

# Gas identification by modulating temperatures of SnO<sub>2</sub>-based thick film sensors

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## Abstract

A new method is presented to identify the presence of two gases in the ambient atmosphere. The method employs only one SnO<sub>2</sub>-based gas sensor in a sinusoidal temperature mode to perform the quantitative analysis of a binary gas mixture (CO/NO<sub>2</sub>) in air. © 1997 Elsevier Science S.A.

*Keywords:* Gas sensor; SnO<sub>2</sub>; Gas analysis; Temperature mode

## 1. Introduction

SnO<sub>2</sub>-based gas sensors have been extensively used to analyse gases [1]. Well known advantages include their low costs and high sensitivities; well known disadvantages concern their lack of stability and selectivity [2,3]. In practical applications, several attempts are usually made to overcome their disadvantages, by, for example, using chromatographic columns to separate the components, by operating at different temperatures, by choosing different burning-in procedures, dopants, measuring frequencies, etc. [1–5]. For common applications of pattern recognition (PARC) and multi-component analysis (MCA) of gas mixtures, arrays of sensors are usually chosen which operate at constant temperature. In these cases a lack of selectivity and therefore overlapping sensitivities of different sensors is of advantage [6,7].

In the present study, a modulated temperature operation mode was chosen as a new approach to change the selectivity of a gas sensor in a controlled way, and to reduce the overall power consumption by employing only a single sensor rather than an array. Earlier inves-

tigations of this kind concern studies which aim at optimizing the response to individual gases (CO, H<sub>2</sub>S, with references given in [8]). A commercial SnO<sub>2</sub> device (TGS 203; Figaro Engineering, Japan) was also operated in a pulsed temperature mode with the gas detection taking place at low temperatures. First attempts have been published to use dynamical sensor data by ramping the sensor temperature [8]. By evaluating the obtained sensor response with Gaussians [9] or by applying fast Fourier transformation [10,11] it was possible to discriminate gas mixtures.

The first attempts to analyse the dynamical sensor data were performed either on thin films deposited on micromachined substrates [9] or on classical Taguchi sensors [10,11]. In the case of thin films deposited on micromachined substrates, the advantages of the fast thermal response and low power consumption of the substrates are hidden by the less sensitive thin film. In the case of the Taguchi sensors, their high sensitivity is counterbalanced by a poor thermal response due to their relatively large substrate, which may induce distortions in the modulated sensor response and, in addition, possess a high power consumption. The present approach takes advantage of the combination of micromachined substrates and thick film layers; in this way we combine the excellent response time to temperature

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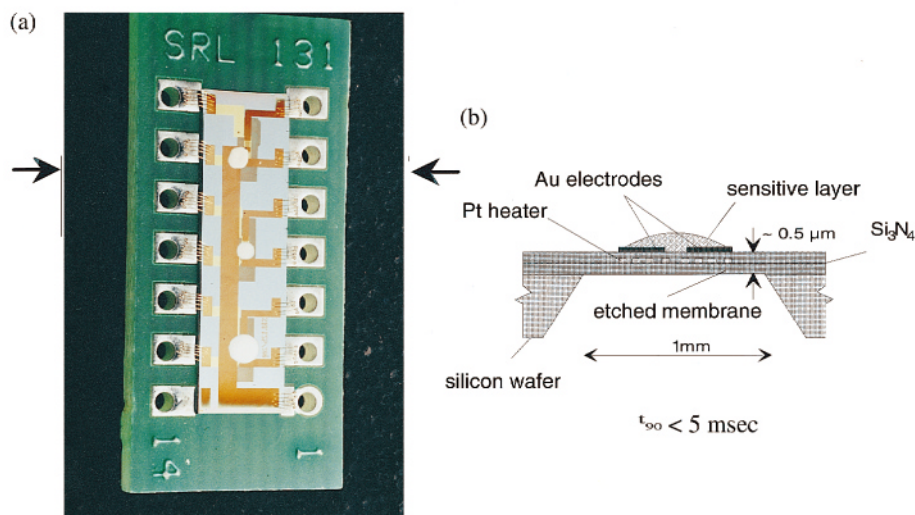


