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Development of graphene layers by reduction of graphite fluoride C_2F surface

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We studied a possibility of reduction of the surface of graphite fluoride obtained by fluorination of highly oriented pyrolytic graphite (HOPG) by a gaseous mixture of BrF_3 and Br_2. X-ray diffraction (XRD) revealed a layered structure of the fluorinated product being a second-stage intercalate due to a presence of bromine molecules between the fluorinated graphite layers. Scanning tunneling microscopy and spectroscopy showed that the "old" surface of graphite fluoride (exposed to the ambient air) has the graphite-like structure, while the fresh cleaved surface is non-conductive. Therefore, the outer layers of graphite fluoride can be reduced by water present in the laboratory atmosphere. The sample was treated by H_2O vapor to confirm that. The reduction was controlled by Raman spectroscopy using intensity of the 1360 and 1580 cm^{-1} bands. The energy dependent photoelectron spectroscopy was used for estimation of thickness of the reduction layer, which was found, does not exceed 2–3 graphite layers. The obtained results indicate the possibility of synthesis of graphene layers on dielectric fluorinated graphite matrix.

1 Introduction The unique electronic properties of graphene, single graphite layer, were supported by numerous physical measurements. Presently it is a stringent necessity to develop the synthesis techniques of a large area graphene. Traditionally the techniques of mechanical exfoliation from bulk single crystals of artificial graphite are used [1]. It is also possible to grow thin graphite layers on SiC single crystal surface at high temperatures [2] or in result of thermolysis of hydrocarbons on metal and other supports [3]. For example, it was reported the formation of graphene single layers on surface of nickel using surface segregation processes [4]. In addition, the techniques of isolation of individual graphene layers were recently developed for graphite [5] and graphite oxide [6] by wet-chemistry based approaches.

Depending on synthesis technique, graphene of different sizes, imperfections, etc. can be obtained. To characterize the obtained graphene various methods were applied: optical microscopy [7], atomic force microscopy (AFM) [8], scanning tunneling microscopy (STM) [9]. The features of the electronic structure are reflected in the specific dependencies of Raman scattering spectra [10] and angle-dependent photoelectron spectroscopy [11].

Here, based on the idea of chemical reduction of oxidized graphite we obtain thin graphite layers and possibly graphene layer using the treatment of fluorinated graphite by water vapor. Graphite fluorides are dielectric and the possibility of controlled reduction of the surface for measuring electrophysical properties is very attractive. The fluorinated graphite of C_2F_x ($x < 1$) composition has a more ordered structure compared to graphite oxide. There are several structural models of graphite fluoride proposed on the basis of X-ray diffraction (XRD) study [12]. Examination of fluorinated graphite by AFM has supported the ordered arrangement of fluorine atoms on the surface [13]. Graphite fluoride C_2F_x ($x < 1$) was obtained by the fluorination of highly oriented pyrolytic graphite (HOPG) by a gaseous mixture of BrF_3 and Br_2. The addition of bromine is necessary for dilution of the fluorinating agent and thus a milder graphite oxidation that prevents the strong deformation of graphitic layers. It was shown before that BrF_3 can be used successfully for the synthesis of graphite fluoride with composition close to C_2F in the case of natural graphite [14]. In addition, the fluorinated multiwall carbon nanotubes with surface composition close to C_2F can be obtained in a similar way. But in the case of single-wall carbon nanotubes the fluorination degree is $C_2F_{0.5–0.4}$ [15] which can be related to surface fluorination of one side only.

2 Experimental

2.1 Synthesis The HOPG, which is commonly used as X-ray radiation monochromator, was taken for fluorination. The sample $5 \times 5 \times 0.5\,mm^3$ in size was placed in a teflon flask and held in the vapors over a solution of BrF_3 in Br_2 for 30 days. As it was shown on natural graphite [14] this time is enough for diffusion processes ensuring achievement of composition close to C_2F. Thereafter, the flask content was dried under a flow of N_2 until the termination of Br_2 evolution (~48 h).

Reduction of the graphite fluoride surface was carried out using a flow of water vapor during 20 min.

2.2 Characterization methods The structure of the obtained material was characterized by means of XRD, STM, AFM, and Raman scattering. The XRD measurements were performed on a DRON SEIFERT RM4 spectrometer (Cu Kα radiation, graphite monochromator). The patterns were registered in a single-step mode in the range of 2θ from 5 to 70°. The Raman scattering spectra were measured on a Triplemate SPEX spectrometer with CCD camera and microscope for detection of the backscattering spectra with excitation by 488 nm laser line. Topography of the fluorinated graphite surface was studied by AFM on a Solver-Pro HT MDT spectrometer. The STM measurements were carried out using a Nanoscope IIIa in a constant current mode with tunneling currents of 0.3–1 nA and bias voltages in the range of 0.1–1 V.

