Photoinduced laser etching of a diamond surface

V.V. Kononenko, M.S. Komlenok, S.M. Pimenov, V.I. Konov

Abstract. **Nongraphitising ablation of the surface of a natural diamond single crystal irradiated by nanosecond UV laser pulses is studied experimentally. For laser fluences below the diamond graphitisation threshold, extremely low diamond etching rates (less than 1 nm/1000 pulses) are obtained and the term nanoablation is used just for this process. The dependence of the nanoablation rate on the laser fluence is studied for samples irradiated both in air and in oxygen-free atmosphere. The effect of external heating on the nanoablation rate is analysed and a photochemical mechanism is proposed for describing it.**

Keywords: *diamond, laser ablation, nanostructurisation of the surface, photoinduced processes.*

1. Introduction

Interest in micro- and nanostructurisation of the surface of diamond is due to the unique physical properties of this material. Diamond is known to be a metastable form of carbon and the sample surface is graphitised upon heating in vacuum [1]. Note that it is this peculiarity of diamond that determines the type of action of high-intensity laser radiation on it because graphitisation changes drastically the physical properties of the surface [2]. In contrast to thermal heating of diamond in air, laser radiation produces a thin graphite-like layer (which remains unoxidised) on the sample surface when laser fluence exceeds a certain value [3, 4]. From the practical point of view, this regime is distinguished by stability of the material removal, which makes it possible to perform high-quality microstructuring of the diamond surface (see, for example, [5, 6]). In this case, however, the depth precision of structuring of the diamond surface is limited by a few tens of nanometres, which is explained by two important reasons. First, the thickness of the graphitised layer is determined by the depth of the heat propagation region and amounts to $\sim 30 - 3000$ nm depending on the laser pulse duration (from 100 fs to 1.5 μs) [7]. Second, it is difficult to provide a

low ablation rate (i.e., a small amount of the material removed per pulse) during laser processing of the surface. This is explained by the fact that being a wide-band gap dielectric, diamond is transparent in a broad wavelength range (the short-wavelength transmission boundary is ~ 220 nm). Upon irradiation by the first laser pulse (before the formation of a graphite-like layer on the surface), a few percent of the incident laser energy is absorbed; in this case, the sample is heated almost uniformly over its thickness. If the laser fluence is low, the surface is not graphitised. If, however, it is high, the entire pulse energy is concentrated after graphitisation in a layer of thickness $30 - 3000$ nm. Therefore, the value of the heat released in the material (and, hence, the temperature increment) before and after graphitisation of the surface differ by $3 - 4$ orders of magnitude.

In the light of the above arguments, it becomes clear that unlike other materials, it is impossible to select an ablation regime for diamond in which the rate of material removal can be made infinitely small. The basic reason behind this is the existence of a phase transition that is inherent in laser ablation. These conclusions are confirmed by experimental observations according to which the minimum rate of diamond surface etching is about 10 nm pulse^{-1} [7].

Thus, the task of forming nanometer-deep ordered structures on the diamond surface is not simple. In this study, we present the results of analysis of nongraphitising etching of the diamond surface obtained by us in [8]. The process observed in the experiments is characterised by extremely low rates of material removal (less than 1 nm per thousand laser pulses), which allowed us to use the term nanoablation for such processes. The main regularities of nanoablation of the diamond surface are described and the dependences of the rate of material removal on the laser radiation parameters and external conditions are analysed.

2. Experimental

The diamond surface was irradiated by a UV KrF excimer laser (CL 7100 model, General Physics Institute, Russian Academy of Sciences) at a wavelength of 248 nm. The laser emitted 15-ns, 400-mJ pulses at a pulse repetition rate of up to 100 Hz. The laser was used in the projection optical setup, illuminating uniformly a square mask (Fig. 1). The reduced (by a factor of 15) image of the template was projected onto the sample surface by a short-focus lens with a numerical aperture of 0.15. The size of the illuminated region was $50 - 100$ μm, and the local laser fluence at the sample surface was constant within the radiation spot,

