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The sensibility of resistance sensor structures with graphene to the action of selected gaseous media

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Abstract. The paper presents resistance sensor structures with a graphene sensing layer. The structures were tested concerning their sensitivity to the affects of hydrogen, nitrogen dioxide and steam in an atmosphere of a synthetic air. Investigations have proved that resistance structures with a graphene layer are sensitive to the presence of the tested gases. The resistance of the structures amounted to about 10Ω, whereas changes in the resistances affected by the external gaseous medium were contained within the range of a several mΩ. The investigations confirmed that the resistance structures with graphene exposed to the affect of hydrogen in atmosphere of synthetic air change their resistances practically at once (within the order of only a few seconds). This indicates that such structures might be practically applied in sensors of hydrogen ensuring a short time of response.

Key words: graphene, resistance sensor, hydrogen sensor, nitrogen dioxide sensor.

1. Introduction

Graphene is a two-dimensional physical structure, consisting of carbon atoms arranged in the form of hexagonal lattices. Between the carbon atoms there are sp^2 bonds [1]. Graphene is a rather recently discovered form of carbon atoms, besides forms which have been known already for many years as diamond, graphite, fullerenes and carbon nanotubes [2]. Graphene was described in the early years of the present century [3, 4]. The theoretically predicted properties of graphene aroused considerable emotions due to its possible applications in widely understood optoelectronics, electrical industry, material engineering and mechanics [2, 5, 6]. Quite a number of publications stress the remarkable importance of graphene in sensor techniques, particularly – in sensors of various gases [7–12].

Ideal graphene is a single monolayer of carbon. Such a structure is characterized by the largest ratio of the surface to the volume – each carbon atom is a surface atom. Therefore, every atom can interact with the molecules and atoms of the external gaseous medium. Practically, most often carbon atoms in graphene form several monolayers [11]. The intensity of the interaction of carbon atoms with the molecules of the external gases varies depending on the type of bonds existing between them – from relatively weak interactions of the Van der Waals type up to strong chemical covalent bonds [6].

Interactions between carbon atoms in graphene with atoms or molecules of the external medium involve changes in the energy band structure of the graphene, and hence also changes of its electron structure, leading among others to changes of its electrical properties, including changes in its resistance. Resistance sensors based on graphene (or its derivatives, viz. graphene oxide and reduced graphene oxide) belong to the most popular graphene sensors of gases [6]. Depending on the kind of the gaseous medium, the molecules of gas sorbed on the graphene surface may result both in an increased electrical conductivity of the structure and its decrease [2]. Changes on the electrical conductivity of the graphene surface are caused by changes in the concentration of electrons in the graphene, but also by changes in the mobility of electrons. Investigations indicate that the sorption of molecules affects considerably the mobility, even to several orders of quantity [6].

Graphene exposed to the effect of the gaseous medium may electrically react to various gases differently. Basing on data quoted in literature [8–10] (and also on the authors' own results of investigations) it is to be observed that in the case of sorption of hydrogen (H_2), ammonia (NH_3) and carbon oxide (CO) the sensor layer of graphene is additionally enriched with electrons [1, 2]. Steam (H_2O) decreases the electric conductivity of the graphene layer [3]. Information provided in literature indicates that nitrogen dioxide (NO_2) may in the presence of steam to entail both an increase and a decrease of the resistance of the graphene layer [4, 5]. The large sensor surface of the graphene layer as well as the accessibility of theoretically every carbon atom for molecules of the external gaseous medium involve the possibility of the formation of a high sensitivity of the sensor structure based on graphene, additionally with a fast reaction of changes of electrical conductivity.

The application of graphene in gas sensors promises the detection of selected gases with extremely low concentrations, within the order of ppb (part per billion). The detection of low

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concentrations is essentially important in applications to detecting the vapour of explosives.

The experimental investigations dealt with further on, concerning the sensitivity of graphene layers in resistance structures to the effect of selected gaseous media, were carried out at the Department of Optoelectronics at the Silesian University of Technology in Gliwice (Poland). The graphene applied in resistance structures was obtained and deposited on interdigital electrodes of resistance transducers at the Institute of Electronic Materials Technology (ITME) in Warsaw.

