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Laser-induced local profile transformation of multilayered graphene on a substrate

V.D. Frolov [a,b], P.A. Pivovarov [a,b], E.V. Zavedeev [a,b], A.A. Khomich [a], A.N. Grigorenko [c], V.I. Konov [a,b,*]

[a] A.M. Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia
[b] National Research Nuclear University MEPhI, Kashirskoye sh. 31, Moscow 115409, Russia
[c] Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, Oxford Road, Manchester M13 9PL, UK

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ABSTRACT

Multi-layered graphene deposited on silicon wafer was irradiated in air by sequences of nanosecond laser pulses. It is shown that ultra-shallow craters (cavities) with depth of ~1 nm and microholes can be formed in graphene sheet on the substrate at laser fluence ~0.04 J/cm^2 well below the experimentally known graphene ablation threshold ≥0.25 J/cm^2. Influence of intensity and number of laser pulses on the depth and roughness of the cavities are described. We suggest that the observed effects are related to laser heating and boiling of the adsorbate at graphene-silicon interface.

1. Introduction

Precise processing of graphene is under active study nowadays. The aim is to develop a technique that allow to fabricate graphene micro- and nanostructures required for various applications of this prospective carbon material (see, e.g. [1–3]). In this connection precise laser nanostructuring of graphene layered on a substrate is of particular interest. Recently, a number of publications devoted to laser-induced structure modification (creation of defects) appeared [4–8]. A limited success was reported for laser ablation: either all graphene layers or selected areas of graphene sheet with the dominant number of layers could be removed by single laser pulses [8–11].

In the present work we found and investigated a novel regime of laser nanoprocessing (local nanoshaping) of graphene in which pulsed laser fluence is much lower than the values (≥0.25 J/cm^2) needed for high temperature heating and removing of graphene by a single laser pulse [9]. The principal condition for the observed profile variation in the irradiated area is a large number of laser pulses (accumulation effect). It should be noted that similar but at different origin accumulation effects were observed, for example, for low intensity ultra-precise (10^{-3}–10^{-1} nm/pulse) ablation of graphite, diamond and diamond-like films [12–14]. They were called nanoablation and are explained as a result of carbon material transformation by photoactivation.

2. Material and methods

Graphene sheets were prepared by a widely used technique – exfoliation and deposited on oxidized silicon [1] (SiO_2 thickness ~100 nm). The number of graphene layers was varied in the range 3–6 and verified by Raman spectroscopy [15]. Experiments on graphene transformation under a pulsed laser action were carried out in the scanning probe microscope (SPM) NTEGRA Spectra M (NT-MDT, Russia). Nd:YAG laser with wavelength λ=532 nm, pulse duration τ=7 ns and repetition rate f=1–2000 Hz was used for local light exposure. Laser beam was focused normally to the sample surface into a spot of ≈0.5 μm diameter at 1/e intensity level. Laser fluence was controlled by photodetector and could be varied in the E=0.01–0.1 J/cm^2 range by means of pump alteration and/or using neutral optical filters. Before and after laser irradiation, graphene surface relief was studied by atomic force microscopy (AFM) with silicon cantilever operated in tapping mode.

The major part of the experiments was carried out with fluence about E_0=0.04 J/cm^2 at fixed position of the beam waist at the sample surface. Graphene sheet transformations were produced by series of N=1–200 pulses in single pulse operation mode and of $N=3\times10^2$–1.8×10^6 pulses in frequency mode with repetition rate f=500 Hz. In addition, 2×2 μm^2 square surface scanning by focused laser beam was done. Pulse repetition rate during

* Corresponding author at: A.M. Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia. Tel.: +7 499 135 76 28.
E-mail address: konov@nsc.gpi.ru (V.I. Konov).

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scanning was $f=1000$ Hz, number of scan lines 512, scan velocity 5 s per line, total pulse number 2.56×10^6. With such samples, Raman spectroscopy at wavelength 488 nm with lateral resolution ~1 μm (LabRAM HR800) was used to compare structural properties of irradiated and non-irradiated graphene.

3. Results

Significant graphene surface relief changes had been found to appear when laser fluence reached threshold value $E=E_0\approx0.04$ J/cm^2. It should be noted that this value is about an order of magnitude less than ablation threshold for graphene $E_a\sim0.25$–0.8 J/cm^2 ($E_a\sim0.3$ J/cm^2 for 4 layer graphene) [9].

3.1. Surface relief transformations at the threshold fluence

During laser treatment with $E=E_0$, visible surface transformations occurred when pulse number exceeded $N\approx300$ value. Pulse quantities $N=300$–1500 led to formation of a crater (cavity) with irregularly located pits and the "rim" at the periphery (Fig. 1a and b). The diameter of the crater grew with pulse number increase until saturated at $N>1000$ at ≈1.2 μm value which significantly exceeds the laser beam diameter. The crater bottom became considerably flatter than the initial sample surface with further increase of N (Fig. 2).

