Sensors and Materials, Vol. 18, No. 5 (2006) 251–260
MYU Tokyo

S & M 0647

Identification of Toxic Gases Using Steady-State and Transient Responses of Gas Sensor Array

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(Received July 27, 2005; accepted January 31, 2006)

***Key words*:** oxide semiconductor sensor, sensor array, principal component analysis, selectivity enhancement

In this paper, we report the performance of a gas identification system based on a metal-oxide gas sensor array. Analyses of single gases, such as ammonia, hydrogen sulphide, carbon monoxide, nitrogen monoxide and acetylene diluted in air, are performed with these nonselective sensors. Both the transient and steady-state behaviors of sensors are measured. The sensor array consists of six gas sensors operating at three temperatures (from 300°C to 500°C). Principal component analysis (PCA) is applied in order to identify the target gases. We obtain a good classification of the four gases using the steady-state response and the dynamic response (response time). However, the dynamic response shows a higher repeatability than the steady-state response.

1. Introduction

Today, the detection of gases brings a major benefit to many fields, such as environmental monitoring, industrial control systems, chemical processes, and food and drink analysis.[1-5] The growing trend toward portable devices has caused an increasing demand for miniaturization. Semiconductor gas microsensors are part of this development. Although the sensors have been miniaturized, their performance remains to be improved. The essential performance of the sensors requires sensitivity, stability and selectivity. The sensitivity is satisfactory in the case of semiconductor, so called "Taguchi," SnO_2 sensors. The surface conductivity of a sensor is modified by the adsorption of gas species and related space-charge effects. In an oxidizing atmosphere, the oxide surface is covered by negatively charged oxygen adsorbates, and the adjacent space-charge region is electron depleted; the SnO_2 layer therefore presents a high resistance. Under reducing conditions, the oxygen adsorbates are removed by reaction with the reducing gas species and the electrons are reinjected into the space-charge layers. As a result, the semiconductor layer resistance decreases. Currently, the sensors are sufficiently sensitive for the majority of

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applications.[6–8] However, their main drawback is the unspecific interaction with almost any oxidizing or reducing gas, giving very large cross-effects. Considering the detection mechanism, it is difficult to design one-sensor systems with significantly improved selectivity. For the late few years, much work has been carried out with the aim of improving the selectivity of gas sensors, but only limited success can be foreseen by adding catalysts or filters.[4, 8–11] Clearly, the lack of selectivity of metal-oxide sensors, drift and low repeatability are barriers to the quantitative analysis of a single gas. It is thus necessary to think about other systems, particularly those using a combination of an array of poorly selective gas sensors or a multisensor device with a pattern recognition method.[13–20] On the other hand, more recent studies have demonstrated that the temperature modulation of a single sensor and measurement strategies (static and dynamic) can be used to enhance sensor selectivity.[10,12]

The purpose of this study is to analyze the ability of an array of cheap sensors associated with a temperature programming procedure to discriminate among various gases. The sensors have different structures (Taguchi-type, a thick or thin-film sensing element with an embedded heater). This choice improves the array selectivity because the gas exposure profile particularly depends on the microstructure, thickness and area of the sensing layer. The response of each sensor to the tested gases (ammonia, hydrogen sulphide, carbon monoxide, nitrogen monoxide and acetylene) is preliminarily characterized at different working temperatures. Both the dynamic and static behaviors of the sensors at the quasi-steady-state resistance change for each gas/air mixture are measured.

Principal component analysis (PCA) is a powerful, linear and nonsupervised pattern recognition technique used to analyze, classify and reduce the dimensionality in a multidimensional dataset.[21] It involves projecting data points on a line, a plane or a subspace of reduced dimensions selected in order to optimize a chosen criterion. Obviously, the dimensionality of the reduced space cannot be higher than three for suitable visualization and analysis of the results. PCA is also a powerful tool for showing the correlations between data (scores plots), and to gather data with similar characteristics (groups of gases). Moreover, the contribution of each sensor, with possible redundancies, is revealed (loading plots).[22,23] The principal limitation of the PCA technique is that it only uses linear data relationships.

