Conference materials
UDC 538.9
DOI: https://doi.org/10.18721/JPM.163.127

Towards nanowire-based selective vapor sensing with an aid of impedance spectroscopy

V.M. Kondratev [1, 2] ✉, I.A. Kozko [3], E.P. Karaseva [1], E.A. Vyacheslavova [1],
T. Shugabaev [1], N.A. Svinkin [1], A.D. Bolshakov [1, 4]

[1] Alferov University, St. Petersburg, Russia;
[2] Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russia;
[3] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia;
[4] Yerevan State University, Yerevan, Armenia
✉ kvm_96@mail.ru

Abstract. This work is aimed at development of highly sensitive silicon (Si)-based sensors allowing for selective detection and analysis of liquid solution composition containing ammonia (NH_3) and hydrochloric acid (HCl) in an indirect manner. To provide enhanced sensitivity, we use Si nanowires obtained with cryogenic plasma etching with high aspect ratio providing large adsorption surface area. The nanowires are placed on a contact platform and electrochemical impedance spectroscopy (EIS) is used to detect the analytes. For optimization of the sensor performance we develop three types of the sensor based on as-fabricated Si nanowires, nanowires treated with hydrofluoric acid (HF) and nanowires decorated with silver (Ag) NPs.

Keywords: silicon, sensors, selective detection, nanowires

Funding: Innovation Promotion Fund of the Russian Federation (Contract 18808GU/2023 dated 04.10.2023, code 0087265, application U-83573); The Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009; agreement 075-03-2023-106, project FSMG-2021-0005).

Citation: Kondratev V.M., Kozko I.A., Karaseva E.P., Vyacheslavova E.A., Shugabaev T., Svinkin N.A., Bolshakov A.D., Towards nanowire-based selective vapor sensing with an aid of impedance spectroscopy, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 151–156. DOI: https://doi.org/10.18721/JPM.163.127

Материалы конференции
УДК 538.9
DOI: https://doi.org/10.18721/JPM.163.127

Селективный анализ состава паров с помощью нанонитей и спектроскопии электрического импеданса

В.М. Кондратьев [1, 2] ✉, И.А. Козко [3], Е.П. Карасёва [1], Е.А. Вячеславова [1],
Т. Шугабаев [1], Н.А. Свинкин [1], А.Д. Большаков [1, 4]

[1] Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;
[2] Московский физико-технический институт (национальный исследовательский университет), г. Долгопрудный, Россия;
[3] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия;
[4] Ереванский государственный университет, г. Ереван, Армения
✉ kvm_96@mail.ru

Аннотация. Работа направлена на разработку высокочувствительных сенсоров на основе кремния (Si), позволяющих селективно определять и анализировать состав жидких растворов, содержащих в малых концентрациях аммиак (NH_3) и соляную кислоту

(HCl). Для определения аналитов используются адсорбционные свойства кремниевых нанонитей и методы электрохимической импедансной спектроскопии (ЭИС).

Ключевые слова: кремний, нанонити, адсорбционные свойства, сенсор аммиака, сенсор соляной кислоты, электрохимическая импедансная спектроскопия

Финансирование: Фонд содействия инновациям (Договор 18808ГУ/2023 от 04.10.2023, код 0087265, заявка У-83573); Министерство науки и высшего образования Российской Федерации (грант № FSRM-2023-0009; Соглашение 075-03-2023-106 от 13.01.2023, проект FSMG-2021-0005).

Ссылка при цитировании: Кондратьев В.М., Козко И.А., Карасёва Е.П., Вячеславова Е.А., Шугабаев Т., Свинкин Н.А., Большаков А.Д. Селективный анализ состава паров с помощью нанонитей и спектроскопии электрического импеданса // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 151–156. DOI: https://doi.org/10.18721/JPM.163.127

Introduction

The effects of analyte adsorption by nanostructures on their electronic characteristics have been widely employed in various sensor applications based on optical, resistive, capacitive, current-voltage characteristics analysis [1–3]. Historically, polycrystalline metal oxide films such as SnO_2 were one of the first materials used for the gas detection fabricated in different geometries [4]. Electronic characteristics of such sensors are mainly governed by the depletion in the vicinity of reactive surface during the adsorption processes. The key disadvantages of these sensors are poor performance in a humid environment and low selectivity [5].

