



CO response of a nanostructured SnO₂ gas sensor doped with palladium and platinum

P. Ménini^{a,*}, F. Parret^a, M. Guerrero^a, K. Soulantica^b, L. Erades^b,
A. Maisonnat^b, B. Chaudret^b

^a Laboratoire d'Analyse et d'Architecture des Systèmes (CNRS-LAAS), 7 Avenue du Colonel Roche, 31077 Toulouse Cedex 4, France

^b Laboratoire de Chimie de Coordination (CNRS-LCC), 205 Route de Narbonne, 31077 Toulouse Cedex 4, France

10 Abstract

11 In this paper, we show the influence of humidity on the sensitivity for CO sensing of the nanoparticulate SnO₂ sensors at an operating
12 temperature of 450 °C. Three different sensors have been studied: un-doped sensors and doped sensors with two doping agents palladium
13 and platinum. It is well known that the resistance of the sensitive layer is largely modified by doping. This study demonstrates that un-doped
14 sensors show under CO a sensitivity less important in humid air than in dry air. Doped sensors display a very different behavior. Indeed, in
15 dry air, a high sensitivity is observed, characterized by an increase in the resistance of the sensitive layer whereas in humid air (>10% RH) a
16 high sensitivity is also observed but characterized by a decrease in the resistance of the sensitive layer. In between, a point of zero sensitivity
17 is found. These results carry out the presence of unexpectedly different electrochemical operating mode for CO sensing according to the
18 humidity content.

19 © 2004 Published by Elsevier B.V.

20 *Keywords:* Gas sensors; SnO₂; Nanoparticles; Doping; CO sensitivity

21 1. Introduction

22 At present time, most of the gas sensors are either electro-
23 chemical or metal-oxide semiconductors in thick-film [1] or
24 in thin-film [2] technology. The main problems of these tech-
25 niques are: moderate level of sensitivity, low reproducibility,
26 low selectivity, long stabilization periods and high power
27 consumption for the thick layer. However, the gas sensor
28 technology has integrated for a few years the development
29 of nanomaterials.

30 This article deals with a new generation of nanopartic-
31 ular SnO₂ gas sensors (Fig. 2) currently studied and de-
32 veloped within the context of an European project entitled
33 “Nanosensoflex” which consists in developing gas sensors
34 for flexible automotive and domestic applications. Due to
35 the reduction of grain size, this new technology of sensitive
36 layer allows a very high surface-on-volume ratio and then
37 may display a high level of sensitivity [3].

38 However, different aspects of this kind of sensors have to
39 be studied to acquire the sensing principles and to improve
40 their present performances.

A way to improve the performance of SnO₂-based sen- 41
sors both in term of sensitivity and response time for a broad 42
range of gases is doping them with small amounts of noble 43
metal [4–6]. In this case, the sensitivity and selectivity 44
properties have been shown to depend greatly on the distri- 45
bution and the crystal size of the added noble metals [7–10]. 46
To achieve a homogeneous Pd and Pt doped SnO₂ sensor 47
layers starting from tin nanoparticles, a new method have 48
been investigated [11]. Operational gas sensors have been 49
obtained by drop depositing the doped or undoped tin col- 50
loidal solutions onto a silicon die and using an integrated 51
heater to perform the oxidation of tin nanoparticles into tin 52
oxide nanoparticles [12]. 53

Electrical response under CO of these new sensors pro- 54
duces a comparison of sensors’ sensitivities according to the 55
different doping agents. The influence of humidity on CO 56
sensitivity is discussed in the following. 57

2. Sensor description 58

The sensor used in this study is formed by a micro- 59
hotplate platform and a nanoparticulate SnO₂ sensing layer 60
(Fig. 2). 61

* Corresponding author. Tel.: +33 561 336218; fax: +33 561 336208.
E-mail address: menini@laas.fr (P. Ménini).

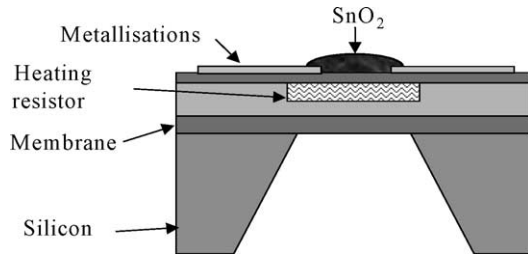


Fig. 1. Schematic view of the SnO₂ gas sensor.