2. Materials and Methods

2.1 *Sensors and experimental setup*

The array consists of six sensors from Figaro Inc. (Japan) and MicroChemical Systems SA (Switzerland). Table 1 shows the sensor characteristics and target gas given by the respective manufacturer. A humidity sensor is also included in the test chamber for monitoring the residual moisture. The sensors were selected for two principal reasons: their low cost and high commercial availability (Figaro is the leader in semiconductor gas sensors and the TGS-type sensors are used in many studies),[24,25] and their differences in sensing layer structure. Models TGS825 and TGS826 are Taguchi sensors: the sensing element is sintered to form a thick film on the surface of an alumina ceramic tube which contains an internal heater. They represent the oldest generation of tin oxide gas sensors.

Table 1
Characteristics of sensors used in array.

Sensor	TGS825	TGS826	TGS2611	MiCS2610	MiCS5131	MiCS5133
Gas	H_2S	NH_3	CH_4	O_3	CO	C_2H_5OH
Range of detection (ppm)	5–100	30–300	500–1000	0.01–10	10–1000	–
Nominal heating voltage (V)	5	5	5	2.35	3.2	3.2

Model TGS2611 has an integrated structure with a non-nanostructured thick film. The MiCS sensors use a nanostructured thin film deposited on an integrated heater.

The experimental setup is shown in Fig. 1. The sensor chamber is connected to a gas mixer using mass flowmeters. The target gases were NH_3, H_2S, CO, NO and C_2H_2 diluted in synthetic air with a constant total flow of 100 ml/min. The concentration was 100 ppm for the tested gases. The sensors were polarized as specified by the constructors. The working temperatures were settled independently for each sensor with heater voltages ranging from 4.75 V to 5.5 V for the Figaro sensors and 2.0 V to 3.4 V for the MiCS sensors. With these voltages, the sensor temperature varied in the range of 300°C to 500°C. A 10-channel multiplexer (Keithley 7001) was used to scan seven sensors of the array (six gas sensors and the humidity sensor) with a cycle period of 7 ms. A multimeter (Keithley 2000) measured the electrical resistance of the sensors, and data acquisition was controlled by a PC via a GPIB bus. The measurements were visualized in real time by a HP-VEE program and stored for further analysis.

2.2 *Test procedure and data processing*

In order to obtain more information for each sensor/gas combination and therefore to improve the selectivity of the semiconductor gas sensors, it is interesting to use different operating temperatures. Indeed, recent works have proved that sensor temperature modulation improves selectivity: a sensor operated at different temperatures behaves as different sensors at constant temperatures.[10,25] The sensors were initially maintained at a high temperature in air until the baseline was obtained, then exposed to gas for 10 min in order to reach the quasi-steady-state response. After gas exposure, the chamber was purged and the sensor heating temperature was regulated to the high temperature. Thus, desorption was enhanced and the response turned over more quickly to the baseline regardless of the temperature. This procedure was applied to each temperature studied. To take into account the low repeatability of the sensors, four identical experiments were performed at different dates. The sensor array was removed from the test chamber and kept in ambient conditions between each experiment.

