Effect of the pulse duration on graphitisation of diamond during laser ablation

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Abstract. **Processes of graphitisation of laser-irradiated polycrystalline diamond surface exposed to multipulse irradiation are studied experimentally. The thickness of the laser-modified layer as a function of the laser-pulse duration ranging from 100 fs to 1.5 μs and the effect of the radiation wavelength on this thickness are studied. It is shown that the diamond graphitisation during multipulse laser ablation is a thermally stimulated process. The dependences of the diamond-ablation rates on the radiation energy density under the action of laser pulses of various durations are presented.**

Keywords*: polycrystalline diamond, laser ablation, graphitisation, thermally stimulated processes.*

1. Introduction

An unremitting interest in studying diamond can be explained by a unique combination of its mechanical, thermal, optical, and electrical properties and a continuous development of methods for chemical vapour deposition (CVD) of synthetic diamond. Regimes of producing polycrystalline diamond, which ensure growth rates of high-optical-quality films of up to 100 μm h^{-1}, were realised recently [1]. To date, efforts are also aimed at a search and study of controllable methods for reconstructing the diamond structure, thereby modifying its properties. For example, attempts to produce n-type conducting diamond by deuterium diffusion into the surface layer of boron-doped diamond accompanied by the subsequent thermal annealing proved to be successful [2]. Since the technique for producing p-type diamond by doping with boron has been long and thoroughly studied, the latest achievements open the way to the development of diamond electronics.

Another approach to a solution of the problem of modifying the diamond structure and surface properties is to use high-power laser radiation for graphitising dia-

mond, which, as is known, is a metastable modification of carbon. Specific features of this approach actually consist in the possibility of exposing a thin near-surface layer or a confined volume of a substance to a local pulsed effect and in a high rate of the initiated processes, such as heating and subsequent cooling of the modified material, proceeding due to the high thermal conductivity of diamond. In this case, in contrast to stationary 'slow' thermal heating in air, a thin graphite-like layer having no time to oxidise remains on the diamond surface [3]. This changes not only the optical and electric characteristics [4] but the chemical properties of the surface as well, making it possible, e.g., to metallise the surface [5]. In addition, laser ablation is an efficient tool for microprofiling the diamond surface and is used in applications that require high-precision processing, e.g., in the manufacture of diamond IR optics [6–8]. These feasibilities account for an interest in studying the laser-etching mechanisms and laser-induced phase transitions in diamond. The main goal of this work was an experimental study of the properties of the laser-induced layer on the diamond surface and the material-ablation conditions depending on the parameters of pulsed laser radiation.

2. Experimental

The polycrystalline diamond plates used in the experiments were produced using the microwave plasma CVD technique [9]. After the plates were separated from the silicon substrate and mechanically polished, the roughness of the irradiated growth side measured using an interference microscope (New View 5000, Zygo, USA) was within 1 nm for 0.5-mm diamond plates.

Table 1 lists the main characteristics of the laser systems with pulse durations ranging from femtosecond to microseconds that were used to irradiate diamond surfaces. More detailed descriptions of laser setups are given in [10, 11]. The experimental technique involved the multipulse irradiation of samples followed by a microscopic analysis of their modified surfaces. The method used in this work to measure the thickness of the laser-graphitised layer is based on the thermal oxidation of graphite and makes it possible to remove step-by-step a nondiamond phase from the sample surface with a resolution of a few nanometers [12]. The laser-irradiated samples were annealed in air at $T = 600\,°C$. Note that, at this temperature, the effect on the material structure in the nonirradiated region and in the sample's depth under the modified layer is negligible. This allows the thickness of the removed layer of the graphite-like phase to be determined by comparing the profiles of the irradiated

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Table 1. Parameters of the used laser systems.

