Relationship between Interfacial Strain and the Elastic Response of Multilayer Metal Films

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We have investigated the structural and elastic properties of three distinct multilayer systems: Mo/Ni, Pt/Ni, and Ti/Ni. We demonstrate that the commonly observed lattice expansion perpendicular to the film plane is not a bulk effect, but is localized at the interface between the contacting metals. Incorporating the measured interfacial expansion into a universal binding relation, we show that the measured elastic softening versus compositional-repeat distance can result from the interfacial strain.

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Investigations of the elastic properties of two-component multilayer metal films have received considerable attention in recent years.[1] In most cases, multilayer films are found to soften as the compositional-repeat distance (bilayer thickness, Λ) is decreased.[2-6] In rare instances, a hardening of elastic properties has been observed and the so-called supermodulus effect continues to be a motivating factor in these studies.[7,8]

The changes in elastic response have been attributed to electronic effects arising from the layering,[9] as well as to the structural changes which accompany an observed lattice strain perpendicular to the film plane.[1,10,11] It is usually assumed that the strain is distributed throughout the bulk of the multilayer film and that correlated elastic changes are bulk effect. Bennett, Leavitt, and Falco[12] have shown that in Mo/Ta films the strain normal to the film plane is localized at the interfaces. This view is supported by the recent calculations of Wolf and Lutsko[13] emphasizing the importance of the atomic scale structure at the interfaces.

We believe that the Mo/Ta system is not unique, and that the observed change in the average lattice spacing is localized at the interface in most of the metal systems studied. In this Letter, we report on the elastic properties of three distinct classes of multilayer films composed of the metal pairs Ti/Ni, Pt/Ni, and Mo/Ni. In spite of the dramatic structural differences, we show for the first time that in all three cases the observed increase in average lattice spacing is localized at the metal-metal interfaces. Furthermore, the observed softening of the longitudinal elastic response can be described by a simple continuum model which incorporates the reduced interfacial adhesive energy resulting from the interfacial strain.

Multilayered samples were prepared by passing oxidized silicon wafers under shielded sputter sources in a cryopumped dual-source magnetron deposition system. The base pressure was 10^{-7} Torr and the deposition pressure was 2.3×10^{-3} Torr of getter-cleaned Ar. The sputter rates (0.3–0.5 nm/sec) were controlled by rate monitors set to produce an equal thickness of each constituent per bilayer. Samples were produced with bilayer periods between 1 and 20 nm, and total thicknesses between 200 and 300 nm. The composition of each film was measured by electron microprobe analysis and composition fluctuations were found to be less than 1% for Mo/Ni, and about 2% for Pt/Ni and Ti/Ni.[14] Film thicknesses were determined by multiplying the number of bilayers and the bilayer thickness measured by low-angle x-ray diffraction.

Most studies of thin-film elastic properties have relied on Brillouin scattering from surface acoustic waves to determine the sound velocities.[1-6] In contrast, we directly measure the longitudinal sound velocity to determine the elastic response in a direction perpendicular to the film plane.[15] Our measurement is based on the generation of an ultrashort duration (4 psec) acoustic pulse by the surface deformation resulting from the absorption of a short optical pulse. The local surface expansion launches a compression pulse which is partially reflected by the acoustic impedance mismatch at the film-substrate interface. We detect the return of the acoustic pulse echo by means of the change in surface reflectivity induced by the dynamic strain of the metal lattice within the optical skin depth. Dividing the film thickness by the measured pulse transit time yields the acoustic velocity. This measurement utilizes two synchronized lasers (excite and probe) which emit visible light pulses of 4-psec duration.[15]

X-ray diffraction was performed using Cu $K\alpha$ radiation in the conventional symmetric reflection geometry which confines the scattering vector to the growth direction. A composition modulation in the growth direction will produce a series of peaks in the low-angle diffraction, and the position of these peaks can be used to determine the bilayer thickness (Λ). The relative peak intensities yield the shape of the composition wave and an upper-limit interface width can be deduced from the highest-order peak resolved. We observe sharp, intense diffraction peaks from all of the samples indicating the presence of a well defined composition modulation. We estimate an upper-limit interface width of 0.5 nm in Pt/Ni and Mo/Ni, and 0.9 nm in Ti/Ni.

