Gas sensor device based on a SnO_2 nanowire network for increased sensing performance

Elise Brunet, Giorgio C. Mutinati, Stephan Steinhauer, Anton Koeck

AIT Austrian Institute of Technology GmbH, Health & Environment Department, Molecular Diagnostics, Donau-City-Street 1, 1220 Vienna, elise.brunet.fl@ait.ac.at

ABSTRACT

The employment of nanowires is a very powerful strategy to improve gas sensor performance. We demonstrate a gas sensor device, which is based on a suspended network of ultralong tin dioxide (SnO_2) nanowires on silicon. The nanowire network exhibits a very high surface-to-volume ratio and provides full access of the target gas to the nanowires. After annealing of two SnO_2 thin film coated Si-wafers glued side by side separated by a gap of ~200µm ultralong SnO_2 nanowires grow from one chip to the other establishing an electrical contact between the two chips. The SnO_2 nanowire network device is able to detect a hydrogen (H_2) concentration of only 20ppm in synthetic air with ~60% relative humidity at room temperature. At an operating temperature of 300°C a concentration of 50ppm H_2 results in a sensitivity of 5%. At this elevated temperature the sensor shows a linear response in a concentration range between 10ppm and 100ppm H_2, which enables a quantitative detection of H_2.

Keywords: gas sensor, tin oxide, nanowires, H_2 sensing

1 INTRODUCTION

Gas sensors have applications in various fields ranging from industrial process control and personal safety to environmental monitoring. Early and reliable diagnosis of diseases, air quality monitoring in heating, ventilating and air conditioning (HVAC), or alert systems for carbon monoxide in household heating systems are examples of applications requiring reliable, compact and efficient gas sensors systems. Metal oxide gas sensors are established devices, which rely on changes of electrical conductance due to the interaction with gas molecules.

The implementation of very thin nanocrystalline films or single crystalline nanowires, which have a high surface-to-volume ratio and thus a strong interaction with the surrounding gases, is a very powerful strategy to improve gas sensor performance. As SnO_2 has been the most prominent sensing material, a major focus has been put on the implementation of SnO_2 thin films and a variety of gas sensor devices has been realized [1–4]. Also numerous gas sensors based on SnO_2 nanobelts and nanowires as sensing elements have been reported so far [5–8]. We have developed nanocrystalline SnO_2 thin film and single crystalline SnO_2 nanowire sensors, which can detect concentrations of toxic gases, such as CO, SO_2 and H_2S in the low ppm region [10–11]. In order to optimize the performance of gas sensing devices, we have recently compared the characteristics of SnO_2 thin film and SnO_2 nanowire sensors for 6 different target gases [13]. Here we present a novel gas sensor device based on a network of ultralong SnO_2 nanowires, which is able to detect the highly explosive gas H_2 at room temperature operation.

2 GAS SENSOR FABRICATION

The network of SnO_2 nanowires is fabricated in a two-step procedure: deposition of nanocrystalline SnO_2 thin films and subsequent annealing for growing the single crystalline nanowires.

First nanocrystalline SnO_2 films are fabricated by a spray pyrolysis process. The experimental setup, shown in Figure 1, consists of a hot plate and a spray setup with an automatic air atomizing nozzle (QuickMist 1/4QMJAU-NC + SUQF-130, Spraying Systems Co.), which is positioned on the side of the hot plate allowing the atomized spray to flow parallel to the surface. Si-wafers with a 50 nm-thick SiO_2-layer on top are coated by sputtering with a 40 nm-thick Cu-layer. The wafers are placed on a hotplate at ~500°C and the thin Cu layer is oxidized to CuO. A 0.28 M solution of tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) in ethyl acetate is sprayed on the substrates on the hot plate. A SnO_2 film is formed with a thickness in the range of 200-300 nm.

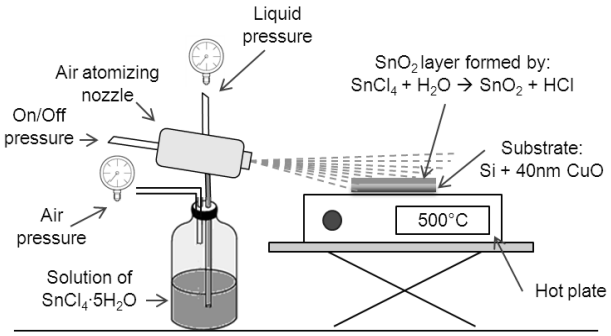

Figure 1: Scheme of the experimental setup for spray pyrolysis.

The SnO_2 thin film coated wafer is cleaved and the two pieces are carefully glued on a substrate base separated by a

gap of ~200 µm. After annealing in Ar atmosphere for 1 hour at ~900°C, ultralong SnO_2 nanowires grow from one chip to the other, bridge the gap between the two wafer pieces and thus electrically connect the chips (Figure 2). The network of SnO_2 nanowires forms a "chip-to-chip" gas sensor with many SnO_2 nanowires connected in parallel.

