New Generation of Micro Machined Silicon Gas Sensors:Nano-structured Pd-and Pt-doped Tin Dioxide Sensitive Layers for the Detection of Hazardous Gases

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New Generation of Micro Machined Silicon Gas Sensors:* Nano-structured Pd- and Pt-doped Tin Dioxide Sensitive Layers for the Detection of Hazardous Gases

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Summary: *In the present work, we demonstrate that organometallic complexes constitute efficient precursors to design nanostructured Pd- or Pt-doped tin dioxide material. We demonstrate also that this material, under the form of colloidal solutions, can be implemented at an industrial scale as sensitive layer by drop deposition process onto micro-machined silicon substrates. Responses of these sensors to CO, H_2, C_3H_8 and NO_2 are presented and discussed.*

Keywords: *SnO_2 micro-machined gas sensors; Platinum and palladium catalysts; organometallic precursors*

Introduction

Metal oxide gas sensors are based on their property of varying their resistance when exposed to oxidizing or reducing gases, thus giving rise to a measurable signal. This property, of special interest for the detection of trace concentrations of flammable or toxic gases in air, is the subject of an extensive exploitation. Despite the fact that commercial devices have been available for a long time, selective and reliable simultaneous detection of several gases, at parts per million ranges, in the presence of other gases, remains a challenge.
In this context we develop researches aiming at improving solid state gas sensor technology by designing a new generation of sensors according to a multi-disciplinary approach which takes advantage of nano-material technology and silicon micro-electronic processes. The use of innovative nano structured materials as sensitive elements as well as filters is supposed to offer a high level of sensing properties, in term of reproducibility, response time, long term-stability and selectivity whereas the semi-conductor manufacturing offers low cost sensors, high miniaturization level and very low power consumption

Results

We recently demonstrated that the organometallic route can be successfully applied for the synthesis of semi conducting nano structured metal oxides of controlled morphology [1,2] and for their homogeneous doping with noble metals. We demonstrated also that these materials can be implemented, by drop deposition process, as sensitive layers on micro machined silicon substrates to generate prototype gas sensors. [3,4]
Optimization of the processes implemented for the preparation of micro gas sensors at an industrial scale (basic chemical processes used for the synthesis and the doping of tin materials; integration and thermal conditioning of the sensitive layer) has been achieved in the frame of NANOSENSOFLEX program.

Typical responses of the as-obtained micro sensors when exposed to test gases, *ie* CO (5, 25 and 50 ppm), H_2 (3, 10 and 20 ppm), C_3H_8 (50, 100 and 200 ppm) and NO_2 (0.5, 1 and 2 ppm), under a humidity content of 50 % and at a non-optimized working temperature of 450°C, are shown on figure 1.
Palladium and platinum-dopings considerably affect the resistances of the sensing materials which typically increase from values close to 20 Kohms for the undoped sensors to 100 Kohms.
Responses of the undoped sensors to small amounts of NO_2 are remarkable with, for example, a sensitivity value $S = [(R_{gas}-R_{air})/R_{air}]$ of 6 under 2ppm of NO_2 (R_{gas} and R_{air} corresponding to the resistance values under test-gas and air respectively).
The palladium and platinum-doping effects on the responses to CO and NO_2 are illustrated through sensitivity profiles shown on figures 2 and 3. Pd- and Pt-doping leads to an increasing in sensitivity for the CO detection and to a strong reduction of the sensitivity toward NO_2. Optimization of

parameters like working temperature, doping rate, operating mode, in order to improve the cross sensitivities between such gases are presently under investigation.

Conclusion

In conclusion, we report in this communication a highly active system for gas detection. It is of special interest that the doping of the sensitive layer leads both to the increase in sensitivity for reducing gasses such as CO and H_2 and to a strong reduction of the sensitivity towards oxidizing gasses such as NO_2. This will, in principle, make the selective detection of NO_2 and CO possible in a bi-sensor system available for automotive applications. In addition, we note that these curves display useful transitory information which will now be studied in detail.

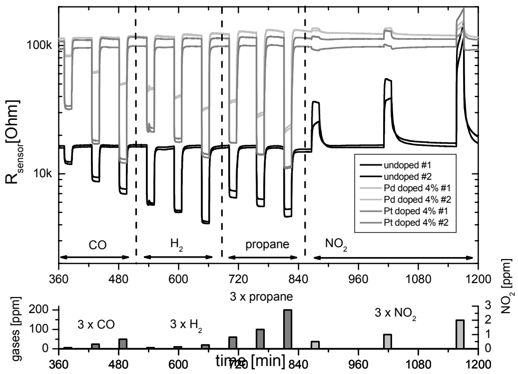

Fig. 1. Gas response of sensors

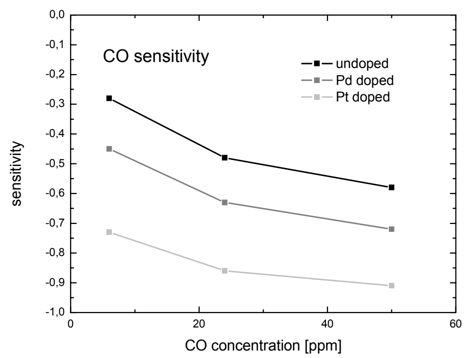

Fig.2. CO sensitivity profile

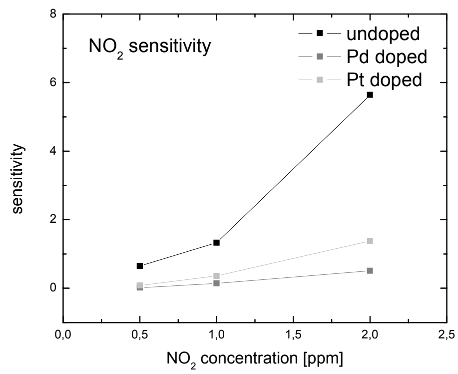

Fig.3. NO_2 sensitivity profile

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