H₂S dosimeter with controllable percolation threshold based on semi-conducting copper oxide thin films

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Abstract. Copper oxides, such as CuO and Cu₂O, are promising materials for H₂S detection because of the reversible reaction with H₂S to copper sulfides (CuS, Cu₂S). Along with the phase change, the electrical conductance increases by several orders of magnitude. On CuO_x films the H₂S reaction causes the formation of statistically distributed Cu_xS islands. Continuous exposition to H₂S leads to island growth and eventually to the formation of an electrical highly conductive path traversing the entire system: the so-called percolation path. The associated CuO_x / Cu_xS conversion ratio is referred to as the percolation threshold. This pronounced threshold causes a gas concentration dependent switch-like behaviour of the film conductance. However, to utilize this effect for the preparation of CuO-based H₂S sensors, a profound understanding of the operational and morphological parameters influencing the CuS path evolution is needed.

Thus, this article is focused on basic features of H₂S detection by copper oxide films and the influence of structural parameters on the percolation threshold and switching behaviour. In particular, two important factors, namely the stoichiometry of copper oxides (CuO, Cu₂O and Cu₄O₃) and surface morphology, are investigated in detail. CuO_x thin films were synthesized by a radio frequency magnetron sputtering process which allows modification of these parameters. It could be shown that, for instance, the impact on the switching behaviour is dominated by morphology rather than stoichiometry of copper oxide.

1 Introduction

Hydrogen sulfide (H₂S) exhibits a characteristic odour of rotten eggs and is released, for example, during the generation of biogas. Due to its toxicity the allowed maximum workspace average concentration is as low as 5 ppm for 8 h in the European Union. H₂S typically causes eye irritation starting at small concentrations (10 ppm); above 150 ppm the nose's receptors accustom to H₂S and above 500 ppm dizziness occurs (IFA, 2016; Schieder et al., 2003; Wellinger and

Lindberg, 2000). Therefore personal monitors are mandatory if working in potentially H₂S-containing environments.

In addition H₂S accelerates abrasion of machine parts due to its corrosive behaviour and high reactivity with iron. Nowadays, filters, mostly based on activated carbon, are used to adsorb these contaminations. The common practice is the exchange of filters in defined periods. This leads to high maintenance costs and to the risk of overlooking filter defects. Reliable and affordable H₂S sensors open up the possibility of using activated carbon filters more efficiently because the filters can be filled completely and are replaced

only if the sensor predicts H$_2$S breakthrough (Schieder et al., 2003; Wellinger and Lindberg, 2000).

There is a variety of H$_2$S sensors commercially available. The most popular detection principle for mass applications is based on an electrochemical process (EC cell, amperometric sensor). The reaction of H$_2$S on an electrode in a liquid electrolyte causes a current flow quantitatively correlated with the gas concentration in the surrounding atmosphere. The EC cells exhibit short response times, are very reliable and the sensing mechanism is understood quite well. However, there are a few drawbacks of this concept. The lifetime even under "mild" process conditions is typically limited to 2 years due to drying out of the electrolyte. Besides this, relatively costly electronics are needed to process the small currents (range of pico-amperes; Jeroschewski et al., 1996). Other principles, for example based on optical methods like high-priced tuneable diode laser absorption spectroscopy (TDLAS), are used for low-quantity applications with high demands on precision (Kim and Kim, 2009; Mullins et al., 2009). However, to the best of the authors' knowledge the only true dosimetric-type principle commercially available is based on lead acetate (e.g. in Dräger tubes). Besides the fact that a regeneration in this case is not easy to achieve, legislation prohibits the use of lead in future electronic devices.

The copper-oxide-based concept presented here aims for the detection of very low concentrations in relatively harsh environments with a simple measurement setup. The dosimetric behaviour of the copper-oxide-based sensors allows the detection of very small concentrations to, for example, predict filter breakthrough. In addition, the simple on/off switching simplifies the detection setup dramatically. For regeneration, only a heater has to be controlled and the trigger time can be directly correlated with the H$_2$S dose (concentration × time). CuO thin films detect quite low doses (~ 10 ppm × 15 min) which are in the same range as supposed working limits (Hennemann et al., 2015a; IFA, 2016).

