

Irradiation of Diamond-like Carbon Films by Picosecond Laser Pulses

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The picosecond laser irradiation of diamond-like carbon (DLC) film on the silicon was investigated. The DLC films were irradiated by Nd:YVO₄ laser with the infrared (1064 nm, fluency 1.02 J/cm²) and ultraviolet (355 nm, fluency 0.79 J/cm²) wavelengths with 1, 10, and 100 pulse numbers per spot. The energy dispersive X-ray spectroscopy and microRaman spectroscopy measurements indicated that the full ablation area of the DLC was narrower than laser beam radius of the 1064 nm wavelength with 10 and 100 pulses. The increase of the oxygen concentration was obtained near the ablation areas after irradiation with the first harmonic. The microRaman and SEM measurements demonstrated that the DLC film was fully ablated in the laser spot when the third harmonic was used. The formation of silicon carbide (SiC) in the center of the irradiated spot was found after 100 pulses.

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1. Introduction

The surface modification of solids by various laser pulses has been studied for a wide range of materials [1-3]. Nowadays surface modification studies of the thin film semiconductors, especially amorphous carbon films by various types of energetic beams, including laser beam are of great technological and fundamental interest [4-10].

The unique physical, mechanical, optical, and electrical properties of amorphous carbon films, such as diamond-like carbon (DLC) or tetrahedral amorphous carbon (ta-C) are attractive for applications in microelectronics, sensor technologies, solar photonic, tribological and biomedical fields [10-12]. It was demonstrated that it is possible to create periodical structures or ripple patterns not only on target surfaces of various materials, but even on surfaces with various semiconductors films such as DLC, SiC, GaN, and etc [4, 7-9]. Recent researches showed that DLC periodic structures have potential applications in lithography or high density data storage [7].

Lasers induced processes in amorphous carbon films, especially on the surface are influenced by the film material properties (sp² and sp³ sites fraction, hydrogen concentration) and laser parameters (wavelength, pulse duration, number of pulses, repetition rate etc.) [12-19]. Y. Dong et al. [13] reported that the ablation threshold of DLC films decreases with increasing number of pulses. T. Roch et al. [9, 14] demonstrated that the direct laser interference patterning of ta-C films reduce the coefficient of friction up to ~30 %. N.T. Panagiotopoulos et al. [6] observed the formation of SiC at the a-C:H film/Si interface and film graphitization, when 35 ps laser irradiation with the 1064 nm and 266 nm, respectively, was used. P. Patsalas [12] managed to vary the structural features and optical properties (refractive index) of a-C:H by picosecond laser radiation. G.Miyaji et al. [7, 16] demonstrated the nanostructure formation on the DLC surface irradiated at low fluence of femtosecond laser pulses.

The ablation and modification of the DLC films by the nanosecond laser pulses are stipulated by the thermal processes and are already well widely investigated. Meanwhile the 2D and 3D nanostructuring of the surfaces with picosecond laser pulses is attractive and promising tool. Although the physical and thermal processes induced in the DLC films by ps laser pulses are not understood yet and well explained. So far no satisfactory researches have been made investigating the picosecond laser pulses effect on the DLC films.

To investigate the influence of the picosecond laser beam wavelength and pulse number on the surface morphology and structure of the DLC films were the main purpose of the work was.

2. Experimental setup

The diamond-like carbon (DLC) film was deposited on the silicon substrate by radio frequency chemical vapour deposition technique using acetylene gas. The thickness of the DLC film was ~300 nm, the refractive index was 2.03, hardness was ~25 GPa, Young's modulus - 190 GPa. The DLC film was irradiated with a picosecond Nd:YVO₄ laser (Ekspla PL10100) using the first (1064 nm) and the third (355 nm), harmonics. The irradiation was performed using the 1.02 J/cm² and 0.79 J/cm² fluency for the first and the third harmonics, respectively. The pulse duration was 10 picoseconds, while the repetition rate was 100 kHz. The radius (r) of the laser beam spots, measured at 1/e² level were 30 μm and 15 μm for the first and the third harmonics, respectively. The pulse number was 1, 10, and 100 per spot. The films surface morphology was investigated by scanning electron microscope (SEM) JEOL JSM6490LV. The irradiated films were analyzed using microRaman spectroscopy (Renishaw inVia spectrometer, 633 nm, 100 s, 1 mW, spot size 2 μm). The energy dispersive X-ray spectroscopy (EDS) (Bruker Quad 5040 spectrometer) was used for the measurement of elemental composition.