Here we fabricate Si NW based sensors and thoroughly examine their electronic properties with an aid of EIS upon exposure to NH_3 and HCl vapors and their mixtures. To optimize the response, we use three types of the NWs, namely, pristine, treated with HF and decorated with silver (Ag) nanoparticles (NPs). EIS spectra of the fabricated sensors subjected under naturally evaporated HCl and NH_3 vapors are analyzed to study response to the analytes. We present an approach based on analysis of an active component of the sensor resistance and characteristic frequency of the transition between two electronic regimes allowing for the simultaneous selective detection of HCl and NH_3. The results demonstrate perspectives for Si NWs utilization in sensorics and open new ways for implementation of EIS for development of highly selective sensors providing indirect detection of health makers in body fluids.

Materials and Methods

Top-down cryogen plasma chemical etching of the [001]-oriented B-doped silicon substrate with resistivity of 12 Ω·cm was used for Si NWs vertical array fabrication by Oxford PlasmaLab System 100 ICP 380 (Oxford instruments, UK) according to the protocol reported previously [6–7]. The as-fabricated Si NWs were studied using scanning electron microscopy (SEM) Zeiss Supra25 (Carl Zeiss, Germany), a typical image demonstrating as-fabricated vertical NWs array is presented in Fig. 1, *a*. On the next step, the growth substrate with the NWs was cleaved into 3 samples of equal area. The first sample was left untreated as a reference. To dispose of the products of the etching process and promote better surface homogeneity the second sample was modified via 10% hydrofluoric acid treatment during 3 min followed by washing in deionized water and drying under pure nitrogen. According to the previous work [8], decoration of Si NWs with plasmonic NPs promotes better sensitivity and long-term operation. So, the NWs in the last sample 3 were decorated with spherical Ag NPs via drop casting of the NPs aqueous solution followed by the same drying procedure under pure nitrogen. The Ag NPs were synthesized according to the protocol reported previously [9].

For the detailed structural characterization, the prepared 3 types of Si NWs were transferred to a Cu grid covered with a carbon lacey film and studied by means of transmission electron microscopy (TEM) (Fig. 1, *b-d*) using Jeol JEM-2100F (accelerating voltage 200 kV, point

resolution 0.19 nm). To get more details on the surface properties of the NWs, high-resolution TEM (HRTEM) images were obtained and represented in Fig. 1, *e-g*.

HRTEM (Fig. 1, *e*) and selected area electron diffraction (SAED) pattern at the [01$\bar{1}$] zone axis (Fig. 1, *h*) corresponding to untreated Si NW (Sample 1) demonstrated high crystalline quality of the NWs after the etching without undergoing amorphization. According to the images, the oxide layer on the surface of the untreated NWs is about 2 nm thick and uncontrolled thickenings up to 20 nm (see Fig. 1, *b*). This phenomenon relates to the non-uniformity of the etching process, not affecting the geometry of the NWs sufficiently. Analysis of the images of the Sample 2 NWs (Fig. 1, *f*) shows that treatment with hydrofluoric acid allows to remove the oxide outgrowths, but the thickness of the oxide uniformly increases up to 5 nm, which is expected to modify the adsorption properties of the NWs. Images of the Sample 3 NWs (Fig. 1, *d* and *g*) demonstrate presence of nearly spherical Ag NPs sparsely decorating NWs sidewalls and having a diameter of 25–40 nm. Sample 3 NWs possess a silicon oxide layer of the same thickness with as-fabricated Sample 1 NWs.

