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# AN EFFICIENT METAL OXIDE GAS SENSOR USING NANOSTRUCTURED-$SNO_2$ FOR INDUSTRIAL APPLICATIONS

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**Abstract**: The sensor presented in this article consists of a nanostructured tin oxide 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 method such as microinjection on a new efficient microhotplate. The microhotplate has been developed with high electrical and mechanical stabilities up to 650°C with a low power of consumption (< 80mW) and allows an efficient control of temperature, useful for detection of gases. In this work, the gas sensor developed is exposed to different polluting gases like carbon monoxide, propane and nitrogen dioxide at different temperatures to determine the optimum operating temperatures which allow obtaining the highest sensitivity for each gas. Then it is demonstrated that these gas sensors present a better sensitivity and above all a better stability compared to commercial metal oxide gas sensors.

**Keywords:** $SnO_2$ gas sensor, High-Temperature Pt-Microhotplate, Nanostructure, Optimization

## 1. Introduction

Until now, gas sensors using metal oxides are subject to increased research. They are common in automotive applications and high consumer applications. Today, they represent an alternative to marketed detectors based on infrared, electrochemical or photo-ionization detectors systems [1, 2]. Those marketed detectors are very expensive, not easy portable. They also consume a lot of energy (on the order of Watt). Metal oxide gas sensors manufacturing combines standard microelectronic technologies and micro-machined silicon devices techniques. That allows reaching the needs of the market such as low cost of manufacturing thanks to miniaturization of

sensors. Moreover, the operating principle based of metal oxide gas sensor facilitates sensor portability. This principle is based on the change in the electrical conductivity of sensitive layer in presence of gas resulting from reactions that occurs at the sensitive material surface, from 200°C [3-5]. The associate electronic that consists in measurement of this electrical conductivity is simple.

Metal oxide gas sensors present a simple structure (Figure 1) [1-5] which could be decomposed into two parts. One part is metal oxide sensitive layer ($SnO_2$, $WO_3$, ZnO…) which reacts with gases. The second part is the microhotplate which is composed of electrodes to easure the conductivity of the metal oxide and a heating platform which supports and thermally activates the sensitive layer for detection. The principal element of platform is a heater which is electrically isolated from the electrodes thanks to an insulating layer.

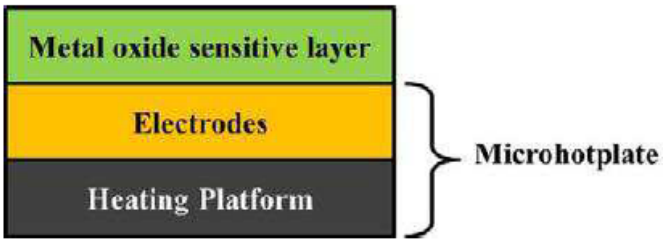


**Figure 1.** Bloc diagram of metal oxide gas sensor

In the market, two kinds of metal oxide gas sensors could be found. There are those based on solid substrate such alumina. As example, the SP series of sensors from FIS Inc. [6] can be cited. The structure is illustrated in Figure 2. It is composed of metal oxide material (generally, $SnO_2$ metal oxide) fo1med on gold electrodes which are printed on the alumina substrate. The heater is printed on the reverse of the substrate.

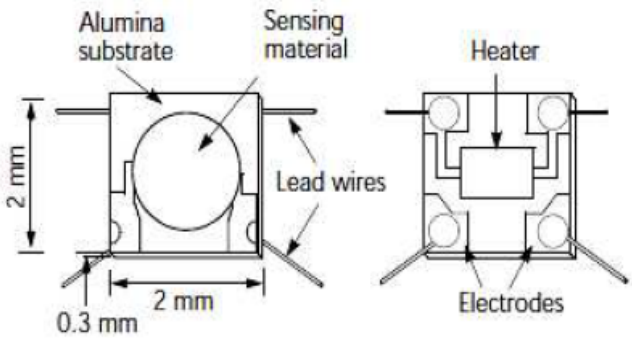


**Figure 2.** Structure of metal oxide gas sensor using a solid substrate [6]

Those sensors needed high power consumption for optimal operation (a typical operating temperature of 400°C for around 400mW). This high consumption can be improved by specific materials. Unfortunately, it is still important (over 200mW).

