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Local CuO Nanowire Growth on Microhotplates: In Situ Electrical Measurements and Gas Sensing Application

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ABSTRACT: We report on local CuO nanowire growth on microhotplates combined with in situ measurement of the electrical resistance for well-controlled integration into conductometric gas sensing devices. Discrete current steps were observed during the CuO nanowire synthesis process, which is attributed to individual nanowire connections being formed. The high gas sensitivity of the CuO nanowire devices was confirmed by detection of carbon monoxide CO in the low ppm-level concentration range. Furthermore, we demonstrate that CuO nanowire growth inside a gas measurement setup allows studies on gas sensor poisoning/deactivation processes. A significant decrease of CO response was found after controlled exposure to humidity, which suggests sensor deactivation by surface hydroxylation. Thus our approach could be a novel and simple way for revealing new insights in various gas sensor degradation mechanisms in the future and might be also adapted for different metal oxide nanomaterials.

Semiconducting nanowires are considered as promising candidates for the realization of next-generation electronic devices ranging from transistors, memories and optoelectronic systems to chemical/biological sensing^{1,2}. Conductometric gas sensors rely on electrical resistance changes due to reactions with surrounding gas molecules, which enables potential applications such as toxic gas alarms or atmospheric pollution monitoring³. Semiconducting metal oxide nanowires were found to be suitable for highly sensitive detection of different target gases and have been thoroughly studied in various device configurations^{4,5}.

Cupric oxide (CuO) nanowires have received growing attention due to high sensitivity for toxic gases such as carbon monoxide CO^{6,7,8}, nitrogen dioxide NO₂^{6,9} or hydrogen sulfide H₂S^{7,10,11}. In addition, this material also shows promising properties for a variety of other applications, such as rechargeable battery electrodes¹², photovoltaics¹³, infrared detectors¹⁴ and field emitting devices¹⁵. CuO nanowires can be grown on a variety of Cu substrates using a simple, cheap and catalyst-free thermal oxidation method¹⁶. Most importantly, CuO nanowire growth was demonstrated on Cu thin films at temperatures compatible with CMOS back-end technology¹⁷, which is a crucial prerequisite for potential integration with standard industrial processes. Thermal oxidation synthesis of CuO nanowires was also achieved by local heating on MEMS-based resistive microheaters¹⁸ (in the following termed microhotplates) as an alternative to conventional techniques relying on heating the whole sample in a furnace or on a hotplate. Furthermore, CuO nanowires were successfully integrated on CMOS microhotplates by local growth between adjacent Cu microstructures leading to functional devices for gas sensing applications¹⁹. In this letter, we report on local CuO nanowire growth in controlled gas atmosphere by heating microhotplate devices inside a gas measurement setup, while measuring the electrical resistance of the devices in situ during the nanowire synthesis process. In contrast to common gas sensor fabrication methods, our approach reveals insights into the electrical properties of single CuO nanowires in an array configuration

and enables the characterization of sensing properties immediately after the nanowire synthesis process. As a consequence, this technique is ideally suited for studying sensor poisoning/deactivation processes, which we demonstrate by comparing sensing performance before and after controlled exposure to humidity. We focus on the colorless and odorless toxic gas CO, a common environmental pollutant which is produced from various different sources such as motor vehicles or gas appliances. Adverse human health effects for CO exposure in the ppm-level concentration range have been reported²⁰, which explains the demand for miniaturized, high-performance gas sensing devices for CO detection.

The microhotplate devices²¹ used for this study were based on a multi-layer SiO₂-SiN_x membrane released by deep reactive ion etching of the Si substrate from the wafer backside. The embedded heater layer consisted of a Ti/Pt thin film and was insulated by a SiO₂ layer deposited by plasma-enhanced chemical vapor deposition. Interdigitated Ti/Pt electrodes with circular shape were used as sensor contacts. More details on the microhotplate layout and device technology can be found in ref 22. On top of the microhotplate surface, Cu microstructures (Cu thickness ~600nm; 15nm Ti adhesion layer) were fabricated by thermal evaporation and lift-off, which is shown in Figure 1. The layout consisted of Cu structures (length of opposing edges 20µm) placed onto the interdigitated electrodes with a gap distance of around 2µm. In the following, these Cu structures will serve as substrate for the growth of CuO nanowires, which bridge the gap between the adjacent electrodes, similar as in ref 23.