The processed samples are glued on micro-heater elements (10×2 PT 6.8–0.4, Delta-R GmbH) combined with a thermocouple (4×1 Pt100B, Delta-R GmbH), which are mounted onto a ceramic chip carrier. This allows for heating the sensors up to a temperature of 450°C and simultaneously for precise temperature control.

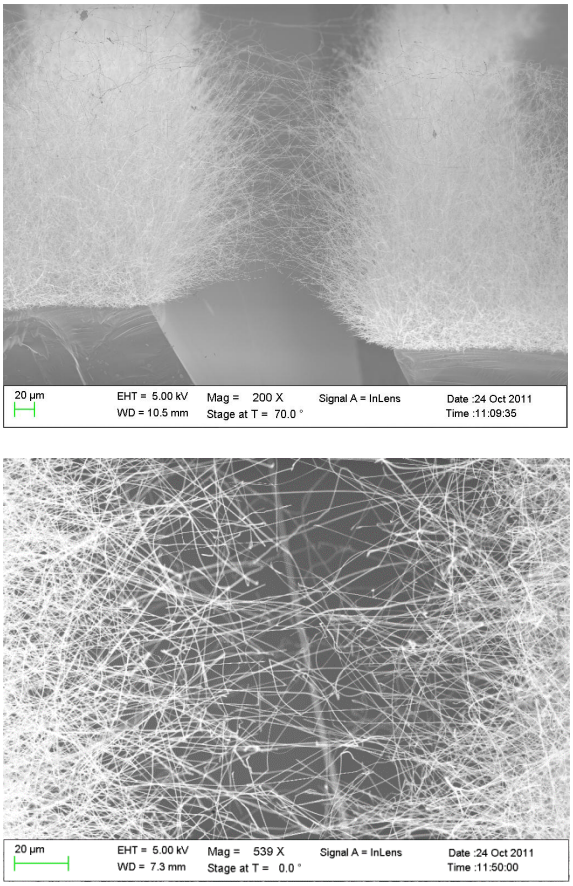

Figure 2: SEM image of the Si-chips bridged by the synthesized SnO_2-nanowire network. Due to cleavage and the crystalline orientation the opposite facets of the Si chip are parallel, but not vertical (top). SEM image of interconnected nanowires forming the network (bottom).

In a next step Ti−Au contact pads (200 nm thickness) have been evaporated on both chips by employing a shadow mask. The pads provide contact to many of the nanowires as well as to the residual SnO_2 layer, which has not been converted to single crystalline nanowires during the annealing process. The sensors are finally bonded to the chip carrier, as schematically shown in Figure 3.

Sensing performance of the single crystalline SnO_2 nanowire network is investigated in an automated measurement setup, which allows precise adjustment of the gaseous environment. Synthetic air (Linde Gas 80% N_2, 20% O_2) is used in all sensing experiments as background gas monitored by a mass flow controller. The synthetic air can be moisturized up to 95% by a bypass flow, which is bubbled through a sequence of water containers and mixed with the dried flow. The percentage of bypass flow and thus humidity is controlled by an additional mass flow controller, while a standard humidity transmitter (KOBOLD Messring GmbH, type AFK-E) is used in order to monitor humidity. The test gas (Linde Gas) is a ready-made mixture of H_2 (294 ppm) in nitrogen, which is mixed to the background gas in a gas mixing vessel. The total flow of background gas and test gas is held constant at 1000 sccm. The measurement is performed as follows: 15 min after the sensor has reached the desired operating temperature in synthetic air the test gas flow is turned on for 5 min and then turned off for 10 min. This sequence is repeated three times at each operating temperature in order to investigate the reproducibility of the gas detection.

Sensor response to H_2 is detected by applying a constant DC-current of 2 µA to the nanowire network sensor and by measuring the voltage drop. The sensor response results from the change of electrical resistance due to the presence of the test gas (here H_2). The response S_{gas} (or sensitivity) of the sensor is calculated from:

$$S_{gas} = \frac{R_{air} - R_{gas}}{R_{air}} \qquad (2)$$

where R_{air} is the sensor resistance in pure synthetic air and R_{gas} the sensor resistance in the presence of the test gas. Response and recovery times are defined as the time necessary for the sensor to reach 90% of the final resistance value during gas exposure and at the end of gas exposure, respectively.

