

Tin Oxide Nanowire Sensors for Highly Sensitive Detection of Toxic Gases

E. Brunet, C. Griessler, T. Maier, G. Mutinati, S. Steinhauer and A. Koeck

AIT Austrian Institute of Technology GmbH, Vienna 1220, Austria, elise.brunet.fl@ait.ac.at

ABSTRACT

This paper presents the gas sensing performance of nanosensors based on SnO₂-nanowires towards the toxic gases SO₂ and H₂S. The nanowires are synthesized in a two-step atmospheric pressure process: first nanocrystalline SnO₂-films (thickness of ~200 nm) are fabricated by a spray pyrolysis process then the films are annealed at 900°C. The electrical resistance of the nanosensor is first decreased in the presence of 26.8 ppm SO₂ and above 350°C it is increased; the highest signal of ~8% is obtained at 400°C. In the presence of 1.4 ppm H₂S, the nanosensor resistance is first increased, then above 300°C it is decreased; the signal reaches 30% at 400°C. This very high sensor signal demonstrates extraordinary sensitivity of the nanowire sensors with a resolution in the ppb range – well below the threshold limit values of 2 ppm for SO₂ and 10 ppm for H₂S. The different behavior (increase and decrease of sensor resistance) should basically allow for a clear discrimination between the two toxic gases.

Keywords: nanosensors, gas sensors, tin dioxide nanowire, toxic gases

1 INTRODUCTION

Numerous applications ranging from industrial process control to personal safety systems and environmental monitoring have a strongly increasing demand for highly sensitive gas detecting equipment. Metal oxide based gas sensors, which rely on changes of electrical conductance due to the interaction with the gas molecules, have been particularly developed over the years.

Many different gas detecting devices based on nanowires as sensing probes have been demonstrated so far [1-4], where the materials are ranging from metal oxides and semiconductors to carbon nanotubes, metals, and polymers [5-12]. As SnO₂ has been the most prominent sensing material, a major focus has been put on implementation of SnO₂ nanobelts and nanowires as sensing probes. The detection of several toxic gases such as CO, NO₂ and H₂S has already been achieved [13-15]. Recently we have reported on SnO₂-nanowire sensors for CO and CH₄ detection [16].

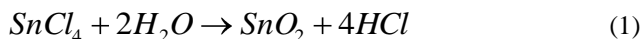
Sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) are two highly toxic gases, whose threshold limit values are 2 ppm for SO₂ and 10 ppm for H₂S. The largest sources of SO₂ emissions are from fossil fuel combustion at power plants and other industrial facilities. SO₂ is linked with a number of adverse effects on the respiratory system. H₂S is

also produced by industrial activities, such as petroleum/natural gas drilling and refining, wastewater treatment, etc. H₂S is both an irritant and a chemical asphyxiant with effects on both oxygen utilization and the central nervous system.

In this paper we present nanosensors based on SnO₂-nanowires, which are extremely sensitive to the highly toxic gases SO₂ and H₂S.

2 EXPERIMENTAL SETUP

The SnO₂-nanowires are realized in a two-step procedure. First nanocrystalline SnO₂-films are fabricated by a spray pyrolysis process. A 0.28 M solution of tin chloride pentahydrate (SnCl₄·5H₂O) and ethyl acetate is sprayed on the substrates, which are placed on a hotplate at a temperature of ~450°C. The substrates are Si-wafers with a 50 nm-thick SiO₂-layer on top, which are coated with a 40 nm-thick Cu-layer. The experimental setup, shown in figure 1, consists of a hot plate and a siphon-fed spray setup with an air atomizing spray nozzle (QuickMistQMJML, Spraying Systems Co.), which is positioned on the side of the hot plate allowing the atomized spray to flow parallel to the surface. N₂ with a pressure of 0.8 bar is used as carrier gas; a siphon height of 10 cm results in a solution flow rate of 10 ml/min. The SnO₂-film thickness lies between 150 and 250 nm. The deposition process is run in ambient air. Tin dioxide is formed according to:



