Elastic-constant softening in nonperiodic Mo/Ni multilayers

G. Richardson, J. L. Makous, H. Y. Yu, and A. S. Edelstein
Naval Research Laboratory, Washington, D.C. 20375
(Received 18 September 1991)

Surface-acoustic-wave velocity measurements on nonperiodic Mo/Ni multilayers show that an electronic mechanism based on minizone boundaries is not responsible for the softening of the c_{44} elastic constant that occurs at small modulation wavelengths in periodic samples. The spacings between the x-ray satellite peaks of the nonperiodic multilayers are not equal. Model calculations predict these spacings and show that the satellite positions depend on the individual atomic interplanar spacings and not just the average modulation wavelength.

Since the early observations[1–3] of 200–400% increases in the biaxial modulus in Cu/Pd, Au/Ni, Ni/Cu, and Ag/Pd metallic multilayers at small values for the modulation wavelength Λ, there has been considerable effort devoted to verifying and understanding this effect. One reason for this interest is that it is normally very difficult to increase the elastic properties of a material by more than a few percent. Despite considerable effort, it has proven difficult to obtain clear answers to many of the relevant questions. Some doubted whether there was any substantial change in the elastic constants. For example, Moreau, Ketterson, and Mattson[4] observed no change in Ni/Cu. In other systems, however, investigations[5,6] have shown that, though the effect is smaller than the large increases originally reported, there are reproducible changes in the elastic constants at small Λ. In Ag/Pd multilayers the reported[7] increase in the C_{55} elastic constant is 50%. In some systems, instead of an increase, there is a decrease in the elastic constants at small Λ. Mo/Ni is one such system where Brillouin scattering measurements of the surface-wave velocity v by Khan *et al.*[6] established that there is a 44% decrease in C_{44} with decreasing Λ where $v \propto (C_{44}/\rho)^{1/2}$ and ρ is the density. Figure 1 shows a fit to the normalized surface-wave velocity data from Ref. 6 for the Mo/Ni system. Three points from our work, which exhibit the same trend, are also shown.

It has been even harder to obtain a theoretical understanding of these changes in the elastic constants. There are several types of suggested explanations. They are coherency strain,[8,9] surface stress,[10] electronic mechanisms,[11–13] changes in the interatomic spacing of atoms that are near the interface,[14,15] and possible compound formation at the interface. Even though several studies[6,16,17] have suggested strain effects as the cause of the observed elastic anomalies in some metallic multilayers, none has been able to determine conclusively the mechanism responsible for these elastic anomalies.

Here we employ nonperiodic multilayers to investigate whether one of the two proposed electronic mechanisms is responsible for the elastic-constant decrease in Mo/Ni multilayers. In the electronic mechanism[11,12] we are investigating, the elastic constants change because of a critical contact between the Fermi surface and one of the minizone boundaries that appear in coherent, composition-modulated multilayers. The critical contact is a nesting of the existing Fermi surface with an added portion caused by the new zone boundary.[18] Although Cammarata[19] has argued against the applicability of this mechanism, no direct, experimental test has been performed previously. This electronic mechanism could be important in Mo/Ni because the orientational order[20] in periodic Mo/Ni samples generates minizone boundaries. The electronic structure of periodic and nonperiodic Mo/Ni samples will be quite different. Thus, if a critical contact between the Fermi surface and the minizone boundary is responsible for the softening, nonperiodic samples should have different elastic constants than the periodic samples. It should be noted that though another type of nonperiodic multilayer system, Fibonacci multilayers, has been studied[21,22] extensively, few studies have been made on random multilayer systems.[23]

We have fabricated two sets of nonperiodic samples in which the average modulation wavelength ⟨Λ⟩, defined as the total film thickness divided by the number of bi-