3. Results and discussions

The spectrum of the non-irradiated DLC indicates a D (1274 cm^{-1}) and G (1499 cm^{-1}) peaks (Fig. 1). The full width at half-maxima (FWHM) of the D band (ΔD) was 217 cm^{-1} , while FWHM of the G band (ΔG) was 174 cm^{-1} . The integral intensity I_D/I_G ratio was 0.53. Such I_D/I_G ratio is typical for the DLC films, indicating that the sp^3 C-C sites fraction are dominating among the sp^2 carbon [11].

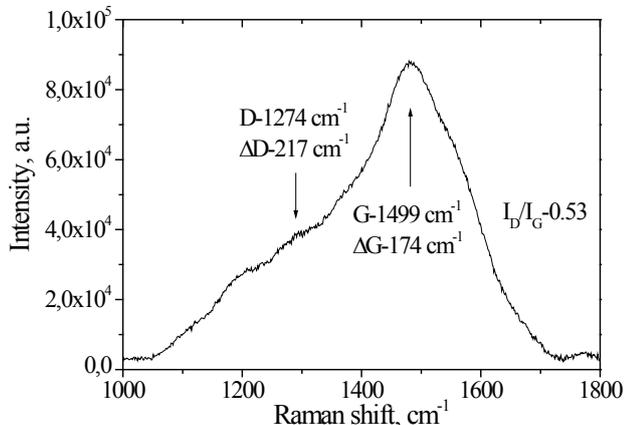


Fig. 1 μ Raman spectrum of the DLC film.

The EDS results of the DLC film before and after laser irradiation are given in the Table 1. It should be noted that the EDS was measured in the depth exceeding the film thickness. The d parameter indicates the distance (radius)

Table 1 Elemental compositions of the DLC film/substrate before and after laser irradiation by 1064 nm

| Pulse number | Distance from the spot center, μm | C, at. % | O, at. % | Si, at. % |
|--------------|--|----------|----------|-----------|
| DLC | - | 55.1 | 2.0 | 42.9 |
| 1 | $d \leq 15$ | 21.8 | 4.1 | 74.1 |
| 1 | $d \geq 15$ | 58.0 | 4.3 | 37.7 |
| 10 | $d < 10$ | 5.6 | 4.6 | 89.8 |
| 10 | $15 \leq d \leq 30$ | 49.9 | 5.6 | 44.5 |
| 100 | $d < 10$ | 2.9 | 1.1 | 96.0 |
| 100 | $20 \leq d \leq 40$ | 18.0 | 30.3 | 51.7 |
| 100 | $d > 40$ | 41.7 | 16.3 | 42.0 |

from the laser spot center, where EDS measurements were performed.

The irradiation of DLC film by the first harmonic with a single pulse at 1.02 J/cm^2 partly removes the film from the Si substrate. The ablated spot diameter is about $30\text{ }\mu\text{m}$ (Fig. 2a). Splats of DLC films still could be found at higher imagination on the surface. The carbon concentration decreased down to 21.8 at.%, while oxygen increased twice (Table 1). Also such laser fluency influenced to the formation of the chaotically distributed ripples (Fig. 2a). The various size micro-fragments outside the ablated area are chaotically distributed. The elemental composition is similar to non-radiated film in radius zone of $15\text{ }\mu\text{m} \leq d \leq 30\text{ }\mu\text{m}$ from the center. The melted Si substrate zone (with diameter of $\sim 30\text{ }\mu\text{m}$) appeared with the increase of the

number of pulses up to 10. The melted silicon area is surrounded by the micro-ripple pattern zone (Fig. 2b). The carbon content decreased down to 5.6 at.%, while the oxygen concentration increased up to 4.6 at.% in the melted zone.

