proceedings

Proceedings

2D SnS_2—A Material for Impedance-Based Low Temperature NO_x Sensing? †

Daniela Schönauer-Kamin [1], Yongxiang Li [2], Wojtek Wlodarski [2], Samuel Ippolito [2] and Ralf Moos [1,*]

[1] Department of Functional Materials, University of Bayreuth, Bayreuth, Germany
[2] School of Engineering, RMIT University, Melbourne, Australia; yongxiang.li@rmit.edu.au (Y.L.); ww@rmit.edu.au (W.W.); samuel.ippolito@rmit.edu.au (S.I.)
* Correspondence: functional.materials@uni-bayreuth.de; Tel.: +49-921-557-401

† Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 9 August 2017

Abstract: The sensor signal of tin disulfide (SnS_2), a two-dimensional (2D) group-IV dichalcogenide, deposited as a film on a conductometric transducer is investigated at 130 °C. The focus is on the detection of the total NO_x concentration. Therefore, the sensor response to NO and NO_2 at ppm- and sub-ppm level at low operating temperature is determined. The results show that the sensing device provides a high sensor signal to NO and NO_2 even at concentrations of only 390 ppb NO_x. Both nitrous components, NO and NO_2, yield the same signal, which offers the opportunity to sense the total concentration of NO_x.

Keywords: 2-dimensional SnS_2; conductometric sensor; total NO_x sensing; sub-ppm NO_x; low temperature

1. Introduction

NO_x sensing at low temperatures is still a difficult task, especially for air-quality monitoring in stationary or transportable air quality monitoring devices [1]. In the past years, strict emission and immission limits for NO_x have been set up, for instance by the EU immission legislation Directive 2008. Currently, the emissions of NO_x by traffic in urban regions are a widely discussed topic since they exceed the regulatory limits. To enforce the limits, the detection of low NO_x concentrations at ppm- and sub-ppm level is required. Reliable and long-term stable sensing devices for the lowest NO_x concentrations are necessary to meet the strict requirements of, for instance, the European legislation, with regard to quality of the data especially in real-time air quality monitoring [2]. In literature, various NO_x gas sensing technologies are discussed [1,3–5]. The sensors have to be accurate, selective, long-term stable, and should have low NO_x detection limits. Especially for air-quality monitoring, the sensors for low-temperature NO_x sensing with a low power consumption are beneficial [1,2].

In this work a new material class based on 2D transition metal dichalcogenides (TMD) is discussed as sensing materials for NO_x sensors [6,7]. Due to the special structure of SnS_2, the charge transfer between *physisorbed* NO_2 gas molecules and the 2D SnS_2 material allows for NO_2 sensing with high NO_2 sensitivity and selectivity at low operating temperatures. In [6], the NO_2 sensor response of SnS_2 is described at 120 °C. In the present work, tin disulfide (SnS_2) flakes are investigated as functional materials for NO_x sensing at 130 °C with focus on the NO sensing performance of SnS_2.

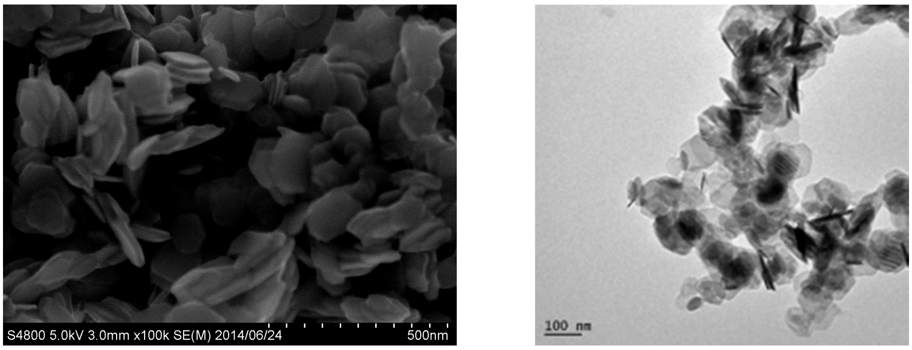
2. Materials and Methods

The transducer composed of an alumina substrate with a screen-printed interdigitated-electrode (IDE) structure (Au-IDE: 100 µm/100 µm). The sensitive film of 2D SnS_2 was synthesized by a wet chemical route and drop-casted on the IDE-structure [6]. The structure and morphology of the SnS_2 film was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The sensor response, the complex impedance $|Z|$ of the SnS_2-film, was determined at 130 °C in a synthetic gas test bench. As base gas, synthetic air with 2 vol.% water was used and NO and NO_2 were added in a concentration range between 390 ppb and 2 ppm. The added NO_x concentration was analyzed downstream the sensing device by a chemiluminescence detector (CLD).