Several works have already shown the principal suitability of CuO in H$_2$S sensors, but the lifetime and precision are currently substantial problems to overcome (Hennemann et al., 2015a, b; Kneer et al., 2016). Since biogas represents a mixture of many gases containing only minor amounts of H$_2$S, the sensors should be insensitive to other reducing gases being present in such mixtures. Copper oxide (CuO) is an excellent candidate fulfilling these requirements. It offers high reactivity to hydrogen sulfide (H$_2$S), but stays nearly unaffected by minor amounts of methane, nitrogen oxides or hydrogen at operating temperature (ca. 160 °C; Choi et al., 2013; Hennemann et al., 2012a). As shown by Choi et al., the conductance changes 2 orders of magnitude under 1000 ppm H$_2$ exposure. In comparison to H$_2$S the conductance step covers at least 3 to 4 orders of magnitude independent of its concentration. Also, previous works have indicated the large impact of structuring CuO on short length (~ 100 nm) scales on sensing properties and long-time stability (Sauerwald et al., 2013). For instance, electrospun CuO nano-fibres

enhanced the magnitude of conductance change due to their higher surface area enlarging the measuring range of the sensors (Hennemann et al., 2013). However, in spite of these encouraging results, the impact of several parameters needs to be understood in more detail. For example, copper oxide can be a mixture of different species, in particular CuO, Cu$_2$O and also Cu$_4$O$_3$, created either due to reducing conditions during the synthesis or by reducing gases during operation at elevated temperatures (Hennemann et al., 2015a). As discussed in previous works (Sharma, 1980) the reaction mechanism of Cu$_2$O in a H$_2$S-containing atmosphere is still not understood in detail. For instance, the role of diffusion effects in the percolation regime reaction of Cu$_2$O films with H$_2$S is not clear yet; see the discussion in the study of Hennemann et al. (2015a). Also, Sharma (1980) noted that the reactivity of Cu$_2$O towards H$_2$S can strongly depend on the humidity (Sharma, 1980).

As another potentially important factor, the morphology of copper oxides (surface area, roughness, grain boundaries, etc.) is expected to exert a significant impact on the conductance increase and percolation effect. For instance, the rate of reaction between a copper oxide (either CuO, Cu$_2$O or Cu$_4$O$_3$) and H$_2$S will certainly increase for a high-surface-area material.

In light of these various factors determining the usage of copper oxide materials for H$_2$S sensors, this paper is intended to introduce and summarize the basics of this special detection principle (Sects. 2 and 3) as well as the fundamental experimental approach (Sects. 4 and 5). Furthermore, two important factors influencing the percolation behaviour are exemplified on thin films possessing thicknesses in the micro-metre range, being generated by radio frequency (RF) magnetron sputtering: first, the conductance increase upon H$_2$S exposure was measured for defined copper oxide films of different composition (CuO, Cu$_2$O or Cu$_4$O$_3$). Second, in the case of Cu$_2$O, the morphology was modified by applying different H$_2$ flow rates during the sputtering process. Since a precise determination of the conductance is inevitable for such comparison, films prepared by RF sputtering are ideal with respect to their overall homogeneity. For these measurements, a H$_2$S concentration range between 1 and 10 ppm was used, being similar to typical applications. Aside from the conductance measurements, the materials were carefully characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2 Copper oxide as H$_2$S sensor

