Laser Induced Nanoablation of Diamond Materials

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Abstract

Possibility of ultra-precise laser induced ablative etching of diamond materials was investigated. Different types of lasers were used. Natural single crystal diamond, poly and nanocrystalline CVD diamond, amorphous diamond-like films were irradiated in air and vacuum at laser fluencies 0.01÷20 J/cm². It is found that depending on material, laser fluence and wavelength physical and chemical regimes of materials ablation can be realized. The role of surface graphitization and oxidation, charge carriers generation in diamond is studied. It is shown that ablation rates as low as 10⁻³⁻¹⁰⁻⁴nm/pulse can be realized and such processing regimes were applied to diamond surface nanostructuring.

Keywords: laser; ablation; oxidation; diamond; nanoprocessing

1. Introduction

Diamond is a unique material [1] showing a number of extreme properties. It has record values of thermal conductivity at room temperature (≥20W/cm·K), hardness (microhardness up to ≈100GPa), sound velocity (18600 m/s). Diamond is transparent in the UV, visible, IR and MW spectral regions, is an excellent electrical insulator and can become a high quality p-type semiconductor (B-doped). Besides, it has unique radiation stability, chemical inertness, biocompatibility and a number of other important features, which determine numerous applications of this material.

In the last few decades the interest to diamond is rapidly growing because it becomes easily available and less expensive. The reason is that nowadays diamond can be obtained not only in the form of natural monocrystals. The techniques have been developed that allow to produce synthetic diamonds with properties and sizes comparable or even exceeding that of the best natural stones. There are two approaches to the problem. The first [2] is based on high pressure high temperature (HPHT) compression of graphitic material mixed with catalysts and allows to synthesis mono and polycrystalline diamond samples with sizes up to 5-10mm. Another approach [3] utilizes chemical vapor deposition of diamond coatings from CH₄:H₂ gas mixture on a hot substrate (CVD technique and the corresponding material is called CVD diamond). The deposition area is determined by the size of a chemical reactor (usually plasma reactors are used) and can reach diameter of about 10 cm. The deposited film thickness can be varied from ≈10nm to few millimeters (thick coatings can be detached from the substrate mechanically or by its...
chemical etching after deposition). For most of the substrates (silicon, molybdenum and some others) CVD diamond is polycrystalline. But if a diamond substrate (e.g. HPHT monocrystal) is used, epitaxial growth of CVD monocrystalline diamond is also possible.

In the case of thin films, an interesting form of CVD diamond exists [4, 5]. It is called nanocrystalline diamond film (NCD), consists of nanograins of diamond (4-20nm) in a matrix of nanographite and polyacetylene, can be deposited at temperatures as low as \( \approx 400^\circ C \), have microhardness up to 80-90GPa. Such films have much smoother surface roughness \( \approx 20-50\text{nm} \), than regular CVD polycrystalline films, have thickness up to 20\( \mu \text{m} \), reasonable transparency and are considered as a perspective IR optical material.

Besides, ion and laser vacuum ablation and deposition of graphite can lead to formation of so called diamond-like carbon (DLC) films [6]. Such films are amorphous but with essential degree of \( \text{sp}^3 \) carbon bonds. They demonstrate also high smoothness and hardness, can reach thickness of several microns and have important technological advantage: DLC films can be deposited at room temperature practically on any substrate.

Some of the above mentioned unique properties of diamond materials lead to great difficulties in their processing: cutting, drilling, polishing, microstructuring, etc. And here the laser turns out to be a unique processing tool. By means of conventional technological lasers it is possible to locally heat and ablate diamond material. Usually pulsed lasers are used for such needs and diamond can be ablated by two ways. The first is realized [7, 8] if the laser radiation is highly absorbed in diamond (e.g. in the case of ArF-laser with photon energy of 6.4 eV exceeding material band gap of 5.45eV). Then direct heating and vaporization of diamond may occur if irradiation energy fluence \( E_\text{S} \) is high enough. In the second case, when the sample is transparent for low intensity laser radiation, material absorption can be switched on by the leading part of the laser pulse or sequence of pulses by heating defects in the sample surface layer (see, e.g. [8, 9]). If the temperature of the diamond surface reaches the critical value \( T=T_g \approx 700^\circ C \) in atmospheric air, surface graphitization takes place and thus instead of initially transparent diamond we have highly absorbing graphitic layer (absorption coefficient in a wide spectral range \( \alpha \approx 10^5 \text{cm}^{-1} \)). That is why further irradiation of the modified layer leads to material evaporation.

