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A New Generation of SnO₂ gas sensor for agro-industrial applications

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Abstract

A new generation of gas sensor which consists of a silicon platform with an integrated polysilicon resistor as heater and a nanoparticulate SnO₂ sensitive layer has been developed and characterized. Methods of deposition and oxidation of the sensitive layer on the substrate were first optimized. Then, a demonstrator was implemented to evaluate the sensor's electrical behaviour under controlled atmospheric conditions. An electrical circuit has been developed to model the electrical behaviour of the sensor. Comparisons between PSPICE simulations and experimental data shows close agreement.

Introduction

Many industrial applications are based on gas detection like individual safety or comfort purpose : for example, H₂S detection in chemical industries, household combustion alarm with CO and H₂ monitoring, cabin quality control in cars (CO, NO_x), emission control of small ozone generators (O₃), industrial health monitoring (NO_x), control of ethylene emission by fruits and/or vegetables in cold storage among others. In order to satisfy to this increasing demand, the actual market offers mainly three basic types of gas sensors for such toxic gas detection :

- Optical infrared sensors (IRGS)
- Electrochemical cells (ECGS)
- Solid state or semiconductors gas sensors (SGS).

In Europe, Japanese Companies sell more than 85% of all SGS used. SGSs offer many advantages : they are from far the least costly class of gas sensors and their properties (sensitivity, long operational life, low power consumption) make them very well suited for a multitude of applications.

An extended international work has been yet focused on new compositions for oxide active layer (ZnO, WO₃, TiO₂, mixed oxides, etc...), but little on the microstructure of the sensitive material itself, since commercial SGSs are still based on standard metal oxide powders. Therefore, SGSs are mainly dealing with tin oxide as sensitive material.

Ethylene has been identified as a phyto-hormone in the process of fruits maturation. Therefore, presence of ethylene closeness of the fruit means that this fruit has already started its maturation phase. So, it can't be kept in stock. Actually, fruit storage rooms are not equipped with gas sensor systems which could allow the control of ethylene concentration in situ and in real time. Only heavy spectroscopy or optical chromatography methods exist to analyse each gas present in the stocking room.

In this context, in collaboration with regional chemists (LCC-CNRS), biologists (INPT-INRA), microtechnologists (LAAS-CNRS) and MICS (Microchemical Systems) firm, a new generation of SGS based on nanoparticulate sensitive layer integrated on a silicon platform has been developed.

After a brief description of different parts of these new gas sensors, test methodologies will be presented.

Sensor description

The detection principle is based on the chemical reaction in air of the heated tin oxide surface with reducing or oxidising gas molecules, giving rise to the modulation of the electrical resistance of the sensitive layer. The known drawback of this device is linked to the stability of the baseline resistance over time and generally the cross sensitivity (or selectivity) to many gases and vapours (humidity, H₂, Ethanol,...). This is due to the technology, which mainly relies on basic ceramic processes i.e. sintered tin oxide powders with a bead shape or deposited onto alumina substrates (fig. 1a, 1b).

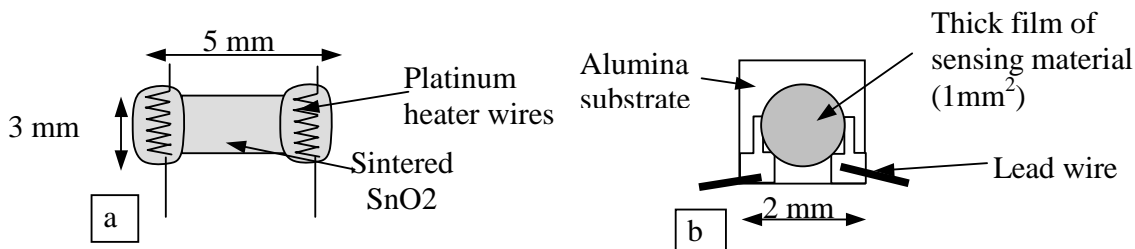


Fig. 1: Commercial semiconductor gas sensor: a) sintered ceramic of gas sensitive material. b) thick sensitive film on alumina substrate

Moreover, it has been also demonstrated that more dispersed matter like nano-particles offers a high surface to volume ratio, correlated with better sensing properties than conventional matter. Microelectronics technology based on **silicon processing and specially on micro-machining** is known to offer **high miniaturisation and integration** possibilities.

