Gallium phosphide nanowires for “biological concentrations” ammonia detection

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Abstract. Ammonia is widespread chemical compound found both in nature and in human body, and its detection is very important in biology and medicine as well as in environmental monitoring systems. This work is aimed at fabrication and study of precise, technological and relatively cheap ammonia sensors compatible with a liquid medium. Here we use GaP epitaxial nanowires (NWs) as adsorption elements capable of ammonia detection fabricated via a simple protocol. The device properties are studied in terms of change in sensor impedance spectrum upon presence of ammonia. Physical interpretation of the impedance spectra in the presence of water and ammonia is given. GaP-based device exhibit sufficient response to the ammonia presence with the detection limit lower than 2.5 ppm.

1. Introduction
Concentration of the order of 1 ppm of ammonia produced with human breath is the biological marker of pathological changes in body, while ammonia in concentrations of the order of 100 ppm is toxic and hazardous. Among modern methods for liquid probes analysis, voltammetry methods are mostly often used. Classical sensor devices based on metal oxides, which have proven themselves in gas sensing, are widely presented [1-3]. To improve the sensitivity features of the semiconductor based adsorption sensors, structures with developed area should be used. Despite the high ratio of the surface area to volume of epitaxial nanostructures 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 poorly studied. Here we fabricate and study several ammonia sensors based on GaP NWs to investigate potential of these nanostructures for sensory applications.

2. Synthesis and study of nanowires
Vertically oriented GaP NWs were synthesized on Si (111) substrates by molecular beam epitaxy, typical parameters and growth conditions can be found in previous reports [4]. The synthesized structures were studied by scanning electron microscopy (SEM), and transferred to an auxiliary substrate for further characterization with Raman scattering spectroscopy. The results of the measurements are shown in Figure 1.
Raman spectrum of the self–catalyzed GaP NWs (about 25 μm long and 150–250 nm cross–sections) is well consistent with the results of the work which examined high crystal quality ZB GaP [5]. All of the studied NWs exhibit faceted geometry governed by their high crystallinity typical for the epitaxial nanostructures and confirmed by the results of the Raman spectroscopy. High aspect ratio with the sub micrometer scale cross section make this NWs perfect candidates for investigation of the absorption capabilities due to sufficient surface area, while their length allows for deposition on substrates with interdigital contacts typically used in sensory applications.

3. Sensor fabrication
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, depending on the NWs length) with subsequent annealing for sensor fabrication. The step–by–step protocol of sensor production and typical image of NWs based sensors are shown in the Figure 2.

![Figure 2](image)

**Figure 2.** The step–by–step sensor fabrication protocol: (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.

The Figure 2 shows: 1 – as–synthesized vertical NWs, 2 – substrate, 3 – isopropyl alcohol, 4 – ultrasonic separation, 5 – diffusion system, 6 – sensor platform, 7 – gold interdigital contacts. The sensor platform with contacts were chosen in terms of minimizing parasitic capacitances and for GaP NWs a 10 μm contact pitch was selected. Gold–NWs contacts type are the Schottky type which was proven with volt–ampere characterization by Keithley 2400.

4. Ammonia detection
This section is devoted to study of ammonia sensors characteristics. The sensitivity (or response) of the sensors was studied in terms of change in the electrical impedance spectrum. To make the analysis straightforward, we first study spectrum of the sensors in a reference medium – distilled water, and then replace water with the solution of ammonia (2.5 and 25 ppm) – and documented the sensor impedance spectra. A typical spectrum of a sensor based on GaP NWs placed in a liquid medium and its physical interpretation are shown in Figure 3.
Following [6], we propose an approach for analysis of the sensor impedance spectra, having a typical shape shown in Figure 3. The spectrum has the following contributions: 1) contact resistance $R_D$ governed by the conductivity of the contact channels is a constant value for the sensor impedance spectra both in water and in ammonia solutions, interpolated with a circle corresponding to the RC circuit discussed below; 2) according to the model of the equivalent RC circuit, diameter of the circle corresponds to the resistance $R_{ct}$, related to the conductivity of the media between the contacts; 3) the diffusion region with the corresponding diffusion resistance $R_d$. The diffusion region of the spectrum lies in the low–frequency regime and is governed by the inertial electrochemical conductivity arising in the sensor, which occurs in the interdigital gap filled with liquid. We assume that two types of parallel processes occur simultaneously in the sensor immersed in a liquid medium – electrochemical conductivity and semiconductor conductivity. Each of the processes becomes more pronounced depending on the operating frequency and affect values of $R_{ct}$ and capacitance of the circuit. The impedance spectra of the sensors based on GaP in water and ammonia solutions are presented in Figure 4.

Analysis of the spectra shows that the discussed conductivities increase when water is replaced with a solution of ammonia. For the electrochemical liquid cell, an increase in the conductivity is associated with an increase in the ionic concentration in the electrolyte, while for the semiconductor contribution (higher frequencies), an increase in the conductivity is associated with the processes of surface hydration and protonation of NWs by OH and NH$_3$ molecules, respectively. By hydration,
we assume chemical reaction leading to the replacement of an electrically neutral surface oxygen atom with a negatively charged OH group followed by emergence of a conduction electron in NW. By protonation, we assume an energetically favorable reaction between the hydrated surface of the NW and the NH$_3$ molecule, which detaches a proton from the OH group becoming a positively charged NH$_4^+$ ion with the formation of another conduction electron in NW. The sum of the described processes leads to a decrease in the $R_{ct}$ value when ammonia appears in the analyzed medium. The difference in the value of $R_{ct}$ in water and ammonia solutions is proposed to be used to characterize the sensory properties of the device. We believe a decrease in the $R_{ct}$ value is due to fall of electrochemical resistance and insignificant contribution to the $R_{ct}$ resistance from the NWs. Thus, in terms of electrical conductivity: the conductivity of the sensor in a liquid medium is determined by the conductivity of the electrolyte between the electrodes and the conductivity of the NWs. The NWs conductivity has a significant contribution to the total conductivity of the sensor at high frequencies and in the presence of a poor electrolyte - water (a comparative medium). Immersion of the sensor in the analyzed ammonia solution leads to an increase in the contribution to the sensor conductivity from the electrolyte between the electrodes, since ammonia ions also begin to participate in electric current. Because of this, the contribution of the NWs to the sensor conductivity decreases. Thus, the presented type of sensors is excellent for the analysis of extremely low (close to biological) concentrations of ammonia in water. This case with GaP NWs fits completely into the concept presented in Figure 3, so we evaluated and presented in Figure 4 all the parameters introduced earlier.

5. Conclusion

Here we fabricate and study ammonia sensory properties of the devices based on GaP NWs which demonstrate ammonia detection limit lower than 2.5 ppm in water. The sensitivity to ammonia can be assessed by the divergence of the impedance spectra corresponding to water and ammonia, as well as the change in characteristic resistance $R_{ct}$. Biocompatibility of GaP nanostructures with respect to slightly alkaline media, which are close in concentration to those of humans are shown.

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