# Doped Zinc Oxide Sensors for Hexanal Detection


**A. Malara, L. Bonaccorsi, A. Donato, P. Frontera and G. Neri**

**Abstract** Hexanal is a volatile compound considered important for food storage and food quality control. Despite this, hexanal has not been extensively studied yet. In a previous work, sensors based on metal oxides semiconductors have been studied and zinc oxide showed promising sensing properties. In this work, the topic was further investigated by preparing zinc oxide-based resistive sensors, together with the aluminum-doped and indium-doped form, for hexanal monitoring in food applications.

**Keywords** Gas sensor · Hexanal · Humidity · Zinc oxide

## 1 Introduction

Metal oxide semiconductor have attracted a lot of attention over the last decade being commonly employed in resistive gas sensors field. Among these, zinc oxide due to high chemical sensitivity, non-toxicity, and low cost, has been widely use [1, 2]. Moreover, the performance of zinc oxide sensor can be easily improved by addition of dopants [3]. In fact, doping with metals enhances the sensitivity and selectivity of gas sensors by changing the energy-band structure and morphology, increasing the surface-to-volume ratio and creating more centers for gas interaction on the metal oxide semiconductor surface, as well its acidity or basicity [1, 4].

In this study, zinc oxide-based resistive sensors (ZnO), together with the aluminum-doped (ZnO:Al) and indium-doped (ZnO:In) form were developed for the monitoring of hexanal. Indeed, the determination of hexanal concentration is of great importance for food quality control and its detection is being a significant indicator of food quality in packaging [5–7]. For instance, hexanal formation is often monitored as a means of determining the onset of rancidity in meat [8]. Anyway,

A. Malara (✉) · L. Bonaccorsi · A. Donato · P. Frontera
Department of Civil, Energy, Environment and Material Engineering, Mediterranean University of Reggio Calabria, Via Graziella, Loc. Feo Di Vito, 89122 Reggio Calabria, Italy
e-mail: angela.malara@unirc.it

G. Neri
Department of Engineering, University of Messina, Contrada Di Dio, 98166 Messina, Italy



G. Di Francia et al. (eds.), *Sensors and Microsystems*, Lecture Notes in Electrical Engineering 629, https://doi.org/10.1007/978-3-030-37558-4_42

despite its importance as a quality marker in the food industry, very few works deal with its detection. To this regard, $In_2O_3$, ZnO, $SnO_2$ based resistive sensors have been proposed for hexanal sensing and monitoring [9, 10]. Indeed, as previously reported [10], ZnO, among the investigated oxides, showed the best compromise between sensing temperature and response. It resulted highly sensitive but saturated at high hexanal concentration. In this study, zinc oxide-based resistive sensors, ZnO, ZnO:Al and ZnO:In, were synthesized and tested for monitoring of low hexanal concentrations, as low as its limit threshold, in dry and humid air, as to accurately replicate the real operating conditions.

## 2 Experimental

### *2.1 Synthesis of Sensing Materials*

The starting materials used for the synthesis of doped zinc oxides were zinc nitrate hexahydrate, aluminium acetate and indium nitrate hydrate. All the reagents used were of analytical grade and were used as received without further purification. Powders were synthesized by chemical co-precipitation method. For this, an aqueous solution of aluminium or indium precursor was added to the zinc aqueous solution, keeping the Al/Zn or In/Zn molar ratio equal to 0.01, and stirred till the homogenization. The solution was then hydrolyzed with an aqueous potassium carbonate solution (1 M). The precipitates were then filtered, washed with deionized water, dried at 110 °C for 12 h and then calcined at 500 °C for 2 h in air.

### *2.2 Characterization*

Samples were characterized by means of complementary investigation techniques. Structural characterization was performed by XRD analysis (Bruker, D2 Phaser) in the $2\theta$ range 10–80°, in steps of 0.02° and a count time of 2 s per step (Cu K$\alpha$1 = 1.54056 Å). Powders morphology was studied by Scanning Electron Microscopy SEM (Phenom ProX) equipped with an energy-dispersive X-ray (EDX). EDX analysis was used to evaluate the content and the dispersion of dopants [11].