This new technology will offer low cost products, high miniaturisation level (operational dice < 1 mm²), very low power consumption, and better sensing properties, stability and selectivity due to nano-sized oxide particles. Our SGS process is based on three main steps :

i) Fabrication of silicon chips with all integrated structures (heater, metal connections, membrane). A first design has been realised and operational dice have been assembled. This structure can be extended to the production of a multi-sensor platform (two or more sensitive areas per single chip).

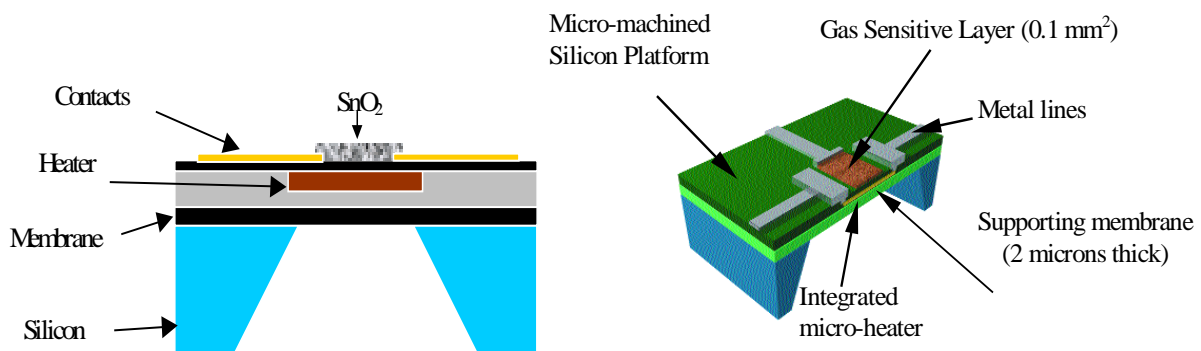


Figure 2 : Cross section of silicon chip

ii) Deposition of the colloidal solution on the silicon chip by dropping. This is the final step of the gas sensor preparation so that we make sure to keep the sensitive layer chemically pure.

Thermal activation of homoleptic tin amido complexes in organic solvents containing controlled traces of water yields spherical nanoparticulate composites of 20 nm diameter, constituted of a tin β core surrounded

by a protecting tin oxide layer. These Sn/SnO_x nanocomposites are thermally oxidised in air to yield crystalline SnO₂ nanoparticles without modification of size or size distribution.

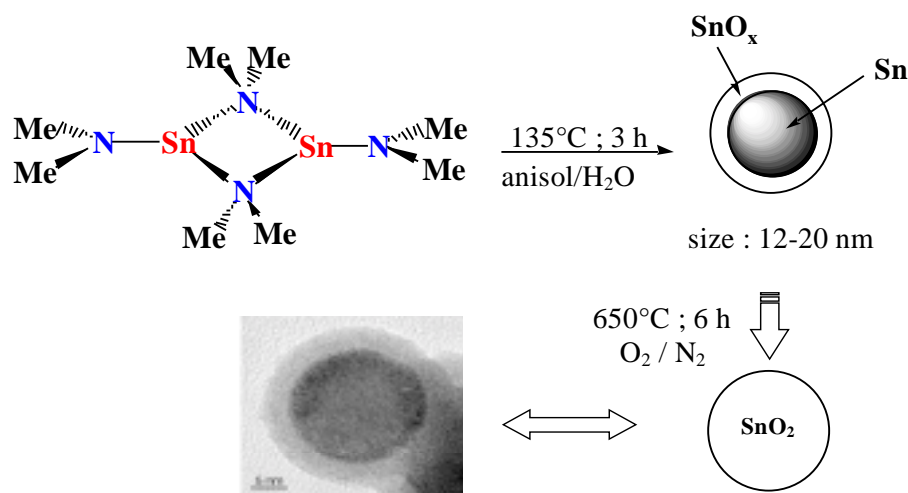


Figure 3 : Syntheses of tin nanoparticles

Two-drop deposition techniques are currently under investigation and have led to realise several hundreds of operational sensors. One of them is described on figure 4.

