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Nanosecond pulsed excimer laser machining of chemically vapour-deposited diamond and graphite

Part II *Analysis and modelling*

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Analysis of the experimental data presented in Part I of this paper and those available in the literature revealed that the mechanism of material removal in laser machining of chemically vapour-deposited diamond is a two-step process: diamond transforms to graphite, and subsequently graphite sublimates. The energy fluence required for the formation of graphite is much lower than its removal by sublimation, and both are sensitive to the wavelength of the laser beam, the impurities present in the film and the environment during machining. When a 248 nm excimer laser beam interacts with diamond, there is an energy loss of 20% by reflection and 10% by transmission. The remaining 70% energy is used for heating the diamond, converting diamond to graphite, and sublimating graphite. Graphite is removed mostly by physical ablation and to some extent by chemical oxidation with the ambient.

A theoretical calculation based on bond strength estimates that the threshold energy fluence for the ablation of diamond is 0.37 J cm^{-2}. The experimental energy fluence was 0.8 J cm^{-2}. Experimental results on the material removal rates as a function of energy fluence closely follow the Beer–Lambert equation, suggesting that physical ablation is the determining mechanism. Temperature calculations showed that both diamond and graphite tend to oxidize in a single laser pulse that contributes to the material removal.

1. Introduction

Laser machining of diamond is an area of considerable technological importance for optical, microelectronic and tribological applications. There exists a clear need to understand the underlying physical mechanisms by which the laser can effectively bring out the benefits. In this paper, the excimer laser beam–diamond interactions is first examined and then the threshold energy fluence for diamond ablation was calculated from fundamental principles. A detailed analysis is made of the results presented in Part I together with data from other investigators. In addition, photochemical and thermal models of laser ablation are used to validate the experimental data and to predict the material removal mechanisms.

2. Excimer laser beam–diamond interactions

When a material is exposed to a sufficiently intense laser beam, an irreversible alteration of the material occurs, and this is called laser-induced breakdown. In a pure transparent dielectric such as diamond, the breakdown process begins with a sparse population of loosely bound electrons. Through various optical processes, these electrons are freed and energized by the large electric field of the laser pulse to the point that they produce more conduction electrons, eventually resulting in a large charge build-up. The resulting solid-state plasma is highly absorbing, and channels energy from the light wave into the material lattice in the form of heat. Two different mechanisms are capable of generating the plasma: avalanche ionization and multiphoton ionization. In avalanche ionization, free electrons are given energy by the oscillating electric field in the laser light. When the electrons gain sufficient energy, they knock additional electrons loose. The new electrons then are also given energy by the electric field, and an avalanche begins, soon forming a plasma. The plasma then transmits energy to the surrounding lattice. In multiphoton ionization, two or more photons are absorbed by an electron. The electron then has sufficient energy to go to a higher atomic energy level or to leave the atom.

The pulse length plays an important role in the formation and effect of the plasma. The plasma is first initiated in the many impurities and crystal imperfections in the sample. If the pulse length is of picosecond duration, overlap of the individual microsites does not occur, resulting in less destruction than generated by nanosecond pulses. Also, for a given quantity of energy, picosecond pulses generate higher electric fields

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than nanosecond pulses. This yields more rapid plasma formation with picosecond pulses, resulting in an increase in plume absorption, which effectively increases the breakdown threshold [1].

Together with the reactions at the atomic level, there are many things occurring on a macroscopic level. These include (i) energy reflected away from the surface, (ii) energy transmitted through the entire workpiece, (iii) heat conducted away by the solid, (iv) conversion of diamond to graphite, (v) sublimation of graphite, (vi) absorption of energy by the plume (vii) kinetic energy of products leaving the surface of the diamond and (viii) absorption of energy by the solid, and then re-emission as luminescence or infrared radiation.

