

## Epitaxial films stabilized by long-range forces

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It has been widely accepted that the stability of an epitaxial film on a substrate of a different material is determined primarily by the competition between surface tension and stress. Here we propose that certain thermodynamic driving forces of different physical origins, acting over longer ranges than atomic length, can be strong enough to compete with elasticity. Specifically, we show that the ubiquitous dispersion force can compete effectively with the stress in thin solid films. We further show that the confined electrons within a metal film can mediate a surprisingly long-ranged force capable of stabilizing metal films of many atomic layers, leading to the existence of a thickness window within which smooth metal films can be formed. [S0163-1829(98)51832-2]

Many electronic and photonic devices require high-quality crystalline films grown on substrates of different crystals. Despite decades of intense study, epitaxy remains largely an art. Its scientific understanding has been challenging because of the marginal size: a film has enough atoms to show complex collective behaviors, but not enough to act like a bulk. This paper focuses on the stability of epilayers during annealing. Consider a film already grown on a substrate, e.g., by a nonequilibrium process. The film covers the substrate, but may be rugged. Upon annealing, atoms diffuse on the surface, driven by various thermodynamic forces. The film may either flatten or form islands. The outcome often depends on the film thickness. On a Si substrate, for example, a flat Ge film is stable up to three monolayers; above this thickness, three-dimensional (3D) islands form.<sup>1</sup> Similar behavior has been reported for many other inorganic and organic semiconductor films, sometimes with much larger critical thicknesses.<sup>2</sup> In particular, Petroff and co-workers<sup>3</sup> demonstrated that the 2D to 3D transition thickness for  $\text{In}_x\text{Ga}_{1-x}\text{As}$  growth on GaAs depends inversely on stress. Recently, Smith *et al.*<sup>4</sup> observed a different kind of thickness dependence. They found that a flat Ag film can be formed on GaAs(110) only when the film *exceeded* a critical thickness of about 15 Å. Similar behaviors have also been confirmed for the same system and for Ag on GaP, GaSb, and Si.<sup>5</sup>

Despite the compelling experimental evidence, the prevailing theory does not predict that the stability of a strained film depends on its thickness.<sup>6</sup> The theory is based on elasticity and capillarity. When a flat film surface is perturbed into a wavy shape, elastic energy decreases but surface energy increases. Stress tends to amplify surface perturbations of all wavelengths. Surface energy can stabilize perturbations of short wavelengths, but not those of long wavelengths. Consequently, the theory concludes that any strained film, regardless of its thickness, is unstable and will break into 3D islands, given enough atomic mobility.

This conclusion clearly disagrees with the experimental observations cited above. One may settle with the thought that the continuum model fails for ultrathin films, and indeed several atomistic model studies have been carried out to address the thickness dependence.<sup>7</sup> However, recent detailed studies have shown that continuum approaches to such problems can be applied down to very small (nanometer) scales.<sup>8</sup> Furthermore, thickness effects of various kinds have been observed in many systems, some of which have stable films of many monolayers.<sup>2-5</sup> Consequently, it is imperative to have a continuum model with a wider applicability. An earlier effort to resolve this issue invoked an assumption that the surface energy depended on film thickness.<sup>9</sup> This modification allowed the theory to give rise to various kinds of film stability, depending on the film thickness. The theory, however, was entirely phenomenological, without providing the physical origin for the key assumption. Consequently, it did not establish whether any force of clear physical origin was strong enough to compete with stress and stabilize a solid film.

In this paper, we show that certain thermodynamic forces, acting over longer ranges than atomic length, are strong enough to compete with elasticity. Specifically, we show that the dispersion force, well known for its role in controlling the morphology of colloids<sup>10</sup> and liquid films,<sup>11</sup> can compete with the stress in thin solid films. We further show that the confined electrons within a metal film can mediate a surprisingly long-ranged force capable of stabilizing metal films of many atomic layers, leading to the existence of a thickness window within which smooth metal films can be formed. We also establish the specific dependence of the transition thickness on stress in the presence of different long-range forces.