Surface composition of the samples was examined using X-ray photoelectron spectroscopy (XPS). The spectra have been obtained at BESSY storage ring using radiation from the Russian–German beamline using a hemispherical analyzer VG CLAM-4. The XPS C 1s spectra were measured at the energy of monochromatized synchrotron radiation in 850–315 eV region. We did not anneal the samples before the experiments to avoid removing of fluorine. During the experiments, the pressure in the chamber was $\sim 10^{-7}$ Pa. The C 1s spectrum with excitation energy of 1486 eV was measured on a SPECS spectrometer.

3 Results and discussion The XRD pattern of the fluorinated HOPG showed reflections from *00l* planes only (Fig. 1). Relative position of the *00l* reflections for graphite fluorides is very sensitive to the real structure which is determined by synthesis method and its parameters [16]. The sample obtained using the procedure described above contained a portion of bromine molecules intercalated between the fluorinated graphite layers. The XRD pattern of the sample is similar to that of intercalates produced by similar treatment of the natural graphite. However, it has some differences. First of all, the identity period calculated from the peak positions of the *00l* reflections is increased in comparison to that for intercalates obtained from natural graphite. In addition, a significant broadening of the *003* reflection was observed. These phenomena are characteristic for layered compounds having mixed layered structure that is disordered alternation of different layer thicknesses. In this case, it is possible that we faced the irregularity of the arrangement of filled and empty layers. For the ideal structure of intercalate of second stage, we have to observe the regular alternation of filled and empty layers and any irregularities lead to the broadening of the *00l* reflections and shift of the peak positions. Both broadening and shift vary for the different order reflections. Therefore, on the basis of the obtained XRD pattern it can be concluded that there are significant irregularities in the package of layers in the sample synthesized from HOPG in comparison to the ideal structure of the second stage intercalate. Most probably, the presence of additional empty and even non-fluorinated carbon layers can be related to the structural irregularity of the sample of pyrolytic graphite.

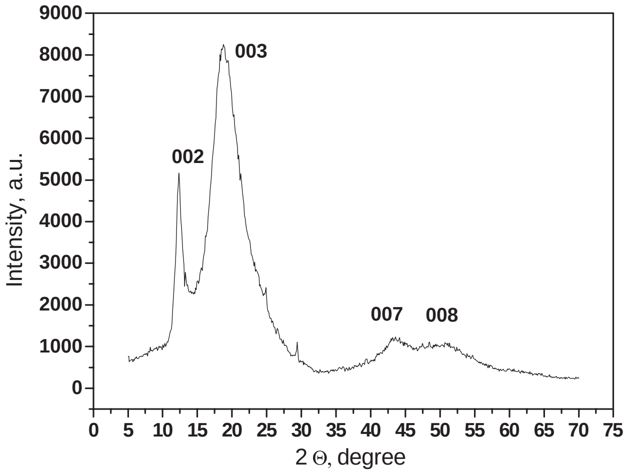

Figure 1 XRD pattern of fluorinated HOPG sample.

STM image of the fluorinated HOPG sample acquired in ambient air is shown in Fig. 2. One can see that this image corresponds to the graphitic one. However, we were unable to measure the surface of the freshly cleaved of the sample due to its lack of conductivity. This fact indicates that the outer surface of the fluorinated graphite is reduced under impact of the laboratory atmosphere and, more probably, water. The entire reduced area has similar atomic arrangement (Fig. 2) that evidences the single crystallinity of graphite layers. After the reduction process the surface exhibited a higher degree of disorder as compared with atomic resolution images of pristine HOPG although both samples were measured under similar conditions.

Examination of the fresh surface of the graphite fluoride by AFM revealed presence of parquet-like structure (Fig. 3). As it was shown [13] the fluorine atoms are ordered on the surface of graphite layer forming covalent bonds directed oppositely relative to the graphite layer for neighboring carbon atoms. The study of the electronic structure of C_2F by X-ray emission spectroscopy allowed establishing of some