Laser	Pulse duration τ	Wavelength λ/nm	Energy distribution in the irradiation spot	Typical size of the irradiation spot/μm
Ti : sapphire	100 fs 6 ps	800	Gaussian	17 (diameter at a 1/e level)
Nd : YAP	300 ps 7 ns 10 ns	539 539 1078	–"–	28 (diameter at a 1/e level)
KrF	15 ns	248	uniform	80 (side of a square)
Nd : YAG	1.5 μs	1064	–"–	$\sim$110 (diameter)

surface before and after oxidation. An interference microscope ensuring vertical and horizontal resolutions of 0.1 nm and 0.5 μm, respectively, was used to measure the topography of the surface relief.

3. Results and discussion

3.1 Laser-induced graphitisation of diamond

The size of individual crystallites at the surface of the diamond plates used was $\sim$ 50 μm, which is comparable to the irradiated spot for all of the laser systems applied (Table 1). This allowed us to ascertain that the modified-layer thickness under identical irradiation conditions is the same within a single diamond crystallite and, as a rule, differs significantly when changing from one crystallite to another; i.e., it is related to the initial crystallographic orientation of diamond grains. This is illustrated in Fig. 1, which depicts optical images of several laser spots shaped as squares on the surface of a diamond plate (Fig. 1a) and distribution profiles of the graphitised-layer thickness (Fig. 1b, 1c) obtained with the New View 5000 interference microscope. Two-dimensional maps of the laser-graphitised-layer thickness (Fig. 1b) and one-dimensional profiles (Fig. 1c) were obtained as a difference between the images (profiles) of the corresponding areas of the irradiated surface before and after the oxidising annealing.

In our opinion, there are two the most probable reasons for such jumpwise changes. First, the observed effect can be explained by variations in the optical and thermal properties of the modified material (the absorption, density, and thermal diffusivity) that determine the temperature distri-
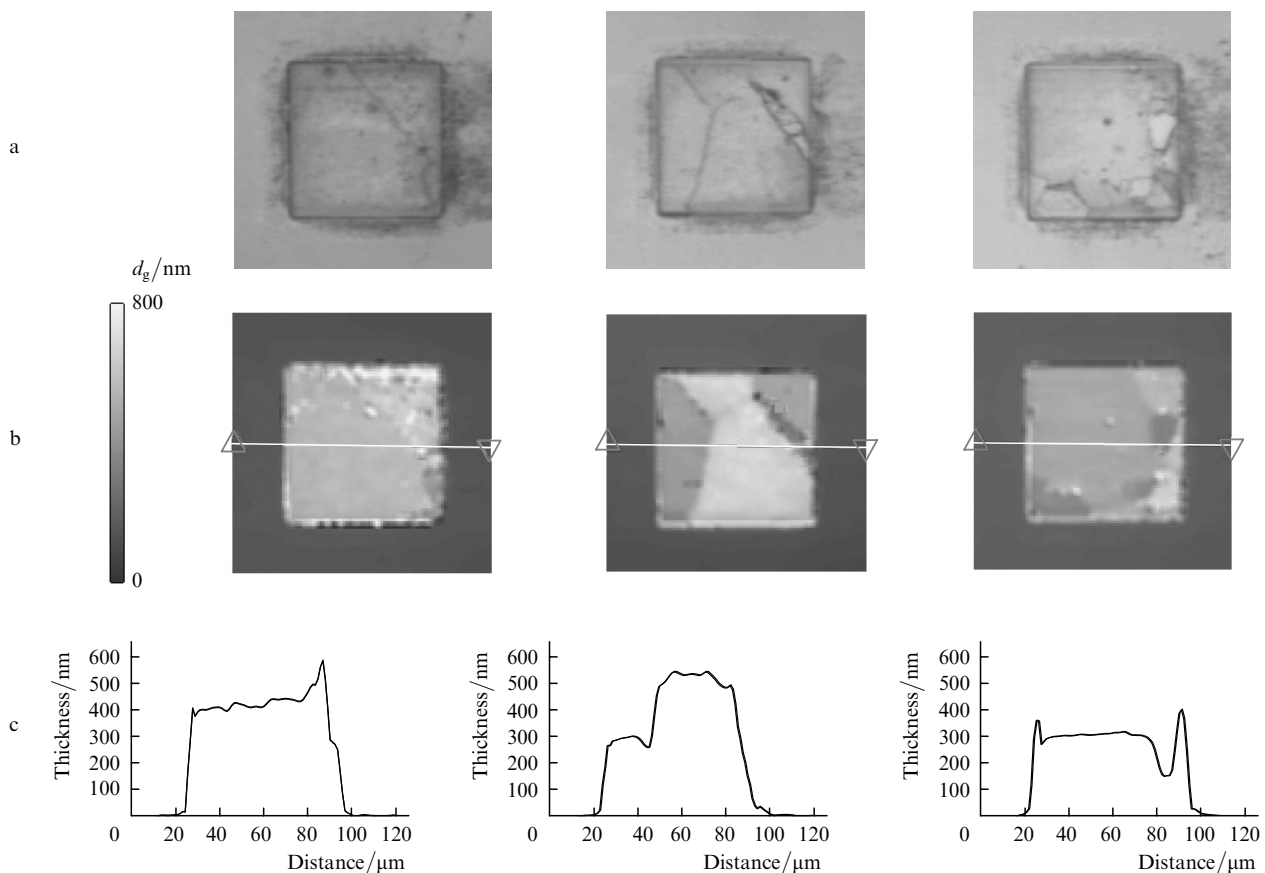

