PHYSICAL INSTRUMENTS FOR ECOLOGY, MEDICINE, AND BIOLOGY

A Gas Sensor Made from a Graphite Paper with a Nanotube Film

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Abstract—A technique for obtaining gas sensor samples from graphite paper with a nanotube film is described. Current-induced annealing of the graphite paper and additional evaporation of a nanotube graphite film in a hydrogen atmosphere are combined in the developed technique. The current−voltage characteristics of the samples have been measured at room temperature in air, in vacuum, and at low concentrations of NH_3, ethanol, and acetone. Experiments demonstrate that these samples containing carbon multiwall nanotubes can be used as a gas sensor to detect the presence of NH_3 and acetone. They are characterized by high sensitivity and selectivity, fast response, restoration, and stability of the characteristics. The estimated sensor sensitivities to NH_3, acetone, and ethanol at a current of 96.8 mA are ~15, ~12, and ~1 mV/Torr, respectively. Their sensitivity is determined by the difference in the behavior of their current−voltage characteristics under exposure to NH_3, ethanol, and acetone. The sensor features fast response (5−20 s) and restoration (within 5 min, restoration to the initial state before the exposure to NH_3 is 100.2%), as well as the stability of its characteristics (the pressure ranges from 1×10^{-6} to 760 Torr).

INTRODUCTION

Gas sensors are actively developed today for industrial, ecological, and medical applications. Sensitive elements based on carbon nanotubes (CNTs) arouse intense interest. In [1, 2], it was proposed using nanotubes (NTs) pressed in the shape of a slate pencil to produce gas chemical sensors. The action of such a sensor is based on a change in the CNT resistance if gas molecules appear on its surface. A precise sensor was developed on its basis in [1, 2]. It is a paper band with gold contacts deposited on it. The contacts are connected by lines drawn with a slate pencil consisting of pressed CNTs. Sometimes, NTs are deposited from an NT suspension in active organic solvents, which is applied to the sensor. The sensor susceptibility to gas of a certain type is attributable to its chemical interaction with NTs. The latter can be regulated by introducing certain additives. It was proposed using the sensor to determine the ethylene concentration in [2]. The inferiorities of the technique in [1, 2] are the inaccurate drawing of the connecting line with an NT slate pencil, the possibility of flaking the picture off the paper, the inadequate durability of the paper, etc.

More complicated constructions of sensors used to investigate the dependences of the electrophysical parameters of samples with CNTs on the gas concentration in a medium were presented in [3–5]. In [3–5], CNT transistors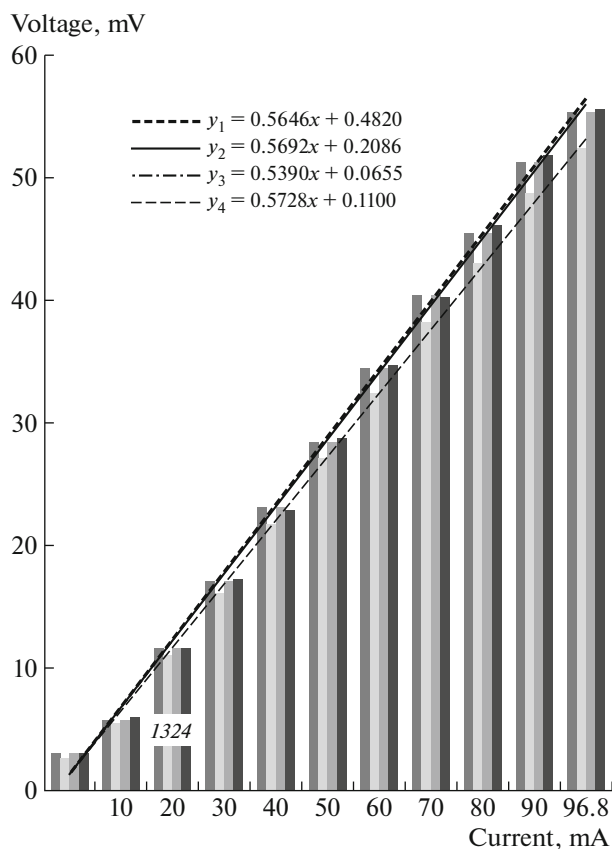 were proposed as gas sensors. Single-wall NTs with a diameter of 18 nm and hole conduction were used to detect NH_3 and NO_2. Within 12 h under normal conditions or in 1 h at a temperature of 473 K, this sensor restored its initial electric parameters. A review of gas sensors based on NTs was presented in [5].

