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The sensitivity of sensor structures with oxide graphene exposed to selected gaseous atmospheres

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Abstract. The paper presents the results of investigations on the resistive structure with a graphene oxide (GO) sensing layer. The effects of dangerous gases (hydrogen and nitrogen dioxide) on the structure were studied; the resistance changes were examined during the flow of the selected gas in the atmosphere of synthetic air. Measurements were performed with a special emphasis on the detection of low concentrations of the analyzed gases. The reactions of the sensing structure to the effect of nitrogen and synthetic air at different humidity were also tested. Much attention was also paid to the fast response of the sensor to the changes in the gas atmosphere. The thin palladium layer ($\sim$2 nm) has been applied in order to improve the sensing properties of the structure. The investigations were performed in the temperature range from RT to 120°C and the analyzed gases in synthetic air were batched alternately with pure synthetic air.

Key words: graphene, graphene oxide, gas sensors, resistive sensors.

1. Introduction

Pollutions of the environment require a permanent monitoring of the concentration of selected gases not only to ensure a compliance with environmental standards, but above all to ensure the safety of population [1, 2]. A lot of attention is paid to development of the technology of hydrogen energetic fuel cells [3], which makes the monitoring of the concentration of hydrogen necessary. Hydrogen is an explosive gas (at a concentration of 4% to 75% in air [4, 5]). An impediment in its detection is the fact that it is odorless and colorless. Another gas, which needs special attention is nitrogen dioxide, particularly its monitoring occurs in large agglomerations. NO_2 is very harmful for the human health, and its presence in the atmosphere contributes to dangerous environmental pollution [6].

Regardless of the composition of the analyzed atmosphere, it is important that the detection of the selected gases is unambiguous and at a low level their concentrations [7]. A special attention should be also paid to the response time of sensors (time of detection), which should be as short as only possible [8]. The properties of sensor structures depend (among others) on the gas sensing layers. Sensors based on carbon nanostructures as sensing layers are characterized by low working temperature [3]. In literature much attention is devoted to sensors with carbon nanotubes [9], graphene [10–13], graphene oxide and reduced graphene oxide [13–15]. The various types of sensors are used (e.g. optical, electrical) for gas detections. In practice, a good solution seems to be a choice of resistive structure [7, 10, 17]. In most cases (regardless of the sensor structure), the presence of water vapor in the analyzed atmosphere is unquestionable and difficult problem. In out-of-laboratory conditions, the humidity is variable and can significantly affect on values of the measured resistance (or the other parameters of a sensor structure). This affects for the proper interpretation of the results. For this, the sensor structures should be very often equipped with a system for measurements of humidity.

2. Preparation of a sensor structure

Resistive structures were made on substrates of BK7 glass. The interdigital electrodes (made of gold on chromium) were made in a lift-off multi stage process. A layer of gold (105 nm) was deposited using the EBPVD method. Between gold and the substrate a chromium layer was applied with a thickness of 35 nm (chromium was also deposited using the EBPVD method). The electrodes were made of gold because of its chemical resistance and good electrical conductivity. The presence of chromium between the gold electrodes and the substrate is necessary for improving the adhesion of gold to the substrate and to reduce its migration on the surface at high temperature. The resistive structure is presented in Fig. 1. The width of the electrodes is 90 μm and the interval between them is equal to 110 μm.

