Development and research carbon nanotube-based resistive gas sensor

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Abstract. Experimental studies of the processes of formation of catalytic centres (CC) and carbon nanotubes (CNTs) at ITO contacts have been carried out. The regularities of the influence of the annealing temperature on the geometric dimensions of CC have been established. An array of interwoven CNTs with a highly developed surface has been grown. A model of a gas sensor with a sensitive element based on a CNT network has been created. The reaction time and reaction of the sensor, its sensitivity to \text{N}_2, \text{O}_2, \text{and} \text{Ar} have been experimentally investigated. It has been shown that the sensor has a maximum sensitivity of 17.2% to \text{N}_2, 16.3% to \text{Ar}, and 18.7% to \text{O}_2 in the range of gas concentrations from 30 to 70 ppm. It has been shown that gas detection is possible at room temperature, despite a rather long reaction and reduction time. In this case, an almost complete restoration of the sensitive element of the initial resistance has occurred without additional heating.

1. Introduction
In a sophisticated man-made situation and terrorist threat danger, one of the problems is gas sensors for environmental monitoring. The main parameters of gas sensors are sensitivity, selectivity, response and recovery times, dimensions, and power consumption. Traditional materials used in resistive sensors (SnO, ZnO, et al.) have good sensitivity, but do not show sufficient selectivity. The long reaction and recovery times, high energy consumption associated with the necessity of heating the sensitive layer [1,2] are the disadvantages of these sensory materials. Therefore, there is a regular research of new materials, which can improve the sensors characteristics. Graphene and carbon nanotubes (CNT) are ones of the most promising materials both for electronic chips [3-5] and gas sensors, which are designed to eliminate the disadvantages of sensors available on the market [6,7].

The aim of this work is the development of the CNT-based resistive gas sensor and experimental study of its sensitivity parameters.

2. Experimental
A model of a gas sensor with a sensitive layer was created on the basis of an array of interwoven multiwalled carbon nanotubes (MWCNT). To create a model, interdigit electrodes based on an ITO film 100 nm thick were formed on a glass substrate. ITO was deposited using the Auto500 unit (BOC Edwards, UK) through a mask. A 10 nm thick Ni film acting as a catalytic layer of CNT growth was deposited over the ITO layer through a mask. After that, the catalytic film was annealed to form catalytic centres (CC) of CNT growth.

The effect of heating temperature on the formation of CC for CNT growth was studied in the range
of 700-800°C. Investigation of the CC parameters of the experimental samples was carried out using a probe nanolaboratory Ntegra (NT-MDT, Russia) (Fig. 1). Geometric parameters of Ni CCs were determined using special software Image Analysis.

Then, at a temperature of 750°C, a network of disordered CNTs was grown in the NANOFAB PECVD module (Fig. 2). CNTs were grown in an atmosphere of acetylene and ammonia.

The gas sensor was placed in a gas measuring stand, where its response to nitrogen, argon, and oxygen was checked. The measuring stand consisted of a vacuum chamber, a controlled gas supply system, and a pumping system. The choice and study of the sensor’s reaction to the presence of these gases is associated with their potential danger during accumulation in confined spaces.

Measurement of resistance was carried out using a universal ohmmeter B7-78/1, at a temperature in the measuring chamber of 300 K. The sensitivity of the device was calculated by the formula:

\[ S_k = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\% \]

where \( R_{gas} \) — sensor resistance in the presence of gas, \( R_{air} \) — sensor resistance before gas supply.

The response time was defined as a time interval of 90% of the time required for the release \((R_{gas} - R_{air})\) to a stationary level after injecting a certain concentration of the analysed gas. Sensor recovery time was defined as the time interval, during which the sensor resistance recovered after injection of the analysed gas to 10% of the maximum value \(0.1(R_{gas} - R_{air}) + R_{air}\).