2. Applied technology of graphene manufacturing

The graphene was deposited on the surface of a copper foil, 23μm thick, in the course of chemical sedimentation from the gaseous phase (CVD method). This process was carried out in two stages. First, in order to improve the quality of the substrate and to augment the size of the copper grains, the substrate was soaked in an Ar atmosphere at a temperature of about 1000°C. Then the substrate was heated up for several minutes at 1020°C with the simultaneous flow of H_2 and C_3H_3 as the source of carbon. Finally, the copper foil, covered with graphene, was kept in the switched off furnace for several hours to cool it down to room temperature. In order to separate the graphene from the copper foil and to transfer it onto the interdigital electrode structure, on the surface of the copper sample (covered with graphene), by means of the spin-coating method a thin layer of poly(methyl methacrylete) (PMMA) was deposited. PMMA prevents graphene from crashing and damages which might arise in the course of etching the copper foil [13]. For the purpose of etching the copper the structure PMMA/graphene/Cu was immersed in a solution of ammonia persulphate. After the copper foil had been thoroughly etched, the polymer with graphene was additionally cleaned in order to remove the remaining metal and insoluble organic impurities [14]. Next the graphene layer was transferred from PMMA to the interdigital resistance transducers. In order to ensure a thorough contact of graphene with the substrate, the structure was heated for several minutes at a temperature of 100°C in the air and then kept for several hours in a vacuum. Finally the PMMA layer was carefully removed by solving it in acetone. The parameters of the process of transferring graphene were chosen in such a way that a formation of gaps and cracks between the graphene layer and the surface of the interdigital electrode structure would be prevented.

3. Sensor structure with graphene

The sensor structure consists of four interdigital transducers, obtained by means of photolithography process on the surface of a quartz-glass plate. The electrodes, 120 nm thick, were made of gold on a substrate of 50 nm chromium. The widths of the gold electrodes and the gaps between them amounted, respectively, to 20 μm and 15 μm. The resistance sensor structures are to be seen in Fig. 1. In ITME the graphene layers were deposited on the interdigital electrodes.

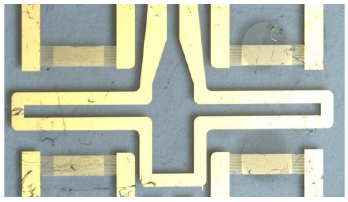

Fig. 1. Sensing structure with 4 resistance interdigital electrode structures

Figure 2 presents the photo of an interdigital structure with the deposited graphene layer.

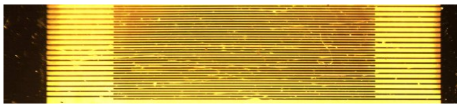

Fig. 2. Interdigital resistance interdigital electrode structure with a layer of graphene

4. Tests of graphene on a sensor structure

The graphene layers (obtained in the process described in Part 2) deposited on an interdigital structures were subjected to various tests, viz. by means of Atomic Force Microscopy (AFM) and Confocal Microscopy methods, making use of the NTEGRA Spectra system, produced by the firm NT MDT in the Netherlands. Figures 3 and 4 are photos of an interdigital structure with a deposited sensor layer of graphene. Figure 3 presents graphene on an interdigital structure achieved by means of the AFM method; Fig. 3a shows the "amplitude image" and Fig. 3b – "the phase image". Figure 3a indicates that the graphene layer is very thin, amounting at the most to only several nm, whereas the thickness of the gold electrode amounts to about 150 nm.

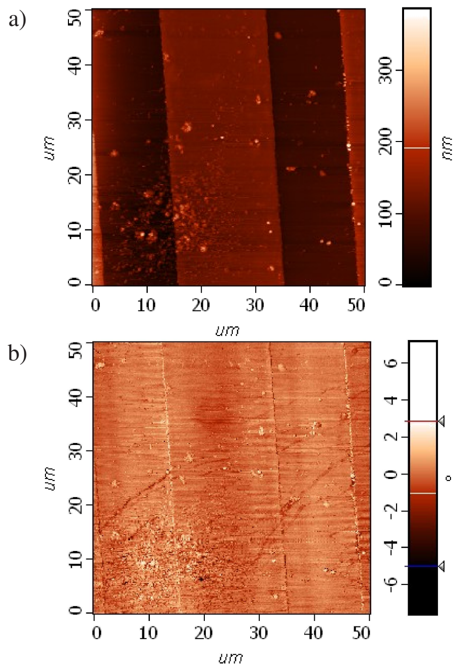

Fig. 3. AFM image of the surface of the electrode structure: a) amplitude image; b) phase image; (the dark spaces in Fig. 3a present graphene on a glass surface, the brighter spaces – graphene on a gold interdigital electrode)

Figure 4 shows the same space, but obtained by applying the technique of Confocal Microscopy (CM). Figure 4b presents the recorded space transversely.

