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Effect of Nanostructured Octahedral SnO_2 Added with a Binary Mixture P-Type and N-Type Metal Oxide on CO Detection †

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† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Received: date; Accepted: date; Published: date

Abstract: In this work, we study the effect of nanostructured octahedral SnO_2 added with a binary mixture p-type and n-type metal oxide semiconductors of CuO and ZnO, on CO detection at two concentrations (100 ppm and 1000 ppm). These metal oxides (SnO_2 and binary mixture of $CuO_{75\%}/ZnO_{25\%}$) are prepared in the form of a serigraphy paste and deposited on an optimized silicon micro-hotplate. The sensors can be operated at temperature of 550 °C with a low energy consumption of only 55 mW. The binary and ternary mixtures of metal oxide are operated at different working temperature to optimize their sensitivity to CO.

Keywords: octahedral SnO_2; CuO nanoparticules; ZnO nanoparticules; binary mixtures; ternary mixtures; gas sensors; sensitivity; CO

1. Introduction

The growing research in the field of metal oxides gas sensors has been deployed on many different applications, among theses, the control of the indoor air quality, which is a major concern of our industrial societies. The monitoring of indoor air quality, especially in offices or classrooms, is one of the objectives of the neoCampus project in the University of Toulouse Paul Sabatier, which also deals with networks of communicating sensors and the treatment of mass of data from these distributed sensors. One way to prepare sensitive and selective metal oxide gas sensors is to develop binary and ternary mixtures of different kind of metal oxides semiconductors (MOS). The binary mixture of two metal oxides n-type and p-type ($CuO_{75\%}/ZnO_{25\%}$), prepared in the form of a serigraphy paste from a mass mixture of the powder of these two metal oxides with 75% CuO and 25% ZnO, shows a high resistivity and different response form (p-type or n-type for CO-reducing gas response) as a function of the operating temperature for 100 ppm and 1000 ppm in a humid atmosphere. However, this high resistance of the base line (even under CO injections) and the form of the response, under the same conditions of the test, are modified in a meaningful way, when adding the octahedral SnO_2 to this binary mixture. This modification also depends on the quantity of this metal oxide with different percentage of the mass at different operating temperature. In this study, we show the effect of adding different proportions of nanostructured octahedral SnO_2 (Figure 1 [1]) to a binary mixture composed by 75% in volume of CuO [2] and 25% of ZnO [3] (Figure 2), on CO detection at different working temperatures. The addition of SnO_2 to $CuO_{75\%}/ZnO_{25\%}$ was used as an intermediate step to improve the adhesion and the chemical functionalization of the surface of $CuO_{75\%}/ZnO_{25\%}$ for

the CO detection between 100 ppm and 1000 ppm at different operating temperatures. This technique allows decreasing the overall level of the sensitive layer resistance and changing the response form of the CO detection, which depends on the applied operating temperature.

2. Materials and Methods

In this work, all the nanoparticles have been prepared through organometallic synthesis procedures. Firstly, ZnO nanorods have been prepared by the reaction of controlled amounts of water (4 equivalents) on Zinc dicyclohexyl ($ZnCy_2$) placed at 40 °C under argon and in the presence of alkylamines ligands (2 molar equivalents octylamine, OA), according to previously published method [1]. The reaction is left running during 4 days and the resulting nanorods (mean diameter 6 ± 1 nm, mean length 36 ± 19 nm) are washed by several precipitation/dispersion stages with acetone.

The second metal oxide is made of ca. 5 nm large CuO nanoparticles. It has been obtained by the reaction of ambient air during 24 h on copper acetamidinate precursor (Cuamd) in the presence of 5 molar equivalents of OA [2]. The excess of OA in the medium is removed by several precipitation stages by centrifugation and washing with THF. To obtain an homogeneous binary blend of these two metal oxides we have mechanically mixed the powders in the defined proportion of 75% mass CuO and 25% mass ZnO. Figure 1 shows the TEM image of the binary mixture of $CuO_{75\%}/ZnO_{25\%}$.

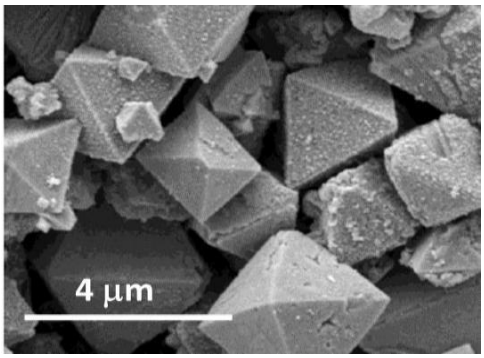

Figure 1. SEM image of SnO_2 octahedra.

