

LETTERS

PACS numbers: 42.30.Va; 78.67.–n; 81.05.uj; 81.07.Bc
DOI: 10.1070/QE2014v044n01ABEH015299

Laser image recording on detonation nanodiamond films

G.M. Mikheev, K.G. Mikheev, T.N. Mogileva, A.P. Puzyr, V.S. Bondar

Abstract. **A focused He–Ne laser beam is shown to cause local blackening of semitransparent detonation nanodiamond (DND) films at incident power densities above 600 W cm^{-2}. Data obtained with a Raman spectrometer and low-power 632.8-nm laser source indicate that the blackening is accompanied by a decrease in broadband background luminescence and emergence of sharp Raman peaks corresponding to the structures of nanodiamond and sp^2 carbon. The feasibility of image recording on DND films by a focused He–Ne laser beam is demonstrated.**

Keywords: *detonation nanodiamond, films, laser blackening, Raman scattering, luminescence, image recording.*

1. Introduction

Optical instrument-making often uses various microstructured plates, such as diffractive optical elements, diverse scales and grids of optical instruments, dials and lens arrays. To produce such optical components, wide use is made of thermochemical microstructuring via visible cw laser beam scanning [1, 2]. Basic to this approach is an effect first described by Veiko et al. [3]: the formation of a latent image in thin chromium films under laser irradiation at a power density below that needed for partial melting of the film. For latent image development, use is made of a selective chemical etchant, which removes the unirradiated part of the chromium film. A surface microprofile of diffractive optical elements on quartz glass substrates can also be produced via laser ablation of thin molybdenum films, which serve as a mask in inductively coupled plasma reactive ion etching [4]. To obtain diffractive structures on metallised dielectric substrates, use can be made of the selective evaporation of metallic film as a result of the interference of two coherent high-power laser beams [5]. Laser microstructuring is also possible on diamond surfaces because, above a certain energy density, pulsed laser radiation produces a graphite-like surface layer [6–8].

Meanwhile, great scientific and technological advances have been made to date in studies of carbon nanomaterials for various applications, including laser engineering and optoelectronics. In particular, single-wall carbon nanotube (CNT) saturable absorbers are used for passive Q-switching of lasers (see e.g. Ref. [9]); fullerene solutions, CNT suspensions, and graphene dispersed in liquids are employed for optical power limiting (see e.g. Ref. [10]); and a fundamentally new laser polarisation analyser, which includes no optical components, has been created using nanographite film [11].

The purpose of this work is to demonstrate the conceptual feasibility of laser image recording on films of detonation nanodiamond, a type of carbon nanomaterial.

2. Inherent features of detonation nanodiamond

Detonation nanodiamond (DND), first synthesised in Russia in 1963 from carbon of high explosives [12], possesses a number of unique properties, which allow one to develop technologies for its application in various areas of industry, science, technology and medicine [13–16]. The specifics of detonation synthesis are such that there are impurities (nitrogen, silicon, oxygen, hydrogen, various metals, hydrocarbon fragments, and functional groups) on the surface of primary nanodiamond crystals of average size 4–5 nm [15], which have a tendency to agglomerate to form larger particles. For this reason, suspensions of DND powders become unstable over time even after ultrasonic processing. Chemical cleaning allows one to reduce the surface impurity concentration and obtain rather stable aqueous suspensions by merely stirring DND powder in deionised water, with no sonication [17]. The DND suspensions thus prepared exhibit nonlinear light absorption and scattering and can be used for optically limiting the laser beam power [18, 19].

DND samples for this investigation were prepared from commercially available nanoparticles (Real-Dzerzhinsk Ltd., Russia). To purify the samples, the DND powder was suspended in deionised water by sonication, and then a NaCl solution was added. This procedure reduced the surface impurity concentration, thereby improving the colloidal stability of the nanoparticles, and enabled differential centrifugation. We used DND powder samples with an average particle size of 38, 50, 110, and 320 nm as determined by dynamic light scattering measurements with a Malvern Zetasizer Nano ZS system (the characteristics of the DND powders were reported in greater detail previously [19]). To prepare aqueous suspensions of predetermined concentration, an appropriate volume of deionised water was added to a weighed amount of the purified DND powder. Films ranging in thickness from 1 to 8 μm were obtained on fused silica or glass substrates 7×7 mm in dimensions through the vaporisation of

