Comparative study of various metal-oxide-based gas-sensor architectures

C.A. Papadopoulos, D.S. Vlachos, J.N. Avaritsiotis

National Technical University of Athens, Electrical Engineering Department, Division of Computer Engineering, 157 73 Zographou, Athens, Greece

Abstract

Reactively sputtered SnO_x and InO_x thin films, plain and surface doped with Pt, have been covered with layers of various insulating films and catalysts. Test gases used are carbon monoxide, methane, ethanol, butane and propane. Filters used are alumina (Al_2O_3), silicon oxide (SiO_2) and tungsten trioxide (WO_3). Palladium has also been added on the surface of alumina filters, while platinum is added on the surface of metal-oxide sensor films. Response to hydrocarbons, and especially to butane and propane is found to be enhanced with the addition of noble metals on the sensing film or on the filter. It is also found that a WO_3 filter improves the carbon monoxide sensitivity at low working temperatures and reduces the sensor response to ethanol with respect to other test gases. The behaviour of indium-oxide-based sensors is qualitatively very similar to that of tin-oxide-based sensors.

Keywords: Gas sensors; Metal oxides

1. Introduction

The detection of gas leaks in houses is a major application in gas-sensor technology. Since ethanol vapour is the main interfering gas in a domestic ambience, the need for selective gas sensors with respect to ethanol is obvious, in order to avoid false alarms. Several methods to suppress the effect of ethanol have been proposed, among which those reported in Refs. [1,2] are of special interest. These methods are based on the fact that the domestic gas, in this case methane, burns at a higher temperature than ethanol, or on the catalytic oxidation of methane on various noble metals, such as Pd or Pt. When a noble metal was incorporated in a filter, it was assumed that the filter would burn all the rest of the gases except methane. In that way only methane would reach the sensing element, providing methane selectivity. However, these devices gave very disappointing results [1]. The results of recent investigations concerning the use of relatively complex geometries of gas filters and catalysts have been presented in Rome during the *5th International Meeting on Chemical Sensors* [3,4]. In Ref. [3] selectively permeable ceramic coatings of SiO_2 and Al_2O_3 were deposited on SnO_2 thin films by r.f. magnetron sputtering or chemical vapour deposition. Coatings of SiO_2 and Al_2O_3 were found to induce pronounced selectivity changes, compared to uncoated SnO_2 films. In Ref. [4] laminating layers, selectively permeable to methane, were deposited on SnO_2 thin films. The ratio of sensitivity to methane against that to hydrogen reached a value of 200 by optimizing the microscopic structure of SnO_2 thin films and optimizing the catalytic activity of the laminating layer.

In this work eight SnO_x- and eight InO_x-based sensors were tested. Pt doping was used on some of the semiconductor oxide films and Pd doping was used on some of the filters. Note that Pd doping was not used on the sensing films, since palladium-doped sensors have not been found to be either selective or stable, in contrast with platinum-doped sensors, which were found to exhibit both selectivity and stability. The fabrication details of the 16 sensors (eight SnO_x- and eight InO_x-based sensors) are shown in Table 1. Doping either on the sensing material or on the filter was used only with alumina filters.

Silicon oxide and alumina were used as filters because these materials are known as gas barriers, and their use is pursued in the food-packaging industry. Moreover, WO_3 was used because of its ability to trap hydrogen [5,6].

2. Experimental techniques

Deposition of SnO_x films was performed with a Leybold Z-400 planar magnetron sputtering system, which was d.c. operated in a controlled, high purity Ar–O_2 mixture. Two different discharge modes may be obtained, the metallic mode and the reactive mode, where the target is respectively free from or covered with reaction products. The compound for-

Table 1
Description of the architecture of the samples used to conduct the present study and maximum sensitivities of the sensors at each test gas at the specified working temperature, in degrees Celsius

