropic surface energy can provide an energy barrier to the formation of surface perturbations, resulting in a linearly stable surface.

Previous theoretical work has treated the film as a single component material; in contrast, much of the experimental literature describes multicomponent films. Here, we examine the conditions governing the stress driven instability in growing, alloy thin films. For our purposes, alloy films differ from single component films in one important fashion: The lattice parameter of the film can be a function of the composition of the film. While this property is routinely used to adjust the misfit between the film and the substrate, and to tailor materials properties such as the band gap, we show that this dependence can have profound effects on the nature of this stress driven instability. In particular, this composition-dependent lattice parameter can stabilize a planar thin film, of any thickness, against this stress driven instability, and leads to a dependence of the morphological evolution of the film on the sign of the misfit. These results hold even for films with isotropic surface energy.

We take the film f to be semi-infinite and in contact with a semi-infinite vapor phase v along the surface Σ. We assume that local equilibrium exists between the film and vapor; thus we limit our discussion to small film growth rates. The system is composed of two species, A and B, which are substitutional in f. The morphology is allowed to evolve by surface diffusion, with an intrinsic diffusivity D^{Σ}, as well as an accretive flux $\mathbf{Q}$ from v.

Stress in the film can result from both misfit strain and variations in the film composition. Composition variations, which can accompany the development of nonplanar surfaces, generate stress because the lattice parameter varies with composition. The magnitude of this effect, for a cubic lattice, is related to the solute expansion coefficient, $\eta = (\partial a^f / \partial C^f)/a^f$ [17], where C is the mole fraction of component A and a^f is the lattice parameter of the film. To isolate the composition dependence of the lattice parameter, we define the misfit as $\epsilon = (\bar{a}^f - a^s)/a^s$, where $\bar{a}^f$ is the lattice parameter of the film in the unperturbed state and a^s is the lattice parameter of the substrate. Throughout this paper, we denote the basic or planar state value of a quantity ξ by $\bar{\xi}$, and the difference between the perturbed and basic state values by $\tilde{\xi} = \xi - \bar{\xi}$.

The motion of the interface, due to surface diffusion and a deposition flux normal to the planar surface Q_n, is determined by mass balance at Σ. We assume, as is typical in molecular beam epitaxy [18], that the composition of Q_n equals the average deposited film composition $\bar{C}^f$, which can differ from the local-equilibrium vapor concentration C^v. Using the procedure outlined previously

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[19–21], the normal velocity of the film is given by

$$\rho_0(C^v - C^f)\mathbf{v}^\Sigma \cdot \mathbf{n} = \boldsymbol{\nabla}_\Sigma \cdot \mathbf{J}^\Sigma + (\bar{C}^f - C^v)Q_n\,, \qquad (1)$$

in which $\boldsymbol{\nabla}_\Sigma$ is the surface gradient, $\mathbf{n}$ is the unit normal to Σ, pointing from f into v, ρ_0 is the molar density of lattice sites in the film, and all densities and concentrations are evaluated at the interface. The flux of component A on Σ is given by $\mathbf{J}^\Sigma = -(\Gamma_0 D^\Sigma / G_m'')\nabla_\Sigma M_{AB}$ [22,23], where Γ_0 is the surface density of lattice sites on Σ, G_m is the molar Gibbs free energy of the film phase, $G_m'' = (\partial^2 G_m/\partial C^{f2})_{C^f=\bar{C}^f}$, and M_{AB} is the diffusion or chemical potential at the surface.

We assume that the system is isotropic and that the elastic compliances are independent of composition. We further assume that the vapor pressure is uniform and negligible, in comparison with the stresses on the film. From the thermodynamics of stressed solids [17,24], we obtain the Gibbs-Thomson relation

$$\tilde{C}^f = -\frac{V_0(\kappa\bar{\gamma} + \tilde{\mathcal{E}} - \Delta\bar{C}\eta\tilde{T}_{kk})}{G_m''(\Delta\bar{C} + \psi)} \qquad (2)$$

on Σ and the surface gradient of the diffusion potential

$$\boldsymbol{\nabla}_\Sigma M_{AB} = \frac{V_0}{\Delta\bar{C} + \psi}\boldsymbol{\nabla}_\Sigma(\kappa\bar{\gamma} + \tilde{\mathcal{E}} + \psi\eta\tilde{T}_{kk})\,, \qquad (3)$$

where κ is the mean curvature of Σ, $\bar{\gamma}$ is the surface energy of Σ, $\tilde{\mathcal{E}}$ is the elastic strain energy density, $\Delta\bar{C} = \bar{C}^v - \bar{C}^f$, $\tilde{T}_{kk}$ is the trace of the stress, $\psi = V_0\eta\bar{T}_{kk}/G_m''$, and V_0 is the molar volume of f. Equation (3) is similar to the result obtained by Spencer, Voorhees, and Davis [5] for an ideal solution of vacancies. In contrast with the usual Gibbs-Thompson equation, (2) is not an explicit expression for the composition at the interface, since the stress is a function of the composition at the interface as well; thus the composition and elastic fields are coupled. Finally, Eq. (3) shows that the presence of composition generated stresses alters the value of the diffusion potential from that used previously [2–7], by the presence of the term involving $\eta\tilde{T}_{kk}$.

