NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (1), P. 130–133

THE INFLUENCE OF THE AMBIENT CONDITIONS ON THE ELECTRICAL RESISTANCE OF GRAPHENE-LIKE FILMS

D. M. Sedlovets, A. N. Redkin

Institute of Microelectronics Technology and High-purity Materials, Russian Academy of Science, Chernogolovka, Russia

sedlovets@iptm.ru, arcadii@iptm.ru

PACS 81.05.ue

Since the discovery of graphene, researchers are not only interested in monatomic layers of carbon, but also in multilayered graphene structures named graphene-like films, which can be used, for example, as sensors. An understanding of the relationship between the growth conditions and the ability of the films to respond to certain gases, the ability to obtain films with desired properties and the ability to operate their sensor properties at the synthesis stage – are all of utmost scientific interest. In our study, we considered these issues. Synthetic conditions are not the only factors that affect the properties of the graphene-like films. In this work, we show that the electrical resistance also depends upon ambient conditions. Depending on the gas present in the environment, the resistance of the films can be changed. It follows from these results that we obtained carbon films possessing a selective sensitivity to ethanol vapor.

Keywords: Carbon films, Gas sensors, Graphene, Synthesis, Electrical properties.

1. Introduction

Since the discovery of graphene, the attention of many scientists has been focused on the study of this unique material. However, researchers are not only interested in the monatomic layer of carbon, but also in multilayered graphene structures, named graphene-like films and used, for example, as sensors. Graphene-based sensors, described in the literature, work on various principles: like field-effect transistors [1,2], surface acoustic waves [3,4], quartz crystal microbalances [5], micro electromechanical systems [6,7], conventional semiconducting metal oxides combined with graphene [8,9]. However, most of the reported gas/vapor sensors mainly operate in the resistive mode [10–12]. This sort of sensor is easy to fabricate and provides the possibility of direct measurement. Because the method of fabrication is based on a change in the electrical conductivity of the material during the interactions with gases, to understand the effect of different factors on the electrical resistance of such films is of great practical value. However, to understand the relationship between the growth conditions and the ability of films to respond to certain gases, and thus to obtain means to fabricate films of desired properties and to control their sensor properties at the synthesis stage – are of utmost scientific interest. These issues were the object of our study.

Earlier, we reported the method of obtaining graphene-like films by pyrolysis of ethanol vapor. This is a simple, low-cost and scalable approach, which excludes the use of flammable gases. At high temperatures (900 – 1000 °C), the pyrolysis of ethanol allows one to obtain carbon films not only on a catalytic metal surface, but also on dielectric substrates. It was found that the final properties of samples can be controlled by changing the growth conditions: for example, the sheet resistance decreased with increasing reaction temperature, while an increase in the synthesis duration led to a reduction of the sheet resistance [13].

TABLE 1. Sensitivities to some gases of the samples obtained at various synthesis temperatures on different substrates

	CH_4	C_2H_4	H_2	C_2H_5OH	i–C_3H_7OH
1000 °C (Cu)	0.13 %	–	–	2.75 %	0.16 %
900 °C (Cu)	–	–	–	2.11 %	0.75 %
800 °C (Cu)	–	–	–	0.72 %	0.94 %
1000 °C (quartz)	0.01 %	0.06 %	-	3.25 %	0.05 %
900 °C (quartz)	0.03 %	0.08 %	1.3 %	13.7 %	2.1 %

Reaction conditions are not only the factors affecting the properties of the graphene-like films. In this work, we show that ambient conditions can influence a film's electrical resistance. Depending on the gas present in the environment, the resistance of the films can vary. This fact led us to test these films as sensors.

2. Experimental technique

The experimental setup consisted of an airtight quartz vessel connected to a controlled gas flow system, and a rigidly fixed sample coupled with a measuring device. The gases used were: hydrogen, carbon monoxide, methane, ethylene as well as ethanol and isopropanol vapors. In the last case, the airflow was bubbled through the liquid reagent so that the concentrations of ethanol and isopropanol vapors were about 2 and 1.5 percent by volume, respectively. The resistance was measured directly between two contacts positioned on top of the sensing graphene films. For this purpose, two copper strips were deposited by vacuum evaporation.

The procedure was as follows: previously the vessel was ventilated with a certain gas for 1 hour to establish stationary conditions. Thus, the concentration of gases, except ethanol and isopropanol vapors, was 100%. A sample was quickly placed in the vessel and a change in the sensor resistance with exposure to the interacting gas/vapor was studied (sensitivity and response time were measured directly). Then, the sample was quickly taken out in air and a recovery time was registered.