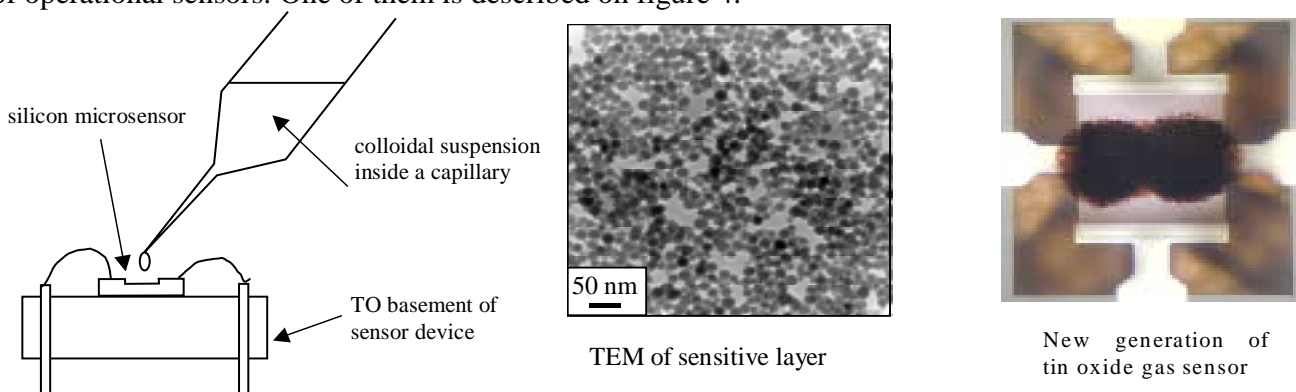


Figure 4 : Deposition system, TEM of sensitive layer and photography of the sensor.

iii) Packaging the sensor with a new generation of active filters made of meso-porous materials in order to improve the selectivity.

Characterization

Before test sequences, the sensors have to be subjected to at least one heating cycle from 25°C to 450°C. Their optimal work temperature has been estimated around 400°C. A temperature of 450°C must not be exceeded to avoid problem of electromigration from metal through polysilicon on contact pads.

Electrical Behaviour

A specific mock-up has been realised to allow DC and AC measurements on the sensitive layer with the heater resistor powered from 0 to 2.5V.

Figure 5 shows an example of different sensors DC responses which represents the resistance of the sensitive layer versus temperature. It clearly appears that the new sensor (curve with diamonds) presents a resistivity four times smaller than that of the traditional sputtered tin oxide sensor (curve with full-squares). Moreover, a local maximum appears for temperature near 320°C. This phenomena is partially attributed to humidity rate ^[6]. Therefore, these kind of electrical tests permit to predict that the new sensor has a better sensitivity than the others.

