Local Synthesis of CuO Nanowires on CMOS Microhotplates for Gas Sensing Applications

S. Steinhauer*, T. Maier**, G.C. Mutinati**, K. Rohracher***, J. Siegert***, F. Schrank*** and A. Koeck*

*Materials Center Leoben GmbH (MCL), Leoben, Austria, stephan.steinhauer@mcl.at
**AIT Austrian Institute of Technology GmbH, Health&Environment Department, Vienna, Austria
***ams AG, Unterpremstaetten, Austria

ABSTRACT

In this contribution, we report on CuO nanowire devices integrated on CMOS microhotplates working as miniaturized, low power consumption gas sensors. The CuO nanowires were synthesized by thermal oxidation of a microstructured Cu thin film by local heating of the CMOS microhotplates. Direct nanowire device integration could be achieved as CuO nanowires form an electrical connection between adjacent oxidized Cu microstructures. By this approach, functional gas sensors were realized which require a low power consumption of less than 20 mW in order to attain the operation temperature around 325°C. The gas sensing properties of the CuO nanowire devices were investigated during exposure to humidity pulses. Moreover, the devices were found to be suitable for detecting the toxic gas CO at concentrations down to 10ppm and thus are potential candidates for future integrated smart gas sensor devices for security applications.

Keywords: CuO nanowire, integration, microhotplate, CO detection

1 INTRODUCTION

After first scientific publications of gas sensitive effects on the electrical conductivity of semiconducting metal oxides in the 1950's and 1960's, these materials have been thoroughly studied up to now for the application in gas sensor devices [1-3].Typically, metal oxide based gas sensors show advantages such as high sensitivity, robustness and low cost. Considerable advances have been made regarding optimization of sensor sensitivity and selectivity by means of morphology control, surface additives or temperature modulation [4]. Therefore, a variety of practical applications has been proposed, for instance environmental monitoring, safety devices or air quality control [5].

The advent of nanoscience, in particular the use of nanoparticles [6] and nanowires [7] in conductometric sensing devices, had substantial impact on gas sensor technology. Due to the large surface-to-volume ratio of nanoscale materials, high gas sensitivities have been typically achieved. One-dimensional nanostructures have shown excellent long-term stability due to high crystallinity [8]. However, CMOS integration of nanomaterials often remains a major challenge, but is a crucial step for the realization of miniaturized, multifunctional, low power consumption gas sensor devices [9].

Among other methods [10], cupric oxide (CuO) nanowires can be synthesized by a simple and cheap thermal oxidation process of Cu substrates [11-13]. In contrast to other gas sensing materials such as SnO_2 or ZnO, CuO exhibits p-type semiconducting properties [14] with a band gap around 1.2eV [15]. CuO nanowires have been employed in conductometric gas sensors using various different device configurations for the detection of several gas species such as hydrogen sulfide H_2S [16], nitrogen dioxide NO_2 [17], or carbon monoxide CO [18].

In this paper, we report on the synthesis of CuO nanowires by local heating on CMOS microhotplates leading to their direct device integration. Although the growth of CuO nanowires on locally heated suspended microbridges has already been demonstrated earlier [19], results on their reliable and efficient device integration on CMOS substrates are still lacking. Gas sensors based on suspended CuO nanowires bridging adjacent oxidized Cu lines have been reported earlier on Si substrates. The excellent gas sensing performance of these devices was validated by the detection of small concentrations of CO (down to 5ppm) and H_2S (down to 10ppb) [20]. Here, we demonstrate that the same approach can be used for CuO nanowire integration on CMOS microhotplates leading to miniaturized, low power consumption gas sensor devices. In the following, CMOS microhotplate performance results will be shown and CuO nanowire synthesis by local heating on suspended membranes will be presented and discussed. Moreover, the gas sensing performance of the CuO nanowire devices will be validated during exposure to water vapor and the toxic gas CO. Eventually, potential implications of the presented technology for future developments in the field of integrated, smart gas sensor devices will be outlined.

2 DEVICE FABRICATION

The CMOS microhotplates used in this study were fabricated in standard 0.35µm CMOS technology. Metal contacts protruding out of the passivated surface were realized by few additional process steps that were all performed in a CMOS environment on wafer-scale. Cu lines were fabricated using a lift-off process of thermally evaporated Cu (thickness 500nm) with a Ti thin film (thickness 5nm) underneath serving as adhesion layer. An isotropic MEMS dry etching process was performed from the wafer front side in order to fully under-etch and release the microhotplate, which is finally suspended by four arms. Fig.1 shows a CMOS microhotplate with eight Cu lines (width 5µm, gap distance 2µm) contacting the metal layer underneath in a specific configuration. CuO nanowires were synthesized by thermal oxidation of the Cu lines, which will be described later on.

