

Review

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Posted Date: 9 August 2023

doi: 10.20944/preprints202308.0617.v1

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Article

Modification of Diamond Surface by Femtosecond Radiation

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Abstract: Basic mechanisms of laser interaction with synthetic diamond are reviewed. The features of the major regimes of diamond surface etching are considered. Besides well-known graphitization and ablation processes, the nanoablation and accumulative graphitization, which attracted the attention relatively recently, are described in detail. The focus is placed on femtosecond (fs) laser exposure which provides a formation of dense cold electron-hole plasma in focal zone and a minimum overheating in surrounding area. This potentially opens the way to develop unique laser-based technologies combining physical and chemical processes for precise surface treatment and functionalization. The physical limitations determining how precisely the diamond surface can be treated by short-pulsed laser radiation and possible pathways to overcome them with the end to remove ultra-thin layers of the material are discussed. Particular attention is devoted to the novel possibility to induce local formation of point active defects - nitrogen vacancy (NV) complexes in the laser-irradiated zone. Both the regimes of NV centers generation with and without graphitization of diamond lattice are reviewed. It is thus shown that intensive pulse laser radiation is a perfect tool for processing of synthetic diamonds on the micro, nano and even on an atomic level that can be well controlled and managed.

Keywords: diamond; femtosecond radiation; ablation; nanoablation; accumulative graphitization; NV centers; surface modification

1. Introduction

For the last 30 years, thanks to the technologies of chemical vapor deposition (CVD) and high-pressure high-temperature (HPHT) growth, diamond has been a technologically accessible material [1]. The first experiments on the gas-phase deposition of diamond were carried out in the end of 1970s [2], and since the deposition regimes have been implemented that provide growth rates of high quality films up to 100 $\mu\text{m}/\text{hour}$ [3]. Today, CVD single crystals meet the requirements for creating not only electronic [4] and photonic [5], but also quantum devices [6]. The only weak point of the synthetic diamond is its complicated processing caused by the extreme hardness and chemical inertness. This problem is one of the key factors currently limiting wide penetration of diamonds into optics, electronics, and other application fields [7]. The great potential of diamond as a new platform for the convergence of electronics and photonics encourages the study of various processes, including laser-stimulated, which would be effective for the bulk and, especially, surface processing of the diamonds.

The interest in the synthetic diamond has passed two stages. Initially, it was explained by the unique combination of mechanical, thermophysical, optical and electrical properties of this crystal [8]. Because of this, diamond was considered an indispensable material in many extreme applications. Diamonds were used as a material for power optics [9], a material for efficient heat sinks [10], a base for high-voltage switches [11], a material for protection against aggressive environments [12], a material for metrology of ionizing radiation [13], etc.

These application areas, as well as many others, require suitable tools for diamond processing at the macro and micro levels. One of the most effective is considered to be ablation, a traditional method of local laser exposure, which is based on pulsed heating and evaporation of the surface layer of the target. The substance removal rate achieved during diamond ablation is typical for metal ablation and, for instance, in the case of nanosecond irradiation is of hundreds of nanometers [14]. A feature of diamond ablation is the inherent intermediate graphitization. Graphite-like surface layer, first spotted in 1960s [15], sharply alternates not only the optical and electrical [16] but also the chemical properties of the surface [17]. This ability of diamond to locally rebuild the structure under the external influence is very important, since it allows to design a surface with desired properties (crystal structure, phase composition, electrical conductivity, etc). The recent investigations have shown that pulse laser systems are quite suitable tools that can boost to realize these fundamental possibilities. Sections 3 - 5 of this survey are devoted to the detailed study of the mechanisms of laser energy transfer to diamond, the mechanisms and rates of its dissipation, the dependencies of the ablation/graphitization rate on the parameters of laser radiation, the properties of the carbon phase graphitized during ablation, and the factors that limit the accuracy of the ablation processing and the possibility of its control.

Since the properties of nitrogen-vacancy complexes (NV centers) in diamond have been studied [18], interest in diamond has taken a new direction. At the moment, diamond is considered an ideal platform for constructing quantum optical microchips [19]. Such a microcircuit basically represents a nanocomposite - an ordered array of single-photon emission active centers and graphitized conducting circuits in the diamond matrix. If such a device is implemented, diamond can significantly replace silicon and become the basis of the element base of active quantum devices with unique characteristics. However, this potential has not yet been realized, since for diamond there is no analogue of photolithographic technologies, which ensured once the development of the silicon electronics. Therefore, today efforts are mainly focused on the search and study of methods for controllable restructuring the diamond lattice, and as a result, modifying its properties at the nanoscale and atomic levels.

The fundamental possibility of the laser surface modification [20–22] and the accompanying generation of defects in different crystals [23–25], as well as in glasses [26,27] has been known for a long time. The possibility of implementing similar processes in diamond, which is characterized by a high rigidity of the crystal lattice and chemical stability of atomic bonds, was first demonstrated in 2003 [28–30]. A specific regime of laser exposure was revealed, in which the etching surface did not stop despite the laser fluence was below the graphitization threshold. In this process as compared with ablation the rate of material removal drew drastically - to values less than 10^{-3} nm per pulse. This factor made to introduce the term “nanoablation” [31] to describe the etching regime given. An important feature of the nanoablative process is the absence of noticeable graphitization, i.e., sp^2 hybridized bonds, if they even arise as a result of laser exposure, their number is very small and does not result in a significant optical absorption. Later in 2017, another key aspect of the nanoablation process was discovered. It was shown that due to the nanoablation NV centers are formed in the surface layer of diamond, both neutral and negatively charged [32].

There is another regime of laser processing of diamond - so-called "accumulative" graphitization [33]. A feature of this regime, as the name implies, is the gradual accumulation of latent defects that develops during prolonged irradiation of the sample and ultimately finishes by the visible graphitization in the laser spot after a certain incubation period [34]. Note that in this regime the generation of active centers in the bulk of diamond was realized too [35]. To this moment the physics of the accumulative regime is studied rather poorly, since it is difficult to characterize weak changes of material properties until macrographitization starts in the irradiated zone. Sections 6 - 9 are devoted to the study of nanoablation and accumulative graphitization as methods of nanoprocessing and nanomodification of the diamond surface.

It should be noted that the main part of the studies described in this review was carried out using ultrashort laser pulses, which make it possible to deposit the required amount of light energy

into the medium in a very short time - much shorter than the lattice response. Particularly, due to this circumstance the femtosecond processing has become a very powerful tool for creating photonic elements in dielectrics [36]. Today, the machining industry relies heavily on the fast laser systems.

2. Materials and Methods

2.1. Diamond samples

The diamonds used in the experiments were obtained by the gas-phase deposition in a microwave plasma reactor. Polycrystalline samples were obtained at the Institute of General Physics of the Russian Academy of Sciences, single crystals were produced by the "Element 6" corp. Face and edge surfaces were polished mechanically, the finished roughness achieved $R_a \sim 1$ nm. Both polycrystalline and single crystal samples had the so-called "optical" purity, which means that the transmission in the far IR range of the spectrum of these samples is close to the maximum (about 70%). The nitrogen concentration in a typical single crystal was estimated at ≈ 1 ppm level reasoning from the absorption coefficient at a wavelength of 270 nm [37].

2.2. Laser systems

In addition to fast lasers, other sources of pulsed radiation were also used to study laser-induced processes in diamond. The main parameters of laser systems are given in the Table 1. The pulse duration was varied in the range from femtoseconds to microseconds. The experiments described consisted, in essence, of multipulse irradiation of samples under varied (if necessary) external conditions, followed by microscopic analysis of the modified surface. Scanning over the sample surface was performed using electromechanical stages, the movement of which was programmatically coordinated with irradiation. A description of the experimental setups can also be found in [31,38–40].

The Gaussian beams were focused by spherical or aspherical lenses, thus obtaining the fluence of up to 1000 J/cm² on the sample surface. This scheme has been used for both the Ti:sapp laser mode-locked laser with a regenerative amplifier and other solid state systems. The Gaussian beam diameter at the 1/e level varied in different systems from fractions of a micron to several tens of microns. In addition to the fundamental harmonic of Ti-sapp laser, the second and third harmonics were used (wavelength $\lambda = 400$ nm and $\lambda = 266$ nm). They were generated using non-linear crystals b-BaB₂O₄ (BBO). For systems with a uniform distribution of radiation intensity in the beam (the excimer lasers), a projection scheme was used. A typical magnification factor was $\sim x20$, which made it possible to obtain a radiation fluence of up to 100 J/cm² on the diamond surface.

2.3. Enviroment

The majority of experiments on laser treatment of diamond surface were performed in an air atmosphere at room temperature. However, to study the key aspects of nanoablation, the environment conditions changed in some experiments. Firstly, the investigation of the surrounding atmosphere effect on the result of laser exposure was carried out under vacuum conditions in order to suppress the process of surface photooxidation. A setup was used, the main element of which is a one-liter vacuum

Table 1. Laser systems used for diamond exposure

laser	Ti:sapp	Nd-YAP	KrF/ArF	Yb:YAG	Nd-YAG
τ	100 fs 6 ps	300 ps 10 ns	15 ns	400 fs 700 fs	1.5 us
λ , nm	800 400 266	539 1078	248 193	515	1064
f , Hz	1000	10	50	$5 \cdot 10^5$	10

chamber with optical inputs. The pressure in the chamber was varied with a turbomolecular pump and a controlled leak. The minimum pressure reached 10^{-7} Torr. The setup allowed the sample to be irradiated through a 100 mm lens, monitoring the state of the irradiation zone and recording the optical transmission through the sample.

Secondly, to assess the effect of ambient temperature on the result of laser nanoablation, experiments under external heating were carried out. Heating was provided using a ceramic element, between the plates of which a diamond sample was tightly clamped. The temperature was controlled with a thermocouple and varied in the range 20C ÷ 600C. At higher temperatures, the surface of a diamond in an air atmosphere began to deteriorate.

2.4. Interference setup for e-h plasma study in diamond

Femtosecond interferometric microscopy [41,42] was used to study the processes of laser-stimulated excitation and relaxation of diamond electronic subsystem. This method makes it possible to monitor the radiation intensity in the irradiated zone and the concentration of quasi-free photocarriers produced by laser pulse with a high time resolution (100 fs) [43], as well as to measure the change in the refractive index resulting from the heating of the lattice [44]. Interferometric microscopy was used in combination with the well-known pump-probe technique: an intense pump beam was focused on the sample, and a weak probe beam passed through the delay line and illuminated the affected area (Figure 1a). This made it possible to capture the "instantaneous" distribution of the change in the refractive index (Δn) in the region of the pump beam waist, as well as to track the dynamics of the Δn value in time.

