

Compensation of siloxane poisoning of metal oxide semiconductor gas sensors in temperature cycled operation

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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 exponential 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 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), H₂ (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 (ams Sensors Germany GmbH) 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:

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

Turning the DSR method around gives the opportunity to evaluate the time constant τ for generation of surface charge (differential surface oxidation, DSO) via an exponential fit of $\ln(G)$ during the high temperature phase.

Results

One cycle with the same, constant gas atmosphere is shown in Fig. 1 after different siloxane dosages. Dosages 6.84 & 18.63 ppm·h are excluded here for better overview but agree with other results. The mean value of the cycle is shifted due to the siloxane exposure and the dynamic response at high and low temperatures is slowed down. This indicates that all processes

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on the sensor surface become slower due to siloxane poisoning, which corresponds to the deactivation of catalyst and other active surface sites. Fig. 2 shows the DSR signal at 200 °C during several characterizations, yielding a concentration proportional signal that is highly affected by siloxane exposure. The total concentration of reducing gases is indicated by the background color intensity. For this temperature at 9.8 and 12.7 ppm·h the signal is completely deteriorated. For quantification of the degradation state the time constant τ for oxidation at high temperature was evaluated, which is – according to the underlying gas sensor model [6] – independent from the ambient gas atmosphere. Fig. 3 shows histograms of τ for the characterization measurements evaluated during the first high temperature phase in each cycle. The width of the distribution mainly originates from the fact that τ 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 should be corrected to allow correct gas quantification. The correction can be carried out using the same method: Fig. 4 shows the relative decrease of the DSR signal vs. the relative increase in τ for every seventh exposure from the total of 50 gas mixtures. The dashed line represents an exponential fit of the form

$$\Delta_{DSR} = 1.06 \cdot \exp(-0.060 \cdot \Delta\tau) \quad (2)$$

which can be directly used to adjust the poisoned sensor signals in Fig. 2.

Outlook

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. Ruffer, F. Hoehne, J. Bühler, *Sensors (Switzerland)*, 18 (2018) doi: 10.3390/s18041052
- [3] C. Schultealbert, I. Uzun, T. Baur, A. Schütze, T. Sauerwald, *Dresdner Sensor-Symposium*, P2.04 (2019); doi: 10.5162/14dss2019/P2.04
- [4] C. Rücker, K. Kümmerer, *Chem. Rev.*, 115 (2015); doi:10.1021/cr500319v
- [5] T. Baur, M. Bastuck, C. Schultealbert, A. Schütze, T. Sauerwald, *Dresdner Sensor-Symposium*, 6.3 (2019); doi: 10.5162/14dss2019/6.3
- [6] T. Baur, C. Schultealbert, A. Schütze, T. Sauerwald, *J. Sens. Sens. Syst.* 7, 411-419 (2018); doi: 10.5194/jsss-7-411-2018

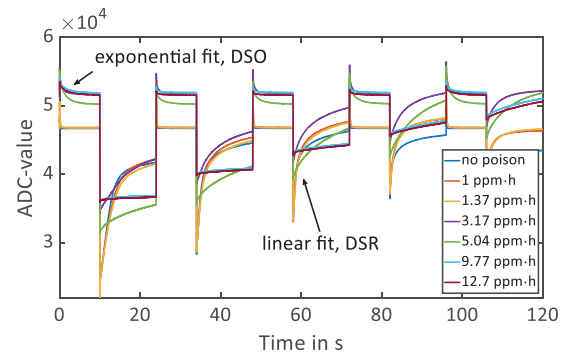


Fig. 1. Signal of one cycle under constant gas atmosphere for different siloxane dosages.

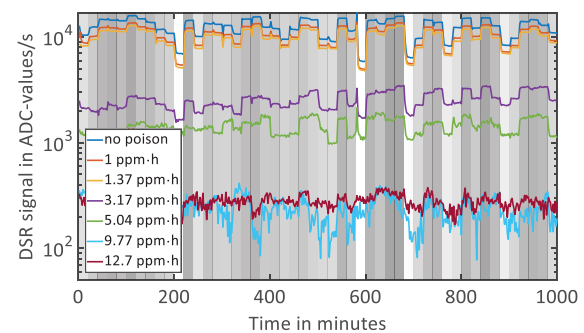


Fig. 2. The DSR signal at 200 °C over time after different siloxane dosages, showing the 50 randomized gas offerings (total concentration indicated by color intensity) held for 20 minutes each.

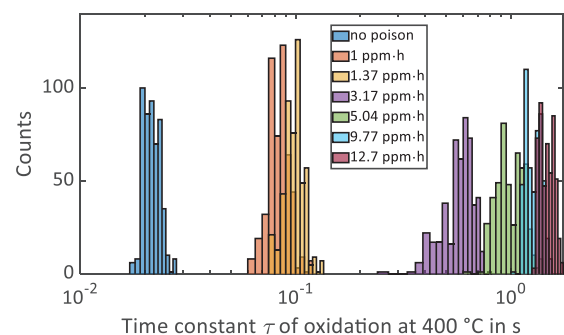


Fig. 3. Histograms of the time constant for oxidation for different siloxane dosages.

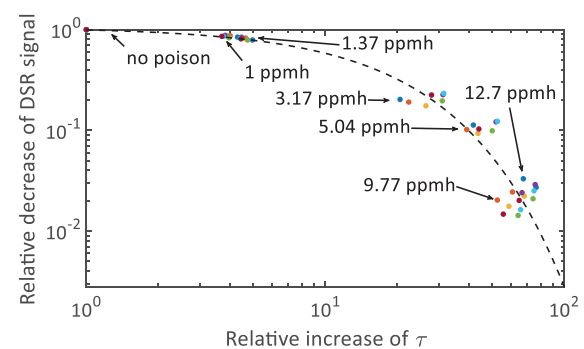


Fig. 4. Relative decrease of the DSR signal used for gas quantification vs. relative increase of the DSO time constant τ indicates that a compensation of siloxane poisoning is possible (every 7th gas offer shown).