

H₂S detection utilizing percolation effects in copper oxide

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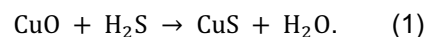
A new type of hydrogen sulfide (H₂S) sensor based on a (chemical) phase transformation in copper oxide (CuO; p-type semiconductor) is presented. Layers of electrospun copper oxide fibers show dosimeter-type behavior if exposed to highly diluted H₂S at operating temperature of 170 °C. The conductance of these layers remains nearly constant for a certain time period (latency time) after which the conductance increases over several orders of magnitude. The latency time shows a linear dependence on the reciprocal H₂S concentration; consequently the layers are acting as dosimeter. The presented sensor shows a switching point at a dose of ca. 210 ppm*s. The effect is reversible; operating the fiber network at 350 °C in air leads to a recovery of the initial conductance; higher doses can therefore be detected by cyclic operation mode. As could be shown the observed behavior is due to the formation of copper sulfide clusters (CuS; degenerate p-type semiconductor) on the outer face of the CuO-fibers. As long as the CuS clusters are disjunct the conductance is not changed effectively. After reaching a critical CuS cluster concentration (percolation threshold) a percolation network is formed. The conductance increases as a function of time and follows a power law for several orders of magnitude, which is in accordance with theoretical model.

Key words: percolation, hydrogen sulfide, copper oxide, copper sulfide, dosimeter

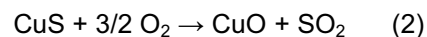
Introduction

The detection of sulfur containing gases has a broad variety of applications. Concerning the high toxicity of hydrogen sulfide safety sensors are required e.g. for the work in sewage water systems. The limit value of hydrogen sulfide (H₂S) for short term exposure (15 min) is 10 ppm in Germany as well as in the United States [1][2]. Hydrogen sulfide is also an important byproduct in digester gas. The purification of digester gas is necessary to prevent damage in storage and combustion processes. For this purposes classical semiconductor gas sensors are not applicable. These sensors typically utilize a change of surface charge caused by oxidizing or reducing gases [3] and can achieve high sensitivity. Nevertheless a lack of selectivity is an obstacle for many applications. Up to a certain extend selectivity can be achieved by choice of sensor material and temperature as well as surface doping [4] [5]. By addition of CuO clusters to tin dioxide (SnO₂) sensing layers different groups utilized their high affinity to sulfur containing species (e.g. H₂S, methyl sulfide, dimethyl sulfide) to increase sensitivity and selectivity compared to other reducing gases e.g. ethanol [6-8]. However, these sensors do still show cross sensitivity to reducing gases. Recently we

have demonstrated that under sound conditions CuO nanofibers can be operated without a SnO₂ transducer as a dosimeter-type gas sensor and that this successfully rules out cross sensitivity to sulfur-free gases (ammonia, carbon monoxide, hydrogen and methane) [9, 10]. The mechanism of the sensor is based on a (surface near) phase transformation of copper oxide to copper sulfide:



The phase transformation (1) is in the following called sulfurization and it is dominant at low temperatures (< 200 °C) whereas at high temperatures (e.g. 350°C) the desulfurization (re-oxidation) reaction (2) is dominating:



The phase transformation is therefore reversible.

A similar sensor principle based on a solid state reaction has also been demonstrated for other gases as e.g. NO_x. There the change of the resistance of a lean NO_x trap during accumulation is utilized as sensor signal [11].

There are various other reports on pure CuO sensors [12, 13]. A CuO sensor using oriented nanofibers was presented by Steinhauer et al. [14]. Although this work is focusing on surface

effects the sulfurization effect at low temperatures is clearly visible.

The conductance of CuS [15] is nearly metallic whereas the conductance of CuO is a weak p-type semiconductor [7,8]. As long as CuS clusters are insulated at the surface of the fibers their contribution to the networks conductance is weak. After a specific dose of H₂S we observed a dramatic increase of the conductance that we interpret as due to highly conducting percolation pathways via the CuS islands, which are then dominating the conductance. In general the conductance of a percolation pathway near the critical concentration p_c (here the concentration of CuS clusters when the first pathway is formed) can be described by a power law with an universal exponent μ (only depending on the dimension of the lattice) [16]. The conductance depending on the concentration p of CuS clusters is then:

$$\sigma \sim (p - p_c)^\mu \quad (3)$$

Numerical values for the exponent μ are 1.3 for 2D- and 1.99 for 3D-systems [16]. Assuming that the concentration of CuS clusters is growing linear with time ($p \sim t$) this would lead to:

$$\sigma \sim (t - t_c)^\mu. \quad (4)$$

This has already turned out to describe the observed conductance increase of CuO fibers exposed to 5 ppm H₂S in air [10] very well.

