Graphitized layer buried in a diamond: photothermal properties and hypersound generation under picosecond optical excitation

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Abstract. We assume that a coherent phonon generation was found out in structures with a single graphitized layer under picosecond laser excitation by means of the Pump/Probe method. The thermal component of the response was calculated that allowed us to define the photothermal coefficient of the graphitized layer as well as its thermal conductivity from the experimental results. The thermal-conductivity coefficient of the graphitized layer appears to grow with the thickness decrease. This makes it possible to assume that the microstructure of the graphitized layer produced during annealing depends on its thickness.

1. Introduction
A unique combination of electrical, optical, structural and thermal properties of diamond makes it an attractive material for production of MEMS as well acoustoelectronic devices in the gigahertz range (filters, surface and bulk waves cavities) [1]. Ion implantation provides a possibility of formation of embedded layers (amorphized and graphitized) built-in the diamond matrix [2]. The thicknesses of the layers produced are typically of about tens and even more nanometers being conductive and perfectly absorbing optical radiation. Optical and thermal properties of such layers are studied in a number of publications [3,4]. However, the structure and acoustic properties excluding [5], which is devoted to the generation of noncoherent acoustic phonons, virtually are not studied. One can obtain information on the sound velocity, attenuation and acoustic mismatch of the implanted layer and a diamond matrix, as well as thermal properties, with the help of picosecond acoustic methods [6]. Such data are of interest both from fundamental – investigation of phase transitions in radiation-damaged materials, and practical points of view – possible using of such layers to form various acoustic wave-guiding systems and phonon crystals. The purpose of this work is to investigate the possibilities to excite coherent phonons by exciting single graphitized layers buried in diamond with a picosecond laser.

2. Experiment
The buried graphitized layers (see table 1) were created by implanting C+ ions with the energy of 350 keV into a IIA-type ~300 μm thick natural diamond wafer. The diamond plane (100) was misoriented by 3.12° against the wafer surface. The implantation was followed by one-hour vacuum annealing at ~1600°C. The depth of location and thickness of the layers were determined by optical methods similarly to [7] and are shown in table 1.
Table 1. Condition of diamond implantation and parameters of graphitized layers. \((d_1, \text{ is the depth, } d_2, \text{ is the layer thickness, } \kappa_{Gr}, \text{ is the layer thermal-conductivity coefficient})\)

| Structure no. | Dose, \(\times 10^{15}\) cm\(^{-2}\) | \(d_1\), nm | \(d_2\), nm | \(\kappa_{Gr}\), W·cm\(^{-1}\)·K\(^{-1}\) |
|--------------|---------------------------------|--------------|--------------|------------------|
| 1            | 12                              | 235          | 283          | 3.4              |
| 2            | 8                               | 250          | 249          | 8.5              |
| 3            | 6                               | 295          | 160          | 17               |

The complex refractive index of the layer was \(n_{Gr}=2.2+j0.88\). The reflected light color of those areas with different implantation doses changed from green to dark blue, which was caused by the interference in optical wavelength range. This allowed us to assume the optical perfection of the diamond/graphitized layer interface [8].

The conventional Pump-Probe method was used to investigate the coherent phonon excitation. The experiment setup is shown in figure 1.

Coherent phonons were excited as a result of the thermoelastic effect arising in the buried graphitized layer (layer 1 in figure 1) being irradiated by picosecond pulses of the MIRA-900P titanium-sapphire laser (wavelength 797 nm, pulse duration 1.5-2.5 ps, repetition frequency 76 MHz). As the heat relaxation time in structures similar to that one under study was \(\sim 100\) ns, a pulse picker was used to make repetition frequency \(\sim 4\) MHz. The laser pulse was split into exciting and probing beams with crossed polarizations. The probing beam could be delayed against the exciting beam by means of the optical delay line based on the translation stage. Beams were focused both at one point by means of the microscope long-focus objective. The size of the laser radiation spot on the sample was \(\sim 12\) \(\mu\)m. Polarization of the probing beam was perpendicular to the incidence plane with the incidence angle being \(\sim 4^\circ\). The maximum incident fluence of the pump beam was 8 J·m\(^{-2}\). The exciting beam was modulated by means of the Pockels cell in order to implement the photodiode output synchronous detection method that allowed registering the probing beam reflected from the sample.

