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Abstract

Plasma treatment of graphene oxide (GO) is of interest for many applications such as gas sensors, flexible electrodes, biological applications, supercapacitors, batteries, etc. Plasma treatment is a high-tech process of processing materials in combination with efficiency, economy and environmental friendliness. At the same time, plasma treatments can lead to an increase in the defectiveness of the surface of GO. Therefore, it is important to know how the treatment in various gas media affects the properties of GO. This is necessary for the correct selection of processing parameters in order to reduce the negative impact of plasma treatment. The review presents the results of experimental studies of the effect of plasma in gases of oxygen, nitrogen, ammonia, sulfur hexafluoride, carbon tetrafluoromethane, hydrogen and methane on the properties of GO. Plasma treatments were used for the functionalization, reduction, doping of graphene oxide, and also for the obtaining GO from graphene by oxidation in oxygen plasma. The effects of plasma treatment are largely determined by the type of ions used and processing conditions: plasma power, processing time and temperature, pressure, as well as the location of the samples in the reaction chamber and their distance from the plasma ignition zone.

Keywords: plasma treatment, oxygen plasma, nitrogen plasma, ammonia plasma, sulfur hexafluoride plasma, carbon tetrafluoromethane plasma, plasma effect on graphene oxide properties

1. Introduction

For several decades, plasma technologies are widely used in the fabrication of microelectronic structures. The main directions of the use of plasma treatments are cleaning of the surface of materials, etching, deposition and modification of the surface properties of materials (changes in hydrophilic, adhesion, conductivity and other properties). With the development of nanotechnologies, plasma methods have found application in the growing and functionalization of
nanomaterials, providing unique properties in combination with the economy and environmental safety in the production process. Thus, plasma technologies are widely used both for the growth of nanomaterials by the method of plasma enhanced chemical vapor deposition (PECVD) and for the modification of surface properties. A low-temperature radiofrequency (rf) plasma containing chemically active particles provides unique possibilities for this. For the functionalization and reduction of graphene oxide, various thermal, chemical, optical, and other methods are used [1–5]. Plasma treatment is effective, eco-friendly and low cost method of functionalization and reduction of graphene oxide (GO). Plasma treatment of GO is of interest for the creation of various devices such as gas sensors [6, 7], photosensitive devices [8], biological sensors [9–11], flexible electrodes [12, 13] and et al. Various methods are used to perform plasma treatments [14, 15], which can be conditionally divided into actions with “low power” and “remote” [14], also low and atmospheric pressures [15]. This largely determines the effect of plasma on the properties of graphene oxide. The most frequently used for the functionalization of graphene oxide are treatments in plasmas of nitrogen, ammonia, oxygen, methane, hydrogen and fluorine. The treatment in each of these plasmas has features related to the chemical activity of ions, activated by the action of ultraviolet radiation, by electrons and other active spices of plasma. At the same time, it should be noted that most of the work devoted to the effect of plasma on carbon nanomaterials is associated with the study of the properties of graphene and carbon nanotubes. Despite the fact that exposure in plasma leads to an effective modification of the properties of graphene oxide, a limited number of studies have been devoted to the study of its properties. Below we will consider the effects of plasma of various gases on the properties of GO, taking into account the processing conditions.

2. Oxygen plasma

Oxygen plasma treatment of graphene oxide can be used to etch surface layers [9, 15–19], to functionalize [6, 9, 20] or to obtain GO from graphene by oxidation [21–25]. On the other hand, the oxygen plasma is very chemically aggressive, usually leading to significant changes in the structural and electronic properties of graphene: a high degree of disorder is induced in the graphene lattice even at low power and after a very short exposure time [26]. At the same time, the intensity of defect formation under the influence of oxygen plasma can be significantly reduced by using mild plasma treatments, which use small power, remote location from the plasma source of samples, the use of protective filters and grids [9, 21, 22, 26–29]. As measurements by the XPS method have shown, the effect of low-pressure O₂ plasma on reduced graphene oxide (rGO) leads to the introduction of different oxygen-containing groups [20, 30]. Similar results were obtained when graphene was exposed to oxygen plasma [9, 15, 21, 22]. Oxygen plasma treatment introduces epoxy (C-O-C) and carboxyl (C-OH) groups in the basal plane and edges of graphene, with the epoxy group being the most energetically favorable [1, 8, 17]. This process is accompanied by a decrease in the carbon regions of sp²-hybridized bonds [27, 30]. Detailed high resolution X-ray photoelectron spectroscopy (XPS) rGO studies after oxygen plasma treatment with a power of less than 50 W have shown that a monotonous increase in the amount of oxygen and a decrease in the carbon content with
increasing processing time does not occur [31]. The content of C-O (epoxy, hydroxyl) groups was maximum after a plasma exposure for 1 min, further decreased after treatment for 5 and 10 min. In contrary, the atomic content of C(O)O (carboxyl/lactone) groups increased at the same processing times. The authors explain this by the fusion of carboxyl groups formed at short plasma treatment times and the formation of lactone groups. This process is accompanied by the loss of one oxygen atom, which leads to a decrease in the oxygen content after 5 min of treatment. With the formation of lactone groups, the authors associate the appearance of new absorption lines in IR spectra at wavelengths at 1730 and 1436 cm⁻¹. It should be noted that in the IR spectra treated in GO plasma, a broad band at 3440 cm⁻¹ bound to hydroxyl groups is significantly enhanced [20, 32].