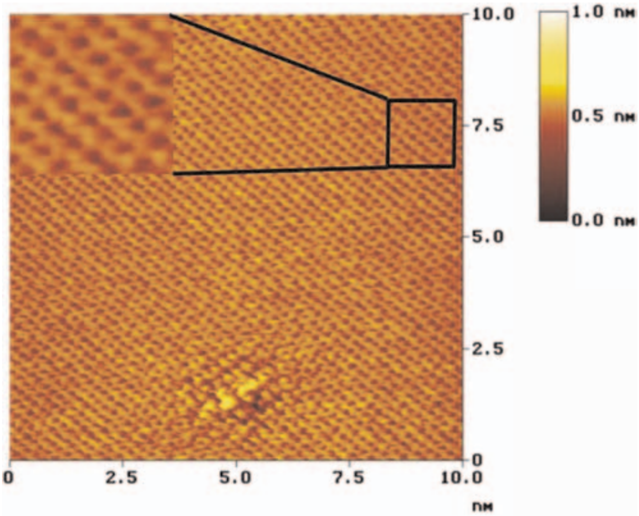

Figure 2 (online color at: www.pss-b.com) STM image of surface of fluorinated HOPG sample.

restrictions on structural model of graphite fluoride of C_2F composition obtained using BrF_3 fluorination [17]. So it was found that in this structure it is impossible for covalently bonded graphite layers to consist of sp^3 carbon atoms. In addition this structure cannot consist of separate double bonds that would lead to localization of the electronic density of π-states in the narrow energy range of the valence band. It was suggested that the main structural motive of the obtained graphite fluoride is the chains of fluorinated and non-fluorinated carbon atoms.

In the AFM image, the structure of graphite fluoride is represented as light and dark bands with characteristic length of 5 nm (Fig. 3). It may be proposed that the light bands correspond to the chains of fluorine atoms bonded with carbon ones and the more dark bands are extensive areas of delocalized π-system. The widths of the fluorinated and non-fluorinated bands are close to 1.2 nm. The mechanism of fluorination assumes the random attachment of primary fluorine atom to graphite network and further random direction of chain formation (one of three). The areas of formation of C_2F structure have limited size and form domains consisting of the C_2F bands ordered at different angles. The borders of domains are non-conductive so that the obtained material has dielectric properties.

The Raman scattering of the freshly prepared sample of the graphite fluoride and that after a long time (at least 3 months) stored in the laboratory atmosphere are compared in Fig. 4. Due to the larger of optical penetration than the thickness of the reduced graphite layers on the surface of the ''old'' sample, the changes in the spectra are less significant. The Raman spectra exhibit the lines at 1580 and 1360 cm^{-1} corresponding to the G and D vibrational modes in graphite. At 1594 cm^{-1} an additional line is observed which relates to the transfer of electron density from carbon to fluorine atoms [18]. As it is seen in the sample stored in the laboratory atmosphere the intensity of the component at 1594 cm^{-1} is decreased because of the lowering of fluorine concentration. Moreover, the D band is shifted to the higher wave numbers that also indicates the decrease of fluorine concentration. Meanwhile, the relative intensity ratio I_D/I_G is decreased from 0.4 to 0.2 that indicates the increase of the crystallinity area in plane graphite layer and decrease of imperfection related to the attachment of fluorine to graphite layer. It can lead to increase of conductivity. In the region of 1420 and 1490 cm^{-1}, the weak lines are observed which can be related to the peculiarities of the phonon state spectra. After treatment of graphite fluoride in water vapor the relative intensity ratio I_D/I_G is decreased significantly.

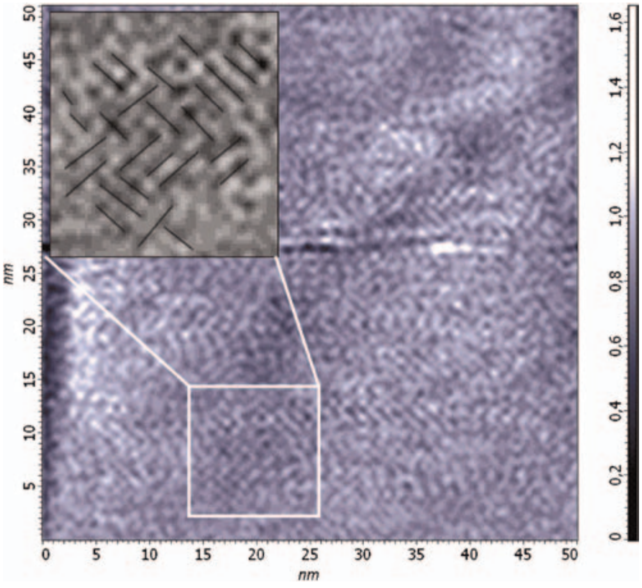

Figure 3 (online color at: www.pss-b.com) AFM image of the fresh cleavage of the fluorinated HOPG sample. The inset shows the formation of a parquet-like structure from dark and light (marked by the lines) bands.

