Accurate measurement of CO concentration in gas mixture with a single SNO2 semi-conducting gas sensor

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ACCURATE MEASUREMENT OF CO CONCENTRATION IN GAS MIXTURE WITH A SINGLE SNO_2 SEMI-CONDUCTING GAS SENSOR

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Abstract: This work demonstrates the feasibility to measure accurately low level of CO concentration diluted with synthetic air and two other gases (C_3H_8 and NO_2) with only one SnO_2 micromachined gas sensor. By consideration of the shape and time constants of the normalized response curves correlated with chemical reactions, it is possible firstly to discriminate different gas mixtures and secondly to evaluate one of the present gas at a ppm level by using two successive Linear Discriminate Analysis (LDA) based on specific variables.

Keywords: SnO_2 gas sensors ; CO sensitivity; Dynamic temperature modulation ; Linear Discriminate Analysis

1. INTRODUCTION

Lots of works are concentrated on the design of metal-oxide gas sensors with for objective to reduce dimensions, consumption [1-2] and response time. Currently, with the combination of nanotechnology and microelectronic processes, it can be possible to reduce both the power consumption and cost. Previous studies have demonstrated the interest to use semi-conducting gas sensor in temperature modulation [3-4] improving these performances in term of selectivity and sensitivity for gasses discrimination [5-6]. In the literature, different type of temperature profiles have been used in order to find significant discrimination variables issues to sensitive layer resistance variations. These features allow extracting useful information of the sensing processes to be applied in gas identification and quantification via mathematical techniques of classification and analysis [7].

This article deals with a Pt-doped nanoparticular SnO_2 gas sensor associated to an optimised temperature profile applied on heating resistor in the goal to correlate the shape of the sensor transient responses to the surrounding atmosphere and more precisely to the concentration of a target gas (i.e. CO in this case). It is shown the significant improvement of selectivity and sensitivity of this kind of gas sensor due to this innovative method of measurement.

2. SENSOR DESCRIPTION

In the frame of the "Nanosensoflex" European project (G5RD-GROWTH, 2002-2005), a new type of semiconducting gas sensors has been developed, formed by a microhotplate platform and a nanoparticular SnO_2 sensing layer with or without doping agent [8]. A SiO_xN_y membrane of 2 μm of thickness supports a n-type polysilicon heater of 2.58×10^{-3} mm^2. Shape and sizes have been optimised to achieve good thermo-mechanical reliability and good homogeneity of temperature on the active area. The heater can reach temperatures of about 500^{o}C with power consumption lower than 100mW. Moreover, this technology allows very fast temperature variations (less than 30ms for temperature varying from ambient to 500°C) and then the possibility to observe dynamically the effect of gas adsorption and desorption phenomena. The metal-oxide, elaborated by LCC-CNRS [9], is a crystalline SnO_2 nanomaterial synthesized by the decomposition and oxidation of a tin based organometallic precursor ($[Sn(Nme_2)_2]_2$), the mean grain size obtained is 15 nm of diameter. This sensing layer has been doped with 4% of platinum to enhance CO detection. This material is then deposited using a microinjector technique over the two electrodes placed in the homogeneous temperature region of the heater. This heater permits the full oxidation into SnO_2 and PtO nanocristals (which mostly remain at the surface of tin) with a controlled temperature cycle from ambient to 500°C.

3. EXPERIMENTS

The experimental set-up consists of a gas delivery system, an exposure glass vessel and an electronic circuit for resistance determination through voltage measurements. The sensing layer resistance of gas sensor is measured at 200 Hz with a 16 bit-resolution acquisition card. The aim of our discrimination system is to obtain the recognition of CO-concentration (from 1 to 200 ppm) in a mixture of 1.8ppm and/or 150 ppm of NO_2 and C_3H_8 respectively. The relative humidity has been fixed at 50% with a constant flow rate of 500cc/min.

According to previous works [10], a specific temperature profile have been designed and applied on the sensor heater (Fig.1). This profile, repeated continuously (cycled), consists of three parts: The first part is defined with a high temperature step, called "Ton", near 500°C during 10 seconds. During this step, most of gases adsorbed on the sensor surface while the sensor was kept at ambient temperature are removed, leading to a stable sensor response in the following steps.

