PERFORMANCES OF A NEW GENERATION OF METAL OXIDE GAS SENSOR BASED ON NANOSTRUCTURED-SnO 2 AND ON HIGH OPERATING TEMPERATURE MICROHOTPLATE

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Abstract

The sensor presented in this article consists of a nanostructured SnO_2 as high sensitive material and an efficient high temperature microhotplate. Tin oxide nanoparticles are in suspension in a solvent (colloidal solution) and then are deposited by contactless methods such as microinjection that insure a good control of thin films deposition. A new efficient microhotplate has been developed with high electrical and mechanical stabilities up to 600°C with a low power consumption (<70mW) and allows an efficient control of temperature, useful for detection of gases. In this work, our new generation of metal oxide gas sensor is exposed to different polluting gases like CO, C_3H_8 and NO_2 at different temperatures to determine the optimum operating temperatures which allow obtaining the highest sensitivity for each gas and then a good selectivity. We also demonstrated that these gas sensors present a better sensitivity and above all a better stability compare to commercial metal oxide gas sensors.

Keywords: Gas sensors, High-Temperature Microhotplate, Tin Oxide, Nanostructures

I- Introduction

Today, gas detection's importance, by using metal oxide materials, is connected to its low cost and its domain of applications which is as well wide as varied. Most of metal oxide gas detectors on the market use a microhotplate mainly based on polysilicon heater and SnO_2 or WO_3 as sensitive element. Studies led to those commercial sensors have shown their poor performances in term of stability, sensitivity and selectivity, essentially due to two main drawbacks: the sensor performances are not stable because of drift phenomena at the sensing layer level (an increase of the mean grain size [1] of polycrystalline SnO_2 obtained by standard methods) and at the polysilicon heater level (resistance drift) at high operating temperatures (450°C). Studies led demonstrated that SnO_2 sensitivity for gas detection should be significantly increased with high porosity level and grains smaller of the sensing layer [1, 2]. Finally, the selectivity of these sensors is poor at constant operating temperature lower than 450°C. Our objective is to develop a new generation of SnO_2 gas sensor with high sensitivity and stability.

II- Performances of the microhotplate

Our gas sensor as describe in [3] (and shown in Fig1) consists of two principle parts. The first part concerns the microhotplate which associates very good mechanical performances and stability at high operating temperature (up to 600°C) [4]. Complementary tests have been achieved to confirm electrical stability of this microhotplate. Particularly, a 6-month ageing test has been carried out. Results are shown in Fig2. It confirms electrical stability of the microhotplate. For a constant voltage up to 7V (which corresponds to around 62mW for a temperature of 500°C (see Fig.3)), it can be observed that the structure shows a very good stability. For higher and constant voltage of 8V (650°C), the microhotplate presents small irreversible increasing of power but seems stable at all.

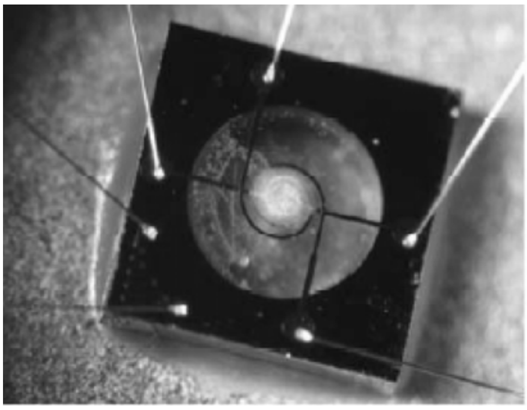

Figure 1: New gas sensor with microhotplate and drop of nanostructured SnO_2

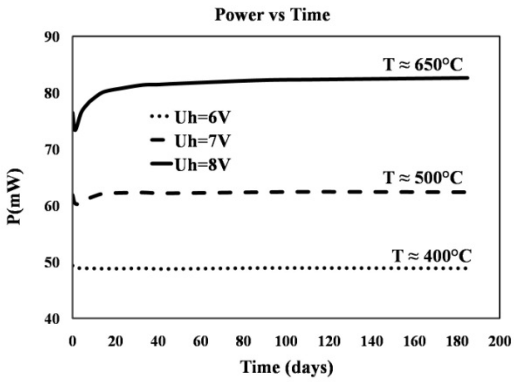

Figure 2: Ageing of heaters at 3 different voltage supplies

III- SnO_2 integration

The second part of the sensor is the SnO_2-nanostructured sensitive layer. It is a sensitive material which has been synthesized in form of colloidal solution obtained by organometallic route [2, 5]. The goal of this kind of synthesis is to prepare individual SnO_x/Sn nanoparticles with small size around 20nm as shown in Fig3. The solution is then deposited on the microhotplate by microinjection technique and then fully oxidized in-situ by a specific temperature profile in order to keep the size of 20nm. A porous nanosensitive layer is obtained without coalescence and cracking (see Fig1 and Fig4).

