PHYSICOCHEMICAL MEASUREMENTS

A SENSOR OF GRAPHITE PAPER WITH
MULTIWALLED NANOTUBES

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The results of a voltage-current characteristics study of sensors made of graphite paper with multiwall nanotubes are presented. It has been found experimentally that these samples are usable as gas sensors for the detection of NH_3, H_2, and Cl_2 in air.

Keywords: *sensor, nanotubes, graphite paper, film, tunneling voltage-current characteristic.*

The principles of operation of gas sensors are based on the physicochemical processes at the interface between two media – gas and solid. The investigated gas, usually air, contains impurities that must be detected using the sensor. The impurities affect the electrophysical properties of the sensing element in the sensor, which registers and converts the changes into the corresponding signal that indicates the presence of impurities in the environment under investigation.

A review of gas sensors and their designs based on nanotubes is given in [1]. These sensors allow one to describe electrophysical parameters of samples with carbon nanotubes as a function of gas concentration in the environment. A new microelectronic sensor based on a thin-film Schottky diode with nanotubes for hydrogen detection, which was used to study the effect of hydrogen flow on the current-voltage characteristics (CVC) of the diode at room temperature, is described in [2].

The authors of [3, 4] suggest to construct a sensor using black lead consisting of pressed nanotubes connecting gold contacts deposited on paper. The use of such lead simplifies the construction of an indicator of impurities in atmosphere. The sensor described in [4] can be used to determine the concentration of ethylene in air as a function of resistance of nanotubes.

Transistors made of carbon nanotubes can be used as sensors in gaseous environments [5–7]. To detect ammonia or nitrogen dioxide, single-walled nanotubes (SWNT) 18 nm in diameter with hole conductivity are used. Conductivity of such a nanotube decreases by a factor of 100 after 10 min in a mixture of ammonia (0.1–1%) and argon. After 12 h at room temperature or after 1 h at 200°C, the initial electrical properties of such a sensor are restored.

In [8], a sensor is described that consists of a resonant circuit in the form of a copper disk coated in carbon nanotubes (a 10 μm thick layer of SWNTs or a 100 μm thick layer of multi-walled nanotubes (MWNTs)). The sensor was placed in a vacuum chamber. Introduction of ammonia vapor caused a change in the resonant frequency of the circuit. The time to restore the initial resonant frequency after removal of ammonia was 10 min. The change in thermoEMF as a function of helium concentration is described in [9]; the time to restore the initial thermoEMF value after removal of helium was 50 min. In [10], an ionization cell is described consisting of an anode-substrate coated with vertically oriented MWNTs, and an aluminum cathode. Nanotube diameter was 25–30 nm, and the distance between them – 50 nm. Under the influence of a high-voltage electric field, an electrical breakdown occurred. A breakdown voltage value was found for each test with different gases. As a result of the breakdown, a discharge current passed between the electrodes, the value of which is proportional to the logarithm of the concentration of the investigated gas (air, Ar, N_2, O_2, NH_3).

In this paper, we propose a method simpler than the previous [1–10] for manufacturing a gas sensor of graphite paper with MWNTs; its current-voltage characteristic is investigated.
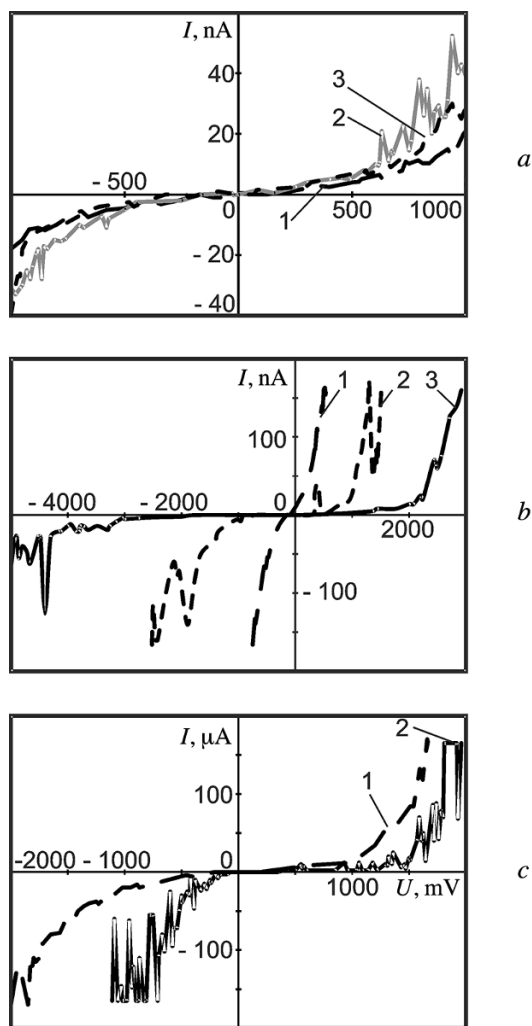

