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Appl Phys A (2011) 105:673–677
DOI 10.1007/s00339-011-6645-0

Applied Physics A
Materials Science & Processing

RAPID COMMUNICATION

Picosecond-laser-induced structural modifications in the bulk of single-crystal diamond

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Received: 6 October 2011 / Accepted: 10 October 2011 / Published online: 21 October 2011
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Abstract Arrays of through laser-graphitized microstructures have been fabricated in type IIa single-crystal 1.2-mm-thick diamond plates by multipulse laser irradiation with 10-ps pulses at $\lambda = 532$ nm wavelength. Raman and photoluminescence (PL) spectroscopy studies of the bulk microstructures have evidenced the diamond transformation to amorphous carbon and graphitic phases and the formation of radiation defects pronounced in the PL spectra as the self-interstitial related center, the 3H center, at 504 nm. It is found that the ultrafast-laser-induced structural modifications in the bulk of single-crystal diamond plates occur along {111} planes, known as the planes of the lowest cleavage energy and strength in diamond.

1 Introduction

Bulk modification and microstructuring of diamonds using ultrashort pulse lasers is of great interest due to its potential in photonic applications and diamond gem marking [1–8]. The interest and need in developing ultrashort laser techniques for three-dimensional (3D) microstructuring of diamond is further caused by huge progress in the chemical vapor deposition (CVD) diamond technology of single crystals [9, 10] which makes large area single-crystal CVD diamond plates (up to $8.0 \times 8.0 \times 1.2$ mm^3 size [11]) readily available material for research and development. Scientific aspects of ultrashort laser damage and structure modification in the bulk of diamond are intriguing and still not completely understood in regard to the mechanisms of ultrafast free-electron generation [2, 4, 12, 13] and laser-induced graphitization [2, 4, 14–16], laser-graphitized structure properties [3, 4, 6] and mechanical damage resulting from bulk graphitization [6, 17, 18]. It is these important problems which are studied in the present work, with placing emphasis on picosecond-laser-induced structural modifications in the bulk of diamond.

In the paper we report on the bulk microstructuring of single-crystal diamonds using a picosecond-laser system with 10-ps pulse widths [19]. Firstly, it is demonstrated that the ps-laser system used allows high-aspect-ratio microstructures ('graphitized' microchannels) to be fabricated at high rates through mm-thick diamond plates. Secondly, the results of two important findings are presented, relating to (i) crystallographic-plane-dependent character of the structure transformation in the bulk of single-crystal diamond, and (ii) appearance of 3H luminescence. Due to the finding of 3H luminescence, particular attention is paid to the behavior of the 3H defect center in correlation with the structure transformation in ps-laser-irradiated diamond.

2 Experimental details

The bulk modification/microstructuring of diamond was carried out using a picosecond MOPA (master-oscillator power-amplifier) laser system—the DUETTO^{TM} laser system [19],

Electronic supplementary material The online version of this article (doi:10.1007/s00339-011-6645-0) contains supplementary material, which is available to authorized users.

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source: https://doi.org/10.24451/arbor.11703 | downloaded: 13.5.2020

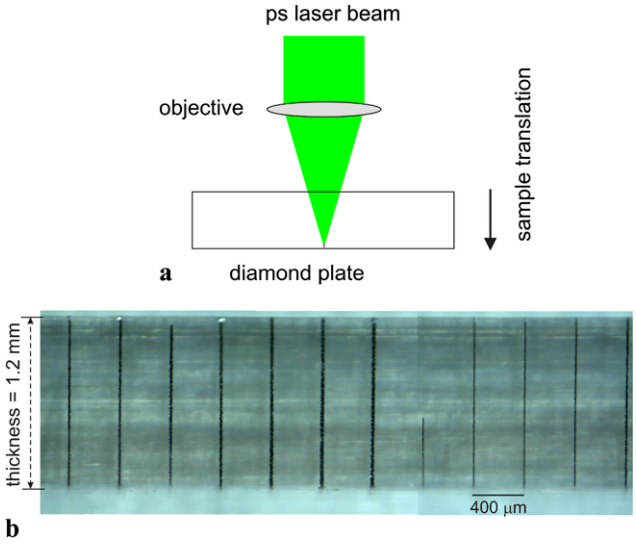

Fig. 1 (**a**) Schematic of ps-laser microstructuring across a diamond plate, (**b**) optical image of ps-laser-induced microstructures fabricated in a 1.2-mm-thick CVD diamond plate at different pulse energies and pulse repetition rates

