CUO NANOWIRE GAS SENSORS FOR CO DETECTION IN HUMID ATMOSPHERE

S. Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Köck
AIT Austrian Institute of Technology GmbH, Vienna, AUSTRIA

ABSTRACT

In this paper we report on conductometric gas sensors based on suspended CuO nanowire arrays for CO detection in humid atmosphere. CuO nanowires with very small diameters (10nm - 30nm) are synthesized by a thermal oxidation process of Cu microstructures. Our approach allows efficient CuO nanowire integration using a CMOS backend compatible technology. We perform CO measurements in a concentration range between 25ppm and 150ppm and investigate humidity interference effects by comparing CO measurements in dry and humid atmosphere.

KEYWORDS

CuO nanowire, on-chip synthesis, gas sensor, humidity interference, CO detection

INTRODUCTION

Various metal oxide semiconductors have been thoroughly studied for applications in conductometric gas sensors [1], as they are favorable in terms of high sensitivity, robustness and low cost [2]. In particular, one-dimensional nanostructures have been extensively investigated due to their advantages over traditional polycrystalline thin- and thick film gas sensors, such as enhanced surface-to-volume ratio and improved stability due to high crystallinity [3]. Cupric oxide (CuO) nanowires can be synthesized by a simple thermal oxidation process of copper substrates [4]. In contrast to other commonly used gas sensing materials such as SnO_2 or ZnO, CuO is known as a p-type semiconductor [5] with a band gap around 1.2eV [6]. Several conductometric gas sensors based on CuO nanowires have been realized for the detection of various gases [7-9], including the toxic gas carbon monoxide (CO) [10,11].

In this paper, we report on gas sensors based on suspended CuO nanowires bridging adjacent copper lines on a Si substrate. As was shown earlier [11], similar devices fabricated with the same technology are able to detect small concentrations of CO (down to 5ppm) and H_2S (down to 10ppb) in dry synthetic air. Here, we investigate the CO sensing performance in dry as well as humid atmosphere (30%, 50% and 70% r.H.) in order to gain a more profound understanding of humidity interference effects. As the fabrication technology of the presented devices can be used in a CMOS backend process, our results may be significant for the realization of smart silicon integrated CuO nanowire devices for CO detection in ambient atmosphere.

DEVICE FABRICATION

The CuO nanowire gas sensors are fabricated as follows: First of all, quadratic contact pads (edge length 150µm) are fabricated by a lift-off process of a thermally evaporated Ti/Au metallization layer (thickness 5nm and 200nm, respectively) on a Si substrate (300nm of thermal SiO_2). Next, a lift-off process of a thermally evaporated Cu layer (thickness 500nm) is used for the fabrication of adjacent Cu lines (width 5µm, length 60µm) with a gap distance of 2µm. An intermediate Ti layer (thickness 5nm) is used in order to improve adhesion and reduce Cu diffusion during the subsequent thermal oxidation step. Eventually, the samples are annealed at 350°C for 3 hours on a hotplate in ambient atmosphere. The final gas sensor device is depicted in Fig.1 with four thermally oxidized Cu lines contacted by the upper and the lower contact pad, respectively.

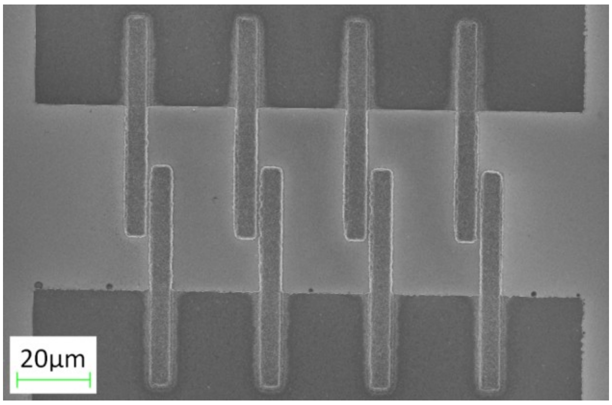

Figure 1: CuO nanowire sensor design consisting of eight oxidized Cu lines and two Ti/Au contact pads.