The main advantage of copper oxides is the reaction with H$_2$S under moderate temperatures (about 160 °C), forming copper sulfides. Since the reaction of Cu$_2$O with H$_2$S is still a matter of discussion (Galtayries and Bonnelle, 1995; Hennemann et al., 2015a; Sharma, 1980), the well-understood CuO is certainly the most suitable copper oxide with respect to the
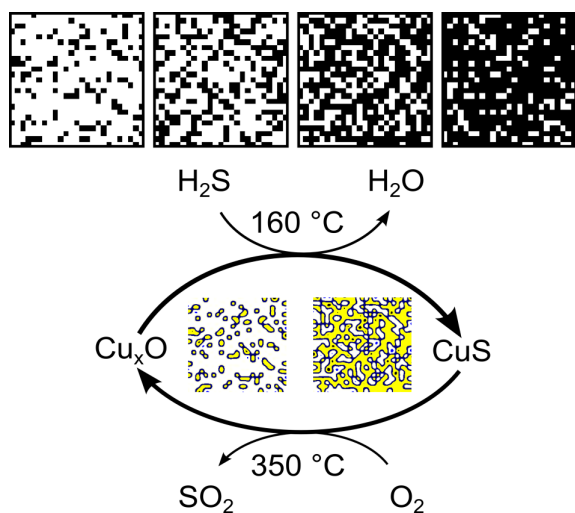
Figure 1. Top: site percolation model on quadratic grid. Left to right: 20, 40, 59 and 80 % occupation with highly conductive material. White pixels depict low conductive and black pixels highly conductive sites. Bottom: scheme of CuO sensor cycle and percolation paths of the conducting sulfide (highlighted in yellow colour) on a CuO film.

usage in H$_2$S sensors. Nevertheless, for both CuO and Cu$_2$O, the generation of the respective sulfide induces a change in conductance from semi-conduction to metal-like conduction behaviour. The drastic difference can be utilized in an electric circuit in which the CuO sensor acts as a chemical on/off switch. The underlying specific reaction is the key to the selectivity of CuO-based sensors. In contrast to many other chemical sensors, the detection is not based on surface adsorption and desorption of oxygen, but on the chemical reaction of CuO with H$_2$S into the respective copper sulfide. As one of the main features, the resulting conductance jump exceeds those of other reducing gases by at least 2 orders of magnitude, facilitating the distinction from interfering effects, e.g. reduction of surface states. Additionally, the continuous reaction of copper oxides with H$_2$S accumulates increasing amounts of sulfur. This offers the possibility to detect the absolute amount of H$_2$S over a defined period of time and estimate the averaged concentration (Hennemann et al., 2012a; Marr et al., 2014; Ramgir et al., 2010).

A steep change in conductance is observed that we interpret as a percolation path (see Sect. 3), which in turn corresponds to a certain amount of H$_2$S having reacted with CuO to form CuS, the latter possessing a much higher conductivity (5 orders of magnitude) than CuO. Measuring the time until reaching the percolation threshold allows the estimation of an average H$_2$S concentration.

As another advantage, the equilibrium of reaction can be easily shifted by increasing the temperature to 350 °C. At this temperature, CuS reacts with oxygen and water in the surrounding air and transforms back to CuO, releasing sulfur in

the form of SO$_2$ (Sauerwald and Russ, 2013). This process resets the sensor for the next detection cycle.

3 Percolation effect

The sensor behaviour of copper oxides towards H$_2$S can be interpreted by percolation theory, which explains the change in conductance after a certain dose or a concentration-depending period of time (Dräger et al., 2013; Sauerwald and Russ, 2013; Ulrich et al., 2004).

In short, standard percolation theory applies to materials of two components, which are allocated statistically to a grid of points on a surface (2-D) or in space (3-D; "site percolation"). This theory allows the calculation of the surface coverage (2-D) or volume fraction (3-D) needed to establish a continuous path of one of the components through the respective entity. We believe that the transition that we observe in our CuO–CuS systems can be simply explained by percolation phenomena, even if some deviations to the standard case can be observed (Hennemann et al., 2015a). We study the behaviour of a composite of two phases possessing a large difference in conductivity, namely conductive CuS and less conductive CuO (or Cu$_2$O).

At the beginning of a typical sensing cycle there is almost no CuS present. With ongoing H$_2$S exposure time, CuS islands start to form. At low concentrations these islands are spatially separated and do not connect to a continuous, conductive cluster through the material. At this point the conductivity is low and mainly determined by the conduction of CuO (or Cu$_2$O). Once the concentration of CuS islands reaches a critical value, the statistically distributed islands connect to each other and form a highly conductive cluster throughout the whole system. This becomes apparent by a steep increase in conductance that we identify as "percolation threshold" (Russ, 2014). For a more detailed description see for example the work of Hennemann et al. (2015a).