Fig. 1. (a) Photograph of a silicon micromachined sensor array (SRL125/MOS) comprising six resistive sensors and three integrated platinum resistive heaters. Each pair of resistive sensors is coated with a thick film of pure, Pt-doped or Pd-doped tin oxide. (b) Schematic cross section of one cell showing the ultra-thin silicon nitride membrane with an internal platinum resistance thermometer/heater and the gas sensitive layer above.

changes of the substrate with the high sensitivity characteristic of thick films tin dioxide sensors. By this approach we also intend to prove that the silicon technology for manufacturing micromachined substrates is perfectly compatible with the thick film technology for depositing sensitive layers. First measurements on such devices, in constant temperature mode, have already been reported [12]. We see advantages of this approach by identifying components in binary mixtures of CO and NO<sub>2</sub> in air at two temperatures. These gases were chosen as they are of practical importance in monitoring pollution from exhaust gases in the automotive industry.

## 2. Experimental

The thick film sensors were made by depositing thick films of Pd-doped tin oxide with two different grain sizes on micromachined substrates [12]. The devices are presented in Fig. 1. The thermal response of the uncoated substrates is presented in Fig. 2. The preparation of the sensitive material was described elsewhere [13]. The grain sizes of the materials were around 20 and 50 nm. The temperature of the sensors was varied between 200 and 420°C by a sinusoidal modulation of the heating voltage with a frequency of 50 mHz. The temperature range and frequency were optimised for the identification of the chosen gases. The dependence of the temperature on the heating voltage was previously calibrated by using an IR thermometer (Maurer-IR KPR 1075-1).

The experimental test setup consisted of computer-driven mass flow controllers, a Teflon chamber and a multimeter for measurements in the millisecond range. The temperature was varied by modulating the heating voltage with a power supply (HP 6035A) driven by a frequency generator (HP 3325B). A flow of humidified synthetic air (200 ml min<sup>-1</sup>, 50% RH) was used as purging gas. Test gases were in the concentration ranges of 50–150 ppm (CO) and 1–2 ppm (NO<sub>2</sub>).

## 3. Results and discussion

Figs. 3 and 4 show the typical time dependencies of the resistance of the sensors realised with the two different materials, during their exposure to different

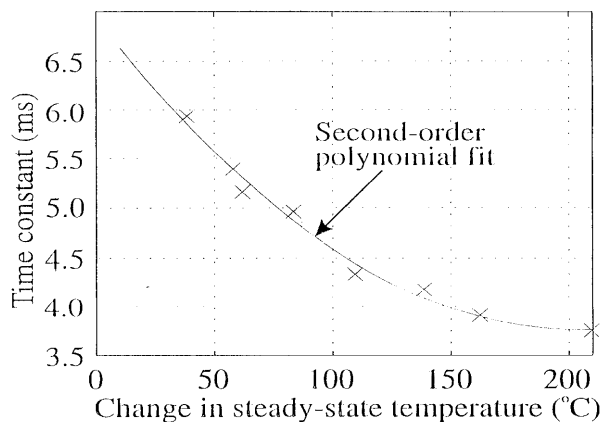


Fig. 2. Dependence of the response time ( $t_{90}$ ) on the temperature change of micromachined substrates.

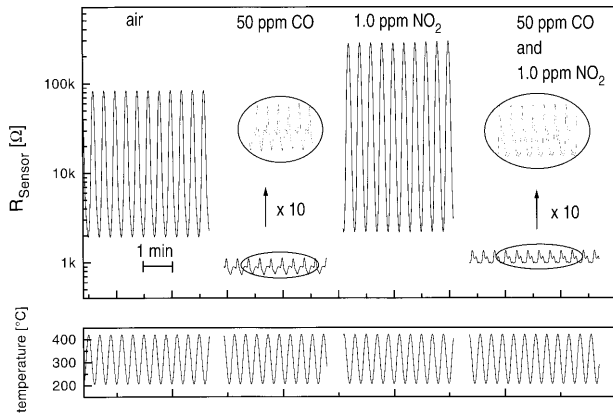


Fig. 3. Time-dependent changes of the resistance  $R$  of a micro-machined sensor in synthetic air (50% RH) and during exposure to 50 ppm CO, 1.0 ppm  $\text{NO}_2$  and a mixture of 50 ppm CO and 1.0 ppm  $\text{NO}_2$ . The coating material was obtained by calcinating  $\text{Sn}(\text{OH})_4$  at  $450^\circ\text{C}$  followed by Pd surface doping (material 1).