High-angle x-ray diffraction measurements indicate

strong crystalline texture within the constituent layers. In the case of the fcc metals, Ni and Pt, the (111) crystalline plane is parallel to the plane of the film. The Mo (bcc) layers are oriented with the (110) plane in the film plane, while Ti (hcp) has the (001) plane parallel to the film. Interface structure can be deduced from the high-angle diffraction where the presence (absence) of superlattice satellite lines indicates crystalline (disordered) interfaces.[16] Despite the modest 10% in-plane lattice mismatch occurring in Pt/Ni (fcc/fcc) we observe sharp and intense diffraction peaks with satellites. This indicates the presence of crystalline interfaces which are found to exist in all of the bilayer thicknesses produced. Analysis of the peak widths indicates that structural coherence extends through several bilayer periods.

Similar behavior is observed in Mo/Ni (bcc/fcc) for $\Lambda > 2$ nm. The observation of long-range coherence in the growth direction may be related to the orientation which matches the spacing between rows of close-packed atoms in the mating (110) bcc and (111) fcc planes.[3,10,17] As in previous studies of this system, long-range crystalline order is not observed for $\Lambda < 2$ nm.[3]

In the Ti/Ni (hcp/fcc) system, the (001) Ti planes and the (111) Ni planes have the same symmetry, but there is a 15% lattice mismatch. For $\Lambda > 4.6$ nm we observe crystalline order within the elemental layers, but the absence of satellite peaks indicates that the interface region is disordered. For $\Lambda < 4.6$ nm, we observe an abrupt transition from crystalline to disordered structure within the elemental layers.[18]

Although these systems appear to exhibit different structural behavior as a function of Λ, they can be analyzed on common ground. When the interfaces are crystalline the position (θ) of the high-angle diffraction satellite peaks follows the relation

$$\frac{2\sin\theta}{\lambda} = (\bar{d})^{-1} \pm \frac{n}{\Lambda}, \tag{1}$$

where $\bar{d}$ is the average lattice spacing in the growth direction, λ is the radiation wavelength, and n is the integral order of a particular satellite peak.[3] The measured $\bar{d}$ will be independent of Λ and given by $\bar{d}_0 = (n_1 d_1 + n_2 d_2)/(n_1 + n_2)$ (where $n_1 + n_2$ equals the total number of planes in bilayer), when the interface spacing is assumed to be the average of the intrinsic interplanar spacings of the constituents (d_1 and d_2, respectively).[3]

A common practice in the analysis of multilayer films is to measure $\bar{d}$, to determine if the difference $\Delta\bar{d} = \bar{d} - \bar{d}_0$ is a function of Λ. This procedure was applied to the Mo/Ni and Pt/Ni systems and the results are shown in Fig. 1. The absence of satellite peaks in the Ti/Ni system required a direct measurement of the Ni lattice spacing in the range of Λ where crystallinity was observed. The Ti/Ni data are actually the relative change in the spacing of the Ni layers, where $\Delta d_{\mathrm{Ni}} = d_{\mathrm{Ni}}^{\mathrm{expt}} - d_{\mathrm{Ni}}^{\mathrm{bulk}}$.

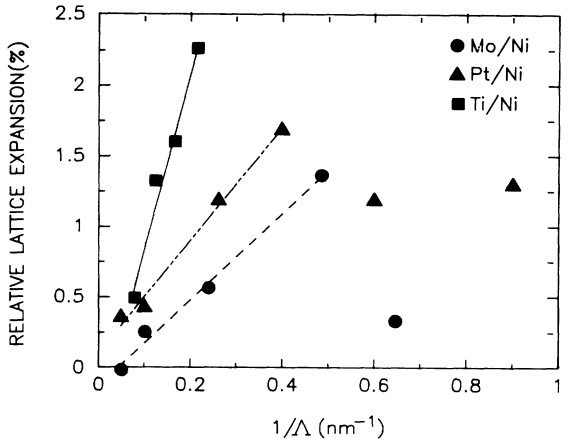

FIG. 1. The relative change in average lattice parameters ($\Delta\bar{d}/\bar{d}$ for Mo/Ni, Pt/Ni, and the Ni lattice in Ti/Ni multilayers) plotted vs the inverse bilayer thickness. The lines are fitted to the regions of apparent uniform expansion.

