Technological improvements of a metal oxide gas multi-sensor based on a micro-hotplate structure and inkjet deposition for an automotive air quality sensor application

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TECHNOLOGICAL IMPROVEMENTS OF A METAL OXIDE GAS MULTI-SENSOR BASED ON A MICRO-HOTPLATE STRUCTURE AND INKJET DEPOSITION FOR AN AUTOMOTIVE AIR QUALITY SENSOR APPLICATION

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***Abstract* — In this paper we present a gas multi-sensor composed by an optimized low consumption (55mW-500°C) and low cost (microelectronics process) micro-hotplate and by three different metal oxides (CuO, ZnO and SnO_2) sensing materials deposited by inkjet directly on the membrane. The realized structures have shown a stable and reproducible behavior. By using a specific temperature-modulated profile associated to a multivariate classifier, we have realized an electronic nose able to detect selectively four gases (alone and mixed) at low concentrations (CO-100ppm, NO_2-0.2ppm, NH_3-5ppm and C_2H_4O-2ppm).**

***Keywords:* Gas Sensors, Metal Oxides (MOX), Micro-hotplate, Inkjet**

I - Introduction

Currently available gas sensors are often rather expensive to fabricate, have high energy consumption and low selectivity. Thus, using novel fabrication techniques and nanomaterials, such as inkjet [1] and screen printing [2], new approaches and functionality of the gas sensors can be achieved.

Up to now, inkjet printing has been less studied than the others techniques [3], but it has the potential to be a versatile, cost-efficient and easy-to-scale-up method for producing a large variety of microstructured materials.

Metal oxide thin film sensors have been widely used for gas sensing applications thanks to their sensitivity toward a large variety of gases [4], but they suffer from a lack of selectivity. Therefore, in this paper, we have explored two ways to overcome this problem: the technological way and the chemical and electrical way.

In the first case, the inkjet printing method has been used to deposit three materials widely used in automotive domain [5]: copper oxide (CuO), zinc oxide (ZnO) and tin dioxide (SnO_2). Each of these materials has a particular behavior under gases, allowing the growth of the selectivity of a multi-sensor composed by them.

In the second case, a post-technological process has been studied to increase selectivity by controlling the heater and sensing resistance. Concerning the heater control, a well-known method which consists in using a temperature modulation of the sensor, by changing the power consumption [6], has been used. This kind of profile allows fast chemical reaction changes, and consequently fast gas sensitivities changes. Sensing resistance changes, which are a less studied specification, are based on the fact that the current/voltage characteristic of MOX films exhibits a non-linear behavior [7]. More details about this phenomenon have already been presented in previous work [8]. Thus, a specific profile associated to the temperature modulation has been developed.

Finally, in order to use the multi-sensor as an electronic nose, a multivariate classifier has to be associated to the dynamical profile of the system. The most used classifier in this domain is the Principal Component Analysis (PCA) [9].

The work presented here aims at presenting and characterizing an optimized MOX multi-sensor structure developed in order to improve sensitivity and selectivity, under different gases related to the automotive domain.

II - Experimental Details

A. Device micro-machining and improvement

The first tested platform consists of a silicon bulk on which a thermally resistive bilayer SiO_2/SiN_x membrane was grown. On top of this bilayer two conductive platinum electrodes were sputtered: one as a heater and a second for the sensing resistor, separated from each other by a passivation layer SiO_2. Finally, the rear side of the chip was etched to reach a suspended membrane in order to increase the thermal resistance and to limit the thermal dissipation (see figure 1). However, it occurs randomly leakage current problem between the two Pt metallization.

In order to solve that random failure, a new platform was then designed. The new model consists in sputtering Pt electrodes: heater resistor and sensing resistor, simultaneously, on top of the bilayer SiO_2/SiN_x. Contacts are opened in a previously deposited passivation layer (see figure 2). This change allows reducing cost and the distance between the two metallization was multiplied by four (from 500 nm to 20 µm).

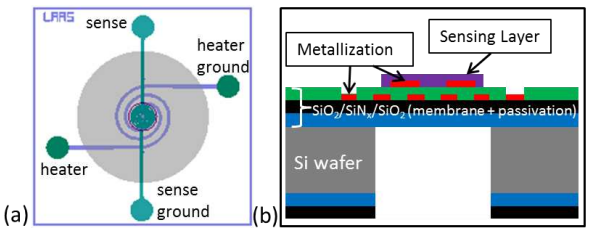

Figure 1: *Old design micro-hotplate gas sensor: (a) chip top view, (b) cross sectional view*

