Silicon nanowires based adsorption sensors for CO and NH\textsubscript{3} 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. The work is aimed at fabrication and study of precise, technological and relatively cheap multi-environment sensors based on Si nanowires possessing high surface area compatible with a gas and liquid medium for CO and NH\textsubscript{3} detection, respectively. We demonstrate the potential of the approach for detection of both ammonia and CO at concentrations as low as 10ppm. The effects of the adsorbates from water and air are discussed.

1. Introduction
The need to control human vital processes stimulates researchers around the globe to develop high-precision sensory devices. The lack of such precision sensors is particularly acute in the medical and biological industries. An important task in these areas is to control the concentration of various inorganic agents in both the environment and biological samples. One of the ways to achieve this goal is the use of semiconductor gas sensors. Adsorption sensorics is a several decades mature technology [1]. Most commonly, such elements are on the basis of films [2] of metal oxides and ceramics [3]. Lately, low–dimensional nanostructures such as metal nanowires (NWs) [4], metal oxide NWs [5] and composite nanostructures [6] have become important and widely used elements for modern adsorption sensors production. High surface area and peculiar electronic properties compare to bulk material are the main reason for use of NWs in sensing. The existing works on Si NWs sensorics [7–8] commonly consider only gaseous media and a small amounts of target adsorbates. Development of multi–environment sensors, such as for CO in gas medium and NH\textsubscript{3} in liquid medium can lead to qualitative breakthrough in modern adsorption sensorics, expand and combine classic applications by one multi–environment case.

2. Nanowires synthesis and study
Vertically oriented structures based on Si NWs are obtained using cryogen plasma etching of Si (001) substrate in Oxford PlasmaLab System 100 ICP380 with SF6/O\textsubscript{2} mixture flow and 5 mTorr pressure according to the previous reports [9–10]. The NWs morphology was investigated with scanning electron microscopy (SEM) Zeiss Supra25. For structural characterization, Si NWs were transferred to
an auxiliary substrate and studied by Raman spectroscopy. The results of the SEM and Raman are shown in Figure 1 (a), (b), respectively.

![Figure 1](image_url)

**Figure 1** – SEM image of the vertically oriented Si NWs – (a), Si NWs Raman spectrum – (b).

Figure 1 (a) demonstrates that the used highly uniform vertical Si NWs without sufficient tapering anticipated for the top-down fabrication approach. The NWs are 10 mkm long and about 350–400 nm thick. RS spectrum in Figure 1 (b) shows 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 [11], respectively, and high–intensity peak at 520 cm⁻¹ (Si NWs), typical for highly crystalline Si NWs [12]. 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 [13]. The obtained spectrum demonstrates high crystalline quality of the NWs and absence of a prominent silicon oxide volume.

Anisotropic etching occurs on the prepared silicon surface in the presence of oxygen in the composition of etcher SF₆/O₂. Primarily etched islands of Si on the surface are passivated by a non-volatile compound SiOₓFᵧ, which prevents lateral etching, but not interferes with the axial. Thus, the primary etched islands become vertical NWs. An increase in temperature after the etching process leads to volatilization of F and conversion of SiOₓFᵧ into the so-called native oxide. On the surface of this oxide are unsaturated covalent bonds and defects of different nature, which in our opinion are adsorption centres. Adsorption of reducing agent molecules on the surface of NWs, leads to saturation of the previously mentioned covalent bonds, formation of near-surface region charge and increase due to the field effect of the conduction channel inside the NW, which connected to the electrical circuit.

### 3. Sensor fabrication

The step–by–step protocol of sensor production is shown in the Figure 2 and includes the procedure for separating NWs from the growth substrate and transferring the array of NWs to the surface of the sensor platform.

![Figure 2](image_url)

**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 gold contacts; (a) – separation of NWs from the growth substrate by ultrasonicication (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 detection.

4. Multi–environment adsorption sensory tests
To investigate sensorics potential of the fabricated device, change in the impedance of the sensor under action of the target adsorbate in gaseous (CO) and liquid (NH₄OH solution) media was measured and compared with the impedance in N₂ and distilled H₂O medium, respectively. 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 NH₃. The constant voltage of 100mV and amplitude of the variable voltage signal is 20mV for impedance measurement are the 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: liquid ammonia and vapor carbon monoxide.

4.1. Ammonia liquid case
First, we measured the sensor impedance spectra in distilled H₂O and NH₄OH 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.

