

Identification of H₂S Impurity in Hydrogen Using Temperature Modulated Metal Oxide Resistive Sensors with a Novel Signal Processing Technique

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Abstract— We report here on the results of a study on the response of copper oxide (*p*-type and mixed) based, low-power microelectromechanical (MEMS) gas sensors to parts per million (ppm) levels of hydrogen sulfide in a hydrogen atmosphere. It is shown that a thermally modulated metal oxide gas sensor can be used for the identification of the H₂S impurity in a reducing environment without the need for a reference gas or baseline signal. It was found that by using this material with a method of transient frequency analysis, a resistive gas sensor can operate reliably in a harsh environment, e.g., pure hydrogen and elevated humidity levels. A linear response in gas concentration was obtained from the analysis of transient sensor signal. This novel temperature modulation technique is more effective than an isothermal method where H₂ background is introduced, due to the elimination of drift and additive noise in the sensor response that limits the practical utilization of these low-cost sensors.

Index Terms—Chemical and biological sensors, gas sensor, hydrogen environment, hydrogen sulfide, temperature modulation.

I. INTRODUCTION

Hydrogen sulfide (H₂S) is an odorous, colorless, noxious, and flammable gas widely produced in different industrial processes. Recent interest in detecting hydrogen sulfide has significantly grown, together with carbon monoxide and ammonia, as a common impurity in hydrogen fuel that typically feeds a polymer electrolyte membrane (PEM) fuel cell stack for automotive applications [1]–[3]. The growing fleet of hydrogen-powered cars creates the need to detect hydrogen contamination at fueling stations to prevent degradation of the fuel cell and vehicle operation [4]. The current method for the in-line monitoring of the hydrogen fuel as a clean energy carrier (no CO₂ or NO_x) requires the use of highly expensive analytical techniques, such as mass spectrometry, gas chromatography and Fourier Transform Infrared spectroscopy. Recent attempts on integration of a contamination detection system based on the technologies listed above into a station face the barriers of technology availability, system integration, cost and maintenance. It is clear that the current prevention strategy must be improved; a more robust method is urgently needed that helps to monitor the quality of the hydrogen supply frequently and alerts station operators.

The application of H₂S detection discussed above requires sensors to operate under harsh conditions, such as absence or low oxygen content and elevated humidity and temperature environments. Some authors including us, have already reported stable gas sensing responses employing *n*-type metal oxides such as WO₃ and doped WO₃ and SnO₂ at trace level oxygen concentrations, focusing mainly on the detection of CO, sulfur compounds and NO₂ [5]–[9]. Metal oxide (MOX) based sensors have the advantage of low cost, long life, high compatibility with microelectronic processing and operation in wide

temperature ranges, especially at higher temperatures (above 300 °C). Among all the *n*-type and *p*-type reported MOX semiconductors, CuO could be a good candidate for detecting H₂S under harsh conditions [10]. It can be anticipated that these sensors rely on sulfurization of copper oxides upon exposure to hydrogen sulfide and such a sensing mechanism does not imply a change in the amount of the surface oxygen species.

Our work focuses on the detection of parts per million (ppm) levels of H₂S in a pure H₂ environment; this condition has not been widely investigated for metal oxide gas sensors. In this paper, we propose a novel signal processing technique for sensors based on pure *p*-type CuO and WO₃ doped with 3 wt% CuO (WO₃:CuO) nanoparticle materials that analyses a temperature modulated change in the electrical resistance of these MOX films and enables the measurement of ppm levels of H₂S in a harsh environment such as a combination of hydrogen, absence of oxygen and elevated humidity level. The principle of novel temperature modulation technique using polymers or metal oxides gas sensors with integrated micro-hotplate has already been reported by our group [11]–[15].

II. EXPERIMENTAL

In this study, a low power microelectromechanical (MEMS) based micro-hotplate gas sensor was used, and the operating temperature was controlled by an adjustable constant current circuit. The schematic cross-section of the micro-hotplate (CCS09C, Cambridge CMOS Sensors Ltd- now ams Sensors UK Ltd) with a sensing layer is shown in Fig. 1. The MEMS structure was fabricated in a commercial foundry and is based on silicon on insulator (SOI) technology [16]. In the membrane structure, a tungsten resistive micro-heater is embedded within a *ca.* 5 μm thick metal/oxide stack ensuring a low DC power consumption (e.g. 65 mW at 600 °C). The membrane is fabricated via a post complementary metal–oxide semiconductor (CMOS) deep