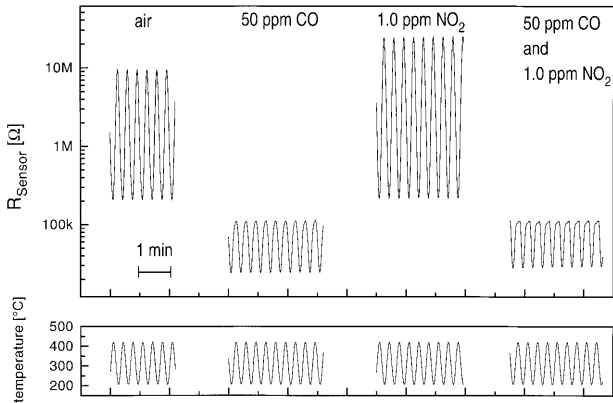


Fig. 4. Time-dependent changes of the resistance  $R$  of a micro-machined sensor in synthetic air (50% RH) and during exposure to 50 ppm CO, 1.0 ppm  $\text{NO}_2$  and a mixture of 50 ppm CO and 1.0 ppm  $\text{NO}_2$ . The coating material was obtained by calcinating  $\text{Sn}(\text{OH})_4$  at  $800^\circ\text{C}$  followed by Pd surface doping (material 2).

test gases and mixtures. One can easily observe the qualitative difference between the response to pure gases and to the mixture. One can also observe the difference between the response corresponding to the two different materials. These facts can be also observed by examining the temperature dependence of the resistances, presented in Figs. 5 and 6. In the last figures one can also observe the huge sensitization to CO, if one measures only at the lowest temperature. This effect can be explained by taking into account the fact that at  $200^\circ\text{C}$ , which is a temperature at which the chemisorption of CO is high, one can find in addition to  $\text{O}_2^-$  species, which are dominating under equilibrium, also  $\text{O}^-$  and  $\text{O}^{2-}$  species, which are dominat-

ing at higher temperatures, and frozen at the surface due to the fast temperature change [14,15]. These last

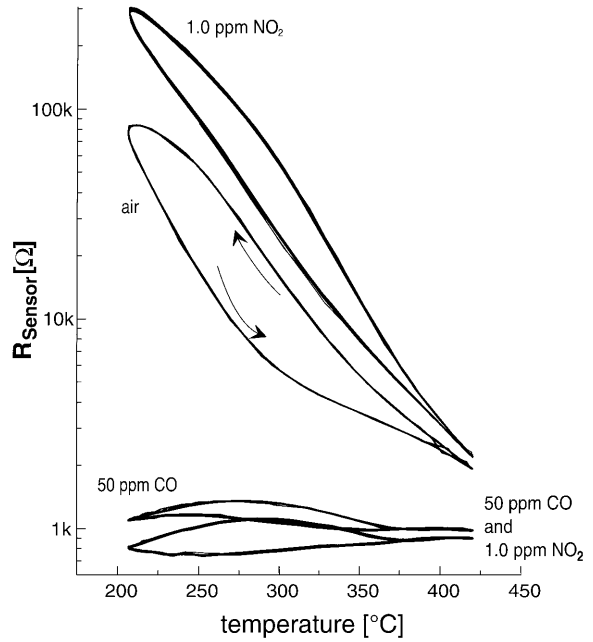


Fig. 5. Dependence of the resistance on temperature during the temperature modulation in synthetic air (50% RH) and during exposure to 50 ppm CO, 1.0 ppm  $\text{NO}_2$  and a mixture of 50 ppm CO and 1.0 ppm  $\text{NO}_2$  (material 1).

