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DEVELOPMENT OF A MICRO-HOTPLATE FOR DIFFERENT METAL OXIDE GAS SENSORS WITH HIGH OPERATING TEMPERATURE

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Abstract *— The main goal of this work is to realize a metal oxide gas sensor with stable operating temperature. This article describes our approach and the technological process used to reach a high and stable operating temperature (650-700°C), with low consumption (100mW) and good thermal homogeneity all over the active area.*

Key Words*: Micro-hotplates, Semi-conducting gas sensor, nano-particles, Micro-cavity, Tin oxides, Micro technology, inter-digitized electrodes.*

I INTRODUCTION

Having a stable operating temperature is very important for the reliability of gas sensors. Bad stability can decrease characteristics of sensor such its sensitivity, selectivity or lifetime. The worst case is the destruction of the sensor. In addition, gas sensors based on thin film of semi-conducting metal oxide such SnO_2, are more and more attractive because of their principal advantages which are a low cost of production and a low consumption in power. They are used in several fields of application like automotive, environment, house automation …

In this article, we firstly deal with our motivation and our approach to realize metal oxide gas sensor with high and stable operating temperature. Then, we describe our new technological process implemented and first characterizations done.

II MOTIVATIONS

The semi-conducting gas sensor has simple and well-known structure (figure 1). It can be decomposed in two parts [1]:

- The sensitive layer.
- The micro-hotplate which consists of heater resistance, thin membrane and silicon substrate as mechanical support of the detection device.

The micro-hotplate is used to heat sensitive layer at high temperature (300-500°C), in order to allow the detection (oxidation or reduction) of various gases. Temperature is an important parameter; it has an influence on the sensitivity and the selectivity of the sensor. So, the more temperature is controlled, the more reliable sensor is.

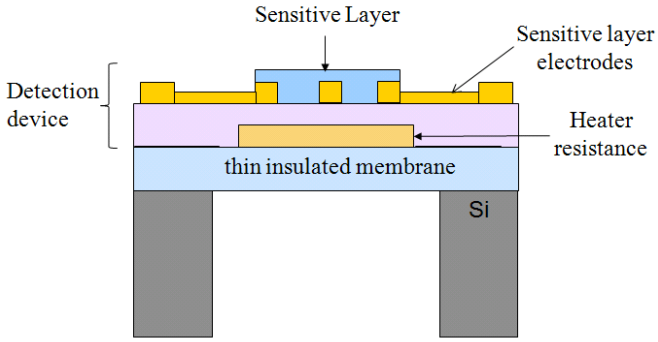

Figure 1: Structure of gas sensor.

Gas sensors developed until day, by LAAS-CNRS as well as some of commercialized sensors, are built on the structure of figure 1. The first structure developed, included a poly-silicon heater on thin film of insulated membranes and metal oxide thin film as sensitive layer (with the collaboration of L2MP and LCC). This structure presents good results for some of applications [5]. The heater reaches 450°C with a power less than 100mW and the thermal inertia from ambient to 450°C is less than 30ms. However, it has been shown that poly-silicon micro-hotplate drifts significantly and in an irreversible way [5]. Indeed this drift induces an increase in the heater resistance of more than 5Ω per month at 450°C; that corresponds to a fall of 12% per month in term of sensitivity. This drift can be explained by a diffusion of doping elements (phosphorus) through grain boundaries in poly-silicon due to high level of current density.

Other examples of tests carried out (~500°C during 120 days [7]) are shown in curves below. Figure 2 shows a drift of micro-hotplate's power for 3 different gas sensors. We can clearly see that heater resistance can decrease up to 15Ω.
Figure 3 shows the time drift of the carbon monoxide (CO) sensitivity for the same 3 sensors that in Figure 2. We can observe that the sensitivity of those sensors decreased of 30-40% in one month.

