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PROPAGATION OF LASER-INDUCED HYPERSOUND WAVES IN POLYCRYSTALLINE DIAMOND WITH SUBMICRON CRYSTALLITES

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Abstract

We investigate the propagation of laser-induced hypersound waves in polycrystalline diamond films by analyzing the spatial changes in the phase and amplitude of the probing laser beam reflected from the surface. We show that the velocity of bulk (longitudinal) acoustic waves is 14300 m/s in films with an average crystallite size of ≈ 0.2 μm and monotonically increases to 17200 m/s with increase in the crystallite size up to ≈ 2 μm. For surface waves, anomalous dispersion is observed, leading to a change in the phase velocity from ≈ 4800 to ≈ 6600 m/s, which is explained by the effective localization of the surface wave field in the diamond films. The values obtained can be used for the design of diamond films and membranes for applications in diamond photonics and acousto-electronics.

Keywords: polycrystalline diamond, membranes, acoustic waves, CVD synthesis.

1. Introduction

In the past decade, significant progress has been made in the field of diamond synthesis by chemical vapor deposition (CVD) in terms of the material quality, chemical purity, deposition rates, and sample sizes [1–3]. The polycrystalline diamond (PCD) films obtained by this method have thermal and elastic parameters close to a natural type-II a diamond; however, the surface roughness of CVD-grown PCD films reaches tens of micrometers, which limits practical applications of such films [4]. To reduce the roughness to a few nanometers, which is important for electronics, acousto-electronics, and MEMS applications, it is possible to use nanocrystalline diamond (NCD) films with crystallite sizes < 100 nm [5]. As the grain size grows with the PCD film thickness [6], smaller size of the crystallites can be achieved in thinner films. The elastic properties of polycrystalline diamond strongly depend on a specific size of the crystallites and can be crucial for a number of applications in diamond acousto-electronics [7]. Moreover, to exclude the influence by the substrate and for the purpose of getting access from both sides of the PCD layer, thin PCD membranes are aimed to be used instead of uniform "diamond-on-Si" films [8].

The aim of this work is to evaluate the acoustic properties of CVD diamond films and membranes, the crystallite size in which falls within the "transitional" range from ∼100 nm to several micrometers. We carry out the study of acoustic properties based on pump-probe laser measurements, in which the fronts of bulk or surface waves are visualized from changes in the phase and amplitude of the probe laser beam reflected from the film surface. This approach made it possible to reconstruct the space–time patterns of propagation of hypersound pulses both in the bulk of the films and along their surfaces.

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2. Experimental

Diamond films were deposited on single-crystal Si (001) substrates using ARDIS-100 CVD reactor (2.45 GHz, Optosystems Ltd.) in CH_4/H_2 gas mixtures with a methane content of 4%. Other process parameters were as follows: a total gas flow of 500 sccm, a gas pressure of 55 Torr, a microwave power of 4 kW, and a substrate temperature of 820°C measured with a two-color pyrometer (Micron M770). The deposition rate and the thickness of the films were controlled *in-situ* using the laser interferometry technique [9]. The final thickness equal to 0.23 – 2.6 μm as well as the average size of the crystallites for each film were determined using scanning electron microscopy (SEM) images of surfaces and cross-sections of the samples. In the lower part of the film, adjacent to silicon during the growth, the crystallite size was on the order of 10 nm. In the upper part of the film, the average crystallite size was on the order of its thickness. The grown PCD films were used for the subsequent fabrication of diamond membranes employing the method described in [8].

For optical excitation of surface acoustic waves (SAW) and bulk acoustic waves (BAW), a metal film was thermally deposited on the surface of the samples such as Al (30 nm) and Au/Ti (50/10 nm).