The scheme involved is based on the interference of plane collinear beams, in which a local change in the refractive index of a transparent object led to a local change in the brightness of the image of this object on the CCD matrix. The advantage of this configuration is high sensitivity: it is much easier to measure a change in brightness than a small fringe shift which is measured commonly. As the signal accumulates in the scheme used, the signal-to-noise ratio increases and a very slight change in the refractive index could be detected. Two interference patterns were always recorded in the experiment: an informative one with the action of the pump pulse and a background one without the pumping. Then the background image was subtracted from the informative image. This approach has significantly increased the measurement accuracy, which in this case is limited only by the vibration of the interferometer mirrors. The use of the Sagnac interferometer, that compensates for this jitter, and the accumulation of data with subsequent averaging provided the sensitivity of the phase shift measurement of $\Delta\phi \approx 10^{-3}$.

3. Results and Discussion

3.1. Plasma in diamond

One of the most important problems in the analysis of laser-induced processes and the permanent consequences of these processes is the understanding of the mechanisms of energy dissipation of an intense electromagnetic field in a medium. In the experiments described below, reversible processes in diamond were studied: the process of excitation of the electronic subsystem stimulated by femtosecond irradiation and the process of heating the diamond lattice stimulated by the electron - hole recombination. In these experiments, interferometric microscopy was used to measure the polarizability of diamond under femtosecond laser irradiation and its temporal dynamics.

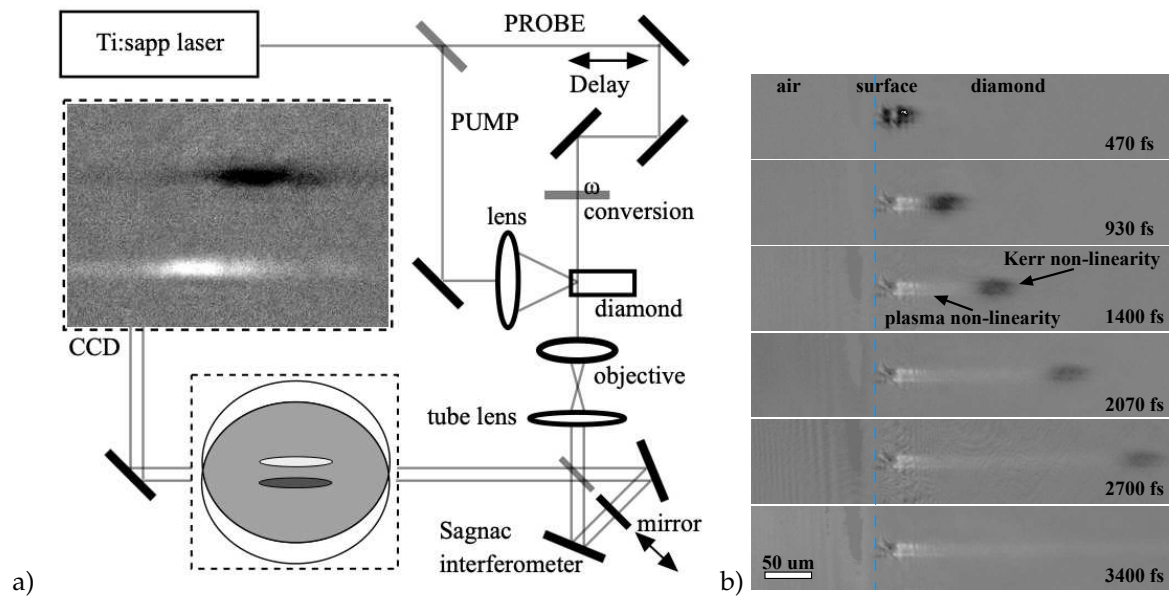


Figure 1. (a) Optical setup for studying laser-stimulated processes in transparent materials using interferometric microscopy. (b) Interference images obtained during the propagation of a femtosecond pulse in a diamond crystal. The pulse (266 nm, 0.36 μ J) moves from left to right. The delay is shown in the photos. The blue dotted line indicates the surface of the diamond sample.

A typical picture of the propagation of a femtosecond laser pulse in the near-surface layer of a diamond sample is shown in Figure 1b [44]. The presented series of interference photographs clearly shows that the polarizability of a crystal in a laser caustic varies greatly with time. In the test described the interferometer was tuned so that a decrease in image brightness indicates an increase in the refractive index (dark areas correspond to $+\Delta n$), and, on the contrary, an increase in brightness indicates a decrease in the refractive index (light areas correspond to $-\Delta n$).

The cloud is clearly seen propagating through the crystal at the speed of light. This image of the light packet arises due to the optical Kerr effect, which locally increases the refractive index of the medium proportionally to the intensity of the radiation: $+n_{kerr} \sim I$. Further exposure to the laser field results in ionization of the covalent bonds of the crystal and, as a consequence, the appearance of electrons in the conduction band and holes in the valence band ($e-h$ pairs). The appearance of both types of free carriers leads to a proportional decrease in n , which is described in terms of classical concepts by the Drude theory: $\Delta n = -(2\pi e^2)/(n_0 \omega^2 m) \cdot N_e$, where n_0 is the refractive index of diamond, ω is the frequency of the laser radiation, $m \approx 0.5m_e$ is the effective optical mass of carriers, N_e is their concentration, e and m_e are the electron charge and mass.

Thus, when intense pulses affect diamond crystal, two mechanisms of light-induced perturbation of the electron subsystem prevail: the optical Kerr effect, which is a manifestation of the anharmonicity of the localized bound electrons, and photoinduced transitions of the electrons, leading to the formation of a free electron-hole plasma. A typical dynamics of n value over subnanosecond time scale is shown in Figure 2a. The presented data have allowed to determine the lifetime of the dense electron-hole plasma in diamond, which is about 10 ps. It was also found that after the complete recombination of carriers, approximately 20 ps later, a region with positive Δn appeared. This induced polarizability slowly decreased with time and after about 40 ns became less than the sensitivity threshold of the measuring system. Simultaneously, the size of the perturbed region gradually increased, so that the integral Δn over space did not depend on time: $\int \Delta n dV = const$.

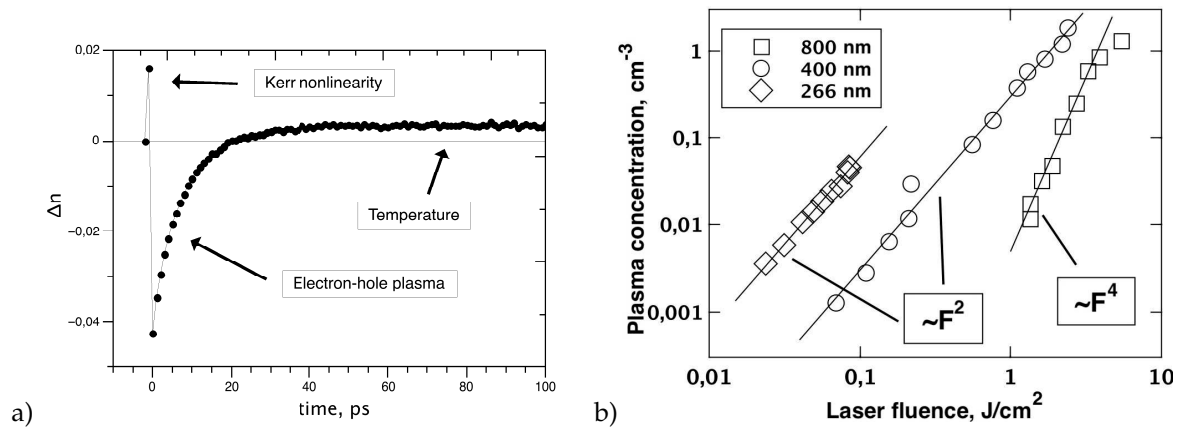


Figure 2. (a) Temporal dynamics of optical polarizability of diamond during and after the action of the field of femtosecond pulse, (b) Concentration of e - h plasma in diamond single crystal as a function of laser fluence.

The observed long-lived $+\Delta n$ perturbation was interpreted as diamond heating, which is confirmed by a good agreement between the measured dynamics of the spatial spreading of the perturbed region and the simulated dynamics of heat propagation from the region initially occupied by photoinduced plasma [44]. A comparison of the experiment and calculation results showed that the heating of the diamond lattice in the pre-ablation regime is relatively low: $\Delta T \approx 400\text{K}$. Close estimates of the increase in temperature were obtained from the energy stored in the electron-hole plasma and released as a result of carrier recombination.

Interferometric microscopy also allows to obtain the dependence of the concentration of photoinduced e - h pairs on the radiation fluence for all three harmonics of the Ti:sapp laser (Figure 2b) [44]. The plasma density was calculated using Drude formalism from the negative change in n . These data demonstrate that the density of the electron-hole plasma can reach $\sim 10^{21}\text{ cm}^{-3}$ without damage of the diamond lattice. The absorption has a multiphoton character in a wide dynamic range of laser fluence (up to surface graphitization and destruction). The corresponding dependences are power-law with an exponent of 4 for 800 nm (four-photon transition), 2 - for 400 and 266 nm wavelength (indirect and direct two-photon transitions, respectively). The contribution of the three-photon direct transition at the 400 nm exposure is not detected. The contribution of inverse bremsstrahlung to the excitation of the electronic subsystem is also not observed even for 800 nm irradiation.

Table 2. Coefficient β_M of multiphoton absorption in diamond.

λ	M	β_M [this work]	β_M [others]
226	2	$0.9 \cdot 10^{-9}\text{ cm/W}$	$1.1 \pm 0.3 \cdot 10^{-9}\text{ cm/W}$ [45]
400	2	$3.7 \cdot 10^{-11}\text{ cm/W}$	–
800	4	$7.6 \cdot 10^{-39}\text{ cm}^5/\text{W}^3$	–

The obtained dependences $N_e = k \cdot F^M$ actually give the quantum yield of phototransitions in diamond and allow us to estimate the M -photon absorption cross sections for all used wavelengths using the formula: $\beta_M = M\hbar\omega k\tau^{M-1}$, where $\hbar\omega$ is the photon energy. The calculated β_M values are given in the Table 2 in comparison with known literature data.

3.2. Multipulse ablation of diamond

Already in the first experiments on laser destruction of natural diamonds by pulsed radiation it was shown that damage to the diamond surface is accompanied by blackening in the laser affected zone, presumably due to the transformation of diamond into graphite [15,46]. Thereafter Rothschild et al. [14] developed these ideas and pointed out that graphitization is indeed the key feature of diamond

ablation. It was shown that when diamond is irradiated with intense UV pulses, two processes occur: the transformation of diamond into graphite and the subsequent evaporation of this graphitized material.