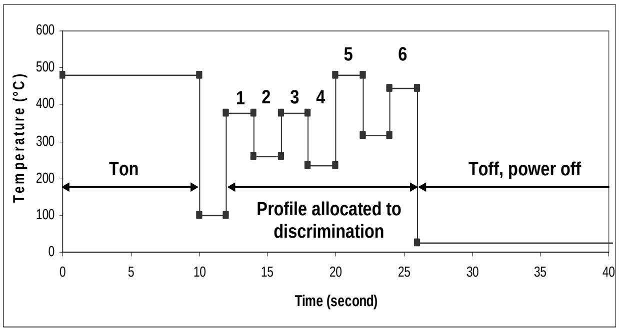

Figure 1. Temperature profile dedicated to CO measurement.

The second part is defined by a specific test profile of temperature dedicated to find out significant discrimination variables issues to transient responses of the sensitive layer on temperature variation. In order to reduce resistance time drift of the sensitive layer, the temperature step duration has been fixed with a compromise of 2 seconds to observe correctly the transient behaviour of sensing layer.

The last part called "Toff" is fixed at ambient temperature (sensor switched off). This time permits firstly a minimisation of sensor consumption and secondly the data treatment to be done before the next cycle.

In order to get more accurate insight on the transient responses of the sensitive layer on each temperature variation, each resistance value R_i is normalized according to the following equation:

$$R_n = (R_i - R_f)/R_f \quad (1)$$

Where R_n is the normalized value for the resistance R_i measured at time t and R_f is the last value measured on each step of temperature.

When complete thermal conditioning (26s per cycle) is repeated continually on the sensing layer, the reproducibility error doesn't exceed 1%/day.

The discrimination approach is dividing in two steps and executed by Linear Discriminate Analysis (LDA) methods. In first time, we classify gasses species independently of CO-concentration. If CO gas is present in surrounding atmosphere, a second LDA method allows quantifying its concentration.

3. RESULTS AND DISCUSSION

We observed that the response curves $R_n(t)$, for a given temperature variation, depends on the surrounding atmosphere. Previous results indicate that certain steps are more useful for gas selectivity and others for gas quantification. From different transient shapes observed with this gas sensor studied under different gases and according to functioning final temperature, results give us three significant points:

- At low temperature, NO_2 (or mixture of NO_2) can be distinguished from others gasses with specific transient response.
- At higher temperature, CO and C3H8 gasses create another type of shape with different time constants for each gas.
- At even higher temperature, only CO gas dominates on sensor transient responses which are quasi-similar, in term of shape and also peak position, when mixture of CO is present. An example of this kind of result is shown in figure 2.

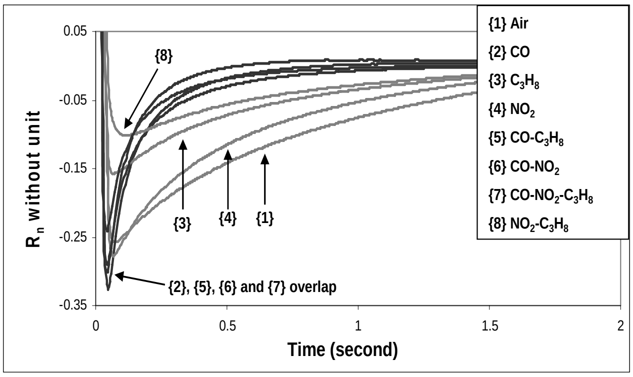

Figure 2. Normalized transient response curves of Pt-doped sensor, from 110 to 500°C

It now appears clearly that some other temperature steps are more efficient for gas sensitivity (possibility to evaluate gas concentration). For example, we can observe in the figure 3, the sensor response under the mixture of CO, C_3H_8 and NO_2, where CO-concentration increases from 1 to 200 ppm. It is clearly possible to discriminate, with the shape analysis by consideration of peak values and time constants, the concentration of CO in this mixture.

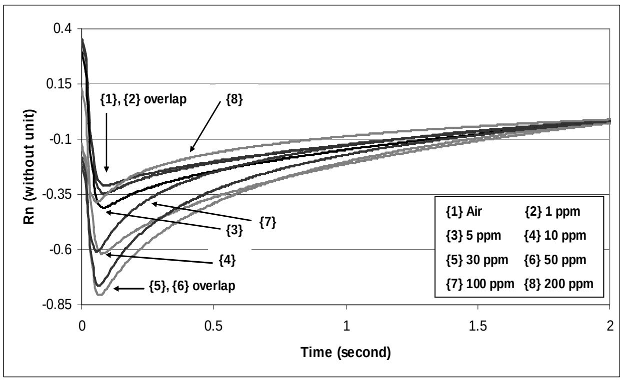

Figure 3. Normalized transient response curves of Pt-doped sensor, from 110 to 500°C

It can be observed on figure 2 and 3 that transient responses of sensor are made up of main features which are shape, peak amplitude and time of peak appearance. These three parameters defined from sensor transient responses depend on gas or gasses mixture but also gas concentration.

