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On the role of multiphoton absorption of light in pulsed laser nanoablation of diamond

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

Abstract. **The rates of multipulse nanoablation of the diamond surface in air by pico- and nanosecond laser pulses that cause single-photon, two-photon, three-photon and four-photon absorption in diamond are measured. In the experiments the radiation of ArF, KrF and Ti:Al_2O_3 lasers and the second harmonic of the Yb:YAG laser was used. The power dependence of the material etching rate on the fluence of laser pulses was found. The power exponent of this dependence appeared to be twice lower than that found earlier for femtosecond pulses. We discuss the causes of the difference in the nanoablation regularities for 'short' and 'long' laser pulses.**

Keywords: *diamond, laser nanoablation, multiphoton absorption.*

1. Introduction

Nanostructuring of surfaces is one of the urgent problems of laser materials processing technology. The diamond micro- and nanostructures are an interesting and important object of high-precision laser technology. Due to unique optical, heat-conducting and other properties, these structures can be used for producing new elements and devices of optoelectronics, e.g., nanoresonators.

The traditional method of laser processing is based on the pulsed heating and evaporation (ablation) of the surface layer of a diamond sample, accompanied by the transformation of this layer into a graphite-like material that, in contrast to the substrate, is strongly absorbing. Varying the laser pulse duration from femtoseconds to milliseconds allows the ablation rates V from a few nanometres to a few micrometres per pulse, respectively (see, e.g., the review [1]).

The ablation process has a threshold character with respect to the fluence of the laser pulse ($F = F_{th}$) [2]. Under low-intensity laser irradiation ($F < F_{th}$) of diamond in air it was found that the removal of the material also occurs, but with a much smaller rate ($V \ll 1$ nm pulse^{-1}). That is why this regime is referred to as nanoablation [3]. Such low rates, when during one pulse only a few individual atoms or atomic clusters are removed, are necessary for ultra-precise processing of the diamond surface. The perspectives of increasing the productivity of this process are associated with the appearance of modern technological lasers with an ultrahigh repetition rate (1–10 MHz) of intense radiation pulses, each of them being capable of providing evaporation of the material from the surface and even more initiating noticeable nanoablation.

The problem of diamond nanoablation mechanisms remains open, in spite of a number of papers devoted to the issue [3–8]. On the one hand, it is clear that two processes play the dominant role, the diamond ionisation that changes the state of the sample surface and the subsequent oxidation of individual carbon atoms, in which the bonds appeared to be perturbed by the optical field. As to the bulk ionisation, the measurements [8] demonstrated that the mechanism responsible for diamond ionisation is the multiphoton absorption of light. At least this refers to the energy densities $F <$ 10 J cm^{-2} for short pulses ($\tau = 100$ fs). It was found that the concentration of charge carriers n is proportional to F^k, where k is the number of quanta for which the sum of energies exceeds the band gap of diamond, $E = 5.4$ eV. Less clear is the relation between the multiphoton absorption and the nanoablation rate. Thus, according to Ref. [8], for $\tau = 100$ fs the nanoablation rate is $V \propto F^{2k}$, while in the case of nanosecond pulses ($\lambda = 248$ nm, $k = 2$) the measurements [6] yielded the dependence $V \propto F^k$.

The main goal of the present paper is to clarify whether the mechanism of laser nanoablation actually changes when the femtoseconds pulses are replaced with longer ones, which is expected to manifest itself in the form of the dependence $V(F)$.

2. Experiment

As a sample we used an optically transparent single crystal of diamond with a thickness ~1.9 mm, obtained using the CVD method at the Iplas microwave plasma growing setup. Before irradiation the crystal surface was mechanically polished.

Irradiation was implemented using three laser sources, providing a different order of multiphoton absorption in diamond ($k = 1–4$). An excimer laser (CL7100, Optosystems) allowed the generation of pulses with the duration $\tau = 20$ ns using an ArF mixture (the radiation wavelength $\lambda = 193$ nm) or a KrF mixture ($\lambda = 248$ nm) with the repetition rate $f =$ 50 Hz. A disk Yb:YAG laser (Varidisk, Dausinger and Giesen) after the frequency doubling generated pulses with a duration $\tau = 1$ ps ($f = 200$ kHz) at a wavelength $\lambda = 515$ nm. Finally, we used a Ti:Al_2O_3 laser ($\tau = 3$ ps, $f = 1$ kHz, $\lambda = 800$ nm).