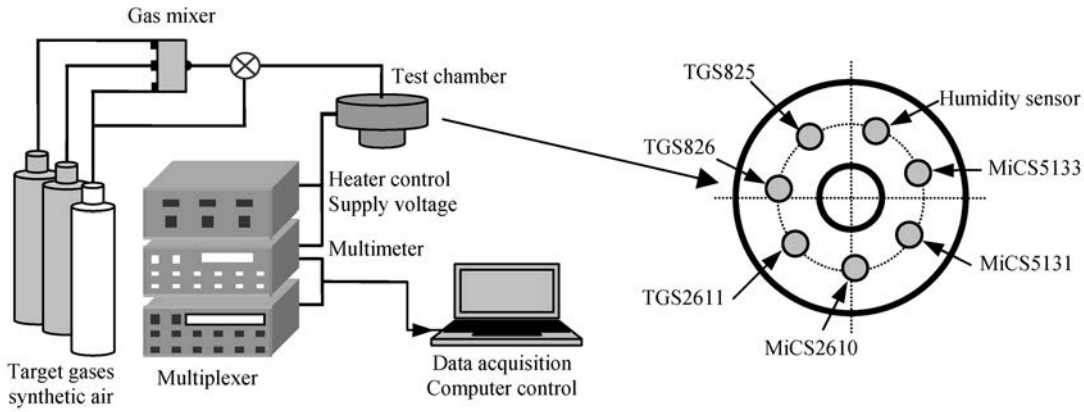

Fig. 1. Experimental setup for gas testing and detail of sensor array.

While the steady-state response of the sensor is usually a processed signal, both static and dynamic parameters were used in this study to characterize the sensor behavior. The static parameter S was the ratio R_{air}/R_{gas}, where R_{air} and R_{gas} are the sensor resistance in air and in a gas/air mixture, respectively. The resistance R_{gas} was measured 10 min after gas exposure, when a steady-state electrical change was reached. The dynamic parameter was the response time t_r defined as the time at which the signal amplitude reaches 90% of the final value recorded for a period of 10 min after the injection of a test gas sample. Figure 2 shows a typical sensor response and specifies the definition of the response time.

For a given gas, the static response S_{ij} and the response time t_{rij} of the sensor i at the temperature j were calculated and collected. We constituted both static and dynamic response matrices of size np, where n is the number of samples and p the number of sensors in the array. These matrices were used as the input data for PCA in order to discriminate among the target gases. The pattern recognition technique was performed using Statistica 6.1.

3. Results and Discussion

3.1 *Characterization of gas sensors*

The sensor characteristics were initially obtained by exposure to a target gas concentration from 50 ppm to 200 ppm. The sensors were heated at a constant operating temperature given by the manufacturers. Figure 3 presents the response of the TGS826 sensor to three reducing gases. Similar results are obtained for the other sensors. The sensors are sensitive, sufficiently stable and have good reproducibity during the same experiment if the first gas exposure is neglected, but they are poorly selective. Because of the detection

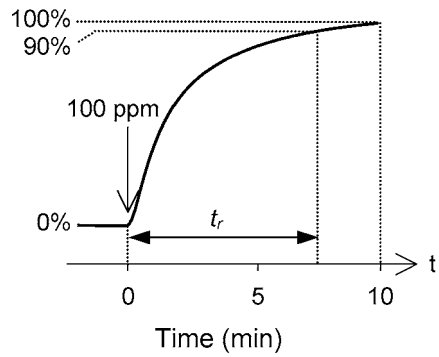

Fig. 2. Response of TGS825 sensor in presence of carbon monoxide. Definition of dynamic parameter t_r.

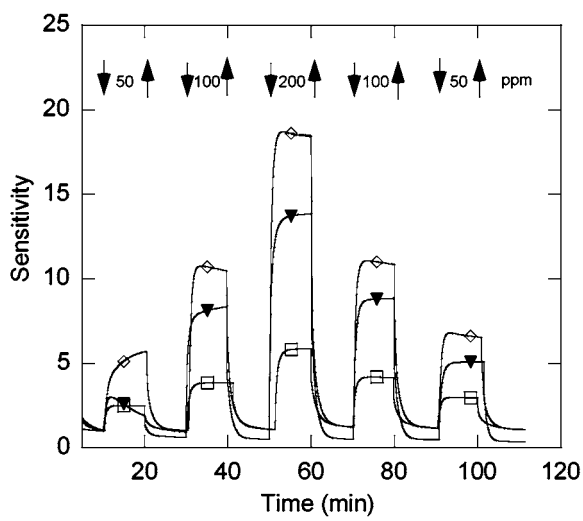

Fig. 3. Sensor response of commercial sensor (TGS 826) to different gases: H_2S (□), C_2H_2 (□) and NH_3 (□), at nominal heating voltage (5 V).

mechanism, they react roughly in the same way to all reducing gases. For example, 200 ppm of NH_3 gives the same response as 50 ppm of H_2S, so we cannot discriminate between various gas/air concentration combinations.

