ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **20**, Number 2, 2017, 86–100

Nanostructured metal oxides semiconductors for oxygen chemiresistive sensing

B. C. ŞERBAN[1, *], M. BREZEANU[2], A. D. LUCA[3], S. Z. ALI[4], O. BUIU[1], C. COBIANU[1], A. STRATULAT[5], F. UDREA[3, 4], V. AVRAMESCU[1], N. VARACHIU[1], O. IONESCU[1], and G. IONESCU[6]

[1]National Institute for Research and Development in Microtechnologies, IMT-Bucharest, Romania
[2]University Politehnica of Bucharest, Romania
[3]University of Cambridge, United Kingdom
[4]ams Sensors, United Kingdom
[5]University Politehnica of Bucharest, Center for Research and Eco - Metallurgical Expertise ECOMET, Bucharest, Romania
[6]Petroleum and Gas University of Ploiesti, Ploiesti, Romania
[*]Corresponding author: bogdan.serban@imt.ro

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 O_2 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 O_2 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 O_2 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 ABO_3 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 chemiresitive gas sensing exhibits other possible disadvantages, such as: high power consumption, drift, material degradation, slow response time [62].

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

Metal oxides semiconductors-based O_2 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 O_2 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 O_2 sensing experiments were performed at room temperature. The porous film exhibited good sensitivity (73%), in the presence of 50 sccm of O_2 flow rate.

Niu *et al.* explored the O_2 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 In_2O_3 nanocrystals was developed by Neri *et al.* [67]. Semiconducting In_2O_3 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 TiO_2 [68, 69], CeO_2 [70, 71], SnO_2 [72, 73], Ga_2O_3 [74, 75], and WO_3 [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 ABO_3 like perovskite structure ($BaTiO_3$, $LaFeO_3$, and $SrTiO_3$), 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.$SrTi_{1-x}Fe_xO_{3-\delta}$ (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.

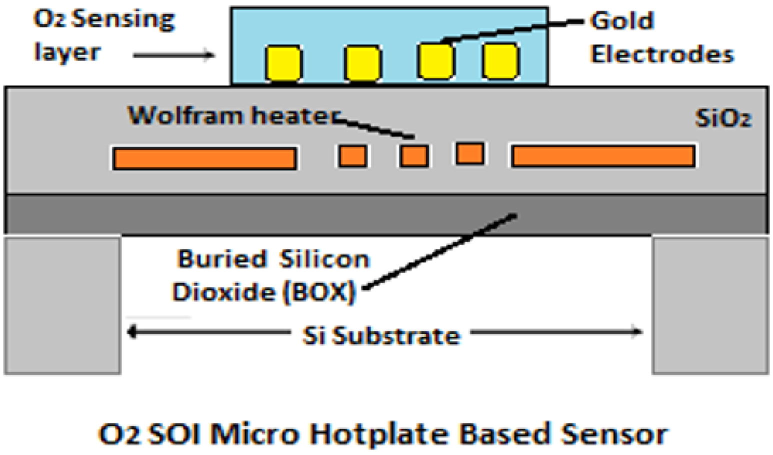

Fig. 1. Chemiresistive sensing structure based on SOI CMOS-compatible micro-hotplate (cross-section).

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).

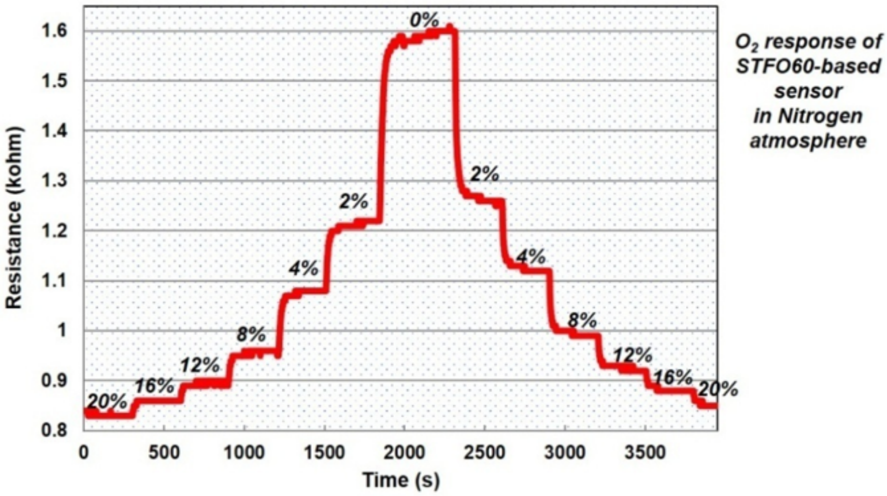

Fig. 2. O_2 response of an STFO60-based sensor in nitrogen atmosphere.

