Silicon nanowires as multi–environment sensor elements for carbon monoxide and ammonia detection

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Abstract. Carbon monoxide and ammonia are inorganic agents found both in nature and in the human body, which is of great interest for modern sensing. First, in concentrations of the order of 1 ppm agents are produced by human and can be markers of changes in human health. Second, at concentrations of the order of 100 ppm, carbon monoxide and ammonia are toxic and hazardous. This work is aimed at fabrication and study of precise, technological and relatively cheap sensors compatible with a gas and liquid medium for CO and NH₃ detection, respectively.

Introduction

Low–dimensional nanostructures such as metal nanowires (NWs) [1] and metal oxide NWs [2] are the main elements for modern adsorption sensors production. High surface area and peculiar electronic properties compare to bulk material are the main reason for using of NWs in sensing. The existing works on Si NWs [3–4] consider only gaseous media and a small amounts of target adsorbates. Development of multi–environment sensors, such as for CO in gas medium and NH₃ in liquid medium can lead to qualitative breakthrough in modern adsorption sensorics, expand and combine classic applications by one multi–environment case.

1. Nanowires synthesis

Vertically oriented structures based on Si NWs with a length of about 10 μm were obtained using cryogen plasma etching of Si (001) substrate in Oxford PlasmaLab System 100 ICP380 with SF₆/O₂ flow and pressure to 5 mTorr according to the previous reports [5–6] and studied by electron microscopy. For structural characterization, Si NWs were transferred to an auxiliary substrate and studied by Raman spectroscopy. The results of the SEM and Raman studies are shown in Fig. 1 (a) and (b), respectively.

Figure 1 – SEM image of the vertically oriented Si NWs – (a) and Si NWs Raman spectrum – (b)
Fig. 1 (a) shows that the Si NWs have a length of about 10 μm and a cross section of 350–400 nm. Fig. 1 (b) demonstrates presence of transverse second order acoustic phonons 2TA (c–Si 2TA) and transverse optical phonons 2TO (c–Si 2TO) at 300 and 970 cm\(^{-1}\) [7] in the Raman spectrum, respectively, and high–intensity peak at 520 cm\(^{-1}\) (Si NWs), typical for highly crystalline Si NWs [8]. The obtained Raman spectrum also shows low–intensity peaks in the range of 400–450 cm\(^{-1}\) and 600–650 cm\(^{-1}\), which are in a good agreement with the studies of low–dimensional Si nanostructures [9].

2. Sensor fabrication
The step–by–step protocol of the sensor development is shown in the Fig. 2.

Figure 2 – The step–by–step sensor fabrication protocol: 1 – as-synthesized vertical Si NWs, 2 – Si substrate, 3 – isopropyl alcohol, 4 – ultrasonic separation tube, 5 – diffusion system, 6 – sensor platform, 7 – gold interdigital contacts; (a) – separating of NWs from the growth substrate by ultrasonic (b) – dispersion of NWs in isopropanol and transfer to the sensor platform, (c) – fabrication of sensor and formation of gold–NWs contacts by annealing

The prototype device based on Si NWs obtained using the presented protocol was used in this work as a multi–environment adsorption sensor for carbon monoxide and ammonia.

3. Sensory tests
The sensory properties of the sensor with the NWs were investigated in terms of the change in the impedance of the obtained sensors under the action of the target adsorbate in gaseous (CO) and liquid (NH\(_3\)) media and compared with the impedance in N\(_2\) and distilled H\(_2\)O medium, respectively. The change in the impedance is represented in the form of Nyquist plot, which allows to selectively characterize the change in real and imaginary parts of the impedance of the sensor in the frequency range from 100 Hz to 500 kHz in the presence of CO and NH\(_3\). The constant voltage signal to measure the impedance of 100mV was selected; the amplitude of the variable voltage signal is 20mV. The presented parameters for impedance measurement are optimal for working with samples with an implicit active and reactive nature of resistance change.

At the same time the concept of a multi–environment sensor is an important aspect of this work, which can be divided into 2 cases: carbon monoxide gas and liquid ammonia.

3.1. Gas case
Working with the gases allowed us to measure the sensor impedance spectrum in N\(_2\) and CO medium not only at normal conditions, but also under heating of the sensor up to 200°C and irradiation with UV light (395nm), which excite the generation of minority charge carriers in NWs. We believe that the processes of adsorption from the gas medium occur by donor–acceptor mechanisms and minority charge carriers can make a useful contribution to the conductivity of NWs connected to the sensor configuration. At the same time, the classical idea of the NWs conductivity in this configuration is the concept of a conducting channel inside the NWs, the width of which varies depending on the adsorption processes on the surface of the low–dimensional structure, leading to the formation of depleted or enriched with the main charge carriers of the regions acting on the conduction channel. An array of conductive NWs is a sensitive part of the sensor produced according to the presented protocol. The second reason of the additional treatment of the sensor is to enhance the overall conductivity of the sensor under the influence of photoconductivity and thermal conductivity, which reduces the shunt effects. However, there no sufficient shift in the sensor impedance spectrum is observed when
changing nitrogen to carbon monoxide under normal conditions and under UV irradiation. On the contrary, the corresponding spectra are very different when the sensor is heated to 200°C during measurements.

