III–V nanowires for ammonia detection

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Abstract. Ammonia is an inorganic agent found both in nature and in the human body, which is of great interest for modern sensory applications. Here we use GaP, GaN and GaAs epitaxial nanowires as sensitive elements of the ammonia sensors fabricated via a simple protocol on the platform with golden interdigital contacts. Impedancemetry is used to study change of the device properties with addition of ammonia to the reference medium (water). GaP and GaN-based devices exhibit sufficient response to the ammonia presence with the detection limit lower than 10ppm. This work is aimed at fabrication and study of precise, technological and relatively cheap ammonia sensors compatible with a liquid medium, and motivated by the possibility of using this type of adsorption sensors in medical, environmental equipment and biological purposes.

1. Introduction
Ammonia in concentrations of the order of 1 ppm is produced by human and is a biological marker of pathological changes in human body, but concentrations of the order of 100 ppm, ammonia is toxic and hazardous. Among modern methods for detection of small concentrations of inorganic agents in liquids, indicator analysis and voltammetry methods are mostly often used. Classical adsorption sensors based on metal oxides, which have proven themselves in gas sensing, are widely presented [1-5]. To improve the sensitivity features of the adsorption-type device, structures with developed area can be used. Despite the high ratio of the surface area compared to volume of nanowires (NWs) and the pronounced conductivity features of quasi-1D structures compared to bulk materials, the adsorption properties of III–V NWs and their correlation with electrical characteristics are still very poorly studied [6–7]. Here we fabricate and study several ammonia sensors based on different III–V NWs to investigate potential of these nanostructures for sensory applications.

2. Synthesis and study of nanowires
Vertically oriented GaAs, GaN and GaP NWs were synthesized on (111) silicon substrates by molecular beam epitaxy, typical parameters and growth conditions are presented in previous works [8–10]. The synthesized structures were studied by scanning electron microscopy, and transferred to an auxiliary substrate for further characterization with Raman scattering spectroscopy. The results of the measurements are shown in Figure 1.
GaAs NWs have a length of about 25 μm and a cross section of 100–200 nm, and their Raman scattering spectra show modes that correspond to the zinc blende (ZB) GaAs crystal structure [11–12]. GaN NWs are about 6–8 μm long and 20–80 nm cross-section have sharp features in Raman spectra corresponding to the wurtzite structure [13]. Raman spectrum of self-catalyzed GaP NWs [14] (about 25 μm long and 150–250 nm cross-section) is well consistent with the results of the work which examined high crystal quality ZB GaP [15].

3. Sensor fabrication and ammonia detection
The NWs were separated from the growth substrate by ultrasonication in isopropanol, and transferred to the surface of a sensor platform with gold interdigital contacts (contact pitch of 5 and 10 μm) with subsequent annealing for sensor fabrication. The step–by–step protocol of sensor production is shown in the Figure 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 gold contacts; (a) – separation of NWs from the growth substrate by ultrasonication (b) – dispersion of NWs in isopropanol and transfer to the sensor platform, (c) – fabrication of sensor and formation of gold–NWs contacts by annealing, (d) – typical image of a III–V NW on Au interdigital contacts obtained by optical microscopy.
Gold–NWs contacts are found to be of the Schottky type, which is proven by the voltage–current characterization obtained using Keithley 2400. Also, 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. A schematic electrical diagram of a sensor based on III–V NWs is shown in Figure 3.

![Figure 3. Schematic electrical diagram of a sensor based on III–V NWs, drawn in accordance with a parallel equivalent circuit: 1 – the III-V NWs impedance; 2 – the electrochemical cell impedance, filled with a liquid sample; 3 – the experimental area with sensor and liquid medium; 4 – the impedance meter Z-500P.](image)

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 \( Z_{\Sigma} \) of the sensor for each \( i \)-th frequency of the voltage measuring signal can be calculated using the expression 1:

\[
\frac{1}{Z_{\Sigma}} = \frac{1}{(Z_{H,O})_i} + \frac{1}{(Z_{NWs})_i};
\]

(1)

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:

\[
Z_i = \operatorname{Re}(Z)_i + j \cdot \operatorname{Im}(Z)_i;
\]

(2)