Figure 1. Laser-induced modification of various areas of the surface of a polycrystalline diamond film: (a) images of the surface obtained with an optical microscope, (b) two-dimensional, and (c) one-dimensional profiles of the graphitised-layer thickness d_g in the irradiation spot (a KrF excimer laser, the energy density $E = 16$ J cm^{-2}, a single pulse).

bution in the near-surface layer under laser-induced heating. Second, from the standpoint of thermodynamics, in order to break an individual interatomic bond, the energy of a given atom that increases due to a thermal fluctuation must exceed a certain energy barrier created by its neighbours [13].

In works devoted to the slow thermal graphitisation of the diamond surface, it was found that the height of this barrier or the activation energy of the process substantially depends on the orientation of the sample surface relative to the crystal planes [14]. This means that, even at one and the same temperature, the probabilities of separate graphitisation events for different grains of a polycrystalline sample are also different; consequently, the graphitised-layer thickness will also vary from crystallite to crystallite. Since the experimental determination and discrimination of grains with an identical crystallographic orientation is a quite difficult problem, considerable statistical data on the sample surface were collected in experiments for revealing the tendency in the behaviour of the properties of the graphite-like layer under study.

It is conventionally considered that the initial surface graphitisation of diamond is initiated by absorption of laser radiation by the present structural defects and nondiamond inclusions and leads during irradiation to the formation of a comparatively homogeneous layer of nanocrystalline graphite on the surface [15]. The experimental results of this study show (Fig. 2) that a graphite-like layer forms during one laser pulse and its thickness does not change after subsequent irradiations (in principle, the pulse that initiates graphitisation can be not the first one, but the analysis of possible causes of such a behaviour, e.g., accumulation processes, etc., is beyond the scope of this paper). This means that the initial graphitisation resulting from the heating of defects in the lattice is a very rapid process and occurs jumpwise in time. At the initial stage, especially in the case of ultrashort pulses, the character of laser graphitisation can be significantly affected by nonequilibrium photostimulated processes associated with the generation/recombination of nonequilibrium carriers. Several recent theoretical works were devoted to this problem [16 – 18].
