Anomalies in the Elastic Properties of Metallic Multilayers

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Using variable-cell molecular dynamics, we have studied the elastic constants of the metallic multilayer system Cu/Pd with embedded-atom potentials. Planar coherency remains intact at very low repeat distances (wavelengths), and the biaxial modulus shows decreases up to about 50%. At small repeat lengths, we predict that these coherent multilayers will become soft, in agreement with recent ultrasonic experiments, but in contrast to bulge-test observations.

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Over the last decade multilayer films have begun attracting the attention of researchers, as reports of unexpected physical properties arising from these artificial structures begin to surface. Although semiconducting films are also of current interest, the multilayer films discussed in this paper constitute a structure of n layers of metal A deposited on m layers of metal B, which is repeated along the direction normal to the layers. The supermodulus effect, which is identified as the anomalous enhancement of elastic constants of a metal-metal multilayer film, has been observed[1] in many transition-metal multilayer systems at small (10–20 Å) repeat lengths (or wavelengths). The biaxial modulus of these (111) films has been reported to increase by 200%–300% over the values of their metallic components. The usual experiment that has been done in most of these cases is referred to as the bulge test.[1]

Around a narrow region of composition wavelength Λ, multilayer films such as Cu/Ni, Cu/Pd, Ag/Pd, and Au/Ni have shown enhancements in their biaxial moduli through bulge-test experiments.[1] The orientation of the films seems to affect these changes. It is also interesting to note that the multilayer system Cu/Au has shown no (bulge test) enhancements in its elastic constants at all. However, longitudinal sound velocity measurements[2] have revealed an about 20% softening of the Young's modulus perpendicular to the films for (111)-like multilayer systems such as Mo/Ni, Pt/Ni, and Ti/Ni. The softening of this elastic constant was accompanied by interplanar expansions. For Pt/Ni, which is a fcc metal on a fcc metal-type multilayer, there was no disorder up to a modulation wavelength of 17 Å and the sound velocity showed a dip in the region 17–50 Å.

The current theories of these anomalies are usually classified into two categories. One is that these are associated with singularities in the dielectric function, or Fermi surface—Brillouin-zone-type interactions. By changing the screening effects drastically it may be possible to produce anomalies in the elastic constants. The second category is based on coherency strains. It is argued that when coherent [i.e., the atom sites in a given layer match those in the neighboring layers according to fcc (as in above examples) stacking, irrespective of the atom type of the neighboring layers] multilayers of two different metals are formed each layer of a given type of metal is under a strain, and that these strains could give rise to changes in the elastic constants. Many authors have discussed the merits of the above and/or searched for the origin of these anomalies.[3]

In this paper we present new and interesting results that may shed some light on these elastic anomalies. (a) According to our knowledge, this is the first calculation that is able to determine a wavelength up to which the interface effects grow and beyond which they begin to die, i.e., the existence of a turning point in the elastic properties. (b) The interplanar distances do change substantially due to the presence of the interface for multilayers of small repeat lengths. For the system Cu/Pd stacked along (001), there are large contractions of the Cu-Cu interlayer spacing together with expansions in the Pd-Pd interlayer spacings compared to their bulk values, while the (common) intralayer distances represent a Λ-dependent spacing closer to that of bulk Pd. (c) We also notice near perfect coherency (within the constraints on our ensembles) of these planes at small repeat lengths (up to $\sim$50 Å). (d) The biaxial modulus is seen to decrease for small Λ in contrast to bulge-test experiments.

In the presence of a massive defect (i.e., the interface), there could be many metastable states and molecular dynamics (MD) allows us to sample a larger portion of the phase space compared to any static approach. However, we do not include any vacancies or dislocations. Our method of calculating elastic constants is based on a direct technique of monitoring the strain due to an applied stress. This is different from conventional static approaches where the symmetry of the system is used to reduce the number of coefficients of the elasticity tensor. Briefly, the calculational method and the details of the calculations are as follows. We use the variable-cell MD technique (with a constant number of particles) introduced by Parrinello and Rahman.[4] It is essential to use a technique where the shape and the size of the cell are varied, since we calculate our elastic constants by applying an external stress and then determining the resulting

strain. The Poisson contraction (or expansion as the case may be) is, of course, allowed under the present scheme, since the shape and the size of the MD cell are allowed to vary. This is by far a better way of theoretically calculating the elastic constants, since we neither make use of any lattice symmetry nor have to (numerically) calculate any derivative of deformation energy.

