Coherent hypersonic closed-pipe organ like modes in supported polymer films

A. V. Akimov, E. S. K. Young, J. S. Sharp, V. Gusev, and A. J. Kent

Coherent hypersonic closed-pipe organ like modes in supported polymer films

A. V. Akimov,[1,a)] E. S. K. Young,[1] J. S. Sharp,[1] V. Gusev,[2] and A. J. Kent[1]

[1]*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*
[2]*Laboratoire de Physique de l'Etat Condensé, UMR CNRS 6087, Université du Maine, 72085 Le Mans, France*

Hypersonic wavepackets were injected into polymer films of various thicknesses on a crystalline substrate, and quantized vibrational modes were detected. The acoustic spectrum showed up to six localized modes with frequencies determined by the boundary conditions for acoustic modes similar to those obtained in closed organ pipes. The decay rate of the modes was found to increase linearly with frequency in the gigahertz range. © 2011 American Institute of Physics. [doi:10.1063/1.3605567]

Recent studies on the generation and detection of coherent gigahertz (GHz) and sub-terahertz (THz) elastic waves in nanometer films have demonstrated their potential for applications in areas such as nanotechnology, communications, medicine, and biology.[1–5] The phonon spectrum in nanometer films can possess quantization of modes corresponding to vibrations of the entire film. The lowest frequency mode of such vibrations occurs when $f_0 = Asd^{-1}$, where s is the velocity of the sound wave, d is the film thickness, and A is a coefficient which depends on the boundary conditions.

Phonon quantization takes place only when the film is strongly acoustically decoupled from the surroundings. This occurs when the materials surrounding the film have acoustic impedances which are very different from that of the film. Two particular situations have been studied previously: namely, films having much higher acoustic impedance than those the surroundings, (corresponding either to free standing membranes or to films deposited on substrates which are acoustically much softer than the film) and films that are supported by a material which has a much higher acoustic impedance. In these types of studies, researchers often draw an analogy with musical instruments, referring to the elastic modes in these two cases as open- and closed-pipe organ like modes, respectively. This is due to the similarity of the frequency dependence and nature of the mechanical displacements within the vibrating films to those of sound waves in pipes. Both types of mode have been studied extensively during the last decade using Brillouin scattering techniques.[6–11] Coherent hypersonic experiments, largely designed to study open-pipe organ modes, have been performed on ultrathin membranes[12,13] and supported films.[1,14,15] So far, very little work has been done on closed-pipe organ modes using coherent hypersonic techniques. A key challenge is to generate and detect coherent hypersonic vibrations in systems which display this type of behavior.[16,17]

In the present work, we performed picosecond acoustic experiments on ultrathin polymer films that were deposited on a crystalline silicon (Si) substrate. The acoustic mismatch between the polymer and Si was high enough to expect the formation of well separated closed-pipe organ like modes in

the phonon spectrum.[9,10] The quantized eigenmodes in the direction perpendicular to the film plane are expected to have frequencies given by

$$f_n = s(2n+1)/4d, \qquad (1)$$

where $n = 0, 1, 2\ldots$ is the mode number. In earlier work performed on a polymer film using an optical transmission pump-probe technique, only the lowest (fundamental) mode ($n = 0$) was observed.[16] In the present work, we detect high-amplitude coherent hypersonic signals and obtain up to six closed-pipe organ like modes in a number of polymer films with different thickness values.

Recent developments in the fabrication of complex block co-polymer nanostructures and arrays by various technologies including nanoimprinting[18] have generated a great deal of interest in the study of thin films of these materials. In this study, thin films of a polystyrene-block-polybutadiene-block-polystyrene block copolymer (PSPBPS, Mw = 140 kDa, 30 wt. % styrene, Sigma, UK) were spin cast from solutions in toluene on to 50 μm thick single crystal silicon wafers. The thickness of the films was controlled by varying the concentration of the solutions and the spin speed used during deposition of the films. The PSPBPS microphase separates to form cylindrical micelles of polystyrene (PS) in a matrix of polybutadiene.[19] The diameter of the cylindrical micelles in this material were measured to be 35 ± 2 nm using an atomic force microscope operating in tapping mode, and the film thickness and refractive index of the films were measured using a self-nulling ellipsometer ($\lambda = 633$ nm). Thin films of PS were also deposited by spin coating solutions of the polymer (dissolved in toluene) on to Si substrates.

