

Electrospun Copper(II)oxide Fibers as Highly Sensitive and Selective Sensor for Hydrogen Sulfide Utilizing Percolation Effects

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Abstract:

We propose a novel sensor for the detection of hydrogen sulfide (H₂S) using a network of electrospun copper(II)oxide (CuO) fibers. The Sensor is very sensitive to H₂S with a detection limit below 0.1 ppm and exhibits no response to reducing gases like carbon monoxide, hydrogen, methane or ammonia. This selectivity to H₂S is advantageous in highly contaminated gas samples e.g. in biogas reactors. These properties are due to a unique sensor mechanism based on a reversible phase transition of p-type CuO to degenerated p-type copper sulfide (CuS) in the vicinity of the surface. At a temperature of 160°C the sensor shows a steep increase of conductance after a time span t_c , which depends on the offered H₂S concentration. We investigated this mechanism by using a CuO thin film as a model sensor and interpret the result in a framework of percolation theory. For regeneration the sensor has to be heated up to 350°C to convert the CuS back into CuO.

Key words: copper(II)oxide, hydrogen sulfide, sensor, sensitive, selective, and percolation

Introduction

In the last few years the production of renewable energies has considerably increased. An important role in this new energy concept plays biogas generation by anaerobic digestion of e.g. sewage or crop residues. Nevertheless unwanted gases like hydrogen sulfide (H₂S) are formed in this process, too. Hydrogen sulfide leads to corrosion of metal parts of the plant, reduces the stability of engine oil in biogas motors and is harmful to human health [1,2]. Only 30 ppm hydrogen sulfide can already lead to heavy disorder of the central nervous system [3]. Therefore, the international occupational exposure limit values are in the range of 1-10 ppm [4]. Therefore, monitoring of H₂S is an important issue for save operation and protection of the plant and the operating personnel.

Since the early nineties it is well known that an addition of copper oxide to the polycrystalline tin oxide (SnO₂) layer of a semiconducting gas sensor increases markedly its sensitivity to H₂S [5]. However, SnO₂ is prone to poisoning by H₂S and shows also (high) sensitivity to various other gases [6,7].

An alternative to the described sensor concept is the usage of pure copper(II)oxide (CuO) as sensor material. It shows a high sensitivity to H₂S and only a small response to other gases like e.g. methane and ammonia. Ramgir [8] described in his work two different reaction mechanisms on a microcrystalline CuO thin film at room temperature. At low concentrations the exposure to H₂S leads to an increase of resistivity caused by a surface reaction. At higher concentrations he observed a decrease of resistivity, which is due to a phase transition of semiconducting CuO to metallic conducting CuS [9,10]. In a paper of Chen CuO is investigated at 160°C. He observed a change of resistance at high H₂S concentrations over several orders of magnitude [11].

In this work we present a new sensor concept. We use electrospun CuO nanofibers at 160°C for the detection of H₂S with sensitivity to below 100 ppb. The dynamic range amounts to over five orders of magnitude. After a time span t_c depending on the offered H₂S concentration the conductance makes a steep increase, which can be described by a power law with a critical exponent μ . We found a value of 2.04 between

the two values that one expects for percolation systems of 2D ($\mu \approx 1.31$) and 3D ($\mu \approx 2.07$), respectively. This should be expected for the investigated nanofibers that can be considered as intermediate between the two special dimensions. In this context, it is of special interest that measurements on 2D CuO thin films [12] show a μ of 1.28 which is in good accordance to the critical exponent of a pure 2D system. In the state of high conductance the sensor can be refreshed at 350°C.

This threshold type behaviour (digital signal) allows us to use simple readout electronics. After the switching of conductance the temperature can be raised to 350°C for getting the initial state back. So the heat pulses can serve as signal to measure the gas concentration for a certain time.

Preparation

The copper(II)oxide nanofibers were produced by using a standard electrospinning setup. A solution of poly vinyl butyrate (PVB) and copper nitrate $\text{Cu}(\text{NO}_3)_2$ in ethanol (PVB:Cu=1:1) was spun on a metal rack to get a nanofiber network pad. During this process an electric field of 25kV and an electrode gap of roughly 20 cm was used (for more details see e.g. [13]).

For electrical readout and heating of the fibers we applied a piece of the polymer nanofibers pad with $\text{Cu}(\text{NO}_3)_2$ salt addition on a commercial sensor substrate from UST GmbH. We used a 3 mm x 3 mm alumina gas sensor substrate with platinum interdigital electrodes and built-in heater (see Fig. 1).

