

Supporting information for

**ZnGa<sub>2</sub>O<sub>4</sub> and ZnGa<sub>2</sub>O<sub>4</sub>:N thin films applied as sensors for detection of  
acetaldehyde in ethanol**

*Idio Alves de Sousa Filho<sup>1,2</sup>, José Fernando Dagnone Figueiredo<sup>3,4,5</sup>, Valerie Bouquet<sup>3</sup>,  
André Luiz Menezes de Oliveira<sup>3,6</sup>, Ronan Lebullenger<sup>3</sup>, Ieda Maria Garcia Santos<sup>6</sup>,  
Maryline Guilloux-Viry<sup>3</sup>, Odile Merdrignac-Conanec<sup>3</sup>, Ingrid Tavora Weber<sup>2,4</sup>.*

<sup>1</sup>*Instituto de Química, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ,  
Brazil 23897-000*

<sup>2</sup>*Instituto de Química, Universidade de Brasília, Brasília, DF, Brazil 70910-900*

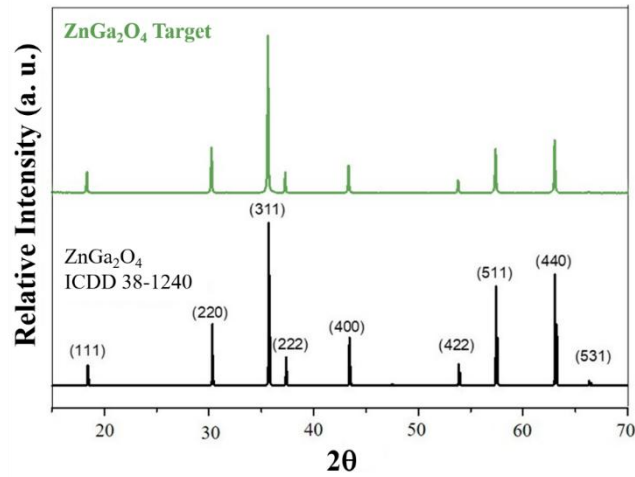
<sup>3</sup>*Univ Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France*

<sup>4</sup>*LIMC, Dept. de Química Fundamental, Universidade Federal de Pernambuco, Recife,  
PE, Brazil 50740-560*

<sup>5</sup>*Universidade Federal Rural de Pernambuco, Cabo de Santo Agostinho, PE, Brazil  
52171-900*

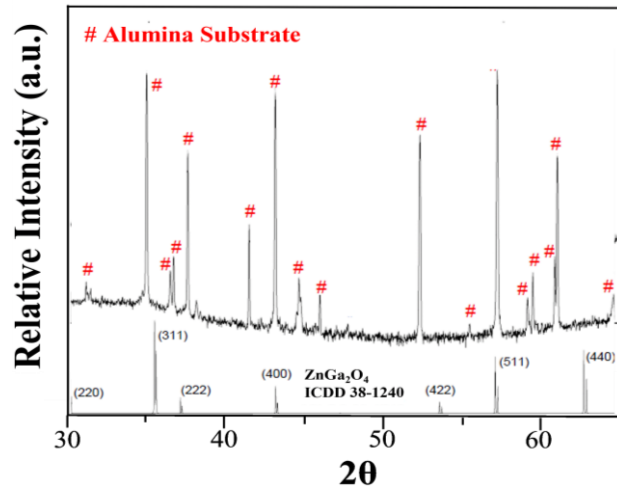
<sup>6</sup>*NPE/LACOM, Dept. de Química, Universidade Federal da Paraíba, Campus I, João  
Pessoa, PB, Brazil 58059- 900*

*\*Corresponding author: idiofilho@ufrj.br*

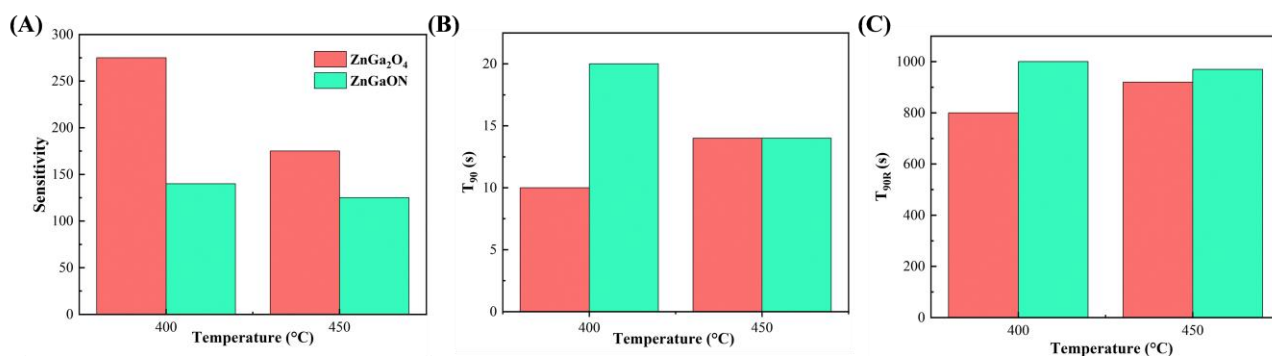


**Figure S1.** XRD pattern of the synthesized ZnGa<sub>2</sub>O<sub>4</sub> target and the corresponding cubic *Fd3m* phase.

