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

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CO response of a nanostructured SnO_2 gas sensor doped with palladium and platinum

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Abstract

In this paper, we show the influence of humidity on the sensitivity for CO sensing of the nanoparticular SnO_2 sensors at an operating temperature of 450 °C. Three different sensors have been studied: un-doped sensors and doped sensors with two doping agents palladium and platinum. It is well known that the resistance of the sensitive layer is largely modified by doping. This study demonstrates that un-doped sensors show under CO a sensitivity less important in humid air than in dry air. Doped sensors display a very different behavior. Indeed, in 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 high sensitivity is also observed but characterized by a decrease in the resistance of the sensitive layer. In between, a point of zero sensitivity is found. These results carry out the presence of unexpectedly different electrochemical operating mode for CO sensing according to the humidity content.

Keywords: Gas sensors; SnO_2; Nanoparticles; Doping; CO sensitivity

1. Introduction

At present time, most of the gas sensors are either electrochemical or metal-oxide semiconductors in thick-film [1] or in thin-film [2] technology. The main problems of these techniques are: moderate level of sensitivity, low reproducibility, low selectivity, long stabilization periods and high power consumption for the thick layer. However, the gas sensor technology has integrated for a few years the development of nanomaterials.

This article deals with a new generation of nanoparticular SnO_2 gas sensors (Fig. 2) currently studied and developed within the context of an European project entitled "Nanosensoflex" which consists in developing gas sensors for flexible automotive and domestic applications. Due to the reduction of grain size, this new technology of sensitive layer allows a very high surface-on-volume ratio and then may display a high level of sensitivity [3].

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

A way to improve the performance of SnO_2-based sensors both in term of sensitivity and response time for a broad range of gases is doping them with small amounts of noble metal [4–6]. In this case, the sensitivity and selectivity properties have been shown to depend greatly on the distribution and the crystal size of the added noble metals [7–10]. To achieve a homogeneous Pd and Pt doped SnO_2 sensor layers starting from tin nanoparticles, a new method have been investigated [11]. Operational gas sensors have been obtained by drop depositing the doped or undoped tin colloidal solutions onto a silicon die and using a integrated heater to perform the oxidation of tin nanoparticles into tin oxide nanoparticles [12].

Electrical response under CO of these new sensors produces a comparison of sensors' sensitivities according to the different doping agents. The influence of humidity on CO sensitivity is discussed in the following.

2. Sensor description

The sensor used in this study is formed by a microhotplate platform and a nanoparticular SnO_2 sensing layer (Fig. 2).

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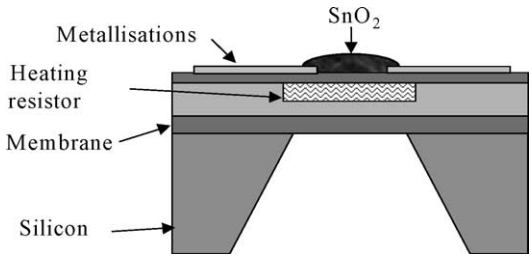

Fig. 1. Schematic view of the SnO_2 gas sensor.

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

Dimensions have been optimised to achieve good thermo-mechanical reliability and good homogeneity of temperature on the active area [13]. The heater can reach temperatures of 500 °C with a power consumption lower than 100 mW. This heater allows in a first time the full oxidation into SnO_2 with a controlled temperature cycle from ambiant to 500 °C, and in a second time the optimisation of the sensor sensitivity and selectivity with a specific temperature operating mode [14].

The metal-oxide used in this sensor is a crystalline SnO_2 nanomaterial synthesized according to the two step process previously described [15]. The Fig. 2 is a scanning electronic microscope image of this type of nanostructured SnO_2. It reveals a very porous sensitive layer.

This process consists, first in the decomposition a tin based organometallic precursor ($[Sn(NMe_2)_2]_2$) to yield a tin/tin oxide nanocomposite of core-shell structure which then can be fully oxidized, in a second step, into well crystallized SnO_2 nanoparticles having a mean diameter near 15 nm, without coalescence. Doping is achieved by decomposing an organometallic precursor $M(dba)_2$ (M = Pd, Pt; dba = dibenzyli-deneacetone) under dihydrogen or carbon monoxide at the surface of the tin/tin oxide preformed particles. Upon heating in situ on the platform the tin material is transformed into SnO_2, whereas the doping agents are oxidized into crystalline palladium and platinum oxides which mostly remain at the surface of tin oxide (Fig. 3).

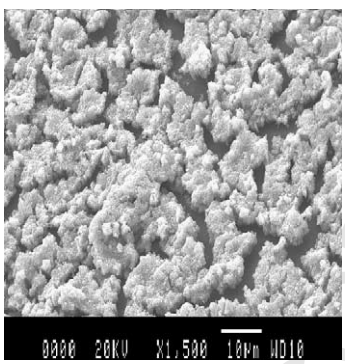

Fig. 2. Scanning electronic microscopy (SEM) image of the nanostructured SnO_2.