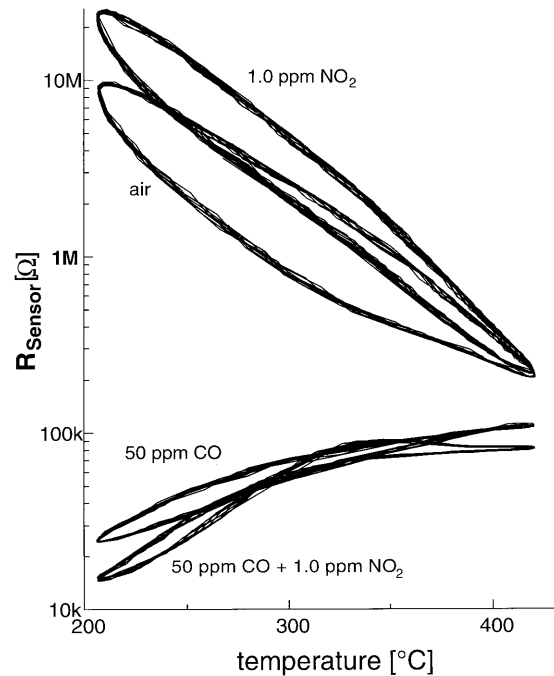


Fig. 6. Dependence of the resistance on temperature during the temperature modulation in synthetic air (50% RH) and during exposure to 50 ppm CO, 1.0 ppm  $\text{NO}_2$  and a mixture of 50 ppm CO and 1.0 ppm  $\text{NO}_2$  (material 2).

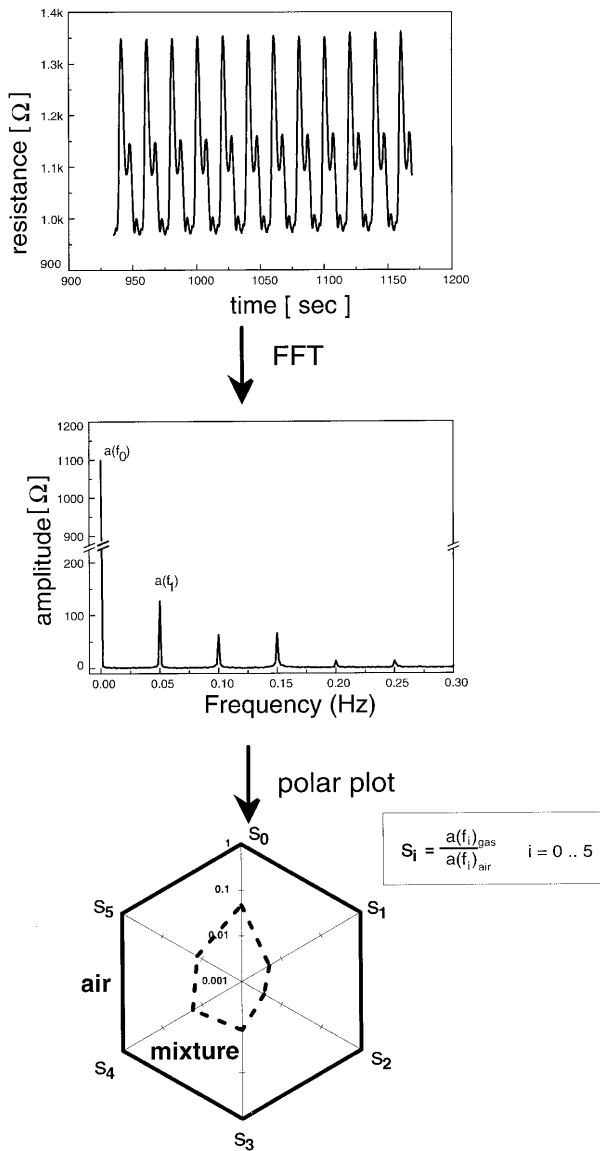


Fig. 7. Illustration showing the way in which the polar plots were constructed. Sensor variables used: the amplitude corresponding to 0 Hz frequency, the amplitude corresponding to the fundamental frequency and the first four harmonics. The values in the polar plot were obtained by normalising each component to the corresponding amplitude in air.

two species are much more reactive with CO, so the sensor response is increased.

