Formation of micro-and nanostructures under the influence of femtosecond laser radiation on carbon samples in liquid nitrogen

K S Khorkov, D A Kochuev, V A Ilin, R V Chkalov and V G Prokoshev

Vladimir State University, 87 Gorky Street, Vladimir 600000, Russia

E-mail: freeod@mail.ru

Abstract. The paper presents the results of an experimental study of carbon nanostructures and microcrystals formation under the influence of femtosecond laser radiation in liquid nitrogen. In addition to the formation of carbon nanopeaks on the surface, graphene exfoliation, it is possible to form carbon microcrystals due to the mechanism of the subsurface overheating.

1. Introduction

Pulsed laser ablation in liquids contributes to the formation of a wide range of nanomaterials in the colloidal state, including metal particles, metal oxides, semiconductors, as well as the production of carbon nanomaterials with unique chemical structures, different shapes and sizes [1]. Obtaining stable colloidal solutions and carbon structures by laser radiation is possible for the production of materials without impurities [2-4].

Use for laser synthesis of carbon targets allows to obtain a wide and diverse range of possible nano-allotropes. A unique variety of structures can be obtained by combining sp²- and sp³-hybridized carbon atoms, as well as, for example, through the use of morphological transformations of sp²-sheets of graphene [5]. In addition to the large variety of allotropic carbon and composite structures that have been characterized experimentally, there are many that have been predicted to exist (especially at high pressures) and are expected to have unusual properties and excellent potential applications [6].

Processes, accompanied by a rapid increase of temperature and pressure, as well as their rapid decrease, are highly unsteady. In this case, it is difficult to talk about the carbon phase diagram which makes sense only for equilibrium states. Under the conditions of exposure, accompanied by an additional laser-induced mechanism - the subsurface overheating of the substance, it is possible to form an intermediate metastable state. At that, it is possible to form a local layer of liquid carbon at high pressure, which allows the synthesis of crystalline carbon structures. The subsurface overheating up to several thousand degrees and the achievement of critical pressure values during the action of a sequence of laser pulses allow the creation of non-equilibrium conditions initiating a phase explosion accompanied by the formation of single-crystal carbon micro-and nanostructures.

A deeper understanding of the processes occurring during laser ablation of solids in liquids opens up opportunities for more efficient synthesis of nano- and microcrystals, where the main factors affecting the formation process are pressure, temperature, raw and the composition of the medium in which the synthesis occurs.
2. Experimental technique

In our experiments we used two femtosecond laser systems: Ytterbium laser system (wavelength $\lambda=1030$ nm, radiation pulse duration $\tau=280$ fs, pulse repetition rate $f=10$ kHz, pulse energy $E_{\text{max}}=150$ $\mu$J) and Titanium-sapphire laser system (wavelength $\lambda=800$ nm, radiation pulse duration $\tau=50$ fs, pulse repetition rate $f=1$ kHz, pulse energy $E_{\text{max}}=1$ mJ). For experiments of processing and micro-nanostructuring of materials by ultrashort laser pulses, a hardware-software laser complex (Figure 1) was developed, combining a number of required technical components and having a single interface for controlling the component elements of the setup. Also the software was developed and the scheme of precision controlled treatment by femtosecond laser radiation of materials for the formation of micro- and nanostructures was implemented [7].

![Figure 1. Scheme (a) and femtosecond laser micromachining complex (b):](image)

3. Results

At the processing of HOPG samples with Ytterbium laser system were obtained graphene sheets (size more than 150 microns), tapes (width up to 50 microns and a length of more than 150 microns); at the glass carbon samples processing – arrays of crumpled graphene (size of the order of 1 microns). It was found that the formation of graphene under the influence of femtosecond laser radiation on carbon samples in liquid nitrogen occurs by the following mechanisms: 1) breaking of weak interplanar $\pi$-bonds due to heating of intercalated nitrogen in the graphite lattice; 2) separation of the surface layers of the target due to the formation of a high pressure region in the walls of the laser cavity [8-10].

At the processing with Ti-Sapphire laser system the diameter of the focused laser spot on the sample surface was about 80 $\mu$m. The laser fluence reached 50 J/cm$^2$ with gaussian distribution. The output laser radiation through the periscope was filed in galvanoscanner enabling the processing of the sample surface at a set rate. For mounting the carbon sample and the subsequent cooling was collected outdoor cryostat, allowing to lock the sample. After thermal stabilization of the sample (cooling), laser radiation treatment was performed at a variable thickness of the liquid nitrogen layer.

It should be noted that when choosing a sample (HOPG or glassy carbon) similar types of nanostructures are formed. However, the ordered formation of nanopics is observed during the processing of the glass carbon sample (Figure 2,a). At the laser processing of pyrolytic graphite arrays of nanostructures with characteristic sizes from 30 nm to 100 nm were obtained on the surface. Meanwhile, the location of nanostructures on the HOPG surface can’t be considered orderly, as in the case of laser processing of samples from glass carbon (Figure 2,b). This occurs as a result of the fact that a single graphite layer, of which pyrolytic graphite is composed, is not able to become the basis of arrays of nanostructures, it is destroyed. Also, there are numerous gaps and pores on the irradiated surface. The edges of breaks and pores often have traces of melting. Linear structures formed from
fused nanostructures are registered. Such structures can be formed if the gap coincides with the boundary of a separate series of carbon nanopics.