The stress state of the film is found by requiring mechanical equilibrium in the infinitesimal strain approximation. The constitutive law relating stress and strain for the isotropic film, subjected to biaxial misfit strain and compositional strain $\eta\tilde{C}^f$, is $\mathsf{T} = \mathsf{C}[\mathsf{E} - (\epsilon + \eta\tilde{C}^f)1]$, where T, C, and E are the elastic stress, stiffness, and strain tensors, respectively, and 1 is the unit tensor. We impose a force balance at the film surface $\mathsf{T}\mathbf{n} = \mathbf{0}$ and require that perturbations in the strain field decay to zero far from the surface.

The composition field in the film, assuming that the diffusivity within the film is zero, satisfies $\partial_t C^f = \mathbf{V} \cdot \nabla C^f$ in a reference frame moving at the velocity $\mathbf{V}$ of the planar interface. The composition perturbation must satisfy Eq. (2) at the surface and decay to zero far from the film-vapor interface. In the limit of a planar surface, the mass balance condition (1) implies that the growth rate of the interface and the deposition flux are related by $V = -Q_n/\rho_0$, since $C^f = \bar{C}^f$.

The basic, or unperturbed, state consists of a compositionally uniform, biaxially stressed film of composition $\bar{C}^f$, with a planar interface, moving at a speed V. Since the film is uniform in composition, there are no compositionally generated stresses (see the definitions of compositionally generated strain and misfit, given above).

The perturbed interface, however, will not have a constant composition [see Eq. (2)]; thus compositionally generated stresses will accompany the development of nonplanar interfacial morphologies. The stability of the interface is determined by linearizing all quantities about the planar state. These linearized equations for the perturbed interface admit usual normal mode solutions of the form $\phi = \exp(\sigma t + i\mathbf{a} \cdot \mathbf{x})$, where the wave numbers a_x and a_y are in the plane of the film and the growth rate of the perturbation is given by σ. If $\mathrm{Re}(\sigma) < 0$, the system is stable, if $\mathrm{Re}(\sigma) > 0$, the system is unstable, and, if $\mathrm{Im}(\sigma) \neq 0$, an oscillatory instability is present.

Solving for the elastic field, and using the result in the Gibbs-Thompson equation, allows us to determine the stress field and composition in the film at all points along the perturbed interface. The value of the diffusion potential is therefore known and Eq. (1) can be used to derive the following dispersion relation for σ [25]:

$$\begin{aligned}\sigma^2 - \sigma(a^3(e^{\star 2} - a) - a\mathcal{V}[1 - \mathcal{N}(\{\epsilon^\star + \eta^\star\}^2 - a)])& \\ -a\mathcal{V}\{a^3(e^{\star 2} - a + \mathcal{N}a\eta^{\star 2})& \\ +a\mathcal{V}\mathcal{N}(\epsilon^{\star 2} + \epsilon^\star\eta^\star - a)\} = 0\,.& \qquad (4)\end{aligned}$$

We have scaled all quantities with the dimensions of length by a characteristic length $\ell = \bar{\gamma}/\chi_0$ and all quantities with the dimensions of time by $\tau = \ell^3/V_0\Gamma_0 D^\Sigma$. The dimensionless magnitude of the wave number is a, $\chi_0 = G_m''\Delta\bar{C}^2/V_0$, the dimensionless growth rate is $\mathcal{V} = V\tau/l$, $\epsilon^\star = [2(1 + \nu)Y/\chi_0]^{1/2}\epsilon$, $\eta^\star = [2(1 + \nu)Y/\chi_0]^{1/2}\eta\Delta\bar{C}$, $Y = E/(1 - \nu)$, E is Young's modulus, and $\mathcal{N} = (1 + \nu)/(1 + \nu + \eta^{\star 2})$. Hence, the conditions for stability depend on the three parameters $\epsilon^\star$, $\eta^\star$, and $\mathcal{V}$. We do not consider variations in Poisson's ratio ν, as it generally ranges between 1/5 and 1/3 for the materials of interest. We take $\nu = 1/4$ throughout.

