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OPTIMISED DYNAMIC TEMPERATURE OPERATING MODE SPECIFICALLY DEDICATED TO MICROMACHINED SnO₂ GAS SENSORS**

F. Parret^{1*}, P. Menini¹, A. Martinez¹, K. Soulantica², A. Maisonnat², B. Chaudret²

¹Laboratoire d'Analyse et d'Architecture de Systèmes (CNRS-LAAS),

E-mail : fparret@laas.fr http://www.laas.fr

7 Avenue du Colonel Roche, 31077 Toulouse-France.

²Laboratoire de Chimie de Coordination (CNRS-LCC),

205 route de Narbonne, 31077 Toulouse cedex 4, France.

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Abstract: In this paper, we show the influence of short temperature variations on the transient response of a SnO₂ nanoparticular gas sensor. By consideration of the shape and time constants of the normalized response curves, we can differentiate different gasses mixtures at a ppm level. This new method of analysis is promising to conceive a gas detector based on combination of temperature profiles and different sensitive layers.

Keywords: Micromachined gas sensor; Temperature cycling; Discriminant variables

INTRODUCTION

Previous studies on the development of gas sensors based on metal-oxides have been designed with for objective to reduce dimensions of these gas sensors. Currently, with the combination of nanotechnology and microelectronic processes, it can be possible to reduce the power consumption with low cost. Previous studies have demonstrated the interest to use this gas sensor in temperature modulation [1] improving these performances in term of selectivity and sensitivity for gasses discrimination [2] and also to reduce the influence of relative humidity [3]. These features allow extracting more useful information of the sensing processes to be used in gas identification and quantification via mathematical techniques of classification and analysis [4].

In the frame of the "Nanosensoflex" project, this type of gas sensors has been developed, formed by a microhotplate platform [5] and a nanoparticular SnO₂ sensing layer [6] with or without doping agent [7].

This article deals with a nanoparticular SnO₂ gas sensor associated to an optimised temperature profile applied on heating resistor in the goal to observe the shape of the sensor transient responses depending of the surrounding atmosphere.

SENSOR DESCRIPTION

The sensor used in this study is formed by a microhotplate platform and a nanoparticular SnO₂ sensing layer. The microhotplate architecture (Fig. 1) was initially developed by Motorola and presently exploited by Microchemical Sensors S.A. A SiO_xN_y membrane of 2 μm of thickness supports a polysilicon heater of 600 μm x 430 μm. Dimensions 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°C with power consumption lower than 100mW.

The metal-oxide used in this sensor is a crystalline SnO₂ nanomaterial synthesized by the decomposition and oxidation of a tin based organometallic precursor ([Sn(NMe₂)₂]₂), the mean grain size obtained is 15 nm of diameter.

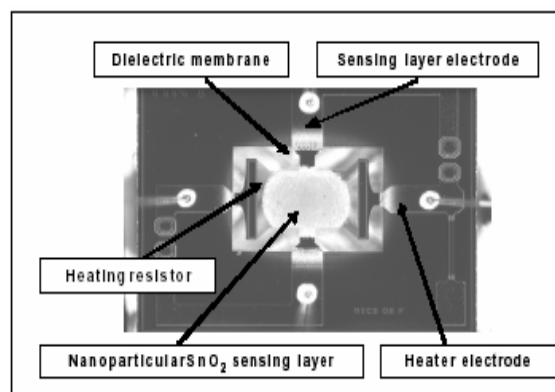


Fig. 1. Top view of a SnO₂ gas sensor

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 SnO₂ with a controlled temperature cycle from ambient to 500°C.

EXPERIMENTAL RESULTS

The experimental set-up consists of a gas delivery system, an exposure glass vessel and an electronic circuit for resistance determination through voltage measurements. Tests have been performed under 3 gasses (CO, NO₂ and C₃H₈) and mixtures of these gasses (with concentrations of 200, 1.8 and 150 ppm respectively). The relative humidity is fixed at 50% for a constant flow rate of 500 ml/min.

