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Electrical properties of thermally reduced graphene oxide

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Graphene oxide produced by the standard Hammers method was annealed at various temperatures. The measurements indicate a monotone enhancement of the electric conductivity of the annealed graphene oxide samples with the increase of the annealing temperature. The most prominent jump in the conductivity (about five orders of magnitude) occurs between 150 and 180 °C. At the annealing temperature of 800 °C, the conductivity of reduced graphene oxide reaches the values typical for highly oriented pyrolytic graphite. The measurements demonstrate a non-linear character of conduction of reduced graphene oxide (RGO) samples, which manifests itself in a sensitivity of the sample conductivity to the magnitude of the applied voltage. This phenomenon is explained in terms of the percolation conduction mechanism of the RGO samples, in accordance with which the charge transport is provided by a limited number of percolation paths formed by contacting RGO fragments. A model simulation performed on the basis of the percolation mechanism of RGO conduction agrees qualitatively with the experimental data obtained.

Keywords: graphene oxide, thermal reduction, non-linear conduction.

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1. Introduction

Realization of a great potential of graphene in practical applications requires the development of effective methods for production of this material in macroscopic quantities. One of the most promising ways to solve this problem is based on the procedure of graphene oxide (GO) reduction. Among various approaches to the realization of such a procedure, the thermal reduction of GO seems to be of the most interest in terms of the practical use [1–4]. This approach is characterized by a relative simplicity in realization and does not require the use of harmful or dangerous chemical compounds. For the development and optimization of this method, it is necessary to understand the nature of physical and chemical processes occurring during the thermal treatment of GO. This problem was stated by many authors, who used various experimental methods. For example, Hall measurements were used in Ref. [5] for determination of the character of conduction in samples of GO reduced at various temperatures. X-ray diffraction analysis has also been used for studying the dynamics of the thermal reduction of GO [3, 4]. Combining approaches such as differential scanning calorimetry, thermal gravimetric analysis and X-ray photoelectron spectroscopy, has permitted the determination of thermodynamic characteristics for the thermal reduction of GO and the main composition of the released gases [2]. The composition of gases evolved during the annealing of GO was also studied by the authors of [6], who used mass-spectrometry and IR spectrometry measurements for this purpose. In distinction of the above-cited papers, in the present work, the electrical properties of partially reduced GO are used as the main indicator of the degree of reduction.

2. Experiment

Graphene oxide, produced by the standard Hummers method [7], was used as the starting material. The paper-like sheets of graphene oxide 40–60 μm thick were about 1.2 g/cm^3 in density, which is about two-fold lower than that of crystalline graphite (2.25 g/cm^3). The sheets were cut into rectangular fragments of 10–15 mm in width and 15–25 mm in length and were studied with the results being presented below.

The thermal treatment of graphene oxide samples was performed in a high temperature furnace planar GROW-2S (PlanarTech). The thermal treatment of samples was performed at a slow flow of Ar (50 cm^3/min sccm) at a pressure of 1 Torr. Heating the samples at a rate higher than 1 °C/s promotes an explosion-like destruction of the material. For this reason the furnace was heated from room temperature up to 200 °C at a rate of 1 °C/min while the rate of the subsequent heating up to the treatment temperature was about 20 °C/min. The duration of the thermal treatment was 10 min for all temperatures.

The density of samples was measured by the use of the balance Sartorius QUINTIX124. Therewith the sizes of samples were measured by means of a micrometer. The measurements show a spread of 20 % of the sample thicknesses. Since this parameter is used for the determination of the conductivity of samples, this non-homogeneity is the main source of measurement error.

