Injection of High-Amplitude Picosecond Acoustic Pulses into Polymer Films

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Picosecond acoustic wavepackets, which are generated in a metal film by femtosecond optical excitation, propagate in a crystalline substrate and are then injected into a polymer film. Such an experimental arrangement allows picosecond strain pulses with amplitude up to $\sim 0.01$ to be injected into the polymer at room temperature without destroying it.

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I. INTRODUCTION

Polymers are prospective materials for the fabrication of submicrometer phononic devices such as hypersonic crystals, nanomechanical oscillators, acousto-optical switches and other devices for realizing attractive “sound ideas” [1]. Polymer nanolayers are easily prepared by spinning the corresponding solutions on to a solid substrate. The technology for producing photonic devices from polymer colloidal suspensions is now well developed, and it can be directly applied to the fabrication of two- and three-dimensional hypersonic crystals [2, 3]. Basic material properties such as the elastic constants and sound velocities are known for a large number of polymer materials. Some polymers [e.g. polyvinylidene fluoride (PVDF)] exhibit the piezoelectric effect, which opens up the possibility of using electric fields and microwave radiation to control acoustic waves and vice-versa.

The non-coherent acoustic properties of a number of polymer films and polymer-based phononic structures have been studied by the Brillouin scattering technique [2–4]. However, to our knowledge, coherent acoustic waves in the GHz and sub-THz frequency range have been studied in only a few experimental works [5, 6], where picosecond strain pulses with amplitudes $<10^{-5}$ were injected into a polymer film directly from a thin metal transducer excited by optical pulses from a laser. Such an experimental arrangement has also been recently used to study GHz acoustic waves in single cells [7].

In the present work, we produce hypersonic wavepackets in polymer films by injecting picosecond strain pulses from the various crystalline substrates on which the films are deposited. Such an experimental arrangement allows us to achieve the generation of high amplitude hypersonic waves in a polymer film without destroying the material via thermal effects.
II. EXPERIMENT

In the experiments, we used polystyrene (PS) and polyvinylpyrrolidone (PVP) polymer films. These materials are technologically suitable for fabrication two-component multilayer structures (e.g., photonic and phononic crystals). The films were prepared by spinning of corresponding polymer solutions on crystalline silicon (100) or sapphire substrates. In the samples on sapphire substrates, a 100-nm layer of silver was deposited on the substrate surface before spinning on the polymer film. The thickness of the prepared polymer films varied from 200 nm up to 500 nm.

The hypersonic wavepacket is injected into the polymer structure from the crystalline substrate by means of the picosecond acoustic technique [8]. The corresponding experimental scheme is shown in Fig. 1. An Al film with a thickness of ~100 nm was deposited on the side of the substrate opposite to the polymer film. The metal film was excited by 60-fs pump pulses generated by a titanium sapphire laser (wavelength 800 nm) followed by a regenerative amplifier with a repetition rate of 5 kHz. The diameter of the excitation spot was 200 μm and the maximum energy density in the pulse incident on the Al film was ~18 mJ/cm². As a result of the optical excitation, the Al film expands due to the thermoelastic effect and a bipolar strain pulse \( \eta(t,x) \) (Fig. 2) is injected into the substrate. The spectrum of the injected hypersound wavepacket peaks at a frequency ~30 GHz, which is in the range of interest for high-frequency acoustics. The strain pulse propagates through the substrate and reaches the substrate/polymer interface in a time \( t_0 = D/s_0 \sim 10 \text{ ns} \) [\( D \sim 100 \mu \text{m} \), and \( s_0 = 8430 \text{ m/s} \) (11100 m/s) are the thickness of the substrate and longitudinal sound velocity in Si (sapphire), respectively]. The strain pulse is partly reflected back to
the substrate and partly transmitted into the polymer film. Calculations based on acoustic mismatch theory give the transmitted strain and displacement pulses in the polymer layer. The shapes of these pulses in a Si substrate and a PVP film are shown in Fig. 3. It is seen that the strain pulse, which represents the hypersonic wavepacket injected into the polymer film, has an amplitude $\eta_0 \sim 10^{-2}$ and occupies in space a distance of $\sim 100$ nm.

