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Elastic anisotropies in 22-tricosenoic acid Langmuir–Blodgett films: surface pressure and dipping direction

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Abstract. We present the Brillouin spectra obtained from 22-tricosenoic acid, deposited onto a silicon substrate using the Langmuir–Blodgett technique, for hypersound propagation both parallel and perpendicular to the dipping direction. The spectra show the expected elastic anisotropy of the films and also demonstrate that the velocities increase with deposition surface pressure. Elastic constants are obtained for a film deposited at a surface pressure of 47.5 ± 2.5 mN m^{-1} by fitting the hypersound velocity data to a model of the film.

1. Introduction

Brillouin scattering is an optical technique for studying propagating acoustic modes in materials. The velocity of the modes are determined by knowing the change in the wavevector (from the scattering geometry) and measuring the frequency shift of the light inelastically scattered from acoustic phonons. This method has proved most useful for the investigation of the acoustic behaviour of thin films because of the non-destructive nature of the technique.

For thin supported films, where the transverse sound velocity in the substrate is greater than that in the film, there can be many phonon modes which correspond to guided acoustic waves. There are generally two types of modes: generalised Lamb modes (which include the Rayleigh mode and the other Sezawa modes) with displacements polarised parallel to the sagittal plane (i.e. the plane defined by the propagation direction and the surface normal) and Love modes with displacements polarised perpendicular to the sagittal plane. The velocities of these modes depend upon the product of the wavevector parallel to the surface ($q_\parallel$) and the film thickness (h) together with multiple elastic constants of the film and the substrate. The number of these modes increase with increasing film thickness. With a suitable acoustic model of the film/substrate combination and measurements of the velocities for different values of $q_\parallel h$ the elastic constants for the film can be obtained (see for example Hillebrands *et al* (1985)).

Langmuir–Blodgett (LB) films are produced by repeatedly dipping a substrate through a monolayer which has been spread on a pure water surface and then compressed. The degree of compression of the monolayer on the water is specified by

the surface pressure, which is the change in surface tension relative to that of the water alone. It is usual to deposit the films at a surface pressure just below the point where the film collapses, giving the best film packing on the substrate (Peterson and Girling 1985).

Brillouin scattering was first used to study LB films formed from cadmium salts of the fatty acid arachidic acid, $CH_3(CH_2)_{18}COOH$, (Zanoni *et al* 1986). Measurements were made on films 11 to 401 monolayers thick and values were given for various elastic constants on the basis of an assumed hexagonal symmetry. Recently Brillouin scattering has been used to obtain values for the elastic constants of octadecylfumorate (ODF) LB films (Lee *et al* 1989) and polyglutamate LB films (Nizzoli *et al* 1989).

A study of LB waveguides has also shown for 22-tricosenoic acid that the angle between the optic axis and the normal to the film reduces with increasing surface pressure (Barnes and Sambles 1987). Monitoring the effect of surface pressure upon the Brillouin spectra from LB films would indicate whether the change in the molecular packing, perhaps in tilt angle, influences the elastic properties of the film.

The results presented here show the effect of deposition surface pressure on the Brillouin spectra from 22-tricosenoic acid for propagation parallel and perpendicular to the dipping direction. The observed changes in the hypersound velocities may not solely correspond to a difference in the molecular tilt angle but also demonstrate that the film becomes more rigid on increasing the surface pressure. Also, for one surface pressure and propagation parallel to the dipping direction a set of measurements have been made which allow an estimate of the elastic constants of the film.

2. Experimental

The LB samples of 22-tricosenoic acid ($CH_2{=}CH{-}(CH_2)_{20}{-}COOH$) were deposited onto silaned (hydrophobic) $\langle 100 \rangle$ silicon at various surface pressures (22.5 ± 2.5, 27.5 ± 2.5, 32.5 ± 2.5, 37.5 ± 2.5 and 47.5 ± 2.5 mN m^{-1}) with thicknesses of 50, 100, 200 and 400 monolayers. These samples were prepared using a fully automated rigid barrier trough at GEC Research Laboratories.

The bilayer thickness for the sample deposited with a surface pressure of 47.5 ± 2.5 mN m^{-1} was 56.5 ± 1.5 Å, as measured by x-ray diffraction. This thickness varies with deposition surface pressure since the actual dimer length is 60 Å(Chollet and Messier 1982) but the tilt of the molecule is a function of surface pressure (Barnes and Sambles 1987). At a lower surface pressure (27.5 ± 2.5 mN m^{-1}) electron diffraction gave the bilayer thickness as 53.7 ± 0.8 Å. The density of the LB film was inferred from the suppression of the silicon edge in a Rutherford back-scattering experiment. The value was found to be approximately 1 g cm^{-3} (for the 400 monolayer sample $\rho = 1.01 \pm 0.03$ g cm^{-3}) and so unity will be used when discussing the elastic constants of the film. The refractive index of the film, perpendicular to the substrate, is taken to be 1.59, as measured using guided wave techniques (Barnes and Sambles 1987).

