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Microelectromechanical gas sensor of resistive type for detection of hydrogen sulphide low concentrations

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Abstract. This article proposes a technology for manufacturing a microelectromechanical (MEMS) resistive gas sensor for detecting low concentrations of analytes and demonstrates the main technological characteristics of the device. MEMS contains a silicon substrate with nickel comb electrodes that act as a microheater. The distance between the teeth on the comb is about 300 microns, and the width of the heater tracks is 100 microns. As a sensitive layer, a thin (100nm) gas-sensitive layer of nickel oxide (NiO) is applied on top of the microheaters. The operating temperature of the sensitive layer in measurement mode is 130–205 °C. All applied meters are made on a silicon membrane of about 50 microns. The proposed work shows the effect of introducing H_2S into a gas mixture from 1 to 100 ppm on the conductivity of a gas sensor. The effective operating temperature of the heating elements was determined, at which the greatest response to the presence of hydrogen sulfide in the gas mixture is observed.

Keywords: microelectromechanical systems, gas sensor, nickel oxide, hydrogen sulfide

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Микроэлектромеханический газовый датчик резистивного типа для определения низких концентраций сероводорода

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Аннотация. В работе предложена технология формирования резистивного МЭМС датчика сероводорода. В качестве газочувствительного материала выбран оксид никеля, способный к изменению своей проводимости при сорбции сероводорода, даже в присутствии паров воды. В работе показано влияние введения в исследуемый газовый поток от 1 до 100 ppm H_2S на электрический отклик МЭМС датчика.

Ключевые слова: микроэлектромеханическая система, газовый датчик, оксид никеля, сероводород

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Introduction

Microelectromechanical systems are used in a variety of applications from gyroscopes and accelerometers to air pollution detection systems [1, 2]. Of particular interest are MEMS gas sensors based on sensitive elements made of thin films of metal oxides. For such sensors, an urgent problem remains the study of the effectiveness of various sensitive layers for different gases and the search for designs that can increase their energy efficiency while maintaining the sensitivity parameter of the sensor.

P-type semiconductors are promising for reducing gases such as hydrogen sulfide due to the acceptor interaction mechanism. An inexpensive and efficient p-type semiconductor material is nickel oxide (NiO). The confirmed possibility of modifying the roughness of NiO films helps to increase the sensitivity of the active layer [3].

Thus, the goal of this work was to create a microelectromechanical gas sensor of a resistive type with a thin-film sensing element made of nickel oxide, suitable for detection in a gas mixture from 1 to 80 ppm H_2S.

Materials and Methods

The sensitive element is made of silicon with a thickness of 0.4 mm and has dimensions of 10×10 mm in the horizontal plane. In the central part, the silicon is thinned to a membrane thickness of about 50 microns. The membrane contains a heater and two nickel comb electrodes, separated by an insulating dielectric. The heater is made of Ni and has the form of a meander, the tracks of which pass between the teeth of the comb electrodes and is also covered with a protective dielectric on top, in contrast to the teeth of the electrodes [4]. The sensitive layer of 80 nm NiO is located on the membrane on top of all elements. The developed technological route is carried out using photolithography and magnetron sputtering methods.

Results and Discussion

NiO coatings obtained by magnetron sputtering were subjected to post-processing – annealing at atmospheric pressure. The effect of annealing on surface morphology was assessed using AFM, XRD and XPS.

AFM images of sensitive layer is shown on Fig. 1. It was found that annealing led to the formation of a pronounced grain structure and an increase in film roughness. The root-mean-square deviation of the surface profile from the average value before and after annealing was 0.7 nm and 1.94 nm. Such changes in morphology should have a positive effect on the sensitivity of the sensor, since the resulting microcracks serve as sites for the emergence of active centers for the addition gas.

X-ray diffraction studies were carried out to evaluate the crystallographic structure of nickel oxide films, shown on Fig. 2, *a*. Three peaks are observed corresponding to NiO (111), (200), (220). Annealing led to a significant increase in the intensity of the peak corresponding to NiO (200). The calculated value of crystallite sizes increased from 3 to 13.4 nm, the lattice

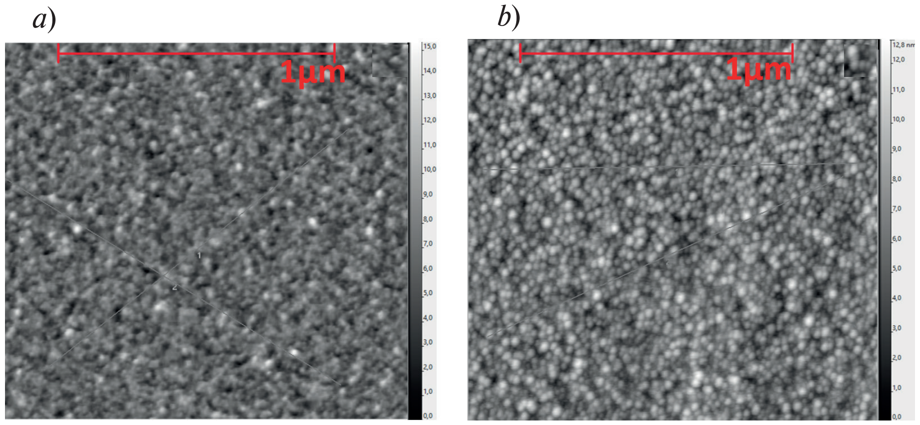

Fig.1. AFM image of NiO sensitive layer (*a*) before annealing, (*b*) after annealing

constant increased from 4.152 to 4.186 angstrom in the case of annealing in an atmosphere at comparison with unannealed samples.