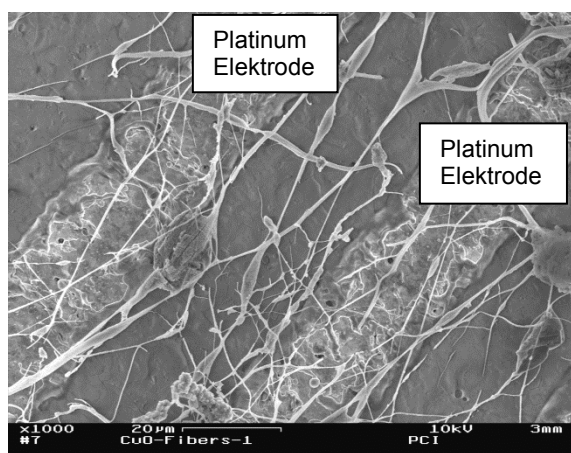


Fig. 1. CuO nanofibers deposited on an UST alumina substrate with IDS platinum electrodes crossing under 45°.

After successive cleaning of the substrates in acetone, isopropyl and distilled water for a few seconds and 5 minutes drying at 600°C, a drop of distilled water was applied to the substrate. So we attained a better connection with the

fibers. Afterwards the substrate was heated up again to 600°C within 30 minutes. At this temperature the fibers were calcinated for 24h in ambient air to convert the $\text{Cu}(\text{NO}_3)_2$ to CuO [14] and remove the polymer. In the last step the fibers cooled down to room temperature during 30 minutes. The mean diameter of the fibers amounts to (483 ± 143) nm.

Experimental Settings

To provide a well-defined gas flow during the gas measurements standard mass flow controllers were used. We used a basic gas flow of synthetic air with 30% relative humidity and added the test gases to the main stream. The heater of the sensor and the electrical readout of the fibers were controlled by custom-built electronics. The data were recorded on a PC by a Lab View program. For the measurement we used electrical pulses of 1 V for 100 ms each second to suppress electromigration effects. The sensor was operated in a two temperature mode. At the low temperature (160°C) the gas measurements were performed and at the high temperature (350°C) the fibers were regenerated [8].

Gas Measurements

The fiber network was exposed to 5 ppm H_2S at low temperature mode. When the exposure has been started at first the conductance has been found decreasing. However, after 54 seconds a slightly steep increase of the conductance over five orders of magnitude occurs (Fig. 2).

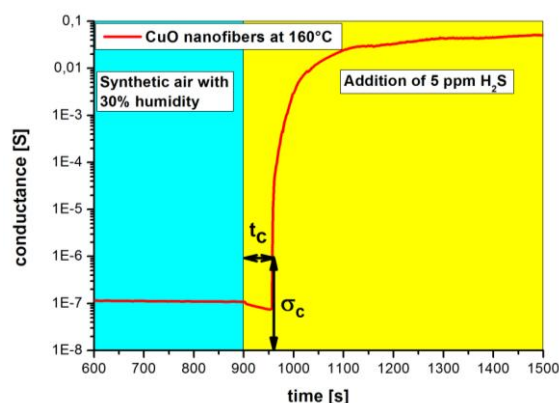


Fig. 2. Conductance change during a continuous H_2S exposure of 5 ppm, where t_c is the time span of the defined switching point σ_c at 10^{-6} S.

We define a critical time span t_c as the interval between the start of the gas exposure and the time, when the critical conductance σ_c equals 10^{-6} S. After exposure to various concentrations of H_2S the fibers show a reciprocal dependency between the offered concentration and the critical time span t_c . Thereby the fibers were always annealed at 350°C prior to each

measurement in the absence of H₂S. Then we offered some other reducing gases to the fibers for 1800 s, too. But for them no switching could be observed (Table 1).

Tab. 1: t_c for different gases and concentrations

gas	concentration	Time until switching
H ₂ S	0.1 ppm	2144 s
H ₂ S	0.5 ppm	481 s
H ₂ S	1 ppm	234 s
H ₂ S	2 ppm	88 s
H ₂ S	5 ppm	57 s
Methane	10000 ppm	No switching
Carbon monoxide	100 ppm	No switching
	20 ppm	No switching
Ammonia	300 ppm	No switching

Regeneration

During regeneration bake out at 350° C the conductance of the fibers decreases within five minutes. Thereafter the conductance remains at a constant level. When the fibers were tempered for 30 minutes without H₂S an EDX analysis showed that the sulfur had been completely removed (Fig. 3). The appearance of platinum and aluminum peaks are due to the sensor substrate.