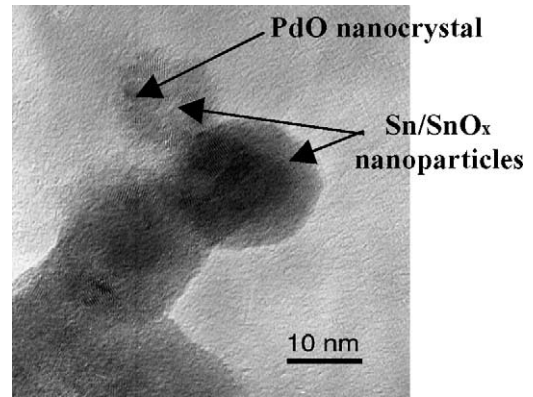


Fig. 3. High resolution transmission electronic microscopy (HRTEM) image of the Pd-doped SnO₂.

62 The microhotplate architecture schematised on Fig. 1 was
63 initially developed by LAAS-CNRS in collaboration with
64 Motorola. A thin dielectric membrane (2 μm of thickness)
65 supports a polysilicon heater of 600 μm × 430 μm. Two
66 pairs of platinum electrodes permit on the one hand to feed
67 heating resistance and on the other hand to recover the signal
68 on the sensitive layer.

69 Dimensions have been optimised to achieve good
70 thermo-mechanical reliability and good homogeneity of
71 temperature on the active area [13]. The heater can reach
72 temperatures of 500 °C with a power consumption lower
73 than 100 mW. This heater allows in a first time the full
74 oxidation into SnO₂ with a controlled temperature cycle
75 from ambient to 500 °C, and in a second time the optimisa-
76 tion of the sensor sensitivity and selectivity with a specific
77 temperature operating mode [14].

78 The metal-oxide used in this sensor is a crystalline SnO₂
79 nanomaterial synthesized according to the two step process
80 previously described [15]. The Fig. 2 is a scanning electronic
81 microscope image of this type of nanostructured SnO₂. It
82 reveals a very porous sensitive layer.

83 This process consists, first in the decomposition a tin
84 based organometallic precursor ([Sn(NMe₂)₂]₂) to yield a
85 tin/tin oxide nanocomposite of core-shell structure which
86 then can be fully oxidized, in a second step, into well crys-
87 tallized SnO₂ nanoparticles having a mean diameter near
88 15 nm, without coalescence. Doping is achieved by decom-
89 posing an organometallic precursor M(dba)₂ (M = Pd, Pt;
90 dba = dibenzylidene-deneacetone) under dihydrogen or carbon
91 monoxide at the surface of the tin/tin oxide preformed parti-

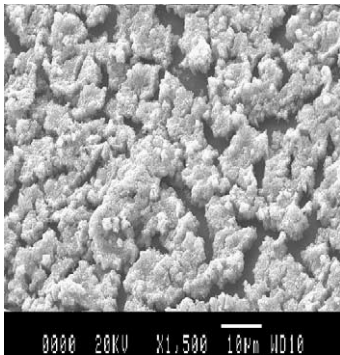


Fig. 2. Scanning electronic microscopy (SEM) image of the nanostructured SnO₂.

92 cles. Upon heating in situ on the platform the tin material is
93 transformed into SnO₂, whereas the doping agents are oxi-
94 dized into crystalline palladium and platinum oxides which
95 mostly remain at the surface of tin oxide (Fig. 3).

96 This material is then deposited using a microinjector tech-
97 nique over the two electrodes placed in the homogeneous
98 temperature region of the heater (Fig. 4).

3. Experimental results

99 The experimental set-up consists of a gas delivery sys-
100 tem, an exposure glass vessel and an electronic circuit for
101 resistance determination through voltage measurements.

102 Before any test sequences, all sensors have to be subjected
103 to several heating cycles in dry air.

104 The optimal operating temperature, i.e. giving the highest
105 sensitivity, has been determined near 450 °C for all tested
106 sensors under 500 ppm of CO.