The hypersonic experiments were performed at room temperature using the picosecond acoustic technique.[20] The experimental scheme is shown in the inset of Fig. 1. A 100 nm thick Al film was deposited on the surface of the Si substrate opposite to the polymer film. The Al film was excited by 60 fs optical pulses (wavelength 800 nm, repetition rate 5 kHz) using a Ti-sapphire laser system with a regenerative amplifier. The energy density of the pump beam focused to a spot with diameter 200 μm did not exceed $W \sim 1$ m J cm^{-2}. As a result, a bipolar strain pulse with amplitude $\sim 10^{-4}$ and total duration of ~ 15 ps was injected into the Si substrate. After the strain

a)Author to whom correspondence should be addressed. Electronic mail: andrey.akimov@nottingham.ac.uk.
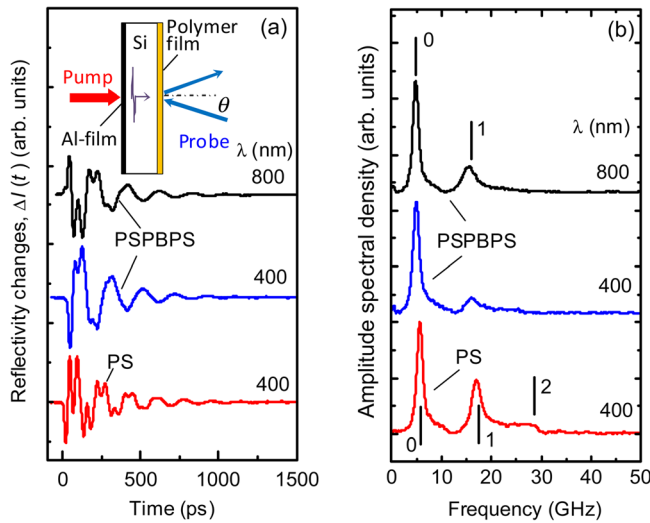
FIG. 1. (Color online) (a) Temporal profiles of the reflectivity signals measured in PSPBPS and PS films with thickness values of 105 nm and 95 nm, respectively. The wavelength λ of the probing light is indicated above the curves. The inset shows the experimental scheme. (b) Amplitude spectra obtained from the signals shown in (a) by fast Fourier transforms. The vertical bars indicate the frequencies of the closed-pipe organ like modes calculated using Eq. (1). The order of the modes, n, are indicated near the corresponding bars.
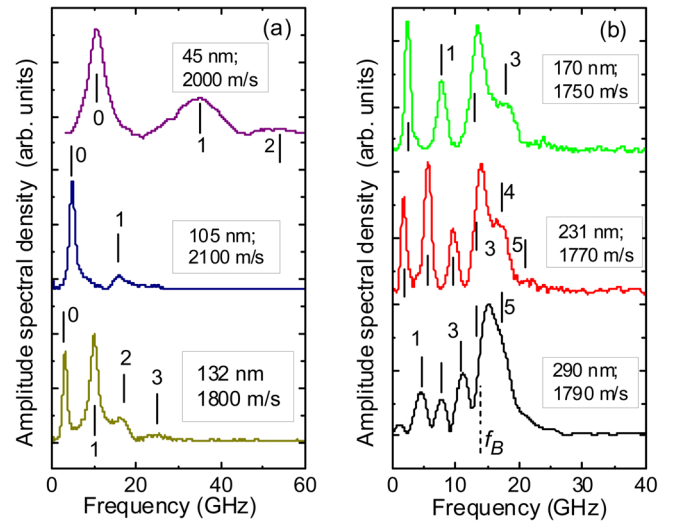

FIG. 2. (Color online) Amplitude spectra obtained from the temporal profiles measured in PSPBPS films with various thickness by probing with λ = 400 nm. The solid vertical bars indicate the frequencies of the closed-pipe organ like modes calculated using Eq. (1). The thickness of the films and sound velocity used in calculations are given in the square frames near each curve. The vertical dashed bar (f_B) indicates the frequency of Brillouin oscillations expected in the bulk material.

pulse propagated through the Si substrate with the velocity of longitudinal polarized (LA) sound (8.3×10^3 ms^{-1}), it reached the polymer film (in a time ~6 ns). The strain pulse was partly reflected from the Si/polymer interface due to acoustic mismatch, and about 25% of the elastic energy was injected into the polymer film. This resulted in a hypersonic wavepacket consisting of coherent LA phonons being excited in the polymer film.