Detection of the hypersound wavepackets in the polymer film is realized by probing the optical reflectivity $R$ with a pulse originating from the same laser system, which excites the strain pulses (Fig. 1). In most of the experiments, the probe pulse was passed through a nonlinear crystal and a wavelength $\lambda = 400$ nm was used for probing the elastic vibrations in the polymer film.

The experimental scheme of a pump-probe setup is shown in Fig. 4. The probe beam is passed through an optical delay line controlled by a stepper motor, thus allowing scanning of the time interval, $t$, between the pump and probe pulses. The probe optical pulse is incident on the polymer sample opposite the pump excitation at an angle $\theta_s$ and the specularly reflected beam is measured by an input of a balance photodetector. The second input of the photodetector was illuminated by the light splitted from the incident probe beam. The detection with the balance photodetector allows to increase signal-to-noise ratio on more than one order of magnitude.

Figure 5 shows the pump probe reflectivity changes $\Delta R(t)/R_0$ ($R_0$ is the reflectivity without strain pulses) measured with probe wavelength $\lambda = 400$ nm in the PS films deposited on the Si (a) and sapphire (b) substrates. The oscillatory behavior is clearly seen. The period of the oscillations is the same in the samples deposited on different substrates. The decay of the oscillation amplitude does not depend strongly on the substrate used or on the exact position on the sample surface probed. The period of the oscillations does not depend on the pump excitation density, $W$, and up to $W \sim 12$ mJ/cm$^2$, the measured $\Delta R(t)/R_0$ increases linearly with $W$ (see Fig. 6). At higher $W$, $\Delta R(t)/R_0$ starts to saturate.
FIG. 5: Relative reflectivity changes measured in PS film deposited on Si (a) and sapphire (b) substrates.

FIG. 6: Relative reflectivity changes measured in PS film deposited on Si substrate for various pump excitation densities at the Al transducer.

which is apparently due to the significant increase in sample temperature.

The signals $\Delta R(t)/R_0$ measured under the same experimental conditions in PVP films are shown in Fig. 7. The signals show oscillations with a different frequency compared to the PS films. However, the variations of $\Delta R(t)/R_0$ for various substrates and excitation/detection points on the films are significantly higher than those in the experiments with PS films. In the example presented in Fig. 7, it is seen that the oscillations for the PVP film deposited on the Si substrate decay faster than those for the film deposited on a sapphire substrate. The reason for this difference can be the difference in the film thicknesses in these two cases. The film deposited on Si was approximately one half the thickness of the film deposited on sapphire and so the strain pulse experiences reflection at the interfaces twice as often. Each time, it is reflected, it loses some amplitude, and this could account for apparently faster decay in signal amplitude with time. The pump excitation density dependence in the experiments with PVP film show saturation of the oscillation amplitude at lower $W$ in comparison with those with PS film. Overall, the PVP films show worse hypersonic acoustic quality for experiments in comparison with PS film, but can be quite suitable for hypersonic applications if their thickness is not too large ($\sim$100 nm).

Figure 8 shows $\Delta R(t)/R_0$ measured in PS films on a sapphire substrate over a long (>2 ns) time interval. The fast oscillations decay in a time $\sim$1 ns and then slow oscillations with frequency $f = 2.6$ GHz are clearly seen. The slow oscillations can be attributed to the vibrations of the whole film with thickness $d$ and are expected to have a frequency $f = s_{ps}/2d$, where $s_{ps}$ is a longitudinal sound velocity. Taking $s_{ps} = 2.3 \times 10^3$ m/s [4, 5]
and \( d = 390 \) nm, we get \( f = 2.9 \) GHz, which is within the experimental resolution of 0.4 GHz.