In the experiments with picosecond pulses, the energy distribution over the beam cross section was Gaussian. The radi-

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ation was focused on the sample surface into spots with the diameter 2–5 μm.

In the case of excimer lasers, the projection scheme of irradiation was used. The image of a square mask measuring 1 mm × 1 mm was projected onto the sample surface into a spot with a size 50 μm × 50 μm and uniform distribution of the fluence. Using two pyroelectric detectors (one placed behind the sample and the other in front of it) the measurements of the transmission were carried out for the sample exhibiting nonlinear absorption of the radiation with λ = 248 nm.

The experiments were performed in the atmospheric air. The depth of the craters created under multiple pulsed irradiation was measured using an interference microscope (Zygo, New View). The ablation rate was determined by dividing the crater depth by the number of laser pulses.

3. Results and discussion

By the example of irradiation with pulses from the ArF laser, Fig. 1 presents a general view of the dependence $V(F)$. One can clearly select two regions with essentially different rates of the diamond laser ablation. For $F < F_{th} \approx 1.5$ J cm^{-2} the ablation rate is $V \approx 10^{-4}$–10^{-2} nm pulse^{-1}. This is the nanoablation regime. If the fluence of the laser pulse exceeds the threshold value F_{th}, the rate abruptly increases (in the present case by two orders of magnitude), which manifests itself in the transition to a purely thermal regime of heating and evaporation of the diamond. The specific feature of irradiation at λ = 193 nm is that the energy of photons exceeds the band gap, and the energy of the laser pulse is efficiently absorbed in the relatively thin near-surface layer (according to Ref. [9], the absorption depth in most transparent single-crystal diamonds of IIa type amounts to ~1 μm). Higher-intensity excitation by the ArF laser at $F > F_{th}$ causes the graphitisation and the evaporation of the graphitised layer, the thickness of which amounts to 40–200 nm [10, 11]. In this case only a small fraction of the layer can be removed, which explains the exclusively small rates of the evaporative ablation $V \approx$ 1–10 nm pulse^{-1} observed in our experiment. Note that similar rates of evaporative ablation and its threshold F_{th} were reported in Ref. [12].

Now let us dwell on the nanoablation regime to consider it in more detail. Figure 2 presents the experimental dependences $V(F)$, obtained in this regime for three radiation wavelengths. The curves have different slopes, determined by the power dependences $V \propto F^k$, where k = 1 (λ = 193 nm), 2 (λ = 248 nm) and 3 (λ = 515 nm). From these observations, it seems logical to conclude that the ablation in these experiments is due to the single-photon, two-photon and three-photon absorption of light, respectively.

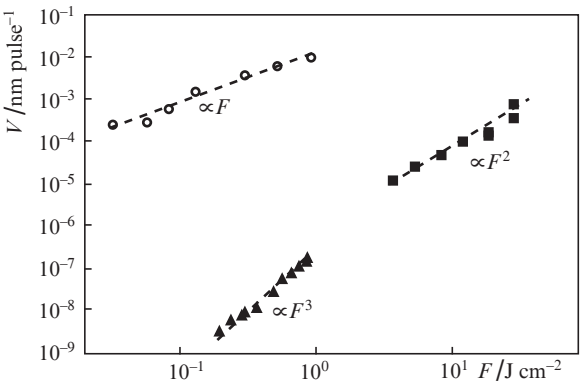

Figure 2. Dependences of the rate of diamond laser nanoablation V on the fluence of the pulse F for the radiation wavelengths λ = 193 (○), 248 (■) and 515 nm (▲).

Note that the dominant role of the two-photon mechanism of the radiation absorption in diamond is not obvious. For the pulses of nanosecond duration, it is quite probable that the comparable role will be played by the inverse bremsstrahlung absorption and impact ionisation. To clarify the situation we measured the sample transmission at different energy densities (Fig. 3). The approximation of the obtained data by the results of numerical modelling taking the real size of the irradiated spots (50 μm × 50 μm at the front face of the sample and 140 μm × 170 μm at the back one) into account yields the coefficient of two-photon absorption $\beta \approx (1–2) \times 10^{-9}$ cm W^{-1}. This value agrees with the known literature data [8, 13].