The hypersonic wavepacket was detected in the polymer film by measuring the changes of the intensity ΔI of the reflected optical probe pulse. The probe beam was focussed on the polymer film directly opposite to the excitation pump spot in the metal film. The time delay, t, between pump and probe optical pulses was scanned using an optical delay line which provides a time resolution of 100 fs. Mechanisms of probing coherent elastic waves in thin optically transparent films by ultrashort optical pulses are described in a number of earlier papers.[21]

The measurements were performed using various probing wavelengths (λ = 400 nm or 800 nm) and excitation pump densities W on a number of PSPBPS and PS films with various values of the thickness d. The films were transparent at both wavelengths used to probe the reflectance of the samples. Figure 1(a) shows the signals $\Delta I(t)$ measured in PSPBPS and PS films with d = 105 and 95 nm, respectively. It is seen that the complex temporal profile of $\Delta I(t)$ includes fast and slow oscillations. The oscillations decay over times of up to $t \sim 1$ ns in both films and it is clear that high-frequency features in $\Delta I(t)$ appear immediately after the injection of the hypersonic wavepacket into the polymer film. At longer times ($t > 500$ ps), the high-frequency components disappear, and the temporal profile possesses decaying oscillations with a single period.

Figure 1(b) shows the amplitude spectrum of the elastic vibrations obtained by the fast Fourier transforms (FFT) of the signals $\Delta I(t)$ presented in Fig. 1(a). All three spectra pos-

sess two well separated peaks with central frequencies f_n that are well described by Eq. (1) for $n = 0$ and $n = 1$. The sound velocities used in Eq. (1) were $s_{LA}^{(PSPBPS)} = 2.1 \times 10^3$ ms^{-1} and $s_{LA}^{(PS)} = 2.3 \times 10^3$ ms^{-1} for PSPBPS and PS films, respectively. The value of $s_{LA}^{(PS)}$ for the PS film is close to the values obtained in earlier works on PS films.[22–24] Hence, the three spectra presented in Fig. 1(b) show the features that are consistent with the presence of quantized phonon modes that are characteristic of closed-organ pipe modes.

The spectra of films with various d values were measured in order to confirm the validity of the organ-pipe mode assignments used for the observed hypersonic modes. The results for PSPBPS films are shown in Fig. 2. The calculated values of f_n are shown by vertical bars labeled by the corresponding values of n. The values of d and sound velocities $s_{LA}^{(PSPBPS)}$ used in the calculations are indicated within the borders above each curve. It is seen that the measured spectral peaks are in good agreement with the calculations. The variation of the value of $s_{LA}^{(PSPBPS)} = (1.78 \pm 0.05) \times 10^3$ ms^{-1} does not exceed 3% for films with $d > 130$ nm. The increase of $s_{LA}^{(PSPBPS)}$ up to 2.1×10^3 ms^{-1} with the decrease of d is in qualitative agreement with the earlier studies in polymer films.[25] Thus, we conclude that the polymer films studied display spectra that are consistent with the presence of closed-pipe organ like modes. Up to four well resolved modes are clearly detected and the spectral features of two further modes are also present in the spectra in Fig. 2(b).

In the films with $d \geq 170$ nm [see Fig. 2(b)], there are spectral peaks centered around $f_B = 14$ GHz, which correspond to the Brillouin frequency indicated by dashed bar,[26,27]