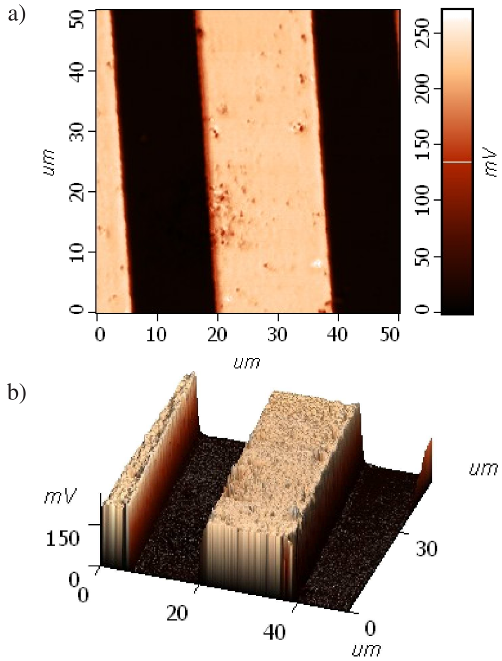

Fig. 4. Sensor structure obtained by means of the confocal microscopy method (the dark spaces – graphene on a glass surface, the brighter spaces – graphene on a gold interdigital electrode)

Figure 5 shows the spectrum of graphene achieved by means of Raman's spectroscopy.

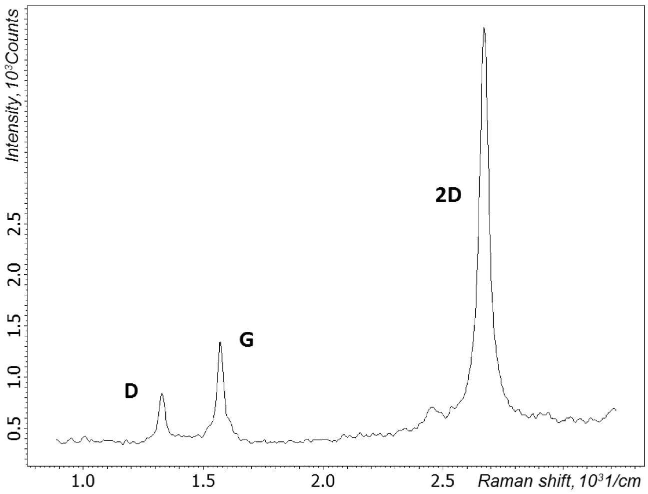

Fig. 5. Raman's spectrum of graphene on the sensor structure

Three Raman peaks of graphene are visible in this spectrogram, viz. D, 2D, and G; Raman's spectrum confirms the fact that the layer deposited on the surface of the resistance transducer is a layer of graphene displaying favorable morphological properties.

5. Results of investigations concerning the graphene structure in selected gaseous atmospheres

The sensitivity of graphene to the effect of various gaseous atmospheres was tested on the test-stand presented in Fig. 6. In all these measurements the atmosphere was synthetic air (20% O_2 and 80% N_2). The tests were run at a flow of synthetic air amounting to 500ml/min. The sensor structures with graphene were tested in the temperature range of 30°C to 130°C.

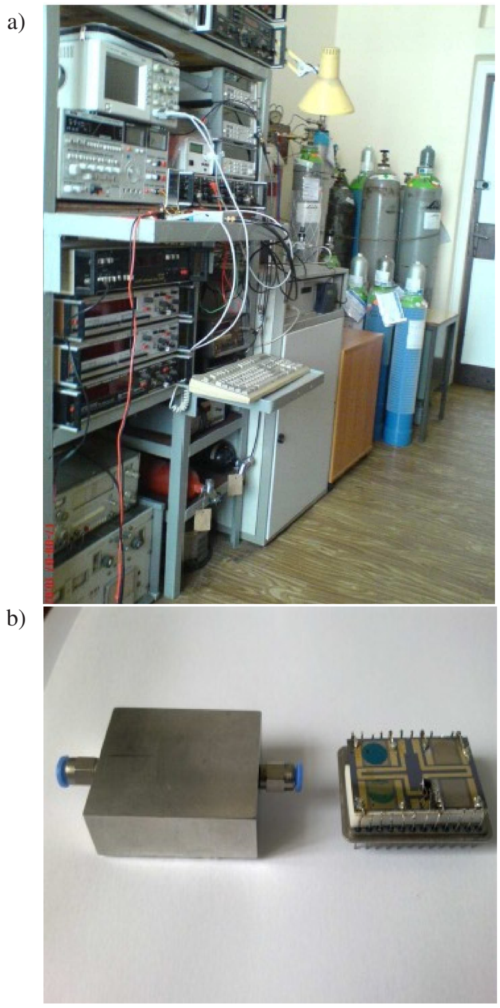

Fig. 6. a) Test-stand for investigations of graphene structures in an atmosphere of synthetic air with the tested gas; b) gas chamber containing the resistance sensor structure