Fig. 1. Resistive sensor structure

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Graphene oxide (GO) (used as a sensors layer) was prepared by means of modified Hummers method. 5 grams of thermally expanded graphite (produced by Asbury Carbons), particle diameter: 300–425 μm and 6.5 g of potassium nitrate (produced by POCh, pure) were added to beaker containing 200 ml of concentrated sulphuric acid (POCh, 96–98%, p. A.). The beaker was cooled in an ice bath to below 5°C and 15 g of potassium permanganate (POCh, pure) were gradually added. After the addition of the last portion, the ice bath was replaced by water (25°C) and left for 16 h. The beaker was put into the ice bath and 230 ml of deionized water (DI) was slowly poured into the suspension. The mixture was then heated for 15 min to 95°C, and then diluted by adding 280 ml of DI water and cooled to room temperature. Finally, 5ml of 30% hydrogen peroxide was added. Graphite oxide suspension were washed with a 3% hydrochloric acid solution and, after the removal of sulphate ions, continuously washed with DI water, until no chloride ions were detected. The purified suspension was then ultrasonicated for 1 h to exfoliate oxidixed graphite sheets. Such an obtained stable suspension of graphene oxide (GO) in water was dried in a lyophilizer. In the next step, GO powder was dispersed in propyl alcohol by ultrasonication in order to obtain a 0.05% GO concentration. The prepared GO suspension was applied to the substrate making use of a spray-coater, holding the applicator at a height of 20 cm from the substrate. As a result, thin, barely noticeable to the naked eye layer was obtained, and next it was dried in the air. During the second part of the investigations the palladium layer was deposited on the selected part of the resistive structure to improve the properties of the sensors. The Pd layer with a thickness of 1.8 nm was deposited using the thermal evaporation method.

3. Characterization of the surface of sensor structures before their application in gas measurements

The sensor structures have been characterized using the atomic force microscopy AFM and the Raman spectroscopy. The NTEGRA Spectra platform (NT-MDT Ltd.) was used in investigations of the graphene oxide (GO) structures. The studies were performed twice, first before the measurements in gaseous atmospheres, then after the completion of the test cycles. (The VIT_P cantilever was used in AFM measurements). A typical image presenting the surface between the electrodes is shown in Fig. 2.

In Raman spectroscopy testing as a light source the laser Nd:YAG was used, which emits a 532 nm light wave. The typical Raman spectra of GO is shown in Fig. 3.

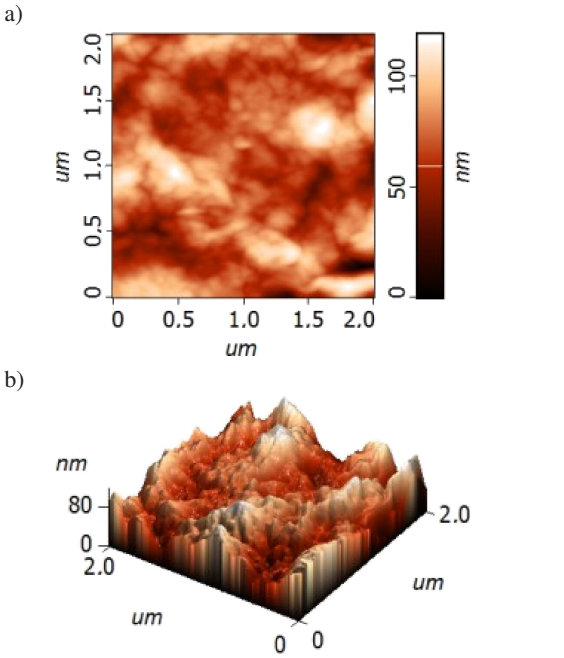

Fig. 2. Topography of the GO sensor structure: a) 2D image, b) 3D image. Measurements were done before the contact of the structure with the analyzed gases

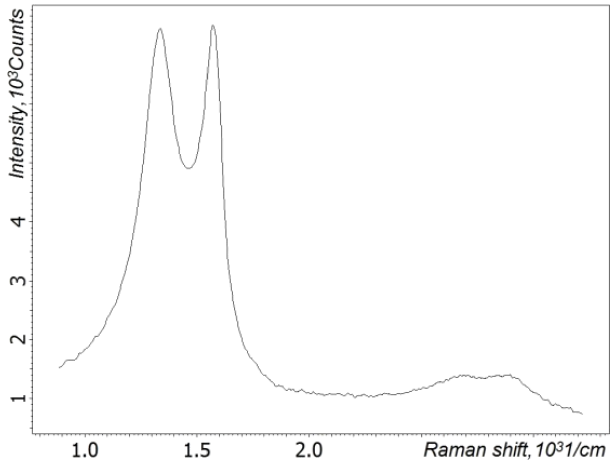

Fig. 3. Typical Raman spectrum received before the contact of the structure with the analyzed gases