$$f_B = 2s_{LA}\sqrt{\varepsilon - \sin^2\theta}/\lambda, \qquad (2)$$

where ε is the dielectric permittivity for the probing wavelength (for PSPBPS, we took $\varepsilon = 2.4$ from ellipsometry data) and $\theta = 10°$ is the angle of incidence of the probe beam [see
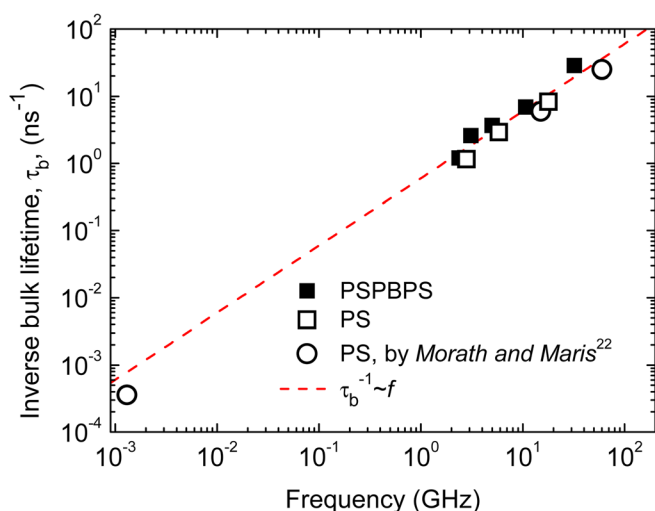
FIG. 3. (Color online) Frequency dependence of the bulk decay rate of the closed-pipe organ like modes in PSPBPS and PS films, after correction for the finite leakage through the polymer/Si interface. The solid line shows the linear frequency dependence of the decay rate due to attenuation in the polymer film and is compared with the data for PS from Ref. 22.

the inset in Fig. 1(a)]. The observation of the signal at the Brillouin frequency only in sufficiently thick films is consistent with the fact that the spectral selectivity of the acousto-optic detection narrows around the Brillouin frequency with increasing film thickness.[10]

The experiments performed here allow us to obtain the decay time (τ) of coherent modes excited in the polymer films. The values of τ for low frequencies, $f < 10$ GHz, were obtained from measured temporal curves $\Delta I(t)$ at long delays, when only one decaying mode, related to $n = 0$, remains in the spectrum. For higher frequencies, the value of τ was derived from the width of the corresponding spectral lines. The experimentally observed lifetime $\tau^{-1} = \tau_b^{-1} + \tau_l^{-1}$, where τ_b and τ_l are the decay times related to the attenuation in the bulk of the polymer film and the leakage from the film to the substrate, respectively. For the leakage time, we have $\tau_l^{-1} = s(2d)^{-1}$ $\ln(R^{-1})$, where $R = 0.75$ is the modulus of the reflection coefficient of the acoustic waves at the film/substrate interface. The results for τ_b are presented in Fig. 3. It is seen that the decay rate τ_b is well described by a linear frequency dependence shown in Fig. 3 by the dashed line. The values of τ_b in PSPBPS are slightly larger than in PS, which is apparently due to additional phonon scattering at the interfaces between the PS and the PB blocks in the polymer. The measured dependence is in agreement with the extrapolation proposed by Morath and Maris[22] between the measurements below 1 GHz accomplished by Brillouin scattering and ultrasonic techniques and high frequency measurements by picosecond laser ultrasonics in the range 10 GHz–100 GHz. Although the observed linear dependence of the acoustic attenuation on frequency below 1 GHz has been attributed to the relaxation on structural defects,[28] this issue is still under debate. Here, the experimental confirmation of the validity of this universal law in the frequency range 1 GHz–20 GHz is reported. The block structure of the PSPBPS copolymer can be excluded as the main reason for the linear dependence of τ_b on f because similar behavior is observed in PS films (see open symbols in Fig. 3), where the polymer structure is homogeneous.

In conclusion, we have observed coherent quantized vibrational modes in supported polymer films. The detected spectra of the vibrational modes consist of up to six spectral lines, which have frequencies that are well described by the spectrum of closed-pipe organ like modes. The observation of more than one mode in the same film opens the possibility for using the same film in nanomechanical circuits operated in a wide frequency range. Polymer films on crystalline substrates have potential applications as sensors for adsorbed molecules including biosensors. The deviations of the spectra from the simple equally spaced lines predicted by Eq. (1) could also be used as a method for characterization of the nanoscale structure of the block copolymer. This will be the subject of future work.