3. Discussion

Figure 2 shows responses of the sample with buried graphitized layers. The responses of structures 1 and 2 had a short \(\sim 3\) ps spike changing into an abrupt dip followed by a slow increase. The maximum of response (depending on depth of location and thickness of the layer) was found \(1\sim 2\) ns after the excitation pulse. The response of structure 3 had an abrupt front and a subsequent decay close to exponential. All responses had evident fluctuations with a maximum value reaching \(4\times 10^{-5}\). A short spike at the beginning of the response arose due to the generation of a large number of hot carriers in the graphitized layer, caused by the laser pulse absorbing. Within a few picoseconds the carriers were thermalized and transferred energy to the phonon system causing the layer temperature to increase by several degrees. The stress induced by this process resulted in exciting elastic waves (coherent phonons). The probing beam reflection coefficient varied due to the disturbance of optical and geometrical parameters of the structure under study, caused by both nonstationary heating and elastic
waves [9]. The location depth of the graphitized layer essentially affected the form of the response as it determines the optical path difference of the beams reflected from the sample surface and the interface between graphitized layer and diamond.

Thus, the interference conditions, when changing depth of location, could be altered from constructive to destructive, making it possible to alter the sign of the optical response. This was the reason why the responses shown in figure 2 were so much different.

To separate the contribution caused by heating into the response, a one-dimensional thermoelastic problem was solved. Elastic properties of diamond and the graphitized layer were assumed to be isotropic. As a result the space-time distribution of temperature and elastic stresses in the structure were obtained. As the thermal-conductivity coefficient of diamond at room temperature is extremely high, we did not neglect the thermal conductivity as usually is used while calculating elastic stresses. Besides, the finite length of the laser pulse was taken into account. The variation of the reflection coefficient was calculated similarly to [9]. As structure 3 was semi-transparent (transmission ~15%), the reflection from both sides of the graphitized layer was taken into account. Results of calculating the response caused by nonstationary heating of the structure, are depicted in figure 2 by dashed curves. The calculations have shown that not only temperature dependence of refraction indices but also the thermal expansion of the sample considerably affected the thermal component of the response.

The best fit was achieved with photothermal coefficients being $\frac{\partial n}{\partial T}=5.5\cdot10^{-6}+5.3\cdot10^{-6}$ K$^{-1}$ for the graphitized layer and $\frac{\partial n}{\partial T}=9.7\cdot10^{-6}$ K$^{-1}$ for diamond, which varies from published [10] by 8%. In addition, thermal-conductivity coefficients of graphitized layers of different thicknesses were defined (see table 1). The decrease of thickness appeared to cause the increase of the thermal-conductivity coefficient. After subtracting thermal components, we obtained the responses caused by propagation of the elastic waves (coherent phonons) (figure 3). It should be noted that all responses have well pronounced rippling. For example, curve 3 has 11 ps-period oscillations at the beginning of the response, curve 2 - spikes repeating every ~30 ps, and curve 3 - groups of 17 ps-period spikes repeating after ~70 ps.

However, we failed to get a quantitative fit between the calculated responses and the experimental ones. In our opinion, this can be explained in two ways. First, because the diamond plane (100) was misoriented against the sample surface (and against the interface between the graphitized layer and diamond), the laser pulse excited a shearing component of deformation [11]. Preliminary calculations taking into account the cubic structure of diamond showed that the maximum value of the shearing deformation component was about 50 times less than the volume component, with mode conversion at the sample surface taken into account. It was found out, however, that the diamond wafer used for implantation is birefringent. That means that the shearing component of deformation could affect the optical response. Second, the graphitized layer is likely to be inhomogeneous depthward. Dependence
of the thermal-conductivity coefficient on the graphitized layer thickness testifies in favor of this assumption. After ion implantation distribution of radiation defects in the near-surface layer had its pronounced maximum.

Figure 3. Responses of the sample with buried graphitized layers caused by propagating stress pulse. 1,2,3 — structures represented in Table 1.

During the annealing process, areas with defect concentration lower than critical restored the crystalline structure while areas with defect concentration higher than critical were graphitized. It seems that those areas with lower defect concentration (yet exceeding critical) appear to be more fully restructured during annealing than those with higher defect concentration. Therefore, elastic properties of the graphitized layer may also be inhomogeneous depthward.

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