The energy reflected from the surface of a material can be determined from the equation $R = [(n_1 - n_2)/(n_1 + n_2)]^2$ where R is the reflectance, n_1 is the refractive index of the incident medium and n_2 is the refractive index of the substrate material [2]. Using values of $n_1 = 1$ for air and $n_2 = 2.65$ for diamond (obtained by chemical vapour deposition (CVD)) at 248 nm [3], we find that $R = 0.20$ for CVD diamond. Of course, this equation assumes only specular reflectance. The energy transmitted through free-standing CVD diamond film has been documented by Thorpe *et al.* [4]. For 248 nm light, approximately 10% of the light incident on the surface is transmitted through to the opposite surface. This value is independent of whether the incident surface is the rough side or the smooth side of the film. The photon energy for 248 nm light is 5.01 eV, which is less than the band gap of diamond which is 5.4 eV. Thus, pure diamond should be transparent to 248 nm light. However, all types of diamond have impurities such as lattice defects or inclusions, all of which absorb 248 nm light to some degree. Excess amounts of nitrogen cause absorption at energies considerably lower than the band gap of diamond. Some common examples of this include the “A centre”, which occurs when two nitrogen atoms replace two adjacent carbon atoms, and the “B centre”, which occurs when four adjacent nitrogen atoms plus a vacancy occur [5].

The remaining 70% of the laser energy is used to heat the diamond surface layers, to cause a phase transition from diamond to graphite and to sublimate the graphite. Once a graphite surface has been formed, the absorption characteristics change dramatically. The reflected and transmitted energies become nearly zero, and the incident laser energy is now divided into just two major components: the energy absorbed by the plume and the energy absorbed by the graphite on diamond substrate. The contribution of the other mechanisms mentioned earlier are assumed to be minimal. The graphite on the surface is then removed by two mechanisms: oxidation with air at about 1150 K, and vaporization by heating at about 4275 K [6]. As graphite is removed, the graphite–diamond interface moves down, and the diamond directly below the interface is converted to graphite. This process continues throughout the duration of the laser pulse, thus removing material from the substrate.

When diamond is transformed into graphite, it forms a distinct layer due to the different crystal structure and lower density of graphite relative to the initial diamond. Graphite has an increased opacity at visible wavelengths and its electrical conductivity is considerably higher than that of diamonds. The rate of the conversion of diamond to graphite was measured by Rothschild *et al.* [7] and Rothschild and Ehrlich [8], who found that this conversion began at a threshold of approximately 60 mJ cm^{-2} and then increased nonlinearly with increasing laser fluence. The graphite generated at the diamond surface has a smaller absorption length than diamond (0.1 μm compared with approximately 10 μm) and a lower thermal diffusivity (1.4 cm^2 s^{-1} compared with 11 cm^2 s^{-1} at room temperature) [7]. Because of this, the energy in the latter part of a laser pulse is localized in the graphite layer, leading to selective vaporization of the graphite. The underlying diamond is relatively unaffected.

Material is removed in two modes when machining diamond with a laser: chemical etching and physical etching, or ablation. When a laser heats the surface, there is a transition to graphite at around 1475 K, and a chemical reaction with oxygen at 1150 K. Small amounts of material are removed by the chemical reaction. Physical ablation (sublimation) begins at around 4275 K. The oxidation mechanism dominates at low fluences (200–500 mJ cm^{-2}), and physical ablation dominates at higher fluences [9,10].

3. Calculation of the threshold fluence for diamond

The threshold energy fluence is a strong function of the wavelength of the light, the type of diamond (including diamond-like carbon (DLC), hydrogenated amorphous carbon (a-C:H) and amorphous carbon (a-C)) and the impurity content, as shown by the data from the experimental study described in Part I and from the literature displayed in Table I.

The threshold energy fluence necessary for ablation to occur in CVD diamond can be estimated using the bond energy of diamond as a starting point. In order to compare the calculated value with the experimental value, the area and volume used in these calculations are the same as that ablated with one laser pulse at the experimental value. At the experimental threshold energy fluence, the surface area and the volume ablated in a single pulse are 0.004 144 cm^2 and 4.97×10^{-9} cm^3, respectively.

