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MULTI-WALLED CARBON NANOTUBE NETWORK FOR GAS SENSING APPLICATION

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In this study, the multi-walled carbon nanotube (mwCNT) network is suggested as a sensitive element of a gas sensor. An increase in the electrical resistance and capacitance of the sensor elements due to the adsorption of ammonia, acetone and ethanol molecules was found. The concentration dependences of the sensing ability and dynamic characteristics of resistive and capacitive type sensors were studied to evaluate the sensor properties of the mwCNTs. The response time of the gas sensor based on the mwCNT network to changing concentrations of ammonia, acetone, and ethanol molecules does not exceed one minute at room temperature. The obtained results expand the perspective of the mwCNTs application in sensor devices.

Keywords: multi-walled carbon nanotubes, gas sensors, sensing ability, response time.

1. Introduction

The development of high-speed sensors compatible with real-time microprocessor signal processing meets the challenges of the Internet of Things paradigm [1, 2]. In particular, the creation of a network of low-cost sensors to detect toxic and flammable gases is important for environmental monitoring [3, 4]. For example, monitoring ammonia concentration in the environment provides data for climate change analysis. Sensors of volatile organic compounds (e.g. ethanol and acetone) are widely used in the chemical, pharmaceutical, food industries, and medicine. Effective and timely detection of flammable vapors is crucial for industrial safety and will avoid potential economic losses and human casualties.

Other requirements for such gas sensors include low energy consumption, operation at room temperatures and miniature sizes of sensitive elements. Sensors based on nanostructures and composite nanomaterials with an ultra-high surface area meet the specified criteria [5–8]. Carbon nanotubes (CNTs) are extremely promising in the field of sensor electronics [9–11]. The small size, large surface-to-volume ratio, mechanical and chemical stability, and adsorption-sensitive electrical properties of CNTs make them excellent candidates for gas-sensing applications.

The main mechanisms of planar gas sensor response are the change in nanotube resistance or capacitance induced by the adsorption of outsider molecules. However, CNTs-based sensors have their own features. Depending on the chirality, single-walled CNTs (swCNTs) can exhibit metallic or semiconducting properties [12, 13]. Their controlled synthesis with uniform chirality is still a challenge. Therefore, single-tube sensor elements do not yet demonstrate good reproducibility due to their chiral deviations. Reproducibility of the results can be achieved by forming a network of disordered swCNTs due to averaging the electrical properties of individ-

ual nanotubes or using multi-walled CNTs (mwCNTs). The low costs and high conductivity of the CNT network are useful for various potential applications, particularly in sensor devices capable of detecting a wide class of gases in real time [14, 15]. Therefore, the study of gas-sensitive properties of mwCNTs can give a push to their use as autonomous and reliable sensors for IoT and various mobile devices to monitor the environment.

This paper presents a sensor element based on the mwCNT network for the detection of ammonia, ethanol, and acetone in air. Special attention is paid to the study of the characteristics of resistive and capacitive type sensors under the influence of various gases, as well as the possibility of their settings to measure the concentration of the selected gas by simple calibration of the sensitive element.

2. Experiment

A silicon wafer with a thickness of 400 μm was used as a substrate for obtaining the mwCNT network. A dielectric layer of SiO_2 with a thickness of about 100 nm was formed on the wafer surface by thermal oxidation of silicon in air for 2 hours at a temperature of 1050 ºC. The mwCNTs with a diameter of 50–80 nm produced by US Research Nanomaterials Inc were used. An aqueous suspension of mwCNTs with a concentration of 0.5 mg per 1 ml was treated with ultrasound for 20 min. After ultrasonic dispersion, the mwCNT suspension was deposited on the surface of the SiO_2 layer on the silicon substrate and air-dried at room temperature. As a result, a disordered network of mwCNTs was formed. Electrical contacts of the planar sensor element were obtained by thermal deposition of an Ag film with a thickness of about 0.5 μm at a distance of 2 mm from each other, as shown in Fig. 1. The working surface of the sensitive element based on the mwCNT network was examined using the "Selmi" scanning electron microscope (SEM).

