Enhanced Instability of Strained Alloy Films due to Compositional Stresses

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A single-component strained film is known to be unstable to the stress-driven morphological instability. Here, we determine how the instability is modified in an alloy film by considering the effect of compositional stresses due to an atomic size difference. We find that the coupling of composition to stress always makes the film more unstable to the formation of stress-driven surface undulations. The destabilization is greatest over a range of intermediate deposition rates.

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The growth of planar strained films is a much sought-after goal in the fabrication of electronic and optoelectronic devices. Unfortunately, elastic relaxation drives a morphological instability of the film surface and results in nonplanar films. Thus, controlling the instability is important to the growth of planar-layer devices. On the other hand, in some cases the instability can result in the formation of small islands, which can form the basis for quantum dot devices. In this case, determining the characteristics of the initial instability gives information about the formation of quantum dots.

The stress-driven morphological instability [1–3] has been studied extensively for single-component films (for a review, see [4]). A small sinusoidal variation of the surface height causes some reduction of elastic stress at the peaks, with an increase in stress at the troughs. The resulting chemical-potential gradient drives diffusion from troughs to peaks, causing the height modulation to increase with time. The surface energy of the film tends to oppose this, but at long wavelengths the elastic effect is always dominant for nonfaceted systems.

While the instability is understood for single-component materials, many strained layers of interest are alloys. It is expected that the stress-driven morphological instability will still occur in strained alloy films; however, the instability might be drastically modified by the interaction between composition and stress. An important issue regarding the instability is whether the linking of composition and stress makes alloy film more or less unstable than the single-component case.

In recent years, there has been much theoretical work aimed at describing this complicated interaction. This work has focused on determining the effect of compositional stresses due to different size atoms, neglecting the influence of variations in the material properties with composition. From thermodynamic considerations it has been shown that a strained alloy film would be unstable if the coupling between the composition and surface modulations could be chosen arbitrarily [5]. Of the recent theoretical models which describe the surface dynamics [6–13], each finds that the strained alloy film can be *less unstable* than the corresponding single-component film, and in some cases the instability can be *completely suppressed,* suggesting that the coupling of composition and stress can be a stabilizing influence on the growth of planar alloy films.

Here, we present a new analysis of the role of compositional stresses in determining the stability of alloy film growth. The difference between our work and previous models is the description of how surface diffusion causes changes in the surface morphology and surface composition of the film, as explained below. We find, for the case of composition-independent material properties, that compositional stresses always make the alloy film *more unstable* than a single-component film. This prediction is a fundamental difference from previous analyses. We also find that the effect of the coupling on film stability is dependent on the deposition rate, with the largest destabilization occurring over a range of intermediate deposition rates. Thus, as in the case of a single-component film, a strained alloy film is *always unstable* for constant, isotropic material properties [14]. These results have important implications for the growth of strained alloy films.

As with the previous work [5–13] we assume that the material properties are independent of composition (the exception is that [12] also permits a composition-dependent Young's modulus). The assumption of composition-independent properties is made to isolate the specific effect of compositional stresses on film stability. A more complete theory, accounting for the composition dependence of material properties, could be developed within the framework presented here. Recent work has shown that species-dependent surface mobilities can control segregation during step-flow growth [15]. It is anticipated that different surface mobilities might significantly modify the stability results presented here, but our concern is with the specific effect of compositional stresses [14].

We consider the growth of a substitutional AB alloy as a strained layer with a surface $z = h(x, y, t)$, and composition of B atoms $C_B(x, y, z, t)$. We assume that the film is grown by a generic deposition process due to a flux of atoms from above, the composition of which determines the average film composition of B atoms, C_0. Atoms deposited on the surface stick can move by surface diffusion before being buried as new material is deposited from above. Once incorporated into the solid, any composition variations are "frozen in" as we assume that bulk diffusion is negligibly slow. Under these assumptions, conservation of atomic species at the surface of the film gives two evolution equations for the normal velocity of the surface V_n and the surface composition:

$$V_n = \Omega[\boldsymbol{F} \cdot \boldsymbol{n} - \nabla_S \cdot \boldsymbol{J}], \tag{1}$$

$$\delta \frac{\partial C_B}{\partial t} + C_B V_n = \Omega[C_0(\boldsymbol{F} \cdot \boldsymbol{n}) - \nabla_S \cdot \boldsymbol{J}_B], \tag{2}$$

where Ω is the atomic volume, $\boldsymbol{F} = -(V/\Omega)\hat{z}$ is the vector deposition flux (in the $-z$ direction giving rise to a nominal growth rate V), $\boldsymbol{n}$ is the outward normal of the surface, ∇_S is the surface gradient, δ is the thickness of the surface layer in which surface diffusion occurs, and $\boldsymbol{J}$ and $\boldsymbol{J}_B$ are the total flux and flux of B atoms, respectively, diffusing along the surface. The surface diffusion flux is based on a standard mobility/driving force model [16]

