Prediction of Impurities in Hydrogen Fuel Supplies Using a Thermally-Modulated CMOS Gas Sensor: Experiments and Modelling

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***Abstract*—We report here on the results of a study on the response of copper oxide based low-power MEMS thermally modulated gas sensor to low ppm levels of hydrogen sulphide (H_2S) in a hydrogen environment. It was found that by using this material with a method of transient frequency analysis, this resistive gas sensor can operate reliably in a harsh environment including hydrogen atmosphere and high humidity levels. We implemented a Bayesian method for data analysis to predict the concentration of H_2S in hydrogen supplies used in fuel cells.**

Keywords—gas sensor; hydrogen atmosphere; Gaussian process

I. Introduction

Hydrogen fuel cells are sensitive to a number of impurities, such as CO, NH_3 and H_2S, that can be found in dispensed fuel at multiple points. Testing of the quality of hydrogen fuel is therefore required to prevent cell degradation. Metal oxide (MOX) based gas sensors have attracted considerable attention due to their potential applications in monitoring poisonous gases in air. It is also well known that atmospheric oxygen plays an important role in these sensors and only a few reports have been published on the mechanism of the response of MOX sensors in the absence or at trace levels of oxygen concentrations [1-4]. Such sensors employ mainly *n*-type metal oxides such as WO_3 and SnO_2 and typically focus on detection of CO and NO_2. Among *p*-type MOX semiconductors, CuO has received much attention for H_2S detection [4]. We have showed that this *p*-type semiconductor with a narrow band gap (E_g = 1.2 eV) is a good candidate for detecting of H_2S at low concentration under harsh conditions. It is anticipated that CuO based sensors rely on sulphurisation of copper oxides upon exposure to hydrogen sulphide and such sensing mechanism does not imply a change in the amount of the surface oxygen species.

In our previous studies, we have also shown the usefulness of thermally-modulated *p*-type and mixed *p*-type/*n*-type sensors in a pure H_2 environment [4]. In this work, we use CuO based sensors to modulate their working temperature in the most suitable range in harsh conditions typical for polymer electrolyte membrane (PEM) fuel cell operation, such as a combination of H_2 and high humidity levels, in order to detect H_2S. We used the obtained data to build up a multi-variate model to predict sensor response to H_2S and associated errors.

II. Experimental Metchods

In this study, a low power MEMS based micro-hotplate gas sensor was used, and the operating temperature was controlled by a switched current circuit. The schematic cross-section of the micro-hotplate (CCS09C, CCS 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 [5]. In the membrane structure, a tungsten resistive micro-heater is embedded within metal/oxide stack ensuring a low DC power consumption. The membrane is fabricated via a post-CMOS deep reactive ion etch (DRIE) and both mechanically supports/thermally isolates the heater from the sidewalls. The MEMS micro-hotplate can reach temperatures of 500°C and has a sub-5V controlled temperature ramp capability of typically 30 ms heating and 60 ms cooling time. This micro-hotplate is therefore ideal to use as a platform for our gas sensors.

In this work, CuO powder (New Metals and Chemicals Ltd) was mixed with an organic dispersant ESL 400 to obtain CuO paste. The weight ratio of the CuO and the organic dispersant was 1:2. The paste was 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 (Fig. 1). After deposition of the CuO paste, the substrate was left to dry in air at room temperature for ~12 h followed by annealing at 450°C using the sensor's heater for 2 h under ambient air to obtain the sensor element consisting of *p*-type CuO.

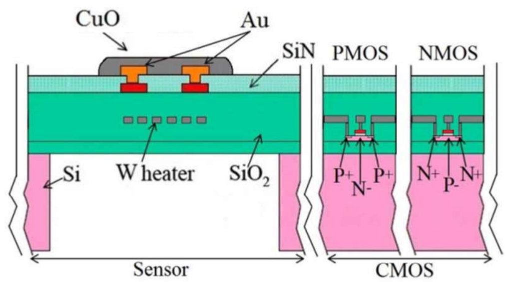

Fig. 1. Schematic cross-section of a chemisensor deposited on an SOI CMOS micro-hotplate with adjacent CMOS electronic cells.