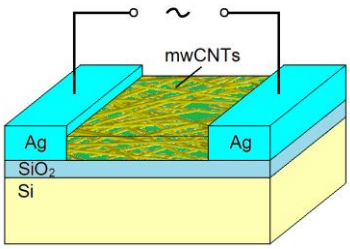


Fig. 1. Scheme of a planar sensor element based on the mwCNT network.

The sensor properties of the mwCNT network on the silicon substrate were studied in a hermetically sealed chamber with a controlled gas environment. Ecologically important gases were used for research: ammonia, acetone and ethanol in a gaseous state. The design of the experimental chamber makes it possible to controllably increase the ammonia concentration in steps of 0.3% and the concentration of acetone and ethanol in steps of 0.4%. The relative humidity in the chamber was additionally measured using the "Honeywell" HIH-4000-004 sensor. The relative humidity during the research was 58–70 %. The electrical resistance and capacitance of the obtained sensor elements based on the mwCNT network were measured using a "Hantek 1833C" RLC meter at the 1 kHz frequency and room temperature.

3. Results and discussion

The study of the morphology of the mwCNTs-based sensor element surface was carried out using SEM in the secondary electron mode (Fig. 2). Analysis of SEM images at different magnifications found the formation of a disordered and heterogeneous network of nanotubes on the silicon substrate after drying the deposited suspension. The connection of individual nanotubes and their agglomerations forms a conductive path between the sensor electrodes. The obtained network of mwCNTs is characterized by greater porosity compared to nanocomposite films based on conjugated polymers [16], which provides a larger area of the working surface of the sensor elements.

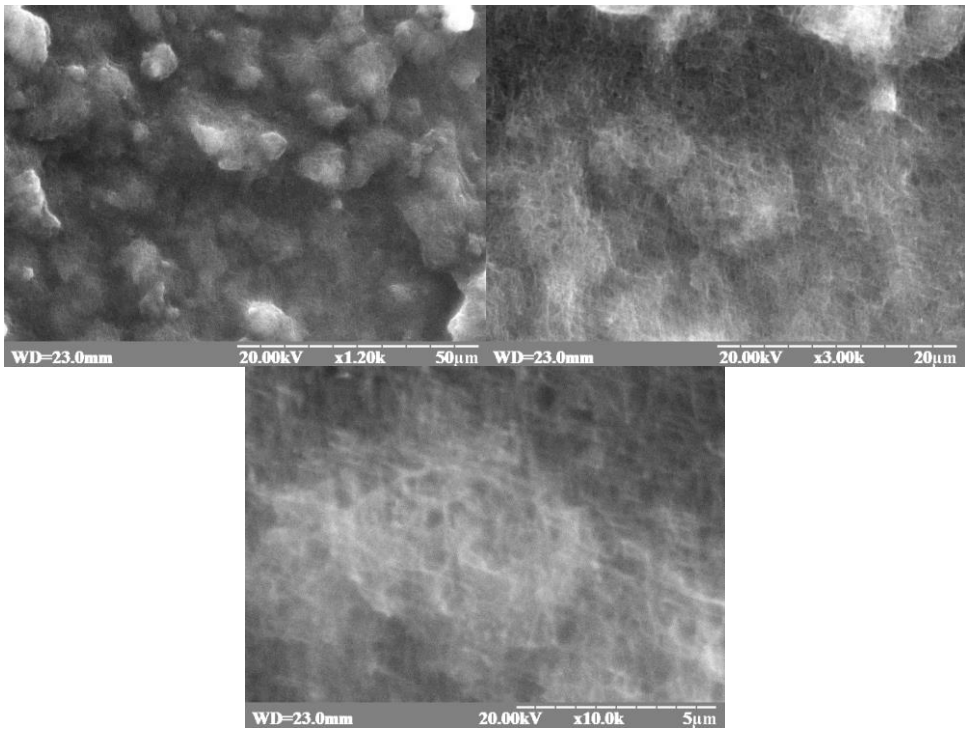
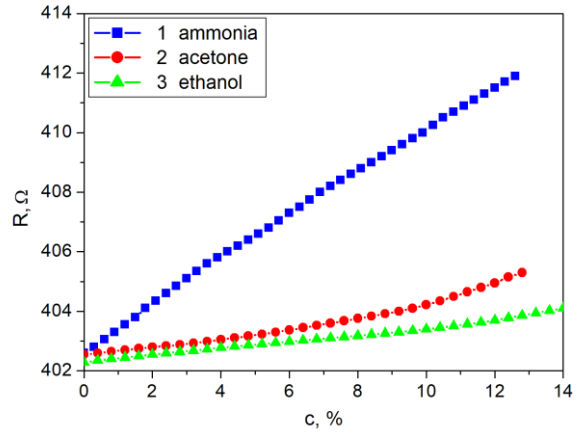