In recent years, a lot of effort was devoted to developing new methods for synthesis of nanostructured 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 $SrTi_{0.6}Fe_{0.4}O_3$ (sono-STFO40) powder. The obtained aqueous mixture (pH $\sim$ 14) was sonicated for 2 h ($\sim$94 W/cm^2 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.

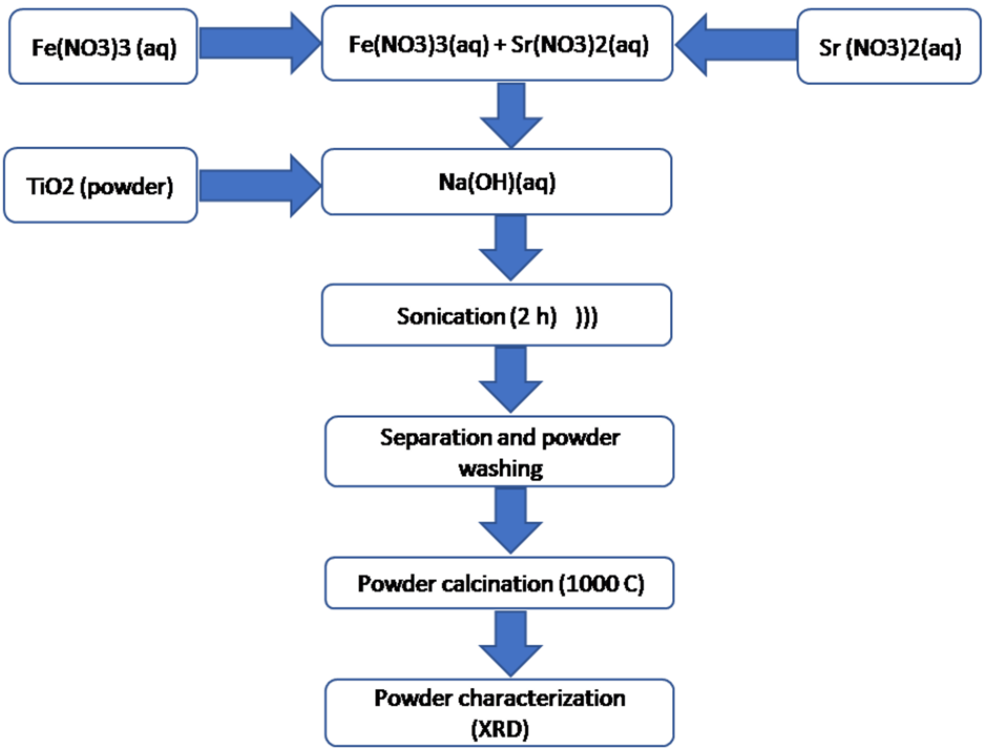

Fig. 3. Route for synthesizing sono-STFO40 employing sonochemical synthesis.

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

In order to produce an O_2 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).

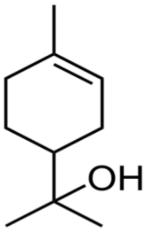

Fig. 5. The structure of terpineol.

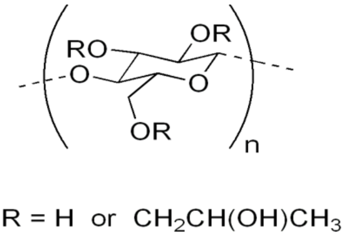

Fig. 6. The structure of hydroxypropyl cellulose (HPC).

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.

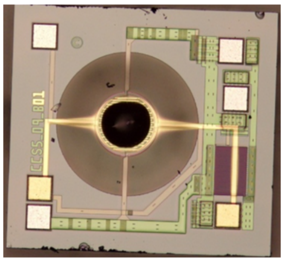

Fig. 7. Top-view of the resistive, SOI micro-hotplate-based O_2 resistive sensor employing sono-STFO40 as sensing layer.

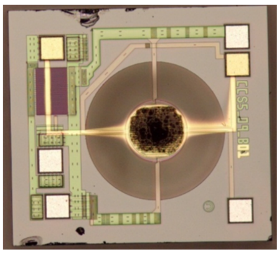

Fig. 8. Top-view of the resistive, SOI micro-hotplate-based O_2 resistive sensor employing sono-STFO40 mixed with SWCNTs as sensing layer.

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 O_2 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 O_2 concentration increases, more holes are generated 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 O_2 and relative humidity (RH) levels. O_2 exposure leads to O_2 molecules being adsorbed by SWCNTs, thus also SWCNTs conductivity is being significantly increased. Consequently, when SWCNTs are mixed with sono-STFO40, even more O_2 molecules are attached to the mixture (compared to sono-STFO40 and SWCNTs alone), and thus the sono-STFO40&SWCNTs mixture has stronger O_2 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 O_2 up to 35%, for O_2 concentration levels lower than 4%. At higher O_2 concentration levels, this effect becomes negligible, most probably due to a saturation of the surface SWCNTs with oxygen molecules.