A frequency-stabilised single-mode argon-ion laser ($\lambda = 5145$ Å) was used as a light source, the output power being typically 50 mW. The back-scattering geometry was used, the scattered light being frequency analysed using a 3+3 pass tandem Fabry–Perot interferometer (see for example Sandercock (1982) and Mock *et al* (1987)). A cooled FW130 photomultiplier tube detected the output from the interferometer and an IBM PC was used to control and stabilise the tandem Fabry–Perot and record the Brillouin spectra.

3. Results and discussion

When studying the effect of deposition surface pressure on the resulting Brillouin spectra p-polarised light was incident on the film at 70° to the substrate normal and the back-scattered light was frequency analysed by the tandem interferometer with a cavity spacing of 5 mm. An acousto-optic modulator was used to limit the amount of elastically scattered light incident on the photomultiplier tube; for clarity the effect of this on the central peak has been removed. Figures 1(*a*) and (*b*) show the Brillouin spectra for different deposition surface pressures for propagation both parallel and perpendicular to the dipping direction respectively, together with the signal from the substrate. For propagation parallel to the dipping direction there are at least two distinct modes in the spectra. The first mode with a frequency shift of between 4.5 and 5.2 GHz is the Rayleigh mode. A second, more distinct, feature with a frequency shift of between 7 and 8 GHz corresponds to a Sezawa guided mode. Figure 2 shows the dependence of the velocities of these two modes upon the deposition surface pressure. The Sezawa wave velocity increases linearly with surface pressure as does the Rayleigh wave velocity. This change in velocity with surface pressure is most clearly seen for the Sezawa mode; however, although the Rayleigh mode is weaker in intensity the same trend is discernible. This increase in velocity can be described by two processes: the change in the elastic constants due to the variation in the molecular tilt and the effect of the film becoming more rigid. Without a knowledge of the film's intrinsic elastic constants it is not possible to prove whether the effect of the change in the molecular tilt dominates the increase in velocity. However, it is likely that this effect does contribute, together with the possible increase in rigidity of the film, to the observed change in the velocites with increased surface pressure. Figure 1(*a*) also shows that for the sample deposited at the lowest surface pressure the mode closely related to that of the substrate, with a frequency shift of approximately 20 GHz, is most prominent.

For propagation perpendicular to the dipping direction there are more modes present in the spectra in comparison with the previous case. This highlights the anisotropic nature of these films, and also shows that the film cannot strictly be considered as having hexagonal symmetry. Again, at the lowest surface pressure the mode closely related to that of the substrate is clearly seen with a frequency shift of approximately 20 GHz. The Rayleigh mode, closest to the central line, is most distinct at the lowest surface pressure (this spectrum had the longest accumulation time, $\simeq$ 15 h). Its velocity at the two lowest values of surface pressure is the same, within experimental error, as for propagation parallel to the dipping direction. At higher surface pressures the frequency shift of the Rayleigh mode for propagation both parallel and perpendicular to the dipping direction also appear to be very similar. This indicates that the response of the films to shear is approximately isotropic as was found with the regular ODF films (Lee *et al* 1989). These results contrast with the Brillouin spectra obtained by Zanoni (1986). For propagation parallel and perpendicular to the dipping direction an anisotropy in the hypersound velocities of approximately 5% was observed. However, there were no differences in the number of modes present in the spectra.