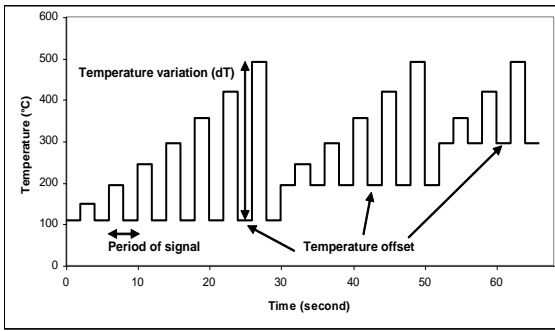


Fig. 2. An example of test profile applied on heater

We have designed different test profiles of temperature applied on heater. These tests are made up of various flexible parameters like temperature offset, temperature variations (noted dT) and period (Fig 2).

In first time, an optimisation on the period has been studied to eliminate the resistance drift over time of the sensitive layer. In order to observe the transient behaviour of sensing layer, the period must be higher at 0.5 second. Then, to eliminate the resistance drift until this isotherm value, the period does not exceed 5 second.

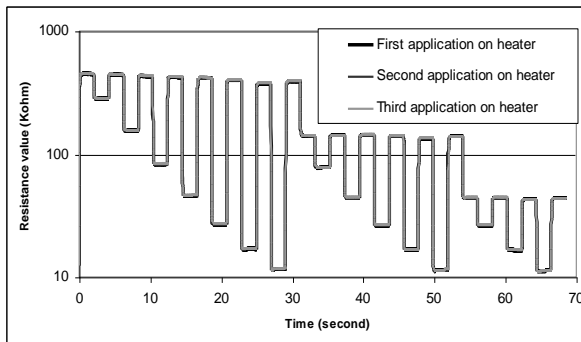


Fig. 3. Undoped sensor response: 3 sequences referenced at the same time.

Typical response curves of the pulsed sensor when exposed to CO (200 ppm) are shown on figure 3. These curves have been obtained reproducibly. Effectively, it can be observed that to a given temperature value always corresponds similar resistance values when the temperature profile is applied at 3 different times.

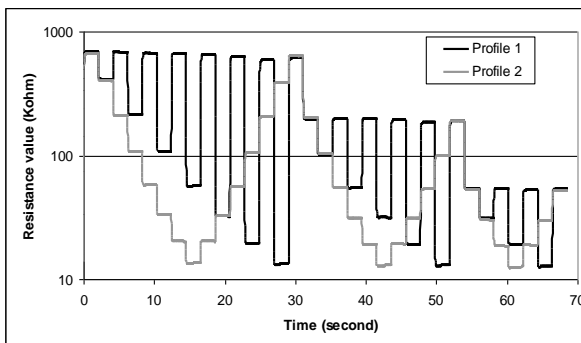


Fig. 4. CO response of an undoped sensor for two different profile.

This reproducibility is also reveals by the figure 4 which shows the sensing layer resistance behavior under 200 ppm of CO, for two different profiles. It can be seen that resistance values, at a given temperature level, are identical independently of the shape of the temperature profile.

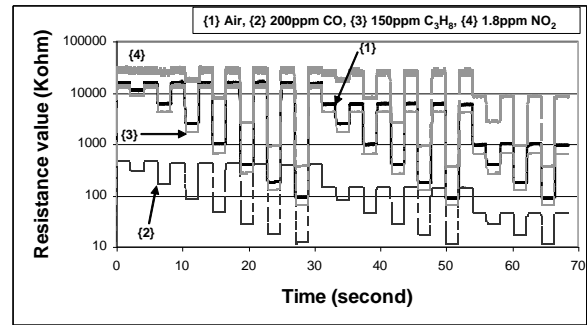


Fig. 5. Undoped sensor resistance response under gas.

Finally, it can be seen on figure 5, reduction and oxidation reactions of the resistance of an undoped sensor, identical like isotherm behaviour, when this one is exposed to reductor gasses like CO and C₃H₈ and oxidant gasses like NO₂.

In order to get a 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 t and R_f is the last value measured on each step of temperature.

We observed that the shape of the response curve $R_n(t)$, for a given temperature variation, depends of the surrounding atmosphere.

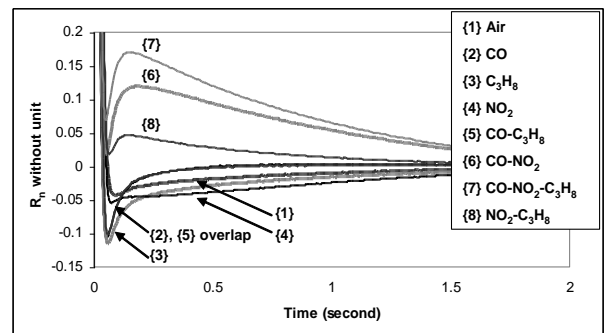


Fig. 6. Normalized transient response curves from 300 to 400°C.

