Compensating the quantitative signal of metal oxide semiconductor gas sensors in temperature cycled operation under the influence of siloxane poisoning

Caroline Schultealbert, Tobias Baur, Tilman Sauerwald[1], Andreas Schütze
Lab for Measurement Technology, Saarland University, Saarbrücken, Germany
c.schultealbert@lmt.uni-saarland.de

Summary:
We present a method for quantifying the degradation state due to siloxane poisoning of a metal oxide semiconductor gas sensor using temperature cycled operation. The time constant for the generation of surface charge at high temperature increases through poisoning and is only slightly dependent on the gas atmosphere. In addition to indicating a necessary sensor replacement, this signal can also be used for drift compensation based on the relation between sensor signal and this time constant.

Keywords: metal oxide semiconductor, gas sensor, siloxanes, poisoning, stability

Motivation

Metal oxide semiconductor (MOS) gas sensors are promising candidates for several applications due to their excellent sensitivity towards many reducing gases. This of course brings along some drawbacks like poor selectivity but also stability issues. Well-known poisons for MOS sensors are siloxanes [1]. Due to their broad occurrence in personal care and household products problems arise in several applications [2]. The impact of siloxanes on sensors operated at constant temperature have been studied extensively, but investigations on temperature cycled sensors are rarely found. We recently presented first results [3]. However, these measurements involved only very high siloxane dosages, the relatively uncommon siloxane HMDS (hexamethyldisiloxane) and only a small set of gases. Here we present a systematic study on the effect of the more prevalent D_4 (OMCTS, octamethylcyclotetrasiloxane, [4]) on MOS sensors in temperature cycled operation (TCO) and an approach for self-compensation.

Experimental setup

Measurements were conducted with our gas mixing apparatus (GMA). The sensors were exposed to a concentration of 2 ppm OMCTS for 1-3 hours several times followed by complex characterization measurements. The following gases and concentration ranges were selected: humidity (30-70 %RH), H_2 (500-2300 ppb), CO (40-1750 ppb), acetone (0-800 ppb), ethanol (0-700 ppb), acetaldehyde (0-900 ppb) and toluene (0-1200 ppb). Gas exposures were generated as described in [5], offering all mentioned gases simultaneously at a randomly chosen concentration within the associated range. 50 mixtures were measured, each held for 20 min. 16 sensors in total were studied (6 different types, 2 working modes, 4 using different types of diffusion barriers). The results presented here focus on the AS-MLV-P2 sensor (ScioSense B.V., NL) in TCO with a cycle length of 120 s. The cycle itself is derived from the differential surface reduction (DSR, described in [6]). This means that the sensor is oxidized at high temperature (here 400 °C, 10 s) followed by fast cool down to a lower temperature (100, 150, 200, 250, 300 °C, 14 s each) where the surface reduction (DSR signal, $k_{reduction}$), which is proportional to the concentration of reducing gases, is measured directly via differentiation of the logarithmic conductance:

$$\frac{d}{dt}\ln(G) \propto k_{reduction} \qquad (1)$$

Turning the DSR method around gives the opportunity to evaluate the simplified time constant t_{50} for generation of surface charge (differential surface oxidation, DSO). This procedure is more stable (higher signal to noise ratio) than using an exponential fit.

Results

One cycle with the same, constant gas atmosphere is shown in Fig. 1 after different siloxane dosages. Dosage 6.84 ppm·h is excluded here for better overview but agrees with other results.

---

[1] currently at: Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany.

The mean value of the cycle is shifted due to the siloxane exposure and the dynamic response at high and low temperatures (DSR and DSO) is slowed down. This indicates that all processes on the sensor surface become slower due to siloxane poisoning, which corresponds to the deactivation of catalyst and other active surface sites. For quantification of the degradation state the time constant t_{50} for oxidation at high temperature was evaluated, which is – according to the underlying gas sensor model [6] – independent from the ambient gas atmosphere. Fig. 2 shows the mean value of $\overline{t_{50}} \pm \sigma$ for the characterization measurements evaluated during the first high temperature phase in each cycle. σ mainly originates from the fact that t_{50} still depends slightly on the atmosphere, but the effect is sufficiently small to allow quantification of the sensor state, e.g., to indicate the need for sensor replacement. Before replacing the sensor, the signal needs to be corrected to allow correct gas quantification. The DSR signal at 200 °C initially shows a correlation of 0.90 with the total concentration, which is lowered only slightly by poisoning (5 % after 1.33 ppm·h). In contrast, the sensitivity of the signal is lowered fast by about 50 % after 1.33 ppm·h (see Fig. 3, blue data points). To perform that correction a relation between the relative change of the DSO signal and the relative change of the DSR-signal is linearly fitted for the first three datapoints (0-1.33 ppm·h). Using higher dosages needs a fit of the form $f(x) = \frac{1}{x}$ but the signal to noise ratio becomes very poor in this case. Applying this compensation to the data points projects them back on the original characteristic line extending the lifetime of the sensor by providing correct quantification results before a replacement is needed.