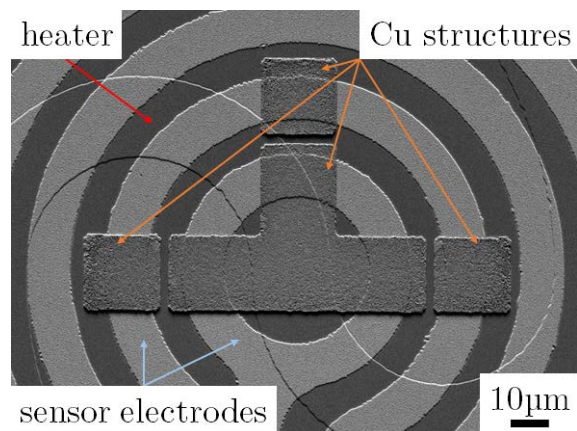


Figure 1. Scanning electron microscopy image of the device design for CuO nanowire growth. The gap distances between Cu microstructures connected to different sensor electrodes are around $2\mu\text{m}$, whereas the lengths of opposing edges are $20\mu\text{m}$. After thermal oxidation, CuO nanowires bridged the gap and formed an electrical connection.

The microhotplate devices were glued onto a printed circuit board and connected to Au pads by wire bonding. CuO nanowire growth and gas sensing measurements were performed inside a test chamber consisting of standard vacuum components. The gas composition was controlled by means of mass flow controllers using a constant total gas flow of 500sccm. A Keithley 2636A dual-channel SourceMeter was employed for microhotplate heating as well as electrical measurements during CuO nanowire growth and gas sensing experiments.

For CuO nanowire growth in dry synthetic air, microhotplates were biased with a constant voltage at a power consumption of 39mW, which corresponds to around 335°C . The nanowire synthesis conditions are comparable to those in previous studies^{19,23}. During the thermal oxidation experiments, a constant voltage was applied while measuring the current between the sensor electrodes. The first 125min of a representative CuO nanowire growth experiment with in situ electrical measurements is shown in Figure 2 (10mV bias). The current increases in discrete steps, which is interpreted by single CuO nanowires bridging the gap between the oxidized Cu microstructures (see inset of Figure 2 for an SEM image after CuO nanowire synthesis for 5h). The total electrical resistance after growth may be interpreted by a parallel circuit of multiple CuO nanowires, whereas the heights of the current steps during the in situ experiments corresponds to the electrical conductance of single nanowires. When assuming cylindrical nanowire geometry and typical dimensions (diameter 20nm, length $1\mu\text{m}$), the observed conductance steps can be correlated with nanowire electrical conductivity. In our growth experiments at 335°C in dry synthetic air, we commonly observed conductance step values of several tens of nS. Considering the geometrical assumptions mentioned above, this corresponds to roughly 10^2S/m . This crude estimation of typical nanowire electrical conductivities leads to values that are reasonably comparable to four point measurements on single CuO nanowires with considerably larger diameters in similar environmental conditions²⁴. Additional transmission electron microscopy results for CuO nanowire characterization can be found in the supporting information (Figure S1). The material composition was confirmed by comparing the electron energy loss near-edge fine structure with literature results for CuO. Furthermore, bicrystalline nanowire structure was typically observed, which is a well-known characteristic of CuO nanowires grown by the thermal oxidation method^{16,17}.

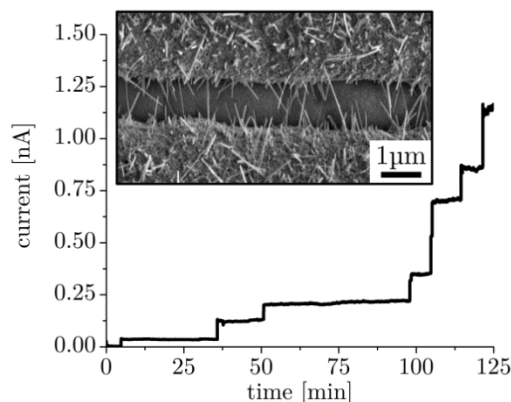


Figure 2. Step-like features of electrical current across sensor electrodes (bias 10mV) during CuO nanowire growth (335°C , dry synthetic air). The inset shows a scanning electron microscopy image of CuO nanowires bridging the gap between oxidized Cu microstructures after the experiment.