The Lagrangian is exactly as defined in Ref. 4. Our MD time step Δt is 2.0362×10^{-15} sec. The system is allowed to evolve for about 5000 time steps and averages are taken during the next 2000 time steps ($=N_{\rm av}$) using standard techniques for low-temperature MD under zero stress. This should be viewed as a search for metastable phases. *We believe that the role of MD is crucial here to overcome energy barriers between metastable phases.* For example, a direct minimization such as used by Dodson[3] is unlikely to sample the different interlayer distances seen here. The initial MD cell is tetragonal in shape with a square base perpendicular to the modulation direction. The sensitivity of our results with respect to the size of the basal plane and other MD parameters such as $N_{\rm av}$ was found to be negligible.

The potentials used here are derived from an embedded-atom method (EAM).[5] The total energy in the embedded-atom approach is given in terms of a short-ranged pair potential and an embedding function which is density dependent and contains the many-body effects. We have used an analytic EAM model which has been successfully applied to calculate thermodynamic properties of Cu.[6] Our approach is similar to that of Johnson,[7] but goes beyond nearest neighbors. The parameters of the model are determined by fitting the experimental values of the lattice parameters, elastic constants, and vacancy formation energies of the pure metals and the heat of solution of a Cu-Pd alloy. The short-ranged, pairwise interaction between Cu and Pd was constructed by taking an arithmetic average of those for Cu-Cu and Pd-Pd. To check the accuracy of this model, we have calculated the lattice parameter of the alloy Cu_3Pd, and found agreement to better than 99% with experiment. Other tests include some comparisons of energetics with more accurate first-principles heats of formation, showing that the energies obtained here are reasonable. The energetics of the multilayers will be discussed again in a later section.

The biaxial modulus Y_B was calculated by applying a biaxial stress in the plane of the film and monitoring the corresponding in-plane strains ϵ_B. According to our experience, Y_B has a relatively large (statistical) uncertainty for small ϵ_B. In order to obtain a reasonably accurate value, a number of different biaxial stresses were loaded and the (extrapolated) limiting value of Y_B as $\epsilon\rightarrow 0$ was identified as the biaxial modulus of the multilayer film corresponding to the given modulation wavelength. This procedure was repeated for multilayers of different modulation wavelengths. As another check, the biaxial moduli of the pure metals were also calculated *with the same procedure* and found to be in reasonable accord with experiment.

The fascinating result we see for coherent Cu/Pd multilayer films with (001) stacking is a *decrease* (by about 50%) of the biaxial modulus with increasing modulation wavelength (from 1 to 4.5 nm); i.e., the multilayer appears to go soft as the repeat distance is increased (Fig. 1). We also know that for large modulation wavelengths the biaxial modulus should be around the average value of the ones corresponding to the pure metals. We have not carried out a MD simulation of such a large cell (a) due to computer time limitations, and (b) because recovery back to bulk may be due to mechanisms such as vacancy formations and dislocations, which were not considered in the present simulation. However, in Fig. 1, we see a clear indication of a minimum and the curve is beginning to rise around 4.5 nm. We have also found that the biaxial and Young's moduli are approximately linear in ϵ_B (similar to Ref. 8) and hence suggest the presence of an anharmonic term in the energy as a function of ϵ_B.

The interplanar distances of this system under *zero stress,* particularly for Cu, show large changes compared to bulk. In Fig. 2, these are shown for $\Lambda=5$ nm. These changes are both qualitatively and quantitatively reasonable. Let us define $a_\parallel(\Lambda)$ to be half of the fcc lattice constant in the coherent planes for a given Λ. For the relaxations shown in Fig. 2 ($a_\parallel=3.65$ a.u., and average interplanar distances of 3.0 and 3.73 a.u. for Cu and Pd,

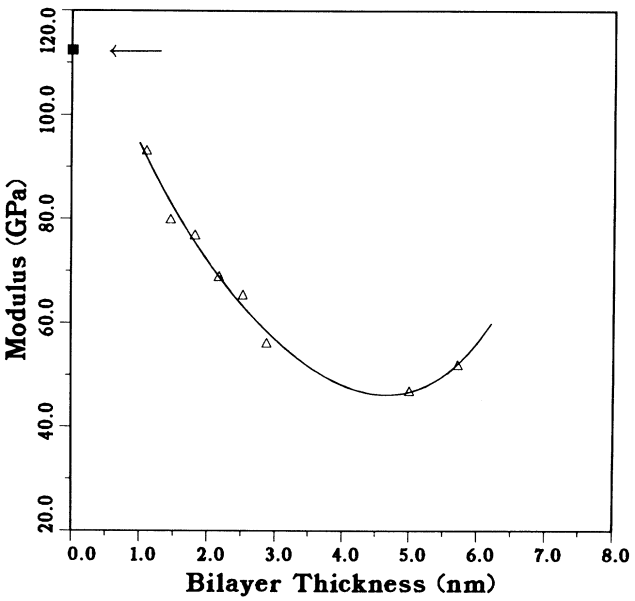

FIG. 1. Biaxial modulus for (fcc) Cu/Pd coherent multilayer stacked along (001) direction vs the modulation wavelength (bilayer thickness) Λ. The arrow indicates the calculated average value of Cu and Pd biaxial moduli for the same stacking, which is about 113 GPa. The interface effects play a crucial role here.