### *2.3 Sensor Fabrication*

In order to prepare the sensor, a paste was obtained by mixing the oxide powder with a proper quantity of ethanol and deposited on an alumina planar substrate (3 mm $\times$ 6 mm) supplied with interdigitated Pt electrodes and a heating element on the

back side. The device was positioned in a stainless steel testing cell and sensing tests were performed flowing a mixture of dry/humid air and hexanal vapor at different concentrations. A moisturizer was used to produce water moisture and the relative humidity level was detected by a humidity meter (Humidity and Temperature Transmitters HMT120, Vaisala). The hexanal vapor was obtained by bubbling dry air in liquid hexanal maintained at a controlled temperature by a refrigerated circulating bath (temperature range −5/−15 ± 0.01 °C) [10]. Fluxes were measured by Brooks mass flow controller systems for a total gas stream of 100 sccm. The sensors resistance data were collected in the fourpoint mode by an Agilent 34970A multimeter while a dual-channel power supplier instrument (Agilent E3632A) allowed to control the sensor temperature. Sensor response S to hexanal was defined as the ratio of the resistance registered in air ($R_{air}$) and that in hexanal vapor ($R_{hexanal}$). Hexanal concentrations as low as 5, 15 and 30 ppm were considered, at different operating sensors temperatures (200, 250 and 300 °C) and different relative humidity (RH) conditions at room temperature (10, 40 and 60%).

## 3 Results and Discussion

The XRD spectra of the ZnO, Al- and In-doped ZnO samples are showed in Fig. 1. Patterns show the characteristic diffraction peaks of hexagonal wurtzite zinc oxide (Fig. 1a). The crystallite size for ZnO and doped ZnO samples was determined by Debye-Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where, D is the crystallite size, K is a dimensionless shape factor assumed 0.9, λ is the wavelength of X-ray, β is the full width at half maximum of the peak and θ is the Bragg angle. The crystallite sizes of the samples are reported in the inset table of Fig. 1b.

The calculated values indicated that crystallite sizes of doped samples changed due to the doping effect. Indeed, the crystal size of In- and Al-doped samples were

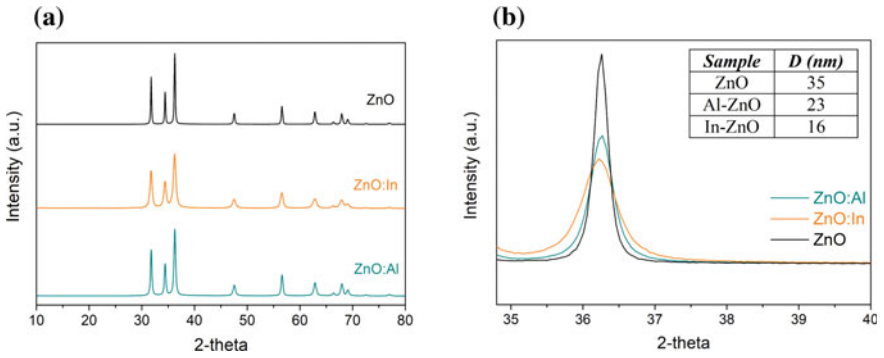


**Fig. 1** XRD spectra of ZnO, ZnO:Al and ZnO:In samples and crystallite sizes determined by Debye-Scherrer equation

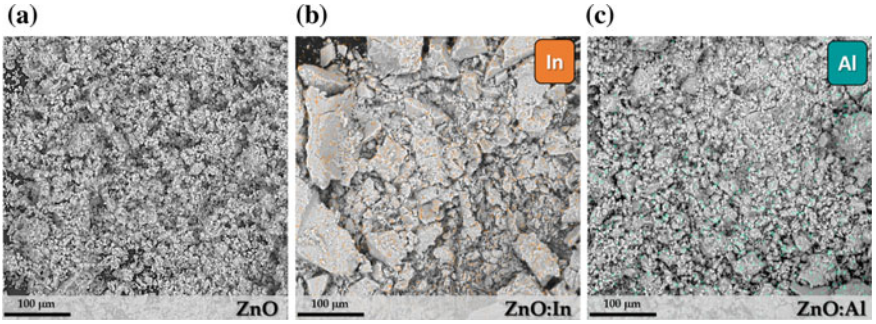


**Fig. 2** SEM micrographs and energy-dispersive X-ray (EDX) maps

smaller than that of the ZnO sample proving that In and Al atoms settled inside the lattice of ZnO and in turn control its nucleation rate, thus a change in the crystal size [12].

From SEM analysis it became clear that the synthesized oxides consisted of grains in the ZnO and ZnO:Al powders (Fig. 2a and c), and composed of fine particles densely aggregated in the case of ZnO:In sample (Fig. 2b). EDX analysis gave the qualitative composition of nanoparticles and also indicated the quantitative presence of indium and aluminum dopants well as their dispersion, homogeneous throughout the zinc oxide matrix (colored points overlapped on the SEM micrographs in Fig. 2b and c).

In Fig. 3, the responses of ZnO, ZnO:Al and ZnO:In as a function of temperature, different hexanal concentrations and relative humidity conditions are shown.