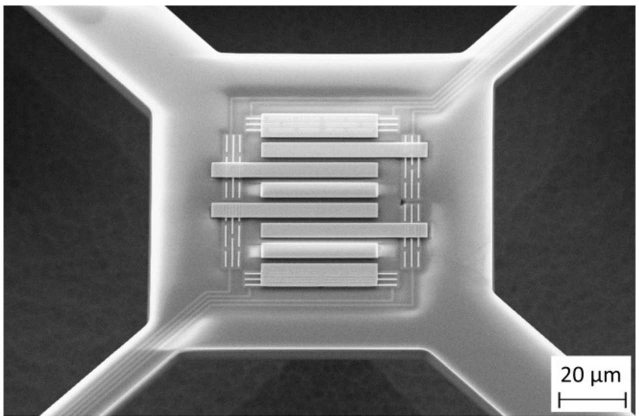

Figure 1: Suspended CMOS microhotplate with eight Cu lines fabricated in a backend process.

3 EXPERIMENTAL

Electrical connections to the device were established by wire bonding between standard CMOS pads and a ceramic substrate. The microhotplates were operated at constant temperatures, which were measured using an integrated temperature sensor. CuO nanowire synthesis was performed by local heating to 350°C in ambient atmosphere for one hour. Gas measurements were performed in an automated gas measurement setup using a constant total gas flow of 1000sccm. The background gas (synthetic air, Linde Gas, 80% N_2 with 20% O_2) was mixed with small concentrations of CO (Linde Gas, 903ppm in N_2) utilizing mass flow controllers. In order to perform gas measurements at different relative humidity levels, water vapor was added by a separate gas flow of synthetic air through bubble humidifiers. The relative humidity level was controlled by a commercial humidity sensor (Kobold AFK-E). The electrical resistance of the CuO nanowire gas sensor devices was measured by a Keithley 2400 SourceMeter in constant current operation.

4 RESULTS AND DISCUSSION

4.1 CMOS Microhotplate Performance

The CMOS microhotplates are based on specifically designed polysilicon heaters in order to ensure a homogeneous temperature distribution all over the suspended membrane. Detailed design, characterization and performance results of the CMOS microhotplates can be found elsewhere [21]. In Fig.2, the temperature versus power curve of a typical device is shown. The CMOS microhotplate can be heated locally to a temperature around 350°C requiring only approximately 20 mW heating power. It has to be noted that optimized CMOS microhotplates (power consumption only around 13 mW for 350°C) have been realized but are not presented here.

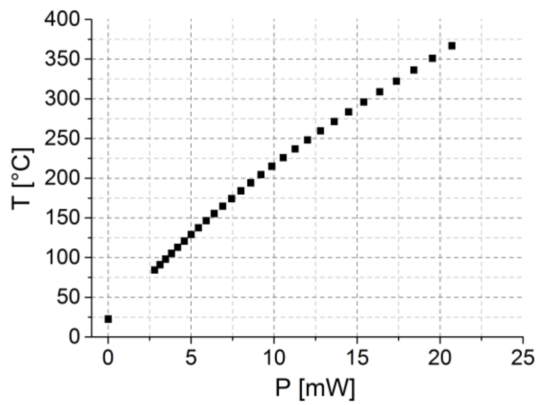

Figure 2: Temperature versus power consumption of a typical microhotplate device.

4.2 Local Synthesis of CuO Nanowires

The local heating of the CMOS microhotplate to a temperature of 350°C in ambient atmosphere leads to thermal oxidation of the Cu microstructures and CuO nanowire growth on the surface. A typical result is shown in Fig.3. As can be seen, CuO nanowires bridge the gap between adjacent oxidized Cu structures and thus form an electrical connection. As a result direct nanowire device integration is achieved on the microhotplate. Changes in electrical resistance of the bridging CuO nanowire arrays during exposure to certain gas species can be employed for conductometric gas sensing.

In earlier studies, CuO nanowires were synthesized by thermal oxidation of similar Cu structures by heating the whole Si substrate [20]. The results achieved by local heating on a CMOS microhotplate are well comparable in terms of nanowire density and diameters. By this thermal oxidation method, CuO nanowires with small diameters between 10nm and 30nm are achieved, which is especially important for gas sensing applications where a high surface-to-volume ratio of the gas sensitive elements is needed.

Local CuO nanowire synthesis on CMOS microhotplates has several advantages as compared to heating of the whole substrate. The proposed method can be performed on already packaged samples directly before gas sensor operation. Furthermore, the described local nanowire synthesis technique may enable the simultaneous integration with other sensing materials that are not able to withstand high temperature treatments, such as conductive polymers for instance. Heating of the whole wafer is advantageous when batch fabrication of multiple CuO nanowire devices is desired. Due to the low temperature for CuO nanowire synthesis (T=350°C), the process is CMOS backend compatible and can be in principle performed on wafer-scale. However, it is desirable for gas sensing applications that no further process steps such as dicing, for example, are performed after CuO nanowire synthesis in order to avoid any surface contaminations, which restricts the available process flow options considerably.