G.M. Mikheev, K.G. Mikheev, T.N. Mogileva Institute of Mechanics, Ural Branch, Russian Academy of Sciences, ul. T. Baramzinoi 34, 426067 Izhevsk, Russia; e-mail: mikheev@udman.ru;
A.P. Puzyr, V.S. Bondar Institute of Biophysics, Siberian Branch, Russian Academy of Sciences, Akademgorodok 50/50, 660036 Krasnoyarsk, Russia

Received 28 August 2013; revision received 21 October 2013
Kvantovaya Elektronika **44** (1) 1–3 (2014)
Translated by O.M. Tsarev

the liquid phase of the DND suspension at room temperature. In contrast to films grown by aerosol-assisted deposition [14], the DND films produced by the above procedure were discontinuous and consisted of many semitransparent islands of various shapes, typically 100×150 μm in dimensions. The transmittance of a 7.7-μm-thick DND film at the He–Ne laser wavelength, λ_{exc} = 632.8 nm, was measured to be 42%.

3. Experimental results and discussion

The DND films were exposed to laser light of wavelength λ_{exc} focused by $10^{\times}$ and $50^{\times}$ objectives. The optical axis of the objectives was normal to the film surface, oriented horizontally. The laser-spot diameter on the film surface, measured with a CCD camera, was 25 and 6 μm for the $10^{\times}$ and $50^{\times}$ objectives, respectively. The laser beam power at the output of the objectives, measured with a calibrated photodetector, was in the order of 8.5 mW.

In our experiments, short-term laser irradiation of the films (by opening and closing a mechanical shutter in front of the objective as fast as possible) led to blackening of the exposed surface area. Laser blackening was observed on all the films prepared from the aqueous DND suspensions, independent of DND particle size (see above). At laser light powers under 3 mW, the laser beam focused by the $10^{\times}$ objective caused no blackening of the 7.7-μm-thick films. Therefore, the threshold incident intensity for film blackening was about 600 W cm^{-2}.

With the mechanical shutter open, manually displacing a film in the horizontal plane at a speed of about 8 mm s^{-1} and incident power of 8 mW we obtained a continuous blackening line. This allowed us to estimate the time needed for film blackening, which was determined to be about 1 ms. Figure 1a shows a square written on a DND film by a laser beam. A diffraction grating written on a film in a similar way is shown in Fig. 1b.

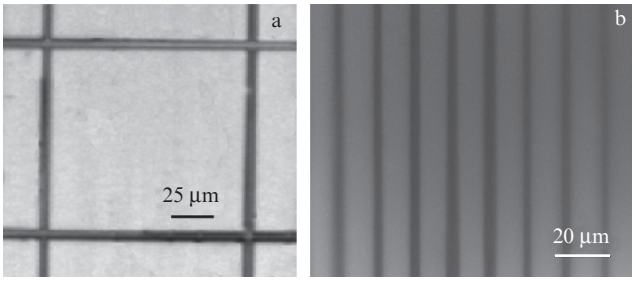

Figure 1. Images of a (a) square and (b) diffraction grating written on a detonation nanodiamond film by a focused He–Ne laser beam.

Figure 2 shows Raman spectra (Horiba Jobin Yvon HR 800 Raman spectrometer) of a film area before [spectrum (*1*)] and after [spectrum (*2*)] laser blackening. The spectra were taken under laser excitation at a wavelength λ_{exc} = 632.8 nm, using a $100^{\times}$ objective to focus the laser beam. The laser beam power at the output of the objective was several times lower than the threshold power for film blackening. The Raman spectrum of the unirradiated DND film has very weak features [spectrum (*1*)]. The Raman spectrum of nanodiamond under excitation at λ_{exc} = 632.8 nm has long been known to contain no sharp peaks [20]. The reason for this is that DND particles contain high densities of various defects and vacancies [21], which give rise to broadband background luminescence (with a maximum at a wavelength of ~630 nm under excitation at a wavelength of 532 or 543 nm [22, 23]). The Raman spectrum of the blackened film area shows two peaks, at Raman shifts of 1326 and 1591 cm^{-1} [spectrum (*2*)]. The Raman shift observed in previous studies of DND [24–27] under excitation in the green spectral region or at shorter wavelengths lies in the range 1325–1329 cm^{-1}. It differs slightly from the Raman shifts of the sharp peaks of CVD nanodiamond films (1330 cm^{-1} [28]) and bulk crystalline diamond (1332 cm^{-1}), which consist of sp^3 carbon. The known dependences of the Raman shift on excitation wavelength [20] and nanoparticle size [25, 26] for carbon nanomaterials lead us to conclude that the peak observed at a Raman shift of 1326 cm^{-1} corresponds to nanodiamond (sp^3 carbon). A similar analysis of the present results and data in the literature (see e.g. Mochalin et al. [25]) suggests that the Raman peak at 1591 cm^{-1} in the spectrum of the blackened area of the DND film corresponds to sp^2 carbon.