For measurements of the resistance of a structure with a graphene layer a high-quality measurement system of the type AGILENT 34970 was applied. The measurements were carried out with an accuracy of $\pm 0.5 \cdot 10^{-3}$ Ω. It is to be stressed that the values of electrical resistance obtained in all these measurements concern the total resistance of the structure (the resistance of the graphene layer and of the interdigital transducer). The total resistance of the sensor structure with a graphene layer amounted at ambient temperature (about 20°C) to about 10 Ω. Figure 7 illustrates the varying resistance of the structure with a graphene layer as a function of its temperature. The temperature was changed every 10 deg in the range 50°C to 130°C.

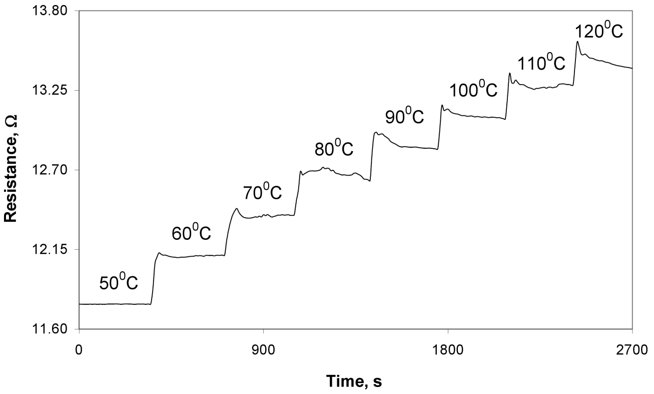

Fig. 7. The influence of temperature on the resistance of a sensor structure with graphene

The resistance of a sensor structure with a graphene layer increases with the growth of temperature only slightly. This dependence is of a linear character. Such an effect is characteristic for metal (e.g. gold). In the interdigital transducer the layer of gold is very thin (about 100 nm) and under this layer there is a layer of chromium, about 30 nm thick. The geometrical structure of the interdigital transducer with electrodes for electrical contacts is complex (Figs. 1 and 2). The resistance of the digital transducer with graphene cannot be measured itself directly. Therefore it is impossible to determine explicitly by means of experiments the character of changes in the resistance of graphene in the function of temperature. Depending on the arrangement of the subsequent layers of the carbon, graphene may be characterized both by the lack of the electron gap or by its presence [1, 6]. Hence, in some samples of graphene its resistance can grow linearly with the temperature, and in some others it may decrease exponentially with the dropping temperature. In the investigated structures the total resistance of a structure with a graphene layer increased with the growth of temperature.

5.1. Investigations concerning the sensitivity of a graphene sensor structure to the presence of hydrogen in the synthetic air. Figures 8 and 9 illustrate the changes in the resistance of a sensor structure with graphene, exposed to the effect of hydrogen in synthetic air. The investigations were carried out at a hydrogen concentration of 4% and humidity of air amounting to 5%, the applied temperature of the sensing structure being 50°C and 120°C.

Both Fig. 8 and Fig. 9 indicate a characteristic decreasing of the resistance of the graphene structure exposed to the effect of hydrogen. This effect, observed in both diagrams, may be accounted for by the influence of cooling due to the flow of gas through the structure. During the investigations the sensor structure is heated up to some given temperature, whereas the temperature of the gas mixture flowing above the structure is lower (room temperature of the gas in the gas cylinder). Figures 8 and 9 present the way in which the thermal conditions of the structure were established due to the gas flow, depending on the temperature of its being heated. Figure 10 illustrates the changes in resistance of a sensor structure with graphene exposed to the effect of hydrogen at different concentrations (1–4%) in synthetic air.