The geometry of the laser hypersound experiment is shown in Fig. 1. An exciting femtosecond pulse consists of the second harmonic of a titanium–sapphire laser ($\tau_P = 160$ fs, $\lambda = 400$ nm, $E = 0.4$ nJ) and a probe beam of the first harmonic of the same laser ($\lambda = 800$ nm, $E = 0.04$ nJ). Upon absorption of an exciting laser pulse, as a result of rapid heating and subsequent thermal expansion of the metal film, an elastic pulse with a pressure of up to 0.3 GPa and a duration of 10 – 30 ps is formed on the sample surface, which excites BAW and SAW. The propagating elastic waves cause oscillations of the sample surface that leads to a phase change ($\sim 10^{-6} - 10^{-4}$) of the reflection coefficient of the probe beam (spot diameter ≈ 2 μm), which is recorded using a Sagnac interferometer [10]; see Fig. 2.

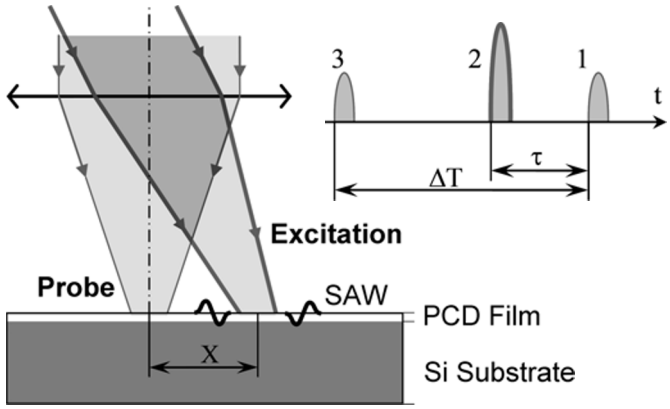

Fig. 1. Scheme of the experiment.

In this interferometer shown in Fig. 1, the probe beam is split into two channels – the reference and the probe, and the pulse from the reference channel (3) falls on the structure under study before the exciting pulse, and from the probe channel (1) after it. As a result of the interference of the reference and probe pulses at the detector of the interferometer, the signal obtained is proportional to the phase difference $\delta\phi = \phi(\tau) - \phi(\tau - \Delta T)$ at times τ and $\tau - \Delta T$. The sensitivity of the technique was ~1 μrad in phase, the spatial resolution was ≈ 2 μm, and the temporal resolution was < 1 ps.

To study the space–time distribution of the elastic wave field, the sample surface was scanned with an exciting beam. In addition, it was possible to change the delay τ between the exciting and probe pulses from 0 to 4 ns.

Analysis of the acoustic properties was carried out both for the initial CVD films and for the diamond membranes obtained from them. After the local removal of silicon, the PCD layer retains its acoustic properties. However, under the weight of PCD material without the support by Si, as well as due to the presence of random stresses, the PCD layer (membrane) loses its flatness. This affects the restoration