The main peaks of Raman spectra of graphene oxide are G band at ~1580 cm⁻¹ wavelength and D band at 1530 cm⁻¹ [18, 33]. The band G is the result of intraplane oscillations of the bound atoms of sp² whereas the D band is due to non-planar oscillations due to the presence of structural defects. In the presence of defects, vacancies and disorderings in the sp²-domain of the structure graphene, are significantly increases the intensity of the D peak [18, 33]. When graphene is exposed in plasma, the intensity of the D band (I_D) Raman spectra are significantly increased [26, 27, 34, 35]. Even a short-term O₂ plasma exposure for up to 5 s at a power of 2 W leads to a sharp increase I_D [34]. The change in Raman intensities associated with the increase in defects occurs also for rGO treated in oxygen plasma [9, 20, 32]. These changes are associated with an increase in the content of oxygen groups and defects formed during plasma oxidation. An increase of the D band intensity is also associated with the formation of sp³-hybridized bonds [9, 22].

An investigation of the electrical conductivity of rGO treated in O₂ plasma showed its decrease both with increasing plasma power and processing time [30]. At high powers and long processing times it becomes impossible to measure the conductivity because it was below the measurement range of the instrument (<0.001 Sxcm⁻¹). Scanning electron microscopy (SEM) measurements showed that most of the rGO disappears [30]. The authors explain this by the fact that the oxygen plasma destroys sp² domains in rGO and introduces various oxygen groups to the sites of rGO defects, which leads to etching of rGO with conversion him to amorphous carbon. At the same time, under ‘gentle’ processing conditions, it is possible preserve the electrical conductivity of graphene oxidized by plasma [22]. It should be noted that the production of GO from graphene by the plasma treatment method makes it possible to obtain GO with an almost undamaged surface, high hydrophilicity and increased adhesion of the surface [21–23].

Gokus et al. show that strong photoluminescence (PL) can be induced in single-layer graphene using an oxygen plasma treatment [36]. The samples are then exposed to oxygen/argon (1:2) rf plasma (0.04 mbar, 10 W) for increasing time (1–6 s).

Surface morphology studies after low-pressure oxygen plasma at 50 W showed that the surface of the GO becomes more porous and corrugated [9, 37]. This leads to an increase in its wettability for both graphene oxide [20] and graphene [22, 27], treated in oxygen plasma. The increase of the wettability allows to improve its surface reactivity with respect to biomolecular interactions [24]. Oxygen-plasma-treated rGO surfaces were employed as reactive interfaces
for the detection of amyloid-beta (Aβ) peptides, the pathological hallmarks of Alzheimer’s disease, as the target analytes [9]. Zhao et al. in [6] proposed a chip based gas sensor NH\textsubscript{3} with oxygen plasma treated GO surface. Owing to the large surface-to-volume ratio of GO and the rich chemical groups on its surface and edges, the sensitivity of the sensor to gas molecule absorption was improved. The response was further improved by oxygen plasma treatment on GO film by introducing numerous site binding defects.

3. Nitrogen and ammonia plasma

In many works, gases NH\textsubscript{3} [38–40] and N\textsubscript{2} [32, 41–43] are used to treat GO in the nitrogen containing plasma. Kim and et al. for nitridation of rGO used NH\textsubscript{3} inductively coupled plasma with a power of 10 W at a pressure of 100 mTorr [38]. The content of many oxygen groups (such as epoxy, hydroxyl, carbonyl and carboxyl) attached to GO films was significantly reduced after treatment with NH\textsubscript{3} plasma, and instead of them, C-N bonds were introduced. The ratios of the nitrogen to carbon concentrations (N/C) and oxygen to carbon concentrations (O/C) in less than 10 min became approximately 10 and 23% and were gradually saturated [38].