Figure 9 shows the fast Fourier transform of the measured \( \Delta R(t)/R_0 \) shown in Fig. 8. There are three peaks clearly observed in the spectrum. The low frequency one \( f = 2.6 \) GHz, as mentioned above, corresponds to the coherent vibrations of the whole film. The high-frequency peak with \( f_B = 19 \) GHz is equal to the Brillouin frequency which is governed by the momentum conservation for photon-phonon interaction in PS-film. The nature of a doublet peak around \( f = 13 \) GHz is related to the phase changes of the coherent wavepacket.

FIG. 7: Relative reflectivity changes measured in PVP films deposited on Si and sapphire substrates.

FIG. 8: Long time temporal reflectivity trace measured in the PS film on sapphire substrate.

FIG. 9: The fast Fourier transform of the long time trace shown in Fig. 8.
III. ANALYSIS AND DISCUSSION

We have performed theoretical modeling of the reflectivity signal $\Delta R(t)/R_0$ in a polymer film. The modeling is based on the theoretical approach developed in earlier works [9]. In the analysis, several contributions to the signal $\Delta R(t)/R_0$ are included. The main contribution comes from the interference of the probe beam reflected from a picosecond acoustic wavepacket propagating in a polymer film with a sound velocity $s$, and the beams reflected from the interfaces of the film. In homogeneous and semi-infinite media when only one interface with air exists, this contribution, known also as the coherent Brillouin signal, shows oscillations with a single frequency $f_B$. For normal incidence of the probe beam:

$$f_B = \frac{2sn}{\lambda},$$

where $\lambda$ is a wavelength of the probe light and $n$ is the refractive index of the polymer.

Another contribution to $\Delta R(t)/R_0$ comes from the Fabry-Perot interference of two probe beams reflected from the interfaces (polymer/air and polymer/substrate interface). When the strain pulses are incident on these interfaces, the modulation of the polymer film thickness results in the modulation of the phase shift between the interfering beams and so the $\Delta R(t)/R_0$ possesses a temporal response.

In the analysis, we model the propagating wavepacket (Fig.3) and get a resulting signal $\Delta R(t)/R_0$, which is shown in Fig.10. The calculations have been performed for $\lambda = 400$ nm, while $s$ and $d$ were used as fitting parameters to get a best agreement with the experimental data for the PS-film grown on the Si substrate [Fig.5(a)]. The value for $n_{ps} = 1.628$ was obtained from ellipsometry measurements. Acoustic attenuation in the PS-film and possible losses in acoustic pulse amplitude due to scattering at the interface with air were ignored.

The result of the modeling (Fig.10) shows the coherent Brillouin oscillations in $\Delta R(t)/R_0$, along with rapid features due to the layer thickness modulation each time the
wave packet reaches an interface. Also, each time the wave is reflected from an interface, a phase lag is introduced into the Brillouin oscillations as the pulse reverses its direction of propagation. The reflection from the PS/Si interface is accompanied by a decrease in the amplitude of the oscillations in $\Delta R(t)/R_0$. Similar modeling for PVP-films has been performed. The corresponding parameters obtained for the polymer films are presented in Table 1.

**TABLE I: Sound velocities and thicknesses of the studied polymer films**

<table>
<thead>
<tr>
<th></th>
<th>Sound velocity (m/s)</th>
<th>Thickness (nm)</th>
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<tbody>
<tr>
<td>PS on Si</td>
<td>2230 +/- 40</td>
<td>240 +/- 20</td>
</tr>
<tr>
<td>PS on sapphire</td>
<td>2260 +/- 40</td>
<td>390 +/- 40</td>
</tr>
<tr>
<td>PVP on Si</td>
<td>2900 +/- 200</td>
<td>230 +/- 30</td>
</tr>
<tr>
<td>PVP on sapphire</td>
<td>2870 +/- 60</td>
<td>450 +/- 70</td>
</tr>
</tbody>
</table>

The obtained values for sound velocities in the PS film are in good agreement with earlier experiments: $s_{ps} = 2350 \text{ m/s}$ [4] and $s_{ps} = 2300 \text{ m/s}$ [5] measured by Brillouin scattering and ultrafast acoustic techniques, respectively.

