

Nanostructured metal oxides semiconductors for oxygen chemiresistive sensing

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Abstract. Nanostructured metal oxide semiconductors have been widely investigated and are commonly used in gas sensing structures. After a brief review which will be focused on chemiresistive oxygen sensing employing this type of sensing materials, for both room temperature and harsh environment applications (particularly, at high ambient temperature and high relative humidity levels), paper reports new results concerning O₂ detection of a structure using a sensing layer comprising nanostructured (typical grain size of 50 nm) SrTi_{0.6}Fe_{0.4}O_{2.8} (STFO40), synthesized by sonochemical methods, mixed with single wall carbon nanotubes. The structure is a *Microelectromechanical System* (MEMS), based on a *Silicon-on-Insulator* (SOI), *Complementary Metal-Oxide-Semiconductor* (CMOS)-compatible micro-hotplate, comprising a tungsten heater which allows an excellent control of the sensing layer working temperature. Oxygen detection tests were performed in both dry (RH = 0%) and humid (RH = 60%) nitrogen atmosphere, varying oxygen concentrations between 1% and 20% (v/v), at a constant heater temperature of 650 °C.

Key-words: Chemiresistive Oxygen Sensing, Metal Oxide Semiconductors, Sonochemistry, STFO, Carbon Nanotubes, CMOS-compatible SOI membrane, MEMSs.

1. Introduction

Industrial applications, such as the control of air-fuel mixture in combustion engine, emission monitoring in automotive, domestic and other small-scale boilers, steel and cement industries,

require low cost, low power oxygen sensors with optimum sensitivity, selectivity and response time [1, 2]. At the same time, monitoring O₂ concentration is essential in other fields, such as medicine, food packaging industries, marine biology, soil aeration, plant respiration, limnology and waste management [3, 4]. The above-mentioned diversity of applications requiring oxygen sensing explains the multitude of sensing principles currently employed by both O₂ detectors available either at academic or commercial level.

The concentration of oxygen in an environment can be determined under ambient conditions using, for instance, optical sensors [5–14], electrochemical sensors [15–23], surface acoustic wave (SAW) sensors [24] or magnetic devices [25]. Oxygen measurements at high temperature levels can be performed with ceramic - based sensors, using different measurement principles: potentiometric [26–28], field effect transistor [29, 30], limiting current amperometric [31, 32].

At the same time, semiconducting metal oxide sensors are widely used in the last years for chemiresistive oxygen sensing. It is important to mention that this inexpensive alternative technology offers solutions both for room and high temperature sensing.

In this review, we provide a summary on nanostructured metal oxides and their chemiresistive oxygen sensing properties. A special attention will be given to metal oxides semiconductors with ABO₃ perovskite structure and their nanocomposites. In addition, new results on the sensing properties of a nanocomposite mixture comprising SrTi_{0.6}Fe_{0.4}O_{2.8} (STFO40) and *Single Wall Carbon Nanotubes* (SWCNTs) are provided.

2. Some considerations about Metal Oxide Semiconductors gas sensors and their characteristics

Metal oxide semiconductors-based gas sensors have been considered a promising candidate for portable gas detection systems because of their significant merits, such as: detection of all reactive gases, high sensitivity, low cost, lightweight, compact size, robustness, portability, and simplicity in both manufacturing and usage.

Basically, metal oxides semiconductors sensors are chemiresistors, the resistance of their sensing layer being changed as result of the interaction with the analyte to be detected.

A p-type semiconductor – based sensing layer is the one where the majority charge carriers are holes. Upon interaction with oxidizing gases, their conductivity increases, while interaction with reducing gas yields to increasing resistance. On the contrary, an n-type semiconductor is a material for which electrons are the majority charge carriers. Upon interaction with oxidizing gases, their conductivity decreases. Conversely, reducing gases will enrich the sensing layer with electrons, thus contributing to a decrease in the resistance [33–36].

Although being matters of high importance, the cross-sensitivity of metal oxide semiconductors-based gas sensors and their increased sensitivity to certain gases are not fully understood. The exact mechanisms that cause the detection of a certain gas and the non-detection of another one are still controversial [37].

There are only few papers which show the importance of discussing the gas molecule and the metal oxide semiconductors in terms of a tandem [38–40]. Moreover, apart from classifying gases as oxidizing or reducing, the nature of the subtle interaction between the analyte and the metal oxide semiconductors-based sensing layer is generally ignored in literature.