Nitrogen forms pyridine (pyridinic-N), pyrrole (pyrrolic-N), and graphite configurations (quaternary, graphitic-N) with carbon atoms in the graphene lattice [36, 44–47]. Pyridinic-N is bonded to two carbon atoms of the hexagonal graphene cell on the edge of vacancy-type defects and introduces 1 p-electron into the π-system; pyrrolic-N introduces 2 p-electrons into the π-system and is connected to two graphene atoms of the pentagonal cell; graphitic-N replaces the carbon atom in the hexagonal ring of graphene [36, 44, 47]. The pyridine and pyrrole configurations of nitrogen form a p-type conductivity, while graphitic N ones increase the electron concentration [44, 48]. Kim et al. [38] showed that when doping in graphene NH\textsubscript{3} plasma, pyridine and pyrrole configurations of nitrogen are predominantly introduced, and the ratios N/C and O/C atoms are inversely related to the processing time in the plasma. The same results were received in Refs. [39, 40]. In the work of other authors [32], the concentration of pyridinic-N (48%) was found to be higher than the Pyrrolic-N (29%) and Graphitic-N (15%). At the same time, treatment with N\textsubscript{2} plasma can lead to an increase in the amount of oxygen [10, 47].

Kim et al. [38] is shown that an increase in the electrical conductivity occurs with an increase in the exposure time in NH\textsubscript{3} plasma with a simultaneous decrease in the optical transmission coefficient. The authors explain the increase in the conductivity from 100 S/m to 1666 S/m rGO films by the combination of the effect of nitrogen doping and the reduction of oxygen. Decreasing of the transmittance is attributed to the restoration of electronic conjugation in rGO film. The surface roughness of the films becomes smoother until the processing time reaches 10 min and further substantially does not change. The main cause of this phenomenon can be explained from the point of view of removing organic impurities in the film, reducing the functional groups of oxygen and extracting the sp\textsuperscript{2}-carbon domains [38].

In [39] the plasma treatment with ammonia of GO and RGO in the reaction chamber with parallel plasma-enhanced chemical vapor deposition (PECVD) diodes was carried out. The conditions of plasma treatment were as follows: plasma power of 200 W at 13.56 MHz, a gas
flow rate of 400 sccm, the substrate temperature 150°C, treatment time 1–5 min. Under these conditions, the level of doping with nitrogen in 6% was reached. Comparison of the intensities of the N1 s peaks associated with the formation of bonds C-N in XPS spectra of GO and RGO after plasma treatments in NH₃ showed that the intensity of this peak in RGO than in GO. The authors explain this by the formation of C-N bonds in the interaction of oxygen groups with ammonia. The intensity ratio of Raman peaks I_D/I_G has a nonmonotonic dependence on the processing time. At initial treatment times (up to 1 min) this ratio increases, then reduces and further gradually enhances with increases exposure time in the plasma. The authors explain the decrease in the I_D/I_G ratio by the formation of an intermediate chemical species, such as hydrazine radicals. The increase can be attributed to the restoration of the sp² bonds in the GO sheets due to the NH₃ plasma, which is consistent with the XPS results [39]. Studies of surface morphology, carried out in the same work, are consistent with these results. Measurements by atomic force microscopy (AFM) showed that exposure to NH₃ plasma for 1 min leads to smoothing of the GO surface. With an increase in the processing time to 5 min, the inhomogeneity of the surface increases due to the destructive effect of the plasma. Four-probe sheet resistance measurements showed that initial treatment with a duration of 1 min leads to a sharp decrease of resistance by 6 orders of magnitude. The resistance reaches a minimum after 3 min of plasma treatment (67.5 ± 4.5 kΩ/sq) and further is a gradual increase of the resistance is observed. The authors attribute the increase in electrical conductivity to the removal of oxygen functional groups and nitrogen doping of graphene oxide.

Kumar and others investigated the effects of plasma N₂ and H₂ (50 sccm each) at a power of 500 W for a time of 1 hour on the GO properties [41]. The microwave plasma source was oriented from the GO sample and the temperature was raised only by 10°C during plasma treatment. After plasma treatment, a slight increase in the Raman intensity ratio of the I_D/I_G peaks from 0.97 to 1.05 was observed. From the XPS data it was obtained that the C/O ratio increases from 2.2 to 5.2. It was found that the nitrogen introduced during the plasma treatment was 5.8 at.% of the material. The decrease in oxygen group content was confirmed not only from XPS measurements, but also from Fourier-transform infrared spectroscopy (FT-IR) spectroscopy data, as well as from other works, for example see [38]. After exposure in plasma, the intensities of the FT-IR peaks corresponding to the oxygen functionalities, such as the C〓O stretching vibration peak at 1726 cm⁻¹, was decreased dramatically.