The dependences of mean crater depth h and crater roughness (mean deviation) on the number of pulses N at $E=0.04$ J/cm^2 are shown in the Fig. 3 (thick and thin lines, respectively). The dashed line indicates roughness of the initial sample surface.

As could be seen, at $N=3\times10^2$–3×10^4 range the mean crater depth grows as $h\sim0.04\log(N)$ and saturates with further increase of N, $h\approx h_{sat}$ ($h_{sat}\approx2$ nm in this case). The speed of crater deepening is very small $\sim10^{-6}$-5×10^{-4} nm/pulse. At the same time, the roughness dependence has a minimum which is significantly lower than the roughness of unirradiated surface. At the first stage of multi-pulsed irradiation, the roughness increases which could be related to redistribution of defects and surface adsorbate as well as inhomogeneity of surface heating. The crater bottom becomes smoother with further growth of pulse number, so at $N=10^4$–10^5 its roughness is essentially below the initial value. After this, at extremely high exposition times ($N=1.8\times10^6$), roughness grows once again and surpasses the initial value.

For estimation of the structural changes using Raman spectroscopy, craters with larger lateral dimensions were made by means of scanning 2×2 μm^2 square graphene surface by the laser beam ($E=0.04$ J/cm^2).

Raman spectra analysis revealed paradoxical situation. After laser irradiation at $E=E_0$ we could find no significant change in graphene structure: the number of layers and quantity of defects stayed at the previous level. A number of graphene layers can be ascertained by relative intensities of G and 2D peaks and by the

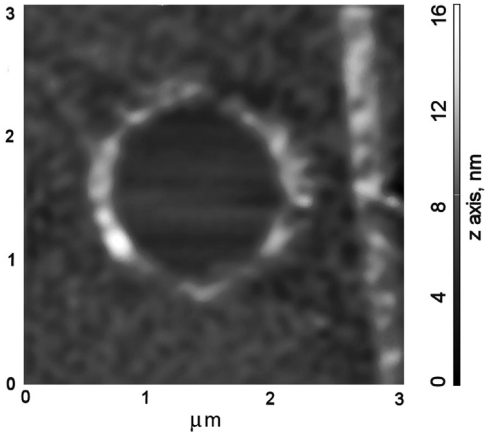

Fig. 2. AFM image of laser irradiated area at $E=0.04$ J/cm^2, high exposition time ($N=3\times10^5$).

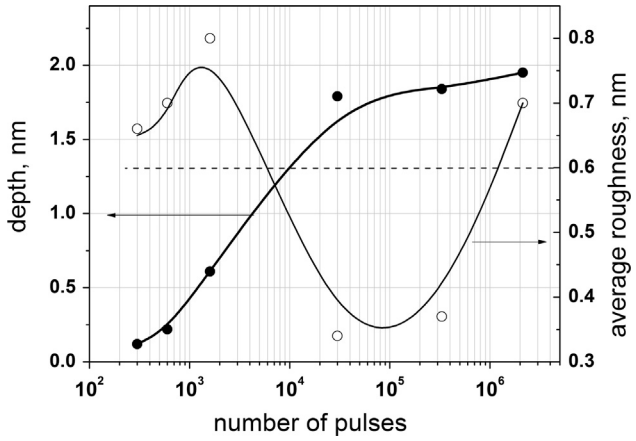

Fig. 3. Dependencies of mean crater depth (the thick line) and bottom roughness (the thin line) on pulse number, $E=0.04$ J/cm^2.

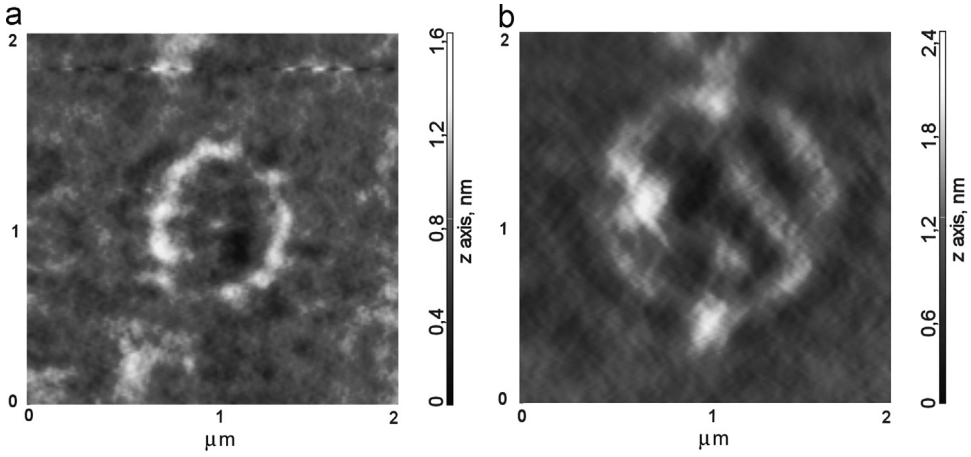

Fig. 1. AFM images of laser irradiated areas at $E=0.04$ J/cm^2: a) $N=300$; b) $N=1500$.