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 corresponding to the current passing through the NWs can be obtained via subtraction of the impedance of the electrochemical cell from the total sensor impedance. Total impedance (Zₜ) of the sensor for each i-th frequency of the voltage measuring signal can be calculated using the expression 1:

\[
\frac{1}{(Zₜ)ᵢ} = \frac{1}{(Z_{H₂O})ᵢ} + \frac{1}{(Z_{NWs})ᵢ};
\]

here (Z_{H₂O})ᵢ is the impedance of the electrochemical cell, (Z_{NWs})ᵢ is the impedance of the NWs. To describe the sensitivity of the sensors, the real and imaginary parts of the impedance were considered:

\[
Zᵢ = \text{Re}(Zᵢ) + j \cdot \text{Im}(Zᵢ);
\]

(2)

where.

\[
\text{Re}(Z_{NWs})ᵢ = \frac{R}{R² + I²}; \text{Im}(Z_{NWs})ᵢ = \frac{I}{R² + I²};
\]

(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. 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.

4.2. Carbon monoxide gas case

Carbon monoxide with a concentration of 10ppm (at the lower threshold of danger to humans) was used as a target adsorbate in vapor experiment and high-purity nitrogen as a control medium. During the vapor measurements, the sensor impedance spectra were obtained at room temperature, under heating of the sensor up to 200°C and irradiation with UV light (395nm), which excite generation of charge carriers in Si NWs. CO adsorption from the gas medium must occur by donor–acceptor mechanisms and charge carriers can make a useful contribution in this case.

The NW conductivity is governed by the cross section of conducting channel inside the NW, which width varies depending on the adsorption processes on the surface, leading to the formation of depleted or enriched regions acting on the conduction channel. An array of conductive NWs is a sensitive part of the sensor produced according to the presented protocol.

No sufficient shift in the sensor impedance spectrum is observed when changing nitrogen to 10 ppm carbon monoxide in nitrogen at RT. During the measurement of the impedance spectrum, the response can be affected by interference. This effect can be suppressed with the photo- or thermogeneration of charge carriers allowing to reduce the electromagnetic interference in AC scheme. Excitation with UV did not succeed – no documentable change in the spectrum was detected. Photogeneration of the charge carriers does not occur at room temperature as such an adsorption process is thermodynamically unprofitable. On the contrary, the spectra in the presence of low concentration CO and without it are distinguishable when the sensor is heated to 200°C during measurements. In accordance with the above, Figure 4 shows the corresponding impedance spectra.

\[
R = \left( \frac{\text{Re}(Z_{\text{Z}_2})}{|Z_{\text{Z}_2}|} \right) \frac{\text{Re}(Z_{\text{H},O})}{|Z_{\text{H},O}|} ; \quad I = \left( \frac{\text{Im}(Z_{\text{Z}_2})}{|Z_{\text{Z}_2}|} \right) \frac{\text{Im}(Z_{\text{H},O})}{|Z_{\text{H},O}|} ;
\]

\[
(4)
\]

in accordance with the above, Figure 3 shows the impedance spectra of the sensor based on Si NWs in a comparative medium – distilled H₂O and in H₂O with the target adsorbate – NH₃.
A plot in Figure 4 demonstrates that 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 to type conductivity and redox interaction between NWs and carbon monoxide during the adsorption. The obtained data demonstrated perspectives of use of the sensors based on Si NWs for the qualitative analysis of gaseous and vapor samples for the presence of carbon monoxide.

5. Conclusion

We present a simple fabrication protocol for creating sensors based on NWs obtained by cryogenic etching which can be interesting in terms of characterization of conductivity nature of low-dimensional epitaxial nanostructures and analysis for the presence of low concentrations of carbon monoxide and ammonia with rapid response and recovery of electrical characteristics in several hundred seconds. Impedansometry is used to study the sensoric potential of the Si NWs based adsorption approach for carbon monoxide and ammonia detecting. Approach demonstrates its potential both for vapor and liquid media.

This Si NWs based sensor configuration with interdigital gold contacts has one significant drawback - cross-sensitivity to water molecules. Cross-sensitivity is essentially the effect on the sensor of other agents that may be present in a liquid or vapour medium simultaneously with ammonia and carbon monoxide. However, we suggest to reduce this effect by heating the sensor in the gas case. The validity of an approach is also shown in this work with sufficient change in impedance under 10ppm of CO in N₂. No sensitivity to CO at RT and under UV exposure is found most probably due to adsorption saturation from ambient air prior to the measurements.

The electrochemical contribution to the sensor signal due to the electric conductivity of electrochemical cell, formed by interdigital contacts and liquid, can be subtracted over the normalization procedure. At the same time, sensitivity of as low as 10ppm is demonstrated for NH₃ dissolved in water. We also demonstrate the possibility of using manufactured sensors according to the previously proposed protocol for both qualitative and quantitative analysis of the ammonia presence.

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Figure 4 – sensor impedance spectra: black – in pure N₂ under heating of the sensor to 200°C during measurements with exposition time over 1000s.; red – in 10ppm CO dissolved in N₂ medium with exposition time 30s.; blue – in 10ppm CO dissolved in N₂ medium with exposition time 630s.; green – recovery of the sensor impedance spectrum after CO exposition in the presence of N₂ medium with exposition time 430s. (this time is needed to restore the original electrical characteristics corresponding to the black spectrum).
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