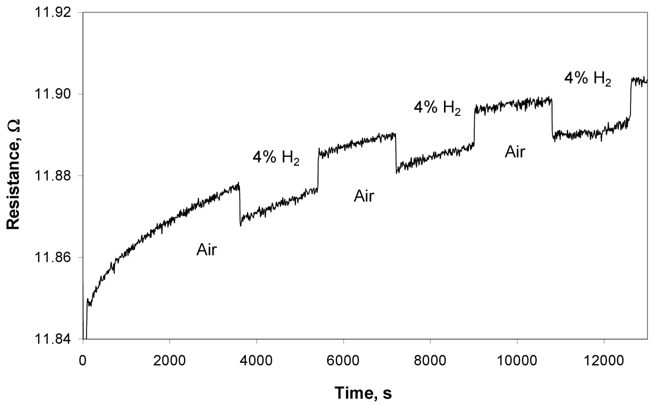

Fig. 8. Sensitivity of the graphene sensor structure to the presence of hydrogen in synthetic air (temperature of the structure 50°C, humidity of the air RH about 5%)

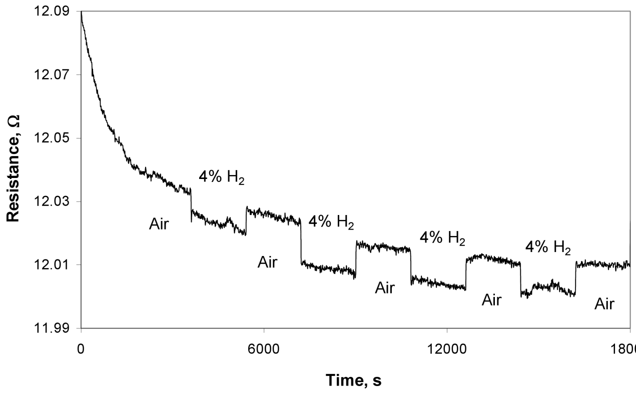

Fig. 9. Sensitivity of the graphene sensor structure to the presence of hydrogen in synthetic air (temperature of the structure 120°C, humidity of the air RH about 5%)

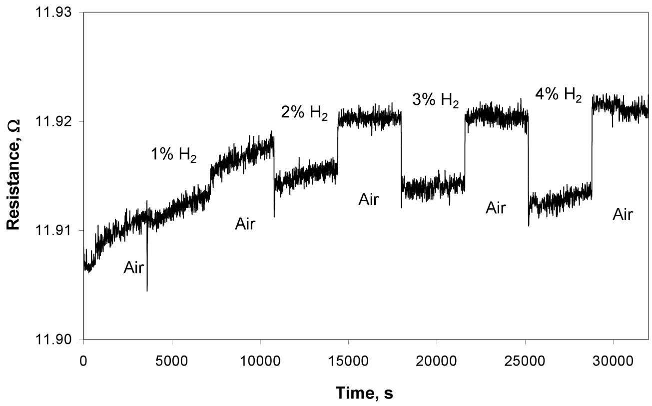

Fig. 10. Sensitivity of the graphene sensor structure to the presence of hydrogen in synthetic air (temperature of the structure 120°C, humidity of the air RH about 5%)

The investigations have proved that the value of the resistance of the structure with graphene is affected both by the presence of hydrogen in the atmosphere and the presence of steam. These dependences are presented in Fig. 11. The effects exerted on the graphene structure by the hydrogen and by steam oppose each other; while the hydrogen molecules contained in the synthetic air reduce the value of the resistance of the structure with graphene, the steam increases the resistance. These changes in the resistance of the structure are, however, rather small (on the whole they do not exceed 1% of the initial value). A characteristic feature of the effect of hydrogen on the structure with graphene is a fast reaction of the structure to the presence of hydrogen. Practically these changes are to be observed immediately after the appearance of hydrogen in the atmosphere of synthetic air.

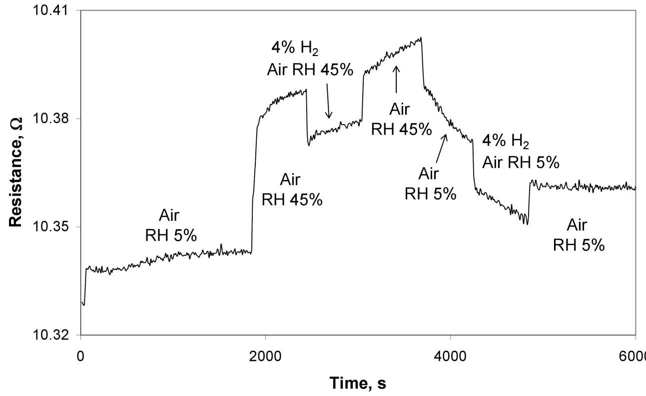

Fig. 11. The influence of humidity and hydrogen on the value of the resistance of the structure with graphene (temperature of the structure 50°C)

6. Investigations of the sensor structure with graphene modified by a nanolayer of palladium exposed to the effect of hydrogen H_2

At the Department of Optoelectronics in Gliwice, investigations concerning the modification of the properties of resistance sensor structures with graphene by depositing on the graphene nanolayers of various elements and molecules are under way. Figure 12 illustrates the system of an interdigital electrode structure with a layer of graphene covered with a 3 nm layer of catalytic palladium by means of magnetron sputtering technology.