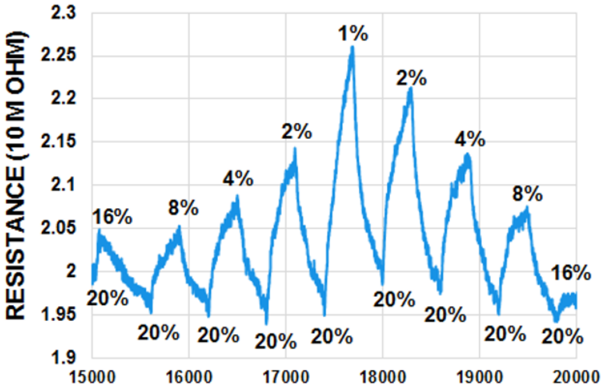

Fig. 9. Resistance of sensor versus time (in seconds), at various oxygen concentrations (in % in graphic) for the SOI micro-hotplate sensing structure employing sono-STFO40 as sensing layer.

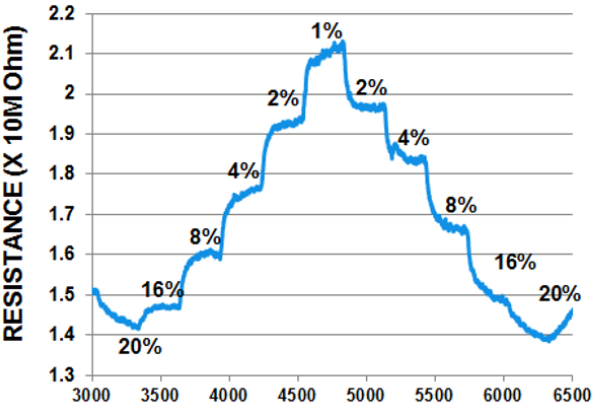

Fig. 10. Resistance of sensor versus time (in seconds), at various oxygen concentrations (in % in graphic) for the SOI micro-hotplate-based sensing structure employing sono-STFO40 & SWCNTs mixture as sensing layer.

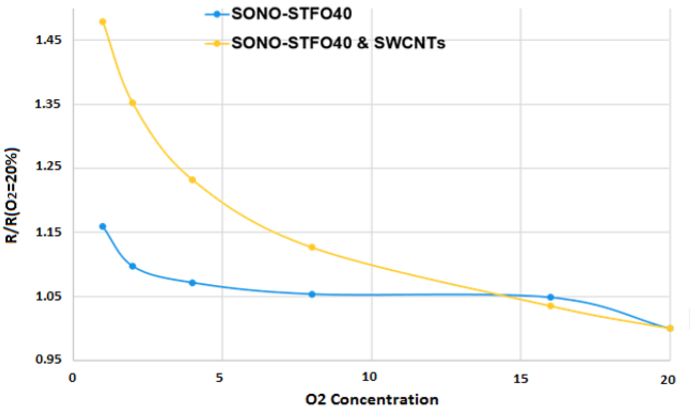

Fig. 11. A comparison of O_2 response of two SOI micro-hotplate based structures employing sono-STFO40 and sono-STFO40&SWCNTs, respectively, as sensing layer.

The influence of RH on the O_2 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.

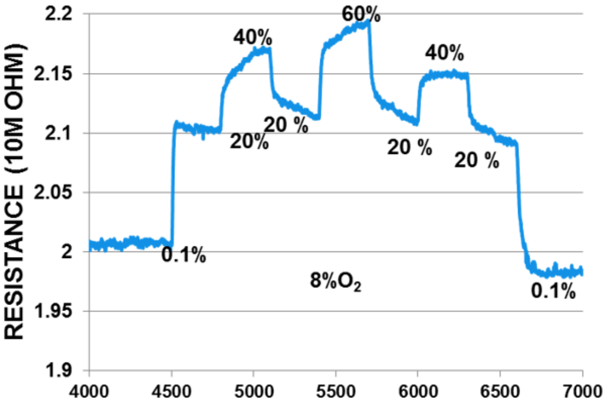

Fig. 12. The influence of RH (% in graphic) on resistance of sensor versus time (in seconds), for a SOI-based structure employing Sono-STFO40 as sensing layer; O_2 level was kept constant at 8% in nitrogen atmosphere.

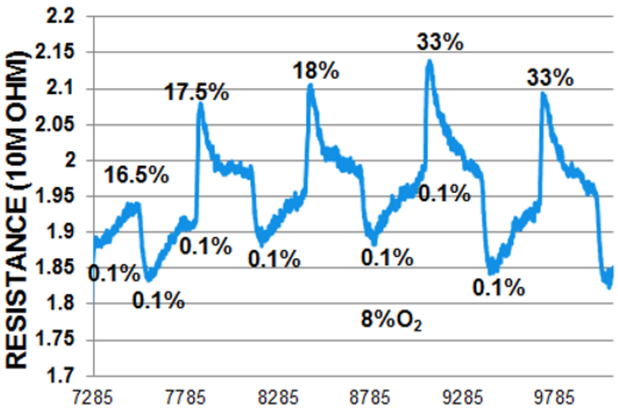

Fig. 13. The influence of RH (in % in graphic) on resistance of sensor versus time (in seconds) for a SOI-based structure employing Sono-STFO40 & SWCNTs as sensing layer; O_2 level was kept constant at 8% in nitrogen atmosphere.