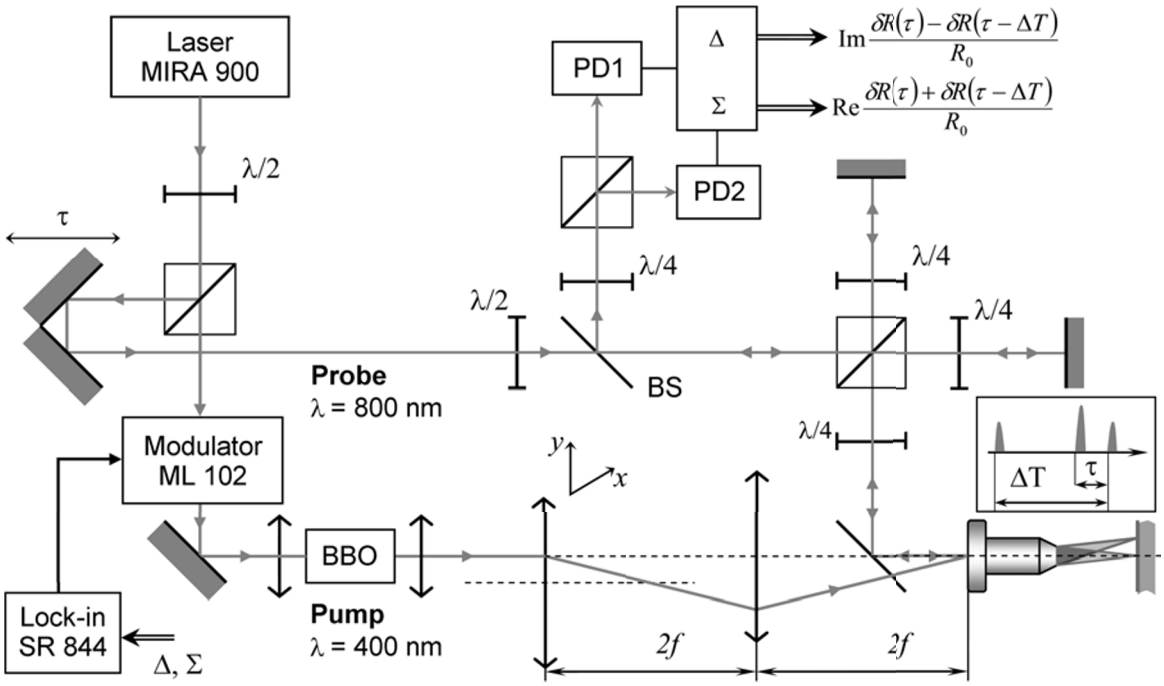

Fig. 2. Scheme of the optical part of the experimental setup.

of the spatial structure of hypersound responses. Therefore, in the analysis of hypersonic properties, the experiments with initial films turned out to be much more informative. Nevertheless, the results regarding BAW properties can be generalized to the diamond membranes as well.

3. Results and Discussion

In Fig. 3, we show responses to picosecond optical excitation obtained on diamond films with different thicknesses. Aluminum with a thickness of 30 nm was thermally deposited on the diamond surface. The responses are vertically shifted for clarity. The arrows show the times of arrival of the echo pulses. For a diamond film with a thickness of 1.7 μm, the amplitude of the reflected pulse was compared with the results of calculations (Fig. 3, the grey curve), which made it possible to estimate the acoustic mismatch at the interface, the value of which turned out to be close to the value for a flat single-crystal diamond/silicon interface.

The measured delay was used to determine the velocity of longitudinal waves in the studied films. The following values were obtained: 14300, 14800,

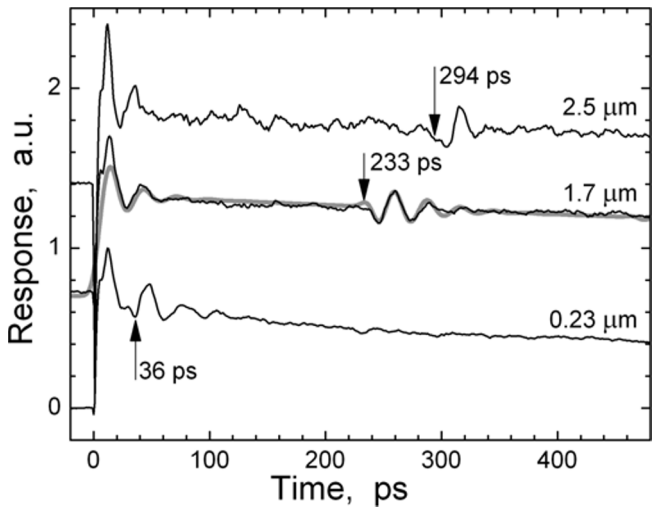

Fig. 3. Responses of Al/PCD/Si structures to picosecond optical excitation.

and 17200 m/s for films with thicknesses of 0.23, 1.7, and 2.6 μm, respectively. These values are in agreement with the data of [11].

To study the propagation of SAWs, the surface of the samples was scanned with an exciting beam. In Fig. 4, we show the distribution of the SAW field investigated on a 1.7 μm diamond film with an Au (50 nm)/Ti (10 nm) layer. Three systems of concentric rings are visible, corresponding to the following excitation pulses in 13.1 ns. The slight deformation of the rings is caused by the symmetry of the fourth order of the Si (001) substrate. The fact that the response to each exciting pulse consists of several rings, and their number increases with increasing distance, indicates the "spreading" of the SAW pulse due to strong frequency dispersion. The dependence of the SAW-field on the X coordinate is shown in more detail in Fig. 5.