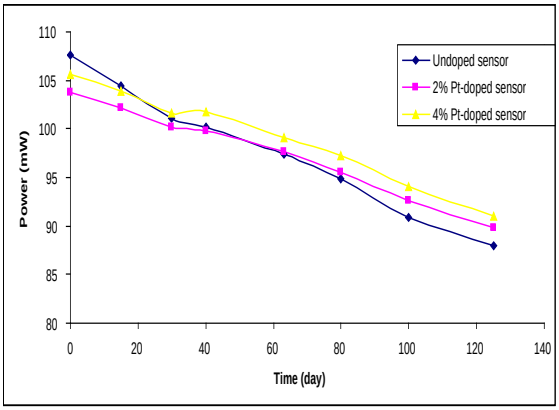

Figure 2: Time drift for 3 gas sensors.

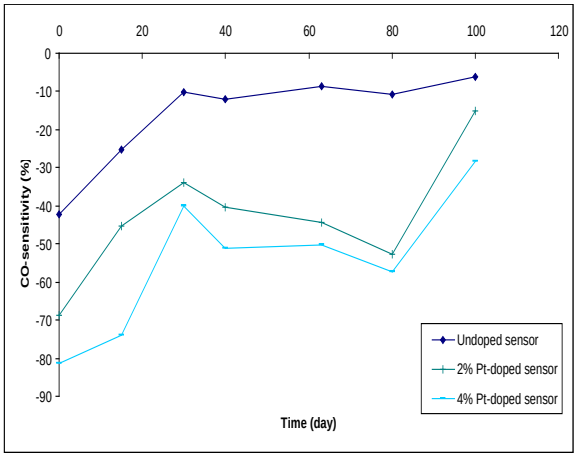

Figure 3: CO-sensitivity versus time (100 days) for the previous gas sensors.

In short, poly-silicon micro-hotplate's drift causes bad stability of the heating and so a bad stability of sensitivity or bad reproducibility. These problems are also due to the uncontrolled morphology of the sensing layer and its thermal drift. So it is very important to elaborate a micro-hotplate more stable with controlled temperature.
A new generation of sensor, where poly-silicon heater had been replaced by a platinum one, has been realized [5]. This new micro-hotplate is able to reach ~475°C with less than 100mW.

Simulation results from numerical modelling with ANSYS Software confirm the Infrared measurement as we can see in figure 4.

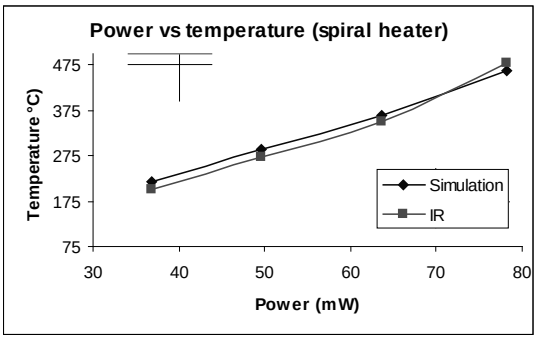

Figure 4: Temperature reach versus power.

Those results with platinum micro-hotplate encourage us to conceive a sensor which can work at high temperature and then detect other gases like CO, NO_x and CH_4. Detection of those gases with metal oxides is essentially done by reactions of surface [3]. Using sensitive layers with nano size or thin CVD layers allow an improvement of those reactions. In addition, some gases' detection appears at more than 500°C (methane oxidation) [4]. So, conceiving sensor for high operating temperature becomes necessary.

III OUR APPROACH

Our approach is to improve and optimize the last developed gas sensor in order to obtain a more stable and controlled temperature beyond 500°C. We also want to make stable and reproducible the deposit of the sensitive layer for a good detection of gases for a long lifetime.

IV IMPROVEMENTS

In spite of the exceptional properties of platinum such stability at high temperature (theoretically up to 650°C) or resistance to oxidation, we observed a drift of the micro-hotplate for temperatures more than 500°C. This drift is supposed to be a degradation of titanium adhesion layer.
Improvements brought to last gas sensor of LAAS-CNRS consist of three main points.

IV.1 NEW TITANIUM THICKNESS

Our current equipment (VARIAN 3/19) enables us to optimize deposits of a 1500/150Å-Pt/Ti with an annealing process in a range of 550-575°C; and this with an aim of avoiding the holes which could

be observed on the surface of platinum according to [2]. Our optimization also enables us to minimize the constraints (less than 100 MPa for annealing temperature higher than 450°C).

