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Graphene Doping in a Spherical Glow Discharge

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Abstract

Multilayer graphene was processed under the conditions of glowing gas discharge in the presence of a central spherical electrode in atmospheres of nitrogen, hydrogen, and air. It is shown that in the case of hydrogen, the most active interaction with plasma-forming gas occurs at positive polarity on the central electrode in atmospheres of nitrogen and air with negative central electrode. In N_2 and air atmospheres with negative polarity of the central electrode, the electrode material is actively sprayed due to ion bombardment and it is deposited on the processed graphene materials.

INTRODUCTION

Possibilities of graphene layer doping by different atoms attracts intensive attention of the scientific community. Graphene doping is possible by introducing the atoms, whose size is similar to C (usually N, B), into the graphite plane - substitutional doping and doping with discharge transfer "Charge-transfer doping", when the adsorbed molecule acts as an electron donor or acceptor [1]. The introduction of nitrogen atoms into the carbon matrix enhances the metal properties, increases the catalytic activity and biocompatibility [2]. In particular, nitrogen-doped graphene can be used for making supercapacitors, lithium-ion batteries, solar cells, etc. Nitrogen-doped graphene has a great potential for replacement of expensive Pt-catalysts in fuel cells and metal-air batteries [3]. The process of hydrogenation, in addition to applications related to the creation of hydrogen capacitors, has an important application in nanoelectronic devices. Formation of the C-H bond leads to sp3 hybridization of a carbon atom and enhancement of semiconductor properties of the graphene sheet. Thus, by changing the degree and topology of hydrogenation, it is possible to control the transport properties of electrons in the graphene layer [4]. The chemical modification of graphene structures allows one to obtain the structures with a non-zero forbidden gap (hydrogenation of graphene to graphane) [5], partial hydrogenation leads to appearance of ferromagnetic properties in graphene [6]. Graphene fluorination makes it possible to obtain a dielectric with a non-zero forbidden gap [7]. Graphene doping with nitrogen and boron allows production of n- and p-type semiconductors [8].

Doping of carbon nanostructures with various elements is possible either directly at the stage of synthesis, introducing various additives (NH_3, N_2, H_2, etc.) into the working mixture, or at subsequent processing of graphene structures. A popular method for doping various carbon materials is plasma treatment under the conditions of a glowing, high-frequency discharge in the atmospheres of NH_3, N_2, O_2, H_2 [9-15]. Graphene was also obtained by irradiating the graphene layers with adsorbed water and ammonia molecules by the electron beam [16] and thermal decomposition of oxidized graphite in the hydrogen atmosphere at high pressures [17].

Plasma treatment of graphene structures can be also used to etch the graphene layers; for example, it is shown in [18] that annealing in hydrogen plasma after the stage of synthesis leads to formation of single-layer graphene from several-layered graphene. When etched in oxygen plasma, it is possible to change controllably the thickness of multilayer graphene [19].

In this work, the original technology of plasma processing of graphene in a discharge with a hollow spherical electrode is tested. The discharge type under investigation may have a number of advantages over the existing technologies of plasma induced chemical deposition from the gas phase. The proposed discharge geometry can ensure spatial symmetry in contrast to traditional types of glow discharge, and this can be an important factor for processing the bulk materials. Advantage over the microwave plasma torches is the absence of dust particles in the zone of material processing; these particles are displaced from the inner zone of cathode by the action of electrostatic forces. It is also the location of the irradiated object outside the zone of the "active" discharge gap, which leads to a decrease in the effect of the object on the parameters of gas discharge and increases the degree of controllability of the discharge parameters.

