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Novel Mesoporous Filters for Selective Gas Absorption

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Abstract

Semiconductor gas sensors have a proven potential for low cost and highly sensitive gas detection. However, selectivity remains one of the main problems for many applications. In this paper we report a new kind of mesoporous ceramic filter with nanoscale pores. The ceramic filter offers mechanical protection and can help to boost selectivity enomously through selective gas absorption. The developed nano-technological filters are based on mesoporous secondary and ternary silicon nitride derivatives with a defined particle size and are prepared via a new sol gel route. The interaction of the filters with CO, NO_2, H_2 and propane were evaluated using broad-band sensors. Highly selective absorption was observed for different gases, especially NO_2. From these experiments a filter efficiency value is calculated which allows easy selection of suitable filter materials for different applications.

Keywords

Mesoporous filters, nanoparticle gas sensors, selective gas absorption.

INTRODUCTION

Semiconductor gas sensors offer high sensitivity, good reliability and low cost making them attractive for a wide range of applications ranging from air quality control to safety applications like explosion warning or fire detection. Current drawbacks are power consumption, especially for handheld devices, and also insufficient selectivity. In the frame of the EU project NANOSENSOFLEX two nano-technological approaches are combined with advanced silicon microtechnology to achieve improved gas sensing systems based on miniaturized semiconductor gas sensors with sensitive layers based on novel doped and undoped metal oxide nanoparticles [1, 2]. The achieved performance of the novel sensors which excels current commercial products was recently reported [3].

To improve the sensors further in terms of reproducibility, long term-stability and especially gas selectivity, filters based on materials exhibiting selective gas absorption are very attractive. For these filters mesoporous materials with nanoscale pores, which exhibit a large inner surface area, seem most suitable. The development and optimization of the synthetic protocols for the preparation of selective gas filters with a defined size and shape by a novel sol gel route to mesoporous secondary and ternary silicon nitride deriva-tives and their evaluation as selective gas filters was a second goal within the NANOSENSOFLEX project. Combined with advanced signal processing, this project aims at developing novel sensor configurations combining high miniaturization level and exceptional selectivity with a very low power consumption at low cost.

EXPERIMENTAL

Filter material preparation

Mesoporous silicon boron nitride was prepared as previously reported using a novel non-oxidic sol-gel procedure [4]. The synthesis of the transition metal containing silicon nitrides using a related procedure will be reported elsewhere [5]. The following table gives an overview of the filter material composition and the preparation route.

Table 1. Overview of material composition and preparation for five tested filter materials

Number	Material composition and preparation
FP1	Si_3N_4-Pd, 1000°C under NH_3 flow
FP2	Silicon nitride membrane on α-Al_2O_3 support (dipping for one time)
FP3	Si_3N_4-BN (Si:B = 2:3)
FP4	Si_3N_4-Ni, 1000°C under NH_3 flow
FP5	Si_3N_4-Pd, 350°C under H_2 flow

These filter materials exhibit a defined particle size and shape with nanoscale pores and a large surface area. After preparation, the mesoporous powder samples were isostatically pressed at 10 tons into a disk using the same process used for the preparation of a KBr disk for IR analysis. The nanosize pores of the ceramic filter material survived this process unchanged. The disks were then cut into 6 mm diameter filters using a cork borer to obtain the filter pellets used for the efficiency tests.

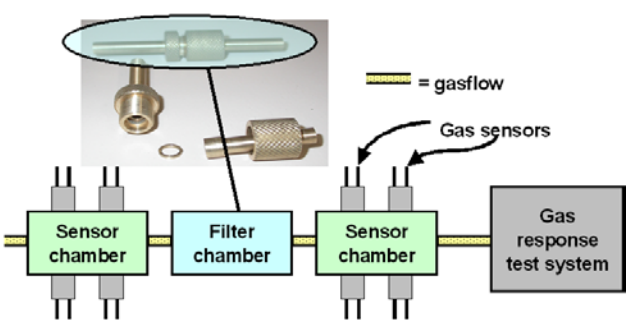
Hardware platform for test measurements

A computer controlled gas test bench was used for the filter tests. The bench allows connection of up to six test gases injected into a carrier gas stream with adjustable relative humidity (r.h.). In these experiments synthetic air at 50% r.h. with a flow rate of 500 ml/min was used. The test gases are injected into the carrier gas stream using three way valves to achieve almost instantaneous changes in the gas concentration. The data acquisition uses a multi-channel DMM (Keithley) for up to ten sensors in parallel.