IV.2 NEW DESIGN OF MICRO-HOTPLATE

We have replaced the previous heater with a 400µm*400µm double spiral and almost square form (figure 5a) by a new double spiral and circular one (figure 5b). The diameter of the new heater is 300µm.

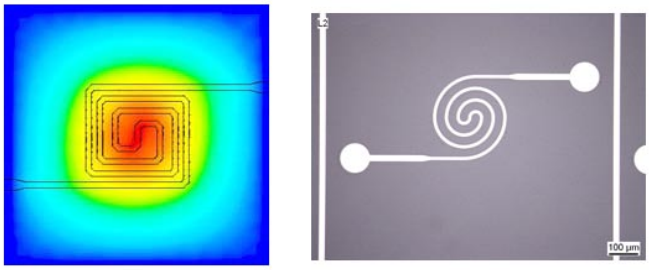

Figure 5: Different designs of micro-hotplate.

The goal of this new design is to obtain the most homogeneous and high temperature on the sensitive layer area, in order to reduce the consumed electric output and then to improve the technical performances of sensor as selectivity, the sensitivity and mechanical reliability.
Simulated tests on the heater in figure 5a give a thermal distribution with an average gradient of 0.3°C/µm from center to border. Even if the gradient of the poly-silicon heater is the best (0.05°C/µm), the gradient of the Pt-heater is interesting for our applications. We expect an improvement of this distribution with the new design (figure 5b).
Modeling and experimental tests are in progress.

IV.3 INTEGRATION OF MICRO-CAVITY

Tin dioxide nano-particles realized by LCC-CNRS are in suspension in a solvent (anisole) [3]. This solution, which is deposited by method of micro-injection, spreads out over the active area, dispersing in uncontrolled way, nano- particles. To avoid that, we are working on integration of a micro-cavity which can contain and fix the size of the drop and so can delimit the active area (260µm of diameter). Following the volume deposited, we will be able to control the reproducibility of active layer from one sensor to another on a wafer. In addition, material used should be compatible with the solvent and removable after SnO_2 deposition if cannot reach high temperature. The first tests of micro-cavity were carried out with SU8 resin. In figure 6, cavity (purple in figure 6a) delimits the active zone precisely.

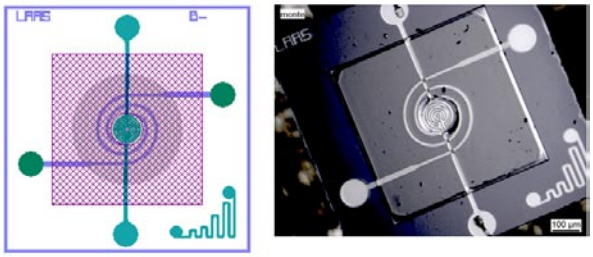

Figure 6: Single gas sensor with SU8 micro-cavity.

In addition, the rounded form of our structure predestines with reception of drops. Moreover, the tests of deposit carried out confirm it as we can see in figure 7. In figure 7b, we can see the spreading out of the same volume of colloid as in figure 7a where all the drop of SnO_2 is well confined (good homogeneity of the thickness).

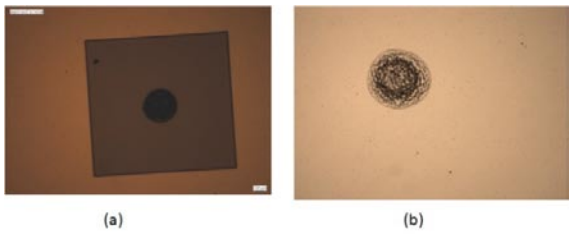

Figure 7: tests of SnO2 deposit with SU8 micro-cavity (a) and without micro-cavity (b).

Another micro-cavity with resin BPR 100 (Boron-modified Phenolic Resin) has been tested as shown in figure 8. This new resin is easily removable even after SnO_2 deposition and first thermal treatment (150°C/1H30 [3] for good adhesion of SnO_2) contrary to SU8 resin.