Fig. 1. Current-voltage characteristics of a sample of graphite paper with MWNTs in air with ammonia (*a*), hydrogen (*b*), and chlorine gas (*c*): *1*) in air without impurities; *2*, *3*) in air at the time of introduction of the specified impurity and 5 min after, respectively.

The simplified method for manufacturing samples of graphite paper with MWNTs by current annealing is given in [11]. Here, we briefly describe this method. Initially a homogeneous solution is prepared: 2 ml tetraethylorthosilicate, 2 ml ethanol, 1.5 ml aqueous solution of nickel nitrate and cobalt nitrate. Then, 0.5 ml of 10% solution of HF is added to the mixture. A silicate gel forms, in which a piece of graphite paper is submerged. The paper is subsequently removed and dried at room temperature. A thin silicate layer with nickel and cobalt nitrates forms on the paper. Then, annealing is carried out at 650–750°C to obtain graphite paper with MWNTs. In the present study, the method described in [11] was improved in the following manner: instead of silica gel, a sample of graphite paper with 81% porosity, consisting of fibers 5–10 μm in diameter, was soaked in 1.5 ml of aqueous nickel and cobalt nitrates (catalysts) and then dried at room temperature. To synthesize samples with MWNTs, a vacuum unit URM-3M was used. In the vacuum chamber (pressure $2.7 \cdot 10^{-4}$ Pa), a 10×1 cm ribbon of graphite paper was placed between the holders of the heater, which was heated to 450°C (for decomposition of nitrates) while passing current through it. Then, the paper was subjected to current annealing at 700–720°C for 2 min in the same chamber. In contrast to [12], where annealing was done under vacuum, here annealing was carried out in hydrogen. In the following step, the vacuum chamber was filled with hydrogen to 1.3 Pa. Inside the chamber, there was a target made of pure graphite for reactors with metal catalysts of nickel, yttrium, and iron. The ribbon was left there. A negative voltage $V = 100$–500 V was

applied to the target, and under this influence a gas discharge with a current strength of 60–100 mA ignited above the ribbon. Positive ions from the gas discharge bombarded the target and dispersed atoms from its surface. Thus, an additional film with nanotubes deposited on the surface of the ribbon. As a result, MWNTs were obtained 10–30 nm in diameter up to 1 μm in length with 10–30 layers. The volume occupied by the nanotubes reached 80–90% of the total volume of graphite film. For further experiments, 1×1 cm samples of paper with carbon MWNTs, cut from the experimentally prepared ribbon, were used.