4. The response of the sensing structure to the effect of selected gas atmospheres

The sensor structure was placed in the measurement chamber (Fig. 4) into which the selected gas was batched (flow: 500 ml/min). During each measurement cycle, the resistance was determined by using the AGILENT 34970A meter. The resistive structure without palladium was 36.57 MΩ (after applying the Pd layer, the resistance significantly decreased about 133 Ω).

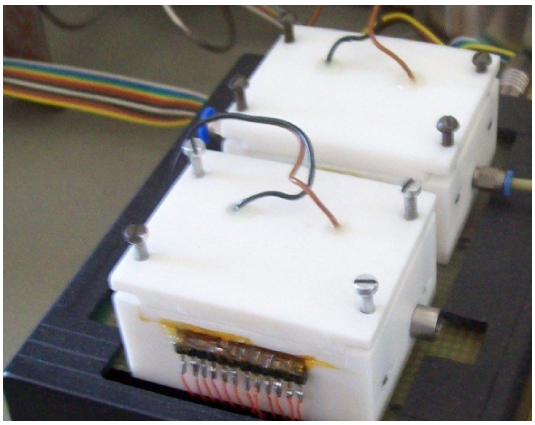

Fig. 4. The measurement chamber applied in the experiments

4.1. The response of the sensing structure to synthetic air at different humidities and with nitrogen at different humidities. At the beginning, the responses of the structure during contact with synthetic air (21% oxygen, 79% nitrogen) at different humidity were tested. The humidity of dosed gases was measured by the SHT1000 sensor with accuracy at the level 4%. These studies were necessary because the resistances of the structure are dependent on atmospheric humidity. The sudden change in moisture content can cause erroneous interpretation of the results of gas detection. The results of the first experiment are shown in Fig. 5. It can be seen that with increasing humidity, the resistance decreases.

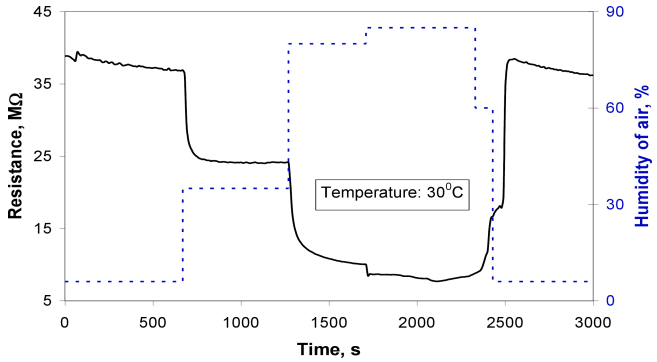

Fig. 5. Responses of the GO sensor structure on acting of synthetic air with various humidity, at temperature 30°C

The investigations shown above indicate that humidity affects considerably the values of the electrical resistance of the GO sensing structure.

Next, the sensor structure was exposed to the effect of hydrogen at various concentrations (1÷4%) in the synthetic air (batched alternately with synthetic air without hydrogen). Unfortunately, the resistance of the structure didn't change significantly during its contact with the hydrogen. In order to improve the sensor properties of the structure, on the graphene oxide layer a thin layer of the catalyst was deposited. Very thin palladium layer (∼2 nm) was evaporated on the selected part of the GO structure. Experiments, at different humidities of synthetic air were repeated. Figure 6 shows the results of measurements in which the substrate was maintained at a temperature of 30°C.

