

## CO<sub>2</sub> sensors based on workfunction readout using floating gate FET devices with polysiloxanes sensing layers

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### 1. Introduction

The reliable detection of CO<sub>2</sub> is a key for demand controlled ventilation (DCV) in buildings, which allows energy savings up to 30%. Presently, optical detection methods are only in use for a small percentage of building ventilation systems due to the relatively high cost of these sensing systems. A reliable low cost CO<sub>2</sub> sensor would allow for widespread use of DCV.

In the past, various transducer principles have been used for CO<sub>2</sub> detection and a number of sensitive materials have been investigated including organically modified silicates [1], also called siloxanes. Due to their ability to form an acid base reaction with the molecule CO<sub>2</sub>, materials using primary amino groups are particularly suitable for the detection of CO<sub>2</sub>. This has been verified using heteropolysiloxanes in mass sensitive [1] and capacitive sensors [2]. Another recent approach makes use of the workfunction readout of these materials, where CO<sub>2</sub> detection at room temperature was demonstrated using a lab-scale Kelvin Probe setup [3]. The underlying detection mechanism has been carefully examined by Stegmeier et al [4].

The readout of gas-induced workfunction changes via hybrid suspended gate field effect devices (HSGFET) has been accepted as a promising technique for the realization of a versatile, low-cost sensor platform for several years [5] and Micronas GmbH is already in the process of industrializing the advanced floating gate FET (FGFET) device [6] as mySENS platform.

In this work we describe the transfer of heteropolysiloxanes sensing layers in the floating gate FET (FGFET) sensor platform [5] in order to enable reliable low-cost CO<sub>2</sub> detection. The actual FGFET setup is schematically depicted in Fig.1 (left). It consists of a CMOS FET structure as readout device and a suspended gate which includes the gas sensitive layer. The floating gate electrode is prolonged forming a capacitive element with the suspended gate electrode on the backside of the sensitive layer. The air gap is of the size of a few microns to allow gas diffusion into the capacitor. The actual design shown on the right in Fig. 1 is able to carry two suspended gates with different sensing layers. Besides the FGFET structure, the CMOS chip includes a temperature sensor and conditioning electronics to convert the sensor signal into digital data, which can be read out via a digital interface.

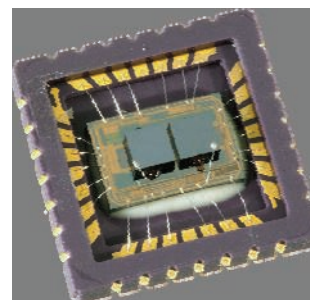
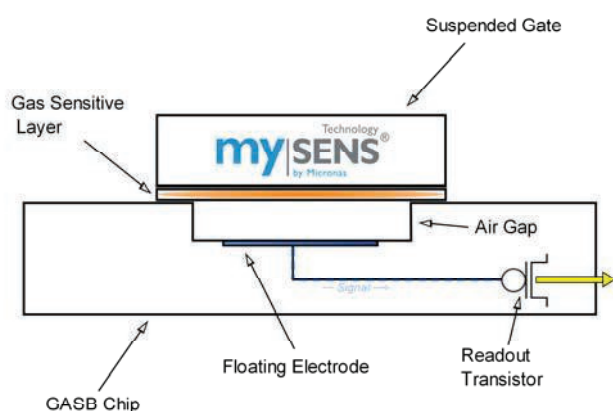


Fig. 1: FGFET schematic depiction (left) and actual setup (right)

## 2. Experimental

The CO<sub>2</sub> sensitive material investigated in this work is a heteropolysiloxane containing AMO (3-aminopropyltrimethoxysilane) and PTMS (propyltrimethoxysilane) in a ratio of 70/30 (v/v). The gas sensitive layers have been prepared by spincoating on Si substrates coated with 160 nm TiN as described in detail in [3].

The suspended gate, a small silicon die coated with a the sensing layer, is mounted on top of the chip with the sensing layer facing the SGFET area, and forming the airgap.

Signals from FGFET sensor are depicted as workfunction change  $d\Phi$ , which is calculated using a calibration pulse with a defined voltage on the contact electrode of the sensing layer simulating a defined change in workfunction.

Gas measurements have been carried out with humidified synthetic air at a total air flow of 1 l/min. The CO<sub>2</sub> and humidity level and other test gas concentrations have been adjusted by a computer-controlled gas-mixing station. In addition, the actual CO<sub>2</sub> concentration has been monitored by a optical filter CO<sub>2</sub> analyzer (Thermo Scientific 410i).

