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Study of quasi 1-D silicon nanostructures adsorption properties

V. M. Kondratev [1,4] ✉, E. A. Vyacheslavova [1, 2], I. A. Morozov [1, 2],
S. S. Nalimova [2], V. A. Moshnikov [2], A. S. Gudovskikh [1, 2], A. D. Bolshakov [1, 3, 4]

[1] Alferov University, Saint Petersburg, Russia;
[2] Saint Petersburg Electrotechnical University "LETI", Saint Petersburg, Russia;
[3] ITMO University, Saint Petersburg, Russia;
[4] Moscow Institute of Physics and Technology, Moscow, Russia
✉ kvm_96@mail.ru

Abstract. The work is aimed at study of quasi 1-D silicon nanostructures (nanowires) adsorption properties via electrical impedance spectroscopy. Nanowires were synthesized by cryogen plasma chemical etching and transferred to auxiliary substrate with interdigital gold contacts. Further, nanowires were exposed to air, unsaturated vapors of ammonia and hydrochloric acid aqueous solutions with concentrations about 0.1—1.0 mmol·l^{-1} followed by measurement of the nanowires impedance spectra. Changes in the impedance spectra of nanowires upon exposure under analyte vapors are considered in terms of a correlation between the adsorption properties of nanowires and their electrical characteristics.

Keywords: silicon, nanowires, 1D, electrical impedance spectroscopy, adsorption properties, acid sensor, alkali sensor

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Исследование адсорбционнымх свойств квази 1-Д наноструктур кремния

В. М. Кондратьев [1,4] ✉, Е. А. Вячеславова [1, 2], И. А. Морозов [1, 2],
С. С. Налимова [2], В. А. Мошников [2], А. С. Гудовских [1, 2], А. Д. Большаков [1, 3, 4]

[1] СПбАУ РАН им. Ж.И. Алфёрова, Санкт-Петербург, Россия;
[2] СПбГЭТУ "ЛЭТИ", Санкт-Петербург, Россия;
[3] Университет ИТМО, Санкт-Петербург, Россия;
[4] Московский физико-технический институт, Москва, Россия
✉ kvm_96@mail.ru

Аннотация. Работа направлена на изучение адсорбционных свойств нанонитей кремния методами спектроскопии электрического импеданса. Продемонстрирована корреляция между адсорбционными свойствами и электрическими характеристиками нанонитей в присутствии воздуха, ненасыщенных паров воды и водных растворов аммиака, а также соляной кислоты.

Ключевые слова: кремний, нанонити, 1Д, спектроскопия электрического импеданса, адсорбционные свойства, сенсор кислот, сенсор щелочей

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Introduction

Active development of low-dimensional nanostructures based on various materials is carried out in all spheres of modern nanoelectronics. Quantum dots (0-D) are widely used in photocatalysis [1]. There are many light emitting [2-4] and waveguiding [2, 5] devices based on nanowires (NWs, 1-D). At the same time, thin semiconductor films is the common basic element of modern electronics [6]. High surface area and peculiar electronic properties compare to bulk material and thin films are the main reason for use of NWs in adsorption sensing [7-10]. Silicon is still the most accessible material for the production of NWs, both by epitaxial and «top-down» techniques [11, 12].

The existing works on Si NWs adsorption properties [13, 14] commonly consider small amounts of target adsorbates. This paper shows the possibility of detection both acidic and alkaline agents at concentrations below the "biological" level via electrical impedance spectroscopy and correlation between silicon NWs electrical impedance and their adsorption properties. For example NH_3 and HCl at concentrations of about 1 mmol·l^{-1} selected as target adsorbates of alkaline and acidic nature because they can be found in body fluids and breath and may indicate pathological changes in the body. At the same time, hydrochloric acid and ammonia are found in human body, nature and waste products of the factories and farms. In high concentrations these agents leads to irritation of respiratory system, as well as eye mucous membranes [15]. So development of novel approaches for their detection is of an importance.

Materials and Methods

In this work silicon NWs are obtained using cryogen plasma chemical etching of Si (001) substrate (boron-doped substrate with the resistivity of 12 Ω·cm) in Oxford PlasmaLab System 100 ICP380. Anisotropic etching occurs on the silicon surface under the flow of oxygen and etcher (O_2/ SF_6) mixture. Primarily etched Si islands on the surface are passivated by a non–volatile SiO_xF_y compound, which prevents lateral etching. An increase in temperature after the etching interruption leads to volatilization of F and conversion of SiO_xF_y into the native oxide. The NWs morphology was investigated by scanning electron microscopy (SEM) by Zeiss Supra25 (Carl Zeiss, Germany) (Fig. 1).

