Investigations of selected physical properties of graphite oxide and thermally exfoliated/reduced graphene oxide in the aspect of their applications in photonic gas sensors

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Abstract—In this work, the results of measurements of two sensing materials: graphite oxide and thermally exfoliated/reduced graphene oxide are presented. The changes of resistance were registered in a changing atmosphere (modified concentration of hydrogen). The authors also try to explain the reasons for different response of the samples to identical external conditions, by measuring the samples by means of the Differential Scanning Calorimetry (DSC) technique.

The materials based on graphene have been focusing a lot of attention especially for the last few years. In 2004 A. Geim, K. Novoselov *et al.* obtained stable graphene layers. Until that time, grapheme had been known only in theory [1]. Nowadays, the basic methods of preparation of graphene include: chemical vapour deposition, epitaxy, reduction of graphite oxide and exfoliation of graphite [2]. The most popular methods of oxidation of graphite are based on Brodie's, Hummer's, Staudenmaier's [3] and Hoffman's [4] technologies. Over the past few year, scientists have been working on the development of production processes and modification of graphene-based materials and other carbon nanomaterials. Due to their unusual physical and chemical properties, these materials can be used in many applications, such as water purification [5], in the form of a sensitive layer in chemical, bio- and gas sensors [6-8] as well in optics, photonics and medicine [9-12]. Due to such a variety of potential usage, further researches of graphene type materials seem to be well-founded and reasonable.

Preparation of the samples: In the presented experiments two similar structures, differing only in a sensitive layer, were used. In both structures, golden comb electrodes were made on silicon substrates (with an oxidized surface). In order to improve the adhesion of the electrodes to the substrate, a chrome layer was introduced between them. On both samples, the sensing layers were prepared in the same way: carbon-based powder graphite oxide (on the sample No I) or exfoliated/reduced graphene oxide (on the sample No II) were mixed with an anhydrous ethanol and (in the next step) imposed on the electrodes. After that, the samples were left for 24 hours in order to evaporate the ethanol.

Preparation of graphite oxide (GrO): Commercial natural graphite powder (90µm), supplied by Graphit Kropfmühl AG (L_a-58 nm, L_c-29 nm, d_{002}-0.338 nm and C^{daf}-99.5%) was oxidized by modifications of the Hummers method [13]. Concentrated H_2SO_4 (95-97%) was used as an acid and $KMnO_4$ and $NaNO_3$. The graphite sample (1g) with a < 20µm particle size (grinded using a planetary ball mill, PM100) was mixed with the acid and placed in a bath of water and ice. When a homogeneous paste was obtained, the oxidizing agent was partially added with continuous mixing and maintaining the reaction temperature in the range 5÷25°C. In a certain method, the following amounts of reagents were used: 30 ml of H_2SO_4, 3g $NaNO_3$. After 2h of mixing, oxidation products were obtained. As the last step, the resulting oxidized mixtures were diluted in 100 ml of mili-Q water with slowly added 3% H_2O_2. The mixture was stirred for 30 min and, finally, centrifuged (5000 rpm for 15 min), the supernatant began to be decanted away. The remaining solid material was washed with 800÷1400 ml of water and centrifuged again - this process was repeated until the pH was neutral. When required, GrO was dried under vacuum at 50°C overnight and stored in the presence of P_2O_5 as a desiccant.

Preparation of graphene oxide (rGO): Graphite oxide (obtained in the above-described method) was reduced by annealing in an inert atmosphere (gas: nitrogen, temperature: 900°C, time: 5 min).

The purpose of the experiments was to investigate the effect of hydrogen on samples No I and II. Hydrogen (in various concentrations: 1%, 2%, 3% and 4%) in a carrier gas (nitrogen or synthetic air) was dosed. The measurements were performed in a temperature range

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from 30^0C to 140^0C. The exemplary results, for 135^oC are presented in Fig. 1.
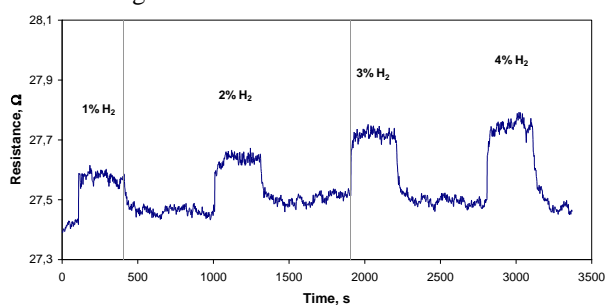

Fig. 1. The resistance of sample II at 135^oC, while dosing various concentrations of hydrogen in synthetic air.