The gas sensing measurements were performed in the Microsensors & Bioelectronics Laboratory at the University of Warwick using a fully-automated custom test rig (Fig. 2). The CMOS micro-hotplate substrates mounted on TO46 packages were connected to a custom made printed circuit board.

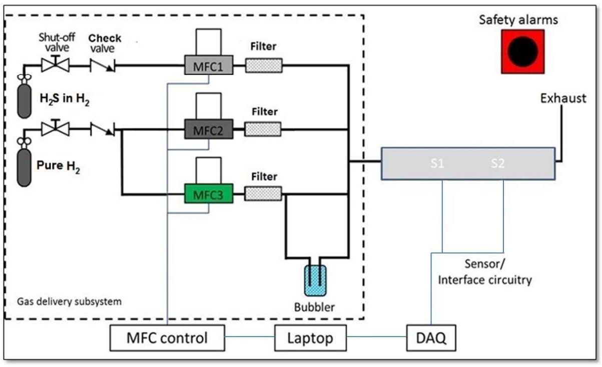

Fig. 2. Block diagram of the fully-automated gas testing rig.

Both the micro-heater and chemiresistor were driven/measured using National Instruments data acquisition unit (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 sensor was placed inside an aluminum sample chamber equipped with standard Swagelock^{TM} gas inlet and outlet connectors. A gas mixture of H_2S in pure hydrogen was introduced into the sample chamber of varying concentrations of 10, 5, 2, 1 and 0 ppm. The total gas flow rate was held constant via mass flow controllers (MFCs) at 0.3 slpm and the measurements were performed at room temperature (23°C) in dry conditions and then at 25, 50 and 75% relative humidity (RH) controlled using a commercial sensor (BME280, Bosh). A LabView (version 13.0, NI) 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 gas sensitive layer was deposited, is switched between two sensor different operating temperatures 200°C (T_1) and 350°C (T_2) in the presence of H_2S in pure H_2 environment. Our previous tests demonstrate that this temperature step showed the highest response of CuO sensors. The principle of this technique using polymers or metal oxides gas sensors with integrated micro-hotplate has already been reported by our group [5-7]. In these experiments, the temperature of the gas sensing films was controlled by applying a square wave voltage to the micro-hotplate. These temperatures used in the experiments require low heater operating voltages of 0.185 V (200°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 H_2S in H_2 at 25% RH. The sampling rate was set at 100 samples per second and the sensor operating temperature was switched every 5 s.

The goal of this work is to demonstrate for the first time the quantitative analysis of ppm levels of H_2S in a pure hydrogen environment using temperature modulated micro-hotplate CuO sensor. The transient signal of the sensing film 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.

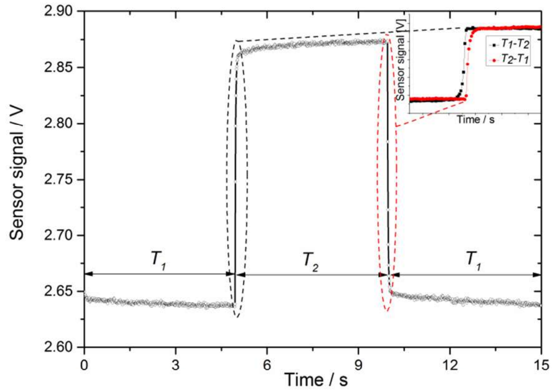

Fig. 3. Typical time behaviour of a gas sensing signal during the measurement phase. Example recorded for CuO sensor in 1 ppm of H_2S in H_2 at 25% RH.

Fig. 4 presents the typical CuO sensor response to H_2S in dry H_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 to H_2S is humidity dependent and on average is between 30% to 50% higher (for RH 25, 50 and 75%) compare to results obtained in dry gas.