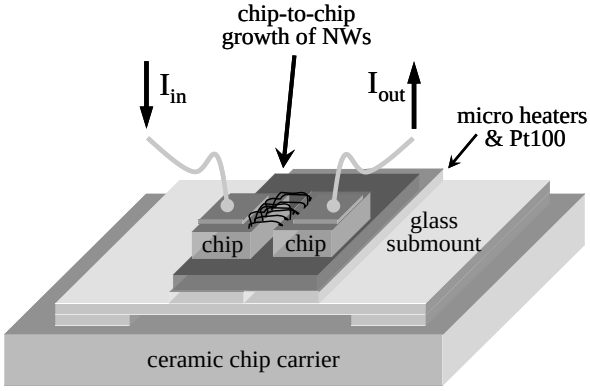

Figure 3: Schematic setup of the gas sensor based on a SnO_2 nanowire network. The nanowires bridge and electrically connect two Si-chips which are separated by a gap of ~ 200µm as result of cleavage.

3 RESULTS

Figure 4 shows the sensor resistance to increasing concentrations of H_2 between 10 and 100 ppm at 300°C in dry synthetic air. We can see that the change of resistance increases with increasing H_2 concentrations. In Figure 5 we plot the sensor response (or sensitivity) in function of H_2 concentration and observe a linear behavior of the sensor response with increasing concentrations, which enables a quantitative detection of H_2 for concentrations at least up to 100 ppm. However, the response time is rather long and after 5 minutes (duration of the H_2 flow pulses) the sensor resistance has obviously not reached saturation yet. Recovery times are relatively long as well (>10 min).

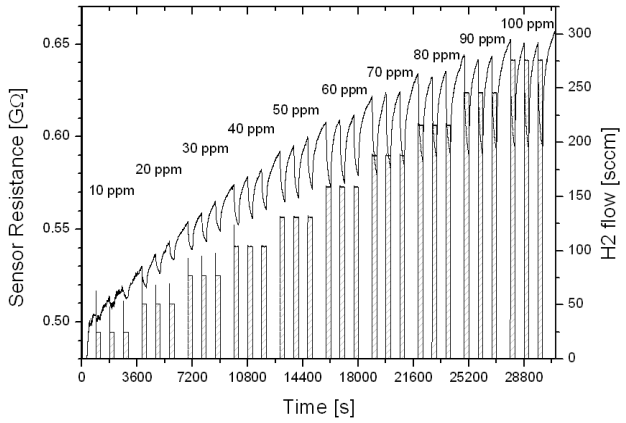

Figure 4: Resistance of the nanowire network sensor to increasing concentrations of H_2 at 300°C in dry synthetic air.

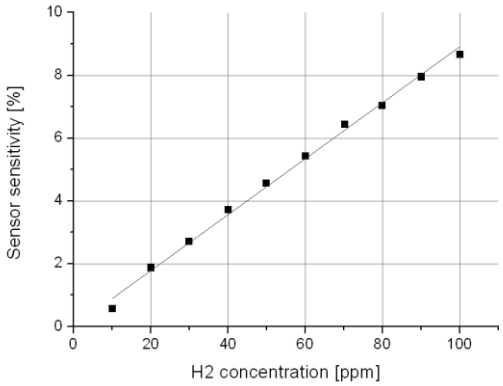

Figure 5: The sensitivity of the nanowire network sensor is linear to H_2 concentrations.

In order to simulate more practical environmental conditions, the sensor response to H_2 was measured when using humid synthetic air as background gas in a range between 7% and 64% relative humidity (rH). At room temperature the sensor starts to detect H_2 at relative humidity above ~ 20%, where the response increases with increasing humidity. Figure 6 shows the gas sensor response to H_2 concentrations of 20 ppm, 40 ppm, and 60 ppm at room temperature, when measured in synthetic air with ~60% relative humidity. In contrast to the measurement at 300°C operating temperature the resistance of the nanowires is increased in presence of H_2.

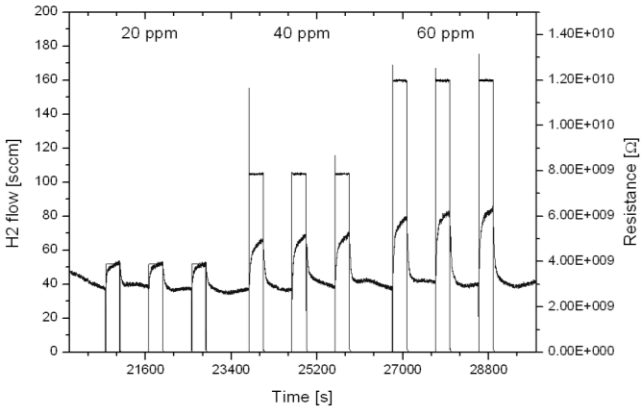

Figure 6: Resistance of the gas sensor device to H_2 concentrations of 20 ppm, 40 ppm, and 60 ppm at room temperature when synthetic air with ~60% rH is used as background gas.

