

Measurements of VOCs with a Semiconductor Electronic Nose

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ABSTRACT

A semiconductor electronic nose with a sensor array of 15 elements has been fabricated by magnetron radio frequency sputtering technique for detecting various volatile organic compounds (VOCs) in a low concentration range from 50 to 250 ppm in air at 300°C. The main components of the array have been titanium oxide and tin oxide (the latter has been doped with different Pt doses) semiconductor oxides with different thicknesses. A good single classification for six tested VOCs (propanal, methyl ethyl ketone, octane, benzene, toluene, and chloroform) has been obtained from this electronic nose through the technique of principal component analysis. In general, good response times, sensitivity, and reproducibility values have been obtained for all sensors, but it is interesting to underline the sensitivity increases to these gases from sensors in which titanium oxide is used for their preparation.

Introduction

It is very important to develop measuring systems that allow one to carry out continuous and in situ measurements of gas mixtures for their recognition in different applications, such as soils, wines, foodstuffs, or perfumes, creating in this way discriminating electronic "noses" that classify various chemical environments. Thus, it will be possible to aid on solving the soil bioremediation or to carry out the quality control of wines,² since these electronic instruments can mimic the human sense of smell and achieve quick information at low cost, with a simple operating procedure compared to classical analytical techniques.

This work is aimed to improve soil remediation by means of the application of remedial technology, due to the contamination suffered from chemical species, such as volatile organic compounds (VOCs), which are dangerous to health as well as to the environment, and which come from wastes or pollution accidents.

Currently, analytical methods for the diagnosis of soils contaminated with VOCs are used. Coupling the use of the solid-phase microextraction technique to the conventional techniques of analysis makes it possible to extract and analyze some of the pollutants from soils. The most used technique is the chromatography in its different variants: thin layer chromatography, gas chromatography (GC), or high performance liquid chromatography, and especially high resolution gas chromatography/mass spectrometry (HRGC/MS), or high performance liquid chromatography/diode array detector. These techniques allow compounds to be identified not only by means of retention time, but also by spectral differences. Mobile methods are also used, such as: GC/MS for analyzing organic compounds, infrared instruments for aliphatic and aromatic hydrocarbons and X-ray fluorescence for heavy metals. Immunoassay and laserprobe are used for analyzing polycyclic aromatic hydrocarbons, and aliphatic hydrocarbons.³ These methods, however, present important problems for carrying out the analysis. For

example, the need of a lot of time and money determines that only a few samples are analyzed. For this reason, it is very important to develop faster and cheaper measuring systems for identification and quantification of contaminants to be used at hazardous waste sites, and that such systems perform continuous and in situ measurements, so that they will offer real-time data and therefore a more efficient detection of contaminated areas.

In this work, a semiconductor solid-state multisensor of small size is developed as a measuring system, and its responses obtained for detection of VOCs in air are shown. Mixtures of these gases have also been measured and their discrimination has been possible through pattern recognition techniques.⁴⁻⁶ The vectorial or matricial response is considered as a characteristic "fingerprint" of the contamination. We are currently working on the integration of the classification and the quantification steps for a VOCs gas analysis model, in which an unknown compound can be identified and the concentration of the gaseous mixture components can be estimated. The results obtained from this work are being used as reference measurements for experiments with wines, since VOCs are present within their composition.

Experimental

A multisensor with 15 different sensor elements distributed in circular sectors on alumina substrate of 1 in. diam was designed. Two semiconductor oxides, tin oxide and titanium oxide, were grown by sputtering (radio frequency-type and magnetron mode) at 250°C using SnO₂ and TiO₂ targets under a 10 to 90% oxygen-argon mixture for SnO₂, and 100% argon for TiO₂ at a total pressure of 0.5 Pa. Some SnO₂ sensors have been doped with different amounts of Pt, changing the deposition time during the sputtering process. Such element was introduced as an intermediate discontinuous layer between two layers equally thickened (sandwich structure). Electrical contacts were also deposited by sputtering from a Pt target. Table I shows multisensor distribution.

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Table I. Multisensor distribution.