We have chosen to plot the relative change in the average interplanar spacing versus the *inverse* bilayer period to illustrate an important and unifying feature. All systems exhibit an apparent wavelength-dependent lattice expansion in the growth direction for 20 nm $> \Lambda > 2$ nm. The fact that this expansion scales *linearly* with $1/\Lambda$, is a crucial trend which can be accounted for by an interface spacing which deviates from the average of the constituent spacings. That is, if $d_i = [(d_1 + d_2)/2] + \delta_d$ (where δ_d represents an expansion of the interfacial lattice spacing), then it can be shown that

$$\Delta\bar{d} = \bar{d} - \bar{d}_0 = 2\bar{d}\delta_d(1/\Lambda), \tag{2}$$

and thus a Λ dependence naturally results. We emphasize that this *apparent change in bulk interplanar spacing is actually the consequence of a constant deviation at the interface and the fact that the number of interfaces per unit volume scales as* $1/\Lambda$.

Although the Ti/Ni system exhibits highly disordered and extended interfaces relative to Mo/Ni and Pt/Ni, the same linear behavior is observed. This can be explained by the presence of Ni planes near the interface which have a larger spacing than the bulk of the Ni layer, leading to a similar expression for $\Delta\bar{d}$ vs $1/\Lambda$. By fitting the linear regions of Fig. 1, we have obtained the interface expansion δ_d for each of the metal systems and the results are given in Table I. Departures from the linear response results from the structural transformations which will be discussed in a future publication.

We now examine the correlation with the observed changes in elastic properties. The results of our sound velocity measurements are shown in Fig. 2, where we have plotted the relative velocity squared versus Λ. The velocity squared is a direct measure of changes in the elastic response with changes in the bilayer period, when the average density of the multilayer film is unchanged.

TABLE I. Observed interface expansion, calculated universal scaling length, and relative interface elasticity. The value for Ti/Ni is an estimated value (see text).

System	δ_d (Å)	l_{AB} (Å)	C_i/C_e
Mo/Ni	0.15	0.54	0.54
Pt/Ni	0.20	0.54	0.44
Ti/Ni	0.32	0.64	(0.5)

We have normalized our measurements relative to the values obtained at the largest Λ, where the effects of layering are minimal. This permits a comparison of all three systems which are found to exhibit longitudinal elastic softening (decreasing sound velocity) in the same region where the lattice expansion is observed to be proportional to $1/\Lambda$. Further softening is observed in Mo/Ni and Ti/Ni as Λ is decreased below the point where long-range order disappears (2 and 4.6 nm, respectively). However, in the case of Pt/Ni which does not disorder at small wavelengths, the sound velocity is observed to increase at $\Lambda=1.7$ nm. This is likely associated with the observed reduction in the average lattice parameter.

The correlation between the interface structure and the elastic response can be explained by the affect of interfacial expansion on metallic adhesion. It has been shown that metallic binding energy versus distance exhibits universal behavior under a simple two-parameter scaling.[19] For adhesion between metals A and B the relation between the elastic stiffness constant perpendicular to the interface (C_i) and the equilibrium adhesion energy (σ_{AB}) is given by

$$C_i=\frac{d_i\sigma_{AB}}{l_{AB}^2}\left[\frac{d^2E^*(a^*)}{da^{*2}}\right]\equiv C_e\left[\frac{d^2E^*(a^*)}{da^{*2}}\right], \quad (3)$$

where l_{AB} and $E^*(a^*)$ are the universal scaling length and energy function, respectively, and C_e is the equilibrium interface elasticity. The universal scaling length is estimated by one averaging the scaling lengths for each metal, and the energy function is well approximated by $E^*(a^*)=-(1+a^*)\exp(-a^*)$.[19,20]

Equation (3) predicts a reduction in the interfacial elastic response for a given interface expansion ($a^*=\delta_d/l_{AB}$), and the results are listed in Table I. This approach is justified when the interface is atomically abrupt (Mo/Ni and Pt/Ni). However, in the case of Ti/Ni, the model is complicated by the presence of diffuse interfaces and we can only estimate a value of $C_i=C_e/2$.

