Lamb Waves in Unsupported Thin Films: A Brillouin-Scattering Study

M. Grimsditch, R. Bhadra, and Ivan K. Schuller
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 15 December 1986)

Using Brillouin scattering we have succeeded in observing the normal modes of vibration of *unsupported* films in a region where the dispersion relationship is quadratic. Extremely low-lying excitations were observed in thin films with thicknesses as small as 200 Å. Contrary to what has been found in work on supported films, we are able to extract information on a number of the elastic moduli because the measured velocities in very thin films do not depend on the properties of the substrate. This technique should be a valuable addition to the tools which can be used in the study of materials in thin-film form.

PACS numbers: 62.20.Dc, 68.55.Pr, 78.35.+c

The current interest in materials in the form of thin films stems from the fact that their properties may be different from those in the bulk.[1-4] It has also been found that the elastic properties of thin films, when incorporated into a superlattice, differ significantly from their bulk values.[5] The determination of the elastic constants of thin solid films has been performed on thick (>5000 Å) films by use of mechanical methods on self-supporting films or Brillouin scattering from films on a substrate. In some of these measurements it was necessary to assume that the elastic properties of the films composing the superlattice are very different from those in the bulk.[5] In order to ascertain whether the elastic anomalies observed to date are due to layering or simply due to the thin-film nature of the samples, it is important to develop a method which allows measurements on self-sustained films which are not affected by the presence of the substrate. Measurements on unsupported films have been used in the study of liquid crystals.[6-10] These experiments rely either on the enormous polarizabilities of these systems, which produce very large intensities in light-scattering experiments,[6-8] or on the fact that very large unsupported films can be produced so that macroscopic mechanical resonances of a film can be detected.[9-10] However, when one is dealing with thin solid films, both of these classes of experiments suffer from serious drawbacks, viz., in order to obtain samples large enough to perform mechanical resonances samples thicker than ~ 1.5 μm are required[11]; on the other hand, since typical polarizabilities of solids are much smaller than those of liquid crystals, Brillouin-scattering intensities are much smaller and the only report[12] is in transparent films thicker than 1 μm. In the case of opaque materials, no Brillouin scattering has been reported on unsupported films. Here we present measurements in very thin ($\gtrsim 200$ Å) opaque self-supporting films.

Brillouin scattering is a technique which has proven to be quite effective[13] in the study of the elastic constants of films with thicknesses $\gtrsim 5000$ Å. This technique, when applied to opaque materials, couples to surface waves (Rayleigh waves) whose amplitudes decay exponentially away from the surface. Provided the thickness is somewhat greater than typical phonon wavelengths (~ 3000 Å), an elastic property is measured with no contribution from the substrate. As films are made thinner, the velocity of the surface waves is strongly influenced by the presence of the substrate and it becomes difficult to extract the properties of the film itself. In Brillouin-scattering experiments on supported films with thicknesses in the range ~ 500–2000 Å, apart from the Rayleigh wave observed in thick films, one also observes features which arise from what are known as Sezawa modes.[13] These modes can be viewed as standing-wave patterns produced by the reflection of acoustic waves between the free surface and the film-substrate interface, and are similar to the Lamb modes of a free-standing plate. For the same reasons given above the extraction of elastic constants from the positions of these modes is not straightforward and has met with mixed success.[14-18]

Here we use Brillouin-scattering techniques to study the Lamb modes of *unsupported* films. The great advantage of these observations is that the measured frequencies depend *only* on the elastic properties of the film even if the thicknesses are much less than the wavelength of the excitation. Our results extend well into the region where the phonon dispersion is quadratic, and our measured Brillouin frequency shift on a 200-Å film is, to our knowledge, the lowest-lying excitation ($0.03\ \mathrm{cm}^{-1}$) ever to be observed in a solid by use of light-scattering techniques (not including quasielastic processes).

