Impact of plasma treatment in CH$_4$/N$_2$ on the properties of reduced graphene oxide

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Abstract. The effect of the two-step process on the properties of graphene oxide (GO) is studied. At the first stage, CH$_4$ (or CH$_2$+N$_2$) plasma treatment was performed. The second one was heat treated at a temperature of 650°C. The formation of thin polycrystalline carbon films on the surface of graphene oxide was detected. The ratio of carbon to oxygen concentration corresponds to graphene oxide. Smooth surfaces of the films were detected by an atomic force microscope. Films have lower sheet resistance and higher carrier mobility than reduced GO (rGO) during the same heat treatment. An analysis of the Raman spectra shows that the formed films have larger graphene domains than the rGO. The presence of nitrogen in methane plasma leads to a decrease in the resistance and mobility of carriers in the carbon film.

1. Introduction

Graphene oxide (GO) belongs to the family of two-dimensional graphene-like materials. Due to its electrical, chemical and mechanical properties, reduced graphene oxide is of interest for use as optoelectronic devices [1, 2], bio- and gas sensors [3-9], electrodes [4, 9, 10] and fuel cells [4, 11, 12]. Graphene oxide can be given individual properties through functionalization [3, 8, 9]. Despite its advantages, GO needs to improve a stability of parameters and the quality of the crystal structure, eliminate oxygen functional groups and increase electrical conductivity. Effective methods for modifying a properties of GO through an addition of various functional groups are also required.

Methane is the main component in the chemical vapor deposition of graphene [10, 11]. By adding nitrogen to the methane stream, graphene can be doped [12]. The use of plasma in the CVD method significantly reduces the synthesis temperature [13, 14]. A modification of this method is the separation of plasma and heat treatment regions (remote PE-CVD) [15, 16]. This method allows to reduce defect formation and eliminate the vertical growth of graphene flakes during exposure in plasma [16]. In addition, plasma exposure to methane is used to functionalization and healing of lattice defects in graphene [17-19]. A feature of this work is the division of a single process in remote PE-CVD into two separate stages. At the first stage, carbon is deposition in methane plasma at room
temperature. At the second stage, heat treatment is performed. This makes it possible to completely eliminate defect formation due to the effect of plasma reactive elements on the synthesis of a carbon film. This technique allows to reduce defect formation during subsequent synthesis of the carbon film during heat treatment. At the same time, this reduces a cost of producing carbon films relative to the remote plasma processing method. Thus, the aim of this work was to study the combined effect of the plasma treatment with methane and nitrogen in a two-step process on the properties of reduced GO.

2. Materials and methods

2.1. Sample preparation and reagents
A graphene oxide was obtained by an improved Hummers method [20] and a detailed description of the production of GO and its properties was carried out in our previous work [21]. To obtain graphene oxide were used graphite powder (Sigma-Aldrich, USA), H$_2$SO$_4$ (Sigma Tek, Russia), NaNO$_3$ and KMnO$_4$ (Chemman Mosreactive, Russia). An aqueous solution of GO on the SiO$_2$ surface of the Si/SiO$_2$ structure was precipitated and evaporated at room temperature for a day. Methane and nitrogen gases with a purity of $\geq 0.999\%$ for plasma processing were used.

2.2. Measurement methods
The Ntegra Spectra atomic force microscope (AFM) was used to measure the surface topography of GO films in tapping mode. To determine the thickness of GO on its surface, scratches with a sharp metal rod were made. As a result of the formation of a scratch, a threshold formed between GO and SiO$_2$. The height of this threshold was measured by AFM. The threshold height was equal to the thickness of the GO film, since the SiO$_2$ surface remained intact upon the formation of a scratch. To measurements of a micro Raman spectra on the Ntegra Spectra platform, a laser wavelength of 473 nm was used. The study of the surface morphology was carried out using a scanning electron microscope (SEM) (JEOL JSM 7800F) and an AFM. Evaluation of the content of chemical elements in the samples was carried out using energy dispersive X-ray spectroscopy (EDS) Inca Energy. The mobility of the samples was measured using the Ecopia HMS-5000 apparatus using the Hall effect method. To electrical measurements were made point contacts based on silver paste. Contacts were previously dried at a temperature of 120° C in air for 15 min.