$$\boldsymbol{J}_i = -C_i M_i \nabla_S \mu_i, \tag{3}$$

where subscripts denote the different species ($i = A, B$), M_i is the (constant) surface mobility, and μ_i is the chemical potential. We assume for simplicity that the A and B atoms have the same surface mobilities $M_A = M_B = M$. From the thermodynamics of stressed solids [17,18], we derive how the chemical potential of a surface atom is modified by the effect of stress,

$$\mu_A = \mu_A(C_B) + \Omega\left[\frac{1}{2} S_{ijkl} T_{ij} T_{kl} + \gamma\kappa + \eta C_B T_{kk}\right], \tag{4}$$

where $\mu_A(C_B)$ is the chemical potential of component A at composition C_B in the absence of stress, T_{ij} is the stress tensor, S_{ijkl} is the linear elasticity compliance tensor, κ is the mean interfacial curvature, and γ is the surface free-energy parameter, taken as composition independent. The important parameter η is the solute expansion coefficient measuring the size difference between A and B atoms, and is defined as $\eta = (a_B - a_A)/a_0$ where a_A, a_B, and a_0 are the relaxed-state lattice parameters for pure A, pure B, and the alloy film of nominal composition C_0. Note that when A and B are the same species, $\eta = 0$ and we recover the chemical potential for a single-component material (see [1,3,4], for example). A result similar to Eq. (4) holds for μ_B. The constitutive law for isotropic linear elasticity in the presence of solute expansion effects is

$$T_{ij} = C_{ijkl}[E_{kl} - \eta(C_B - C_0)\delta_{kl}], \tag{5}$$

where C_{ijkl} is the tensor of elastic constants, E_{kl} is the elastic strain tensor measured with respect to the stress-free film, and $\eta(C_B - C_0)\delta_{kl}$ is the strain due to composition variations of different size atoms on a perfect crystal lattice. We focus here on the generic stability results of the film, so we take the elastic constants in the film and substrate to be identical and independent of composition. The equilibrium stress state of the epitaxially strained film with lattice mismatch strain ϵ is then accurately modeled as a semi-infinite solid with an applied biaxial strain due to the misfit [19]: the state of stress in the film is described by a divergence-free stress tensor in the solid, a traction-free film surface, and strains in the solid approaching that of uniform biaxial misfit strain ϵ as $z \to -\infty$.

The difference between our work and previous analyses [6–9,11–13] is in the surface dynamics. Guyer and Voorhees [6–9] assume that the surface of the film is in local equilibrium. By equating the chemical potential of surface atoms with that of atoms in the overlying vapor, the local equilibrium condition determines the surface composition C_B in terms of the local surface curvature and stress. The dynamics for the surface V_n are then determined from an equation of the form of Eq. (2) with the surface layer thickness δ set to zero. While the local equilibrium assumption may be appropriate at high vapor overpressures, we argue that for typical molecular beam epitaxy conditions the overlying vapor pressures are so small that local equilibrium is not established during growth. Instead, surface compositions are determined dynamically from the conservation of mass equations (1) and (2) in which the surface flux of each species is determined by Eq. (3). Leonard and Desai [11–13] use dynamics for the surface equivalent to Eqs. (1) and (2); however, they assume a different form for the total surface flux of atoms along the surface $\boldsymbol{J}$. Instead of each species diffusing independently according to Eq. (3) with $\boldsymbol{J} = \boldsymbol{J}_A + \boldsymbol{J}_B$, their model for the total flux is equivalent to a gradient of a composition-weighted chemical potential, $\boldsymbol{J} = -M\nabla_s(C_A\mu_A + C_B\mu_B)$. In our work the surface flux is $\boldsymbol{J} = -[C_A M_A \nabla_s(\mu_A) + C_B M_B \nabla_s(\mu_B)]$, and the different $\boldsymbol{J}$ leads to different stability predictions. We argue that the underlying physics of different species diffusing independently along the surface is more correctly represented by Eq. (3) rather than the total surface flux used by Leonard and Desai.

The stability of a compositionally uniform planar film during growth is determined from a linear stability analysis of the evolution equations (1) and (2). The growth or decay of perturbations is determined using normal modes, which for the surface shape takes the form

$$h(x, y, t) = Vt + \hat{h}\exp(\sigma t + i a_x x + i a_y y), \tag{6}$$

where $\hat{h}$ is the amplitude of the surface perturbation, and σ is the growth rate of the perturbation with wave numbers a_x and a_y in the x and y directions, respectively. Similar representations for the composition and stress involve the amplitudes of the composition perturbation $\hat{c}$ and stress perturbation $\hat{T}_{ij}$. The existence of nontrivial solutions to the linearized system for the perturbation determines the growth rate σ of the perturbation in terms of its wave numbers.