When $\eta^\star = 0$, such that there are no compositionally generated stresses, the solutions to Eq. (4) are $\sigma = (\epsilon^{\star 2} - a)(a^3 + a\mathcal{V})$ and $\sigma = -a\mathcal{V}$; only the first can produce unstable modes. When there is no deposition, $\mathcal{V} = 0$ and we recover the results of Asaro and Tiller [2]. The elastic stress, represented by $\epsilon^\star$, is destabilizing and the surface energy, which gives rise to the $-a$ term, is stabilizing. If the film is growing, however, $\mathcal{V} \neq 0$ and both the wave number dependence and amplification rate of the instability are altered from the Asaro and Tiller predictions. In the limit of very small surface diffusivity, $\mathcal{V} \gg 1$, the instability evolves as a result of the deposition process itself. This is possible because the composition of the beam is uniform and fixed, whereas the composition of the film varies with position, as a result of the nonplanar surface. Thus, in this limit, the growth rate of the perturbations should scale as the amplitude of $\tilde{C}^f$, evaluated on Σ. The consequences of this scaling are easiest to see in the limit $\epsilon^\star = 0$, when $\tilde{C}^f(\Sigma) \sim -a^2\phi$ [see Eq. (2) in the small slope limit]; therefore $\sigma \sim -a^2\mathcal{V}$, as given above. While the mechanism is different, a similar wave number dependence for the growth of the instability is possible for an evaporation/condensation mass transport process [4,22].

Figure 1 shows neutral stability curves for $\eta \neq 0$. In all cases, $\sigma < 0$ for large wave numbers, due to the stabilizing influence of interfacial energy. For $\epsilon^\star > 0$, regardless of the magnitude of either $\eta^\star$ or the growth velocity, the long-wave elastic-stress-driven instability is still present. Furthermore, $\eta^\star$ tends to be destabilizing, as the band of unstable wavelengths increases with $\eta^\star$. In contrast, for $\epsilon^\star < 0$, the presence of compositionally generated stresses acts to stabilize very long wavelength perturbations near $a = 0$ (see $\mathcal{V} = 10^{-2}$ in Fig. 1). As the velocity increases, this effect becomes more important and eventually stabilizes the growing film. This suggests that sufficiently rapid deposition on appropriate substrates will enable the growth of planar alloy films. This window of stability increases in size as $\mathcal{V}$ increases. Above the upper limit of $\eta^\star$ at which the system is stable when $\epsilon^\star < 0$, the instability returns. The compositionally generated stresses, however, still tend to stabilize the surface, giving rise to a smaller band of unstable wavelengths with lower perturbation growth rates than for positive $\epsilon^\star$ of identical magnitude.

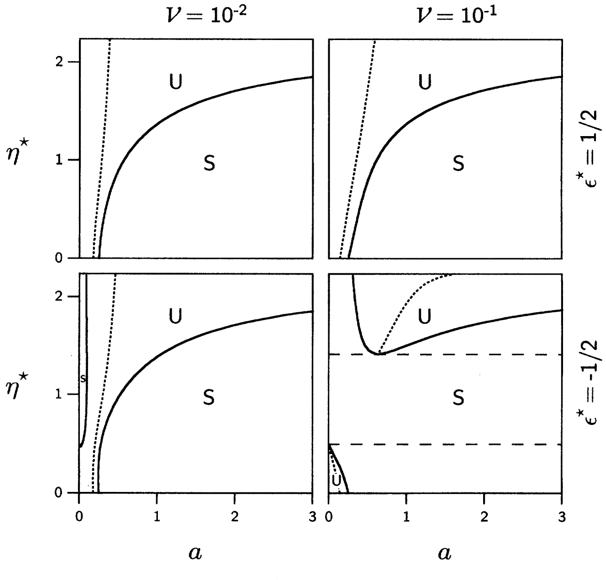

FIG. 1. Regions of stable (S) and unstable (U) wave numbers a, for different compositional strains $\eta^\star$ and growth rates $\mathcal{V}$. Misfit is compressive in the upper pair of plots and tensile in the lower pair. The solid line denotes $\sigma = 0$. The dotted line denotes the wave number that maximizes the growth rate σ. The region between dashed lines is stable for all a.

Stress induced by a nonuniform composition field stabilizes a growing thin film by changing the concentration of the film relative to that of the beam. To illustrate, we choose a system in which $\bar{C}^v \approx 0$ and $\eta > 0$, such that $\eta^\star < 0$. Therefore an increase in concentration dilates the lattice; i.e., the solute atoms are larger than the host lattice atoms. When $\epsilon^\star < 0$, the lattice parameter of the flat, coherent film is larger than its stress-free value. Thus the lattice parameter of the film at a protuberance on the interface will be smaller than that of the planar, coherent film. This smaller lattice parameter makes it more difficult to insert the larger solute atoms into the lattice than at a planar interface, causing the concentration at the interfacial bump to decrease. As the concentration of the beam is unchanged, this decrease in concentration allows the bump to grow faster than the planar interface, which destabilizes the system. In contrast, if $\epsilon^\star > 0$, the lattice at a bump will expand and the solute concentration will increase. Since the concentration of the beam is fixed, this increase in concentration is stabilizing.