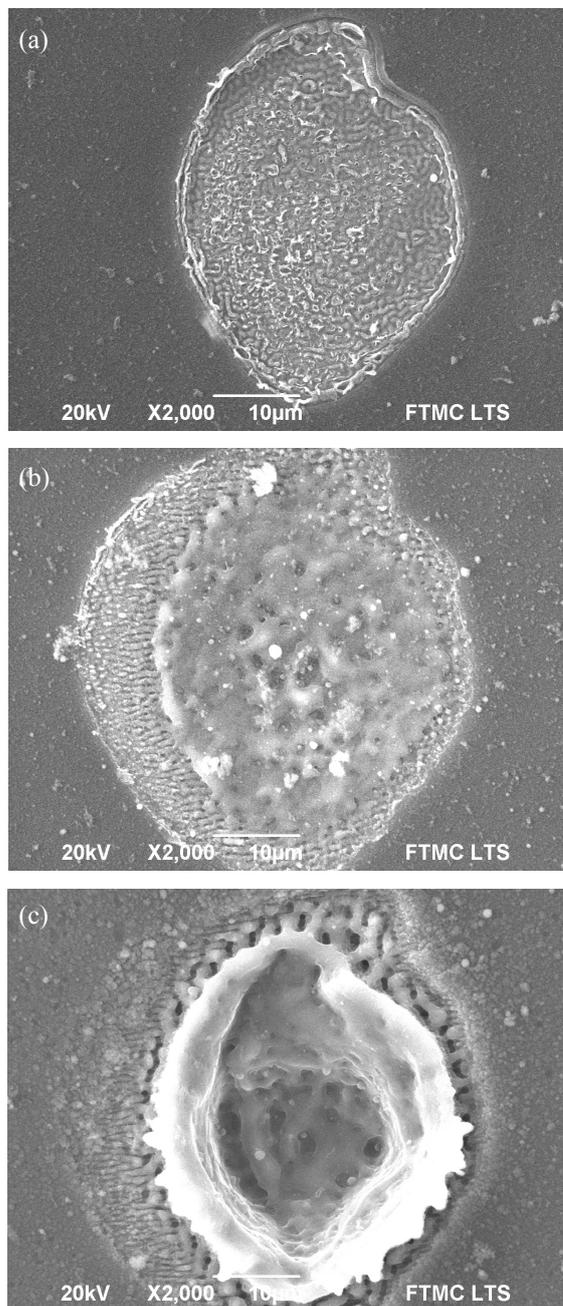


Fig. 2 Surface morphology of DLC films irradiated by the first harmonic with 1.02 J/cm^2 at different laser pulses a) 1, b) 10, and c) 100.

The hole of $10\text{ }\mu\text{m}$ depth and $\sim 20\text{ }\mu\text{m}$ diameter was observed after irradiation with 100 pulses. EDS results indicated very low amount of carbon (2.9 at.%) and oxygen (1.1 at.%). However similar to 10 pulses per spot, the narrow ripple zone around the hole also was formed (Fig. 2c). EDS measurements showed only 18 at.% of carbon and high concentration (30.3 at.%) of oxygen in the radius area $20\text{ }\mu\text{m} \leq d \leq 40\text{ }\mu\text{m}$ from the center. It should be noted that even at $d > 40\text{ }\mu\text{m}$ away from the spot center the oxygen

fraction was higher compared to the non-affected DLC film (Table 1).

The μ Raman spectrum measured from the spot center irradiated by 100 laser pulses indicates the low intensity D (1335 cm^{-1}) and G (1591 cm^{-1}) peaks, and intense broad band at $\sim 960\text{ cm}^{-1}$ (Fig. 3 b). The broad band can be deconvoluted into several Gaussian peaks. The peak around 960 cm^{-1} is attributed to the Si (2nd order) and the peak around $980\text{-}1020\text{ cm}^{-1}$ corresponds to the stretching mode of Si-O-Si configuration in which Si atoms were in turn back bonded to the oxygen atoms [20-21]. The EDS and RS measurements confirmed that DLC film was removed in the laser spot center. Existence of low intensity D and G peaks can be conditioned feedback DLC fragments after films spallation. Moreover, it is also probably that the low amount of carbon is dissolved into Si substrate. The D (1338 cm^{-1}) and G (1588 cm^{-1}) peaks became separated in the μ RS spectrum measured at the $20\text{ }\mu\text{m} \leq d \leq 40\text{ }\mu\text{m}$ zone (Fig. 3a). The Δ D peak narrowed to 127 cm^{-1} , while Δ G narrowed to 101 cm^{-1} . As a result of this, I_D/I_G ratio increased up to 1.27. The increase of the I_D/I_G ratio represents a reduction of the amount of sp^3 C-C sites and an increase of the amount of the graphite structure [11]. The appearance of the low intensity peaks at $\sim 1120\text{ cm}^{-1}$ and $\sim 1480\text{ cm}^{-1}$ are assigned to trans-polyacetylene segments at grain boundaries [20, 22]. These results indicate that the modified film is composed from a mixture of sp^3/sp^2 sites with dominant sp^2 C=C sites and formation of the nanocrystalline graphite or glass carbon phase.