Outlook

If the found compensation factor can be transferred to new unpoisoned sensors or is individual for every single device needs to be evaluated. Additionally, the presented results include only a small part of the collected data from the corresponding study. More results including other sensors and operating modes, selectivity of MOS sensors and classification as well as other concepts to deal with siloxane poisoning are in preparation.

References

[1] G. Korotcenkov, B. K. Cho, *Sensors Actuators, B Chem*., 156 (2011); doi: 10.1016/j.snb.2011.02.024

[2] D. Rüffer, F. Hoehne, J. Bühler, *Sensors (Switzerland)*, 18 (2018) doi: 10.3390/s18041052

[3] C. Schultealbert, I. Uzun, T. Baur, A. Schütze, T. Sauerwald, *J. Sens. Sens. Syst.* 9, 283-292 (2020), doi: 10.5194/jsss-9-283-2020

[4] C. Rücker, K. Kümmerer, *Chem. Rev*., 115 (2015); doi:10.1021/cr500319v

[5] T. Baur, M. Bastuck, C. Schultealbert, A. Schütze, T. Sauerwald, *J. Sens. Sens. Syst.* 9, 411-424 (2020), doi:10.5194/jsss-9-411-2020

[6] T. Baur, C. Schultealbert, A. Schütze, T. Sauerwald. *J. Sens. Sens. Syst*. 7, 411-419 (2018); doi: 10.5194/jsss-7-411-2018
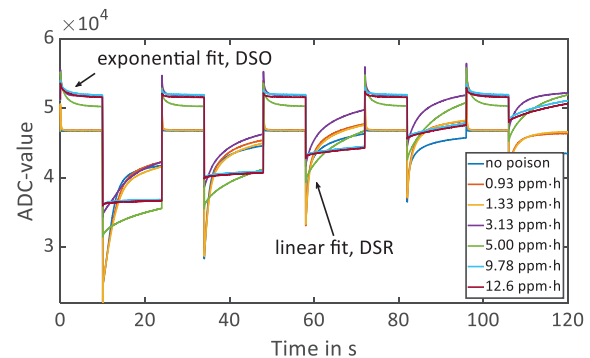
Fig. 1. *Signal of one cycle under constant gas atmosphere for different siloxane dosages.*
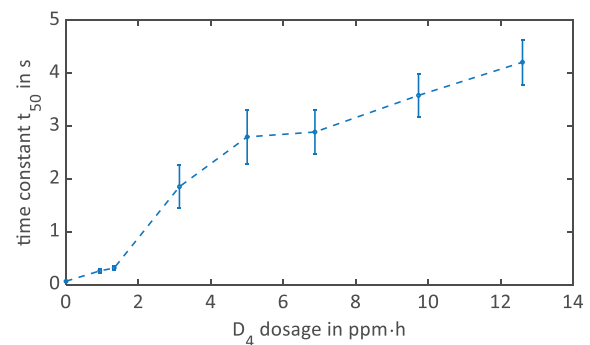

Fig. 2. *The DSO signal evaluated on the first high temperature phase as a mean value over all 50 gas exposures and the corresponding standard deviation as error bars. A quantification of the poisoning state is easily possible by this feature.*
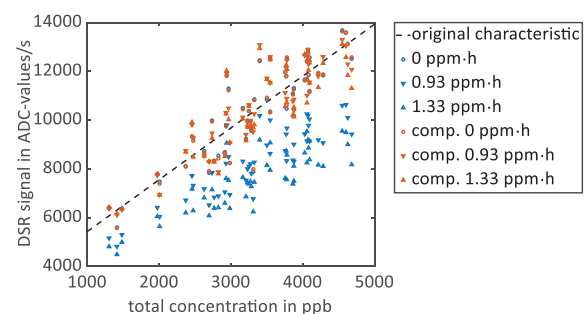

Fig. 3. *DSR signal at 200 °C over total concentration: blue (original measured values at 0, 0.93 and 1.33 ppm·h) and red (compensated values). Each data point represents the mean value of one gas exposure.*