We present our main idea by generalizing the existing model, whose essentials are summarized as follows. Figure 1 illustrates a film of thickness  $D$  on a semi-infinite substrate. The surface tension of the film  $\gamma$  is taken to be isotropic.<sup>12</sup> This stress in the film  $\sigma$  results from the difference of the

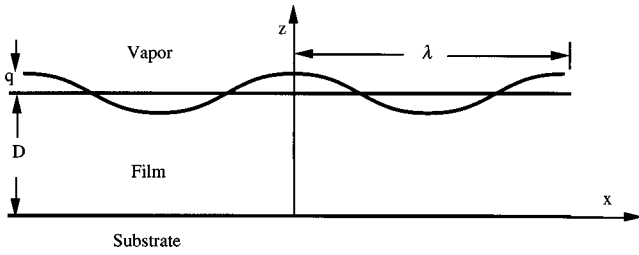


FIG. 1. An epitaxial film on a substrate. the film surface is perturbed into a wavy shape of wavelength  $\lambda$  and amplitude  $q$ .

film and the substrate in, for example, crystal structure, lattice constant, or thermal expansion coefficient. When the surface is flat, the stress is uniform in the film. Consider a two-dimensional problem, representing the substrate by a semi-infinite plane, and the film by an overlaying strip; atoms can diffuse along the curve representing the film surface. The model is based on a stability analysis. Atomic diffusion on the surface conserves the mass of the film. Consequently, one can perturb the surface into a wavy shape above and below the average film thickness  $D$ , namely,

$$z = D + q \cos(2\pi x/\lambda), \quad (1)$$

where  $z$  is the perturbed film thickness,  $q$  the wave amplitude, and  $\lambda$  the wavelength. The  $x$  axis coincides with the film-substrate interface.

To highlight the thermodynamic nature of this instability, we focus on energetics and avoid details of the mass transport process. All energies are computed for one period of the system, per unit thickness in the direction normal to the plane, to the leading order in the perturbation amplitude  $q$ . The surface energy  $U_S$  is  $\gamma$  times the length of the curve that represents the surface. One can readily show that the perturbation increases the surface energy by

$$\Delta U_S = \pi^2 \gamma q^2 / \lambda. \quad (2)$$

Elementary considerations dictate that, when the surface undulates, the elastic energy stored in the system  $U_E$  should decrease, and its change should take the form

$$\Delta U_E = -\beta \sigma^2 q^2 / Y. \quad (3)$$

Here  $Y$  is Young's modulus of the film, and  $\beta$  a positive dimensionless number, which has been calculated by solving the boundary value problem of a strained, perturbed film on a substrate.<sup>6</sup> If the film and the substrate have identical elastic constants,  $\beta = \pi$ . The total free energy  $U_S + U_E$  increases for short wavelengths, but decreases for long wavelengths. Consequently, the flat film of any thickness is unstable. For the film and the substrate having different elastic constants,  $\beta$  depends on  $\lambda/D$  and ratios of the elastic constants. Nonetheless, the conclusion remains essentially unchanged: except for a film on a rigid substrate, the stressed film of any thickness is unstable.

We now include long-range force effects, as described by the interaction energy  $W(D)$  between the surface of the film and the film-substrate interface. The change in the interaction energy associated with the surface undulation is

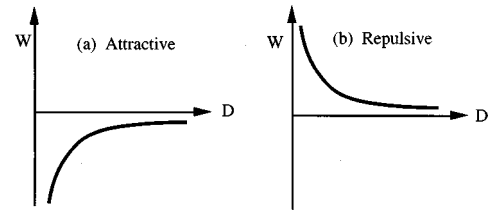


FIG. 2. Two representative long-range interactions.

$$\Delta U_L = \int_0^\lambda W(z) dx - W(D)\lambda. \quad (4)$$

This expression is reasonable when the wavelength of the perturbation is larger than the film thickness, and the amplitude of the perturbation is small. To the leading order in  $q$ , the change is

$$\Delta U_L = \frac{\lambda}{4} \frac{\partial^2 W}{\partial D^2} q^2. \quad (5)$$

When the function  $W(D)$  is concave up, i.e.,  $\partial^2 W / \partial D^2 > 0$ , the long-range force tends to stabilize a flat film. When  $\partial^2 W / \partial D^2 < 0$ , it tends to destabilize the flat film.

Observe from Eqs. (2), (3), and (5) that the surface tension is effective in stabilizing the film against perturbations of short wavelengths, the long-range interaction (assuming  $\partial^2 W / \partial D^2 > 0$ ) is effective in stabilizing the film against perturbations of long wavelengths, and the stress destabilizes the film for all wavelengths. Summing Eqs. (2), (3), and (5) we conclude that the net free energy increases for perturbations of all wavelengths only if

$$\partial^2 W / \partial D^2 > \sigma^4 / Y^2 \gamma. \quad (6)$$

This is the condition under which the flat film is stable against any small perturbation. We have taken  $\beta = \pi$  in using Eq. (3) because elastic constants are often not too dissimilar between the film and substrate. The condition is similar to that derived previously in the model based on the thickness-dependent surface energy,<sup>9</sup> but with distinctly different physical grounds.