The performance of metal oxides semiconductors-based chemiresistive sensors is significantly influenced by the chemical components [41–45], surface modifications by noble metals

[46–49], humidity [50–55], and temperature [56–58]. In the last years, a lot of efforts were devoted towards the synthesis of nanostructured metal oxide semiconductors. High surface area and controlled structure have a paramount importance in order to improve gas sensing properties [59–61].

Besides selectivity issue, metal oxides semiconductors-based chemiresistive gas sensing exhibits other possible disadvantages, such as: high power consumption, drift, material degradation, slow response time [62].

3. Metal Oxide Semiconductors based oxygen chemiresistive sensing at low temperature

Metal oxides semiconductors-based O₂ chemiresistive sensing can be performed at low temperature. Chaabouni *et al.* have used ZnO films for oxygen sensing at room temperature [63]. The metal oxide semiconductor was deposited by RF magnetron sputtering in an argon atmosphere, on glass and p-silicon substrates. It was demonstrated that the O₂ sensitive properties are strongly correlated with the deposition parameters and the substrate nature.

A recent report by Shafura *et al.* uses sol-gel spin coated method to synthesize nanostructured aluminium doped zinc oxide sensing layer [64]. The O₂ sensing experiments were performed at room temperature. The porous film exhibited good sensitivity (73%), in the presence of 50 sccm of O₂ flow rate.

Niu *et al.* explored the O₂ sensing capability of ZnO nanowires at room temperature [65]. The piezotronic effect and the pre-treatment of metal oxide surface in UV light trigger an increase of the sensitivity toward oxygen molecules. A recent study by Chou *et al.* presents a novel ultraviolet irradiation (370 nm) assisted nanostructured ZnO sensing layer for high sensitivity oxygen sensing at 50 °C [66]. The chemiresistive response of the UV-assisted ZnO sensing layer is 4.66 times larger than the same sensing layer in the absence of UV exposure.

A highly sensitive oxygen sensor operating at room temperature based on platinum-doped In₂O₃ nanocrystals was developed by Neri *et al.* [67]. Semiconducting In₂O₃ nanocrystals, synthesized using a non-aqueous sol-gel method and doped with 1 wt% of platinum, exhibit superior performance in comparison with the state-of-the-art sensors.

4. Metal Oxide Semiconductors – based oxygen chemiresistive sensing at high temperature

In harsh environment applications, especially at high relative humidity levels and at high ambient temperature levels [1], metal oxide semiconductors-based oxygen chemiresistive sensing is an inexpensive technology that could be an alternative to the well-known lambda sensor. Oxygen sensors operating at high temperature and employing, as sensing layers, semiconducting metal oxides such as TiO₂ [68, 69], CeO₂ [70, 71], SnO₂ [72, 73], Ga₂O₃ [74, 75], and WO₃ [76] were fabricated and tested in the last decades.

Their sensing mechanism, explained by the Kröger and Vink model [77], is based on the reaction between the oxygen vacancies - which are an intrinsic part of their structure - and the oxygen gas. Metal oxides, with ABO₃ like perovskite structure (BaTiO₃, LaFeO₃, and SrTiO₃), were also studied as sensing layer for oxygen detection [78].

Recently, doped perovskites have been explored as promising candidates for use in manufacturing of chemiresistive oxygen sensors. $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STFO) with different Ti: Fe ratios have been proposed in the literature as suitable alternatives for O_2 resistive sensing layers. This type of material exhibits several advantages, such as:

- ✓ For a certain Ti:Fe ratio, STFO has zero temperature coefficient;
- ✓ Depending on the manufacturing method, STFO exhibits TCR=0 either for 35% Fe and 65% Ti (STFO35), or for 60% Fe and 40% Ti (STFO60);
- ✓ For STFO60, TCR is 0 if the layer is heated between 450°C and 650°C;
- ✓ STFO60 accommodates large levels of dopants without displaying phase changes [79–81].

Avramescu *et al.* [82] have reported the design and characterization of a *Microelectromechanical System* (MEMS) chemiresistive O_2 sensor, based on an ultra-low-power, CMOS-compatible, *Silicon on Insulator* (SOI) micro-hotplate membrane, depicted in Figure 1. The membrane comprises a tungsten heater that can be safely operated at temperatures up to 650 °C. Other important advantages of the SOI micro-hotplates are their very low power consumption (tens of mW) and high temperature uniformity across the heater sensing area.