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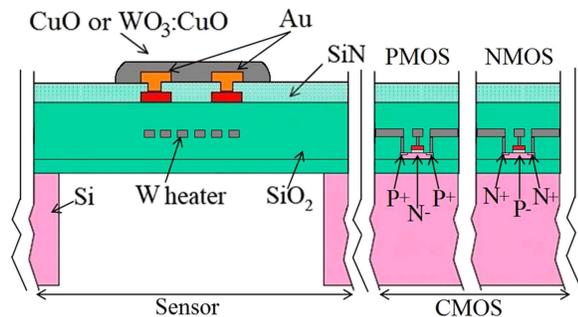


Fig. 1. Schematic cross-section of a chemisensor deposited on an SOI CMOS micro-hotplate.

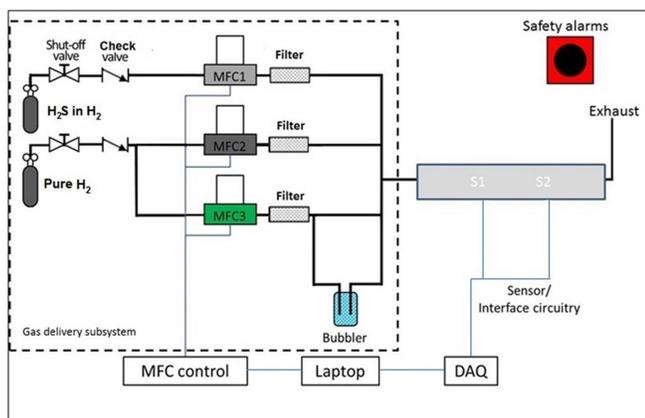


Fig. 2. Block diagram of the fully-automated gas testing rig. MFC: mass flow controller; DAQ: data acquisition unit.

reactive ion etch (DRIE) and both mechanically supports and thermally isolates the heater from the sidewalls. The MEMS micro-hotplate can reach temperatures well in excess of 500 °C and has a sub-5V controlled temperature ramp capability of 30 ms heating time and 60 ms cooling time from ambient to 500 °C.

In this work, CuO and WO₃ powders (New Metals and Chemicals Ltd.) were mixed with an organic dispersant ESL 400 to obtain CuO and WO₃:CuO pastes. The weight ratio of the CuO and WO₃:CuO powders and the organic dispersant was 1:2. The pastes were drop cast onto the 1 mm × 1 mm silicon die, which consisted of gold interdigitated electrodes on top of the membrane as a single-chip solution (see Fig. 1). After deposition of the CuO and WO₃:CuO pastes, the substrates were left to dry in air at room temperature for ~12 h followed by annealing at 450 °C for 2 h under ambient air to obtain the sensor elements consisting of *p*-type CuO and *n*/*p*-type WO₃:CuO.

The gas sensing measurements were performed at the Microsensors and Bioelectronics Laboratory at the University of Warwick using a fully-automated custom test rig (see Fig. 2). The CMOS micro-hotplate substrates mounted on TO46 packages were connected to a custom made printed circuit board. Both the micro-heater and chemiresistor were driven/measured using National Instruments DAQ (NI-6343) hardware and software. The gas sensing properties of the sensor element were characterized using a flow type sensing measurements apparatus. The gas sensors were placed inside an aluminum sample chamber equipped with standard Swagelock gas inlet and outlet connectors. A gas mixture of H₂S in pure hydrogen was introduced

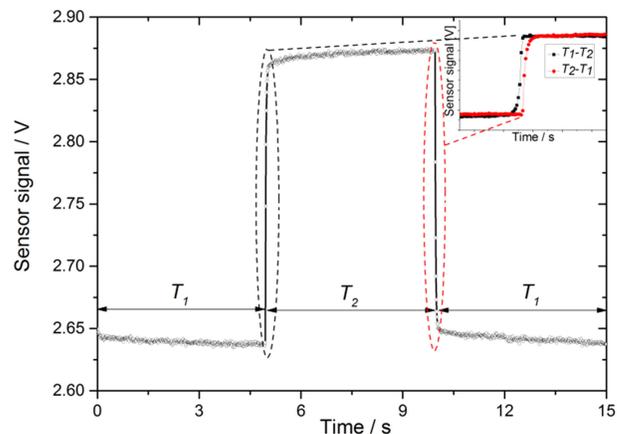


Fig. 3. Typical time behavior of a gas sensing signal during the measurement phase. Example recorded for CuO sensor in 1 ppm of H₂S in H₂ at 25% RH.

into the sample chamber of varying concentrations of 10, 5, 1, and 0 ppm. The total gas flow rate was held constant at 0.3 slpm and the measurements were performed at room temperature (23 °C) in dry conditions and then at 25% relative humidity (RH). A LabView (version 13.0, National Instruments) interface allowed fully automated control of the digital mass flow controllers of the gas testing system.