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 O_2 response of SOI micro-hotplate-based structures employing, as sensing layer, nanostructured sono-STFO40 (synthesized by a sonochemical method) mixed with SWCNTs. O_2 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 O_2 response up to 35% for O_2 concentration levels lower than 4%.

References

[1] QUARANTA M., BORISOV S.M., KLIMANT I., *Indicators for optical oxygen sensors*, Bioanal. Rev., **4**, pp. 115–157, 2012.

[2] RAMAMOORTHY R., DUTTA P. K., AKBAR S. A., *Oxygen sensors: materials, methods, designs and applications*, Journal of Materials Science, 38, 21, 4271–4282, 2003.

[3] HITCHMAN, M. L., *Measurement of dissolved oxygen*, Ed. John Wiley & Sons, 1978.

[4] SMIDDY M., et al., *Use of oxygen sensors for the non-destructive measurement of the oxygen content in modified atmosphere and vacuum packs of cooked chicken patties; impact of oxygen content on lipid oxidation*, Food Research International 35, 6, 577–584, 2002.

[5] PAPKOVSKY D. B., *New oxygen sensors and their application to biosensing*, Sensors and Actuators B: Chemical, 29, 1–3, 213–218, 1995.

[6] PUKLIN E., et al., *Ideality of pressure sensitive paint. I. Platinum tetra (pentafluorophenyl) porphine in fluoroacrylic polymer*, Journal of Applied Polymer Science 77.13: 2795–2804, 2000.

[7] AMAO Y., ASAI K., OKURA I., *Photoluminescent oxygen sensing using palladium tetrakis (4-carboxyphenyl) porphyrin self-assembled membrane on alumina*, Analytical Communications, 36, 5, 179–180, 1999.

[8] AMAO, Y., OKURA, I., *An oxygen sensing system based on the phosphorescence quenching of metalloporphyrin thin film on alumina plates*, Analyst, 125, 9, 1601–1604, 2000.

[9] LO L-W., KOCH C. J., David F., *Calibration of oxygen-dependent quenching of the phosphorescence of Pd-meso-tetra (4-carboxyphenyl) porphine: a phosphor with general application for measuring oxygen concentration in biological systems*, Analytical biochemistry 236, 1, 153–160, 1996.

[10] SERBAN B., COSTEA S., BUIU O., COBIANU C., DIACONU C., *Pyrene-1-butyric acid-doped polyaniline for fluorescence quenching-based oxygen sensing*, Proceed. IEEE International Semiconductor Conference CAS, 265–268, 2012.

[11] SERBAN B., BREZEANU M., COBIANU C., COSTEA S., BUIU O., STRATULAT A, VARACHIU N., *Materials selection for gas sensing.* An HSAB perspective, Proceed. IEEE International Semiconductor Conference CAS pp.21–30, 2014.

[12] SERBAN B., MIHAILA M., BUIU O., *Fluorescence quenching based oxygen sensor*, United States Granted Patent, US8747750B2, 2014.

[13] SERBAN B., MIHAILA M. BUIU O., *Fluorescent polymers for oxygen sensing*, United States Granted Patent, US8, 778, 501 B2, 2014.

[14] SERBAN B., MIHAILA M., BUIU O., COSTEA S., *US Patent Application, Oxygen sensors based on hard-soft acid-base relationships*, US Patent Application 2013/0171027A1, 2013.

[15] HOBBS B.S.et al., *Liquid Electrolyte Fuel Cells*, Techniques and Mechanisms in Gas Sensing, Ed. P.T. Moseley, J. Norris, D. Williams, CRC Press, 1991.

[16] KITAZAWA N., et al., European Patent Application EP 1593962 A1, 2005.

[17] GAMBERT, R., U.S. Patent Application US2007/0272553 A1, 2007.

[18] COBIANU C., SERBAN B., AVRAMESCU V., HOBBS B., PRATT K., and WILLETT M., *Lead-free galvanic oxygen sensors-a conceptual approach*, Proceed. IEEE International Semiconductor Conference CAS, pp.161–164, 2012.

[19] COBIANU C., SERBAN B., AVRAMESCU V., HOBBS B., PRATT K., and WILLETT M., *Lifetime considerations for lead-free oxygen galvanic sensors*, Academy of Romanian Scientists, Series on Science and Technology of Information, **5** (2), 2012.

