Characterization of Dynamic Measurements with Nanoparticular SnO 2 Gas Sensors

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Abstract

A temperature step dynamic measurement on a nanoparticular SnO_2 gas sensor is studied. Different sequences applied on the heater sensor are investigated to determine the best way to have a reproducible response. The sensor performances are then compared for CO detection in isotherm mode and in dynamic mode, with the previously highlighted sequence. A characterization of the step length is also led to its influence on sensor sensitivity.
Finally, the best temperature profile to use for dynamic measurements is presented to improve significantly sensor sensitivity, reproducibility and stability.

Keywords :
SnO_2 gas sensor, temperature step dynamic mode, stability, reproducibility, CO sensitivity.

I- Introduction

The SnO_2 gas sensors are based on the principle of chemisorption/desorption phenomena. They are used for management of air quality systems in low cost applications. Many domains are concerned such as medical, military, automotive … They are many interests in their developments but natural barriers limit their selectivity, reproducibility and reliability. The use of a dynamic measurement mode is one way to improve their performances, lowering these problems [1, 2].
Many dynamics mode exists as sinusoidal or triangular signal applied on the heater. We propose in this paper a characterization of a dynamic mode with temperature steps. The main goal is to make a measurement protocol giving the best results in term of reproducibility, sensitivity, response time and stability.

II- Methodology

A gas sensor is composed by 2 parts; a sensing layer which interacts with gas and microhotplate as a heating part permitting to increase reactions between gas and the sensing material. In our experimental work, we use sensors designed in LAAS-CNRS[3]. The heater is in platinum and the sensing material is a nanoparticular SnO_2 synthetized by LCC-CNRS.
The sensing layer temperature is linked to the power applied to the heater by a linear law: 60mW corresponds to 500°C and 30mW to 250°C approximatively.
The principle of the dynamic mode used is summed up in the Figure 1. A sequence of N temperature steps is continuously applied on the heater through the power control. An experiment is defined by:

- Number N of temperature steps.
- Power values of these steps.
- M continuous repetitions of the sequence.
- Gases on the sensing layer during the time of experiment.
- Resistance measurements made on the sensitive layer during experiment.

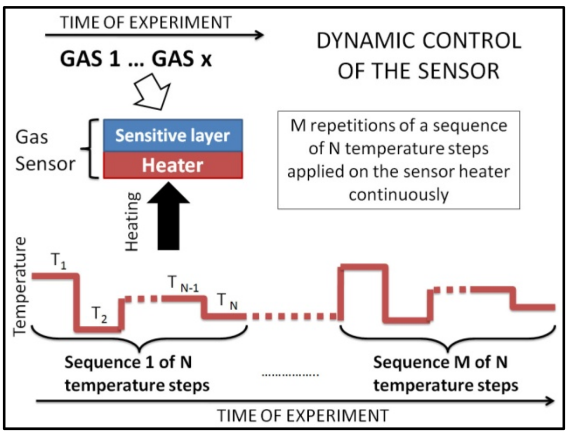

Figure 1 : Dynamic control of the heater. It consists in a loop of identical sequences composed by several temperature steps.

A specific test bench has been developed at LAAS-CNRS firstly to control the atmosphere (gas concentration; working gas temperature, relative humidity); secondly to control the working temperature of the sensor through the control of power on the heater and finally, to permit fast acquisition rate (250 samples by second).
Some parameters are fixed in the following part (ambient temperature and 0% rate humidity). In this study, we only use the last measured point of each step. We show in previous work that it is the most reproductible and the most steady point of all the step. The heating power is between 30 and 60mW. 60mW is the maximum defined by the used microhotplate [3] and 30mW is fixed by the measurement constraints (resistance variations more than 10MOhm).

III- Choice of a sequence

This study is based on similar temperature steps organized in different sequences. Measurements of each temperature are displayed to study the impact of the sequence on the sensor response.
The first sequence is presented in Figure 2. It corresponds to regular stairs shape: a constant sweep between 30 and 60mW with a 10mW step (~80°C).

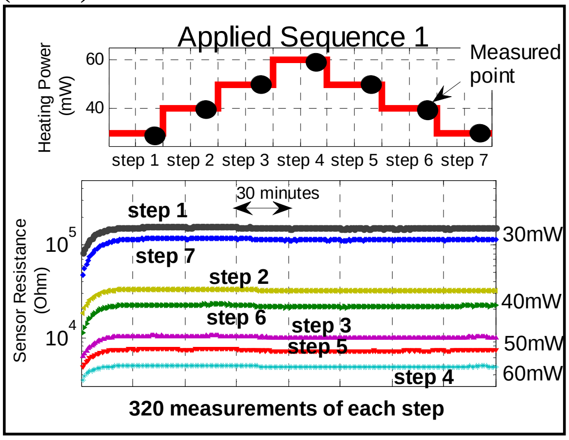

Figure 2 : Comparison between two equivalent steps (same power) from the first sequence (in regular steps).