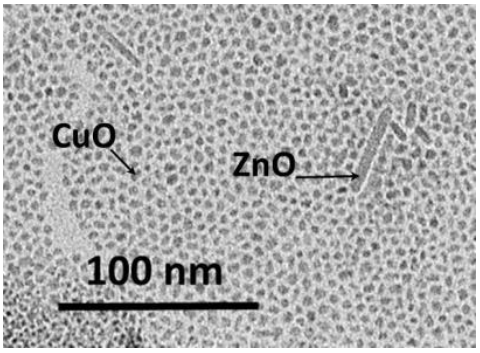

Figure 2. TEM image of $CuO_{75\%}/ZnO_{25\%}$ blend.

The third metal oxide used in this study is made of nanostructured SnO_2 octahedra. This metal oxide has been obtained by the reaction of controlled amounts of water (8 molar equivalents) on tin amidure precursor ($Sn(NMe_2)_2$) in the presence of small amounts of hexadecylamine (HDA) (0.1 molar equivalent) [3]. Figure 1 shows SEM image of the as-obtained SnO_2 octahedra.

The $CuO_{75\%}/ZnO_{25\%}$ and SnO_2 powders have been mixed with ESL commercial organic binders (30 % mass) in order to prepare screen-printing pastes intended for the deposition on a silicon platform integrating a platinum microhotplate [4]. The variable fractions of $CuO_{75\%}/ZnO_{25\%}$ and SnO_2 have been achieved by the weighting of each of the pastes and their blending with suited mass proportions. In this context, we have firstly studied the behavior of pure $CuO_{75\%}/ZnO_{25\%}$ blend and we have compared it to two types of ternary mixtures: (i) 25% of SnO_2 with 75% of $CuO_{75\%}/ZnO_{25\%}$

and (ii) 50% SnO_2 with 50% $CuO_{75\%}/ZnO_{25\%}$. These different pastes have been deposited on silicon microhotplates [4] by the same method (drop deposition technique) (Table 1).

Table 1. The different sensors.

Sensor	Type	MOX Blend (% mass)
Sensor 1	Binary mixture	$CuO_{75\%}/ZnO_{25\%}$
Sensor 2	Ternary mixture	SnO_2 (25%) $CuO_{75\%}/ZnO_{25\%}$ (75%)
Sensor 3	Ternary mixture	SnO_2 (50%) $CuO_{75\%}/ZnO_{25\%}$ (50%)

The sensor microhotplate of this study has been designed in the technology center of LAAS-CNRS in Toulouse. It is optimized to be operated up to 600 °C with a low power consumption (< 55 mW) [4]. Each deposited paste has been annealed in ambient air from room temperature to 500 °C at a slow rate (1 °C/min) before cooling to room temperature. This thermal pretreatment is necessary to gently remove the organic binders from the powders and insure densification and therefore an electrical continuity between the oxide grains. It also generates ionized oxygen species in atomic or molecular form at the oxide surface and therefore improve the reactivity between the reacting gas and the sensor surface [3]. The sensors have been characterized in an automatized experimental set-up comprising a 250 mL test chamber. After a stabilization phase under humidified synthetic air (RH = 30 %), each sensor has been tested under two different CO concentrations (100 ppm and 1000 ppm) and at different working temperatures (500 °C, 400 °C, 300 °C and 200 °C). Before the onset of the gas injections, the sensors follow a stabilization phase during 2 h under humid air (30 % RH) in order to clean up the test chamber, the surface of the metal oxide and to stabilize the sensor base line. A 30 minutes stabilization phase is applied between two reacting gas injections for the same purpose.

3. Results and Discussion

The first part of the test under gas investigates the characteristic of the $CuO_{75\%}/ZnO_{25\%}$ sensor response to the CO gas injections. This sensor was tested with two CO concentrations (100 ppm and 1000 ppm) under 30 % RH air at different operating temperature (200 °C, 300 °C, 400 °C, and 500 °C). The results are presented in Figure 3.