2.3. Processing method
Plasma treatments were performed in radio-frequency (13.56 MHz) inductively coupled plasma. Figure 1 shows schematic diagram of the microwave plasma source and the reaction chamber. The samples of GO in the reaction chamber were arranged so that a surfaces of the samples were turned down (“face down”) and were not subjected to bombardment by the reaction products in plasma, as was described in our previous works [22, 23]. After placing the sample in the center of the reaction chamber a reactor was evacuated to a pressure of less than 10$^{-3}$ mbar. Methane (30 sccm) was introduced in the reaction chamber and a plasma was ignited at a pressure of 0.04 mbar with a microwave power of 150 W and 200 W. The same powers were used for plasma processing in a mixture of methane (30 sccm) and nitrogen (10 sccm). Then, a pressure in the chamber was 700 mbar. The process parameters for plasma treatment of samples are shown in table 1. It should be noted that the time of one process was 3 min and a total processing time was 12 min. After plasma treatment, all samples were annealed at 650° C in an argon atmosphere for 30 min.
Figure 1. Schematic diagram of the microwave plasma source and the reaction chamber.

Table 1. Process parameters for plasma treatment of samples.

| Symbol | CH$_4$-flow, sccm | N$_2$-flow, sccm | Power, W | Pressure, mbar |
|--------|------------------|-----------------|----------|---------------|
| Process 1 | 30               | -               | 150      | 400           |
| Process 2 | 30               | -               | 200      | 400           |
| Process 3 | 30               | 10              | 150      | 700           |
| Process 4 | 30               | 10              | 200      | 700           |

3. Results and discussion

Figure 2a presents an AFM image of the GO surface prior to plasma treatment. Measurements of the heights of the steps formed by the interface of GO with the surface of the substrate were carried out with the help of AFM, showed that the thickness of the film under study is in the range from 1 to 5 nm (Figure 2d). Figures 2b and 2f show the corresponding patterns of the sample surface and the profile of the step after plasma processing in methane with a power of $P=200$ W for 6 min. Figures 2c and 2f show similar images for a sample processed in a CH$_4$ + N$_2$ plasma with a power of $P=200$ W for 12 min. Table 2 presents the changes in thickness $\Delta h_1$ and $\Delta h_2$ after plasma treatment for 6 and 12 min, respectively. As can be seen, the deposition processes dominate the etching processes in plasma. These results can be explained by the deposition of carbon and the formation of an amorphized carbon (a:C) film as a result of plasma treatment [24]. For methane plasma, the deposition rate of an a:C film depends on the plasma power and increases with increasing power. The deposition rate is irregular and at the initial exposure times of the plasma reaches the highest value. The lowest deposition rate of an a:C film in plasma CH$_4$ + N$_2$ mixture was observed. Most likely, this is due to more intensive nitrogen etching of the deposited film. After annealing at 650$^\circ$ C, part of the
amorphized carbon film was removed and part of the carbon atoms forms bonds with a GO film. As a result, a thickness of the initial GO film increased by 10–16 nm.

### Table 2. The change in the thickness of the deposited film during plasma processing.

| Change the thickness of the samples | CH₄, 150 W | CH₄, 200 W | CH₄+N₂, 200 W |
|-----------------------------------|------------|------------|---------------|
| Δh₁, nm                           | 40         | 65-75      | 30            |
| Δh₂, nm                           | 60-70      | ~120       | ~(40-50)      |

In the inserts of figures 2a, 2b and 2c it is shown a surface roughness for the initial GO, after CH₄ (200 W, 6 min) and CH₄+N₂ plasma treatment obtained by AFM. Measurements showed that the surface roughness before and after plasma treatment decreased from ~2 nm to ~1 nm, respectively (Figures 2a and 2b). On the contrary, when using a mixture of methane + nitrogen plasma, the roughness increased to ~(4-5) nm (Figure 2 c). This confirms that etching occurs in a plasma involving nitrogen.

Figures 3a and 3b show SEM images of the surface of the initial GO and the surface of the sample after treatment in 200 W methane plasma for 6 min. As can be seen from the figure 3b, no wrinkles and corrugations typical for GO are observed due to the deposition and the formation of an a:C film. The surface roughness of the samples after heat treatment is not noticeably changed and remains the same.