[20] COBIANU C., AVRAMESCU V., SERBAN B., HOBBS B., PRATT K. and WILLETT M., *Experimental evidence of long life lead-free oxygen galvanic sensors*, Proceed. Of IEEE International Semiconductor Conference CAS, pp. 47–50, 2013.

[21] COBIANU C., SERBAN B., AVRAMESCU V., Hobbs B., Pratt K., Willett M., *Long-life, lead-free, oxygen galvanic sensor*, European Granted Patent, EP 2 813 843 B1, 2015.

[22] COBIANU C., SERBAN B-C. HOBBS, B.S., *Lead-free electrochemical galvanic oxygen*, US Patent Application, US9557289B2, 2017.

[23] CLARK L C., et al., *Continuous recording of blood oxygen tensions by polarography*, Journal of Applied Physiology, 6, 3, 189–193, 1953.

[24] SERBAN B., COBIANU C., BREZEANU M., STRATULAT A., BUIU O., *Acoustic wave based sensors*, European Patent Application, EP 3106868 A1, 2016.

[25] KARRER, H. E., *Paramagnetic oxygen sensor*, United States Patent (4), 563, 94, 1986.

[26] MASKELL W.C., STEELE B.C H., *J. Appl. Electrochem.* 16, 475, 1986.

[27] NISHIO K., *The Fundamentals of Automotive Engine Control Sensors*, Fontis Media, The Netherlands, 2001.

[28] RAMAMOORTHY R., RAMASAMY S. SUNDARARAMAN D., *Annealing effects on phase transformation and powder microstructure of nanocrystalline zirconia polymorphs*, J. Mater. Res. 14, 90, 1999.

[29] BREZEANU M., SERBAN B., DUMITRU V., BUIU O., *Method and system for diamond-based oxygen sensor*, United States Patent 2016/ 0056239 A1, 2016.

[30] BREZEANU M., SERBAN B., BUIU O., DUMITRU V., *Diamond-based gas sensors for adverse environments*, 3rd French-Japanese workshop on Diamond Power devices, Nimes, pp. 21, 2015.

[31] HITCHMAN M.L., *Measurement of Dissolved Oxygen*, Ed. John Wiley & Sons, New York, 1978.

[32] REINHARDT G., MAYER R., ROSCH M., *Sensing small molecules with amperometric sensors*, Solid State Ionics 150, 79, 2002.

[33] YAMAZOE, N., FUCHIGAMI J., KISHIKAWA M., SEIYAMA T., *Interactions of tin oxide surface with* O_2*,* H_2O *and* H_2, Surf. Sci., 86, 335–344, 1979.

[34] BARSAN N., SCHWEIZER-BERBERICH M., GOPEL W., *Fundamental and practical aspects in the design of nanoscaled* SnO_2 *gas sensors: a status report*, Fresenius J. Anal. Chem. 365, 287–304, 1999.

[35] BARSAN N., WEIMAR U., *Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with* SnO_2 *sensors in the presence of humidity*, J. Phys. Cond. Matt. 15, R813, 2003.

[36] FINE G. F., et al., *Metal oxide semiconductor gas sensors in environmental monitoring*, Sensors, **10**(6), 5469-5502, 2010.

[37] WANG, C., et al., *Metal oxide gas sensors: sensitivity and influencing factors*, Sensors, **10**(3), 2088–2106, 2010.

[38] SERBAN B., BREZEANU M., BUIU O., COBIANU C., STRATULAT A., *Semiconducting metal oxides for gas sensing - An HSAB perspective*, The 8th International Conference on Advanced Materials: ROCAM, pp. 53, 2015.

[39] COBIANU C., SERBAN B., AVRAMESCU V., BREZEANU M., STRATULAT A., BUIU O., *Novel materials for oxygen sensing technologies*, Proceed. IEEE International Semiconductor Conference (CAS), pp. 17–26, 2016.

[40] SERBAN B., et al. *Selection of gas sensing materials using the Hard Soft Acid Base theory; application to Surface Acoustic Wave* CO_2 *detection*, Proceed. IEEE International Semiconductor Conference (CAS), pp. 247–250, 2010.

[41] ZHU C.L., CHEN Y.J., WANG R.X., WANG L.J., CAO M.S., SHI X.L., *Synthesis and Enhanced Ethanol Sensing Properties of -*Fe_2O_3*/ZnO Heteronanostructures*, Sensors and Actuators B., 140, 185–189, 2009.

[42] GOPEL W., SCHIERBAUM K.D., SnO_2 *Sensors-Current Status and Future Prospects*, Sensors and Actuators B. 26-27, 1–12, 1995.

[43] YU J.H., CHOI G.M., *Electrical and CO Gas Sensing Properties of ZnO-*SnO_2 *Composites*, Sensors and Actuators B, 52, 251–256, 1998.