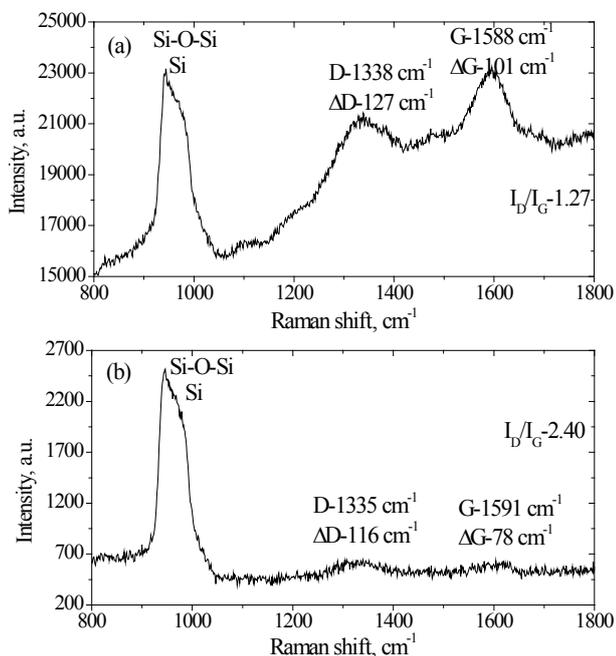


Fig. 3 μ Raman spectra of the DLC film irradiated by the 1064 nm laser beam by 100 pulses (a) near ablated zone, (b) spot center.

The irradiation by the first harmonic demonstrated the increase of the ablation area with the increase of the pulse numbers. The radius of ablation zone was smaller than the radius of the laser beam spot measured at $1/e^2$ level. The DLC film fully ablation occurs only in the 15-20 μm radius area depending on the pulse number.