In [9] GO was processed in an N₂ inductively coupled plasma (ICP) (P = 50 W, 50 mTorr, flow rate of 10 sccm). As a result of plasma exposure, the ratio of I_D/I_G Raman intensities of the samples increased from 0.851, which corresponds to graphene oxide, to 1.08. The authors note that when comparing treatments in nitric and oxygen plasmas, in the latter case, significant surface distortions are observed due to the high-energy particles present in the oxygen plasma. From the results of measurements of the FT-IR spectra, it was found that treatment in plasma N₂ leads to a significant decrease of the absorption band corresponding to the O-H group, in contrast to the O₂ plasma treatment. Also in the IR spectra new peaks appear at 1331 cm⁻¹, which confirms the presence of the amide functional group corresponding to N-H in-plane stretching, and the peaks 1608 cm⁻¹ belong to C-N bond stretching.
Lee and et al. used inductively coupled NH$_3$ plasma with a power of $1 \times 10^3$ W/m$^2$ at a pressure of 500 mTorr [40]. Samples were processed in the two plasma regions: the bulk plasma region ($R_{\text{bulk}}$) and the sheath region ($R_{\text{sheath}}$). In both regions, reduction and nitridation processes began immediately once the NH$_3$ plasma was exposed to the GO films. Just like in Kim’s work XPS measurements showed that in both cases a gradual increase N-pyrrolic and a decrease N-quaternary with an increase of treatment time of up to 30 min were observed. The authors also observed an increase in the ratio of N/C and a decrease of the O/C, which can be explained by the substitution of nitrogen compounds at the sites of oxygen functional groups on the r-GO films. At the same time, the electrical conductivity of the r-GO films in the bulk plasma region increased significantly after 10 min of treatment. On the other hand, the optical transmittance of the r-GO films in the $R_{\text{bulk}}$ decreases gradually with increasing processing time, while for the sheath plasma region it first decreases, then after 5 min of processing starts to increase gradually. The observed effects are attributed to the fact that the reactions in each region were shown to be different. The authors explain the observed effects by the difference in the reactions in these regions. In the $R_{\text{sheath}}$, the physical reaction was dominant because of the accelerated ion bombardment by the strong electric field. In general, comparing these sample locations in the reaction chamber, the authors conclude that the reduction in the $R_{\text{bulk}}$ is more effective.

Mohai et al. in [42] estimated the penetration of nitrogen and argon ions into the GO using the stopping and range of ions in matter (SRIM-2013) program. Calculations have shown that at energies of 20–50 eV, the depth is equal for the two ions. Thus, plasma can only modify narrow near-surface regions.

It was shown in [43] that, as a result of nitrogen plasma treatment, the defect formation causing an increase in the intensity of the Raman peak D of the spectra depends on location of the samples in the reaction chamber. The substrate was placed “face down” into the plasma chamber (Figure 1), which significantly reduced the formation of defects in the rGO. In the investigated rGO samples, the electrical resistance increased, it is possible that this is due to the predominance of defect formation over doping and restoration of the graphene lattice.

Figure 1. Schematic view of plasma system used for nitridation of graphene oxide.
Qin et al. [49] demonstrated that N\textsubscript{2} plasma treatment is an efficient technique to prepare rGO with simultaneous introduction of N doping and ferromagnetism. The structural characterizations clearly demonstrate that the pyrrolic N bonding configuration is the main source of ferromagnetic moments. At the same time, the N\textsubscript{2} plasma exposure time plays the key role in tuning the magnetization of nitrogen doped rGO.

Recently Wang et al. have shown that the nitrogen plasma treatment is used to modify graphene oxide to enhance the oxygen reduction reaction (ORR) performance, which implicates a burst open and high-energy electron/ion collision mechanism for doping and exfoliating [50].

Zhu et al. [51] devoted much attention to the study of the electrical properties of graphene oxide exposed to ammonium and hydrogen plasmas with the addition of argon in the ratio (9:1). Field effect transistors (FET) of rGO were manufactured for the study of electrical characteristics. It was found that the action of ammonium plasma for 8, 5 min leads to electronic conduction. It was found that the action of ammonium plasma for 8, 5 min. Leads to an n-type conductivity with an electron mobility of 5.43 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. At the same time, with a processing time of up to 5.5 min, the p-type conductivity predominates with a hole mobility of 2.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. At intermediate exposure times, ambipolar conductivity is observed. The results of the work performed show that treatment with nitrogen plasma leads to the reduction of graphene oxide due to the removal of oxygen containing groups, as well as to n-doping. From the analysis of the XPS spectrums, the authors believe that nitrogen atoms in the pyridine configuration are responsible for the formation of n-type conductivity. With a short plasma exposure time, oxygen doping dominates, leading to a p-type conductivity of FET transistors.