The results are conveniently expressed in nondimensional variables using a length scale $L = \gamma(1-\nu)/2E(1+\nu)$, a time scale $\tau = L^4/M\Omega^2\gamma$, and a stress scale $\sigma_0 = 2E(1+\nu)/(1-\nu)$, where E is Young's modulus and ν is Poisson's ratio. Typical values for the length and time scales at 800 K are $L \approx 6 \times 10^{-10}$ cm and $\tau \approx 3 \times 10^{-12}$ s (τ is sensitive to material and temperature because of the dependence on the surface diffusion coefficient). These length and time scales are typically multiplied by factors of $1/\epsilon^2$ and $1/\epsilon^8$ to give the actual length and time scales relevant to the instability [19] (for $\epsilon = 0.02$ this gives $L/\epsilon^2 \approx 15$ nm and $\tau/\epsilon^8 \approx 2$ min), but we have kept ϵ separate from the scalings to more clearly illustrate its role. The δ term appearing in Eq. (2) is negligible as long as the time scale for the instability is much longer than the time it takes to deposit a monolayer, $1/\sigma \gg \delta/V$. Since this criterion is generally valid except at very low growth rates, high misfits, and high temperatures, we present results here for $\delta = 0$.

Using these scalings for all variables, the characteristic equation for the *nondimensional* growth rate of perturbations can be written

$$\sigma = \epsilon^2 a^3 - a^4 + \left[\frac{C\epsilon^2\eta^2 a^5}{\mathcal{V} + Ca^2(g - \eta^2 p)}\right] \times \left[\frac{a}{(a + \sigma/\mathcal{V})}\right], \tag{7}$$

where $a = (a_x^2 + a_y^2)^{1/2}$ is the *nondimensional* magnitude of the wave number vector, and $p = a/(a + \sigma/\mathcal{V}) - 1/(1+\nu)$. In addition, the new nondimensional parameters C, $\mathcal{V}$, and g quantify the nominal film composition $C = C_0(1 - C_0)$, the deposition rate $\mathcal{V} = V\tau/L$, and the chemical energy $g = G_M''/V_0\sigma_0$, where G_M'' is the second derivative of the molar Gibbs free energy at the nominal film composition, and V_0 is the molar volume. Note that only combinations of ϵ^2 and η^2 appear in the equation for the growth rate, which means that the stability results are independent of the sign of ϵ and η.

Case (i): no solute stresses ($\eta = 0$, $\epsilon \neq 0$).—In this case we recover the usual stability results for the stress-driven instability [1,3,4], with $\sigma = \epsilon^2 a^3 - a^4$. Thus, the surface is always unstable to a range of wave numbers with $0 < a < \epsilon^2$. The mode of instability in this case is purely morphological; the surface develops undulations but the composition remains uniform because there is no coupling between the composition and stress. Also, the stability of the surface is independent of the nominal composition C, the growth rate $\mathcal{V}$, and the chemical energy g. (Note that, even though the film is unstable, if the growth rate σ is small, then over the time it takes to deposit the film the instability will not become apparent [20].)

Case (ii): coupled case ($\epsilon \neq 0$ and $\eta \neq 0$).—For a given set of conditions the growth rate of the instability depends on the wave number of the perturbation. The wave number that gives the largest growth rate corresponds to the perturbation that dominates the initial stages of the instability. Figure 1 shows that for $\eta \neq 0$ the maximum growth rate of the instability is increased, indicating that compositional stresses destabilize the alloy film relative to the corresponding single-component case. For large η at intermediate deposition rates the growth rate of the instability can be orders of magnitude larger than that of the $\eta = 0$ case.

When η exceeds a critical value (not shown in Fig. 1) such that $g < \eta^2\nu/(1+\nu)$ the growth rate of the instability becomes unbounded as $a \to \infty$, even if there is no misfit strain. This divergence is a manifestation of the compositional-stress instability [6–9,21], also known as the kinetic instability [22–24]. In this case, the growth process enables a fine-scale surface decomposition of the alloy, even at temperatures above the chemical spinodal. The divergence in our model occurs because we do not include gradient-energy terms which become important when the wavelength of the perturbation approaches the lattice spacing. Including these gradient-energy terms would cause very short wavelength perturbations to decay, and eliminate the nonphysical divergence in our results when $g < \eta^2\nu/(1+\nu)$.