Special attention should be paid here to the fact that graphite is a semi-metal and its absorption in the optical range of the spectrum is orders of magnitude higher than that of diamond. This circumstance leads to a sharp jump in the optical absorption in laser affected zone during the primary formation of the graphite-like layer and, consequently, to different mechanisms of diamond ablation at the stage of formation of the graphite layer and after it. Three situations should be distinguished: (i) graphitization has not yet begun and the radiation energy is absorbed in the diamond, subjecting the relations described in Section 3.1. In particular, this is always true for the first laser pulse. (ii) If the graphitized carbon phase has formed and completely covers the zone irradiated, the laser energy is dissipated completely in the target and the ablation process resembles the ablation of metals. This is exactly the established regime of multipulse processing that usually refers to "diamond ablation" term. (iii) An intermediate situation is also possible, when the radiation energy is close to the threshold and graphitization is spread over time - a gradual accumulative formation of the graphite layer occurs. In this regime, the role of both multiphoton absorption in diamond and one-photon absorption on "non-diamond" inclusions is important (see Section 3.4).

The correctness of the two-stage ablation mechanism (through graphitization and evaporation) was fully corroborated in the later works [47,48]. To date, the generally accepted model of the ablation under multipulse irradiation is the "graphite piston" model, which combines the evaporation of graphitized material from the surface and graphitization at the diamond-graphite interface into a single self-consistent process (Figure 3a). According to this model, the energy of the next laser pulse is completely absorbed in a rather thick graphitized layer and heats it up. As a result, the temperature in the zone affected reaches values higher than the evaporation temperature of graphite, thus removing material from the surface. Simultaneously, the diffusive penetration of heat into the sample increases the temperature of the graphite-diamond interface and initiates the transformation of the next portion of the diamond. In this way the repetitively pulsed laser radiation "push" the "graphite piston" into the diamond plate, involving more and more new diamond layers in the graphitization process.

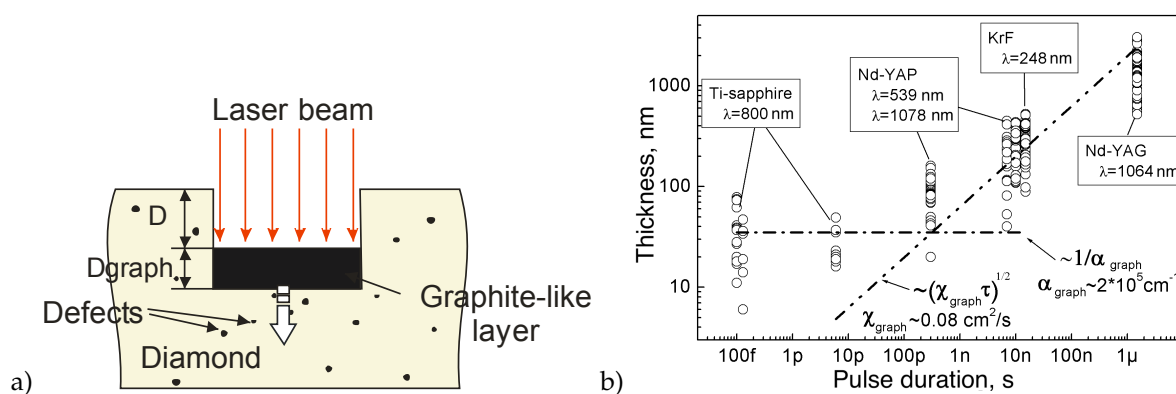


Figure 3. (a) The generally accepted model of laser ablation of diamond and (b) experimental data and theoretical estimates of the thickness of the layer graphitized under multipulse exposure, depending on the pulse duration.

Studies of the properties of the graphite-like layer formed during multipulse ablation also confirm that diamond ablation is a thermally stimulated process [48]. In particular, it is shown that the thickness of the graphitized layer varies over a wide range (10 nm ÷ 3 μm) depending on the duration of the laser pulse. The layer thickness, as the "graphite piston" model implies, is determined by the depth of the heat-affected zone: for long pulses - by the thermal conductivity of the graphite-like phase; for short pulses (up to femtosecond ones) - by the depth of radiation absorption in this phase. This conclusion was made on the basis of the experimental results and the corresponding assessments of the thickness

of the graphitized layer depending on the laser pulse duration (Figure 3b). The absorption coefficient and thermal conductivity of polycrystalline graphite at a temperature of 2000K ($\alpha_g \approx 2 \cdot 10^5 \text{ cm}^{-1}$ and $\chi_g \approx 0.08 \text{ cm}^2/\text{sec}$ [49]) were taken as the corresponding values for the graphitized carbon phase. Note, that the influence of the laser wavelength on the layer thickness was found to be illusive: its small variations are rather caused by differences in the pulse duration of the used laser systems.

The laser ablation of diamond has a pronounced threshold character [14]. In other words, a noticeable rearrangement of the structure of the material is observed if only the laser fluence exceeds a certain threshold. It is interesting to analyze the value of the graphitization threshold depending on the pulse duration (Figure 4a). The ablation threshold value is approximately constant for short pulses (up to 10 ps), and then increases with increasing pulse duration proportionally to the fourth root of the pulse duration. (The exception is a sharp decrease in the threshold for a nanosecond excimer KrF laser (248 nm), associated with the high absorption of diamond in the UV spectral range.) The observed dependence is much weaker than the proportionality to the square root of the pulse duration, which is expected as a consequence of the material cooling due to thermal conductivity. A possible explanation is that the probability of an elementary graphitization event obeys the Boltzmann statistics, and, therefore, the amount of the graphitized phase during laser irradiation depends not only on the laser heating temperature, but also on the time interval during which this temperature is sustained.

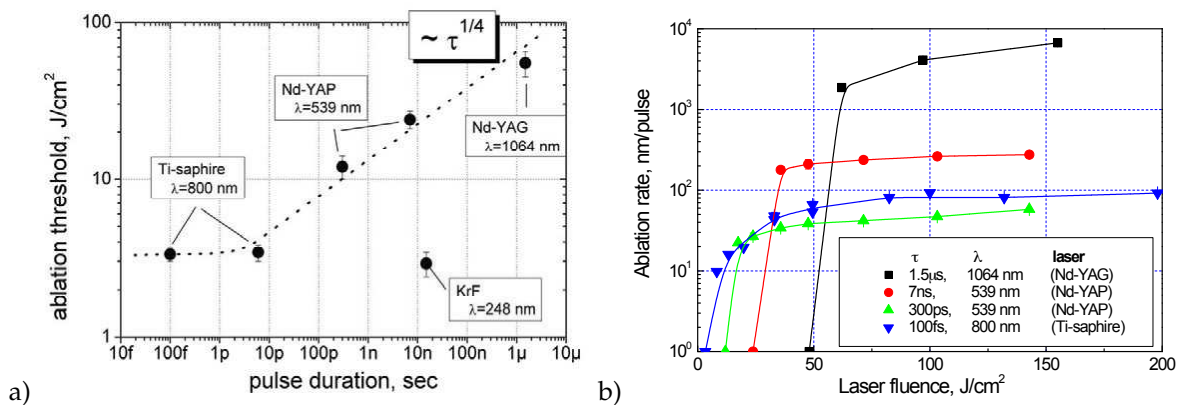


Figure 4. (a) Threshold of diamond ablation versus laser pulse duration and (b) rates of diamond ablation versus laser fluence for different laser systems.

As already mentioned, typical ablation rates are similar for diamond and metals due to one-photon absorption in both cases. Figure 4b shows ablation curves for various laser systems [48]. For all laser pulse durations used, when the ablation threshold is exceeded, the regime of developed evaporation is attained; the laser heating and the further evaporation of the substance occur so rapidly that the thermal conduction process does not have time to spread a significant part of the energy in the depth of the material.

The dependencies given show that for radiation of microsecond duration the material removal has the highest efficiency. Moreover, simple estimates demonstrate that when using long laser pulses, diamond ablation occurs with virtually no loss of optical energy. For shorter pulses, the ablation rates decrease, which is usually attributed to radiation screening by the ablation plume and material overheating due to a very high laser intensity - the substance does not have time to evaporate or cool. It is interesting to note that, as compared to picosecond lasers, the ultrafast (femtosecond) sources provide the increase in the ablation rate, because one of these two effects - screening by evaporated carbon vapor - disappears.

We emphasize once again that laser ablation, being a thermally stimulated process, is characterized by a threshold value of the laser fluence at which it can develop. At fluencies exceeding this threshold, diamond graphitization and ablation are initiated. In this case a clearly defined crater has to be formed in the zone irradiated, the depth of which is determined by the number of pulses (Figure 5a). However,

the structural inhomogeneity of diamond can lead to uncontrolled and non-local surface or volume destruction (Figure 5b,c, respectively), which is also accompanied by graphitization.

This effect is attributed to the presence of microscopic absorbing inclusions in the diamond bulk and, as a rule, manifests strongly in polycrystalline diamond, which has multiple defects and their clusters at the boundaries between crystallites. Such inclusions are able to provide stronger, as compared to the surface, heating of the underlying parts of the crystal and their graphitization. Subsurface graphitization, in turn, will entail explosive destruction of the diamond in the bulk or on the surface, depending on how far the absorbing center was from the surface. This is due to the fact that the material density of graphite is less than the material density of diamond, and during graphitization the substance tends to expand. Similar features should be taken into account in high-precision laser micromachining of diamonds.

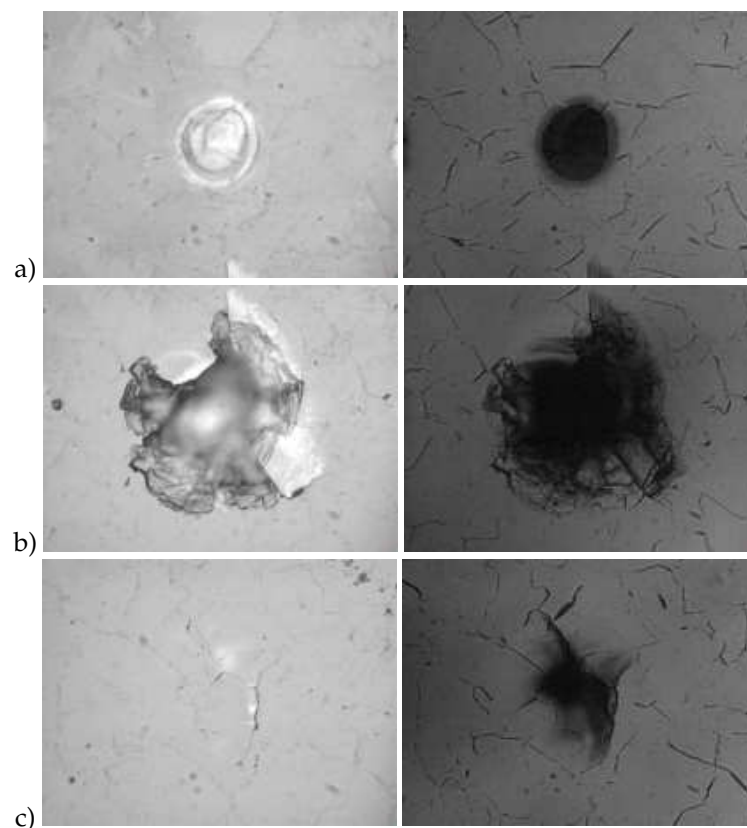


Figure 5. Typical results of single pulse femtosecond exposure to the surface of polycrystalline diamond: (a) surface ablation, (b) surface destruction, (c) bulk destruction. Left images were made with transmission light microscopy, right ones - reflection light microscopy.