Fig. 12. Graphene resistance structure covered with a 3 nm layer of palladium

Figure 13 presents changes in the resistance of a graphene sensor structure covered with a 3 nm layer of palladium. The character of the changes of resistance is similar to that presented in Fig. 7. Also in this case the resistance of the whole structure grows with its temperature. The "metallic" character of the sensor structure with graphene is dominant.

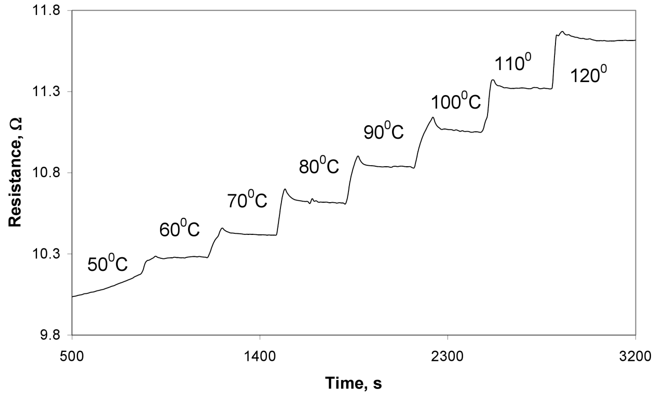

Fig. 13. Investigations concerning the influence of temperature on the resistance of a sensor structure with graphene and palladium

Investigations concerning the resistance structure with a graphene layer modified by palladium exposed to the atmosphere of synthetic air and to the effect of synthetic air containing hydrogen are presented in Fig. 14. Measurements were taken similarly as in the former case, i.e. at 50°C and 120°C (humidity of the gas about 5%).

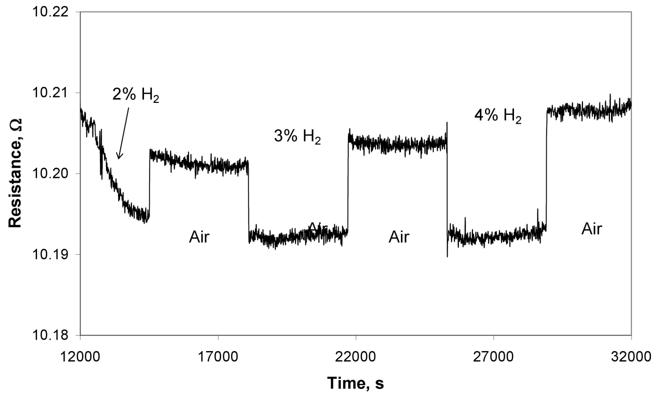

Fig. 14. Sensitivity of a resistance graphene structure with a 3nm layer of Pd to the presence of H_2 in an atmosphere of synthetic air (temperature 50°C)

Figure 15 presents the changes in the resistance structure depending on the humidity of the gaseous atmosphere. Investigations have proved a considerable sensitivity of the structure to the presence of steam.

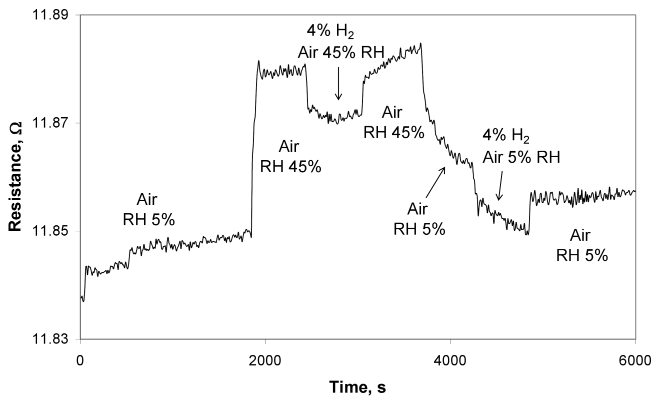

Fig. 15. The influence of humidity and the effect of hydrogen on the value of the resistance of a graphene sensor structure with a 3nm palladium layer (temperature of the structure 50 °C)

Figure 15 shows that the structure with graphene/Pd first of all is sensitive to moisture in the synthetic air. After the steam action on graphene/Pd, its surface changes irreversible. (The more detailed analysis of steam influence on physical properties of graphene was presented in [15].)

