ELSEVIER

Sensors and Actuators B 24–25 (1995) 883–885

SENSORS AND ACTUATORS B CHEMICAL

# The effect of film oxygen content on $SnO_x$ gas-sensor selectivity

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

*National Technical University of Athens, Electrical Engineering Department, 15773 Zographou, Athens, Greece*

**Abstract**

The effect of the oxygen content in tin oxide films on selectivity in gas detection has been studied. The experimental results show that sensors with different Sn:O ratios exhibit different behaviour in response to CO and ethanol. A theoretical explanation of this phenomenon is presented, which is based on the density of oxygen vacancies at the surface. Moreover, a simple parametric method using three sensors with different Sn:O ratios has been tested to distinguish between CO and ethanol.

*Keywords:* Gas sensors; Tin oxide

## 1. Introduction

Semiconductor gas sensors based on tin oxide are widely used for the detection of toxic and explosive gases in air. Their advantages are high sensitivity, simple design, low power consumption and cost. But the selectivity of these sensors to different gases has been found to be poor. For this reason, various techniques have been used to increase the selectivity. The four [1] popular ways of doing this (i.e., catalysts and promoters in order to increase the response to a specific gas, temperature control to obtain maxima at different temperatures, specific surface additives and the use of filters) have reached a technical bottleneck.

Pattern-recognition methods have been successfully used [2] as an alternative treatment of the selectivity problem. In the case of neural networks, one should use sensors that, without being selective, exhibit different correlation factors to various gases. The small differences in sensor behaviour can then be compiled to give a very selective device. But serious problems may arise in such networks, like the continuous repetition of the learning procedure due to sensor instabilities.

In contrast, the use of a parametric method can only be successful in the case of the parameterization of a specific phenomenon. For example, using some parameters that describe the curve of the sensor behaviour as a function of temperature, one can compile the different maxima of this curve.

In this work, a method is proposed that produces sputtered thin-film tin oxide sensors with different correlation factors to CO and ethanol. The flow of oxygen during deposition affects the Sn:O ratio of the produced film and consequently differentiates the sensitivity. The differences in the behaviour of these sensors can be parameterized and they give the opportunity of applying a simple method and three sensors with different Sn:O ratios to distinguish between CO and ethanol.

## 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 formation reactions are desirable in the metallic mode for high rate depositions, and for a more precise control of the Sn:O 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 [3], with the tin emission-line intensity at 450 nm as a measurand for the control loop of the reactive gas mass-flow controller.

Films were fabricated at a relatively high total gas pressure of approximately $1.0\times10^{-2}$ mbar. The substrate holder was at a distance of 7 cm from the 10 cm diameter target. The total power into the tin target


*SSDI* 0925-4005(94)01486-2

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 to 20 ml $min^{-1}$, while the oxygen intake was controlled by the above-mentioned PEM control unit, so that the intensity of the tin 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 [4] 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 [5]. Films are compact for total pressures less than $5\times10^{-2}$ mbar, but become columnar for pressures up to 0.8 mbar and then spongy for pressures higher than 0.8 mbar.

The effect of substrate temperature during film deposition was also studied for substrate temperatures between 100 and 500 °C. XRD studies of films prepared at different temperatures gave the results presented in Fig. 1. It is apparent from Fig. 1 that a preferential crystallite orientation occurs mainly at a substrate temperature of 300 °C. Consequently, all subsequent films were deposited at 300 °C, a substrate temperature that ensures both preferential crystallite orientation and columnar structure, as observed by XRD analysis and SEM studies, respectively.

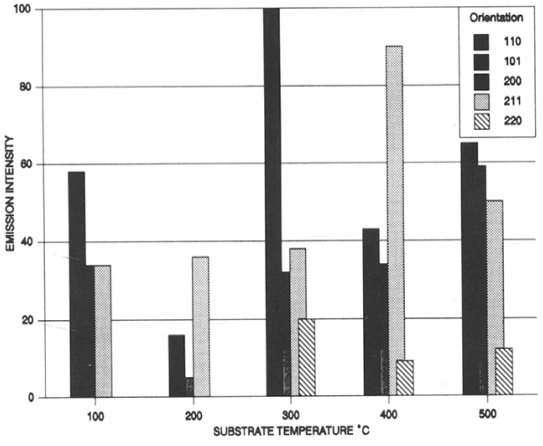


Fig. 1. Tin oxide film structure obtained from XRD measurements vs. substrate temperature during film deposition.

Film dimensions were approximately 1.2 mm×2.0 mm after using an appropriate metal contact mask. The mask was cleaned in an HCl solution before sputtering, in order to remove $SnO_x$ remains from previous deposition runs. The films were fabricated with a constant Ar flow of 20.0 ml $min^{-1}$ and with variable $O_2$ flows, in order to achieve different Sn:O ratios in each film. When the oxygen flow was varied from 24 to 45 ml $min^{-1}$, the Sn:O ratios were varied from 0.8 to 0.44. If the Sn:O ratio is high, the films have a metallic form and cannot function as gas sensors; if the Sn:O ratio is relatively low the fabricated films are highly resistive (small concentration of oxygen vacancies) and again cannot function as sensors. The sputtering system was operated in constant-current mode. The thickness of all films fabricated was equal to 2000 nm (20 min sputtering time).

The set-up for the sensor characterization was designed in order to measure the steady-state and transient responses of the samples, and to test them under different temperatures and different ambient gases. The testing conditions were rigorously controlled via a fully automated computer-controlled system.