which has demonstrated excellent performance in microprocessing of various materials [20]. A type IIa CVD single-crystal diamond plate of 6.0 × 6.0 × 1.2 mm size, {100} orientation and nitrogen content [N] < 1 ppm (from Element Six Ltd) [11] was an original sample. It was cut into three plates followed by mechanical polishing of side faces. For diamond microstructuring with the DUETTO system (which generates pulses of 10-ps duration), we used the second laser harmonic ($\lambda = 532$ nm). The laser beam radius (r) in the focal plane of an objective was $r = 7$ μm. A video imaging system was applied for real-time observation of the growth of a laser-modified region in the bulk of diamond—from the rear side to the front side of the plates—in the course of multipulse irradiation, as described elsewhere [4] and shown schematically in Fig. 1a, and also in a video clip (see Fig. S1 and the video in the Electronic Supplementary Material).

3 Results and discussion

Using the developed technique (described above), arrays of through laser-graphitized microstructures have been fabricated in 1.2-mm-thick diamond plates. Figure 1b displays an optical image of such microstructures located at 400 μm spacing. In these experiments the pulse energy (E) was varied from 1 μJ to 7 μJ, the pulse repetition rate (f)—from 10 kHz to 50 kHz, and the translation speed (V_z) was 100 μm/s. A video clip (see Fig. S1 and the video in the Electronic Supplementary Material) shows the real-time growth of a through microstructure under irradiation at $E = 7$ μJ and $f = 10$ kHz. It takes about 4 sec (average growth rate $V_{gr} = 260$ μm/s) for the structure to grow from the back side to the front side, forming a laser-graphitized microchannel in the 1.2-mm-thick diamond plate.

It should be noted that the maximum growth rate is achieved when the 'graphitization' rate at the focal position (determined at $V_z = 0$) is equal to the translation speed of the sample [2, 4]. Under the irradiation conditions used, the maximum growth rates were found to increase from $V_{gr} = 1$ mm/s to $V_{gr} = 4$ mm/s with increasing pulse energy from $E = 2$ μJ to $E = 6$ μJ ($f = 50$ kHz). The occurrence of high rates of the structure transformation is a characteristic feature of the bulk microstructuring of diamond with the DUETTO ps-laser system.

In addition, an advantage of ps-laser pulses for bulk microstructuring is pronounced in higher thresholds for the beam self-focusing than for femtosecond pulses. Using the formula for the critical power $P_{cr} = 3.77 \cdot \lambda^2/(8\pi \cdot n_0 \cdot n_2)$ [2, 21, 22] (where λ is the laser wavelength, $n_0 = 2.4$ is the refraction index, and n_2 is the nonlinear refraction index of diamond) and the reported value of $n_2 = 4 \times 10^{-13}$ esu for $\lambda = 532$ nm [23], we estimate the self-focusing threshold as $E_{cr} = P_{cr} \cdot \tau/(1 - R) = 9.3$ μJ (for $\tau = 10$ ps, $R = 0.17$, R is the reflection from the front surface), which is higher than the laser pulse energies used in our experiments.

Optical microscopy examination of the bulk microstructures with higher resolution reveals the following distinctive features of the ps-laser-induced structural modifications, which are shown in Fig. 2. First, the diameter of the bulk microstructures is increased with the pulse energy (see Figs. 2a–c), while the change in the pulse repetition rate from 10 kHz to 50 kHz does not essentially influence the diameter, compare Fig. 2a with Figs. 2d, e.