Tin-oxide-based sensors	Doping on metal oxide	Doping on filter	CO 2000 ppm	CH$_4$ 10 000 ppm	Ethanol 26 ppm	Butane 20 000 ppm	Propane 20 000 ppm
SnO$_x$ plain			148/450	200/450	11000/400	200/330	600/370
SnO$_x$ + SiO$_x$			116/450	171/450	4400/400	264/210	400/210
SnO$_x$ + Al$_2$O$_3$-40			100/450	100/450	2900/420	100/200	300/200
SnO$_x$ + Al$_2$O$_3$-100			195/450	100/450	1220/450	131/270	200/380
SnO$_x$ + WO$_3$			100/450	88/420	1000/380	70/300	235/360
SnO$_x$ + Al$_2$O$_3$-40 + Pd		Pd	142/380	255/420	4980/390	747/210	939/360
SnO$_x$ + Pt + Al$_2$O$_3$-40	Pt		135/240	282/420	2460/450	940/240	1790/240
SnO$_x$ + Pt + Al$_2$O$_3$-40 + Pd	Pt	Pd	176/450	96/450	1160/420	243/330	1460/270
Indium-oxide-based sensors							
InO$_x$ plain			80/450	112/450	3300/450	94/350	270/420
InO$_x$ + SiO			70/450	117/450	2790/400	170/330	276/420
InO$_x$ + Al$_2$O$_3$-40			69/450	97/450	2820/450	73/250	225/420
InO$_x$ + Al$_2$O$_3$-100			79/450	92/450	2780/450	77/280	181/420
InO$_x$ + WO$_3$			93/420	75/450	1200/430	94/370	234/380
InO$_x$ + Al$_2$O$_3$-40 + Pd		Pd	214/250	196/250	5095/420	1448/200	1120/370
InO$_x$ + Pt + Al$_2$O$_3$-40	Pt		47/240	300/210	1325/450	1713/220	1404/280
InO$_x$ + Pt + Al$_2$O$_3$-40 + Pd	Pt	Pd	652/210	416/210	2720/420	7030/210	3090/260

mation reactions are desirable in the metallic mode for high deposition rates and for a more precise control of the O$_2$/ metal (Sn or In) ratio of the deposited film. This necessitates the use of a plasma emission monitor (PEM) system, which allows us to select and maintain the degree of target oxidation [7], with the tin or indium emission line intensity at 450 nm as a measurand for the control loop of the reactive gas mass-flow controller. This technique has proved adequate for the fabrication of reproducible films.

Films were fabricated at a relatively high total gas pressure of approximately 1.0×10^{-2} mbar. The substrate holder was at a distance of 7 cm from the 10 cm diameter target. The total power into the target was 115 W with a total current of 0.36 A, thus achieving a deposition rate of approximately 100 nm min^{-1}. The argon flow was adjusted manually at 20 ml min^{-1}, while the oxygen intake was controlled by the afore-mentioned PEM control unit, so that the intensity of the tin or indium emission line remained constant.

By varying the deposition temperature and pressure we can control the film structure. Density and crystallite size increase with temperature. It was found [8] that at a deposition temperature of 460 °C we have a low-density film (43% single crystal) with a medium crystallite size (11 nm) and a high specific area (50 m^2 g^{-1}). This structure is suitable for high sensitivity, but the mechanical properties of the film depend on the density in an opposite sense to the sensitivity. For even higher deposition temperatures (560 °C) the microstructure is even more dense (85% single crystal) with a larger crystallite size (30 nm) and a lower specific area (15 m^2 g^{-1}). A scanning electron micrograph of such a sample shows a fine modular microstructure with spherical grains. Moreover, we know that the total pressure during deposition affects the film structure [8]. Films are compact for a total pressure less than 5×10^{-2} mbar, become columnar for pressures up to 0.8 mbar and become spongy for pressures higher than 0.8 mbar.

The deposition of our films was carried out on Al$_2$O$_3$ substrates with dimensions 12 mm × 26 mm, heated at 300 °C, a temperature which ensures that the film consists mainly of [110] crystallites [9].

Platinum was deposited on the SnO$_x$ or InO$_x$ films with electron-beam evaporation, with a thickness of the order of a few nanometres. Platinum films with thicknesses in this region are expected to be discontinuous and non-conducting [10]. Palladium was also deposited on the alumina filters with electron-beam evaporation, with thicknesses slightly above those of platinum. Note that the roles of platinum on the sensing layer or palladium on the filter are expected to be different.

SiO$_2$ was formed by thermal evaporation of SiO powder and subsequent oxidation at 500 °C for 48 h. WO$_3$ was formed by thermal evaporation of WO$_3$ powder. Alumina was formed by thermal evaporation of pure aluminium and subsequent oxidation at 500 °C for 48 h. This procedure was found to be adequate for full oxidation of a 100 nm aluminium film. Note that all sensors (even plain ores) were submitted to a 48 h annealing at 500 °C, so that all the samples have the same pretreatment. The thicknesses of the silicon oxide and tungsten trioxide were measured with a Talystep profile meter and found to be around 100 nm. Two alumina filters were used, one 40 nm thick and one 100 nm thick.