The first specific type of long-range force we consider is the dispersion force. In a many-particle system, the fluctuations in the polarization of one particle correlate, via electromagnetic waves, with those of all other particles. This correlation gives rise to the dispersion force, commonly known as the van der Waals force. For two bulk media separated by a film of thickness  $D$ , the interaction energy per unit area takes the form

$$W(D) = -A / (12\pi D^2), \quad (7)$$

where  $A$  is the Hamaker constant, which depends on the dielectric spectra of the three media.<sup>10,13</sup> When two identical media interact across a film of another medium the dispersion force is attractive [ $A > 0$ , Fig. 2(a)]. The attraction plays central roles in colloids<sup>10</sup> and ceramics with glassy films on grain boundaries.<sup>14</sup> When two dissimilar media interact across a film of a third medium, the dispersion force can be either attractive or repulsive [ $A < 0$ , Fig. 2(b)]. Due to its

robust physical origin, the dispersion force exists for any system of media, including a substrate interacting, across a film, with vacuum (or air), in which case  $W(D)$  is better understood as the excess free energy of a thin film relative to a very thick film. The repulsive dispersion force has manifested itself in several startling phenomena involving liquid films. When a suitable liquid is placed in a beaker, a film of the liquid climbs up the wall, and soon all the liquid leaves the beaker.<sup>15</sup> In another phenomenon, a film of one liquid can lie stably above another liquid of lower density.<sup>16</sup> In both cases, the repulsion tends to thicken the film, counteracting the gravity.

Now a centrally important question is, is the dispersion force strong enough to stabilize a solid film against stress?

Despite its truly ubiquitous nature, to the best of our knowledge the dispersion force has never been considered in any stability analysis of solid films where elasticity is important. We tentatively attribute this ignorance to the existence of the following conceptual barrier. The dispersion force is responsible for the bonding of van der Waals solids, which are much weaker than covalent, ionic, or metallic solids. This might give the impression that the dispersion force was too weak to be important in driving morphological changes in most solids. This perception is misguided. Morphological changes are driven by a small deviation from the cohesive energy, such as elastic energy, rather than the cohesive energy itself. Consequently, one should compare the dispersion energy with the elastic energy, instead of the cohesive energy. In the following, we show that the dispersion force is indeed strong enough to be competitive with elasticity.

We now apply Eq. (6) to the dispersion force. When the force is attractive [Fig. 2(a)], a flat film of any thickness is unstable. When the force is repulsive [Fig. 2(b)], a thin film is stable, but a thick film is unstable; a comparison of Eqs. (6) and (7) defines the critical thickness:

$$D_c = \left( \frac{-A \gamma Y^2}{2 \pi \sigma^4} \right)^{1/4}. \quad (8)$$

Qualitatively, Eq. (8) shows the inverse dependence of the transition thickness on stress, as observed experimentally.<sup>3</sup> Quantitatively, we are unaware of any evaluation of the Hamaker constant  $A$  for epitaxial films. Fortunately, the critical thickness depends weakly on  $A$ ; an order of magnitude,  $10^{-20}$  J, representative of extensive tabulations of many systems,<sup>10,14</sup> serves our purpose. What is more crucial here is the sign of  $A$ : only the repulsive interaction can stabilize a film. Judging from the dependence of  $A$  on dielectric spectra,<sup>10</sup> one expects that, of all substrate-film-air systems, repulsion should be as prevalent as attraction. Consequently, it is reasonable to take  $A = -10^{-20}$  J in this first estimate. Other quantities in Eq. (8) are better established. Using values representative of inorganic semiconductor films,  $\gamma = 1$  J/m<sup>2</sup>,  $Y = 10^{11}$  N/m<sup>2</sup>, and  $\sigma = 4 \times 10^9$  N/m<sup>2</sup>, we find that  $D_c = 5$  Å. This estimate is of the same order as that which has been observed experimentally in some systems.<sup>1-3</sup> One should not, however, accept this agreement as a validation of the model because we have not established that the systems having wetting films indeed have *repulsive* dispersion force. Furthermore, long-range forces of other origins may coexist.