7. Investigations concerning the sensitivity of the resistance structure with graphene to the presence of NO_2 in synthetic air

While testing the properties of the resistance sensor structure with graphene also the sensitivity of the structure to the presence of nitrogen dioxide in the atmosphere of synthetic air was investigated. The results of these investigations have been gathered in Fig. 16. Humidity of the atmosphere amounted to about 5%. The steam was present in a gas cylinder containing NO_2.

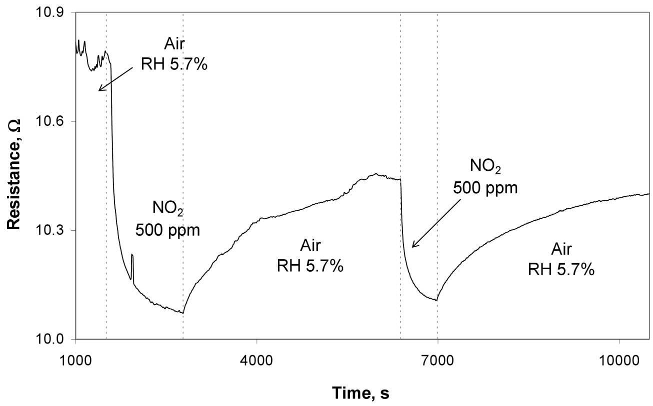

Fig. 16. Sensitivity of the sensor structure with graphene to the presence of NO_2 in the atmosphere of synthetic air (temperature of the structure 50°C, humidity RH about 5%)

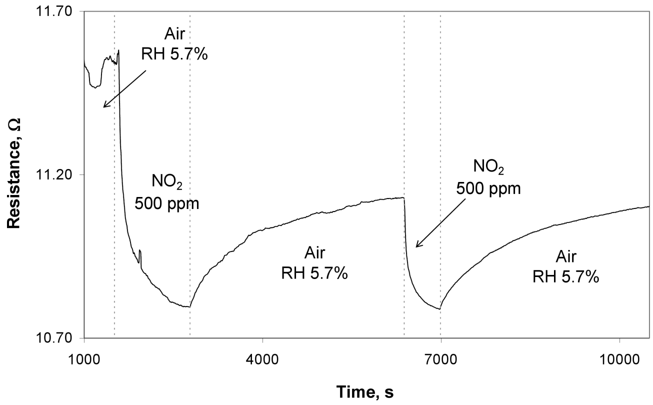

Fig. 17. Sensitivity of the sensor structure with graphene to the presence of NO_2 in the atmosphere of synthetic air (temperature of the structure 120°C, humidity RH about 5%)

Results of investigations of the resistance structure with modified graphene by a 3 nm palladium layer exposed to the effect of NO_2 in the atmosphere of synthetic air at 120°C and the humidity RH $\approx$ 5% have been illustrated in Fig. 18.

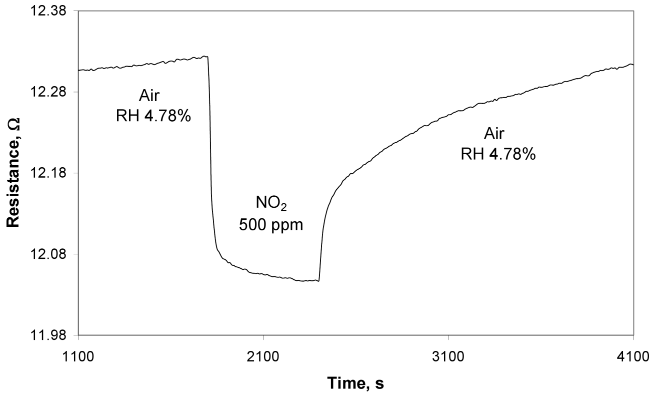

Fig. 18. Sensitivity of the sensor structure with graphene modified by a 3 nm Pd layer to the presence of NO_2 in the atmosphere of synthetic air (temperature of the structure 120°C, humidity RH about 5%)

The modification of graphene by a 3 nm layer of Palladium resulted in a very fast reaction of the resistance structure to the effect of nitrogen dioxide. This has also been confirmed by investigations carried out on other transducers of the tested four-transducer structures shown in Fig. 1. It is to be stressed that in the performed investigations the presence of NO_2 leads to an increase of electrical conductivity of the sensor structure with graphene [11, 15].

