Research of Properties of a Carbon Film Formed in Methane Plasma and the Following Annealing

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Abstract. In the work, the properties of graphene oxide processed in methane plasma and plasma of a mixture of methane and nitrogen and subjected to subsequent annealing at T = 650 °C in an argon atmosphere are investigated. It is shown that during plasma treatment, the hydrogenated amorphous carbon film is deposited on the surface of the exhaust gas. During heat treatment, a significant part of this film is removed, another part of the carbon atoms participates in the formation of bonds with the structure of the exhaust gas. This process leads to a decrease in the density of defects introduced by the plasma. The inclusion of nitrogen in methane plasma leads to n or p doping depending on the plasma power level. This effect is explained by the predominant formation of graphite and pyridine nitrogen configurations, which are donor centers in structures with fewer defects. At a high density of defects, pyrrole nitrogen structures, which are acceptor centers, are mainly introduced.

1. Introduction

Graphene oxide (GO) is an oxidized form of graphene and is of interest in the creation of various sensors (optoelectronic, biological, gas) [1-4], supercapacitors [5], the basis for organic light-emitting diodes [6] and polymer nanocomposites [7]. In many ways, the electrical and optical properties of GO are associated with the possibility of its chemical functionalization using molecules and atoms. Functionalization allows you to change the bandgap of graphene oxide, affects the concentration of charge carriers and their mobility, conductivity, optical absorption [4,8]. One of the effective methods for functionalizing graphene and its derivatives is plasma treatment. Thus, the treatment of graphene oxide in methane plasma saturates the surface with hydrogen and promotes the removal of oxygen groups [9]. Besides, due to the incorporation of carbon atoms into the lattice of the OG, the crystal structure of the lattice is restored and the number of structural defects decreases [9-11]. The use of heating in the process of plasma treatment allows the simultaneous removal of defects to carry out the
reduction of graphene oxide [12]. Yang and other was demonstrated a simple and easy method for the reduction of graphene oxide without heating in an inductively coupled methane plasma with characteristics exceeding the results achieved when hydrogen plasma was reduced at room temperature [13]. The authors of the process of exhaust gas recovery in methane-containing plasma are divided into two stages that occur simultaneously.

First, under the influence of high-energy electrons, CH4 molecules decompose into hydrogen and CHx radicals (x < 4). Active hydrogen interacts with oxygen functional groups and removes them from the exhaust gas lattice. This process dominates at the initial plasma treatment times. With an increase in the exposure time of the sample in the plasma, the amount of oxygen on the surface decreases, and the process of carbon deposition (CHx radicals and amorphous carbon) onto the surface of the exhaust gas begins to dominate. This process leads to an increase in film thickness and a decrease in electrical conductivity. The deposition of carbon from methane plasma at low temperatures and the formation of hydrogenated amorphous carbon films were observed in [14, 15]. Investigation of the effect of heat treatment on tetrahedral amorphous films showed that at temperatures of about 700 °C, sp3 and sp2 bonds are transformed [16]. In the presence of hydrogen, the loss of sp3 bonds occurs at lower temperatures of 300–400 °C [16].

During plasma treatment in nitrogen (N2), N atoms decorate graphene flakes and shift the Fermi level, causing the doping effect [17]. Therefore, doping with N can play an important role in controlling the electronic properties of exhaust gases. Three types of binding of a nitrogen atom to a graphene lattice are distinguished — pyridine, pyrrole, and graphite (substitution) [17–20]. In this case, graphite and pyridine configurations form sp2 bonds, while pyrrole configurations form sp3 bonds [19]. Plasma treatment in nitrogen leads to an increase in the fraction of pyrrole and pyridine bonds, while the fraction of graphite bonds does not increase [17, 20, 21]. In the graphite and pyridine configuration, nitrogen atoms lead to the n-doping of graphene [21,22]. Regarding pyrrole nitrogen, the opinions of the authors differ and some authors consider it to be an acceptor [21], others consider it to be a donor [22,23]. The type of conductivity will depend on the ratio of the nitrogen configurations leading to n- or p-doping. On the other hand, the electrical conductivity of graphene films will be influenced by the fact that at high content of dopant N, carbon nitride films can be formed, which have an extremely low electrical conductivity [24]. The same effect is caused by an increase in the density of defects caused by doping and prolonged (or higher powerful) plasma exposure, which is necessary to increase the doping level [25].

