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Percolation-Based Chemical Switch for H_2S Gas Detection

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Abstract:
We present a nanocomposite material based on semiconducting copper oxide that exhibits stable chemical switching behavior when exposed to hydrogen sulfide (H_2S). The switching is characterized by a fully reversible increase in conductance of up to seven orders of magnitude and can be explained by means of percolation theory. Exposure to distinct amounts (dosimetric sensing) of H_2S at low operating temperature (160 °C) leads to the formation of a percolation path due to the selective phase transition of copper oxide (CuO, low conductivity) to copper sulfide (CuS, high conductivity). The initial state can be recovered by high-temperature treatment. However, in conventional layouts (films) this typically leads to degradation of the sensing layer structure caused by a volume decrease during CuO recovery, resulting in a low cycle stability. The nanocomposite material presented here is based on a porous silica matrix that allows for structural stabilization of the CuO/CuS system and a stabilization of the percolation threshold. The selective formation of CuS inherently minimizes cross-sensitivity to H_2, CH_4, CO, NH_3, or NO. The material is therefore suitable for such applications as monitoring the degradation process in biogas plants. In addition to the high stability during more than 900 sensing-recovery cycles, theoretical simulations will be presented that allow insight into details of the chemical mechanism.

Key words: percolation effect, chemical switch, dosimetry, hydrogen sulfide, biogas

Sensing Mechanism

Exposure of a thin CuO film to H_2S gas at moderate temperatures (160-200 °C) leads to a phase transition from p-type semiconducting CuO to metallic conducting CuS. This chemical reaction can be reversed by high-temperature (~350 °C) treatment. Due to the lower density of CuS compared to CuO, the volume of the copper compound decreases by a factor of 0.6 during regeneration which causes changes in the film morphology and reduces the life time of the sensor to only a few sensing cycles [1,2,3]. It was already shown that the cycle stability of a matrix of electrospun nanofibers [4] can lead to an improved cycle stability. Here we use different types of mesoporous silica as a support matrix to inhibit the migration of the CuO/CuS grains in order to improve the long-term stability of the sensor. Furthermore, the volume change is utilized as an advantage. The porous matrix is filled only partially with CuO, so that the grains are not in contact with each other (see fig. 1). This is the “insulating”, or rather, the low conducting state. During exposure to H_2S gas, CuS forms; the grains expand, and contact each other at a distinct amount of H_2S.

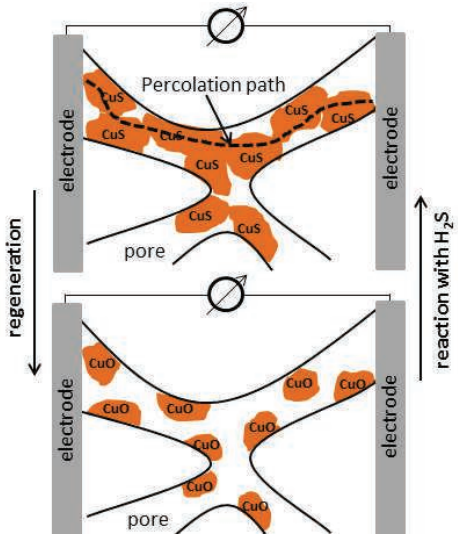

Fig.1 Scheme of the insulating CuO (bottom) and the conducting CuS state (top).

A percolation path is formed and the measured conductance rises several orders of magnitude. It switches from the “insulating” to the “conducting” state. During regeneration by high

temperature treatment the H_2S gas can still be present, without interfering with the formation of the initial state of the sensor. Therefore, this sensor can be used while permanently environed by the gas to be detected.

Experimental

Copper oxide (CuO) is created in the pores of mesoporous silica (e.g. KIT-6 [5]) by impregnation with $Cu(NO_3)_2$ and subsequent thermal conversion. The composite material is deposited on a commercially available inter-digitated sensor substrate from UST Umwelt-sensortechnik GmbH. A constant voltage of 1 V is applied to the interdigitated electrodes; the measured current allows calculation of the conductance. Temperature is adjusted via the build-in Pt-heater. An automated gas mixing equipment based on mass flow controllers was used to supply the different gas concentrations.

Results and Discussion

Upon exposure to H_2S gas at 160 °C the reaction to CuS occurs. The grains grow up to the point where they are in contact with each other. A percolation path is formed (fig. 1 top). As a result, the electric conductance increases seven orders of magnitude (fig. 2).

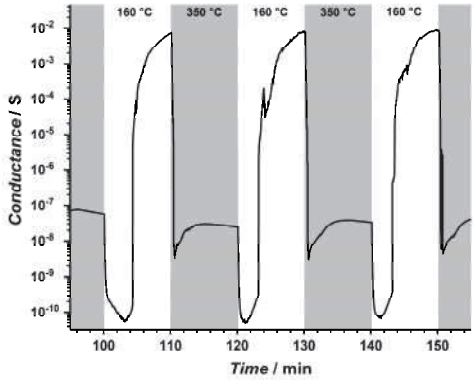

Fig. 2. Conductance of the CuO/CuS@SiO_2 composite during 10 ppm H_2S gas exposure

This increase cannot be only due to the formation of CuS (increase of about 10^5 S). We rather assume the expansion of the grains to be responsible. In total two different percolations mechanisms occur in our system, which superimpose each other and lead to this large increase in conductance. Subsequently the initial state is recovered by raising the temperature up to 350 °C (fig. 1 bottom left).

To test the long-term cycling stability a custom built setup including a simple percolation threshold detection algorithm was utilized. Contrary to CuO film samples, over 900 sensing cycles could be measured. In addition statistical simulations of the percolation mechanism will be presented, which allow the interpretation of the measured data by means of percolation theory, i.e. critical exponents and percolation thresholds are determined. Figure 3 shows an example for the analysis of chemical noise during percolating path formation for a finite lattice.

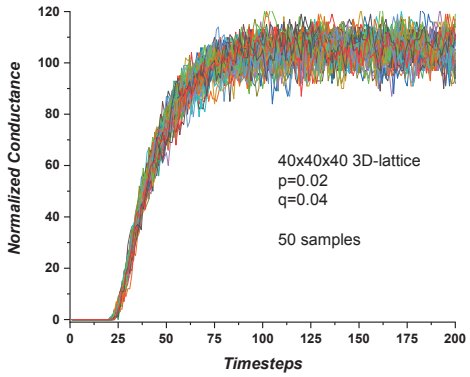

Fig. 3. Simulation of chemical noise during percolation path formation for bond percolation on a 40x40x40 lattice; probability for conducting bond formation p and for insulating bond formation q.

Acknowledgements

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