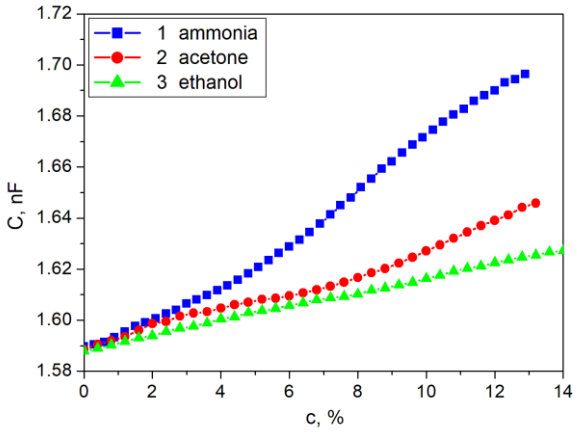
Fig. 2. SEM image of the mwCNT-based sensor element surface at various magnifications.

The electrical characteristics of the obtained mwCNT network depend on the surrounding atmosphere. As can be seen in Fig. 3, filling the working chamber with the investigated gases with donor properties causes an increase in the resistance and capacity of the mwCNT-based sensor element. The obtained dependencies can be explained by the interaction of adsorbed molecules with the surface of mwCNTs, which are usually characterized by acceptor-type conductivity if the absence of their functionalization [17]. As a result, adsorption-electric effects lead to a decrease in the conductivity of nanotubes. It should be noted that a larger range of changes in the sensor resistance and capacitance was observed in the case of the adsorption of ammonia molecules for the same change in the concentration of the studied gases. This is probably due to the strong donor properties of ammonia and an increase in the relative humidi-

ty of the air in the experimental chamber. In addition, almost linear concentration dependences of electrical characteristics of the sensor elements based on the mwCNT network were observed at low concentrations of the gases-analyte.



a)



b)

Fig. 3. Resistance (a) and capacitance (b) of the mwCNT-based sensor element as functions of the concentration of the ammonia (1), acetone (2) and ethanol (3) molecules.

To evaluate the sensory properties of the mwCNTs network, its sensing ability γ was calculated using the expression [18]

$$\gamma = \frac{\Delta S/S}{\Delta c/c}. \quad (1)$$

Here, $\Delta S/S$ is the relative change in the electrical characteristics (resistance or capacitance) of the sensor element, $\Delta c/c$ is the relative change in the concentration of analyte molecules in the

working chamber. The dependences of the sensing ability of the mwCNT-based sensor element of resistive and capacitive types on the concentration of ammonia, ethanol and acetone molecules are shown in Fig. 4.

