ULTRA-LOW-POWER CHEMIRESISTIVE MICROSENSOR ARRAY IN A BACK-END CMOS PROCESS TOWARDS SELECTIVE VOLATILE COMPOUNDS DETECTION AND IOT APPLICATIONS

N. Marchand[1], T. Walewyns[1], D. Lahem[2], M. Debliquy[3], L. A. Francis[1]

[1]*Electrical Engineering Department (ELEN), ICTEAM Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium; laurent.francis@uclouvain.be*
[2]*Materia Nova, Mons, Belgium*
[3]*Department of Materials Science, Université de Mons, Mons, Belgium*

ABSTRACT

We describe an ultra-low-power volatile compounds microsensor array towards increased selectivity and sensitivity. The chemiresistive transducers are 100 nm-thick interdigitated gold microelectrodes coated with polypyrrole-based polymer. Two sensors arrays were implemented with respectively 3 x 3 and 2 x 2 pixels², showing a surface per pixel down to 400 x 200 µm². The fabrication is fully CMOS-compatible and the polymer coating is performed at wafer level by electropolymerization, using a differential pulse method from 1.1 to 1.5 V. The polymer film thickness varies from 1.2 to 1.5 µm. Looking at ammonia detection, a sensitivity up to 80 % at 5 ppm in nitrogen is achieved, while consuming below 20 µW continuously. Finally, temperature and humidity effects are analyzed at 25 and 45 °C, from 45 to 95 % RH. Such devices are very promising for remote environmental monitoring applications requiring low-cost low-power sensors associated with dedicated electronics.

Index Terms *— microsensors, sensors array, volatile compounds, ammonia, VOC, conductive polymer, polypyrrole, CMOS-compatible, ultra-low-power, ULP, IoT.*

1. INTRODUCTION

Looking for a better environmental monitoring and increased control in the industry, ultra-low-power and low-cost gas sensors are of main interest in the interconnected sensors nodes vision of the Internet of Things (IoT). By spreading a large number of embedded devices providing high sensitivity and selectivity to specific gaseous species, associated with on-chip processing and communication capabilities. Selectivity and power consumption still remains a big issue in chemical gas detection systems, mostly based on heated metal oxide sensors, and raises challenges for new developments, particularly in the field of miniaturized devices [1]. Looking at volatile (organic) compounds (VOC) monitoring, indicators such as "total VOC" (TVOC) are irrelevant to applications focusing on healthcare or safety. For example, ethanol is not a dangerous volatile compound at ppm level compared to ammonia or hazardous solvents, but will be part of the TVOC value [2].

A large-scale association of sensors on a single chip might provide a good screening of species present in an environment through dedicated data analysis [3,4]. Moreover, the integration of conductive polymers as sensitive layer is a great alternative to metal oxides for an ultra-low-power consumption and selective detection at room temperature [5,6].

We propose a new way for the integration of large-scale microsensor arrays using conducting polymers as sensitive layers. The fabrication process is fully CMOS-compatible with a back-end step of electropolymerization to simultaneously coat the polymer on a large number of sensors. In a first step, polypyrrole (PPy) has been used as functional material for ammonia detection. Thanks to its versatility, the platform enables all kind of functionalization based on electrodeposition.

2. MODELING AND FABRICATION

2.1 Device Modeling

The chemiresistive microsensor array is based on interdigitated electrodes (IDE) as schematized in Figure 1, where L_{finger} is the microelectrode length, W_{finger}, the microelectrode width, g, the gap, L_{IDE}, the transducer length, R_{film}, the functional material resistance and C_{IDE}, the interdigitated electrode capacitance. We define n, the number of interdigitated electrodes or fingers:

$$n = {L_{IDE}}\Big/{\left(W_{finger} + g\right)} \quad . \tag{1}$$

The microsensor resistance is approximated by:

$$R_{sensor} \cong \frac{R_{film}}{2n-1} \cong {\rho_{film} g}\Big/{\left(t L_{finger}\right)(2n-1)} \tag{2}$$

where ρ_{film} is the functional material resistivity, and t, the film thickness.

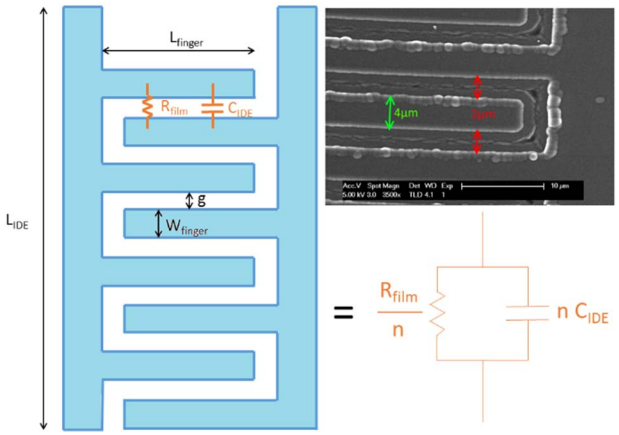

Figure 1 : Schematic and equivalent circuit of an IDE. Inset: SEM picture of the IDE edge after electropolymerization.