In our experiments, we used a thermal modulation technique in which the temperature of the SOI CMOS micro-hotplate, onto which CuO or WO₃:CuO gas sensitive layers were deposited, is switched between two sensor different operating temperatures T_1 and T_2 ($T_1 < T_2$) in the presence of H₂S vapor in pure H₂ environment and, there is no need to switch to reference gas. Temperature modulation was carried out between the following T_1 and T_2 : 200 °C and 250 °C, 200 °C and 300 °C, 200 °C and 350 °C, 250 °C and 300 °C, as well as 250 °C and 350 °C. In our experiments, the temperature of the gas sensing films was controlled by applying a square wave voltage to the micro-hotplate, where the peak and trough of the square wave were set in the LabView program. These temperatures used in the experiments require low heater operating voltages of 0.185 V (200 °C), 0.205 V (250 °C), 0.220V (300 °C), and 0.239 V (350 °C). Fig. 3 shows a typical temperature modulation response between 200 °C and 350 °C based on the recorded data for the CuO sensor in 1 ppm of H₂S in H₂ at 25% RH. The sampling rate of the sensor signals was set at 100 samples per second and the sensor operating temperature was switched every 5 s.

III. RESULTS AND DISCUSSION

The goal of this work is to demonstrate for the first time the quantitative analysis of PPM levels of H₂S in a pure hydrogen environment using temperature modulated micro-hotplate CuO and WO₃:CuO sensors. The transient signal of the sensing films was recorded and then FFT analyses of the fractional difference of transient sensor resistance were used to characterize the sensor response. The FFT was calculated over 3 time periods of the signal and averaged to demonstrate stability of the sensor performance. Five temperature steps T_1 and T_2 were studied for thermal modulation analysis and the highest response of CuO sensor was observed for the temperature step 200 °C and 350 °C for T_1 and T_2 , respectively. Fig. 4(a) and (b) present the highest average CuO sensor response to H₂S in dry and humid H₂ obtained

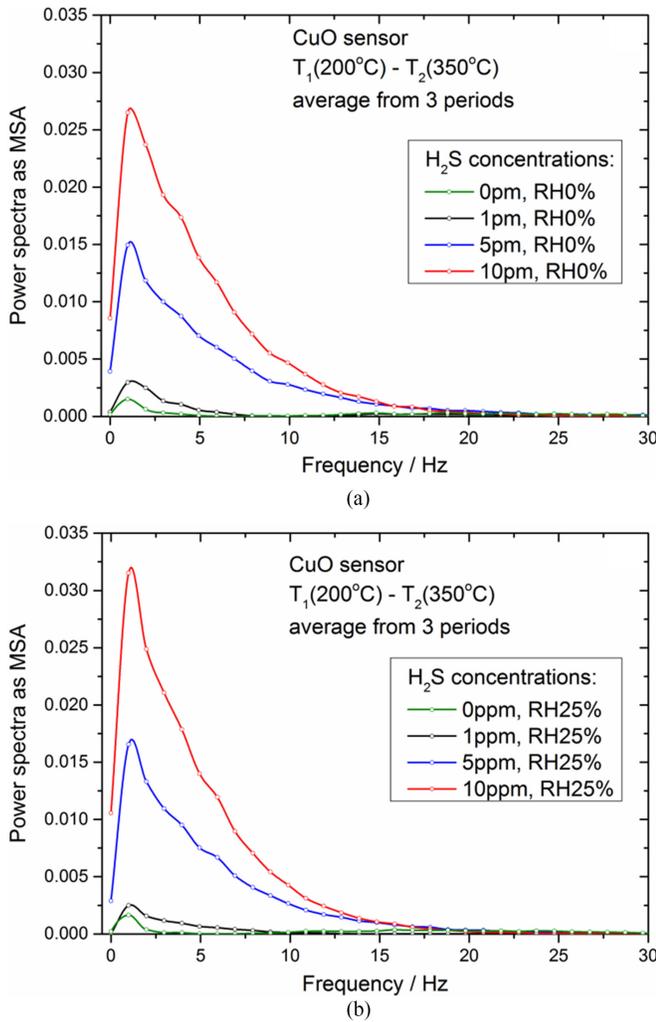


Fig. 4. Power spectra as mean square amplitude (MSA) of the average signal response of CuO sensor to H₂S impurities in dry (a) and 25% RH (b) H₂.