In this work, we studied the effect of plasma treatment in methane and a mixture of methane and nitrogen on the optical, structural, and electrical properties of graphene oxide. The exhaust gas was functionalized by plasma treatment and subsequent heat treatment at a temperature of 650 °C.

2. Experimental technique

For research, graphene oxide samples obtained by the modified Hammers method with a thickness of several units to tens of nm were taken. Modification of the properties of the exhaust gas was carried out by treatment in plasma of methane or plasma of a mixture of methane and nitrogen. To conduct a comparative analysis, the SiO2 / Si substrates without GO were plasma treated. Further, all samples were heat-treated at a temperature of 650 °C. Inductively coupled plasma was excited by a high-frequency generator at a frequency of 13.56 MHz with a rated power of up to 300 watts. The power of the generated plasma ranged from 150 watts to 200 watts.

Figure 1 shows the installation diagram of the plasma-chemical etching Etna-100 PT (NT-MDT). The Si / SiO2 substrates (GO / SiO2 / Si) (or GO on glass for optical studies) were placed in the reaction chamber in the middle of the lower substrate holder with a diameter of 120 mm (Fig. 1) at a distance of 100 mm from the upper electrode. The reaction was carried out in a chamber evacuated to a pressure of 0.001 mbar. After gas injection, the working pressure in the chamber increased to 0.03 mbar at a flow rate of methane and nitrogen of 30 and 10 cm³ / min, respectively. The total exposure time of the samples in the plasma did not exceed 12 minutes and was no more than 6 minutes in one process. The temperature of the sample during the process did not exceed 50 ° C. After plasma
treatment, the samples were subjected to heat treatment at a temperature of 650 °C for 30 min in an argon atmosphere. The obtained carbon films were studied using scanning electron microscopy (SEM) (JEOL JSM 7800F), atomic force microscopy (AFM) (Ntegra Spectra), X-ray energy dispersive spectroscopy (EMF) (INCA Energy, Oxford), and an IR spectrometer (Perkin Elmer Spotlight 200i), micro-Raman spectroscopy (Ntegra Spectra).

Figure 1. Scheme of installation of plasma-chemical etching ETNA-100 PT.

3. Results
During the processing of exhaust gas samples in methane plasma, carbon is deposited on a substrate, which, in particular, manifests itself in a change in the color of the substrate from blue (for SiO2 substrate) to yellow-green. To determine its thickness, cuts were made on the surface of a carbon film deposited on the surface of SiO2. The height of the formed step at the SiO2 / film interface was measured using an AFM. Figure 2 shows the step height for a sample exposed in a plasma with a power of P = 200 W for 9 min. The cross-section of this threshold in the selected area is shown in the right figure. The thickness of the deposited film was approximately 100 ± 10 nm. Thickness measurements were performed at various points on the surface of the sample. Thus, it can be argued that a carbon film is deposited on the surface of the substrate at a rate of about 10-12 nm/min. It should be expected that a similar carbon deposition also occurs on the surface of the exhaust gas, which is also accompanied by a change in color from the initial (depending on the film thickness) to blue-green. The inset in Figure 2 shows the surface roughness of the carbon film, which does not exceed 2 nm.
Figure 2. AFM image of the SiO2 film interface / deposited carbon film and step height (right). The inset shows the surface roughness of a carbon film deposited in a methane plasma.