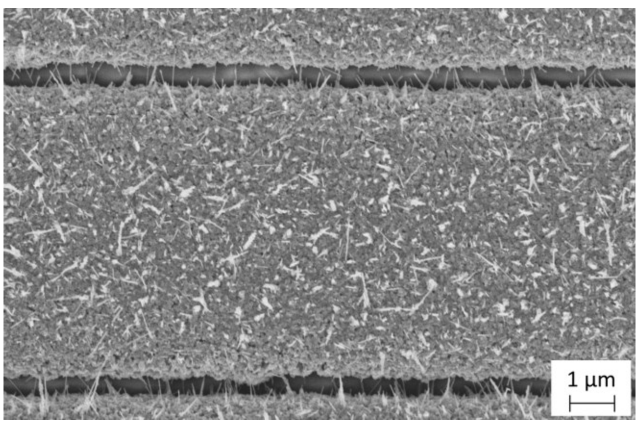

Figure 3: The gap between neighboring thermally oxidized Cu lines is bridged by suspended CuO nanowires.

4.3 Gas Measurements

It is obvious from the device design (see Fig.1) that the electrical resistance can be measured between several contact electrodes resulting in different numbers of CuO nanowire arrays contributing to the overall sensor resistance. In the following, gas sensing results for two CuO nanowire arrays in series are shown while the CMOS microhotplate was operated at a constant temperature around 325°C (power consumption 18.2 mW). In Fig.4, the electrical resistance change of the CuO nanowire gas sensor during exposure to three pulses of humidity is presented. Large sensor responses up to a factor of two were achieved. As expected for a p-type semiconductor, the resistance increases in the presence of water vapor, which was explained by a decrease of charge carriers in the accumulation layer at the metal oxide surface [22].

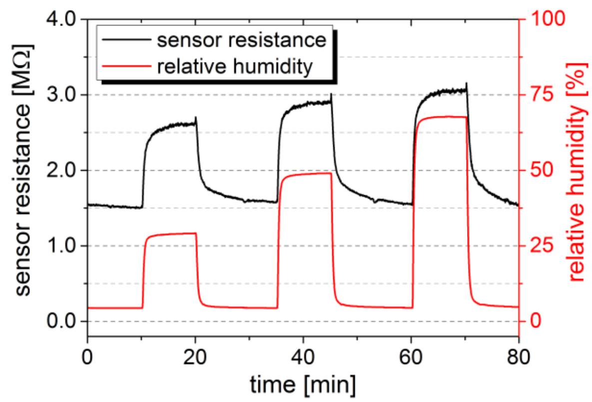

Figure 4: Humidity response of a CuO nanowire sensor (T~325°C) in dry synthetic air.

The sensor response of the CMOS integrated CuO nanowire device is also investigated during exposure to pulses of CO with concentrations ranging from 10ppm to 100ppm (Fig.5). As can be seen, the CuO nanowire device is able to detect CO in the investigated concentration range with a sensor response around 17% for the 100ppm CO pulse. These results are well comparable with those achieved earlier on similar CuO nanowire devices on Si substrates assembled with external heating elements [20]. Similar as during humidity exposure, CuO nanowire resistance increases in the presence of CO. In literature, this was explained by the reaction of CO with ionosorbed oxygen O^- to CO_2 resulting in a reduction of the negative charge trapped at the surface [22]. As a consequence, CO exposure leads to a decrease of hole concentration in the surface accumulation layer and an increase of electrical resistance.

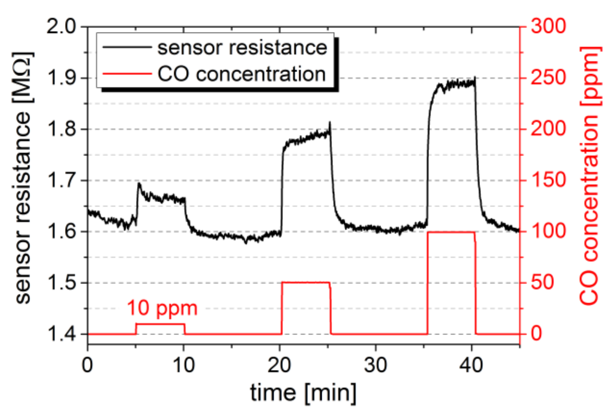

Figure 5: CO response of a CuO nanowire sensor (T~325°C) in dry synthetic air.

5 CONCLUSION

In summary, CuO nanowires were locally synthesized on CMOS microhotplates leading to the realization of functional gas sensing devices. This technique has advantages in terms of heterogeneous materials integration and extended fabrication process flow options. As the toxic gas CO could be detected in a concentration range relevant for safety applications, the CMOS integrated CuO nanowire gas sensors may find applications as security devices. Most importantly, the presented technology combines device miniaturization, low power consumption and CMOS integration of nanomaterials, which are crucial factors for the future realization of smart gas sensors for daily life applications.

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