for 200 °C (T_1) and 350 °C (T_2). It is clearly seen that the amplitude of the fractional signal curve depends on the gas concentration and can be used for quantification. The response of CuO based sensor to H₂S is humidity dependent and on average is 15% higher compare to the results obtained in dry gas.

Analysis of the WO₃:CuO sensor response revealed that two temperature steps were suitable for modulation: 200 °C and 350 °C; 250 °C and 350 °C as T_1 and T_2 , respectively. Fig. 5(a) and (b) show the average WO₃:CuO sensor response to H₂S in dry and 25% RH H₂ for T_1 and T_2 200 °C and 350 °C, respectively. Although the height of the peaks shown in Fig. 5(a) and (b) increases with increasing H₂S concentration, the outputs from this analysis are noisier and the bandwidth wider compared to the results obtained for CuO sensor. The response of WO₃:CuO sensor to H₂S in 25% RH H₂ was three times lower for all studied temperature steps compare with the response obtained in dry gas. These sensors have longer shelf life and can be used at a wider range of operating temperature compared to CuO based sensors.

The peaks from the power spectra typically occur at *ca.* 1 Hz for CuO and *ca.* 2-3 Hz for WO₃:CuO sensors tested both in dry and

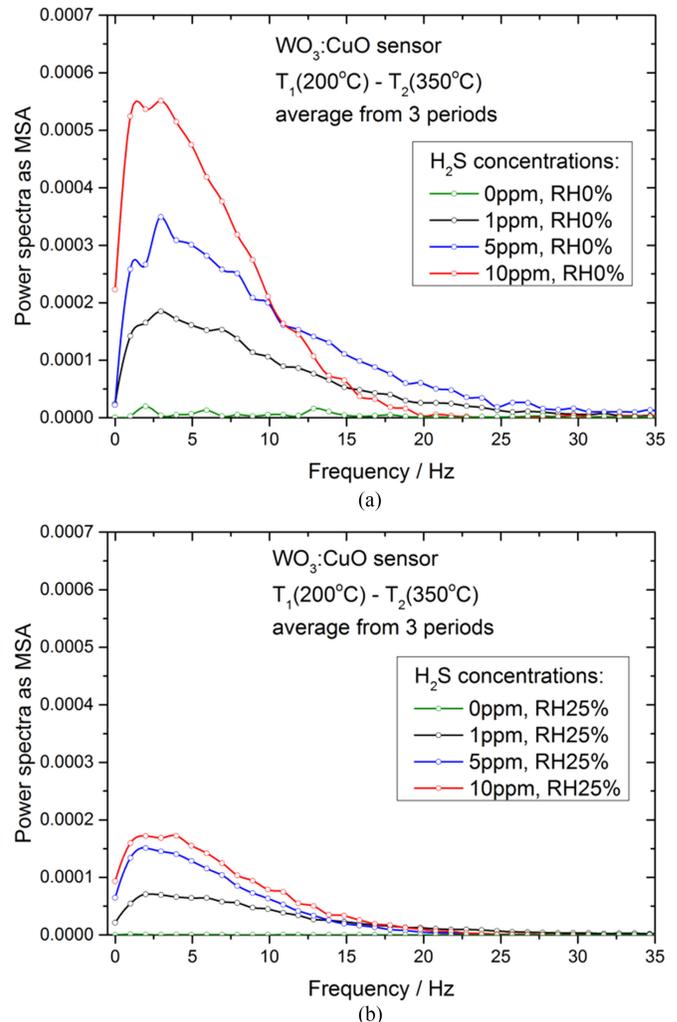


Fig. 5. Power spectra as mean square amplitude (MSA) of the average signal response of WO₃:CuO sensor to H₂S impurities in dry (a) and 25% RH (b) H₂.