The "critical" concentration at which the percolation threshold is reached depends on the shape and dimension of the grid. For standard cases, it can be calculated by percolation theory. For example in a quadratic grid the highly conductive islands have to cover 59.3 % of the surface sites to form a conducting path between two sites of the lattice, the so-called infinite cluster.

4 Typical conductance data of CuO used in a H$_2$S sensor

Figure 2 depicts an exemplary conductance measurement of a CuO-based sensor exposed to H$_2$S. Four different sections occur as a function of exposure time, corresponding to different effects. Over the whole measurement, the relative humidity is kept constant at 30 % measured at room temperature. Section I: The sensor is exposed to synthetic air and the heater is powered to bring the sensor to its sens-
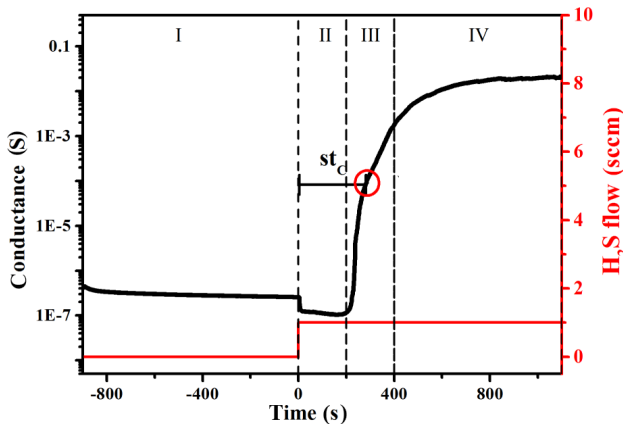
Figure 2. Typical conductance change of CuO under exposure to H$_2$S.

Figure 3. Scheme **(a)** and image **(b)** of measurement setup for thin films. 1: gas inlet, 2: temperature sensor, 3: resistive heater, 4: contact pins and 5: sample.

Figure 4. H$_2$S sensing **(a)** of CuO thin films prepared by different heat treatment **(b)** applied to Cu films oxidized in an oxygen-containing atmosphere (according to Hennemann et al., 2012b; see Sect. 5).

ing temperature of typically 160 °C. As is typical for p-type semi-conducting metal oxides, equilibration effects of the lattice oxygen concentration with the surrounding atmosphere cause the conductance to decrease slightly. Section II: H$_2$S exposure after 900 s leads to an immediate, steeper conductance decrease due to a reaction of H$_2$S with chemisorbed surface oxygen releasing the binding electrons to the valence band. This is the expected sensing reaction for a *p*-type semi-conductor in reducing atmosphere. Simultaneously, the formation of CuS islands takes place. However, the overall conductance is dominated by the conductivity of CuO, which separates the CuS islands, and therefore no significant change in overall film conductance is observed. After another 200 s, in section III, the conductance increases over at least 4 orders of magnitude. This is attributed to the formation of highly conductive pathways on the film surface (interconnection of the CuS islands, percolation threshold). The percolation time is defined here as the time difference between the start of H$_2$S exposure and when the conductance reaches the mid-value between minimum and maximum on a logarithmic scale. A typical value for this point is around 10^{-4} S (Hennemann et al., 2015a).