Sensor No.	Semiconductor materials	Dopant (time)
1	SnO ₂ (1 layer ~100 nm)	
2	SnO ₂ (1 layer ~150 nm)	
3	SnO ₂ (1 layer ~200 nm)	
4	SnO ₂ (1 layer ~250 nm)	
5	SnO ₂ (2 layers ~100 nm each)	Pt (2 s)
6	SnO ₂ (2 layers ~100 nm each)	Pt (4 s)
7	SnO ₂ (2 layers ~100 nm each)	Pt (6 s)
8	SnO ₂ (2 layers ~100 nm each)	Pt (8 s)
9	SnO ₂ (2 layers ~150 nm. each)	Pt (2 s)
10	SnO ₂ (2 layers ~150 nm each)	Pt (4 s)
11	SnO ₂ (2 layers ~150 nm each)	Pt (6 s)
12	SnO ₂ (2 layers ~150 nm each)	Pt (8 s)
13	SnO ₂ (1 layer ~100 nm) + TiO ₂ (1 layer ~100 nm)	
14	SnO ₂ (1 layer ~150 nm) + TiO ₂ (1 layer ~150 nm)	
15	SnO ₂ (1 layer ~200 nm) + TiO ₂ (1 layer ~200 nm)	

Before carrying out the electrical characterization, the multisensor was thermally treated in air during 4 h at 520°C; thus the semiconductor morphology and resistance stability of each sensor were controlled.

The electrical measurements were carried out in the laboratory with a field measuring system or electronic nose (Fig.1), which comprises the described array of electronic chemical sensors, an electrical heater, a test chamber, and an electrical connector for the personal computer (PC),

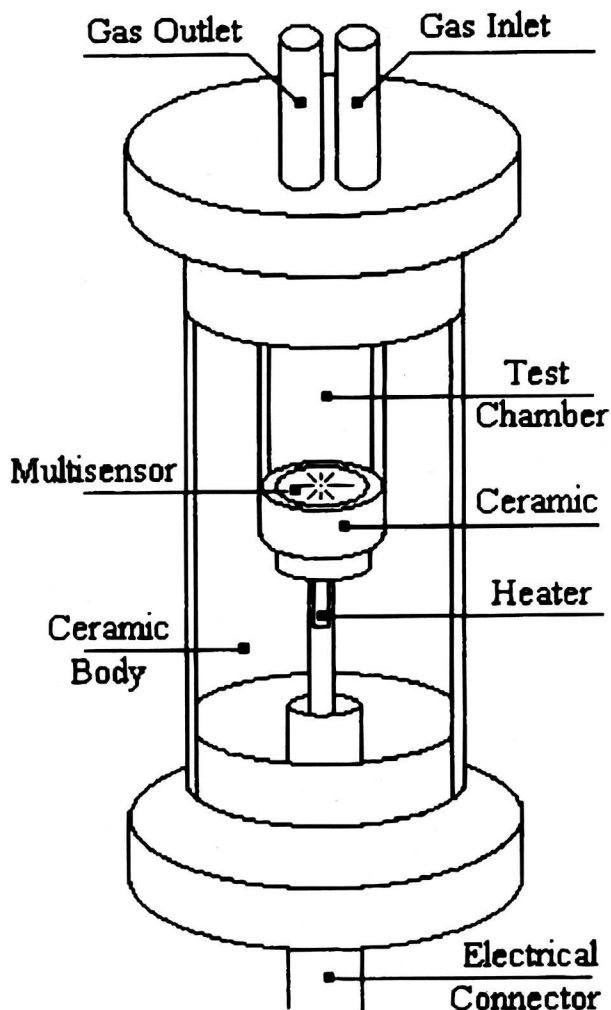
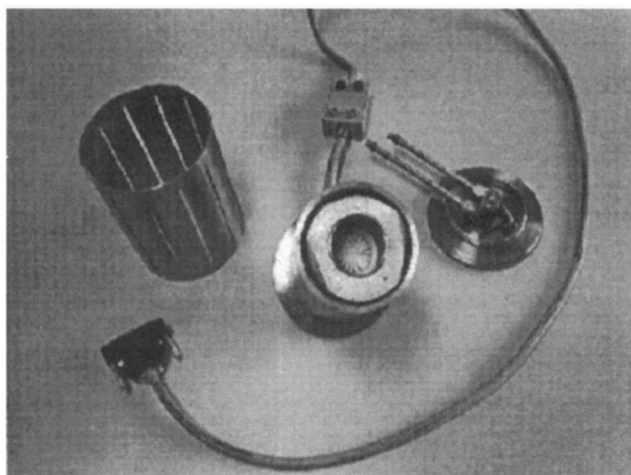


Fig. 1. (top) Field measuring system. (bottom) Parts of the measuring cell.

which accomplishes the data acquisition and analysis through an appropriate pattern-recognition system, capable of recognizing simple or complex mixtures of gases/vapors. The electrical heater placed within an isolating ceramic material, can reach up to an operating temperature of 500°C. The test chamber has an effective volume of 20 cm³, and the gas inlet and outlet are located at the top of the chamber.