The sensor characterization set-up was designed to measure the steady-state and transient response of the samples, testing them at various working temperatures and under different gas compositions. The testing conditions were rigorously controlled via a fully automated computer-controlled

system. All sensors have been characterized according to the following experimental procedure:

- The samples were heated to 450 °C and cooled back to 150 °C in zero-grade air (ZGA, dry synthetic mixture of 80% N_2 and 20% O_2). This step was repeated three times before starting film characterization, in order to clean water vapour remains from the samples.
- The samples were heated to 450 °C and cooled back to 150 °C in 2000 ppm carbon monoxide diluted in ZGA.
- The samples were heated to 450 °C and cooled back to 150 °C in ZGA.
- The last two steps were repeated four times again, but with test-gas compositions of 10 000 ppm methane, 26 ppm ethanol, 20 000 ppm butane and 20 000 ppm propane in ZGA, instead of CO.

During the aforementioned measuring cycles, the resistance of the samples was recorded at 5 °C intervals as the samples were cooled from 450 to 150 °C. The cooling speed was 10 °C min^{-1}. At temperatures above 250 °C, this speed ensures that no significant transient effects have been recorded [11].

3. Experimental results and discussion

Experimental results are shown in Figs. 1–4. Fig. 1 and Fig. 2 show the response of a plain tin oxide sensor and a tin oxide sensor covered with a WO_3 filter, respectively, while Fig. 3 and Fig. 4 show the response of a plain indium oxide film and an indium oxide film with WO_3 filter, respectively. Each Figure shows the conductance of each sensor to ZGA

(empty circles), to 2000 ppm CO (squares), to 10 000 ppm methane (triangles), to 26 ppm ethanol (diamonds), to 20 000 ppm butane (hexagons) and to 20 000 ppm propane (shaded circles). Note that the Figures show the logarithm of the conductance versus reciprocal temperature ($1/T$). The values for maximum sensitivity (which is defined as the maximum conductance change in the presence of a reducing gas over conductance in ZGA) of each sensor at each test gas are shown in Table 1.

Table 1 shows that both SnO_x- and InO_x-based devices exhibit similar sensitivity values to the same test gases. For most sensors the sensitivity to ethanol is about one order of magnitude higher than the sensitivities to the other test gases, although the ethanol concentration is almost three orders of magnitude lower.

3.1. SiO_2 gas barriers

3.1.1. Tin oxide

From Table 1 one can see that an SiO_2 filter has little effect on the SnO_x sensor behaviour. Maximum sensitivity values for the two sensors (without filter and with SiO_2 filter) are very close and the conductance versus temperature curves have the same shape (i.e., the conductance maxima appear at the same temperature regions). However, the conductance of the sensor with an SiO_2 filter is slightly higher than that of the plain sensor under the presence of all test gases (and under the presence of ZGA as well), except ethanol. In order to explain such a behaviour we could simply accept that the SiO_2 filter prevents oxygen from adsorbing on the SnO_x surface. Possibly a thicker SiO_2 filter would show a more pro-
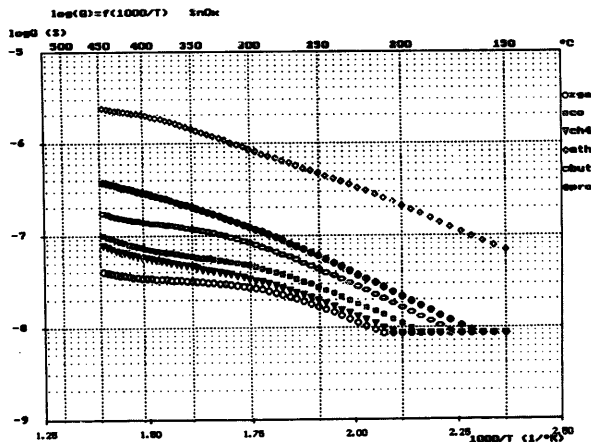