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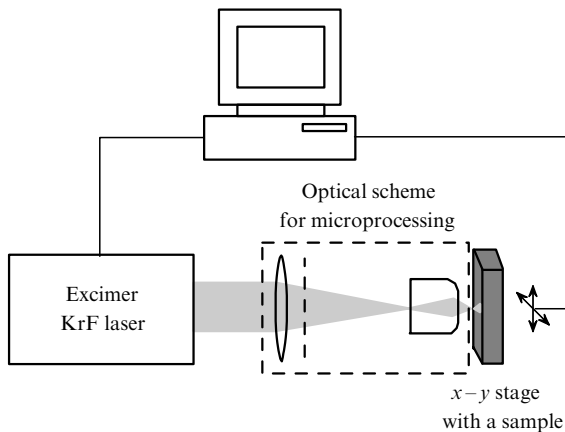
Figure 1. Scheme of the setup for irradiating a diamond plate surface.

amounting to ~ 40 J cm^{-2}. Experiments were performed in air and vacuum for laser fluence varying from 4 to 20 J cm^{-2} and up to 300000 laser pulses.

We used in our experiments single-crystal diamond samples of type IIa. The transmission of diamond plates at 248 nm varied from 45 % to 65 % and was apparently determined by the concentration of impurity defects (nitrogen) in the crystal lattice [9].

The surface relief was measured before and after laser action with an interference profile meter (New View 5000, Zygo Corp.). The error of measuring the surface-profile height was less than 1 nm, which allowed us to reliably detect the variation in the sample surface topology at the radiation spot caused by nanoablation.

To study experimentally the effect of sample temperature on the nanoablation rate, we worked out a diamond sample heating system consisting of a ceramic heater, an autotransformer as the voltage source, a thermocouple and a microvoltmeter for measuring the sample temperature. The diamond sample was pressed between the plates of the heating element which in turn was fastened in a clamp on an electromechanical $x-y$ translation stage. About half the sample area remained open from two sides. Such a positioning provided the efficient heating of the diamond due to a good thermal contact and a simultaneous exposure of the open part of the sample to laser pulses. The thermocouple was inserted between the diamond sample and one of the plates of the ceramic heater. After calibration, this system could control and maintain the diamond plate temperature from room temperature to 700 °C with an error of up to 10 °C. In this case, the ceramic heating element did not react chemically with diamond even at the highest temperatures.

3. Experimental results

As mentioned above (see also [8]), irradiation of a sample by nanosecond ultraviolet pulses from an excimer KrF laser with an intensity lower than the graphitisation/ablation threshold for diamond leads to the formation of a crater at its surface. Figure 2 shows the image of the laser spot (70-nm deep crater) formed at the surface of a diamond single crystal after irradiation by 100000 laser pulses in the absence of any visible surface graphitisation. This image was obtained with the help of a New View 5000 interference

profile meter. Figure 3 shows the dependences of the crater depth on the number of pulses for various laser fluences in the radiation spot. The rate of material removal was determined from the slope of the corresponding straight line for each laser fluence. The dependence of the nanoablation rate on the laser fluence obtained in this way is shown in Fig. 4. This dependence shows, in particular, that the maximum nanoablation rate at room temperature is ~ 0.7 nm/1000 pulses. A further increase in the laser fluence in the experiment was limited by the development of traditional ablation with the threshold ~ 14 J cm^{-2} for the given material.
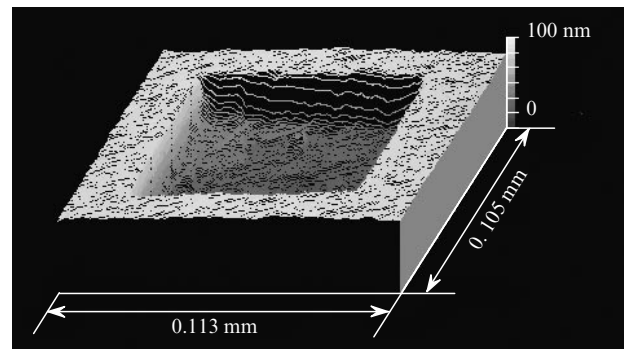