The predicted interfacial softening can be used to calculate the change in sound velocity of a multilayer film as a function of Λ. We have extended the formalism of Rytov[21] to include an interface of finite extent, and we find that the expression for the longitudinal sound velocity in the presence of perturbed interfaces (V_i) relative to that without (V) is given by

$$\left[\frac{V_i}{V}\right]^2=\left\{1-\frac{2n_id_i}{\Lambda}\left[1-\frac{2}{C_i}\left[\frac{C_AC_B}{C_a+C_B}\right]\right]\right\}^{-1}. \quad (4)$$

The indices A, B, and i represent metal A, metal B, and the interface region, respectively, where the interface is n_i lattice spacings (d_i) thick with the density equal to the average of the constituent densities.[6,21,22] We see from this expression that the effective elastic constant of a lamination of A and B is $C_e=2C_AC_B/(C_A+C_B)$, and if the interface elasticity (C_i) departs from this value then a Λ dependence will occur.

The results of our model calculation are shown in Fig. 3 where we find qualitative agreement with the experimental results shown in Fig. 2. Although we have used an estimated interfacial softening in Ti/Ni, we have modeled the diffuse interfaces by using the values $n_i=4$

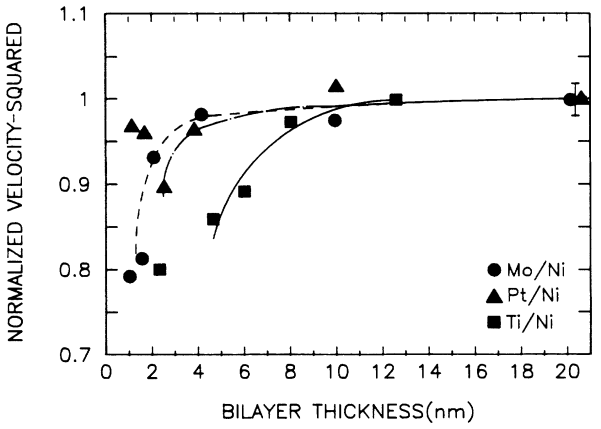

FIG. 2. Measured sound velocity (squared and normalized) vs bilayer thickness. The velocities measured at the largest Λ are $V=5866$ m/sec Mo/Ni; 4496 m/sec Pt/Ni; 5800 m/sec Ti/Ni. The error bars correspond to a maximum ± 2-psec error in the pulse-echo time delay. The curves are a visual aid.

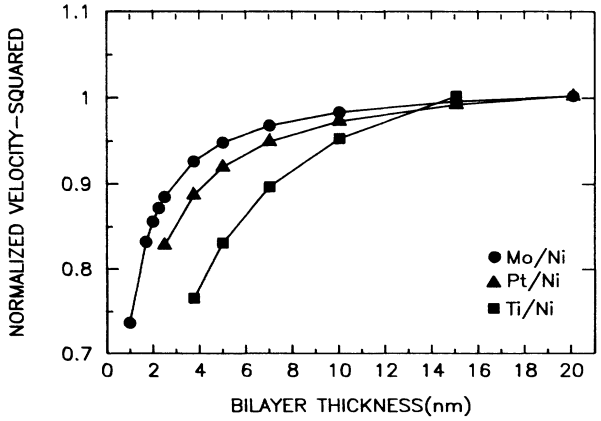

FIG. 3. Model calculation of the sound velocity (squared and normalized).

and $d_i = d_{Ni} + \delta_d/4$, in agreement with previous studies of the Ni/Ti system.[18]

In conclusion, we have shown that the measured expansion in the average lattice spacing of metal multilayer films can be attributed to a local expansion at the interfaces. The distinct differences in the interfacial structure we have examined leads us to conclude that this phenomenon is not unique to the particular metals studied. This interfacial expansion can explain the apparent softening of the bulk elastic response in multilayer metal films as the compositional modulation distance is decreased.[23] Furthermore, our measurements of the longitudinal sound velocity are in agreement with our model of the elastic softening.

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[22]If the interface density (ρ_i) is different from the average density of the two metals (ρ_{av}), an additional factor of $[1-(2n_i d_i/\Lambda)(1-\rho_i/\rho_{av})]^{-1}$ multiplies the right-hand side of Eq. (3). Determination of the interface density is a three-dimensional problem which is beyond the scope of this work.

[23]If the interface lattice spacing contracts, the universal binding model will predict an increase in the interfacial adhesion and our formulation for the sound velocity will infer an increased stiffness as Λ decreases.