ABSTRACT

of the dissertation work of Ikramova Saltanat on the topic «The effect of porosity on the electrical and optical properties of nanostructured semiconductor sensors», submitted for the degree of Doctor of Philosophy (PhD) in the specialty «6D071900 - Radio Engineering, electronics and telecommunications»

General description of work. The dissertation work presents the results of an experimental study of the parameters and characteristics of sensitive elements of molecular sensing, which can be integrated with devices and devices of solid-state electronics, consisting of layers of silicon wire nanostructures with gold nanoparticles deposited on their surface.

Relevance of the dissertation theme

Chemical sensors with low operating temperature, fast dynamic response and high selectivity are in demand for environmental and health monitoring. The sensitivity and selectivity of sensors are determined by the properties of the sensitive material. Thus, the study of electrical and optical sensory responses of a semiconductor sensitive element is one of the urgent problems of modern electronics.

Various types of gas sensors are actively developed and used, mainly based on porous wide-gap semiconductor metal oxides, such as: SnO_2, TiO_2, WO_3, MoO_3, Nb_2O_5, ZnO, CuO, Co_3O_4, Cr_2O_3, NiO, PdO, In_2O_3. Nevertheless, the significant disadvantages of such sensors include the insufficient stability of their response, as well as the need to heat the sensitive element to temperatures (250-500°C), which can lead to additional energy consumption, degradation of the material of the sensitive layer over time and to certain risks, associated with work in a flammable and explosive atmosphere. Therefore, the development of new semiconductor sensitive elements for detecting molecules in the environment at temperatures close to room temperature is very important.

Among various sensitive materials, silicon nanowires have attracted close attention due to their promising sensory properties, biocompatibility, large specific surface area, the ability to modify it with various functional groups, fast time response and good reproducibility of optical and electrical characteristics at room temperature, as well as compatibility with modern silicon-based semiconductor technology.

The growth of porous silicon layers using metal stimulated chemical etching (MACE) leads to the formation of arrays of silicon nanowires, which can serve as an active sensor material for the adsorption of gas and liquid molecules. Despite the large number of research papers on the formation patterns and physical properties of silicon nanowires, there are no completed studies on molecular sensing in such structures.

It is known that the presence of highly conductive metal nanoparticles in arrays of porous silicon nanowires leads to the appearance of a number of new unique properties in such systems, which are important for sensor applications. Among them, such as localized surface plasmon resonance, which consists in the interaction of electromagnetic radiation in the visible region of the spectrum with free surface electrons of metal nanoparticles, resulting in surface enhancement of Raman scattering

of light (giant Raman scattering or SERS effect). Currently, the SERS effect is widely used to detect low concentration target molecules important for numerous applications, from ecology and chemistry to biosensors, including biomedical diagnostics. The efficiency of SERS-active surfaces is usually characterized by the gain, which depends on the morphology of the substrate and the physical properties of the plasmonic nanoparticles. The maximum efficiency of SERS is often associated with the formation of so-called "hot spots" of the electric field, formed by the close proximity of metal nanoparticles. The reproducibility and stability of the SERS signal is an important indicator for evaluating the effectiveness of SERS active surfaces, which means that the surface must be well controlled and stable for a long time. Thus, the search for a universal and highly efficient substrate for SERS biomolecules to create efficient electronic devices (sensors) is still ongoing, new technologies are being developed, and new nanostructured materials and methods for their use are proposed.

Despite the fact that the main physicochemical properties of silicon nanowires for optoelectronic devices have been studied in detail, a number of issues important for sensorics, such as the effect of semiconductor sensing element porosity on electrical and optical sensory responses, have not been adequately studied. One of the possible reasons preventing the use of electrical sensory responses of porous silicon nanostructures in molecular sensing is the factor of gradual oxidation of their surface, which also depends on porosity. Today, one of the urgent tasks of radio electronics and optoelectronics is the creation of efficient electronic sensor devices based on the use of simultaneous electrical and optical responses in the structures of porous silicon nanowires.

The aim of this work is to experimentally study the effect of porosity on the electrical and optical sensory responses of semiconductor sensor elements based on layers of silicon filamentary nanostructures with gold nanoparticles deposited on their surface.

Research objectives

1. To establish and optimize technological modes of manufacturing a semiconductor element of a molecular sensor based on silicon nanowires with gold nanoparticles deposited on their surface.

2. To investigate the effect of the porosity of the sensitive element of a molecular sensor on electrical sensory responses in gaseous ammonia vapor and to determine the optimal value of porosity to achieve maximum sensitivity.

3. To investigate the influence of porosity on the signal of the relative intensity of Raman scattering of light from molecules of organic dyes in sensor structures and to reveal the main regularities in the formation of a sensor signal in such structures.

Objects of research: molecular sensor elements based on porous silicon nanowires, gold nanoparticles, surface plasmons, porosity.

Subject of research: morphology, electrical and optical properties of sensor materials based on silicon nanowires with gold nanoparticles deposited on their surface, surface enhanced raman scattering, plasmonics, molecular sensorics

Research methods: metal-assisted chemical etching, scanning and transmission electron microscopy, energy dispersive x-ray spectroscopy, raman spectroscopy, box-counting, ImageJ, mercury porosimetry, chemical precipitation of metals from aqueous

solutions, technique for measuring the current-voltage characteristics of the samples under study using the NI ELVIS II+ digital universal station, registration of optical characteristics of sensors using Ntegra Spectra, NT-MDT spectrophotometer.