Zinc oxide response to hexanal concentration of 5, 15 and 30 ppm in dry air, at different operating temperatures is shown in Fig. 1a. The sensor is sensitive in all the tested conditions, giving the highest response at 250 °C. In order to study the effect of humidity, the sensor response to different humidity range was registered operating at the temperature of maximum sensitivity. Figure 1b reports the response of ZnO sensor when humid air at 10, 40 and 60% RH (@ 25 °C) was used. As clearly evident, increasing humidity the response has worsened and, moreover, the recovery time has increased as shown in Fig. 4. For a sensor temperature higher than 150 °C, the water vapor in the air stream cannot forms a continuous monolayer covering the oxide surface but is partially chemisorbed by interaction with the surface hydroxyl groups [13].

The chemisorbed water increases the electrical conductivity of the semiconductor oxide mainly for two reasons: the displacement of the adsorbed oxygen species and the interaction of hydronium ions with the lattice oxide [14, 15]. The combined effect of these two mechanisms, however, caused the reduction of the sensor response with humidity observed for ZnO in Fig. 3b. The oxygen species displacement by the adsorbed water molecules lowered the sensitivity of the ZnO sensor because a decrease of oxidation sites available for the hexanal detection [13–15].

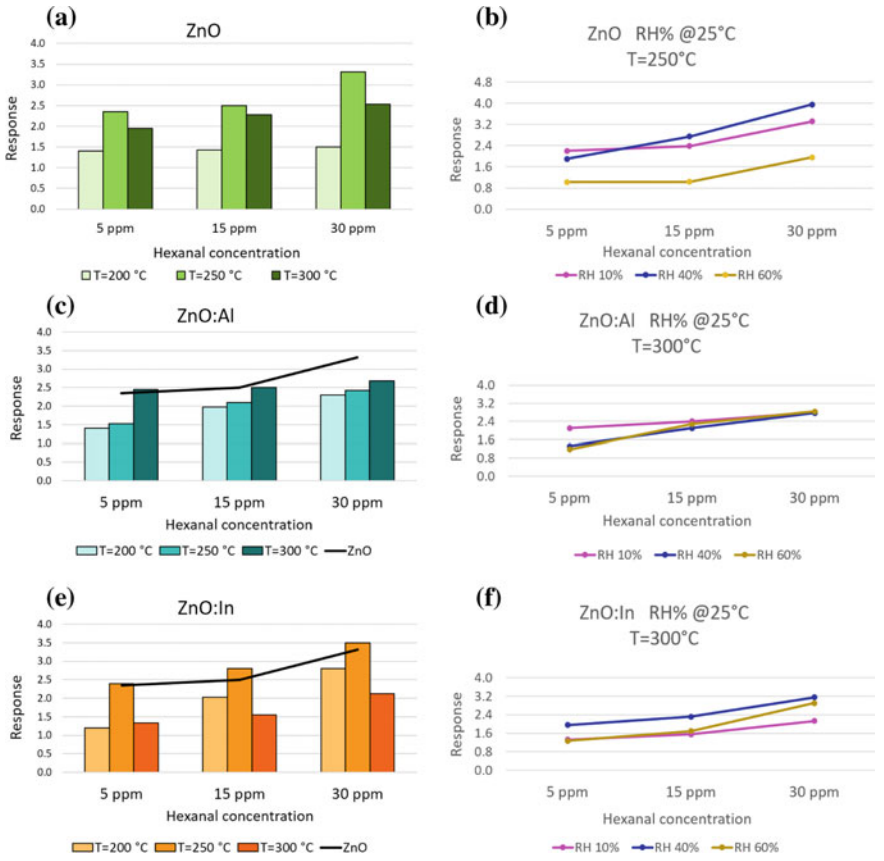


**Fig. 3** Sensors response evaluated as $R_{air}/R_{hexanal}$ as function of temperatures and hexanal concentrations in dry air (**a**, **c**, **e**) and RH (**b**, **d**, **f**)

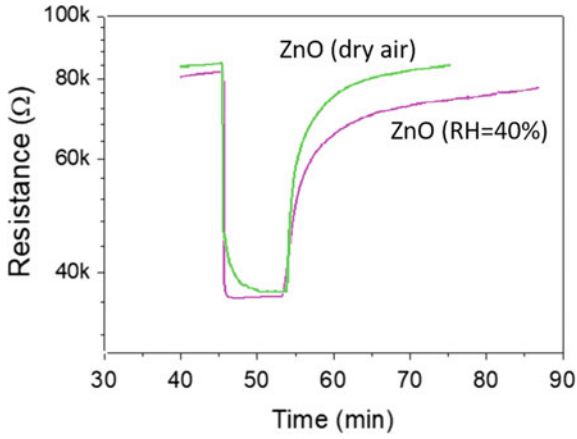


**Fig. 4** ZnO sensor response at 250 °C and 15 ppm hexanal in dry and wet air (RH 40% @ 25 °C)

An increasing trend with T, reaching the highest response at 300 °C, was observed for the ZnO:Al sample (Fig. 3b), even if, unless for the higher operating temperature (300 °C), the sensitivity resulted lower than pure ZnO, proving the inefficient effect of Al dopant at low temperatures. The Al doped zinc oxide showed a sensitivity decrease at increasing RH% similar to the undoped metal oxide, as shown in Fig. 3d.