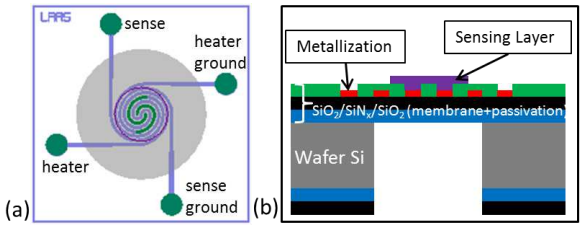

Figure 2: *New design micro-hotplate gas sensor: (a) chip top view, (b) cross sectional view*

B. Inkjet printing

Before jetting, a surface treatment was realized on the substrate in order to reduce the surface energy leading to a hydrophobic surface except the deposition zone. Perfluorodecyltrichlorosilane (FDTS) molecules bond onto surfaces, terminated with hydroxyl (-OH) groups, such as SiO_2 forming a regular covalent bond. The coating is performed by vapor phase deposition and the substrate was treated with standard processes as oxygen plasma prior to the FDTS deposition.

For the ink fabrication, 5 or 10 wt% of each material were dispersed in ethylene glycol by ultrasonic bath for an hour. The obtained dispersion was left to sediment for 1 day. The supernatant dispersion on top was collected and then used for inkjet printing.

Inkjet printing was performed with Altadrop equipment using a 50µm nozzle head from Microfab.

The chuck temperature and the addition of diethylene glycol (DEG) were optimized for each sensing material in order to avoid the coffee ring effect. The jetting parameters are gathered in the table1.

C. Characterization technique

The sensor was placed into a chamber flown by different gases. The composition and humidity of the gas mixture was controlled by Mass Flow Controllers and the global flow rate was checked by a debimeter and set to 200 sscm. Temperature and sensor resistance were controlled by Source Measurement Units.

The sensing layer was heated to 500°C prior to the test in order to desorb the surface from contaminating species. The working temperature was set in the range of 200-500°C. After a period of stabilization under dry synthetic air (two hours), the specific gases were introduced during a given time while ensuring the global flow remains constant.

Responses of different materials gas sensor toward four gases (CO, NH_3, C_2H_4O and NO_2) were characterized and the corresponding sensitivities were compared.

Sensing material morphologies were characterized using a classic SEM S4800 (see figure 3).

Table 1: *Jetting conditions for each material*

Sensing Materials	wt (%)	DEG (%)	Chuck Temperature (°C)
CuO	5	0	25
ZnO	10	2.5	25
SnO_2	10	0	25

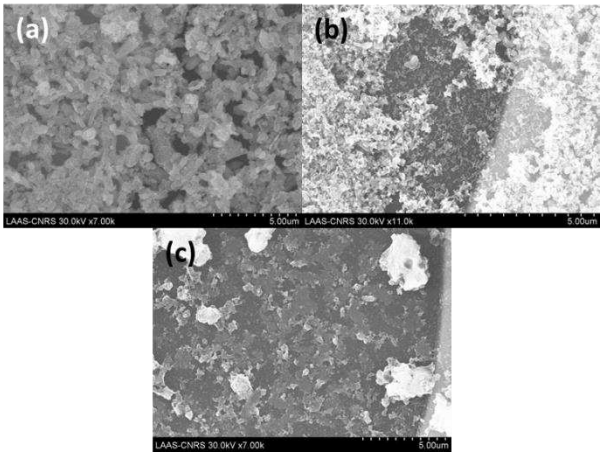

Figure 3*: SEM micrographies of (a) CuO, (b) ZnO, (c) SnO_2.*

III - Results and Discussion

A. Comparison of the two designs

Before performing the new technological process in clean room, a multiphysics modeling has been realized with COMSOL software to compare both designs.

The physics model used to simulate this work was the Joule Effect model. Different heater voltages have been applied (between 0.5 and 6V) in stationary mode and the temperature changes at the surface of the micro-hotplate have been observed (see figure 4).

In addition to reducing costs, achieving the two metallization simultaneously made several significant improvements on temperature distribution. First, the fact to intercalate the sensing electrode in the heater one generates a more circular distribution of the temperature. Moreover, the inkjet deposits being circular too, so this characteristic was very important. Then, the temperature gradient between the center of the surface of the micro-hotplate and the outer limit of the contact open area has been improved by 25% with the new design. Thus, the temperature uniformity of the sensing layer has been improved too and the chemical reactions are better controlled.

The metallization modification brought a better temperature distribution at the surface of the micro-hotplate.

