

ABSTRACT

Dissertation submitted for the Philosophy Doctor (PhD) degree in educational program “8D06201 – Radio engineering, electronics and telecommunications”

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“ELECTRONIC SYSTEMS BASED ON SEMICONDUCTORS WITH RESISTIVE SWITCHING EFFECTS AND ORGANIC COMPOUND SENSING PROPERTIES”

General Characteristic of the work

This thesis presents the results of a study examining resistive switching effects and gas-sensing properties aimed at detecting volatile organic compounds using semiconductor electronic systems. Using modern analytical methods, as well as ellipsometry, a method first applied in gas sensing, the potential for determining gas adsorption processes is demonstrated. It is shown that semiconductor structures based on porous silicon and metal oxide heterostructures exhibit memristor properties, manifested as electrical hysteresis. Calculations are performed and the mechanisms of gas adsorption kinetics are confirmed using density functional theory (DFT) methods.

Relevance of the study

The modern development of micro- and nanoelectronics is associated with the transition toward new paradigms of information processing and storage, including neuromorphic computing systems, the Internet of Things (IoT), flexible electronics, and intelligent sensor networks. The rapid growth of data volumes and the increasing demand for energy-efficient data processing require the development of novel functional materials and devices capable of combining multiple functions within a unified architecture. In this regard, significant attention is focused on the creation of energy-efficient, scalable, and multifunctional electronic components characterized by high switching speed, low power consumption, and compatibility with advanced computing platforms.

One of the most promising directions in modern electronics is represented by semiconductor systems exhibiting resistive switching effects, which form the basis of memristive devices. Memristors are considered key elements of next-generation non-volatile memory technologies (ReRAM) due to their high storage density, low energy consumption, and fast switching performance. Moreover, owing to their ability to continuously modulate and retain intermediate resistance states, memristive structures are regarded as promising building blocks for neuromorphic computing systems that emulate the operation of biological neural networks. The capability for analog conductance modulation enables the use of such devices as artificial synapses in hardware-based artificial intelligence and machine learning applications.

Particular interest is devoted to metal-oxide semiconductors such as ZnO, TiO₂, SnO₂, and their composite structures, which exhibit high chemical stability, developed surface morphology, and strong sensitivity to external stimuli. These materials are

actively investigated not only as functional layers for memristive devices but also as highly sensitive sensing materials for the detection of gases and volatile organic compounds. The high sensitivity of metal-oxide structures is mainly attributed to surface adsorption and desorption processes, which alter the concentration of charge carriers and consequently modify the electrical properties of the material.

Alongside the development of sensing technologies, there is growing interest in next-generation intelligent sensors capable not only of detecting external stimuli but also of performing preliminary signal processing and information storage directly at the hardware level. In this context, the integration of resistive switching behavior and sensing functionality within a single structure opens broad opportunities for the development of multifunctional devices combining memory, signal processing, and sensing capabilities. Such systems may become the foundation of advanced adaptive sensor platforms for IoT applications, robotics, and autonomous electronic systems.

It should be noted that the mechanisms responsible for resistive switching and sensor response are closely related and are governed by similar physicochemical processes. In both cases, a crucial role is played by the migration of oxygen vacancies, redistribution of structural defects, formation and rupture of localized conductive filaments, as well as adsorption and desorption processes occurring on the material surface. Control over defect concentration and surface morphology enables targeted tuning of both resistive switching parameters and sensing characteristics.

Despite substantial progress in the field of memristive and sensing materials, several challenges remain unresolved, including issues related to stability, reproducibility, and long-term reliability of device performance. The characteristics of such devices are strongly influenced by surface morphology, defect distribution, conductive filament formation mechanisms, and degradation processes occurring during repeated switching cycles. Furthermore, the interaction mechanisms between sensing effects and resistive switching in hybrid structures are still insufficiently understood, which limits their practical implementation.

Therefore, the investigation of metal-oxide semiconductor structures exhibiting combined memristive and sensing properties represents an important scientific and technological challenge in modern micro- and nanoelectronics. The development of such materials and devices may enable the creation of a new generation of intelligent electronic systems integrating memory, information processing, and sensing functionalities within a single compact architecture.