Typical diamond materials ablation rates depend on laser fluence, wavelength and pulse duration, exceed 10nm per pulse and even can reach few microns per pulse for \( E_\text{S} \geq 100J/cm^2 \) [10].

The aim of the work is to show that there are irradiation regimes when diamond ablation can proceed with much lower rates and, correspondingly, much higher precision. We call such regimes as laser nanoablation of diamond materials [11, 12].

2. Experimental details

A number of diamond materials were used in the experiments:

- natural monocrystalline diamond stones
- polycrystalline CVD diamond
- nanocrystalline diamond films
- DLC films

Surfaces of diamond samples were mechanically polished before laser irradiation. The NCD films of two types were deposited with addition of 30% \( N_2 \) to the gas mixture. In this case the structure of NCD transforms to the net of diamond nanorods in graphitic shells surrounded by amorphous carbon [13]. The thickness of non-doped and nitrogen-doped NCD films was 3.6 and 0.8\( \mu \text{m} \), correspondingly. The thickness of ta-C type DLC films was 1 and 2\( \mu \text{m} \). They were deposited on steel substrates by laser-arc process [14].

The diamond material samples could be irradiated both in atmospheric air and in vacuum. Most of the results were obtained with excimer KrF-laser (\( \lambda = 248\text{nm} \)) with pulse duration \( \tau = 15\text{ns} \). Laser fluence on the target surface varied from 0.01J/cm\(^2\) up to 20J/cm\(^2\). In control experiments ArF-laser (\( \lambda = 193\text{nm} \), \( \tau = 15\text{ns} \)), Ti:Al\(_2\)O\(_3\) (\( \lambda = 800\text{nm} \), \( \tau = 100\text{fs} \)), Nd:YAG (\( \lambda = 1.06\mu\text{m} \), \( \tau = 1.5\mu\text{s} \)), Nd:YAP (\( \lambda = 0.54\mu\text{m} \), \( \tau = 300\text{ps} \)) and TEA CO\(_2\) (\( \lambda = 10.6\mu\text{m} \), \( \tau = 1\mu\text{s} \)) lasers were also used.

The surface morphology and depth profiles of the craters produced by laser irradiation were examined with white-light interferometric (WLI) microscope (New View 5000, Zygo Corp.) and scanning electron microscope (QUANTA). Carbon structure modification was controlled by Raman spectroscopy (scattering excitation at 514 nm wavelength).
3. Results and discussion

As it has been already mentioned above, diamond ablation by material vaporization in most cases requires surface graphitization. Moreover, in such case at the bottom of the crater a graphitic layer is formed during the vaporization process and surface cooling stage (from the boiling temperature down to $T_g$).

In this work we have focused on irradiation conditions when neither diamond nor laser induced surface graphitized layer can be vaporized, it corresponds to the sample surface temperature $T \leq T_g$.

Surface graphitization is characterized by changing (drop) of the sample optical transmittance because the graphitic phase of carbon absorbs laser light much more than the diamond phase. But laser graphitization dynamics strongly depends on diamond material. In the case of polycrystalline diamond, graphitization starts in local defects (graphitic phase on grain boundaries and others). Laser produced graphitic microvolumes can overlap in the course of a single pulse action if the laser pulse fluence $E_1$ is relatively high or in a sequence of pulses with $E_2 < E_1$.