Typical normalized response curves of an undoped sensor can be observed on figure 6. The shape of this response curve (peak position and slope of the quasi linear part) is considerably affected by exposed gasses (i.e. CO, 200 ppm or C₃H₈, 150 ppm, or NO₂, 1.8 ppm or mixtures of these gasses). With the same gas sensor but on a different temperature variation, an other shape of the transient response can be observed on figure 7

which is pronounced when NO₂ (or mixture of NO₂) are exposed on the gas sensor.

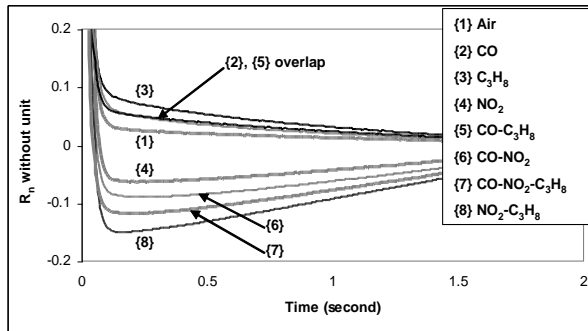


Fig. 7. Normalized transient response curves from 110 to 240°C.

When the temperature increases, the shape of the normalized resistance variations can be sum up with the curves of previous figures. Typical response curves of an undoped gas sensor can be defined with negative slope and a long time constant (170 ms about) when NO₂ (or mixture with NO₂) are exposed on the sensor for low temperature variations. For the other gasses, CO and C₃H₈ gasses, the behavior is quasi the same than under synthetic air.

In order to modify the shape of the response curves, at the time of CO and C₃H₈ gasses exposition, the operating temperature level must be higher. From 250°C until the allowed maximum temperature (about 500°C), the influence of NO₂ is less pronounced. Then, CO and C₃H₈ gasses exposition creates peaks or the combination of peaks and slopes for the gasses mixture. The discrimination of these gasses can be realize with the time of peak position corresponding at 54 and 63 ms respectively for CO and C₃H₈ gasses. Moreover, the temperature offsets induce few influences on the shapes.

It's also very interesting to observe the response curves when temperature level goes down.

In order to compare transient response curves when temperature level goes down and up, we have inverse the normalization with the following relation:

$$R_n = (R_f - R_i) / R_f \quad (2)$$

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

It can be seen three phenomena according to temperature level.

In first time, with low operating temperature, the response of an undoped sensor is more affected when this one is exposed to NO₂ gas and mixture with NO₂ (Fig. 8).

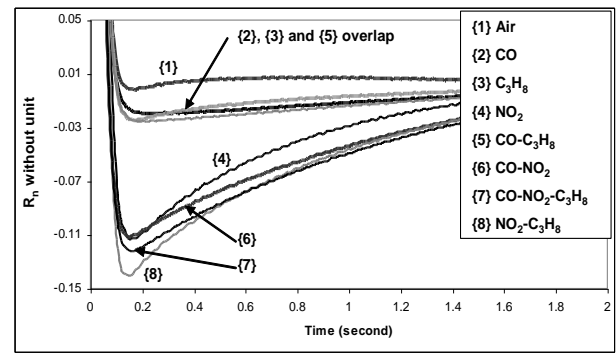


Fig. 7. Normalized transient response curves from 440 to 60°C.

Next, with a temperature upper to 250°C, the shape under NO₂ gas and mixture with NO₂ is fully changed with simple slopes. Moreover, the sensor response under CO becomes different from synthetic air and C₃H₈ (Fig. 9).

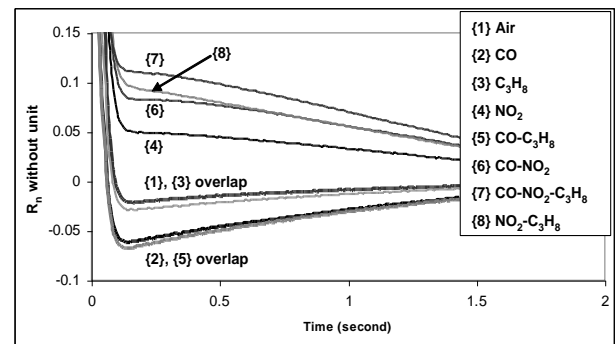


Fig. 8. Normalized transient response curves from 440 to 200°C.