3. Results and Discussion

The microstructure of the SnS_2 film is shown in Figure 1. The SEM image (Figure 1a) of the deposited film shows SnS_2 particles with a hexagonal shape which appear to from flake like structures. This is proven by the TEM image (Figure 1b). The shape of the particle is a hexagonal plate, with an average diameter of 100 nm and a thickness of less than 10 nm. This planar 2-dimensional flake structure was selected due to its very high active surface area resulting in a high adsorption capability for physisorbed NO_x molecules.



(**a**) (**b**)

Figure 1. (**a**) SEM image of SnS_2 particles; (**b**) TEM image of SnS_2 particles.

Initial impedance spectra of a SnS_2 sensor, shown in Figure 2 in the form of Nyquist-plots (frequency between 1 MHz and 1 Hz, root-mean-square value of the amplitude 200 mV, temperature 130 °C), present a semi-circular behavior with a high sensor signal when exposed to 390 ppb NO_x. The sensor signal in synthetic air is very stable (shown are two measurement curves). The complex impedance increases strongly in presence of NO_x, even at a NO_x concentration in the sub-ppm range.

As stated in [6] for NO_2 exposure, the strong resistance increase can be explained by the effect that the adsorbed NO_2 gas molecules act as electron acceptors. Charge is transferred from the SnS_2 flakes to the adsorbed NO_2 and the SnS_2 flakes deplete with charge carriers. The reduced number of free electrons leads to the increasing resistance.

For further measurements, we selected a constant frequency of 1 Hz. The sensor was exposed to varying NO and NO_2 concentration steps, and the resulting $|Z|$ is presented in Figures 3 and 4. The impedance of the SnS_2 sensor is around 600 MΩ in synthetic air, and increases when exposed to 1 ppm NO or NO_2 to 2.2 GΩ with the same sensor signal for NO and NO_2. The oscillating of the sensor signal is due to temperature fluctuations of the furnace (around 10 °C). The response time is quite good, but the signal recovery is relatively slow. The sensor seems to be a total NO_x sensing device.

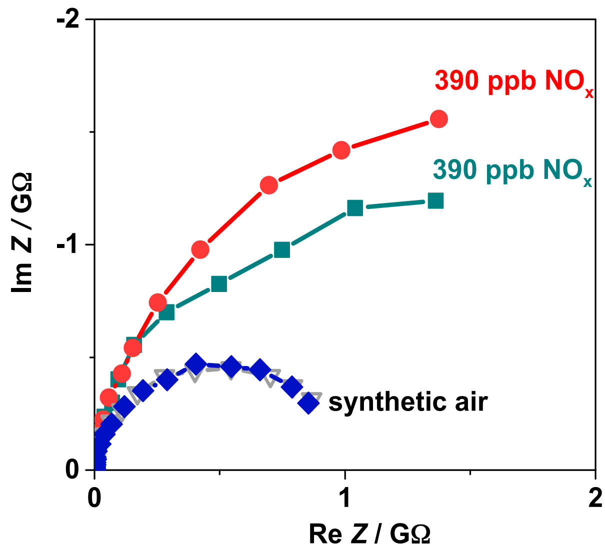


Figure 2. Impedance spectra of a SnS_2 sensor at 130 °C in synthetic air and with 390 ppb NO_x in the Nyquist-plot representation; spectra determined with U_{eff} = 200 mV and between 1 Hz and 10 MHz.

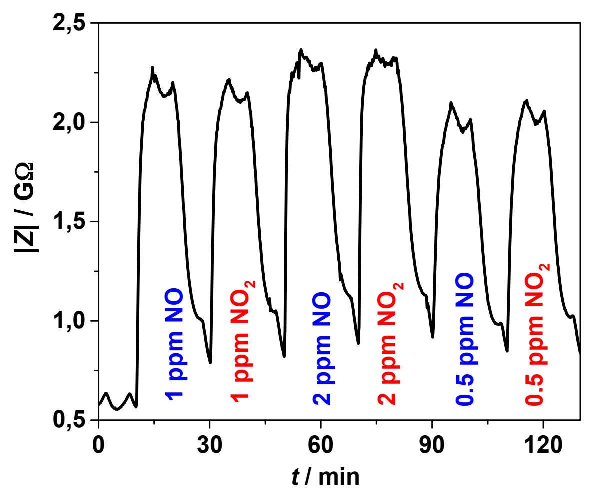


Figure 3. Complex impedance |Z| signal of the SnS_2 sensor determined at f = 1 Hz at 130 °C during NO_x exposure to 1 ppm, 2 ppm and 0.5 ppm NO res. NO_2.