In order to obtain more information about the analyzed gas, the sensors were operated at various operating temperatures. Figure 4 presents the responses of the TGS825 sensor to different gases, at three working temperatures. The other sensors, TGS and MiCS, give similar results. Both the static and dynamic parameters of three experiments are shown in Figs. 4(a) and 4(b), respectively. The cross-effects with the static response are more important than those with the dynamic one; the sensor clearly has a different dynamic response to each gas. Moreover, the repeatability is better with this parameter: the data dispersion is lower in Fig. 4(b) than in Fig. 4(a).

3.2 *Discrimination of target gases*

PCA was performed for the steady-state response and response time matrices. The system was studied to discriminate among four gases (NH_3, H_2S, CO and NO, each gas concentration at 100 ppm). The matrices consist of forty eight lines (four tests × four gases × three sensor temperatures) and six columns (six sensors). The results of the PCA are shown in Fig. 5 using the static response data and the dynamic response data. In both cases, the first two principal components present a high cumulative variance (more than 83%): the PC1-PC2 plane is highly descriptive for classifying the tested gases. The gas classification with the first parameter reveals in Fig. 5(a) an overlap between the score plots of NH_3 and H_2S and, therefore, was not satisfactory. However, a perfect classification of the four gases in clearly separated clusters is obtained in Fig. 5(b) with the dynamic response of the sensor array.

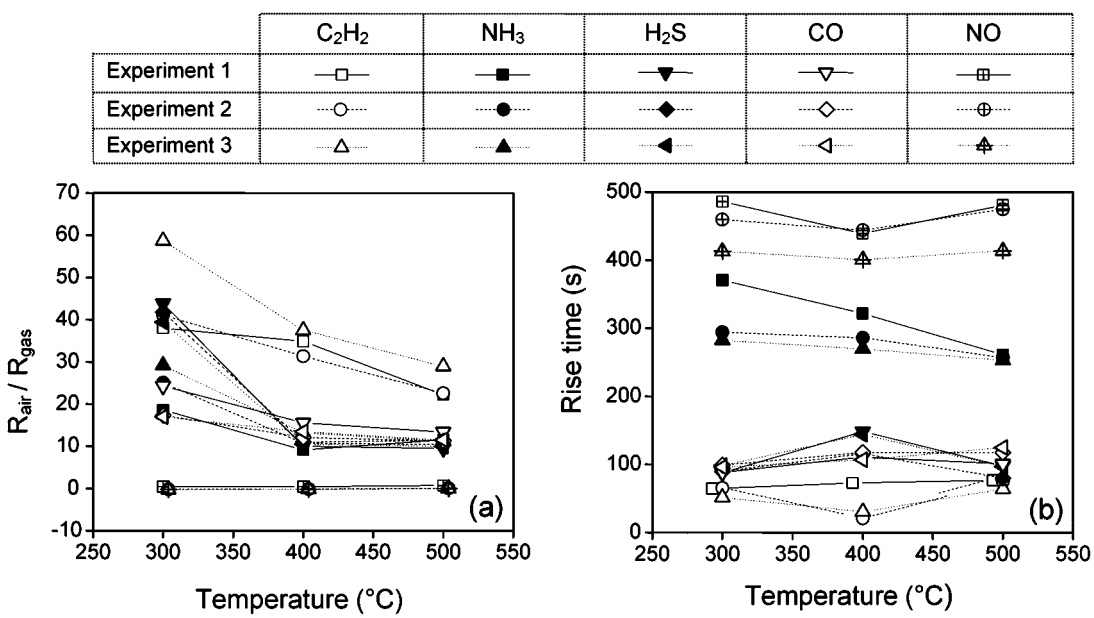

Fig. 4. Response of TGS825 sensor to different gases at three temperatures (a) static response and (b) dynamic response (response time). Each gas concentration: 100 ppm.