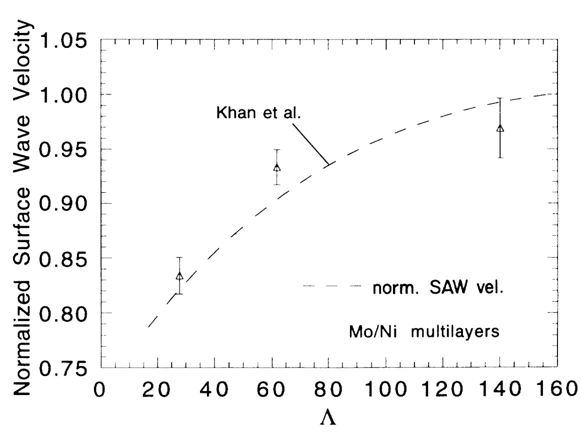

FIG. 1. Normalized surface-wave velocities observed by Khan *et al.* in Brillouin scattering measurements (Ref. 6), represented by the dashed line, and the present SAW measurements on periodic Mo/Ni multilayers. The Khan data have been fitted to a fifth-order polynomial and divided by 2.54. Our SAW data have been divided by 2.10.

layers, is kept constant within each set. The first set, with $\langle \Lambda \rangle = 26.8$ Å, was chosen to correspond to the region shown in Fig. 1 where the softening is large, while the second set, with $\langle \Lambda \rangle = 140$ Å, was chosen to correspond to the region where the softening is small. The average layer thicknesses t of both the Mo and Ni layers were equal so that $t = \langle \Lambda \rangle /2$. For a particular sample, the layer thicknesses of only one element was varied. The deposition was made such that the layers of that element had one of three equally likely thicknesses, t, $t - \Delta t$, or $t + \Delta t$. The thickness selections were determined by a pseudo-random-number generator. For each set, several samples were prepared with $0 \le \Delta t < 0.7$. In all cases but one, we varied the Mo-layer thickness and not the Ni thickness. The reason for keeping the Ni-layer thickness constant was to minimize structural changes in the Ni layers, since the elastic-constant softening in Mo/Ni has been attributed[6] to structural changes in the Ni layers.

The samples were prepared in a computer-controlled, ion-beam-sputtering system described previously.[24] The substrates were either Si, glass, or quartz. The Ni and Mo films are preferentially oriented with the high atomic density (111) fcc planes of Ni and the (110) bcc planes of Mo parallel to the substrate. The total film thicknesses were approximately 4000 Å.

Figure 2 shows the x-ray spectrum taken with Cu $K\alpha$ radiation of three samples, each with an average modulation wavelength $\langle \Lambda \rangle = 26.8$ Å and Ni layers that are approximately 13.4 Å thick. The Mo layers also had t approximately 13.4 Å but $\Delta t = 0.0$, 4.2, and 8.4 Å for the three different samples. The spectrum for the periodic sample, $\Delta t = 0.0$ Å, has the usual characteristics of satellite lines evenly spaced around a central peak. The satellite spacing of the periodic sample was used to determine the value of $\langle \Lambda \rangle$.[25] For the nonperiodic samples, since the average periodicity is unchanged, one might have expected that the satellite positions would be unchanged and that the randomness would increase their width and decrease their intensities. The broadening does occur, but the changes in the positions and intensities of the satellites are not in agreement with these simple expectations. For example, instead of being unchanged, the positions of the satellite, S_{+1}, on the right of the central peak, S_0, is shifted to a lower value of 2θ and, though the satellite on the right loses intensity as one increases Δt, the satellite, S_{-1}, on the left, *gains* intensity relative to S_0.