Fig. 1 illustrates dynamics of CVD diamond sample transmittance for picosecond pulses with $\lambda=0.54\mu$m. One can see, that intense surface graphitization (drop of transmittance) can start in the first irradiation laser pulse ($E=10\, \text{J/cm}^2$) or may require a number of laser pulses (N=20 for $E=4.3\, \text{J/cm}^2$). Raman spectroscopy confirms that nanographite phase appears in the irradiated volume. For $E=2.8\, \text{J/cm}^2$ no graphitization was observed for N≈500 but even in this case accumulation process works and local changes of carbon phase already take place and for much higher N a visible surface graphitization will occur. To realize a single shot diamond graphitization the difference between optical properties of initial diamond material and laser graphitized layer should be minimized and to make this layer uniform it is desirable to work with diamond material that uniformly absorbs the laser light or concentration of initially absorbing defects in the material should be high. Such a regime was realized for KrF-laser irradiation of polycrystalline CVD diamond. Fig. 2 shows the microscopic image of the KrF laser ($\lambda=248\, \text{nm}$) irradiated zone (the square with $\approx300\, \mu$m sides). Not only optical properties of diamond material were changed but also the surface morphology varies. Instead of initially flat surface (or a crater which is usually formed when vaporization of the target material takes place) we can see a bump in the irradiated zone. This effect can be easily explained by the difference in mass density between the diamond and graphite ($\rho_{\text{diam}}=3.5$ and $\rho_{\text{grap}}=2.2$ g/cm$^2$, correspondingly). Such a difference in mass densities leads to material expansion when such carbon transformation takes place.

![Figure 1. Dynamics of CVD diamond transmittance caused by multiple laser irradiation ($\tau = 220\, \text{ps, } \lambda = 539\, \text{nm}$) at different fluencies.](image)
Example of another diamond material single pulse surface graphitization is shown in Fig. 3a. A photomask was irradiated by a single-pulse KrF-laser beam and its image was projected on the surface of diamond-like ta-C film. Thus by a single shot with the fluence $E = 5J/cm^2$ the sample surface was laser graphitized and electrically conductive strips were produced on the surface of the DLC film. The height (over the flat film surface) of the laser produced structures was only 70nm. The width was 2 µm, but with improved photomask and better objective applied, the structures width can be diminished to about $(0.5-1)·\lambda\approx100$nm. It was also found that graphitized material can be removed by chemical etching (oxidation) after laser irradiation. The result of such a treatment is shown in Fig. 3b. Instead of graphitic pathways the grooves with depth of about 200nm were formed. It should be also mentioned that the depth of etched grooves plus the height of the bumps give the total thickness of the laser produced graphitized layer. This data, in particular, is valid for laser fabrication of conductive structures on the surface of diamond-based devices.

It is important to know what are the maximum values of laser fluence $E_{max}$ that induce surface graphitization but still prevent diamond sample vaporization. Fig. 4 represents the dependence of $E_{max}$ on the laser pulse duration for a polycrystalline diamond. From these measurements it follows that $E_{max}$ value is determined by the thickness $\ell$ of laser heat affected zone. The lower is the $\ell$ value the smaller is $E_{max}$. The observed $E_{max}(\tau)$ dependence is well correlated with the formula $\ell=\max\{\ell_1, \ell_2\}$, where $\ell_1=1/\alpha$ (\alpha - laser light absorption coefficient in the target material) and $\ell_2=(\chi\tau)^{1/2}$ - heat diffusion length ($\chi$ - material thermal diffusivity). In the case of femtosecond pulses and if UV laser radiation is absorbed in a very thin layer and $\ell\approx\ell_1$, the threshold $E_{max}(\tau)$=Const while for longer pulses and radiation not so well absorbed in the target material $\ell\approx\ell_2$ and $E_{max}$ grows with $\tau$. The observed dependence $E_{max}\propto\tau^{1/4}$ slightly differs from the predicted $E_{max}\propto\tau^{1/2}$. It can be explained by diamond material properties changes in the process of diamond-graphite transformation.
It was found that if a surface graphitization takes place, then for efficiently large number \( N \) of laser pulses a crater in the irradiated zone can be formed. This regime is well observed for DLC and NCD samples and is illustrated in Fig. 5. The process is triggered by the first KrF-laser pulse that produces the graphitized bump with height of about 400nm, formed on the surface of ta-C DLC film. But after a few laser pulses the graphitized layer can be fully below the sample surface and the crater starts to be formed. If the laser fluence is high (Fig. 5a), then the ablation of a graphitic layer starts from the second pulse and ablation rate is \( V \approx 30-200 \text{nm/pulse} \) for \( E = 1.2-3.8 \text{J/cm}^2 \). This is a typical material vaporization regime and is observed both in air and vacuum. For lower \( E \approx 0.34-0.55 \text{J/cm}^2 \) (Fig. 5b) the created graphitic bump stays for about 5000 laser pulses and only after that removal of the material from its top starts but proceeds with much lower rates \( V \approx 0.01 \text{nm/pulse} \). Ambient environment is essential for this regime which we call nanoablation regime 1. Such a nanoablation does not take place in vacuum as it follows from laser processing curves, presented in Fig. 6. So we can come to the conclusion that the regime 1 is not pure thermo physical but also have a chemical nature. It could be observed with all lasers used in the experiments.

