*INTERACTION OF LASER RADIATION WITH MATTER*

# Laser nanoablation of diamond surface at high pulse repetition rates

V.V. Kononenko, V.M. Gololobov, V.P. Pashinin, V.I. Konov

*Abstract*. **The chemical etching of the surface of a natural diamond single crystal irradiated by subpicosecond laser pulses with a high repetition rate ($f \leqslant 500$ kHz) in air is experimentally investigated. The irradiation has been performed by the second-harmonic (515 nm) radiation of a disk Yb : YAG laser. Dependences of the diamond surface etch rate on the laser energy density and pulse repetition rate are obtained.**

## 1. Introduction

Precise nanoprocessing of the surface of diamond is one of the key technologies, which currently determine the prospects of application of this material in optics and electronics [1]. This circumstance stimulates the study of laser-induced processes in diamond, which are diverse and efficient from the point of view of controlled and productive processing of the surface of this extremely hard and chemically inert crystal.

Historically, most of the works in this field were devoted to the evaporative ablation of diamond with a high material removal rate ($r > 10$ nm pulse$^{-1}$) [2–5]. A specific feature of this processing regime is the formation of a rather thick (more than 10 nm [4]) strongly absorbing graphite-like layer on the surface [2]. In principle, this layer can be removed using various chemical methods; however, the structure of the initial crystal is damaged to some extent, which is not always acceptable in practice [6]. At the same time, with a decrease in the laser beam energy density in the laser-irradiated region, the development of the initial surface graphitisation slows down and then even stops.

It turns out that, if the laser energy density is below some threshold value, extremely slow photochemical etching of the diamond surface is observed instead of graphitisation [7]. This etching occurs when diamond is irradiated in air. It is believed to be due to the photostimulated surface reaction of carbon oxidation. It was found that the laser-stimulated surface oxidation is a thresholdless process; hence, reduc-

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ing the pulse energy, one can obtain arbitrarily low material removal rates. As will be shown below, rates as low as $r < 10^{-8}$ nm pulse$^{-1}$ can experimentally be set; hence, this processing regime can in fact be considered as a key element of diamond surface nanoprocessing technology and referred to as nanoablation.

The efficiency problem is urgent at such low etch rates. As numerous experimental data show, no more than one atomic layer of material is generally removed by photoetching during a pulse [8]. The reason for this limitation is that the photoreaction occurs directly between the surface-layer atoms and adsorbed molecules. Before implementing a contact between the adsorbent and lower layers of material, the reaction products must be removed from the reaction zone. Since the agent activation time under pulsed irradiation is limited by the pulse duration and relaxation processes, the second and subsequent layers are unlikely to be etched during one pulse.

The expected limiting etch rate for diamond is $r_{lim} \leqslant a = 0.178$ nm pulse$^{-1}$ ($a$ is the average interatomic distance in the diamond lattice). In practice, the maximum photooxidation rate $r_{max}$ of the diamond surface is lower than $r_{lim}$. The $r_{max}$ value is determined, in particular, by the maximum plasma density that can be induced in the irradiation zone without developing graphitisation; it also depends strongly on the pulse wavelength and width. For example, for 100-fs pulses with $\lambda = 266$ nm, $r_{max} \approx 10^{-3}$ nm pulse$^{-1}$ [9]. For 20-ns pulses with $\lambda = 193$ nm, $r_{max}$ is much higher: $\sim 10^{-2}$ nm pulse$^{-1}$ [10]. Note also that an external heating of the target increases the nanoablation rate up to a factor of 10 [11]. Thus, etch rates $r_{max}$ close to $r_{lim}$ can experimentally be implemented within one pulse.

Obviously, a complementary way to improve the nanoablation processing efficiency is to increase the laser pulse repetition rate. Currently, the development of modern industrial lasers with an ultrahigh repetition rate (1–10 MHz) and average power no less than 100 W has opened interesting prospects in this line of research.

However, in the case of surface reactions induced by pulsed irradiation, this approach may have limitations related to the adsorption rate of agents (oxygen molecules in our case) on the surface. For example, the results of the experiments on silicon etching in a chlorine-containing atmosphere [12] indicate that the chlorine adsorption even does not start if the time between pulses is not long enough for the irradiated region to be cooled. The characteristic times are $\sim 1$ µs; i.e., at a pulse repetition rate of 1 MHz, the silicon etch rate may even drop to zero. To date, this problem has not been studied for diamond photoetching. Our experiments are aimed to fill in this gap.