Survey XPS spectra of the layer are shown in Fig. 2, *b*. The spectrum contains Ni $2p_{3/2}$ lines (868.6 ÷ 850 eV). The valency of nickel corresponds to two different oxidation states, so it can be concluded that highly defective nanocrystalline nickel oxide was used as a sensitive layer.

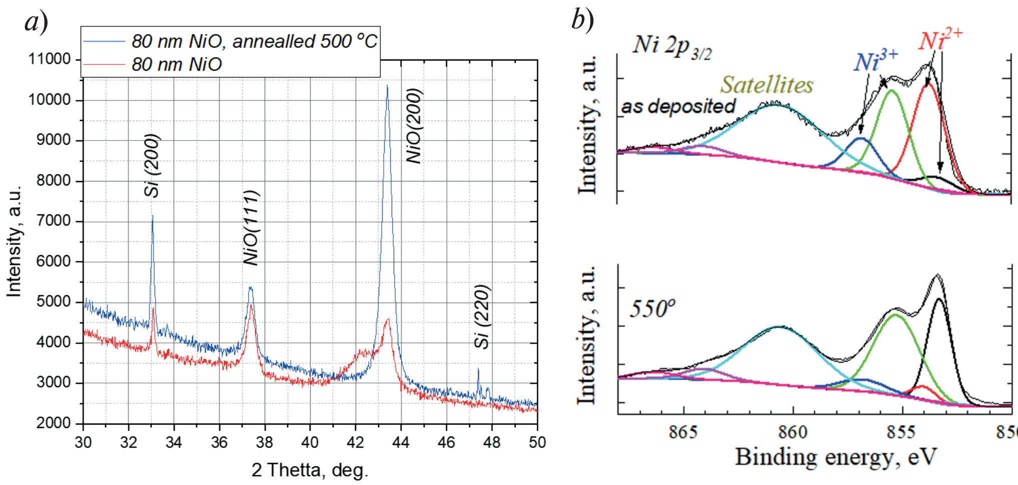

Fig.2. XRD spectrum of NiO films (80nm) before and after annealing (*a*), Ni $2p_{3/2}$ core level spectrum of NiO films (80 nm) before and after annealing (*b*)

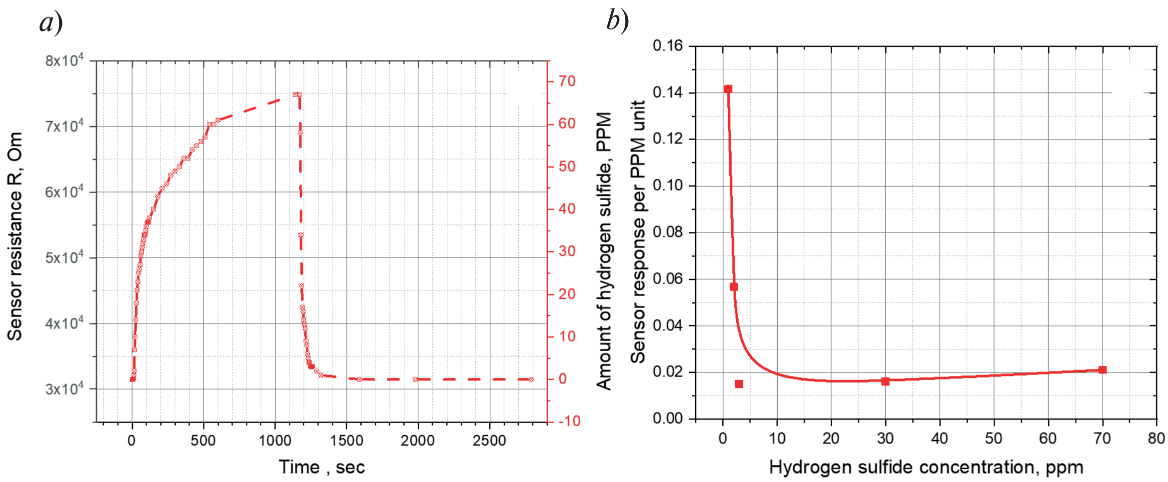

Fig. 3. Sensor response to the introduction of hydrogen sulfide vapor (*a*), sensor response per ppm unit at different H_2S concentrations (*b*)

The results of the study of the gas-sensitive properties of the MEMS sensor to the presence of hydrogen sulfide vapor are shown in Fig. 3 for a heater temperature of 205 °C in the range of hydrogen sulfide concentrations from 1 to 80 ppm. The determined parameter is the electrical response, defined for donor gases as the ratio of the resistance R_g measured in the presence of the substance being detected to the resistance in a pure model medium R at the same temperature. For acceptor gases, the inverse ratio is used [5]. The manufactured MEMS sensor makes it possible to determine the presence of hydrogen sulfide in the gas mixture under study with varying degrees of efficiency from 1 to 80 ppm. The operating power of the sensor was 1.5 W. The sensor response time ranged from 3 to 15 seconds, the recovery time was up to 30 minutes. The response speed increased with increasing operating temperature.

Conclusion

In this work, a technology for manufacturing MEMS hydrogen sulfide sensors with a sensitive layer of nickel oxide was proposed and tested. A sensitive layer of nickel oxide (NiO) deposited on the membrane showed sensitivity to hydrogen sulfide from 1 to 80 ppm, for annealed layer, the optimal operating temperature was 205 °C. This MEMS sensor is a resistive type with a self-heating thin NiO film is suitable for energy-efficient gas sensing applications, but requires selectivity testing and optimization temperature modes work.

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