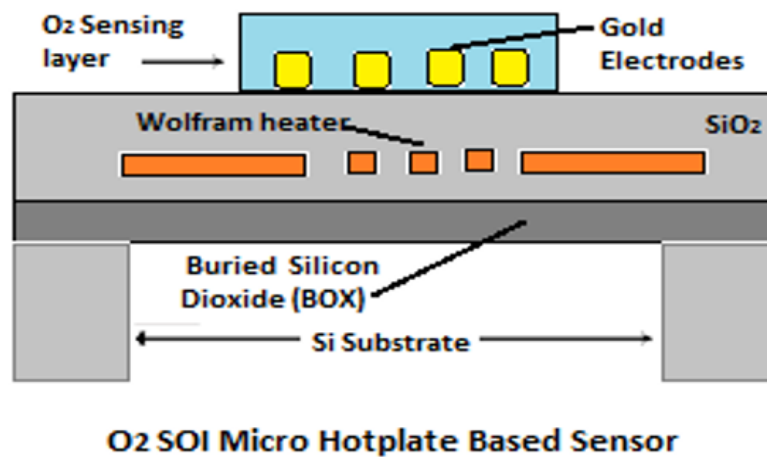


Fig. 1. Chemiresistive sensing structure based on SOI CMOS-compatible micro-hotplate (cross-section).

In the described work, STFO60 was used as sensing layer [62]. The resistive O_2 sensing structure was experimentally tested in an N_2 atmosphere, where the O_2 concentration was varied from 1% to 20%. The heater temperature was set at 600°C. The results, presented in Figure 2, show a p-type behavior (i.e., conductivity increases with oxygen concentration), characterized by good sensitivity and fast response.

Electro spinning [83], co-precipitation [84], self-propagating high-temperature synthesis [85], microwave-assisted hydrothermal [86] are several methods for obtaining micro/nano-structured STFO_x , nanofibers, nanocubes and (nano)-powders (particles size in the 40 nm–1.5 μm range).

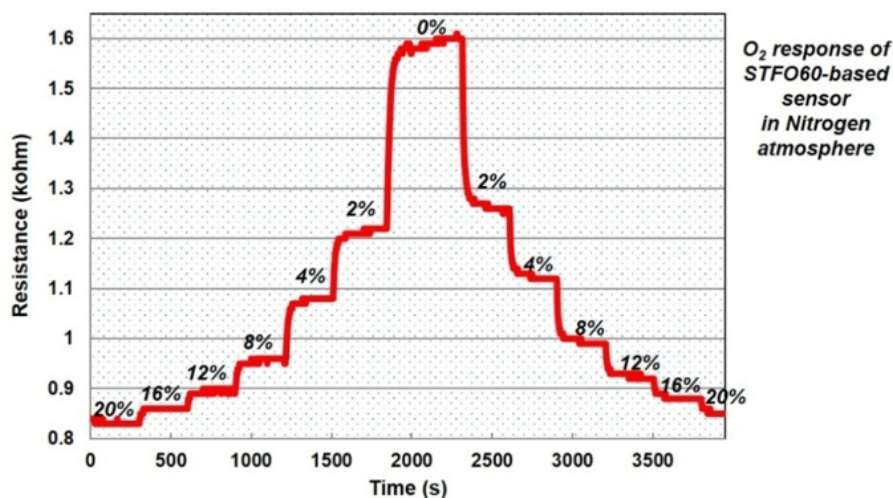


Fig. 2. O₂ response of an STFO60-based sensor in nitrogen atmosphere.

In recent years, a lot of effort was devoted to developing new methods for synthesis of nano-structured materials with controlled size and morphology.

Among these, the sonochemical methods have proved to be a suitable tool for the synthesis of materials with high surface area materials and uniform particle size [87–97].

Matrix nanocomposites comprising sonochemical synthesized STFO_x and different carbon-based nano-structures (single-wall, double-wall, and multi-wall carbon, graphene, nanotubes, fullerene-C60, fullerene-C70, nanobuds, carbon nanohorns, carbon nanofibers) were also proposed as sensing layers for chemiresistive oxygen detection [98–100].

5. Proposed synthesis, theoretical considerations and experimental results

Figure 3 introduces the route followed for the sonochemical synthesis of SrTi_{0.6}Fe_{0.4}O₃ (sono-STFO40) powder. The obtained aqueous mixture (pH ~ 14) was sonicated for 2 h (~94 W/cm² intensity) in argon (5 L/min flow), using a Hielscher UP200St (200 W, 26 kHz) ultrasonic generator with a titanium 14 mm sonotrode, set-up shown in Figure 4.