## 2. Experimental

A schematic of the experimental setup is presented in Fig. 1a. We applied a disk Yb:YAG laser (Varidisk, Dausinger and Giesen) with a built-in frequency doubling system ($\lambda$ = 515 nm), generating subpicosecond pulses. The irradiation was performed in two lasing regimes, with pulse repetition rates of 200 or 500 kHz and pulse durations of 400 or 700 fs, respectively. To obtain lower repetition rates, the setup was equipped with an optical pulse selector, which made it possible to reduce the pulse repetition rate to 1–10 kHz. This selector, consisting of a Pockels cell with external cooling, a high-voltage generator and a control unit with a delay generator, provided a certain sequence of linearly polarised laser pulses.
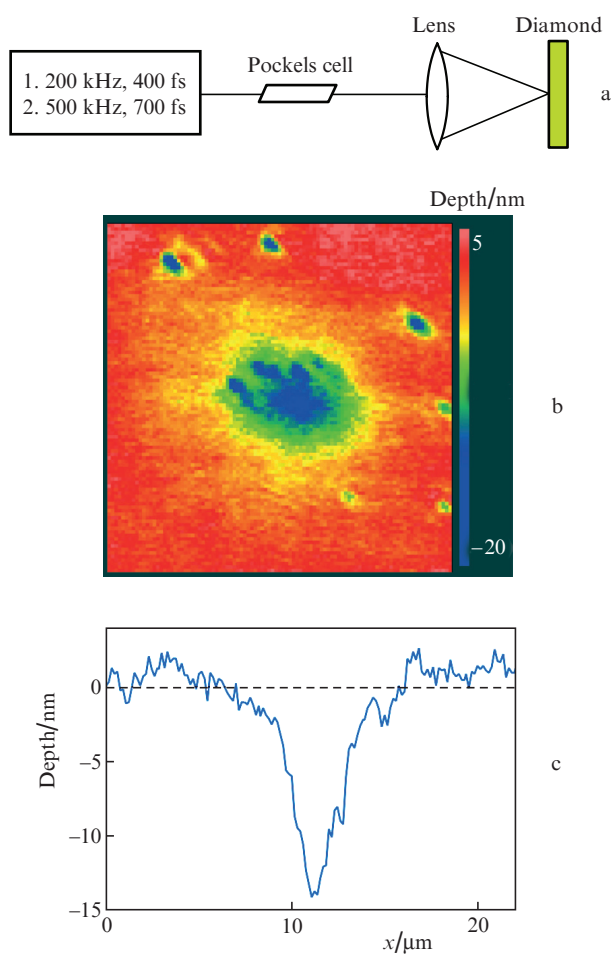


**Figure 1.** (a) Experimental setup, (b) diamond surface after laser processing, and (c) crater profile (pulse duration 400 fs, pulse energy 400 nJ, repetition rate 200 kHz).

The diamond sample under study ($1.17 \times 5.2 \times 1.9$ mm) was obtained by vapour-phase deposition in a microwave plasma reactor. After removing the substrate, it was mechanically polished (to an rms roughness of $\sim$1 nm) and subjected to laser irradiation in air, with variation in the pulse energy and repetition rate. The laser beam was focused on the sample surface using a lens with a focal length of 50 mm; under these conditions, the beam waist radius at an intensity level of 1/e was 4 µm. The nanoablation rate was determined with the aid of a New View 5000 interference profilometer (Zygo Corp.).

This instrument made it possible to measure (with a nanoscale accuracy) the depth of the craters formed by a specified number of laser pulses. An example of the surface morphology after laser irradiation is shown in Fig. 1b. Under the conditions of three-photon absorption, the characteristic nanoablation rate turned out to be very low: $\sim 10^{-7}$ nm pulse$^{-1}$. To provide an acceptable measurement accuracy, the irradiation time was chosen so as to make the crater depth be in the range of 10–20 nm (Fig. 1c).

## 3. Results and discussion

Figure 2 shows the dependences of nanoablation rate $r$ on laser energy density $F$ for the two laser operation regimes, corresponding to pulse repetition rates of 200 and 500 kHz. A pronounced third-order nonlinearity ($r \sim F^3$) is observed in both regimes, which is in good agreement with the photochemical mechanism proposed previously to describe the nanoablation [11, 13].
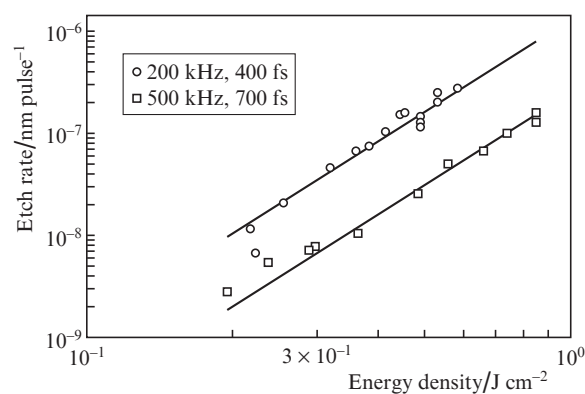


**Figure 2.** Power-law dependences $r = CF^3$ of the diamond laser nanoablation rate on the energy density in the irradiated region for two high-frequency irradiation regimes: 400 fs, 200 kHz and 700 fs, 500 kHz.