The gap (2µm distance before thermal oxidation) between neighboring Cu lines is bridged by suspended CuO nanowires after the thermal oxidation process (Fig.2), which results in an electrical connection between the two contact pads. The sensor resistance is dominated by the suspended CuO nanowire bridges, which form the gas sensitive elements in our sensor devices. In terms of equivalent circuit model, the CuO nanowire gas sensor device can be regarded as a parallel circuit of four equivalent CuO nanowire arrays, each of them containing multiple bridging CuO nanowires in parallel.

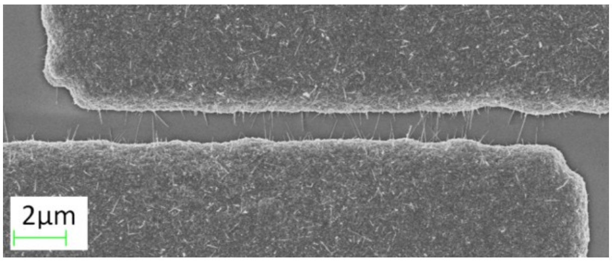

Figure 2: Multiple CuO nanowires bridging the gap between adjacent thermally oxidized Cu lines.

Two representative examples for CuO nanowires bridging the gap between oxidized Cu structures are shown in a high magnification SEM image in Fig.3. As can be seen, our specific nanowire synthesis technology allows the integration of CuO nanowires with very small diameters between 10nm and 30nm as electrical connection between adjacent oxidized Cu lines. A more detailed discussion of the CuO nanowire growth mechanism on the oxidized Cu microstructures can be found in [11].

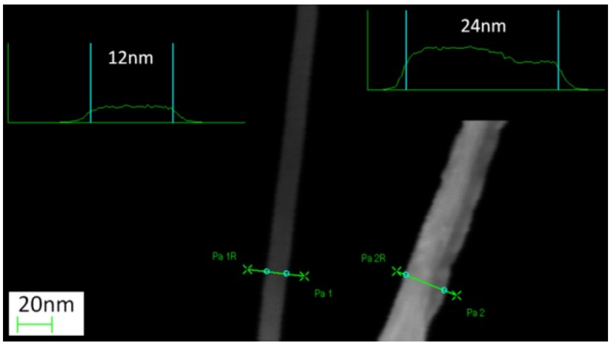

Figure 3: High magnification SEM image of typical suspended CuO nanowires, which exhibit very small diameters between 10nm and 30nm.

EXPERIMENTAL

The substrates of the CuO nanowire gas sensing devices are glued to commercially available microheaters (10x2 Pt6,8-0,4, Delta-R GmbH) and a Pt100 temperature sensor (4x1 Pt100A, Delta-R GmbH), which are soldered to a ceramic sensor mounting. Wedge bonding is used for establishing electrical connections from the Ti/Au contact pads on the sensor chip to the sensor mounting. The sensor device resistance is measured by a Keithley 2400 SourceMeter in constant current operation. During the gas measurements in the automated gas measurement setup, the total gas flow is kept constant at 1000sccm. Mass flow controllers are used to mix the background gas (synthetic air, Linde Gas, 80% N_2 with 20% O_2) with small concentrations of CO (Linde Gas, 903ppm in N_2). The duration of single CO pulses is ten minutes for all the presented measurements. Humidity is added by a separate gas flow of synthetic air through bubble humidifiers and the relative humidity level is controlled by means of a commercial humidity sensor (Kobold AFK-E).

RESULTS AND DISCUSSION

Fig.4 shows the sensor response to CO at three different operation temperatures (T=300°C, T=325°C, T=350°C) in dry as well as humid synthetic air (50% r.H.). As can be seen, the baseline resistance of the CuO nanowire sensor is strongly temperature dependent. It is important to notice that this sensor behavior does not exclusively reflect the semiconducting properties of the material. CuO is a p-type metal oxide semiconductor with a surface accumulation layer in oxygen atmosphere [12]. Elevated temperatures favor the formation of ionosorbed O^- oxygen species. Consequently, the sensor resistance will be also influenced by a change of CuO nanowire surface charge. The sensor response S towards CO is evaluated according to:

$$S = R_{CO} / R_{air} \tag{1}$$

S is found to be between 1.04 and 1.13 for CO concentrations between 25ppm and 100ppm and is widely constant for the three investigated temperatures. When comparing the measurements in dry and humid synthetic air, it is evident that humidity influences the sensor baseline resistance. However, the humidity influence on the CO response is rather small and will be further investigated in additional measurements later on. In general, this sensor behavior is beneficial for practical sensor application in ambient atmosphere with varying relative humidity.