Subsequently the SnO₂-coated samples are tempered in Ar-atmosphere at 900°C for 1h, which results in the growth of single-crystalline SnO₂-nanowires with diameters of 30 to 400 nm and lengths up to several 100 µm. The samples with surface-grown nanowires are sonicated in isopropanol to remove the nanowires from the surface and to form a nanowire-in-isopropanol solution, which is then spin-coated on Si-wafers with a 300 nm-thick SiO₂-layer on top, so that SnO₂-nanowires are approximately uniformly distributed on the substrate. The last process step is the evaporation of Ti-Au contact pads (thickness of ~ 200 nm) in a regular arrangement.

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 thermally insulated onto a ceramic chip carrier. This allows for heating the sensors up to a temperature of 450°C and simultaneously for precise temperature control. The sensors are finally bonded to the chip carrier.

Sensing performance of the single-crystalline SnO₂-nanowires is investigated in an automated measurement setup, which allows precise adjustment of the gaseous environment. Synthetic air (Linde Gas 20% O₂, 80% N₂) is used in all sensing experiments as background gas monitored by a mass flow controller. The test gases (Linde Gas) are ready-made mixtures of SO₂ (997 ppm) and H₂S (52.2 ppm) in nitrogen. They are 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. Sensor response to SO₂ and H₂S is detected by applying a constant DC-current of 2 μA to a single sensor element and by measuring the voltage drop. The electrical resistance – calculated by Ohm’s law – is defined as the sensor response.

The resistance of our nanowire sensor is measured at operating temperatures of 200°C, 250°C, 300°C, 350°C and 400°C, when exposed successively to the test gases SO₂ and H₂S. Once the sensor has reached the operating temperature in synthetic air, the test gas flow is turned on during 5 min and then turned off during 10 min. This sequence is repeated three times at each operating temperature in order to show the reproducibility of the gas detection.

The sensor sensitivity *S* towards a test gas is calculated according to:

$$S_{gas} = \frac{R_{air} - R_{gas}}{R_{air}} \times 100\% \quad (2)$$

where *R*_{air} is the sensor resistance in synthetic air and *R*_{gas} the sensor resistance in the presence of the test gas.

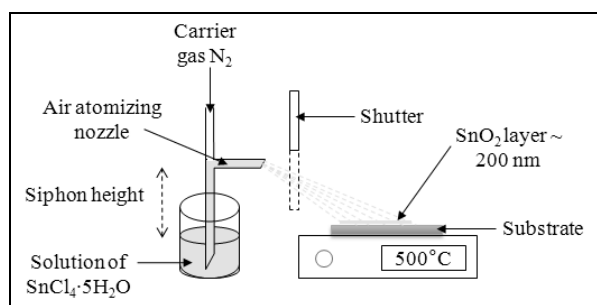


Figure 1: Setup of spray pyrolysis process.

3 RESULTS

Figure 2 shows a SEM image of a SnO₂-nanowire on a SiO₂/Si substrate contacted by two Au-Ti electrodes, thus building our gas sensor. The nanowire is 54 μm long (distance along the nanowire between the two electrodes) and has a diameter of 220 nm.

The I-V characteristic of this nanowire has been measured at room temperature (figure 3). The characteristic is linear, which demonstrates the ohmic nature of the contacts between the electrodes and the SnO₂-nanowire.

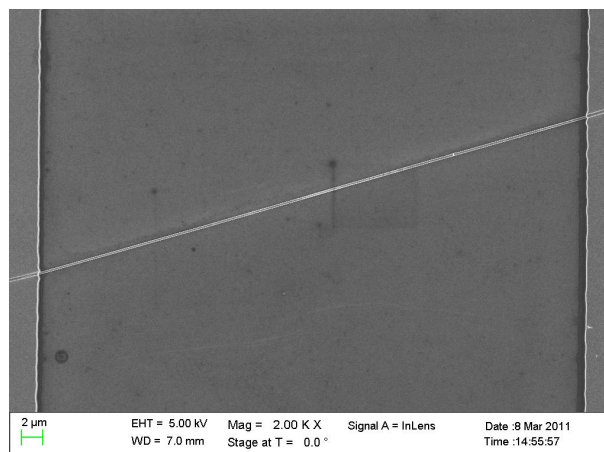


Figure 2: SEM image of a SnO₂-nanowire between two electrodes building a gas sensor.

