

Evidence for the supermodulus effect and enhanced hardness in metallic superlattices

A. Fartash

*Physics Department 0319, University of California–San Diego, La Jolla, California 92093
and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

Eric E. Fullerton and Ivan K. Schuller

Physics Department 0319, University of California–San Diego, La Jolla, California 92093

Sarah E. Bobbin, J. W. Wagner, and R. C. Cammarata

Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

Sudha Kumar and M. Grimsditch

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 3 September 1991)

A study of the mechanical properties of Cu/Nb superlattices shows that for modulation wavelengths below ~ 50 Å the biaxial modulus increases by $\sim 15\%$, the shear modulus decreases by $\sim 30\%$, and the flexural modulus does not change. These observations show that anomalies with different signs for elastic moduli can coexist in the same material. Measurements performed on both supported and unsupported films show that the anomalous effects are not induced by the presence of a substrate. The superlattices are also found to have a hardness larger than either Cu or Nb.

In spite of the fourteen years that have elapsed since large enhancements in the biaxial moduli of Au/Ni and Cu/Pd superlattices were reported,¹ these findings are still controversial.² Subsequent studies on Cu/Ni (Refs. 3 and 4) and Ag/Pd,⁵ which found biaxial moduli larger than that of diamond, intensified the controversy. The reason for the controversy is the great difficulty in measuring elastic properties of thin films. The initially reported enhancements of the biaxial modulus, measured using the bulge tester technique, have been questioned regarding problems of initial warping of the films and the resulting uncertainties in the data analysis.⁶ Since the early bulge tester measurements^{1,7} a number of other techniques have been used to investigate the presence or absence of elastic anomalies ("supermodulus effect"). The shear and compressional moduli of superlattices have been studied by Brillouin scattering^{8–12} and picosecond-reflectance¹³ techniques, respectively, and in all cases anomalies were found. Other techniques,^{14–17} based on the excitation of macroscopic normal modes of the film, have been used to study compositionally modulated films (Cu/Ni and Ag/Pd) have usually found no anomalies at all. None of the above techniques however has measured the biaxial modulus directly.

Here we present a comprehensive study of the biaxial, flexural, and shear moduli of Cu/Nb superlattices. Our results exhibit anomalies; an increase of the biaxial modulus, and a decrease of the shear modulus which correlate with a lattice expansion as the modulation wavelength Λ is decreased to 20 Å. The biaxial modulus enhancement ($\sim 15\%$) is however considerably smaller than the previously reported 700% and 100% for Cu/Ni

(Refs. 3 and 4) and 230% for Au/Ni.¹

Although it might appear that an obvious choice of material for the present study should be either Cu/Ni or Ag/Pd, the already conflicting results reported on these systems imply that there could be effects related to the preparation technique. To avoid these complications Cu/Nb was chosen for the present studies because it is known that its shear constant behaves in an unexpected, but reproducible, manner as shown by two independent groups^{8,9} both of which reported a decrease in this constant. We note however, that Cu/Nb, contrary to Cu/Ni and Ag/Pd is a eutectic system with sharp interfaces so that care should be exercised in generalizing our results to compositionally modulated systems.

Equal thickness Cu/Nb multilayers, 7 μm thick, with modulation wavelengths $\Lambda=22, 30, 55, 85, 125,$ and 250 Å and 7 μm Cu and Nb films were prepared by dc magnetron sputtering on silicon substrates.¹⁸ The base pressure was $\sim 10^{-7}$ Torr and the argon pressure during deposition was $\sim 3 \times 10^{-3}$ Torr. Deposition was finished with niobium in the outermost layer since this produces a shinier surface and thereby facilitates the Brillouin scattering experiments.⁸

The structure was determined from reflection θ - 2θ x-ray diffraction performed using Cu $K\alpha$ radiation. The films show a strong preferential orientation with the Nb [110] and Cu [111] axes perpendicular to the layers but with randomly oriented crystallites in the plane of the substrate. Well-resolved superlattice diffraction peaks were observed for all the superlattice samples. The average lattice spacing $\langle d \rangle$ and modulation wavelength Λ are obtained from

$$Y_B = C_{11} + C_{12} - 2C_{13}^2 / C_{33} \quad (3)$$

Similarly to the flexural modulus (see below), the experimental value of Y_B for Cu lies below the calculated range (0.222–0.262 TPa) (Ref. 22) while that of Nb lies close to the top of the expected range (0.137–0.157 TPa). It can be easily shown²¹ that the biaxial modulus of a superlattice is given by the weighted average of the biaxial moduli of the constituents. This average, obtained using the experimentally determined Y_B 's for Cu and Nb films, is indicated by the dashed line in Fig. 1(c). For $\Lambda \geq 50$ Å the measured values of Y_B are consistent with this average. The most striking feature of the results shown in Fig. 1(c), is the enhancement of Y_B as the modulation wavelength is decreased below 50 Å.