Figure 2. Image of a diamond single crystal surface obtained after irradiation by 100000 pulses from KrF laser (laser fluence 10 J cm^{-2}, intensity $\sim 10^9$ W cm^{-2}).
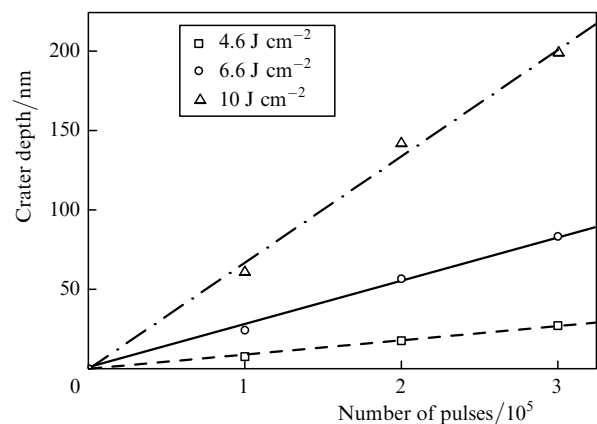

Figure 3. Dependence of the etching depth on the number of radiation pulses for different laser fluences in the laser spot.

Upon the external heating of the sample, the rate of material removal increases and achieves 1 nm/1000 pulses at 600 °C. This corresponds to a laser fluence of 5.4 J cm^{-2} (the ablation threshold for the given sample decreased to 7 J cm^{-2} with increasing temperature). The temperature dependence of the nanoablation rate of the sample presented in Fig. 5 was obtained for the same laser fluence. One can see that the dependence is close to a straight line in the Arrhenius coordinates. This means that the probability of detachment of a carbon atom from the surface of the target obeys the Boltzmann statistics and strongly depends on temperature.

Experiments on laser irradiation of diamond single crystals in the absence of oxygen were decisive for clarifying
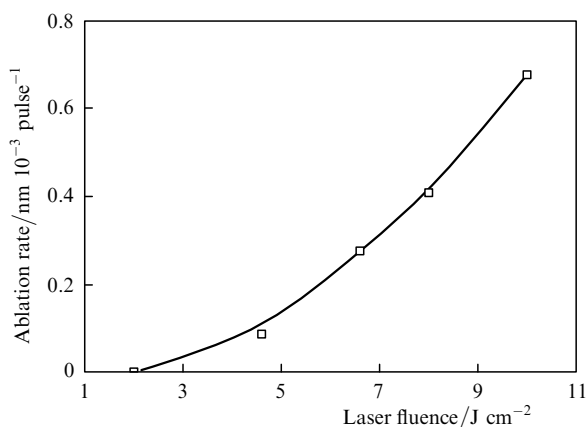
Figure 4. Dependence of the laser nanoablation rate on the laser fluence at room temperature.
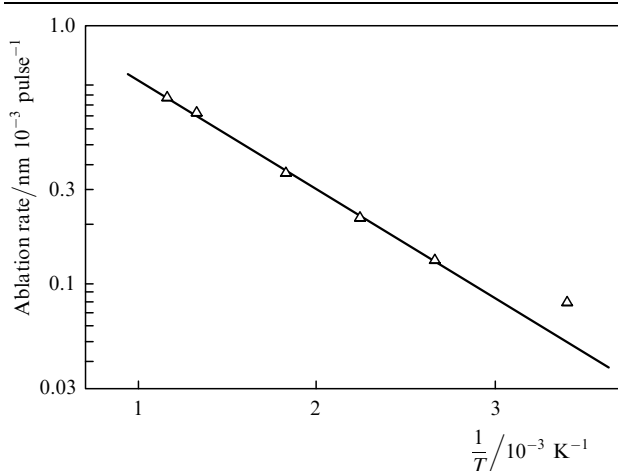

Figure 5. Dependence of the laser nanoablation rate on the temperature of the externally heated sample for a laser fluence of 5.4 J cm^{-2}.

the nanoablation mechanism. These experiments were performed in vacuum and in inert helium atmosphere. In both cases, the number of radiation pulses reached 3×10^5, while the laser fluence at the spot was only 15 % – 20 % below the ablation threshold. No traces of crater formation were detected at the surface of the single crystal. Thus, atmospheric oxygen obviously plays a key role in the process of material removal from the surface of the diamond target. It is well known that oxidation reaction is the main process occurring in the presence of oxygen. Taking into account the Arrhenius temperature dependence of the etching rate of the material, we can assume that it is oxidation that occurs in the phenomena described.