For the filter evaluation a special filter chamber was designed into which the filter pellets are inserted. This filter chamber consists of several parts:

- housing for the filter pellet with male thread
- stamp and screw nut with female thread
- O-ring to center the filter-pellet in the housing and to avoid breaking the pellet when the stamp is screwed in

Rubber O-rings were used to achieve gas tight seals so that the gas can only pass the filter chamber through the filter pellet. Two sensor tests chambers for up to four sensors where installed, one in front of the filter chamber, another after the filter chamber to measure directly the difference in sensor response due to the filter pellet. The carrier gas stream passes through all three chambers. Before each experiment a leak test was performed to ensure that the gas passes through all three chambers. Fig. 1 shows the set-up for the filter tests. The total volume off the three chambers was approx. 10 ml, so that the gas concentration is changed in approx. 1,2 sec. These fast concentration changes allow determination of the sensor response time.



Note that the chosen set-up actually forces the gas under test through the filter. Effective removal of a given test gas under these conditions is therefore a better criterion for the filter efficiency than placing a filter pellet in front of the sensor element with the gas passing through by diffusion only. On the other hand, materials that prove effective under these test conditions should show an even better performance if gas transport in through diffusion only.

Four gases, CO, NO_2, H_2 and propane (C_3H_8), were chosen for the filter evaluation tests to cover a broad spectrum of common gases which might interfere with the target gas for a given application. We chose sensors with a broad detection spectrum to be able to evaluate all four gases using the same sensor. The sensors are microstructured Si-sensors with SnO_2 gas sensitive layer and noble metal doping mounted in standard TO-5 metal cans. These were screwed tightly into the sensor chambers. In all experiments, four sensors were placed in front of the filter and four behind to ensure correct operation of the gas test bench. The reported data compare the response of one sensor placed behind the filter chamber with the response of the same sensor in a reference measurement without filter so that a direct comparison of the response behavior is possible.

RESULTS AND DISCUSSION

For evaluation of the filter performance, the sensor response without filter is compared to the response with the different filter pellets placed in the filter chamber. The duration of the exposure was 20 min for each gas. Fig. 2 gives an overview of the sensor response to for all four gases and all five filter materials. It is immediately obvious that all filter materials except FP 1 are very effective for absorption of NO_2, while FP 1 only slows the sensor reaction but ultimately leads to the same resistance change as the reference curve. After NO_2 is switched off the sensor resistance remains higher than in the reference measurement and only slowly returns to the base line. Both effects can be explained with NO_2 adsorbing on the filter material: when NO_2 is injected in the carrier gas stream the full concentration reaches the sensor only after the filter is saturated. Then, when the gas is switched off again, NO_2 is desorbing from the filter slowly so that the sensor is still exposed to a small NO_2 concentration. Conversely, the response to H_2 is nearly unaffected by all filters except FP 4, which drastically reduces the sensor reaction.

To allow fast determination of the effectiveness of the different materials, we define the FE (filter efficiency) value as

$$FE_{red} = 1 - \frac{\left(\frac{R_0 - R_{gas}}{R_0}\right)_{with\ Filter}}{\left(\frac{R_0 - R_{gas}}{R_0}\right)_{without\ Filter}} \qquad (1)$$

for reducing gases and

$$FE_{ox} = 1 - \frac{\left(\frac{R_{gas} - R_0}{R_0}\right)_{with\ Filter}}{\left(\frac{R_{gas} - R_0}{R_0}\right)_{without\ Filter}} \qquad (2)$$

for oxidizing gases. With these definitions a FE-value of 1 denotes complete suppression of a given gas by the filter material while a value of 0 denotes no effect of the filter.