## 3. Discussion

It is well known [6,7] that CO is chemisorbed mainly on already chemisorbed oxygen atoms. Thus, the sensitivity to CO is proportional to the number of oxygen adatoms. Moreover, the density of oxygen adatoms is proportional [6] to the density of oxygen lattice vacancies, and these vacancies are inversely proportional to the oxygen flow during sputtering. Thus, an almost linear dependence of sensitivity on oxygen flow is expected. On the other hand, in the case of ethanol, the mechanism is a little more complicated. First ethanol is weakly chemisorbed on tin atoms, via the oxygen atom of its OH group. Thus, the chemisorption is proportional to the oxygen vacancies. Afterwards, one or two hydrogen atoms from ethanol may react with oxygen adatoms, giving one or two electrons to the crystal. The sensitivity $S$ is then given by

$$S \propto \theta_V \theta_O^x \quad (1)$$

where $\theta_O$ is the density of oxygen adatoms, $\theta_V$ is the density of oxygen lattice vacancies and $x$ is a number between 1 and 2, which depends on the ratio of the amount of ethanol molecules that dissociate by giving one hydrogen atom over those molecules that dissociate by giving two hydrogen atoms. Since the density of oxygen adatoms is proportional to the density of vacancies, it means that the sensitivity to ethanol is inversely proportional to the $(1+x)$th power of the oxygen flow during sputtering. Fig. 2 shows the sensitivity

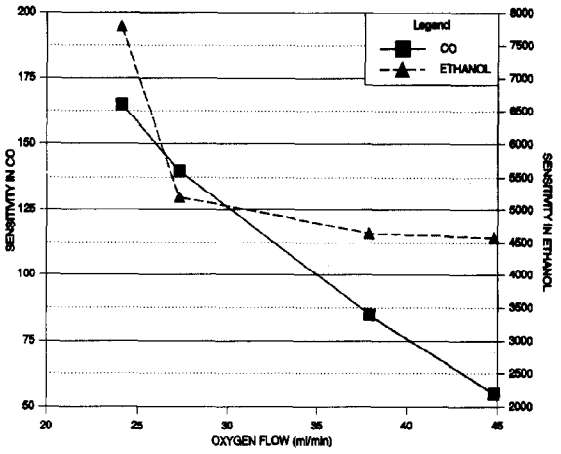


Fig. 2. Sensitivity of $SnO_x$ films to CO and ethanol vs. oxygen flow during the sputtering of the films.

of $SnO_x$ films to ethanol and CO as a function of the oxygen flow during the sputtering of the films.

Under these assumptions, we can select three sensors with different Sn:O ratios. Let $f_i$ be the oxygen flow during deposition of the sensor $i$. Then, the sensitivity $S_i$ of the sensor $i$ may be given by

$$S_i = S_3 + (S_1 - S_3)\left(1 - \frac{f_i - f_1}{f_3 - f_1}\right)^y \tag{2}$$

where $y$ is close to one in the case of CO and equals $(1+x)$ in the case of ethanol, which means a value greater than two. After collecting the data $S_i$, points $S_1$ and $S_3$ are immediately fixed. Then we can find the exponent $y$ that fixes the curve (2) with the point $S_2$. Then $y$ is given by

$$y = \frac{\log\left(\frac{S_2 - S_3}{S_1 - S_3}\right)}{\log\left(\frac{f_3 - f_2}{f_3 - f_1}\right)} \tag{3}$$

Then, the value of $y$ can monitor the two gases. For example, in the case of sensors deposited with oxygen flows of 24.1, 27.4 and 44.8 ml $min^{-1}$, one gets in the case of CO the value $y=0.9$ and in the case of ethanol the value $y=2.41$. One of the basic characteristics of this method is that $y$ depends on the chemisorption mechanism, but must be independent of the oxygen deficiency of the sensors.

## 4. Conclusions

The deposition of thin-film tin oxide gas sensors with reactive magnetron sputtering using different oxygen flow rates has been found to produce films with different Sn:O ratios. Then the amount of lattice oxygen may be related to the oxygen flow rate during deposition. It was shown that, since the interaction of both carbon monoxide and ethanol with tin oxide surfaces is related to the degree of oxidation of tin, a simple parametric method can be developed in order to distinguish between the two gases.

## References

[1] S.R. Morrison, Selectivity in semiconductor gas sensors, *Sensors and Actuators, 12* (1987) 425–440.

[2] J.W. Gardner and P.N. Bartlett, in P.T. Moseley, J.O.W. Norris and D.E. Williams (eds.), *Techniques and Mechanisms in Gas Sensing*, Adam Hilger, Bristol, 1991, Ch. 14, pp. 347–380.

[3] C.D. Tsiogas and J.N. Avaritsiotis, Monte Carlo simulation of high rate reactive sputtering of tin oxide in planar d.c. magnetron systems, *Thin Solid Films, 219* (1992) 270–277.

[4] B. Gautheron, M. Labeau, G. Delabouglise and U. Schmatz, Undoped and Pd-doped $SnO_2$ thin films for gas sensors, *Sensors and Actuators B, 15–16* (1993) 357–362.

[5] C. Pijolat, P. Breuil, A. Methivier and R. Lalauze, An electrical percolation model for tin dioxide polycrystalline thin films, *Sensors and Actuators B, 13–14* (1993) 646–648.

[6] P.D. Skafidas, D.S. Vlachos and J.N. Avaritsiotis, Modelling and simulation of tin oxide based thick-film gas sensors using Monte Carlo techniques, *Sensors and Actuators B, 18–19* (1994) 724–728.

[7] D. Kohl, Surface processes in the detection of reducing gases with $SnO_2$-based devices, *Sensors and Actuators, 18* (1989) 71–113.