[44] YOON, D.H., YU, J.H., CHOI, G.M., *CO Gas Sensing Properties of ZnO-CuO Composite*, Sensors and Actuators B, 46, 15–23, 1998.

[45] DE LACY COSTELLO, B.P.J., EWEN R.J., JONES P.R.H., RATCLIFFE, N.M., WAT, R.K.M. *A Study of the Catalytic and Vapor-Sensing Properties of Zinc Oxide and Tin Dioxide in Relation to 1-Butanol and Dimethyldisulphide* , Sensors and Actuators B., 61, 199–207, 1999

[46] HARIDAS, D., GUPTA, V., SREENIVAS, K., *Enhanced Catalytic Activity of Nanoscale Platinum Islands Loaded onto SnO2 Thin Film for Sensitive LPG Gas Sensors*, Bull. Mater. Sci., **31**, 397–400, 2008.

[47] HYODO, T., BABA Y., WADA, K., SHIMIZU, Y., EGASHIRA, M., *Hydrogen Sensing Properties of SnO2Varistors Loaded with* SiO_2 *by Surface Chemical Modification with Diethoxydimethylsilane*. Sensors and Actuators B, 64, 175–181, 2000.

[48] LU Y., LI J., HAN J., NG, H.-T., BINDER, C., PARTRIDGE, C., MEYYAPPAN, M., *Room Temperature Methane Detection Using Palladium Loaded Single-Walled Carbon Nanotube Sensors*, Chem. Phys. Lett., 391, 344–348, 2004.

[49] WANG, D., MA Z., DAI S., LIU J., NIE Z., ENGELHARD, M.H., HUO Q., WANG C., KOU, R., *Low-Temperature Synthesis of Tunable Mesoporous Crystalline Transition Metal Oxides and Applications as Au Catalyst Supports*, J. Phys. Chem. C., 112, 13499–13509, 2008.

[50] TRAVERSA, E., *Ceramic Sensors for Humidity Detection: The State-of-the-art and Future Developments*, Sensors and Actuators. B., 23, 135–156, 1995.

[51] MCCAFFERTY, E., ZETTLEMOYER, A.C. *Adsorption of Water Vapour on* α*-Fe2O3*, Discuss. Faraday Soc., 52, 239–263, 1971.

[52] HBNER, M. et al., *Influence of humidity on CO sensing with p-type CuO thick film gas sensors*, Sensors and Actuators B, 153, 2, 347–353, 2011.

[53] STRIKE, D. J.; MEIJERINK, M. G. H.; KOUDELKA-HEP, M. *Electronic noses - A mini-review*. Fresenius' Journal of Analytical Chemistry, 364, 6, 499–505, 1999.

[54] Qi, Q., ZHANG, T., Zheng X., FAN, H., LIU, L., WANG, R., ZENG, Y., *Electrical Response of* Sm_2O_3*-Doped* SnO_2 *to* C_2H_2 *and Effect of Humidity Interference*, Sensors and Actuators B., 134, 36–42, 2008.

[55] GONG J., CHEN Q., LIAN M., LIU N., STEVENSON, R.G., ADAMIC, F., *Micromachined Nanocrystalline Silver Doped* SnO_2 H_2S *Sensor*, Sensors and Actuators B., 114, 32–39, 2006.

[56] CAO M., WANG, Y., Chen, T., ANTONIETTI, M., NIEDERBERGER, M.A., *Highly Sensitive and Fast-Responding Ethanol Sensor Based on* $CdIn_2O_4$ *Nanocrystals Synthesized by a Nonaqueous Sol-Gel Route*, Chem. Mater., 20, 5781–5786, 2008.

[57] DUY N.V., HIEU N.V., HUY P.H., CHIEN, N.D., THAMILSELVAN, M., YI, J., *Mixed* SnO_2/TiO_2 *Included with Carbon Nanotubes for Gas-Sensing Application*, Physica E., 41, 258–263, 2008.

[58] BICELLI, S et al., *Model and experimental characterization of the dynamic behavior of low-power carbon monoxide MOX sensors operated with pulsed temperature profiles*, IEEE Transactions on Instrumentation and Measurement, 58, 5, 1324–1332, 2009.

[59] LU, F., LIU, Y., DONG, M., WANG, X.P., *Nanosized Tin Oxide as the Novel Material with Simultaneous Detection towards CO,* H_2 *and* CH_4, Sensors and Actuators B., 66, 225–227, 2000.

[60] ANSARI S.G., BOROOJERDIAN P., SAINKAR, S.R., KAREKAR, R.N., AIYER, R.C., KULKARNI, S.K., *Grain Size Effects on* H_2 *Gas Sensitivity of Thick Film Resistor Using* SnO_2 *Nanoparticles*, Thin Solid Films, 295, 271–276, 1997.

[61] BARSAN, N., WEIMAR, U., *Conduction Model of Metal Oxide Gas Sensors*, J. Electroceram., 7, 143–167, 2001.