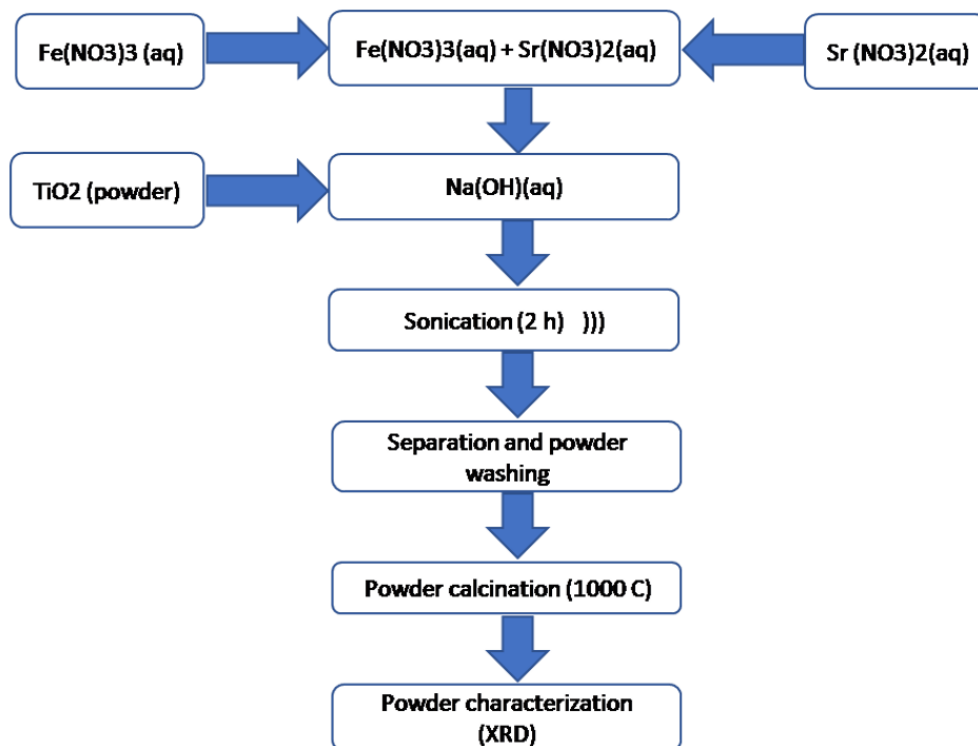


Fig. 3. Route for synthesizing sono-STFO40 employing sonochemical synthesis.



Fig. 4. Argon set-up for sono-STFO40 sonochemical synthesis.

In order to produce an O₂ sensing layer, sono-STFO40 slurry is required. Sono-STFO40 slurry was obtained by mixing sono-STFO40 (powder, 55% w/w, obtained following the route in Figure 3), terpineol (solvent, 35% w/w, having the formula depicted in Figure 5), hydroxypropyl cellulose (HPC) (binder, 5% w/w, having the formula depicted in Figure 6) and capric acid/caprylic acid (equimolecular mixture, surfactant, 5% w/w).

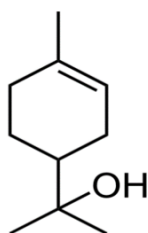


Fig. 5. The structure of terpineol.

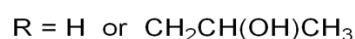
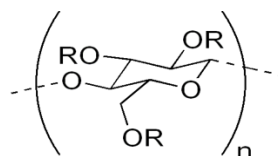


Fig. 6. The structure of hydroxypropyl cellulose (HPC).

A Sono-STFO40 & SWCNTs matrix nanocomposite slurry was also synthesized, by mixing sono-STFO40 (powder, 50% w/w), SWCNTs (5%), terpineol (solvent, 35% w/w), hydroxypropyl cellulose (HPC)(binder, 5% w/w) and capric acid/caprylic acid (equimolecular mixture, surfactant, 5% w/w). Sono-STFO40 and sono-STFO40 & SWCNTs matrix nanocomposite were deposited onto the SOI-based micro-hotplate membranes presented in Figure 1, using a dip pen nanolithography (DPN) system (NLP2000 by NanoInk). The obtained structures are depicted in Figures 7 and 8.