The number, M_c, of moles of carbon in the volume is calculated as $M_c = V\rho/M_c$ where V is the volume (4.97×10^{-9} cm^3), ρ is the density (3.51 g cm^{-3}) and M_c is the molar weight of carbon (12.011 g mol^{-1}). Substituting the values, $M_c = 1.45 \times 10^{-9}$ mol. Each single bond (sp^3) in diamond is shared equally among adjoining atoms; thus, for each bond, an atom “owns” half of the bond. In diamond, there are four strong σ bonds shared among neighbouring atoms; so each diamond atom “owns” two bonds. In comparison, graphite has three strong σ bonds and one weak π bond. The π bond is very weak compared with the σ bonds; so each graphite atom “owns” approximately $3 \times 1/2 = 1.5$ bonds. In this calculation, it is assumed that the diamond bonds are broken directly

TABLE I Threshold energy fluence values

Source	Wavelength (nm)	Diamond type	Fluence ($J cm^{-2}$)
Present study	248	Free-standing CVD diamond	0.8
Ageev *et al.* [11]	308	CVD diamond	1.0
Rothschild *et al.* [7]	193	Natural diamond	3.9
Douglas-Hamilton and Haag [12]	10 600	Natural diamond	10^6
Rothschild and Ehrlich [8]	193	DLC	0.13
Prawer *et al.* [13]	530	DLC	1.60
Konov *et al.* [14]	248	a-C:H	0.07
Malshe *et al.* [15]	248	a-C:H	0.11
Malshe *et al.* [15]	248	a-C	0.035

instead of being transformed to graphite first and then broken.

For diamond, the total number, N_b, of atomic bonds in the volume is given by $N_b = 2M_c = 2.9 \times 10^{-9}$. The energy, E_b, required to break all the bonds in the given volume would be $E_b = N_b E_d$, where E_d is the energy for breaking a single bond (sp^3) which is given by $370 kJ mol^{-1}$ [16]. This results in a value of $E_b = 0.001\,077$ J. In laser processing, this energy must all be initially absorbed at the surface; so the fluence F_s at the surface, would be $F_s = E_b/A$, where A is the surface area ($0.004\,144 cm^2$). This results in a value of $F_s = 0.26 J cm^{-2}$. As shown earlier, only 70% of the energy in a laser pulse is totally absorbed within the volume. Thus, the threshold fluence required for ablation is estimated to be $F = F_s/0.7 = 0.26/0.7 = 0.37$ $J cm^{-2}$. The calculated value for the threshold fluence is about 50% less than the experimental value ($0.8 J cm^{-2}$) obtained in this work. The difference between the calculated and experimental values may be due to plasma absorption, conduction and other miscellaneous effects such as impurities that were ignored to simplify the calculation. The energy-absorbing plasma is very likely to form at $0.8 J cm^{-2}$ which corresponds to a power density of $10^7 W cm^{-2}$ because it has been demonstrated that, between 10^7 and $10^{10} W cm^{-2}$ (depending on wavelength), the vapour plume becomes partly ionized and absorbs a substantial fraction of the laser energy. Of course, the plume emits black-body radiation, which can then be partially absorbed by the target material [17].

As a side note regarding the threshold fluence, some discussion should be given regarding the octahedron (1 1 1) surfaces typical of CVD diamond surfaces. For light that is normal to the macroscopic plane of the surface, the four faces on the top of an octahedron crystal may initially tend to focus light to a point inside the crystal. This point inside the crystal will then be exposed to a fluence that is roughly four times the fluence received on each face. This could generate a situation where ablation can be initiated in as-grown CVD diamond at fluences much lower than the threshold fluence for polished diamond. Ablation at these low fluences will continue until the crystal faces have been severely modified by the ablation process, thus eliminating the focusing effect.

4. Analysis of material removal rate

The experimental study described in Part I confirms that the material removal in nanosecond pulsed 248 nm excimer laser machining of free-standing CVD diamond films involves two steps: conversion of diamond to graphite, followed by the sublimation of graphite. The material removal rate increased with an increase in the energy fluence. In the present study, material is removed at the rate of 0.15 μm per pulse at an energy fluence of $40 J cm^{-2}$. Rothschild *et al.* [7] performed machining of single-crystal diamond using ArF (193 nm) laser pulses and achieved etch rates of up to 0.2 μm per pulse. They used a focused energy density that varied from 0.1 to $200 J cm^{-2}$ and type IIA crystalline diamond with (1 0 0) orientation and diamond-like hard-carbon films. Rothschild *et al.* [7] also used reactive ambient vapours to react with the heated graphite layer to reduce the temperature and to eliminate accumulation of graphite. The best results were obtained with gases simultaneously photolysed during the pulse, such as Cl_2, O_2 and N_2. In the higher-temperature ranges, a hydrogen ambient increased the etching rate of graphite.