In section IV an infinite conductive cluster connecting the electrode conductive path is established, now growing in diameter due to further formation of CuS. Additionally, oxygen diffuses from the film's interior to the surface, and simultaneously sulfur diffuses from the surface into the bulk. Therefore, the CuS layer grows perpendicular to the surface, resulting in a further increase in conductance. Both effects, percolation and diffusion, partially overlap in time, but can be well separated by different exponents of a power-law-like increase in conductance (which is 0.5 for diffusion; Hennemann, 2014). In case of Cu$_2$O, diffusion contributes more to the overall increase in conductance, thus aggravating a fine separation of the conductance into the effects of percolation and diffusion, as shown recently by Hennemann et al. (2015a).
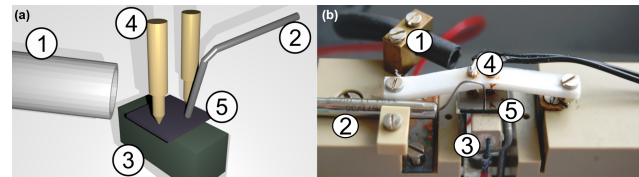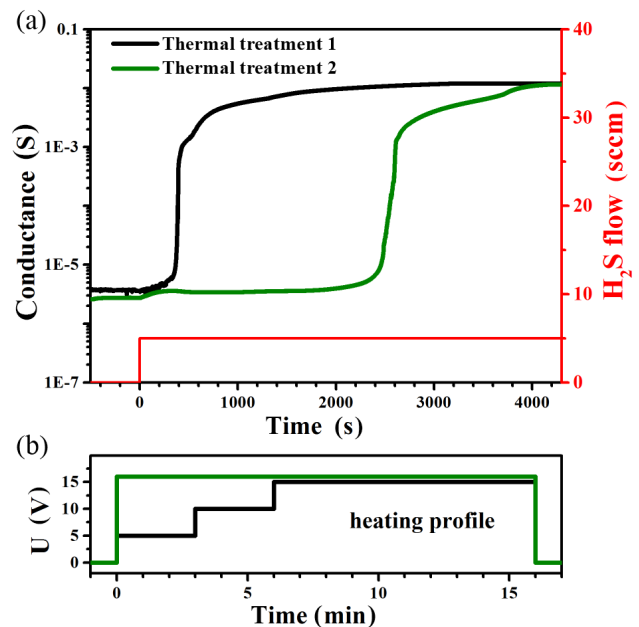
5   Experimental

All films were deposited on glassy microscope slides, purchased from Roth. For first measurements (the evaluation of heat treatment), thin films of copper (50 nm) were produced by thermal evaporation under a vacuum ($\sim 10^{-4}$ mbar) and afterwards heated by a 10 Ω heating resistance by applying a constant voltage depicted in the graphs in Figs. 2, 4, 6 and 9. The heat treatment was performed directly in the measurement setup (see Fig. 3) in ambient air. For all other measurements the copper oxide films were synthesized by RF magnetron sputtering using Argon as a sputter medium (Meyer et al., 2012). Oxygen was added with different flow rates as reactive gas. The base pressure was 3.7×10^{-7} mbar and working pressure 4.8×10^{-3} mbar. The power used was 75 W with an Argon flow of 35 sccm at a temperature of 650 °C. Oxygen was added with flow rates of 3.9, 5.1 and 6.3 sccm as reactive gas to deposit Cu$_2$O, Cu$_4$O$_3$ and CuO,
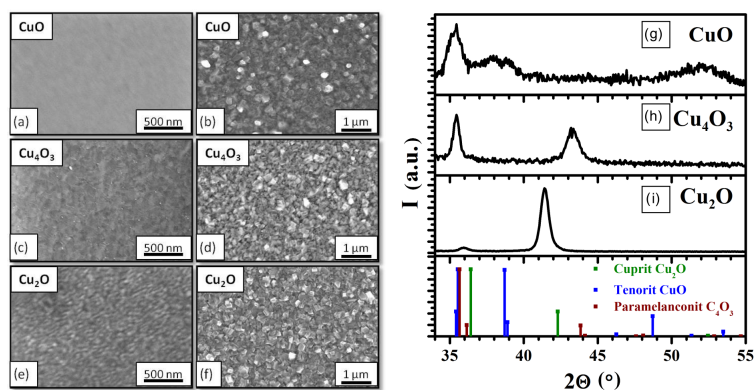
Figure 5. Scanning electron microscope images **(a–f)** and X-ray diffractograms **(g–i)** of copper oxide thin films, with CuO on top, Cu$_4$O$_3$ in the middle and Cu$_2$O on the bottom. The images **(a)**, **(c)** and **(e)** depict samples before and images **(b)**, **(d)** and **(f)** depict samples after H$_2$S treatment. Part **(g)** to **(i)** shown according to Hennemann et al., 2015a.
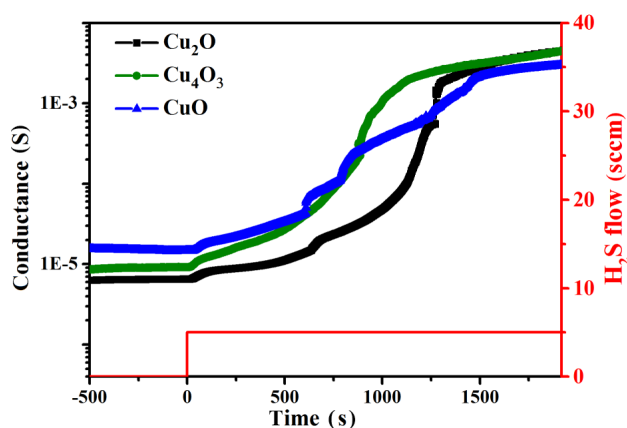
Figure 6. Conductance change of CuO, Cu$_2$O and Cu$_4$O$_3$ due to H$_2$S exposure treatment (according to Hennemann et al., 2015a).