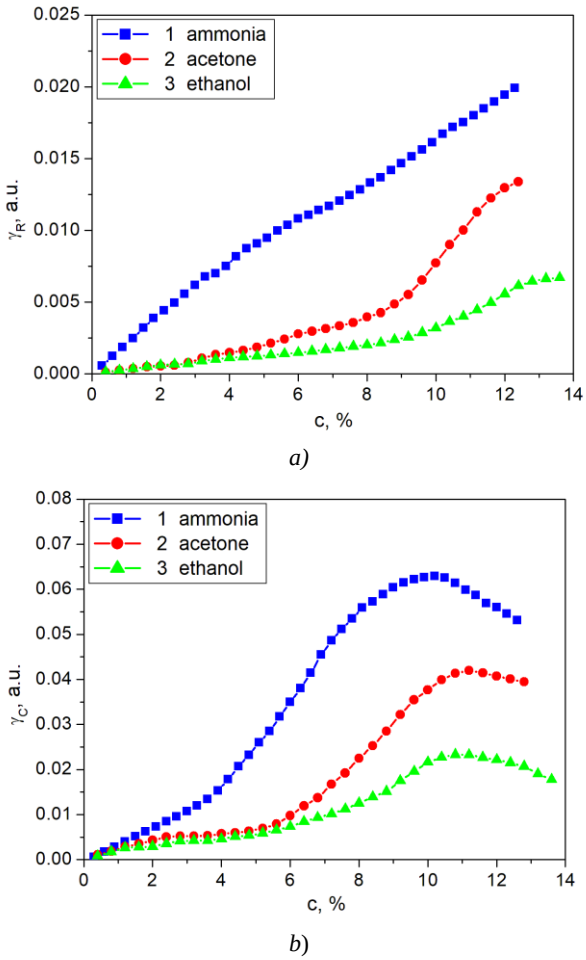


Fig. 4. Sensing ability of the mwCNT-based sensor element of resistive (a) and capacitive (b) types as functions of the concentration of the ammonia (1), acetone (2) and ethanol (3) molecules.

The mwCNT network shows an increase in sensing ability with the increasing concentration of the analyzed gases in the low concentration range due to reducing the denominator in the expression (1) in contrast to the constant sensitivity of the sensor element in the same range (see almost linear curves in Fig 3). The analysis of the obtained dependencies indicates a greater sensitivity of the mwCNT-based sensor of the capacitive type to the action of molecules of the analyzed gases than the resistive type sensor. In addition, the sensing ability of mwCNTs shows maximum values in the concentration range of 10–11 %. The sensitivity of both resis-

tive and capacitive type sensors was the highest for ammonia and the lowest for ethanol molecules.

Since the sensitivity of the electrical characteristics of the mwCNT network is high to the adsorption of molecules of various gases, ensuring the selectivity to the analyte gas requires the use of additional gas recognition mechanisms. One such mechanism can be a computer analysis of the cross-sensitivity of a matrix of sensor elements, each of which is characterized by an individual profile of the transfer function. Analysis of the total response of the multi-element sensor system will make it possible to identify the gas and determine its concentration with correction for the value of the relative humidity.

An important dynamic characteristic of sensor materials is the response time of the sensor element to changes in the analyte gas concentration. Fig. 5 shows the response time of mwCNT-based gas sensors of resistive and capacitive types.

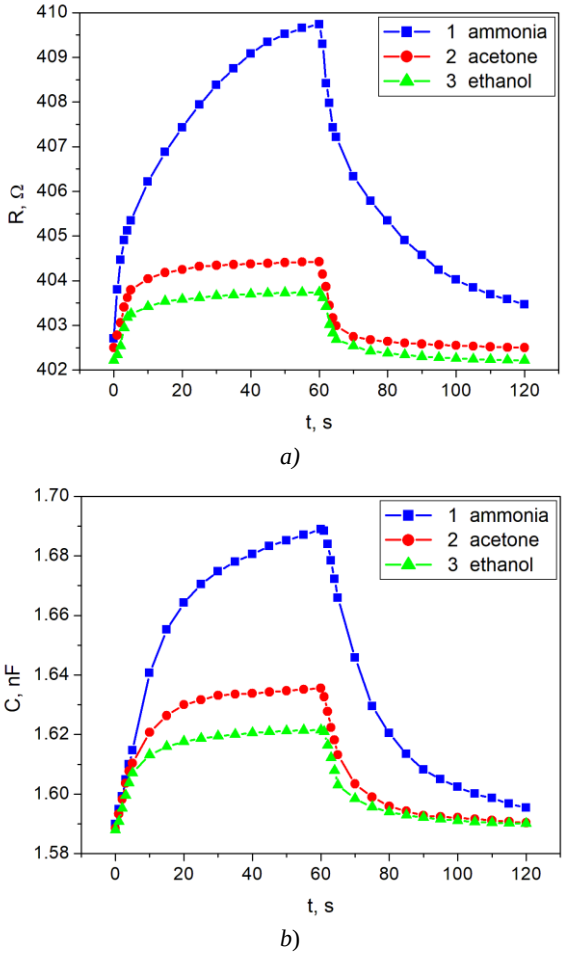


Fig. 5. Response of resistance (a) and capacitance (b) of the mwCNT-based sensor element to changing the concentration of the ammonia (1), acetone (2) and ethanol (3) molecules.