Figure 2. SEM-images of formed nanostructures on the surface of carbon samples:

a) glassy carbon, b) HOPG

Under the regimes of action accompanied by subsurface overheating of the substance initiating a phase explosion, it is possible to form an intermediate liquid state. The effect of laser radiation on the sample leads to the separation of sufficiently thick layers of pyrographite. In case of femtosecond laser action on carbon samples in liquid nitrogen, the effect of subsurface overheating occurs, which is confirmed by experimental data and simulation results. On the basis of SEM-images, it is shown that the depth of formation of the subsurface overheating region, where the crystals were registered, was 200-300 nm, the estimated calculation was less than 1 \( \mu \)m [11].

A model of subsurface overheating under laser action on carbon samples in liquid nitrogen was also developed. The model allows to make a qualitative assessment of the temperature distribution in the volume of the material. The temperature distributions as a result of energy transfer to the target material and the imposition of the thermal effect in the bulk sample from a series of laser pulses are simulated. The simulation results confirm the phenomenon of subsurface overheating [12].

Carbon microcrystals of different shapes and sizes 1÷10 \( \mu \)m were obtained in liquid nitrogen under the influence of titanium-sapphire laser system radiation on carbon samples (Figure 3).

Figure 3. SEM-images of different forms of carbon crystal structures formed under the action of femtosecond laser radiation in liquid nitrogen
The study of microcrystals obtained using scanning electron microscopy (Quanta 200 3D) and energy dispersive X-ray microanalysis (EDAX) showed the absence of any other elements except carbon. X-ray analysis did not allow to accurately determining the affiliation of the obtained structures to any group.

As an approach to determining the external shape of the obtained samples, a method for comparing the habitus with a set of growth polyhedra constructed within the framework of the model of layered growth of partitions and graphs for known crystal modifications of superhard carbon is proposed. As a periodic neighborhood graph on which layer-by-layer growth is realized, it is proposed to use a graph whose vertices coincide with carbon atoms of some diamond-like structure with edges corresponding to chemical bonds of atoms in the crystal structure, as well as subgraphs of this graph obtained by removing some edges. Figure 4 shows the dynamics of carbon crystal growth using the layer-by-layer growth method.

As a result, a set of polyhedra of layer-by-layer growth, called the spectrum of polyhedra of layer-by-layer growth of the crystal structure, is obtained for one structure. Based on the model compared the external shape of the obtained carbon monocrystals, the spectra of the polytopes of layer-by-layer growth of M-carbon (spatial symmetry group C2/m, a=9.089 Å, b=2.496 Å, C=4.104 Å and β=96.96º) is constructed [13].

4. Conclusion
In addition to the fundamental nature of the search for new possible crystalline forms of carbon, their description, study of the mechanisms of formation and the conditions under which they can be obtained, the study of carbon structures can lead to the discovery of allotropic forms of carbon with improved mechanical and electronic properties. The development of a new method for the synthesis of superhard allotropic forms of carbon, the production of "new diamonds", is an important direction of research in the field of materials science and laser physics, as a means of obtaining conditions for the formation of new carbon forms.

5. Acknowledgements
This work was performed as a part of Vladimir State University’s State Task 3.5531.2017/8.9 GB-1106/17.

References
[1] Al-Hamaoy A, Chikarakara E, Jawad H et al 2014 Appl Surf Sci 302 141-4
[2] Russo P, Hu A, Compagnini G, Duley W W and Zhou N Y 2014 Nanoscale 6(4) 2381–9
[3] Tsuji T, Kakita T and Tsuji M 2003 Appl Surf Sci 206(1) 314-20
[4] Chakif M, Essaidi A, Gurevich E et al 2014 Mater Eng Perform 23(7) 2482-6
[5] Tapia J I, Larios E, Bittencourt C et al 2016 Carbon 99 541-6
[6] Georgakilas V, Pernan J A, Tucej J and Zboril R 2015 Chem Rev 115(11) 4744-822
[7] Chkalov R V, Khorkov K S, Kochuev D A et al 2018 J Phys Conf Ser 1109(1) 012029
[8] Abramov D, Arakelian S, Kochuev D et al 2016 Nanosyst Physics, Chem Math 7(1) 220-5
[9] Ilin V A, Khorkov K S, Kochuev D A et al 2018 International Conference Laser Optics (ICLO) 421
[10] Khorkov K S, Kochuev D A, Ilin V A et al 2018 J Phys Conf Ser 951(1) 012014
[11] Khorkov K S, Abramov D V, Kochuev D A et al 2016 Phys Procedia 83 182-7
[12] Khorkov K S, Zvyagin M Y, Kochuev D A et al 2017 Bull Russ Acad Sci Phys 81(12) 1433-7
[13] Khorkov K S, Maleev A V, Chkalov R V et al 2018 J Surf Investig X-ray, Synchrotron Neutron Tech 12 392-4