[62] http://www.eunetair.it/cost/training/Barcelona/50-TRAINERS%20PRESENTATIONS/02_ TrainerPresentation_Morante.pdf

[63] CHAABOUNI, F.; ABAAB, M.; REZIG, B., *Metrological characteristics of ZnO oxygen sensor at room temperature*, Sensors and Actuators B, 100, 1, 200–204, 2004.

[64] SHAFURA, A. K. et al., *Oxygen-sensing characteristics of nanostructured Al-doped ZnO thin films*, Electronic Design (ICED), 2014 2nd International Conference on. IEEE, 446–449, 2014.

[65] NIU, S. et al., *Enhanced Performance of Flexible ZnO Nanowire Based Room-Temperature Oxygen Sensors by Piezotronic Effect*, Advanced Materials, 25, 27, 3701–3706, 2013.

[66] CHOU, C-S; WU, Y-C; LIN, C-H., *Oxygen sensor utilizing ultraviolet irradiation assisted ZnO nanorods under low operation temperature*, RSC Advances, 4, 95, 52903–52910, 2014.

[67] NERI, G et al., *A highly sensitive oxygen sensor operating at room temperature based on platinum-doped* In_2O_3 *nanocrystals*, Chemical communications, 48, 6032–6034, 2005.

[68] WANG,H et al., *A micro oxygen sensor based on a nano sol-gel* TiO_2 *thin film*. Sensors, 14.9: 16423–16433, 2014.

[69] HAIRONG, W et al., *Design and fabrication of* TiO_2 *thin films oxygen sensors*, Manipulation, Manufacturing and Measurement on the Nanoscale (3M-NANO), 2013 International Conference on. IEEE, 238–242, 2013.

[70] JASINSKI, P; SUZUKI, T; ANDERSON, H. U., *Nanocrystalline undoped ceria oxygen sensor*, Sensors and Actuators B: Chemical, 95, 1, 73–77, 2003.

[71] BEIE, H.-J. GNRICH, A., *Oxygen gas sensors based on* CeO_2 *thick and thin films*, Sensors and Actuators B: Chemical, 4, 3–4, 393–399, 1991.

[72] KOLMAKOV, A. et al., *Detection of CO and* O_2 *using tin oxide nanowire sensors*, Advanced Materials, 15, 12, 997–1000, 2003.

[73] ADAMOWICZ, B., et al., *Response to oxygen and chemical properties of* SnO_2 *thin-film gas sensors*, Vacuum, 82, 10, 966-970, 2008.

[74] OGITA, M., et al., Ga_2O_3 *thin film for oxygen sensor at high temperature*, Applied Surface Science, 175, 721–725, 2001.

[75] FLEISCHER, M., MEIXNER, H., *Sensing reducing gases at high temperatures using long-term stable* Ga_2O_3 *thin films,* Sensors and Actuators B: Chemical, 6, 1-3, 257–261, 1992.

[76] LI, X. et al., WO3/W *Nanopores Sensor for Chemical Oxygen Demand (COD) Determination under Visible Light*, Sensors, 14, 6, 10680–10690, 2014.

[77] KROGER, F.A., Vink, H. J., *Relations between the concentrations of imperfections in crystalline solids*, Solid State Phys., 3, 307–4359, 1956.

[78] SHIMIZU, Y. et al., *Perovskite-type oxides having semiconductivity as oxygen sensors*, Chemistry Letters, 14, 3, 377-380, 1985.

[79] KOROTCENKOV, G., *Handbook of Gas Sensor Materials*, 1st ed.; Springer: New York, NY, USA, pp. 49–116, 2013.

[80] ROTHSCHILD, A., TULLER, H.L., *Gas sensors: new materials and processing approaches*, J. Electroceram., 17, 1005–1012, 2006.

[81] ROTHSCHILD A. et al., *Temperature-independent resistive oxygen sensors based on SrTi1-xFexO3-δ solid solutions*, Sensors and Actuators B: Chem., 108, 223–230, 2005.

[82] AVRAMESCU V., DE LUCA A., BREZEANU M., ALI S.Z., UDREA F., BUIU O., COBIANU C., SERBAN B., GARTNER J., DUMITRU V., STRATULAT A., *CMOS-Compatible SOI Micro-Hotplate-based Oxygen Sensor,* Proceedings of the 46th European Solid-State Device Research Conference (ESSDERC), pp. 280–283, 2016.

[83] CHOI, S.-H., CHOI, S.-J., MIN, B.K., LEE W.Y., PARK J.S., KIM I. D., *Facile Synthesis of p-typePerovskite SrTi0.65Fe0.35O3-δ Nanofibers Prepared by Electrospinning and Their Oxygen Sensing Properties*, Macromol. Mater. Eng., 298, 521–527, 2013.