In principle, the presented method enables controlling the number of CuO nanowire connections during device fabrication. The rise and fall times of microhotplate temperature are in the ms range (20-30ms) and thus the thermal oxidation process may be stopped with high temporal precision. Thus in situ electrical measurements during CuO nanowire growth might be used for studies on devices with single or few nanowires bridging the gap between the oxidized Cu structures in the future. Here, we chose a constant time of five hours for CuO nanowire growth in order to maximize the number of connecting nanowires in the array devices. CuO nanowire growth rate was previously reported to follow a parabolic law over time and is becoming increasingly low after few hours²⁵. Although we assume that in situ electrical measurements might be useful in order to gain insights on CuO nanowire growth kinetics, we restrict ourselves to the gas sensing application in this letter.

In Figure 3, the CO sensor response of a typical CuO nanowire device, which was grown inside the gas measurement setup, is shown. The measurement was performed after sensor stabilization at a temperature of around 325°C (microhotplate power consumption 37mW) after a CuO nanowire synthesis process at around 335°C for five hours. The presented CuO nanowire device showed sensor responses from 6.4% to 27.6% for CO concentrations from 1ppm to 30ppm, respectively. Supplementary data on the CO response can be found in the supporting information (Figure S2). CuO nanowires are suspended and entirely surrounded by the gas atmosphere, which is a highly favorable configuration. It is known from literature that suspended nanomaterials are advantageous due to faster adsorption/desorption kinetics²⁶, maximization of surface area exposed to the gas atmosphere²⁷ and improved signal-to-noise ratio²⁸. The excellent CO sensing performance is comparable to literature results on SnO₂ nanowire array devices²⁹ and thick films of CuO microspheres³⁰ in dry air. Increased CuO nanowire resistance was found, which is in accordance with previous results on similar devices⁷ and with other literature reports^{6,8,31}. It can be assumed that the CO response can be explained by sensing mechanisms of metal oxides proposed in literature, which rely on the oxygen chemisorption model³². In the case of the p-type metal oxide CuO, CO molecules are expected to react with chemisorbed oxygen ions to form CO₂, which leads to a reduced hole concentration in the surface accumulation layer and thus an increase in electrical resistance^{30,31}. Additional gas measurement results showed increased CuO nanowire resistance in the presence of H₂S and decreased resistance during NO₂ exposure (Figure S3), which is in accordance with the oxygen chemisorption model^{9,11}.

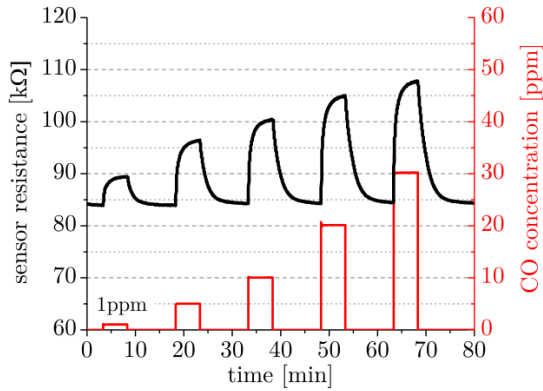


Figure 3. Electrical resistance of CuO nanowire gas sensor device in dry synthetic air during pulses of carbon monoxide CO exposure (1-30ppm) at an operation temperature of 325°C.

CuO nanowire device integration by growth between adjacent Cu microstructures does not require any further post processing steps and thus avoids nanowire surface contamination, which is most commonly detrimental to the device performance of sensors and detectors³³. Furthermore, local CuO nanowire growth on microhotplates inside a gas measurement setup offers the possibility of performing sensing experiments immediately after nanowire synthesis. The sensors may be characterized without exposure to ambient atmosphere, which usually contains a variety of reactive species, for instance water vapor and volatile organic compounds. As a consequence, this enables gas sensing measurements on devices with pristine CuO nanowire surfaces, which is an ideal starting point for studies on sensor deactivation mechanisms. Various degradation mechanisms have been reported in literature, such as sensor poisoning by sulfur or carbon compounds and humidity-induced changes³⁴. Here, we restrict ourselves to the influence of water vapor as exemplary case.