The second kind of commercial gas sensors use 1nembrane -type structure as microhotplate whose main goal is to reduce power consumption and minimize the thermal inertia. That appears more interesting. Metal oxide gas sensors from MICS Company E2V Sensors [7] can be cited, as example. The structure of such sensors (illustrated in Figure 3) consists in an

opening in the rear face of a silicon substrate so as to leave a thin diaphragm acting as mechanical support. $SnO_2$ is generally used as sensitive material and is made by a physical vapor deposition (PVD) method. Most of those devices have a heater made of polysilicon. They require an average power consumption of around 80mW for a temperature of around 400°C. Studies conducted on this kind of metal oxide sensors exhibit some drawbacks essentially linked to a drift of the resistance of the polysilicon heater observed at high operating temperatures over 450°C [8-10] and a poor thermo mechanical stability of sensors which can lead to a progressive loss of sensor performances upon time [11].

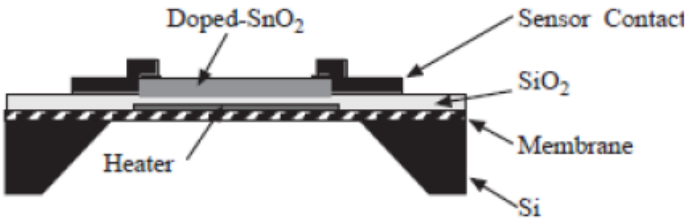


**Figure 3.** Membrane-type structure of commercial metal oxide gas sensor [7]

Concerning the sensitive material, the advantage of PVD methods is a precise control of deposit (thickness and size). However, those techniques which are very expensive, allow having compact deposit of sensitive layer. That induces small area for surface reactions and therefore that provides poor performance in terms of sensitivity [12]. Recently, research has been directed towards the synthesis of nanostructured materials with significant inter-granular porosity to greatly improve the effective area and hence the sensitivity [13-16].

This work proposes solutions to those problems in order to develop a more efficient sensor remaining miniature and inexpensive. In the first step, this article will present separately, the new microhotplate which is the membrane-type structure of commercial metal oxide gas sensor, optimized and the sensitive material which is a highly sensitive nanosized $SnO_2$. Then the combination of the two components will be described. Finally, results of conducted tests and conclusion will be provided.

## 2. Material and methods

### 2.1 An optimized microhotplate

The membrane-type structure of commercial metal oxide gas sensor [7] platform has been used as basis for this work. The device is commonly composed of a silicon substrate with SiNx membrane and integrates polysilicon plate as heater. Manufacturing of such gas sensors follows standard microelectronic technology and silicon micromachining techniques. Sensors present a very good homogeneity with a temperature gradient of 0.05°C/µm on the area where sensitive material will be deposited (active area). However, as stated above, these devices have reliability problems over time, when operating at high temperature s (particularly, over 450°C). They showed an irreversible degradation of the polysilicon layer and that degrades the performances of the sensor and limits its life.

Design and material 1nodifications have been brought in order to reach excellent stability (thermal and mechanical stabilities), to keep a low power for high temperature (< 1OOmW for temperature over 450°C) and to have low response time (< 30ms). The goal of those optimizations has also been having good temperature homogeneity on active area. Temperature homogeneity is an important parameter for metal oxide gas sensors. lndeed, bad homogeneity (or high temperature gradient) on active area can lead to instability or uncontrolled drift over time.

The optimized platform is composed of a silicon substrate on which it has been deposited successively:

Design and material modifications have been brought in order to reach excellent stability (thermal and mechanical stabilities), to keep a low power for high temperature (< 100mW for temperature over 450°C) and to have low response time (< 30ms). The goal of those optimizations has also been having good temperature homogeneity on active area. Temperature homogeneity is an important parameter for metal oxide gas sensors. Indeed, bad homogeneity (or high temperature gradient) on active area can lead to instability or uncontrolled drift over time.