The purpose of the work

The aim of this dissertation is to establish the relationships between the structural, morphological, electrical and optical characteristics of metal oxide semiconductors and their gas-sensing properties, as well as to develop scientifically sound approaches to creating multifunctional electronic systems with non-volatile memory functions (based on the resistive switching effect) and organic substance sensors.

Objects of research

The object of the research is semiconductor structures based on porous silicon and metal oxide heterostructures, intended for the implementation of sensor and memory elements of electronics.

The subject of the study

The subject of the study is the physical mechanisms and patterns of formation of gas-sensitive response, as well as the effects of resistive switching in semiconductor structures based on porous silicon and metal oxide heterostructures, which determine their electrical and optical characteristics and functional parameters of sensor and memory elements.

Research methods

The study utilized a combination of methods for the formation and study of semiconductor structures. Porous silicon was obtained electrochemically, while metal oxide heterostructures were formed using magnetron sputtering. The structural and morphological characteristics were studied using scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray diffraction (XRD). Surface properties were assessed by measuring the wetting angle. Electrophysical characteristics were determined using the van der Pauw method and by analyzing the current-voltage (I-V) characteristics. Optical parameters of the samples were measured spectrophotometrically. Gas-sensitive properties were studied under the influence of organic substances. Spectral ellipsometry was used as a sensitive method for in situ recording of the gas-sensitive response caused by adsorption processes on the surface of the structures. The results were processed and interpreted using experimental and analytical methods.

Research objectives

1. To develop and characterize a sensor element based on porous silicon obtained by electrochemical etching and evaluate its gas-sensing characteristics, such as sensitivity, response time, and selectivity, when detecting organic substances as part of an electronic measurement system.
2. To study the effect of the metal oxide layer thickness in a $\text{SnO}_2/\text{por-Si}$ heterostructure on the gas-sensing response when exposed to organic vapors using spectral ellipsometry.
3. To study the effects of resistive switching in a NiO/MgO heterostructure and determine the parameters of anisotropic conductivity and the HRS/LRS state ratio depending on the electrical stimulation mode and electrode configuration.

The novelty of the dissertation work:

1. The patterns of formation of the gas-sensitive response of porous silicon depending on its electrochemical synthesis modes were established, ensuring maximum sensitivity to ammonia and minimum response time during integration into an electronic measurement system.
2. The influence of the metal oxide layer thickness in $\text{SnO}_2/\text{por-Si}$ heterostructures on the magnitude of the gas-sensitive response to organic vapors was revealed, and the informative value of the spectral ellipsometry method for recording adsorption processes at the phase interface was demonstrated.

3. The effects of anisotropic resistive switching in NiO/MgO heterostructures were discovered and systematized, determining the high HRS/LRS state ratio and substantiating the possibility of their application in non-volatile memory elements and new types of functional electronic devices.

The main provisions for the defense:

1. A porous silicon sensor element integrated into an electronic system, obtained by electrochemical etching with a current density of $j = 12 \text{ mA/cm}^2$, voltage $U = 9 \text{ V}$, and etching time $t = 45 \text{ min}$ (porosity 52%), demonstrates the highest sensitivity to ammonia – 42%, with a response time of $t_{\text{res}} = 35 \text{ s}$.

2. In an ellipsometry study of the $\text{SnO}_2/\text{por-Si}$ heterostructure, the gas-sensitive response to ethanol and propanol vapors increases by more than 50% with an increase in the metal oxide layer thickness from 100 nm to 300 nm.

3. The resulting NiO/MgO heterostructure with anisotropic resistive switching yields the highest high-to-low-resistance HRS/LRS ratio of 10^2 , at voltage values of $\pm 5 \text{ V}$ and a parallel electrode configuration.