The key process in this model is the diamond ionisation: the laser irradiation provides the transition of some part of electrons (up to $\sim 10^{19}$ cm$^{-3}$) from the valence band to the conduction band, thus reducing for a time the binding energy for the corresponding number of atoms in the diamond lattice. From the microscopic point of view, this process changes the state of the sample surface (either directly due to the field effect or as a result of the hole diffusion from the crystal bulk), and many atoms with perturbed bonds arise on the surface. Atmospheric oxygen oxidises these atoms, after which the volatile reaction products (SO and $CO_2$) leave the surface.

From the point of view of thermodynamics, laser irradiation radically reduces the height of the energy barrier that must be overcome by an individual carbon atom during chemical reaction with oxygen and subsequent removal from the surface of newly formed oxide. It was experimentally shown that the activation energy of photoreaction is much lower than that of the thermal oxidation of diamond: about 0.1 eV atom$^{-1}$ [11], which is smaller than the thermal oxidation activation energy by a factor of 25 [14].

Within the above-described model, the nanoablation rate $r$ is directly proportional to the number of surface atoms with excited bonds (i.e., in the first approximation, to the plasma density in the crystal). Indeed, it has been demonstrated for a

number of laser sources that the dependence of $r$ on the energy density in the irradiated region obeys the power law; note that the power exponent coincides with the order of multiphoton light absorption in diamond at the wavelength used. Thus, the observed dependence $r \sim F^3$ is the consequence of three-photon absorption: the indirect transition in diamond ($E_g$ = 5.4 eV) at the wavelength $\lambda$ = 515 nm and photon energy $\hbar\omega$ = 2.26 eV involves three photons.

At first glance, these data indicate that the nanoablation rate for a pulse repetition rate of 500 kHz is lower than that for a rate of 200 kHz by a factor of about four.

The aforementioned circumstance and the fact that the characteristic nanoablation rate under high-rate irradiation ($\sim10^{-7}$ nm pulse$^{-1}$) is much lower than in the case of low-rate irradiation ($\sim10^{-5}$–$10^{-2}$ nm pulse$^{-1}$) for different sources [9, 10]) suggest that the oxidation reaction, as well as the adsorption and desorption processes, do not have enough time to evolve at high pulse repetition rates.

However, the measurements of the diamond etch rates for different pulse repetition rates at a fixed pulse duration (400 fs) and energy density, performed with an electro-optical selector, indicate that the nanoablation rate remains constant in the range of 1–200 kHz (Fig. 3). Even if there is a weak tendency to a change, it most likely indicates an increase in the etch rate with an increase in frequency. This observation does not contradict the model in use and can be explained by the rise of the average temperature in the irradiated region.
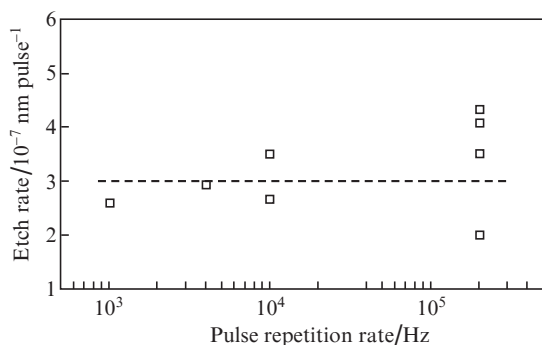


**Figure 3.** Dependence of the laser nanoablation rate at $\tau$ = 400 fs and $F$ = 0.93 J cm$^{-2}$ on the pulse repetition rate.

The difference in the nanoablation rates, observed for the two lasing regimes (Fig. 2), is due to their different durations $\tau$ rather than to the difference in the pulse repetition rates. Indeed, taking into account only the multiphoton absorption (which is quite reasonable for the $\tau$ values in use), one can estimate the number of electron–hole pairs excited per unit volume during a pulse:

$$n_e = \frac{\beta_k F^k}{k\hbar\omega\tau^{k-1}}, \tag{1}$$

where $\beta_k$ is the nonlinear absorption coefficient and $k = 3$. Then the nanoablation rate, being proportional to the plasma density, is inversely proportional to $\tau^2$, a fact explaining the observed decrease in the oxidation rate for longer pulses. The decrease in $r$ should be $\sim(700/400)^2 \approx 3$, which is close to the observed drop: $\sim4$.

Thus, we did not reveal any pronounced tendency of the nanoablation rate to decrease with an increase in the laser pulse repetition rate up to 500 kHz. This circumstance is undoubtedly positive for scaling the nanoablation etching of diamond surface.