respectively. Film thicknesses were kept constant at 1 µm for each deposition. By adding hydrogen flows of 0.05, 0.5 and 3.0 sccm, the surface roughness was influenced.

To visualize the structure, SEM ("Merlin" by Zeiss, Germany) was used. Voltage was kept at 5 kV with a sample current of 90 pA.

The conductance measurements were performed in a custom-built measurement setup. The sample was contacted by two gold-plated pogo pins with a distance of 2 mm and heated by a 10 Ω resistive heater to 160 °C; temperature was monitored by a thermocouple (type K). Resistance was recorded utilizing a Keithley 6517A Electrometer/ High Resistance Meter. H$_2$S-containing atmospheres were supplied by mass flow controllers with a constant relative humidity of 30 % at room temperature and a flow rate of 200 sccm. This high flow rate was chosen to ensure the atmosphere is exchanged very fast so that the reaction is not influenced by a depletion of H$_2$S. The displayed setup was put into a closed chamber with a volume of approximately 1 L to reduce the influence of surrounding atmosphere. Sample size and position were kept constant over the different experiments.

To minimize the influence of the electrical measurement on the sample composition (e.g. electromigration within the sample), the conductance was read out at 1 s intervals with 100 ms measurement pulses and a measurement voltage of 1 V. Applying short pulses has shown no difference compared to using alternating +1 and −1 V pulses. For the sake of ease of the experiment, it was decided to only apply DC pulses. Reproducibility of the experimental method was already shown by Hennemann et al. (2015b) utilizing the same setup; a couple of different samples of one batch measured under same conditions exhibited variations in switching time of ±5 %. Comparison of this earlier work with the actual results also reveals high reproducibility of the chosen methodology.

6   Results and discussion

In order to identify the relevant factors for manipulation of the percolation threshold, Cu thin films were oxidized by different thermal programs; the resulting changes in the oxide growth causes changes in the surface morphology of the samples.