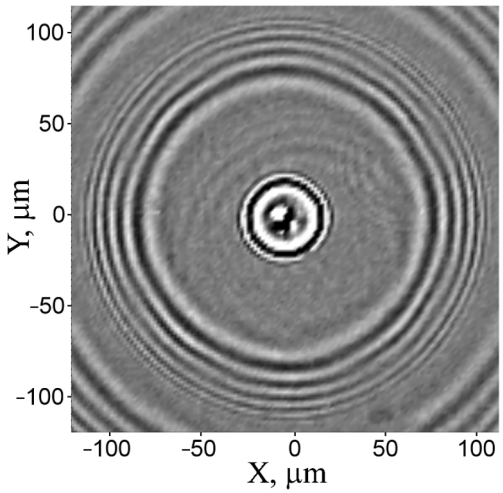

Fig. 4. Spatial distribution of the SAW field.

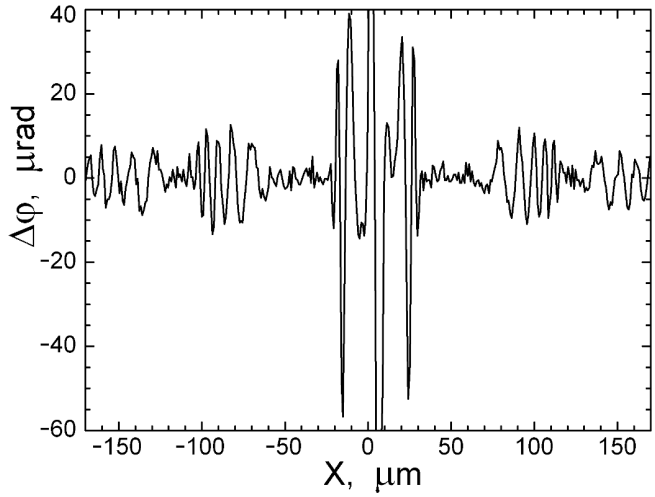

Fig. 5. Dependence of the SAW field on the X coordinate.

One can note that with an increase in the frequency of the spectral component of the SAW pulse and, accordingly, with a decrease in the wavelength, the propagation velocity increases. This follows, in particular, from the fact that the wider rings in Fig. 4 "lag" behind the narrower ones. This situation corresponds to the so-called "anomalous" dispersion of SAWs. Analyzing the position of the local maxima/minima in Figs. 4 and 5, it is easy to assess the range of changes in the phase velocities of the SAWs. For higher-frequency components, it is measured as 6600 m/s, while for low-frequency components it is ≈ 4800 m/s. The appearance of anomalous dispersion is associated with an increase in the localization of the wave in the PCD layer, in which the speed of sound is noticeably higher than in Si.

As it is known [12], in structures "layer on half-space" in the case where the velocity of the transverse wave in the layer is greater than the velocity of the transverse wave in the half-space, Rayleigh surface waves exist provided that the thickness of the elastic layer is smaller than a certain critical value; they have a narrow range of admissible values of phase velocities. Therefore, with increase in the SAW frequency above the critical value, the Rayleigh wave is transformed into a damped pseudosurface wave. Calculations show that the critical frequency for a 1.7 μm diamond layer on the silicon surface is ≈ 400 MHz, and the phase velocity is ≈ 5400 m/s. At the same time, the spectral width of the SAW pulse under experimental conditions is ≈ 1 GHz. Estimates of the phase velocity of the high-frequency (∼1 GHz) components of the experimentally recorded SAW pulse give a value of ≈ 6600 m/s, which is significantly higher than the maximum velocity of the Rayleigh wave. Therefore, in this case, apparently, a pseudosurface

wave is excited. However, for the further determination of the speed of a shear (transverse) wave in a diamond film, it is necessary to numerically simulate the process of SAW excitation/propagation in the metal/PCD/silicon structure.