3.3. Single-pulse ablation of diamond

In the Section 3.2, it was shown that the multipulse ablation rate and the thickness of the graphitized layer produced by femtosecond pulses are limited by the depth of radiation absorption in the target. In fact, the portion of graphitized/ablated material per pulse is determined by the density of the plasma with which the radiation interacts. When the graphitized surface is irradiated, this plasma consists of $\sim 10^{23} \text{ cm}^{-3}$ π -electrons. Therefore, the well-absorbing graphite limits the radiation penetration depth to $\sim 10 \text{ nm}$. On the other hand, during the first pulse, when initially non-conductive diamond is irradiated, the plasma arisen is not so dense: the concentration of $\sim 10^{21} \text{ cm}^{-3}$ corresponds the graphitization threshold (see Section 3.1). This plasma interacts dynamically with the pulse itself and also limits the penetration of radiation into the diamond. However, the penetration depth in this case becomes noticeably higher and reaches tens and hundreds of nanometers.

Figure 6 shows the experimental depths of the ablation craters as a function of the laser fluence under the single pulse exposure [50,51]. In these conditions the main mechanism of laser energy deposition was two-photon absorption ($\tau = 100$ fs, $\lambda = 266$ nm). As is evident in the data of Figure 6, the dependence is complex and consists of three parts revealing three different regimes of graphitization under single-pulse laser irradiation. The first regime is realized at energies close to the threshold. For two-photon absorption the penetration depth is given as: $D(F) = \tau/\beta(1/F_{th} - 1/F)$ (β is two-photon absorption coefficient of diamond, F_{th} is threshold of graphitization). The field penetrated into the crystal by $\sim 1\mu\text{m}$, and $D(F)$ dependence describes well the initial sharp increase in the thickness of the graphitized layer from 10 nm to 70 nm (black curve, Figure 6).

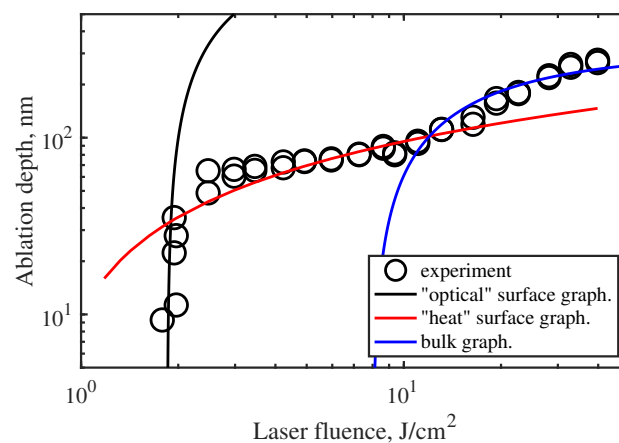


Figure 6. Dependence of ablated crater depth measured after oxidation of graphitized layer on the laser fluence. The exposure was made with 3rd harmonic of Ti-sapp laser (266 nm). Curves exemplify different regimes of surface and bulk graphitization induced by femtosecond radiation.

At energies just above the threshold, a transition to the second graphitization regime, which is characterized by strong saturation, is observed. The depth of graphitization grows slowly, according to a logarithmic law (red curve, Figure 6). The key factor which restricts the ablation rate in this regime is a finality of graphitization wave velocity. Calculations show that the diamond lattice rearrangement occurs layer by layer at a typical velocity of 1 atomic layer (~ 0.2 nm) per 0.1 ps [52]. The graphitization wave starts from the surface and, as the diamond has a record thermal conductivity ($\chi_g \sim 10$ cm²/s), the subsurface layers have time to cool down before the graphitization wave reaches them. On the other hand, the heat released in the near-surface graphitized region turns out to be "locked," since the thermal conductivity of graphite is much less than that of diamond ($\chi_g \sim 0.1$ cm²/s). As a result, the increase in the absorbed energy in the second regime causes incremental superheating of graphitized layer instead of growth of its thickness.

The third regime is realized when the laser fluence exceeded a certain threshold and bulk graphitization started in the crystal. Opposed the previous case, such graphitization is not sourced by the surface but occurred simultaneously in the entire excited volume ($\sim 1\mu\text{m}$). Indeed, the surface swelling in the laser spot reaches $\sim 0.5\mu\text{m}$, indicating implicitly the thickness of the graphitized phase is close to $\sim 1\mu\text{m}$. In this regime, the dependence of the graphitization depth on the laser fluence is also well described within the model of optical field penetration into diamond and two-photon absorption (blue curve, Figure 6). The simulation shows that a threshold of the bulk graphitization is around 8 times a threshold of the surface graphitization.

3.4. Graphitization of (111) diamond face

Single-shot laser exposure made it possible to investigate a relationship between the crystallographic orientation of a diamond sample and the structure of the graphitized phase. This task is of interest in terms of carbon composites consisting of insulating diamond phase and conducting

graphite phase. Laser processing can easily produce graphitic inclusions in diamond, however the crystal perfection of the graphitized phase is rather low. Raman spectroscopy identified laser-modified diamond as a disordered form of carbon [47,53], which is much closer to glassy carbon than to highly oriented pyrolytic graphite (HOPG) [54]. Essentially, laser-graphitized diamond is the mixture of the sp^2 -bonded amorphous carbon intermixed with nanocrystalline graphite with a grain size of approximately 3 nm [54,55]. The high amorphization in the laser-graphitized phase deteriorates its conduction. The typical resistivity of the laser-graphitized surface layer exceeds $10^{-4}\Omega \cdot \text{cm}$ [56,57]. In the case of HOPG the conductivity along basal (0001) plane is substantially higher ($R \approx 3 \cdot 10^{-5}\Omega \cdot \text{cm}$).

The remarkable improvement of the crystal perfection of the graphitized phase produced on the diamond surface was achieved due to the processing of the (111) face. This face graphitization is preferable, as the energetically favorable diamond-graphite transition is realized via transformation of two diamond (111) planes into a graphite (0001) plane as Figure 7a illustrates [58]. As a result, graphite produced on any diamond face always tends to arrange itself so that its basal plane (0001) was parallel to the (111) plane of the diamond crystal [59]. Thus, the crystallographic orientation of the irradiated surface strongly affects the performance of crystal structure of graphitized phase. Graphitized layer produced on the (111) surface has minimal internal stresses thus improving its structure. It should be noted that the formation of highly oriented graphite on the (111) surface was predicted by molecular dynamics simulations performed for both stationary furnace heating [52] and pulsed laser heating [60].

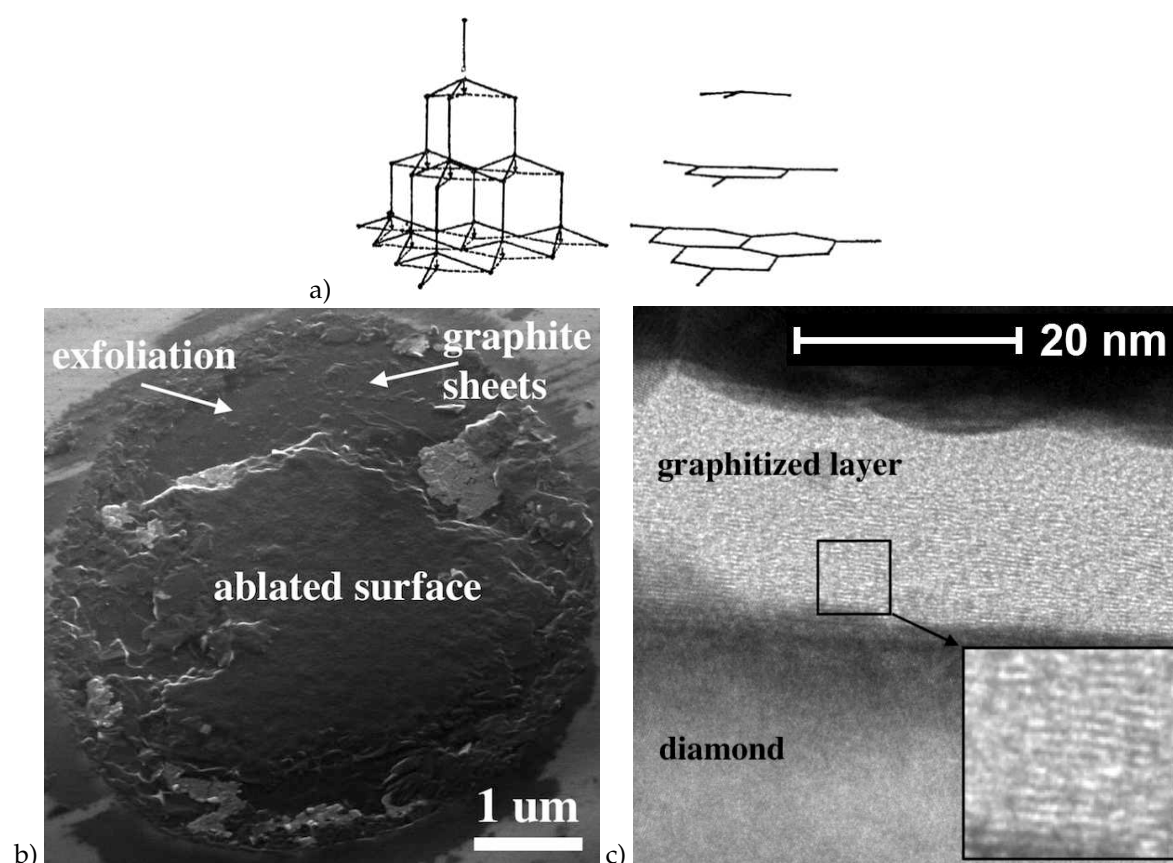


Figure 7. (a) Graphitization model of (111) diamond, (b) SEM and (c) TEM images of the laser-graphitized phase on (111) face ($F = 3.8 \text{ J/cm}^2$).