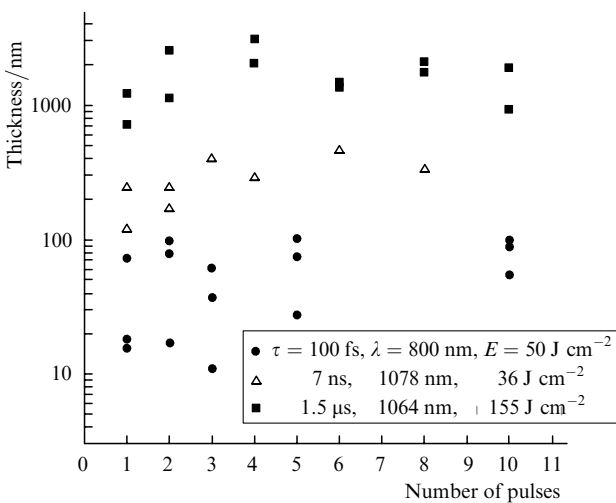
After an absorbing graphitised layer is formed, it moves into the sample's depth under the action of each subsequent laser pulse as a result of sublimation of the substance from the surface at $T \sim 4000$ K, accompanied by a simultaneous reconstruction of carbon crystal structure at the interface between the graphite-like and diamond phases [19]. In this case, if the graphitisation process is thermally stimulated, the thickness of the modified layer is then determined by the distribution dynamics of the absorbed laser energy and, as a consequence, by the temperature distribution in the material. For a laser-heated surface, the temperature distribution in the depth depends on the absorption coefficient α_g of the graphite-like phase and the heat redistribution due the heat conduction. For short radiation pulses when a heat transfer during the pulse duration can be neglected, absorption plays the determining role. The dependence of the temperature on the depth is close to an exponential function (Bouguer law), and the thickness d_g of the graphitised layer satisfies the expression
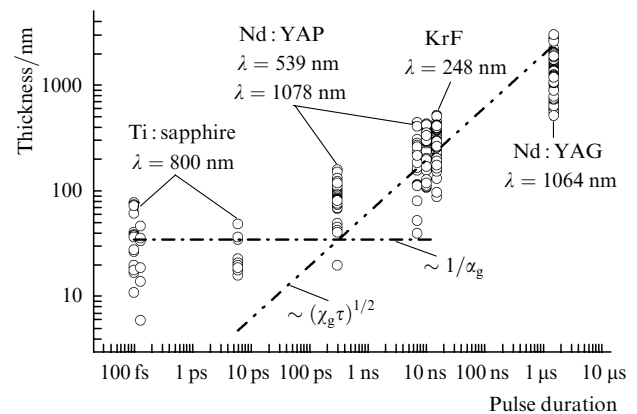
$$d_g \approx \frac{\ln(T_s/T_g)}{\alpha_g} \approx \frac{0.7}{\alpha_g}, \qquad (1)$$

where $T_s \approx 4000$ and $T_g \approx 2000$ K are the graphite evaporation and diamond graphitisation temperatures, respectively. The heat penetration depth to the material bulk for long pulses is determined by the pulse duration τ:

$$d_g \approx \ln(T_s/T_g)(\chi_g\tau)^{1/2} \approx 0.7(\chi_g\tau)^{1/2}, \qquad (2)$$

where χ_g is the thermal diffusivity for the modified layer.

Figures 3 and 4 show the thicknesses of the graphitised layers as functions of the pulse duration and laser wavelength obtained experimentally and estimated from (1) and (2). The absorption coefficient and the thermal diffusity of the modified surface layer used in these calculations were the same as those for polycrystalline graphite at $T = 2000$ K: $\alpha_g \approx 2 \times 10^5$ cm^{-1} and $\chi_g \approx 0.08$ cm^2 s^{-1} [20]. The correlation between the experimental data and estimates indicates that the process of diamond graphitisation with high-power laser multipulse radiation is really thermally stimulated. The thickness of the modified layer is determined by the depth of the heat-affected zone: at long laser pulses, by the thermal

Figure 2. Thickness of the graphitised layer as a function of the number of irradiation pulses for femtosecond, nanosecond, and microsecond laser systems.

