Dynamically stable growth of strained-layer superlattices

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In heteroepitaxy, misfit stress leads to a well-known instability of planar films against ''roughening.'' In contrast, we find that growth of a strained-layer *superlattice* is *dynamically stable* under a range of growth conditions. Outside the stable range, the modulations of successive layers may be in phase, out of phase, or more complex, as summarized in a dynamical phase diagram. This remarkable behavior results from the collective influence of the buried interfaces, via their strain fields, on the evolution of the surface morphology.
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In recent decades, materials physics has increasingly turned toward the problem of growing materials far from equilibrium. A classic example is the semiconductor superlattice. The early fabrication of these nonequilibrium structures was a triumph, requiring precise control of temperature and deposition. A still greater challenge was incorporation of strained layers, to allow a far wider range of materials combinations. Tremendous efforts have been devoted to understanding and controlling the instability of strained layers with respect to elastic relaxation (by surface roughening) and plastic relaxation (by dislocations).

Strained layers become unstable to plastic relaxation only above a critical thickness.[1,2] Elastic relaxation represents a more fundamental problem, rendering even the thinnest strained layers unstable against morphological modulations.[3–8] It is generally believed that this strain-induced roughening can be slowed down, but never entirely suppressed.

Here we consider the growth of strained-layer superlattices. Unlike the familiar single-layer case where stresses are associated with misfit with respect to the substrate, each layer in a heteroepitaxial superlattice grows under a stress that includes contributions from all (possibly nonplanar) buried layers. This difference, though subtle, leads to dramatically different behavior. We predict that roughening can be *entirely suppressed* by an appropriate choice of growth rates and layer thicknesses. Superlattice growth is then *dynamically stable*, even though the system is strained throughout and thus very far from equilibrium.

Recent studies of strain-balanced superlattices have found fascinating lateral modulations, which can persist in an apparent steady state for many periods.[9–12] Our results may explain a key element of the behavior. There is a range of growth conditions where the superlattice is stable, and also a range where it is only weakly unstable. Thus, inclusion of nonlinear terms could give a steady-state structure with finite-amplitude modulations. Such a structure might have applications as a ''vertical superlattice,'' or as a two-dimensional array of ''quantum wires.'' [At low growth temperatures, facetting provides the key nonlinearity, and stable self-organized island array somewhat analogous to Fig. 1(b) have been studied.][13]

We consider growth of alternating layers of materials A and B on a substrate C. The lattice constant of material C is taken to be intermediate between A and B, so the layers are

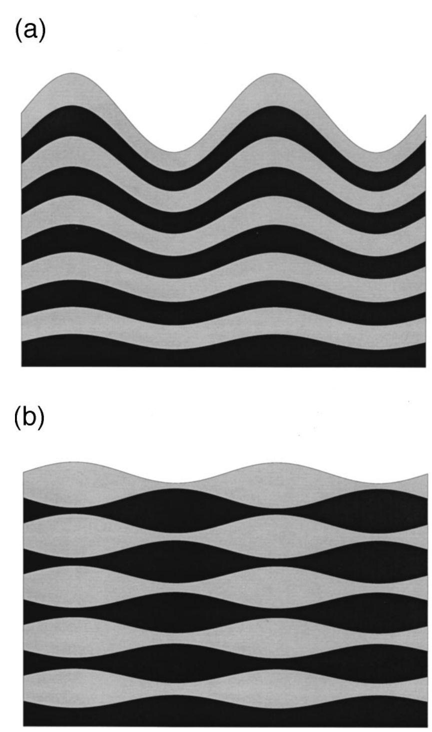

FIG. 1. Multilayer film morphology resulting from perturbation growth: (a) corresponds to the in-phase mode of the instability and (b) corresponds to the out-of-phase mode. In this case the structure is modulated not only morphologically, but also compositionally.

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alternately under tensile and compressive stress. The layers are assumed to be free of dislocations. For simplicity, we assume the same elastic constants throughout the system, and neglect any intermixing or alloy decomposition of the respective materials. For typical semiconductors, bulk diffusion may be neglected at the growth temperature, so we assume that the morphological evolution is determined entirely by deposition and diffusion along the growth surface.

We begin with the simplest case, the symmetric strain-balanced superlattice. Here the two materials have exactly the same surface energy, surface diffusivity, and other materials parameters, except for equal and opposite stress; and the growth rate and thickness are the same for all layers. For small deviations from planarity, the evolution of the surface profile $h(x,y,t)$ is[14]

$$\frac{\partial h}{\partial t}=r+\frac{D\Omega\,\theta}{k_BT}\nabla_s^2\mu_k^s. \tag{1}$$

Here $\mu^s{}_k$ is the chemical potential of the atoms at the surface of the growing layer k and the two-dimensional Laplacian is evaluated along the surface, D is the surface diffusion coefficient (assumed the same for both materials), r is the deposition rate, k_B is the Boltzmann constant, and Ω and θ are atomic volume and atomic surface density. We use a constant deposition rate r, as when impinging atoms have fixed sticking coefficient and negligible desorption.