Fig. 1. Log conductance vs. reciprocal temperature plot of the plain SnO_x sensor response in the presence of the test gases. Test gas concentrations are 2000 ppm for CO, 10 000 ppm for CH_4, 26 ppm for ethanol, and 20 000 ppm for butane and propane. Measurements were taken at a cooling speed of 10 °C min^{-1}.
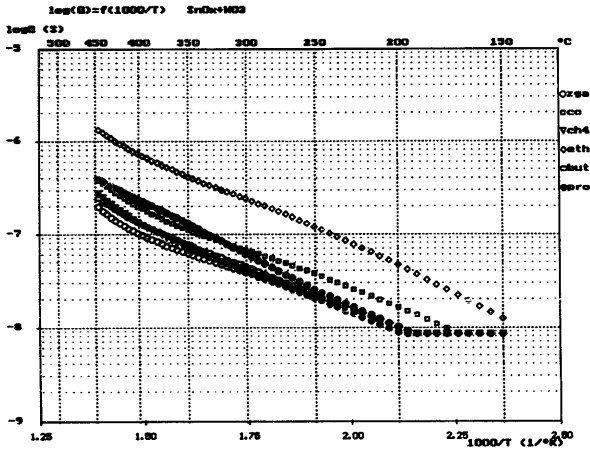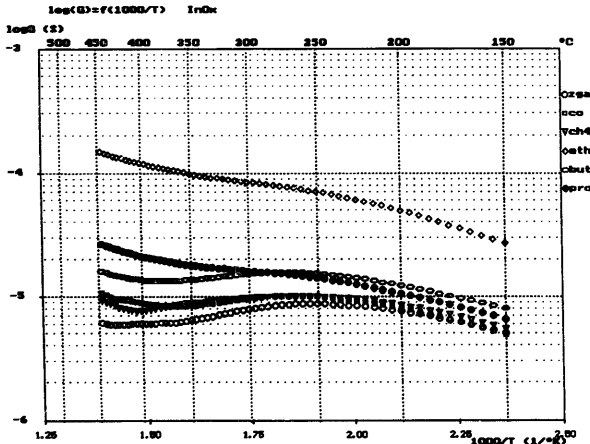
Fig. 2. Log conductance vs. reciprocal temperature plot of the $SnO_x + WO_3$-100 nm sensor response in the presence of the test gases. Test gas concentrations are 2000 ppm for CO, 10 000 ppm for CH_4, 26 ppm for ethanol, and 20 000 ppm for butane and propane. Measurements were taken at a cooling speed of 10 °C min⁻¹.

Fig. 3. Log conductance vs. reciprocal temperature plot of the plain InO_x sensor response in the presence of the test gases. Test gas concentrations are 2000 ppm for CO, 10 000 ppm for CH_4, 26 ppm for ethanol, and 20 000 ppm for butane and propane. Measurements were taken at a cooling speed of 10 °C min⁻¹.

nounced effect, if the aforementioned mechanism is valid. It is widely known that oxygen molecules adsorbed on an SnO_x surface decrease the conductance, and lack of oxygen increases the conductance [12–14]. As a consequence, the lower oxygen partial pressure due to the filter leads to higher conductance. In order to explain the lower sensitivity values for the test gases, reactions of test gases with an SnO_x surface should be considered.

Carbon monoxide is adsorbed on pre-adsorbed oxygen species (O^-, O^{2-}, O_2^-) or hydroxyl groups, forming car-
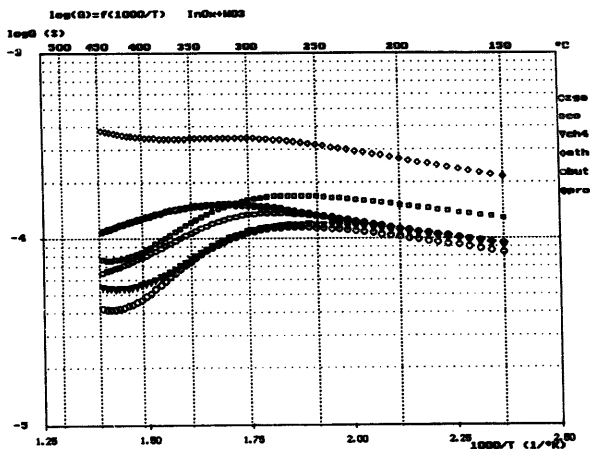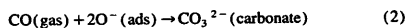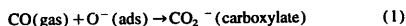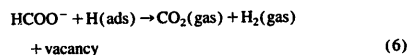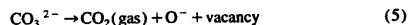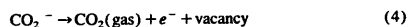
Fig. 4. Log conductance vs. reciprocal temperature plot of the $InO_x + WO_3$-100 nm sensor response in the presence of the test gases. Test gas concentrations are 2000 ppm for CO, 10 000 ppm for CH_4, 26 ppm for ethanol, and 20 000 ppm for butane and propane. Measurements were taken at a cooling speed of 10 °C min⁻¹.