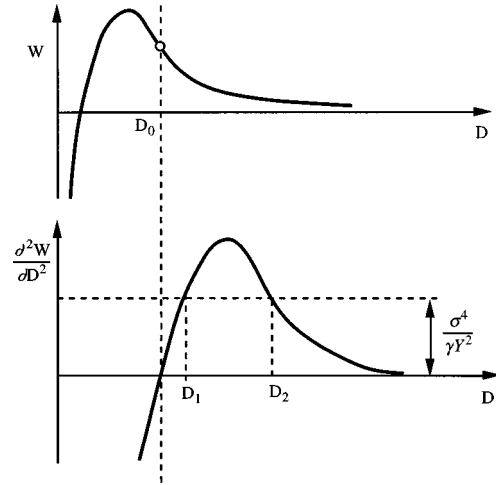


FIG. 3. The top figure shows the qualitative shape of the function  $W(D)$  for Ag on GaAs, where the inflection point is marked by a small circle. The bottom figure shows the qualitative shape of the curvature  $\partial^2 W / \partial D^2$ .

These uncertainties aside, insofar as it gives the correct magnitude for the critical film thickness, the dispersion force should be at least as important as any other force that affects the stability.

With the above first encouraging order-of-magnitude estimate, it is highly desirable to make a more precise comparison between the strengths of stress and the dispersion force for a given system. This in principle is just becoming feasible, given the recent advancement in the density-functional account of van der Waals interactions between two solids.<sup>17</sup>

Next we consider a metallic film on a semiconductor substrate. A recent model has highlighted forces of two origins: quantum confinement and charge transfer.<sup>18</sup> In a metallic thin film, electronic states form discrete subbands, and these quantized states can manifest themselves in various ways.<sup>19,20</sup> In particular, when insulated, the film has higher average electronic energy than the bulk. This difference results in an excess free energy of the film relative to the bulk. (As an approximation, ions in the film and in the bulk are taken to have identical free energy.) On the other hand, when the metallic film is brought in contact with a semiconductor substrate, electrons transfer between the two media to equalize the Fermi level. This lowers the free energy. For Ag on GaAs, calculations<sup>18</sup> showed that the attraction due to charge transfer dominates for films of a few monolayers, and the repulsion due to quantum confinement dominates for thicker films. Figure 3 shows the qualitative shape of the combined interaction energy  $W$ . The curve is concave down for thin films, but concave up for thick films; the small circle on the curve marks the inflection point, corresponding to the film thickness  $D_0$ , which is about a few monolayers. As pointed out in Ref. 18, if the effect of stress is negligible, such a long-range interaction destabilizes a film thinner than  $D_0$ , but stabilizes a film thicker than  $D_0$ . This trend agrees with the experimental observations cited in the beginning of this paper.<sup>4,5</sup>

The previous work<sup>18</sup> ignored the effects of the stress and surface tension, which we now include. The bottom part of Fig. 3 shows the shape of  $\partial^2 W / \partial D^2$  as a function of  $D$ . The quantity  $\sigma^4 / \gamma Y^2$  is a horizontal line. According to the stabil-

ity condition (6), three situations exist. (a) When the horizontal line is too high to intersect with the curve, the flat film is unstable for any thickness. (b) When the horizontal line is tangent to the curve, the flat film is stable only for one particular thickness, and unstable for any other thicknesses. (c) When the horizontal line intersects with the curve at two points, corresponding to films of thickness  $D_1$  and  $D_2$ , the flat film is stable if its thickness falls in between, and unstable otherwise. Using  $\gamma=1 \text{ J/m}^2$ ,  $Y=76 \text{ GPa}$ , and  $\sigma=500 \text{ MPa}$  (a relatively large stress in metallic films), we obtain  $\sigma^4/\gamma Y^2=10^{13} \text{ J/m}^4$ . Our calculations, including both quantum confinement and charge transfer, with either finite or infinite potential well, gave the magnitude of the maximum curvature  $(\partial^2 W/\partial D^2)_{\text{max}} \approx 10^{18} \text{ J/m}^4$ . Note the huge difference between  $\sigma^4/\gamma Y^2$  and  $(\partial^2 W/\partial D^2)_{\text{max}}$ . Consequently, for films of several monolayers, the quantum confinement effect prevails over the stress by a large margin. Situation (c) is readily accessible experimentally: very thin films are destabilized by charge transfer, films of intermediate thickness are stabilized by quantum confinement, and thick films are destabilized by stress.