In figure 3 shows the SEM image of the same SiO2 / interface (GO + deposited film). In the figure, the region designated in the figure as “Spectra 1” corresponds to a film deposited from methane plasma, and the region “Spectra 2” corresponds to the surface of SiO2. SEM image confirms that the surface has a slight roughness. EMF measurements in these areas showed the presence of carbon and oxygen in a 4:1 ratio (Table 1), while, as expected, only oxygen and silicon atoms in a ratio close to 2:1 were detected for the surface of the SiO2 substrate. It should be noted that the EMF method does not detect the presence of hydrogen in the samples.

The presence of hydrogen in plasma-deposited films was carried out in samples on SiO2 / Si substrates using IR spectroscopy. In figure 4 shows the absorption spectra in the infrared region of carbon films deposited in a methane plasma with a power of P = 200 W for a duration of 9 minutes on glass substrates. In the IR spectra can be distinguished

Figure 3. SEM image of the sample surface after exposure to methane plasma with a power of 200 W for a duration of 9 min.
Table 1. The content of the elements in the areas indicated in Figure 3 as “Spectra 1” and “Spectra 2”.

| Elements | Spectra 1 | Spectra 2 |
|----------|-----------|-----------|
| C        | ~80       | -         |
| O        | ~20       | ~70       |
| Si       | ~30       | ~30       |
| Summary  | 100       | 100       |

the following absorption bands in the IR spectra due to the presence of hydrogen: a wide absorption band in the region from 3000 to 3700 cm⁻¹ with a maximum at ~ 3400 cm⁻¹, associated with OH hydroxyl groups [26–28]; a weak “shoulder” at 1445 cm⁻¹, the nature of which can be caused by OH bonds [28]; peaks in the vicinity of ~ 2868 cm⁻¹ and ~ 2933 cm⁻¹ are explained by vibrations of CH bonds [28]. The nature of the absorption band with a maximum at ~ 1710 cm⁻¹ can also be associated with vibrations of carboxyl groups [29]. The nature of the remaining peaks is associated with vibrations of carbon bonds and epoxy groups [29, 30]. Thus, measurements of the light absorption coefficient in the IR spectrum confirm the presence of hydrogen in the deposited film.

Figure 4. Absorption spectra in the infrared region of carbon films deposited in a methane plasma with a power of 200 W for a duration of 9 minutes on a glass substrate.

Figure 5. Raman spectra of exhaust gases after plasma treatment in methane (P = 200 W, 12 min) and annealing at 650 °C for 30 min in an argon atmosphere. The inset shows the Raman spectra for the same sample before annealing.

In figure 5 shows the Raman spectra of the exhaust gas after plasma treatment in methane plasma with a power of P = 200 W for t = 12 min after annealing at 650 °C. The Raman spectrum for the same sample is shown in the inset of the figure before heat treatment. The broad photoluminescence band observed in the inset is characteristic of hydrogenated films of amorphous carbon (α-C: H) [31]. After heat treatment in the Raman spectra, this photoluminescence band practically disappears and D (~ 1350 cm⁻¹) and G (~ 1590 cm⁻¹) peaks characteristic of graphene oxide appear [32]. The main peak G in the Raman spectra characterizes the vibrations of sp2-hybridized bonds in the carbon plane [33,34]. The nature of the D peak is associated with out-of-plane vibrations of the sp3 bonds and disordering of the lattice [33, 34]. The 2D band in the Raman spectra is the second order of the D peak, but unlike it, it does not require defects for activation [33]. The D + G band is a combination of
D and G peaks and is also associated with defects [35]. The “shoulder” of the D + G peak observed at \( \sim 3150 \text{ cm}^{-1} \) is presumably caused by vibrations of the carbon--hydrogen bonds of the aromatic carbon ring [35]. The band observed in the region from 920 cm\(^{-1}\) to 1050 cm\(^{-1}\) is most likely a manifestation in the Raman spectra of the silicon substrate [36,37]. An increase in its intensity after annealing can be associated with a decrease in the thickness of the carbon film during heat treatment. The observed results can be explained by the deposition of an amorphized carbon film on the surface of the exhaust gas, which is partially removed after heat treatment, and part of the carbon atoms forms bonds with the surface atoms of the exhaust gas, consisting of graphene flakes. Also, Raman spectra confirm the presence of hydrogen in the GO film.