Figure 11 shows the fast Fourier transform of the calculated signal $\Delta R(t)/R_0$ (Fig.10). The spectral peaks at the Brillouin frequency at $f_B = 18 \text{ GHz}$ and low-intensity sidebands are observed. These sidebands are the result of a combination of the phase shifts and decreases in amplitude, which take place at the reflection of the acoustic wavepacket at the interfaces. These modulate the signal at frequencies of $f = s_{ps}/d$ and $f = s_{ps}/2d$. In the case of a semi-infinite film, the side-bands are absent and only one line centered at the Brillouin frequency, as given by Eq.(1), is present in the spectrum. The presence of the modulation splits this central line into the observed spectrum of side bands with the weights of each line depending on the exact nature of the modulation. Thus the exact spectrum of the finite film depends strongly on the thickness of the film, the relative contributions to $\Delta R(t)/R_0$ from Brillouin and Fabry-Perot interference mechanisms and the loss of the amplitude on the reflections. Qualitatively, we can attribute the experimentally observed sideband (Fig.9) at $f \approx 13 \text{ GHz}$ to the phase shift of the $\Delta R(t)/R_0$.

There is still uncertainty in the calculations of the absolute amplitude of the oscillations. The temporal shape of $\Delta R(t)/R_0$ in PS films deposited on various substrates are similar but the amplitude of the oscillations in the sample on the Si substrate is one order of magnitude higher [compare $\Delta R(t)/R_0$ in Fig.5 (a) and (b)]. The reason for this can be understood from the detailed analysis of the interference of the light reflections from the substrate and the strain pulse. A qualitative explanation is that because the silver film has an amplitude reflection coefficient close to -1, the signal due reflection of light directly from the strain pulse and due to reflection from the substrate, then the strain pulse, then the substrate again cancel each other out to a significant degree. Detailed numerical calculations confirm that there is a change of order 10 times in signal strength when a silicon substrate is replaced by one with optical amplitude reflection coefficient near -1. The modeling was based on the method developed by O.B. Wright [9].
The quantitative modeling does not include attenuation of the acoustic wave-packet during propagation through a polymer film. Obviously, this attenuation plays an important role and it is partly responsible for the decrease in the oscillation amplitudes in $\Delta R(t)/R_0$ (Figs. 5, 6 and 7). The saturation of amplitude in the measured $\Delta R(t)/R_0$ observed for the PVP films could be the result of an increase in the attenuation with the sample temperature, which apparently takes place at high $W$. The frequency-dependent attenuation (mean free path $l \sim f^{-2}$ [5]) could be responsible for the relatively high intensity of the spectral sideband shown in Fig. 9. This frequency in the acoustic wavepacket should not decay as rapidly as the main Brillouin spectral component at $f = 19$ GHz, resulting in comparable amplitudes of the main Brillouin and sideband peaks. However, from the comparison of various experimental temporal traces, it is not clear whether the attenuation occurs mostly during the reflection at the interfaces or while the acoustic wavepacket propagates in the bulk of the polymer film. More systematic studies are required to make a certain conclusion about the attenuation of GHz sound in the polymer films.

IV. CONCLUSIONS

We have performed experiments where coherent acoustic wavepackets are injected into polymer films from crystalline substrates. Such an experimental arrangement allows the generation of a polymer film of picosecond strain pulses with an amplitude of $\sim 1\%$. The detected signals are free from thermal and electronic backgrounds, which are typical in traditional experiments, when the acoustic wavepacket is injected into the polymer film directly from the opaque substrate or metal film. Polystyrene and polyvinylpyrrolidone films with thicknesses of $\sim 200–400$ nm, deposited by spinning of corresponding solutions on silicon and sapphire substrates, have been shown to be realistic materials for operations with high-amplitude acoustic waves in the frequency range up to 20 GHz. The experimental results, supported by a theoretical modeling, provide a firm background for further hypersonic experiments with complex polymer-based nanostructures.

References

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