4 DISCUSSION

The results demonstrate a high sensitivity of the SnO_2 nanowire network sensor to H_2 in particular in humid environment conditions. The linear bahavior of the sensor response with the gas concentration at room temperature and in humid environment (see Figure 6) demonstrates that a quantitative detection of H_2 should be possible at least up to 100 ppm. The high sensitivity of the SnO_2 nanowire network can be explained by the chip-to-chip sensor configuration, where the network of SnO_2 nanowires bridges the gap between the two chips and exhibits a huge surface-to-volume ratio. Consequently, the nanowires are completely surrounded by the gas, which is basically an ideal gas sensor configuration. Moreover, the network is composed of hundreds of nanowires, which have different diameters between 30 nm and 300 nm. The variation of the nanowire diameters might be an advantage for a more defined response at higher gas concentrations as compared to SnO_2 ultrathin film, where saturation can occur at low levels of concentration. We have found that the sensor response of SnO_2 thin films first increases with increasing gas concentration, but starts to saturate at higher concentrations [11]. In case of the nanowire network a low gas concentration might be sufficient to saturate the nanowires with smaller diameter, while the thicker nanowires still exhibit a linear response. Thus the chip-to-chip nanowire network sensor should exhibit a larger dynamic range. This will be investigated in detail employing test gases with higher concentration.

5 CONCLUSION

We have realized a novel gas sensor device, which is based on "chip-to-chip" synthesized ultralong SnO_2 nanowires. The SnO_2 nanowire fabrication procedure is performed at atmospheric pressure, requires no vacuum and allows upscale of the possible substrate to wafer size. The SnO_2 nanowire device is able to detect humidity and a H_2 concentration of only 20 ppm in synthetic air with 60% relative humidity at room temperature. At an operating temperature of 300°C a concentration of 50 ppm H_2 results in a sensitivity of 5%. At this elevated temperature the sensor shows a linear response in a concentration range between 10 ppm and 100 ppm H_2, which should enable a quantitative detection of H_2 at least up to 100 ppm.

6 ACKNOWLEDGEMENT

This work was partly funded by the FFG-Austrian Research Promotion Agency within the MNT-Eranet project "NanoSmart" (No. 828691) and the WWTF Vienna Science and Technology Fund within the project "Mathematics and Nanosensors" (No. MA09-028).

REFERENCES

[1] H. Meixner et al., Thin-film gas sensors based on semiconducting metal oxides, Sens. Actuators B 23, 119–125, 1995.

[2] G. Korotcenkov, Metal oxides for solid-state gas sensors: what determines our choice? Mater. Sci. Eng. B 139 1–23, 2007.

[3] C. Wang et al., Metal oxide gas sensors: sensitivity and influencing factors, Sensors 10, 2088–2106, 2010.

[4] D. Zhou et al., p-Type metal oxide doped SnO2 thin films for H_2S detection, Sens. Lett. 9, 651–654, 2011.

[5] E. Comini et al., Stable and high-sensitive gas sensors based on semiconducting oxide nanobelts, Appl. Phys. Lett. 81, 1869–1871, 2002.

[6] A. Kolmakov et al., Enhanced gas sensing by individual SnO_2 nanowires and nanobelts functionalized with Pd catalyst particles, Nano Lett. 5, 667–673, 2005.

[7] F. Hernández-Ramírez et al., High response and stability in CO and humidity measures using a single SnO_2 nanowire, Sens. Actuators B 121, 3–17, 2007.

[8] Y.-J. Choi et al., Novel fabrication of an SnO_2 nanowire gas sensor with high sensitivity, Nanotechnology 19, 095508, 2008.

[9] B. Wang, L. F. Zhu, Y. H. Yang, N. S. Xu, G. W. Yang, "Fabrication of a SnO_2 Nanowire Gas Sensor and Sensor Performance for Hydrogen", J. Phys. Chem. C 112, 6643-6647, 2008.

[10] L. V. Thong, N. D. Hoa, D. T. T. Le, D. T. Viet, P. D. Tam, A.-T. Le, N. Van Hieu, "On-chip fabrication of SnO_2-nanowire gas sensor: The effect of growth time on sensor performance", Sens. Act. B 146, 361–367, 2010.

[11] A. Tischner et al., Ultrathin SnO_2 gas sensors fabricated by spray pyrolysis for the detection of humidity and carbon monoxide, Sens. Actuators B 134, 796–802, 2008.

[12] A. Köck et al., Atmospheric pressure fabrication of SnO_2-nanowires for highly sensitive CO and CH4 detection, Sens. Actuators B 138, 160–167, 2009.

[13] E. Brunet et al., Comparison of the gas sensing performance of SnO_2 thin film and SnO_2 nanowire Sensors, Sens. Actuators B 165, 110–118, 2012.