Figure 1(d) shows the measured velocity of the symmetric Lamb mode^{28,29} as a function of modulation wavelength for Cu/Nb superlattices and pure Nb and Cu films. The velocity of symmetric Lamb modes is given by

$$v = [(C_{11} - C_{13}^2 / C_{33}) / \rho]^{1/2} = (F / \rho)^{1/2}, \quad (4)$$

where F is the flexural modulus. Similarly to the biaxial modulus results, the value obtained for the pure Cu film (4.19 km/sec) is below that calculated from bulk values (4.43–4.60 km/sec) whereas the Nb velocity (3.69 km/sec) is slightly higher than the expected range (3.42–3.65 km/sec) obtained from bulk values. The measured values in the superlattices are close to the average of the measured velocities in pure Cu and Nb.

Although the results presented in Fig. 1 are the most complete elastic study of any system which shows anomalous behavior, it is still not possible to decisively isolate the behavior of any single C_{ij} . The velocity of the surface wave [Fig. 1(b)] is strongly dependent on C_{44} [Eq. (2)] and only weakly dependent on C_{11} , C_{33} , and C_{13} . Given the weak modulation wavelength dependence of the biaxial and flexural moduli which are functions of the latter C_{ij} 's it is almost certain that C_{44} depends strongly on Λ . Since a decrease solely in C_{33} (with no changes in the other C_{ij}) would produce an increase in both the biaxial and flexural moduli with the change in Y_B being roughly twice as large as in F , our results of Y_B and F are consistent with a decrease of C_{33} similar to that found in a number of systems.¹³ The results given in Ref. 9, however, show only small changes in C_{33} of Cu/Nb superlattices. The possible enhancement of C_{12} reported from an investigation of Love waves in Cu/Nb (Ref. 30) is consistent with our results but has such large error bars that no quantitative comparison can be made.

Knoop microhardness of the Cu/Nb superlattices was measured using an Anton Paar MHT4 Microhardness Tester with an applied load of 4 g (see Fig. 2). Ten widely spaced indents were made on each sample. In accordance with the established procedure for hardness measurements,³¹ the depth of the indents were less than 10% of the total film thickness. As seen in Fig. 2, the superlattices are harder than either of the constituents. Noting that the hardness is a measure of the yield strength,²⁷ it has been suggested that an enhanced hardness in multilayers may be the result of a supermodulus effect on the

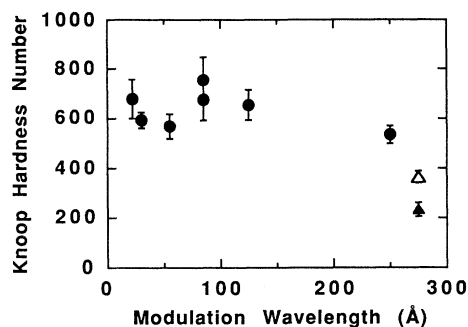


FIG. 2. Knoop microhardness vs modulation wavelength for Cu/Nb.

line tension of dislocations.³² However, nanohardness indentation studies of Cu/Ni films give hardness enhancements without any anomalous elastic behavior during indenter unloading.³³ Those results, coupled with the fact that the hardness enhancements presented here are much greater than the elastic anomalies, suggest that another mechanism is responsible. Proposed mechanisms have involved either effects of image forces on dislocations,³⁴ where no modulation wavelength dependence is predicted, or a Hall-Petch-like interface hardening effect,³³ where a modulation wavelength dependence is expected. Unlike the hardness behavior of TiN/VN (Ref. 32) and Cu/Ni,³³ which displayed a modulation wavelength dependence, the hardness results for Cu/Nb [as well as those for Mo/Ni (Ref. 35)] showed no modulation wavelength dependence, which suggests that image force effects dominate in these films.