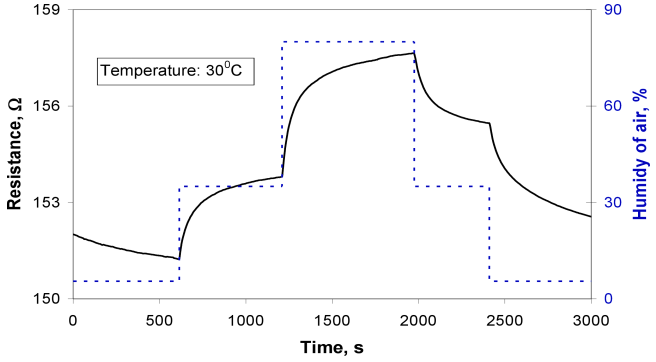

Fig. 6. Response of the sensor structure with a palladium layer affected by humid synthetic air; temperature of the structure: 30°C

The response of the sensor structure with a palladium layer affected for actions moist synthetic air at temperature of 30°C is opposite to the response of this structure without palladium. The problem of the impact of water vapor on the structure is a complex issue. One should keep in mind that the catalyst has been applied only on the part of the sensitive layer.

When the sensor layer is affected by hydrogen, atoms of the gas can penetrate the layer [19]. In that case, some part of the electrons from the structure is absorbed by OH^- ions causing an increase of the resistance of the sensitive layer. If the sensing structure isn't covered by palladium, the free electron as a product of dissociation ($OH^- + H^+ + e^-$) is connected with the structure and in consequence increases its conductivity.

In the next series of measurements, the substrate was heated to a temperature of 80°C and after that the synthetic air (at various its humidities) was batched. Similar measurements were performed for various humidities of nitrogen (temperatures of the substrate were equal to 30°C and 80 °C). The results of the experiments are shown in Figs. 7–9.

In both cases of measurements, in the nitrogen atmosphere and in synthetic air atmosphere, the electrical resistances of the structure with palladium increases with the increasing humidity of the tested gases.

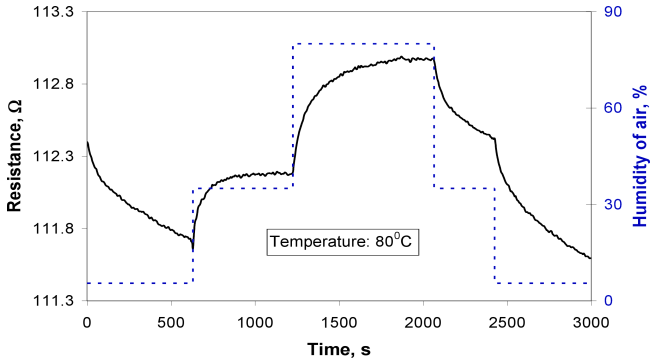

Fig. 7. Response of the structure with a palladium layer affected by the humid synthetic air; temperature of the structure: 80°C

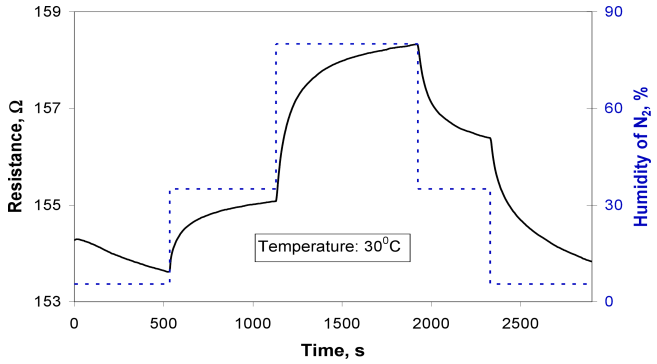

Fig. 8. Response of the structure with palladium layer affected by humid nitrogen; temperature of the structure: 30°C

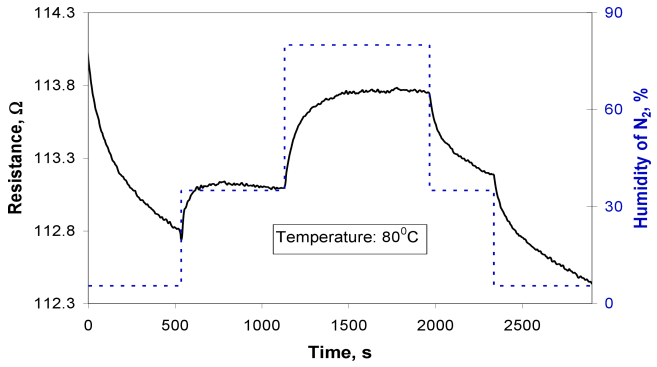

Fig. 9. Response of the sensor structure with a palladium layer affected by humid nitrogen; temperature of the structure: 80°C