The electric characteristics of partially reduced GO (RGO) samples were measured by means of a standard apparatus. A sample was clamped between contacts of the measurement device by means of copper foil crampons providing a homogeneous flow of the electrical current through all the film. X-ray photoelectron (XPS) and Auger spectra of initial samples and those experienced to the thermal treatment were measured by the use of the spectrometer PHI 5500 ESCA (Physical Electronics). The photo emission was initiated by MgK_α radiation with the energy of quantum of 1253.6 eV and 350 W in the power. The analysis area was 1.1 mm in diameter. The spectra C1s and O1s were measured at the analyzer transmission energy of 11.75 eV and the density of data collection of 0.1 eV/step, for the spectra C *KLL* these quantities were equal to 93.9 eV and 0.8 eV/step, correspondingly.

3. Experimental results

Figure 1 presents the measured dependence of the conductivity on the treatment temperature. As is evident from the figure, the most prominent change in the conductivity of the samples occurs within the temperature interval between 150 and 200 °C, where the conductivity changes by about five orders of magnitude – from 10^{-3} up to 100 S/m. The maximum value of conductivity ($\sim$ 3500 S/m) reached at the temperature of 800 °C is about one order of magnitude lower than the reference value of the conductivity of graphite. However taking into account that the density of RGO treated at a temperature of 800 °C is about 0.5 g/cm^3 (see Fig. 2) which is about 4.5 times as low as the density of crystalline graphite, one obtains that the conductivity of the material accounted for one graphene layer is only two times lower than that for graphite. Fig. 2 presents the dependence of the sample density on the thermal treatment temperature. As it is seen heating the samples to 800 °C results in a decrease of their density by about 2.4 times – from 1.2 to 0.5 g/cm^3.

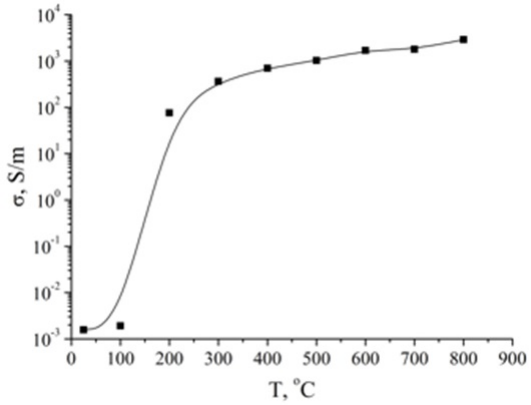

FIG. 1. The conductivity of samples RGO vs thermal treatment temperature

The quantitative data on the content of oxygen and other elements in the samples RGO subjected to the thermal treatment at various temperatures have been obtained as a result of the analysis of XPS spectra. Such an analysis was performed using the standard approach described in particular in [8, 9]. This allowed one to determine the dynamics of changing of the chemical composition of the material depending on the treatment temperature. These data are given in Table 1.

Figure 3 presents typical current–voltage characteristics of RGO samples annealed at various temperatures. The conductivity of RGO increases at higher annealing temperatures. Fig. 4 presents the dependences of the conductivity of RGO samples annealed at various temperatures on the applied voltage. The degree of non-linearity of RGO conductivity can be characterized by the parameter k defined through the relation $\sigma = \sigma_0[1+k(U-U_0)/U_0]$ where σ is the conductivity of a sample at applied voltage U_0. Fig. 5 (points) presents parameter k as a function of the annealing temperature. This dependence simulated on the basis of the percolation model of the conductivity is also shown in Fig. 5 by the solid line. The reason of dependence of the degree of sensitivity of the conductivity to the applied voltage is in the dependence of the contact resistance on the applied voltage.

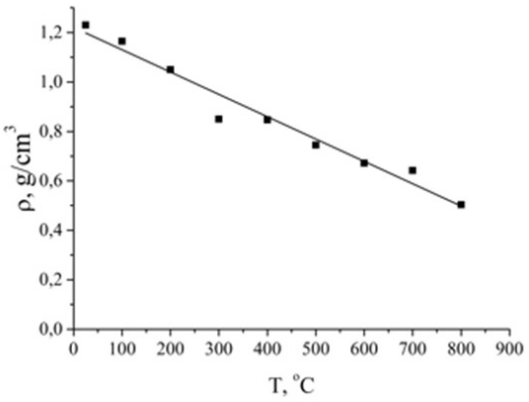

FIG. 2. Dependence of the density of samples RGO on the thermal treatment temperature