EXPERIMENT

In this study we used graphene paper, obtained by ultrasonic treatment in the medium of dimethylforamide of few-layer graphene [20-21], formed at destructive thermal decomposition of an intercalated polyfluoride-carbon compound with chlorine trifluoride with an idealized formula [22] $(C_2F{\cdot}0{,}13ClF_3)_n$ by method [20]. After dispersion, the suspension was filtered through a Whatman filter with pore sizes of 20 nm. As a result, graphene paper containing single-layer graphenes (~ 25% by weight), double-layer graphenes (~ 25% by weight), triple-layer graphenes (~ 25% by weight) and four-layer graphenes (~ 25% by weight) was obtained [23-24].

CVD graphene was synthesized from methane on a copper foil by the technology described in detail in [25].

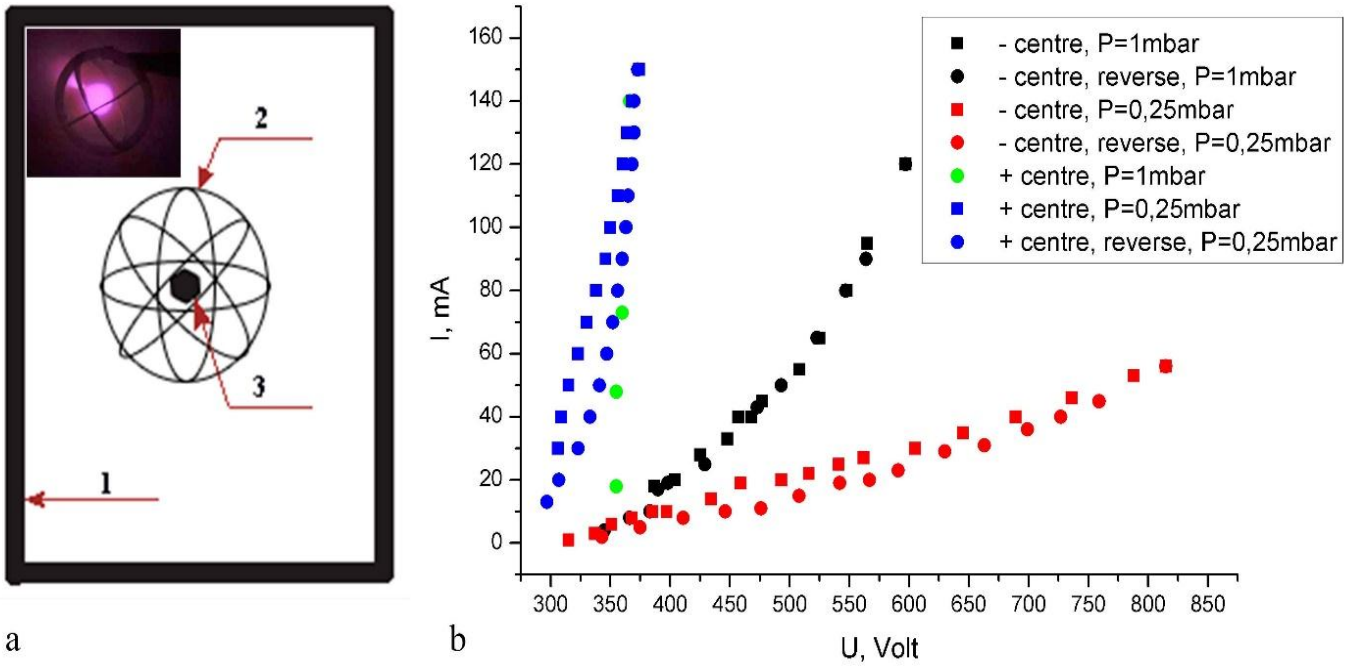

Figure 1 (a) Scheme of plasma reactor with a spherical cathode (1 – outer electrode, vacuum chamber, 2 – inner spherical electrode, 3 – sample). **(b)** current-voltage characteristic of discharge with a spherical central electrode at different polarities and pressures in nitrogen.