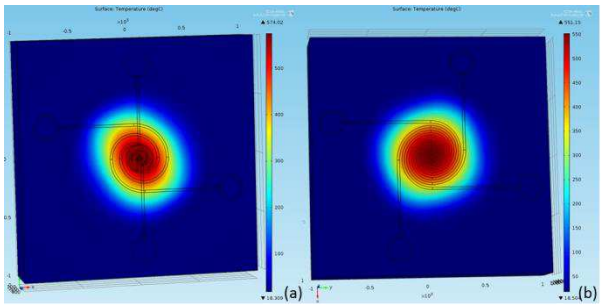

Figure 4: *Temperature variation at the surface of the micro-hotplate; comparison between old and new design; heater voltage = 5V*

In order to validate the results obtained, the maximum temperature obtained by simulations for different voltages applied across the heater has been compared to infrared measurements with a real sensor (see figure 5). The two plotted curves are very close and the maximum deviation was below 25°C.

B. Gas testing

As presented in the introduction, a specific dynamic test profile has been developed into obtained the best information of each sensor. This profile includes heater and sensing layer bias changes.

Several profiles have been observed, and one that allows good reproducibility, the fastest stabilization and the best discrimination was selected (see figure 6). The temperature profile is the following: each step lasts 2 seconds; the temperature baseline is the highest operating temperature (500°C in this case); the others steps are at lower temperatures (400-300-200°C); a complete cycle lasts 12 seconds.

During one temperature cycle, one bias current is applied to the sensing resistor; three different polarizations are successively set (0.01-0.1-1 µA in this example); a complete cycle lasts 36 seconds. Both profiles are repeated throughout the test, under various gaseous atmospheres.

Four different gases at two different concentrations have been injected, firstly individually and then by binary mixtures. One gas injection lasts fifteen minutes and two air sequences are interposed between each one.

The sensitivity (at a given concentration) is calculated as the ratio of the absolute difference between the stabilized resistances of the device under dry air and under the specific gas to the resistance under dry air:

$$S = \left(R_{gas} - R_{air}/R_{air}\right) \times 100. \qquad (1)$$

During one complete cycle (36 seconds), we obtained 36 different mean values and information about each sensor. It therefore generates a huge amount of information for each test and several comparison parameters are possible (temperature, sensing layer bias, sensor, gas …).

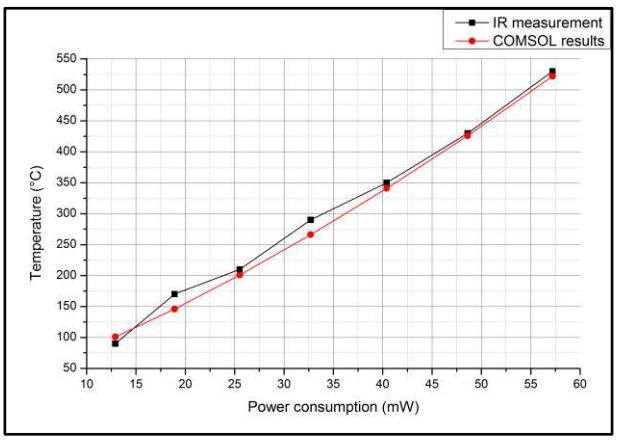

Figure 5: *Temperature versus power consumption at the surface of the micro-hotplate; comparison between simulation and measurement*

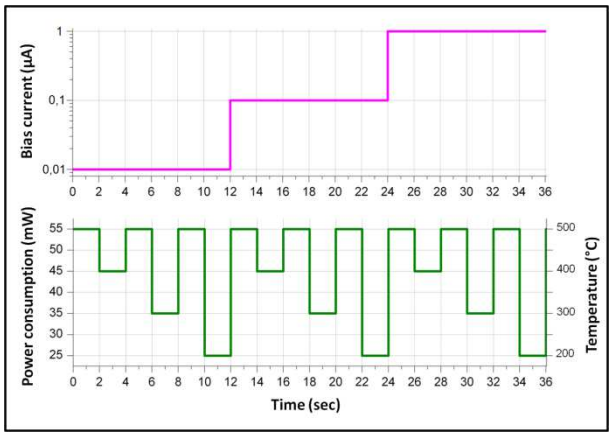

Figure 6: *Power consumption and bias current profiles applied to the sensors*

For example, if we only consider 4 gases at 1 concentration (CO-100ppm, NO_2-0.2ppm, NH_3-5ppm, C_2H_4O-2ppm), 2 temperature from the profile (500 and 200°C), and 2 bias current (10 nA and 1 µA), we can already draw several conclusions (see figure 7).

Concerning the CuO-layer, at 10 nA, decrease the temperature reduces the response to CO; the opposite was observed at 1 µA. For the ZnO-layer, the sensor was not responding to NH_3 at 10 nA, but it had a good response at 1 µA. And for the SnO_2-layer, responses were almost always the same whatever the current applied.