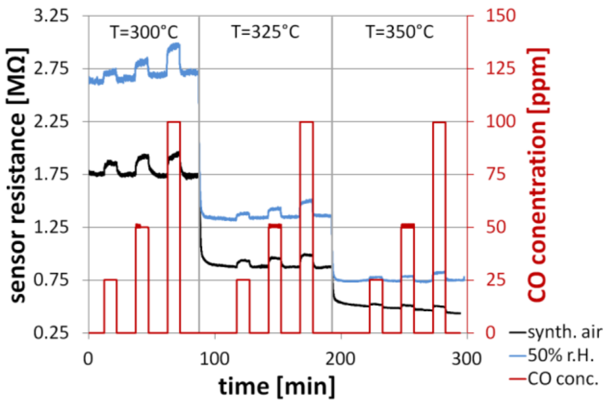

Figure 4: CO response of a CuO nanowire sensor in dry and humid synthetic air at three operation temperatures.

In literature, the following reaction of water vapor with a CuO surface was proposed [13]:

$$H_2O + O^-_{(ad)} + 2Cu_{Cu} + h^+ \rightarrow 2(Cu_{Cu}^+ - OH^-) + S_O \tag{2}$$

Due to the formation of terminal hydroxyl groups the concentration of ionosorbed O^- oxygen species and free holes is reduced which should result in an increased resistance. This is consistent with the different baseline resistance values in the experimental results of the CuO nanowire devices.

The reaction of CO with a CuO surface was explained by the following equation [13]:

$$CO + O^-_{(ad)} \rightarrow CO_2 + e^- \tag{3}$$

During CO exposure the concentration of ionosorbed oxygen species is decreased leading to a decrease of free hole concentration and an increased resistance. In our measurements, we observe increased CuO nanowire sensor resistance during CO exposure, which is in accordance with this literature model for CO sensing.

In order to investigate the influence of different water vapor concentrations during CO sensing, we performed additional measurements at a constant operation temperature of 325°C in dry synthetic air and at different relative humidity levels (30%, 50% and 70% r.H.). The measurement results of the CuO nanowire sensor resistance can be seen in Fig.5. Again, a considerable difference in baseline resistance can be observed when comparing dry and humid synthetic air. For the three investigated relative humidity levels the difference in baseline resistance is small, which indicates that the sensor surface is almost saturated with water vapor molecules for the three relative humidity levels.

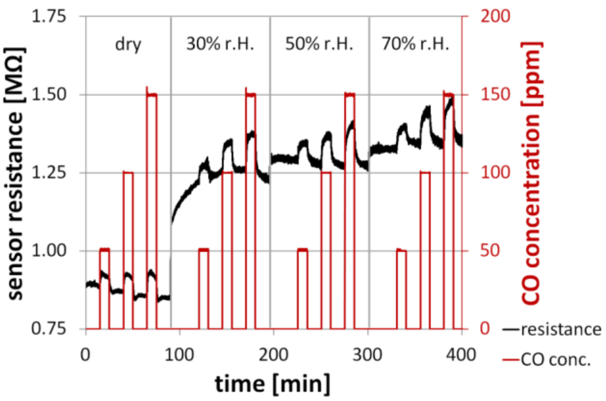

Figure 5: CO response of a CuO nanowire sensor in dry and humid synthetic air (operation temperature 325°C).

The evaluation of the CO response of the CuO nanowire sensor is shown in Fig.6. As can be seen, the influence of humidity on the CO response of the CuO nanowire sensor is comparatively small, which is of high importance for practical applications. The CO response values in humid synthetic air are higher than in dry synthetic air. From a sensing mechanism point of view, this finding is interesting as the opposite behavior was expected. In [13], decreased CO response in the presence of humidity was reported for CuO thick film sensors, which was explained by competition between CO molecules and H_2O molecules for O^- reaction partners.