We can see that this operating mode (with M repetitions) lead to rapid stabilization of sensor response for each temperature steps. This stabilization time (about 10minutes) is longer for weak powers (30mW and lower).
The figure 2 highlights also the non reproducibility in the sequence for 2 identical steps. For example, in spite of the identical temperature of step 2 and 6, (40mW), the sensor response is different even at the end of 320 cycles (M=320). We can conclude that the sensor response at a given power step depends on the previous steps.

As the step before is important, we decided to fix it to the same value. In consequence, in the second sequence a 0mW reference step between each step is included. Figure 3 shows an identical effect. The sensor resistance is different depending on the place of the step in the sequence. This difference seems to be as greater as the power is high. We suppose that it depends on the height between measured step and reference one.
We can also notice that the stabilization time of the sensor response is much longer than with the first sequence.

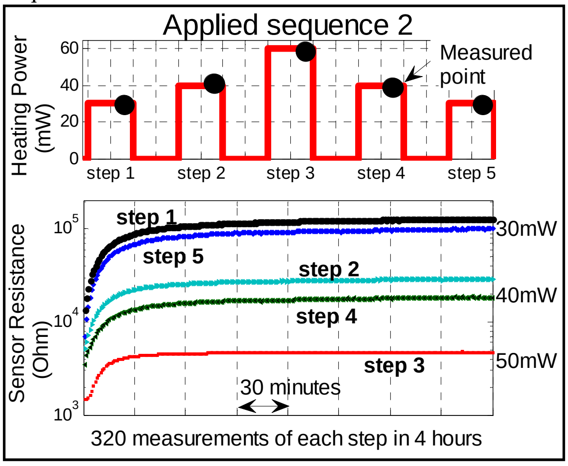

Figure 3 : Second sequence used for the characterization. A 0mW reference is inserted between the measured steps.

Sequence 3 is illustrated in Figure 4. It uses a 60mW step as reference. This new profile leads to a very good reproducibility from one step to another equivalent. In a dynamic sequence, we can obtain the same sensor response (in term of resistance) for a temperature step if previously we apply a higher level of temperature. Concerning the stabilization time, we can observe the same results as the sequence 2: the stability depends on the height between the steps.

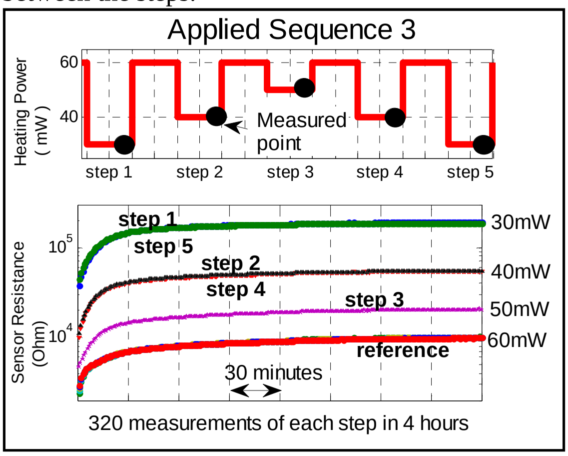

Figure 4 : Third sequence studied: same power steps with previous sequences but with 60mW as reference.

This result can be explain by chemisorption/desorption phenomenon. For a given temperature, interaction between sensing layer and surrounding gas leads to the formation of specific species and the release of others. The higher the temperature is, the more the surface species are released. Consequently, using a high temperature step before a measured step is like cleaning the surface. The sensor will be in a reproducible configuration if this step is the same.

IV- Measurements under CO

A part of the sequence 3 has been used to characterize the sensor sensitivity to CO which is defined by the following formula:

$$S_{CO} = \frac{R_{CO} - R_{air}}{R_{air}} \quad (1)$$

R_{CO} and R_{air} correspond to sensor resistance under CO and air respectively. The sensitivity will be all the more different from 0 since the sensor reacts with CO.

The reference step is 60mW and 2 others steps of 30 and 40mW are used. The sequence is shortened with the lowest temperatures, for the best sensitivity. A comparison with the one obtained with isotherm operating mode is made. In this mode, heater power is constant and the values are taken after 1 hour under the considered atmosphere. In dynamic mode, the used values correspond to the last measure of each step after 1 hour in air or CO (Figure 5).