Following[7] we write the chemical potential at the surface as $\mu=\mu_0+\gamma\Omega\,\kappa+\boldsymbol{\sigma}_k^s\mathbf{S}\boldsymbol{\sigma}_k^s\Omega/2$, where μ_0 is the chemical potential of the unstrained bulk material. The other two terms in this expression are the surface energy and elastic contributions: κ is the sum of the two principle surface curvatures, γ is the surface energy[15] of the materials, $\boldsymbol{\sigma}_k^s$ is the stress tensor evaluated at the surface of layer k, and $\mathbf{S}$ is the elastic compliance tensor.

We perform a linear stability analysis of the multilayer growth. Each interface has a shape perturbation which formed during the growth of the layer underneath. The average thickness $\overline{h}$ of the growing film at time t is $\overline{h(t)}=(k-1)H+h_k(t)$, where layers up to $k-1$ are fully grown to thickness H, and layer k has average thickness h_k measured from the interface between layers $k-1$ and k. The profile of the film, therefore, is $h(t)=\overline{h(t)}+\Delta(t)$, where $\Delta(t)$ is the perturbation of the growing surface.

If the interfaces and surface were flat, the stress in Eq. (1) would be determined simply by the misfit of whichever material is at the surface. However, here we must also include the stresses at the surface due to the nonplanar interfaces beneath, up to linear order in the amplitude. For this purpose, we evaluate the stress (and hence, μ) using the Green's function for a buried sinusoidal interface between layers of different stress.[16] We do this in two spatial dimensions [where the surface is at $h(x,t)$] using plane strain elasticity. Then each Fourier component $\Delta(\xi,t)$ of the surface profile of the growing layer k evolves as

$$\begin{aligned}\frac{\partial\Delta}{\partial t}=&\frac{D\Omega^2\,\theta}{k_BT}|\xi|^3\left(-\gamma|\xi|\Delta+2\frac{\Sigma_k^2}{M}\Delta\right)\\&-\frac{D\Omega^2\,\theta}{k_BT}|\xi|^3\left(\sum_{j=1}^{k-1}\Delta_j\frac{\Sigma_k}{M}(\Sigma_{j+1}-\Sigma_j)\right.\\&\times\left\{2-\frac{|\xi|[(k-j-1)H+h_k]}{1-\nu}\right\}\\&\left.\times\exp\{-|\xi|[h_k+(k-j-1)H]\}\right),\end{aligned} \tag{2}$$

where Δ_j is the amplitude of the perturbation for the fully grown layer j. Here M is the elastic modulus $[E/(1-\nu^2)$ for a flat layer in the plane strain approximation], and Σ_j is the macroscopic misfit stress in layer j with respect to the substrate (Σ is positive or negative, for odd- or even-numbered layers, respectively).

We put the equations into a dimensionless form, scaling all lengths by the wave vector of the most unstable mode of a pure material,[7] $\xi_0=3\Sigma^2/(2M\gamma)$. This gives a dimensionless wave vector $\xi^*=|\xi|/\xi_0$ and a dimensionless thickness of a fully grown layer $H\xi_0=H^*$. Scaling time by the growth rate r gives a dimensionless composite diffusivity parameter $D^*=D\Omega^2\,\theta\Sigma^2\,\xi_0^2/(rk_BTM)$.

To obtain the amplitude of the instability after layer k is fully grown, we integrate Eq. (2) over the growth time of layer k. The details will be given elsewhere. The integration results in a linear recurrence relation for the amplitude Δ of the interface modulation with an asymptotic solution

$$\Delta_k=\alpha_1\lambda_1^{k-1}, \tag{3a}$$

where λ_1 is the largest characteristic number of the recurrence relation. When the maximum characteristic numbers form a complex conjugate pair, this becomes

$$\Delta_k=2\,\mathrm{Re}(\alpha_1\lambda_1^{k-1}). \tag{3b}$$

This asymptotic expression for the perturbation amplitude is sufficient to analyze the stability. Moreover, it usually provides a good approximation to the full evolution, since the additional terms in Eqs. (3) make fractional contributions that decay as a power of the ratio of the eigenvalues. The asymptotic response to a perturbation is fully determined by the dependence of λ_1 on the parameters ξ^* (normalized wave vector), H^* (normalized thickness of an individual layer), and D^*.

