Effects of Surface Stress on the Elastic Moduli of Thin Films and Superlattices

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A thermodynamic model which predicts a significant sample-size effect on the elastic properties of very thin films and small-period superlattices is presented. Compressive surface stresses cause the in-plane interatomic distances in a thin metal film to decrease as the thickness decreases. For copper films with a thickness of 0.75 nm, a 1% in-plane biaxial compressive strain is obtained which gives rise to a 50% increase in the biaxial modulus. This model also predicts a similar modulus enhancement (supermodulus effect) in multilayered thin films due to strains caused by incoherent interfacial stresses.

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The elastic properties of artificially multilayered and superlattice thin films have been the subject of several recent reviews.[1-4] For systems involving layered fcc metals (e.g., Cu/Ni [5]), enhancements of 100% or more of the in-plane biaxial modulus, as measured by a bulge test, have been reported for a range of composition-modulation wavelengths (layer repeat lengths) centered around 1.5 to 2.5 nm. Such behavior has been termed the "supermodulus effect." The shear moduli of thin films composed of alternating fcc and bcc layers (e.g., Cu/Nb [6]), determined from Brillouin scattering measurements, have displayed a softening of about 35% for a composition-modulation wavelength Λ of about 2.0 nm. For these systems, it was found that an expansion in the interplanar spacing accompanied the modulus decrease.[1] Recently, Clemens and Eesley[7,8] determined Young's modulus *perpendicular* to the plane of the film in Mo/Ni, Pt/Ni, and Ti/Ni multilayered thin films from longitudinal sound velocity measurements. In each case, a softening of approximately 20% was observed at small Λ. Also, it was found that the softening was accompanied by an interplanar expansion, this expansion being proportional to $1/\Lambda$.

Any model of the supermodulus effect must explain both the magnitude of the enhancement (or decrease), and also why the effect occurs only for a limited range of modulation wavelengths (equivalently, why the effect is lost at small and large modulation wavelengths). Most theories have been based either on electronic effects due to the interaction of the Fermi surface with reduced Brillouin zones created by the periodic nature of the composition modulation,[9-11] or on nonlinear elastic effects due to coherency strains.[2,12]

In this Letter we discuss the elastic properties of very thin films of thickness t, and of compositionally modulated thin films of wavelength $2t$, within the framework of nonlinear elasticity and Gibbsian thermodynamics. We present a self-consistent calculation showing that for very thin ($t < 5$ nm) films and small-period superlattices with *incoherent* interfaces, surface stresses[13] can act to significantly displace atoms from the equilibrium positions which they normally occupy in bulk macroscopic assemblies. This change in interatomic distance affects the elastic properties of nanoscale structures. The analysis indicates that the surface stress induces lattice strains which vary approximately as t^{-1} (or Λ^{-1}). Using reasonable values of the surface-stress parameter we obtain in-plane lattice contractions of the order of 1%, causing the biaxial modulus to increase by $\sim 50\%$, and owing to a Poisson effect, a corresponding lattice expansion is induced in the thickness direction with a concomitant decrease in modulus.

A supermodulus effect for the multilayered structure in our analysis results because *all* of the layers undergo in-plane lattice contractions. This is in contrast with the coherency strain model, which attempts to explain the supermodulus effect as due to strains generated by *coherent* interfaces. Coherent films have one type of layer under compression and the other under tension. As a result, the higher-order elastic effects in each type of layer will in large part cancel, resulting in only a small net change in the overall elastic modulus.[14,15] Several difficulties with the model based on electronic effects have been discussed previously.[3]

The surface-stress tensor f_{ij} derives from the variation of the surface free energy per unit area γ with strain e_{ij}, and in the Lagrangian formulation it is given by[16]

$$f_{ij} = \partial \gamma / \partial e_{ij} .$$

For an isotropic surface, the surface stress can be expressed as a scalar f which represents the reversible work required to form a unit area of surface by elastic deformation.[17] It is to be distinguished from the specific surface free energy, γ, which corresponds to the reversible work required to form a new surface by a process such as cleavage. Ackland and Finnis,[18] using an embedded-atomic-type model,[19] calculated the surface stresses of bcc transition metals. They found that in all cases the in-plane relaxation of the {100} surface layer was inward with strains ranging from 1% in tungsten to 16% in niobium. Also, the surface stress acting on these {100} surface layers was larger in magnitude than the corresponding surface free energy for all the elements they examined. Similar results have been obtained by Baskes[20] for the fcc metals using the embedded-atom method.