The aim of this study was to obtain samples of gas sensors consisting of a graphite paper with an NT film and to study their current−voltage characteristic (CVC) in various media.

EXPERIMENT

The proposed method for producing the gas sensor from multiwall NTs has the following advantages: it is free from the inferiorities of the technique in [1, 2] and is simpler than the constructions in [3−5]. This method is based on obtaining multiwall NTs from a graphite paper with an additional synthesized NT film. Samples obtained thereby were tested as gas sensors. The technique for preparing multiwall NTs by current-induced annealing of a graphite paper was proposed earlier in our work [6]. Nevertheless, some essential changes have been introduced in it.

The URM-3M vacuum facility was used to synthesize multiwall NTs by the current method. A graphite paper shaped as a band with dimensions of 10×1 cm was placed in the vacuum chamber of the facility

Voltage, mV

$y_1 = 0.5646x + 0.4820$
$y_2 = 0.5692x + 0.2086$
$y_3 = 0.5390x + 0.0655$
$y_4 = 0.5728x + 0.1100$

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Current, mA

Fig. 1. The CVCs of a sample with multiwall NTs, measured at room temperature: (*1*) in air at 1 atm; (*2*) in a vacuum of 2×10^{-2} Topp; (*3*) in vacuum upon supplying some NH_3 to a pressure of 2×10^{-1} Torr (the lowest bar); and (*4*) after lowering the pressure down to 2×10^{-2} Torr and holding at this pressure for 5 min.

between the heater holders, and current was passed though it. The graphite paper consisted of fibers 5–10 μm in diameter and had a porosity of 81%. By contrast to [6], catalysts (Ni and Co) were added to the paper in the following way. A sample was impregnated with 1.5-mL water solution of nickel nitrate and cobalt nitrate. Afterward, it was dried out at room temperature, thereafter, was fixed in place at the heater electrodes in the URM-3M vacuum facility, and heated to a temperature of 450°C at a pressure of 2×10^{-6} Torr for decomposition of the nitrates and oxidation of the metals. For multiwall NTs to be obtained, the paper was annealed with a current for 2 min at a temperature of 700–720°C and the same pressure.

At the nest stage, the chamber was filled with a working gas (hydrogen) to a pressure of 1×10^{-2} Torr. A target made of a pure reactor-grade graphite with metal catalysts Ni, Y, and Fe were placed in the vacuum chamber. By contrast to the method described in [7], the working gas was hydrogen, and the conditions for preparing graphite films with multiwall NTs were

changed. After negative voltage $U = -(100-500)$ V was applied to the target, a gas discharge was initiated over it, and the discharge current was 60–100 mA. Positive ions from the gas discharge bombarded the target and dispersed atoms from its surface. An additional NT film was deposited thereby on the graphite paper surface.

As a result, multiwall NTs with a diameter of 10–30 nm, a length of up to 1 μm, and with 10–30 layers have been obtained. In the total volume of the graphite film, the volume occupied by nanotubes may vary from a fraction of percent to 80–90%, depending on the NT preparation conditions. The NT characteristics were determined by the atomic-force microscopy method, while the scanning tunneling microscopy and electron microscopy techniques described in detail in [6, 7] were used at the initial stage of modification of sensor samples.

