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2D SnS₂ — A Material for Impedance-Based Low Temperature NOₓ Sensing? †

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Abstract: The sensor signal of tin disulfide (SnS₂), 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 NOₓ concentration. Therefore, the sensor response to NO and NO₂ 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 NO₂ even at concentrations of only 390 ppb NOₓ. Both nitrous components, NO and NO₂, yield the same signal, which offers the opportunity to sense the total concentration of NOₓ.

Keywords: 2-dimensional SnS₂; conductometric sensor; total NOₓ sensing; sub-ppm NO₂; low temperature

1. Introduction

NOₓ 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 NOₓ have been set up, for instance by the EU immission legislation Directive 2008. Currently, the emissions of NOₓ by traffic in urban regions are a widely discussed topic since they exceed the regulatory limits. To enforce the limits, the detection of low NOₓ concentrations at ppm- and sub-ppm level is required. Reliable and long-term stable sensing devices for the lowest NOₓ 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 NOₓ gas sensing technologies are discussed [1,3–5]. The sensors have to be accurate, selective, long-term stable, and should have low NOₓ detection limits. Especially for air-quality monitoring, the sensors for low-temperature NOₓ 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 NOₓ sensors [6,7]. Due to the special structure of SnS₂, the charge transfer between physisorbed NOₓ gas molecules and the 2D SnS₂ material allows for NOₓ sensing with high NOₓ sensitivity and selectivity at low operating temperatures. In [6], the NOₓ sensor response of SnS₂ is described at 120 °C. In the present work, tin disulfide (SnS₂) flakes are investigated as functional materials for NOₓ sensing at 130 °C with focus on the NO sensing performance of SnS₂.
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 SnS₂ was synthesized by a wet chemical route and drop-casted on the IDE-structure [6]. The structure and morphology of the SnS₂ film was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The sensor response, the complex impedance |Z| of the SnS₂-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 NO₂ were added in a concentration range between 390 ppb and 2 ppm. The added NOx concentration was analyzed downstream the sensing device by a chemiluminescence detector (CLD).

3. Results and Discussion

The microstructure of the SnS₂ film is shown in Figure 1. The SEM image (Figure 1a) of the deposited film shows SnS₂ 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 NOx molecules.

![Figure 1. (a) SEM image of SnS₂ particles; (b) TEM image of SnS₂ particles.](image)

Initial impedance spectra of a SnS₂ 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 NOx. The sensor signal in synthetic air is very stable (shown are two measurement curves). The complex impedance increases strongly in presence of NOx, even at a NOx concentration in the sub-ppm range.

As stated in [6] for NO₂ exposure, the strong resistance increase can be explained by the effect that the adsorbed NO₂ gas molecules act as electron acceptors. Charge is transferred from the SnS₂ flakes to the adsorbed NO₂ and the SnS₂ 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 NO₂ concentration steps, and the resulting |Z| is presented in Figures 3 and 4. The impedance of the SnS₂ sensor is around 600 MΩ in synthetic air, and increases when exposed to 1 ppm NO or NO₂ to 2.2 GΩ with the same sensor signal for NO and NO₂. 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 NOx 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 $U_{\text{eff}} = 200$ 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


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