As regards ZnO:In behavior, the response versus temperature in dry air showed a slight increment compared to ZnO (Fig. 3e) with a maximum sensitivity at T = 250 °C. In wet air, the ZnO:In response was higher at the highest operating temperature (300 °C) and, surprisingly, demonstrated to be less sensitive to water interaction even at the maximum tested humidity of 60% RH (@ 25 °C), as evident in Fig. 3f. The reasons for this improved behavior of In doped zinc oxide was ascribed to lower grain size (Fig. 1b) that is know to improve the sensor response in general [2, 3, 14] but that effected in this case also the water chemisorption on the sensor surface [15].

## 4 Conclusion

In conclusion, zinc oxide and doped zinc oxide based sensors, synthesized by chemical co-precipitation method, were used for hexanal sensing. Very low hexanal concentrations both in dry and humid air were tested. The comparison of the three sensors demonstrated that ZnO is an interesting candidate although negatively influenced by a humid environment. The inefficient effect of Al dopant at low temperatures was reported, whereas doping zinc oxide with indium oxide showed to improve the sensor response in dry air and to be only partially influenced by wet air up to 60% RH if an operating temperature of 300 °C is used.

## References

1. Hjiri M, El Mir L, Leonardi SG, Pistone A, Mavilia L, Neri G (2014) Al-doped ZnO for highly sensitive CO gas sensors. Sens Actuators B: Chem 196:413–420
2. Zhang J, Qin Z, Zeng D, Xie C (2017) Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration. Phys Chem Chem Phys 19(9):6313–6329
3. Qi J, Zhang H, Lu S, Li X, Xu M, Zhang Y (2015) High performance indium-doped ZnO gas sensor. J Nanomaterials 16(1):74
4. Angiolini L, Benelli T, Giorgini L, Mauriello F, Salatelli E (2007) Chiroptical and optical thermoplastic acid sensors based on chiral methacrylic polymers containing azoaromatic moieties. Sens Actuators B: Chem 126(1):56–61
5. Spadafora ND, Amaro AL, Pereira MJ, Müller CT, Pintado M, Rogers HJ (2016) Multi-trait analysis of post-harvest storage in rocket salad (*Diplotaxis tenuifolia*) links sensorial, volatile and nutritional data. Food Chem 211:114–123
6. Jayasena DD, Ahn DU, Nam KC, Jo C (2013) Flavour chemistry of chicken meat: a review. Asian-Australas J Anim Sci 26(5):732
7. Schindler S, Krings U, Berger RG, Orlien V (2010) Aroma development in high pressure treated beef and chicken meat compared to raw and heat treated. Meat Sci 86(2):317–323

8. Skibsted LH, Mikkelsen A, Bertelsen G (1998) Lipid-derived off-flavours in meat. Flavor of meat, meat products and seafoods. Blackie Academic, London, pp 217–256
9. Huang K, Zhu C, Yuan F, Xie C (2013) Nanoscale $SnO_2$ flat-type coplanar hexanal gas sensor arrays at ppb level. J Nanosci Nanotechnol 13(6):4370–4374
10. Malara A, Bonaccorsi L, Donato A, Frontera P, Piscopo A, Poiana M, Leonardi SG, Neri G (2018) Sensing properties of indium, tin and zinc oxides for hexanal detection. Convegno Nazionale Sensori. Springer, Cham, pp 39–44
11. Malara A, Paone E, Frontera P, Bonaccorsi L, Panzera G, Mauriello F (2018) Sustainable exploitation of coffee silverskin in water remediation. Sustainability 10(10):3547
12. Hendi AA, Alorainy RH, Yakuphanoglu F (2014) Humidity sensing characteristics of Sn doped zinc oxide based quartz crystal microbalance sensors. J Sol-Gel Sci Technol 72(3):559–564
13. Helwig A, Müller G, Sberveglieri G, Eickhoff M (2009) On the low-temperature response of semiconductor gas sensors. J Sens 2009
14. Farahani H, Wagiran R, Hamidon M (2014) Humidity sensors principle, mechanism, and fabrication technologies: a comprehensive review. Sensors 14(5):7881–7939
15. Wang C, Yin L, Zhang L, Xiang D, Gao R (2010) Metal oxide gas sensors: sensitivity and influencing factors. Sensors 10(3):2088–2106