### 4. Plasma fluorination

Plasmas of carbon tetrafluoromethane (CF\textsubscript{4}) and sulfur hexafluoride (SF\textsubscript{6}) are more often used for the fluorination of GO by plasma [8, 52–54]. In [8], the effect of plasma treatment of SF\textsubscript{6} and CF\textsubscript{4} ions on GO in the structure of an organic solar cell was investigated by methods of Raman spectroscopy, XPS, ultraviolet (UV) and infrared (IR) spectroscopy, and photoelectric characteristics measurements. For this purpose, reactive ion etching in a plasma with a power of 20 W with a duration of 10 to 60 s at a pressure of 20 mTorr was used. The results of the research showed that the use of GO films functionalized in the SF\textsubscript{6} and CF\textsubscript{4} plasma makes it possible to increase the conversion efficiency of solar energy from 0.56 to 2.72%. And the best result was achieved by processing in plasma SF\textsubscript{6}. From measurements of Raman spectra it follows that the ratio of the Raman spectra of I\textsubscript{D}/I\textsubscript{G} spectra as a result of plasma fluoride treatment increases slightly (from 1.17 to 1.21). This means an increase in disturbances in the graphene lattice. The XPS method revealed the presence of two peaks of C1s and F1 s in the spectra. C1s peak authors are considered responsible for the formation of C-F and C-F\textsubscript{2} bonds with energies at 288.7 and 290.9 eV after SF\textsubscript{6} and CF\textsubscript{4} plasma treatment. The peak F1 s shows the presence of two components of the C-F bond with energies of 685.4 and 688.1 eV corresponding to the semimetallic and semiconductor bonds. In this case, as the authors
believe, fluorine should change the electrostatic potential on the outer surface. The large difference in the electronegativity between carbon (2.55) and fluorine (3.98), according to the authors, means that the C-F bonds on the surface are polar. This is equivalent to introducing a layer of dipoles over the entire surface, which can increase the electrostatic potential energy on the surface with covalent bonds [8].

Zhou et al. used XPS, X-ray diffraction (XRD), AFM and transmission electron microscopy (TEM) methods to study GO obtained by the Hammers method [52]. The CF$_4$ plasma treatment conditions were as follows: gas flow rate of 1.5 l/h, operating pressure of 20 Pa, a bias voltage of 200 V, the power of 240 W, and process duration of 1, 3, 5, 10, 15, 20 min, respectively. From XPS data it is shown that fluorination in plasma of CF$_4$ leads to the formation of C-F, C-F$_2$ and C-F$_3$-bonds. Moreover, the intensity of the peak (C-F) increased at small times (up to 10 min) of treatment, and then sharply decreased. As the authors believe, this decrease may have resulted from the reduction in the conjugated $\pi$-domains. At the same time, the proportion of components CF$_2$ and CF$_3$ only increases with increasing processing time. On the other hand, the content of C-C and C-O decreases. The fluorination of GO can occur due to the substitution of hydrogen atoms in C-H and O-H bonds, as well as oxygen atoms in oxygen-containing groups. Using AFM and TEM, a thinning effect for GO exposed to plasma in CF$_4$ was observed. The thickness of pristine GO after plasma exposes decreased from ~1.9 to 1.3 nm. The hydrophobicity of GO showed that with increasing treatment time to 20 min, super hydrophilic GO becomes neither hydrophilic nor hydrophobic [52].

In Ref. [53] studied the effect of an inductively coupled Ar/SF$_6$ plasma with a power from 100 to 250 W at a pressure of 15–30 Pa on the property of graphene oxide. Using the X-ray energy dispersive spectroscopy, the fluorine content on the GO surface was found to increase depending on both the plasma power and the fluorination time. In this case, the ratio of the fluorine to oxygen concentrations (F/O) ratio content changes more rapidly than the change in fluorine to carbon concentrations (F/C). This can mean that fluorination is more due to the displacement of oxygen than carbon atoms. There is also a slight change in Raman spectra after plasma treatment lasting up to 30 min. Measurements of the volt-ampere characteristics showed a gradual increase in resistance with increasing processing time.