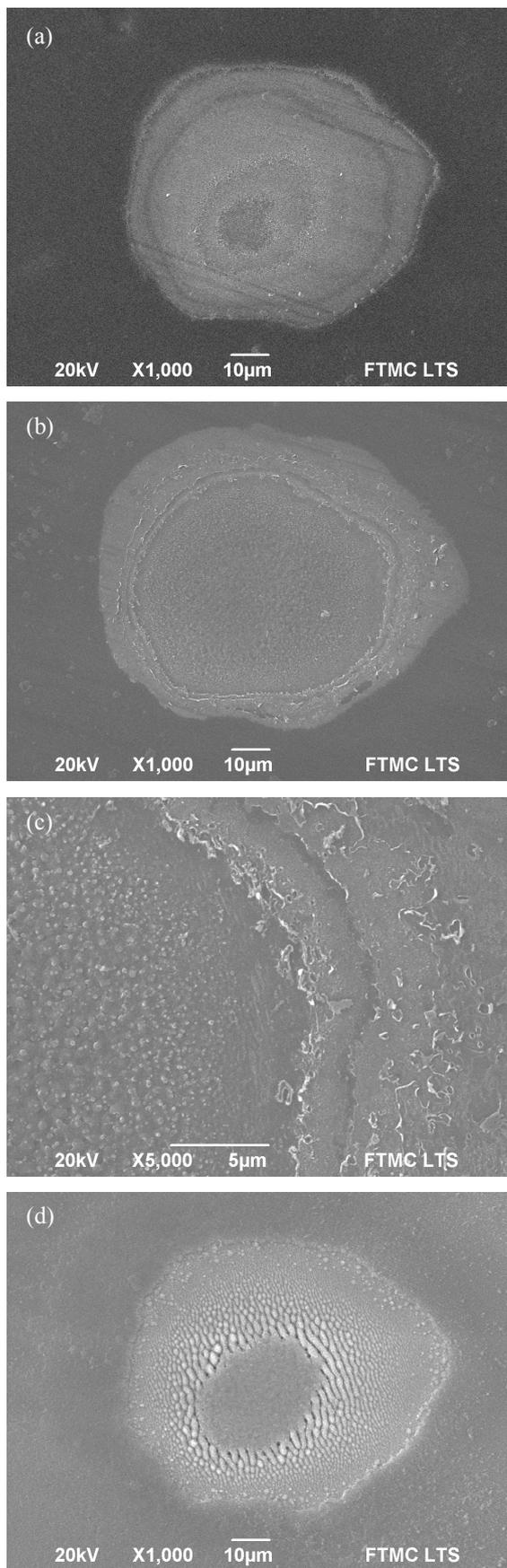


Fig. 4 Surface morphology of DLC films irradiated with 355 nm at various laser pulses a) 1, b) and c) 10, d) 100.

The explanation of obtained results is related with band gap of the irradiated DLC film and Si substrate. The photon

energy (1.165 eV) of the laser beam is below the energy band gap of DLC (1.5 – 2 eV) film, for the case of the 1064 nm wavelength, but it is above the band gap of Si (1.11 eV). Thereby the laser photons can pass through DLC film and then be absorbed by silicon substrate inducing local annealing. The increase of the pulse number rises the temperature in the irradiated zone, which induces melting of the Si and formation of pinholes in the substrate as well.

The irradiation of the DLC film with a single pulse at 0.79 J/cm² induced the uneven ablation and slight stratification of the film (Fig. 4a). The DLC film was ablated and Si substrate was local melted in the area of ~60 μm diameter when irradiation by 10 pulses per spot was used (Fig. 4b). The ablated zone is surrounded by the terrace-like relief (Fig. 4c). The appearance of such structure demonstrates the multilayer delamination.

Different morphology depending on the position in the laser spot is observed at the surface after 100 pulses (Fig. 4d). In the radius of the laser spot $d \leq 15 \mu\text{m}$, the energy fluence was high to ablate the DLC film and to melt and ablate the silicon substrate. The DLC layer was ablated and the formation of non-regular ripples around the melted Si was observed ($15 \mu\text{m} \leq d \leq 30 \mu\text{m}$). The DLC film was ablated and micro size fragments on the surface were distributed at position $30 \mu\text{m} \leq d \leq 40 \mu\text{m}$ (Fig. 4d). The μRaman spectrum of the melted and ripples formation areas showed a broad peak (~960 cm⁻¹) indicating amorphous/nanocrystalline Si and Si-O-Si sites [20]. Also a broad low intensity peak at ~820 cm⁻¹ was observed (Fig. 5). The peak at 820 cm⁻¹ is attributed to the silicon carbide (SiC) [6, 23]. The μRaman spectrum does not demonstrate any D and G peaks, indicating that the film is completely ablated.

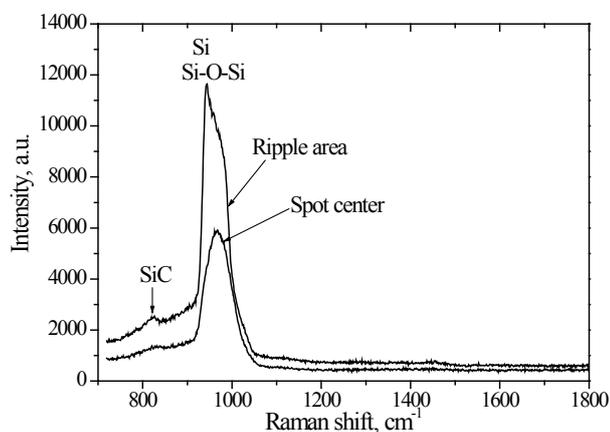


Fig. 5 μRaman spectra of the DLC film irradiated with the 355 nm laser beam by 100 pulses.