The cadmium arachidate (CdA) LB film previously studied using Brillouin scattering had a molecular tilt of 5° with respect to the substrate normal (Zanoni 1986). Using a hexagonal model for the film, a fit to the velocity against $q_{\parallel}h$ data gave a set of elastic constants. Other elastic constants were measured using two separate experiments (Zanoni *et al* 1986).
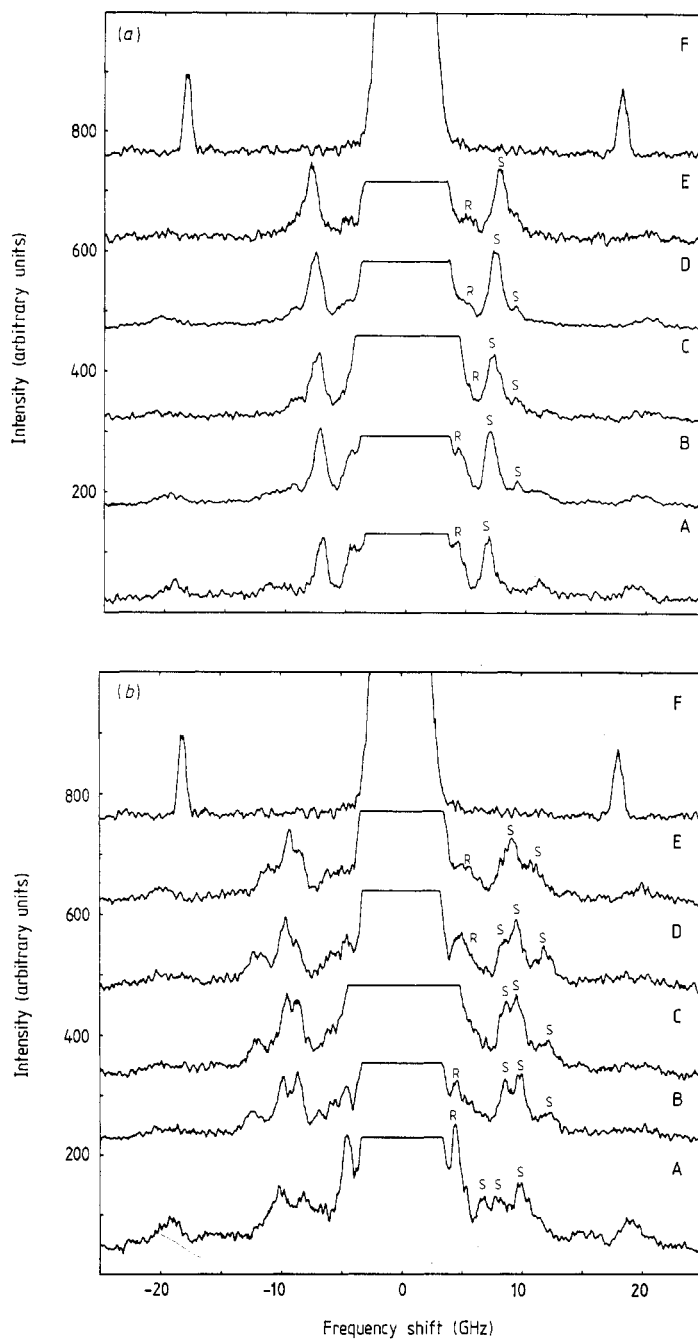
Figure 1. Brillouin spectra for 22-tricosenoic acid deposited on $\langle 100 \rangle$ silicon with deposition surface pressures of (A) 22.5 mN m^{-1}, (B) 27.5 mN m^{-1}, (C) 32.5 mN m^{-1}, (D) 37.5 mN m^{-1} and (E) 47.5 mN m^{-1}. Back-scattering configuration with the light incident at 70° to the subtrate normal. The Rayleigh and Sezawa modes are denoted by the letters R and S respectively. Curve F is the Brillouin spectrum from the silicon substrate. The propagation is (*a*) parallel and (*b*) perpendicular to the dipping direction.
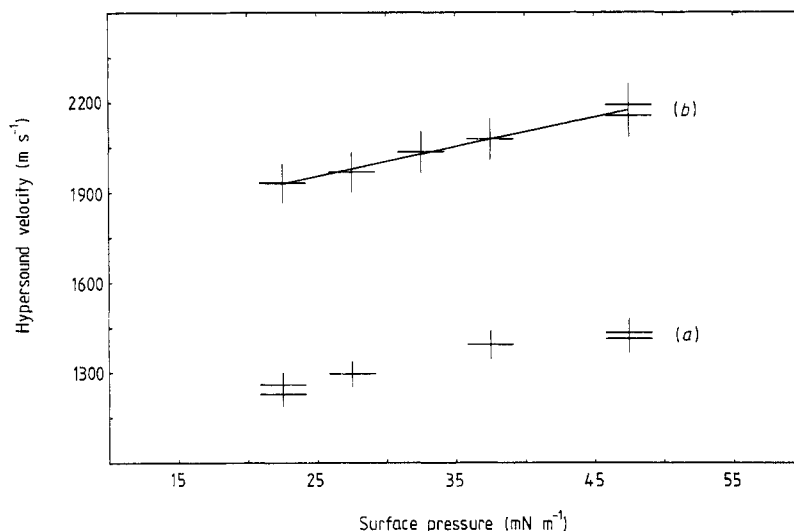
Figure 2. The variation in the velocity of (a) the Rayleigh mode and (b) the Sezawa mode with deposition surface pressure (propagation parallel to the dipping direction).