Figure 4 shows the sensor resistance in the presence of 26.8 ppm SO₂. The detection of SO₂ is already visible at a temperature of 200°C. However, the signal is much higher at 250°C and 300°C, where a neat decrease of resistance can be observed in the presence of SO₂. After the gas flow has been turned off, the sensor signal recovers although a visible drift at temperatures below 400°C. At 350°C, the sensor response is not well defined, but at 400°C an increase of the electrical resistance is clearly noticed, when SO₂ is introduced into the measurement chamber. The maximum sensitivity of 8% is reached at 400°C operating temperature.

Figure 5 shows the sensor resistance in the presence of 1.4 ppm H₂S. The nanowire sensor detects already the toxic gas at a temperature of 200°C. It is very interesting to notice that the sensor resistance is decreased in the presence of H₂S at each operating temperatures between 200°C and 400°C, except at 250°C. Indeed, at 250°C the sensor resistance is clearly increased during the detection of H₂S. The highest sensor signal is obtained at 400°C, where the sensitivity to only 1.4 ppm H₂S reaches 30%.

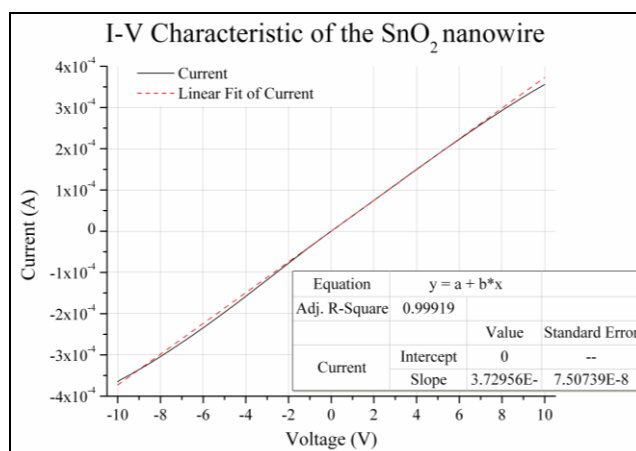


Figure 3: I-V Characteristic of the SnO₂ nanowire.

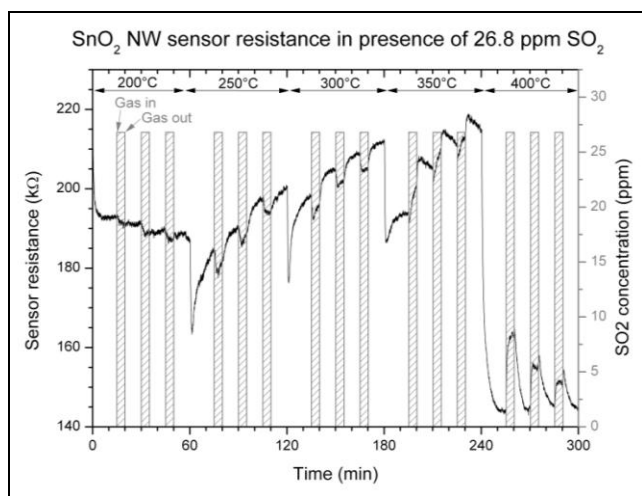


Figure 4: Sensor resistance at 200°C, 350°C, 300°C, 350°C and 400°C when exposed to a 26.8 ppm SO₂.