Finally, with a temperature upper to 380°C, it can be observed on the figure 9, the discrimination between C₃H₈ and synthetic air that constitutes a good result.

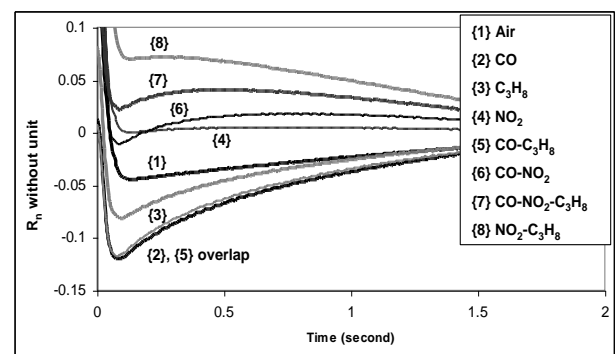


Fig. 9. Normalized transient response curves from 440 to 350°C.

These results demonstrate the interest to observe the shape of the normalized sensing layer response which depends of the temperature variations and, especially, affected via the surrounding atmosphere.

Moreover, it can be possible to discriminate, with the shape analysis by consideration of peak values and time constants, the concentration of one gas in a mixture. In example, with the figure 10, we can

observe the sensor response under the mixture of CO, C₃H₈ and NO₂, where CO-concentration increases.

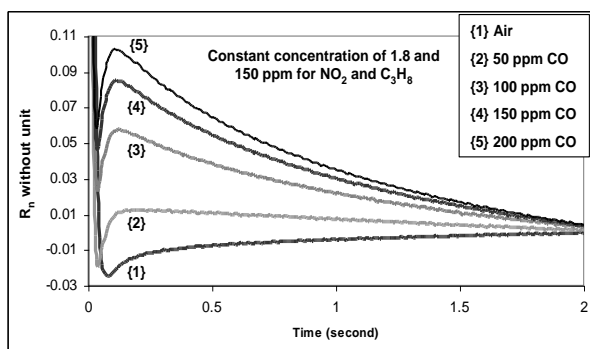


Fig. 10. Normalized transient response curves from 350 to 520°C.

DISCUSSION

Figures 6 and 7 show the normalized variation of resistance against time for injection of various resistive and oxidative gas mixtures upon increasing the temperature whereas figures 8-10 display the same phenomena but upon decreasing the temperature. These curves bring to our attention several interesting points :

- at low temperature the resistive gas CO and C₃H₈ do not play a role in the resistance modification (figure 8); this can be easily interpreted in terms of absence of reaction between CO or propane on one side and O₂ on the other catalysed by the SnO₂ sensitive layer;

- at higher temperature (figure 9), the barrier of activation of the oxidation reaction of CO is low enough for the reaction to proceed whereas that for C₃H₈ is higher; it is therefore possible to discriminate one from the other;

- at even higher temperature (figure 10) both CO and C₃H₈ are oxidized and they are more difficult to distinguish; only the peak position reveals the different nature of the gasses

- there is a somewhat similar phenomenon for oxidizing gasses but reverse. Thus, at low temperature (figure 7) NO₂ displays an oxidizing power larger than air and is therefore detected by a transient peak; this peak tends to disappear at higher temperature where the oxidation rate of the sensitive layer is fast enough

- the mixture of NO₂ and a reducing gas only reveals NO₂ at low temperature whereas the opposite effects are clearly seen at 350°C (figure 10).

These data demonstrate the complexity of catalytic reactions at the surface of the tin oxide layer and associated to the gas detection. This is clearly revealed by the transient peaks which are associated with difference in kinetics of the various reactions involved. This can be associated with the thermodynamic characterization of the reactions associated with the final resistance measured when exposing a sensitive layer to a define gas and can

lead to a finger print of various gasses and gas mixtures.

CONCLUSION

A new generation of gas sensors based on nanoparticular SnO₂ sensitive layer has been elaborated. We have developed and optimised a test profile of temperature to find the best variation competent to get reproducible information for the gas detection. First results show that the shape of the sensing layer response on a temperature variation is significantly affected by a gas or gasses mixture. These shapes, formed with peak and slope, can be treated and exploited. These results are promising and a study is in progress for the realisation of a gas detection prototype based on the shape analysis and the time constants with an optimise temperature profile.

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