The resistance measurements were carried out at 300°C with a constant flow rate of 200 mL/min for single VOC in synthetic air with concentrations varying from 50 to 250 ppm. The mixtures were prepared by means of mass-flow controllers into an automated gas line. The exposure time to each VOC concentration was 10 min. The electrical resistance values of each sensor were measured through digital multimeters with scanner cards connected to the PC by means of an IEEE data acquisition board.

The experiment for each VOC concentration was performed in two steps. First, the semiconductor resistance in synthetic air (baseline) was measured; and thereafter known VOC concentrations were introduced into the test chamber and the resistance changes were measured.

The sensitivity values for each sensor was calculated in the following way

$$S(\%) = (G_{\text{gas}} - G_{\text{air}})/G_{\text{air}} \times 100 = (R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}} * 100$$

where G is the electrical conductance.

Results and Discussion

Six VOCs were chosen for the electrical characterization as the most representative VOCs families in soils: propanal, methyl ethyl ketone (MEK), octane, benzene, toluene, and chloroform.

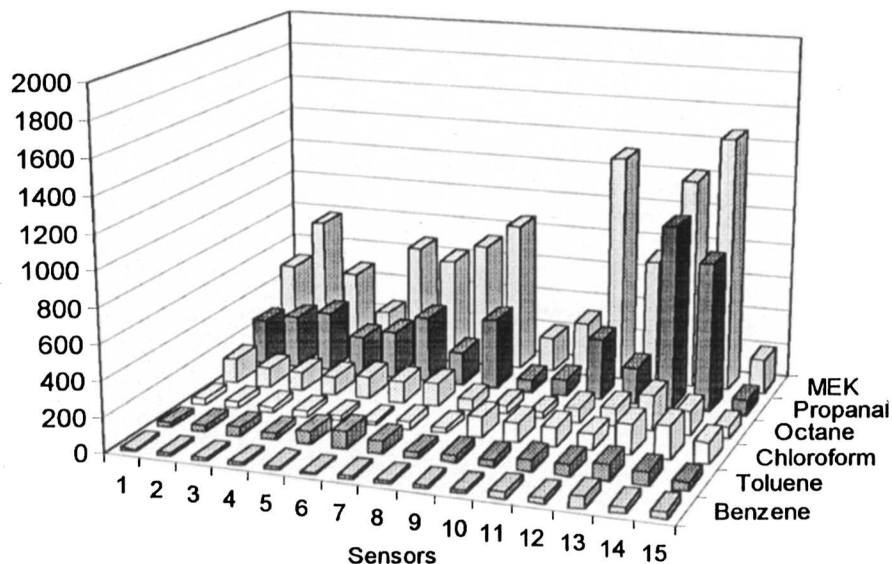
The sensitivity values obtained from the multisensor for 100 ppm of each VOC in air at 300°C are shown in Fig. 2. The best detection responses for each VOC are given from sensors no. 13 and 14, mainly for the most oxygenated compounds (MEK and propanal). Therefore, it is possible to conclude that the titanium oxide added to the tin oxide activates the oxidation reactions produced by these reducing gases on the semiconductor surface, so that the oxidation of such compounds is enhanced at greater extent than those prepared with SnO₂.⁷ Such fact is even greater than for tin oxide sensors doped with typical metals, such as Pd and Pt,⁷ used to catalyze oxidation reactions. An interpretation of the detection mechanism for these chemical compounds can be also seen in Ref. 7.

On the other hand, the film thickness has an important role in the sensitivity, because among sensors with only tin oxide those of lower thicknesses (100 to 200 nm) had a better response than the sensor with thickness of ~250 nm. With regard to Pt-doped tin oxide sensors with the lowest total thickness (~200 nm), the best sensitivity value was achieved in general for the sensor prepared with a deposition time of 8 s, although there were no important differences among results for various deposition times. However, those sensors with a thickness of approximately 300 nm showed the best behavior when the deposition time was 6 s. It is very important to get the optimum dose of dopant with regard to the semiconductor thickness. Considering titanium oxide films the sensor with greater thickness showed also a worse detection. This is due to the fact that those reactions take place on the sensor surface.

In general, all sensors showed short response (immediate) and equilibrium (few minutes) times to the VOCs and a good reproducibility. This last feature is observed in Fig. 3 for propanal in a concentration range varying from 50 to 250 ppm/air each 10 min.