Yu et al. in [54] the high density plasma etcher was employed to carry out the fluorination at room temperature with the CF$_4$ flow rate fixed at 20 sccm and the pressure kept at about 0.16 Pa. XPS measurements showed that after fluorination the C/F ratio increased from 17.2 to 27%, depending on the treatment time. The study of surface morphology by AFM showed that the structure of the graphene substrate is well preserved after the plasma treatment, implying negligible damage for the samples. These data are confirmed by the Raman spectra data, from which it follows that the ratio of the peak intensities D (at 1340 cm$^{-1}$) G (at 1601 cm$^{-1}$) and the ratio of these two peaks ($I_D/I_G$) all remain practically the same after fluorination. At the same time, unlike the work of [51], the thickness of the graphene substrate increases from ~0.4 to ~1.0 nm, which the authors associate with fluorination. Perhaps this difference is due to the short processing times, which in this work were up to 20 s, while in Zhou’s work—up to 20 min. Studies of electrical properties after treatments with a duration of up to 10 s showed that the current–voltage (IV) characteristics remained practically unchanged, which indicates,
in the opinion of the authors, that the structure of rGO was not damaged by plasma treatment. After the fluoridation of GO authors noted a weak p-doping accompanied by a decrease in mobility due to the appearance of new scattering sites associated with F-containing groups.

The study of the fluorination of various carbon materials by plasma makes it possible to understand more fully the effect of such treatment on the properties of graphene oxide. The effect of plasma SF₆ fluorination on the properties of graphene was investigated in [55–59]. Baraket et al. the chemical vapor deposition (CVD) graphene was treated with a pulsed Ar/SF₆ plasma (pulse duration 2 ms and period 20 ms, plasma exposure time was 6 s and the total treatment time was 60 s) at a pressure of 50 mTorr, where the reactive gas was 5% of the total flow rate [55]. The ion energy was on the average 3 eV, which is the latter is lower than the bonding energy of C-C (3.6 eV) or C≡C bonds (6.35 eV) that form the graphitic plane of graphene. The total fluorine content after plasma treatment, measured by the XPS method, was 18 at.%. Moreover, no sulfur or sulfur compounds were observed after treatment. The intensity of the D band in Raman spectra caused by the disturbances increases significantly and exceeds the intensity G of the peak. Although the incident ion energies are low to cause impact-driven physical defects, the ion energies are sufficient to drive chemical reactions at the surface when reactive ions and/or neutrals are present during irradiation. Fluorine forms two types of bonds with carbon: ionic and semi-ionic bonds, which do not violate the planar character of graphene, and covalent sp³-hybridized bonds. The increase in the intensity of the D band in the Raman spectra indicates an increasing amount of carbon bound to sp³ in the structure of the modified graphene [18, 33]. After heat treatment at T = 500°C in an Ar atmosphere with a duration of 10 min, the fluorine is completely removed, the intensities of D and D’ peaks, as well as the I_D/I_G ratio drastically decrease [55]. In [56] the effect of pure SF₆ plasma generated in a reactive ion etcher (RIE) system at a radio-frequency of 13.56 MHz on epitaxial graphene. An rf power of 50 W and an SF₆ partial pressure of 100 mTorr were used for all experiments. From XPS, ultraviolet photoelectron spectroscopy (UPS) and Raman spectroscopy of multilayer epitaxial graphene, the authors concluded that the configuration of sp² graphene remains unchanged after plasma treatment, and fluorination is limited to one or two surface layers. The authors believe that fluorination to the carbon atoms at the edges of graphite domains generated by ion-bombardment. Similar studies of the effect on graphene obtained by a micromechanical method were carried out by Yang [57]. The plasma processing conditions were as follows: 5 Pa of pressure, 5 W of power and a 5 sccm gas feed rate by different durations. From Raman spectra studies, the authors report that fluorination of single-layer graphene occurs is much more feasible than that of bilayer and trilayer graphenes, for which high fluorination times are required. Studies have shown that the process of plasma fluorination of graphene is a reversible process. The annealing carried out by the authors at a temperature of 970°C for 1 hour completely restored the original graphene structures.

Chen et al. [58] from the Raman analysis of spectra of graphene exposed in plasma SF₆ (5 Pa, 5 W, 5 sccm) concluded about p-doping of graphene. Moreover, the p-doping of the edges of monolayer graphene is more significant than its central part.