Figure 3. Experimental data (circles) and theoretical estimates (straight lines) for the thickness of the graphitised layer as functions of the laser-pulse duration at an irradiation-energy density $E = 15 – 150$ J cm^{-2}, $\chi_g \sim 0.08$ cm^2 s^{-1}, $\alpha_g \sim 2 \times 10^5$ cm^{-1}.

diffusivity of the graphite-like phase; at short pulses (down to femtoseconds), by the radiation-absorption depth in it. Figure 4 shows that the laser wavelength has a weak effect on the layer thickness: its variations are more likely due to different pulse durations of laser systems. Within the scope of the model used, this is explained by almost the same absorption of graphite at wavelengths of $250-1100$ nm: : $\alpha_g(\lambda) \approx (2-6) \times 10^5$ cm^{-1} for highly oriented pyrolytic graphite (HOPG) [21, 22]. Formula (1) allows for an estimate of the effect of the graphite absorption spectrum on the modified-layer thickness, which does not exceed 50 nm. This is confirmed by the experiment (Fig. 4).
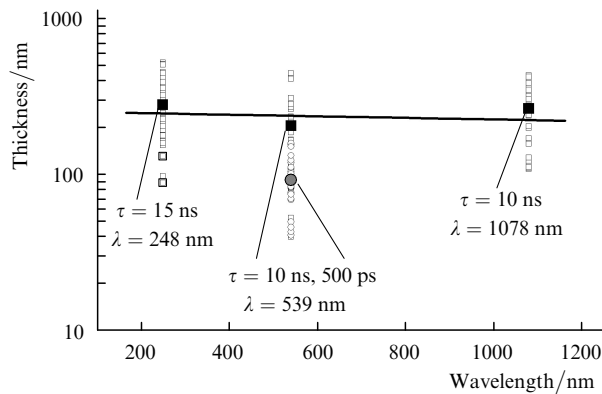
Figure 4. Experimental data (open circles and squares) and the corresponding averaged values of the graphitised-layer thickness (dark circles and squares) as functions of the radiation wavelength for picosecond and nanosecond pulses at an irradiation-energy density $E = 15 - 150$ J cm^{-2}.

3.2 Laser-induced diamond ablation

The laser systems described in Section 2 were used to measure the diamond-ablation rates as functions of the energy density under multipulse irradiation of surfaces (Fig. 5). The ablation rate, i.e., the thickness of a material evaporated per pulse of fixed energy, was measured from the slope of a linear dependence of the depth of a crater forming under laser irradiation on the number of irradiating pulses. The initial points in each curve, at which the ablation rate is zero, correspond to an irradiation regime, in which no changes on the irradiated area of the sample surface were observed for several tens of pulses. As is seen, the ablation threshold increases with the pulse width, which can be explained by increasing energy losses due to the heat conduction. The efficiency of material removal γ, i.e., the ratio of the energy needed to heat and then evaporate the substance to the entire deposited energy, simultaneously increases as well. It is of interest that this efficiency is very high for pulses of microsecond duration. At a thickness of the graphite-like layer of ~ 1 μm (Fig. 3), the total laser energy, except for the reflected light, is absorbed. Then,

$$\gamma = \frac{[q_s + c_g(T_s - T_g) + c_d T_g]\rho_d D}{E(1 - R)}. \tag{3}$$

Assuming that the specific heat of evaporation for graphite $q_s = 6 \times 10^4$ J g^{-1}, the diamond density $\rho_d = 3.5$ g cm^{-3}, the specific heats for diamond and graphite $c_d = 0.5$ J g^{-1} K^{-1} and $c_g = 0.7$ J g^{-1} K^{-1}, the reflectivity for