The optimized platform manufactured, consisted of a silicon substrate on which it has been deposited successively:

- A thinner $SiO_2$/SiNx membrane for low thermal conductivity and low stress. The method of manufacturing used in [17] provides a bilayer membrane with minimal residual stress (better than SiNx alone).
- A Ti/Ptheater to activate sensitive metal oxide layer with a homogeneous temperature. The polysilicon has been replaced by platinum (Pt) one to solve drifts problems. Platinum has better thermal properties and more stable over time. Titanium (Ti) has been used as adhesion for Pt on silicon substrate.

The design of the heater was obtained after study of several geometries simulated by finite element method (FEM method). Following this study, it was shown that the geometry of the rounded spiral (Figure 4) gave a good compromise between power of consumption and thermal homogeneity unlike other geometries (meander shape, circular shape and square spiral shape) previously used [10]. The rounded shape of the spiral allowed having a better temperature distribution on the active area and reducing hot spots which appeared, particularly, in the corners of square spiral shape, for example [10].

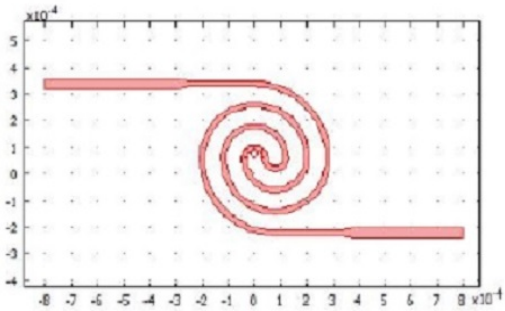

**Figure 4.** Simulated design of heater using COMSOL multiphysics software

- A thin film of PECVD-$SiO_2$ insulated layer to separate the heater from measurement electrodes (electrical isolation)
- Interdigitated Ti/Pt electrodes for good electrical contact with the sensitive layer and for measuring their high resistance.

The last step of the process was the backside releasing of the membrane by DRIE (Deep Reactive Ion Etching). A bad membrane releasing could decrease sensor's reliability by allowing heat losses [10, 17]. Packaged microhotplate is illustrated in Figure 5.

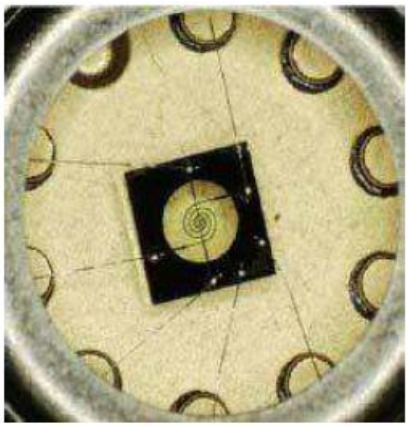

**Figure. 5.** Optimized microhotplate

### 2.2 $SnO_2$ Sensitive material

$SnO_2$ sensitive material has been used in our work because of its high sensitivity to gases. Although very selective and highly dependent on the ambient humidity, sensors based on $SnO_2$ are recognized as having a high sensitivity to reducing gases (CO, hydrocarbon, hydrogen …) and a good stability during operation reducing atmosphere. They represent the best compromise to detect both reducing and oxidizing [18].

### 2.3 Nanoparticles $SnO_2$ sensitive elements and their integration on the optimized microhotplate

$SnO_2$ -nanostructured has been used as sensitive layer of the sensor. lt is a sensitive material which has been synthesized in the form of colloidal soluti on obtained by organometallic route [19]. The goal of this kind of synthesis is to prepare individual SnOx/Sn nanoparticles with small size around 20nm. The solution is then deposited on the microhotplate by microinjection technique. Figure 6 illustrates the process of integration of nanoparticles Sn02 on the optimized microhotplate (see Figure 6a). The apparatus used is composed of a microscope, a capillary tube (filled with the colloïdal solution) surrounded by a piezoelectric actuator and a control unit controlled by PC [20]. The solution is ejected by applying a pulse to the actuator that contracts. A pressure wave is created in the liquid through the tube using ADK401 pipette (see Figure 6b). Solution is accelerated and a part is ejected from the tube to form a micro droplet of few picoliters.