The samples used in the experiments as sensors were obtained by pyrolysis of ethanol under the following conditions: reaction temperature was varied from 800 – 1000 °C, quartz and metal foil were used as substrates.

3. Results and discussion

It was determined experimentally that there was no film response upon exposure to carbon monoxide. Sensitivities of the samples obtained at various reaction temperatures on different substrates to other gases are given in Table 1. These values were estimated as changes in the materials resistance upon interaction with different gases, using the equation (1).

$$\text{Sensitivity} = (R_{\max} - R_0)/R_0, \qquad (1)$$

where $R_{\max}$ and R_0 – maximum resistance of the response and initial resistance, respectively.

The sensitivity values were negligible (about 1% or much less) for all gases except ethanol vapor. So, we can assume that our sensors exhibit a high selectivity for ethanol vapor. The result is of great practical value, because a lot of sensors usually respond to a number of different gases. A better chemical affinity can be achieved by functionalization of graphene [14,15]. Because films obtained by pyrolysis of ethanol vapor contain carboxyl groups on the surface [16], the good chemical selectivity of our sensors is evidently due to this fact.

The efficiency of graphene sensors was recently found to be improved by increasing their surface area [17]. In our case, this is easy to achieve, because the size of the films we obtained is only limited by the size of the reactor. Furthermore, with our technique, thin carbon films can be directly grown onto almost any dielectric substrate (as long as it can be heated up to the growth temperature and not subjected to strong thermal expansion). Generally, films formed on quartz substrates possess a higher sensitivity than structures obtained on copper foil. Perhaps this can be explained by the inevitable damage of the films during transfer.

Figure 1 shows changes in response for the last sample towards a mixture of C_2H_5OH vapor with air. The response time was determined to be 10 minutes. As follows from the insert in Fig. 1, the sensor possesses good recover ability.

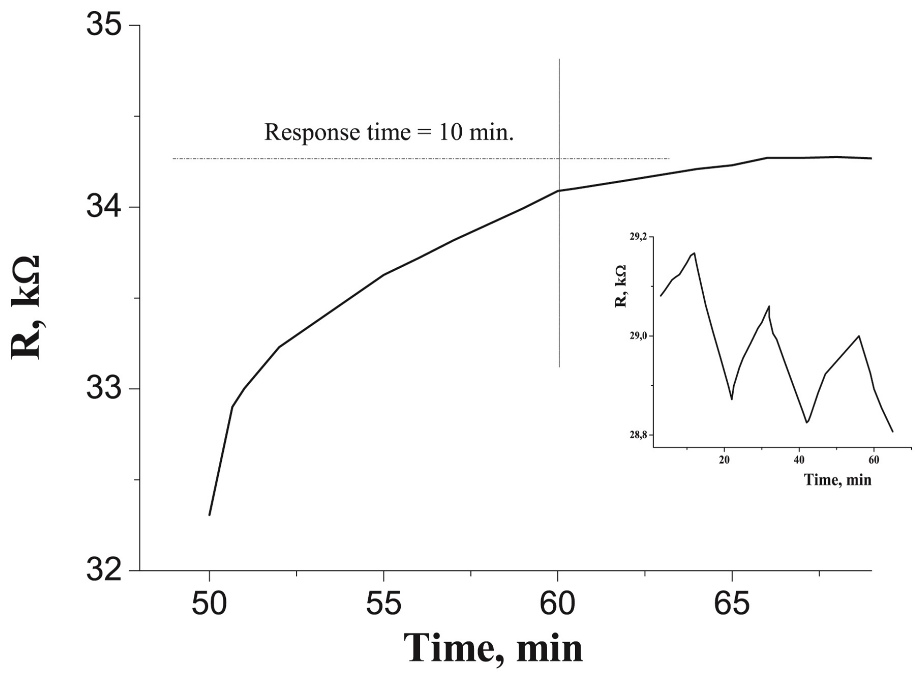

FIG. 1. The time response of the electrical resistance R to the exposure to ethanol vapor for the sample obtained at 900 °C on a quartz substrate. Insert: dynamic changes in response of the sensor during an "in/out" cycle (one step of cycle = 10 min)

4. Conclusions

We show that a relationship exists between the growth conditions and the ability of films to respond to certain gases. But the synthetic conditions are not the only factor influencing the properties of graphene-like films. Their electrical resistance also depends on the ambient conditions. Selective sensitivity of different samples to some gases of various concentrations was studied. The obtained results suggest that the proposed method is highly promising for obtaining carbon films, which possess a selective sensitivity to ethanol vapor.

A more detailed study of the sensor characteristics (including a detection limit) of the films in relation with their synthesis conditions will be the subject of future investigations.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (project No. 11-02-00498a).

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