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Study of quasi 1D silicon nanostructures adsorption properties via impedance spectroscopy

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Abstract. The work is aimed at study of correlation between quasi 1D silicon nanostructures adsorption properties and their electrical characteristics in terms of change in Si nanowires impedance under action of different environments with a target adsorbate. Here we fabricate silicon nanowires based gas sensor and demonstrate the possibility of qualitative and quantitative gaseous media analysis for the presence of ammonia. The equivalent electric circuits of the sensor under action of air, water vapour and water ammonia solutions are considered. The sensor response under action of the different adsorbates and optimal impedance spectroscopy parameters are discussed.

Keywords: silicon, nanowires, 1D, electrical impedance spectroscopy

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Исследование адсорбционных свойств квазиодномерных наноструктур кремния методом спектроскопии электрического импеданса

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Аннотация. Работа направлена на изучение адсорбционных свойств нанонитей кремния методом спектроскопии электрического импеданса. Продемонстрирована корреляция между адсорбционными свойствами и электрическими характеристиками нанонитей.

Ключевые слова: кремний, нанонити, сенсор, спектроскопия импеданса

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Introduction

There are many research activities in the field of modern electronics, based on nanomaterials, especially nanowires. The possibility of development of efficient light-emitting [1], resonator [1–2], and waveguide [2] structures, based on III–V and II–VI nanowires [3–4], as well as sensor elements [5–9], are widely presented. Despite the possibilities these highly crystalline nanostructures bring, their synthesis protocols are rather expensive and incompatible with modern CMOS processes.

As such, development of devices, based on silicon-cheap and technologically feasible material, and study of adsorption properties of quasi 1D Si nanowires is an important field being the subject of this work.

Synthesis

Silicon nanowires with a length of 10–12 μm and thickness of about 350 nm were obtained using cryogenic plasmachemical etching of Si (001) substrate in Oxford PlasmaLab System 100 ICP380 (Oxford instruments, Abingdon, UK). Anisotropic etching occurs on Si surface under flow of oxygen and etcher (O_2/SF_6) mixture. Primarily etched Si islands on the surface are passivated by 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. Typical parameters, growth conditions and result of the structural characterization via Raman spectroscopy are reposted previously [10–11]. The nanowires morphology and geometry were investigated by scanning electron microscopy (SEM) Zeiss Supra25 (Carl Zeiss AG, Jena, Germany) (Fig. 1, *a*).

As-synthesized Si nanowires 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. 1, *b*). Gold-nanowires contacts are found to be of the Schottky type, which is proven by the voltage-current characterization, obtained using Keithley 2400 source-meter (Tektronix, Beaverton, USA) (Fig. 1, *c*).

The current-voltage (I-V) characteristic of the sensor demonstrates symmetry and a diode shape with a knee voltage of about 5 V, which indicates the barrier nature of the sensor conductivity. The phenomenon of barrier conductivity at the nanowire-gold interfaces can be effectively used for ammonia detection as shown below via electric impedance spectroscopy of sensor under exposure of analyte vapour at 100 mV bias in the frequency range from 100 Hz to 500 kHz (by impedance meter Z500P (Elins, Chernogolovka, Russia)). The impedance spectra were represented in Nyquist's plots — in the form of a dependence of the imaginary part of the sensor impedance on the real one, and analyzed for a shift followed by the change in the sensor environment. Impedance spectrum of the sensor in a reference medium, air, is shown in Figure 1, *d*.

Study

Vapour media with adsorbates were delivered to the sensor by natural evaporation of water and aqueous ammonia solutions (room temperature, atmospheric pressure) from a reservoir 4 cm