Theoretical significance

The theoretical significance of the dissertation lies in establishing the relationship between the structural, morphological, electrical, and gas-sensitive properties of semiconductor structures based on porous silicon and metal-oxide heterostructures. The obtained results expand the understanding of resistive switching mechanisms, gas adsorption processes, and the influence of metal-oxide layer thickness on the formation of gas-sensitive response. The перспективность of applying spectral ellipsometry for studying adsorption processes in gas sensing applications has also been demonstrated.

Practical significance

The practical significance of the work lies in the possibility of using the developed semiconductor electronic systems for the detection of volatile organic compounds (VOCs) in environmental monitoring, industrial safety, and medical diagnostics systems. The obtained results can also be applied in the development of non-volatile memory elements and next-generation functional devices based on resistive switching effects. In addition, the research results open up prospects for developing a new class of devices – gasistors, combining sensing and memristive properties.

Reliability and validity of the results

The reliability and validity of the results of the thesis are confirmed by the availability of publications in the publications of the MSHE of the Republic of Kazakhstan, in journals included in the international information resources Web of Science (Clarivate Analytics, USA) and Scopus (Elsevier, the Netherlands) and in international scientific conferences, as well as in accordance with the results obtained by other authors.

Personal contribution of the author

The author fully participated in the research work at all stages of the thesis. The author has carried out work on obtaining low-conductivity nanostructures, studying the effect of gas particles on their electrical characteristics, as well as processing and

analyzing the results of studies of optical, morphological and electrical characteristics of samples. The tasks and work plan were approved, and the results were discussed jointly with the scientific supervisors.

Approbation of the dissertation work

4 papers were published on the topic of the dissertation in the international information resources Scopus/Web of Science. There is also an author's certificate.

Articles with a high impact factor in publications included in the international scientific database Scopus/Web of Science:

1. A.Skabylov, L.Abdizhalilova, M.Ibraimov, B.Khaniyev, Y.Tezezbay, M.Abdullah, R.Azamat, O.Toktarbaiuly and **T.Duisebayev**. Wireless ammonia gas sensor based on p-type porous Si: methods, materials and design. Engineered Science, 2025, V.37. [IF = 12.5, Percentile 96%] <http://dx.doi.org/10.30919/es1704>
2. M.Ibraimov, B.Khaniyev, Y.Tezezbay, R.Azamat, N.Yakovlev, O.Toktarbaiuly, M.Zhazitov, M.Karibayev, B.Akilbekov, S.Piskunov, J.Liu, **T.Duisebayev**. Ellipsometry optical gas sensor of SnO₂/porous-Si heterostructure for organic compounds detection. Advanced Sensor Research [Q2, IF = 3.5, percentile 70%] <https://doi.org/10.1002/adsr.202500194>
3. **T.Duisebayev**, B.Khaniyev, M.Ibraimov, O.Toktarbaiuly, M.Zhazitov, M.Abdullah, Y. Tezezbay, A. Syrlybekov, T. Serikov, N. Nuraje. Anisotropic resistive switching in NiO thin films deposited on stepped MgO substrates. Nanomaterials. [Q1, IF = 4.3, percentile 76%] <https://doi.org/10.3390/nano15221703>
4. **T.Duisebayev**, M.Ibraimov, B.Khaniyev, A.Tileu, D.Alimbetova. Development of memory elements based on surface-modified nanostructured porous silicon. WSEAS Transactions on Electronics, 15 2024 [IF=1.1, percentile 25%] <https://doi.org/10.37394/232017.2024.15.8>

Copyright certificate:

No. 685501 dated March 11, 2026, “Ellipsometric Method for Detection of Organic Substances,” Duisebayev T.S., Ibraimov M.K.

Relationship of the study to scientific projects:

The study was carried out within the framework of Project No. AP19678266, “Development of a Selective Gas Sensor for Explosive and Harmful Substances Based on Nanostructured Semiconductors to Ensure Industrial Safety,” funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (2023–2025).

The structure and scope of the thesis:

The dissertation consists of an introduction, 3 sections, a conclusion and a list of references. The work includes 66 figures, 28 formulas, 4 tables, 106 references and 107 pages.