107 The sensitivity of the sensor is determined by:

$$S = \frac{R_{\text{gas}} - R_0}{R_0} \quad (1)$$

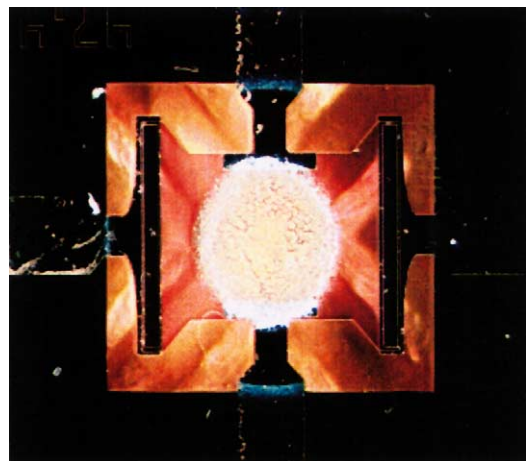


Fig. 4. Top view of the SnO₂ gas sensor.

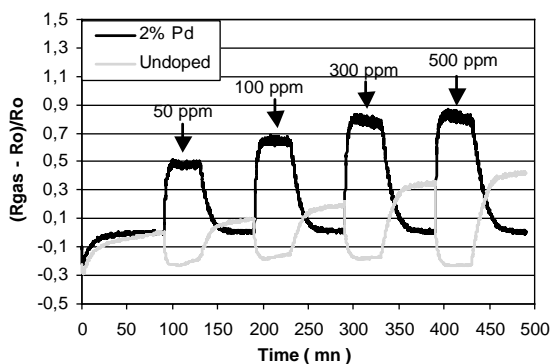


Fig. 5. Undoped and Pd-doped sensor responses under CO in dry air.

where R_0 is the sensitive layer resistance without CO and R_{gas} the resistance measured under CO.

Even if un-doped sensor response is not stabilized, it can be seen in Fig. 5 that, in dry air, responses of Pd-doped and un-doped sensors to CO are characterized by opposite variations of the resistances. Similarly, Fig. 6 shows that the responses of Pd-doped sensors in humid air and in dry air are characterized by opposite variations of the resistances. Moreover, doped and un-doped sensors display the same variation (in term of sign) in humid atmosphere as generally observe in ref. [16].

So, the doped-sensor exhibits a zero sensitivity for a low level of relative humidity (about 5%) as it is shown in Fig. 7.

Last recent results shown that this inversion of sensitivity has been also obtained with Pt-doped sensors (Fig. 8) where the catalyst Pt has been inserted by the same surface-doping method.

4. Discussion

The accepted mechanism of detection of a reducing gas such as CO, involves the partial chemical reduction of the surface of the sensitive layer, in the present case SnO_2 nanoparticles. The result of this chemical reduction is an increase of the conductivity of the sensitive layer. The inversion of CO sensitivity from undoped to Pd-doped (and/or

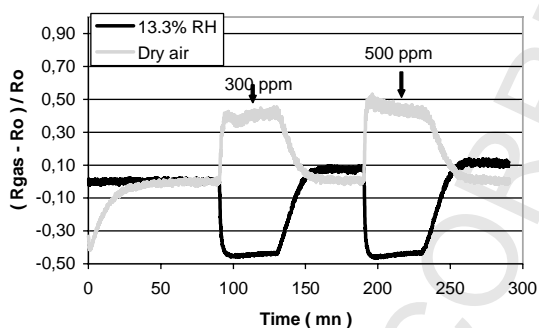


Fig. 6. Pd-doped sensor responses under CO in dry and humid atmosphere.

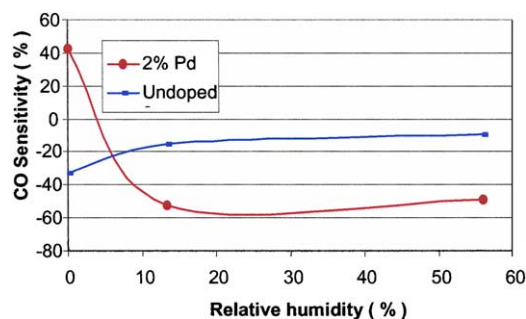


Fig. 7. Sensitivity vs. humidity content for un-doped and 2% Pd-doped sensors.