\(Z_i\) is the impedance, \(\operatorname{Re}(Z)_i\) is the real component of the impedance, \(\operatorname{Im}(Z)_i\) is the imaginary, \(j = (-1)^{1/2}\). Then the expression for signal normalization, which consists in subtracting the contribution from the electrochemical cell from the sensor impedance formed between the interdigitated contacts can be represented in the form:

\[
\operatorname{Re}(Z_{NWs})_i = \frac{R}{R^2 + I^2}, \quad \operatorname{Im}(Z_{NWs})_i = \frac{I}{R^2 + I^2};
\]

(3)

where

\[
R = \left( \frac{\operatorname{Re}(Z)_i}{|Z_{\Sigma}|} - \frac{\operatorname{Re}(Z_{H,O})_i}{|Z_{H,O}|} \right), \quad I = \left( \frac{\operatorname{Im}(Z)_i}{|Z_{\Sigma}|} - \frac{\operatorname{Im}(Z_{H,O})_i}{|Z_{H,O}|} \right);
\]

(4)

In accordance with the above, Figure 4 shows the impedance spectra of the sensors based on III-V NWs in a comparative medium – distilled H\(_2\)O and in H\(_2\)O with the target adsorbate – NH\(_3\). In this paper, we designate the exposure time as an interval during which the sensor is exposed to liquid adsorbates before the measurement of the impedance spectrum begins. At the same time, the exposure of the comparative medium-water was carried out for about 1000 s, in order to achieve an equilibrium of the adsorption processes on the surface of the NWs.
4. Impedance spectra of the sensors based on: (a) – GaAs, (b) – GaN, (c) – GaP; Plots: black – in pure deionized H$_2$O with exposure time over 1000s.; red - spectrum in 100ppm NH$_3$ dissolved in distilled H$_2$O with adsorbate exposure time 30s.; blue – sensor impedance spectrum in 10ppm NH$_3$ dissolved in distilled H$_2$O with adsorbate exposure time 30s.

The GaAs NWs based sensor allowed us to qualitatively determine the presence of ammonia in distilled water followed by reduction of the imaginary part of the impedance over the entire range of voltage frequencies relative to the sensor impedance spectrum in the presence of distilled water. However, no restoration of the original electrical performance was observed. We assume that this may be due to the defective nature of the adsorption centers on the NWs and the degradation of the GaAs crystal surface, which together determines the capacitive nature of the GaAs NWs sensor and makes a significant contribution to the reactive component of the impedance. The optimal frequency range for working with GaAs sensors is 200 Hz–8 kHz, where the strongest separation of the impedance spectra corresponding to water and ammonia are observed.

GaN and GaP NWs demonstrated high chemical stability in liquid medium. The first demonstrated the possibility of reproducible ammonia detection with the restoration of the electrical characteristics of the sensor. In the presence of ammonia, an increase in the imaginary part of the sensor impedance was observed with the real part almost unchanged over the entire frequency range under consideration. The second sensor is suitable for quantitative detection of ammonia with reduction of the imaginary and real part of the impedance during adsorption of ammonia, with the restoration of the original electrical characteristics in water. In this case, the entire considered range of measuring frequencies is found suitable.

4. Conclusion
Here we fabricate and study ammonia sensory properties of the devices based on GaP, GaAs and GaN NWs in liquid medium. The signal normalization is proposed, which makes it possible to study
changes in the NWs conductivity due to the ammonia molecules adsorption on the NW sidewalls. Normalization consists in subtracting the electrochemical contribution of the liquid between the interdigitated contacts to the sensor impedance spectrum and allows us to evaluate the electrical properties of NW and their correlation with the adsorption properties.

The fabricated GaN- and GaP-based devices demonstrate ammonia detection limit lower than 10ppm in water. Conclusions are drawn about the biocompatibility of quasi-one-dimensional nanostructures of compounds III-V with respect to slightly alkaline media, which are close in concentration to those of humans.

We demonstrated an effective protocol for manufacturing sensors based on NWs III–V and showed the optimal frequencies for working with this type of sensor when using impedance engineering - as a way to control the effect of adsorption on the electrical properties of NWs in terms of sensitivity to ammonia.

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