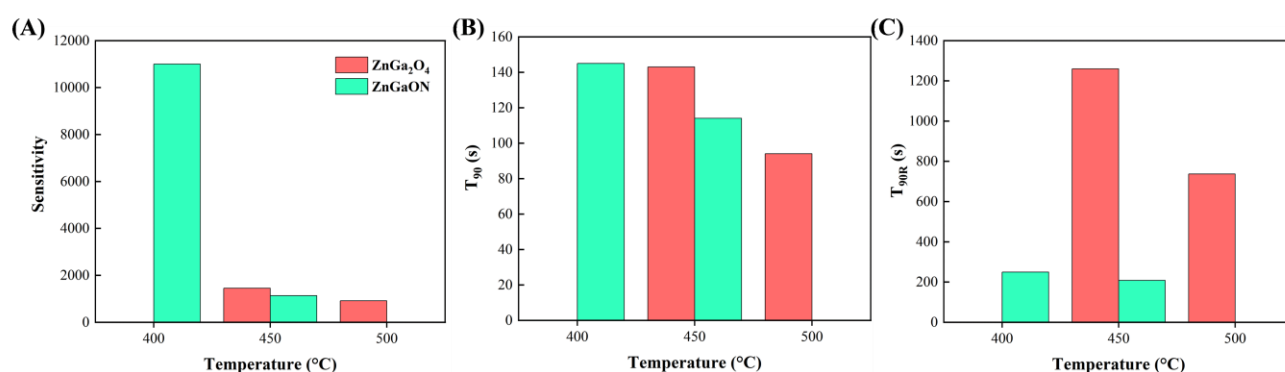
All the reflections peaks were assigned to the cubic spinel structure ZnGa<sub>2</sub>O<sub>4</sub>, with space group *Fd3m* (ICDD 38-1240). No other peak assigned to any related compounds was observed.



**Figure S2.** XRD patterns of the amorphous ZnGa<sub>2</sub>O<sub>4</sub> film deposited at room temperature by PLD on Pt/alumina substrates.



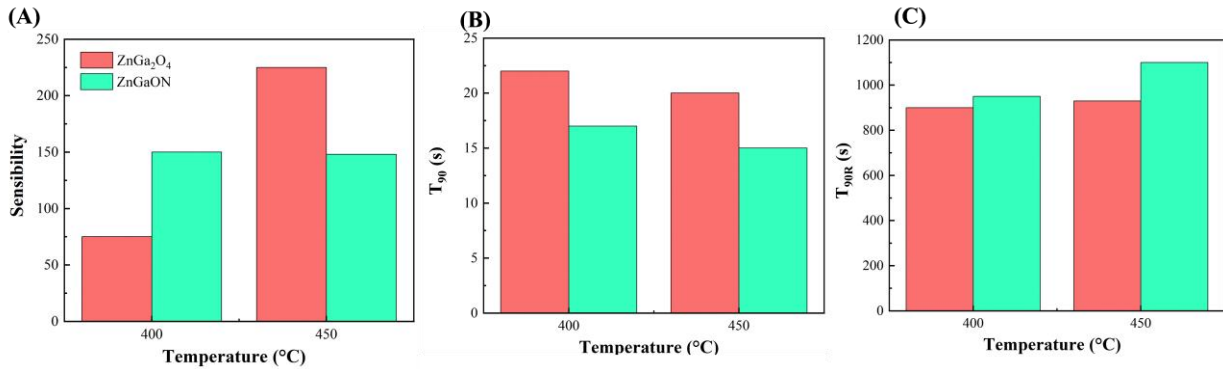
**Figure S3.** (A) Sensitivity ( $R_0/R_{gas}$ ), (B) response time and (C) recovery time to ethanol of ZnGa<sub>2</sub>O<sub>4</sub> and “ZnGaON” sensors as a function of work temperature.



**Figure S4.** (A) Sensitivity ( $R_0/R_{gas}$ ), (B) response time and (C) recovery time to acetaldehyde of ZnGa<sub>2</sub>O<sub>4</sub> and “ZnGaON” sensors as a function of work temperature.