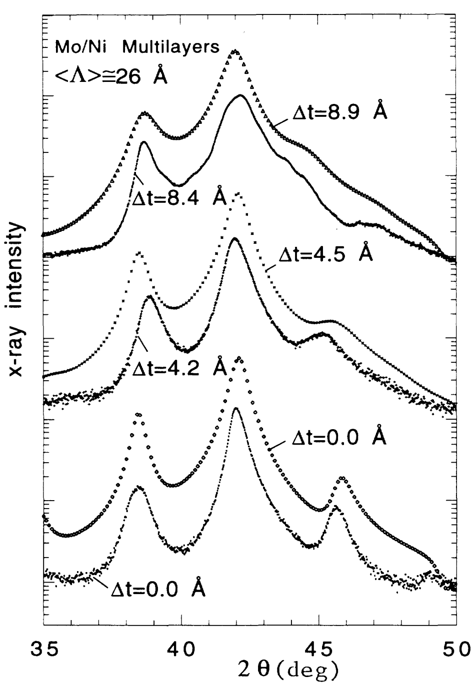

FIG. 2. Three pairs of measured and calculated x-ray spectra of one periodic ($\Delta = 0.0$ Å) and two nonperiodic Mo/Ni multilayer samples, all having an average modulation wavelength of approximately $\langle \Lambda \rangle = 26$ Å ($\langle \Lambda \rangle$ experimental $= 26.8$ Å, $\langle \Lambda \rangle$ calculated $= 25.6$ Å). The experimental spectra are below the calculated spectra.

Calculations which incorporated the nonperiodicity were performed to see if they could reproduce the unusual features of the experimental x-ray spectra shown in Fig. 2. We represented the periodic sample as a repetition of bilayers containing six Ni (111) planes and six Mo (110) planes. The randomness was incorporated by allowing the number of Mo planes in the layers to take on one of three equally likely values, but the Ni and Mo plane spacings and the average interface spacing $\bar{d}_i$ were kept constant for different values of Δt. The convergence of the calculations is very slow if one averages the scattering from a large number of bilayers. Instead, we used analytic results obtained by Fullerton *et al.*,[26] who showed how one could properly average over a single bilayer if the bilayers are statistically independent. In their work Fullerton *et al.* assumed that the spacing at the interface between the Mo and Ni layers, d_i, satisfied a Gaussian probability distribution about the average, $\bar{d}_i$.

In agreement with previous work,[6,15] we found it necessary to increase the average spacing between the planes in order to fit the positions of the peaks for the periodic sample. Previously, data on periodic Mo/Ni multilayers[15] were modeled by assuming that $\bar{d}_i$ is larger than the value usually assigned to it, namely $(d_1 + d_2)/2$, where d_1 and d_2 are the Ni and Mo interplanar spacings, respectively. For periodic multilayers, the position of the satellites is determined solely by the value of Λ and not the individual interplanar spacings d_1, d_2, or $\bar{d}_i$. In contrast, for nonperiodic structures the calculated positions of the satellites depend differently on the separate interplanar spacings. For example, we find that changing $\bar{d}_i$ from the usual value $(d_1 + d_2)/2$ shifts the position of the satellite S_{+1} only approximately half as much as the satellites S_0 and S_{-1}, whereas changing d_1 or d_2 shifts all three satellites by approximately the same amount.

In fitting the spectra shown in Fig. 2, we assumed that d_1 was increased by 1.6% from its bulk value but still maintain $\bar{d}_i = (d_1 + d_2)/2$. Alternatively, we could have increased d_2, but increasing $\bar{d}_i$ from the value given by $(d_1 + d_2)/2$ does not provide as good a fit. The width of the Gaussian was taken to be 0.25 Å, and the number of bilayers was taken to be equal to the number of bilayers in our samples, 150. For the nonperiodic samples we assumed that the thickness of the Ni layer is six atomic layers, while the Mo layers took on one of three equally likely possibilities. For one nonperiodic sample the Mo layers were taken to be either four, six, or eight atomic layers thick, i.e., $t=13.352$ Å and $\Delta t=4.451$ Å. For the other nonperiodic sample the Mo layers were taken to be either two, six, or ten atomic layers thick, i.e., $t=13.352$ Å and $\Delta t=8.902$ Å.

The model predictions, presented in Fig. 2, show most of the unusual features of the experimental spectra, namely the shift in the position of S_{+1} and the large intensity of S_{-1} relative to S_{+1}. One difference is that while the experimental ratio of the intensities of S_{-1} to S_0 increases as one increased Δt, the calculated ratio shows a small decrease. The general agreement between the experimental and model spectra shows that most of the unusual features of the x-ray spectra are due to nonperiodicity.