The wavelength of the instability that maximizes the growth rate is strongly influenced by compositionally generated stresses. Asaro and Tiller found that $a_m = (3/4)a_c$, where a_c is the wave number at which $\sigma = 0$ and a_m is the wave number with the maximum growth rate. In our analysis, this relationship does not hold, even at $\eta^\star = 0$, due to the influence of the deposition process. For $\eta^\star \neq 0$, a_m increases with increasing $\eta^\star$ and $\mathcal{V}$. Thus, the wavelength of the instability that is observed experimentally can depend on the deposition rate.

As the dispersion relation (4) is quadratic, an oscillatory instability is possible. For relatively large values of $\eta^\star$ and $\mathcal{V}$, within the band of linearly unstable wave numbers, both unstable steady and oscillatory instabilities can be present. The presence of an oscillatory instability is a result of the composition of the film surface being out of phase with the surface perturbation, due to the nonlocal effects of stress [26]. This causes more material to deposit on one side of a bump than the other and makes perturbations travel laterally across the surface. As the onset of the instability is not oscillatory, however, only a nonlinear analysis will determine whether steady or oscillatory modes will be observed experimentally.

The predictions of our theory are summarized on a stability map, shown in Fig. 2, indicating the regions in which a growing thin film will be stable or unstable, for any wave number perturbation. The system is stable when $\epsilon^\star = 0$ and it is unstable when $\eta^\star = 0$ and $\epsilon^\star \neq 0$.

Most experiments have been performed in the region in which the film is predicted to be unstable, $\varepsilon^\star > 0$, $\eta^\star > 0$. Two experiments, however, indicate that the system may be stable when $\epsilon^\star$ and $\eta^\star$ are of different signs. Xie *et al.* [27] deposited $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ films on SiGe(001) substrates of different compositions. They showed a

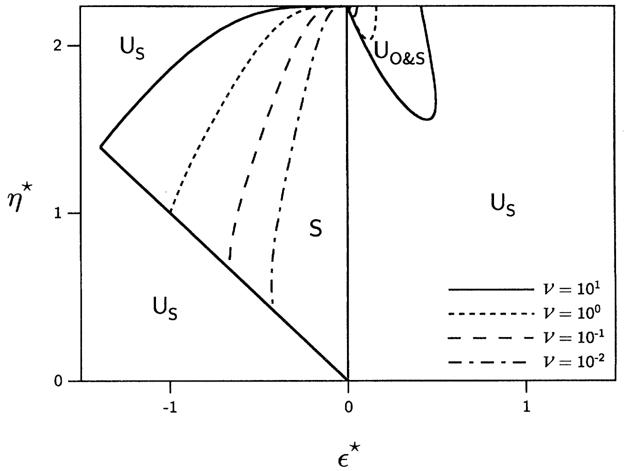

FIG. 2. Stability map, as a function of misfit $\epsilon^\star$, compositional strain $\eta^\star$, and deposition rate $\mathcal{V}$, where S, U_S, and $U_{O\&S}$, denote regions of stability, instability, and combined oscillatory and steady instability, respectively. The map is antisymmetric about $\epsilon^\star = \eta^\star = 0$, such that $(\epsilon^\star, \eta^\star)$ maps to $(-\epsilon^\star, -\eta^\star)$. For most systems, $\eta^\star > 0$.

strong stabilization of films under tension ($\epsilon^\star < 0$). Based on molecular dynamics simulations, they have ascribed this phenomenon to changes in step-edge energies. Thus, in Si-Ge, both the variation in the surface energy with strain and compositionally generated stresses act to stabilize a planar film. Ponchet *et al.* [28] deposited a multilayer structure of GaInP and InAsP on InP(001). The first, tensile layer of the superlattice structure was stable, whereas the second layer, with $\epsilon^\star > 0$, was unstable. Weatherly [29] has observed a similar dependence of thin film stability on the sign of the misfit in quaternary III-V alloys.

We have demonstrated that stresses generated by a nonuniform composition field can have a profound effect on the nature of the stress driven instability in thin films. Such stresses can stabilize a system against the instability, induce oscillatory modes, alter the wave number at which the instability develops, and result in an instability which is controlled by the sign of the misfit. These effects are intimately related to the dynamical process of thin film deposition and are not present in static systems. Finally, we have shown that the deposition process itself can lead to the development of the instability as well as alter its experimentally observable wavelength.

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