The majority of publications and reviews present data on the study of traditional electrophysical properties of samples with NTs [1–10, 13]. More sophisticated methods for determining parameters of materials with nanotubes can be used. For example, within the framework of solving nanometrology problems, studies of CVC by scanning tunneling spectroscopy (STS) were performed with a scanning probe microscope (SPM) SMM-2000 (Proton-MIET, Zelenograd) for a number of metals [14]. This paper presents the study of electrophysical properties of samples of graphite paper with carbon MWNTs conducted using a Nanoedyukator scanning probe microscope (NT-MDT, Zelenograd) in different gas environments. Linearity of the scanner in YXZ <0.1%, noise in YX <0.3 nm, noise in Z <0.04 nm. Tunneling CVC of graphite paper with carbon MWNTs were collected in STS mode. In this mode, electron tunneling between the conductive probe and the sample were studied under external voltage. A sharpened tungsten needle with a tip curvature radius on the order of 50 nm was used as the probe. Test gasses were run over the graphite paper samples using a remote probe in the shape of a piston with a capillary with an inner diameter of 0.3 mm. CVC dependences of the sample in the presence of impurities in air were collected without changing the position of the probe over the selected sample point and from the moment the impurity was introduced, so the response time of the sensor was 5–20 sec.

Figure 1a shows the experimental results on the measurement of CVC of the sample of graphite paper with MWNTs in air (curve 1), in air at the time of introduction of ammonia impurity (curve 2), and 5 min after the introduction (curve 3). It turned out that in the specified voltage range the interval of the measured values of current for curves 2, 3 widened in comparison with the curve 1, the tilt angle of the right positive branches of the curves 2, 3 increased, and the left – decreased. Also, the sensor responded to small gas flow values from the remote probe, even to the minimum recorded flow of test gases of $\approx 9.3 \cdot 10^{-8}$ m³·Pa/sec. These features of the CVC observed immediately after introducing the impurity can be explained by the interaction of ammonia molecules with MWNTs [1]. From the curve in air with impurity 5 min after its introduction, it follows that the CVC parameters began to stabilize and approach the initial values in air (curve 1), distortions decreased. This indicates recovery of the initial characteristics of the sample 5 min after the start of effect of ammonia. In [2], it is shown that adsorption of the test gases can noticeably affect the electronic characteristics of nanotubes, changing their resistance, and as a result the CVC is significantly distorted.

In the following experiment, the CVC of the sample of graphite paper with MWNTs under a constant flow in air (Fig. 1b, curve 1) and in air with hydrogen impurity (curve 2) was determined in scanning tunneling microscopy mode at room temperature and atmospheric pressure. Experiment methodology was similar to the previous case. The minimum registered gas flow was also $9.3 \cdot 10^{-8}$ m³·Pa/sec. The following features of the CVC dependencies are notable. The central part of curve 2 in air with hydrogen impurity became flatter, tunneling transition widened and shifted by –0.7 V compared to curve 1. After 5 min, the CVC started to stabilize (curve 3) compared to CVC in air at the moment of introduction of hydrogen, however, the distortions increased.

Sample preparation procedure was modified. Some of the graphite ribbon was pulverized into a powder. To obtain the powder, either the upper layer of the graphite ribbon with MWNTs was simply scraped, or a piece of the ribbon was ground in an agate mortar using an agate pestle. Square pieces of textolite coated in copper foil on both sides were used as the substrate. These samples were 10×10 mm² in size. The two surfaces were connected with conducting contacts on the sides for unobstructed flow of the tunneling current. The powder was diluted with water; the suspension was applied to the front surface of the samples, and then the suspension was dried. In scanning tunneling spectroscopy mode, the CVC was obtained of the sample of graphite paper with MWNTs in air with gaseous chlorine admixture (Fig. 1c). The branches of the CVC in air at the moment of introduction of chlorine are severely distorted, the central part of the curve 2 becomes flatter compared with curve 1.

Conclusion. A method of manufacturing a gas sensor of graphite paper with a film of carbon MWNTs is investigated. The electrophysical properties of these sensors in various gaseous media were investigated in scanning tunneling spectroscopy

mode. It is shown experimentally that the obtained samples can be used as gas sensors to detect ammonia, hydrogen, and chlorine gas impurities in air. The response time and recovery time of the characteristics is shorter or commensurate with other types of sensors. CVC of the sensors vary for the investigated admixtures of ammonia, hydrogen, and chlorine in air.

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