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Multi-Gas sensor array based on SnO_2 and CuO thin films functionalized with Ag and Cu nanoparticles

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Summary:
We have realized a multi-gas sensor array, which employs 4 different sensor materials: bare SnO_2, and CuO films, and SnO_2, and CuO films, functionalized with Ag- and Cu-nanoparticles. The sensors have been screened towards 6 specifics get gases (CO_2, CO, NO, acetone, NH_3, specific hydrogen carbide mixture) which are relevant for air quality monitoring in the harsh environment of mines. The sensing materials show specific response to the test gases, which enables an identification of the test gases by adjusting the operation temperature and applying a proper calibration method.

Keywords: metal oxide, nanomaterials, nanoparticles, gas sensors, sensor array

Introduction

Indoor air quality (IAQ) monitoring plays an important role in public health and well-being, Poor IAQ has been linked to a variety of health issues ranging from transient discomfort and headache, to respiratory diseases and cardiovascular problems. In particular in harsh environment, such as industrial settings or mines, AQ monitoring is key to maintain a safe working environment.

Conductometric gas sensors, which rely on changes of the electrical conductance of a gas sensitive material due to the surrounding gas, are very good candidates for IAQ. Mostly, metal oxides (MOx) like SnO_2, ZnO or CuO are used because of their high sensitivity to a large variety of gases [1]. For AQ, however, selectivity – the property to distinguish a single target gas out of a gas mixture – is a most important issue. A very promising approach to achieve a high degree of selectivity is to functionalize the surface of MOx sensors by metallic nanoparticles such as Au, Pd, or Pt [2, 3].

We have realized a 4 x multi-gas sensor array, which employs 4 different sensor materials: bare SnO_2, and CuO films, and SnO_2, and CuO films, functionalized with Ag- and Cu-nanoparticles. The goal of this sensor array is to monitor the AQ in the harsh environment of mines. Hence, the sensors have been screened towards 6 specifics get gases: CO_2, CO, NO, acetone, NH_3, and a hydrogen carbide mixture (HC_{mix}, equal mixture of 500 ppm of acetylene, ethane, ethene and propene). Table 1 lists the target gases relevant for AQ in mines and includes the required measurement range as well as the maximum workplace concentrations.

Target Gas	Concentration Range	MAK* concentration
CO_2	400 - 5000 ppm	5000 ppm
CO	1 - 50 ppm	30 ppm
NO	1 - 50 ppm	25 ppm
Acetone	1 - 5 ppm	500 ppm
HCmix**	1 - 30 ppm	not defined
NH_3	1 - 50 ppm	20 ppm
* Maximum workplace concentration		
** HCmix = mixture of acetylene, ethan, ethen and propen		

Sensor Fabrication

SiN-based micro-hotplate chips incorporating a heating structure (up to 500°C) and electrodes, have been used as carriers for the sensing films. The sensors are fabricated as follows: First, a negative lift-off resist mask is structured by photolithography. Then the chips are coated with 50 nm SnO_2 and CuO, respectively, using reactive magnetron sputtering. This is followed by a lift-off process to structure the sensing films into a circular shape (diameter 450 µm) and an annealing process at 400°C in dry synthetic air. Finally, two out of four sensors are functionalized with Ag, and Cu nanoparticles via

magnetron sputter inert gas condensation. The 4 chips are mounted on a Kyocera socket, wire bonded, and form the multi-gas sensor array.

Sensor characterization and results

All sensors have been characterized simultaneously in an automated gas measurement setup. Synthetic air, with controlled humidity (25% and 75% rh), serves as the background gas. The target gases are subsequently introduced into the setup for 5 min at low concentration (500 ppm CO_2, 5 ppm CO, 1 ppm NO, 1 ppm acetone, 1 ppm NH_3, and 5 ppm HC_{mix}). After 10 min in synthetic air, the target gases are introduced for 5 min at high concentration around the MAK limits (2500 ppm CO_2, 25 ppm CO, 5 ppm NO, 5 ppm acetone, 5 ppm NH_3, and 25 ppm HC_{mix}).

The relative resistance changes due to the interaction with the test gas, i.e. the sensor response S, has been calculated according to:

$$S = \frac{R_{air} - R_{gas}}{R_{air}} \quad (1)$$

where R_{gas} is the sensor resistance in the presence of the test gas and R_{air} is the sensor resistance in pure synthetic air.

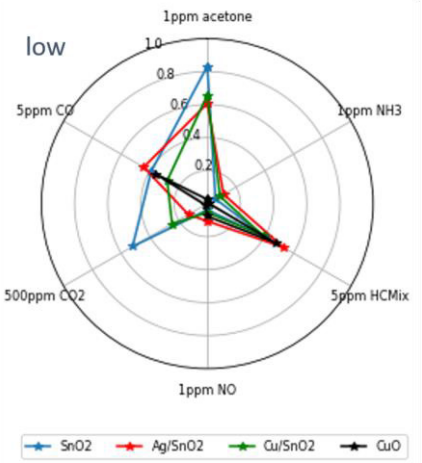

Fig.1 Response of four sensors towards 6 test gases for low concentrations (300°C operation temperature, 75% rh in background gas).

In order to accurately identify the target gases, we analyzed sensor drift and developed a calibration method to evaluate the sensitivity and selectivity of all devices. Fig. 1 presents the results for 4 sensor devices towards the 6 target gases at low concentration values at 300°C operating temperatures and 75% relative humidity. The high humidity was chosen to simulate the humidity levels in mines.

Discussion and Conclusion

As obvious from Fig. 1 and Fig. 2, the different sensing materials show specific responses to the test gases, which enables an identification of the test gases. This demonstrates the potential of our sensor system in real-world environments where variations in temperature and humidity are common. Future work will focus on refining the calibration process to enhance accuracy and reliability under varying environmental conditions, thereby improving the system's applicability for industrial and safety-critical applications.

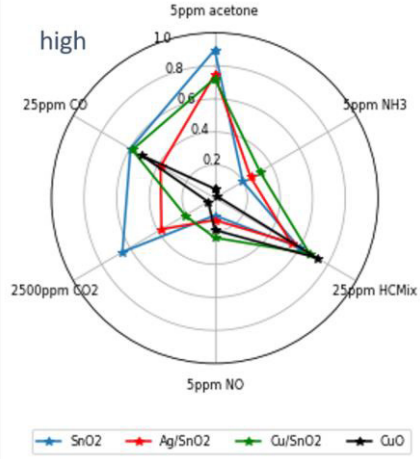

Fig.2 Response of four sensors towards 6 test gases for high concentrations (300°C operation temperature, 75% rh in background gas).

References

[1] N. Barsan, D. Koziej, U. Weimar, Metal oxide-based gas sensor research: How to? *Sensors Actuators, B* Chem., vol. 121, no. 1, pp. 18–35, 2007, https://doi.org/10.1016/j.snb.2006.09.047

[2] C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal Oxide Gas Sensors: Sensitivity and Influencing Factors, *Sensors*, 10, 2010, 10, 2088-2106, https://doi.org/10.3390/s100302088

[3] F. Sosada-Ludwikowska, L. Reiner, L. Egger, E. Lackner, J. Krainer, R. Wimmer-Teubenbacher, V. Singh, S. Steinhauer, P. Grammatikopoulos, Anton Koeck, Adjusting surface coverage of Pt nanocatalyst decoration for selectivity control in CMOS-integrated SnO_2 thin film gas sensors", *Nanoscale Adv.*, 2024, https://doi.org/10.1039/D3NA00552F

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