Because of the variety of elastic anomalies exhibited by different systems, a detailed comparison of our experimental results to theory could only be done if model calculations for bcc/fcc structures reported specific estimates for the individual moduli. Since model calculations are not yet that specific, only the general features: i.e., a large reduction in C_{44} and a small increase in Y_B , can be qualitatively compared. Molecular dynamics (MD) calculations for Mo/Ni (Ref. 36) found that expansion of the out-of-plane Ni lattice constant could explain the measured reduction in the shear modulus and predicted a slight enhancement of (8–10%) of Young's and biaxial moduli in excellent agreement with our measured results on Cu/Nb. The coherency strain model³⁷ (which assumes that the in-plane structures are coherent at the interface and hence may not be applicable to bcc/fcc systems) uses the measured $\langle d \rangle$ as an input parameter, and predicts a reduction of C_{44} in Cu/Nb which is comparable to the measured values.

Recent calculations assuming incoherent or grain boundary interfaces³⁸ in fcc/fcc systems have found decreases in C_{44} and increases in the biaxial modulus in agreement with the measured results found for Cu/Nb. This model also predicts the measured out-of-plane lattice constant expansions. Another model³⁹ has been proposed based on interfacial stresses associated with incoherent (or semicoherent) interfaces which induce lattice parameter variations as a function of Λ . The model pre-

dicts elastic behavior that is in reasonable agreement with the increases in Y_B and the decrease in C_{44} reported here. Other proposed models^{40,41} have not yet produced quantitative results pertaining to the behavior of the different moduli.

To summarize, we have shown that elastic anomalies of different sign and magnitude can coexist in a single system. More specifically, the Cu/Nb system shows simultaneously an enhancement of the biaxial (15%), a decrease of the shear (30%), and Λ -independent flexural

modulus. The changes are concomitant with an out-of-plane expansion of the average lattice spacing. These results are in qualitative agreement with model calculations which either use the lattice expansions as an input parameter^{36,37} of which predict concomitant lattice expansions.^{38,39}

This work was supported by the ONR under Contract No. N00014-91-J-1177 and the U.S. DOE, BES-Materials Sciences under Contract No. W-31-109-ENG-38.