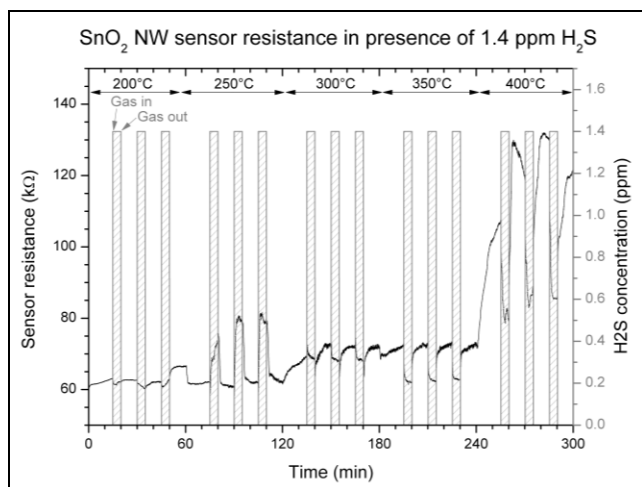


Figure 5: Sensor resistance at 200°C, 350°C, 300°C, 350°C and 400°C when exposed to 26.8 ppm H₂S.

4 DISCUSSION AND OUTLOOK

The results demonstrate a very high sensitivity of the SnO₂-nanowire sensor with a resolution in the ppb range, which is well below the threshold limit values of 2 ppm for SO₂ and 10 ppm for H₂S.

The two gases SO₂ and H₂S are reducing gases, which means that electrons shall be transferred from the gas molecule to the SnO₂ material during the chemisorption of the gas at the SnO₂ surface, thus increasing the sensor conductivity and decreasing the resistance. The signal inversion observed at 400°C for SO₂ and at 250°C for H₂S, where the sensor resistance is increased, is therefore unexpected.

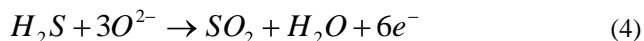
Bukun et al. reported that SO₂ chemisorption on SnO₂ can actually proceed in two forms: donor and acceptor chemisorption [17]. They presented thermodesorption spectra in order to identify the SO₂ sorption species. In

particular, two large peaks around 200°C and 400°C are attributed to a donor and an acceptor, respectively. This theory of two different kinds of sorption species is an interesting approach for the interpretation of our results. The decreasing sensor signal observed between 200°C and 300°C may be due to the chemisorption of donor species, which contribute to the increase of the sensor conductivity. The increasing signal at 400°C may be the consequence of the chemisorption of acceptor species, which decreases the sensor conductivity.

No similar study has been found in the literature to explain the behavior observed for the detection of H₂S. However, consideration of surface reactions is surely the key for the understanding of such phenomena. It has already been reported [18] that surface reactions of SnO₂ with H₂S and SO₂ lead to unreversible transformation of the metal oxide into sulfides at temperature above 200°C:



As reported by Malyshev et al., H₂S gas molecules react also with oxygen species, which are chemisorbed on the SnO₂ surface, according to:



This reaction results in the release of electrons in the metal oxide lattice and thus the conductivity of the sensor is increased. Those equations show the complexity of the surface reactions and further investigation is required.

However, this signal inversion may be used for a selective detection of the two toxic gases. Indeed, if the sensor signal shows an increase of resistance at 400°C, the gas detected shall be SO₂ and if an increase of resistance is observed at 250°C, it shall be due to the presence of H₂S.

A main advantage of our nanowire sensor device is the simple and low cost production process. The fabrication of the SnO₂-nanowires by spray pyrolysis and subsequent tempering requires no vacuum. With the present experimental setup utilizing a single spray nozzle a sample size of about 4×4 cm² can be coated homogeneously with the nanocrystalline SnO₂-film. The subsequent fabrication process requires only one photolithographic step for the metal contacts.

Further development of the present SnO₂-nanowire sensor to a real-world device is focused on improvement of sensor selectivity and on specific control of nanowire growth. Both issues will be tackled by means of our fabrication technology. The spray pyrolysis process in particular offers a comparable simple way to modify the chemical composition of the nanocrystalline SnO₂-layers by adding chemicals to the spray solution. This should result in a shift of nanowire material composition which should have considerable influence on sensor selectivity. This approach as well as controlled surface doping are presently investigated in detail.