At the same time, our experiments showed that the use of radiation with a longer wavelength, in particular, the transition from linear to two-photon [10] and then to three-photon (this study) absorption, sharply (by five orders of magnitude) reduces the material removal rate. This fact cannot be explained only in terms of the interaction of laser radiation with diamond, because the degree of ionisation of crystal in the pre-ablation irradiation regime depends weakly on the photon energy. According to our experimental data [15], the maximum carrier concentration that can be generated in diamond without initiating surface graphitisation is $10^{20}$–$10^{22}$ cm$^{-3}$ for different radiation sources ($\lambda$ = 193–800 nm); this parameter depends to a greater extent on the pulse duration. To explain why UV light oxidises diamond surface much more efficiently, it is necessary to consider other possible aspects of nanoablation. Examples are the additional field-induced excitation of oxygen-containing reagents or, as an intermediate stage, cluster graphitisation in the presence of an oxygen-containing catalyst.

Note also that the type of the oxygen source involved in the photoreaction is not quite clear. Until now, all experiments have been performed in air, which contains, along with molecular oxygen, a rather large amount of water. However, a thin layer with a high concentration of water molecules and hydroxyl groups can also be formed on the diamond surface [16].

To clarify the role of water in the nanoablation, we performed an experiment on irradiation of a diamond surface immersed in water. It showed that the surface etching stops under these conditions. A 3-h irradiation of diamond in the pre-ablation regime at a pulse repetition rate of 500 kHz did not lead to the formation of any pronounced (more than 1 nm) crater on the surface. Thus, the etch rate did not exceed $10^{-10}$ nm pulse$^{-1}$, a fact suggesting the dominant role of atmospheric oxygen in the reaction.

Thus, irradiating a diamond single crystal with a high pulse repetition rate, we obtained dependences of the rates of graphitisation-free surface etching on the laser energy density in the irradiated region, which are consistent with the photochemical mechanism proposed previously to describe the nanoablation. It was established that an increase in the pulse repetition rate up to 500 kHz does not change the material removal rate at a fixed energy density. This finding opens new possibilities for developing highly efficient methods of diamond nanoprocessing.

# References

1. Aharonovich I., Greentree A.D., Prawer S. *Nat. Photon.*, **5**, 397 (2011).
2. Rothschild M., Arnone C., Ehrlich D.J. *J. Vacuum Sci. Technol. B*, **4**, 310 (1986).
3. Preuss S., Stuke M. *Appl. Phys. Lett.*, **67**, 338 (1995).
4. Kononenko V.V., Kononenko T.V., Pimenov S.M., Sinyavskii M.N., Konov V.I., Dausinger F. *Kvantovaya Elektron.*, **35**, 252 (2005) [*Quantum Electron.*, **35**, 252 (2005)].

5.  Shinoda M., Gattass R.R., Mazur E. *J. Appl. Phys.*, **105**, 053102 (2009).
6.  Khomich A.V., Kononenko V.V., Pimenov S.M., Konov V.I., Gloor S., Luethy W.A., Weber H.P. *Proc. SPIE Int. Soc. Opt. Eng.*, **3484**, 166 (1998).
7.  Kononenko V.V., Gololobov V.M., Konov V.I. *Appl. Phys. A*, **122**, 1 (2016).
8.  Bauerle D.W. *Chemical Processing with Laser* (Berlin: Springer, 1986) pp 1–241.
9.  Kononenko V.V., Gololobov V.M., Komlenok M.S., Konov V.I. *Laser Phys. Lett.*, **12**, 096101 (2015).
10.  Komlenok M.S., Kononenko V.V., Gololobov V.M., Konov V.I. *Kvantovaya Elektron.*, **46**, 125 (2016) [*Quantum Electron.*, **46**, 125 (2016)].
11.  Kononenko V.V., Komlenok M.S., Pimenov S.M., Konov V.I. *Kvantovaya Elektron.*, **37**, 1043 (2007) [*Quantum Electron.*, **37**, 1043 (2007)].
12.  Kuzmichov A.V. *Appl. Surf. Sci.*, **86**, 559 (1995).
13.  Mildren R.P., Downes J.E., Brown J.D., Johnston B.F., Granados E., Spence D.J., Lehmann A., Weston L., Bramble A. *Opt. Mater. Express*, **1**, 576 (2011).
14.  Davies G., Evans T. *Proc. R. Soc., London, Ser. A*, **328**, 413 (1972).
15.  Kononenko V.V., Konov V.I., Gololobov V.M., Zavedeev E.V. *Kvantovaya Elektron.*, **44**, 1099 (2014) [*Quantum Electron.*, **44**, 1099 (2014)].
16.  Ristein J. *Appl. Phys. A*, **82**, 377 (2005).