We investigated the elastic properties of the Mo/Ni samples using a surface-acoustic-wave (SAW) technique described in detail elsewhere.[27,28] Measurements[27] on Ni/V multilayers demonstrated that SAW measurements and Brillouin scattering measurement are complementary techniques for determining the surface-wave velocity. For our SAW measurements, films were deposited onto ST quartz substrates and the surface-wave velocity determined from time-of-flight measurements. The substrate contribution to the SAW velocity is subtracted using an analytic expression relating the surface-wave velocity of the film to the film thickness and the SAW velocity of the bare substrate.[27] Because this relation is not exact, the absolute values of the velocities determined by the SAW technique are not accurate. This technique for interpreting SAW measurements has been used to observe the wavelength dependences of the velocity in periodic Mo/Ni samples.[28] Figure 1 shows that though we had to normalize the Brillouin scattering and SAW data differently, both sets show the same trend as a function of Λ. Thus the SAW technique can be used to reliably determine whether nonperiodicity changes the velocity v in the long-wavelength region, $\langle\Lambda\rangle=140$ Å, where the softening is not very pronounced and the small-wavelength region, $\langle\Lambda\rangle=26.8$ Å, where it is pronounced.

Figure 3 shows a plot of v determined by SAW measurements versus the ratio $\Delta t/t$ where Δt is the deviation of the layer thickness of one element from its average thickness t. As discussed above, we chose to vary the thickness of the Mo layers and keep the Ni-layer thickness constant, except in one case. In that case $\langle\Lambda\rangle=26.8$, $\Delta t/t=0.3$, and the thickness of the Ni layers was varied and the Mo-layer thickness was kept constant. One sees that the v is essentially independent of

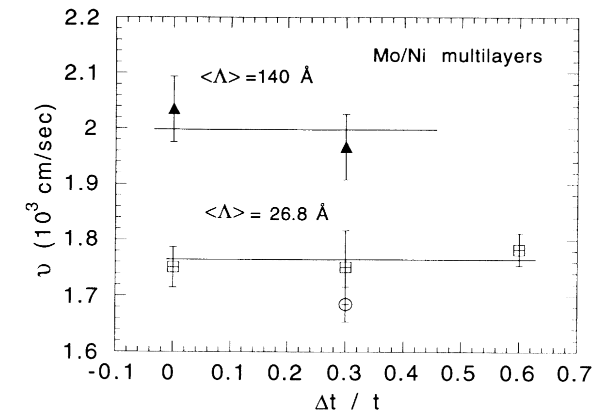

FIG. 3. SAW determination of the velocity v at $\langle\Lambda\rangle=26.8$ and 140 Å vs the ratio of the deviation of the layer thickness of one element, usually Mo, to the average thickness of that element, $\Delta t/t$. The measurement denoted by an open circle was made on a sample for which the Ni-layer thickness varied instead of the Mo thickness. The lines serve only as visual guides.

$\Delta t/t$ in both the long-wavelength region, where an effect might not be expected, and the more relevant small-wavelength region where the elastic softening occurs; the nonperiodic samples show the same elastic softening at small $\langle\Lambda\rangle$ as observed in the periodic samples.

The fact that the elastic softening observed on these nonperiodic samples agrees with that taken on periodic samples indicates that the presumed minizone boundaries of the Fermi surface in periodic multilayers is probably not the cause of the softening in Mo/Ni. For our samples the softening depends only on the number of interfaces per unit volume. Thus, it appears that the cause of the softening is localized near the interface, or the effects of the nonperiodicity cancel one another, or the softening is associated with the Ni layers, which were not varied in most of our experiments. This last possibility is in agreement with previous studies,[6,16] in which the softening was attributed to strains in the Ni layers. Further, we have found that the calculated positions of the satellite peaks in nonperiodic samples depend upon the individual interplanar spacings. Thus, one may be able to use measurements of these peak positions to determine the individual interplanar spacings.