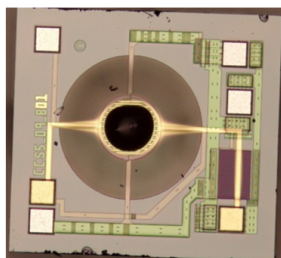


Fig. 7. Top-view of the resistive, SOI micro-hotplate-based O₂ resistive sensor employing sono-STFO40 as sensing layer.

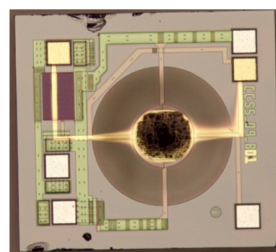


Fig. 8. Top-view of the resistive, SOI micro-hotplate-based O₂ resistive sensor employing sono-STFO40 mixed with SWCNTs as sensing layer.

After setting the tungsten heater temperature at 650°C, the resistance of sensor was measured at various oxygen concentrations (varying from 1% to 20%). Figures 9 and 10 show how the resistance of the sensor changes with the O₂ concentration, as a function of time, in seconds. Both structures show p-type semiconductor behavior, good stability and reduced drift.

Sono-STFO40 has p-type semiconducting behavior in atmospheres where the oxygen partial pressure is larger than 10⁻⁵ bar. When the O₂ concentration increases, more holes are gene-

rated due to the oxygen atoms incorporation in the positively charged oxygen vacancies of sono-STFO40. Thus, sono-STFO40 conductivity is increased, in agreement with the results in Figure 9. At the same time, the conductivity of SWCNTs is strongly influenced by both O₂ and relative humidity (RH) levels. O₂ exposure leads to O₂ molecules being adsorbed by SWCNTs, thus also SWCNTs conductivity is being significantly increased. Consequently, when SWCNTs are mixed with sono-STFO40, even more O₂ molecules are attached to the mixture (compared to sono-STFO40 and SWCNTs alone), and thus the sono-STFO40&SWCNTs mixture has stronger O₂ detection properties, in agreement with the results in Figure 10.

These theoretical considerations are confirmed by the experimental results presented in Figure 11; these demonstrate that the presence of SWCNTs enhances the response to O₂ up to 35%, for O₂ concentration levels lower than 4%. At higher O₂ concentration levels, this effect becomes negligible, most probably due to a saturation of the surface SWCNTs with oxygen molecules.

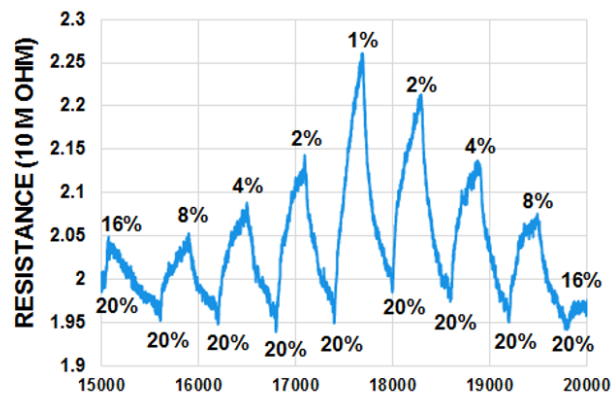


Fig. 9. Resistance of sensor versus time (in seconds), at various oxygen concentrations (in % in graphic) for the SOI micro-hotplate sensing structure employing sono-STFO40 as sensing layer.

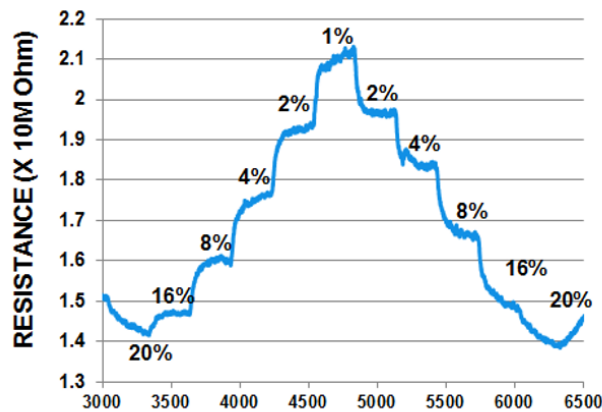


Fig. 10. Resistance of sensor versus time (in seconds), at various oxygen concentrations (in % in graphic) for the SOI micro-hotplate-based sensing structure employing sono-STFO40 & SWCNTs mixture as sensing layer.