Thanks to these three parameters measured on the transient responses from each of the sixth temperature variation, the LDA carry out to the separation of different CO-concentration points. In the worst case of three gasses mixture (fig. 4), it can be seen that each concentration is well distinguished with a good reproducibility (10 plots overlapped). Also, we obtain a minimum level of detection between 1 and 5 ppm of CO.

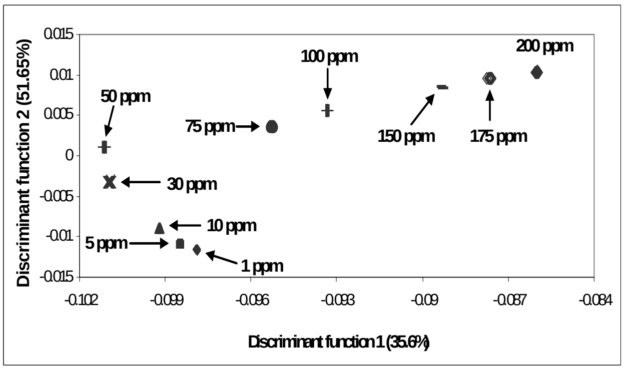

Figure 4. LDA Graph: results of CO concentration

Then, in order to determinate CO-concentration, we can execute second order polynomial regressions. In example for the mixture of 3 gasses (Fig. 5), the two axis of LDA projections are used: factorial axis 2 to quantify the low concentration range between 1 to 50 ppm, and factorial axis 1 to quantify the CO concentration from 50 to 200 ppm.

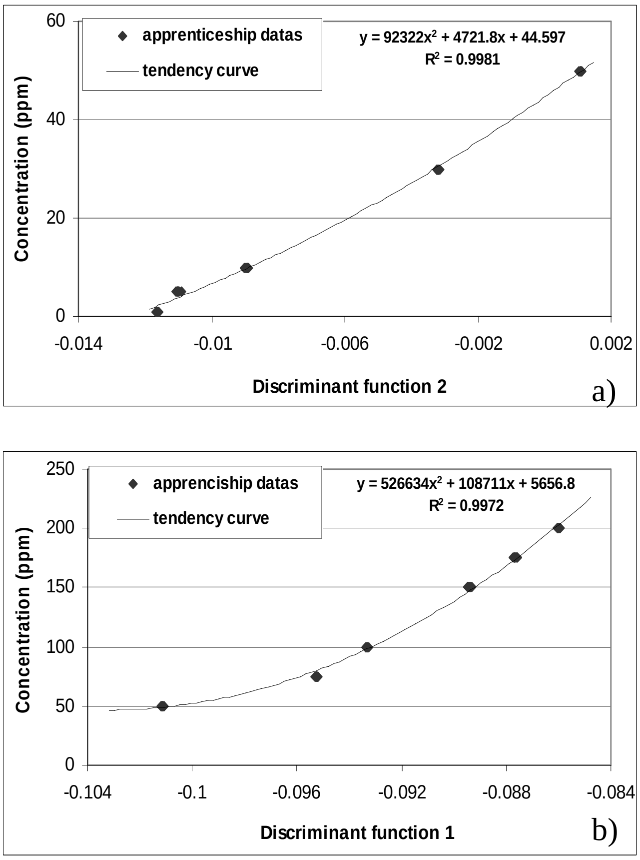

Fig. 5: LDA projection dedicated to qualitative analysis: a) regression for low concentration (<50 ppm) ; b) regression for high concentration (>50ppm)

4. CONCLUSION

We have developed and optimized a test profile of temperature to find the best variation competent to get reproducible information for the gas detection. Results show that the shape, formed with peak and slope, of sensing layer response on a temperature variation is significantly affected by a gas or gasses mixture. From these results, we have designed a temperature profile dedicated to CO quantification in a mixture of NO_2 and C_3H_8. The discrimination method, based on Linear Discrimination Analysis, permits us firstly to classify gasses species and secondly to quantify CO-concentration in a range from 5 to 200 ppm with a good precision, with a measuring time lower than 30s. This new method is promising to conceive a smart gas detector based on combination of temperature profiles and a reduced number of sensors.

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