The scheme of plasma-chemical reactor based on a discharge with a central cathode is shown in Figure 1(a). A spherical electrode (2) consisting of metal rings was placed in the center of vacuum chamber (1). Similar electrode geometry is used by the method of inertial electrostatic plasma confinement for nuclear fusion (Farnsworth-Hirsch fusor) at low pressures [26].

When the pressure increases to 0.1 mbar or more, the collisional processes increase, mean free path of electrons and ions becomes smaller than the electrode size (less than 1 mm), and discharge turns to the glowing regime [27]. The current-voltage characteristics of discharge [see Fig. 1(b)] correspond to an anomalous glow discharge with negative potential on the central electrode, and normal glow discharge with positive polarity. Inconsistency of the current-voltage characteristics at increasing and decreasing discharge voltage is connected with gas and electrode heating.

Experiments on functionalization of graphene were carried out under the conditions of gas discharge with a spherical electrode at different polarities on electrodes, in the center "+" and "-", pressure of 0.25 mbar, processing time of 30 minutes, discharge current of 30 mA in nitrogen, hydrogen and air plasma. For each gas, the discharge parameters were chosen to achieve the maximal luminescence intensity in the central cavity of the cathode with negative polarity at the central electrode; for the positive central electrode, the current value was set equal to the current at reverse polarity. The discharge voltage for nitrogen (air) is 700V for the central negative electrode and 310V for the central positive electrode, for hydrogen, it is 910 and 385V, respectively. The procedure for sample preparing was as follows: a flake of "graphene paper" was pinned onto a quartz rod with the diameter of 1 mm, fixed on a spherical electrode in such a way that the sample was in the center of the electrode.

Raman spectra for the synthesized materials were taken on a T64000 Raman spectrometer produced by Horiba Jobin Yvon with a wavelength of exciting radiation of 514.5 nm.

Fourier transform infrared (FTIR) spectra were recorded using a Scimitar series instrument (Varian). For FTIR measurement, samples were mixed with KBr powder and pressed into discs shape.

DISCUSSION

When the graphene paper is processed in nitrogen and air plasmas, defectiveness (the ratio of ID/IG lines) of graphene layers increases, which may be caused by formation of C-N bonds. Figure 2(a,b) implies that in the case of the central cathode, a broad peak appears in the region of 500-600 reverse centimeters.

After graphene paper processing in hydrogen plasma with the central anode, defectiveness of samples does not increase. With the central cathode, an increase in graphene defectiveness occurs and slight reflexes [see Fig. 2(c)] are observed in the region of 500-700 cm^{-1}. When graphene is processed in hydrogen plasma, the material (carbon) evaporates intensely.