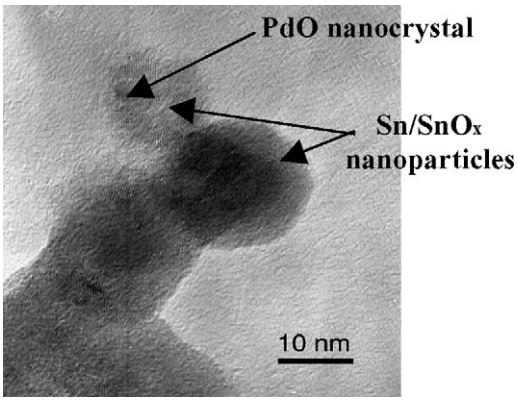

Fig. 3. High resolution transmission electronic microscopy (HRTEM) image of the Pd-doped SnO_2.

This material is then deposited using a microinjector technique over the two electrodes placed in the homogeneous temperature region of the heater (Fig. 4).

3. Experimental results

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

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

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

The sensitivity of the sensor is determined by:

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

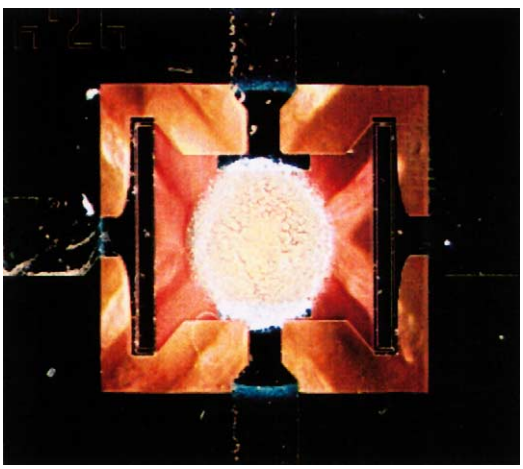

Fig. 4. Top view of the SnO_2 gas sensor.

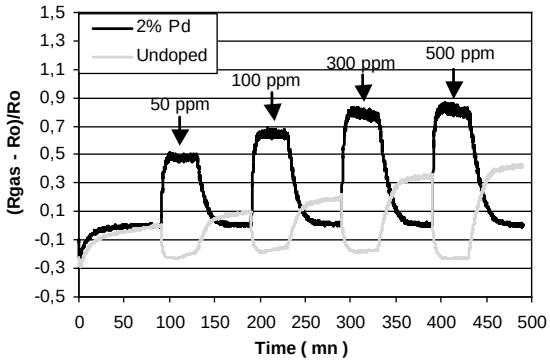

Fig. 5. Undoped and Pd-doped sensor responses under CO in dry air.

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

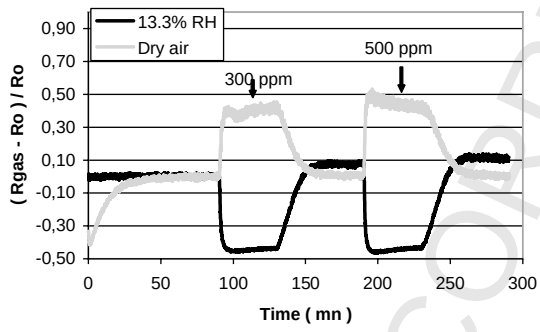

Fig. 6. Pd-doped sensor responses under CO in dry and humid atmosphere.

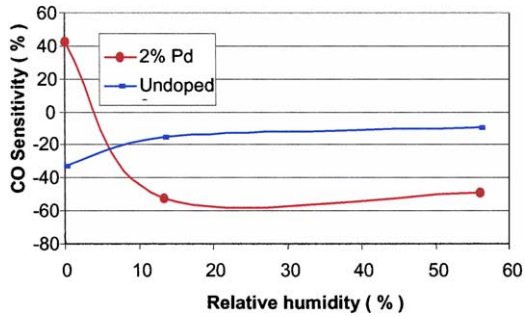

Fig. 7. Sensitivity vs. humidity content for un-doped and 2% Pd-doped sensors.

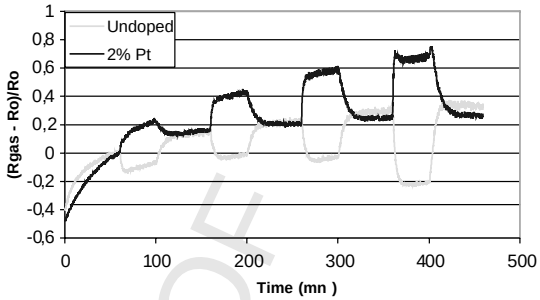

Fig. 8. Comparison between un-doped and Pt-doped sensor responses under CO injections in dry air.

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 ambiant 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.

Acknowledgements

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Biographies

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

F. Parret received the DEA (post-graduate diploma) in electronics in 2002 from National Polytechnic Institute, Toulouse, France. He is working towards a PhD in micro and nano technology and more specifically on smart SnO_2 gas sensors.

M. Guerrero was born in 1969 in Columbia. He works as associated professor at the university "Los Andes" in Bogota, Columbia, since 1997. He joined the CNRS-LAAS in 1999 as a PhD student. He works on architecture of electronic systems specially in data treatment of microsystems.

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

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

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

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