Zhang [59] used SF₆ plasma to fluorinate the CVD graphene (37.5 mTorr, P = 5 W, at a gas flow rate of 2 sccm, DC bias voltage 13 V, the processing time was from 10 to 90 s). From the analysis
of Raman spectra and XPS, the authors concluded that fluorination leads to covalent bonds and p-doping of graphene occurs. At the same time, the ratio $I_D/I_G$, which increased to ~ 2.9 after initial treatments of up to 50 s, starts to decrease continuously with further increase in the processing time. The authors explain this effect by the formation of a less stable fluorine group, which decays with increasing processing time.

The results of the plasma fluorination of graphene in CF$_4$ are reported in Refs. [26, 60–66]. Cheng et al. used the RIE system to treat CVD graphene CF$_4$ with plasma (40 W, 700 mTorr) [67]. As a result of plasma processing in Raman spectra of graphene, after 10 s of processing, the intensities of the peaks (D, D', D + G), associated with the introduction of structural lattice disorderings [18, 33, 62], significantly increased. According to the authors, the reason for this can be the conversion of sp$^2$-carbon to sp$^3$-hybridization due to the adsorption of fluorine, which coincides with the conclusions of other authors [61, 62]. With an increase in processing time to 300 s, Raman peaks become almost invisible. This result is typical of strongly fluorinated graphene [68–70]. It was shown in report [60] that the ratio of the intensity D of the peak to the G peak increases significantly with initial treatments and then goes to saturation with a further increase in the fluorination time. At the same time, the ratio of $I_{2D}/I_G$ intensities shows the opposite trend and reaches to saturation gradually. The intensity of the 2D Raman peak is related to two phonon double-resonance Raman processes [33, 71]. The saturation yield can mean the absence of chemical etching by fluorine of carbon, if there is no ion bombardment [62]. At the same time, Shen and other [63] methods of optical microscopy and Raman spectroscopy observed thinning of graphene layers and an increase in structural disturbances during fluorination in CF$_4$ plasma (at a power of 20 W at a pressure of 0.8 Torr), as well as in the report [52]. Exposure of graphene in a plasma with a duration of 5 s resulted in the removal of the upper layer of graphene. The paper notes that functionalization occurs due to the formation of covalent bonds that distort the lattice structures of graphene. As a result, the intensities of D and D’ peaks in the Raman spectra increase. It should be noted that different authors have no common opinion on this matter. From the analysis of XPS data and the results of measuring electrical characteristics, Cheng et al. in [60] state that at low fluorine content, ionic bonds of C-F components are introduced. With a high content of fluorine, covalent bonds dominate. The above increase in $I_D/I_G$ and a decrease in the $I_{2D}/I_G$ ratio in the Raman spectra, with short processing times (up to 10 s), was observed in [26, 61, 62] under close fluorination conditions in plasma. The Raman $I_D/I_G$ peak ratio mapping images of fluorinated graphene showed that the flat portions of graphene are uniformly fluorinated [60]. While, in multilayered CVD graphene containing wrinkles, wrinkles, etc., heterogeneous fluorination occurs. As the authors argue, these areas are less susceptible to fluoridation. Similar results were obtained in [26, 61], who found that single-layer graphene is more efficiently fluorinated by plasma than two and three-layer graphene films. Measurements of the resistance of CF$_4$ CVD-graphene fluorinated in plasma showed a significant increase in electrical resistance from several kΩ to several MΩ [65] and even more than 100 GΩ [64]. Despite the high values of electrical resistance, there were regions with low resistances (such as bilayer islands, folds (2-layer height, width ~ 100 nm), wrinkles (line width < 50 nm), and ripples (fine parallel lines with spacing ~ 150 nm), which have small resistance [64]. In the authors’ opinion, this is due to the weak fluorination of these regions. The increase in the resistance of fluorinated graphene is associated with the formation of covalent bonds [64, 65]. Annealing in a 30-min nitrogen atmosphere showed
that the fluoride desorption process is heterogeneous, due to the presence of various C-F bonding components, and can begin at temperatures of 150°C with a low fluorine content [60]. Annealing of samples with a high content of fluorine, which has predominantly covalent components, showed that at T = 300°C, the ratio of $I_D/I_G$ intensities increases to 1.8, and then decreases to ~ 1.5 when annealed to 600°C [60]. In [62], from the measurements of topography and currents obtained by the AFM method, fluorinated clusters sp3, with dimensions of ~ 20–30 nm, were detected.

An increase in the covalent bound fluorine content during plasma fluorination was observed on the surface of graphene nanoplates (GNPs), multi-wall carbon nanotubes (MWCNT) [72, 73] and highly ordered pyrolytic graphite (HOPG) [72]. Fluorination of GNPs and MWCNT in CF4 plasma leads to covalent bonding of fluorine with irregularities, defects, boundaries and with sp2 carbon atoms inside graphene sheets of both carbon materials [72]. Thus, the surface area of both materials is a parameter that partially determines the degree of functionalization. This is confirmed by the fact that surfaces of CNTs are easier to fluorinate than HOPG surfaces. This is the expected result, since the hybridized compound sp2 in graphite is much more stable than the distorted sp2 compound observed in nanotubes [21].

