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Summary: In this work, the authors present a new approach to detect and discriminate sub-ppm level of formaldehyde with metal oxide semi-conductors (MOS) gas sensors based on nanostructured layers of SnO_2, CuO, or a combination of the two. These sensitive layers are deposited on silicon micro-hotplates and operated with a pulsed temperature modulation between 100 and 500°C under 50% of relative humidity (%RH). This method allows a very specific sensor response to formaldehyde compared to other gases such as CO or NO_2. This sensor set up (combination of sensitive layers and pulsed temperature mode) opens the way toward an efficient formaldehyde detection method for indoor air quality applications.

Keywords: Formaldehyde, gas sensor, metal oxides semiconductors, pulsed temperature modulation, selectivity, indoor air quality.

1. Introduction

During the last years, indoor air pollution has become a real health concern due to the awareness of presence of numerous gas pollutants issued from our direct environment (building, decoration or wooden materials, paints, etc...) [1]. These materials may release various volatile organic compounds (VOCs) such as formaldehyde, acetaldehyde, benzene, toluene etc. According to the World Health Organization (WHO), formaldehyde (CH_2O) is considered as the main pollutants found in indoor air and it is known to be carcinogenic even for short-term exposure conditions. Its detection has consequently become urgent [2]. We report in this paper a new MOS sensor based on a dual sensitive layer made of nanostructured SnO_2 and CuO, which can detect and discriminate sub-ppm concentration of formaldehyde at low energy consumption. This sensor performance is compared to sensors with simple layers of SnO_2 and CuO in order to evidence the role of the dual layer setup. All these sensors are operated with a pulsed temperature modulation, which is a key feature for selective gas detection.

2. Materials and Methods

The different sensitive layers of this study are prepared in the form of serigraphy pastes and deposited on a silicon micro-hotplate [3] before being slowly annealed in ambient air from room temperature up to 500°C. In this paper, we propose to study three different gas sensors: SnO_2, CuO and a dual-layer sensor made of the successive deposition of SnO_2 (bottom) and CuO (top) material. All these device are operated with a pulsed temperature modulation applied to the integrated heater at a power of 12 mW and 50 mW, during 30 s each (corresponding to temperature steps of 100°C and 500°C, respectively). This temperature procedure reduces the total power consumption of the device compared to the continuous high temperature mode. In addition, it offers a very specific response of the dual layers sensor to formaldehyde exposure. The sensors are tested in a test chamber under 50% of RH and to the following successive gas injections: CH_2O (5 and 10 ppm), CO (100 and 50 ppm) and NO_2 (0.3 and 0.5 ppm).

3. Results and Discussion

The normalized resistance Rn of the sensors is calculated according the following expression (1).

$$Rn = \frac{Rgas - Rref}{Rref} * 100$$

In the following part, we presents the responses Rn measured at 100°C and 500°C of the different sensors to CO, NO_2 and CH_2O. In Figure 1, we show the respose of SnO_2 layer behaves as a n-type semiconducting oxide with a large resistance decrease

(- 90 %) to 5 ppm formaldehyde at 100 or at 500°C. It presents a moderate response to CO 100 ppm (- 25%) and a huge resistance increase to 0.5 ppm NO_2 at 100°C (+ 350%).

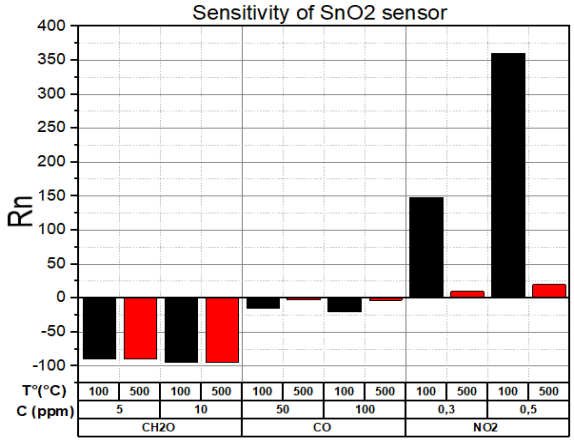

Fig. 1. Response of SnO_2 gas sensors operated with pulsed temperature modulation in different gaseous environment