Samples with multiwall CNTs with dimensions of 1×1 cm (cut out of the primary band) were investigated at the URM-3M vacuum facility. This facility was used to produce vacuum and a gas medium to investigate samples with multiwall NTs. The facility contained vacuum-tight current leads, which were connected via copper conductors and pressure contacts with experimental samples. These current leads were connected to the measuring instrumentation.

The four-contact dc technique was used to investigate the CVCs. Power supplies Elektronika and HY1502D, universal voltmeters V7-21 and V7-35, a resistor bank, and a measuring resistance of 1 Ω were used to measure the CVC of samples based on multiwall NTs in various gases, air, and vacuum. The CVCs of test samples were investigated in air, in a vacuum of down to 2×10^{-2} Torr, and in the presence of small amounts of NH_3, ethanol, and acetone.

Figure 1 presents the CVC of the sample with multiwall NTs, measured at room temperature at the URM-3M facility. The CVCs are presented as histograms with trend lines and with expressions for these lines. The histogram elements consist of four bars each of which corresponds to an individual experiment with the number shown on the bar and as a subscript of y in the respective expression. The CVCs were measured under the following conditions:

(1) in air at a pressure of 1 atm ($y_1 = 0.5646x + 0.0482$);

(2) after the pressure was lowered to 2×10^{-2} Torr ($y_2 = 0.5692x + 0.2086$);

(3) after inleakage of a small amount of NH_3 over a few seconds via a microvalve to a pressure of 2×10^{-1} Torr ($y_3 = 0.539x + 0.0655$; the lowest bar); and

(4) after subsequent pressure reduction to 2×10^{-2} Torr and holding at this pressure over 5 min ($y_4 = 0.5728x + 0.11$).

Comparison of the CVC of the sample with multiwall NTs has shown that the CVC measured in air at a

Voltage, mV
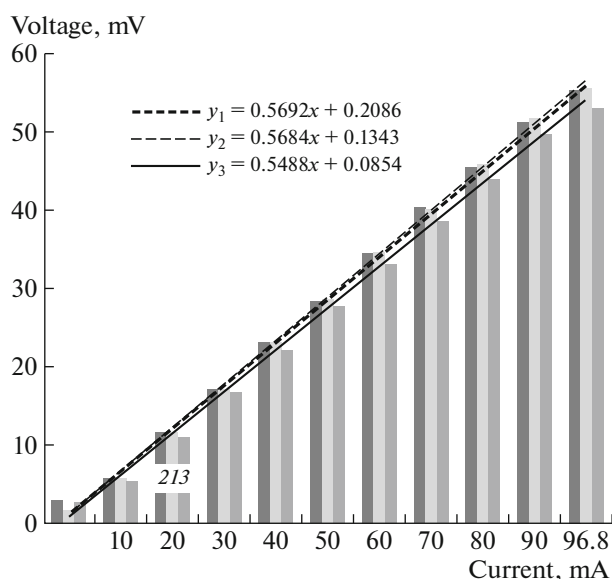
Fig. 2. The CVCs of a sample with multiwall NTs, measured at room temperature: (*1*) in a vacuum of 2×10^{-2} Torr; (*2*) in vacuum upon supplying some ethanol to a pressure of 2×10^{-1} Torr; and (*3*) in vacuum upon adding some acetone to a pressure of 2×10^{-1} Torr.

pressure of 1 atm and room temperature coincides with the CVC obtained after pressure reduction to 2×10^{-2} Torr. This indicates that the presence of air does not affect the CVC behavior for a particular sensor. Subsequent inleakage of some NH_3 to a pressure of 2×10^{-1} Torr leads to a noticeable change in the CVC trend line slope ($y_3 = 0.539x + 0.0655$, the lowest bar). For this volume, this NH_3 concentration is $0.26‰$ relative to its value under normal conditions, which is the evidence of the high sensor sensitivity. Further NH_3 pressure reduction down to 2×10^{-2} Torr with exposure over 5 min has shown that the CVC has recovered its initial shape (before experiment no. 3). This indicates that the characteristics of the sensor based on these samples are stable to a certain degree.