Figure 4 shows the Raman spectra of the initial GO samples after plasma treatment in methane and in a mixture of CH₄+N₂ for 12 min and subsequent annealing at T = 650° C. The Raman spectra of the initial samples have a typical form for GO, containing G and D peaks at ~1600 cm⁻¹ and ~1350 cm⁻¹, respectively. The G peak characterizes the vibrations of the sp² carbon bond system in the planar structure of graphene [25, 26]. The D peak is related with sp³ vibrations of hybridized carbon bonds and its activation requires the presence of structural disorders and/or edge effects [25, 26]. In the figure the intensity of the Raman peaks is normalized relative to the height of the G peak. After plasma treatment, a broad photoluminescence peak characteristic of amorphized carbon appears [24]. This band is most noticeable for samples treated in a CH₄ + N₂ gas mixture plasma (Figure 4b). The maximum of this band also shifted towards lower frequencies with increasing power and duration of the CH₄ + N₂ plasma exposure. During subsequent heat treatments (650° C, 30 min), the intensity of this peak becomes noticeably less and the D and G peaks become the most significant again. Table 3 shows the Raman parameters of the peaks of the initial GO samples, control sample (only annealing) and samples after plasma treatment and subsequent annealing at 650° C. Exposure of samples in plasma leads to a greater redshift of the maximum intensity of the G peak than in the control sample. The red shift of the G peak means an increase in the size of graphene domains or their number [27]. Estimates of the sizes of graphene domains were also performed according to the method proposed in [28].
For this was used the formula [25, 29, 30]:

\[ L_a (nm) = (2.4 \times 10^{-10}) \lambda_{\text{laser}}^4 \left( \frac{I_D}{I_G} \right)^{-1}, \]

where \( I_D/I_G \) is a ratio of the intensities D and G of the Raman peak of the spectra, \( \lambda_{\text{laser}} \) is the laser radiation wavelength. The evaluation showed that the size of the graphene domains after plasma treatment is approximately 14-16 nm. This is 1-2 nm more than for samples that are subject to thermal reduction only and 3-4 nm more than for the initial GO. An increase in the size of graphene domains is consistent with the results of work [17, 18, 31], in which treatment in the plasma of methane led to healing of defects in the graphene lattice. When using plasma power of 150 W or a shorter processing time (6 min), the size of the domains is not noticeably different from the size of the thermally reduced GO.

\[ \text{Figure 2. AFM image of the surface at the GO/SiO}_2 \text{ interface for a) initial GO, b) after plasma processing in CH}_4 \text{ (P= 200 W for 6 min) and c) after plasma processing in CH}_4+\text{N}_2 \text{ (P= 200 W for 12 min). The insets of the figures show the corresponding surface roughness. Figures d, e and f show surface profiles along the white lines shown in figures a, b and c respectively.} \]
Figure 3. SEM images of a) the original GO surface and b) after exposure to 200 W methane plasma for 6 min.

Figure 4. Raman spectra of samples of GO treated in plasma a) CH$_4$ and b) CH$_4$ + N$_2$ in accordance with processes 2 and 4, respectively. In the figures, the numbers indicate: 1 - initial GO, 2 - after exposure to plasma, 3 - after annealing at 650° C for 30 min.

Table 3. The parameters of the Raman spectra peaks for the initial samples of GO and after plasma treatment with CH$_4$ and CH$_4$ + N$_2$ and subsequent annealing.

| Processing conditions | $\lambda_G$, sm$^{-1}$ | $I_D/I_G$ |
|-----------------------|-------------------------|-----------|
| Parameters Raman Spectra before processing (Initial GO) | 1590 | 1.10 |
| Parameters Raman Spectra of control sample (only annealing) | 1584 | 0.88 |
| Parameters Raman Spectra after processing 2 | 1581 | 0.76 |
| Parameters Raman Spectra after processing 4 | 1580 | 0.81 |

Figure 5 shows the spectra of energy dispersive x-ray spectroscopy. As can be seen from the figure for the samples, plasma treatment of methane (process 2) and a mixture of methane + nitrogen (process 4) leads to an increase in the ratio of carbon to oxygen (C / O) on the surface of materials. It should be noted that the highest C / O values are observed upon exposure to methane plasma. The lower rates of formation of an amorphous carbon film during plasma treatment in a methane +
nitrogen mixture can decrease the C / O value. After annealing, the C / O ratio for two plasma-treated samples decreases. To the control sample of GO, as expected, the C / O ratio increases due to the removal of oxygen functional groups during heat treatment.