The decrease in the thickness of the carbon film deposited during plasma treatment in methane after annealing is shown in Fig. 6, which shows the AFM image of the SiO\(_2\) / carbon film interface after heat treatment. Carbon film thickness measurements carried out in different regions at the interface showed values from 2 to 4 nm. Thus, the thickness of the deposited film after heat treatment decreases by several tens of times from the initial value shown in figure 2.

![Figure 6](image_url)

**Figure 6.** The surface of the sample at the interface between the carbon-containing film and SiO\(_2\) after annealing at 650 °C for 30 minutes in an argon atmosphere and the step cross section between them. The insert of the figure shows the roughness of the carbon-containing film.

The surface roughness remains approximately at the same level as before annealing (~ 2 nm) (inset in figure 6). Similar values of surface roughness were also observed during deposition on the surface of the exhaust gas. At the same time, the roughness of the recovered exhaust gas at \( T = 650 \text{ °C} \) for \( t = 30 \text{ minutes} \) is much larger due to the presence of wrinkles and wrinkles on its surface.

Measurements by the Hall effect method showed that the mobility of the charge carriers (holes) of the GO treated in a methane plasma is \( \sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). With the addition of nitrogen to the methane plasma, the mobility decreases during the processing of exhaust gases in a plasma with a power of 150 W, while at higher power (200 W) they do not noticeably change. This behavior is explained by the fact that when using a plasma of lower power, fewer structural defects are introduced, which are subsequently eliminated by heat treatment during the incorporation of amorphous carbon atoms into the structure of the exhaust gas. As a result, the nitrogen impurity introduces donor centers in the pyridine and graphite configurations. In this case, the Hall measurement gives the weighted average effective mobility of holes and electrons, which becomes very small. At high plasma powers, which is accompanied by significant defect formation, the crystal structure of the lattice does not completely recover during heat treatment and nitrogen predominantly forms a pyrrole configuration. As noted
above, pyrrole N can lead to the introduction of acceptor impurities; as a result, the introduction of nitrogen into the methane plasma does not substantially change the hole mobility.

4. Conclusion
In the work, the properties of graphene oxide processed in methane plasma and plasma of a mixture of methane and nitrogen and subjected to subsequent annealing at \( T = 650 ^\circ C \) in an argon atmosphere are investigated. Using Raman spectroscopy, SEM, AFM, EMF, and IR spectroscopy, it was shown that the plasma treatment of GO and SiO2 leads to the deposition of a hydrogenated amorphous carbon film. During heat treatment, a significant part of this film is removed, the remaining carbon atoms participate in the formation of bonds with the structure of the exhaust gas. As a result, the crystal lattice is restored, which, in particular, manifests itself in the form of a decrease in surface roughness. The introduction of nitrogen into the nitrogen plasma leads to n-doping at lower plasma powers (150 W); at higher plasma powers, the type of conductivity does not change. This effect is explained by the predominant formation of graphite and pyridine nitrogen configurations, which are donor centers, in structures with fewer defects. The formation of these structures occurs both in the course of plasma treatment and in the process of subsequent heat treatment during the incorporation of amorphous carbon atoms into the GO structure, which eliminates lattice defects. At a high density of defects, pyrrole nitrogen structures, which are acceptor centers, are mainly introduced. Heat treatment does not completely remove defects, which contributes to the formation of N pyrrole. Thus, the introduction of nitrogen and control of the plasma power makes it possible to control the level of doping in the GO film.

5. References
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