The structure of the layer graphitized with single femtosecond UV pulse on the (111) diamond face was studied in detail in [61]. The SEM inspection of graphitized diamond surface confirm that the graphitic sheets arranged along (111) plane (Figure 7b). The thin flakes graphite are found to be of

about 100 nm laterally. The adhesion of these flakes to the substrate was rather low; the modified phase could be easily scratched by a steel tip. According to the data of bright-field TEM microscopy the structure of the carbon in the bulk of the graphitized layer (Figure 7c) is highly ordered. The laser-modified material resembles HOPG and consists of regular sheets which are parallel to the diamond surface. The closer to graphite-diamond interface, the higher the structural performance of graphitized material is and the more it resembles HOPG. On the other hand, the sub-surface (~ 5 nm) graphitized structure is rather amorphized.

Besides the fact that the structure of the graphitized layer is determined by the crystallographic orientation of the irradiated face, it essentially depends on the laser fluence. Figure 8 compares the Raman spectra obtained on the (111) and (100) faces. The spectrum of original diamond, that exhibits a single intensive "diamond" peak at 1333 cm^{-1} , is depicted in the bottom part of both panels. In the case of (111) graphitization the lowest fluencies are characterized by the emergence of the narrow G peak ($\Gamma_G \approx 25\text{ cm}^{-1}$), while the D and D' peaks are relatively low and can hardly be distinguished. Taken as a whole these spectra are close to the HOPG spectrum [62]. (The typical Raman spectrum of HOPG is presented in the top part of the Figure 8). Note that above SEM and TEM images correspond exactly this regime. At the elevated pulse energy the Raman spectra acquired the typical features of the graphitization on the (100) diamond face: the D and G peaks become wider, attributing the formation of disordered nanocrystalline graphite [62]. It is noteworthy that the disorder diminishes in the bulk graphitization regime (see Section 3.3). The D and G peaks get relatively narrow (Figure 8a, $F = 60.9\text{ J/cm}^2$) and the correspondent spectra resemble the spectra of a diamond graphitized at the low fluence.

Nothing similar happens when the (100) or (110) diamonds are graphitized. In the case, as a number of studies proved the graphitized material is close in structure to nanocrystalline graphite with a significant content of the amorphous phase [47,54,55,63–65]. The typical Raman spectra for the (100) face irradiated at different laser fluencies are shown in Figure 8b.

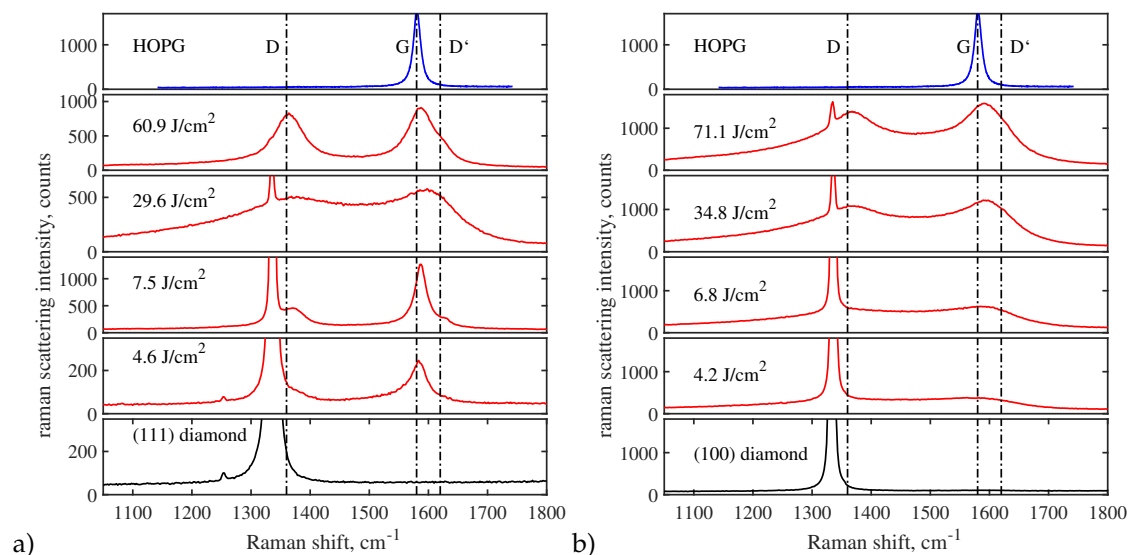


Figure 8. Raman spectra of graphitized (111) diamond (a) and (100) diamond (b) for different laser fluence. Bottom spectrum relates to untreated diamond. Top spectrum is given for comparison and relates to monocrystalline HOPG

3.5. Accumulative graphitization of diamond

Before the discussion of subthreshold regimes of exposure to diamond, a few words should be said about the accumulative regime of irradiation [33,39]. In this regime the laser fluence is less than the single-pulse graphitization threshold but higher than the multipulse one. During multipulse irradiation the surface in the laser focus remains uncovered with an absorbing graphitized layer, and

the diamond is directly exposed to radiation. The effect of each individual pulse is too small to be measured and it introduces a tiny change (damage) in the lattice. However, being permanent, these changes accumulate from pulse to pulse. And after a certain time they appear in the form of the rapid graphitization of the diamond surface, which can be easily detected (Figure 9).

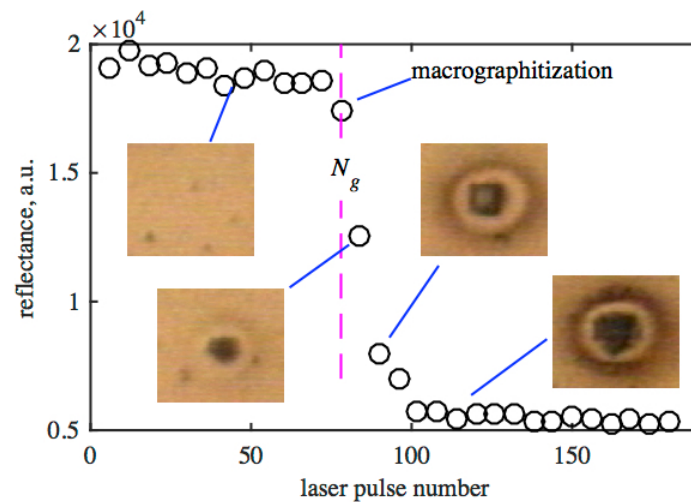


Figure 9. Evolution of the diamond surface reflectance during femtosecond 400 nm laser exposure ($F = 3 \text{ J/cm}^2$). The insets - the bright field illuminated images of irradiated surface - demonstrate the state of surface.

To date, understanding the mechanisms of accumulative graphitization is rather poor. In [39] a model of accumulative graphitization of diamond under the femtosecond irradiation is proposed. It is based on two-stage growth of graphite-like nanodroplets and transformation of diamond into graphite around initial point nuclei (accumulation stage). When the droplet reaches a certain critical size R_{cr} , its heating by a femtosecond pulse becomes effective and the critical temperature required for thermal graphitization of diamond is reached. In this moment the growth of the droplet accelerates and the droplet increases to a micron size in several pulses.

It is substantiated experimentally that the duration of the accumulation stage (N_{accum} pulses) can serve as a measure of the rate of structural changes in the lattice at a fixed laser fluence. This makes it possible to estimate the graphitization rate at the accumulation stage as $r_{accum} \approx R_{cr} / N_{accum}$. Experimental dependences of $1/N_{accum}$ on laser fluence for Ti-sapp laser radiation (800 nm, 400 nm and 266 nm) are shown in Figure 10. Their analysis shows that the growth rate of graphite clusters on the diamond surface obeys the Arrhenius law. In other words, accumulative graphitization is a thermally stimulated process. On the basis of the experimental data, the assessments of the rate of accumulative graphitization under femtosecond irradiation were obtained: graphite nanodroplets on the diamond surface grow at a rate of $\sim 10^{-4} \div 1 \text{ nm/pulse}$. The corresponding dependence on laser fluence will be discussed in Section 3.7.

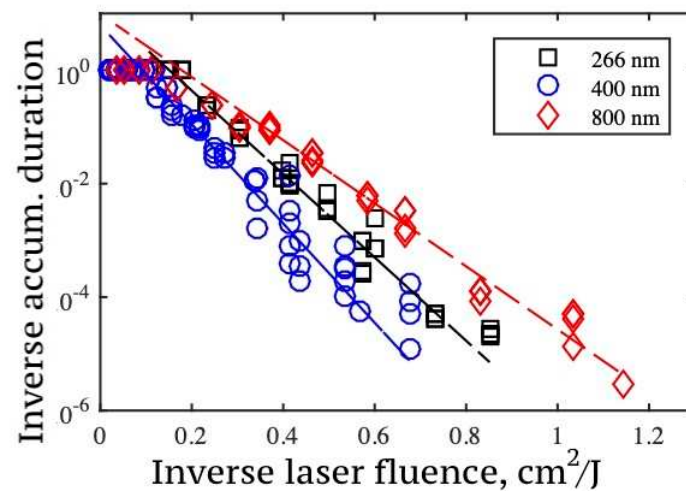


Figure 10. Arrhenius plot of a quantity $1/N_{accum}$ which is proportional to the average rate of diamond graphitization in its latent stage.

3.6. Nanoablation of diamond

This Section discusses the main regularities of the process of laser nanoablation of diamond - slow etching of a sample surface in the air atmosphere at laser fluence below the multipulse graphitization threshold. The first observations of such a graphitization-free etching process took place in the works studying laser annealing of ion-implanted crystals [28–30]. These observations initiated a series of experiments when already pure diamonds, which were free of introduced defects and characterized by high optical transparency, were subjected to long-term irradiation with nanosecond KrF laser pulses. It was found that visible graphitization of the surface did not develop at laser fluence of 15 J/cm^2 during millions of pulses [31]. Simultaneously, the removal of carbon inside the laser spot happened, the rate of which was about $2 \cdot 10^{-5} \text{ nm/pulse}$. To emphasize the extremely low etching rates, this process was called "nanoablation".

The experiments, comparing the rates of nanoablative diamond etching in air and in a helium flow [31], showed the importance of atmospheric oxygen deficiency. More detailed studies had been demonstrated that the etching rate dependence on the ambient pressure is essentially nonmonotonic (Figure 11). The nanoablation rate (r) increases almost linearly with pressure in the high vacuum of 10^{-7} to 10^{-5} Torr. However, a further increase in pressure leads to a sharp drop in the carbon removal rate, and in the range from 10^{-3} Torr to atmospheric pressure, this rate remains constant at $5 \cdot 10^{-7} \text{ nm/pulse}$.