Using 308 nm XeCl light on CVD diamond films, Ageev *et al.* [11] achieved an etch rate that was almost an order of magnitude greater than that obtained in the present work. This shows that 308 nm light can ablate graphite better than 248 nm light. The existence of impurity absorption in CVD diamond films, as well as the formation of an absorbing graphite layer on the surface during illumination, can result in effective etching.

Ageev *et al.* [11] carried out comparative studies of changes induced in polycrystalline diamond films by light from an XeCl laser (energy, 4.08 eV) and a CO_2 laser (energy, 0.12 eV). Light from the XeCl and CO_2 sources was focused on the workpiece to spot sizes of 150 μm and 500 μm, respectively. The pulse repetition frequency was varied from 1 to 10 Hz while the energy density was varied to a maximum of $30 J cm^{-2}$. Appreciable etching occurred only with the XeCl source beginning near $1 J cm^2$. At $8 J cm^{-2}$, the etch rate was 0.3 μm per pulse, which is almost an order of magnitude higher than that obtained by Rothschild *et al.* [7] using 193 nm light at comparable energy densities. Ageev *et al.* believed that this discrepancy occurs because diamond film has a lower thermal conductivity

($k = 410\,\mathrm{W\,m^{-1}\,K^{-1}}$) than does single-crystal diamond ($k = 2000\,\mathrm{W\,m^{-1}\,K^{-1}}$). Lower thermal conductivity results in intensified pulsed heating of the film surface and causes faces which are more active than the (1 0 0) direction used by Rothschild *et al.* to participate in the graphitization of the diamond film.

When Ageev *et al.*, were conducting their experiments, the transmission of the film remained constant until a through-hole appeared and corresponded to an effective absorption coefficient $\alpha = 2000\,\mathrm{cm^{-1}}$. This provided evidence that a steady-state absorbing layer of graphite was present at the bottom of the crater, supporting the Rothschild *et al.* model of two-stage etching. The Rothschild *et al.* model involves the transformation of diamond to graphite in the first few laser pulses, followed by the sublimation of graphite with additional laser pulses. Ageev *et al.* also found that, after irradiation in a xenon gas atmosphere or a vacuum, a graphite halo always formed around the spot. This was caused by the deposition of carbon ejected from the crater. When irradiated in air, the oxygen did not appreciably accelerate etching, but it did react with carbon in the gaseous phase, forming CO and CO_2. This process prevents the formation of a graphite "breastwork" at the edge of the laser spot, and the boundary of the hole becomes sharper.

Regarding the experiments using a CO_2 laser on CVD diamond films, Ageev *et al.* calculated an absorption coefficient $\alpha = 200\,\mathrm{cm^{-1}}$, and the ablation threshold value was determined to be $18\,\mathrm{J\,cm^{-2}}$. This threshold fluence is much lower than the value of $10^6\,\mathrm{J\,cm^{-2}}$ reported by Douglas-Hamilton and Haag [12] and may be due to the different absorption coefficients of type IIA natural diamond and CVD diamond.

Potamac Photonics [18, 19] used a KrF laser producing 50 μJ pulses of 80 ns duration at pulse repetition rates extending to 2 kHz to machine diamond. In general, fluences between 0.1 and $10\,\mathrm{J\,cm^{-2}}$ were required for ablation, and the single pulse ablation depth in diamond was typically a few tens of nanometers. With this precision depth control, Potamac Photonics used raster scanning techniques to fabricate a variety of microstructures from bulk diamond. The diamond substrate was mounted on motorized stages, and laser pulse generation was synchronized with stage motion to assure uniform exposure of selected surface areas. No effort was made to homogenize the laser beam since the scanning process produced a spatial averaging effect that minimized the effect of fluence variation in the focal spot. A surface roughness of a few hundred nanometers was typical of the scanned area. The graphite layer produced by the laser beam was subsequently removed by abrasive sonication with an Al_2O_3 slurry.