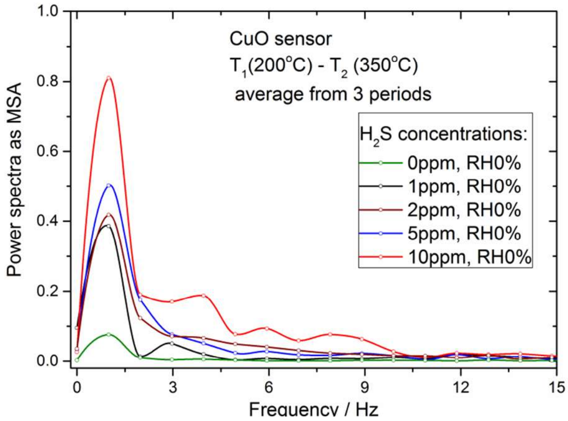

Fig. 4. Power spectra showing mean square amplitude (MSA) of the average signal response of CuO sensor to H_2S impurities in dry H_2.

III. EXPERIMENTAL DATA ANALYSIS

In this section we conduct a quantitative analysis using the raw data. For the real-time application, the time-varying signal $s(t)$, where t denotes time, could be monitored for some fixed time interval and stored as a vector $\boldsymbol{s}$. The observed ppm level y is assumed to be an output of an unknown but well-defined function corrupted with additive Gaussian noise. The unknown function can be approximated in a statistical sense given observations from experiments. This is essentially a multi-input-single-output (MISO) learning problem. Gaussian process (GP) models are Bayesian statistical learning methods for regression and classification. Compared to non-Bayesian methods such as the neural networks, GP models provide full statistical descriptions of the predicted outputs and do not

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require cross-validation for training process [8]. Thus, they are suitable for problems where data are limited due to high experimental cost, as in the present case. Previous work using GP models for signal processing can be found in [9,10], though the focus and applications are mainly related to communications. GP models can naturally deal with Gaussian noise in the output. It is shown in [11] that input signal noise could be dealt with by modifying the kernel function and introducing more hyperparameters. This may consequently increase the computational burden and also require more training data. To avoid this issue, we assume the noise could be filtered out by discarding the high frequency signal. In practice, we apply a FFT to the signal to gain a power spectrum and retain the first 25 power coefficients (from 0 to 8Hz) by testing and comparing the final results. The remaining power spectrum is denoted as $\boldsymbol{x}$. Another advantage of FFT pre-processing is that the power coefficients x_i are independent. This simplifies the model structure and consequently reduces the computational cost and number of training data required.

The model we assume is, $y = f(\boldsymbol{x}) + \epsilon_y$, where ϵ_y is a Gaussian noise term. Given sufficient observations $\boldsymbol{D} = \{\boldsymbol{x}^{(i)}, y^{(i)}\}_{i=1}^{n}$ as training data, the unknown function f could be approximated in a statistical sense. A GP model does not specify $f(\boldsymbol{x})$ explicitly. Instead, it describes the input-output relationship using a conditional Gaussian distribution: $y(\boldsymbol{x})|\boldsymbol{\theta} \sim GP(0, \mathbb{c}(\boldsymbol{x}, \boldsymbol{x}', \boldsymbol{\theta})$ in which we assume $\mathbb{E}[y(\boldsymbol{x})]$=0 by centering $\{y^{(i)}\}_{i=1}^{n}$. The covariance function $\mathbb{c}$ fully specifies the model, and in this paper we adopt a Gaussian kernel with a noise term:

$$\mathbb{c}(\boldsymbol{x}, \boldsymbol{x}', \boldsymbol{\theta}) = \theta_0 \exp\left(-(\boldsymbol{x} - \boldsymbol{x}')^T \, diag(\theta_1, \ldots, \theta_l)(\boldsymbol{x} - \boldsymbol{x}')\right) + \theta_{l+1}\delta(\boldsymbol{x}, \boldsymbol{x}')$$