Because  $(\partial^2 W/\partial D^2)_{\text{max}} \gg \sigma^4/\gamma Y^2$ , from Fig. 3 we see that  $D_1 \approx D_0$ . However,  $D_2$  must be estimated by using the long-range tail of the interaction energy. Everything else being equal, better confinement of electrons can stabilize thicker films. As an estimate of the magnitude of the long-range tail, consider electrons confined in a metallic film by infinite potentials on both sides. The energy levels are determined by the one-electron Schrödinger equation. The total free energy is estimated by the sum of energies over all electrons in the ground state of the film. Let  $W(D)$  be again the excess energy per unit area of the film relative to that of the bulk of the same thickness. Our analysis shows a long-ranging tail:

$$W(D) = \frac{3\pi^2 \hbar^2 n}{32mD} \equiv \frac{B}{D}, \quad (9)$$

where  $\hbar$  is the Planck constant,  $m$  the electron mass, and  $n$  the number of free electrons per unit volume. Figure 4 compares this asymptotic result with the exact numerical solution: they agree well beyond a few monolayers. A combination of Eqs. (6) and (9) gives

$$D_2 = (2B\gamma Y^2/\sigma^4)^{1/3}. \quad (10)$$

Note that this transition thickness also depends inversely on the stress, and more strongly than the case of the dispersion force (the exponents are  $4/3$  vs  $1$ ). For Ag,  $n=5.86 \times 10^{28} \text{ m}^{-3}$  and  $B=6.62 \times 10^{-10} \text{ J/m}$ . A stress of magnitude  $\sigma=500 \text{ MPa}$  leads to  $D_2=496 \text{ \AA}$ . The available experimental data do not permit a critical comparison. Equation (9) ignores fine oscillations that are invisible on the scale of Fig. 4. For finite confinement potentials, our numerical calculation shows that each of the interaction energies due to quantum confinement and charge transfer has a  $1/D$  tail, but with different proportionality constants. Consequently, these details do not change the qualitative behaviors at large  $D$ .

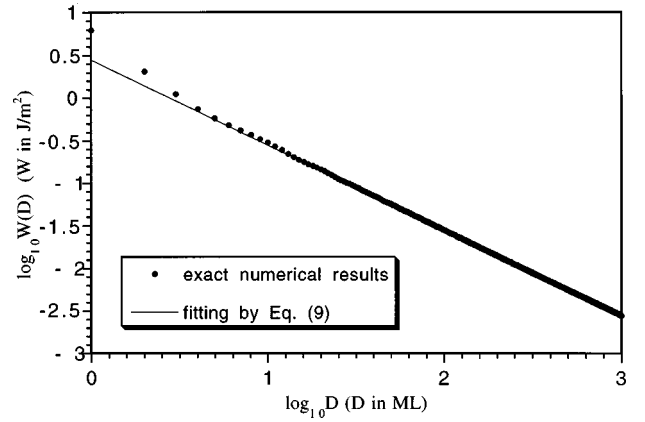


FIG. 4. Comparison between the asymptotic long-range tail with numerical results for a silver film confined by infinite potential on both sides.

Regardless of the physical origins of the long-range forces, our model predicts that the critical film thickness depends inversely on the stress. This fact can be readily exploited in experiments. For example, the stresses in  $\text{In}_x\text{Ga}_{1-x}\text{As}$  films on GaAs substrate depend on the composition  $x$ ; the wetting layer thickness is known to be a strong function of the composition.<sup>3</sup> Furthermore, for a metallic film on a semiconductor substrate, thermal expansion misfit is large; for example, for Ag on GaAs a temperature change can cause a change in stress by  $1.4 \text{ MPa/K}$ . One therefore expects that the critical thickness can be tuned by changing the temperature, as suggested in some experiments.<sup>2-5,21</sup>

In summary, we have shown that suitable long-range interactions of clear physical origins, allied with surface tension, can stabilize epitaxial films against stress. The dispersion force, ubiquitous in all media, can compete with the stress in thin solid films. The electrons confined in metal films can mediate a very long-ranged force capable of stabilizing films of many atomic layers, leading to the existence of a thickness window within which smooth films can be formed. We have also established the dependence of the transition thickness on stress in the presence of these long-range forces. The present work is expected to motivate first-principles-based theoretical efforts aimed at firmly establishing the importance of the dispersion force in stabilizing thin solid films. It is also hoped that experiments will soon establish the existence of the thickness window for the formation of smooth metal films on semiconductor substrates.

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