boxylate (CO_2^-), carbonate (CO_3^{2-}) or formate ($HCOO^-$) species, depending on the kind and density of available pre-adsorbed species and on temperature [12,15]:

$$CO(gas) + O^-(ads) \rightarrow CO_2^-(carboxylate) \qquad (1)$$

$$CO(gas) + 2O^-(ads) \rightarrow CO_3^{2-}(carbonate) \qquad (2)$$

$$CO(gas) + OH^-(ads) \rightarrow HCOO^-(formate) \qquad (3)$$

Decay of the above species is believed to be the dominant mechanism contributing to carbon monoxide sensitivity:

$$CO_2^- \rightarrow CO_2(gas) + e^- + vacancy \qquad (4)$$

$$CO_3^{2-} \rightarrow CO_2(gas) + O^- + vacancy \qquad (5)$$

$$HCOO^- + H(ads) \rightarrow CO_2(gas) + H_2(gas)$$
$$+ vacancy \qquad (6)$$

Above 500 K formate on SnO_x can react to give formaldehyde:

$$HCOO^- + OH^-(ads) \rightarrow H_2CO(gas) + 2O^-(ads) \qquad (7)$$

Noting that since carbon monoxide adsorbs only on pre-adsorbed species (reactions (1), (2) and (3)), the presence of a filter preventing oxygen from adsorbing on the SnO_x surface (like SiO_2) is expected to reduce the sensitivity to carbon monoxide, as indeed happens (Table 1). However, the conductance of the sensor with an SiO_2 filter in the presence of CO is higher than that of the plain sensor, although the sensitivity of the sensor with an SiO_2 filter is lower than that of the plain sensor (Table 1). This is due to the higher

base (i.e., in the absence of a reducing gas) conductance of the sensor with the filter.

In addition, the presence of the silicon oxide filter seems to have no effect on the response of the sensor to hydrocarbons (methane, butane and propane), as can be derived from Table 1. The higher conductance of the sensor with the filter in the presence of hydrocarbons, compared to those of the plain sensor, is due to the higher base conductance.

3.1.2. Indium oxide

From Table 1 we can see that an SiO_2 filter also has little effect on the InO_x sensor behaviour. Maximum sensitivity values for the two sensors (without and with an SiO_2 filter) are very close and the conductance versus temperature curves have the same shape (i.e., conductance maxima at the same temperatures). The conductance of the sensor with an SiO_2 filter is slightly higher than that of the plain sensor, denoting that the filter has a similar effect on both tin- and indium-oxide-based sensors. Although a conductance mechanism for indium oxide has not been explicitly proposed, the assumption that it is very similar to that of tin oxide (i.e., due to conduction electrons attributed to oxygen vacancies) seems to be supported from the aforementioned behaviour.

3.2. Al_2O_3 gas barriers

3.2.1. Tin oxide

The base conductance of the sensors with an alumina filter is increased compared to that of the plain sensor, implying that, like an SiO_2 filter, alumina is an oxygen barrier. It is

interesting to note that the response of the sensor with a thin (40 nm) alumina filter is very similar to the response of the sensor with the SiO_2 filter. However, the thick (100 nm) alumina filter remarkably reduces the sensor response to ethanol, as can be seen in Table 1.
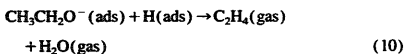
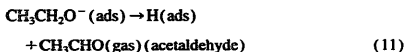Ethanol adsorbs on tin atoms of the tin oxide surface via the oxygen atom of its hydroxyl group:

$$CH_3CH_2OH(ads) \rightarrow CH_3CH_2O^-(ads) + H(ads) \qquad (8)$$
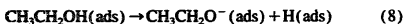
Hydrogen of Eq. (8) can react to form water and desorb. Near 400 K and between 660 and 750 K ethylene and water are desorbed:

$$CH_3CH_2OH(ads) \rightarrow C_2H_4(gas) + H_2O(gas) \qquad (9)$$

Ethylene may also be evolved by decomposition of the ethoxy group of Eq. (8):

$$CH_3CH_2O^-(ads) + H(ads) \rightarrow C_2H_4(gas)$$
$$+ H_2O(gas) \qquad (10)$$

Acetaldehyde desorption has also been detected:

$$CH_3CH_2O^-(ads) \rightarrow H(ads)$$
$$+ CH_3CHO(gas)(acetaldehyde) \qquad (11)$$

Since no pre-adsorbed species are required for the chemical adsorption of ethanol on tin oxide surface (ethanol adsorbs on tin atoms of the crystal, Eq. (8)), we should accept that the reduced response of the sensor with the thicker (100 nm) alumina filter to ethanol is due to the effect the filter has on the reactions of ethanol with the tin oxide surface. Alternatively, we could accept that the thicker alumina filter prevents ethanol from adsorbing on the tin oxide surface.