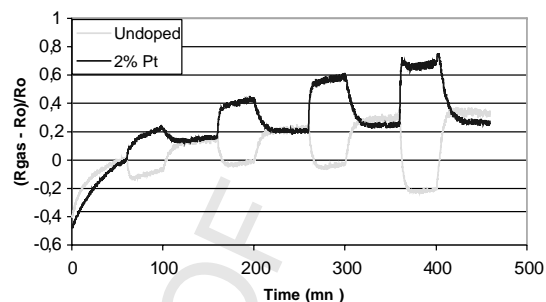


Fig. 8. Comparison between un-doped and Pt-doped sensor responses under CO injections in dry air.

Pt-doped) sensors observed in this study is therefore surprising and, to the best of our knowledge, unprecedented. The correlation with the rate of humidity is clear and the observation of a point of zero sensitivity confirms it. The origin of this behavior is as yet unclear but probably results from different catalytic properties of the doping nanoparticles according to the presence of humidity. The surface chemistry of this system has therefore to be studied in detail. A hypothesis would be the variation of rates of CO oxidation on the catalyst and adsorption on SnO_2 according to the rate of humidity.

5. Conclusion

A new generation of gas sensors based on nanoparticulate SnO_2 sensitive layer with two doping catalysts—palladium and platinum—has been elaborated and tested. The maximal sensitivity to carbon monoxide has been obtained at the upper temperature of 450°C for all of the sensors. First results in dry air reveal that the palladium is the best doping agent for CO detection, but, at the moment, that in wet ambient air, the best sensitivity is achieved for a Pt-doped sensor in agreement with the literature [16].

The inversion of sensitivity from dry to wet air introduces firstly, a new concept of electrochemical operating mode between oxygenated gases and the superficially doped sensing layer and secondly, an potential opportunity to increase the selectivity using a sensor array.

161 **Acknowledgements**

162 Authors would like to thank CNRS and European Com-
163 mission for funding this work within the context of Nanosen-
164 soflex project (Growth-G5RD-CT-2002-00722).

165 **References**

- 166 [1] K. Ihokura, et al. The stannic Oxide Gas Sensor, Principle and
167 Applications, CRC Press, Boca Raton, Floride, 1994.
- 168 [2] E. Leja, et al., Phase composition of SnO_x thin films obtained
169 by reactive D.C. sputtering, Thin Solid Films 59 (1979) 147–
170 155.
- 171 [3] N. Yamazoe, et al., New approaches for improving semiconductor
172 gas sensors, Sens. Actuators B B5 (1991) 7–19.
- 173 [4] J.O.W. Norris, The Role of Precious Metal Catalysts, Adam Hilger,
174 Bristol, 1987.
- 175 [5] M. Schweizer-Berberich, J.G. Zheng, U. Weimar, W. Göpel, N.
176 Barsan, E. Pentia, A. Tomescu, The effect of Pt and Pd surface
177 doping on the response of nanocrystalline tin dioxide gas sensors to
178 CO, Sens. Actuators B B31 (1996) 71.
- 179 [6] Y. Shimizu, M. Egashira, Basic aspects and challenges of semicon-
180 ductor gas sensors, MRS Bull. 24 (6) (1999) 18–24.
- 181 [7] S. Matsushima, et al., Electronic interaction between metal additives
182 and tin dioxide in tin dioxide-based gas sensor, Jpn. J. Appl. Phys.
183 27 (10) (1988) 1798–1802.
- 184 [8] S. Matsushima, et al., TEM Observation of the Dispersion State of
185 Pd on SnO₂, Chemistry Letters, 1989, pp. 1651–1654.
- 186 [9] M. Labeau, et al., Pt nanoparticles dispersed on SnO₂ thin films:
187 a microstructural study, J. Solid State Chem. 102 (2) (1993) 434–
188 439.
- 189 [10] A. Dieguez, et al., Influence on the gas sensor performances of the
190 metal chemical states introduced by impregnation of calcinated SnO₂
191 sol–gel nanocrystals, Sens. Actuators B Chem. 68 (1–3) (2000) 94–
192 99.
- 193 [11] C. Nayral, et al., Synthesis and use of a novel SnO₂ nanomaterial
194 for gas sensing, Appl. Surf. Sci. 164 (2000) 219–226.
- 195 [12] P. Fau, et al., Nanosized tin oxide sensitive layer on a silicon platform
196 for domestic gas applications, Sens. Actuators B 78 (2001) 83–
197 88.
- 198 [13] S. Astie, Ph.D. Thesis, Integration d'un capteur de gaz a
199 oxyde semi-conducteur sur silicium, LAAS Report, No. 98537,
200 1998.
- 201 [14] M. Guerrero, et al. Method of C₂H₄ detection in humid atmospheres
202 using a nanoparticulate SnO₂ gas sensor, Eurosensors'02, Proceeding,
203 Prague, Czech-Republic, 15–18 September 2002, pp. 1019–1022.
- 204 [15] C. Nayral, et al., Synthesis of tin and tin oxide nanoparticles of low
205 size dispersity for application in gas sensing, Chem. Eur. J. 6 (22)
206 (2000) 4082–4090.
- 207 [16] V.N. Mishra, R.P. Agarwal, Sensitivity, response and recovery time
208 of SnO₂ based thick-film sensor array for H₂, CO, CH₄ and LPG,
Microelectron. J. 29 (1998) 861–874.