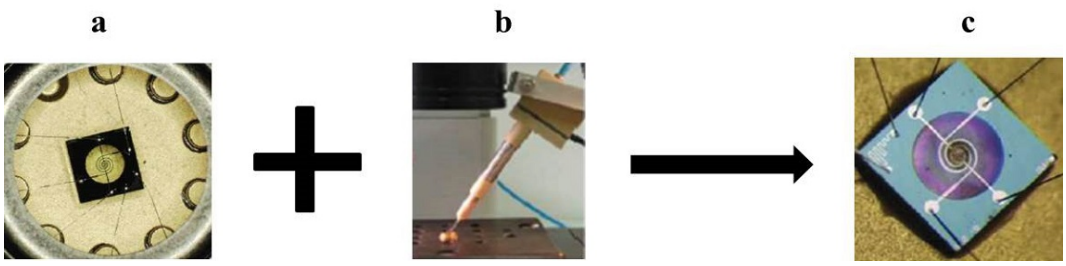


**Figure 6.** Process of integration of nanoparticles SnO2 on the optimized microhotplate

Then, the drop has been slowly and fully oxidized in-situ by a specific temperature profile (empirically defined and applied to our sensitive layers) in order to keep the size of 20nm. A porous nanosensitive layer (Figure 7) is obtained without coalescence and cracking.

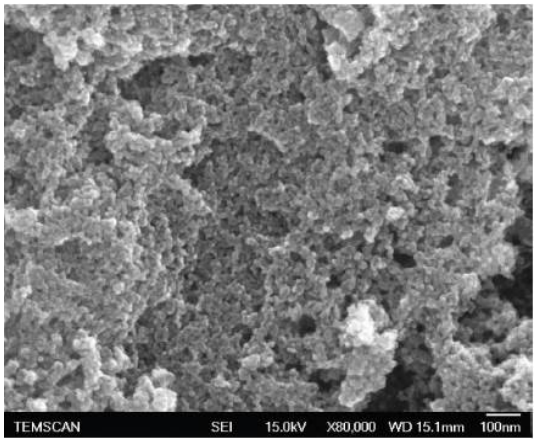


**Figure. 7.** TEM image of $SnO_2$ nanoparticles obtained after oxidation

## 3. Results and discussion

### 3.1 Performances of our optimized microhotplate

Tests conducted on the optimized microhotplates showed that the devices could reach 650°C for consumption lower than 100mW. This result was excellent in comparison with to the classical commercial heater (450°C for less than 100mW).

From ambient temperature, the device could reach 550°C in about 25ms. The cooling time was of the same order.

Thermal distribution simulations carried out on 200µm diameter of active area and centered on heater have been conducted. An average temperature gradient of 0,25°C/µm was obtained with maximal temperature of 550°C (Figure 8). This interesting result for our applications at high temperature was confirmed experimentally.

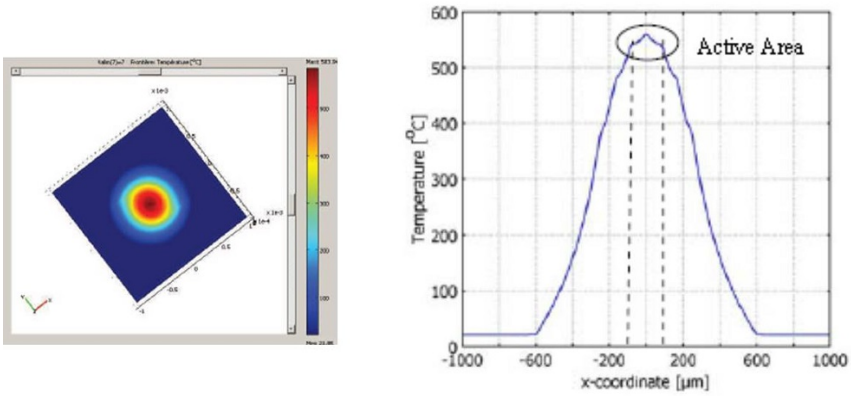


**Figure 8.** Electrothermal simulation of optimized microhotplate using COMSOL Multiphysics software

Tests have been conducted to confirm electrical stability of this microhotplate. Particularly, a 13-month ageing test has been carried out. Results are shown in Figure 9. It appears that the heater is remarkably stable at very high temperature up to 550°C.