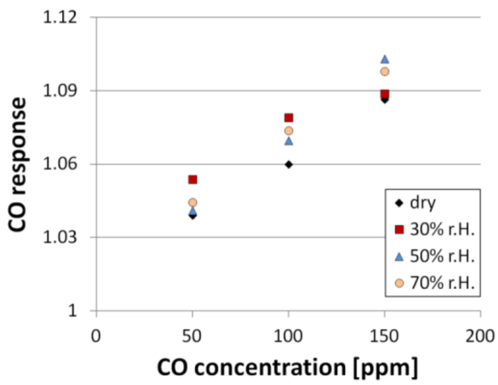

Figure 6: Evaluation of the CO response of the CuO nanowire gas sensor in dry synthetic air and at different relative humidity levels (operation temperature 325°C).

In order to confirm our results, additional measurements are performed using the following procedure: the CuO nanowire sensor is exposed to ten repeated pulses of CO (100ppm concentration) in dry synthetic air followed by ten pulses in humid synthetic air (50% r.H.) and then ten pulses in dry synthetic air again resulting in a total measurement time of 23h. The evaluation of the CO response is depicted in Fig.7 for a sensor operation temperature of 325°C. The mean values of S account for 1.054±0.005 for the first series of CO pulses in dry synthetic air, 1.072±0.005 for the series of CO pulses at 50% r.H. and 1.058±0.003 for the second series of CO pulses in dry synthetic air. Consequently, the increased CO response of the CuO nanowire sensor in humid synthetic air could be verified.

We assume that two main reasons are responsible for our results, which are in contrast to [13]: Firstly, the comparatively high operation temperatures above 300°C should ensure fast kinetics of the chemical reactions at the CuO nanowire surface. Secondly, due to the specific sensor configuration employing suspended CuO nanowires, gas species can be readily adsorbed at / desorbed from the sensor surface. Both these factors should contribute to high adsorption / desorption rates, which in turn may lead to reduced competition between CO and H_2O molecules for O^- reaction partners. However, a more detailed model for the increased CO response in humid atmosphere is currently under development by comparison with other CuO nanowire sensing structures.

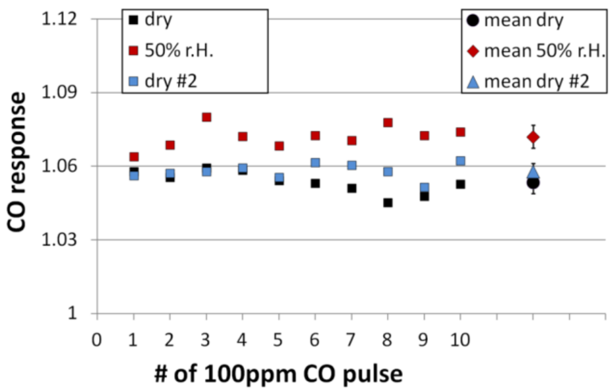

Figure 7: CuO nanowire gas sensor response towards 10 repeated 100ppm CO pulses in dry and humid synthetic air (operation temperature 325°C).

As is known from literature results from heterogeneous catalysis, several different factors influence the oxidation of CO on CuO nanowire surfaces, such as surface oxidation state, morphology and size. The authors of [14] report on poorly-crystallized CuO nanorods prepared by electrochemical methods with a coarse structure and high surface oxidation states, both leading to a high CO oxidation rate. In [15] it was found that the catalytic CO oxidation on CuO nanowires prepared by thermal oxidation can be significantly increased by plasma treatment, which is responsible for the formation of grain boundaries within the CuO nanowires. Motivated by these literature results, plasma treatment methods are currently investigated in order to further improve the CO response of the CuO nanowire gas sensors.

Moreover, the integration with CMOS fabricated microhotplates [16] is under progress in order to realize low power, silicon integrated CuO nanowire sensors for CO detection in humid atmosphere, which is of high importance for safety applications, for instance.

CONCLUSION

CuO nanowires with very small diameters between 10nm and 30nm are synthesized by thermal oxidation of a structured Cu thin film and are thereby successfully integrated as electrical connection between adjacent oxidized Cu lines. The CuO nanowire devices are operated as conductometric gas sensor and are found to be suitable for CO detection in the low ppm range. Humidity interference effects during CO sensing are thoroughly studied and are found to be comparatively small. Due to this beneficial sensing behavior and the CMOS backend compatible fabrication technology, the presented CuO nanowire devices may find applications as integrated CO sensors in ambient atmosphere.