The most interesting effect observed in the microstructure formation is a crystallographic-plane-dependent character of the structure transformation in the bulk of diamond, which is seen in all images of Fig. 2 as pronounced sharp boundaries (between original and laser-modified regions) set at a fixed angle to the {100}-aligned diamond plate surface. This angle is 54.5° and corresponds to the angle between the (001) and {111} crystal planes. It means that the ps-laser-induced structure transformation propagates preferably along {111} planes, which are known to exhibit the lowest cleavage energy and strength in diamond crystals [24].

The obtained data confirm the supposition of the crystallographic-plane dependence of laser fracture made in our previous paper on the bulk microstructuring of diamond with 120-fs pulses [4]. So, the character of the bulk modifications, controlled by the anisotropy of the strength of diamond, appears to be alike for ultrashort pulses of different durations from 10 ps to 120 fs. The mechanism behind the observed structure modifications is suggested to involve ultrafast free-electron generation by avalanche ionization [2, 13], interaction of the excited electron system with the

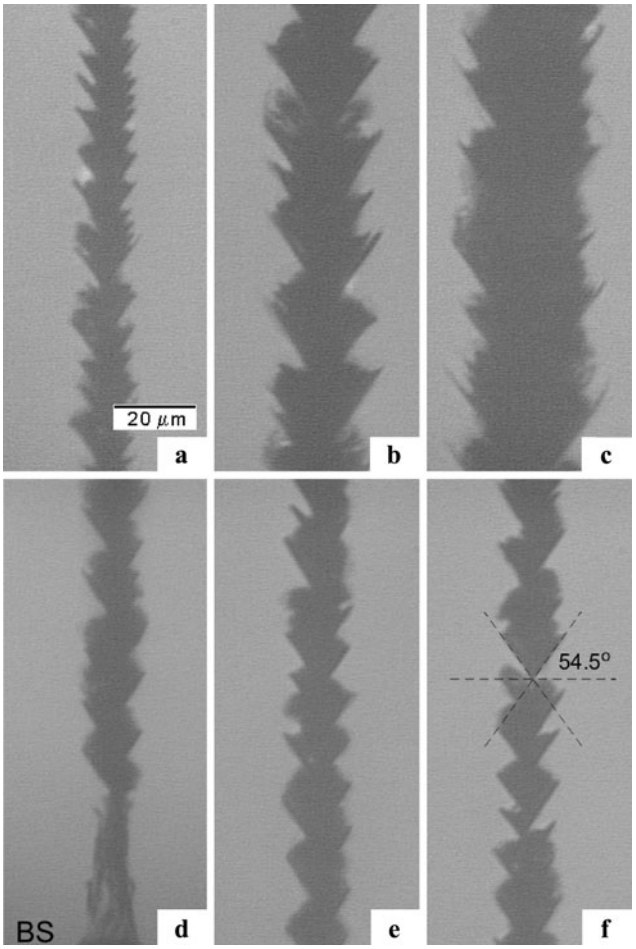

Fig. 2 Optical images of the microstructures produced in the bulk of a CVD single-crystal diamond plate at different pulse energies: (**a**) 1 μJ, (**b**) 3 μJ, and (**c**) 5 μJ (at $f = 10$ kHz), and of different parts of a through microstructure formed at $E = 1$ μJ and $f = 50$ kHz—at/near the back side (BS) (**d**) and two regions in the bulk (**e**, **f**). The angle of 54.5° is between the (001) and {111} crystal planes