### 3.1. Data evaluation and feature extraction

Two ways of analysing the data were used, a qualitative one by using polar plots and a quantitative one by using neural networks. In both cases the feature extraction was performed by FFT. The analyzed sensor variables were the amplitudes corresponding to the resistance offset (corresponding frequency = 0 Hz), the

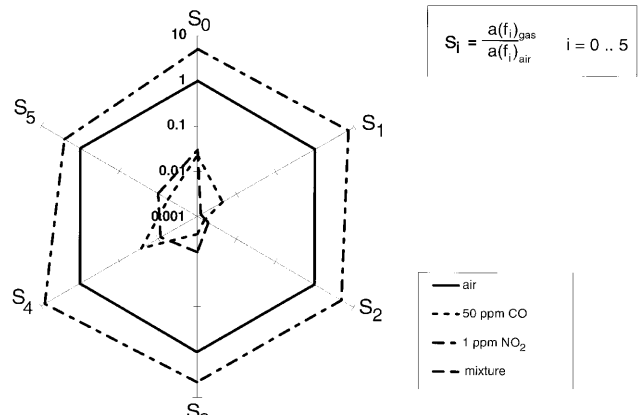


Fig. 8. Polar plot of the different gases (material 1).

fundamental frequency, which is in our case the frequency of the temperature modulation (50 mHz), and the first 4 harmonics. Fig. 7 shows the way in which the polar plots were constructed, i.e. the represented values being obtained by the normalization of the above listed amplitudes in the test gases to the amplitudes in reference air. In Figs. 8 and 9, typical polar plots are given for the two different sensing materials. One can clearly distinguish between the cases in which one or the other of the target gases are present in the test atmosphere. In this way one can perform a identification of both gases.

Qualitative and quantitative discrimination can also be performed by artificial neural network algorithms. The output values of the FFT were used as input variables to the network. To show the feasibility of a complete system, a simple and fully connected 5:5:2 classical feed forward net was used (5 input nodes/5 hidden neurones/2 neurones). The 5:5:2 network was found sufficient to solve our prediction problem. The learning was done with the *Quickprop* algorithm (comparable to backpropagation). As transfer function the sigmoid one was chosen and the gas concentrations were correspondingly scaled down. Fig. 10 presents the

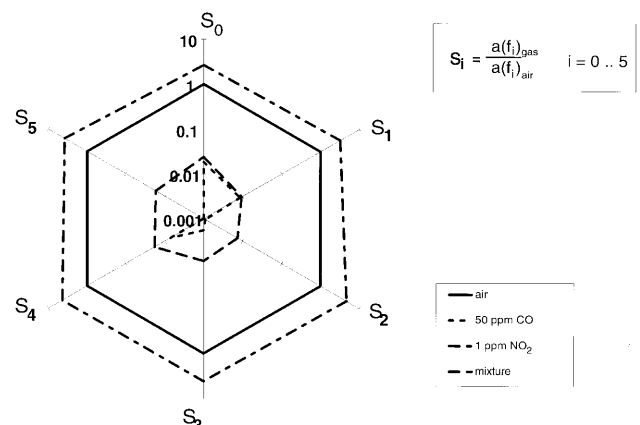


Fig. 9. Polar plot of the different gases (material 2).