The design contains two types of interdigitated electrodes gathered in a pixel array to form a die of 3 mm². The combinations allow 4 pixels of 1 x 1 mm², and 9 of 400 x 200 µm², as shown in Figure 2 (insets).

2.2 Device fabrication

Prototypes have been fabricated in the WINFAB Class 1/ISO 3 cleanroom facilities (UCL, Belgium). A lift-off lithography followed by an e-beam evaporation of gold is realized to define the 100 nm-thick interdigitated microelectrodes on top of a 300 nm wet oxidized silicon wafer. Bottom and top parts are used as electrical contacts.

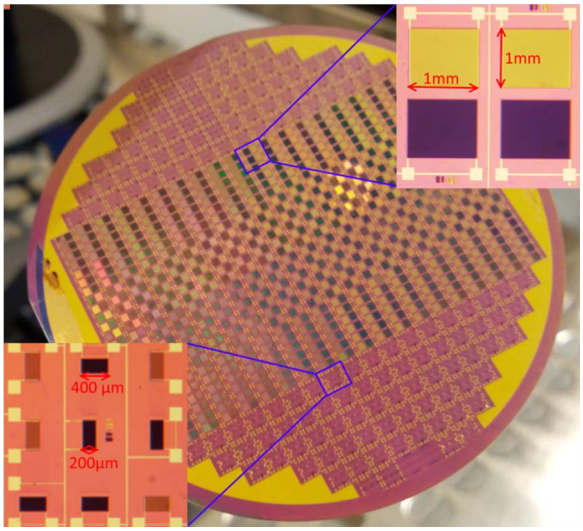

Figure 2 : Picture of a 3-inch wafer after the process of electropolymerization. Insets: optical microscope pictures of a 3 x 3 and a 2 x 2 sensor array.

A PECVD nitride is applied on the entire wafer, and then selectively etched in order to locally coat the electrodes, as depicted in Figure 2.

The electropolymerization is performed by a potentiostat-galvanostat PGSTAT302N controlled by the NOVA 2.0 software from Autolab Metrohm B.V., using a traditional 3-electrodes configuration. The counter electrode is in inox and the reference electrode is a Ag/AgCl(sat). The solution for PPy is composed of 50 ml of acetonitrile, 0.355 ml of pyrrole, 0.05 g of pyrrole carboxylic and 0.612 g of $NaCLO_4$.

A differential pulse method with 500 pulses from 1.1 to 1.5 V vs reference is applied to reach the target thickness. A Dektak® profilometry reveals a homogeneous PPy layer thickness of 1.2 to 1.5 µm, totally recovering the electrodes, as shown in Figure 3. Finally, an aqua regia etching of the gold wires is carried out to open the short-circuits used for electroplating.

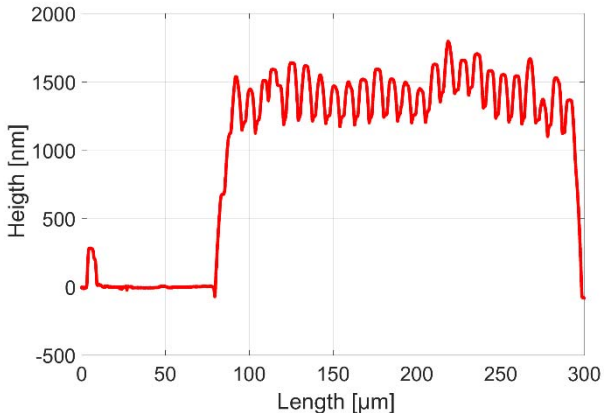

Figure 3 : A down-up profilometry of the PPy sensitive layer on a 400 x 200 µm² IDE.

3. ELECTRICAL CHARACTERIZATIONS

3.1 Humidity and temperature dependence

Both humidity and temperature effects are analyzed from 45 % to 95 % RH, at 25 and 45 °C, as presented in Figure 4 for a 1 x 1 mm² microsensor.

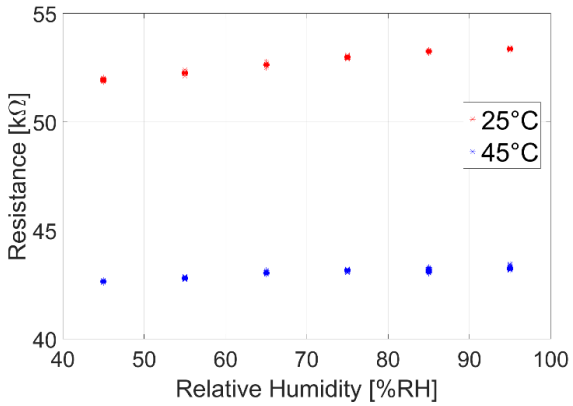

Figure 4: Resistance of a 1 x 1 mm² microsensor at 25°C to 45°C from 45 to 95 % RH.