Also, the principal component analysis (PCA) method was used to obtain the classification of single VOCs. The number of experiments was 51 per each single gas and therefore the total number was 306. All gases were tested for concentrations of 50, 100, 150, 200, and 250 ppm in air. The measurements were repeated ten times for each concentration except for the 50 ppm concentration that was repeated eleven times. In order to recognize VOCs mix-

Fig. 2. Sensitivities to 100 ppm in synthetic air for VOCs at 300°C.



tures, by artificial neuronal networks methods, different mixtures were used combining up to the six VOCs tested in this work; Ref. 8 shows the results obtained.

The following preprocessing algorithm of normalized fractional conductance, $X_{i,j}$, was used

$$X_{i,j} = \frac{\frac{G_{i,j} - G_{i,air}}{G_{i,air}}}{\sqrt{\sum_{i=1}^p \frac{(G_{i,j} - G_{i,air})^2}{G_{i,air}^2}}}$$

where $G_{i,j}$ and $G_{i,air}$ are the conductances of sensor i in the gas j and in air, respectively, and p is 15 in this case.

The optimum rank calculated for this system from PCA was 2, thus with the first two principal components all data were represented. The other principal components represented only noise. The results obtained showing the scores of the single gases tested and the loadings of the sensors can be seen in Fig. 4 and 5, and it can be concluded that it is possible to separate all gases because the points are clustered around the mean values of each gas. Some overlaps are observed that would lead to ambiguities in the identification. The experiments of octane, MEK, and propanal are near each other, whereas those corresponding to chloroform, benzene, and toluene are quite separated (Fig. 4). Results showed a good classification for these VOCs from the first two principal components. With regard to the loadings of the first two principal components, these show the relative contribution of each one of

the sensors to the recognition process: sensors with loading values next to zero indicate that they are redundant and sensors with similar loading values indicate collinearity in the response matrix. Figure 5 shows that the loading values are not very similar, and therefore, most sensors in the array contributed to the analysis process, since there was no dependence among them. The same results were obtained from the correlation coefficients calculated from

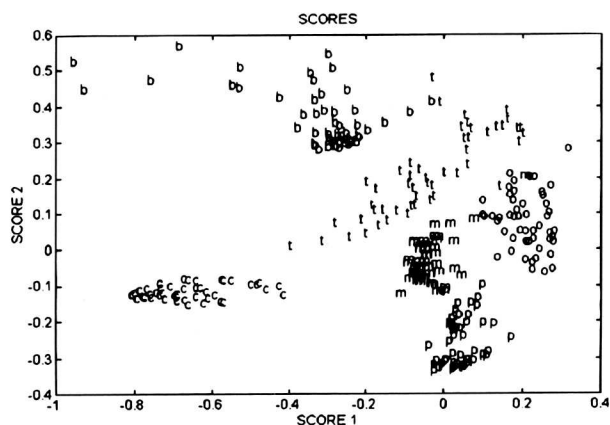


Fig. 4. Results of PCA showing the scores of benzene (b), chloroform (c), toluene (t), octane (o), propanal (p) and MEK (m).

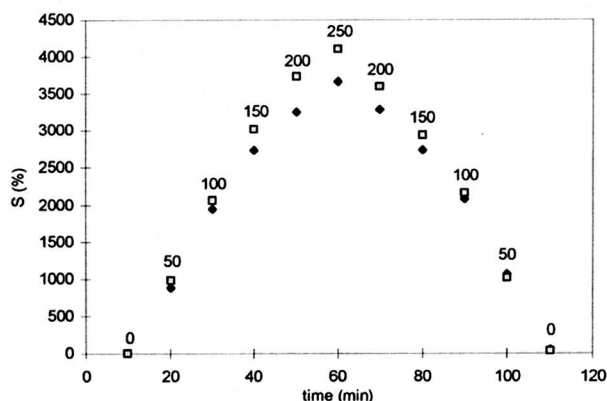


Fig. 3. Reproducibility of two experiments sweeping propanal concentrations from 0 to 250 ppm in synthetic air.

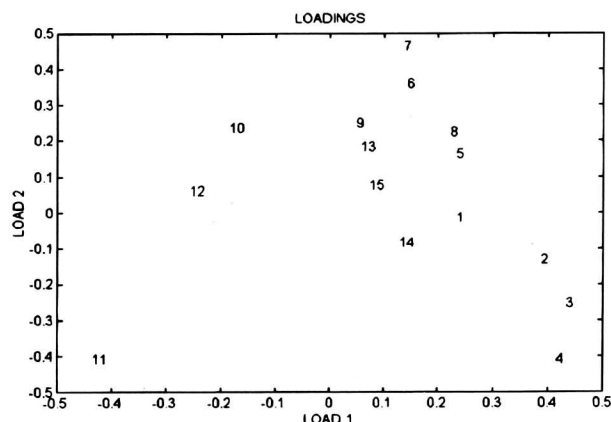


Fig. 5. Loadings of sensors array for the first two principal components.

an analysis of variance. All correlation coefficients were lower than 0.8, so there were no strong interdependence.