There have been few experimental results which have given insight into the proper value of f. Mays, Vermaak, and Kuhlman-Wilsdorf[21] measured the lattice parameter of small gold particles as a function of particle size and used these results to estimate the magnitude of the surface stress. Their results indicate that there is a lattice contraction for small gold particles of radius ~ 3 nm compared to the bulk, and therefore f is a compressive stress. Also, they concluded that the magnitude of the surface stress is of the order of the specific surface free energy γ. More recently, Marks and co-workers[22,23] have analyzed the enthalpy and Gibbs free energy of small gold particles in their description of multiply twinned structures, and have assumed that the magnitude of f is of the order of γ. In the following analysis, we take f to be of the same order as γ and to be a compressive stress.

We consider a disk-shaped film of radius r and thickness t. If $t \ll r$, the only surfaces that will contribute a significant surface stress will be the planar surfaces. For a very thin film, a compressive surface stress will biaxially strain the film, reducing the in-plane interatomic distance relative to that of a bulk solid where surface effects are negligible. Assuming the film to be isotropic, the change in internal energy ΔU is given by

$$\Delta U = \int \pi r^2 ts\, de + \int 2\pi r^2 f\, de .$$

In this equation, e is the elastic biaxial strain due to the surface stress, and $s = \int Y de$ is the elastic stress response of the strained film, where Y is the biaxial modulus. The first and second terms represent the volume and surface contributions to the change in strain energy in the film, respectively. The strain e can be determined by minimizing ΔU with respect to e; if the strain dependences of Y, f, and t are ignored, the biaxial strain is given by[24] $e = -2f/Yt$. Thus, we obtain the approximate result that $e \sim 1/t$. However, since e may be large enough that nonlinear elastic effects can be important, the strain dependence of the surface stress and the biaxial modulus should be taken into account. The surface stress f can be expanded in a Taylor series about $e=0$, retaining terms to first order in e: $f = f_0 + (\partial f/\partial e)_0 e$. The biaxial modulus is most conveniently expressed[25] as $Y = Y_0(1 - Be)$. It is also necessary to incorporate the strain dependence of the radius and thickness of the film: $r = r_0(1+e)$, and $t = t_0(1 - \nu e)$, where ν is Poisson's ratio. In each case, the naught subscript refers to values the parameters would adopt under zero strain, i.e., values representative of bulk behavior.

Using the condition $d(\Delta U)/de = 0$, and retaining terms up to $O(e^2)$, we obtain a quadratic equation with roots

$$e = \frac{[2(\partial f/\partial e)_0/Y_0 t_0 + 1] \pm \{[2(\partial f/\partial e)_0/Y_0 t_0 + 1]^2 + (8 f_0/Y_0 t_0)(B/2 + \nu)\}^{1/2}}{2(B/2+\nu)} .$$

The term $(\partial f/\partial e)_0$ may be thought of as a surface stiffness which can be considered to have a value of the order of $Y_0 d_0$, where d_0 is approximately the interplanar spacing. Choosing values appropriate for copper, $Y_0 = 1.6 \times 10^{11}$ Pa, $\nu = 0.3$, $f = 1$ J m^{-2}, $d_0 = 0.21$ nm, and $B = 25$, and evaluating the root corresponding to $e < 0$ yields a value of $e \sim -0.01$ for $t_0 = 0.75$ nm.

Dividing ΔU by the volume $\pi r^2 t$ of the film yields the strain energy density, and differentiating this twice with respect to the strain results in an expression for the effective biaxial modulus Y^* of the thin film,

$$Y^* = Y_0(1 - Be) + (\nu f_0 + Y_0 d_0)/t_0 .$$

Again choosing values appropriate for copper, and for $t_0 = 0.75$ nm, we calculate a relative increase in the modulus $\Delta Y/Y_0 = (Y^* - Y_0)Y_0$ of the order of 50%. This is in good agreement with computer simulations performed by Wolf and Lutsko[26] for thin slabs (and grain boundary superlattices). On account of the Poisson effect, the compressive radial strains give rise to a tensile strain of $-\nu e$ in the thickness direction which results in a decrease in the modulus measured perpendicular to the plane of the order of $-\nu Be$.