For a constant voltage up to 7.5V (which corresponds to around 65mW for a temperature of 550°C, it can be observed that the structure showed a very good stability. For higher and constant voltage of 8V (650°C), the microhotplate presented an increasing of power before stabilization.

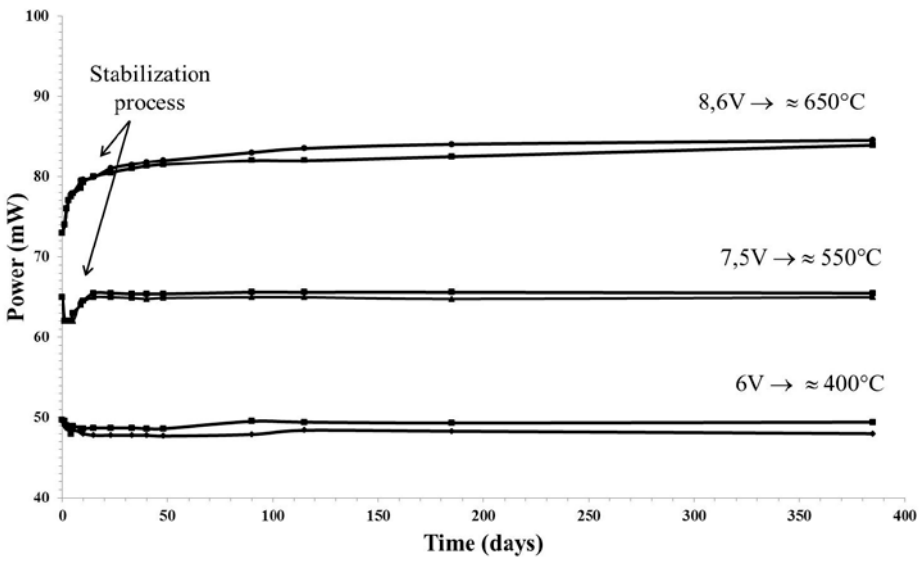


**Fig. 9.** Ageing test of optimized microhotplate using 3 different continuous voltage supplies (6V, 7,5V and 8,6V): parameter T is the operating temperature

Concerning electromechanical performances, two geometries based on square and rounded membranes have been developed and evaluated after membrane releasing. Tests led on those two types of membrane gave following results:

- First, the interest of the circular platform can be observed in Figure 10(a). Indeed, the cross deformations of square membrane were eliminated with the circular shape.

- Then for the square membrane form, maximal deformation of the structure was about 8µm at rest with nonlinear variations up to 2µm when functioning (see Figure 11).
- The rounded structure (Figure 10(b)) allows reducing the deflection around 0,5µm only with low variations in functioning (some hundreds of nm) as shown in Figure 11.

In view of the results, the rounded geometry appeared the most reliable. The optimized microhotplate will participate to the reliability of the device.

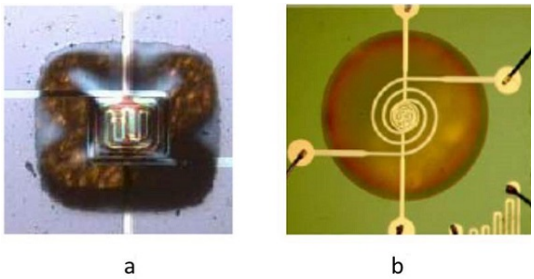


**Figure 10.** Microhotplates for metal oxide gas sensors: (a) square membrane structure; and (b) optimized structure (rounded shape)