Biographies

Ph. Ménini was born in Toulouse, France, in 1970. He received the
209 PhD degree in electronics from the Paul Sabatier University, Toulouse
210 in 1998. His doctoral studies were concentrated on characterization and
211 modelling of capacitive pressure sensors. Since 1999, he has been an
212 assistant professor at Paul Sabatier University. At the same time, he
213 joined the “Laboratoire d'Analyse et d'Architecture des Systèmes du
214 Centre National de Recherche Scientifique” (LAAS-CNRS), Toulouse. His
215 research interests include microtechnology, analogue IC for Microsystems,
216 instrumentation, electrical modelling and design of MEMS.
217
218

F. Parret received the DEA (post-graduate diploma) in electronics in 2002
219 from National Polytechnic Institute, Toulouse, France. He is working
220 towards a PhD in micro and nano technology and more specifically on
221 smart SnO₂ gas sensors.
222

M. Guerrero was born in 1969 in Columbia. He works as associated pro-
223 fessor at the university “Los Andes” in Bogota, Columbia, since 1997. He
224 joined the CNRS-LAAS in 1999 as a PhD student. He works on archi-
225 tecture of electronic systems specially in data treatment of microsystems.
226

K. Soulantica received her PhD in chemistry in 1995 from the Chemistry
227 Department of the University of Athens (Greece). After a post-doctoral
228 stage in Spain (Universidad de Valladolid) where she worked on
229 organometallic chemistry, she joined the Laboratoire de Chimie de Coor-
230 dination (Toulouse) where she currently works as a post-doctoral student
231 on the synthesis of metal and metal oxide nanoparticles.
232

L. Erades holds a master of chemical sciences (Maitrise de Chimie) and
233 a post graduate diploma (DEA) in “chemistry and physicochemistry of
234 the transition elements” from the university “Paul Sabatier”, Toulouse, in
235 1999. Then he received the PhD degree in January 2003 on the synthesis
236 and development of metal and metal-oxide nanoparticles for use in gas
237 sensor devices.
238

A. Maisonnat obtained his Doctorat d'Etat from Université Paul Sabatier
239 (Toulouse, Pr. R. Poilblanc) in 1978. During 10 years, for the Region
240 Midi-Pyrénées (France), he has been in charge of industrial relationships
241 with CNRS. He is currently working as Directeur de Recherche CNRS
242 since 1990. His research interest are focused on nanoparticles of metal
243 and metal oxides and related applications to microelectronics.
244

B. Chaudret holds an Engineering Diploma from Ecole Nationale
245 Supérieure de Chimie de Paris in 1975, and a PhD obtained in 1977
246 from the Imperial College of Science and Technology (Londres, Pr. G.
247 Wilkinson). He received his Doctorat d'Etat from Université Paul Sabatier
248 (Toulouse, Pr. Poilblanc) in 1979. He is currently working as a Directeur
249 de Recherche CNRS since 1988 at the Laboratoire de Chimie de Co-
250 ordination CNRS. His scientific interests are: organometallic chemistry
251 (synthesis and applications of sigma-bond complexes), homogeneous
252 catalysis; synthesis, physical and chemical properties of nanoparticles of
253 metal and oxides; applications in microelectronics.
254