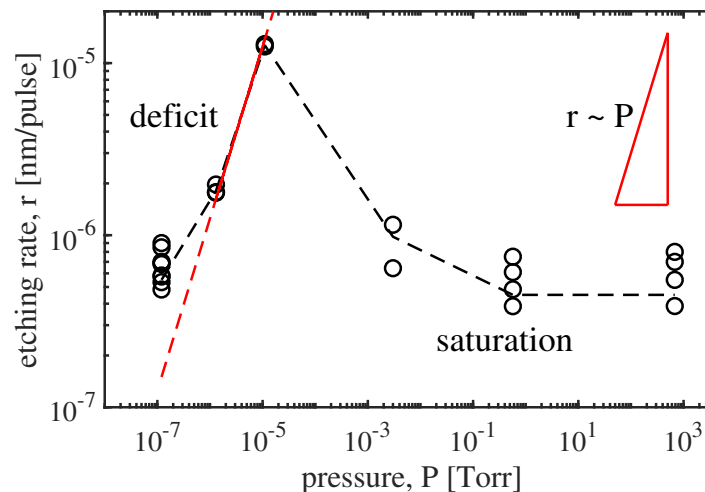


Figure 11. Dependence of the nanoablation rate on the atmospheric pressure obtained with 2nd harmonic of Ti-sapp laser ($\tau = 120$ fs, $\lambda = 400$ nm).

The increase in the nanoablation rate ($r \sim P$) observed at low pressures suggests to exclude the evaporative mechanism of substance removal and leads to the conclusion that the nanoablation is a chemical reaction. A main reactant in this reaction is, obviously, oxygen, which (i) is chemically active and (ii) reacting with carbon creates volatile components (CO , CO_2).

Detailed analysis of the $r(P)$ curve shows that its complex character cannot be explained solely in terms of the reaction with oxygen. A sharp drop in the nanoablation rate at pressures of $\sim 10^{-5}$ Torr indicates the presence of some inhibitor of laser stimulated oxidation of diamond. The most likely candidate for this role is water contained in the atmosphere and easily adsorbed on the hydrophilic surface of diamond, up to the formation of a thin aquatic layer there [66]. Indeed, water vapor significantly slows down the oxidation process. For example, 2.5% water vapor increases in the activation energy of thermal oxidation of diamond by 1.5 times [67].

The ambient pressure also affects the topology of craters formed during nanoablation. This influence has two aspects, shown in the Figure 12. The first is that the depths of the craters obtained at the same dose of radiation differ by several times (see craters obtained at 10^{-5} Torr and at 680 Torr). The second aspect is that at low pressures (in the region of linear growth of the nanoablation rate) the shape of the profile changes: at a pressure of 10^{-6} Torr the crater bottom noticeably flattens, and at 10^{-7} Torr an elevation appears in the crater center. In other words, at low pressures, the rate of nanoablation in the center of the irradiation zone is significantly lower than on its periphery, despite the fact that the radiation intensity in the center is higher.

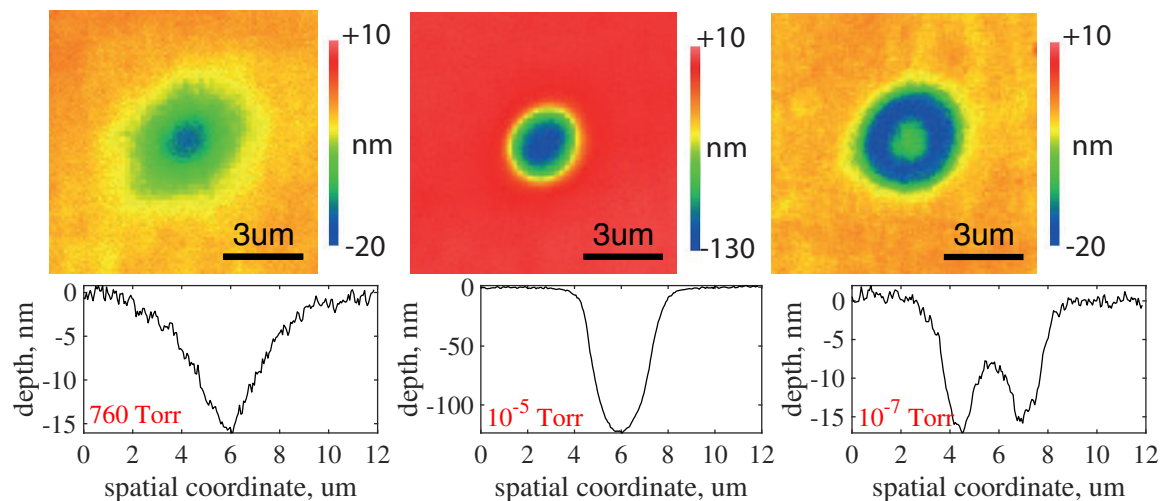


Figure 12. Two-dimensional surface profiles of the laser irradiated zone at varied atmospheric pressure.

The effect arises due to a mechanism that becomes important in the shortage of the atmospheric oxygen. This mechanism is surface oxygen diffusion, which allows additional amount of oxygen to appear inside the laser affected zone. Indeed, laser heating leads to desorption of oxygen, thus forming a gradient in the surface concentration of oxygen: its amount in the center of the laser spot turns out to be significantly lower than at the periphery. The surface diffusion of adsorbed oxygen develops in the direction opposite to the concentration gradient, i.e., to the center of the laser spot. As a result, much more oxygen piles up on the periphery of the crater due to the diffusion than was adsorbed in the center of the spot from the gas phase. This eventually causes the flattening of the crater bottom and even its uplift (Figure 12, 10^{-7} Torr).

The understanding nanoablation as a chemical reaction is crucially supported by the investigations of its kinetics under external heating. The nanoablation rates were measured for various temperatures in the range $20\text{C} \div 600\text{C}$ at a fixed laser fluence (Figure 13). It has been found that the nanoablation rate increases approximately 10 times as the temperature rises from room temperature to 600C and reaches $\approx 10^{-3}$ nm/pulse. In this case, the temperature dependence is close to Arrhenius law with an activation energy of about $E_a^{\text{las}} \approx 0.1$ eV/atom.

For comparison purposes, the Figure 13 presents data on thermally stimulated oxidation of diamond [68]. The corresponding activation energy is $E_a^{\text{term}} \approx 2.7$ eV/atom and exceeds the activation energy under combined action (laser exposure + external heating) by a factor of 25. These data show that the laser action drastically reduces the height of the potential barrier, which must be overcome in each oxidation event. For this reason, under laser excitation the reaction rate sharply increases, and so much so that the carbon removal becomes noticeable even at room temperature.

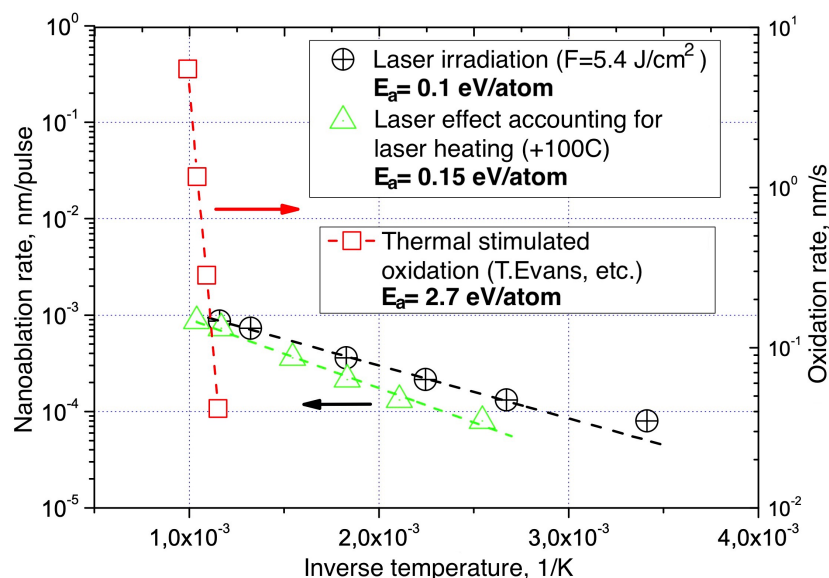


Figure 13. The rate of laser nanoablation depending on the temperature of the sample.

Thus, nanoablation is a photostimulated process and the parameters of laser radiation largely determine its efficiency. This is confirmed by the nanoablation rate dependencies on the laser fluence, radiation wavelength, and laser pulse duration [69–71]. Unlike conventional thermally stimulated ablation, nanoablation is a non-threshold process, and for all used laser sources, the material removal rate r was found to depend on the laser fluence F in a power-law manner: $r \sim F^s$, where the exponent s depends on the radiation wavelength and pulse duration (Figure 14a).

As in any photo-stimulated process, the wavelength dependence is expectedly critical. In particular, etching of the diamond surface does not take place under IR irradiation. When using radiation in the visible or UV spectral ranges (193 nm - 515 nm), two regimes of nanoablation were observed, depending on the duration τ of laser pulses. At $\tau \geq 1$ ps, the nanoablation rate is proportional to the concentration of carriers excited by radiation, while for femtosecond pulses ($\tau \approx 100$ fs) this dependence turns out to be nonlinear, namely, quadratic (Figure 14 b). (Figure 14b is a recalculation of nanoablation data (Figure 14a) using diamond photoionization data (Figure 2)). It was also found that as the pulse repetition rate increases (at least, up to $f = 500$ kHz), the nanoablation rate remains stable, that opens up new possibilities in the development of high-performance nanomachining methods for the diamond surface.

Therefore, the nanoablation proceeds through a three stages. The first step is dissociation of molecular oxygen on the surface, which is known to be effective at room temperature [72]. Oxygen chemisorption takes place between laser pulses and causes oxygen species to saturate dangling bonds and form ether-like bridge [73] or ketone on-top sites [74]. The second step is realized when light is absorbed and the energy imparted makes the excited electrons leave the bonding orbitals and transfer to nonbonding or antibonding states. This runs the third step that is a C–O group desorption, which hypothetically consists of six elementary transformations, including β -scission of the C–CO bond, formation of a dimer C–C bond, and cleavage of the second C–CO bond [75]. Two of these transformations have high activation barriers ($\approx 1.1 - 1.7$ eV) and control the overall reaction kinetics. Without laser pumping these barriers stop the oxidation at room temperature, whereas photo activation enables the C–O group desorption. So, in the last third step the oxides desorb from the surface, resulting in gradual removal of the substance from an irradiated zone.