8. Remarks and conclusions

After numerous (several scores) cycles of measurements, in which the structure with graphene was exposed to the effect of various gases (H_2, NO_2, H_20, O_2, N_2) at varying temperatures (20–130°C), the structure was again tested making use of the methods of Raman's spectroscopy and AFM. The obtained results have been presented in Fig. 19. The area of the graphene layer composed in these investigations was the same as that presented in Fig. 5. Comparing both these diagrams it becomes obvious that after many cycles of testing the structure has changed, viz. the height of the peak D (by about 1350 cm-1) in relation to the peaks 2D and G, as well as the height of background at which the spectrogram of graphene had been recorded. (More detailed results of these investigations will be published).

Molecules of NO_2, which are absorbed into the graphene surface in presence the steam in synthetic air, may cause forming nitric acid. Nitric acid oxides graphene and generates defects in the graphene structure. These defects change stably the structure of graphene and hence its electrical properties. Figure 20 presents the AFM picture of graphene after its deposition on synthetic air containing NO_2 and steam. On the graphene layer mechanical defects can be observed. In Fig. 20 there is presented approximately this same region as in Figs. 3 and 4.

As it has been described in Sec. 2, graphene was deposited on the interdigital electrode structure mechanically from a PMMA foil. Such a mechanical deposition of graphene damaged the interdigital structure – some electrodes of the structure were broken. This leads to the conclusion that the electrode resistance structures should rather be constructed of thicker layers of gold (above 200nm) deposited on a chromium substrates (about 50 nm). The width of the interdigital electrodes (as well as the distance between them) should exceed, for instance, 100 μm, thanks to which the structure would be more durable and less liable to injury. The investigations have proved that a resistance structure with a graphene layer is sensitive both to the presence of hydrogen and nitric oxide in the atmosphere of synthetic air. The observed changes of resistance were on the level of a score (sometimes of several score) of mΩ. This structure was also sensitive to the effect of steam contained in synthetic air. Changes in the resistance of the structure due to the presence of steam were often larger than changes caused by the presence of hydrogen or nitrogen dioxide. In the case of resistance sensors of gases the problem of eliminating the steam from the investigated gaseous atmosphere is an important metrological and technical challenge. (The problems of steam presence in the gaseous atmosphere on the accuracy of detecting of selected gases were investigated and discussed in [16–20]). The performed investigations proved that the presence of steam in the monitored gaseous medium is a problem, which requires a solution concerning also gas sensors based on graphene.

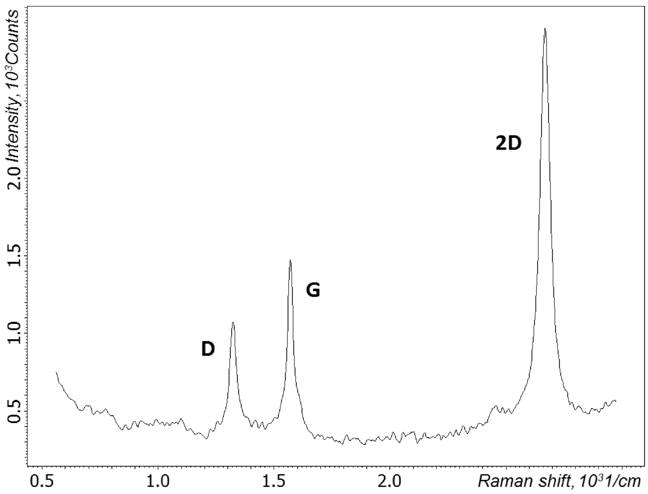

Fig. 19. Raman's spectrum of graphene on the sensor structure after its using in complex investigations

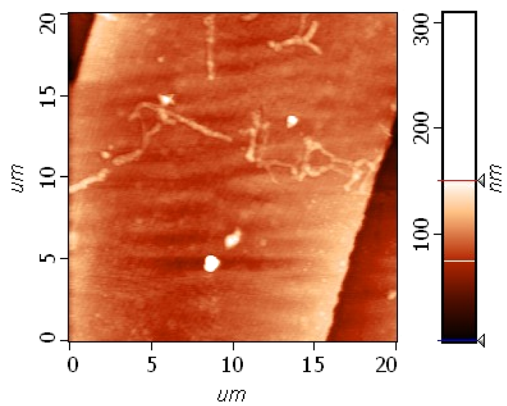

Fig. 20. AFM phase image of the surface of the electrode structure with graphene after numerous cycles of deposition of the synthetic air with NO_2 and steam

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