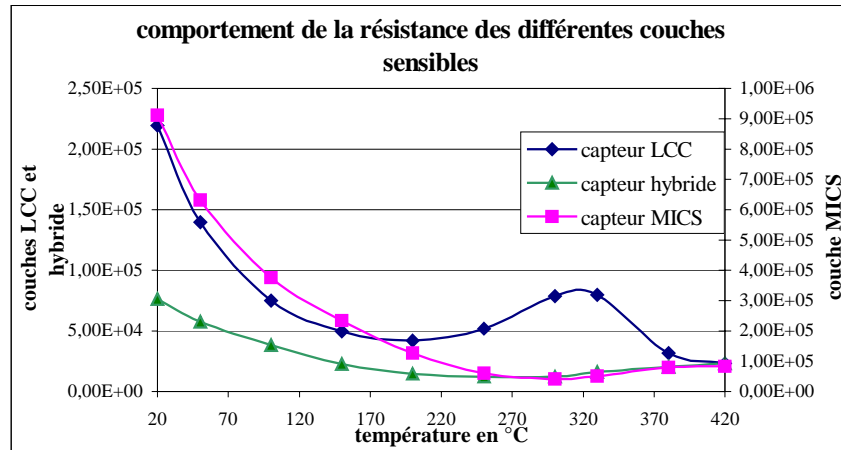


Figure 5 : Resistance of different sensitive layers versus temperature

AC measurements constitute the second part of the sensor's electrical behaviour study. A 7600Quadteck impedance meter were used to achieve measurements versus frequency from 10 to 2 MHz. Real and imaginary parts have been extracted and shown in fig. 6. It can be made the comparison between frequency behaviour of three different kinds of sensitive layer. The curve with diamonds represents the nanoparticular SnO₂ while the one with squares represents the traditional sputtered SnO₂. The third curve with triangles points out a hybrid sensitive layer behaviour elaborated from both aforesaid processes.

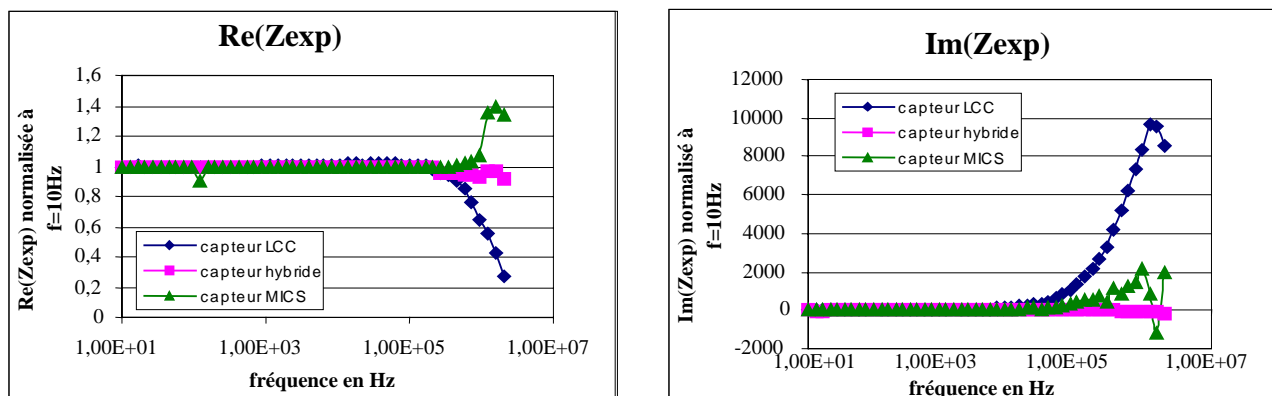


Figure 6 : Impedance measurements : a) Real part vs frequency ; b) Imaginary part vs frequency

In this range of frequency, according to PSPICE simulations, the three of the sensors can be modelled by the same equivalent circuit shown in figure 7. In fact, different values of each parameter permit to fit with experimental data of each sensors. Same measurements with different operating temperature reveal that all of the circuit parameters present the same temperature dependency.

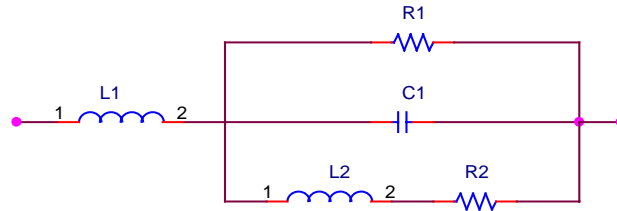


Figure 7 : Equivalent circuit of the encapsulated SnO₂ gas sensor.

Behaviour under ethylene

The detection principle is well known, based on the chemical reaction in air of the heated tin oxide surface with reducing gas molecules giving rise to the modulation of the electrical resistance of the sensitive layer.

