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"Supermodulus effect" in Cu/Pd and Cu/Ni superlattices

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The elastic and structural properties of Cu/Pd and Cu/Ni superlattices have been determined. Microstructurally the films have the same growth mechanisms, growth textures, and composition modulation amplitudes, as in past studies where the "supermodulus effect" was reported. Advanced techniques have been used to measure the flexural, shear, and Young's moduli of the thin films, and *no* significant anomalous elastic behavior has been observed.

The linear elastic properties of a material of a given chemical composition are found to be relatively insensitive to macroscopic processing steps.[1] Thus, the finding that various measured elastic moduli of a number of transition metal–noble metal superlattices varied radically, as a function of the wavelength of the composition modulation, λ, has been greeted with much interest and some skepticism. This so-called supermodulus effect has been previously reported in the Cu-Ni,[2,3] Cu-Pd,[4] Ag-Pd,[5] and Au-Ni (Ref. 4) systems; for composition modulation wavelengths in the vicinity of 2 nm, the measured elastic moduli (biaxial, flexural, shear, and Young's) were reported to be 2–4.5 times greater than the values predicted from the bulk elastic constants of the two metals. Films with $\lambda \leq 1$ nm or $\lambda \geq 3.5$ nm were found to have elastic moduli approximately equal to the values predicted for such a microstructure, based on the bulk elastic constants of the two metals. Since the initial reports of these experimental findings a number of theories have been presented attempting to explain or rationalize the supermodulus effect.[6–9] There have also been reports of anomalous elastic properties in superlattices consisting of two materials which are immiscible in each other,[10] but the effect reported in these studies is an order of magnitude smaller, generally of the opposite sign—i.e., a softening—and probably has a different physical origin.

In all but one of the previous studies[2,4,5] the elastic properties were determined using the bulge test, and there is a serious problem with respect to the interpretation of the raw data for this technique.[11] Furthermore, some of the procedures used in the remaining study[3] are problematic. To help resolve this controversy, we have performed a detailed reexamination of the elastic properties of two of the systems in which a supermodulus effect was previously reported.

Both the Cu/Pd and Cu/Ni superlattices were prepared in a high-vacuum (HV) chamber which contains two electron beam guns, computer-controlled substrate and shutter wheels, and separate quartz-crystal monitors to control the deposition process.[12] The films were grown using the constant-thickness procedure[13] on mica substrates. The Pd was 99.99 wt.% pure, while the Cu and Ni were 99.999 and 99.99 wt.% pure. To obtain a strong [111] growth texture, a 0.15 μm thick Cu predeposition layer was deposited at 573 K at a rate of 2 Å s^{-1}; the same rate was used to deposit the superlattice layers. The vacuum in the chamber was approximately 1×10^{-12} bar prior to deposition, and $\leq 3\times10^{-11}$ bar during deposition. After the predeposition layer was deposited, the substrate temperature was decreased to 363–393 K for the Cu/Ni films and 338–348 K for the Cu/Pd films. The total thickness (and hence the number of superlattice wavelengths) was chosen so that the thin films could be removed from their substrates and their mechanical properties tested. This required that the total thickness of each thin film, including the predeposition layer, be roughly 1.2–1.5 μm; details of the deposition process are presented in Refs. 14 and 15. The major difference between the present growth conditions and those employed in prior studies[2–5,11] was the background vacuum; it was approximately 2 orders-of-magnitude better in the present studies.

The films were characterized using x-ray diffraction from which the value of λ and the composition modulation amplitude, A, were determined; when the composition profile is written out as a Fourier series, the term A is the amplitude of the leading Fourier component. Details used to determine A in this study are presented in Ref. 14. All of the films in the present study were found to possess a strong [111] growth texture; no other growth texture was observed via x-ray diffraction studies. Low- and high-angle first-order satellite peaks were found straddling the central (111) Bragg peak for all of the films; no higher-order satellite peaks were observed. The values of A determined from the raw data for the Cu/Pd films are shown in Fig. 1. In past studies it was found that a strong [111] growth texture was critical for the observation of

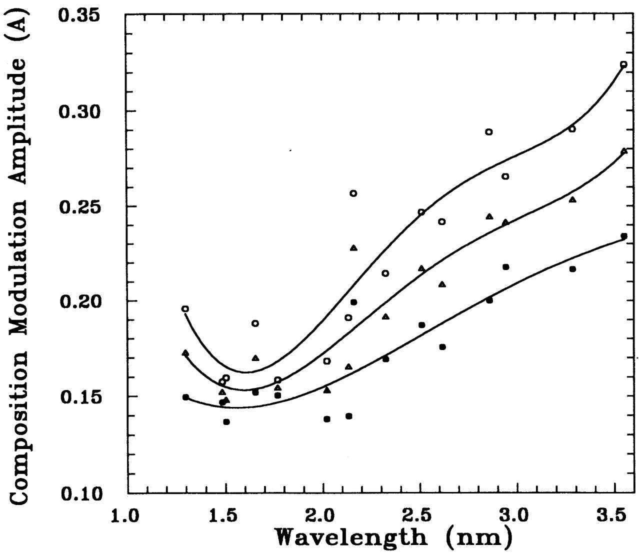

FIG. 1. The calculated values of A as a function of λ (nm) for the Cu/Pd superlattices. The open circles were calculated based on the data obtained on the high-angle satellite peak and the central (111) Bragg peak. The solid circles are based on the data obtained from the low-angle satellite peak and the central (111) Bragg peak. The triangles are the average of these two values. The solid lines are curves fitted to the data. The procedure outlined in Ref. 14 was used to calculate the value of A.