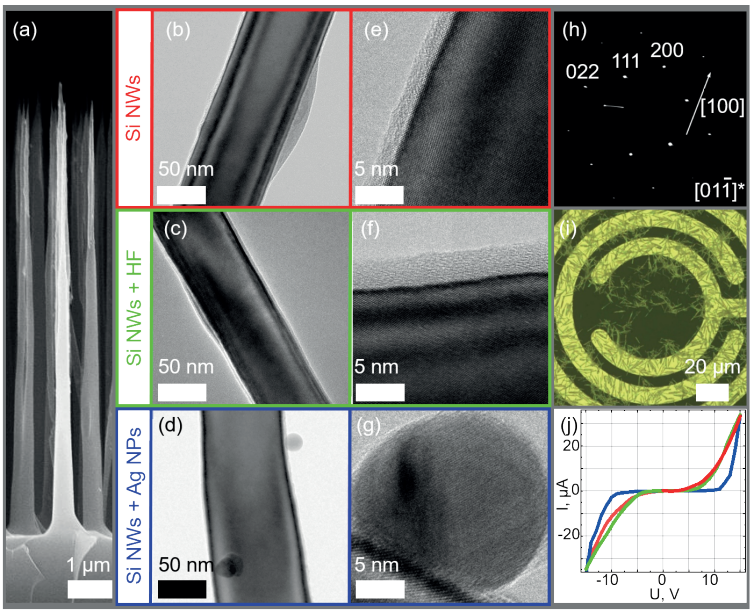

Fig. 1. Fabricated NWs and sensors. (*a*) typical SEM image of the as-fabricated vertical Si NWs array on the native substrate. (*b-d*) TEM images and (*e-g*) HRTEM images of individual as-fabricated Si NW, NW treated with hydrofluoric acid and NW decorated with Ag NPs, respectively. (*h*) selective area electron diffraction (SAED) pattern of a Si NW at the [01$\bar{1}$] zone axis. (*i*) typical 20x optical image of Si NWs drop casted on a substrate with interdigital concentric golden contacts. (*j*) current–voltage characteristics of the fabricated sensors based on as-fabricated (red), treated with HF(green) and decorated with Ag NPs (blue) Si NWs

For fabrication of sensors, the prepared NWs were transferred on a 0.7 cm wide platform with concentric interdigital 10 μm gold (Au) contacts with a pitch of 10 μm (DropSens Co. Ltd., Spain). A protocol of the sensors' preparation including the NWs separation from the growth substrate to isopropanol via ultrasonication followed by drop casting of the NWs solution on the contact platform was reported in detail previously [10]. Typical optical image (×20) of the fabricated sensor is presented in Fig. 1, *i* demonstrating dense coverage of the platform with randomly distributed NWs. For the study, three types of sensors were fabricated corresponding to the three prepared NW samples.

To study electrical contact between the NWs and interdigital contacts of the sensors, current-voltage (I-V) characterization was carried out. The I-V curves were measured with Keithley 2401 source-meter and normalized over the surface density of the transferred NWs and depicted in Fig. 1, *j*. The Au–NW contacts are found to be Schottky-type. According to the previous results, these contacts provide efficient variation of the sensor electronic parameters upon exposure to the analyte vapors promoting good sensing [10–11].

Study of the sensor's electrical properties under HCl and NH_3 vapors was carried out with the use of a Z500P impedance meter (Elins, Russia). The impedance spectroscopy was employed at 100 mV bias in the 100 Hz–500 kHz frequency range, allowing for analysis of various electronic processes that may occur upon the analyte adsorption [12].

Results and Discussion

The fabricated sensors were tested upon exposure to HCl and NH_3 vapors. To provide indirect measurement of the fluid chemical composition, aqueous solutions of NH_3 and HCl were poured into 3 ml pools with a diameter of 4 cm and evaporated naturally at ambient conditions. The sensor was located at a distance of 5.0 cm above the pool. To provide accurate electrical measurements, the setup was put into a Faraday box. Due to the small air gap between the aqueous solution and the sensor, humidity was close to 100%. Such an experimental setup mimics non-invasive or indirect analysis of the biological or chemical samples. Schematic of the experimental setup is presented in Fig. 2, *a*.

