Laser modification of high-pressure high-temperature nanodiamonds

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Abstract. Micro-thin semitransparent films of purified high pressure high temperature nanodiamonds were produced on a glass substrate. A focused 632.8 nm He-Ne laser irradiation is shown to cause an emission of light in the green region of the optical spectrum accompanied with laser-induced blackening of the obtained films. Possible mechanisms of the observed phenomenon are discussed.

1. Introduction

Recently, investigations of laser radiation interactions with carbon nanostructures revealed interesting and useful phenomena [1–4]. One of the most interesting carbon nanostructures is nanodiamonds (NDs), which are attractive for many applications due to their unique mechanical, chemical, thermal and optical properties [5]. For example, use of focused laser radiation can trigger physical and chemical processes that lead to a local laser-induced modification of the surface of the ND material [6]. Such modification may be of interest for obtaining various microstructured optical plates, which are diffractive optical elements, various scales and grids, limbs, rasters, etc [7–9].

It is well known that NDs synthesized using hydraulic presses at high pressure and high temperature (HPHT) [10] contain nitrogen-vacancy [N-V] defects (neutral [N-V]⁰ and negatively charged [N-V]⁻), which consist of one nitrogen atom N in a substitutional position and one carbon vacancy [V] [11]. These centers show particularly strong electronic transitions, allowing optical detection of individual centers [12]. The HPHT NDs can also contain a number of nickel related optical centers [13,14]. These centers can affect the laser modification of HPHT NDs, depending on the wavelength. In this paper, we show that low-power laser irradiation of HPHT ND films at 632.8 nm leads to transformation of the sp³-carbon of NDs into sp²-carbon. Such transformation is accompanied by luminescence in the green spectral region and a significant decrease in the luminescence level in the Stokes region. This phenomenon can be explained by photoionization of [Ni-N] and [N]-centers leading to the formation of electrons in the conduction band of the ND film and an increase of the local temperature of the sample transforming the NDs into sp²-carbon.

2. Characterization of the films

HPHT NDs with an average size of 150 nm were used in the experiments. The particles obtained from the vendor (Diamond Innovations, USA) were first purified from sp²-carbon by treatment in air at 500 ºC for 2 hours followed by treatment in HCl at 70 ºC for 2 hours. The particles were dispersed in deionized water at 1 wt% concentration and the suspensions were stored in plastic vessels. Films with
a thickness of 20 \( \mu \text{m} \) (see figure 1a) were prepared by drying the ND suspension on a glass substrate at ambient conditions. Figure 1b shows the extinction spectrum of the 0.5 \( \mu \text{m} \)-thick HPHT ND film on a quartz substrate, recorded relative to an identical quartz substrate. The spectrum is determined by the absorption and scattering of light by the film nanoparticles and film inhomogeneities which arise due to the method of production not ensuring the uniformity of the film thickness. It is seen that the extinction spectrum has a maximum at a wavelength of 208 nm, due to single-photon absorption between the valence band and the conduction band of diamond. The photon energy corresponding to this maximum is 5.96 eV, which is higher than the energy of the forbidden band gap of a bulk diamond (5.6 eV). Figure 1b also shows that with increasing wavelength, the extinction of the film decreases monotonically, which is explained by the decrease in Rayleigh light scattering by ND particles and film inhomogeneities with the increasing light wavelength.

Figure 1 (a, b, c). (a) Photo of 20 \( \mu \text{m} \) thick HPHT ND film on a quartz substrate; (b) Extinction spectrum of the 0.5 \( \mu \text{m} \)-thick HPHT ND film on a quartz substrate, recorded relative to an identical quartz substrate; (c) Raman spectrum of ND film.

Figure 1c shows the Raman spectrum of an arbitrarily selected point on the ND film measured by a Horiba HR800 Raman spectrometer at \( P = 5 \) kW/cm\(^2\), where \( P \) is excitation power density of 632.8 nm laser radiation. It can be seen that the presented spectrum consist of a broad luminescence band and one sharp peak with a frequency shift of about 1331 cm\(^{-1}\), which coincides with the frequency shift of bulk crystalline diamond with \( sp^3 \)-hybridization [15]. Note that Raman shifts of NDs depend on the exciting laser wavelength and the average size of nanoparticles [16,17], and varies in the range 1325-1331 cm\(^{-1}\) [18].
Figure 2a shows a typical image of the surface of the ND film, obtained with a scanning electron microscope (SEM) Inspect S50. One can see the granular structure of the film surface. The characteristic size of the particles in the suspension used to prepare the film measured by dynamic light scattering using a Malvern Zetasizer ZS device is about 150 nm (see figure 2b).

Figure 2 (a, b). (a) SEM image of the HPHT ND film surface; (b) the ND particles size distribution.

3. Experimental section

Experiments on laser modification of HPHT ND films were carried out using a He-Ne laser at the wavelength of 632.8 nm, embedded in a Horiba HR800 Raman spectrometer in a backscattering geometry. In these experiments the HPHT ND film was located on the coordinate stage (see figure 3a). Using an objective, laser radiation was focused on the surface of the film. Laser modification of the films was carried out while the film was moved relative to the focused laser beam using the coordinate stage. The maximum $P$ of laser radiation on the surface of the films under study did not exceed 65 kW/cm$^2$.

Figure 3 (a, b, c). (a) The sketch of the experiment on laser modification of HPHT ND film using focused laser radiation; images of laser exposure area at (b) $P = 14$ kW/cm$^2$ and (c) $P = 65$ kW/cm$^2$.

The emission from the surface of the film during laser modification was recorded using a Canon photocamera after passing through a color optical filter to attenuate the 632.8 nm laser radiation, reflected from the film surface (see figure 3).