The normal modes of vibration of a free-standing plate can be calculated by means of the usual equations of motion and appropriate boundary conditions corresponding to stress-free surfaces.[19] Rather than use the method described in Ref. 19 we have used an equivalent approach usually used for surface waves in semi-infinite media[20] and for surface and Sezawa modes in supported films.[11,21] The computer programs we used to perform the calculations on supported and unsupported films were general enough to allow calculations of surface-wave velocities in any system in which, by symmetry, a bulk transverse mode is polarized in the surface plane

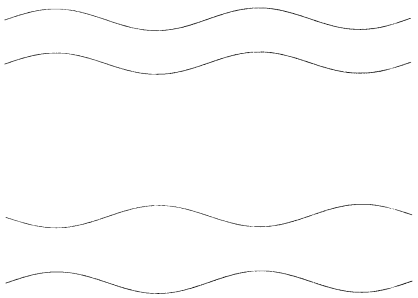

FIG. 1. Schematic of the lowest-lying two modes in an unsupported film.

and hence is decoupled from the other two modes. Thus, we are able to handle the following cases: isotropic, propagation in the basal plane of hexagonal crystals, and propagation along principal axes of cubic, tetragonal, and orthorhombic crystals with a high-symmetry plane normal to the surface. These conditions apply to film and substrate. We have not attempted to include the calculation of the scattered intensities into our calculations.[22] However, if the ripple mechanism is the dominant effect, as it is for most metals,[23] any mode which produces undulations at the surface is, in principle, observable in a Brillouin-scattering experiment.

In Fig. 1 we show a schematic of the lowest-lying two modes in a thin, *unsupported* film. From this figure it is easy to comprehend that when the films are made very thick and hence the top and bottom surfaces become essentially decoupled, the velocity of both modes converges to that of a Rayleigh mode on a semi-infinite medium (cf. Fig. 2) and also to that of a thick *supported* film (cf. Fig. 3). Measurements have been performed on self-sustained films of Al, Ag, and Au prepared by electron-beam gun evaporation or molecular-beam epitaxy on temperature-controlled cleaved NaCl substrates. The data presented here are for electron-beam-gun–evaporated Au films on room-temperature cleaved NaCl substrates. For this first report we choose Au since it is relatively easy to produce in thin films and oxidation problems should be minimal. X-ray studies using Cu $K\alpha$ radiation showed that the samples grew with preferential orientation along the [111] direction and that (200) and (220) reflections were 5 to 20 times weaker than the (111) peak. The films were removed from the substrate by our placing them in contact with a thin, grease-coated mask with holes and then dissolving the substrate in water. Typically, free-standing surfaces could be obtained over areas of ~ 1 mm^2. Brillouin spectra were recorded on a tandem Fabry-Perot interferometer[13] which used between 15 and 100 mW of 5145-Å radiation from a single-mode Ar laser.

From the measured frequency shifts (ω) the velocities (v) were calculated from

$$v = \omega/q \tag{1}$$

and

$$q = k_i(\sin\theta_i + \sin\theta_s), \tag{2}$$

where k_i is the wave vector of the incident light, and θ_i and θ_s are the angles between the surface normal and the incident and scattered wave vectors, respectively.

The experimentally determined velocities for the unsupported Au films are shown in Fig. 2. The dashed line is the fit obtained if we assume elastic isotropy, (viz., $2C_{44} = C_{11} - C_{12}$). Since these films have a preferential growth orientation they consequently have cylindrical ($\equiv$hexagonal) elastic symmetry. We have also performed a fit assuming this symmetry; the result is the

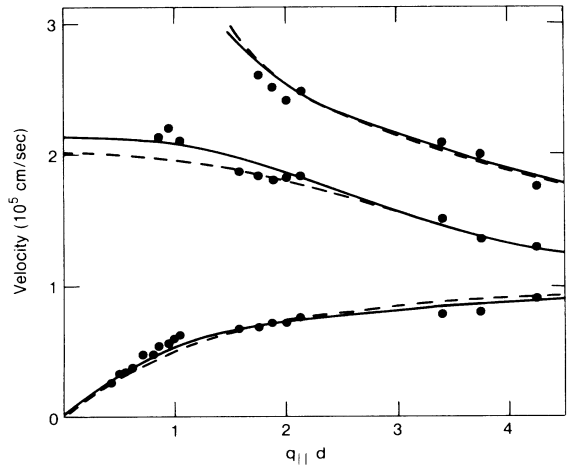

FIG. 2. Measured velocity in unsupported Au films as a function of the product of the thickness (d) and wave vector ($q_{\|}$). The full and dashed lines are fits based on hexagonal or isotropic symmetry of the Au layer.

