

Gas sensing applications of CuO doped with metallic catalyst fabricated by spark ablation

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Summary:

In this work, we present chemical nanosensors based on thin CuO films, which are fabricated by spark ablation paired with a dry printing system and subsequent oxidation on Si₃N₄-based micro-hotplate chips. The sensors are tested against various target gases like carbon monoxide (CO), carbon dioxide (CO₂), hydrocarbons (HC_{Mix}) and formaldehyde (CH₂O). An investigation was conducted into various combinations of metallic catalysts, with a particular focus on the CuO, with the objective of reducing the operational temperature.

Keywords: metal oxide, CuO, nanomaterials, spark ablation, gas sensors

Introduction

The detection of hazardous or toxic gases—such as volatile organic compounds (VOCs), CO₂, CO and CH₂O—that adversely affect human health has become essential for monitoring both indoor and outdoor air quality. Conductometric gas sensors operate by measuring changes in the electrical conductivity of a gas-sensitive material when it interacts with surrounding gases. Metal oxides such as SnO₂, ZnO, and CuO are commonly used for this purpose because they exhibit high sensitivity to a wide range of gases [1]. The performance of these sensors can be further optimized through doping with metallic nanoparticles, such as Au, Pd, or Pt, which is considered a promising strategy for enhancing sensor selectivity. [2,3] In particular, the use of CuO is a promising candidate, as it demonstrates significant potential for functionalization with Au nanoparticles, which can enhance the detection of CO₂. [4] In this study, we investigate a solvent-free printing system based on spark ablation, a novel fabrication technique, to print CuO thin layers with metallic catalysts such as Au for gas sensing applications.

Sensor Fabrication

The fabrication technique for producing the sensitive gas-sensing layer of CuO is the patented technology from VSParticle based on spark ablation that can locally deposit the material without use of any patterning/lithography step. Then, the layer is printed directly onto the Si₃N₄ micro hotplate chip with an electrode structure covering an area of 340 × 340 μm². The principle behind

spark ablation involves generation of high-energy electrical sparks between two bulk electrodes (metals or properly doped semiconductors) in a hermetically sealed chamber at atmospheric pressure, with a high purity gas (Ar) being flown through the system. In summary, the spark ionizes the gas and ablates the material from the electrodes. This process creates a vaporized material that rapidly cools down due to the temperature difference between the spark zone and the surrounding environment. [5] The present study focuses on a specific aspect of the spark ablation process, namely the variation of layer thickness, post-annealing temperatures and mixtures with Au metal catalysts during the printing step by using two generators in parallel.

Sensor Characterization & Results

The sensor devices have been operated at 150 and 300 °C and tested against CO, CO₂, HC_{Mix} (an equal mixture of 500 ppm of acetylene, ethane, ethene and propene) and formaldehyde. Synthetic air consisting of 80% N₂ and 20% O₂ with 50% relative humidity (r.h.) has been used as the background gas. A comparison has been made between bare CuO sensors and CuO/Au sensors. Fig. 1 shows the electrical resistance behaviour of CuO/Au sensors when exposed to 0.1, 1 and 5 ppm formaldehyde, measured at an operating temperature of 150 °C. The resistance of the baseline of the bare CuO is enhanced with an increase of Au in the sensing layer. The sensors demonstrate a rapid response time and an extended recovery time.

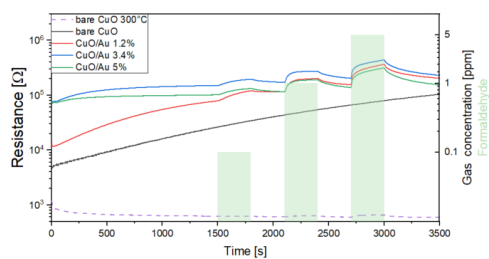


Fig. 1. Resistance measurement during exposure to 0.1 / 1 / 5 ppm formaldehyde at 150 °C (black), 300 °C (violet) operation temperature and 50% r.h. of CuO fabricated by spark ablation, and CuO with different Au content (red 1.2%, blue 3.4% and green 5%)

As illustrated in Fig. 2, the responses of CuO mixed with different concentrations of Au are compared. The sensor response (S), has been calculated according to the following formula:

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} * 100\% \quad (1)$$

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. The sensors are operating at an optimal temperature of 150 °C. The sensors have already reached a state of saturation at low concentrations of each test gas, with the exception of formaldehyde. As demonstrated, the sensors with the highest Au content (5%) correspond to the highest sensor response for each test gas. The highest sensor response was achieved for CO₂, with a result of 77%. Conversely, the sensor response of formaldehyde is not influenced by the Au content; all three Au concentrations demonstrate a comparable sensor response. Notably, these results suggest distinct optimal operating temperatures depending on the target gas with a concentration-dependent response: CuO/Au at 150 °C is well suited for formaldehyde detection, while bare CuO at 300 °C is suited for CO₂.

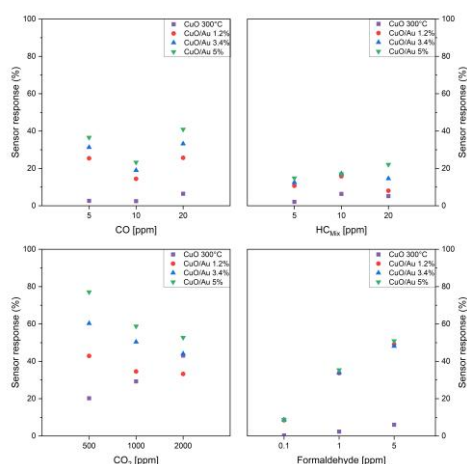


Fig. 2. Sensor response of bare CuO at 300 °C and CuO with different Au content operated at 150 °C towards CO, HC_{Mix}, CO₂ and formaldehyde at different concentrations.

Discussion & Conclusion

We have demonstrated that a combination of CuO and Au is sensitive towards different test gases. The highest sensor response of 77% was achieved for CO₂ with 5% Au content. Typically, CuO gas sensors are operated at 300 °C to ensure optimal sensor response. However, the incorporation of Au serves to reduce this operating temperature from 300 °C to 150 °C, thereby decreasing the energy requirements of the entire system. In addition, the drift of the baseline resistance of the CuO/Au mixture is reduced in comparison with that of the bare CuO.

It is asserted that the pathway for enhancing sensitivity to different test gases with low-energy consuming devices, as outlined here, is a highly promising approach for the development of chemoresistive based sensors to be commercialized.

References

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Funding

The work has been performed within the projects "RealSens- Advanced Nanomaterials for Real-time Environmental Monitoring Sensor System (project No 922632), which receive funding from the Austrian Funding Agency FFG.