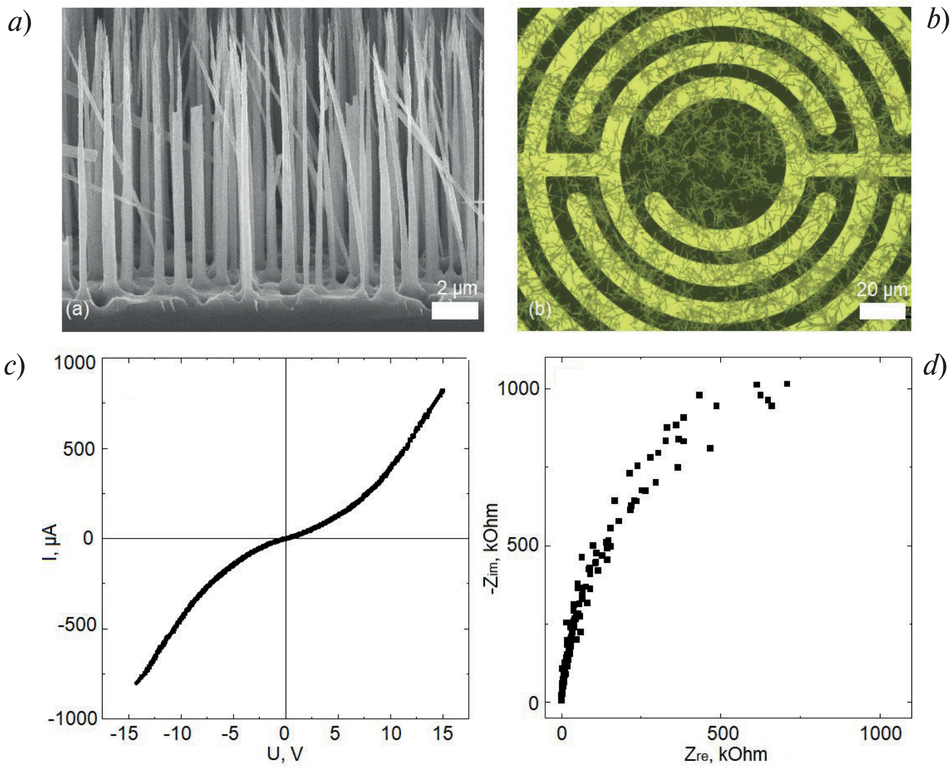

Fig. 1. SEM image of the vertically oriented structures based on plasma chemically etched Si nanowires (*a*); typical optical image of the Si nanowires on the surface of an auxiliary substrate with concentric interdigital gold contacts (further — sensor) (*b*); current-voltage characteristic of the sensor (*c*); measured sensor impedance spectrum in ambient conditions (*d*)

(1.6 in) in diameter, located at a distance of about 5 cm (2.0 in) below the sensor. A change in the sensor electrical impedance under action of the target adsorbates (vapours of NH_3 aqua solutions with concentrations of 0.125, 0.250, and 0.500 mmol·l^{-1}) (Fig. 2, *b*–*d*) was measured and compared with the impedance in the water vapours medium (Fig. 2, *a*).

Analysis of the dependencies in Figure 2 showed presence of characteristic plot regions, typical for impedance spectra of semiconductor materials — semicircular at frequencies of the order of 10–500 kHz and quasi-linear at frequencies of the order of 100 Hz–10 kHz. The first of these regions is associated with the contribution to the sensor impedance from the electrical resistance and capacitance of silicon nanowires, connected in parallel by interdigital contacts. The second region is largely determined by barrier phenomena at Schottky contacts between nanowires and gold [12–15].

Discussion

The conductivity of nanowires is determined by the cross section of the conducting channel inside the nanowire, the width of which varies depending on the adsorption processes on the surface, which leads to the formation of depleted or enriched regions that act on the conduction channel [12, 16]. In this work the sensitive element of the sensor is an array of conducting nanowires, connected in parallel through a Schottky contact, and the sensor impedance spectra carry information about the correlation between the adsorption properties and electrical characteristics of silicon NWs (semicircular region of the spectrum), as well as about contact phenomena at the NW-gold interface (quasi-linear region).

As follows from Figure 2, the projection of the semicircular part of the sensor impedance spectrum (the active resistance of silicon nanowires) decreases, when the sensor passes from air to unsaturated water vapour and vapours of aqueous ammonia solutions.

The oxidation of nanowires surface occur 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 [10–11]. The adsorption interaction presumably proceeds through two main mechanisms [16]:

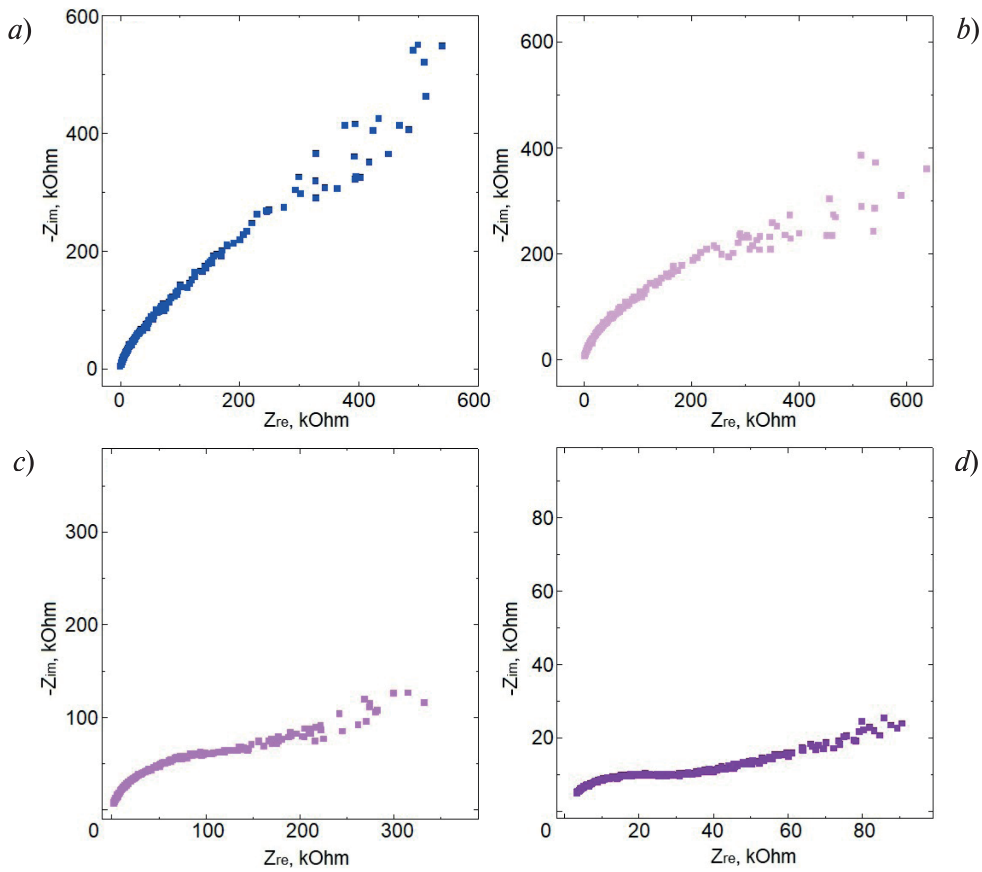

Fig. 2. Measured impedance spectra exposed under vapours of H_2O (*a*), and 0.125 (*b*), 0.250 (*c*), and 0.500 (*d*) mmol·l^{-1}of NH_3

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

2) protonation of the hydrated surface of the nanowire by 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.

In both cases described, conduction electrons enter silicon, which affect the resistance and impedance of nanowires.

In addition, it is necessary to take into account the small transverse dimensions of single nanowires and the huge ratio of the surface area to the volume of NWs, as a result of which there is a strong bending of the energy bands in the axial direction of the NWs. In the case of quasi 1D silicon nanostructures such effects lead to an inversion of conductivity from p-type (substrate) to n-type (NWs), as well as a predominant effect on the conductivity of silicon NWs from adsorbates [16].

The estimation of the projection of the semicircular part of the sensor impedance spectrum (the active resistance of silicon nanowires) value makes it possible to estimate the total resistance of the nanowire array (sensitive element of the sensor). This resistance under action of ammonia less than resistance of the sensor in the air (2250 kOhm) and water vapour environment (200 kOhm) and decreases with increasing ammonia concentration (150, 55, and 12 kOhm for 0.125, 0.250, and 0.500 mmol·l^{-1}, respectively).

The optimal frequency of the measuring voltage is in the range from 10 to 500 kHz, at which there is no significant contribution to the sensor impedance spectrum from the Schottky contacts between nanowires and gold, and the sensor impedance is determined mainly due to the active and reactive resistance of silicon nanowires, which correlates with the composition of the environment.

Conclusion

Correlation between silicon nanowires adsorption properties and their electrical characteristics demonstrate the possibility of qualitative and quantitative gaseous (vapour) media analysis for the presence of ammonia in extra low concentration with the fabricated sensor.

The semicircular part of the sensor impedance spectrum corresponds to the resistance of the sensor is used to analyze change in the resistance under the vapour adsorption. The resistance of the sensor changes, when water vapour is replaced by vapour of an aqueous solution of ammonia to 25, 73, and 94% (for 0.125, 0.250, and 0.500 mmol·l^{-1}, respectively).

The optimal frequencies of the measuring voltage at which there is no significant contribution to the sensor impedance spectrum from the Schottky contacts are shown. These frequencies can be used to perform real-time detection.

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