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PERFORMANCE OF MOX GAS SENSORS OBTAINED BY MIXING P-TYPE AND N-TYPE METAL OXIDES FOR RELIABLE INDOOR AIR QUALITY MONITORING

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Novelty

In this work, we study the effect of n-p heterojunctions in metal oxides (MOX) gas sensors, and particularly on their gas sensitivity and relative humidity dependence for indoor air quality applications. This effect depends on the relative proportion of MOX in the mixture. This study was achieved in order to build a MOX gas sensor that overcomes the effects of humidity variations and to improve the overall sensitivity of MOS gas sensors.

Background

Indoor air quality is major health concern in our societies but European recommendations (directive 2008/50/EC) will be still difficult to fulfill without the help of simple and efficient air quality monitoring systems. MOX gas sensors have proven their interest for the air quality monitoring in open air or indoor areas [1]. The main drawback of theses sensors concerns their stability over time and lack of selectivity among mixtures of gases as well as in variable humidity environment. While a great attention has been focused on n-type semiconducting oxides, few studies have been devoted to the p-type gas sensors. Among p-type oxide semiconductors, single phase, or CuO as part of heterojunction sensors, have demonstrated considerable potential for detection of gases such C_2H_5OH, NO_2, H_2S, H_2, CO and NH_3 [2]. Some of these sensors exhibited interesting selectivity properties towards investigated gases.

Description of the New Method

In order to increase the sensitivity and the selectivity of semi-conducting gas sensors, SnO_2, WO_3, CuO and ZnO nanopowders of this study have been synthesized by a metalorganic approach and mixed in binary or ternary blends in order to prepare efficient sensitive layers integrated on silicon substrates. The mixture of n-type and p-type metal oxides have been used to modify the response gas sensor [3], but there is still a lack of knowledge about the role of n-p heterojunction to overcome the effect of the hygrometry changes. In this work, the optimum blending of different metal oxides (n-type and p-type) is achieved by mixing and grinding the nanoparticles previously suspended in an organic solvent. Then the mixed metal oxides have been prepared in the form of a screen-printing paste in order to facilitate their deposition on silicon micro hotplates [4]. Gas sensors have been realized with nanostructured SnO_2 (Fig. 1) and a blend (Fig. 2) composed by 75% in volume of CuO and 25% of ZnO (Table 1).
With an experimental set-up, we applied a gas injection protocol (Fig. 3). All injections with the reactive gas concentrations are summarized in Table 2. Another preparation mixture was set up where WO_3 particles (fig. 4) mixed with various amounts of nanosized SnO_2 or CuO were used. The performances (sensitivity, stability) of the gas sensors are presented and compared with simple MOX sensors.

Experimental Results

In Figure 5 we present the result of SnO_2. The sensor sensitivity decreases in dry air, and the resistance baseline is different between dry and humid air. This suggests that the humidity influence is prominent for a single metal oxide composition as SnO_2.
In Figure 6 we show the effect of mixing 25% mass of SnO_2 with 75% mass of a binary CuO/ZnO blend. The sensor response sensitivity is lowered in dry and humid air but the baseline has only slightly changed.
In Figure 7 we present the result of the ternary mixture made of SnO_2 (50%) and CuO/ZnO (50%). The resistance baseline remains unchanged between dry and humid air conditions, so that it overcomes the effect of humidity, and thus improves the gas

sensitivity in humid air conditions (30% RH).
The interest of p-n junctions in gas sensing sensitivity and humidity variation for indoor air quality are discussed and justified.

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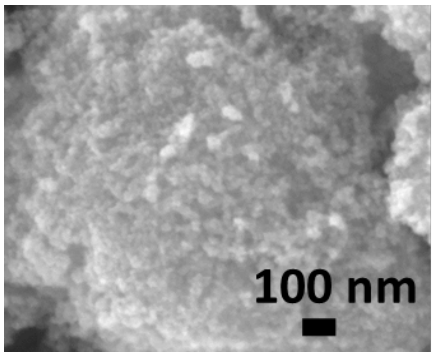


