Fluorographene with nanoswell surface relief obtained by hydrofluoric acid treatment

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Fluorographene (FG) is one of the main derivatives of graphene attracting huge interest for last few years. It is a stoichiometric derivative of graphene with fluorine atom attached to each carbon atom [1]. FG is stable material (up to temperature 400°C) and a high-quality insulator (resistivity > 10^{12} Ohm) with optical bandgap 3 eV [1, 2]. In the present report, we demonstrate a new, very simple approach for creation of FG. This process uses treatment of graphene or few-layer graphene in aqueous solution of hydrofluoric acid yielding fluorogrphene or few-layer FG with nanoswell relief on the surface.

Fluorination of graphene or few-layer graphene (with thickness below 10 nm) by means of HF treatment resulted in dramatic changes of structural and electrical properties of the material. The interaction of graphene with HF observed as a function of HF treatment duration exhibited a two-stage behavior.

At the first stage, Raman spectra of samples treated in HF:H_2O solution demonstrated an increase in D-peak intensity (1350 cm^{-1}) and a decrease in the intensity of G and 2D peaks (respectively ~1580 cm^{-1} and ~2700 cm^{-1}). A network relief with height 3-4 nm was revealed on the surface of such samples by atomic force microscopy (AFM). Grain boundary mapping is assumed to be responsible for the formation of this network. The resistivity of the graphene structures remained roughly unchanged at this stage of HF treatment. A surprising finding was that in HF-treated structures the current value in the $I_{ds}(V_g)$ characteristics measured in transistor configuration using the substrate as the gate electrode varied over 4–5 orders of magnitude with variation of gate voltage V_g. On the contrary, reference (not treated in HF:H_2O) few-layer graphene samples demonstrated variation of drain-source current I_{ds} within 30%. This effect was found to be due to an increase of carrier mobility. Thus, our films shortly treated in HF:H_2O demonstrated a high potential in management with their conductivity.

The second stage of the graphene-HF interaction proceeded over HF treatment times of 30 s for graphene proper and over times of 5 min for structures with thickness 3-5 nm. At this stage, graphene-related peaks disappeared from Raman spectra. A step-like increase in resistivity (up to 100 GΩ) was observed in such structures. This modification of few-layer graphene properties suggests the formation of FG during treatment of graphene in HF:H_2O solution. A periodic nanoswell relief (step ~ 50 – 100 nm and height ~ 2–6 nm depending on treatment duration and sample thickness) was observed by AFM on the surface of the samples. Thermal stability of our FG samples was tested by giving them an additional anneal. It is known that hydrogen desorption from graphene occurs at temperatures ~200 – 290°C [3]. On the other hand, C-F bonds are stable up to ~400°C [1, 2]. We have performed an annealing of one of the FG samples at temperature 300°C for 1 h. The properties of the annealed structure showed no changes after annealing. Repeated measurements performed over a one-year period proved time stability of created material.

Fluorine ions present in HF/water solution were found to be necessary for the fluorination reactions. For comparison, several graphene samples were given treatment in HF vapor. The duration of the latter treatment was varied from 1 min to 17 hours. It was found that the resistivity value remained unchanged over 17 h of HF vapor treatment. We would like to mention here that such samples showed no changes in Raman spectra as well.

The fluorination process could be made controllable using a preliminary treatment of graphene in isopropyl alcohol. The latter treatment was found to suppress fluorination of graphene in HF/water solution. Combination of the two treatments gives one a key for nanodesign of graphene-based devices.

References

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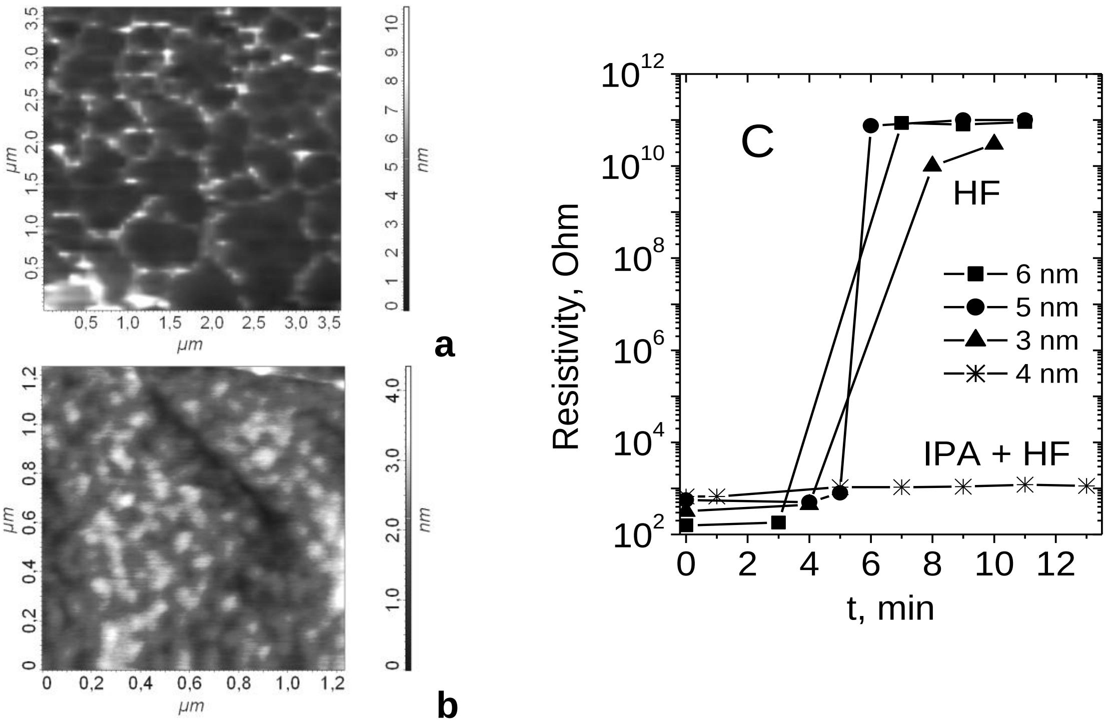

Fig. 1. *(a) AFM images of the surface of samples treated in 5 % solution of HF in water during different times, 4 (a) and 9 min (b). (c) Resistivity of various few-layer graphene flakes versus the HF-treatment duration t. The few-layer graphene thickness is given in the figure sheet as a parameter. The curve labeled IPA+HF in (c) refers to the sample that was preliminarily (before HF-treatment) treated for 20 min in isopropyl alcohol (IPA).*