The heating profiles and the resulting sensor measurements in H$_2$S atmosphere are summarized in Figure 4. Ostwald ripening causes the growth of crystallites. The velocity of the growth is highly dependent on temperature. With increasing temperature, the crystallite grains grow faster (Ostwald, 1897), probably resulting in a more pronounced roughness. If the surface area is increased due to a higher roughness, more CuO is exposed to the atmosphere to react with the surrounding H$_2$S. Therefore, on the one hand a higher reaction speed of the CuO conversion occurs, but on the other hand the CuS conduction pathways are interrupted more often by Cu$_x$O, and it takes longer to obtain the same surface concentration of CuS than in a smooth sample.
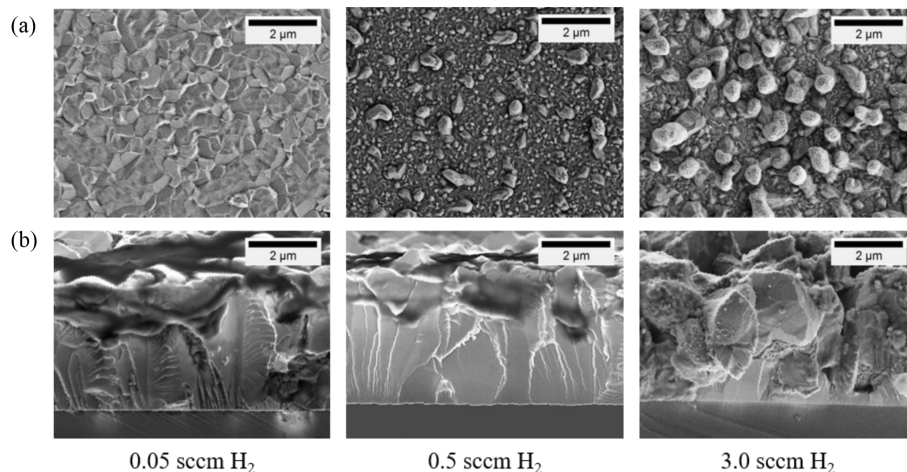
Figure 7. Scanning electron microscopy images of Cu$_2$O thin films sputtered under 0.05, 0.5 and 3.0 sccm H$_2$ flow. Top: top-view. Bottom: cross-section view.
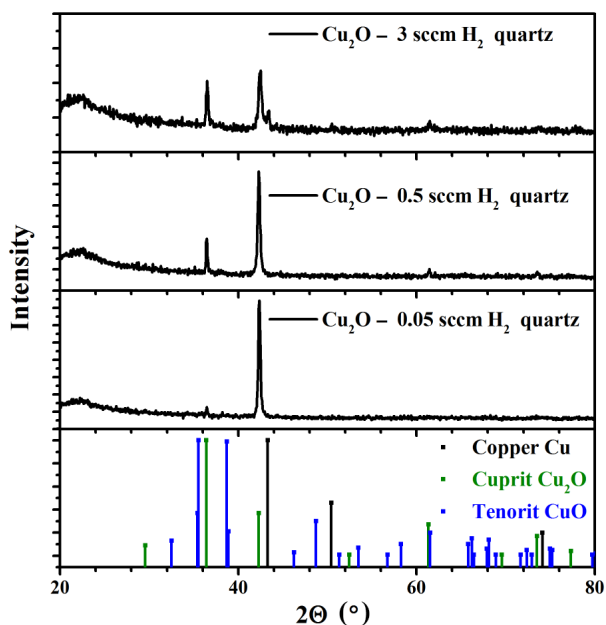

Figure 8. X-ray diffraction of copper oxide thin films on quartz substrate prepared by 0.05, 0.5 and 3 sccm H$_2$ flow, respectively.

Figure 9. Sensing behaviour of Cu$_2$O thin films with different roughness.

6.1 Influence of sample stoichiometry

Another important issue is the stoichiometry and composition of the copper oxide films. Since copper possesses two stable oxidation states (+I and +II), mixtures of Cu(I) and Cu(II) oxides are often found in copper oxide materials. Here, thin films of pure-phase CuO, Cu$_2$O and Cu$_4$O$_3$ were prepared under carefully chosen conditions, by RF sputtering (see Sect. 5) by changing the oxygen flow. X-ray diffraction reveals that only reflexes correlated to the desired compounds indicate that no other crystalline phase is present in the films
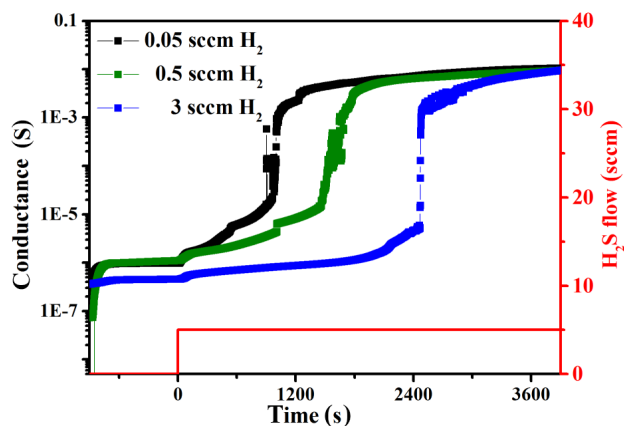
(Fig. 5g–i). Deviation from theoretical intensities can be explained by preferred oriented growth seeded by the substrate. SEM images display that the roughness of non-heat-treated films increases slightly with increasing amount of Cu (see Fig. 5a to e). However, the roughness after H$_2$S treatment has increased for all three samples, which is attributed to the volume expansion of material, since the CuS unit cell has about twice the volume than that of the CuO unit cell.