TABLE 1. Chemical composition of the initial sample and the samples experienced to the thermal processing at various temperatures as determined on the basis of XPS spectra

Temperature annealing, °C	C, at%	O, at%	N, at%	S, at%	Si, at%
25	74.7	23.0	1.3	0.5	0.4
150	73.6	25.1	0.7	0.5	–
200	82.0	15.2	1.6	0.5	0.7
600	90.6	8.1	0.5	–	0.7

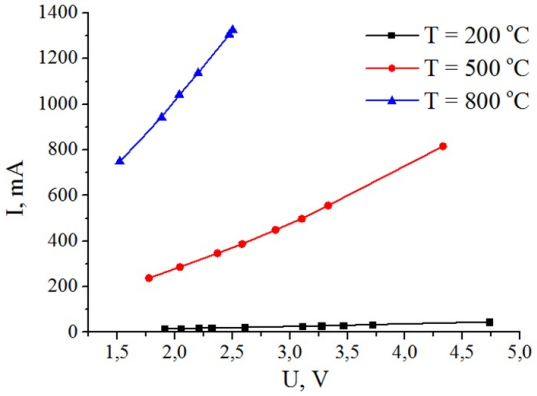

FIG. 3. Current-voltage characteristics of GO samples annealed at various temperatures

4. Conclusion

Thermal treatment results in a reduction of GO, which is indicated by a rise of the conductivity. The most abrupt rise is observed at the annealing temperature of between 150 and 180 °C when the conductivity increases by about 5 orders of magnitude. At the annealing temperature of 800 °C the conductivity reaches about 3500 S/m, which corresponds to that of crystalline graphite (with taking into account the loss in the density of samples). Experiments imply a non-linear conduction of RGO samples, so that the conductivity increases with the applied voltage. This feature is explained qualitatively within the framework of the percolation model of conduction. The non-linear electrical behavior of the samples is caused by a dependence of the contact resistance on the applied voltage.

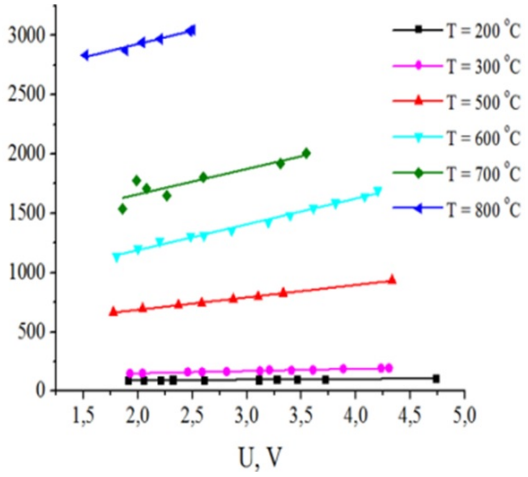

FIG. 4. Dependences of the conduc-tivity of RGO samples annealed at various temperatures on the applied voltage

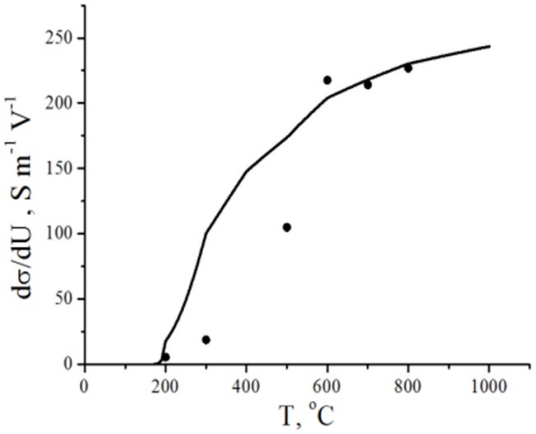

FIG. 5. Dependence of the degree of non-linearity of the RGO conductivity on the annealing temperature: points – experiment; line – model simulation

Acknowledgements

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