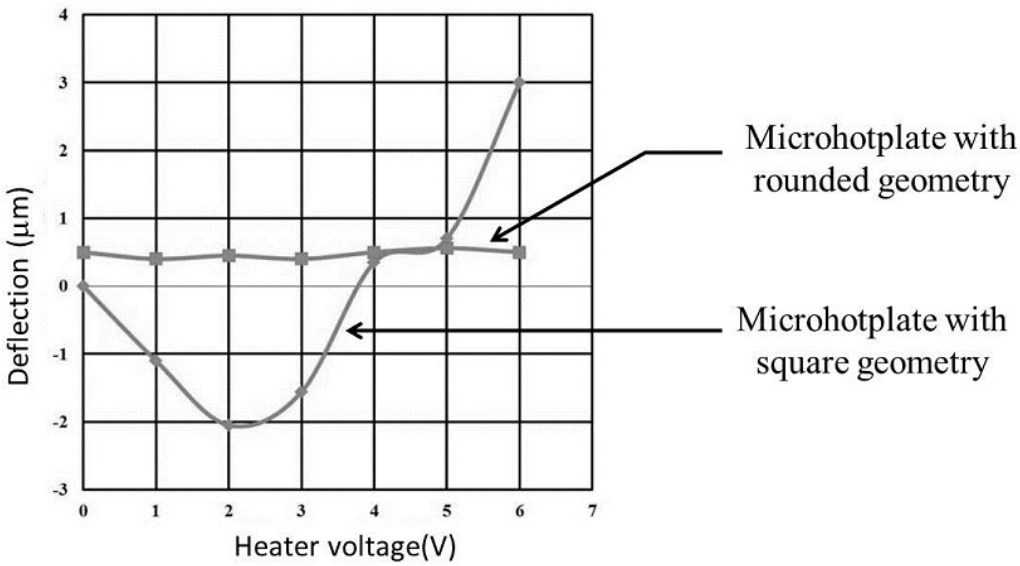


**Figure 11.** Measurements of membrane deformations from optical profiler: membrane deformations for different voltages applied to the heater

### 3.3 Performances in gas detection

Tests were conducted to check stability of the optimized sensors after depositing sensitive layer. Before any tests, an initial stabilization period under operating conditions (air, 50% HR) was necessary for the sensor signal to reach a stable baseline. Then sensor's resistance was measured when it is exposed under three concentrations (50 ppm, 200 ppm and 500 ppm) of CO and $C_3H_8$ at 500°C.

Results shown in Figure 12 revealed that sensitivity to CO was approximately twice higher than $C_3H_8$ one.