CuO nanowire growth inside a gas measurement chamber followed by gas sensing characterization was utilized in order to study the sensor response to CO before and after controlled exposure to water vapor. This methodology differs from previous literature reports investigating the humidity influence on gas sensing properties of CuO nanomaterials^{23,35,36}, as they compared the gas sensor response in dry and humid air. In contrast, we address irreversible changes of CuO nanowire gas sensor performance induced by the presence of water vapor. Experiments were performed as follows: CuO nanowire gas sensors at a microhotplate temperature around 325°C were exposed to a 5min pulse of humidity by applying a mixed gas flow of 300sccm dry air and 200sccm humid air (through bubble humidifier), which corresponds to around 30% relative humidity at room temperature. During the humidity pulse, the device resistance increased to more than three times of its value in dry air. The CuO nanowire gas sensor response to 30ppm CO in dry air was characterized before and after humidity exposure (sensor recovery for 3h), which is shown in Figure 4. As can be seen, the CO sensor response of the CuO nanowire device considerably decreased after humidity exposure, whereas the sensor resistance baseline was markedly increased. Comparable CuO nanowire gas sensor deactivation characteristics after humidity exposure were found in multiple experiments. These findings underline the crucial influence of CuO nanowire device pre-treatment on gas sensor performance for CO detection.

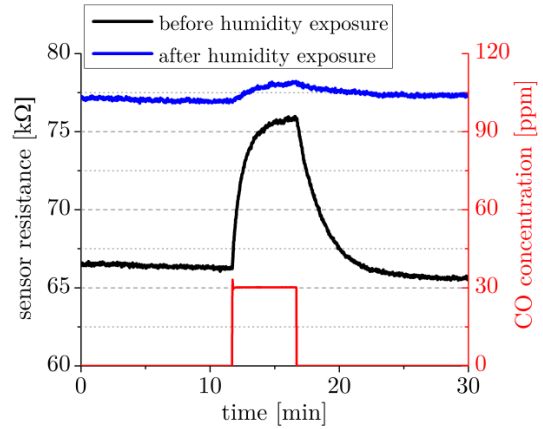


Figure 4. Comparison of CuO nanowire gas sensor response to 30ppm carbon monoxide CO (dry synthetic air; operation temperature 325°C) before and after humidity exposure.

We assume that the notable decrease of CO sensing response after water vapor exposure may be explained by hydroxylation of the CuO nanowire surfaces. It is expected that hydroxyl groups lead to a decrease of surface sites for oxygen chemisorption, similar as was suggested due to experimental results on CuO thick films³⁶ and theoretical calculations for the case of SnO₂³⁷. This argument is consistent with the increased sensor baseline resistance (see Figure 4) after humidity exposure, because a decrease of chemisorbed oxygen ions would result in a lower number of holes in the CuO surface accumulation layer³⁶ leading to decreased surface conductivity. Furthermore, a lower number of chemisorbed oxygen ions is expected to result in a decrease of CO surface reactions, which would explain the lower sensor response. However, a detailed understanding of the underlying mechanisms is lacking at the moment and would require extensive atomistic modelling, which is beyond the scope of this work.

The decreased CO response of CuO nanowire sensors after water vapor exposure has to be considered for practical gas sensing applications in ambient air. In order to enhance CO sensing performance in humid atmosphere, CuO nanowire devices may be decorated with noble metal nanoparticles for increased catalytic activity. We recently demonstrated that magnetron sputter inert gas aggregation is ideally suited for the deposition of size-selected Pd nanoparticles on CuO nanowire surfaces, which improved the CO sensor response in humid air considerably⁸. Furthermore, nanoparticle decoration is expected to improve sensor selectivity to other gases such as H₂S or NO₂, which is a common limitation of metal oxide-based devices³. Alternatively, sensor properties might be enhanced by plasma treatments, as the latter were found to enhance the catalytic activity of CuO nanowires for CO oxidation³⁸.

In summary, we performed local CuO nanowire growth on microhotplates and observed discrete current steps during simultaneous in situ measurements of the electrical resistance, which is attributed to individual nanowire connections being formed. Our approach offers the possibility of performing gas sensing experiments immediately after nanowire growth on devices with pristine CuO surfaces. Excellent gas sensor performance for the detection of CO concentrations down to 1ppm was observed. However, a considerable decrease of CO response was found after exposure to humidity, which is attributed to surface hydroxylation and gives valuable insights in sensor deactivation mechanisms of CuO nanowire devices. It can be assumed that the presented method might be adapted for other gas-sensitive metal oxide materials, in particular those that allow nanowire synthesis by thermal oxidation at moderate temperatures such as ZnO³⁹ or Fe₂O₃⁴⁰. As a consequence, we expect that metal oxide nanowire growth inside a gas measurement

setup combined with in situ electrical measurements will lead to new insights on various gas sensor degradation mechanisms in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

CuO nanowire characterization and gas sensing results (PDF).

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Notes

The authors declare no competing financial interests.

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