**Figure S5** shows results observed for the sensors prepared in the present work in presence of methanol. Differently from what observed for ethanol, there is a displacement of  $S_{max}$  for both sensors. Following the same discussed for ethanol, the difference maximum response temperature between ZnGa<sub>2</sub>O<sub>4</sub> and ZnGaON for methanol may be related to the gas oxidation rate on sensor surface, that is, the higher the oxidation rate, the lower the maximum response temperature [1]. The  $t_{90}$  continuously decreased with increasing temperature. At 400 °C, the  $t_{90}$  is ~22 s for ZnGa<sub>2</sub>O<sub>4</sub>, decreasing to ~17 s at 450 °C. A similar trend in the curve of  $t_{90}$  as a function of temperature is observed for ZnGaON, but it starts at 400 °C with 20 s and decreases to  $t_{90} = 15$  s at 450 °C (Figure S4B). At the studied temperatures, ZnGaON showed a reduction  $t_{90}$ , which can be correlated to the fact that this sample has a rougher and grained and nanostructured surface morphology and is accessible to gas molecules, which may have favored the faster adsorption and desorption of the species than in ZnGa<sub>2</sub>O<sub>4</sub> sensor.

Regarding the recovery time, one can be observed that at 250 °C,  $t_{90R}$  reaches maximum values of about 1100 s for ZnGaON sensor. In the case of ZnGa<sub>2</sub>O<sub>4</sub> samples the time is ~950 s at both studied temperatures. The stability observed for ZnGa<sub>2</sub>O<sub>4</sub> throughout the temperature range suggests greater sensor surface stability against methanol. In all cases, for both ethanol and methanol, a tendency to high surface recovery times is observed.



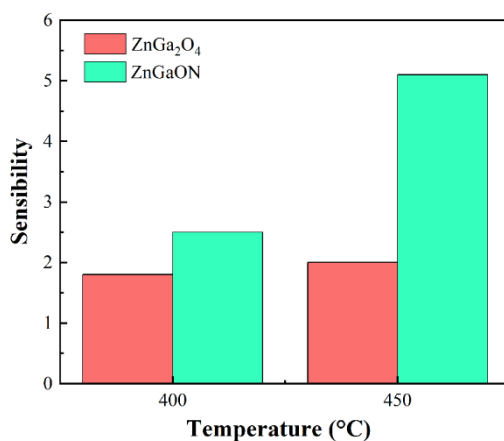
**Figure S5.** (A) Sensitivity ( $R_0/R_{gas}$ ), (B) response time  $t$  and (C) recovery time  $t_{90R}$  towards methanol detection using ZnGa<sub>2</sub>O<sub>4</sub> and “ZnGaON” sensors as a function of work temperature.

It is well known that sensors must have high sensitivity, short response time, long-term chemical, and thermal stability as well as good selectivity. In addition, the sensor must be able to maintain a stable signal in variable concentrations of humidity and temperature or even in aggressive atmospheres[2,3].

To the best of our knowledge about SnO<sub>2</sub> sensors, it is assumed that surface interaction with water vapor leads to adsorption of molecular water and hydroxyl groups. Above 200 °C, the water molecules adsorbed by physisorption are no longer present on the surface, however the hydroxyl groups remain chemisorbed [4]. Upon heating, the desorption of hydroxyl groups should only occur from 450 °C [5,6]. Considering this, a preliminary test was initially performed to evaluate the effect of humidity on sensor performance as shown in **Figure S6**. The presence of H<sub>2</sub>O vapor does not cause a large signal variation in ZnGa<sub>2</sub>O<sub>4</sub> showing a small decrease in resistance at 400 °C, and above this temperature the signal seems to be only a change related to flux fluctuation. For ZnGaON, the electrical resistance varies more sharply throughout the studied temperature range, showing a greater change on surface states due to the presence of H<sub>2</sub>O. Furthermore, an inversion in resistance behavior due to the

presence of H<sub>2</sub>O is observed. This suggests that in ZnGaON, H<sub>2</sub>O is adsorbing on surface capturing electrons due to surface-adsorbate charge transfer. From 450 °C, the sensor resistance starts to decrease when H<sub>2</sub>O vapor is introduced into the chamber. This may be associated with the desorption of hydroxyl groups, which would leave only oxygen acting as the adsorption site [7].

It is important mentioning that the ZnGaON film was not tested at 500 °C to avoid thermal oxidation of the surface. Still, it is possible to work safely to preserve the stability of the sensor at temperatures of 450 °C, as a possible thermal oxidation should only effectively occur from 750 °C [8,9], which would compromise not only the sensor's operation but also the interpretation of the data.



**Figure S6.** (A) Sensitivity of ZnGa<sub>2</sub>O<sub>4</sub> and “ZnGaON” sensors towards humidity as a function of work temperature.

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