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Formation monocrystalline carbon micro- and nanostructures under femtosecond laser irradiation of graphite in liquid nitrogen

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Abstract

The combination of high energy and ultra short duration of femtosecond laser pulses allow to reach in the area of impact the local conditions which can change the phase composition of irradiated material. Traditional methods of structural phase transformation of the graphite at high pressures do not provide the abrupt simultaneous cancellation of the applied pressure and temperature. As a result, some of the synthesized nanostructures and metastable forms of carbon are destroyed. The suggested method allows to eliminate this disadvantage. Femtosecond laser radiation provides ultrafast heating of the target material, and the use of liquid nitrogen dramatically accelerates the process of it cooling. The formation of new carbon micro- and nanostructures has been registered at experimental approbation of the proposed method. The check of elemental composition of the created crystals showed that they are formed solely of carbon. The experimental results show the possibility of creation of new (less studied) carbon forms with a variety of properties.

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1. Introduction

The variety of forms of carbon modifications is very large. A separate group consists of superhard form of carbon, such as diamond and longsdaleite (hexagonal diamond). The development of nanodiamond synthesis technology has made it possible to use them in a wide range of applications, such as in tribology, medicine delivery,

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biovisualization, tissue engineering, and others [1]. Numerous studies in the field of methods of synthesis of diamonds are aimed to simplifying and reducing the cost of technologies of superhard materials production for modern industry. Direct transformation of graphite into diamond is one of the most known structural phase transitions in condensed matter physics. But the main mechanism of this transformation is not fully understood, despite decades of experimental and theoretical studies. The presence of carbon atoms in various hybridized states proves the possible existence of less studied carbon forms with various electronic and mechanical properties. Therefore, the interest in searching new forms of crystal carbon has been growing for the recent years.

Numerous calculations and modeling works show existence of various hypothetic forms of carbon structures, such as bct-C4, K4-, M-, H-, R-, S-, T-, W-, Z-carbon and others [2-8]. These structures are the most important element for solving the age-old challenge of understanding the phase transformation of graphite into diamond under high pressure and high temperature. The study of the so-called M-carbon takes a special place. The article [9] deals with a monoclinic structure with C2/m symmetry, as a low-energy polymorph, which is more profitable under the pressure of more than 13.4 GPa. This crystal carbon form and diamond can be compared by their hardness. Earlier monoclinic structures were obtained by generating more covalent bonds between the graphite layers in conditions of high pressure. According to the calculations in [10] the structure C2/m-carbon is dynamically stable at pressure from 0 to 100 GPa. In any case, the synthesis of new carbon forms requires the creation of conditions under which the formation of the energetically more advantageous structures can not be realized. The action of ultrashort laser pulses at low temperatures is a method that is able to provide such conditions. The set of processes that occur under the action of femtosecond laser radiation makes it possible to activate the mechanism of formation of carbon structures.

For example, one of the ways of obtaining the graphene structures is the method of laser-induced exfoliation of graphite in the liquid nitrogen medium with the use of ultrashort laser pulses [11]. In this case there is the possibility of formation of graphene structures of the two types. The first type is a multilayer graphene sheets and lengthy ribbon which can be used in devices of nanooptics. The second type is the crumpled graphene, which is preferred for use in devices of energy conversion and storage. The considered method allows to increase the productivity of producing of graphene by several orders of magnitude compared to other laser experiments [12]. Furthermore, the use of liquid nitrogen as the buffer medium may cause a spatial modulation of the laser intensity. This effect leads to the formation of ordered micro- and nanostructures on the surface of the irradiated materials.

2. Experimental Setup

Scheme of the experimental setup for generating carbon structures is shown in fig. 1. To produce carbon structures we used Ti-Sapphire femtosecond laser system *1* with following parameters: λ=800 nm, τ=50 fs, f=1 kHz, P_{avg}=500 mW. By means of periscope *2* the output laser radiation was put into galvanoscanner *3* enabling to treat the sample surface at the required speed. The diameter of the laser beam on the surface of the sample was about 80 µm, the intensity of laser radiation was up to $2\cdot10^{14}$ W/cm^2 and had distribution close to Gaussian. The carbon sample *5* was mounted in an open cryostat *4*. Laser treatment of the sample surface was carried out after thermal stabilization of system "sample-cryostat" in multipulse mode. Highly oriented pyrolytic graphite (HOPG) and glassy carbon were used as materials for experimental samples.

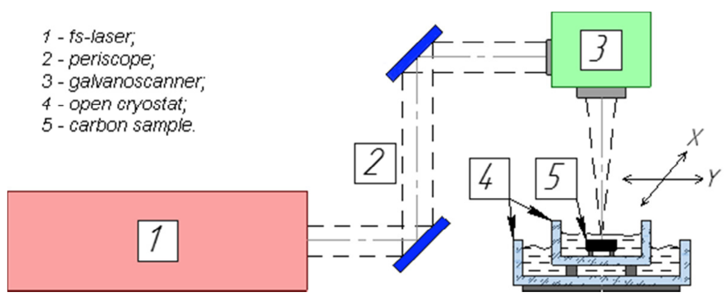

Fig. 1. Scheme of the experimental setup for generating carbon structures.