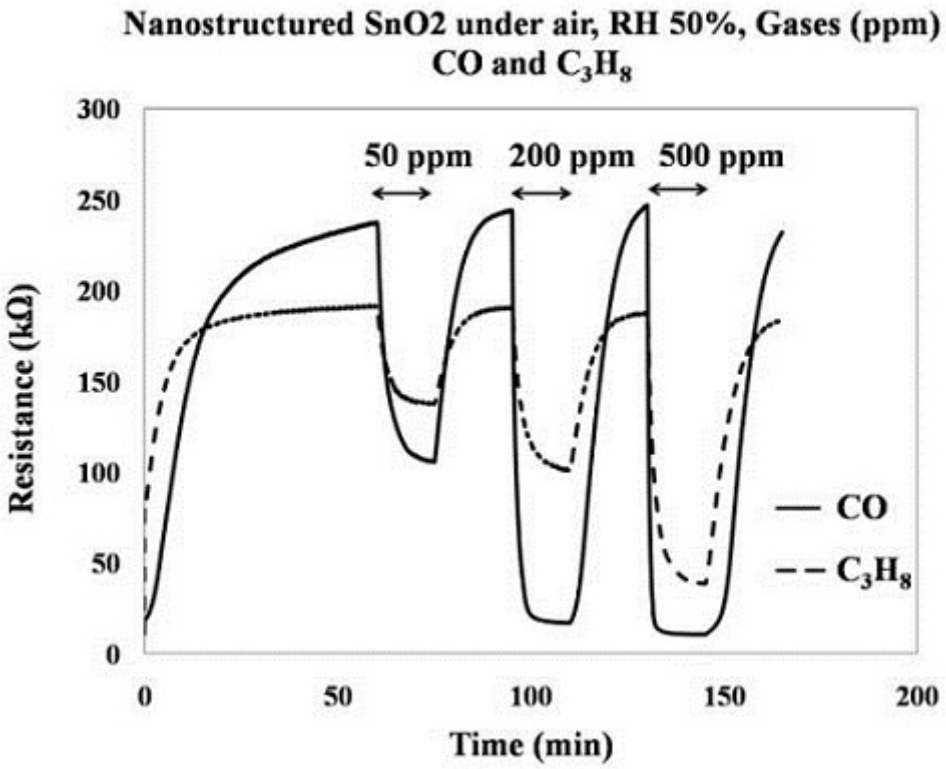


**Figure 12.** Transient Response to CO and $C_3H_8$ at 500°C

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

$$S=\frac{R_{air}-R_{gas}}{R_{air}}$$

$R_{air}$: resistance of sensor under the air
$R_{gas}$: resistance of sensor under gas

**Table 1**: Gases relative sensitivities of nanostructured $SnO_2$ to CO and $C_3H_8$ for three concentrations (50ppm, 200ppm and 500ppm)

| | **50 ppm** | **200 ppm** | **500 ppm** |
|---|---|---|---|
| **CO** | 55% | 93% | 96% |
| **$C_3H_8$** | 28% | 47% | 79% |

These results showed that a specific gas had an optimum temperature at which it is detected as confirmed in literature [21]. More tests had been led to find the optimum temperature for each gas. Those tests consisted in applying different supplies to the heater in order to reach various temperatures from 300°C to 650°C. A concentration of 200ppm of gases was used. Results helped plot the relative sensitivity S according to the working temperature, as presented in Figure 13. This test provides the highest CO and C3H 8 responses (on the order of 90% at 500°C for CO and 70% at 550°C for C3H 8) with a significant fall for lower and higher temperatures. These results had never been shown before. Indeed, the foregoing sensors do not function beyond 450°C.

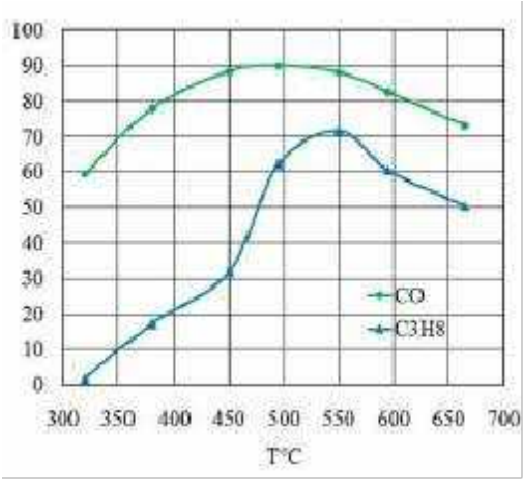


**Figure 13.** Relative sensitivity to CO and $C_3H_8$ at 500°C versus operating temperature

Another test bas been led under an oxidative gas ($NO_2$) and dry air to compare responses of our nanostructured-$SnO_2$ gas sensor with some MICS $SnO_2$ gas sensors (those commercial sensors were used as reference during this project). Exposure under 2ppm of gas was led for different operating temperatures (250°C, 350°C, 450°C and 550°C). Results presented in Figure 14 and Figure 15 showed performances sensibly better than the commercial one in term of sensitivity and stability for our gas sensor. Moreover, in accordance with literature, the better sensitivity of $NO_2$ gas sensor is obtained at low operating temperatures [22, 23]. The transient response to $NO_2$ was more stable with the optimize gas sensor as shown in Figure 15.