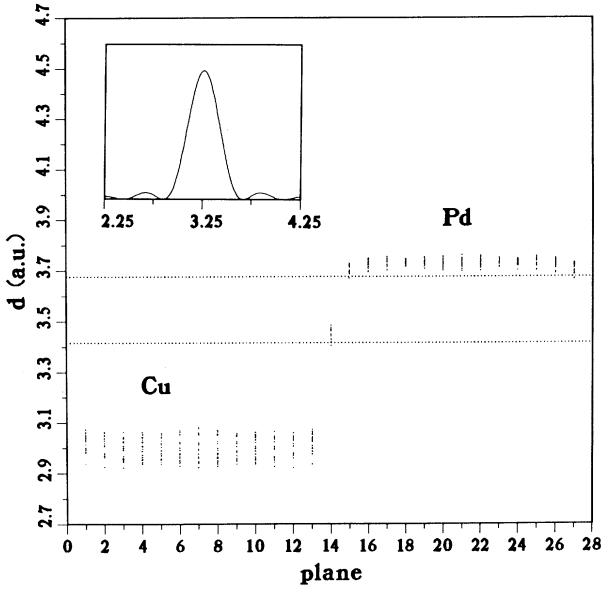

FIG. 2. Interplanar distances over a time period of 2000 time steps after equilibration under zero stress for 14 layers of fcc Cu on 14 layers of fcc Pd, stacked along (001). The horizontal dotted lines show the (observed) bulk interlayer spacings for Cu (at 3.42 a.u.) and Pd (3.68 a.u.), which were used to fit the embedded-atom method. The modulation wavelength Λ is about 5 nm. Inset: In-plane (1D) structure factor for 14Cu/14Pd. The horizontal scale is in Å^{-1}. The peak corresponds to a value of 3.65 a.u. for $a_{\parallel}$. Note that $a_{\parallel}$ depends on Λ. Both Cu and Pd planes give rise to an identical curve after equilibration, indicating almost perfect coherency.

respectively), a simple calculation of an average volume per atom for each species turns out to agree to better than 99.5% with the bulk metallic values; i.e., the equilibrium values are such that the metallic volume per atom is conserved for each species. Note that the equilibrium value of $a_{\parallel}(\Lambda)$ in Fig. 2 *happens to be not* at the average of the bulk Cu and Pd values, but closer to that of Pd. Although the films remain coherent, the equilibrium structural parameters for the multilayers show significant changes from their initial values in the simulation. We would also like to stress that coherency was only an initial condition, and during the simulation there were no explicit constraints forcing the films to be coherent. Even with initial conditions somewhat away from coherency, the films (rapidly) relax back to being coherent.

There are much more accurate first-principles multilayer calculations[9] that show a similar behavior with respect to volume per atom, which gives us more confidence in our potentials. These calculations also find that in a multilayer of the type considered here, the change in the heat of formation due to the layering can be understood to a remarkable degree by considering a simple model consisting of structural (elastic) and bonding energies. Similar concepts may be used to understand our results as follows.

The range of Λ values considered here ($0 < \Lambda < 5$ nm) is the experimentally relevant range.[2,3] Following Ref. 9, there are two competing energies that will determine the energy surface and hence the elastic constants. One is the (elastic) distortion energy (compared to stable, pure phases), which stays positive. The other is the interface bonding energy ξ, as defined in Eq. (2) of Ref. 9. For $\Lambda = 5$ nm, we have estimated ξ to be about -0.2 eV per interface atom, using the total energies of the multilayer, bulk Cu, bulk Pd, and an estimate of the (elastic) distortion energy of the multilayer film. For this case, the interface bonding energy is (in close agreement with heats of similar alloys and) of the same order of magnitude as the elastic energy of the cell, but opposite in sign. This clearly shows that we have not reached the elastic limit and that continuum elastic theory alone will not be sufficient to explain the behavior seen in Fig. 1. The initial drop of the biaxial modulus is due to this comparable (negative) interface energy which is affecting the curvature of the total energy surface. We have also seen a direct correlation between the in-plane biaxial modulus and $a_{\parallel}(\Lambda)$, which shows a weak maximum around the turning point of the in-plane biaxial modulus.