3.2 Ammonia detection

Devices have been exposed to concentrations from 1 to 5 and 1 to 20 ppm NH_3 in N_2 at 50 % RH and 0.1 V, as presented in Figures 5 and 6, respectively for a 200 x 400 µm² and a 1 x 1 mm² microsensor. No differences were observed when carrying the experiment in air, as the transduction mechanism does not involve O_2 adsorption unlike metal oxides [1].

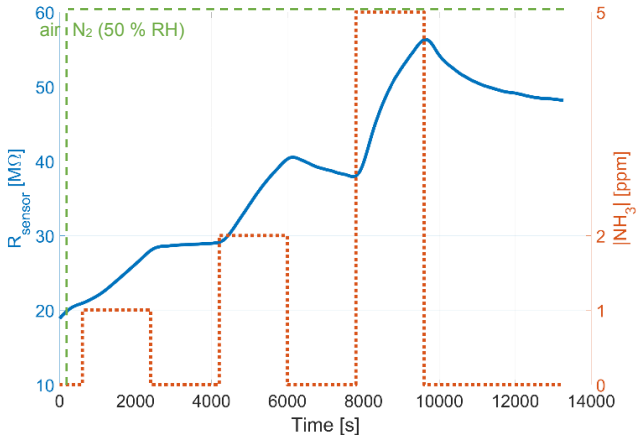

Figure 5: Resistance of a 200 x 400 µm² microsensor under 1 to 5 ppm NH_3 in N_2 at 50 % RH. The supply voltage is 5 V.

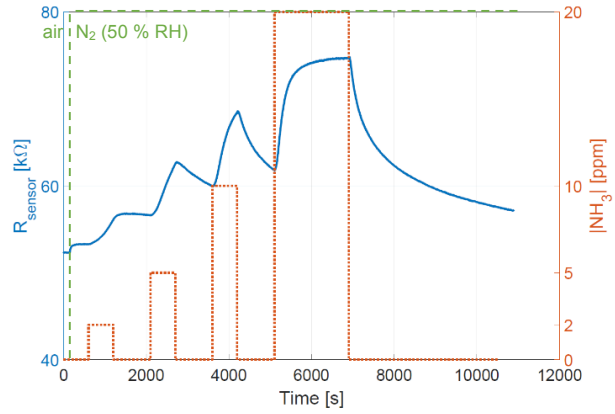

Figure 6: Resistance of a 1 x 1 mm² microsensor under 2 to 20 ppm NH_3 in N_2 at 50 % RH. The supply voltage is 0.1 V.

4. DISCUSSION

As depicted from Figures 5 and 6, a small surface, with a thicker polymer layer, has a better sensitivity than a big one, but exhibits a lower response time. The small surface presents a sensitivity of about 80 % at 5 ppm, where the biggest surface has around 20 %. The response (T90) and recovery (T10) times at 20 ppm are respectively around 15 minutes and over 60 minutes for the biggest surface, with a quasi-absence of drift. With the small surface, a more important drift is observed and both response and recovery times are above 60 minutes. However, the initial slope of the resistance variation as a function of time is roughly proportional to the gas concentration and highlights the chemisorption kinetic. Finally, the detection limit is down to 500 ppb.

The conductivity of the polypyrrole layer can be extracted from Equations 1 and 2, given $\sigma_{film} = 1/\rho_{film}$. Conductivities of approximately 1.2 10^{-4} and 7.29 10^{-4} S/m are achieved, respectively for the small (n = 25) and big surfaces (n = 250). This variation can be explain by a different polymer density between the IDEs, as for both sensitivity and response time. An ultra-low-power consumption down to 20 µW continuously has been reached.

Considering the humidity effect on the PPy layer, the Figure 4 shows an increase of the resistance below 2 % from 45 to 95 % RH, which is negligible. On the other side, the temperature effect decreases the resistance by almost 20 % for an increment of 20 °C. These effects will be compensated by using dedicated temperature and humidity sensors.

5. CONCLUSION

We successfully developed a low-cost method to fabricate chemiresistive microsensors in a back-end CMOS fabrication process. A 1.2 to 1.5 µm-thick sensitive layer has been electropolymerized with good adhesion. The coating process is simultaneously performed on a large number of microsensor arrays at wafer level, significantly reducing the production cost while preserving performances.

Future developments will focus on the co-integration with a dedicated analog interface for signal conditioning, as well as on the integration of other functional material towards increased selectivity. In addition, sensitivity, response time and drift will be optimized in a new design.

Such a multi-pixel approach is promising for low-cost ultra-low-power multi-gas analysis, as preventive qualitative monitoring and warning system through dosimetry analysis, within IoT applications.

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