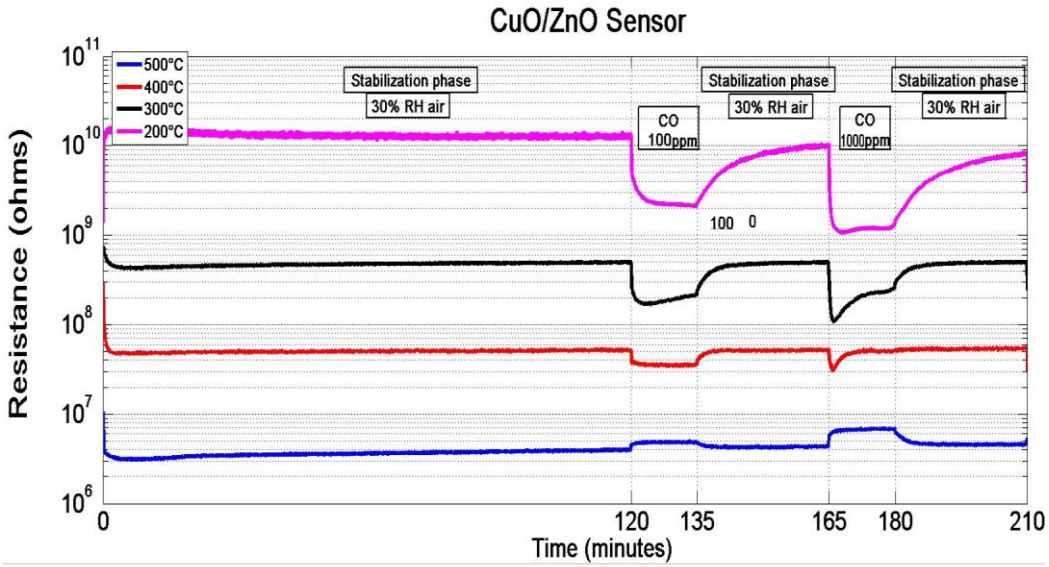

Figure 3. Responses of $CuO_{75\%}/ZnO_{25\%}$ gas sensor at different operating temperatures.

On Figure 3, we can firstly observe that the resistance of this sensing layer depends on the working temperature. Secondly, the highest CO response is achieved at a low working temperature

(200 °C and 300 °C) but with a sensor resistance very high (some GOhms). At a higher working temperature (400 °C and 500 °C) the resistance decreases down to several MOhms. One very important result is that the leading conduction type of the mixed oxide layer indicated by the CO response nature is reversed at high temperature. The CO response corresponds to n-type semiconductor (ZnO) at 200 °C, 300 °C and 400 °C, but at 500 °C the CO response follows the CuO characteristic (p-type) where the electrical conduction is controlled by holes. In the second part of our test, we studied the role of adding nanostructured octahedral SnO_2 to the binary mixture $CuO_{75\%}/ZnO_{25\%}$.

Firstly, we started by a ternary mixture composed by 25% of SnO_2 and 75% of $CuO_{75\%}/ZnO_{25\%}$. In this test, we applied the same test protocol. Figure 4 and Figure 5, presents the result of this test. The addition of SnO_2 significantly decreases the resistance of the sensing layer (under several MOhm), allowing an improved signal to noise ratio and a more stable base line. The presence of 25 % in mass of SnO_2 significantly changes the sign of the CO response. The n-type CO response is obtained only at the lowest operating temperature (200 °C), whereas almost no response is measured at 300 °C and a clear p-type behavior is recorded at 400 °C and 500 °C.

Finally, we tested the sensor with a ternary mixture composed by 50% of SnO_2 and 50% of $CuO_{75\%}/ZnO_{25\%}$. Sensor responses are shown in the Figure 5. In that case where a large amount of SnO_2 (50%) is employed; the CO sensitivity is drastically reduced. The sensor behavior is now controlled by CuO at low temperature (200 °C), whereas all other temperatures lead to a n-type gas response due to SnO_2 sensitive layer. This first study on the preparation of a blend of various sensing oxides types for gas sensing shows that a complex sensor response is obtained. The CO response doesn't show a linear evolution with the increase of the of the n-type oxide proportion in the blend according to different working temperatures. This complex behavior may be an advantage in order to design an array of gas sensors for the detection and recognition of gas mixtures with a PCA analysis (principal components analysis) protocol designed for advanced applications.