The reason for this may be associated with a decrease in the thickness of the amorphized carbon film at annealing. For thin films, the EDS results may be affected by the content of elements in the silicon substrate, in which the oxygen content is high. At the same time, a bound oxygen atoms of GO, protected by an amorphized film, will be removed less than in the control samples. As a result, a quantity of carbon atoms will decrease faster than oxygen and C / O will decrease. In contrast, plasma exposure to a CH$_4$ + N$_2$ mixture results in a higher C / O value after annealing. This can be explained, firstly, by the formation of a smaller thickness of the deposited carbon film. Secondly, by replacing oxygen with nitrogen under the action of plasma on the surface of GO. This is confirmed by the EDS data, which shows an increase in the number of nitrogen atoms relative to the initial content by ~ 5%.

![Figure 5. The change in the C/O ratio depending on the processing conditions.](image)

![Figure 6. Carrier mobility in samples rGO (reduction GO), rGO (CH$_4$+N$_2$) and rGO (CH$_4$).](image)

The sheet resistances of the samples were determined from the I-V characteristics measured at room temperature. After plasma treatment in methane and in a mixture of methane + nitrogen, the resistance of the samples after 12 min of treatment reaches hundreds of MΩ/sq. Heat treatment at T = 650°C reduces the resistance to several units of kΩ/sq. The ratio of the sheet resistances of the samples of the control sample and the samples treated according to methods 4 and 2 was 4:3:1, respectively. It should be noted that when nitrogen was added to plasma with lower power (process 3 in Table 1), a change in the type of conductivity from the p-type to the n-type was observed. It is possible that with a gentle plasma effect, the formation of nitrogen bonds with surface carbon atoms predominates over the etching processes, which leads to n-doping of graphene domains during subsequent heat treatment. Measurements of charge carrier mobility by the Hall effect method showed that, when using methane plasma (rGO(CH$_4$) in figure 6), the mobility was on average about two times higher than in the case of CH$_4$ + N$_2$ (rGO(CH$_4$ + N$_2$) in figure 6) plasma treatment and reduction GO (rGO in figure 6). This may be due to the fact that heat treatment of amorphized carbon films deposited in plasma leads to the formation of films with a larger domain structure on the GO surface relative to the initial ones. Less resistance and mobility in samples exposed to CH$_4$ + H$_2$ plasma can be associated by a stronger surface damage during processing in such plasma leads to the formation of a smaller domain structure.

4. Conclusion

In this study, a simple two-step process was carried out for the treatment of GO in methane plasma (with or without the addition of nitrogen) and subsequent heat treatment. The experiment used radio frequency (13.56 MHz) inductively coupled plasma. Processing in plasma was carried out in the "face down" position to have a mild effect on the surface of GO. Heat treatment was carried out at T =
650 °C in an argon atmosphere for 30 min. Structural, optical, and electrical studies were carried out after plasma treatment and annealing. It follows from a results of investigations that, in a first stage of the process, plasma treatment in methane and in a mixture of CH₄ + N₂ leads to the deposition of amorphous carbon on the GO surface. The thickness of this film increases with enhancing processing time and plasma power. Sheet resistance of the films reaches hundreds of MΩ/sq. The presence of amorphous carbon is the cause of broadband photoluminescence in the Raman spectra in the range from 1000 to 3500 cm⁻¹. After the second stage of the process (heat treatment), a thickness of the carbon film decreases noticeably. Sheet resistance is reduced to several units of kΩ/sq. The intensity of broadband photoluminescence also decreases. In contrary, the intensities of the D and G peaks associated with the formation of ordered carbon structures significantly increase. It is most likely that the remaining carbon atoms form a crystalline structure with a GO substrate. As a result, an increase in the thickness of the relative initial GO film is observed (before plasma exposure). In addition, the red shift of the maximum intensity of the G peak of the Raman spectra and the decrease in the I_D/I_G ratio suggest that larger graphene domains are formed in comparison with initial samples. This is confirmed by the lower value of the layer resistance and the higher mobility of charge carriers in the samples treated in methane plasma. The surface roughness of this film is slightly less than that of the initial GO. Processing in a CH₄ + H₂ plasma increases the surface roughness, apparently due to more intense etching in the presence of nitrogen. As a result, such processing leads to the formation of a smaller domain structure. This is confirmed by lower mobility and higher layer resistance. The research results are supposed to be used to obtain GO-based carbon films with improved quality.