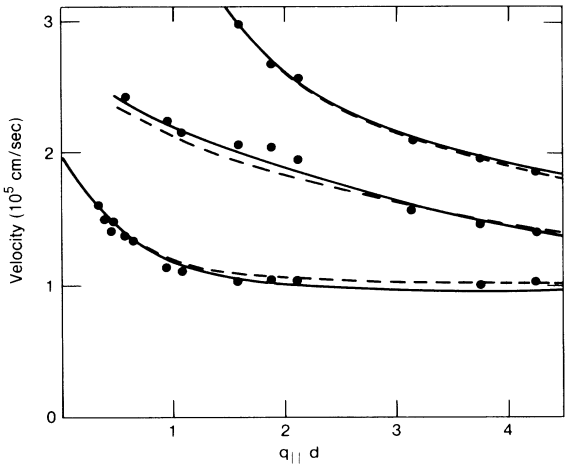

FIG. 3. Same as Fig. 2 for Au films on (001) NaCl substrates. The propagation direction is along a [100] direction of the substrates.

full line in Fig. 2. The elastic constants obtained from these fits are given in Table I. In these fits the bulk value (19.3 g/cm^3) for the density of gold was used since the lattice constant determined with x rays remains constant to within 0.1% as the film thickness is changed. The errors given in Table I for our elastic moduli are estimates based on the changes that variations in one constant produce on the quality of the fit and on the overall accuracy of the frequency shifts. We have not attempted to incorporate errors arising from the fact that variations in two or more of the constants may tend to compensate. Because of this difficulty, and because both the isotropic and hexagonal fits are in good agreement with experiment, we are not able to attribute definite significance to their differences.

With the constants obtained from the fits to the data in Fig. 2 we have calculated the mode positions in Au films supported on NaCl substrate[24] and compared them with our experimental results in Fig. 3; the agreement is excellent.

The elastic constants determined from our data are compared with other values for Au in Table I. In Ref. 15 Brillouin-scattering data of gold on silicon were fitted with only C_{44} as a parameter. In Ref. 14 Brillouin-scattering data of gold on glass were fitted with use of the density and the velocities of the transverse and Rayleigh waves as fitting parameters. The last entry is that of "hard-drawn" gold.[25] It is not clear if this last entry should be compared with the others since being hard drawn it probably has suffered work hardening and furthermore does not have the same preferential growth characteristics as evaporated films. In spite of the differences that exist between the first, third, and fourth entries in Table I, it is interesting to note that the velocity of the transverse mode calculated for each case is $(1.07, 1.13, \text{and } 1.08)\times 10^5$ cm/sec, respectively. This indicates that the actual Brillouin measurements are very similar and most of the discrepancies arise during the fitting procedure. We believe that since we have eliminated the effects of the substrate the present results should be more reliable.

Figure 2 shows that for the lowest mode in unsupported films the velocity is proportional to the product of the thickness (d) and the component of the wave vector parallel to the surface ($q_\parallel$). This behavior illustrates the unusual dispersion relationship

$$\omega \propto q_\parallel^2 \tag{3}$$

displayed by these vibrations.

Although we have shown here that Brillouin scattering is capable of yielding information on unsupported films as thin as 200 Å, it would certainly be interesting to extend these results to thinner films. Even in these very thin films it was not the signal-to-noise ratio that limited the measurements, but the resolution of the interferometer which depends on the maximum distance at which the plates of the instrument can be placed (4 cm in our interferometer). Although it may be possible to gain somewhat with a Fabry-Perot interferometer of higher resolution (which must also be multipassed), a more interesting possibility is the use of light-beating techniques similar to those used in the experiments on liquid crystals.[6-8] With this technique it should be easily possible to detect the smaller frequency shifts expected from films, conceptually even as thin as a few monolayers. Whether or not this technique would possess the necessary contrast remains to be investigated. Further measurements on unsupported Al and molecular-beam-epitaxy-grown Ag films are in progress in order to test in greater detail the potential of the technique described here.

In summary, we have measured for the first time the elastic constants of an unsupported thin film down to a thickness of 200 Å; we have observed the low-frequency normal modes which exhibit a quadratic dispersion law and we have been able to extract information on a variety of elastic constants by fitting the experimentally measured velocities. We believe that the demonstrated viability of this technique provides an additional powerful tool in the study of the many novel materials which

TABLE I. Elastic moduli of gold (10^{11} dyn/cm^2). An asterisk indicates that it was not a fit parameter but a value taken from the literature; N.A. indicates that it was not applicable.