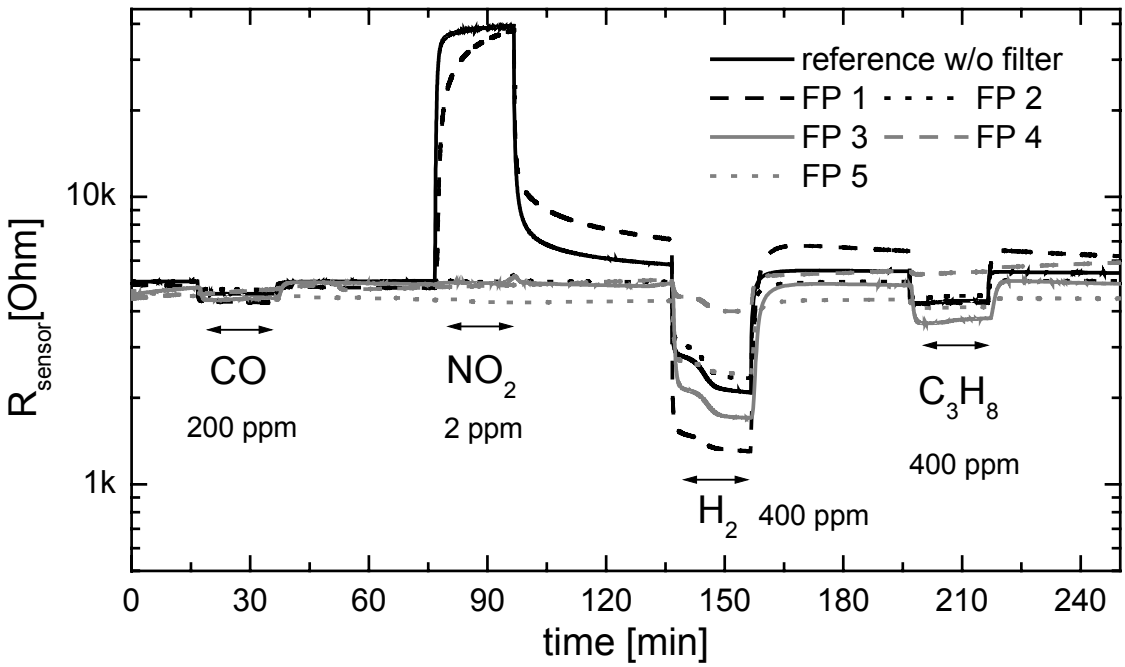


Fig. 3 gives an overview of the FE-values of all tested filter materials for all four test gases. With this plot, it is immediately obvious that FP 1 has no effect on the sensor response (although delaying the NO_2 response as discussed above). The most promising materials seem to be FP 3, which removes NO_2 very effectively without affecting the reaction to the other gases much, and FP 4, which effectively removes all gases except H_2. The sensor response with these two filter materials is therefore shown in more detail in Fig. 4 in comparison with the reference curve without filter.