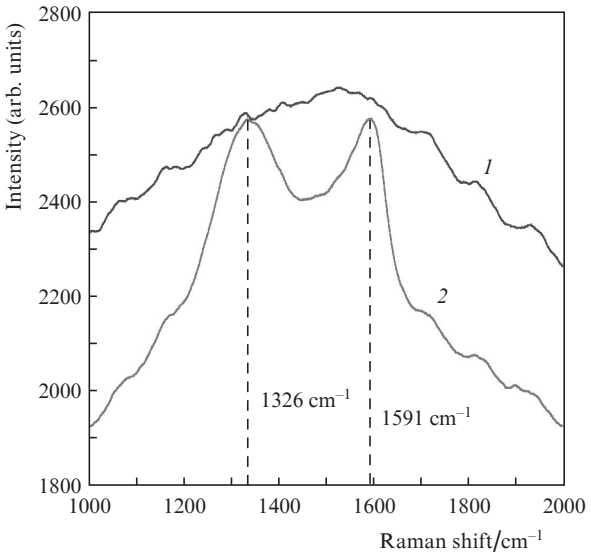

Figure 2. Raman spectra of an area of a detonation nanodiamond film (*1*) before and (*2*) after laser irradiation; excitation wavelength, 632.8 nm.

Analysis of the luminescence of defects in nanodiamond films [22, 23, 29, 30] and the optical properties of DND [31] suggests that the present results can be accounted for in terms of laser annealing of the DND films. The annealing leads to the decay and reduces the density of various defects and functional groups in the nanoparticles, which luminesce in the red spectral region. Laser annealing may also result from the photoionisation of some defects in DND [32] and functional groups on its surface. Such annealing reduces the disguising luminescence level and produces a sharp Raman peak corresponding to nanodiamond particles. In addition, local heating of the film by the laser beam probably causes some of the DND to transform into sp^2 (nondiamond) carbon, which increases the optical density of the film. The possibility of this transformation has been demonstrated in Refs [33, 34]. We believe that the above factors are responsible for the two peaks (1326 and 1591 cm^{-1}) dominating the Raman spectrum of the blackened areas at λ_{exc} = 632.8 nm.

The present results demonstrate conceptual feasibility of laser image recording on films produced form DND suspensions. This approach to image recording is possible at considerably lower incident power densities (by thousands of times), in contrast to the laser-assisted thermochemical synthesis of optical elements on chromium films [1, 2]. It requires no vacuum system for producing thin films on a substrate and no selective chemical etching for developing the latent image produced by exposing a chromium film to a laser beam. It is worth noting however that the ability to produce high-quality images by the proposed method will depend crucially on advances in the technology of large-area, homogeneous DND films with good adhesion to substrates, which will be the subject of further investigation.

Thus, the present experimental data demonstrates that exposure to a low-power He–Ne laser beam causes local blackening (an increase in the optical density) of semitransparent DND films. In the future, this effect will possibly be used to record images via blackening of a semitransparent film under the effect of a laser beam scanned in a programmed manner. The conceptual feasibility of such recording has been demonstrated in this study by the examples of a square and diffraction grating written on DND films.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 13-02-96016 r_ural_a) and the Presidium of the Ural Branch of the Russian Academy of Sciences (Project No. 12-C-1-1003).