![Figure 1](image-url)

**Figure 1.** Dependence of CC geometric parameters on processing temperature: (a) example of AFM image of CC; (b) dependence of CC geometric parameters on processing temperature; (c) dependence of CC surface density on processing temperature.
3. Results and discussion

The geometric dimensions (height and diameter) and the surface density of CC are the main factors affecting the geometric parameters of the grown CNTs. The study of the size of the CC at the annealing stage made it possible to optimize the modes of their formation. The results of the AFM study of the CC showed that the annealing temperature had a significant effect on the geometric parameters of the CC. Analysis of the obtained AFM images made it possible to determine the average diameter, height, and surface density of the formed CCs (Fig. 1). It can be seen that with increasing annealing temperature from 700 to 750°C, both the height and diameter of the CC decrease, which indicates the occurrence of evaporation and sublimation of Ni from the substrate surface. This leads to a decrease in the average geometric dimensions of the CC, and also reduces their dispersion in the array. With a further increase in temperature, the processes of atomic diffusion over the surface are manifested, which is reflected in the combination of small droplets into larger ones and, correspondingly, an increase in the size of formed CCs. It is established (Fig. 1) that the temperature of 750°C allows the formation of the smallest CC (223 ± 20 nm) with the maximum density (9.2 µm⁻²).

Thus, for the subsequent formation of the sensitive element of the model (Fig. 2a,b) of a CNT-based gas sensor, a temperature of 750°C was chosen. To ensure maximum sensitivity of the sorption gas sensor, an array of interwoven MWCNTs with a high surface development was grown (Fig. 2c). The formation of interwoven CNTs is due to the fact that the sensitivity of the sensor is proportional to the surface area of the CNTs. Thus, nanotubes can adsorb more gas molecules onto themselves.

The initial resistance of the structure was found to be 516 kΩ. Figure 3 shows the sensor's response time to different gases.

Table 1 summarizes the results of measuring the change in sensor resistance, converted to gas sensitivity according to formula (1), as well as the response and recovery time for each gas.

| Parameters     | N₂   | Ar    | O₂         |
|----------------|------|-------|------------|
| Gas sensitivity, ppm |      |       |            |
| 10             | -    | (5 ± 1.3) % | -          |
| 30             | (8.7 ± 2.1) % | (9.7 ± 3.2) % | (10.4 ± 2.2) % |
| 50             | (9.4 ± 1.4) % | (16.3 ± 4.1) % | (16.6 ± 2.5) % |
| 70             | (17.2 ± 3.6) % | -       | (18.7 ± 3.3) % |
| Response time, s | 153 ± 12 | 186 ± 15 | 141 ± 7    |
| Recovery time, s | 280 ± 19 | 130 ± 11 | 190 ± 8    |
Thus, the maximum measured sensitivity to oxygen, argon, and nitrogen was 18.7%, 16.3%, and 17.2%, respectively, with a response time of 141 s, 186 s, and 153 s, respectively. The onset of exposure to all three gases causes a fairly fast response of the sensor (on average 160 sec), which is a good result for a sensitive layer operating at room temperature. The fastest recovery time of 130 s was shown after exposure to argon. After exposure to oxygen, the sensor was restored for 60 s longer, which might be due to the high chemical activity of oxygen and a large mass of adsorbed molecules. The long recovery time of the sensor after exposure to nitrogen may be associated with the formation of C-N bonds and partial nitrogen chemisorption. Also, the argon atom is 2.5 times heavier than oxygen one, which also complicates the desorption process. However, the patterns that affect the recovery time of the gas-sensitive layer require additional research. Moreover, in all experiments, the restoration of the sensor model occurred without heating, at room temperature. From the obtained results, we can conclude that the developed gas sensor sensitive element has a high sensitivity and speed, as well as does not need to be heated for degassing.

4. Conclusion
A model of a sorption gas sensor with a CNT-based sensitive element was developed, and its performance was measured. It was shown that the sensor had a maximum sensitivity of 17.2% to N₂, 16.3% to Ar, and 18.7% to O₂ in the range of gas concentrations from 30 to 70 ppm. It was also found that even at room temperature, despite a rather long reaction and recovery times, an almost complete restoration of the sensitive element of the initial resistance occurred.

Obtained results can be used in the development of promising sensor devices based on carbon nanotubes, in particular portable wearable devices as well as multisensory systems, which will expand the range of sensitivity and increase the selectivity of devices.
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