[84] GUO L., LIANG F., ZHOU W., HE L., CHEN, C., *One-Dimensional Nanomaterials: Synthesis, Characterization and Properties*, World J. Eng., Supplement, 279–280, 2008.

[85] NERI G., BONAVITA A., MICALI G., RIZZO G., LICHERI R., ORRU R., CAO G., *Resistive λ-sensors based on ball milled Fe-doped $SrTiO_3$ nano-powders obtained by self-propagating high-temperature synthesis (SHS)*,Sensors and Actuators B, 126, 258–265, 2007.

[86] DA SILVA, L.F., AVANSI W., MOREIRA M.L., ANDRES J., LONGO E., MASTELARO V.R., *Novel $SrTi_{1-x}Fe_xO_3$ nanocubes synthesized by microwave-assisted hydrothermal method*, Cryst. Eng. Comm., 14, 4068–4073, 2012.

[87] GEDANKEN, A., *Using sonochemistry for the fabrication of nanomaterials*, Ultrason. Sonochem.11, 47–55, 2004.

[88] SUSLICK, K.S., PRICE G.S., *Applications of ultrasound to materials chemistry*, Annu. Rev. Mater. Sci., 29, 295–326, 1999.

[89] STRATULAT A., SERBAN B., COBIANU C., AVRAMESCU V., BREZEANU M., BUIU O., DIAMANDESCU L., FEDER M., UDREA F., DE LUCA A., ALI S.Z., *Novel sonochemical route for manufacturing O_2 sensitive STFO*, Proceed. NATO Advanced Research Workshop Functional nanomaterials and devices for electronics, sensors, energy harvesting, pp.78–79, Lviv, Ukraine, 2015.

[90] COBIANU C., SERBAN B., BREZEANU M. DUMITRU V., BOSTAN C., BUIU O., *Oxygen sensing: A review (Part 2: Solid state technology)*, Annals of the Academy of Romanian Scientists, Series on Science and Technology of Information 7, 2, 2014.

[91] COBIANU C., STRATULAT A., SERBAN B- C., BREZEANU M., BUIU O., *Sonochemical syntheses of metal oxide nanocomposites for gas sensing*, Annals of the Academy of Romanian Scientists, Series on Science and Technology of Information, 9, 1, pp. 5–12, 2016.

[92] STRATULAT A., SERBAN B., DE LUCA A., AVRAMESCU V, COBIANU C., BREZEANU M., BUIU O., DIAMANDESCU L., FEDER M., ALIS.Z., and UDREA F., *Low power resistive oxygen sensor based on sonochemical $SrTi_{0.6}Fe_{0.4}O_{2.8}$ (STFO 40)*, Sensors, 15, pp. 17495–17506, 2015.

[93] COBIANU C., SERBAN B-C, BREZEANU M., BUIU O., BOSTAN C-G., *Sonochemical synthesis of iron doped strontium titanate powder*, European Patent Application EP2848589A1, 2015.

[94] COBIANU C., SERBAN B- C., *Hydrothermal or solvothermal synthesis of iron doped strontium titanate powder*, European Patent Application EP 2 883 839 A1, 2015.

[95] COBIANU C., STRATULAT A., SERBAN B., BREZEANU M., BUIU O., *Sonochemical synthesis of metal oxide nanocomposites for gas sensing*, Annals of the Academy of Romanian Scientists, Series on Science and Technology of Information, 9, 1, 2016.

[96] COBIANU C., SERBAN B- C., BREZEANU M., BUIU O., BOSTAN C-G., *Sonochemical synthesis of iron doped strontium titanate powder*, European Patent Application EP2848589 A1, 2015.

[97] COBIANU C., SERBAN B. C., *Hydrothermal or solvothermal synthesis of iron doped strontium titanate powder*, European Patent Application EP 2 883 839 A1, 2015.

[98] DE LUCA A., UDREA F., LI G., ZENG Y., ANDRE N., POLLISSARD-QUATREMERE G., FRANCIS L.A., FLANDRE D., RACZ Z., GARDNER J.W., ALI S.Z., BUIU O., SERBAN B.C., COBIANU C., WOTHERSPOON T., *Sensors and Sensor Systems for Harsh Environment Applications*, Book chapter in Semiconductor Devices in Harsh Condition, CRC Press, Taylor & Francis Group, pp. 87–111, 2016.

[99] SERBAN B., COBIANU C., BREZEANU M., AVRAMESCU V., DUMITRU V., MIHAILA M., BOSTAN G., *Sensing layers for oxygen detection,* European Granted Patent, EP 2 848 927 B1, 2015.

[100] BREZEANU M., SERBAN B-C., AVRAMESCU V., BUIU O., COBIANU C., STRATULAT A., *Nanocomposites-based Oxygen Gas Sensors*, International Conference of Smart and Multifunctional Materials, Structures, Systems, CIMTEC, Perugia, abstract, invited paper, 2016.