With increasing values of Λ (> 5 nm), the elastic distortion energy will continue to increase and dominate over the interface energy (which will be roughly independent of Λ). To lower this energy cost, both Cu and Pd will begin transforming into pure, bulklike regions far way from the interface, through various mechanisms, such as vacancies, misfit dislocations, etc. *Our simulation did not consider such mechanisms and hence the turning point of Fig. 1 may not be directly compared to the real experimental situation where disorder will be the key mechanism for the above transformations.* However, we believe that the initial softening of the modulus seen for these coherent multilayers is realistic and supported by experiments such as Ref. 2; i.e., elastic anomalies do exist even for coherent multilayers.

According to a model developed by Rytov[10] and extended to a finite interface in Ref. 2, the longitudinal velocity of sound in the multilayer films is given (approximately) by

$$\left[\frac{V_i(\Lambda)}{V}\right]^2 = \left[\frac{2C}{C_i(\Lambda)} - 1\right]^{-1}, \tag{1}$$

with $C = 2C_A C_B/(C_A + C_B)$ being an average (longitudinal) elastic constant. (A and B refer to the two types of metals and V is an average sound velocity. C_i and V_i indicate the new values of C and V in the multilayer for a given Λ.) Note that we have assumed the interface to extend over a length Λ, and the main point here is to show that the behavior of the elastic constants in the multilayers is directly transformed into a closely related functional form for the velocity of sound. In fact, as seen in Fig. 1, the deviations of the elastic constants and hence of the velocity of sound from their average values

will grow up to about 5 nm. However, for $\Lambda > 5$ nm, the interface effects on the elastic properties and on the velocity of sound will disappear as Λ^{-1}.

There is one other calculation, using a Morse potential and variable-cell MD, reported in the literature.[11] There are some similarities and important differences seen when our results are compared with the above, in which only a Ni supercell was studied (hence no explicit Λ dependence). The role of the other metallic component was said to be "passive." However, according to our picture, it is the different atomic environment across the interface which is the driving force of the anomalies. The calculation of Ref. 11 is unable to obtain the interface-driven distortions in the interlayer spacings as there is simply no interface in that calculation. Note that our definition of these moduli is in the limit when the strain (ϵ) goes to zero, and, as a function of increasing strain, our calculated moduli increase (as those in Ref. 11). However, for these multilayer films, the calculated limiting value of the biaxial modulus (for $1 < \Lambda < 5$ nm) is less than that for either of the pure metallic components. This comparison leads us to the conclusion that one has to be careful in interpreting some reported enhancements, since at least according to our experience the moduli are strain dependent and show enhancements with increasing strain. The slope of Y_B vs ϵ_B shows signs of being sensitive to the model. As noted in Ref. 12, the inner components of the elastic constants do not vanish for noncentrosymmetric solids and can be complex functions of force constants.

The experimental picture is far from being clear. As mentioned previously, the mechanical bulge-test results show huge enhancements in elastic constants (biaxial moduli) for Cu/Ni, Cu/Pd, etc. Brillouin light scattering[13] can be used obtain a surface wave velocity which is closely tied to that of a bulk transverse wave with a polarization perpendicular to the free surface. These experiments have been used to calculate a softening in a shear modulus for V/Ni, Nb/Cu, etc. There are recent ultrasonic experiments which seem to show a softening of Young's and biaxial moduli for Mo/Ni, Pt/Ni,[2] and Cu/Pd,[14] and all these changes are at least an order of magnitude smaller than those reported in the bulge-test experiments. The quality of the films and the interface could be crucial for a systematic comparison. Up to now there has not been much of an effort to compare different experimental techniques with respect to obtaining elastic constants of high-quality multilayer films. It is important to work with single crystals and make the measurement without damaging the film.

In conclusion, we have seen anomalous behavior in the biaxial modulus of coherent multilayer films with respect to the changes in the modulation wavelength. We see a decrease in the biaxial modulus of Cu/Pd of about 50% (and expect the Young's modulus to show similar behavior) as seen in ultrasonic methods for Pt/Ni (Ref. 2) and Cu/Pd (Ref. 14). Another important finding is that the interplanar distances show rather substantial changes from their bulk values, while the intraplanar interatomic distances for each layer remain at a (common but not necessarily average) value between those of the two metallic components, resulting in near perfect coherency. The volume per atom for each species remains very close to the metallic bulk values. The interface effects are essential to understand these anomalies which are about an order of magnitude smaller than those reported by bulge-test experiments (and opposite in sign) but about the same magnitude as those reported in the Brillouin light scattering and ultrasonic experiments. We conclude that the interface region is elastically soft and hence easy to distort in the coherent metallic multilayer Cu/Pd. These results should hold true for similar metallic multilayers.

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