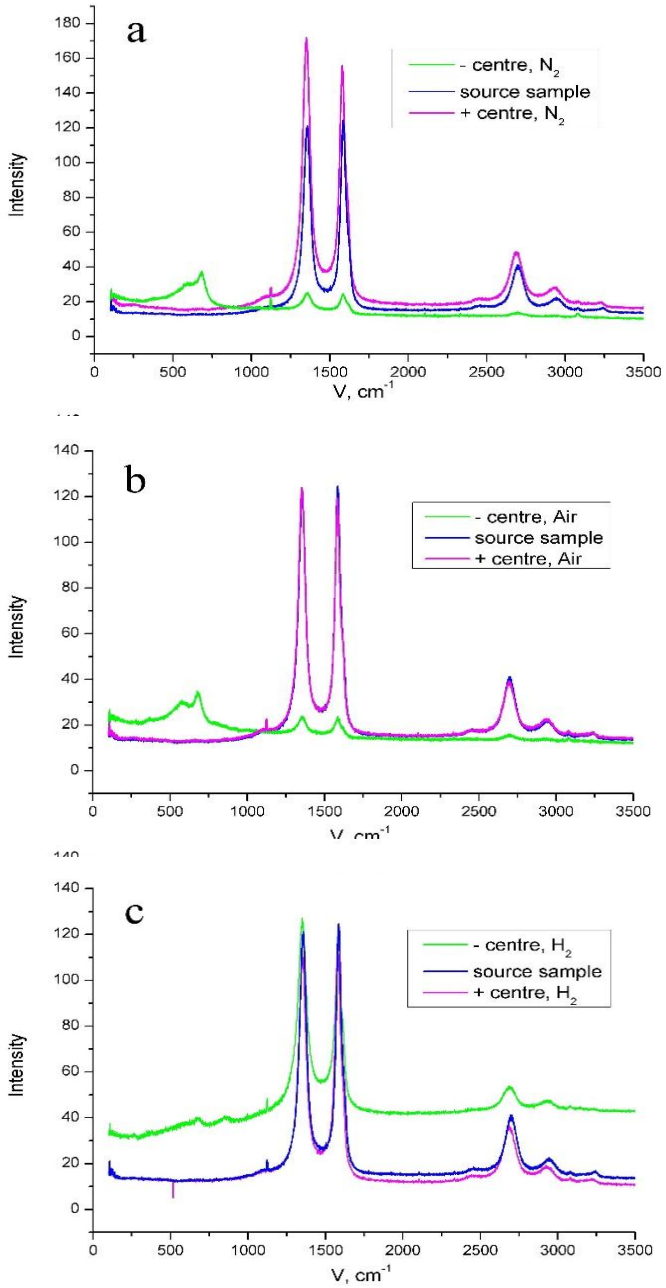

Figure 2. (a) Raman spectra of graphene paper before and after processing by nitrogen plasma. **(b)** Raman spectra of graphene paper before and after plasma processing in air. **(c)** Raman spectra of graphene paper before and after processing by hydrogen plasma.

After plasma processing with a central cathode in nitrogen and air, the signal from the graphite D and G lines weakens, only 2D (G + D, G + G is not visible) remains visible, and there are wide peaks in the range of 500-700 cm^{-1}, not corresponding to the compounds with C, N, O. To analyze the origin of these peaks, EDAX from the surface of samples was made; the results are given in Table 1.

Table 1. Elemental composition of a sample of thermally expanded graphene after nitrogen plasma processing with the negative central electrode.

Element	Weight %	Atomic%
C K	41.59	57.88
O K	32.65	34.11
Al K	0.30	0.19
Si K	0.37	0.22
S K	0.50	0.26
Cr K	3.89	1.25
Fe K	4.70	1.41
Ni K	15.02	4.28

It can be seen that on the surface of graphene structures, there are metals corresponding to the components of stainless steel of the central electrode. Thus, the peaks in the range of 500-700 reverse centimeters correspond to carbides and metal oxides. The metal atoms are knocked out when the central electrode is bombarded with nitrogen ions, and this effect is weak in hydrogen discharged because of the small mass of the molecule.

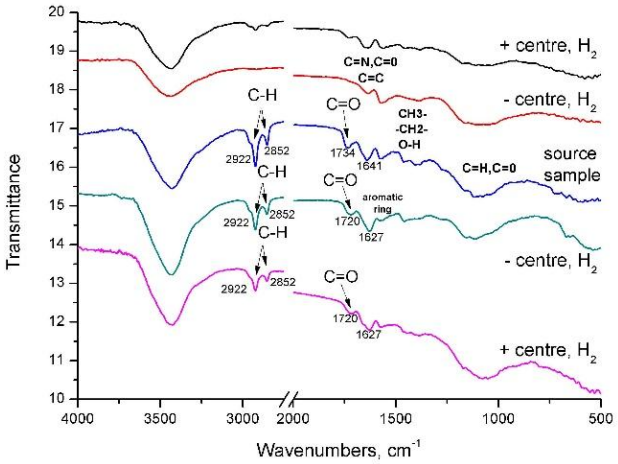

Figure 3. FTIR spectra of graphene paper before and after processing by hydrogen plasma.