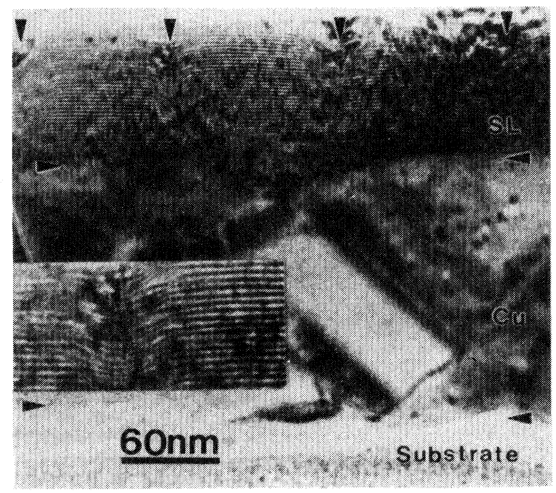

FIG. 2. A cross-sectional TEM micrograph, showing the crystal structures of an as-deposited Cu/Pd superlattice thin film. An enlarged image of the superlattice structure is shown as an inset in the lower left-hand corner.

the supermodulus effect, and the value of A should be as large as possible; the magnitude of a supermodulus effect was found to be approximately proportional to A^2.[2-5] The values of A obtained in the present studies are comparable to those obtained in past studies, and thus evidence for a supermodulus effect should have been observed if it is a real effect.

A number of Cu/Pd superlattices were also studied using high-resolution-electron microscopy (HREM).[16] Figure 2 is a typical cross-sectional transmission-electron-microscope (TEM) micrograph of an as-deposited Cu/Pd superlattice film. It shows the growth morphology of the crystallites, the crystal structures of the mica substrate, the Cu predeposition layer, and the Cu/Pd superlattice layers. The horizontal arrows indicate the interface between the mica substrate and the Cu predeposition layer, as well as the interface between the Cu predeposition layer and the Cu/Pd superlattice layers. The films were found to grow via a columnar growth mechanism. The vertical arrows indicate the interface between columnar gains. TEM images of superlattice thin-films show a structure consisting of well-defined alternating layers of Cu and Pd. In this image the light and the dark contrast regions are associated with the Cu and Pd layers, respectively. The thin films were found to contain microtwins. Also, the layers in the films undulate and the degree of waviness was found to vary from film to film. In Fig. 2 note that the alternating Cu and Pd layers are curved at the interface between the columnar grains, as shown in the inset. The major finding of the present HREM study is that the present set of Cu/Pd films are strikingly similar to the Cu/Ni films[17,18] used in past studies. Both sets of superlattice thin-films grew via the same growth mechanism and exhibit similar defect structures.

The elastic properties of the superlattice thin films were studied extensively using three separate techniques that allow the determination of four different elastic moduli. Brillouin scattering[19,20] was used to measure the surface or Rayleigh wave velocity. The Rayleigh wave velocity is closely related to that of a bulk shear-wave polarized perpendicular to the surface. Also, a number of techniques were developed to measure the elastic properties of thin films by coupling acoustic waves from surface-acoustic-wave (SAW) transducers into the films and measuring the phase velocity of various film modes.[21] Using this latter technique the flexural and shear moduli—for a shear-wave polarized in a plane parallel to the film surface—can be measured. The final technique employed was a uniaxial tension test to determine Young's modulus. This technique is similar to a procedure used in past studies,[3] but several important modifications were made that improve the reliability of the technique. The measurement of four separate elastic moduli makes this the most detailed study to date of the elastic properties of a thin film.

Typical results obtained from the films are presented in Figs. 3 and 4. In Fig. 3 the shear velocity of the Cu/Pd films, as measured using Brillouin scattering, is presented as a function of λ. In the range of λ where a supermodulus effect has previously been reported, the measured shear velocity is essentially *independent* of the value of λ. Figure 3 also shows the estimated upper (C-average) and lower (S-average) bounds for the Rayleigh shear-wave velocity using the techniques outlined in Refs. 22 and 23. It is noted that the thin films have a shear velocity that is approximately 8% less than the lower bound of the predicted value. (This corresponds to the films having a shear modulus roughly 16% less than the predicted lower bound.) The measured shear velocity of the Cu/Ni films[14] also showed no evidence for a supermodulus effect; a typical thin film has a shear modulus that is approximately

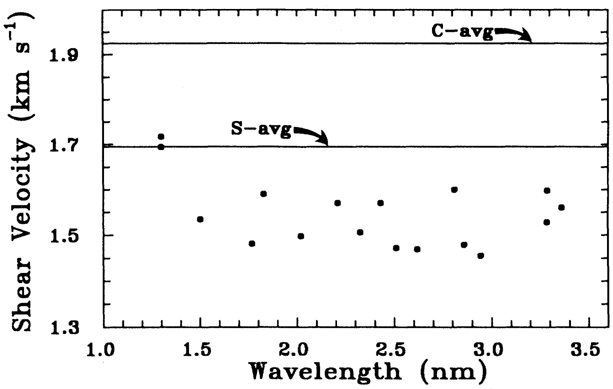

FIG. 3. The value of the velocity of a shear wave measured using Brillouin scattering as a function of λ (nm) for all of the Cu/Pd superlattices examined. Also shown are the calculated velocities for a Cu/Pd superlattice based on the bulk elastic constants of Cu and Pd.