where $\theta_1, \ldots, \theta_l$ measure the impact of each component of the spectrum, θ_0 measures the overall impact and θ_{l+1} is the variance of the Gaussian noise. It can be shown that the distribution conditioned on the training data is also Gaussian: $y(\boldsymbol{x})|\boldsymbol{\theta}, \{y^{(i)}, \boldsymbol{x}^{(i)}\}_{i=1}^{n} \sim GP(\boldsymbol{c}^T\boldsymbol{C}^{-1}\boldsymbol{y}, c(\boldsymbol{x}, \boldsymbol{x}, \boldsymbol{\theta}) - \boldsymbol{c}^T\boldsymbol{C}^{-1}\boldsymbol{c})$, where: $\boldsymbol{c} = \left(c(\boldsymbol{x}, \boldsymbol{x}^{(1)}, \boldsymbol{\theta}), \ldots c(\boldsymbol{x}, \boldsymbol{x}^{(n)}, \boldsymbol{\theta})\right)^T$, $\boldsymbol{y} = \left(y^{(i)}, \ldots y^{(n)}\right)^T$ and $\boldsymbol{C}$ is covariance matrix of $\{\boldsymbol{x}^{(i)}\}_{i=1}^{n}$ with elements $C_{ij} = \mathbb{c}(\boldsymbol{x}^{(i)}, \boldsymbol{x}^{(j)}, \boldsymbol{\theta})$. To make predictions, the hyper-parameters of the model $\theta_0, \ldots, \theta_{l+1}$ can be integrated out in a fully Bayesian approach by Monte Carlo sampling. This approach, however, is computational expensive. Instead, we use a Type-II maximum likelihood estimate to obtain point estimates: $\boldsymbol{\theta}_{MLE} = \arg\max_{\boldsymbol{\theta}}(-\frac{1}{2}\ln|\boldsymbol{C}| - \frac{1}{2}\boldsymbol{y}^T\mathbf{C}^{-1}\boldsymbol{y})$.

For each RH condition, the analysis using the GP model is done through a k-fold cross-validation with k=3. The result is shown in Fig. 5 for different RH with an error bar indicating the predictive variances. It is clear that the GP predictions are accurate at low ppm in most cases and reasonably good at high ppm. Also, notice that the predictions are poor at 5 ppm. The reason lies in the lack of observations at the medium ppm level. We also took the RH level h as an input and approximated $y = f'(\boldsymbol{x}, \mathrm{h}) + \epsilon_{\mathrm{y}}$. The GP model required modification of the covariance function $\mathbb{c}$ to incoperate the impact of h. We used the same Gaussian kernel and found that the predictions slightly improved with larger variance. We believe significant improvements could be achieved with more training observations and a careful design of $\mathbb{c}$.

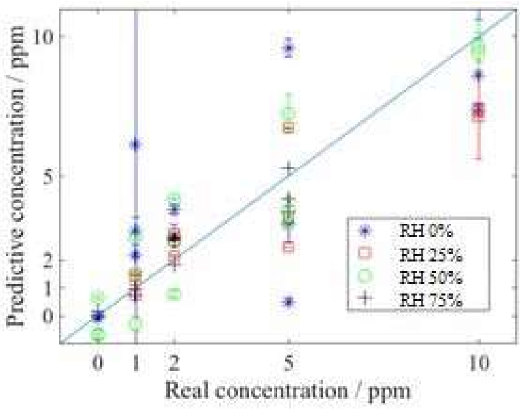

Fig. 5. Predictive ppm versus real ppm at different RH levels (3-fold).

IV. CONCLUSION

A novel temperature modulation technique for CuO based sensor has been used to detect sub ppm levels of H_2S impurity in pure H_2 and various RH levels. This method enables accurately identify H_2S species in harsh conditions using only few seconds of the signal response. The results from GP model used to predict sensors response to H_2S were reasonably accurate for low and high RH levels. Further improvements can be made by incorporating more data, the choice of covariance function, and perhaps through different learning approaches, e.g. taking the signal input directly to the machine-learning pipeline.

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