

A reproducible, metal oxide based gas sensor for ppb level hydrogen sulfide detection

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Abstract

Metal oxide based gas sensors generally feature high sensitivity but have serious drawbacks in terms of selectivity and reproducibility. The latter is a main obstacle preventing the use of this type of sensors in demanding scenarios, where the determination of concentrations of a specific gas is required. In this contribution we present a novel, reproducible gas sensor approach based on CuO nanoparticles that is capable of determining the hydrogen sulfide concentration down to the ppb level. Employing a thermal modulation scheme and using a percolation phase transition we demonstrate that the sensor response towards H₂S is independent on layer morphology. Using six equally produced sensing layers we show that each device reacts the same upon exposure towards H₂S thus exhibiting repeatability in a metal oxide based gas sensor.

Key words: hydrogen sulfide, reproducibility, metal oxide, CuO, percolation

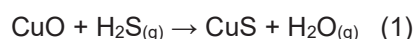
Introduction

The sensitive, selective and reliable detection of toxic trace gases is of great interest in many areas including safety and security applications. To enable mass deployment of chemical sensors the possibility for low cost production and high reliability are crucial. With regards to production cost, metal oxide (MOX) based gas sensors are popular with manufacturers. However, the lack of specificity and repeatability of this gas detection technique limits the field of operation to scenarios where a rough estimate of environmental conditions is sufficient. So far, metal oxide based devices have not been used in analytical equipment since it is inherently difficult to determine the concentration of a specific target gas because of sensor drift, cross sensitivities and a lack of repeatability even between sensor chips of the same batch. Using a scheme for the selective detection of hydrogen sulfide (H₂S) [1] that employs pure CuO nanoparticles with narrow size distribution [2] we show that a repeatable performance of MOX sensors is possible. To this end we have fabricated six CuO layers and evaluated their performance.

Experimental

The six gas sensitive layers are produced via inkjet printing of a colloidal dispersion of Cu₂O nanospheres onto hotplate devices [3] also allowing for precise control of layer thickness. The dispersion has been obtained via a facile

precipitation reaction [4] and heating the layers for 1 hour to 400°C converts the material to pure CuO of the same shape and size, which is subsequently used in gas sensitive characterization. Instead of using the resistivity of the layer to determine the gas concentration, we use the thermal modulation scheme presented in [1] and measure the so-called percolation time. To do this the layer is heated to 450°C first. The timer then starts upon lowering the temperature to 150°C, which makes the substitution reaction:



dominant. The timer stops upon passing a pre-defined threshold of 300 Ω layer's resistivity. Since the electric conductivity of CuS is almost metallic, the emergence of a continuous path heralds a H₂S concentration dependent phase transition from semiconducting to conducting. We exploit this by deducing the H₂S concentration from the time it takes for the phase transition to occur. The layers are reset by heating them to 450°C for 5 min, thus converting CuS back to CuO, even in the presence of H₂S. We have performed a comprehensive gas sensitive characterization in the range from 70 ppb – 5 ppm and varying humidity levels. While the percolation time for 5 ppm H₂S is only seconds, it increases to several minutes for 70 ppb. Figure 1 shows an exemplary layer exposed to 1 ppm H₂S in dry synthetic air. The baseline resistivity at 450°C changes considerably after each percolation

event but the percolation time remains constant.

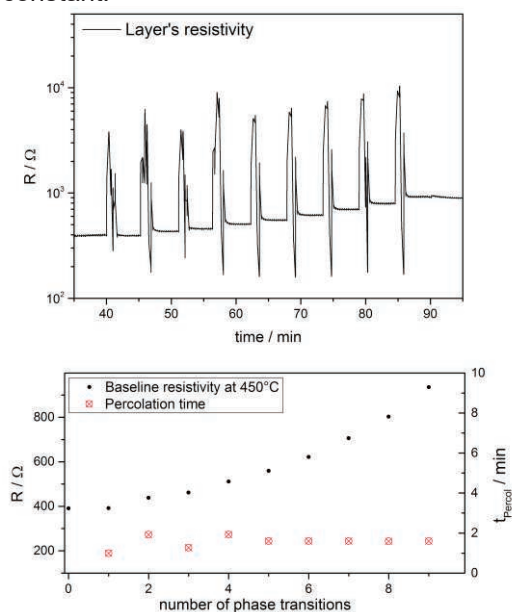


Fig. 1. (top) Transient response of a sample CuO layer during exposure to 1 ppm H₂S and employing the thermal modulation scheme. (bottom) While the baseline resistivity changes more than 100% during the course of 9 percolation events, the percolation time remains constant scattering randomly around a concentration dependent average.

Morphology independence

To highlight the independence of this scheme on the layer's morphology we have performed scanning electron microscope (SEM) analysis of the functional layer right after conversion to CuO and after 9 percolation events. The results are shown in Figure 2 and demonstrate that the percolation time is independent on the surface morphology. In fact, the originally well-defined CuO spheres disintegrate completely and an amorphous layer remains. Nonetheless, the layer's response remains the same. We anticipate that layer thickness is an important parameter for the percolation time, which is why exact control of layer thickness is crucial.

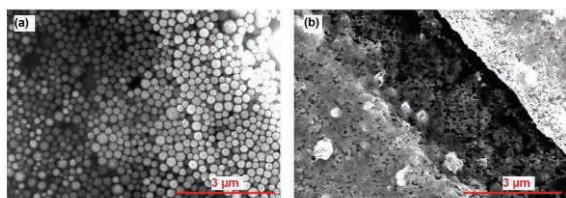


Fig. 2. (a) SEM images of the functional layer right after conversion from Cu₂O to CuO reveals spherical CuO nanoparticles with narrow size distribution. (b) After 9 percolation events the spherical particles have dissolved.

Reproducibility

To check the reproducibility we have operated six layers in parallel and have analyzed the

percolation time for varying levels of H₂S. Each individual layer has showed a random distribution scattering around an average. The average percolation time of the individual layers and total average of all layers are within one standard deviation of each other. This demonstrates that the performance is reproducible and independent on both the layer's morphology and the individual layer.

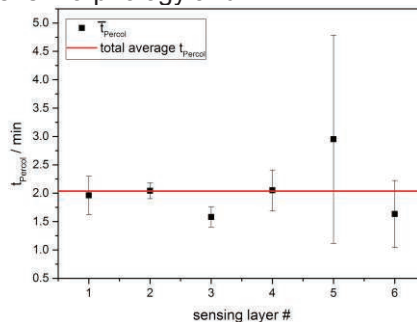


Fig. 3. Analysis of the percolation time of the six layers upon exposure to 1 ppm H₂S in dry synthetic air as well as the global average.

Summary

In this contribution we present a reproducible, morphology-independent, highly selective metal oxide based sensor for the detection of hydrogen sulfide. The functional layers are based on CuO nanospheres, whose shape is destroyed during the course of operation. Because changes in morphology and electrical particularities of the individual sensing layers do not influence the percolation time, a reproducible chemical analysis of the H₂S concentration is possible.

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