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References
[1] Shelke N T, Karche B R 2017 Ultraviolet photosensor based on few layered reduced graphene oxide nanosheets Applied Surface Science 418 374-379
[2] Fernandes G E, Kim J H, Oller D and Xu J 2015 Reduced graphene oxide mid-infrared photodetector at 300 K Applied Physics Letters 107 111111
[3] Xu J, Wang Y and Hu S 2017 Nanocomposites of graphene and graphene oxides: synthesis, molecular functionalization and application in electrochemical sensors and biosensors Microchimica Acta 184 1-44
[4] Singh R K, Kumar R and Singh D P 2016 Graphene oxide: strategies for synthesis, reduction and frontier applications RSC Advances 6 64993-65011
[5] Yu X, Cheng H, Zhang M, Zhao Y, Qu L and Shi G 2017 Materials 2 17046
[6] Lu G, Ocola L E and Chen J 2009 Nanotechnology 20 445502
[7] Hu N, Yang Z, Wang Y, Zhang L., Wang Y, Huang X and Zhang Y 2013 Nanotechnology 25 025502
[8] Chen D, Feng H and Li J 2012 Chemical reviews 112 6027-6053
[9] Georgakilas V, Tiwari J N, Kemp K C, Pernan J A, Bourlinos A B, Kim K S and Zboril R 2016 Chemical reviews 116 5464-5519
[10] Li X, Colombo L. and Ruoff R S 2016 Advanced Materials 28 6247-6252
[11] Chen X, Zhang L and Chen S 2015 Large area CVD growth of graphene Synthetic Metals 210 95-108
[12] Wei D, Liu Y, Wang Y, Zhang H, Huang L and Yu G 2009 Nano letters 9 1752-1758
[13] Terasawa T O and Saiki K 2012 Carbon 50 869-874
[14] Azam M A, Zulkapli N N, Dorah N, Seman R N A R, Ani M H, Sirat M S, Ismail E, Fauzi F B, Mohamed M A and Majlis B Y 2017 ECS Journal of Solid State Science and Technology 6 M3035-M3048
[15] Nandamuri G, Roumimov S, Solanki R 2010 Applied Physics Letters 96 154101
[16] Cuxart M G, Šics I, Goñi A R, Pach E, Sauthier G, Paradinhas M, Foerster M, Aballe L, Moreno Fernandez H, Carlino V and Pellegrin E 2017 Carbon 117 331-342
[17] Baraket M, Walton S G, Wei Z, Lock E H, Robinson J T and Sheehan P 2010 s Carbon 48 3382-3390
[18] Cheng M, Yang R, Zhang L, Shi Z, Yang W, Wang D, Xie G, Shi D and Zhang G 2012 Carbon 50 2581–2587
[19] Zhu D, Pu H, Lv P, Zhu Z, Yang C, Zheng R, Wang Z, Liu C, Hu E, Zheng J, Yu K, Wei W, Chen L and Chen J 2017 Carbon 120 274-280
[20] Hummers W S and Offeman R E 1958 J. Am. Chem. Soc. 80 1339
[21] Neustroyev E P, Aleksandrov G N and Nogovitsyna M V 2015 Vestnik SVFU 50 6 87 (in Russia)
[22] Neustroev E P, Burtseva E K, Soloviev B D, Prokopiev A R, Popov V I and Timofeev V B 2018 Nanotechnology 29 144002
[23] Neustroev E P, Nogovitsyna M V, Soloviev B D, Kurkina I I and Nikolaev D V 2018 Journal of Structural Chemistry 59 793-798
[24] Hamelmann F, Aschentrup A, Brechling A, Heinzmann U, Abrashev M, Szekeres A and Gesheva K 2004 Vacuum 76 139-142
[25] Beams R, Cançado L G and Novotny L 2015 Journal of Physics: Condensed Matter 27 083002
[26] Kudin K N, Ozbas B, Schneipp H C, Prud’Homme R K, Aksay I A and Car R 2008 Nano letters 8 36-41
[27] Jacobsohn L G, Franceschini D F, Maia da Costa, M E H and Freire Jr F L 2000 Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 18 2230-2238
[28] Tuinstra F and Koenig J L 1970 The Journal of Chemical Physics 53 1126-1130
[29] Pimenta M A, Dresselhaus G, Dresselhaus M S, Cancado L G, Jorio A and Saito R 2007 Physical chemistry chemical physics 9 1276-1290
[30] Dresselhaus M S, Jorio A, Souza Filho A G and Saito R 2010 Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 368 5355-5377
[31] Yang C, Gong J, Zeng P, Yang X, Liang R, Ou Q and Zhang S 2018 Applied Surface Science 452 481-486