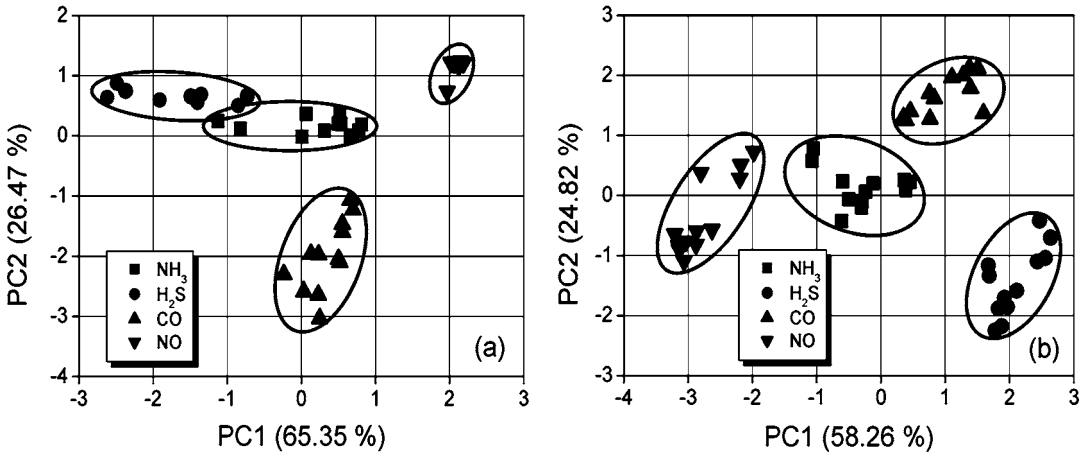

Fig. 5. Discrimination of four gases by six-sensor array operating at three temperatures using (a) static response and (b) dynamic response (response time).

In order to find the basic configuration of the matrix, i.e., to find the minimum number of sensors for gas identification, the relative importance of each sensor was evaluated by the analysis of loading plots: similar loadings indicate redundancy and colinearity in the response matrix. Three sensors had a small contribution, so they were removed from the sensor array. Figure 6 shows the discrimination of four gases using the dynamic response with only three sensors (TGS825, TGS2611 and MiCS5133). The score plot in the PC1-PC2 plane reveals a good classification of the four gases with distinct clusters. No satisfactory results were obtained with fewer than three sensors.

The performance of the complete array in discriminating various gases was evaluated with five gases. Data of another gas (C_2H_2) were added into the databases (both static response and dynamic response matrices). The matrices consist of sixty lines (four tests × five gases × three sensor temperatures) and six columns (six sensors). Figures 7(a) and 7(b) show both PCA results using the static response matrix and using the dynamic response matrix. An overlap between the scores plots of various gases reveals the limits to discriminating among five gases with the static responses, as shown in Fig. 7(a). This overlap is reduced in Fig. 7(b) using the dynamic responses but it remains between H_2S and C_2H_2 scores plots. These results prove that the dynamic response of sensors contains more information than the static response and gives a better gas classification.

This study emphasizes the measured parameter of the sensor response used for PCA. The steady-state electrical change (the static response) is the usual measure of such sensors. The other way is to study the complete transient (dynamic) behavior, characterized through the measurement of its electrical-change response time due to a step change in the gas exposition. This method has been developed in order to obtain rapid information on the sensor array and gives satisfactory results for the identification of various gases.[12,19,20]

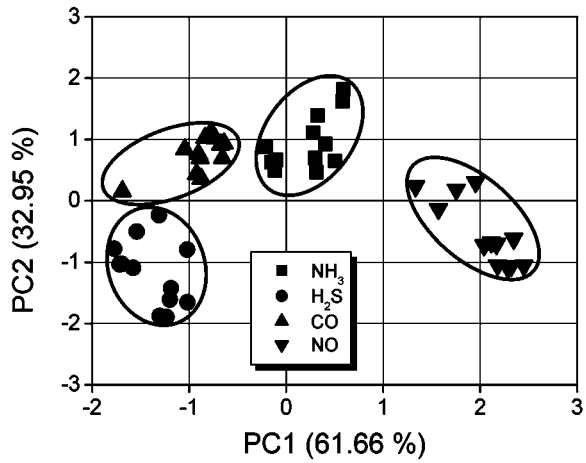

Fig. 6. Discrimination of four gases by reduced sensor array operating at three temperatures using dynamic response (response time).