We wish to thank E. Fullerton for communicating his results on calculating the x-ray spectrum prior to their publication, W. Pickett for helpful conversations of the electronic mechanism, and the Office of Naval Research for supporting this research. J.L.M. thanks the Office of Naval Technology for financial support.

[1] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977).

[2] G. E. Henein and J. E. Hilliard, J. Appl. Phys. **54**, 728 (1983).

[3] T. Tsakalakos and J. E. Hilliard, J. Appl. Phys. **54**, 734 (1983).

[4] A. Moreau, J. B. Ketterson, and J. Mattson, Appl. Phys. Lett. **56**, 1959 (1990).

[5] J. Mattson, R. Bhadra, J. B. Ketterson, M. Brodsky, and M. Grimsditch, J. Appl. Phys. **67**, 2873 (1990).

[6] M. R. 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).

[7] John R. Dutcher, Sukmock Lee, Jeha Kim, George I. Stege-

man, and C. M. Falco, Phys. Rev. Lett. **65**, 1231 (1990).

[8]T. Tsakalakos and A. F. Jankowski, Annu. Rev. Mater. Sci. **16**, 293 (1986).

[9]A. F. Jankowski and T. Tsakalakos, J. Phys. F **15**, 1279 (1985).

[10]R. C. Cammarata and K. Sieradzki, Phys. Rev. Lett. **62**, 2005 (1989).

[11]W. E. Pickett, J. Phys. F **12**, 2195 (1982).

[12]T. B. Wu, J. Appl. Phys. **53**, 5265 (1982).

[13]M. L. Huberman and M. Grimsditch, Phys. Rev. Lett. **62**, 1403 (1989).

[14]D. Wolf and J. F. Lutsko, Phys. Rev. Lett. **60**, 1170 (1988).

[15]B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988).

[16]I. K. Schuller and A. Rahman, Phys. Rev. Lett. **50**, 1377 (1983).

[17]J. L. Makous and C. M. Falco, Solid State Commun. **72**, 667 (1989).

[18]In the second electronic mechanism, Ref. 13, the changes in the elastic constant are due to a charge-transfer effect that is necessary to match the Fermi levels at the interface.

[19]R. C. Cammarata, Scr. Metall. **20**, 479 (1986).

[20]Bain *et al.* [J. A. Bain, L. J. Chyung, S. Brennan, and B. M. Clemens, Phys. Rev. B **44**, 1184 (1991)] believe there is Nishiyama-Wasserman epitaxial orientation. Such orientation is discussed by E. Bauer and J. H. van der Merwe, *ibid.* **33**, 3657 (1986).

[21]D. Toet, M. Potemski, Y. Y. Wang, J. C. Maan, L. Tapfer, and K. Ploog, Phys. Rev. Lett. **66**, 2128 (1991).

[22]W. Feng, N. Liu, and X. Wu, Phys. Rev. B **43**, 6893 (1991).

[23]Merlin *et al.* (R. Merlin, K. Bajema, J. Nagle, and K. Ploog, in *Proceedings of the Third International Conference Modulated Semiconductor Structures* [J. Phys. (Paris) Colloq. **48**, C5-503 (1987)]), however, did perform Raman-scattering measurements on random multilayers.

[24]C. Kim, S. B. Qadri, M. Twigg, and A. S. Edelstein, J. Vac. Sci. Technol. A **8**, 3466 (1990); C. Kim, S. B. Qadri, P. Lubitz, T. E. Schlesinger, R. C. Cammarata, and A. S. Edelstein, Mater. Sci. Eng. A **126**, 25 (1990).

[25]I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980).

[26]E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruynseraede, Phys. Rev. B **45**, 9292 (1992).

[27]R. Danner, R. P. Huebener, C. S. L. Chun, Grimsditch, and I. K. Schuller, Phys. Rev. B **33**, 3696 (1986).

[28]J. L. Makous and S. M. Hues, Phys. Rev. B **44**, 10 848 (1991).