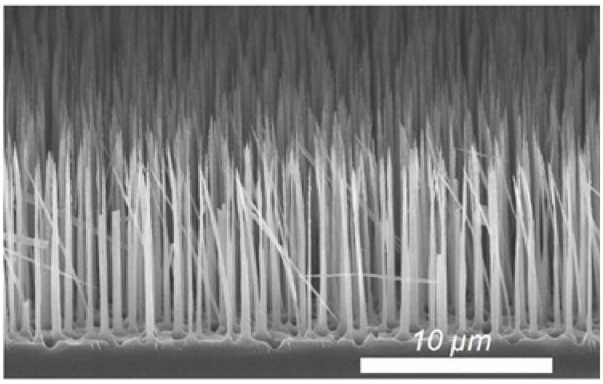

Fig. 1. SEM image of the vertical Si NWs

As-synthesized Si NWs (Fig. 1) were separated from Si (001) substrate by ultrasonication and transferred to an auxiliary substrate with concentric interdigital gold contacts (contact step of 10 μm) (Fig. 2, *a*). Gold–NWs contacts are found to be of the Schottky type, which is proven by the voltage-current characterization obtained using Keithley 2400 source-meter, (Tektronix, USA) (Fig. 2, *b*). The current-voltage (I-V) characteristic demonstrates symmetry and a diode shape with a knee voltage of about 5V, which indicates the barrier nature of the conductivity.

The phenomenon of barrier conductivity at the nanowire-gold interfaces can be effectively used for NH_3 and HCl detection as shown below via electric impedance spectroscopy of Si NWs under exposure of analyte vapor at 100mV bias in the frequency range from 100 Hz to 500 kHz (by impedance meter Z500P (Elins, Russia)). Impedance spectrum in a reference medium – air – is shown in Fig. 2, *c*.

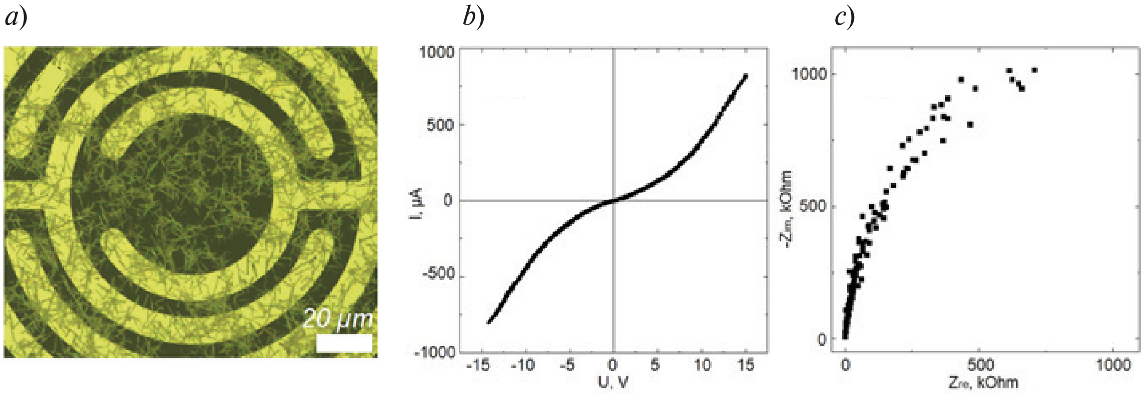

Fig. 2. Typical optical image of the Si NWs on the surface of an auxiliary substrate with concentric interdigital gold contacts (*a*); current-voltage characteristic (*b*); measured impedance spectrum in air conditions (*c*)

The impedance spectra were represented in Nyquist's plots – in the form of a dependence of the imaginary part (Z_{im}) of the Si NWs impedance on the real one (Z_{re}) – and analyzed for a shift due to the change in the environment.

Results and Discussion

Vapor media with adsorbates were delivered to the NWs by natural evaporation of water and aqueous ammonia solutions (room temperature, atmospheric pressure) from a reservoir 4 cm (1.6 in) in diameter located at a distance of about 5 cm (2.0 in) below the NWs. A change in the NWs electrical impedance under action of the target adsorbates (vapors of NH_3 and HCl aqua solutions with concentrations of 0.1 and 1.0 $mmol \cdot l^{-1}$) (Fig. 3, *b*, *c*, *e*) was measured and compared with the impedance in the water vapors medium (Fig. 3, *a*).

Analysis of the dependencies in Fig. 3 showed the presence in all spectra of a characteristic region in the frequency range from 25 kHz to 500 kHz which can be approximated by a semicircle with the center lying on the abscissa axis. At the same time, the diameter of such a semicircle decreases when water vapor changes to vapor of aqueous ammonia solutions and increases when changing to vapor of aqueous solutions of hydrochloric acid. In previous works, it was shown that the projection of this high-frequency region of the nanowire impedance spectrum onto the abscissa (real resistance) axis makes it possible to estimate the active resistance of NWs transferred to gold contacts and electrically connected in parallel to each other [11–12].