As can be seen in Fig. 5, the interaction of the mwCNTs with ammonia, acetone, and ethanol molecules has a physical adsorption nature because the initial resistance and capacitance values of the sensor elements are restored after the removal of the analyzed gases from the experimental chamber even without heating. Besides, the response speed of the acetone and ethanol sensors at room temperature was slightly higher than that of the ammonia sensor. In general, the response time of the gas sensors based on the mwCNT network does not exceed one minute.

4. Conclusions

The sensor elements have been obtained by depositing an aqueous suspension of mwCNTs on the surface of the silicon substrate with the SiO_2 layer and subsequently drying at room temperature. Based on the analysis of the SEM image of the sensor element surface, it was established that mwCNTs form the disordered and non-homogeneous in density terms network, the porous morphology of which contributes to increasing the sensor sensitivity to the adsorption of gas molecules.

It was established that the adsorption of ammonia, acetone and ethanol molecules causes an increase in the resistance and capacitance of the sensor elements based on the mwCNT network. Analysis of concentration dependences of electrical characteristics and sensing ability of the obtained sensor elements in the 0.4–12.8 % range indicates that mwCNTs are most sensitive to ammonia molecules. In addition, the mwCNT-based sensor of the capacitive type is characterized by a higher sensing ability compared to the resistive one. The response speed of the sensor to changing analyzed gas concentration (i.e. the time after which the output signal reaches 90% of the set value) is less than 1 minute at room temperature.

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МЕРЕЖА БАГАТОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК ДЛЯ ГАЗОСЕНСОРНИХ ЗАСТОСУВАНЬ

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Вуглецеві нанотрубки (ВНТ) є надзвичайно перспективними для створення газових сенсорів, які характеризуються низьким енергоспоживанням, роботою при кімнатних температурах і мініатюрними розмірами чутливих елементів. Система автономних і надійних сенсорів на основі ВНТ може забезпечити екологічний моніторинг навколишнього середовища у режимі реального часу. Тому мета роботи полягала у вивченні можливості використання мережі багатошарових ВНТ як недорогих сенсорів токсичних і вибухонебезпечних газів.

Для виготовлення сенсорних елементів було використано багатошарові ВНТ діаметром 50–80 нм, водну суспензію яких після ультразвукової обробки було нанесено на кремнієву підкладку з шаром SiO_2. Після висихання осадженої суспензії була сформована невпорядкована і неоднорідна за щільністю мережа ВНТ. Сенсорні властивості одержаної мережі ВНТ досліджено в режимі змінного струму вимірюванням електричного опору та ємності за впливу адсорбції молекул аміаку, ацетону та етанолу.

Зареєстровано збільшення опору та ємності сенсорних елементів внаслідок адсорбції досліджуваних газів. На основі аналізу залежностей електричних характеристик та адсорбційної здатності мережі багатошарових ВНТ від концентрації молекул аміаку, ацетону та етанолу у діапазоні 0,4–12,8 % встановлено, що сенсори як резистивного, так і ємнісного типів мають найбільшу чутливість до аміаку. Крім того, сенсорні елементи ємнісного типу характеризуються більшою адсорбційною здатністю порівняно з резистивними. Проте, однозначна ідентифікація газу-аналіту і визначення його концентрації у суміші потребує додаткового аналізу сукупного відгуку матриці сенсорних елементів, кожен з яких характеризується індивідуальним профілем функції перетворення. Час реакції і час відновлення сенсорів аміаку, ацетону та етанолу на основі багатошарових ВНТ не перевищує однієї хвилини. Отримані результати демонструють значний потенціал застосування мережі багатошарових ВНТ у сенсорних пристроях.

Ключові слова: багатошарові вуглецеві нанотрубки, газові сенсори, адсорбційна здатність, час відгуку.

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