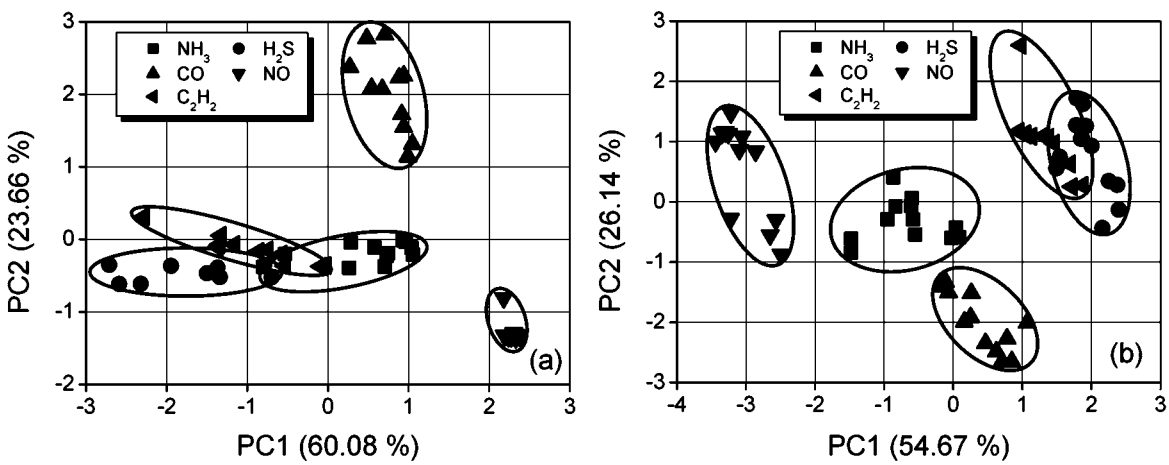

Fig. 7. Discrimination of five gases by six-sensor array operating at three temperatures using (a) static response and (b) dynamic response (response time).

Both parts of the gas-exposure profile bring information: the transient response reflects the kinetics of the gas/sensing film interaction, whereas the steady-state change reflects the thermodynamics of that reaction.[16] The experimental results of this work point out that the capability for gas identification is improved by using the dynamic response of the sensors rather than the usual steady-state electrical change. This result can be due to our array consisting of sensors with different structures. Indeed, the final electrical change is principally related to the sensing material, whereas the kinetics of the gas/sensing film interaction is related to the sensing material and to the structures of both the sensing layer and sensor.

4. Conclusions

In this work, we studied the ability to carry out gas analyses with a metal-oxide sensor array. The advantages of these sensors are their high commercial availability and low cost, but their selectivity is poor. PCA was performed as a pattern recognition method in order to identify different gases (ammonia, hydrogen sulphide, carbon monoxide, nitrogen monoxide and acetylene) diluted in synthetic air. Whereas the steady-state response of the sensors was usually used to characterize the sensor response, we used both steady-state and dynamic responses. Matrices were composed of steady-state measurements (static response) or the response time (dynamic response) of six sensors operating at three temperatures and used as the input data in a simple PCA. We showed that the dynamic behavior gives more information than the static one in the discrimination of gases and, using the former, a good classification of four gases (ammonia, hydrogen sulphide, carbon monoxide and nitrogen monoxide) was obtained. Moreover, the transient response shows higher repeatability and gives more information than the steady-state response. Indeed, the sensor response is dependent on the sensing layer structure. The results also point out the importance of a sensor temperature programming procedure and confirm that different sensor temperatures give more information on the chemical response. In spite of the low selectivity of metal-oxide sensors, improved gas detection is realizable with cheap sensors and a simple temperature programming method.

Acknowledgements

The authors wish to thank Alain Combes (laboratoire L2MP) for technical support.

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