Our results indicate that there are significant sample-size effects on the elastic properties of thin solids. In a compositionally modulated thin film, a similar effect will result for modulation wavelengths ~ 1 to 2 nm if the interfacial stresses are sufficiently large. We expect that values of γ for incoherent interfaces formed between different metals will be no less than the interfacial energy of a high-angle grain boundary in the lower-melting-point metal. This is supported by experimental measurements of interphase and grain-boundary energies in many metals,[27,28] as well as theoretical calculations based on the embedded-atom method.[29] These interfacial energies are all of the order of J m^{-2}. If we assume that the interfacial surface stress for an incoherent surface is also of this order, then our previous calculations would also be applicable for multilayered incoherent thin films, when the modulation wavelength is given by $\Lambda = 2t_0 = 1.5$ nm. The analysis predicts an in-plane modulus enhancement $\Delta Y/Y_0$ of approximately 50%, which is the correct order of magnitude when compared to experimental results (though somewhat smaller).[1-5] This enhancement would be (approximately) inversely proportional to Λ.

The biaxial modulus in the direction perpendicular to the plane of the film in superlattices should decrease by a factor of $-\nu Be$. Also, this modulus should fall off approximately as $1/\Lambda$. Perfectly coherent interfaces have relatively little specific surface free energy,[27,28] and assuming that this represents the approximate situation for the surface stress, then we would predict that no elastic-modulus anomalies would occur in structures containing coherent interfaces (characteristic of small-repeat-length superlattices).

Based on the above model the supermodulus effect in superlattices is explained (at least in part) as due to nonlinear elastic effects caused by large elastic biaxial strains generated by interfacial stresses in *incoherent* films. As λ is decreased, the strains become larger, and the modulus changes increase. Eventually, a critical layer repeat length Λ_c is reached below which it becomes more energetically favorable for the interfaces to be *coherent*. As a consequence, the large interfacial stresses of the incoherent interfaces disappear along with the associated compressive strains, and thus, the modulus anomalies are lost.

The above predictions are in good general agreement with the recent experimental results of Clemens and Eesley.[7,8] X-ray diffraction studies[8] of Mo/Ni, Pt/Ni, and Ti/Ni multilayered thin films revealed that decreases in the moduli perpendicular to the plane of the films occurred in superlattices possessing incoherent interfaces. These decreases, as well as the expansion in the interplanar spacings in the direction of the layering, were inversely proportional to Λ. X-ray diffraction characterization[8] of Pt/Ni films showed that this multilayered system had a critical layer repeat length Λ_c of approximately 1.0 nm; when the repeat length of these films went below Λ_c, the elastic modulus abruptly reverted to its large values (i.e., the modulus decrease of incoherent films was lost when the films became coherent at small Λ).[7,8] All of these results are in agreement with the theory presented here.

In conclusion, we have presented a theory concerning anomalous elastic properties of thin films and superlattices based on large elastic strains created by surface stress effects. This theory gives several predictions that can be tested experimentally. It is predicted that the in-plane biaxial modulus should increase (the supermodulus effect), the biaxial modulus perpendicular to the plane of the film should decrease, and the ratio of this decrease to the enhancement should be of the order of Poisson's ratio. The predicted modulus increases for superlattices (approximately 50%) can account for at least part of the supermodulus effect. Unlike the coherency strain model[2,12] that predicts a supermodulus effect for coherent superlattices, we predict that elastic anomalies occur in incoherent multilayers, and that these anomalies disappear when the films become coherent at very small repeat lengths. These modulus changes, as well as the elastic strains that give rise to them, should be approximately proportional to $1/\Lambda$. As discussed above, all of these predictions have been borne out experimentally.[7,8] Also, in contrast to models that claim that the changes in lattice constant perpendicular to the plane of the film are due to strains localized at the interface in superlattices,[7,8] we predict that within each metal layer (of thickness t_0) there will be a *uniform* expansion in the d spacing in this direction. This expansion will depend on the elastic and thermodynamic properties of the particular layers and the incoherent interfaces. Sensitive x-ray analyses should be able to address this issue.

It should be mentioned that there is a caveat associated with these considerations with regard to our conventional notions of epitaxy which have been developed over the past forty years. Equilibrium elastic theories describing the maintenance of coherency consider a balance between the elastic strain energy in the overlayer and the energy which would result if part or all of this strain were relieved by the formation of misfit dislocations causing the interface to become partially or completely incoherent.[30] As the overlayer relaxes, it is assumed that it approaches its normal equilibrium (zero strain) lattice constant. Our analysis predicts that a thin overlayer will relax to a strained condition and that this should be considered in the overall energy balance determining the maintenance of epitaxy. This effect will be important for layers of thickness ~ 10 nm or less and will tend to alter the predictions of the coherent-to-incoherent transition based upon misfit and film thickness.

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