In Figure 6 the sensing behaviour of these Cu$_x$O thin films with different stoichiometry is shown. It is seen that the initial conductivities differ by a factor of about 3, which can be attributed to the different semi-conducting properties of the three copper oxides themselves. Even though all three copper oxides reveal a percolation threshold, CuO reaches the threshold first and Cu$_2$O last. It is interesting to note that in our case Cu$_2$O also exhibits a well-defined percolation behaviour, in contrast to some other publications where Cu$_2$O

is not expected to react with H_2S under low relative humidity (Sharma, 1980). Evaluating these results, it can be concluded that a higher amount of oxygen in the compound leads to a faster transformation to CuS. This could be due to the fact that compounds with low oxygen amount intrinsically contain less oxidized copper species and have to be oxidized before they can form highly conductive CuS, which in turn results in a longer period of time taken to reach percolation threshold.

6.2 Influence of sample morphology

In another set of experiments the influence of surface roughness was addressed. By adding hydrogen to the sputtering gas a variation in surface roughness of the Cu_xO films could be achieved. Owing to the presence of H_2, in this case Cu_2O thin films were formed. SEM images (Fig. 7, top view and cross-section) show that the roughness of samples increases as a function of H_2 flow rate. On the left-hand side the top view shows a homogeneous film surface, confirmed by cross-sectional analysis.

In XRD analysis (Fig. 8) all reflections can be attributed to the Cu_2O phase (green reference). The relative intensities vary among the samples, which indicates preferential crystallite growth in one specific crystallographic direction and can be seen in the cross-section SEM images, too. However, the preferred orientation can be regarded as negligible with respect to the sensing properties. For flow rates of 3.0 sccm H_2 within synthesis, minor reflexes of pure copper appear indicating the limit of synthesis flow rate of H_2. Percolation behaviour seems not to be affected, which is probably due to a copper concentration well below percolation threshold leading only to a (small) overall increase in conductance.

In the sensing measurement (Fig. 9) the samples reveal large variations in switching times, while start and end conductances remain nearly constant. This indicates that composition of these three Cu_2O samples is similar, and minor amounts of copper do not significantly contribute to the conductance for the sample prepared at 3.0 sccm H_2S flow. The small deviations can be explained by the different amount of grain boundaries causing a decrease in conductance. Less rough samples, namely the ones sputtered at H_2 flow of 0.05 sccm, display the percolation-induced increase in conductance already after 16 min. In contrast, the sample prepared with the highest H_2 flow exhibits this change after approximately 41 min. The small effect of sample composition and the fact that the samples consist of the same phases lead to the interpretation that the variations in sensing behaviour are mainly due to different sample morphology. By varying sputter parameters, the surface roughness can be influenced. Therefore the percolation time was increased by a factor of 3.

7 Conclusions and outlook

As was shown, CuO thin films serve as excellent model materials to examine the influence of chemical and morphological parameters on the percolation threshold, even though they are known to exhibit a poor cycling stability (due to inter-layer stress as a consequence of the volume difference between CuO and CuS). Several film parameters can be controlled independently by RF magnetron sputtering. Variation of oxygen flow in the sputter process allowed controlling the composition of Cu_xO layers from CuO to Cu_2O. This change in stoichiometry induced small but measurable changes in percolation time and in the starting conductivities. Furthermore, the morphology of thin layers of Cu_xO was influenced by adding H_2 to the reactive gas in the sputter process. This change in roughness increased the percolation time dramatically, by up to a factor of 3. This result can be used later to systematically control the sensor threshold depending on the addressed application by, for example, micro structuring. Further experiments have to be conducted to increase the cycling lifetime of this sensing material. Taking into account the dramatic influence of morphology on the percolation threshold, the results shown indicate how to advance in understanding and optimization of nano-structured CuO for its application in H_2S sensing.

One possible strategy for further improvement is embedding nano-particles in a host species to reduce inter-layer stress. For multi-cycle applications sensors, hybrid materials need to be developed containing nano-structured copper oxides, allowing for relaxation of the stress associated with the conversion of CuO into CuS upon exposure to H_2S.

Edited by: A. Nocke
Reviewed by: two anonymous referees

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