	C_{11}	C_{13}	C_{44}	C_{33}	ρ (g/cm^3)
Isotropic fit	19 ± 1	$C_{11}-2C_{44}$ (14.6)	2.2 ± 0.1	C_{11}	19.3*
Hexagonal fit	23 ± 1	16 ± 1	1.85 ± 0.15	19 ± 1	19.3*
Au on Si[a]	20.7*	$C_{11}-2C_{44}$ (15.7)	2.5 ± 0.1	C_{11}	19.75*
Au on glass[b]	N.A.	N.A.	2.8 ± 0.3	N.A.	24.2 ± 6.1
Bulk polycrystal Au[c]	20.3	$C_{11}-2C_{44}$ 14.7	2.80	C_{11}	N.A.

[a]Reference 8.
[b]Reference 7.
[c]Reference 18.

can now be fabricated with thin-film techniques.

We thank G. Güntherodt, B. Hillebrands, C. Falco, and M. B. Brodsky for useful conversations. This work was supported by the U.S. Department of Energy, Basic Energy Science–Materials Sciences, under Contract No. W-31-109-ENG-38, and by the U.S. Office of Naval Research under Contract No. N00014-83-F-0031.

[1]B. G. Orr, H. M. Jaeger, and A. M. Goldman, Phys. Rev. Lett. **53**, 2046 (1984).

[2]J. Graybeal and M. Beasley, Phys. Rev. B **29**, 4167 (1984).

[3]Sung I. Park and T. H. Geballe, Phys. Rev. Lett. **57**, 901 (1986).

[4]R. C. Dynes, A. E. White, J. M. Graybeal, and J. P. Garno, Phys. Rev. Lett. **57**, 2195 (1986).

[5]For a review see, I. K. Schuller, *IEEE 1985, Ultrasonics Symposium,* edited by B. R. McAvoy (IEEE, New York, 1985), p. 1093 and references therein.

[6]C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. **40**, 773 (1978).

[7]C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. **42**, 1220 (1979).

[8]C. Rosenblatt, R. B. Meyer, R. Pindak, and N. A. Clark, Phys. Rev. A **21**, 140 (1980).

[9]R. Pindak, D. J. Bishop, and W. O. Sprenger, Phys. Rev. Lett. **44**, 1461 (1980).

[10]K. Miyano, Phys. Rev. A **26**, 1820 (1982).

[11]See for example, D. Baral, J. B. Ketterson, and J. E. Hilliard, J. Appl. Phys. **57**, 1076 (1985).

[12]J. R. Sandercock, Phys. Rev. Lett. **29**, 1735 (1972).

[13]J. Sandercock, in *Light Scattering in Solids III,* edited by M. Cardona and G. Güntherodt, Topics in Applied Physics Vol. 51 (Springer, New York, 1982), p. 173.

[14]B. Hillebrands, P. Baumgart, R. Mock, G. Güntherodt, and P. S. Bechthold, J. Appl. Phys. **58**, 3166 (1985).

[15]L. Bassoli, F. Nizzoli, and J. R. Sandercock, Phys. Rev. B **34**, 1296 91986).

[16]B. Hillebrands, R. Mock, G. Güntherodt, P. S. Bechthold, and N. Herres, to be published.

[17]B. Hillebrands, P. Baumgart, R. Mock, G. Güntherodt, A. Boufelfel, and C. M. Falco, Phys. Rev. B **34**, 9000 (1987).

[18]F. Nizzoli, R. Bhadra, O. de Lima, M. Brodsky, and M. Grimsditch, to be published.

[19]B. A. Auld, *Acoustic Fields and Waves in Solids* (Wiley, New York, 1973), Vol. 2.

[20]See, for example, G. W. Farnell, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. 6, p. 109.

[21]G. W. Farnell and E. L. Adler, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1972), Vol. 9, p. 35.

[22]V. Bortolani, F. Nizzoli, G. Santoro, A. Marvin, and J. R. Sandercock, Phys. Rev. Lett. **43**, 224 (1979).

[23]V. Bortolani, F. Nizzoli, G. Santoro, and A. Marvin, J. Phys. (Paris), Colloq. **42**, C6-804 (1981).

[24]The parameters used for the NaCl substrate are as follows: surface (001), propagation along [100], $\rho=2.165$ g/cm^3, $C_{11}=4.91$, $C_{44}=1.28$, and $C_{12}=1.28$ in units of 10^{11} dyn/cm^2.

[25]*American Institute of Physics Handbook* (McGraw-Hill, New York, 1972), p. 3–104 (we have used $\rho=19.3$ g/cm^3 to extract the C_{ij} from the velocities).