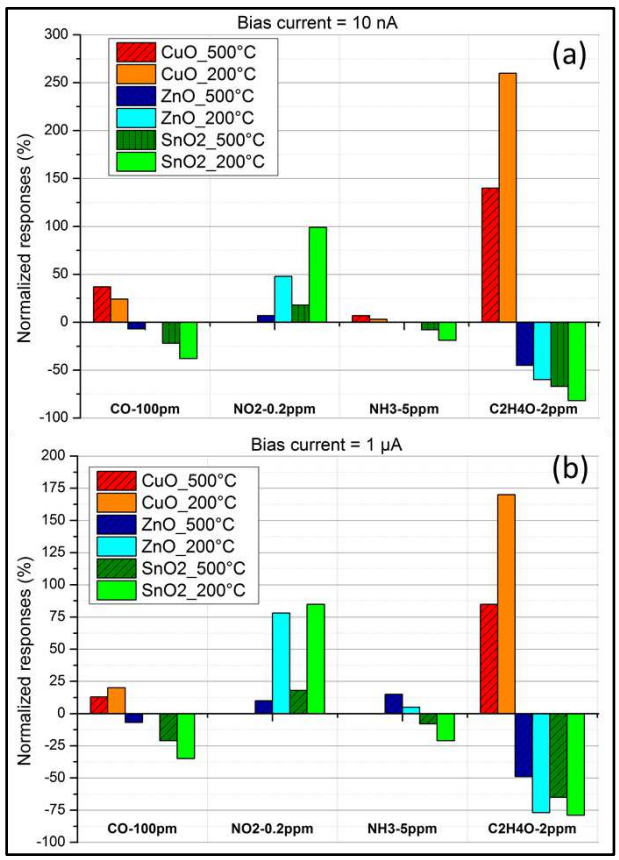

Figure 7: *Normalized responses for the 3 sensing layers at the 4 gases with 2 bias current (10 nA and 1 µA)*

Each sensing layer has presented a specific behavior towards various changes, so it is necessary to use a decision-making system to ensure all information.

C. Towards an electronic nose

As presented before, each sensing material has furnished a specific behavior in presence of different gaseous ambiances. The best way to associate all information was to use a multivariate analysis. The most commonly used is the PCA.

This kind of analysis has been tested on our samples. The correlation matrix was composed by the normalized responses in function of the temperature and the bias current for each gaseous ambiance. Each sensor has been treated individually and then all together (see figure 8).

Using all these results, it has been possible to classify all tested ambiances.

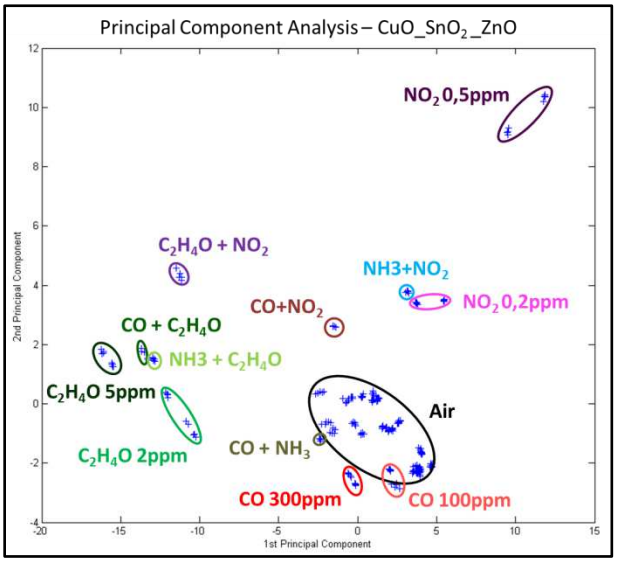

Figure 8: *Cross-PCA of the 3 sensing layers*

IV - Conclusion

The optimization of MOX sensors thanks to technological and electrical control improvements has been investigated.

A new optimized micro-hotplate has been presented. This structure has shown a better temperature distribution, due to the metallization rearrangement, avoiding any leakage current through the passivation layer. The inkjet deposition has been realized directly on the membrane, what constitutes a technological novelty. The deposited layers have shown a stable and reproducible behavior.

A specific optimized dynamic temperature and bias current has been developed. It includes temperature changes between 200 and 500°C, and bias current changes between 10 nA and 1 µA.

The responses to three sensing materials (CuO, ZnO and SnO_2) with four different gases related to the automotive domain (CO, NO_2, NH_3 and C_2H_4O) have been observed. The behavior under gases of each sensing layer was totally different with the temperature and bias influence. Thus, these responses have been analyzed with PCA, and a fully classification of all ambiances have been realized.

To complete this work, it could be considered to replace the PCA by a supervised decision-making system, as a decision tree or a discriminant analysis, to design a recognition system.

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