Material preparation and experimental setup

Fibers are obtained by an electrospinning process of a 1:1 solution of copper nitrate in polyvinylbutyrate. The process is described in details in [9]. The process yields in a tuft of arbitrarily oriented fibers that is cut in piece for characterization and sensor preparation. The fibers are transformed to copper oxide (CuO) fibers by thermal oxidation at 600 °C. The CuO-fibers have a mean diameter of 480 nm with a broad distribution of 140 nm. For sensor preparation a piece of the as synthesized fiber network is fixed on a sensor substrate (UST x330) [10, 17] by adhesion using a small water droplet using subsequent thermal oxidation. The sensor substrate has an integrated platinum heater used for heating as well as for temperature control. The CuO wires are connected by two interdigital electrodes with an electrode width and gap width of approximately 25 μ m each. Figure 1 (a) shows a section of the sensor surface which is covered by CuO wires. The network is very thin with little interconnections between the wires (b). The lengths of the wires are much higher than the electrode gap. The conductance of the network,

therefore, is dominated by the conductance of parallel fibers. It is assumed that weak connections between fibers are not contributing significantly. It can be seen that the fibers themselves are mesoporous (figure 1b) with a grain and pore size in the order of approximately 50 nm. Therefore not only the outer surface of the fiber is considered to be active.

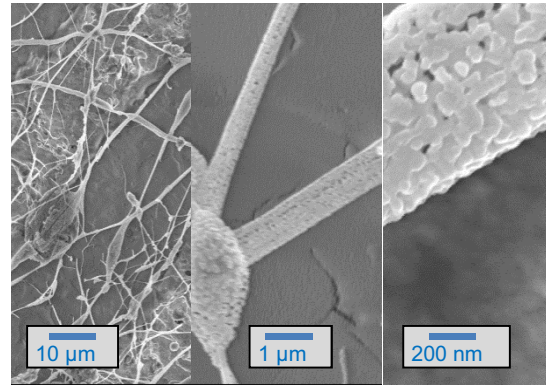


Figure 1: Scanning electron micrographs of the CuO fibers on a sensor substrate with different magnifications (M): (a) on the left ($M=1000$) the interconnections between the electrodes are shown [10]; (b) in the middle ($M=10000$) the connection of two fibers is visible; (c) on the right ($M=50000$) the grains and pores of a single fiber are depicted [9].

Material characterization

The incorporation of sulfur in the CuO layer was measured by (spatially resolved) EDX [9]. It was proven that the concentration of sulfur in the fiber is continuously increasing while exposed to H₂S at operating temperatures below 200 °C. After thermal treatment at 350 °C in air there is no residual sulfur detectable in the fibers. The process can therefore be considered to be reversible concerning the metal oxide phase. Nevertheless, the results also showed that there is a significant change in morphology over one sulfurization/ desulfurization cycle. We argue that this change is mostly due to a mismatch of molar volumes of CuO and CuS. The phase transformation to CuS leads to a strong growth of the molar volume. The porous structure of the nanofibers seems to be very advantageous to buffer this volume growth. Even after several regenerations still reproducible measurements are possible for this material whereas measurements utilizing compact CuO films show significant alteration of the film behavior in the for subsequent sulfurization cycles. The formation of copper sulfide was proven by using a secondary ion mass spectrometer (TOF-SIMS V, IONTOF GmbH). The analysis of fiber sample is shown in figure 2 for a H₂S treated fiber tuft. The treatment was 20 ppm H₂S in air at 170 °C for

20 min in a tube furnace. It shows that the SIMS spectra of copper, oxygen and copper sulfide are coexisting. Especially a significant formation of CuS in the fiber sample can be observed (the signals are not calibrated for quantification). The resolution is not high enough to discriminate individual fibers or even single CuS clusters.

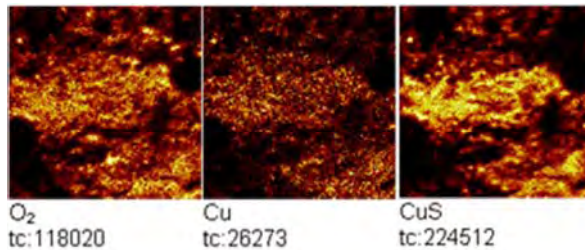


Figure 2: Spatial resolved SIMS measurement of a H_2S treated tuft of CuO fibers (not calibrated for quantification). The area of the tuft is $500 \times 500 \mu m^2$.

Sensor measurements

A CuO nanofiber sensor was exposed to 100 ppb H_2S in synthetic air at 30 % relative humidity supplied by a computer controlled gas mixing system. A custom-built electronics was used for the conductance measurement; the measurement voltage was kept constant at 0.25 V. The conductance prior to the H_2S exposure (but with carrier gas flow) is approximately $0.05 \mu S$. Figure 3 shows the sensors conductance during the H_2S exposure.

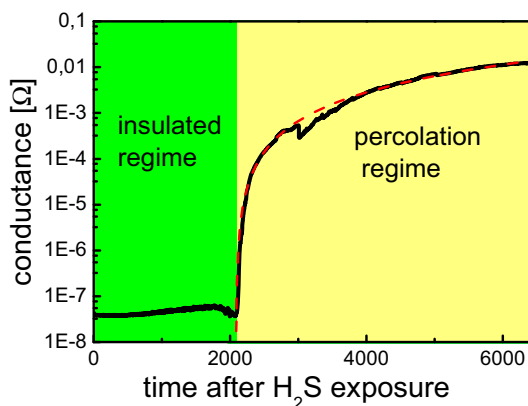


Figure 3: Conductance of a CuO nanofiber sensor exposed to H_2S (black line). The conductance in the percolation regime (yellow area; $t_c=2088$ s) is fitted by a power function with an exponent $\mu=1.99$ (dashed red line).