In reports of Tahara et al. [74] to suppress ion bombardments and improve the reaction with fluorine radicals on graphene, the substrate was placed “face down” in the plasma chamber. Graphene samples were investigated prepared by the mechanical exfoliation from graphite. For the fluorination process was used a RIE system. The graphene samples were exposed to Ar/F2 (90%/10%) plasma with a relatively low rf power of 5 W, a gas pressure of 0.1 Torr, and a total gas flow rate of 75 sccm at room temperature. The reaction time ranged from 0.5 to 30 min. The fluorination of graphene led to a sharp increase in the intensity of D-peak caused by the defects (1350 cm$^{-1}$). At the same time, with increasing reaction time, the D peak intensity shown non-monotonic behavior and had the maximum at 3 min, while the 2D peak intensity decreased monotonously. As the authors believe, such behavior of the peak intensities indicates an increase of amount of fluorine atoms attaching to the graphene. The authors explain the decrease in the D-peak intensity by the competition between the defect-phonon scattering processes and the decrease in the lifetime of the electronic states, caused by an increase in the defect concentration. The paper also shows that the monolayer graphene was more reactive than bilayer. In addition, an annealed the fluorinated graphene samples in the atmosphere for 90 min at 573 K showed that fluorination in a plasma is a reversible process.

5. Conclusion

A review of the literature shows that plasma treatments in various gases are primarily used for the functionalization of graphene oxide to produce graphene oxide from graphene. Summarizing the effects of GO processing in various gases, the following conclusions can be drawn:

1. The effect of an oxygen-containing plasma leads to rapid etching of the GO layers, accompanied by the formation of a large number of defects. The etching rates depend on the type of plasma source used, the location of the samples in the reaction chamber and the distance
from the plasma, as well as the plasma power, gas pressure and processing temperature. The aggressive effect of oxygen plasma can be reduced by using ‘gentle’ treatments. In addition, plasma treatment in oxygen can be used to produce GO from graphene. The graphene oxide obtained in this way has a higher wettability of the surface, this circumstance is of interest in the development of biological sensors and gas sensors.

2. Treatment in nitrogen plasma does not lead to aggressive etchings in oxygen, but if special measures are not taken to protect the exhaust gas from the plasma, defect formation can be significant. Exposure of graphene oxide in a nitrogen plasma can be used for n-doping graphene oxide, but p-doping has been observed in some studies. This effect depends on the type of binding of nitrogen atoms to carbon (formation of pyridine, pyrrole and graphite configurations) and, depending on this, both donor and acceptor charge carriers can be introduced. The use of ammonia NH$_3$ plasma allows for both reduction and simultaneous alloying of graphene oxide.

3. Plasma treatment in fluorine-containing plasma (CF$_4$, SF$_6$) is an effective method of fluorination of GO, mainly due to the displacement of oxygen atoms. The intensity of etching in the fluorine plasma is low, which allows the use of treatments lasting up to tens of minutes. The effect of plasma leads to an increase in the electrical resistance, accompanied by a weak p-doping. Plasma fluorination is a reversible effect and when heat treatments above 500°C, complete removal of fluorine atoms occurs.

The general effects of the action of plasma treatment can be reduced to the following points: the most noticeable functionalization of graphene oxide occurs at the initial processing times in plasma, duration, as a rule, up to 1 min. The effect of plasma on GO properties is limited to several atomic layers and does not affect the bulk properties of GO. When plasma treatments GO one of the primary tasks remains to protect the surface from the defect formation and etching of GO films.

In general, it should be noted that the effect of plasma treatments on GO properties is still poorly understood. If we compare the amount of work devoted to the plasma treatment of graphene and graphene oxide, then this amount for GO is much lower. A still poorly studied region remains the study of the effect of a plasma of a mixture of various gases on the properties of graphene oxide. Mechanisms of functionalization of graphene oxide in various plasma media have not been fully investigated. The problem of the “gentle” effect of plasma on the surface of graphene oxide has not been completely solved. When using plasma treatments to control the properties of graphene oxide, these problems must be solved in the future.

Author details

Efim Petrovich Neustroev

Address all correspondence to: neustr@mail.ru

Institute of Physics and Technologies, North-Eastern Federal University (NEFU), Yakutsk, Russia
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