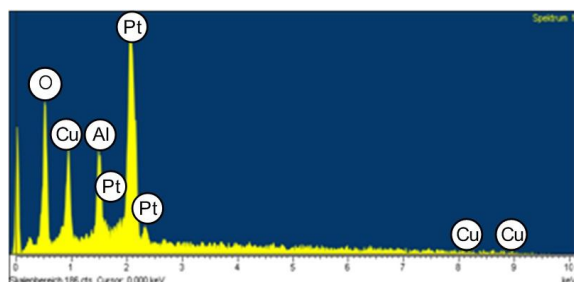


Fig. 3. EDX analysis of the tempered fibers after 30 minutes at 350°C.

Data Analysis

An analysis of the steep conductance increase of the 5 ppm measurement shows two different regimes that we interpret as a transition between two different power laws. In figure 4, to discover the exponents of these regimes, we plot $\sigma - \sigma_c$ versus $t - t_c$ in a double-logarithmic plot, i.e. we start the presentation at the switching time. A fit of the critical exponent of the first regime (green line) shows a behavior as [15]

$$\sigma \sim (t - t_c)^\mu \quad (1)$$

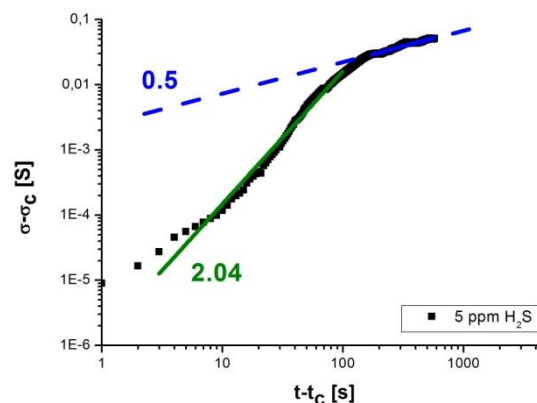


Fig. 4. Measurement of the 5 ppm concentration plotted as a function of $t - t_c$ and $\sigma - \sigma_c$ in a double logarithmic scale.

with $\mu \approx 2.04$. This strong increase is followed by much smoother increase with an exponent of about 0.5 (blue line).

Discussion

When CuO is exposed to H₂S at low temperatures (e.g. 160° C) it undergoes a successive phase transformation by generating highly conductive copper sulfide (CuS) clusters [11]. We assume that as long as the CuS clusters are disjunct they do not contribute significantly to the conductance. If the fraction p of surface covered by CuS clusters in relation to the entire surface of a fiber / film exceeds a critical value p_c , percolating pathways are formed. The conductance is almost immediately dominated by the CuS pathways. The influence of the confined geometry of the disordered CuS structure on the conductivity can be described by percolation theory [15].

The assumption that the CuS density after the formation of the percolating pathways (which takes place at the switching time t_c increases proportional to the time t , $(t - t_c) \sim (p - p_c)$, leads to the following prediction (see also [12]) for the increase of the conductivity

$$\sigma_{DC} \sim (t - t_c)^\mu \quad (2)$$

with $\mu = v(d_w - 2) + v(d - d_f)$. Here the anomalous diffusion exponent d_w , the fractal dimension d_f and the exponent v are universal for percolation systems leading to $\mu = 1.31$ in $d = 2$ and $\mu = 2.07$ in $d = 3$. Recently, we have proven for copper oxide thin films that the conductance characteristics after the switching time t_c follows a power law with the exponent $\mu = 1.28$ predicted by percolation theory for 2 D disordered systems. This shows that the CuS network can be seen as a constantly growing, fractal network on a 2-dimensional plane. Figure 4 shows that for the fiber network the increase of conductance above the percolation threshold is steeper than

in the 2D system [12] with an exponent of $\mu=2.04$. The complex CuS-structure growing on the fiber network seems to feature 3D effects. After a long exposure to H₂S the surface is completely covered by CuS clusters. At this stage the increase of conductance is dominated by the growth of the film thickness. Considering a growth mechanism dominated by bulk diffusion the thickness and thus the conductance of CuS films should increase proportional to $t^{0.5}$, which is in good accordance to our experimental data (fig. 4 inset blue line). The EDX analysis verifies that during the annealing process at high temperature the CuS is reoxidized to CuO. The other test gases do not cause switching.

Conclusion

The sensor operation will involve a change between a low temperature state at 160° C and a high temperature state at 350°C. Here we are using the time span t_c describing the formation of a percolation path in the low temperature state as sensor signal. The fiber structure shows a high sensitivity above 100ppb over 5 orders of magnitude to H₂S. The sensor does not show any cross sensitivities to the other test gases. The critical exponent of the fibers is steeper than expected for a pure 2-dimensional percolation system. This nearly digital signal helps to simplify measurement electronics.

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