- ¹W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, *J. Appl. Phys.* **48**, 876 (1977).
- ²For a recent review see I. K. Schuller, A. Fartash, and M. Grimsditch, *Mat. Res. Bull.* **XV**, 33 (1990).
- ³T. Tsakalakos and J. E. Hilliard, *J. Appl. Phys.* **54**, 734 (1982).
- ⁴L. R. Testardi, R. M. Willens, J. T. Krause, D. B. McWhan, and S. Nakahara, *J. Appl. Phys.* **52**, 510 (1981).
- ⁵G. E. Henein and J. E. Hilliard, *J. Appl. Phys.* **54**, 728 (1983).
- ⁶H. I. Itozaki, Ph.D. thesis, Northwestern University, 1982.
- ⁷For a review of the original work see J. E. Hilliard, in *Modulated Structures—1979 (Kailua Kona, Hawaii)*, Proceedings of the International Conference, edited by J. M. Cowley, J. B. Cohen, M. B. Salamon, and B. J. Wuensch, AIP Conf. Proc. No. 53 (AIP, New York, 1979), p. 407.
- ⁸A. Kueny, M. Grimsditch, K. Miyano, I. Banerjee, C. M. Falco, and I. K. Schuller, *Phys. Rev. Lett.* **48**, 166 (1982).
- ⁹J. A. Bell, W. R. Bennett, R. Zannoni, G. I. Stegeman, C. M. Falco, and C. T. Seaton, *Solid State Commun.* **64**, 1339 (1987).
- ¹⁰R. Danner, R. P. Huebener, C. S. L. Chun, M. Grimsditch, and I. K. Schuller, *Phys. Rev. B* **33**, 3696 (1986).
- ¹¹R. Khan, C. S. L. Chun, G. P. Felcher, M. Grimsditch, A. Kueny, C. M. Falco, and I. K. Schuller, *Phys. Rev. B* **27**, 7186 (1983).
- ¹²J. R. Dutcher, S. Lee, J. Kim, G. I. Stegeman, and C. M. Falco, *Phys. Rev. Lett.* **65**, 1231 (1990); this work reports an enhancement of the C_{11} and C_{55} in Ag/Pd for $\Lambda \leq 60$ Å.
- ¹³B. Clemens and G. Eesley, *Phys. Rev. Lett.* **61**, 2356 (1988).
- ¹⁴B. S. Berry and W. C. Pritchett, *Thin Solid Films* **33**, 191 (1976).
- ¹⁵A. Moreau, J. B. Ketterson, and B. C. Davis, *J. Appl. Phys.* **68**, 1622 (1990).
- ¹⁶A. Moreau, J. B. Ketterson, and J. Mattson, *Appl. Phys. Lett.* **56**, 1959 (1990).
- ¹⁷B. M. Davis, D. N. Seidman, A. Moreau, J. B. Ketterson, J. Mattson, and M. Grimsditch, *Phys. Rev. B* **43**, 9304 (1991).
- ¹⁸I. K. Schuller, *Phys. Rev. Lett.* **44**, 1597 (1980).
- ¹⁹I. K. Schuller and M. Grimsditch, *J. Vac. Sci. Technol. B* **4**, 1444 (1986).
- ²⁰I. K. Schuller, E. E. Fullerton, H. Vanderstraeten, and Y. Bruynseraede, in *Structure Property Relationships for Metal-Metal Interfaces*, edited by A. D. Romig, Jr., D. E. Fowler, and P. D. D. Bristowe, MRS Symposia Proceedings No. 229 (Materials Research Society, Pittsburgh, 1991), p. 41; and E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruynseraede (unpublished).
- ²¹M. Grimsditch, *Phys. Rev. B* **31**, 6818 (1985); M. Grimsditch and F. Nizzoli, *ibid.* **33**, 5891 (1986).
- ²²G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties* (MIT Press, Cambridge, 1971).
- ²³*Numerical Data and Functional Relationships in Science and Technology*, edited by K. H. Hellwege, Landolt Börnstein, Group III, Vol. II (Springer, New York, 1979), p. 9-10.
- ²⁴G. W. Farnell, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1969), Vol. 6, p. 109.
- ²⁵A. Fartash, I. K. Schuller, and M. Grimsditch, *Appl. Phys. Lett.* **55**, 2614 (1990).
- ²⁶A. Fartash, I. K. Schuller, and M. Grimsditch, *Rev. Sci. Instrum.* **62**, 494 (1991).
- ²⁷D. Tabor, in *Microhardness Techniques in Materials Science*, edited by P. J. Blau and B. R. Lawn (American Society for Testing and Materials, Philadelphia, PA, 1985), p. 90.
- ²⁸A. Moreau, J. B. Ketterson, and J. Huang, *Mat. Sci. Eng.* **A126**, 149 (1990).
- ²⁹S. E. Bobbin, J. W. Wagner, and R. C. Cammarata, *Appl. Phys. Lett.* **59**, 1544 (1991).
- ³⁰J. A. Bell, R. J. Zannoni, C. T. Seaton, G. L. Stegeman, W. R. Bennett, and C. M. Falco, *Appl. Phys. Lett.* **51**, 652 (1987).
- ³¹*Hardness Testing*, edited by H. E. Boyer (ASM International, Metals Park, OH, 1987).
- ³²U. Helmersson, S. Todorova, S. A. Barnett, J. E. Sundgren, L. C. Markert, and J. E. Greene, *J. Appl. Phys.* **62**, 481 (1987).
- ³³R. C. Cammarata, T. E. Schlesinger, C. Kim, S. B. Qadri, and A. S. Edelstein, *Appl. Phys. Lett.* **56**, 1862 (1990).
- ³⁴J. S. Koehler, *Phys. Rev. B* **2**, 547 (1970).
- ³⁵T. Baumann, J. B. Pethica, M. Grimsditch, and I. K. Schuller, in *Interfaces, Superlattices and Thin Films*, edited by J. D. Dow and I. K. Schuller, MRS Symposia Proceedings No. 77 (Materials Research Society, Pittsburgh, 1981), p. 527.
- ³⁶I. K. Schuller and A. Rahman, *Phys. Rev. Lett.* **50**, 1377 (1983).
- ³⁷A. F. Jankowski, *Mat. Sci. Eng.* **B6**, 191-197 (1990).
- ³⁸D. Wolf and J. F. Lutsko, *J. Appl. Phys.* **66**, 1961 (1989), and references therein.
- ³⁹R. C. Cammarata and K. Sieradzki, *Phys. Rev. Lett.* **62**, 2005 (1989).
- ⁴⁰A. J. Jankowski and T. Tsakalakos, *J. Phys. F* **15**, 1279 (1985).
- ⁴¹M. L. Huberman and M. Grimsditch, *Phys. Rev. Lett.* **62**, 1403 (1989).