3.2.2. Indium oxide

From Table 1 we can see that Al_2O_3 filters little affect the InO_x sensor behaviour. Ethanol sensitivity dominates and all corresponding curves have the same shape. The thicker alumina filter increases the base conductance of the InO_x sensor. If we accept that the conduction mechanism of indium oxide is similar to that of tin oxide (i.e., the conductance is controlled by the concentration of oxygen vacancies, acting as donors and providing conduction electrons to the bulk), we observe an effect of the alumina filter proportional to its thickness. The behaviours of both SnO_x-based and InO_x-based sensors are very similar, and their maximum sensitivity values are very close (Table 1), although InO_x-based sensors are generally two orders of magnitude more conductive than SnO_x-based ones.

3.3. WO_3 gas barriers

3.3.1. Tin oxide

A WO_3 filter on a tin oxide surface (Fig. 2) has a larger effect both on the shape of the conductance versus temperature curves and on the ethanol sensitivity, which is reduced with respect to the sensitivities to other test gases. This may

be attributed to the fact that WO_3 can react with hydrogen atoms released from ethanol reaction with the SnO_x surface and form a bronze; this traps the hydrogen atoms necessary for the next steps of ethanol interaction with the sensor, critical for film conductivity (reactions (8) to (11)). Another difference in the behaviour of this sensor compared to the behaviour of sensors covered with silicon oxide or alumina is the higher sensitivity to carbon monoxide at low temperatures (compare Fig. 2 with Fig. 1). Note that hydrogen is necessary for reaction (6) to take place. Lower availability of hydrogen may favour Eqs. (4) and (5), having a larger effect on the sensor conductivity.

3.3.2. Indium oxide

In the case of the InO_x sensor with a WO_3 filter, the conductance in the presence of all test gases is remarkably increased by almost one order of magnitude (compare Fig. 3 with Fig. 4). It is also interesting to note that the conductance of the $InO_x + WO_3$ sensor above 300 °C shows a negative temperature coefficient to all gases except ethanol. Another interesting observation is that the conductance of the InO_x sensor with WO_3 barrier in the presence of CO at low temperatures (less than 300 °C) is remarkably high, just as in the case of the SnO_x sensor with WO_3 filter. A very similar behaviour of the indium-oxide-based sensors to that of the tin-oxide-based sensors is observed, forcing us to accept that reactions analogous to the ones found for tin oxide should occur on the InO_x surface.

From the previous observations we may conclude that silicon oxide and alumina may be characterized as inert filters, reducing the sensitivity to all test gases uniformly. On the other hand, a tungsten trioxide (WO_3) filter on both SnO_x- and InO_x-based sensors increases the response to carbon monoxide and decreases the response to ethanol. This behaviour is expected, given that WO_3 adsorbs hydrogen [5,6]. Lack of hydrogen may affect the reactions of ethanol on the sensor surface that affect the film conductance.
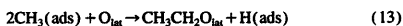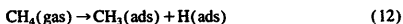
3.4. Effect of additives

3.4.1. Pd doping onto alumina filter

3.4.1.1. Tin oxide

From Table 1 it is obvious that the palladium addition on the filter seems to have a large effect on sensor response. The conductance of the sensor in the absence of a reducing gas was reduced. This behaviour may be due to spillover of oxygen [16,17]. The conductance in the presence of hydrocarbons, especially butane and propane, is remarkably increased, giving large sensitivity values for these gases, as shown in Table 1. Reactions of methane on a tin oxide surface are given in the next paragraph.

Methane dissociates on an SnO_x surface to a methyl group and a hydrogen adatom. Two methyl groups can combine to form a rooted ethoxy-like species [15]:

$$CH_4(gas) \rightarrow CH_3(ads) + H(ads) \qquad (12)$$

$$2CH_3(ads) + O_{lat} \rightarrow CH_3CH_2O_{lat} + H(ads) \qquad (13)$$

Ethylene and water may be formed from ethoxy-like species:

$$CH_3CH_2O_{lat} + H(ads) \rightarrow H_2O_{lat} + C_2H_4(gas) \qquad (14)$$

$$CH_3CH_2O_{lat} + H(ads) \rightarrow H_2O(gas)$$
$$+ C_2H_4(gas) + vacancy \qquad (15)$$
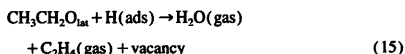
Ethoxy-like species can be converted to acetate-like species:

$$CH_3CH_2O_{lat} + O_{lat} \rightarrow CH_3CO_{lat}O_{lat} + 2H(ads) \qquad (16)$$

Finally, formate-like species may be formed, which in turn may decay to carbon dioxide, as in the CO case (Eq. (6)) and produce oxygen vacancies, increasing the conductivity:

$$CH_3O_{lat}O_{lat} + 2H(ads) \rightarrow CH_4(gas) + HCO_{lat}O_{lat} \qquad (17)$$

Note that pre-adsorbed oxygen species are not required for methane reactions. Hydrogen adatoms are required for the decay of formate-like species.