The results of research on DLC films are also useful. In contrast with CVD diamond, DLC films are amorphous and very smooth [10]. DLC films contain a mixture of sp^2 and sp^3 bonds; so their structure may be described as being between that of diamond and graphite [13]. However, the band gap of a-C is 1.0 eV, and for a-C:H it is 1.4 eV [15]. These values are considerably lower than the 5.4 eV band gap of pure diamond; so a comparison of results must be performed with caution. Konov *et al.* [14] performed experiments on a-C: H films using KrF (248 nm) radiation and fluences ranging from 0.07 to $1.0\,\mathrm{J\,cm^{-2}}$ to determine the most efficient etching conditions for these films. Prawer *et al.* [13] used a frequency-doubled neodymium-doped yttrium aluminium garnet laser (534 nm) on DLC films in the range 0.2–$1.6\,\mathrm{J\,cm^{-2}}$. Their intention was to create conducting pathways on insulating DLC films for microelectronic applications, and they reported a minimum fluence near $1.6\,\mathrm{J\,cm^{-2}}$. Rothschild and Ehrlich [8] used 193 nm light to produce lines 0.13 μm wide on DLC films with fluences ranging from 0.1 to $1.0\,\mathrm{J\,cm^{-2}}$. They reported an ablation threshold of approximately $0.13\,\mathrm{J\,cm^{-2}}$. Malshe *et al.* [15] used 248 nm light and fluences ranging from 0.2 to $1.2\,\mathrm{J\,cm^{-2}}$. They showed that a-C:H films had etch rates approximately ten times higher than a-C films. Malshe *et al.* believed that this difference was because etching of a-C:H removed material without redepositing the graphitic phase, which occurs when ablating a-C. Minimum ablation fluences of $0.035\,\mathrm{J\,cm^{-2}}$ for a-C and $0.11\,\mathrm{J\,cm^{-2}}$ for a-C:H were estimated from the data. A detailed comparison of results on the laser–DLC interaction obtained by different workers is hampered because, in most cases, the optical, thermophysical and structural parameters of DLC films were not reported; yet these properties can be varied in a wide range by the proper choice of deposition conditions.

5. Modelling of material removal

The results obtained in this work suggest that the etching of CVD diamond may be photochemical in nature and may follow the Beer–Lambert relation given by $E(z) = E_i \exp(-\alpha z)$, where $E(z)$ ($\mathrm{J\,cm^{-2}}$) is the attenuated fluence (at depth z), E_i($\mathrm{J\,cm^{-2}}$) is the incident fluence and α ($\mathrm{cm^{-1}}$) is the absorption coefficient. If one assumes that the etch depth is equal to the depth at which the attenuated fluence reaches the threshold fluence (E_t) value, then the equation can be rearranged to estimate the etch depth. The etch depth, D (cm), per pulse is then given by $D = (1/\alpha)\ln(E_i/E_t)$, where E_t is the threshold ablation fluence equal to $0.8\,\mathrm{J\,cm^{-2}}$ for CVD diamond.

Based on the experimental data obtained, the calculated values of α (including the effects of transformation of diamond to graphite) range from approximately 10^5 to $10^6\,\mathrm{cm^{-1}}$. The variation in α with fluence is shown in Fig. 1. It can be seen that α^{-1} is quite high for low fluences and then it gets smaller for higher fluences. This is probably due to the production of thicker graphite films on the diamond surface at higher fluences. Graphite has a higher absorption coefficient than diamond. The average value of α^{-1} is 4×10^{-6} cm, which is low compared with the value of 5×10^{-4} cm obtained by Ageev *et al.* [11] using 308 nm light on single-crystalline diamond. However, it compares favourably with the value of 10^{-6} cm obtained by Kononenko *et al.* [9], who modelled the ablation rate of DLC films using the Beer–Lambert equation.