The electrical resistance of samples was increasing during the dosage of hydrogen. The changes in thermal conductivity of the carrier gas (which contains hydrogen) or molecular reactions of hydrogen with graphene-based sensitive materials could be a cause of this effect. Unfortunately, both structures do not react to the changes in the composition of a dosed atmosphere at low temperatures (below 80^oC). Additionally, above 80^oC the sensitivities of the structures change with temperature (Figs. 2-3). Moreover, the optimum ranges of temperatures can be observed in which the changes of resistance (difference between resistances of the structure in the atmosphere without and with hydrogen) were maximal (for both samples).

The "optimal" temperatures were both observed when the nitrogen and synthetic air was used as a carrier gas, but at various temperatures (Figs. 2-3). To ensure that the structures work stable in time, the measurements were repeated several times (over a two-month period). Unfortunately, after the first measurement cycle, the sample No I stopped to react to a changing concentration of hydrogen while the sample No II worked correctly at all times.
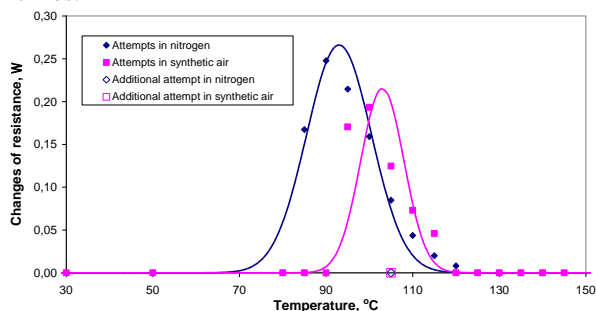

Fig. 2. The changes of resistance of sample No I (measured when carrier gas and 4% of hydrogen in carrier gas was dosed) in function of temperature.

Figures 4 and 5 show changes in the resistance as a function of time, measured after two months from the first experiments.
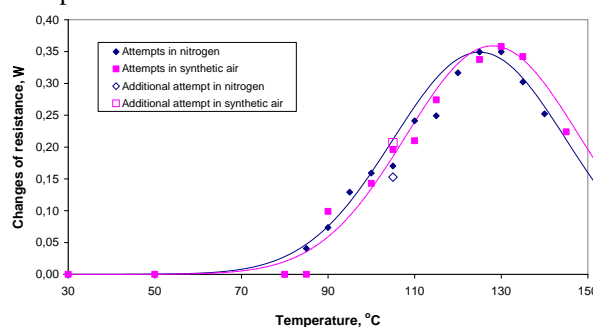

Fig. 3. The changes of resistance of the sample No II (measured when a carrier gas and 4% of hydrogen in a carrier gas was dosed) as a function of temperature.
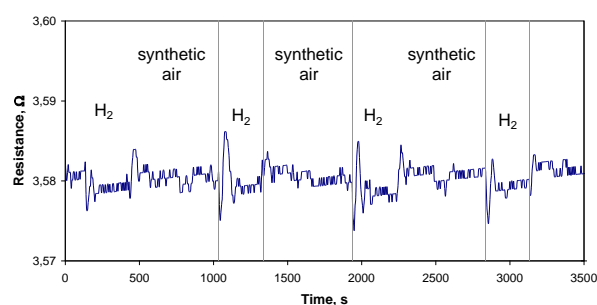

Fig. 4. Resistance of the sample no I vs. time, temperature of the sample at 120^0C, measurements made two months after the first experiments.
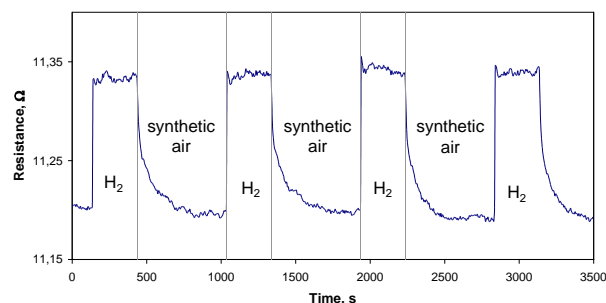

Fig. 5. Restistance of the sample No II vs. time, temperature of the sample $\approx 120^0$C, measurements made two months after the first experiments.