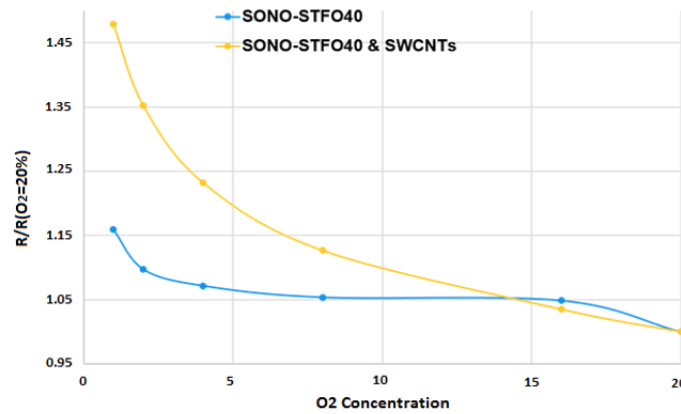


Fig. 11. A comparison of O₂ response of two SOI micro-hotplate based structures employing sono-STFO40 and sono-STFO40&SWCNTs, respectively, as sensing layer.

The influence of RH on the O₂ response of sono-STFO40 and sono-STFO40 & SWCNTs was also investigated. The results are summarized in the Figures 12 - 13. As predicted by theory, RH has a stronger impact on the sono-STFO40 & CNTs based sensor. This effect was expected given the high RH sensitivity of SWCNTs.

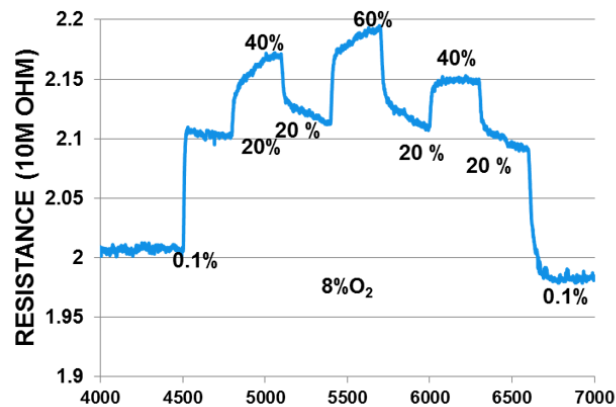


Fig. 12. The influence of RH (% in graphic) on resistance of sensor versus time (in seconds), for a SOI-based structure employing Sono-STFO40 as sensing layer; O₂ level was kept constant at 8% in nitrogen atmosphere.

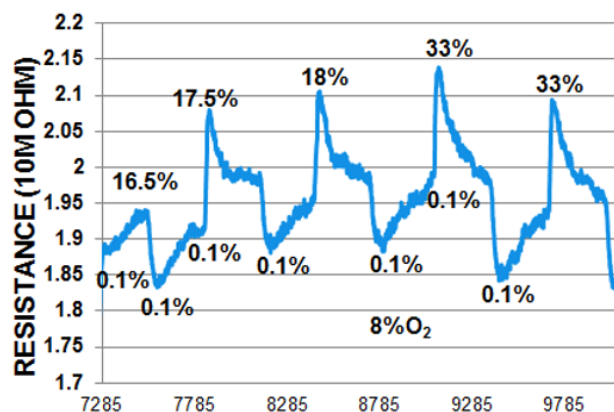


Fig. 13. The influence of RH (in % in graphic) on resistance of sensor versus time (in seconds) for a SOI-based structure employing Sono-STFO40 & SWCNTs as sensing layer; O₂ level was kept constant at 8% in nitrogen atmosphere.

6. Conclusions

The development of nanostructured metal oxides semiconductors for oxygen chemiresistive sensing has been accelerated over the past 10 years. After reviewing some aspects regarding metal oxide semiconductors-based oxygen sensing, both at room temperature and in harsh environment applications (especially at high ambient temperature and high relative humidity levels), the paper introduces new results regarding the O₂ response of SOI micro-hotplate-based structures employing, as sensing layer, nanostructured sono-STFO40 (synthesized by a sonochemical method) mixed with SWCNTs. O₂ detection tests, performed in both dry (RH = 0%) and humid (RH = 60%) nitrogen atmosphere and varying oxygen concentrations between 1% and 20% (v/v), showed that the presence of the SWCNTs enhances the O₂ response up to 35% for O₂ concentration levels lower than 4%.

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