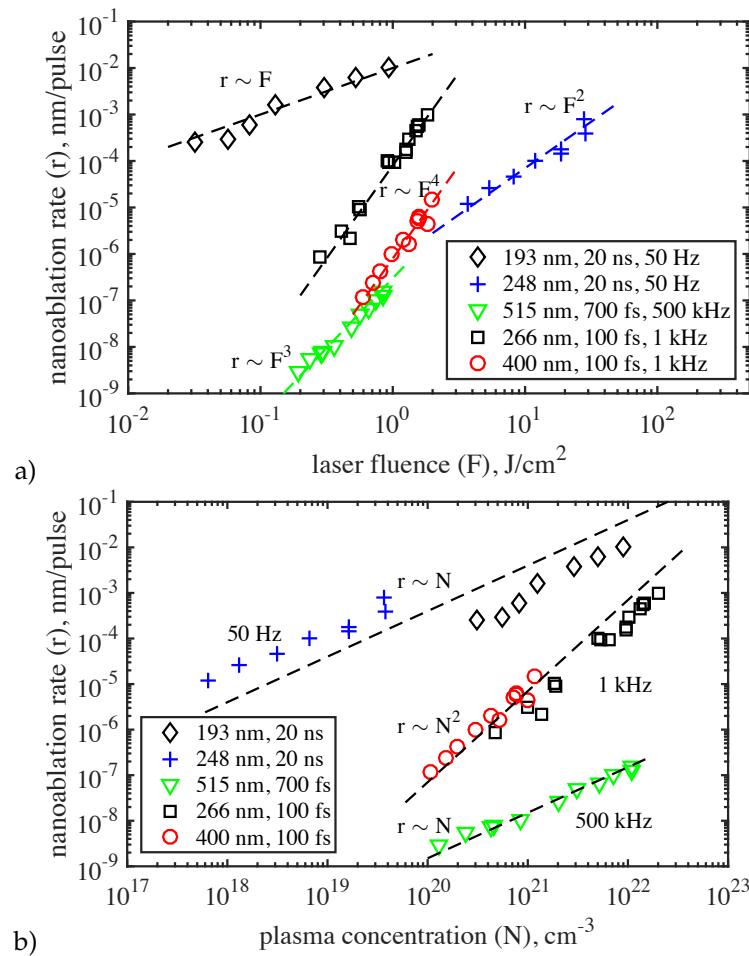


Figure 14. (a) Diamond nanoablation rate versus optical fluence for different lasers, (b) Nanoablation rate versus the concentration of optically excited carriers.

3.7. Overall picture of laser-induced processes in diamond

It is interesting to comprehend the relationship of various laser-stimulated processes and compare their rates. The instance of such data combining the rates of (i) nanoablation, (ii) accumulative graphitization and (iii) evaporative ablation for the case of 2nd harmonic of Ti-sapp laser are shown in the Figure 15. Data for nanoablation and evaporative ablation were measured directly (as crater depth divided by the number of pulses). The data for the accumulation regime were calculated as $r_{accum} = R_{cr}/N_{accum}$, where $R_{cr} = 10$ nm is a constant calculated from the conditions of heating a graphite drop with a femtosecond pulse [39]. These data show that, taken as a whole, the laser pulse exposure on diamond is not a threshold process, as previously thought. Intense radiation initiates a complex of fast or slow interrelated processes resulting in diamond transformation or destruction.

It is apparent, the result of multipulse irradiation critically depends on the laser fluence. There are two key points: single pulse graphitization threshold $F_g^s \approx 10 \text{ J}/\text{cm}^2$ and multipulse graphitization threshold $F_g^m \approx 1.4 \text{ J}/\text{cm}^2$. At low laser intensity ($\leq F_g^m$), nanoablation takes place. Typical rates for this laser are 10^{-5} nm/pulse and below. At moderate fluence ($F_g^m \div F_g^s$) during long-term multipulse exposure the diamond lattice gradually transforms into a graphite-like phase. Typical rates for this laser are $10^{-5} - 1$ nm/pulse.

The observed behavior suggests the hypothesis of a competition between photooxidation and graphitization in diamond. If the optical energy fluence is below the multipulse graphitization threshold ($F < F_g^m$), photooxidation dominates. Its rate is much higher than the rate of thermally stimulated graphitization. Any graphite cluster produced will be exposed to oxygen and etched away instead of continuing to absorb light and grow. It is the regime that is referred by the term nanoablation.

The situation changes on going to a higher laser fluence $F > F_g^m$: in the case photooxidation can not completely remove graphitized clusters, and they grow faster and faster. Accumulative graphitization develops, as detailed in the Section 3.5. Thus, the lower limit of the accumulative graphitization rate is determined by the competition between it and nanoablative etching.

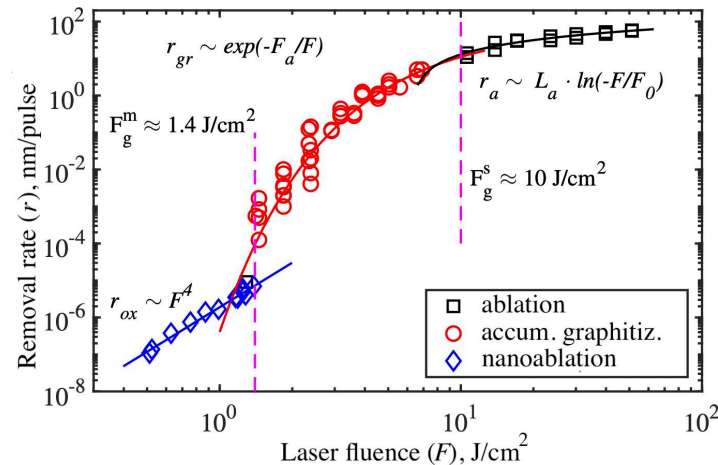


Figure 15. The rates of laser-induced processes in diamond: evaporative ablation of diamond, accumulative graphitization, nanoablation. The data are presented for the 2nd harmonic of the Ti-sapp laser ($\tau = 120$ fs, $\lambda = 400$ nm). Ablation data are fitted with logarithmic curve; accumulative graphitization - function of the Arrhenius type; nanoablation is a 4th order polynomial.

In turn, the upper limit of the accumulative graphitization rate is limited by the development of single-pulse ablation, the typical rates of which are > 10 nm/pulse (Figure 15). This regime is completely determined first (before graphitization) by the process of multiphoton absorption in diamond and then (after graphitization) by single-photon absorption in graphite, and is described in detail in Sections 3.2 - 3.3.

3.8. Laser-induced NV centers in diamond

This Section is devoted to another important aspect of laser interaction with diamond: the possibility of modifying its lattice at the atomic level, in other words, to the formation of structural defects. The nitrogen-vacancy complexes (NV centers) are of main interest due to the perspectives of their application in quantum optics, probing, and other fields [18]. Since nitrogen is an impurity that is difficult to get rid and which is always present in diamonds (including synthetic ones), the main difficulty lies in the controlled and preferably local generation of diamond lattice vacancies. Significant efforts are being made to use ionic [76], electronic [77], and laser exposure [35,78,79] for this purpose.

It turned out that different regimes of laser generation of NV centers are possible: with graphitization of the diamond lattice and without it. It is rather simple to obtain generation of NV centers in the graphitization regime, since such a strong lattice damage is a natural source of vacancies that relatively easily diffuse into diamond over distances of $\sim 100\mu\text{m}$. In the experiment, a strong enhancement of the luminescence of NV centers was found near the regions of laser graphitization, which were created both on the surface [78] and in the bulk of diamond [79]. However, the use of such structures is very limited, since damage to the crystal lattice negatively affects properties of NV centers, in particular, the inhomogeneous broadening of optical transitions in the defect increases dramatically.

Recently, Chen et al. [35] showed the possibility of the formation of NV centers with a femtosecond laser in the bulk of diamond without total destruction of the lattice. A narrow range of pulse energies was found in which vacancies can be generated using single-pulse laser irradiation avoiding visible graphitization. Above, we have described this regime as the accumulative graphitization (see Section 3.5). We emphasize that Chen et al., working in the accumulative regime, affected the diamond by a

single shot only and, thus, deliberately prevented the development of macrographitization. In order to heal the created laser damage to the lattice, the crystal was annealed at the temperature of $\sim 1000^\circ\text{C}$. Such a procedure led highly likely to the formation of $1 \div 2$ centers in the irradiated region, which was buried at the depth of several microns from the surface.

The next reasonable step in order to mitigate the lattice damage was made in [32,80]. The technique consisted in creating vacancies on the diamond surface, which appear during nanoablation. Figure 16a,b illustrates two effects that occur inside the irradiated zone after nanoablative etching: (i) the appearance of a nanoablated crater and (ii) a sharp increase in photoluminescence (PL) intensity. The latter indicates the formation of new color centers. The PL signal after irradiation was about ten times greater than before it.

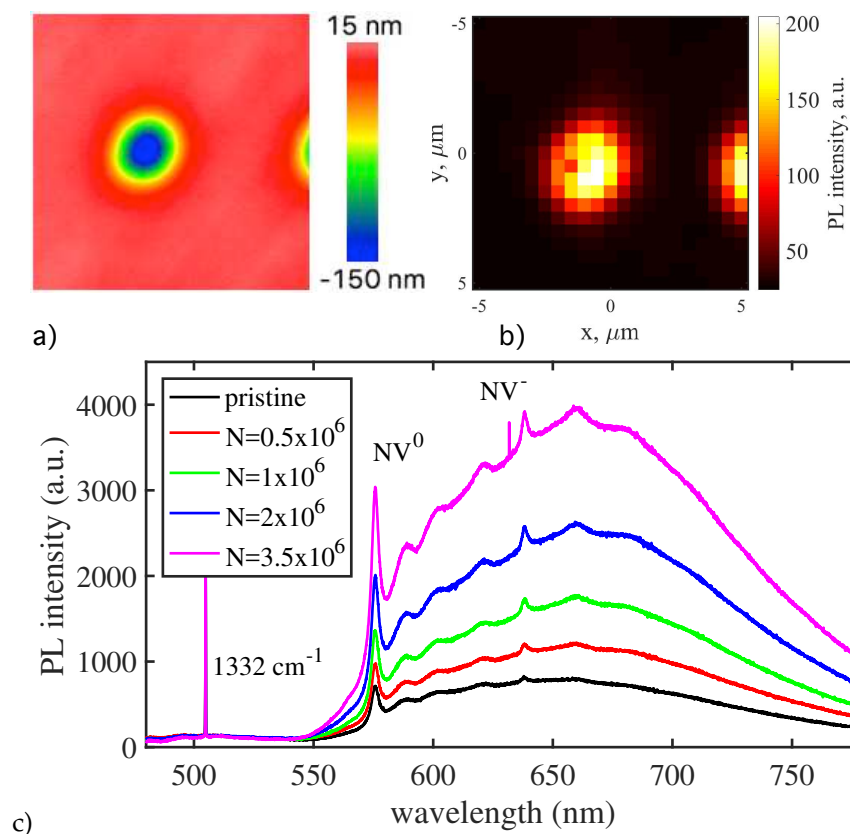


Figure 16. Result of laser irradiation of diamond ($\lambda = 266 \text{ nm}$, $\tau = 100 \text{ fs}$, $F = 0.4 \text{ J/cm}^2$, $2.6 \cdot 10^6$ pulses): (a) formation of a 130 nm nanoablated crater; (b) photoluminescence enhancement caused by the formation of NV complexes in the irradiated area, (c) photoluminescence spectra measured inside and outside the laser irradiated area at different irradiation doses. The 505 nm line corresponds to Raman scattering (1332 cm^{-1}).