## 3. Results

Fig. 2 shows a characteristic CO<sub>2</sub> response curve of a FGFET sensor with a heteropolysiloxane sensing layer, recorded under room air conditions. Since the sensor is operated at ambient temperature without additional heating, the power consumption is reduced to the needs of the CMOS device and the related data acquisition circuit so that the low-power operability of the CO<sub>2</sub> sensor is demonstrated.

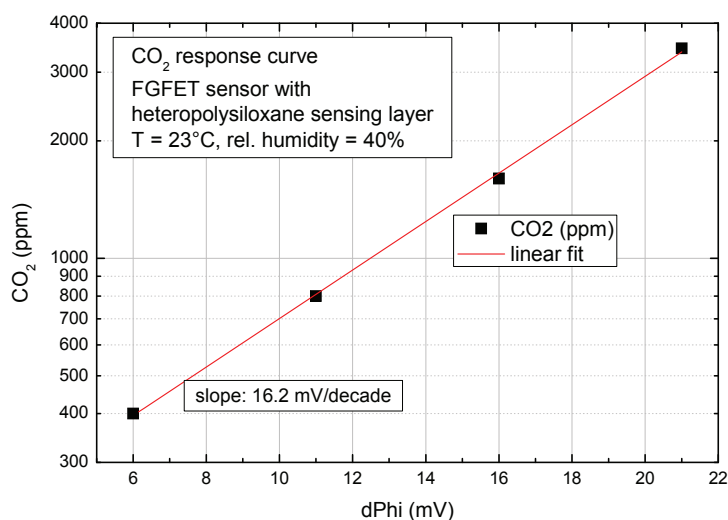


Fig. 2: Characteristic CO<sub>2</sub> response curve of a FGFET sensor with heteropolysiloxane sensing layer.

The type of curves as depicted in fig. 2 are used as calibration curves in order to calculate CO<sub>2</sub> concentrations out of the FGFET signals. For room air monitoring applications changes of 100ppm of CO<sub>2</sub> have to be distinguishable. This is verified for the FGFET CO<sub>2</sub> sensor as displayed in Fig. 3. Here, CO<sub>2</sub> concentrations calculated from transient response of a FGFET sensor are compared to the signal of a commercial optical CO<sub>2</sub> analyzer. This test demonstrates that FGFET sensors can resolve changes in CO<sub>2</sub> concentrations < 100ppm at room temperature operation.

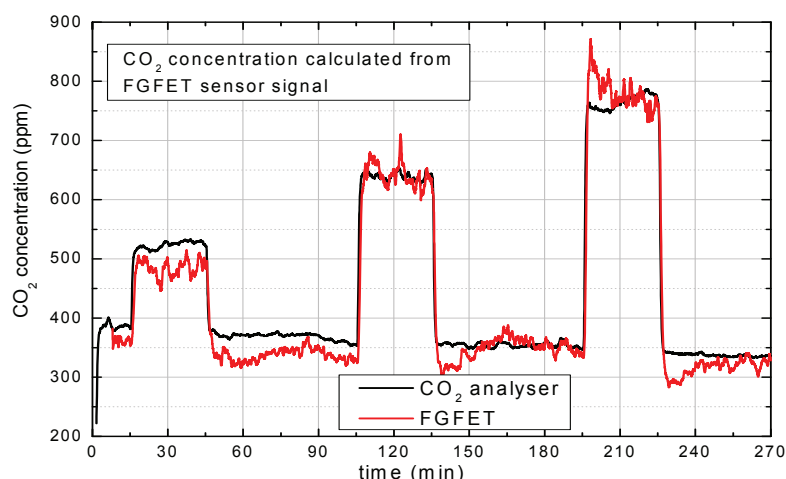


Fig. 3: Transient CO<sub>2</sub> response of a FGFET sensor with heteropolysiloxane sensing layer (red line) compared to a commercial CO<sub>2</sub> analyser (black line). The sensor is operated at room temperature.

Besides the CO<sub>2</sub> response itself, the stability of a sensor signal towards ambient influences like temperature, humidity and interfering gases is crucial for the overall performance. Therefore the FGFET sensor has been tested regarding these ambient parameters.

Both, the sensing mechanism and the transducer itself exhibit an inherent temperature influence. Since the main application for the sensors is room air control, climate chamber tests up to 50°C maximum have been performed (fig. 4). The workfunction changes calculated from the raw signal show a very strong dependency on temperature changes. Assuming a linear dependency of the sensor signal on temperature, the influence of temperature can be minimized efficiently using the integrated temperature sensor as can be seen in the curve named as “T compensated”.