Given the parameters H^* and D^*, for a given wave vector ξ^* the evolution of the multilayer structure can be classified according to the value of λ_1. When the absolute value of λ_1 is smaller than 1, the planar superlattice is dynamically stable against perturbations of this wave vector—such a perturbation does not propagate through the stack of multilayers but, rather, decays exponentially with growth. When the absolute value of λ_1 is greater than one, the amplitude of the perturbation grows exponentially with the number of layers, so superlattice growth is dynamically unstable. The morphology of the multilayer structure is determined by the phase of λ_1. If λ_1 is real and positive, the modulations of successive layers are in phase [as illustrated in Fig. 1(a)], while for negative values the modulations of

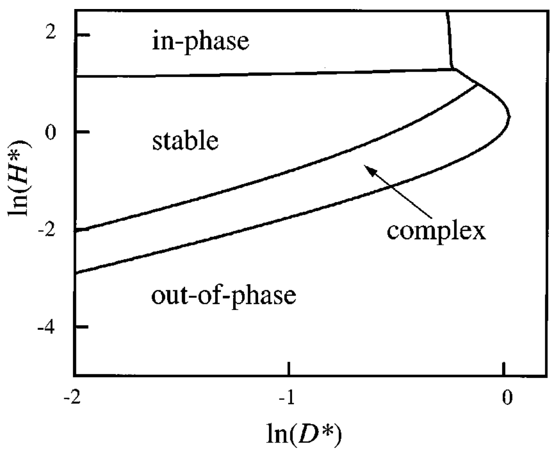

FIG. 2. Stability diagram for a growing multilayer film. The four domains in this diagram are classified according to the eigenvalue λ_{max}.

successive layers are 180° out of phase [Fig. 1(b)]. For complex values of λ_1, the perturbation amplitude still varies with layer m as λ_1^m. This gives an overall trend $|\lambda_1|^m$, which determines the stability or instability. But this is modulated by a factor $\cos(m\phi)$, where ϕ is the phase of λ_1; so despite the overall trend, the amplitude may increase, decrease or even reverse from one layer to the next.

For any given set of material and growth parameters, the overall stability is determined by the value of λ_1 for the most-unstable mode, i.e., $\lambda_{max}=\max_{\xi}\lambda_1(\xi^*)$. For the symmetric case, there are only two dimensionless parameters characterizing the system, H^* and D^*. We can characterize the stability of this system by computing the value of λ_{max} as a function of H^* and D^* and then determine the type of behavior depending on the values of λ_{max}. The four types of behavior that are found are presented in the stability map of Fig. 2. The region corresponding to $|\lambda_{max}|<1$ is the area of decaying perturbation for all wavelengths. This region is labeled ''stable'' because growth of a planar superlattice is stable against perturbations in this range of growth parameters. For the region of unstable growth ($|\lambda_{max}|>1$), the mode of the instability is determined by the phase of λ_{max}, as discussed earlier, and the regions in Fig. 2 are labeled accordingly. Note that for large D^*, the system is always unstable with out-of-phase modulations. This corresponds to large surface diffusivity (high temperature) or large misfit stress. For small D^*, there is a stable regime at intermediate layer thickness.

To check whether the symmetric case is typical of the more general behavior of strained-layer superlattices, we have repeated these calculations for systems with unequal stress, layer thickness, diffusivity, etc. Details will be given elsewhere. In all cases that we have studied, the stability diagram is qualitatively similar to Fig. 2. Stable growth occurs over a range of layer thickness H^*, and this stable range increases for small D^*. For sufficiently large D^*, the system becomes unstable for any layer thickness.

In practice the system may be stable over an even larger range of parameters than suggested by the region of absolute dynamical stability in Fig. 2. At small layer thicknesses, the nominal instability is rather weak compared with that at large layer thicknesses. Moreover, the instability only occurs at extremely short wavelengths, well below the instability range for a single layer.[7] Thus any initial perturbation at such short wavelengths may be smoothed out in the first layer, so that these modes begin from extremely weak initial amplitude.

It is also important to consider the possibility of plastic relaxation by dislocations. As long as the individual layers are below their Matthews–Blakesley critical thicknesses, relaxation will only occur when the system as a whole exceeds a much larger critical thickness, which is set by the much smaller *average* stress of the superlattice. Thus, at temperatures where bulk diffusion is negligible, superlattice growth can be stable against both elastic and plastic deformations, up to a total thickness which is limited only by the imperfect stress compensation. We expect that stable growth will be most easily seen for short-period superlattices (small H^*); but because key materials parameters are poorly known, or vary exponentially with temperature, it is difficult to predict the stable growth range for specific systems.

In conclusion, we have shown that growth of a strained-layer superlattice may be dynamically stable, despite the well-known instability of single strained layers. This stabilization occurs over a substantial range of layer thickness and growth conditions, even when there is a substantial asymmetry between alternate layers. Outside the stable regime the instability can take various forms, depending on the layer thickness and diffusion length. We hope that an understanding of this effect may prove useful in growing technologically important superlattice structures.

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