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STM observation of a box-shaped graphene nanostructure appeared after mechanical cleavage of pyrolytic graphite

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ABSTRACT

A description is given of a three-dimensional box-shaped graphene (BSG) nanostructure formed/uncovered by mechanical cleavage of highly oriented pyrolytic graphite (HOPG). The discovered nanostructure is a multilayer system of parallel hollow channels located along the surface and having quadrangular cross-section. The thickness of the channel walls/facets is approximately equal to 1 nm. The typical width of channel facets makes about 25 nm, the channel length is 390 nm and more. The investigation of the found nanostructure by means of a scanning tunneling microscope (STM) allows us to draw a conclusion that it is possible to make spatial constructions of graphene similar to the discovered one by mechanical compression, bending, splitting, and shifting graphite surface layers. The distinctive features of such constructions are the following: simplicity of the preparation method, small contact area between graphene planes and a substrate, large surface area, nanometer cross-sectional sizes of the channels, large aspect ratio. Potential fields of application include: ultra-sensitive detectors, high-performance catalytic cells, nanochannels for DNA manipulation, nanomechanical resonators, electron multiplication channels, high-capacity sorbents for hydrogen storage.

1. Introduction

From the moment of graphene discovery and until the present time, several methods of its preparation have been suggested [1–5]. Among the suggested methods, the method of mechanical exfoliation of graphene planes from highly oriented pyrolytic graphite (HOPG) [1,5] deserves a special mention since mechanical exfoliation of graphene planes apparently underlies mechanism of formation of the spatial box-shaped graphene (BSG) nanostructure described in the present work.

A surface of HOPG having unusual appearance is presented in Fig. 1 [6]. The surface has been either formed or uncovered after mechanical cleavage. As a rule, plane atomically smooth areas with sizes from several hundreds of nanometers to several microns are produced after cleaving this sort of graphite [7]. In the case considered, the graphite surface represents a multilayer system of parallel hollow channels which plane facets/walls are apparently graphene sheets.

A periodical microstructure that appeared after mechanical cleavage of HOPG is described in work [8]. The microstructure is a system of parallel folds periodically repeating through approximately 100 μm. The width of a fold area makes about 2 μm. The microstructure consists of several graphite layers and reaches 1–2 μm in depth. The microstructure and the detected nanostructure have some similarities: both structures extend in one dimension, periodically repeat, their folds are formed across the cleaving front, they both have layer shifts and channels with quadrangular cross-section. The observed similarities may imply similarity of the processes of formation of those surface structures, i.e., scalability of the phenomenon when passing from micrometer to nanometer fold sizes.

The main objectives of the presented work are

(1) Demonstration of the existence of BSG nanostructure.
(2) Analysis of the sizes and morphology of elements of BSG nanostructure.