After silicon removal, the bulk properties of polycrystalline diamond, such as longitudinal hypersound velocity, should be retained. Therefore, the results presented in Table 1 are applicable to diamond membranes. The role of the boundary conditions at the diamond-silicon interface obviously does not allow to generalize this statement to surface waves. However, the SAW structure in Fig. 4 unambiguously indicates the homogeneity of the acoustic properties of diamond films obtained, both in contact with silicon and freely hanging.

Table 1. Experimental Results.*

D, μm	τ, ps	V_L, m/s
0.23	36	14,300
1.7	233	14,800
2.6	294	17,200

*Here, D is the thickness of PCD films, τ is the time of arrival of the elastic pulse reflected from the diamond/silicon interface (pulse echo), and V_L is estimated value of the longitudinal speed of sound.

4. Summary

Thus, by analyzing the spatial changes in the phase and amplitude of the probing laser beam reflected from the surface, we investigated the propagation of laser-induced hypersound waves in polycrystalline diamond films on silicon substrates. Bulk and surface waves were excited by sharply focused femtosecond laser pulses. We showed that the velocity of bulk (longitudinal) acoustic waves is 14300 m/s in films with a crystallite size ∼0.2 μm and monotonically increases to 17200 m/s with an increase in the crystallite size to ∼2 μm. For surface waves propagating along the diamond film, a significant anomalous dispersion was discovered; it leads to a change in the phase velocity from ≈ 4800 m/s to ≈ 6600 m/s. We explain the sharp dependence of the phase velocity on the frequency by the localization of the SAW in the diamond film. The results obtained can provide a foundation for the design of thin diamond films and membranes that can be used for applications in diamond photonics [13, 14] (UV photodetectors, quantum optics dealing with embedded diamond color centers, photoelectrochemical cells for water splitting, and others) as well as acousto-electronics [15].

Acknowledgments

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References

1. M. A. Prelas, *Handbook of Industrial Diamonds and Diamond Films*, Routledge (2018).
2. V. Sedov, A. Martyanov, A. Altakhov, et al., *Coatings*, **10**, 939 (2020).
3. M. Schreck, S. Gsell, R. Brescia, and M. Fischer, *Sci. Rep.*, **7**, 1 (2017).
4. V. Sedov, A. Martyanov, S. Savin, et al., *Diam. Relat. Mater.*, **114**, 108333 (2021).
5. V. Podgursky, A. Bogatov, V. Sedov, et al., *Diam. Relat. Mater.*, **58**, 172 (2015).
6. V. G. Ralchenko, E. Pleuler, F. X. Lu, et al., *Diam. Relat. Mater.*, **23**, 172 (2012).
7. B. P. Sorokin, G. M. Kvashnin, A. S. Novoselov, et al., *Ultrasonics*, **78**, 162 (2017).
8. V. S. Sedov, A. A. Voronin, M. S. Komlenok, et al., *J. Russ. Laser Res.*, **41**, 321 (2020).
9. V. S. Sedov, A. K. Martyanov, A. A. Khomich, et al., *Diam. Relat. Mater.*, **109**, 108072 (2020).

10. T. Tachizaki, T. Muroya, O. Matsuda, et al., *Rev. Sci. Instrum.*, **77**, 043713 (2006).
11. J. Philip, P. Hess, T. Feygelson, et al., *J. Appl. Phys.*, **93**, 2164 (2003).
12. G. W. Farnell and E. L. Adler, "Elastic Wave Propagation in Thin Layers," in: *Physical Acoustics*, W. P. Mason and R. N. Thurston (Eds.), Academic Press, New York (1972), Vol. 9, p. 35.
13. X. Chang, Y.-F. Wang, X. Zhang, et al., *Appl. Phys. Lett.*, **112**, 032103 (2018).
14. P. Hill, E. Gu, M. D. Dawson, and M. J. Strain, *Diam. Relat. Mater.*, **88**, 215 (2018).
15. B. P. Sorokin, G. M. Kvashnin, A. S. Novoselov, et al., "Application of thin piezoelectric films in diamond-based acoustoelectronic devices," in: *Piezoelectricity–Organic and Inorganic Materials and Applications*, IntechOpen (2018), pp. 15–41.