The same model was used in order to allow estimates for some values of the elastic constants of 22-tricosenoic acid. Clearly this is a simplification of the actual situation since the molecular tilt is approximately 20°, but it is currently the only available model which may be used to extract values for the elastic constants. Brillouin spectra were obtained from the sample deposited at 47.5 ± 2.5 mN m^{-1} at angles of 50°, 60° and 70° to the substrate normal and thicknesses of 50, 100 and 200 monolayers. A further experiment was performed on the 400 monolayer thick sample at normal incidence to obtain a value for C_{33}. Figure 3 shows the data obtained in the first experiment together with theory lines for the fitted dispersion curve. Table 1 compares the elastic constants obtained from the fit with those for the other LB materials studied using Brillouin spectroscopy.

Table 1. Comparison of the elastic constants for 22-tricosenoic acid with CdA (Zanoni *et al* 1986), ODF (Lee *et al* 1989) and polyglutamate (poly(γ-methyl-L-glutamate-co-γ-n-alkyl-L-glutamate)) (Nizzoli *et al* 1989) LB films.

Material	C_{11} (10^9 N m^{-2})	C_{13} (10^9 N m^{-2})	C_{33} (10^9 N m^{-2})	C_{44} (10^9 N m^{-2})
22-tricosenoic acid	6.4 ± 0.6	5.9 ± 0.6	13.5 ± 1.3	0.95 ± 0.1
CdA	11.0 ± 0.7	10.0 ± 0.6	21.0 ± 1.2	0.40 ± 0.01
Unpolymerised regular ODF	6.21 ± 0.31	3.50 ± 0.17	7.68 ± 0.38	1.10 ± 0.05
Polyglutamate	4.74 ± 0.24	3.57 ± 0.18	10.8 ± 0.54	0.91 ± 0.05

The elastic constants for the materials are of the same order, those for CdA being greater than those for the other films. This is most probably due to the presence of cadmium ions in the film. Apart from a double carbon bond, the CdA and 22-tricosenoic acid films are similar in nature, both of these films are generally more rigid than the other LB films. An upper limit for the value of C_{44} for CdA was obtained due to not observing phonon modes greater than 3 GHz in a depolarised scattering
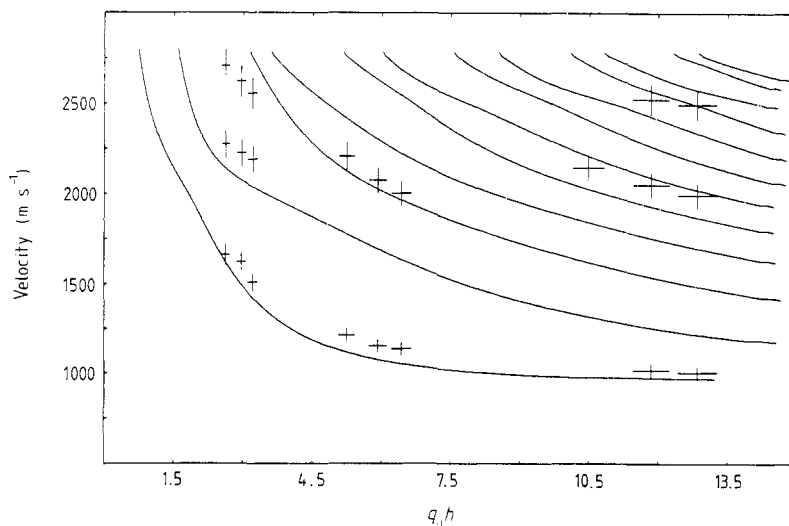
Figure 3. The dispersion curves obtained from fitting the velocity against $q_\parallel h$ data to an acoustical model of the LB film. Propagation parallel to the dipping direction for the sample deposited with a surface pressure of $47.5 \pm 2.5\,\mathrm{mN\ m^{-1}}$.

experiment (Zanoni *et al* 1986) whereas for the other films it was obtained from the parameterised fit to the data. For this reason it is not surprising that there is some difference between the values of C_{44} for CdA and the other materials.

4. Conclusion

We have presented Brillouin spectra showing the general acoustic behaviour of 22-tricosenoic acid on $\langle 100 \rangle$ silicon as a function of deposition surface pressure. The measurements were made using the back-scattering geometry where the light was incident on the sample (50 monolayers thick) at $70°$ to the substrate normal. For propagation parallel to the dipping direction there is a linear increase in the guided wave velocity with surface pressure. The spectra for propagation perpendicular to the dipping direction have more phonon modes compared with the case of propagation parallel to the dipping direction indicating the anisotropic nature of the material. Using a model for the acoustic properties of the film, based on a film/substrate combination with uncoupled Love modes, a set of elastic constants have been obtained for the sample prepared with a surface pressure of 47.5 ± 2.5 mN m^{-1}.

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