Due to the fact that the structures do not behave in the same manner, an additional elemental analysis and Differential Scanning Calorymetry (DSC) measurements were performed.

	GrO, %	rGO, %
Nitrogen	0,080(30)	0,260(50)
Carbon	63,80(50)	89,80(60)
Hydrogen	2,170(50)	0,440(30)
Sulfur	1,620(60)	0,950(60)
Oxygen	32,29(33)	8,53(17)

The nitrogen, carbon, hydrogen, sulphur and oxygen content of the samples was determined directly by means

of an automatic elementary analyser Vario Macro Cube (Elementar Analysensysteme GmbH Company).

It should be noted that the percentage contents of the above-mentioned elements were decreasing after a thermal exfoliation/reduction process (especially the percentage content of oxygen). This should be explained by the fact that the graphene planes are exfoliated and the attached functional groups containing oxygen (carbonyl, carboxyl, hydroxyl and epoxy groups) are reduced during a rapid high temperature operation. In thermal processing of the graphite oxide, the bonds in the functional groups were broken. In this process CO, CO_2 and water vapor are received. Such gases are responsible for the defects in the final product- thermally exfoliated/reduced graphene oxide. Finally, graphene oxide had a greater percentage of carbon and a smaller percentage of oxygen, hydrogen and sulfur [14-16].

Additionally, the Differential Scanning Calorimetry (DSC) measurements using METTLER TOLEDO (STAR^e SW 8.10) equipment were performed (the fragment of characteristic was presented in Fig. 6). The purpose of such measurements was to determine whether and to what extent the residual presence of ethanol in the sensor layer could affect its sensitivity to hydrogen. Two groups of graphite oxide were used for the measurements. The first of them, denoted as "A", was prepared with ethanol (it was prepared exactly in the same way as graphite oxide in the sample No I). The second sample (denoted as "B") was the reference one - it was prepared without ethanol.
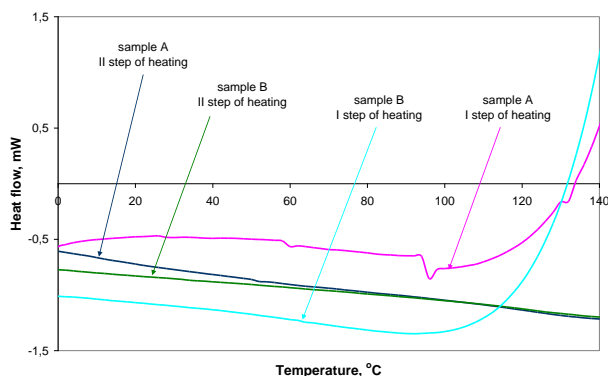

Fig. 6. Changes of heat flow vs. temperature, sample "A" and "B".

Both groups of graphite oxide were annealed in two cycles (from $-10^{\circ}C$ to $180^{\circ}C$). In the first annealing process, the flow of heat was changing significantly for both samples. Additionally, it should be noted that there are additional endothermic changes (at ~$55^{\circ}C$, at ~$95^{\circ}C$ and at ~$130^{\circ}C$). They can be explained by the evaporation of ethanol and water from the sample (a low evaporation temperature is the result of residual amounts of ethanol). Such changes are not visible during the first heating of the

sample "B"- the course is linear, without characteristic changes. The lower temperature of the reduction of sensitive oxygen groups is a consequence of ethanol used for preparation of the sample "A". For both samples, the processes of changing the heat flow vs. temperature are very similar, the intake energy has changed to a small extent.

In conclusion, by modifying the technology of graphene-based materials we can essentially change their properties. It has to be taken into consideration while designing their new applications. During the modification of physical properties of graphite oxide, the temperature of processes is very important, because this material is rich in various functional groups. For this reason, the measurements of graphite oxide properties and those of thermally exfoliated/reduced graphene oxide are well-founded and required.

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