However, the role of laser radiation in this process remains unclear. Obviously, the laser pulse must produce a substantial additional optical or thermal action for the oxidation rate to be higher at the radiation spot than in the unexposed region. Let us try to compare the possible contributions of these effects to the nanoablation process. We will estimate the additional increase in the sample temperature caused by laser heating itself and averaged over the depth,

$$\Delta T_{las} = \frac{EA}{D\rho c} \leqslant 100 \text{ K}, \qquad (1)$$

where $E \leqslant 20$ J cm^{-2} is the laser fluence; $A \leqslant$ 20 % is the film absorption; $D = 300$ μm is the sample thickness; $\rho = 3.5$ g cm^{-3} is the density of diamond; and $c = 0.5$ J g^{-1} K^{-1} is the specific heat of diamond. Obviously, this additional heating cannot substantially affect the processes mentioned above. The diamond surface oxidation rate at a temperature of 100 °C amounts to about 10^{-19} nm s^{-1}. This quantity was obtained by interpolating the experimental values of the oxidation rate of the diamond surface with a crystallographic orientation {111} in air upon a continuous heating of the sample in the temperature range 600 – 700 °C [1]. Even if we assume that laser irradiation maintains a constant (in time) temperature ~ 100 °C, the depth of the crater formed by 1000 laser pulses, i.e., over a time period of 10 s, would be only 10^{-18} nm.

Thus, one can see that additional heating of the target by laser radiation does not ensure the experimentally observed rates of local oxidation of the diamond surface. At the same time, a fixed (~ 100 °C) laser-induced heating of the sample may be responsible for the discrepancy between the measured temperature dependence of the nanoablation rate and the Arrhenius dependence observed at low temperatures (Fig. 5).

It is interesting to note that the activation energy calculated from the experimental data (see Fig. 5) amounts to only ~ 0.1 eV at.$^{-1}$, which is 25 times lower than the activation energy of thermal oxidation obtained in [1]. Therefore, the experimental data indicate that the action of UV radiation drastically lowers the height of the energy barrier that must be surmounted by an individual carbon atom during its chemical reaction with oxygen followed by the removal of the formed oxide from the surface. A quantum-mechanical description of possible mechanisms of graphitisation of diamond in a laser field [10, 11] is based on the fact that the rearrangement of bonds in a diamond crystal may be an essentially nonequilibrium photoinduced process which occurs individually in some atoms. Such an approach can also be used for considering the nanoablation mechanism. The photoconduction effect representing an increase in the electrical conductivity of a dielectric (including diamond) upon irradiation is well known [12, 13]. This effect is explained by the appearance of free charge carriers in the conduction band upon absorption of photons. For the object of investigation of this study, it is important that laser-induced excitation of the electron system in diamond (i.e. the transition of electrons from localised states to the free state) suppresses the atomic bonds for a part of atoms in the crystal lattice. It can be assumed that due to the high efficiency of this process, the number of partly ruptured bonds formed in the lattice during a laser pulse due to photoexcitation of valence electrons is large enough to cause a considerable increase in the surface oxidation rate, thus providing the observed etching of the diamond surface. Note also that nanoablation at the atomic level can be an even more complex process and may include, in particular, photoinduced surface graphitisation [10, 11] of several monolayers or even individual atomic nanoclusters at the surface as the intermediate stage.

The efficiency of excitation of free electrons in a diamond single crystal by nanosecond UV laser pulses can be judged from the change in the optical properties of the material during irradiation. It is found that transmission of the sample decreases with increasing the laser

fluence (up to the ablation threshold) (Fig. 6). After exposure to laser radiation, the transmission was restored to its initial value, thus indicating that no irreversible changes occured in diamond. The maximum detected decrease in transmission was $\sim 12\,\%$ for a laser fluence of ~ 18 J cm^{-2} in the spot (the ablation threshold is ~ 20 J cm^{-2}).
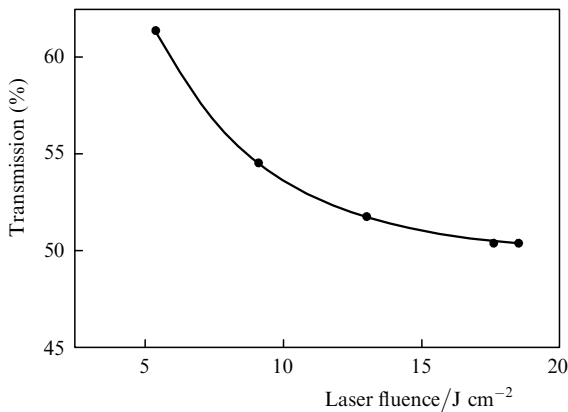

Figure 6. Transmission of a diamond plate irradiated by 248-nm laser pulses.

