V_2O_5 nanofiber-based chemiresistors for ammonia detection

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Abstract. Vanadium pentoxide (V_2O_5) nanofibers with a cross-section of 15 nm^2 were obtained by self-assembly in aqueous solution. These fibers - the length of which can reach 10-15 μm - have been deposited as a thin network on interdigitated electrode structures with 10 μm electrode gap. Exposure to ammonia at room-temperature changes the conductance of the networks, which makes them useful as chemiresistors for gas-sensing applications. By evaluating the concentration dependence of the sensor response, we found that the gas adsorption follows the Langmuir adsorption isotherm.

INTRODUCTION

Classical metal oxide gas sensors have to be operated at elevated temperatures (typically above 250 °C) to achieve sufficient sensitivity [1]. In order to reduce the power consumption, it is desirable to develop gas sensors operating at room-temperature. Recently, advances have been achieved with nanosized materials, due to their large surface/volume ratio [2, 3, 4]. Although carbon-nanotubes could be used as gas sensors [3, 4], they have the disadvantage to be entangled in ropes of metallic and semiconducting tubes, decreasing the surface/volume ratio. Furthermore the conductivity is dominated by the metallic tubes, which are less sensitive to gases than the semiconducting tubes [4]. This encouraged us to investigate vanadium pentoxide (V_2O_5) nanofibers as sensor material, because each fiber shows an identical hopping like conductance [5, 6]. In addition the very large surface/volume ratio of these fibers is comparable to that of an isolated carbon nanotube.

EXPERIMENTAL

V_2O_5 nanofibers were prepared from 0.2 g ammonium(meta)vanadate (NH_4VO_3) and 2 g acidic ion exchange resin (DOWEX 50WX8-100) in 40 ml water, as described previously [5]. Due to a polycondensation process, fibers are formed as an orange colored gel. In order to obtain fibers with a mean length exceeding 5 μm, the solution was aged for several weeks under ambient conditions.

Interdigitated electrode structures with 50 fingers, a separation of 10 μm, and an overlap of 1800 μm were fabricated by optical lithography. The structure was amino-

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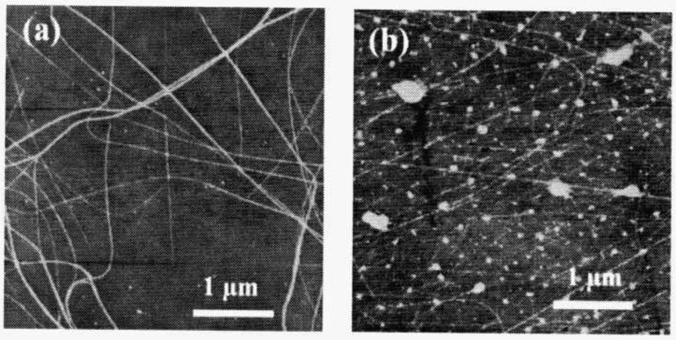

FIGURE 1. Scanning Force Microscopy image of (a) unmodified and (b) with 1 nm gold modified V_2O_5 network.

silanized (using N-[3-(Trimethoxysilyl)propyl]ethylenediamine) prior to dip coating with a 1:10-diluted V_2O_5 solution. Figure 1a shows a typical scanning force microscopy image of these networks, whereas Figure 1b displays a network, modified by evaporating 1 nm gold on top.

The resistances of the networks are on the order of 10 kΩ and were monitored as a function of time in the constant current mode, with the current adjusted to obtain ~100 mV prior gas exposure. Sensors were placed within a teflon cell and a constant gas-flow of 0.4 l/min was supplied by a mass flow system, that also generated the appropriate gas-concentrations. Ammonia was obtained from a gas cylinder containing 1% of the test gas in nitrogen. All experiment were performed under dry conditions at room-temperature, in each case involving three steps: an equilibration time (0-1 min), an exposure phase (1-3 min) and a recovery period (3-8 min).

RESULTS AND DISCUSSION

Figure 2a shows the response $\Delta R/R_{ini}$ (change of resistance ΔR, normalized to initial resistance R_{ini}) of an unmodified V_2O_5 network, when exposed to various concentrations of ammonia. A fast resistance drop over a time scale of ~1 min is observed. In addition, the recovery occurs in less than 5 min. The high sensitivity with a detection limit below 5 ppm and the reversibility at room-temperature, make this material a promising candidate for sensor applications.