In air conditions a NWs surface is oxidazed due to increase in temperature after the cryogenic plasmachemical etching interruption and volatilization of F with subsequent conversion of SiO_xF_y into the native oxide [11-12]. The interaction of H_2O, NH_3 and HCl vapors with NWs occurs by redox mechanisms:

1) hydration of the silicon oxidized surface by OH^- molecules from water vapors (breaking the bond between oxygen and silicon in the near-surface native oxide and its replacement with a more energetically advantageous one) [11-12];

2) for ammonia aqueous solution vapors it is a protonation of the hydrated surface of the nanowire by neutral NH_3 molecules (separation of the proton H^+ from the OH molecule on the surface of the nanowire) with formation of the NH_4^+ ion (gas) [13-15];

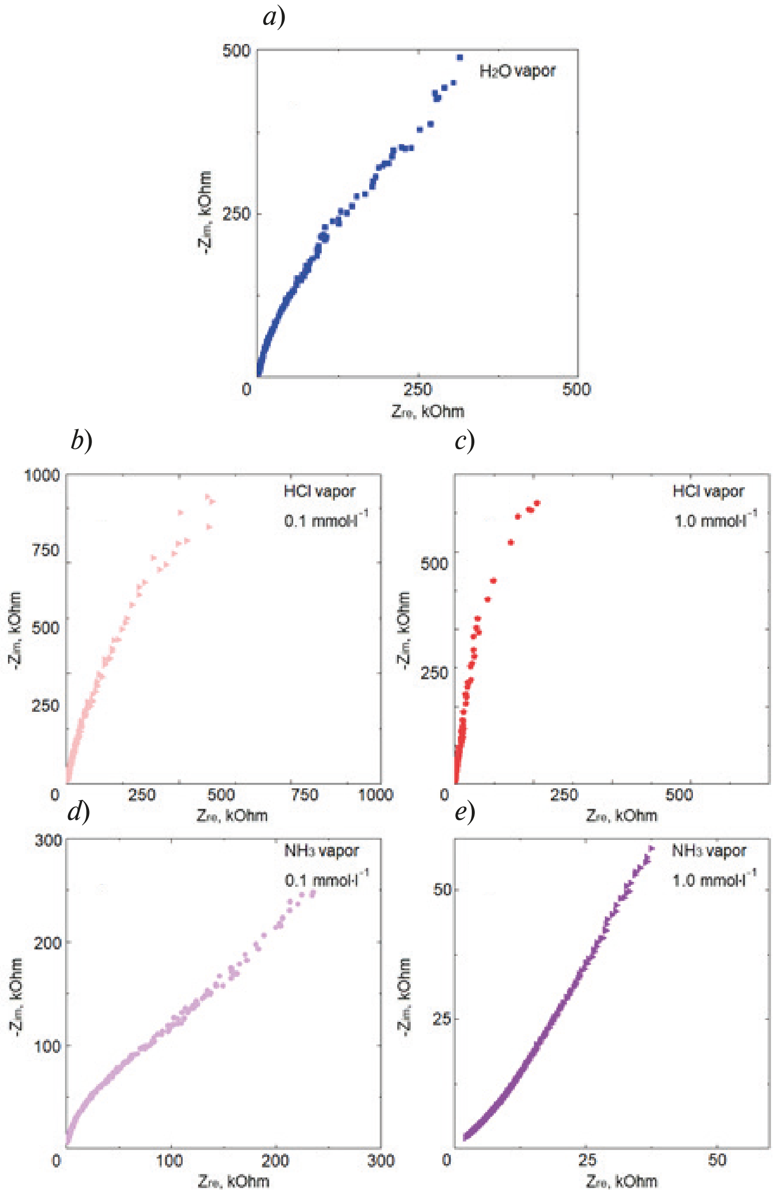

Fig. 3. Measured impedance spectra in: comparative medium of water vapor (*a*), 0.1 (*b*) and 1.0 mmol·l⁻¹ HCl aqueous solution vapors (*c*), 0.1 (*d*) and 1.0 mmol·l⁻¹ NH_3 aqueous solution vapors (*e*)

3) vapors of hydrochloric acid aqueous solution contain neutral Cl ions which presumably interact with the silicon surface followed by the removal of electrons from NWs with a subsequent increase in its resistance [16].

At the same time in both first and second cases described conduction electrons are injected into silicon NWs which affect the resistance and impedance of NWs.

It is also necessary to consider the multiple Schottky barriers at the gold-NWs interfaces which make a significant contribution to the impedance of NWs in air in the non-ohmic mode (Fig. 2). We believe that the impedance of silicon NWs in air is determined precisely by the contact resistance of the Schottky barriers, and the NWs themselves are significantly depleted.

However, in the presence of water vapor, ammonia, and hydrochloric acid, the impedance of NWs is determined precisely by the injection and rejection of electrons during the adsorption of molecules. Thus, the measurement concept proposed in Fig. 2 is suitable for silicon NWs adsorption properties analysis.

Conclusion

Changes in the impedance spectra of NWs in the presence of air, H_2O, NH_3 and HCl were considered in terms of a correlation between the adsorption properties of NWs and their electrical impedance.

We demonstrate the possibility of qualitative and quantitative gaseous (vapor) media analysis for the presence of ammonia and hydrochloric acid in extra low concentration via silicon NWs and impedance spectroscopy.

The selectivity between oxidizing and reducing gasses can be used for Si NWs based sensor fabrication.

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THE AUTHORS

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

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

MOROZOV Ivan A.
morivan@mail.ru

NALIMOVA Svetlana S.
sskarpova@list.ru

MOSHNIKOV Vyacheslav A.
vamoshnikov@mail.ru

GUDOVSKIKH Alexander S.
gudovskikh@spbau.ru

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

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