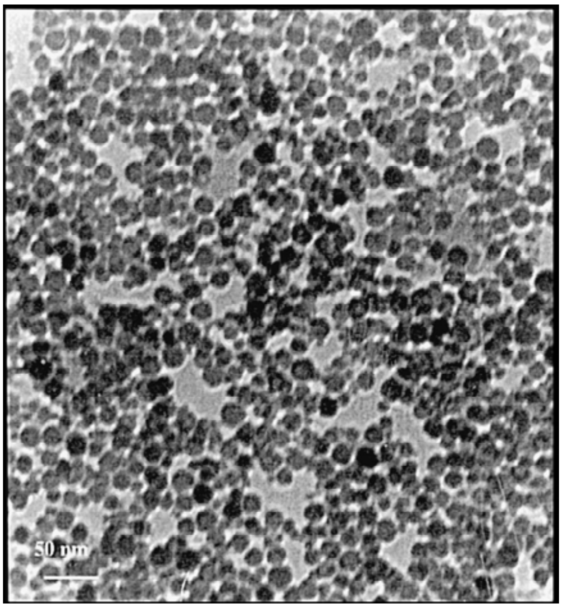

Figure 3: TEM image of SnOx/Sn nanoparticles obtained by organometallic route.

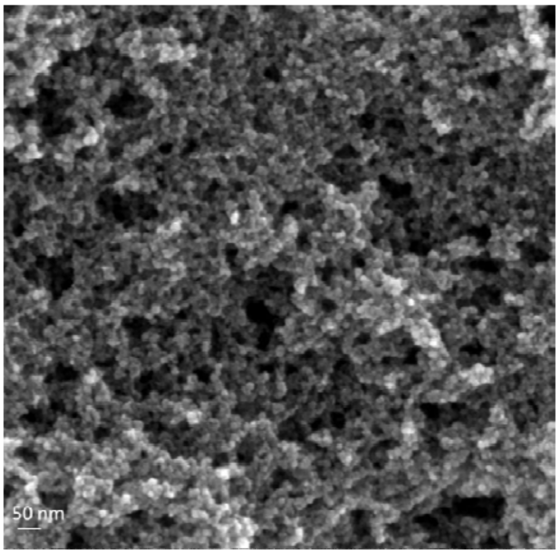

Figure 4: TEM image of SnOx/Sn nanoparticles obtained after specific oxidation

IV- Performances in gas detection

First tests were achieved to check stability of our sensors after depositing sensitive layer. It corresponds to the resistance responses of our sensors under 3 concentrations (50ppm, 200ppm and 500ppm) of CO and C_3H_8 at 500°C. First of all, these results shown in Fig5 reveal that the sensors present a very stable basic line response. Sensitivity to CO is approximatively twice higher than C_3H_8 one. We can also observe a saturation effect for CO concentrations higher than 200ppm. This last point depends mainly on the sensing layer porosity and thickness.

Corresponding relative sensitivity S to those gases are shown in table 1 with S defined by

$$S = \frac{(R_{air} - R_{gas})}{R_{air}} \qquad (1)$$

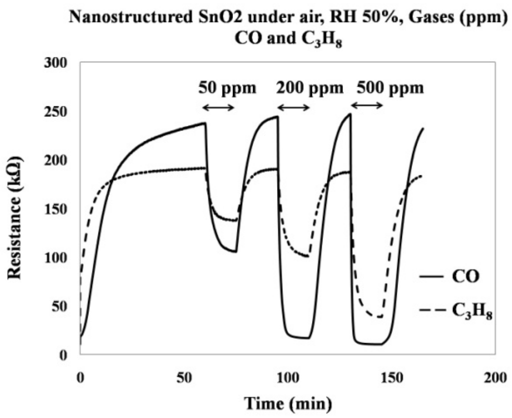

Figure 5: Transient Response to CO and C_3H_8

Table 1: Gas relative sensitivity of nanostructured SnO_2 to CO and C_3H_8

	50ppm	200ppm	500ppm
CO	55%	93%	96%
C_3H_8	28%	47%	79%

Fig6 presents an example of sensitivity responses to 200ppm of C_3H_8 of our gas sensor in dry atmosphere. This test was led for different operating temperatures from 250°C to 550°C. Results show a better relative sensitivity for the highest operating temperature (550°C). It is twice better than sensitivity at 450°C; that justifies our technology improvements.