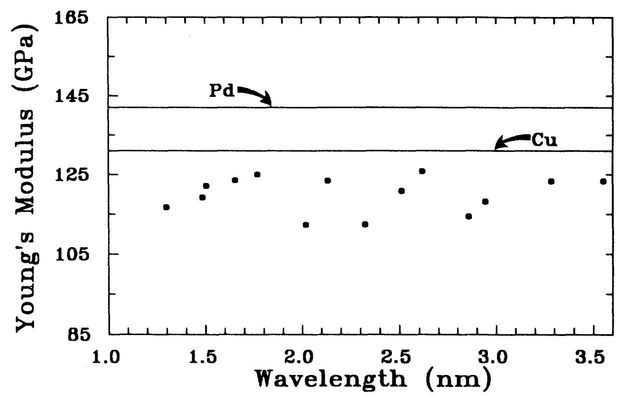

FIG. 4. The value of Young's modulus as a function of λ (nm) for the Cu/Pd superlattices. Also plotted are the measured values of the Young's modulus of Cu and Pd thin films with [111] texture.

equal to the predicted S-average.

Using the acoustic-wave measurement techniques, the flexural and shear moduli of both sets of films were also determined. No evidence for a supermodulus effect was found in these measurements. The measured values for both moduli[24,25] are independent of the value of λ for both thin-film sets over the entire range of λ in which a supermodulus effect had previously been reported. The measured shear moduli of both sets of films is found to be approximately equal to the predicted lower (S-average) bound. On the other hand, the measured flexural moduli exhibit a value that is within 10% of the predicted lower bound.

Finally, the measured Young's modulus of the Cu/Pd superlattices and pure Cu and Pd films—also with a [111] growth texture—are presented in Fig. 4. As can be seen, the Young's modulus of the films is again independent of λ. Also, the measured Young's modulus of the superlattices is approximately 6% less than the average of the measured values for Cu and Pd.

In summary, the elastic property results exhibit *no* evidence for a supermodulus effect for the present sets of superlattices. For all of the measurements, the estimated S-average —based on the bulk elastic constants of the two materials—gives a good first-order approximation to the elastic properties for the films. From a microstructural standpoint, the present sets of films are very similar to those used in the earlier studies. The high-resolution-electron microscopy study[16] shows that our superlattice films are microstructurally similar, and have basically the same defect structures, as the films utilized in the earlier studies.[17,18] The values of A predicted for the films in the present study are also approximately equal to those of the thin films in past studies. The one major difference between the thin films in the present study and those employed in past studies where a supermodulus effect was noted is the background vacuum during deposition. The elastic constant results presented in this paper are in agreement with the results from a recent theoretical study that used embedded-atom method potentials[26] to study the elastic properties of Cu/Ni, Cu/Pd, and Ag/Pd superlattices.[27] Recently, a 14% enhancement of c_{11} and a 50% enhancement of c_{55} were measured, employing Brillouin light scattering, for Ag/Pd superlattices when λ was decreased below 6–0.5 nm.[28] These enhancements are small compared with enormous enhancements originally observed for the Ag/Pd system,[5] and hence do *not* constitute a significant supermodulus effect.

Based on the results obtained in these recent studies, employing detailed and improved techniques to measure the elastic and microstructural properties of the thin films, the existence of a significant—i.e., 2–4.5 times greater elastic constants than the values predicted from the bulk elastic constants of the two metals—supermodulus effect has to be seriously questioned.

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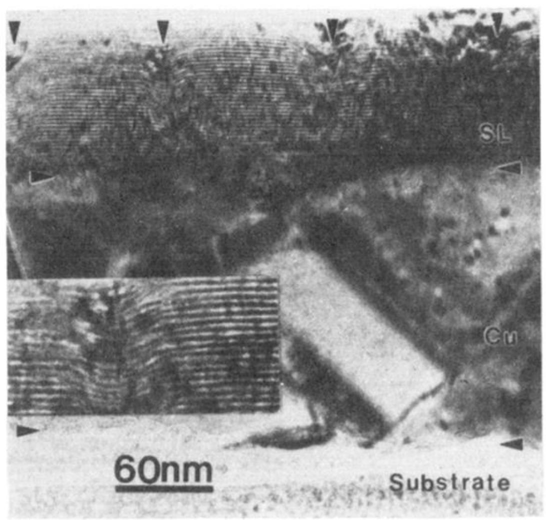

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