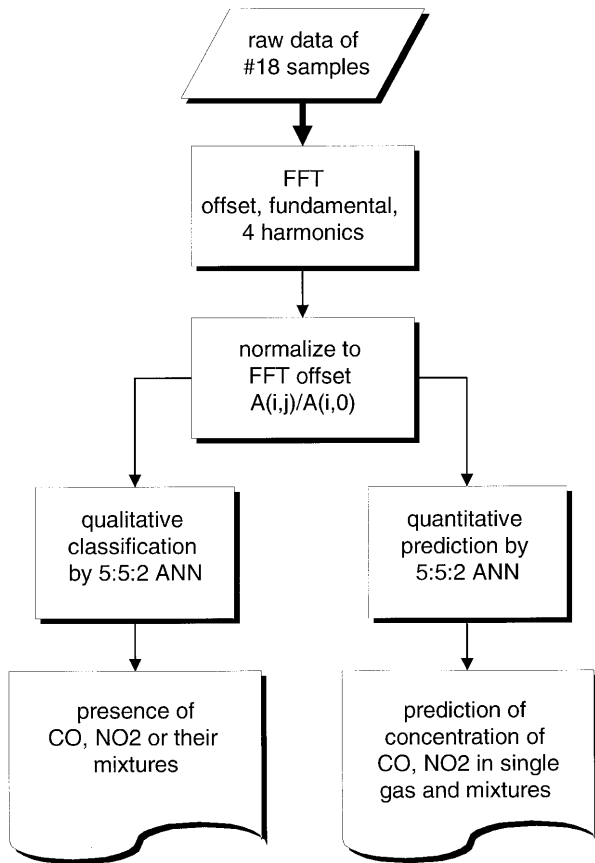


Fig. 10. This flow chart illustrates signal processing methods used to analysis the temperature response of a single tin oxide sensor.

feature extraction and data preprocessing as well as the multicomponent analysis in a flow chart. We present this sample to demonstrate the principle but not an optimal solution. The 18 measurement vectors were divided into two groups: one for the training and the other one for classification. This causes the problem of reducing the size of the training data-set, however an acceptable result was obtained as can be seen in Figs. 11 and 12 in the case of the quantitative prediction. First a fast Fourier transform (FFT) was performed on the raw data. Secondly the fundamental frequency and the first four harmonics were normalized to the offset value. Afterwards a qualitative or a quantitative prediction was executed. In case of the qualitative prediction the target gas concentrations were set to 0.5 if a gas was present, and  $-0.5$  if not. The training was done with half of the data set and vice versa (i.e. 2-fold validation). A total of 100% of the vectors of the two component mixture in the other half (not used for training) could be classified. In the case of the qualitative prediction the results were not so good. This was because of the limited data-set. An extrapolation with this model was hindered. Therefore only 4 and 6 ob-

jects, respectively, out of 18 were used for the verification. As can be seen in Figs. 11 and 12, the prediction is good with the exception of one outlier. This can be improved with a larger calibration set, which totally describes the concentration domain.

### 3.2. Sensitization by temperature modulation

The explanation of the possibility of gas identification in a temperature modulated mode is related to the different reaction kinetics of the interacting gases at the tin oxide surface. By temperature modulation it becomes possible to provide at the surface oxygen species at temperatures at which, in equilibrium conditions, would not exist. In this way the reaction with the reducing and oxidizing gases is dramatically influenced, e.g. at lower temperatures the response to CO becomes dominant in comparison with the response to  $\text{NO}_2$ . For constant temperature measurements one can observe the opposite, see Fig. 13. This fact is determined by the presence of oxygen species at lower temperatures which are normally present only at high temperatures and

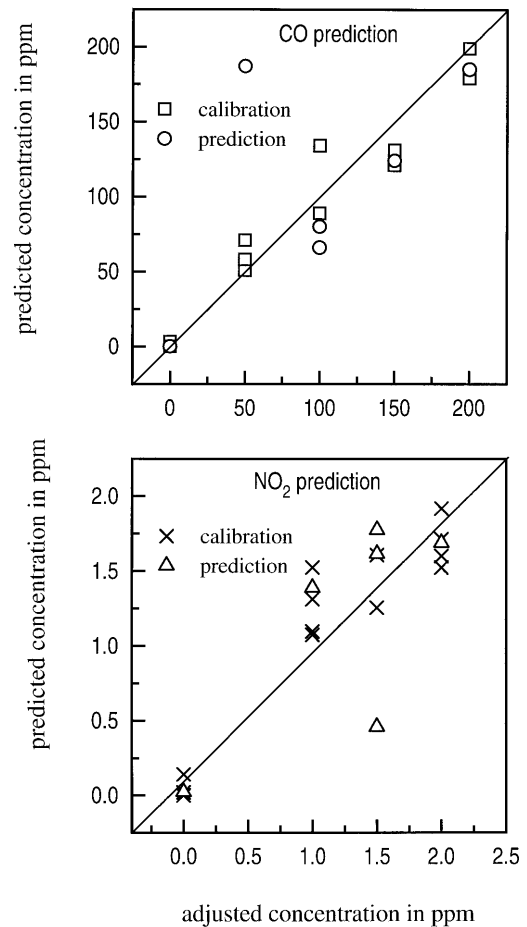


Fig. 11. Dependence of the predicted concentration on the adjusted concentration (material 1).