5 CONCLUSION

We presented the gas sensing performance of nanosensors based on SnO₂-nanowires towards the toxic gases SO₂ and H₂S. The fabrication process of the SnO₂-nanowires by spray pyrolysis and subsequent tempering is simple and requires no vacuum. The nanowire sensor studied consists in a single nanowire (54 μm long and 220 nm of diameter) contacted by two metallic electrodes. The contacts established are ohmic as demonstrated by the linear I-V characteristic. In the presence of 26.8 ppm SO₂, a sensor signal of ~8% is obtained at 400°C. In the presence of 1.4 ppm H₂S, the sensor signal reaches 30% at 400°C. This very high sensor signal demonstrates extraordinary sensitivity of the nanowire sensors with a resolution in the ppb range – well below the threshold limit values of 2 ppm for SO₂ and 10 ppm for H₂S. The sensor shows a strong temperature dependence and even a signal inversion (increase of the electrical resistance) for SO₂ at 400°C and for H₂S at 250°C, which enables a certain degree of selective detection for the two gases.

REFERENCES

- [1] Y. Cui, Q. Wei, H. Park, C. Lieber, *Science* 293, 1289–1292, 2001.
- [2] Z. W. Pan, Z. R. Dai, Z. L. Wang, *Science* 291, 1947–1949, 2001.
- [3] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, Z. L. Wang, *Appl. Phys. Lett.* 81, 1869–1871, 2002.
- [4] L. Samuelson, *Materials Today* 6, 22–31, 2003.
- [5] B. Murray, E. Walter, R. Penner, *Nano Letters* 4, 665–670, 2004.
- [6] D. Zhang, Z. Liu, C. Li, T. Tang, X. Liu, S. Han, B. Lei, C. Zhou, *Nano Letters* 4, 1919–1924, 2004.
- [7] F. Patolsky; C. M. Lieber, *Materials Today* 8, 20–28, 2005.
- [8] A. Kolmakov, D. Klenov, Y. Lilach, S. Stemmer, M. Moskovits, *Nano Letters* 5, 667–673, 2005.
- [9] A. Ponzoni, E. Comini, G. Sberveglieri, J. Zhou, S. Deng, N. Xu, Y. Ding, Z. L. Wang, *Appl. Phys. Lett.* 88, 203101, 2006.
- [10] U. Yogeswaran, S.-M Chen, *Sensors* 8, 290–313, 2008.
- [11] I. Hwang, J. Choi, S. Kim, K. Dong, J. Kwon, B. Ju, J. Lee, *Sens. Act. B* 142, 105–110, 2009.
- [12] L. Xu, B. Dong, Y. Wang, X. Bai, Q. Liu, H. Song, *Sens. Act. B* 147, 531–538, 2010.
- [13] X. Kong, Y. Li, *Sens. Act. B* 105, 449–453, 2005.
- [14] C. Yu, Q. Hao, S. Saha, L. Shi, X. Kong, Z. Wang, *Appl. Phys. Lett.* 86, 063101, 2005.
- [15] F. Hernández-Ramírez, A. Tarancón, O. Casals, J. Arbiol, A. Romano-Rodríguez, J. Morante, *Sens. Act. B* 121, 3–17, 2007.

- [16] A. Köck, A. Tischner, T. Maier, M. Kast, C. Edtmaier, C. Gspan, G. Kothleitner, *Sens. Act. B* 138, 160–167, 2009.
- [17] N. Bukun, A. Vinokurov, M. Vinokurova, L. Derlyukova, Yu. Dobrovolsky, A. Levchenko, *Sens. Act. B* 106, 153–157, 2005.
- [18] V.V. Malyshev, A.V. Pisyakov, *Sens. Act. B* 47, 181–188, 1998.