In accordance with the above, Fig. 3 shows the impedance spectra of a sensor based on Si NWs in a reference medium—nitrogen and in the medium of the target adsorbate—carbon monoxide, under conditions of heating the sensor to 200°C.

Figure 3 – The shift of the sensor impedance spectrum when changing N\textsubscript{2} to CO under heating of the sensor to 200°C during measurements: N\textsubscript{2} 200°C (>1000s. before CO) – in N\textsubscript{2} with exposition time over 1000s.; CO 200°C (10ppm in N\textsubscript{2}, 30s.) – in 10ppm CO with exposition time 30s.; CO 200°C (10ppm in N\textsubscript{2}, 630s.) – in 10ppm CO with exposition time 630s.; N\textsubscript{2} 200°C (430s. after CO) – recovery of the sensor impedance

The impedance spectra in the presence of N\textsubscript{2} and of CO are qualitatively different. CO presence leads to decrease of real and imaginary parts of the impedance in all of the frequency range. The latter effect may be due amorphization of the NWs surface, n– type defective conductivity and redox interaction between NWs and carbon monoxide during adsorption. The obtained data together indicate the possibility of using sensors based on Si NWs for the qualitative analysis of gaseous and vapor samples for the presence of carbon monoxide.

3.2. Liquid case

Working with the liquids allowed us to measure the sensor impedance spectrum in distilled H\textsubscript{2}O and NH\textsubscript{3} medium at room temperature and atmospheric pressure. We believe that the previously presented scheme of conductivity of low-dimensional nanostructures in the presence of adsorbates can be also used for liquid adsorbates, however, it is necessary to take into account the strongly polar nature of water molecules and the pronounced alkaline nature of water-ammonia solutions with reducing properties.

In analysis of the obtained results, it is necessary to take into account the contribution to the overall conductivity of the sensor from the electrochemical cell formed between the interdigital contacts when the sensor is placed in liquid medium. The impedance of the NWs and electrochemical cell in this sensor configuration are connected in parallel. Based on the latter assumption, the signal normalization algorithm, which consists in subtracting the impedance of the electrochemical cell from the total sensor impedance, is proposed further. Then the total impedance (Z\textsubscript{∑}\textsubscript{i}) of the sensor for each i-th frequency of the voltage measuring signal can be calculated using the expression 1:

\[
\frac{1}{(Z_{\text{H}_2\text{O}})_{i}} = \frac{1}{(Z_{\text{H}_2\text{O},i})} + \frac{1}{(Z_{\text{NWs}})_{i}};
\]

the (Z\textsubscript{H}_2\textsubscript{O\textsubscript{i}}) is the impedance of the electrochemical cell, (Z\textsubscript{NWs\textsubscript{i}}) is the impedance of the NWs. To describe the sensitivity of the sensors, the real and imaginary parts of the impedance were considered:

\[
Z_{i} = \text{Re}(Z)_{i} + j \cdot \text{Im}(Z)_{i};
\]

then the expression for signal normalization, which consists in subtracting the contribution from the electrochemical cell from the sensor impedance spectrum formed between the interdigitated contacts can be represented in the form of expression 3:
the ratio for the coefficients $R$ and $I$ is presented as an expression 4.

\[
R = \frac{\text{Re}(Z_{\Sigma})_i - \text{Re}(Z_{H,O})_i}{|Z_{\Sigma}|^2 - |Z_{H,O}|^2}, \quad I = \frac{\text{Im}(Z_{\Sigma})_i - \text{Im}(Z_{H,O})_i}{|Z_{\Sigma}|^2 - |Z_{H,O}|^2};
\]

in accordance with the above, Fig. 4 shows the impedance spectra of a sensor based on Si NWs in a comparative medium – distilled H$_2$O and in the medium of the target adsorbate – NH$_3$.

Ammonia adsorption at NW sidewalls in liquid medium leads to decrease of imaginary part of the impedance and signal normalization allows one to evaluate the electrical properties of NWs and their correlation with adsorption properties. The impedance spectra of a sensor based on Si NWs corresponding to different concentrations of ammonia dissolved in water and distilled water are distinguishable in the entire frequency range of measurements, which indicates the possibility of using fabricated sensors according to the previously proposed protocol for the qualitative and quantitative analysis of liquid samples for the presence of ammonia.

4. Conclusion
In all the studied cases, the shift of the impedance spectrum demonstrates perspectives of Si NWs use for both quantitative and qualitative multi–environment analysis for the presence of low concentrations of carbon monoxide and ammonia.

We also demonstrate a protocol for development of multi–environment sensors based on Si NWs which can be interesting in terms of characterization of conductivity nature of low–dimensional epitaxial nanostructures and future sensory applications.

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References
[1] Nano Letters 2003, 3, 9, 1229–1233.
[2] Advanced Materials 2003, 12, 997–1000.
[3] Chemical Physics Letters 2003, 369, 220–224.
[4] Nanotechnology 2010, 21, 9, 015501.
[5] Phys. Status Solidi A 2020, 217, 1900535.
[6] Energy Procedia 2013, 38, 866–871.
[7] Physical Review B 1999, V. 59, N. 3, 1645–1648.
[8] Materials Science and Engineering C 2003, 23, 931–934.
[9] Nanotechnology 2012, 23, 275706.