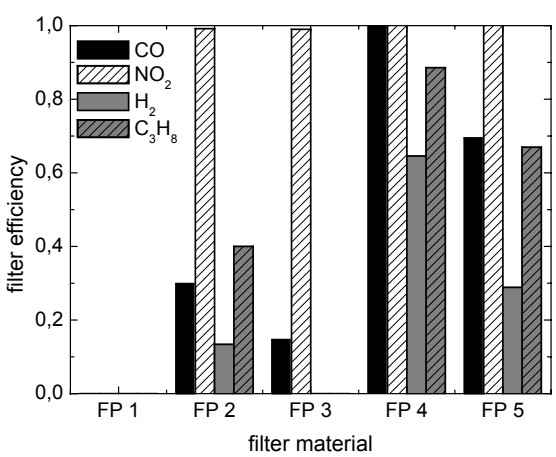
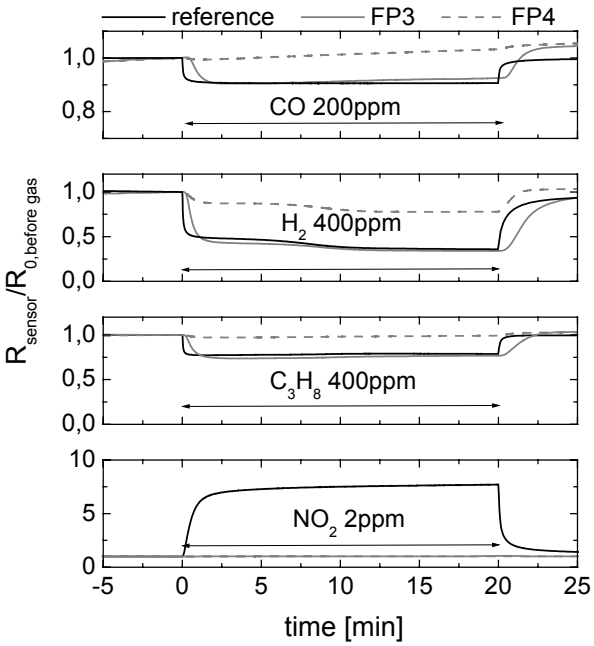
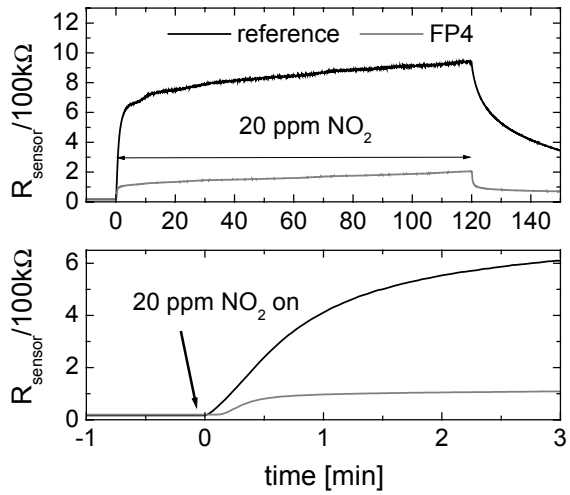


Figure 3. Filter efficiency for the five tested filter materials and the four test gases allowing fast assessment of the filter performance.

Both materials suppress the sensor response to NO_2 completely so that the sensor resistance remains constant during the 20 min exposure. FP 3 leaves the sensor reaction to CO, H_2 and C_3H_8 practically unchanged. However, for all three gases a slight change in the response is evident: the raction is slower after the gas is switched on and the sensor resistance returns slowly to the baseline after the gas exposure. As for FP 1 and NO_2 (see above) this can be explained with adsorption of gas molecules on the filter materials which then desorb slowly after the gas is switched off. FP 4, on the other hand, also suppresses the sensor response to CO and C_3H_8 almost completely and also reduces the response to H_2 considerably. It is interesting to note that for this materials and the reaction to H_2 the sensor signal return to the baseline is as fast as without filter. In this case, hydrogen obviously does not desorb from the filter material. This can either mean that the adsorption energy is too high for desorption at room temperature or that the filter catalyses a reaction between hydrogen and oxygen.

Of course, it is interesting to see if the sensor performance is unchanged for high gas concentrations, especially for NO_2 where the tests were performed with a concentration of only 2 ppm, and for longer exposures. We checked this by increasing the NO_2 concentration to 20 ppm for an exposure of two hours. For this experiment, an undoped SnO_2 sensor with extremely high NO_2 sensitivity was chosen. The results for FP 4 are shown in Fig. 5. As can be seen, the sensor response is not completely suppressed as for the smaller concentration but still the resistance





increase is reduced by a factor of approx. 5. Note that in this case, the initial response time with the filter material is shorter than without filter. This is due to a faster response time of the sensor at low NO_2 concentrations. Note that even for the long exposure no filter breakthrough is evident. The slight increase during the exposure is the same with and without filter so this is probably not due to a breakdown of the filter but to a slow drift off the sensor during long exposure.

CONCLUSIONS AND OUTLOOK

These first tests have proven that the novel mesoporous filter materials offer considerable potential to improve the selectivity of gas sensor systems. With the materials studied so far, suppression of NO_2 interference seems possible, especially for low concentrations. Also for hydrogen detection, FP 4 seems a promising material as it suppresses many different gases.

Further tests are required to investigate the mechanism of the filter performance: thermal desorption experiments will show if the filter function is due to an adsorption/desorption process or if catalytic effects play a role at least for some gases. In addition, tests need to be made with filter pellets placed in the sensor housing to check the filter performance if the gas is not pressed through the filter but is instead transported to the sensor by diffusion.

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