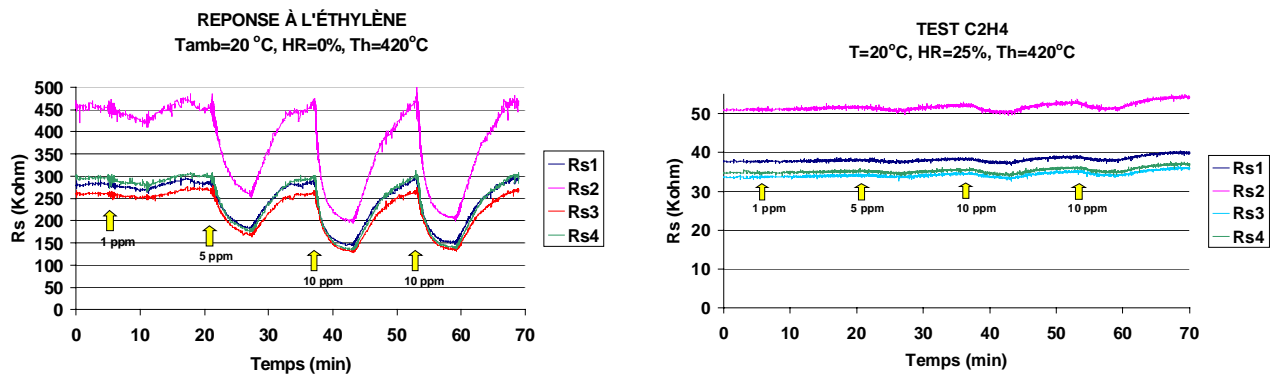


Figure 8 : Sensitive layer resistance variation with different injections of ethylene ; a) in dry air – b) with 25% HR

Figure 8 shows the nanoparticular sensitive layer resistance variation with different ethylene concentration. All these measurements have been made with constant operating temperatures.

In dry air, it can be seen first that these sensors are reversible and reproducible. In these conditions (0%RH, T=420°C) the detection limit has been evaluated around 0.6 ppm and the sensitivity defined by the ratio $R_s(10\text{ppm})/R_s(0)$ reaches 53%. In humid air with just 25% RH, this sensitivity decreases to only 5%. On the other hand, the sensitivity (at 10 ppm and 25%RH) can be increased again up to 30% if the operating temperature is pulsed as it is shown in figure 9. In this case, the sensitivity is defined by the ratio $\Delta R_s(10\text{ppm})/\Delta R_s(0)$ at the hot level.

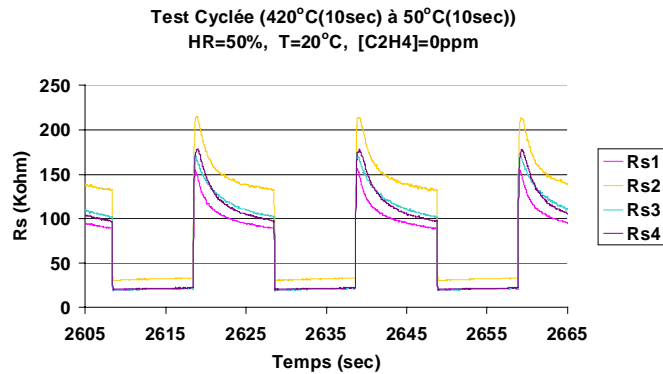


Figure 9 : Resistance of sensitive layer versus time with pulsed operating temperature

Conclusion

This paper allows the comparison of several characteristics between sensors based on standard SnO₂ sensitive layer with those elaborated with nanometer-scaled sensitive layers which use metal oxide nanoparticles.

An electrical study of three different sensitive layers reveals that they can be modelled by the same equivalent circuit.

Experimental results under ethylene indicate that the colloidal SnO₂ presents better features than those of the traditional SnO₂ : first, the resistivity of the material is at least 4 times smaller. Then, the sensitivity is also better as it is possible to detect C₂H₄ concentrations lower than 1 ppm in dry air. Even if humidity degrades sufficiently the sensitivity, a dynamic mode of temperature operation minimizes this dependency. The sensitivity of this new generation of gas sensor is already (without any doping process) between 3 and 5 times better than actual commercial sensors.

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