Basic provisions for defense

1. An optoelectronic sensor for detecting molecules with optical and electrical signal acquisition at room temperature, based on layers of silicon nanowires with subsequent deposition of gold nanoparticles on their surface, shows the highest efficiency with the following parameters: the length of silicon nanowires is from 5 to 35 μm with a cross section of about 100 nm, the sizes of gold nanoparticles are about 10 nm and the porosity of the films is in the range from 50 to 85%.

2. The electrical sensor response to ammonia vapor at a concentration of about 100 ppm in sensor structures based on an array of silicon nanowires about 10 μm long and about 70% porosity increases by a factor of 5–7 when gold nanoparticles are added to the nanowire surface and is observed at a voltage of 1 -10 V and flowing current 1-25 mA.

3. The optical sensor response based on the effect of Surface enhanced Raman scattering of light from organic dye molecules adsorbed in the structures of silicon nanowires with gold nanoparticles reaches the highest values at an active element porosity of about 50%, the relative intensity sensor signal amplification factor is about 10^5, and analyte molecules are detected with detection threshold 10^{-15} mol.

The scientific novelty of the work is as follows

1. The effect of porosity on the electrical sensory responses of sensitive semiconductor materials based on silicon nanowires with gold nanoparticles deposited in ammonia gas has been experimentally studied, and the optimal porosity value of about 70% to achieve maximum sensitivity has been found.

2. Optical sensory responses from organic dye molecules in nanostructured sensor materials based on silicon nanowires with deposited gold nanoparticles have been researched, and it has been found that the optimal porosity of such structures for detecting molecules is about 50%.

3. It has been found that sensor materials based on silicon nanowires with deposited gold nanoparticles can be used to detect organic dye molecules at a concentration of about 10^{-15} mol.

Scientific and practical significance of the research

1. The results of the research make it possible to find technological modes for obtaining sensor elements that produce dense arrays of silicon nanowires with gold nanoparticles for detecting small target molecules, which can be useful in preparing the sensitive element of an optoelectronic sensor for biomedical and environmental applications.

2. The results obtained in studying the effect of the porosity of silicon nanowires on the electrical and optical responses of sensor materials can be applied in the manufacture of new types of molecular sensors and in increasing the efficiency of their operation.

The sources of the research are the main experimental provisions of modern nanoelectronics, as well as related fields of science and technology, such as sensor

technology, plasmonics, as well as the results of original scientific papers listed in the list of references.

Personal contribution of the author. The main stages of work, obtaining samples of silicon nanowires and deposition of metal nanoparticles on their surface, applying contacts to the surface of samples, research electrical and optical properties, determining porosity and analyzing the results were performed personally by the author. Microphotographs obtained with the help of a scanning and transmission electron microscope, the author received personally as part of an internship in Astana. The main research work was carried out at the National Nanotechnology Laboratory of Open type and in the Laboratory of Semiconductor Instrumentation of the Faculty of Physics and Technology of Al-Farabi Kazakh National University. Micrographs of pure porous silicon nanowires and porous silicon nanowires with gold and silver nanoparticles, measurement of optical properties were carried out in Astana at the Laboratory of Advanced Research of Materials and Laser Technologies (AMRELAT) of Nazarbayev University. The author, as part of a research group, has worked out the technology for obtaining and the method of structural and plasmonic modification of the electronic and optical properties of thin films of silicon nanowires. Protected provisions, main results and conclusions are made jointly with scientific consultants.

The reliability of the results of the work is ensured by the use of a complex of complementary structural, electrical, and optical research methods: transmission and scanning electron microscopy, X-ray energy-dispersive spectroscopy, Raman spectroscopy, optical reflection spectroscopy, measuring the current-voltage characteristics of sensors, and determining the porosity of nanostructures.

Approbation of work

Based on the results of the research, 11 papers were published, including 4 in publications recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the RK, 2 in international scientific journals indexed by Web of Science and / or Scopus (International Journal of Molecular Sciences - Q1 , IF 6.628; Applied Sciences - Q2, IF 2.921), 1 in scientific publications, included in the database of the Russian Science Citation Index, 3 publications in collections of abstracts of international conferences, incl. 1 foreign (The 6th International Symposium and Schools for Young Scientists on Physics, Engineering and Technologies for Biomedicine. November 20-24, 2021. Moscow) and there is 1 copyright certificate (No. 28638, 09/07/2022).

The connection of the dissertation topic with the plans of scientific work

The dissertation work was carried out within the framework of research work under the program of grant funding for scientific research of the CS MSHE RK on the topic: «The relationship of nonlinear electrical, optical and fractal-geometric characteristics of nanostructured semiconductors», No. GR 0118RK00200 (in 2018 - 2020) and the joint research program of Nazarbayev University (CRP) « Development and validation of hybrid Brillouin-Raman spectroscopy for non-invasive assessment of mechano-chemical properties of urine proteins as biomarkers of kidney diseases» No. 091019CRP2105 (2020-2022).

The structure and scope of the dissertation. The work consists of an introduction, main part (literature review, experimental part, results and their

discussion), conclusion, list of references. The volume of the dissertation is 109 pages of typewritten text, including 82 figures, 6 tables, 31 formulas and 1