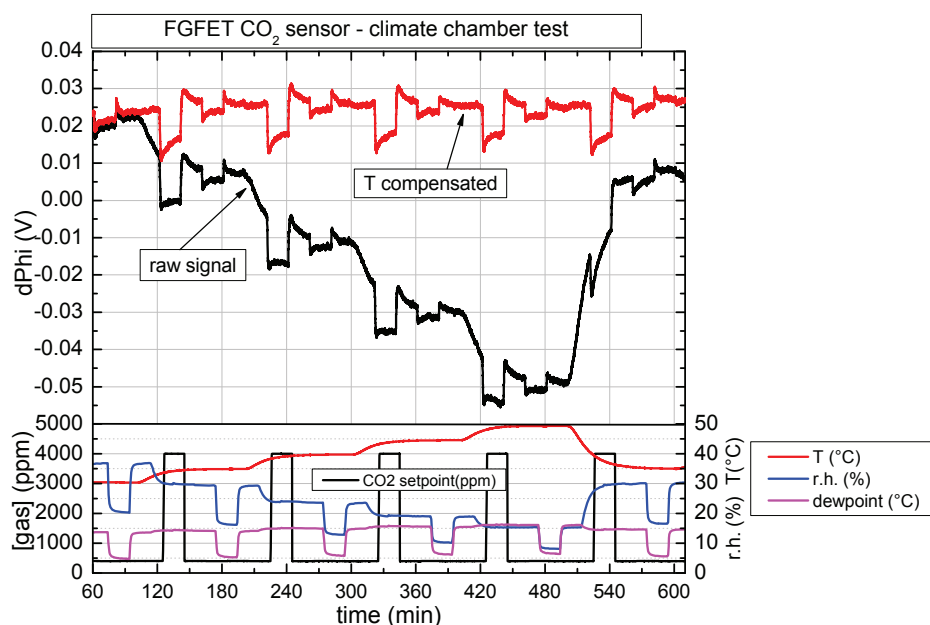


Fig. 4: Transient response of a FGFET sensor with heteropolysiloxane sensing layer at changing temperatures from 30°C to 50°C. Since the raw signal (black line in the upper part of the graph) exhibits a strong dependency on temperature, this dependency is significantly reduced after linear temperature compensation using the integrated temperature sensor (red line). CO<sub>2</sub> concentration, temperature and relative humidity (r.h.) are shown in the lower part of the graph.

The same approach can be applied on compensation of humidity effects. If the signal of a second sensor for the humidity level is used to compensate the dependency of the CO<sub>2</sub> response on humidity, a significantly improved accuracy in CO<sub>2</sub> detection can be achieved. This is illustrated in fig 5. for an temperature range from 25°C to 35°C and varying humidity levels from 25% to 60% relative humidity (r.h.). If the CO<sub>2</sub> concentration is changed stepwise, a steep response of the sensor signal is caused, followed by a slower decline. This effect was also observed in previous Kelvin Probe measurements and is assumed to be related to two concurring reactions (e.g. formation of carbamate species and loss of adsorbed water [7]).

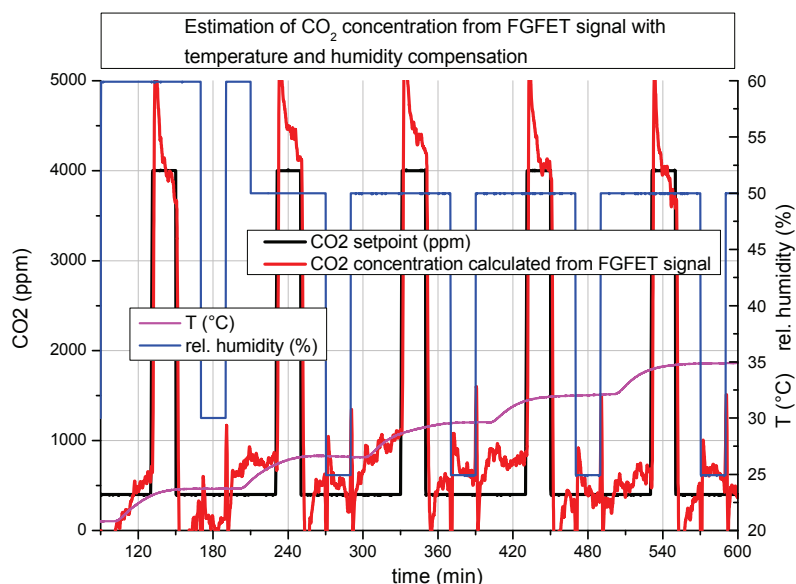


Fig. 5: Transient CO<sub>2</sub> response of a FGFET sensor to stepwise changes in CO<sub>2</sub> concentration at temperatures from 25°C to 35°C and at changing humidity levels from 25% to 60% r.h.).