4.2. Response of the sensor structure affected by various concentrations of hydrogen in synthetic air. In the next research stage, measurements were carried out at different concentrations of hydrogen (1÷4%). The temperature of the substrate amounted during measurements from 21°C to 120°C, respectively. The results are shown in Figs. 10 and 11.

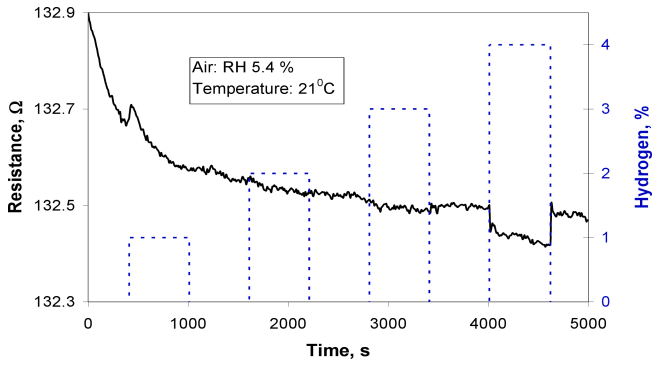

Fig. 10. Response of the sensor structure with a palladium layer affected by various concentrations (1÷4%) of hydrogen in synthetic air; temperature of the substrate: 21°C, humidity of air: 5.4%

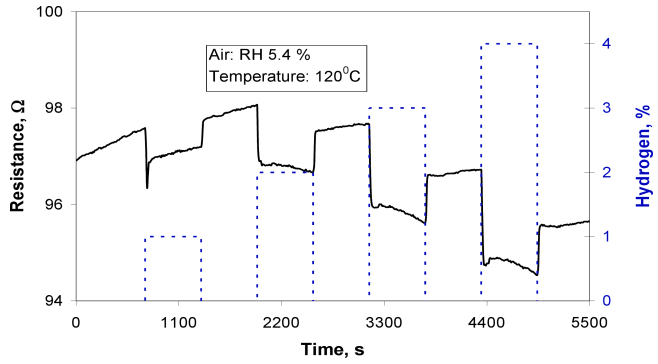

Fig. 11. Response of the sensor structure with a palladium layer affected by various concentrations (1÷4%) of hydrogen in synthetic air; temperature of the substrate: 120°C, humidity of air: 5.4%

When the temperature of the substrate was equal to 21° C, H_2 in synthetic air could be detected only at its concentration exceeding 4%. When the substrate was heated to 120° C, it is possible to distinguish not only which gas is batched (synthetic air with hydrogen or pure synthetic air) but also the concentration of the hydrogen in the analyzed atmosphere. Regardless of the temperature, the electrical resistance decreased when hydrogen was batched. It is important that the response time of the sensor was very short (only a few seconds).

4.3. The response of the sensing structure affected by various concentrations of nitrogen dioxide in synthetic air. In the next experiments the responses of the sensor structure exposed to nitrogen dioxide were studied. The results are shown in Figs. 12 and 13.

The electrical resistance undergoes changes in a wider range when the temperature of the substrate equals 50°C. But when a temperature of the substrate amounts to 120°C, the reaction times for changing the gas atmosphere are shorter. It can be also seen that the times of responses are longer during the detections of the nitrogen dioxide in comparison to detections of hydrogen. As in the case of hydrogen, the resistance decreases when structure is affected by nitrogen dioxide.