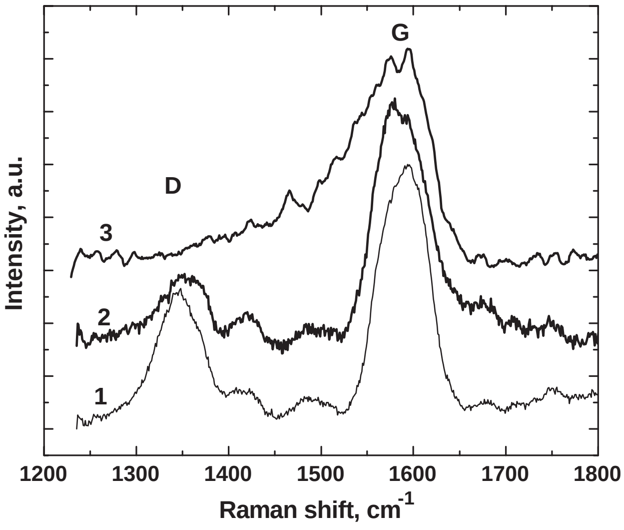

Figure 4 Raman scattering spectra of C_2F samples freshly prepared (1), stored in the laboratory atmosphere (2), after interaction with water vapor (3).

The XPS C 1s spectra of the samples obtained at different excitation energies are shown in Fig. 5. The excitation energy influences the kinetic energy of C 1s electrons, which in our measurements constituted 1200, 565, 395, 65, and 30 eV. As an escape depth of photoelectrons depends on kinetic energy, so information about electronic state of surface layer comes from depth from 3 to 0.5 nm in the photon energy range under study. The spectra obtained with excitation energy of 1486.7 eV correspond to states of electrons at depth 3 nm. The peaks *A* and *B* in the C 1s spectra are from bare carbon atoms and carbon atoms forming chemical bond with fluorine atoms, correspondingly. From the relative intensity ratio $I_A/I_B = 1.4$ at normal electron emission relative to surface it is possible to estimate the stoichiometric composition of near surface layer as $C_{2.4}F$. When the electron take-off angle increases, the intensity ratio I_A/I_B also increases (1.5 at take-off angle 45°). It shows an increase of carbon concentration on the surface. Decrease of the electron kinetic energy causes *B* peak intensity to drop which, in turn, is evidence of decrease of fluorination degree of the surface top layer. In the spectrum measured at excitation energy of 315 eV the *B* peak is practically not observed. That corresponds to STM measurements, showing absence of fluorine atoms on the surface. The change of the spectral shape with decreasing energy is worth noting. The broadening and shift of the *A* component to the higher binding energy takes place. It is possibly related to non-equivalence of the graphite layers. The lower reduced layer of graphite has donor–acceptor interaction with the fluorinated graphite layer and also the surface shift of top graphite layer may be observed. Interaction with water vapor causes the reduction of surface layer as *B* peak disappears in the spectrum.

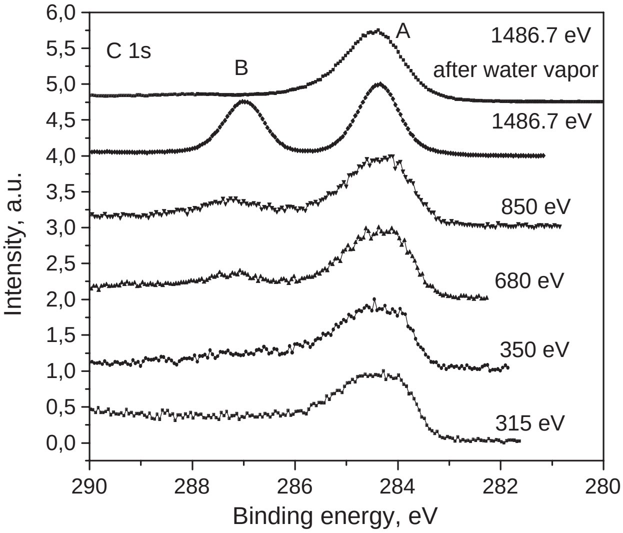

Figure 5 XPS C 1s spectra of graphite fluoride stored in the laboratory atmosphere obtained at excitation energies 1486.7, 850, 689, 350, 315 eV and graphite fluoride after the treatment with water vapor.

4 Conclusions

Fluorination of HOPG produces dielectric graphite fluoride with composition close to C_2F. Structure of the obtained layered material is stable to defluorination in temperatures up to 400 °C. Exposure to air, however, leads to reduction of several top layers as a result of hydrolysis by water vapor present in the atmosphere. Measuring XPS C 1s spectra with different excitation energies can give estimates of graphite layer thickness being less than 1 nm. Direct interaction with water vapor causes reduction to penetrate deeper than 3 nm.

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