Reactions for non-methane hydrocarbons have not been explicitly proposed, but it may be assumed that reactions similar to those of methane take place. Hydrocarbons with more carbon atoms in their molecule are expected to dissociate easier than methane [15]. Higher response to butane or propane compared with that to methane can be ascribed to the high energy required for reactions (12) and (13) to occur. Hydrogen atoms are needed for reactions (14) and (15). Palladium may act as a catalyst for the dissociation of hydrogen [18,19] on the sensor surface, favouring reactions (14) and (15). It is also interesting to note that conductance under a butane- or propane-containing environment exhibits maxima at temperatures below 400 °C. Response to ethanol is slightly decreased. Concluding, a Pd-doped alumina filter results in high sensitivity to butane and propane. If we accept that palladium acts as a catalyst for hydrogen (in addition to oxygen), we would expect an increased sensitivity to hydrocarbons, according to the reactions postulated for methane (and as a consequence for hydrocarbons). Increased sensitivity to methane is not observed due to the high energy required for the adsorption of a methane molecule on an SnO$_x$ surface, in addition to the high energy required for the combination of two methane molecules to form one ethane molecule.

3.4.1.2. Indium oxide
Similar response was observed for the indium oxide sensor with an alumina filter doped with palladium. The conductance of the sensor under most test gases was increased with respect to the sensor without palladium on the alumina filter, while the conductance in the presence of ZGA remained practically unaltered (it was slightly reduced at temperatures above 350 °C). The sensitivity to butane or propane was remarkably increased as can be seen in Table 1. The sensitiv-

ity to CO was also slightly enhanced. The assumption that Pd acts catalytically (oxygen spillover) is confirmed, since SnO$_x$- and InO$_x$-based sensors exhibit comparable behaviour.

3.4.2. Pt doping onto metal oxide film

3.4.2.1. Tin oxide
While Pd on the filter is expected to affect the adsorption mechanisms of some gases on the sensor surface (and further diffusion through the alumina filter to the sensing layer), Pt on the semiconductor film is expected to have a large influence on the conduction mechanism of the sensor. Experimental results for the SnO$_x$ and InO$_x$ sensors with platinum doping under the alumina filter are shown in Table 1.

From Table 1 one can see that Pt doping on the tin oxide film reduces the sensitivity to ethanol. As a result, the effect of propane or butane dominates, exhibiting a peak at around 320 °C. This sensor exhibits high sensitivity to hydrocarbons and especially propane.

3.4.2.2. Indium oxide
More interesting is the behaviour of the InO$_x$-based device, which exhibits remarkably low sensitivity to ethanol, in contrast to that to hydrocarbons. In order to explain such a behaviour we should accept that platinum acts catalytically, resulting in a different conduction mechanism, perhaps tunnelling between discrete Pt clusters [20].

3.4.3. Pt doping onto metal oxide film and Pd doping onto alumina filter

3.4.3.1. Tin oxide
The combined effect of palladium addition on the filter and platinum under the alumina filter results in a reduction of sensor conductance under all testing conditions. The conductance of the SnO$_x$-based sensor under a ZGA environment is unmeasurable with the equipment used (lower than 10 nanosiemens). This can be explained if we assume that oxygen molecules dissociate on palladium clusters and diffuse to the bulk, occupying vacant sites (spillover effect [16,17]). In addition, the presence of noble metals on the metal oxide grains creates a depletion layer due to the difference of the noble metal work function and the electron affinity of the metal oxide semiconductor. As a consequence, the combination of these two mechanisms may be responsible for the large conductance decrease. The sensitivity to propane remains high, while that to ethanol is low. Recall that the peak conductance in the presence of propane was at about 320 °C for the SnO$_x$ + Pt + Al$_2$O$_3$ sensor, while it was reduced to about 280 °C with palladium addition (SnO$_x$ + Pt + Al$_2$O$_3$ + Pd sensor).

3.4.3.2. Indium oxide
An analogous effect to Pd addition on the InO$_x$ + Pt + Al$_2$O$_3$ sensor was also observed. The base conductance of the sensor was reduced by one order of magni-

tude, while the conductance in the presence of propane and butane remained at the same values, resulting in a sensor highly selective to propane and butane.