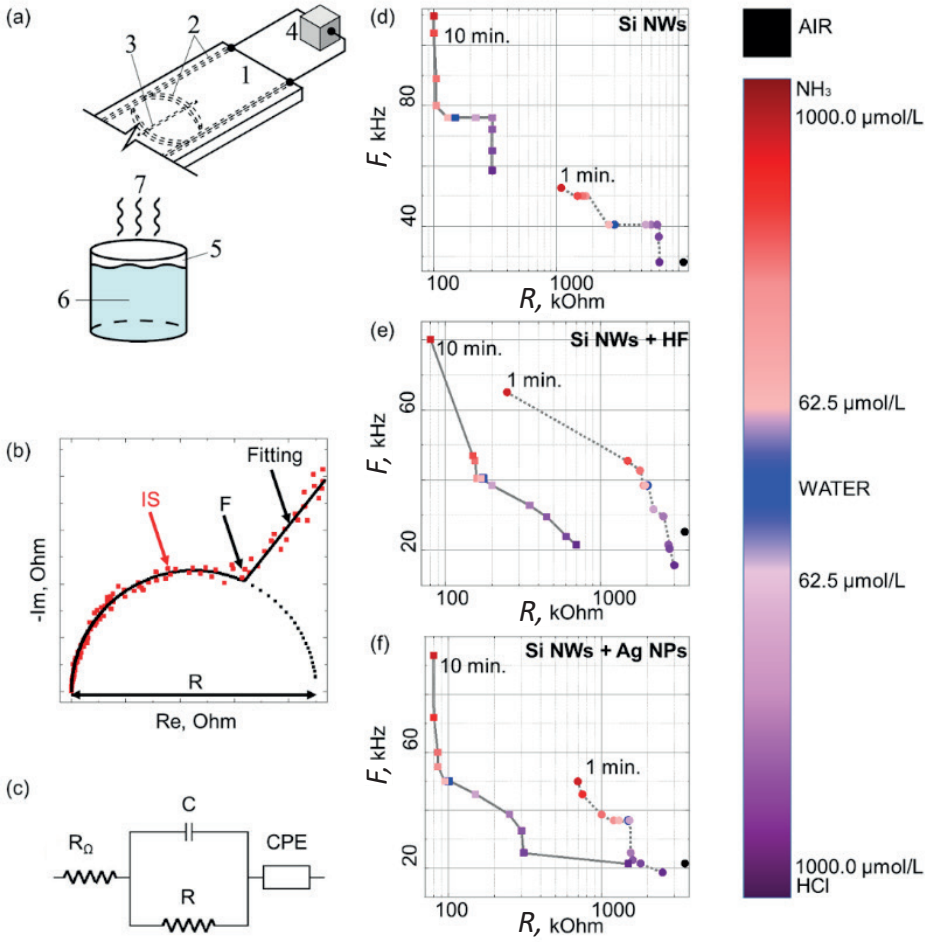

Fig. 2. Sensors characterization. Schematic of the measurement setup: 1 – contact platform, 2 – gold electrodes, 3 – NW, 4 – impedance meter, 5 – pool, 6 – solution, 7 – analyzed vapor (*a*); typical EIS spectrum of a sensor (*b*); equivalent circuit: R_Ω – resistance of the gold electrodes, R – resistance of the sensor, C – capacitance of the sensor and constant phase element (CPE) (*c*); $F(R)$ maps for 1 and 10 min vapor exposures for the sensors based on: as-fabricated Si NWs, NWs treated with HF and decorated with Ag NPs, respectively, exposure time 1 min – round dots, 10 min – square dots (*d-f*)

To study the sensitivity of the sensors, interdigital electrodes were connected to the impedance meter and EIS spectra were obtained in the presence of air, reference medium – water vapor, and vapors of NH_3 and HCl aqueous solutions in a wide concentration range of 62.5 (1.25 ppm for NH_3 and 1.88 ppm for HCl) to 1000.0 μmol·l^{-1} (20 ppm for NH_3 and 30 ppm for HCl).

The impedance spectra were depicted as the Nyquist plots, typical spectrum is presented in Fig. 2, *b*. The obtained curves consist of high-frequency (100 kHz to 500 kHz) and low-frequency (< 100 kHz) domains. The high-frequency domain corresponds to the impedance of the NWs and Schottky barrier and represented by a semicircle. The low frequency domain follows nearly linear dependence and is considered as the result of the diffusion processes at the nanowire-gold interface [8].

All the obtained EIS spectra were fitted using the equivalent electrical circuit method. The employed circuit (Fig. 2, *c*) contains: R_Ω – contact resistance corresponding to the resistance of the gold interdigital electrodes, R – resistance related to the Si NWs and Schottky barriers (referred to as the sensor resistance), C – capacitance of the sensor and CPE – constant phase element associated with the linear low frequency part of the spectra. These parameters evolve with adsorption of the analyte species on the NW sidewalls, so their analysis allows us to quantify the sensor response with the change in the resistive and capacitive characteristics. The carried out fitting allows one to obtain two parameters in the presence of various vapors: R and characteristic EIS frequency F (see Fig. 2, *b*) corresponding to the transition between the predominant action of the contact processes described by CPE at low frequencies, to the major role of the resistance R and capacitance C of the NWs and Schottky barriers at higher frequencies. According to the data analysis results, the R and F parameters are the fingerprint of the atmosphere surrounding the sensor due to the corresponding change in the spectra governed by the analyte species adsorption. So, exposure under NH_3 and HCl vapors of different concentrations can be quantified via $F(R)$ mapping of the sensory response in order to obtain selectivity in sensing.