4. Results and discussion

Experiments have shown that when the ND film is irradiated by laser radiation with $P > 33$ kW/cm$^2$, blackening can occur on the film surface in the area of the laser beam waist. We note that this blackening occurs only when the film is moving relative to the laser beam, i.e. when the film is
motionless and irradiated by laser radiation with $P > 33 \text{ kW/cm}^2$ no blackening is observed. Visual observation of the area irradiated by the laser beam through a glass filter, according to the scheme presented in figure 3a, showed that the blackening of the film is accompanied by blue-green emission (see figure 3c). Photographs of the waist region of a focused laser beam taken with the camera (see figure 3a) at $P = 14$ and 65 kW/cm$^2$ are shown in figure 3b,c. It was found that at $P < 33 \text{ kW/cm}^2$, the camera registers only the red glow of the laser, and at $P > 33 \text{ kW/cm}^2$, green emission is observed from the waist area, accompanied by blackening of the film. It should be particularly noted that repeated long-term irradiation of the blackened area of the film at the maximum $P = 65 \text{ kW/cm}^2$ does not generate any emission.

Figure 4a illustrates the Raman spectra measured for three different points located on the $x$-axis perpendicular to the symmetry line of the laser-modified (blackened) region of the film (the symmetry line is parallel to the $y$-axis) (see figure 4b, inset). Here, the coordinate $x = 0$ is the intersection point of the $x$-axis and the line of symmetry. The Raman spectra were recorded at $P = 5 \text{ kW/cm}^2$ using a 100$\times$ objective. It can be seen that the spectra obtained at $|x| > 2 \mu$m contain a pronounced diamond peak with a frequency shift of 1331 cm$^{-1}$. In the Raman spectrum of the point $x = 0$, the diamond peak is absent (see figure 4a, curve 3). Instead, the Raman spectrum shows two distinct peaks with frequency shifts of 1320 and 1580 cm$^{-1}$, characteristic for $sp^2$-carbon. Figure 4(b) shows the ND peak intensity as a function of the $x$ coordinate. It can be seen that this dependence in the first approximation is symmetrical relative to the point $x = 0$. In addition, it is clearly seen that the decrease in the ND peak intensity occurs for points with coordinate $|x| < 10 \mu$m.

Thus, during the movement of a laser beam spot with $P > 33 \text{ kW/cm}^2$ relative to the HPHT ND film the transformation of ND particles into $sp^2$-carbon can occur which is accompanied by a green emission. Partial transformation of ND particles into $sp^2$-carbon also occurs in the region adjacent to the waist, the size of which is several times larger than the waist diameter.

Though the structural transformation of $sp^3$ to $sp^2$-carbon was previously observed [19] while irradiating powders of detonation nanodiamonds [20,21] with continuous radiation from a 325 nm He-Cd laser ($P = 1300 \text{ W/cm}^3$), such transformation was due to high-temperature heating with strong absorption of the incident radiation by the ND particles. In our case the result could not be explained by simple high-temperature heating. Firstly, in figure 5, the Raman spectra are presented of arbitrarily
selected points on the motionless film, which were irradiated for different periods of time by laser radiation with $P = 65$ kW/cm$^2$ (before measuring the Raman spectrum). The spectra were all measured at the same $P = 65$ kW/cm$^2$. All of the spectra contain the ND peak, with approximately the same intensity. This means that irradiation of the motionless film with focused laser radiation at the maximum $P = 65$ kW/cm$^2$ for a long time does not lead to blackening and structural changes. Secondly, the process of laser modification of the film surface is accompanied by a blue-green emission (see figure 3c). Thirdly, we found that after blackening of the film has occurred repeated irradiation of the same segment of the film at the maximum $P$ does not lead to any further visible changes. Furthermore, it is known that the HPHT NDs can contain Ni and N impurity complexes [13,22–25]. This means that in the studied HPHT NDs there is a set of energy levels that provide the possibility of the absorption of one or two photons at 633 nm. When absorption occurs, the upper-levels of the energy transitions of the Ni centers and the Ni – N complexes get populated, which can lead to the emission in the blue-green region due to various mechanisms of up-conversion luminescence. Simultaneously with this process, ionization of impurity centers, similar to the ionization of the [N-V] - centers during laser irradiation may occur [12,26]. As a result, free electrons are generated in the zone of laser exposure, which begin to effectively absorb the incident laser radiation. These processes lead to the fact that the temperature of the material in the zone of laser exposure increases sharply to significant temperatures, leading to the transformation of the diamond material into $sp^2$-carbon, i.e. to blackening of the material under study. Subsequent laser irradiation of the blackened area devoid of impurity centers does not result in multi-photon absorption, and due to the low $P$ of the laser radiation, the film cannot be heated up to a high temperature resulting in thermally induced light emission, as was reported by Osswald et al. [19]. Obviously, the Ni – N complexes scattered randomly on the film surface that explain the fact that blackening occurs only when the film is moving relative to the laser beam. In addition, recently, it was reported on intense broadband white emission with maximum at 620 nm obtained from the irradiation of HPHT diamonds by focused beam of 975 nm laser diode lead, suggesting that the white light emission may originate from the laser-induced $sp^2 \leftrightarrow sp^3$ hybridization change as a result of the mechanism analogous to the intervalence charge transfer in Sr$_2$CeO$_4$ nanocrystals [27].

5. Conclusions

Thus, we have shown the possibility of modifying films obtained from HPHT NDs using low-power He-Ne laser radiation at 632.8 nm. Laser modification occurs due to the transformation of the diamond material into $sp^2$-carbon and is accompanied by the emission of light in the blue-green region.
of the optical spectrum. The possibility of laser modification of HPHT NDs is explained by photon absorption at 633 nm, leading to the ionization of the impurity complexes of Ni and Ni – N contained in diamond nanoparticles.

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