For ca. 2000 s (green) the change of conductance is very low. This is considered the regime of insulated CuS clusters on the surface of the CuO fibers. At 2088 s after the start of the exposure a steep increase of the conductance is observed. This is considered

the start of the percolation regime (yellow). The increase of conductance as a function of time for all data points in the percolation regime is fitted (OriginPro™ 8.6, function type *Belehradek*) by power functions as defined in (4). We use a nonlinear fitting algorithm with three free parameters (a , t_c , μ) yielding a value of 2088 s for t_c and a value of 1.985 for μ , which is already in good agreement with the predicted value for 3D percolation. (Figure 3, dashed red line).

The switching time t_c could be shown to be reciprocal to the concentration in the range of 100 ppb to 5 ppm [10] (Table 1). In order to compare the t_c -values independently from small conductance changes caused by surface effects or drift t_c was defined as the time after the conductance exceeds 10^{-6} S.

Table 1: H_2S -Dose (concentration multiplied by time) until switching for different concentrations [10]

concentration	t_c (at $\sigma \geq 10^{-6}$ -S)	conc. * t_c
0.1 ppm	2144 s	214 ppm s
0.5 ppm	481 s	242 ppm s
1 ppm	234 s	234 ppm s
2 ppm	88 s	176 ppm s
5 ppm	57 s	285 ppm s

The sensor cannot be operated in a continuous way since the desulfurization needs an elevated temperature. However, it could be shown that there are possible quasi-continuous modes of operation, e.g. as shown in Figure 4.

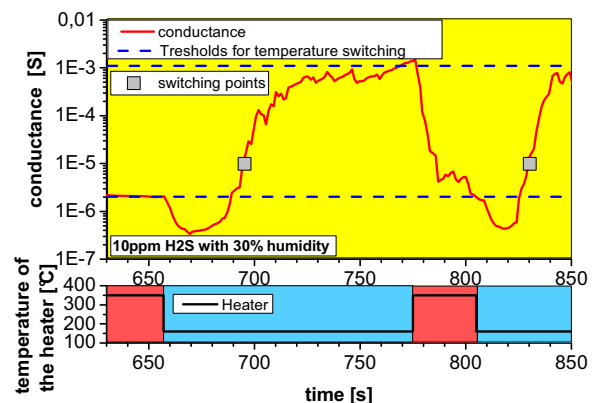


Figure 4: Quasi-continuous operation mode: The operating temperature of the sensor is controlled by the conductance. The high temperature (350 °C) is applied after exceeding a "regeneration" threshold (10^{-3} S, upper dashed blue line) of the conductance. The low temperature (170 °C) is applied after running below the "measurement" threshold ($2 \cdot 10^{-6}$ S, lower dashed blue line). The time between reaching "measurement" threshold and switching point ($\sigma \geq 10^{-5}$ S) could be defined as sensor signal.

In this mode there are 3 conductance thresholds. Two thresholds are used to control the sensors operating temperature (I) and therefore operation mode and one is used to generate a sensor signal(II):

- (I) Reaching a “regeneration” threshold triggers an operation temperature increase (350 °C) leading to a desulfurization of the fibers even if the sensor is exposed to 10 ppm H₂S in air. This regeneration phase until the sensors conductance does fall below the “measurement” threshold. Then the operating temperature is decreased to 170 °C and the CuO fibers start to accumulate sulfur. This point is also used as the starting point for the signal generation.
- (II) Reaching the switching point (conductance marks the end of one measurement cycle. Since the increase is very steep it might be beneficial to choose a value well above the baseline conduction in order to avoid false switching caused e.g. by electrical noise. The reciprocal time span between the starting point for signal generation and switching point could be defined as sensor signal. Higher concentrations of H₂S lead to shorter time span values and therefore higher reciprocal time span values respectively.

This modus operandi is suitable for applications where e.g. very low concentrations have to be detected and the demands on the sampling rate are not too high.

Conclusion

Sulfurization of copper oxide fibers at a temperature of 170°C has been proven to be suitable method for detection of small H₂S concentrations. As could be shown this effect is reversed by heating the fibers to a temperature of 350 °C. The presented fibers showed a switching point at a dose of ca. 210 ppm*s. Therefore, the sensor presented is sensitive enough for monitoring H₂S pollution in working environments, where the short term exposure limit equals a dose of 9000 ppm*s in 15 min [1]. The transient of the conductance increase can be described by a simple percolation model for a 3D percolation system. The high porosity of the fibers indicates that the use of a 3D model for the percolation process is suitable. An (quasi-continuous) operation mode for the sensor was suggested where alternating accumulation (measurement) and regeneration cycles have been used to generate a continuous sensor signal.

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