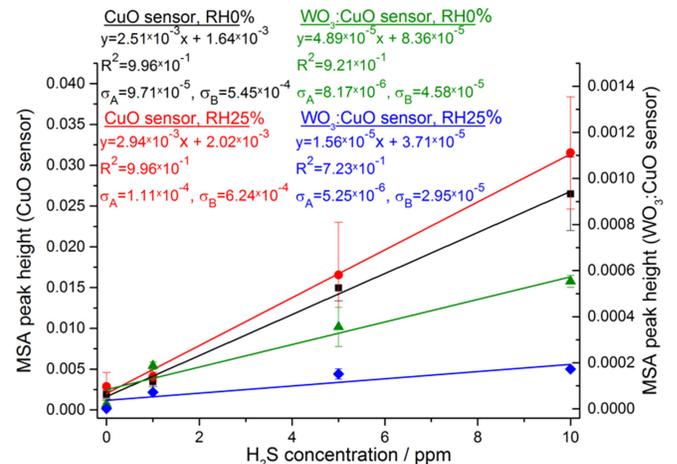


Fig. 6. Plot of average peak height from power spectra vs. H₂S concentration. The error bars represent the standard deviation of three periodic temperature pulses. σ_A and σ_B indicate uncertainties of slop and intercept, respectively.

humid gas. The height of these peaks shown in Fig. 6 increases with the increasing concentration of H₂S in dry and humid hydrogen environment and is approximately linearly proportional to these low level gas concentrations.

Both CuO and WO₃:CuO laboratory sensors along with a commercial sensor (TGS 2602 supplied by Figaro), were also tested in a static (isothermal) mode where H₂S in H₂ and pure H₂ were introduced alternately for 5 minutes. In the case of *p*-type CuO based sensor during exposure to H₂S, the release of electrons led to increase in sensor resistance showing response defined in this measurement method as the ratio of the electrical resistance of the copper oxide in H₂S and H₂ (R_{H_2S}/R_{H_2}), 1.32, 1.49 and 1.65 for 1, 5 and 10 ppm of H₂S in 25% RH H₂ at 250 °C. The average sensor response time (t_{90}) was 30 s and the occurrence of negative baseline drift (27% after 1 h from initial R_{H_2}) was observed. In case of *n*:*p*-type WO₃:CuO sensor, introduction of H₂S impurities decreased the resistance suggesting *n*-type behavior. By cutting off the H₂S flow, the sensor resistance increased but did not reach its initial value. Such sensors had slow response, did not reach steady state after 5 minute exposure to the sensing gas and did not recover to baseline. The significant baseline drift of 58% after 1 h from initial R_{H_2} was observed due to incomplete recovery of the WO₃:CuO sensing element. These sensors responses to H₂S impurities in H₂ were reproducible and, may indicate that for these gases there are two interaction paths: a direct interaction with metal oxides, which does not involve lattice oxygen and a reaction with pre-adsorbed oxygen. These devices have been stored in ambient conditions and showed 5% lower overall response in the same operating temperature range after 4 months. The sensors were also tested for cross-sensitivity in the presence of CO from 1 to 400 ppm in dry and humid H₂ and no signal changes were observed. In case of metal oxide commercial sensor, during exposure to H₂ the signal was not stable, thus the device was unsuitable for application in reducing environment.

The drift of the sensor signal observed during the static measurements limits their practical application. In our novel temperature modulation method, sensors are exposed to the target gas only for several seconds making it not only faster but more robust against baseline drift and unspecific noise than static experiments, where sensors have to be exposed to the target gases for significantly longer and need zero gas calibration or reference point.

IV. CONCLUSION

In this paper, a novel temperature modulation technique for CuO and WO₃:CuO based sensors has been proposed in order to detect sub ppm levels of H₂S impurities in pure H₂. This novel temperature modulation method enables accurately identify H₂S species in harsh environment using only few seconds of the signal response. It was found that the sensor response was, as expected, humidity dependent and linearly proportional to the gas concentration. This novel signal processing technique based on analysis of transient sensor signal, combined with CMOS micro hotplate sensors, could lead to a new generation of low-cost gas sensors with embedded software that could

be used e.g., for a hydrogen fuel cell in the real world where fast indication (under 1 s) of impurities in hydrogen gas line is required. Clearly, compensation of the impact of humidity would be needed in variable ambient conditions. Further development of resistive gas sensors for operation in H₂ at higher RH levels (50-75%) is in progress to demonstrate detection in the multi-component environment required for hydrogen fuel cells.

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