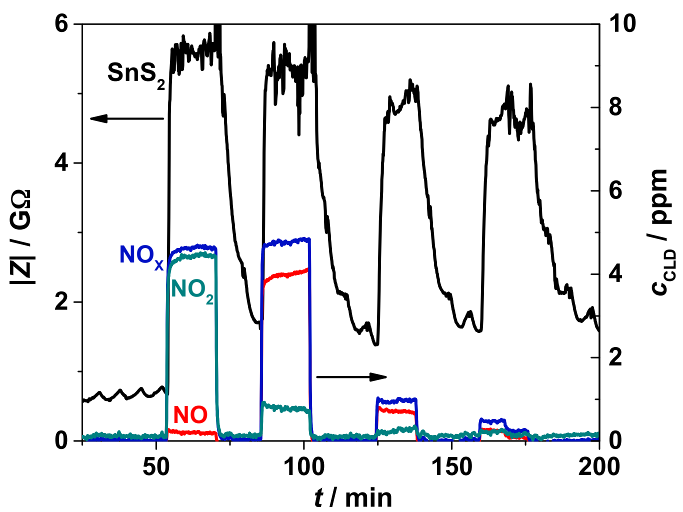


Figure 4. Complex impedance |Z| of the SnS_2 sensor determined at f = 1 Hz at 130 °C during NO_x exposure and the added NO_x concentration analyzed by CLD downstream the sensor device.

To investigate this more in detail, Figure 4 includes the NO and NO_2 concentrations determined by a CLD gas analyzer. Comparing the first two NO_x peaks, almost the same sensor response is visible for 5 ppm total NO_x (5 ppm NO_2 res. 4 ppm NO with 1 ppm NO_2). A huge sensor signal can determined even for NO_x concentrations below 1 ppm.

4. Conclusions

The SnS_2 sensors show a huge NO_x gas response even for low concentrations that needs to be investigated with respect to the behavior as a total NO_x sensor. The developed sensing device provides high impedance values. The impedance changes strongly when exposed to low concentrations of NO or NO_2 and the sensor seems to be suitable for sub-ppm level NO_x detection. The dependence of the resistance on the thickness of the SnS_2 film is an interesting task for further investigations. Additionally, the concentration dependent sensor response has to be analyzed and the response and the recovery time need to be improved.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Borrego, C.; Costa, A.M.; Ginja, J.; Amorim, M.; Coutinho, M.; Karatzas, K.; Sioumis, T.; Katsifarakis, N.; Konstantinidis, K.; De Vito, S.; et al. Assessment of air quality microsensors versus reference methods: The EuNetAir joint exercise. *Atmos. Environ.* **2016**, *147*, 246–263, doi:10.1016/j.atmosenv.2016.09.050.
2. Van den Bossche, J.; Peters, J.; Verwaeren, J.; Botteldooren, D.; Theunis, J.; de Baets, B. Mobile Monitoring for mapping spatial variation in urban air quality, development and validation of a methodology based on an extensive dataset. *Atmos. Environ.* **2015**, *105*, 148–161, doi:10.1016/j.atmosenv.2015.01.017.
3. Marr, I.; Moos, R. Resistive NO_x dosimeter to detect very low NO_x concentrations—Proof-of-principle and comparison with classical sensing devices. *Sens. Actuators B* **2017**, *248*, 848–855, doi:10.1016/j.snb.2016.12.112.
4. Marr, I.; Groß, A.; Moos R. Overview on Conductometric Solid-State Gas Dosimeters. *J. Sens. Sens. Syst*. **2014**, *3*, 29–46, doi:10.5194/jsss-3-29-2014.
5. Geupel, A.; Schönauer, D.; Röder-Roith, U.; Kubinski, D.J.; Mulla, S.; Ballinger, T.H.; Chen, H.-Y.; Visser, J.H.; Moos, R. Integrating nitrogen oxide sensor: A novel concept for measuring low concentrations in the exhaust gas. *Sens. Actuators B* **2010**, *145*, 756–761, doi:10.1016/j.snb.2010.01.036.
6. Ou, J.Z.; Ge, W.; Carey, B.; Daeneke, T.; Rotbart, A.; Shan, W.; Wang, Y.; Fu, Z.; Chrimes, A.F.; Wlodarski, W.; et al. Physisorption-Based Charge Transfer in Two-Dimensional SnS_2 for Selective and Reversible NO_2 Gas Sensing. *ACS Nano* **2015**, *9*, 10313–10323, doi:10.1021/acsnano.5b04343.
7. Donarelli, M.; Prezioso, S.; Perrozzi, F.; Bisti, F.; Nardone, M.; Giancaterini, L.; Cantalini, C.; Ottaviano, L. Response to NO_2 and other gases of resistive chemically exfoliated MoS_2-based gas sensors. *Sens. Actuators B* **2015**, *207*, 602–613, doi:10.1039/c5nr06121k.