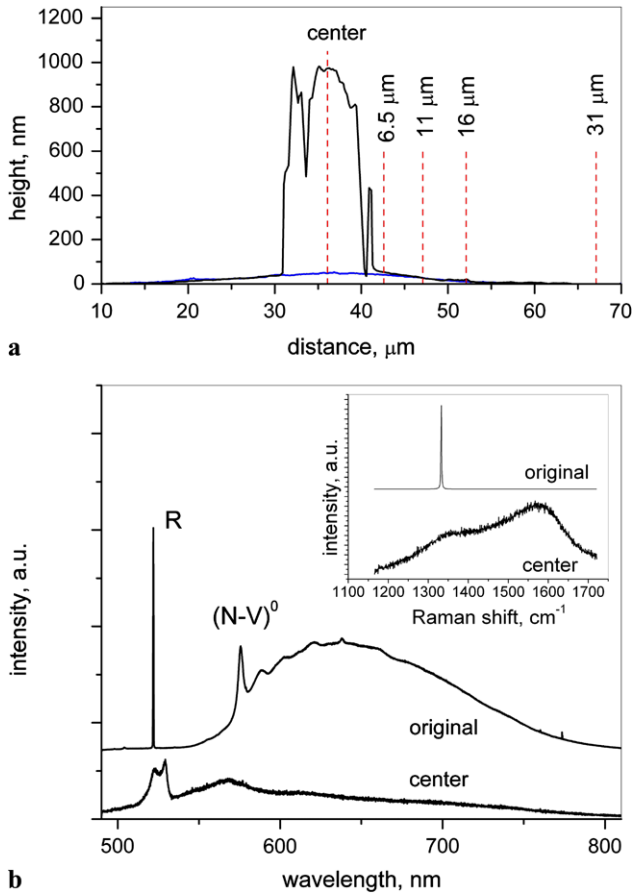

Fig. 3 (**a**) The back side (BS) surface profile of the end of the microstructure fabricated at $E = 1$ μJ and $f = 10$ kHz, the positions at different distances from the center mark the sites of PL spectra measurements; (**b**) PL and Raman (in the *inset*) spectra of the original plate and ps-laser-modified diamond, measured at the BS in the center of the microstructure as shown in (**a**); the PL and Raman spectra are shifted and plotted at different intensity scales for clarity

lattice and ultrafast collective motion of carbon atoms [24], resulting in the structural changes and phase transitions in the bulk of diamond.

The morphology of the laser-structured diamond plates was studied using a 3D surface profiler "Zygo" (model New View 5000). A typical back side (BS) surface profile of the end of a through microstructure is presented in Fig. 3a, which shows the surface swelling of 1 μm height due to lower density of the laser-graphitized diamond [25]. At the front side (FS) surface, a crater of several micron depth was formed by laser ablation.

The microstructural properties of the laser-modified regions were examined using micro-Raman and photoluminescence (PL) spectroscopy at the 488 nm excitation wavelength. Raman and PL spectra were measured mainly on the back side of diamond plates. The laser light was focused onto the surface in a spot of 2-μm-diameter, the spectra were recorded at room temperature.

Raman and PL spectra of the original diamond plate are shown in Fig. 3b. The Raman spectrum is characterized by a single narrow line at 1332 cm^{-1}, revealing a high phase and structural quality of the single crystal. In the PL spectrum, a zero-phonon line of the NV defect at 575 nm accompanied by a red-shifted phonon side-band is observed. In spite of the low concentration of the N impurity ([N] < 1 ppm) the N-related defects are still detectable by high-sensitive PL technique. Raman and PL spectra of the laser-modified diamond, measured in the center of the BS spot of the microstructure fabricated at $E = 1$ μJ and $f = 10$ kHz, are also shown in Fig. 3b. The broad band with two maxima at 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band) dominated in the Raman spectrum (see inset in Fig. 3b) is typical of amorphous carbon structures; e.g. similar spectra were observed for tetrahedral amorphous carbon (ta-C) films annealed at 1000–1100°C and characterized by high sp^3 content (80–85%) [26]. No essential luminescence is observed in the spot center.