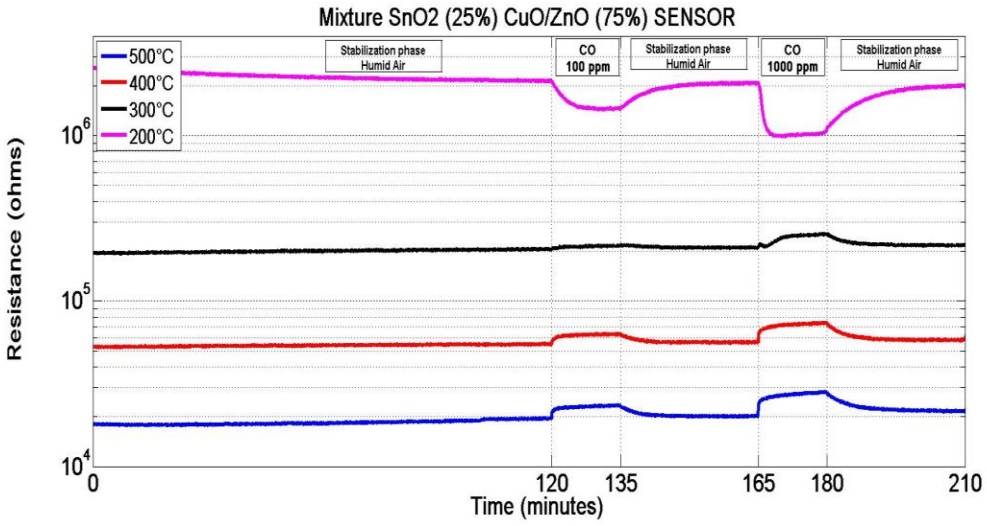

Figure 4. Responses of gas sensor at different operating temperatures for the MOS: mixture SnO_2 (25%) and $CuO_{75\%}/ZnO_{25\%}$ (75%).

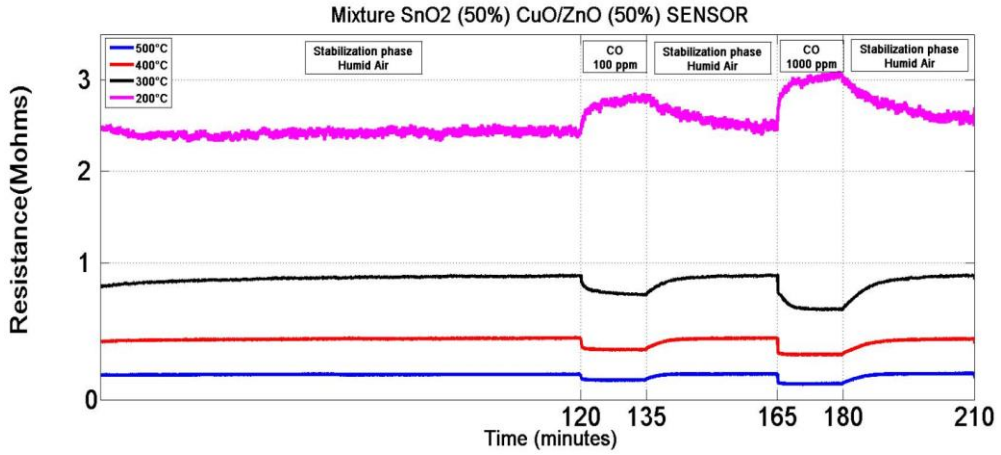

Figure 5. Responses of gas sensor at different operating temperatures for the MOS: mixture SnO_2 (50%) and $CuO_{75\%}/ZnO_{25\%}$ (50%).

A more detailed study of the microstructural interaction between the different oxides in the blend is undergoing and will help to explain these results under CO and more generally to rationalize the gas response of mixed nanosized sensitive layers.

Conclusions

The present work describes our study on the effect of the mixtures of SnO_2 octahedra with a binary blend of 75% p-type (CuO) and 25% n-type (ZnO) metal oxides on the detection of CO. Indeed, the addition of different weight proportions of SnO_2 octahedra nanoparticles to the binary mixture modifies the response of $CuO_{75\%}/ZnO_{25\%}$ blend. The ternary mixture of MOX (SnO_2, $CuO_{75\%}/ZnO_{25\%}$) presents different response level and response type (n-type or p-type) depending on the operating temperature. The distinct gas response of the sensitive oxide blends may allow to improve the detection of gas mixtures by applying a PCA analysis to multi sensors arrays comprising various blended oxides and operated at different temperature.

Acknowledgments: The authors express their gratitude to neOCampus program, the university Paul Sabatier project and the region Occitanie, for the financial support. This work was also partly supported by the French RENATECH network through technology developments in the CNRS-LAAS cleanroom.

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