The influence of these concurring effects becomes neglectable, when only slow changes in CO<sub>2</sub> concentration have to be recorded. In this case the sensor response can follow the transient CO<sub>2</sub> concentration within the required accuracy range (fig. 6).

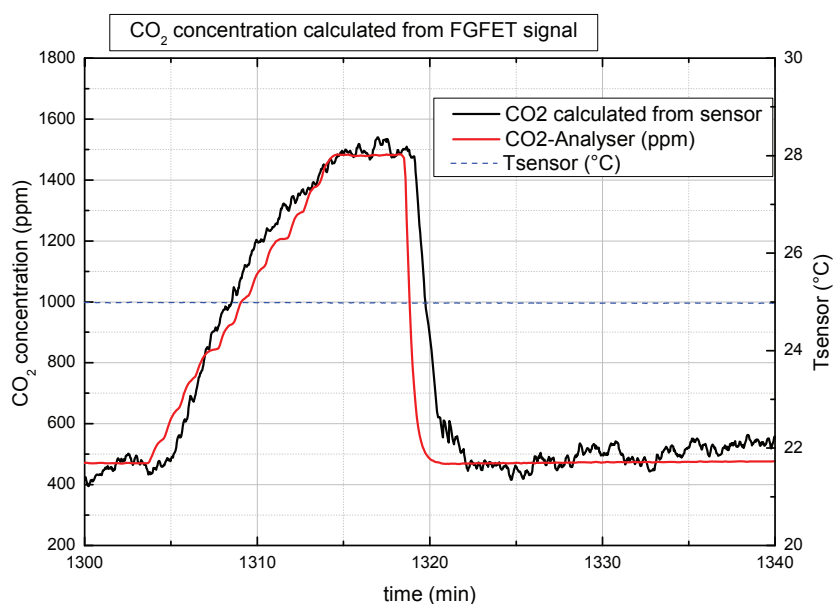


Fig. 6: Transient CO<sub>2</sub> response of a FGFET sensor to a slow change in CO<sub>2</sub> concentration of approx. 100ppm/min.

#### 4. Conclusion

The promising CO<sub>2</sub> sensing characteristics of heteropolysiloxane sensing layers have been successfully transferred to the FGFET platform. The reported results illustrate the capability of the FGFET platform for room air monitoring applications using the ability of the FGFET technology for low power operation. The obtained resolution in CO<sub>2</sub> concentration and the response time can meet the requirements for room air monitoring. Inherent effects of ambient temperature on the sensor response can be reduced to a large extent by benefit of the temperature sensor integrated on the FGFET chip. A first approach for compensation of humidity cross interference has been validated using an external humidity sensor. An extended version of the mySENS sensor platform with integrated humidity sensor is already under investigation and will allow further reduction of humidity cross interference. Future investigations will aim on the long term stability and reproducibility of the FGFET CO<sub>2</sub> sensors in respect to room air control applications.

#### References

- [1] R. Zhou, S. Vaihinger, K.E. Geckeler, W. Göpel, Reliable CO<sub>2</sub> sensors with siliconbased polymers on quartz microbalance transducers, *Sens. Actuators B: Chem.* 18–19 (1994) 415–420.
- [2] H.-E. Endres, R. Hartinger, M. Schwaiger, G. Gmelch, M. Roth, A capacitive CO<sub>2</sub> sensor system with suppression of the humidity interference, *Sens. Actuators B: Chem.* 57 (1999) 83–87.
- [3] S. Stegmeier, et al., Sensing of CO<sub>2</sub> at room temperature using work function readout of (hetero-) polysiloxanes sensing layers, *Sens. Actuators B: Chem.* (2010), doi:10.1016/j.snb.2009.12.071
- [4] S. Stegmeier, et al., Sensing mechanism of room temperature CO<sub>2</sub> sensors based on primary amino groups, *Sens. Actuators B: Chem.* (2010), doi:10.1016/j.snb.2010.01.022
- [5] M. Fleischer, Advances in application potential of adsorptive-type solid state gas sensors. 2008 *Meas. Sci. Technol.* 19 042001
- [6] Ch. Wilbertz, H.-P. Frerichs, I. Freund, M. Lehmann, Suspended-Gate- and Lundstrom-FET integrated on a CMOS-chip, *Sens. Actuators A* 123-124 (2005) 2–6
- [7] S. Stegmeier, et al., Stepwise improvement of (hetero-) polysiloxane sensing layers for CO<sub>2</sub> detection operated at room temperature by modification of the polymeric network, *Sens. Actuators B: Chem.* 148 (2010) 450–458