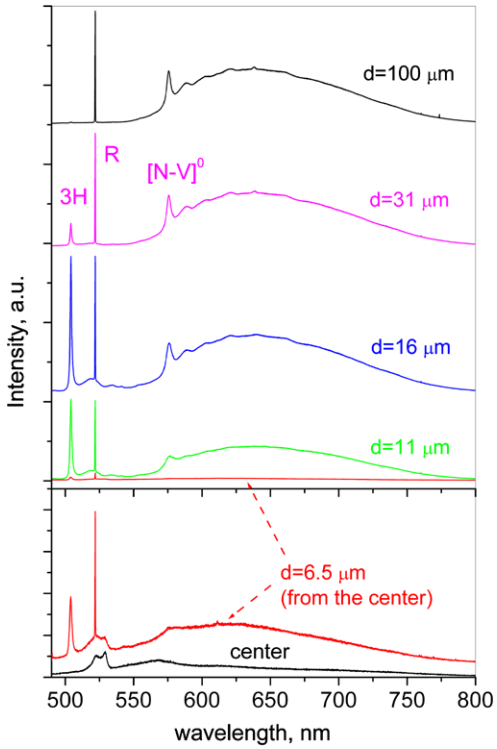

Fig. 4 PL spectra recorded at the BS surface and at different distances from the spot center as marked in Fig. 3a. Two PL spectra in the lower part of the plot are shifted for clarity. PL spectra in the upper part (at $d = 11$, 16, 31 and 100 μm) are also shifted for clarity along the Y-axis, and the two lowest spectra show a sharply enhanced intensity as the distance changes from $d = 6.5$ μm to $d = 11$ μm

Significant changes in the PL spectra are revealed as the laser probe is shifted away from the spot center (see Fig. 4). Particularly, the appearance of a strong PL line at 504 nm is observed, which is identified as PL from the 3H center, related to one of the configurations of self-interstitial defects and usually observed in diamonds irradiated by high-energy electrons [27–29]. The PL characteristics of the 3H center are the zero-phonon line at 504 nm and a weak vibronic structure consisting of at least four local modes (clearly seen in the PL spectrum 'at $d = 16$ μm' in Fig. 4) [27, 28]. It also follows from Fig. 4 that the 3H centers migrate at a distance of tens of micrometers away from the bulk microstructure similar to the migration of 3H defects in electron-irradiated diamonds [27, 28].

The 3H luminescence is observed in a wide variety of natural, HPHT and CVD diamonds irradiated with electrons of high energies ranged from a few hundred keV to MeV [27, 29], but the data are lacking on the formation of the 3H centers by irradiation with ultrashort lasers. We believe that the finding of the ps-laser-induced formation of the 3H defect centers in high-purity CVD single-crystal diamond supports the role of avalanche impact ionization in the mechanisms of optical breakdown and structure modification in the bulk of diamond. However, the mechanism of the 3H center formation during bulk microstructuring of diamond with ps-pulses is not clear and requires further investigations. Other questions of interest are related to the possibilities of using ultrashort laser pulses for creation and control of other optical centers (vacancies, NV defects), which are considered highly promising for quantum information applications [30].

4 Conclusions

Bulk modification and microstructuring of single-crystal diamonds have been studied using an advanced ps-laser system which showed excellent performance in fabricating high-aspect-ratio microstructures ('graphitized' microchannels) in mm-thick diamond plates. Raman and PL spectroscopy studies of the bulk microstructures have evidenced the diamond transformation to amorphous carbon and graphitic phases and the formation of radiation defects pronounced in the PL spectra as the self-interstitial related center, the 3H center, at 504 nm. The picosecond-laser-induced structural modifications in the bulk of single-crystal diamond are found to occur along {111} planes, known as the planes of the lowest cleavage energy in diamond. Based on the data obtained, it is concluded that the character of the bulk modifications, induced by ultrashort pulses of different durations (in the range of 10 ps to 100 fs), is controlled by the anisotropy of the strength of diamond.

Acknowledgements The authors are grateful to E.V. Zavedeev for the surface profile measurements. The work was supported by the SNSF project IZ73Z0-128088/1.

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