Without surprise, CuO sensor presented in Figure 2 behaves as a p-type oxide with resistances increase under reducing gases (CO and formaldehyde) and resistances decrease under oxidizing one (NO_2). The very high response of this sensor to formaldehyde is remarkable (+ 450% for 10 ppm at 100°C).

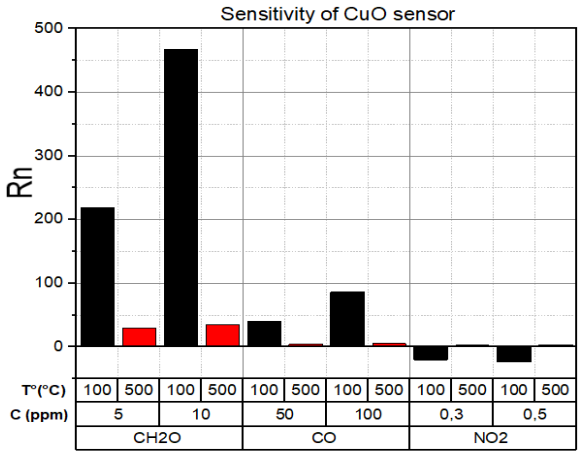

Fig. 2. Response of CuO gas sensors operated with pulsed temperature modulation in different gaseous environment

The striking result of these experiments concerns the behavior of the dual layer sensor made of a SnO_2 layer covered by a CuO layer illustrate in Figure 3. This sensor presents a very complex response depending on the temperature of the operating cycle and the nature of the reacting gas. Under CO, the response of this sensor is controlled by the p-type behavior of the top CuO layer, whatever the temperature of the cycle (100 and 500°C). Under NO_2, the sensor is not sensitive at 500°C and only presents a weak n-type (bottom SnO_2 layer) response at 100°C (+ 10%) whatever the concentration. For formaldehyde concentration of 5 or 10 ppm, the sensor response is even more complex since the response type (n or p) varies depending on the measurement temperature. At 100°C, the sensor response is controlled by the SnO_2 layer with up to – 30% of resistance drop for 10 ppm formaldehyde. Surprisingly, at 500°C the response type is reversed with around + 25 % of the measured resistance increase to 5 ppm formaldehyde.

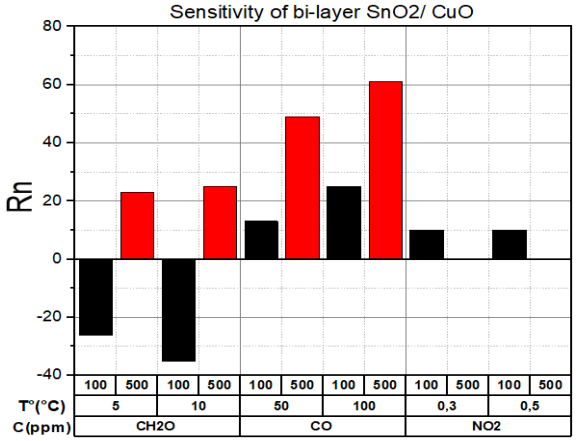

Fig. 3. Response of Bi-layer SnO_2/CuO sensor gas sensors operated with pulsed temperature modulation in different gaseous environment

4. Conclusions

We can conclude that the reversed response depending on the temperature has been observed solely for CH_2O and may represent a specific signature of the presence of this gas in the atmosphere. The combination of n and p type stacked layers coupled with pulsed temperature mode of the device represent an original and relevant way to improve the selectivity of MOS gas sensors.

Acknowledgements

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