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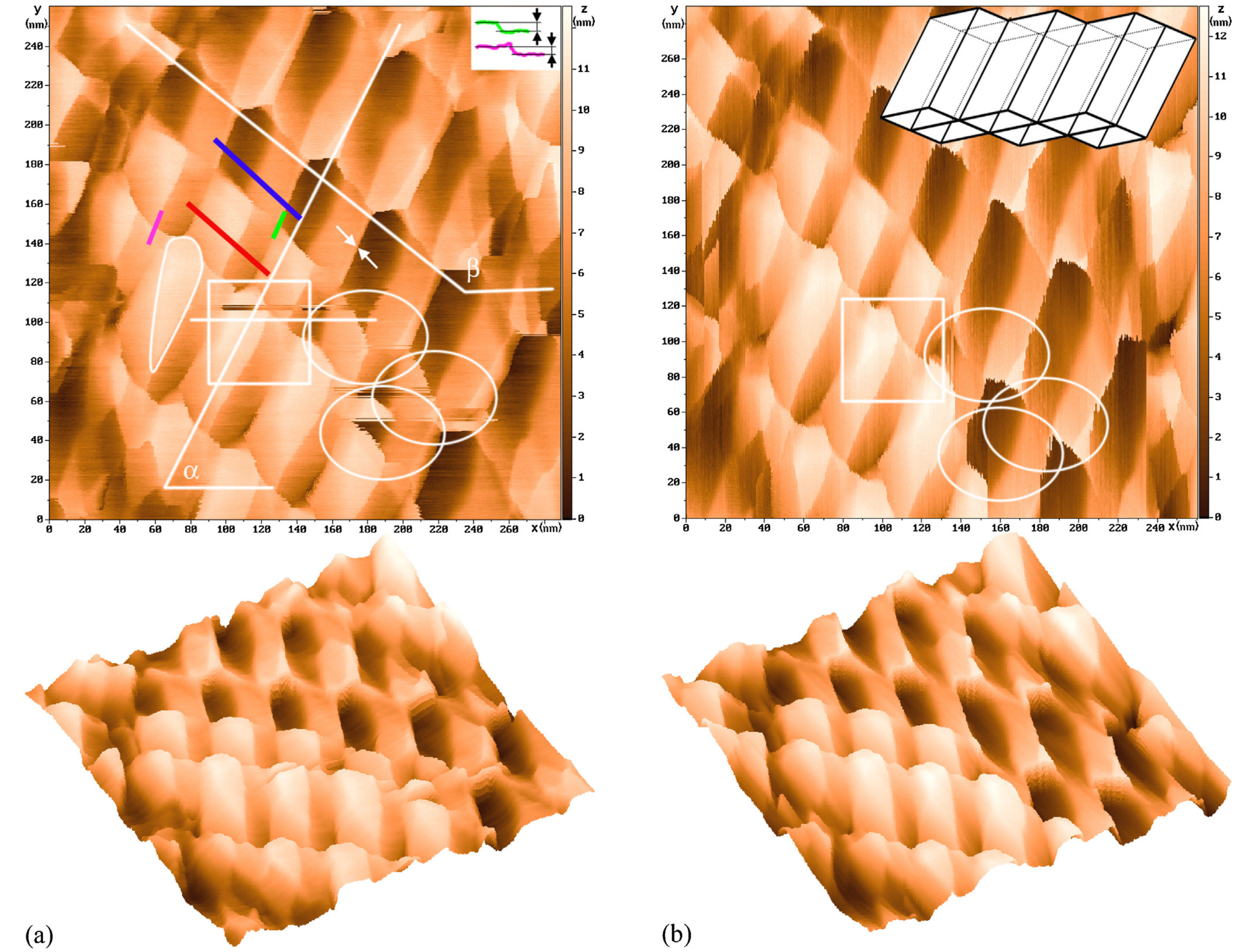

Fig. 1. 3D box-shaped nanostructure of graphene. The nanostructure represents a multilayer system of parallel hollow channels of a parallelogram shape in cross-section. A schematic view of the nanostructure is shown in the inset to figure part b. The wall/facet thickness (shown with white/black arrows) of the nanostructure channels makes about 1 nm. The 512×512 points STM-image is obtained in air in constant-current mode, U_{tun} = 50 mV (sample positive), I_{tun} = 890 pA. Fast-scan direction coincides with axis (a) *x*, (b) *y*. Structure regions inside the ovals became severely deformed as the direction of fast scanning had changed from *x* to *y*. Channel orientation $\alpha = 62.7^\circ$, orientation of the facet cuts of the open channels $\beta = 143.8^\circ$.

(3) Development of a possible mechanism (a qualitative model) of the BSG nanostructure formation.
(4) A brief estimation of the prospects of possible applications of BSG nanostructure (to prove the need of further research).

Theoretical analysis and computer modeling of the discovered nanostructure as well as attempts of its reproduction are planned to be implemented at the next stages of the research. Based on the study of the BSG nanostructure, possible areas of its application were defined: detectors, catalytic cells, nanochannels of fluidic devices, nanomechanical resonators, multiplication channels of electrons, hydrogen storage and some others.

The notions of a channel wall and a channel facet used below are close to each other. Wall, as a rule, refers to a flat surface common to two adjacent channels. Facets usually refer to outer flat surfaces of the upper channel layer.

2. Specimen and measurement method

HOPG (Research Institute of Graphite, Russia) with mosaic spread angle 0.8° (density 2.24 g/cm^3, purity 99.999%) was used as a specimen. The specimen was as thin as 0.3 mm strip of 2 mm×4 mm. Electrical insulation adhesive tape (KLL, Taiwan) of polyvinylchloride 0.13 mm in thickness was used for cleavage. The images of the BSG nanostructure of 512×512 points were obtained with the scanning tunneling microscope (STM) Solver™ P4 (NT-MDT Co., Russia) in the air at room temperature, in the constant current mode. The bias voltage made 50 mV (sample positive), the tunneling current 890 pA. A mechanically cut Ø0.3 mm NiCr wire was used in the capacity of the tip. The typical noise level of the tunneling current in the course of the measurements made about 20 pA (peak-to-peak).

3. Experimental observations

The following experimental facts point out the small thickness of the walls/facets of the detected nanostructure. First, the direct measurement of the wall thickness (see the white arrows in Fig. 1(a)) of an "open" channel gives a size of order of 1 nm (an open channel is the one that has no top facets). Second, the direct measurement of the facet thickness (see the black arrows in the inset) also gives a size of order of 1 nm.