4. Conclusions

From the study of the effect of various filters on semiconductor-oxide-based gas sensors the following conclusions may be drawn:

- Inert filters like alumina or silicon oxide do not provide significant selectivity enhancement.
- Tungsten trioxide as a filter has an opposite result to ethanol than to other gases. The conductance of tin-oxide-based sensors in the presence of ethanol is reduced, while the conductance in the presence of carbon monoxide is slightly increased at low temperatures. For indium-oxide-based sensors, the conductance is generally increased, but again the sensitivity to ethanol is reduced with respect to those to the other test gases, especially carbon monoxide at low temperatures. In general a tungsten trioxide filter on SnO_x and InO_x films improves the sensor selectivity for CO at relatively low working temperatures and it also dramatically reduces the sensor response to ethanol over the entire working temperature region, as can be seen in Fig. 2 and Fig. 4. The sensitivity values of Table 1 may be misleading, due to the higher base conductance of the sensors with WO_3 filters.
- The use of an inert filter such as alumina in conjunction with a very thin palladium layer on it enhances the sensitivity to butane and propane, while the response to ethanol is practically unaffected.
- The use of a very thin platinum layer under an inert filter (alumina) acts catalytically for sensitivity to hydrocarbons with respect to ethanol. In the case of the InO_x-based sensor, even methane exposure caused a significant response in sensor conductance.
- The combined use of a palladium additive on the inert filter and a platinum additive under it reduces the sensor conductivity, but the conductance in the presence of butane and especially propane remains high.
- Indium-oxide-based devices are generally two orders of magnitude more conductive than tin-oxide-based ones. However, the behaviour of indium-oxide-based devices is qualitatively very similar to the behaviour of tin-oxide-based ones, considering all sensor structures and all test gases used. This experimental observation provides evidence to postulate that the sensing mechanisms of tin and indium oxide films should be very similar. Reactions of reducing and oxidizing gases occurring on an InO_x surface should be very similar to the ones found for SnO_x films. Oxygen partial pressure seems to play the same role for the conductance of both films [12–15].

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Biographies

C.A. Papadopoulos was born in Greece in 1966. He received the B.E. degree in electrical engineering from the

National Technical University of Athens in 1990. He is currently enrolled in the Ph.D. program in electrical engineering at the National Technical University of Athens.

Since 1993 he has been working for the National Technical University of Athens, Department of Electrical Engineering, Division of Computer Science, Microelectronics Technology Laboratory as a research engineer. His research interests include automation and control, chemisorption theory and fabrication of solid-state gas sensors.

He is a student member of the IEEE.

D.S. Vlachos was born in Pireas, Greece, in 1967. He received the B.E. degree in electrical engineering from the National Technical University of Athens in 1991. He is currently enrolled in the Ph.D. program in electrical engineering at the National Technical University of Athens.

Since 1992 he has been working for the National Technical University of Athens, Department of Electrical Engineering, Division of Computer Science, Microelectronics Technology Laboratory as a research engineer. His research interests include modelling and simulation of gas–solid interface interactions, chemisorption theory, fabrication of solid-state gas sensors, neural networks and fuzzy neural networks for gas sensing.

John Avaritsiotis was born in Greece in 1948. He received his B.Sc.(Hons.) degree in physics from the Department of Physics of the University of Athens in 1972. His M.Sc. and Ph.D. degrees were obtained from Loughborough University of Technology, UK, in 1974 and 1976, respectively, in the field of thin-film technology and the fabrication of thin-film devices.

From 1976 to 1979 he was employed as a research fellow in the Thin Film Group of Loughborough University of Technology. From 1980 to 1986 he was a lecturer at the Electronics Laboratory of Athens University, and in 1986 he was elected associate professor in the Department of Electrical Engineering of the National Technical University of Athens. In 1990 he was elected professor of microelectronics in the same department.

He has worked as a technical consultant to various British and Greek industrial firms for the incorporation of new thin-film deposition techniques in their production processes.

He has published over 30 technical articles in various scientific journals, and has presented more than three dozen papers at international conferences.

His research activities have been focused in the field of microelectronic materials and thin-film deposition techniques for use in the fabrication of semiconductor devices. His present research interests concern the study of the electrical properties of thin insulating and semiconducting films deposited by sputtering, on-chip interconnections and MCMs for high-speed circuits, design of ASICs, development of fabrication processes for the production of solid-state gas sensors and design and prototyping of smart sensors.

Professor Avaritsiotis is a member of the Editorial Advisory Board of the journal *Active and Passive Electronic Components*, a Guest Editor of *IEEE Transactions on Components, Packaging and Manufacturing Technology*, and a senior member of IEEE and a member of IOP and ISHM.