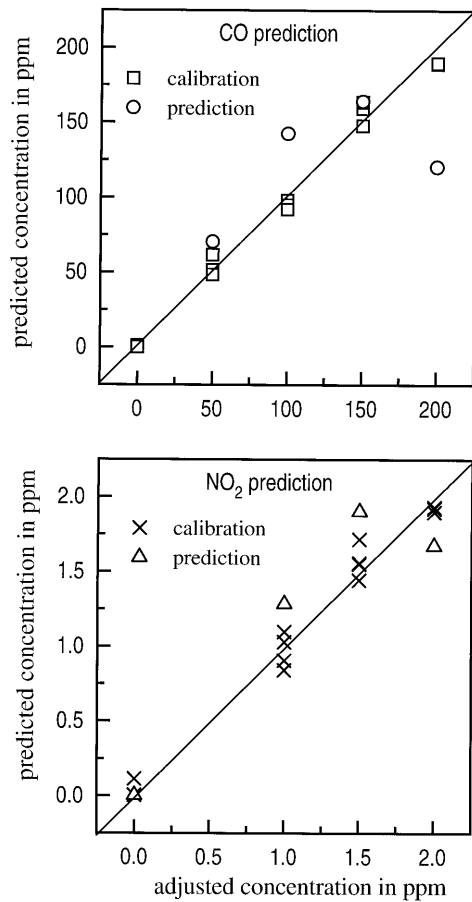


Fig. 12. Dependence of the predicted concentration on the adjusted concentration (material 2).

which will compete with  $\text{NO}_2$  in the capture of electrons, diminishing its effect on the sensor resistance. On the contrary, for CO the effect is enhanced due to the higher reactivity of the non-equilibrium oxygen species. The FFT is probably not the best way of analysing the time dependence of the resistance, due to the fact that it is a linear technique and is limited to the linear harmonics of the fundamental frequency, which will be the frequency of the temperature modulation. In order to get the basic information it would be necessary to decompose the time-dependent resistance in the real simple components and to relate the characteristic frequencies to the surface reaction kinetics.

The approach can be extended to other combinations of target gases; the doping and microstructure of the sensitive material, the temperature range and the frequency of the modulation of the temperature are the parameters which will permit the tuning of the method according to specific goals. Also, alternative methods for the feature extraction can improve the performances of the method.

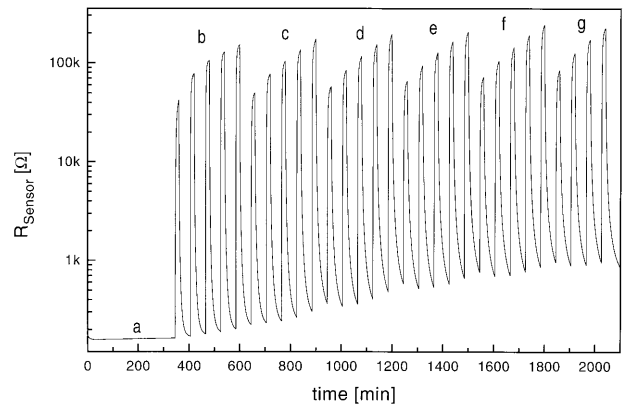


Fig. 13. Time-dependent changes of the resistance  $R$  in synthetic air (50% RH) at constant temperature ( $T = 200^\circ\text{C}$ ) and during exposure to (a) only CO (50, 100, 150, 200 and 250 ppm), (b) only  $\text{NO}_2$  (1, 1.5, 2, 2.5, 3 ppm), (c) mixture of 50 ppm CO with  $\text{NO}_2$  (1, 1.5, 2, 2.5, 3 ppm), (d) mixture of 100 ppm CO with  $\text{NO}_2$  (1, 1.5, 2, 2.5, 3 ppm), (e) mixture of 150 ppm CO with  $\text{NO}_2$  (1, 1.5, 2, 2.5, 3 ppm), (f) mixture of 200 ppm CO with  $\text{NO}_2$  (1, 1.5, 2, 2.5, 3 ppm), and (g) mixture of 250 ppm CO with  $\text{NO}_2$  (1, 1.5, 2, 2.5 ppm).