References

1. Veiko V.P., Korol'kov V.I., Poleshchuk A.G., et al. *Kvantovaya Elektron*., **41**, 631 (2011) [*Quantum Electron*., **41**, 631 (2011)].
2. Koronkevich V.P., Poleshchuk A.G., Churin E.G., Yurlov Yu.I. *Kvantovaya Elektron.*, **12**, 755 (1985) [*Sov. J. Quantum Electron.*, **15**, 494 (1985)].
3. Veiko V.P., Kotov G.A., Libenson M.N., Nikitin M.I. *Dokl. Akad. Nauk SSSR*, **208** (3), 587 (1973).
4. Volkov A.V., Moiseev O.Yu., Poletaev S.D. *Komput. Opt.*, **37** (2), 220 (2013).
5. Mikheev G.M., Zonov R.G., Kalyuznyi D.G. *Izv. Vyssh. Uchebn. Zaved., Priborostr*., **47** (8), 62 (2004).
6. Kononenko V.V., Kononenko T.V., Pimenov S.M., et al. *Kvantovaya Elektron.*, **35** (3), 252 (2005) [*Quantum Electron*., **35** (3), 252 (2005)].
7. Kononenko V.V., Komlenok M.S., Pimenov S.M., Konov V.I. *Kvantovaya Elektron*., **37** (11), 1043 (2007) [*Quantum Electron*., **37** (11), 1043 (2007)].
8. Komlenok M.S., Kononenko V.V., Ralchenko V.G., et al. *Phys. Procedia*, **12**, 37 (2011).
9. Tausenev A.V., Obraztsova E.D., Lobach A.S., et al. *Kvantovaya Elektron*., **37**, 847 (2007) [*Quantum Electron*., **37**, 847 (2007)].
10. Lim G.-K., Chen Z.-L., Clark J., et al. *Nat. Photonics*, **5**, 554 (2011).
11. Mikheev G.M., Styapshin V.M. *Prib. Tekh. Eksp*., (1), 93 (2012).
12. Danilenko V.V. *Fiz. Tverd. Tela*, **46**, 581 (2004).
13. Dolmatov V.Yu. *Usp. Khim*., **70**, 687 (2001).
14. Feoktistov N.A., Sakharov V.I., Serenkov I.T., et al. *Zh. Tekh. Fiz*., **81** (5), 132 (2011).
15. Mochalin V.N., Shenderova O., Ho D., Gogotsi Y. *Nat. Nanotechnol.*, **7** (1), 11 (2012).
16. Samsonova Yu.S., Priezzhev A.V., Lugovtsov A.E., et al. *Kvantovaya Elektron*., **42**, 484 (2012) [*Quantum Electron*., **42**, 484 (2012)].
17. Bondar V.S., Puzyr A.P. *Fiz. Tverd. Tela*, **46**, 698 (2004).
18. Mikheev G.M., Puzyr A.P., Vanyukov V.V., et al. *Pis'ma Zh. Tekh. Fiz*., **36** (8), 23 (2010).
19. Vanyukov V.V., Mogileva T.N., Mikheev G.M., et al. *Appl. Opt*., **52**, 4123 (2013).
20. Ferrari A.C., Robertson J. *Philos. Trans. R. Soc. London, Ser. A*, **362**, 2477 (2004).
21. Say J.M., Vreden C., Reilly D.J., et al. *Biophys. Rev*., **3**, 171 (2011).
22. Chung P.-H., Perevedentseva E., Cheng C.-L. *Surf. Sci*., **601**, 3866 (2007).
23. Shalaginov M.Y., Naik G.V., Ishii S., et al. *Appl. Phys. B*, **105**, 191 (2011).
24. Dubois M., Guerin K., Petit E., et al. *J. Phys. Chem*., **113**, 10371 (2009).
25. Mochalin V., Osswald S., Gogotsi Y. *Chem. Mater*., **21**, 273 (2009).
26. Vlasov I.I., Shenderova O., Turner S., et al. *Small Group. Res.*, **6**, 687 (2010).
27. Zou Q., Wang M.Z., Li Y.G. *J. Exp. Nanosci.*, **5**, 319 (2010).
28. Zolotukhin A.A., Ismagilov R.R., Dolganov M.A., Obraztsov A.N. *J. Nanoelectron. Optoelectron.*, **7**, 22 (2012).
29. Rabeau J.R., Stacey A., Rabeau A., et al. *Nano Lett*., **7**, 3433 (2007).
30. Doherty M.W., Manson N.B., Delaney P., et al. *Phys. Rep.*, **528**, 1 (2013).
31. Aleksenskii A.E., Vul' A.Ya., Konyakhin S.V., et al. *Fiz. Tverd. Tela*, **54**, 541 (2012).
32. Manson N.B., Harrison J.P. *Diamond Relat. Mater.*, **14**, 1705 (2005).
33. Geis M.W., Rothschild M., Kunz R.R., et al. *Appl. Phys. Lett*., **55** (22), 2295 (1989).
34. Pimenov S.M., Shafeev G.A., Konov V.I., Loubnin E.N. *Diamond Relat. Mater.*, **5**, 1042 (1996).