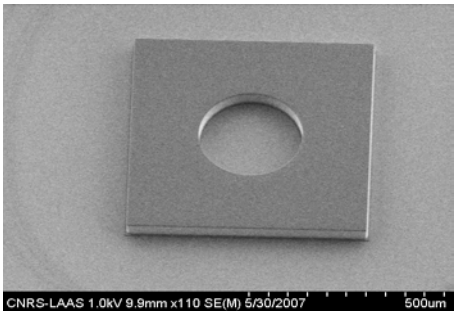

Figure 8: Picture BPR 100- micro-cavity.

The size of micro-cavity will also allow a good thermal homogeneity on the active area.

IV.4 DESCRIPTION OF TECHNOLOGICAL PROCESS

Our technological process is a new process based on that of [5]. It integrates modifications described here before. Initially, the LPCVD bi-layer membrane with low residual stress [7] is deposited on each side of a 400µm-Silicon substrate. Then, micro-hotplate is realized by optimized process of IV.1. The heater is then insulated by a PECVD deposit of SiO_2, followed by heater's contacts opening. After that, inter-digitized electrodes are realized by similar method than the heater (Pt/Ti). The next step is the realization of micro-cavity (height more than 10µm). We finish backside releasing of membrane by DRIE (Deep Reactive Ion Etching).
Final structure of our sensor is schematized on figure 9.

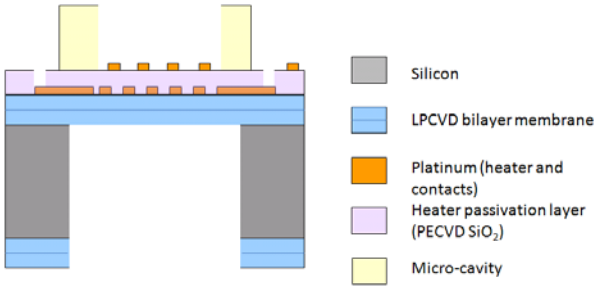

Figure 9: Structure of new gas sensor.

Then we can deposit different sensitive layers with a good control of size and position.

V CHARACTERIZATIONS

Electro-thermal characterizations of the active area are being realized. First carried out characterizations consisted with Infrared measurement of temperature versus power. With the new heater design, we can reach 550°C for less than 100mW (figure10). That is interesting for the current applications. Next characterizations (thermal homogeneity…) are in progress. We are working on titanium time drift observed for temperature higher than 500°C. We are also working on membrane deformation which can be caused either by resistance heating or by layers (with high residual stress such Pt and resin) on membrane. We are also carrying out simulations to evaluate this deformation.

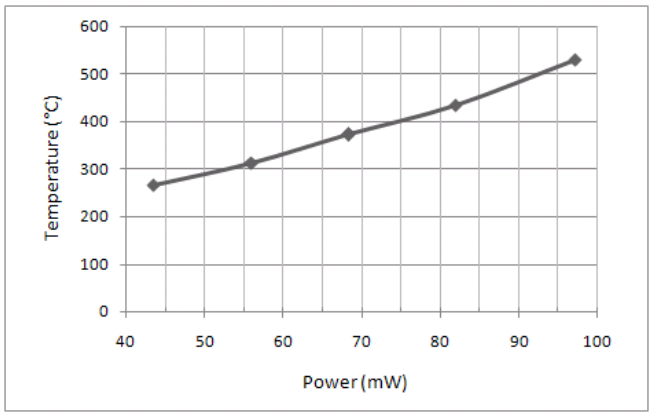

Figure 10: Temperature reached versus power.

CONCLUSION

We succeeded in stabilizing the process allowing making a micro-hotplate with Ti/Pt. Our first results showed that the characteristics are stable until 500°C. That corresponds to an improvement compared to the structure using the poly-silicon. The disadvantage of this type of metallization is its drift of the resistivity for temperature higher than 500°C. Hence, for operating temperatures higher than 500°C, it is preferable to use refractory materials like molybdenum for example.
In addition we proved the feasibility of a platform with interdigitated electrodes and circular micro-cavity allowing to a stable and reproducible deposit of sensitive layers for different modes of deposits such micro-injection or screen printing.

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