The DLC film was modified at the distance higher than $d \geq 40 \mu\text{m}$. The spectrum of modified carbon film is composed from the superposition of separated D (1349 cm⁻¹) and G (1576 cm⁻¹) peaks (Fig. 6). The appearance of the peak at 1473 cm⁻¹ is related to the trans-polyacetylene segments [20]. However, this peak can be related to the A₁ mode for five membered rings [24]. The position of D and G bands shifted to higher wave numbers, and both peaks narrowed, compared to non-irradiated DLC film (Fig. 6). The I_D/I_G ratio increased from 0.53 up to 1.31. The rise of

the D band and peaks splitting are the indication of the graphitization of the DLC film [18].

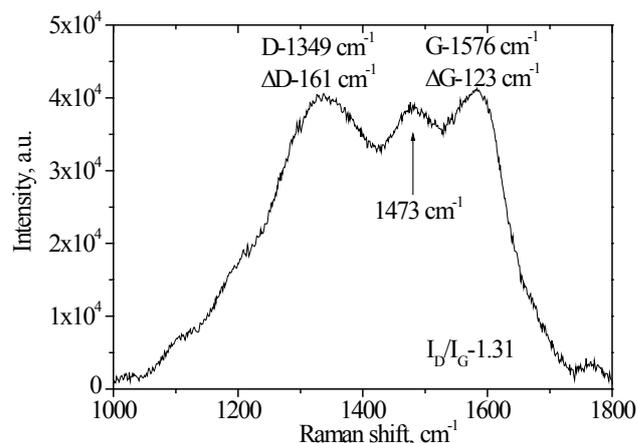


Fig. 6 μRaman spectrum of the DLC film after irradiation with the 355 nm laser beam by 100 pulses at $d > 40 \mu\text{m}$ distance.

The irradiation of the 355 nm laser beam resulted in the fully DLC ablated zone radius twice larger than the laser spot radius at 1/e² level. The dimension of the ablated DLC zones increases with the increase of the number of the pulses. The increase of the ablation zone related to the laser beam wavelength. The photon energy of the 355 nm laser beam is ~3.5 eV. Thus the photon energy is higher than the energy band gap of DLC film and Si substrate as well as above the spectral energy of the π-π* interband transition. It will result the strong optical absorption in the volume of the carbon film and laser annealing of the DLC film. The annealing of the a-C:H film by the 266 nm laser beam was obtained by N.T. Panagiotopoulos et al. [6].

The laser photon energy is absorbed by the film, not reaching the silicon substrate when one pulse is used. The delamination of the film after one pulse reflects the spatial distribution of Gaussian beam intensity. The fluency of 0.79 J/cm² was enough to reach the melting temperature and start the evaporation of the DLC in the center of laser spot. The Gaussian energy distribution of the laser beam resulted non-homogeneous heating and temperature distribution in the film. The ablated area is increasing with the number of laser pulses due to accumulation of the energy. The irradiated DLC film is graphitized, the swelled surface is removed and finally the energy is transformed to the Si substrate resulting to the melting and partly ablation (Fig. 4d). G. Miyaji et al. [16] obtained changes in the bonding structure from DLC to graphite carbon certainly proceeds the ablation to form the nanostructures. T. Roch [14] found that at low fluences (<500 mJ/cm²) the ablation rate is low and the surface swelling (graphitization) is dominating compared to the film ablation. However in our case, the fluence of 0.79 J/cm² was high enough to induce the graphitization of the film and when partly ablate the film even after one pulse.

4. Conclusions

The radius of ablated zone was smaller than the radius of the laser beam spot measured at 1/e² level when the first

harmonic (1064 nm) was used. The DLC film was removed from the laser spot center ($d < 15 \mu\text{m}$) after irradiation with 1064 nm by 10 pulses and 1.02 J/cm^2 fluence. The irradiation of the 355 nm laser beam by 10 and 100 pulses per spot resulted in the fully DLC ablated zone radius twice larger than the laser spot radius. The irradiation with the third harmonic resulted to the delamination of the DLC. The picosecond laser irradiation stipulated graphitization of the DLC film near the ablated areas. The degradation of the Si substrate was minimized, and the area of the DLC film ablation was enlarged by the decrease of the laser wavelength. The investigations demonstrated that the ablation of the DLC proceeded due to the annealing of the Si substrate when the 1064 nm wavelength was used. Meanwhile, the irradiation with the third harmonic directly ablated the DLC film.

Acknowledgments

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