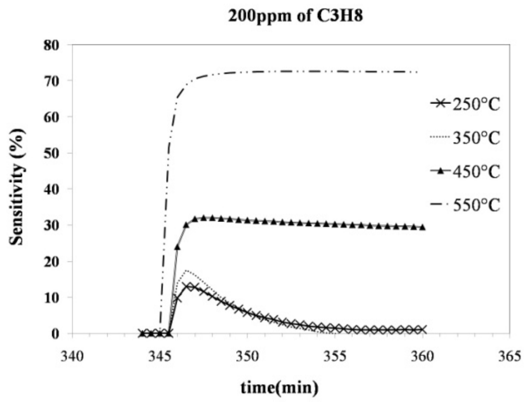

Figure 6: Example of sensor relative sensitivity under 200ppm of C_3H_8 in dry atmosphere at different operating temperatures

Another test has been led under an oxidative gas (NO_2) and dry air to compare responses of our nanostructured SnO_2 gas sensor with a specific commercial NO_2-gas sensor. Exposition under gases was achieved for different operating temperature (250°C, 350°C, 450°C and 550°C). Results presented in Fig7 and Fig8 show better performances in term of sensitivity and stability for our gas sensor than the commercial one. In accordance with literature, the better sensitivity is obtained for low operating temperature.

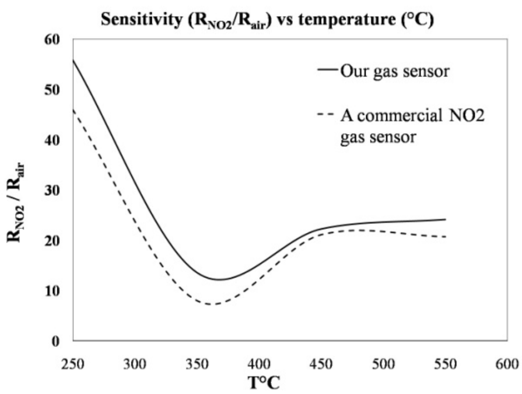

Figure 7: Comparison of gas sensitivities of nanostructured SnO_2 gas sensor and a commercial one's to 2ppm of NO_2

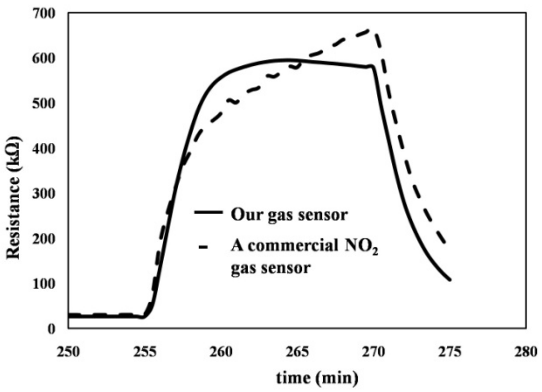

Figure 8: Stability of transient response of nanostructured SnO_2 gas sensor and commercial one's to 2ppm of NO_2

V- Conclusion

This article presents our new generation of metal oxide gas sensor using an efficient microhotplate based on Ti/Pt heater in term of mechanical deformation, temperature homogeneity, power consumption, and long term stability at high operating temperature. We have also integrated nanostructured tin oxide as sensitive material. Gas detection tests show better responses in term of sensitivity, of stability at high operating temperature (base-line and response of gas detection) compare to commercial gas sensors.

Moreover, concerning microhotplate, performance tests in pulsed heating mode are in progress. This operating mode is useful to improve sensors selectivity [6]. We are also working on integration of other nanostructured sensitive materials as ZnO or bilayers by microdrop deposition or inkjet for low cost array of different sensors.

VI- References

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