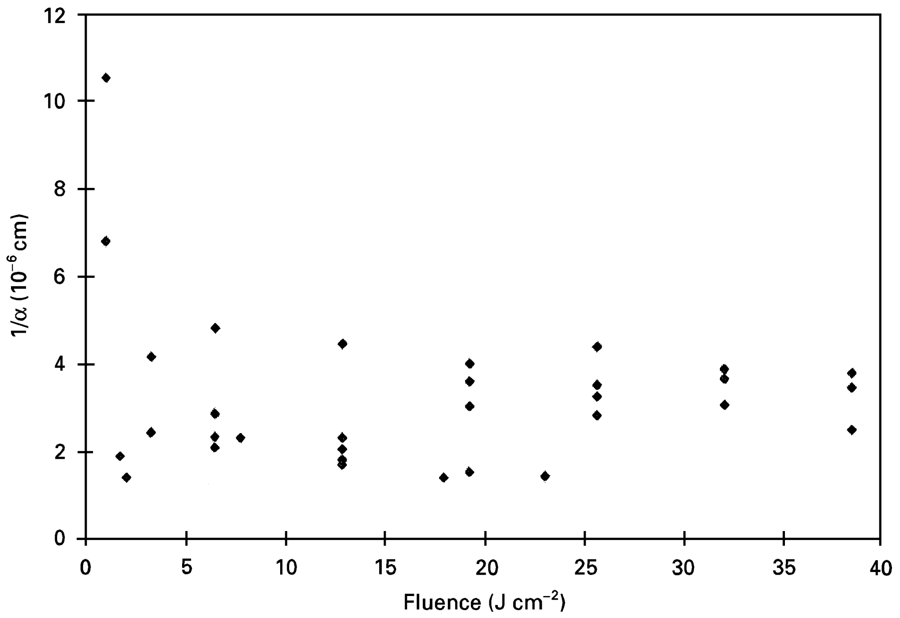

Figure 1 Variation in absorption coefficient with energy fluence for CVD diamond.

TABLE II Properties of diamond and graphite

Material	Thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)	Thermal diffusivity ($\mathrm{m^2\,s^{-1}}$)
Diamond	2100	0.001
Graphite	290	0.000 165

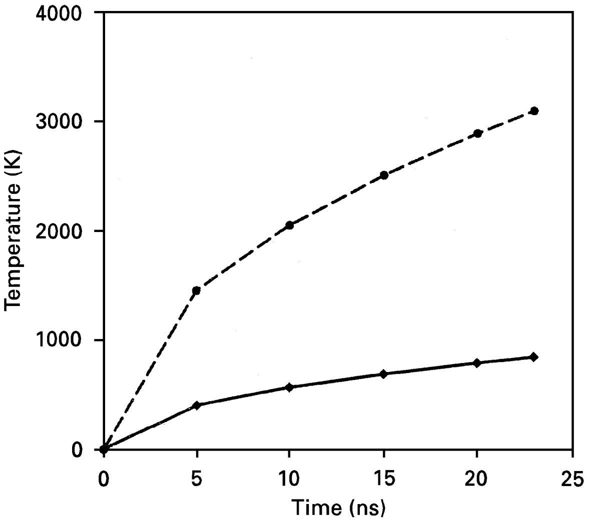

Figure 2 Calculated surface temperatures in diamond (—◆—) and graphite (– – –●– – –) during a 23 ns laser pulse.

Pettit [20] noted that, for many materials exposed to fluences slightly above threshold, the etch depth per pulse varies according to the Beer–Lambert equation. However, for higher fluences, there are considerable deviations from this logarithmic relationship. In many cases, the relationship between etch depth and fluence becomes approximately linear as given by $D = C(E_i - E_0)$ where C and E_0 are constants. Data in the present work did not follow this linear equation.

In addition to ablation, the material removal may occur by oxidation. A thermal model is used to determine the oxidation of diamond or graphite, and the transformation of diamond to graphite in a single laser pulse. Table II lists the thermal properties for CVD diamond and the highly oriented pyrolytic graphite (HOPG) used in this work.

The energy distribution across an excimer laser beam can be approximated as uniform and constant. Assuming a semi-infinite solid, the solution to the heat transfer equation for the surface temperature is $T(0, t) = (I_0/K)\ (4\kappa t/\pi)^{1/2}$ where I_0 is the absorbed power density, K is the thermal conductivity and κ is the thermal diffusivity. This equation ignored the energy loss by plasma absorption. In addition, this equation is valid when the thickness of the part exceeds $(4\kappa \mathrm{t})^{1/2}$. For diamond and graphite, the values of $(4\kappa t)^{1/2}$ are 10 μm and 4 μm, respectively, both of which are considerably smaller than the thickness of the samples used in these experiments. Thus, the above equation should give a reasonable estimate of the temperatures in the samples when they are exposed to a laser pulse.

The surface temperature of both diamond and graphite during a single laser pulse with a fluence of $0.94\,\mathrm{J\,cm^{-2}}$ was calculated, and the temperature is plotted as a function of time in Fig. 2. The reflectances used for calculating I_0 are 0.20 for diamond and 0 for graphite. Diamond begins to oxidize at around 1150 K and begins to convert to graphite at 1475 K. Graphite oxidizes between 625 and 675 K and sublimes around 3975–4275 K [16]. It is seen from Fig. 2 that both diamond and graphite oxidize during nanosecond pulsed laser machining, and that diamond transforms to graphite.