Figure 1: SEM image of nanosized SnO_2 sensitive layer–100nm

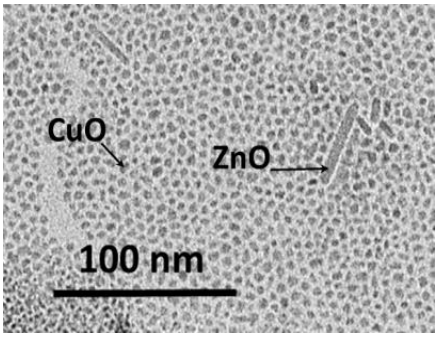


Figure 2: TEM image of CuO 75%/ZnO 25% blend – 100nm

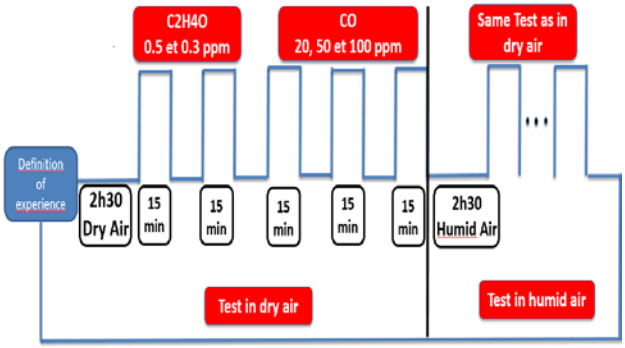


Figure 3: Synoptic representative of gas injections and their concentrations in dry and humid air.

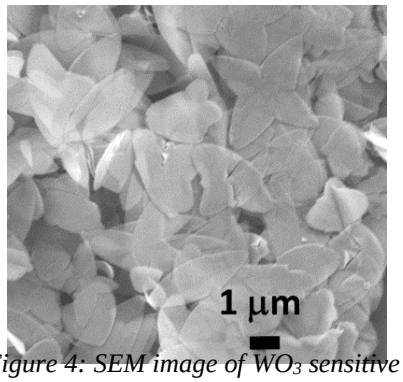


Figure 4: SEM image of WO_3 sensitive layer

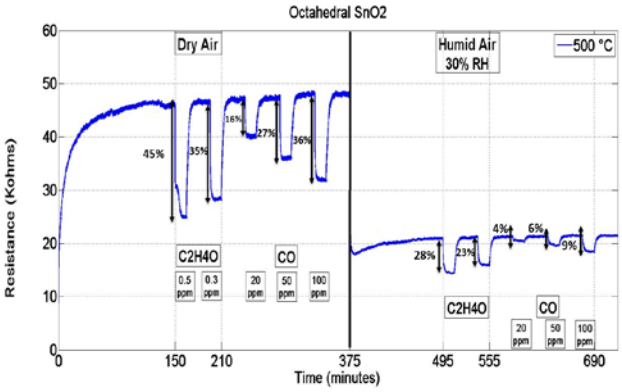


Figure 5: Responses of gas sensor at 500°C for the SnO_2 in dry and humid air.

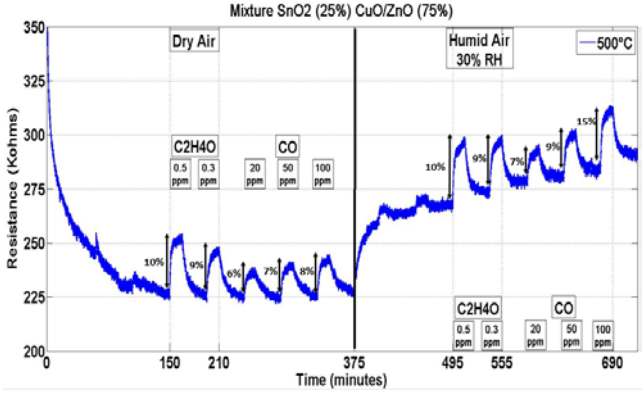


Figure 6: Responses of gas sensor at 500°C for the ternary mixture 25% SnO_2 and 75% of CuO/ZnO in dry and humid air.

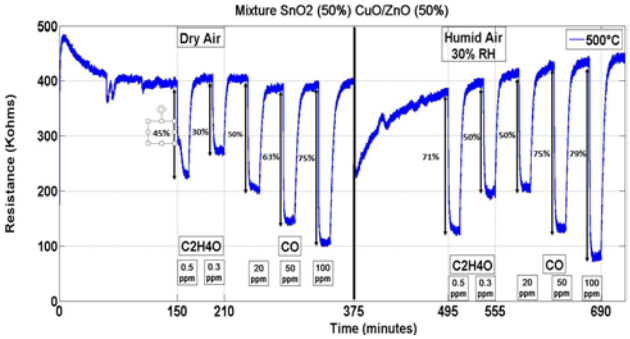


Figure 7: Responses of gas sensor at 500°C for the

ternary mixture 50% SnO_2 and 50% of CuO/ZnO in dry and humid air.

Table 1: The different sensors and their composition

Sensors	Type	MOX Blend (% masse)
Sensor 1	Single	SnO_2 100%
Sensor 2	Ternary mixture	25% SnO_2 and 75% of CuO/ZnO
Sensor 3	Ternary mixture	50% SnO_2 and 50% of CuO/ZnO

Table 2: Injected gas concentrations

Gas	Concentrations
Acetaldehyde	500 ppb
	300 ppb
Carbon Monoxide	20 ppm
	50 ppm
	100 ppm

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