It was found that metal evaporation improves the performance of the sensors. For that purpose, nominally 1 nm of gold was evaporated onto the same network, which resulted in clusters of various sizes, as can be seen in the scanning force microscope image of Figure 1b. The response of the sensor was measured prior and after the modification to various concentrations of ammonia, revealing a sensitivity increase by a factor of 7 (at 100 ppm NH_3).

Figure 2b compares the traces of the unmodified (dashed line) and the modified (solid line) sensor in the case of 100 ppm ammonia exposure. Obviously the improved

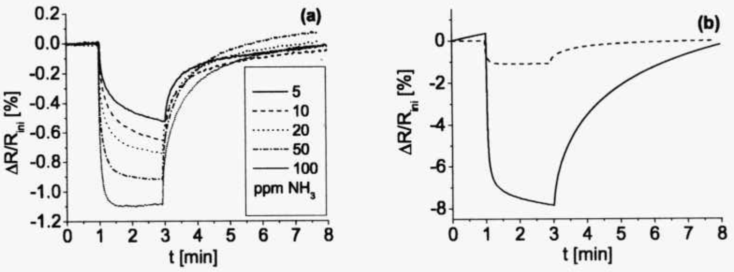

FIGURE 2. (a) Response of an unmodified V_2O_5 sensor to various concentrations of ammonia. (b) Comparison of responses of an unmodified (dashed line) and a gold modified (solid line) V_2O_5 sensor, when exposed to 100 ppm of ammonia.

sensitivity has the disadvantage of an increase in recovery time. For applications, one defines the t_{90}-time, as the time needed to give either 90 % of the response in the case of adsorption or a 90 % recovery in the case of desorption. For an exposure to 100 ppm ammonia, we obtain recovery-values for t_{90} of 100 s and 180 s for the unmodified and the modified V_2O_5 network, respectively. Both, the increased response and the slower recovery indicate a stronger interaction of ammonia with the gold-nanoparticle/V_2O_5-system, compared to the non-modified sample.

To shine more light onto the gas-nanofiber interaction, we analyzed the sensor response measured as a function of the gas-concentration c. Assuming, that the response $\Delta R/R_{ini}$ is proportional to the gas coverage θ on the nanofibers, we can apply the Langmuir adsorption isotherm [7]:

$$\theta_c = \frac{K \cdot c}{1 + K \cdot c}, \tag{1}$$

where θ_c is the gas-dependent coverage ($0 \leq \theta_c \leq 1$), and K is the binding constant. It is noted that after the exposure time, the sensor response did not fully reach its equilibrium. This is especially true for the lower ammonia concentrations. Nevertheless, Figure 3 shows reasonable agreement between the experimental results (symbols) and the Langmuir fits (lines), for both undoped (triangles) and gold nanoparticle doped (squares) V_2O_5 sensors.

In addition, the observed deviation from ideal Langmuir adsorption behavior can be explained by the presence of different adsorption sites, such as the electrode-fiber contact, on the fiber or on fiber-fiber interconnects.

CONCLUSIONS

V_2O_5 nanofiber networks show a high sensitivity to ammonia at room-temperature. This sensitivity can be improved via the deposition of gold-clusters.

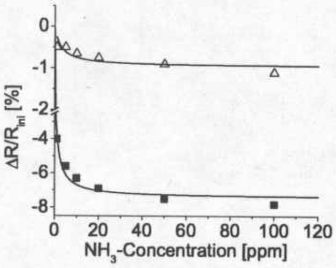

FIGURE 3. Response of unmodified (triangles) and modified (squares) V_2O_5 network as a function of ammonia-concentration. The solid lines correspond to the Langmuir fits.

The observed resistance decrease is in accordance with the known electron donor property of ammonia and the n-type semiconducting behaviour of V_2O_5 [6]. On this basis, we currently assume that the ammonia predominantly interacts with the gold nanoparticles and changes the conductivity in the underlying V_2O_5 fibers. However, further investigations are required to clarify by which extent the gold particles enhance the e^- transfer from the NH_3 to V_2O_5.

In future experiments, our goal is to achieve a higher selectivity by specific doping, similar to what has been demonstrated for carbon nanotube sensors, where palladium modification introduces a high selectivity to hydrogen [4].

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