Spectroscopic measurements confirmed that the induced color centers are indeed NV complexes. Both before and after laser exposure, the PL spectra are typical for NV centers and consist of narrow zero-phonon lines (ZPL) and broad phonon wings (Figure 16c). Both neutral (ZPL at 575 nm) and negatively charged (ZPL at 638 nm) centers are observed. Note that laser irradiation increases the PL intensity, while the shape of the spectra remains unchanged. The ratio of NV^- to NV^0 is constant. To check how much the laser action damages the lattice, the width of zero-phonon lines at low temperatures ($T = 5 \text{ K}$) was measured. In the PL spectra of irradiated diamond, as compared to pristine one, no changes in the width of the lines at 575 nm and 638 nm were found. The ZPL width at half maximum intensity was found around 0.3 nm for both NV^0 centers and NV^- centers.

The fact of a stable correlation between the process of creating NV centers and the process of nanoablative etching has been confirmed experimentally. Figure 17a shows that the intensity of

photoluminescence (i.e., the number of NV centers) does not depend on the parameters of the radiation that stimulates nanoablation process, but depends only on the depth of the obtained nanoablative crater. The kinetics of the generation of NV centers was also studied and the dependences of their formation rate on the laser energy density were obtained (Figure 17b). It turned out that while the nanoablation rate is proportional to the fourth power of the laser fluence (as a result of two-photon absorption - see Section 3.6), the generation rate of NV centers is proportional to the sixth power of the laser fluence. Allowing for the absorption mechanism, these rates are proportional respectively to the second and third powers of the concentration of the electron-hole plasma. The power-law nature of the dependences suggests laser-stimulated generation of defects in diamond, like nanoablation, to be a photostimulated process.

A possible interpretation of the obtained results is that the process of formation of NV centers goes through three successive stages. First, intense light strongly perturbs the electronic subsystem of diamond, but the accompanying heating is still insufficient to run a thermal graphitization transition. Ionization stimulates the second stage - surface reactions with adsorbed oxygen, and as a result of nanoablative etching, empty atomic nodes are formed on the surface in the carbon lattice - nodes that are not filled with carbon atoms. Actually, being on the surface, these empty nodes are not yet full-fledged vacancies, however, some of them diffuse deep into the crystal, thereby transforming into real vacancies. Third, the vacancies created in this way diffuse further inside the crystal until impurity nitrogen atoms capture them and form NV complexes. In this scheme, the trapping of vacancies is a secondary process, and the rate of formation of NV centers is determined by the mechanism of laser-induced formation of vacancies and their laser-stimulated diffusion.

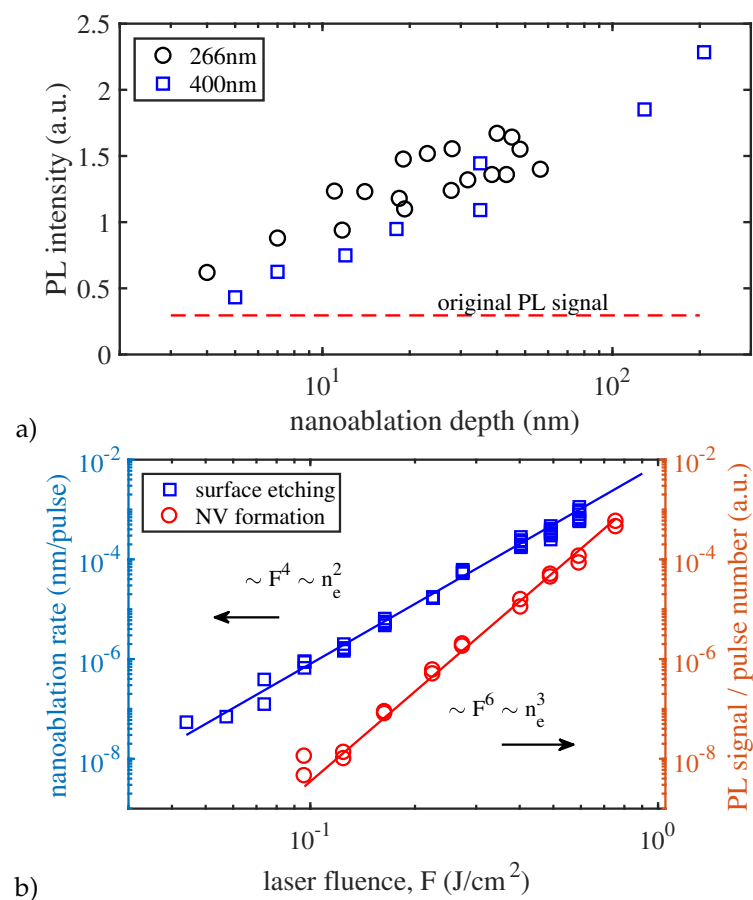


Figure 17. (a) Integral PL signal as a function of nanoablation depth for laser treatment at 400 nm and 266 nm ($F \approx 0.8 \cdot F_g$), (b) Nanoablation rate and rate of formation of NV centers depending on laser fluence.

The results obtained show that femtosecond laser nanoablation is a promising tool for controlling the formation of NV centers in diamonds. This is a relatively slow process, and at a sufficiently low laser fluence, the formation of single NV center requires several laser pulses, which makes it possible to control a number of NV centers and, particularly, to create single-photon emitters in the pre-given points on the surface in a controlled manner.

4. Conclusions

The main fundamental aspects of the laser-diamond interaction reviewed here can be summarized as follows:

1. Multipulse evaporative ablation of the diamond surface is accompanied always by the surface graphitization, which is essentially a thermally stimulated process and can develop gradually, over a sufficiently long accumulation period. In a steady-state mode (when the graphitized layer has been already emerged), both the thickness of this layer and the thickness of the material removed during a laser pulse are proportional to the depth of the heat-affected zone and vary in the range of $\sim 10 \text{ nm} \div 1 \text{ }\mu\text{m}$ depending on the duration of the laser pulse.

2. Laser graphitization occurs during a single pulse, when a certain threshold of laser fluence is exceeded. In this case, depending on the irradiation energy, three regimes of diamond ablation are realized: (i) if the pulse energy is close to the threshold, the graphitization rate is determined by the penetration of the optical field into the crystal; (ii) then, with increasing the irradiation energy, the penetration depth of the graphitization front reaches saturation, that refers to the limitation of the graphitization wave velocity; (iii) when the laser fluence exceeds a certain next threshold, bulk graphitization is initiated, which is not associated with the surface, but occurs simultaneously in the entire excited volume ($\sim 1 \text{ }\mu\text{m}$).

3. The crystalline perfection of the graphitized phase crucially depends on the orientation of the diamond face irradiated. The carbon phase produced on the (100) or (110) face is close to nanocrystalline graphite with a significant content of the amorphous phase. The structure of a layer obtained on the (111) crystalline face resembles highly ordered pyrolytic graphite.

4. As the laser energy decreases below the multipulse graphitization threshold, nanoablative etching of the diamond surface occurs, which is intrinsically photostimulated oxidation and which is characterized by the extremely low rate - less than 10^{-2} nm/pulse . Optical excitation of the electronic subsystem results in a significant decrease in the activation energy of the oxidation process: from $\approx 2.7 \text{ eV/atom}$ (thermal oxidation) to $\approx 0.1 \text{ eV/atom}$ (nanoablation).

5. Nanoablation is found to be a multiphoton process - the removal rate of diamond material r depends on the laser fluence F as $r \sim F^k$, where the exponent k depends on the laser wavelength and the pulse duration. For the case of femtosecond irradiation the role of photoexcitation of the electronic subsystem of diamond was clarified experimentally: the nanoablation rate was shown to be determined by the concentration of photo-excited carriers independently on the pump radiation wavelength.

6. The above-mentioned process of accumulative graphitization is a thermally stimulated process, in which diamond is gradually (from pulse to pulse) transformed into a graphite-like form of carbon. The typical rates of the transformation range from 10^{-4} to 1 nm/pulse . The upper limit of this rate is limited by the development of single-pulse graphitization, while the lower limit is determined by the competition between graphitization and nanoablative etching.

7. Laser processing makes it possible to modify the structure of the diamond not only at the nanoscale, but even at the atomic level. The zone graphitized by laser radiation is a source of vacancies diffusing outward into diamond and creating there nitrogen-vacancy complexes. Besides the graphitization process, the NV centers can be formed both in the accumulative regime (during single-pulse irradiation) and in the nanoablative regime (during long-term irradiation). Nanoablation is apparently the most promising technique for creation of the active centers in diamond, since it refers to the generation of NV centers in the subsurface layer without graphitization damage to the lattice.

The experiments using different harmonics of Ti:sapp laser proved a clear correlation between the nanoablative surface etching and the formation of NV complexes. Thus, laser-induced generation of NV centers is a non-threshold and photostimulated process, where the defect formation rate is proportional to the third degree of the plasma concentration induced in diamond regardless of which wavelength was chosen for pumping.

Funding: This research was funded by Russian Science Foundation, grant no. 22-72-10108.

Acknowledgments: The author is thankful to his colleagues from the General Physics Institute, first of all to Vitaly Konov, Taras Kononenko, Sergey Pimenov, Andrey Khomich, Evgeny Zavedeev, Alexander Khomich, Maxim Komlenok, Igor Vlasov, and many others for important contributions in the presented researches.

Conflicts of Interest: The author declares no conflict of interest.

Symbols and Abbreviations

The following symbols and abbreviations are used in this manuscript:

λ	radiation wavelength
τ	duration of laser pulse
f	laser repetition rate
F	laser fluence
r	rate of material removal
HPHT	high pressure - high temperature
CVD	chemical vapor deposition
BBO	β -barium borate

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