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

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10 Abstract

11 In this paper, we show the influence of humidity on the sensitivity for CO sensing of the nanoparticular 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.

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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 nanoparticular SnO₂ sensing layer 60
(Fig. 2). 61

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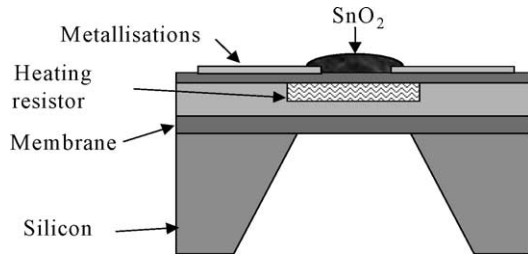


Fig. 1. Schematic view of the SnO₂ gas sensor.

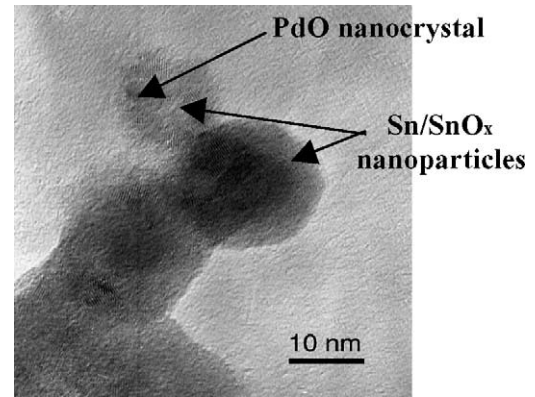


Fig. 3. High resolution transmission electronic microscopy (HRTEM) image of the Pd-doped SnO₂.

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 = dibenzylideneacetone) under dihydrogen or carbon
91 monoxide at the surface of the tin/tin oxide preformed parti-

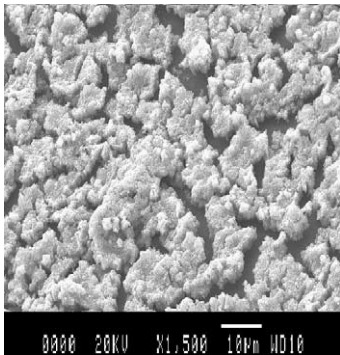


Fig. 2. Scanning electronic microscopy (SEM) image of the nanostructured SnO₂.

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:

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

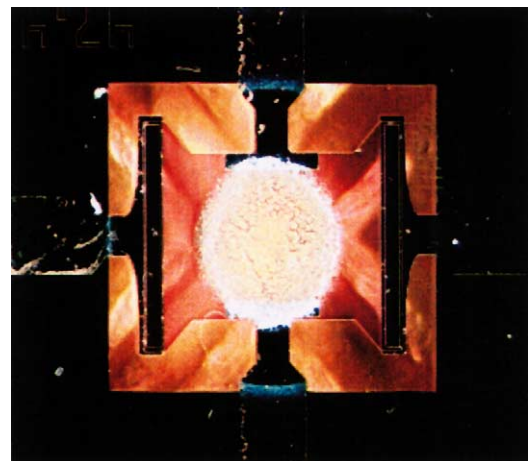


Fig. 4. Top view of the SnO₂ gas sensor.

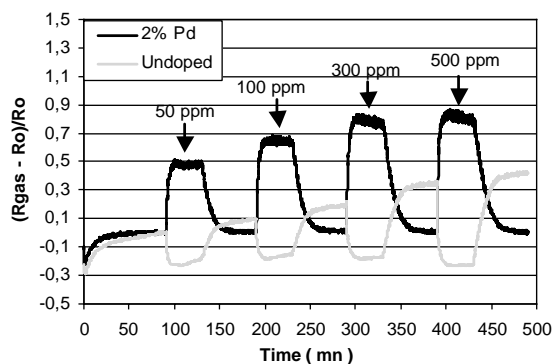


Fig. 5. Undoped and Pd-doped sensor responses under CO in dry air.

where R_o 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

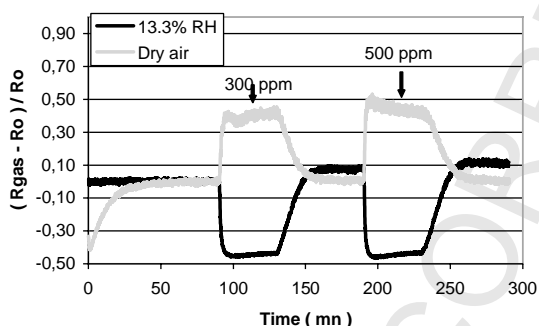


Fig. 6. Pd-doped sensor responses under CO in dry and humid atmosphere.

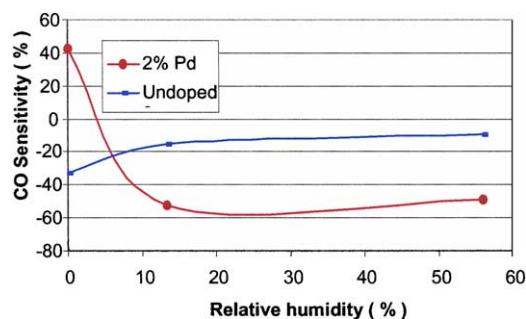


Fig. 7. Sensitivity vs. humidity content for un-doped and 2% Pd-doped sensors.

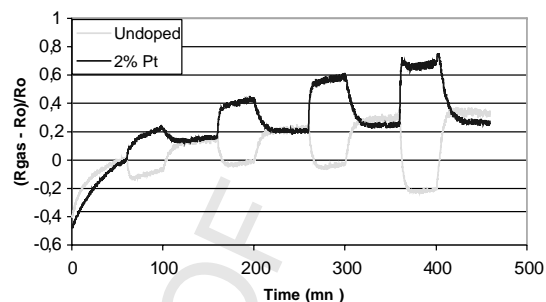


Fig. 8. Comparison between un-doped and Pt-doped sensor responses under CO injections in dry air.

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 nanoparticular 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.

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