ACKNOWLEDGEMENTS

This work was partly funded by the FFG - Austrian Research Promotion Agency within the MNT-Eranet project “NanoSmart” (No. 828691) and the WWTF Vienna Science and Technology Fund within the project “Mathematics and Nanosensors” (No. MA09-028).

REFERENCES

[1] G. Korotcenkov, “Metal Oxides for Solid-State Gas Sensors: What Determines Our Choice?”, *Mater. Sci. Eng. B*, vol. 139, pp. 1-23, 2007.

[2] G.F. Fine, L.M. Cavanagh, A. Afonja, R. Binions, “Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring”, *Sensors*, vol. 10, pp. 5469-5502, 2010.

[3] E. Comini and G. Sberveglieri, “Metal Oxide Nanowires as Chemical Sensors”, *Mater. Today*, vol. 13, pp. 36-44, 2010.

[4] X. Jiang, T. Herricks, Y. Xia, “CuO nanowires can be synthesized by heating copper substrates in air”, *Nano Lett.*, vol. 2, pp. 1333-1338, 2002.

[5] A. M. B. Gonçalves, L. C. Campos, A. S. Ferlauto, R. G. Lacerda, “On the growth and electrical characterization of CuO nanowires by thermal oxidation“, *J. Appl. Phys.*, vol. 106, pp. 034303, 2009.

[6] F. Marabelli, G. B. Parravicini, F. Salghetti-Drioli, „Optical gap of CuO“, *Phys. Rev. B*, vol. 52, pp.1433, 1995.

[7] Y. S. Kim, I. S. Hwang, S. J. Kim, C. Y. Lee, J. H. Lee, “CuO nanowire gas sensors for air quality control in automotive cabin”, *Sens. Act. B*, vol. 135, pp. 298-303, 2008.

[8] D. Li, J. Hu, R. Wu, J.G. Lu, “Conductometric chemical sensor based on individual CuO nanowires”, *Nanotechnol.*, vol. 21, pp. 485502, 2010.

[9] B.J. Hansen, N. Kouklin, G. Lu, I.K. Lin, J. Chen, X. Zhang, “Transport, analyte detection, and opto-electronic response of p-type CuO nanowires”, *J. Phys. Chem. C*, vol. 114, pp. 2440-2447, 2010.

[10] S. Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Köck, O. Freudenberg, “Single Suspended CuO Nanowire for Conductometric Gas Sensing”, *Proc. Eng.*, vol. 47, pp. 17-20, 2012.

[11] S. Steinhauer, E. Brunet, T. Maier, G.C. Mutinati, A. Köck, “On-Chip Synthesis of CuO Nanowires for Direct Gas Sensor Integration”, in *Nanotechnology (IEEE-NANO), 2012 12th IEEE Conference*, Birmingham, August 20-23, 2012.

[12] N. Barsan, C. Simion, T. Heine, S. Pokhrel, U. Weimar, “Modeling of sensing and transduction for p-type semiconducting metal oxide based gas sensors”, *J. Electroceram.*, vol. 25, pp. 11–19, 2010.

[13] M. Hübner, C.E. Simion, A. Tomescu-Stanoiu, S. Pokhrel, N. Bârsan, U. Weimar, “Influence of Humidity on CO Sensing with p-type CuO Thick Film Gas Sensors”, *Sens. Act. B*, vol. 153, pp. 347-353, 2011.

[14] K. Zhong, J. Xue, Y. Mao, C. Wang, T. Zhai, P. Liu, X. Xia, H. Li, Y. Tong, “Facile synthesis of CuO nanorods with abundant adsorbed oxygen concomitant with high surface oxidation states for CO oxidation”, *RSC Adv.*, vol. 2, pp. 11520, 2012.

[15] Y. Feng, X. Zheng, “Plasma-Enhanced Catalytic CuO Nanowires for CO Oxidation”, *Nano Lett.*, vol. 10, pp. 4762, 2010.

[16] C. Griessler, E. Brunet, T. Maier, S. Steinhauer, A. Köck, T. Jordi, F. Schrank, M. Schrems, “Tin oxide nanosensors for highly sensitive toxic gas detection and their 3D system integration”, *Microelectr. Eng.* vol. 88, pp. 1779-1781, 2011.

CONTACT

*S. Steinhauer, tel: +43-50550-4302;
stephan.steinhauer.fl@ait.ac.at