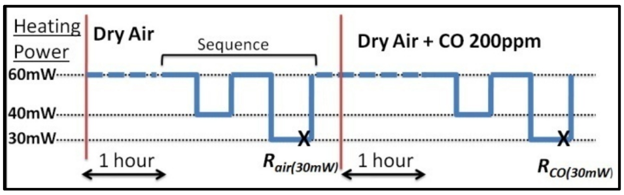

Figure 5 : Measurements used for the Sensitivity calculus in dynamic mode.

The formula 2 is then used for the calculation of the dynamic sensitivity for each temperature step. For example, concerning the step at 30mW, the sensitivity is given by:

$$S_{CO(30mW)} = \frac{R_{CO(30mW)} - R_{air(30mW)}}{R_{air(30mW)}} \quad (2)$$

The comparison between the dynamic and the isotherm mode are represented on the Figure 6. The behaviors are opposite. On one hand, for the dynamic mode, the less the power is, the more the sensitivity increases. On the other hand, the isotherm mode gives a better reaction to CO for higher heating power.

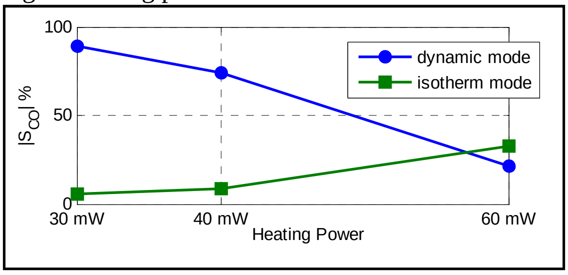

Figure 6 : Sensitivity of the sensor under CO 200ppm for dynamic and isotherm mode.

The chemical mechanisms involved in the sensor response are totally different following the way of utilization. From these results, we can conclude that the use of short dynamic steps improves significantly the performance in CO detection of a nanoparticular SnO_2 sensor. The sensitivity is all the higher since the applied shift of temperature is important.

The effect of step length has been also studied. The Figure 7 highlights the sensitivity of the sensor to CO, in dynamic mode. Three different durations of steps in the sequence previously defined are taken.

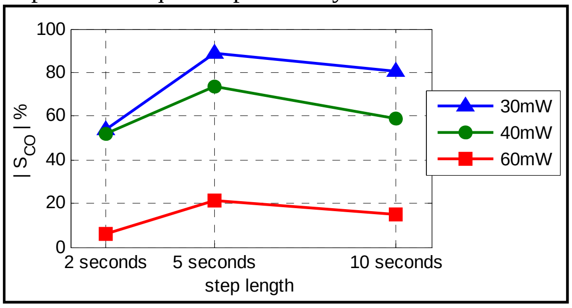

Figure 7 : Sensitivity of the sensor under CO 200ppm for different step times for the dynamic mode.

We can see that the dynamic mode presents an optimum of sensibility for a step length of five seconds. The tendency of a better detection for a lower temperature is confirmed.

From these preliminary results, optimal sequence for CO detection is a sweep between 30 and 60mW. The high power is the reference step and the 30mW step gives the best sensitivity. The optimal length step is 5 seconds.

Using a dynamic mode also offers a good reproducibility of the sensor performances. Five measurements have been made along fifty hours of experiment. In the same conditions, another acquisition has been made one week later. The figure 8 shows the mean value and the standard deviation of all these measurements.

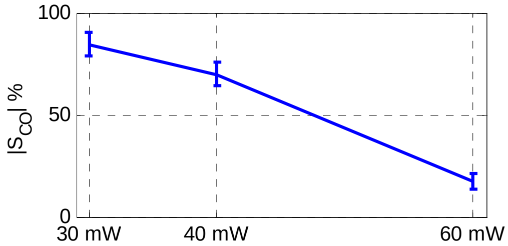

Figure 8 : Reproducibility of the Sensitivity of the sensor under CO 200ppm. 5 measurements are 10 hours spaced out and a last one a week after.

There is a good long term reproducibility with a sensitivity difference less than 10% for one week spaced out utilizations. This method leads to a good reliability of the results.

V- Conclusion

Different studies on the dynamic measurement of a nanoparticular SnO_2 sensor have been led. We have focused on the utilization of temperature steps on the sensor heater. The best results are obtained using a step reference of 60mW between each step of the applied sequence. It gives a good reproducibility of the sensor response. For an identical power step, we have the same resistance value, avoiding effects of previous steps.
Such a sequence has been applied to the heater under 200ppm of CO diluted in dry air. The sensor shows higher sensitivity to the gas than isotherm mode. The lower is the power step the higher is the CO sensitivity. An optimal heater sequence for temperature step dynamic measurement. has been determined with a sweep of 5 seconds between 30 and 60mW. This operating mode gives the best results with our sensor in term of CO sensitivity, reproducibility and stability.

VI- References

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