Conclusions

A sensitive selective electronic nose has been built that has various semiconductor oxides to detect and analyze low VOCs concentrations coming from soils. Titanium oxide plays an important role as catalyst of oxidation reactions produced for these compound types on the surface-sensor. Perhaps future research work will reveal that titanium oxide is, by itself, a better semiconductor oxide than tin oxide for detecting these compounds, or if the mixture of both is what produces a better detection. In any case it is clear that the number of O_2 vacancies increase and therefore better detections are achieved.

A good single classification of these VOCs has been obtained using the PCA method. The problems of collinearity and redundancy in the gas response, shown in previous prototypes of semiconductor electronic noses based on monolayer sensor array,^{6,8} were eliminated. In this device, each one of the sensors contributes to the analysis process.

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Interface States Distribution in Electrical Stressed Oxynitrided Gate-Oxide

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ABSTRACT

Quasi-static capacitance measurements and deep level transient spectroscopy measurements were combined to analyze the density of interface states in N_2O oxynitrides after constant-current Fowler-Nordheim injection from the silicon. Two defect levels are found, around $E_{t1} = E_c - 0.33$ eV and $E_{t2} = E_c - 0.2$ eV, having capture cross sections of 2×10^{-17} cm² and 3×10^{-18} cm², respectively. The stress creates a very high density of E_{t1} in the control sample. Stress-induced E_{t1} are associated with P_b centers, and their density decreases with increasing N_2O treatment temperature, from 850 to 1050°C. E_{t2} are detected in the oxynitrided layers before and after the stress and are much less affected by electrical stress than E_{t1} .

Introduction

The tendency toward the use of more severe electric fields across the dielectrics in the design of complementary metal oxide semiconductor (CMOS) and electronically erasable programmable read-only memory (EEPROM) devices demands a better understanding of the nature of SiO_2/Si interface states, their distribution, and their robustness against hot-electron stress.^{1,2} One of the types of defects most sensitive to high field stress or to irradiation involves a P_b center.³ This defect is a dangling silicon bond, backbonded to three other silicon atoms, or to two silicon atoms and one oxygen atom. This defect is amphoteric and has energy around $E_v + 0.30$ eV and $E_v + 0.8$ eV. Passivation of these interface states is possible via hydrogen annealing treatments⁴ which form Si-H bonds. However, when the devices are electrically stressed, the interface states appear again as these strained Si-H bonds are broken. In addition to these interface states, which have a peaked energy distribution, another type of defect is also found which seems to have a flat energy distribution.^{5,6}

Several techniques for improving gate oxide reliability have been studied, such as two-step oxidation,⁷ use of an oxidized-nitrided oxide,^{8,9} incorporation of Cl or F in the

oxide,^{10,11} and use of stacked dielectric films.^{12,13} Oxynitridation has shown very promising results for the improvement of metal oxide semiconductor (MOS) gate oxide. Different techniques have been attempted to form oxynitrides at the Si/SiO_2 interface, such as reoxidation of NH_3 -nitrided SiO_2 ,¹⁴ oxidation of Si in pure N_2O ,^{15,16} and oxynitridation of thermally grown SiO_2 in N_2O .¹⁷ Improved reliability under hot-carrier stressing is achieved by an N_2O -based approach as opposed to an NH_3 nitridation approach, because the N_2O process is hydrogen-free. Using Auger electron spectroscopy, secondary ion mass spectroscopy, and electrical characterizations, Hori et al.¹⁸ suggested that the improved electrical properties are caused by the presence of nitrogen atoms (N) at the Si/SiO_2 interface. Possible mechanisms that could account for these phenomena are: (i) the nitrogen may cause the rearrangement of the SiO_2 at or near SiO_2/Si interface which may increase the resistance against constant-current Fowler-Nordheim (CCFN) stress and (ii) P_b center formation is prevented by blocking or retarding the hydrogen arrival at the interface.¹⁹⁻²¹

In this article, quasi-static capacitance (QS) and deep level transient spectroscopy (DLTS) techniques are used to investigate the concentration of interface states and their distribution, in polysilicon-oxide-silicon devices after

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