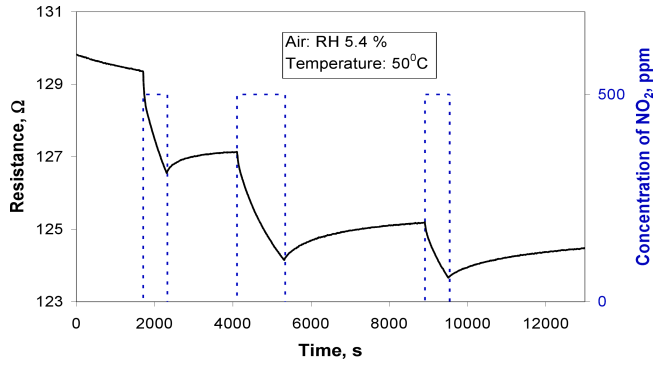

Fig. 12. Response of the sensing structure with a palladium layer affected to nitrogen dioxide in synthetic air; temperature of the substrate: 50°C, humidity of air: 5.4%

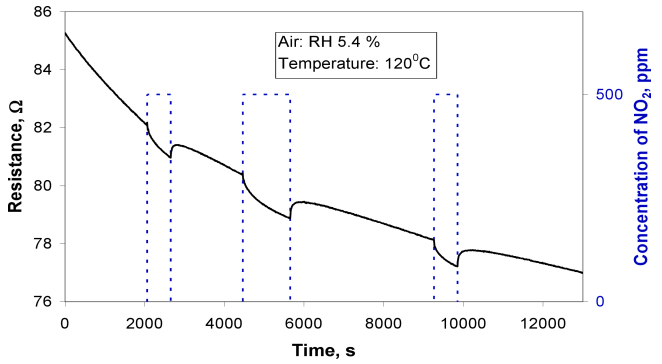

Fig. 13. The response of the sensor structure with a palladium layer exposed to nitrogen dioxide in synthetic air; temperature of the substrate: 50°C, humidity of air: 5.4%

4.4. Response of the sensor structure affected by various concentrations of hydrogen and nitrogen dioxide in synthetic air batched alternately. In the last experiment various concentrations of nitrogen dioxide (from 125 to 500 ppm) and hydrogen (2% and 4%) in synthetic air were batched in one test cycle. Analyzed gases (in synthetic air) were batched alternately with pure synthetic air (at RH = 5.5%).

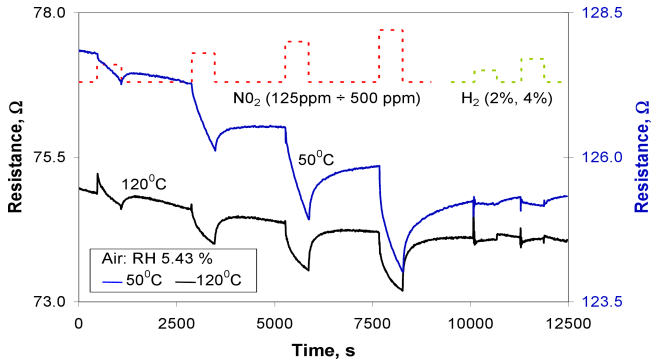

Fig. 14. Response of the sensor structure with a palladium layer affected by various concentrations of hydrogen (1÷4%) and nitrogen dioxide (125÷500 ppm) in synthetic air (temperature of the substrate: 50°C and 120°C, RH: 5.4%)

The resistance of the sensor structure changes more intensively during its exposition to nitrogen dioxide when temperature of the substrate equals 50°C than at temperature of 120°C, which confirms earlier observations. When hydrogen is batched the resistance changes less than in the case of batching nitrogen dioxide.

5. Characterization of the sensor structure subjected to effect of various gas atmospheres

The final stage of the studies comprises re-characterizations by means of atomic force microscopy and the Raman spectroscopy. Results of this re-characterization are shown in Figs. 15 and 16. In comparison with measurements performed before the contact of the inflicted gas atmospheres with the structure, it can be seen that the difference is particularly visible in the Raman spectrum (especially in the peaks observed in the area from 2500 cm^{-1} to 3000 cm^{-1}). This may indicate that the amount of hydroxyl and oxygen groups on the surface of graphene oxide was reduced. Most likely, in contact with hydrogen or nitrogen dioxide these groups began to react chemically with these gases.