The excitation of an electron plasma in diamond is the most probable reason for the observed time variation in optical properties. We believe that two-photon absorption of UV radiation cannot be the main mechanism of the measured decrease in the sample transmission. The radiation intensity in our experiments was $\sim 10^9$ W cm^{-2}. According to numerical estimates, the probability of two-photon absorption under these conditions is such that $\sim 10^{15}$ conduction electrons appear during a pulse in 1 cm^3. Such a concentration of free carriers is too low to explain the observed laser-induced absorption in diamond. A more probable process is one in which the free-electron concentration in the conduction band noticeably increases long before the end of the pulse due to absorption by defects. These free electrons provide an increase in absorption at the middle and end of the pulse. In other words, the dependence of the sample transmission on the laser fluence is due not to multiphoton absorption, but to excitation of the electron system of the crystal and hence a change in the absorption of material with time.

4. Conclusions

Irradiation of the surface of a diamond single crystal (of the type IIa) by nanosecond pulses from an excimer KrF laser at intensities lower than the graphitisation/ablation threshold for diamond led to the nanoablation in diamond, i.e., a slow (less than 1 nm/1000 pulses) removal of the material from the surface in the irradiation region. Unlike traditional laser ablation, this process occurs without intermediate graphitisation of diamond. The rate of diamond nanoablation as a function of the laser fluence of UV radiation, the temperature of the externally heated sample, and the composition of the surrounding gaseous medium has been measured experimentally. The effect of pulsed UV radiation on the optical absorption of diamond is studied. Our investigations lead to the assumption that nanoablation is governed by a photochemical mechanism which implies laser-induced photoexcitation of the electron system of diamond during a pulse and, as a consequence, the emergence of suppressed atomic bonds in the lattice. This is the reason behind an abrupt increase in the surface oxidation rate in the laser radiation region.

References

1. Evans T., in *The Properties of Natural and Synthetic Diamond* (London: Acad. Press, 1979) Ch. 13.
2. Ralchenko V.G., Pimenov S.M. *Diam. Films Technol.*, **7**, 15 (1997).
3. Rothschild M., Arnone C., Ehrlich D.J. *J. Vac. Sci. Technol. B*, **4**, 310 (1986).
4. Ageev V.P., Bouilov L.L., Konov V.I., Kuzmichov A.V., Pimenov S.M., Prokhorov A.M., Ralchenko V.G., Spitsyn B.V., Chapliev N.I. *Sov. Phys. Doklady*, **33**, 840 (1988).
5. Kononenko V.V., Konov V.I., Pimenov S.M., Prokhorov A.M., Pavelyev V.S., Soifer V.A., et al. *Kvantovaya Elektron.*, **26**, 9 (1999) [*Quantum Electron.*, **29**, 9 (1999)].
6. Kononenko V.V., Konov V.I., Pimenov S.M., Prokhorov A.M., Pavelyev V.S., Soifer V.A., Lüdge B., Duparré M. *Proc. SPIE Int. Soc. Opt. Eng.*, **4426**, 128 (2002).
7. 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)].
8. Kononenko V.V., Kononenko T.V., Pimenov S.M., Konov V.I., Fischer P., Romano V., Weber H.P., Khomich A.V., Khmelnitskiy R.A., Strekalov V.N. *Proc. SPIE Int. Soc. Opt. Eng.*, **5121**, 259 (2003).
9. Collins A.T. *J. Phys. C: Solid State Phys.*, **13**, 2641 (1980).
10. Strekalov V.N., Konov V.I., Kononenko V.V., Pimenov S.M. *Appl. Phys. A: Mat. Sci. Process.*, **76**, 603 (2003).
11. Strekalov V.N. *Appl. Phys. A: Mat. Sci. Process.*, **80** (5), 1061 (2005).
12. Rohre E., Nebel C.E., Stutzmann M., Floter A., Zachai R., Jiang X., Klages C.-P. *Diam. Relat. Mater.*, **7**, 879 (1998).
13. Souw E.-K., Meilunas R.J., Szeles C., Ravindra N.M., Tong F.M. *Diam. Relat. Mater.*, **6**, 1157 (1997).