[1]N. Nakamura, A. Uranishi, M. Wakita, H. Ogi, M. Hirao, and M. Nishiyama, Appl. Phys. Lett. **98**, 101911 (2011).
[2]W. Xu, S. Choi, and J. Chae, Appl. Phys. Lett. **96**, 053703 (2010).
[3]F. Bender, P. Roach, A. Tsortos, G. Papadakis, M. I. Newton, G. McHale, and E. Gizeli, Meas. Sci. Technol. **20**, 124011 (2009).
[4]C. Rossignol, N. Chigarev, M. Ducousso, B. Audoin, G. Forget, F. Guillemot, and M. C. Durrieu, Appl. Phys. Lett. **93**, 123901 (2008).
[5]R. C. Hughes, A. J. Ricco, M. A. Butler, and S. J. Martin, Science **254**, 74 (1991).
[6]X. Zhang, R. Sooryakumar, A. G. Every, and M. H. Manghnani, Phys. Rev. B **64**, 081402(R) (2001).
[7]X. Zhang, R. S. Bandhu, R. Sooryakumar, and B. T. Jonker, Phys. Rev. B **67**, 075407 (2003).
[8]R. S. Bandhu, X. Zhang, R. Sooryakumar, and K. Bussmann, Phys. Rev. B **70**, 075409 (2004).
[9]J. Groenen, F. Poinsotte, A. Zwick, C. M. Sotomayor-Torres, M. Prunnila, and J. Ahopelto, Phys. Rev. B **77**, 045420 (2008).
[10]N. Gomopoulos, W. Cheng, M. Efremov, P. F. Nealey, and G. Fytas, Macromolecules **42**, 7164 (2009).
[11]R. S. Bandhu, R. Sooryakumar, and K. Bussmann, Ann. Phys. **523**, 107 (2011).
[12]A. Bruchhausen, R. Gebs, F. Hudert, D. Issenmann, G. Klatt, A. Bartels, O. Schecker, R. Waitz, A. Erbe, E. Scheer, J.-R. Huntzinger, A. Mlayah, and T. Dekorsy, Phys. Rev. Lett. **106**, 077401 (2011).
[13]F. Hudert, A. Bruchhausen, D. Issenmann, O. Schecker, R. Waitz, A. Erbe, E. Scheer, T. Dekorsy, A. Mlayah, and J.-R. Huntzinger, Phys. Rev. B **79**, 201307(R) (2009).
[14]H. Ogi, M. Fujii, N. Nakamura, T. Yasui, and M. Hirao, Phys. Rev. Lett. **98**, 195503 (2007).
[15]H. Tanei, N. Nakamura, H. Ogi, M. Hirao, and R. Ikeda, Phys. Rev. Lett. **100**, 016804 (2008).
[16]G. S. Kanner, Z. V. Vardeny, and B. C. Hess, Phys. Rev. B **42**, 5403 (1990).
[17]C. Mechri, Ph.D. thesis, Université du Maine, Le Mans, France, 2009.
[18]R. A. Farrell, N. Kehagias, M. T. Shaw, V. Reboud, M. Zelsmann, J. D. Holmes, C. M. Sotomayor-Torres, and M. A. Morris, ACS Nano **5**, 1073 (2011).
[19]Q. Zhang, O. K. C. Tsui, B. Du, F. Zhang, T. Tang, and T. He, Macromolecules **33**, 9561 (2000).
[20]C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, Phys. Rev. B **34**, 4129 (1986).
[21]V. Gusev, Acust. Acta Acust. **82**, S37 (1996).
[22]C. J. Morath and H. J. Maris, Phys. Rev. B **54**, 203 (1996).
[23]W. Cheng, R. Sainidou, P. Burgardt, N. Stefanou, A. Kiyanova, M. Efremov, G. Fytas, and P. F. Nealey, Macromolecules **40**, 7283 (2007).
[24]P. M. Walker, J. S. Sharp, A. V. Akimov, and A. J. Kent, Appl. Phys. Lett. **97**, 073106 (2010).
[25]Y. C. Lee, K. C. Bretza, F. W. Wise, and W. Sachse, Appl. Phys. Lett. **69**, 1692 (1996).
[26]H. N. Lin, R. J. Stoner, H. J. Maris, and J. Tauc, J. Appl. Phys. **69**, 3816 (1991).
[27]O. B. Wright, J. Appl. Phys. **71**, 1617 (1992).
[28]K. S. Gilroy and W. A. Phillips, Philos. Mag. B **32**, 202 (1980).