Therefore, experiments have shown that samples with multiwall CNTs exhibit a fast response, are suitable for detecting NH_3 molecules, and have a high sensitivity to small amounts (down to 2×10^{-1} Torr) of NH_3. After adding some NH_3, the CVC was measured within 5–20 s after the moment of its supply. Therefore, the response time of the sensor is 5–20 s (slightly shorter than in the review [5]). Therefore, the sensor sensitivity to NH_3 estimated at a current of 96.8 mA is ~15 mV/Torr. In [5], the sensitivities of gas sensors were mentioned as dependences of ratios of resistance R_s in the medium under study to the sensor resistance in air (or before exposure to the gas being tested) $R_{s\,air}$ on the gas concentration in terms of ppm for various gases. In our case at a pressure of 2×10^{-1} Torr, the NH_3 concentration was $0.26‰ = 260$ ppm and $R_s/R_{s\,air} \approx 0.94$. In this case, the restoration of the initial sensor state after the pressure in the chamber was lowered down to 2×10^{-2} Torr and the sensor was kept at this pressure for 5 min is considered to be a fast restoration of the sensor parameters.

Figure 2 presents the CVC of a sample with multiwall NTs, measured at room temperature at the URM-3M facility. The CVCs are shown as histograms with trend lines and expressions for them. The CVCs were measured under the following conditions:

(1) in vacuum after pumping down to a pressure of 2×10^{-2} Torr ($y_1 = 0.5692x + 0.2086$);

(2) after lowering the pressure to 2×10^{-2} Torr, holding at this pressure for 5 min, and fast (in a few seconds) inleakage of some ethanol via a microvalve to a pressure of 2×10^{-1} Torr ($y_2 = 0.5684x + 0.1343$); and

(3) after the previous experiment, upon lowering the pressure again to 2×10^{-2} Torr and, within 5 min, after inleakage of some acetone over a few seconds via a microvalve to a pressure of 2×10^{-1} Torr ($y_3 = 0.5488x + 0.0854$).

Comparison of the CVCs measured thereby shows that the CVCs of the sample in a vacuum of 2×10^{-2} Torr differ only slightly from the CVC of the sample after adding some ethanol to a pressure of 2×10^{-1} Torr. This is the evidence that the tested sensor exhibits a low sensitivity to ethanol molecules. Apparently, special additives must be introduced to allow ethanol detection. On the contrary, inleakage of some acetone over a few seconds via a microvalve to a pressure of 2×10^{-1} Torr has lead to a substantial change in the CVC slope (see Fig. 2); i.e., samples with multiwall CNTs demonstrate a high sensitivity to low acetone concentrations and a fast response. The sensor response time for acetone vapor is 5–20 s (shorter than in the review [5]). Therefore, the sensor sensitivity estimated at a current of 96.8 mA is ~12 mV/Torr for acetone and ~1 mV/Torr for ethanol. In this case, at a pressure of 2×10^{-1} Torr, the acetone (ethanol) concentration is $0.26‰ = 260$ ppm and $R_s/R_{s\,air} \approx 0.96$ (for ethanol, $R_s/R_{s\,air} \approx 0.996$). One can easily see the distinctive differences in the CVC behavior in a residual vacuum and after some acetone is added.

Thus, the experiments have shown that our samples with multiwall CNTs are applicable as a gas sensor for detecting the presence of NH_3 or acetone molecules. In this case, one can easily discern the difference in the CVC behavior in the presence of NH_3 (see Fig. 1, $y_3 = 0.539x + 0.0655$), acetone (see Fig. 2, $y_3 = 0.5488x + 0.0854$), and ethanol (see Fig. 2, $y_2 = 0.5684x + 0.1343$); in other words, the sensor possesses a certain selectivity.

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