Figure 4. Dependence of CVD diamond vaporization threshold on laser pulse duration

Figure 5. Dependence of bump height/crater depth on pulse number after ta-C film laser irradiation (\( \lambda = 248 \text{nm} \)) for two different ablation regimes: (a) graphitized surface layer is vaporized; (b) laser induced oxidation of graphitic material takes place
Even at lower laser fluences another nanoablation regime (regime 2) was discovered. It works only with UV lasers but can be realized for all diamond materials under study. Irradiation of the samples by KrF or ArF laser pulses with laser fluence lower than the graphitization threshold leads to formation of craters. Fig. 7 shows the image of the irradiated spot (70nm deep crater) formed at the surface of a diamond single crystal. To produce such a shallow and fine structure it was necessary to use as many as $10^5$ laser pulses with $E=10\text{J/cm}^2$. At such level of $E$ no surface graphitization is observed and estimated surface temperature was below 100°C. When $E$ was increased to $E=20\text{ J/cm}^2$ traditional diamond ablation with much higher rates took place.

Experiments on irradiation of diamond single crystals in the absence of oxygen were very important for clarifying the regime 2 nanoablation mechanism. It was found that both in vacuum and inert helium atmosphere no traces of crater are formed. The number of pulses reached $3\cdot10^5$ while the laser fluence was only 15-20% below regular ablation threshold. Thus we can conclude that oxidation reaction plays a key role in this nanoablation regime. This conclusion is also supported by the experiment when the sample was externally heated in atmospheric air to the temperature 600°C and simultaneously irradiated by KrF-laser. In this case the rate of nanoablation increased by about 30% and regular ablation threshold dropped to $7\text{J/cm}^2$. 

![Figure 6. Dependence of bump height/crater depth on pulse number after ta-C film laser irradiation in air and low vacumm](image)

![Figure 7. Microscopic image of the crater on the single crystal diamond surface after laser nanoablation ($\lambda=248\text{nm}$, $10^5$ pulses, $10\text{ J/cm}^2$)](image)
Main features of regime 2 nanoablation were also observed with DLC films. Besides, with this material a special experiment was performed. After laser induced graphitization, the sample was shifted by about half (20µm) of the spot size in the direction perpendicular to the laser beam. The effect of further irradiation with $10^5$ pulses with fluence less than the surface graphitization threshold, was monitored on graphitized (half the spot) and initial DLC film surface. The result was surprising: laser nanoablation took place only on non-graphitized sample surface while for traditional oxidation you would expect that graphitized material should react with oxygen much faster than the diamond-like. At the same time, we should take into account that UV laser photons can effectively produce carriers in diamond materials. Laser induced excitation of the electron system in diamond (transition of electrons from localized states to free states with further relaxation or trapping) can change bonding for part of the atoms in the crystal lattice. As a result some carbon atoms (or atomic clusters) on the sample surface may be more weakly bonded than in diamond and can react with oxygen atoms more efficiently. Besides, high density electronic cloud near the wide band gap material surface can influence oxidation reaction. The efficiency of free carriers generation in diamond can be quite high. This is confirmed, for example, by our measurements of the dependence of single crystal thin plate transmittance upon the KrF-laser pulse fluence (Fig. 8). Our investigations with pump-probe laser interferometry and photoconductivity measurements have shown that under the above mentioned E levels electron density inside the diamond sample can reach $10^{16}$-$10^{19}$cm$^{-3}$. It is also worth mentioning that for diamond ionization by multiphoton absorption a high intensity femtosecond laser can be applied. But our tests with Ti:Al$_2$O$_3$ laser did not lead to regime 2 nanoablation of diamond. Probably, this failure is the result of the short (~ps) life-time of carriers in diamond and correspondingly more prolonged action of carriers in the nanosecond than femtosecond laser pulse duration.