Conclusion

We propose a novel approach for the analysis of the EIS spectra via analysis of the response in $F(R)$ space. The frequency F and resistance R of the sensor were obtained by analyzing the impedance spectra of the sensor based on Si NWs in the presence of hydrochloric acid and ammonia. The possibility of qualitative and quantitative detection of ammonia and hydrochloric acid in water vapor has been demonstrated in a wide concentration range from 62.5 to 1000 $\mu mol \cdot l^{-1}$. The dynamics of the sensory response is shown in the range from 1 to 10 min. of vapor exposure.

Protocols for modifying the adsorption properties of silicon nanowires via HF acid and Ag NPs were proposed. The difference in response in $F(R)$ space for sensors based on modified and unmodified nanowires is shown with the possibility of increasing sensitivity to both NH_3 and HCl.

REFERENCES

1. **Kondratev V.M., et al.,** Gallium phosphide nanowires for “biological concentrations” ammonia detection, 2022 J. Phys.: Conf. Ser. 2172 012006.

2. **Nalimova S.S., Kondratev V.M.,** Study of Surface Acid-Base Properties Of Gas-Sensitive Metal Oxides, 2020 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus), 2020, 987–990.

3. **Kadinskaya S.A., Kondratev V.M., Kindyushov I.K., Kuznetsov A., Punegova K.N.,** Hydrothermal ZnO-based Nanostructures: Geometry Control and Narrow Band UV Emission, 2022 Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), 2022, 958–961.

4. **Seiyama T., Kato A., Fujiishi K., Nagatani M.,** Analytical Chemistry 1962 34 (11), 1502–1503.

5. **Kondratev V.M., Kuznetsov A., Gridchin V.O., Fedina S.V., Aubekerov K.,** III–V Nanowires for Biological Ammonia Concentrations Detection, 2022 Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), 2022, 970–974.

6. **Kondratev V.M., et al.,** Silicon nanowires as multi—environment sensor elements for carbon monoxide and ammonia detection 2021 J. Phys.: Conf. Ser. 2015 012068.

7. **Kondratev V.M., et al.,** Silicon nanowires based adsorption sensors for CO and NH_3 detection, 2021 J. Phys.: Conf. Ser. 2103 012229.

8. **Kim D., et al.,** Improved Long-Term Responses of Au-Decorated Si Nanowire FET Sensor for NH_3 Detection, IEEE Sensors Journal. 20 (5) (2020) 2270–2277.

9. **Houshen L., Haibing X., Dayang W., Xutang T.,** Simple Synthesis of Monodisperse, Quasi-spherical, Citrate-Stabilized Silver Nanocrystals in Water, Langmuir. 29 (16) (2013) 5074–5079.

10. **Kondratev V.M., Morozov I.A., Vyacheslavova E.A., Kirilenko D.A., Kuznetsov A., Kadinskaya S.A., Nalimova S S., Moshnikov V.A., Gudovskikh A.S., Bolshakov A.D.,** Silicon Nanowire-Based Room-Temperature Multi-environment Ammonia Detection, ACS Applied Nano Materials. 5 (7) (2022) 9940–9949.

11. **Hunter G.W., et al.,** Editors' Choice—Critical Review—A Critical Review of Solid State Gas Sensors, 2020 J. Electrochem. Soc. 167 037570.

THE AUTHORS

KONDRATEV Valeriy M.
kvm_96@mail.ru
ORCID: 0000-0002-3469-5897

KOZKO Ivan A.
ivkozko@gmail.com
ORCID: 0009-0006-0923-1501

KARASEVA Elizaveta P.
liza.karaseva@gmail.com
ORCID: 0009-0005-0777-6746

VYACHESLAVOVA Ekaterina A.
cate.viacheslavova@yandex.ru
ORCID: 0000-0001-6869-1213

SHUGABAEV Talgat
talgashugabaev@mail.ru
ORCID: 0000-0002-4110-1647

SVINKIN Nikita A.
nik-svinkin@mail.ru
ORCID: 0000-0002-8604-5829

BOLSHAKOV Alexey D.
acr1235@mail.ru
ORCID: 0000-0001-7223-7232

Received 18.07.2023. Approved after reviewing 04.09.2023. Accepted 04.09.2023.