The analysis of materials by the FTIR method is presented in Figure 3. The main difference between the samples treated in nitrogen from the initial material is displacement of 1750-1700 cm^{-1} and 1650-1600 cm^{-1} peaks, which can associated with formation of C = N bonds; the effect is the same for both discharge polarities. In the case of hydrogen, the intensity of peaks associated with vibrations of C-H (2800-3000cm^{-1}, 1450cm^{-1}, 1300-900 cm^{-1}) and C-O (1300-900 cm^{-1}) weakens. Thus, when processing the materials in nitrogen plasma, formation of a chemical bond with nitrogen is possible; in the case of hydrogen plasma, the material is etched with formation

of volatile CH_x fragments and oxide reduction. The etching rate of defective graphite regions (the defect relates to the bond with oxygen or hydrogen) is higher than that of defect-free graphite fragments, therefore, concentration of CH and CO groups decreases.

After CVD graphene processing under the conditions of nitrogen and hydrogen plasma, no carbon peaks were detected in the presence of central cathode; this was due to carbon etching under the discharge conditions. In this connection, experiments were carried out on a methane-hydrogen mixture: in this case, along with carbon structures etching, their healing from ionized fragments of the plasma-forming gas is possible.

After plasma processing in methane-hydrogen mixture with the central anode, defectiveness of graphite planes decreased (ID/IG ratio decreased from 0.5 to 0.4, see Fig. 4) and this may be caused by the effect of defect "healing" described in [28]. With the central cathode, the Raman spectrum of the resulting material corresponds to amorphous soot, i.e., sp2 material with a large number of unconfined bonds. Apparently, soot is formed from the gas phase by plasma-activated thermal deposition.

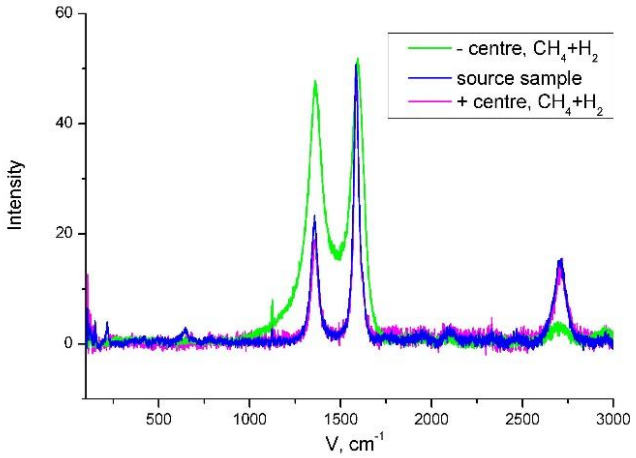

Figure 4. Raman spectra of CVD graphene after processing by methane-hydrogen plasma.

In all cases, plasma treatment involves etching of carbon structures. When working with graphene paper, the volume of carbon material is sufficiently large, and the evaporated part is insignificant (except for the case of processing in hydrogen plasma, when volatile CH_n compounds are formed intensely). When graphene structures are processed on a copper substrate, complete evaporation of carbon material occurs in mixtures that do not contain hydrocarbon.

Functionalization of graphene structures occurs in nitrogen plasma in the presence of the central anode and this causes an increase in the defect D line in the sample. Annealing of functionalized samples to 400°C in argon leads to complete restoration of materials.

CONCLUSION

A new technique for doping the graphene structures with hydrogen and nitrogen in gas discharge plasma in the presence of a central spherical electrode is proposed. It is shown that the most effective interaction of graphene with hydrogen occurs in the presence of central spherical cathode, without material hydrogenation; the main effect is graphene plane etching. In the plasma of nitrogen and air with the central spherical anode, the materials are doped with nitrogen. At negative polarity on the central electrode, the electrode material can be sprayed onto the processed sample. At plasma processing in a methane-hydrogen mixture in the presence of a central positive electrode, it is possible to heal the defects of graphene structures.

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