The obtained dependences $V \propto F^2$ for λ = 248 nm correlate well with the data of Ref. [6], where the irradiation of diamond was performed at λ = 266 nm (τ = 11 ns), also providing the two-photon absorption. However, a serious contradiction remains between our results and those of the mea-

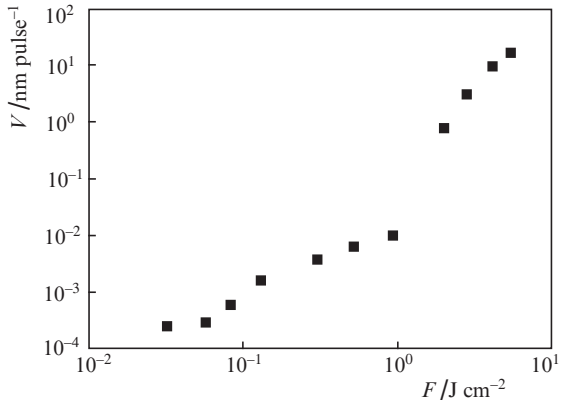

Figure 1. Dependence of the diamond ablation rate V on the fluence F under the exposure to the radiation of the excimer ArF laser (λ = 193 nm, τ = 20 ns).

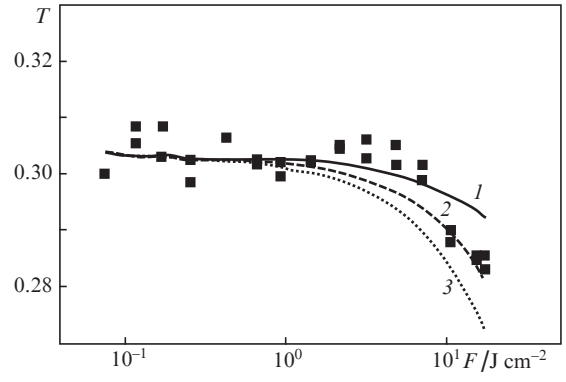

Figure 3. Nonlinear transmission T of the diamond sample under irradiation by the excimer KrF laser (λ = 248 nm, τ = 20 ns). The curves present the result of numerical modelling for β = (*1*) 1×10^{-9}, (*2*) 2×10^{-9} and (*3*) 3×10^{-9} cm W^{-1}, and the points present the experimental results.

surements performed in Ref. [8], where for shorter femtosecond laser pulses the stronger dependence of nanoablation rate on the laser fluence, $V \propto F^{2k}$, was recorded.

This difference in the nanoablation caused by the short ($\tau \approx 100$ fs) and the long ($\tau \geqslant 1$ ps) laser pulses is probably due to the different character of the second stage of the process of the material removal, i.e., the oxidation of surface carbon atoms weakly bound to the lattice. One can suppose that at $\tau = 100$ fs the oxidation has the photolytic nature, and the nonlinear character of the dependence $V(F)$ is determined by the sum of the contributions from the bulk multiphoton diamond photoionisation and the surface photooxidation, both mechanisms acting only during the laser pulse. At $\tau \geqslant 1$ ps one can expect essential contribution from the thermal oxidation mechanism.

In the experiments with the radiation at $\lambda = 800$ nm the nanoablation regime was not observed even after the impact of 10^8 pulses, i.e., the etching rate did not exceed 10^{-8} nm pulse^{-1}. Above the definite threshold ($F_{\text{th}} \approx 1$ J cm^{-2}) the graphitisation of the diamond surface gradually occurred in the accumulation regime [14]. In our opinion, this specific feature is due to the relatively low degree of the diamond ionisation, which is caused by the four-photon character of absorption at this wavelength. Therefore, before the ionisation degree attains the values at which the nanoablation becomes noticeable, the sample absorbs the energy sufficient for heating and graphitisation of its surface. This is also facilitated by the much stronger inverse bremsstrahlung absorption of the IR radiation by electrons (since the coefficient of the bremsstrahlung absorption of light is proportional to $\alpha \propto \lambda^2$).

4. Conclusions

It is shown experimentally that there are two regimes of laser nanoablation, determined by the duration of radiation pulses in the visible and UV spectral ranges. For $\tau \geqslant 1$ ps the dependence of the ablation rate on the pulse fluence is described by the expression $V \propto F^k$, while for femtosecond pulses ($\tau = 100$ fs) this dependence is much stronger. This effect is related to the different character of the oxidation of the irradiated surface, modified by the multiphoton light absorption and diamond ionisation. In the case of ultrashort pulses the surface oxidation has a photolytic character, while for the pulses with the duration of a few picoseconds and longer the considerable contribution of thermal oxidation is possible.

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