graphite $R = 0.02$ [22], and the thickness of the removed material per laser pulse $D = 6700$ nm at an energy density $E = 165$ J cm^{-2} (Fig. 5), we obtain a value of γ close to 100 %. This estimate is certainly quite rough. For example, the temperature dependence of the specific heat and a small amount of energy released during graphitisation are neglected. However, this estimate shows that, for long laser pulses and radiation intensities $< 10^8$ W cm^{-2}, carbon sublimates almost without material overheating.
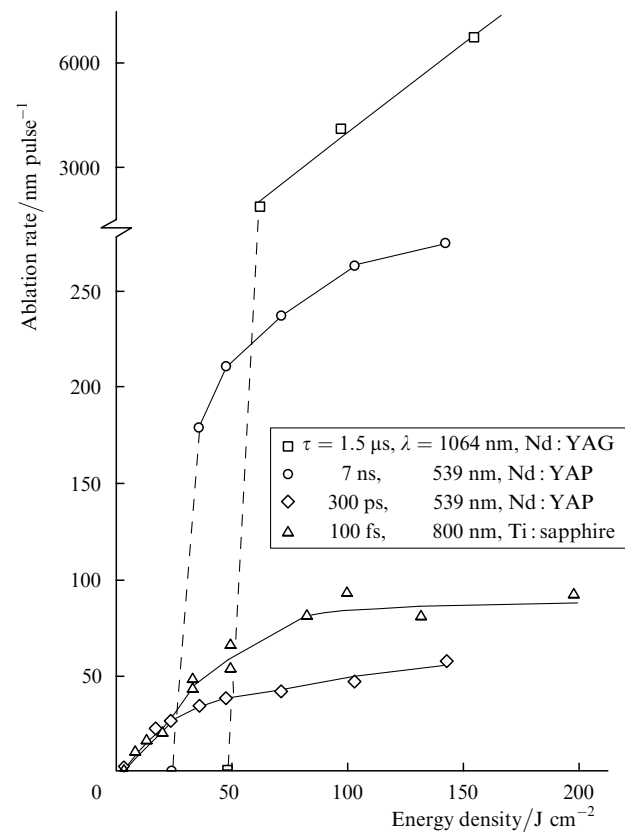
Figure 5. Ablation rate as a function of the energy density per pulse for various laser systems.

Estimating γ for nanosecond laser pulses yields $\sim 5\,\% - 13\,\%$ depending on the energy density. The data in Fig. 5 and the efficiency values testify to a saturation of the ablation rate with an increase in the energy of picosecond and nanosecond pulses, although this effect is appreciably weaker for the latter. This behaviour is usually considered to be associated with the radiation screening by a low-temperature plasma [22] being formed during evaporation of the irradiated substance. Short pulses are thus characterised by a comparatively low efficiency of material removal due to, primarily, the material overheating and, secondly, the ablation-rate saturation. When femtosecond pulses are used, the etching rates are higher than with picosecond pulses. This is obviously determined by the fact that, for ultrashort pulses, the screening by a vapour flame is impossible, since a laser pulse terminates before the substance is heated and evaporates. At the same time, the ablation rate under irradiation with 100-fs pulses saturates (at a level of ~ 80 nm per pulse) at energy densities > 100 J cm^{-2} as a result of an optical breakdown of air.

4. Conclusions

We have ascertained the main properties of laser-induced graphitisation of the surface of polycrystalline diamond during ablation and determined the thickness of the graphitised layer as a function of the irradiation conditions. It has been shown that the crystallographic orientation of individual diamond crystallites affects considerably the thickness of the modified layer. It is found that the thickness of the graphitised layer is 10 – 3000 nm depending on the laser-pulse duration (from 100 fs to 1.5 μs) and is determined by the depth of the heat-affected zone: by the thermal diffusivity of the graphite-like phase for long pulses and by the radiation-absorption depth in this phase for short pulses. The studied dependences of the ablation rates on the energy density allow one to estimate the efficiency of laser processing of diamond at various pulse durations. This study has shown that pulse laser radiation is an efficient tool for controlled local reconstruction of the diamond surface structure and, thus, for modification of its properties.

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