#### 4. Conclusions and outlook

The results show that it is possible to identify the gases CO and  $\text{NO}_2$  in the ambient atmosphere by using only one sensor operated in the modulated temperature mode. They also illustrate that it is possible to use successfully sensors prepared in a hybrid technology, i.e. by combining silicon technology for manufacturing micromachined substrates with thick sensitive layers. Additional studies are now on the way to extend this approach to identify other gas mixtures with more components and to understand the basic physical phenomena. Future work will also be devoted to the development of appropriate feature extraction procedures for this non-linear frequency-time problem.

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#### References

- [1] W. Göpel, K.D. Schierbaum,  $\text{SnO}_2$  sensors: current status and future trends, *Sensors and Actuators B* 26–27 (1995) 1–12.
- [2] K. Ihokura, J. Watson, *Stannic Oxide Gas Sensors, Principles and Applications*, CRC Press, Boca Raton, FL, 1994.
- [3] P. Moseley, B. Tofield, *Solid State Gas Sensors*, Adam Hilger, Bristol, 1987.

- [4] N. Bârsan, R. Ionescu, A. Vancu, Calibration curve for SnO<sub>2</sub>-based gas sensors, *Sensors and Actuators B* 18–19 (1994) 466–469.
- [5] U. Weimar, W. Göpel, AC measurements on tin oxide sensors to improve selectivities and sensitivities, *Sensors and Actuators B* 26 (1995) 13.
- [6] H.V. Shurmer, J.W. Gardner, Odour discrimination with an electronic nose, *Sensors and Actuators B* 8 (1992) 1–11.
- [7] K.D. Schierbaum, U. Weimar, W. Göpel, Multicomponent gas analysis: an analytical chemistry approach applied to modified SnO<sub>2</sub> sensors, *Sensors and Actuators B* 2 (1990) 71–78.
- [8] R.E. Cavicchi, J.S. Suehle, K.G. Kreider, M. Gaitan, P. Chaaprala, Optimized temperature pulsed sequences for the enhancement of chemically-specific response patterns from micro-hotplate gas sensors, *Conf. Proc. of Transducers '95 and Eurosensors IX*, p. 823–826, Stockholm, 1995.
- [9] S.W. Wlodek, K. Colbow, F. Consadori, Signal-shape analysis of a thermally cycled tin-oxide gas sensor, *Sensors and Actuators B* 3 (1991) 63–68.
- [10] S. Nakata, H. Nakamura, K. Yoshikawa, New strategy for the development of a gas sensor based on the dynamic characteristics: principle and preliminary experiments, *Sensors and Actuators B* 8 (1992) 187–189.
- [11] S. Nakata, S. Akakabe, M. Nakasuji, K. Yoshikawa, Gas sensing based on a nonlinear response: discrimination between hydrocarbons and quantification of individual components in a gas mixture, *Anal. Chem.* 68 (1996) 2067–2072.
- [12] J.W. Gardner, A. Pike, N.F. de Rooij, M. Koudelka-Hep, P.A. Clerc, A. Hierlemann, W. Göpel, *Sensors and Actuators B* 26–27 (1995) 135–139.
- [13] M. Schweizer-Berberich, J.G. Zheng, U. Weimar, W. Göpel, N. Bârsan, E. Pentia, A. Tomescu, The effect of Pt and Pd surface doping on the response of nanocrystalline tin dioxide gas sensors to CO, *Sensors and Actuators B* 31 (1996) 1–5.
- [14] P.T. Moseley, D.E. Williams, oxygen surface species on semiconducting oxides, in: P.T. Moseley, J. Morris, D.E. Williams (Eds.), *Techniques and Mechanisms in Gas Sensing*, Hilger, Bristol, 1991, pp. 46–59.
- [15] M.J. Willett, Spectroscopy of Surface Reactions, in: P.T. Moseley, J. Morris, D.E. Williams (Eds.), *Techniques and Mechanisms in Gas Sensing*, Hilger, Bristol, 1991, pp. 61–107.