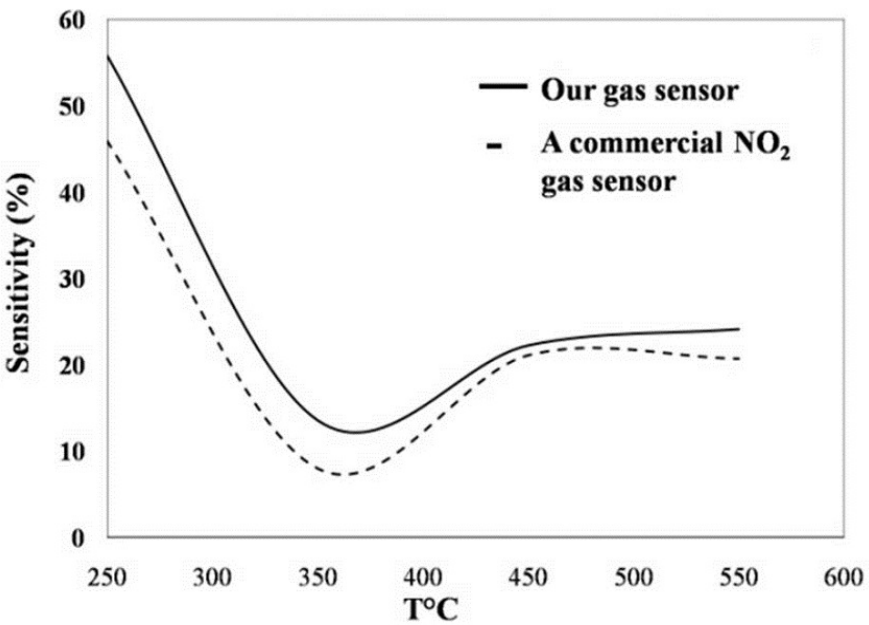


**Figure 14.** Comparison of sensitivities of nanostructured-$SnO_2$ gas sensor and a commercial one's to 2ppm of $NO_2$ at different operating temperatures

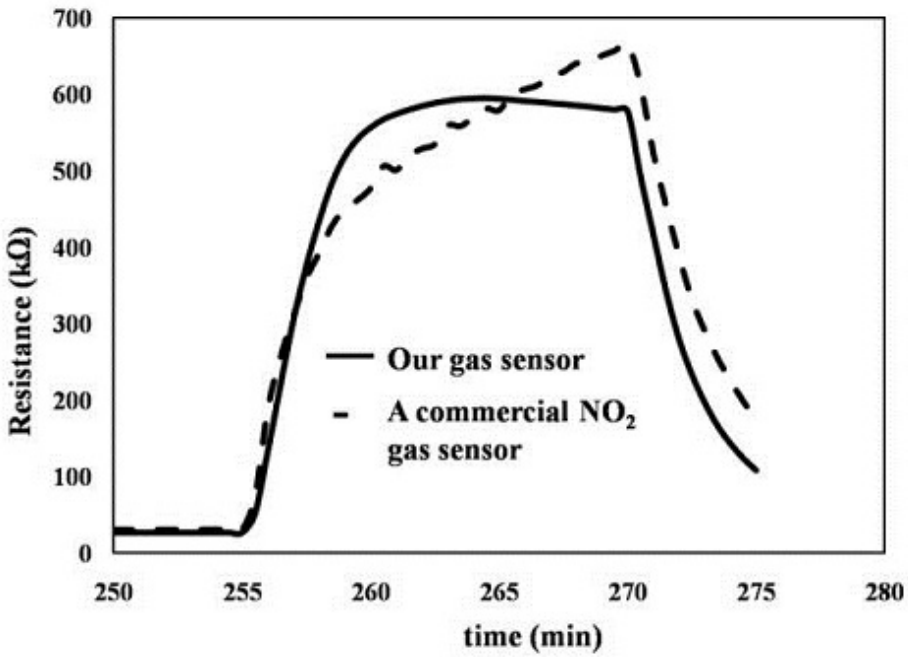


**Fig. 15. S**tability of transient response of nanostructured-$SnO_2$ gas sensor and commercial one's to 2ppm of $NO_2$ at 250°C

## 4. Conclusion

An industrializable metal oxide gas sensor with thermal, electrical and mechanical performances vastly superior to those of common commercial sensors has been developed. The optimized sensor allows reaching a stable temperature of 550°C for less than 70mW. The platinum microhotplate shows an excellent robustness and quick time response around 25ms. The temperature gradient of 0,25°C/µm obtained is suitable for our applications.
Nanostructured-$SnO_2$ has been integrated as high sensitive material. Gas detection tests show better responses in term of sensitivity and stability in comparison with to commercial gas sensors.

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