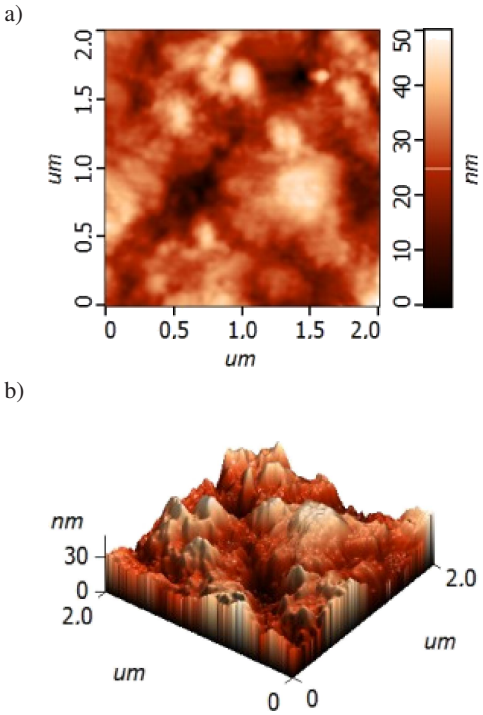

Fig. 15. Topography of the sensor structure with a palladium layer: a) 2D image, b) 3D image. (Measurements were curried out after the contact of the structure with the analyzed gases)

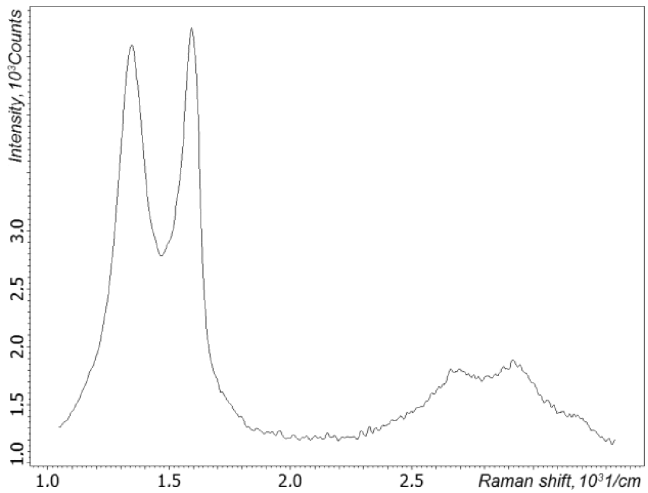

Fig. 16. Raman spectrum of the GO layer after its affected by analyzed gases

6. Conclusions

Basing on the performed studies, it may be concluded that graphene oxide seems to be an interesting gas sensor material. After imposing the catalyst (palladium) the layer changed its physical (and chemical) properties and the sensitivity of

the structure improved due to its exposure to the gas. The resistant sensor based on graphene oxide allows detecting a low concentration of hydrogen and nitrogen dioxide in synthetic air. In the case of hydrogen the sensor is characterized by a short time of reaction due to changes of the gas atmosphere. The detection of hydrogen is better at an elevated temperature of the substrate (120°C). When nitrogen dioxide is batched the changes of the resistance are larger at a the lower temperature of the substrate (50°C). The unquestionable advantage of such a system is its low work temperature.

The effect of the detected gases (H_2, NO_2) on physical (and chemical) properties of the GO structure was observed in the Raman spectra. This indicates that the amount of oxygen and hydroxyl groups has decreased. The sensitivities of the GO structure on the water vapour allow concluding that the system should be equipped with a element for measuring the humidity of air (the resistance changes caused by changes in water vapour content in the atmosphere during the measurements ought to be included). In future, researches concerning the improvement of the sensitivity of the sensor structure on the base of graphene oxide will have to be taken up.

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