6. Conclusions

Experiments, analysis and modelling of laser hole drilling of CVD diamond and HOPG with a 23 ns pulsed KrF excimer laser provided insight into the mechanisms of material removal. In a single laser pulse, diamond oxidizes as well as transforms to graphite. The material removal mostly occurred through physical ablation of graphite. The threshold energy fluence for ablation of diamond was theoretically calculated as $0.37\,\mathrm{J\,cm^{-2}}$ which is 50% of the experimentally obtained value. The discrepancy between these values may be due to absorption of energy in the plume, conduction losses and impurities in the diamond. The threshold energy fluence decreased with decrease in the wavelength. Information regarding the threshold ablation fluence of HOPG could not be found in the literature; so a comparison with other values could not be made.

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References

1. W. L. SMITH, *Opt. Engng* **17** (1978) 489.
2. J. LUXON and D. PARKER, "Industrial lasers and their applications, 2nd Edn (Prentice-Hall, Englewood Cliffs, NJ, 1992).
3. P. D. OWNBY and R. W. STEWART, in "Engineered materials handbook", edited by T. Reinhart (American Society for Metals, Metals Park, OH, 1987) pp. 821–834.
4. T. P. THORPE, A. A. MORRISH, L. M. HANSSEN, J. E. BUTLER and K. A. SNAIL, in "Diamond optics III", Proceedings of the SPIE, Vol. 325, edited by A. Feldman and S. Holly (Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1990) pp. 230–237.
5. J. WILKS and E. WILKS, "Properties and applications of diamond" (Courier, Boston, MA, 1991).
6. H. D. GRESSER, Society of Manufacturing Engineers, Dearborn, MI, Technical Paper MR76-855 (1976).
7. M. ROTHSCHILD, C. ARNONE and D. J. EHRLICH, *J. Vac. Sci. Technol. B* **4** (1986) 310.
8. M. ROTHSCHILD and D. J. EHRLICH, *ibid.* **5** (1987) 389.
9. T. V. KONONENKO, V. I. KONOV and V. G. RALCHENKO, in "Diamond optics V", Proceedings of the SPIE, Vol. 1759, edited by A. Feldman and S. Holly (Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1992) pp. 106–114.
10. V. I. KONOV, V. G. RALCHENKO, S. M. PIMENOV, A. A. SMOLIN and T. V. KONONENKO, in "Laser microprocessing of diamond and diamond-like films", Proceedings of the SPIE, Vol. 2045, Laser processing of thin films and microstructures, edited by I. Boyd (Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1994) pp. 184–192.
11. V. P. AGEEV, L. L. BUILOV, V. I. KONOV, A. V. KUZMICHEV, S. M. PIMENOV, and A. M. PROKHOROV, *Dokl. Akad. Nauk SSSR* **303** (1988) 598.
12. D. H. DOUGLAS-HAMILTON and E. D. HAAG, *J. Opt. Soc. Amer.* **64** (1974) 36.
13. S. PRAWER, R. KALISH and M. ADEL, *Appl. Phys. Lett.* **48** (1986) 1585.
14. V. I. KONOV, T. KONONENKO, S. PIMENOV, A. SMOLIN and N. CHAPLIEV, *Sov. J. Quantum Elec.* **21** (1991) 112.
15. A. P. MALSHE, S. T. KSHIRSAGAR and K. S. CHARI, *Mater. Lett.* **11** (1991) 175.
16. H. O. PIERSON, "Handbook of carbon, graphite, diamond and fullerenes" (Noyes Publications, Park Ridge, NJ, 1993).
17. M. von ALLMEN, "Laser–beam interactions with materials, 2nd Edn (Springer, Berlin, 1995).
18. C. P. CHRISTENSEN, in "Lasers as tools for manufacturing", Proceedings of the SPIE, Vol. 2062, edited by L. Migliore and R. Walker (Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1993) pp. 14–21.
19. C. P. CHRISTENSEN, *Ind. Laser Rev.* June (1994) 9.
20. G. H. PETTIT and R. SAUERBREY, *Appl. Phys.* A **56** (1993) 51.

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