The summary of laser ablative etching of diamond materials is given in Fig. 9 basing on KrF laser irradiation experiments with a broad range of $E=0.01$-10J/cm$^2$. 

![Figure 8. Dependence of single crystal diamond transmittance on laser fluence](image1)

![Figure 9. Dependence of ablation rates for different diamond materials on excimer laser fluence](image2)
The most important result is that there are different ablation regimes which are characterized by the material removal rates. For all diamond materials, represented on Fig. 9, we can easily trace 3 regions of ablation rates values.

a) $v \geq 10^{-10} - 100 \text{nm/pulse}$

The mechanism of ablation is entirely physical and determined by thermal heating, phase-transformation (diamond-graphite) and vaporization of carbon material. Near the threshold of ablation and for a few laser pulses craters (and correspondingly surface structures) with submicron depth can be fabricated in this regime.

b) $v \sim 0.01 - 0.1 \text{nm/pulse}$

This regime, that we call nanoablation regime 1, is determined by oxidation of laser graphitized surface layer during thermal laser pulse action. The ablation or etching rates in this case well correlate with the data, obtained in various experiments on laser induced pulsed chemical reactions. For example, in [15] numerous results on dry chemical etching of metals, semiconductors and insulators in Cl$_2$, NF$_3$ and other gases by short pulsed eximer and CO$_2$ lasers are summarized. In all cases the etching rate was in the same $v$ range. This can be explained by specificity of pulsed laser induced surface chemical reactions in gases when the reaction rate is limited by diffusion of reagents (in our case oxygen molecules) to the sample surface [16].

c) $v \sim 10^{-3} - 10^{-4} \text{nm/pulse}$

The proposed mechanism for this nanoablative regime 2 is the removal from the diamond surface of weakly bonded individual atoms and clusters by oxidation. The peculiarity of this regime, observed only with UV lasers, is that such weakly bonded carbon species formation is determined by diamond ionization by high energy photons. Additional proof of such a model comes from the comparison of ablation rates for NCD (30% N$_2$) obtained for $\lambda=248\text{nm}$ (less than diamond bandgap) and $\lambda=193\text{nm}$ (more than bandgap) laser pulses. Increased photon energy resulted in about an order of magnitude growth of ablation rates for the same laser fluence range (Fig. 9).

It is also important to note that for investigated diamond materials, which have very different optical and thermophysical (e.g. thermal conductivity of single crystal diamond and NCD films differs by 3 orders of magnitude), the regions of the above discussed ablation regimes can be shifted along E axis in Fig. 9. For instance, nanoablation regime 2 takes place for diamond at much higher E than for NCD and DLC films. The same reason is for the E shift in regime 2 to higher values $E \approx 0.5 - 1 \text{J/cm}^2$ for NCD (0% N$_2$) in comparison with $E \approx 0.1 \text{J/cm}^2$ for better absorbing NCD (30% N$_2$).

4. Conclusions

It was found that depending on laser fluence there are three different regimes of diamond materials (mono and polycrystalline diamond, nanocrystalline diamond films, diamond-like coatings) ablation:

- vaporization by single and multiple pulsed irradiation of initial material or laser graphitized surface layer
- surface thermal graphitization and oxidation (multiple pulsed)
- UV light photoinduced material modification, defects formation and further oxidation (multiple pulsed)

The latter two regimes allow to realize ultra precise diamond surface nanostructuring with material removal rates as low as $10^{-3} - 10^{-4} \text{nm/pulse}$. Such regimes were called laser nanoablation.

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References