The wave number of the most unstable mode is shown in Fig. 2 for the same set of parameters as in Fig. 1. The general trend is that the interaction of composition and stress causes a shift in the most unstable wave number to larger values. For sufficiently large η (e.g., $\eta = 0.2$)

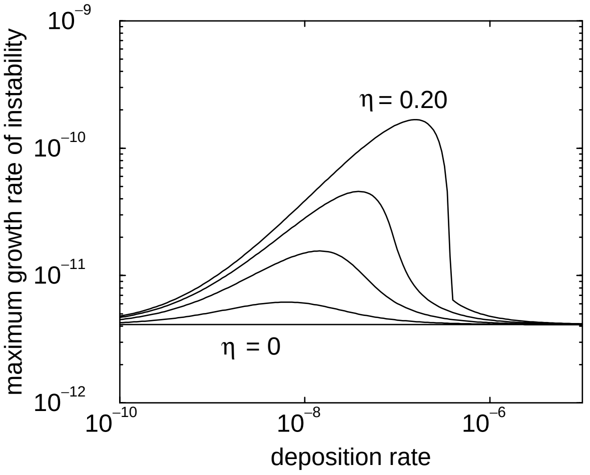

FIG. 1. Maximum growth rate σ of the instability as a function of nondimensional deposition rate $\mathcal{V}$ for $\eta = 0, \ldots, 0.20$ in steps of 0.05. Other parameters here are $\epsilon = 0.05$, $C = 0.25$, $\nu = 0.25$, and $g = 0.01$. The perturbation grows as $e^{\sigma t}$.

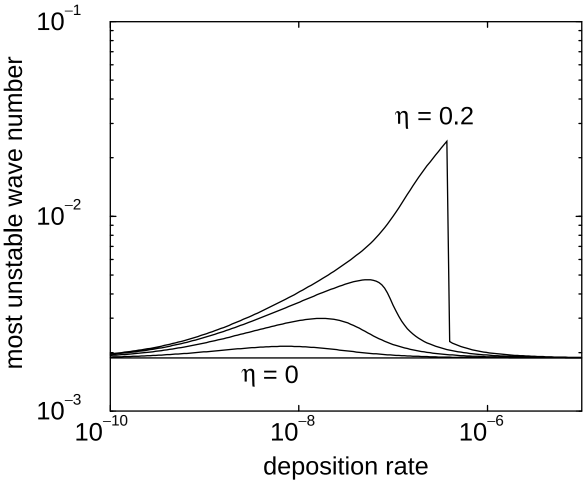

FIG. 2. Wave number a of the most unstable mode. Parameters are the same as in Fig. 1. The initial instability is dominated by undulations with wavelength $2\pi/a$.

there is a discontinuous change in the most unstable wave number at a specific deposition rate. This discontinuity is due to a double peak in the $\sigma(a)$ curve: the relative height of the peaks changes as the deposition rate is changed, leading to a shift in the maximum growth rate from one peak to the other.

The eigenfunctions derived in the linear stability analysis reveal the mechanism for how compositionally generated stresses destabilize the film relative to the single-component case. Consider a compressive misfit $\epsilon < 0$ and take $\hat{h} > 0$. At a bump on the surface the stress is relaxed relative to that of a planar film, so the stress at a bump has a tensile deviation $\hat{T}_{kk}$ from the uniform state. If B atoms are large ($\eta > 0$), for example, then there is a preferential motion of B atoms to bumps on the surface ($\hat{c} > 0$). As these composition variations are incorporated into the solid during growth, they result in a further expansion of the crystal lattice at surface bumps, increasing the amplitude of the tensile stress perturbation. The increase in the stress perturbation leads to a positive feedback through increasing the compositional segregation. Even without the compositional effects, the stress nonuniformity is sufficient to drive the surface instability (as in a single-component film). Here, composition variations cause an enhancement of the instability in two ways. First, the composition variations increase the stress nonuniformity, causing a larger driving force for the surface instability. Second, the stress nonuniformity results in the enhanced diffusion of one atomic species to surface peaks, causing the instability to grow faster. For a film with compressive misfit, this results in the preferential motion of large atoms to surface peaks. Thus, the enhancement of the instability is due to the feedback of the composition variations on the stress, causing increased net transport via the usual stress-driven instability, as well as additional mass transport through the enhanced motion of large atoms to surface peaks. The mechanism for destabilization is independent of the choice of signs for ϵ and η. This mechanism, which predicts that large atoms preferentially segregate to peaks if the misfit is compressive and to valleys if the misfit is tensile, is consistent with experimental evidence in the GeSi/Si system [25,26] and in the AlAs/InAs system [27].

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