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# OXYGEN SENSING: A REVIEW PART 2: SOLID STATE TECHNOLOGIES

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**Abstract**. *This paper reviews the status of oxygen sensing for combustion control and environmental monitoring at both commercial and research level. The evolution of potentiometric and chemoresistive sensor for automotive applications is described in detail, but also the optical principles for $O_2$ sensing in medical applications are treated. The main limitations of the existing devices are pinpointed, and the emerging technologies based on SOI-CMOS hot places and their challenges are also described.*

**Keywords:** Oxygen Sensing, Zirconia Potentiometric Sensor, Resistive Gas Sensor, SOI Micro-hotplate, CMOS-compatible

## 1. Introduction

The high efficiency of fossil fuel burning in automotive and process industries, and the demand for a cleaner exhaust gas of internal combustion systems have been made possible by the extensive use of robust $O_2$ sensors, used both for the control of an optimum air-fuel mixture admission (as part of closed-loop feed-back control algorithm), as well as for monitoring the operation and ageing status of the exhaust gas after treatment systems [1]. This was possible due to the introduction (Bosch, 1976) of the thimble-type potentiometric, solid-electrolyte, galvanic $O_2$ sensors based on stabilized zirconia ($ZrO_2$) – well known under the name of "Lambda Sensor"; since then these sensors have played a very important role for the control of air/fuel (A/F) ratio (named $\lambda$) in internal combustion engines.

In these sensors, also known as "$O_2$ Nernst concentration cell", for a small change of the air-fuel mixture, moving from a fuel rich-region ($\lambda < 1$) to a fuel – lean – region ($\lambda > 1$), the voltage response will sharply decrease from about 0.8 V to about 0.2 V. Due to this huge Nernstian type response, combined with a rather small sensitivity outside this value, we can conclude that this "Lambda Sensor" has a "quasi-digital" (switch-like) operation.

In general, a two-electrode galvanic sensor is made of a solid electrolyte with high oxygen ionic conductivity (yttria-stabilized –zirconia ($Y_2O_3$-$ZrO_2$) – for example), which is sandwiched between two platinum electrodes (these being the place where the redox $O_2/O^{2-}$ electrode reactions occur).

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In this potentiometric sensor, the catalytic cathode (Pt) is exposed to the exhaust gas to be monitored ($P'_{O_2\ test}$) for chemically reducing this very low amount of $O_2$ from the exhaust gas and consuming thus four electrons; at the same time, the other Pt electrode (anode) is exposed to a clean air reference chamber ($P''_{O2ref}$), where the corresponding oxidation takes place for generating four electrons. In other words, during the sensor operation at high temperatures, the $O^{2-}$ ions will diffuse rapidly from cathode to anode, where they will suffer the oxidation reaction, thus retrieving the $O_2$ molecule [2]. This galvanic cell, in an open circuit configuration, will generate a Nernst voltage proportional to the ratio of partial pressure of oxygen from the two regions ("test" – cathode and "reference" – anode), as follows:

$$E = \frac{R_T}{4F} \ln\left(\frac{P''_{O2}}{P'_{O2}}\right)$$

where $T$ is the medium temperature (in K) and $F = 9.6485 \times 10^4$ C mol$^{-1}$ is Faraday's number.

For gasoline-powered engines, operating near the stoichiometric ratio ($\lambda = 1$), the limited amounts of gases resulted from combustion (both reducing - $CH_4$, CO - and oxidizing - $NO_x$ species) can be almost 100% converted to the exhaust gases like $CO_2$, $N_2$, $O_2$ [3], by means of a three way catalyst (TWC) [4]. The efficiency and ageing status of the TWC-based exhaust gas after treatment system is differentially monitored by installing one $O_2$ sensor at the input and another one at the output of the TWC. Such a scheme will allow detecting any variation of $O_2$ concentration between its input and the output. This variation is due to the net $O_2$ generated in the TWC through reduction reactions of $NO_x$ and $O_2$ consumed by CO oxidation in order to produce $CO_2$.

For diesel engines, operating in fuel-lean region ($\lambda > 1$), a big amount of the resulting $NO_x$ will not be reduced by such a classical TWC. For these engines, urea generating ammonia is introduced in the exhaust gas after the treatment chamber (the so-called "selective reduction catalysts – SRC" [5]), thus reducing $NO_X$ to $N_2$ and $H_2O$. [1].

Such SCR systems will be also equipped with $O_2$ sensors at its input and output for the same purposes of monitoring the efficiency of the catalyst in reducing emissions, and thus improving the quality of exhaust gas.

Current and forthcoming EU regulations focusing on the minimization of the environmental air pollution generated by the automotive industry were the main incentive behind a major research and development activity focused on the design and realization of super ultra - low emission vehicles (SULEV), driven by very efficient combustion, where the exhaust gases like - reducing hydrocarbons (CH) and oxidizing $NO_x$, as well as reducing agent $NH_3$ - are to be monitored [6].

Nowadays, even modern gasoline engines are operating under lean conditions ($\lambda>1$) in order to better adapt to these SULEV requirements and for further increase in the fuel economy. This trend is bringing new challenges and specific working requirements to the classical $\lambda$ sensors, which are not so sensitive to $O_2$ partial pressure in this lean operating region. We must note that the same requirements apply also when monitoring the burning processes in boilers and industrial furnaces. Thus, novel $O_2$ sensors have been developed, which are able to detect $O_2$ with a monotonic response in a larger $\lambda$ range from 0.7 to 11 [3]. In answering to these new demands, a novel planar multi-layer technology - such as High Temperature Co-Firing Ceramic (HTCC) - has been developed by Bosch, where a referenced-potentiometric and a pumped-amperometric $O_2$ sensor were combined together. In the case of amperometric sensors, an electric current proportional to the $O_2$ concentration on a broader band of $\lambda$ is obtained [1, 3]. Further developments of this HTCC zirconia tapes-based technology by "NGK Insulators Ltd" have led to the development of a new multifunctional $O_2$ (both digital and quasi-linear response) and $NO_x$ sensors; in both cases, the Nernst cells and pumped-amperometric cells are developed using the HTCC process.

Finally, by employing a thick film of yttrium - stabilized zirconia (YSZ) as solid electrolyte (prepared in planar technology), a solid state reference made of 25% mole of zirconia in ceria (instead of the air reference chamber), and Pt electrodes, a novel miniaturized concept for $O_2$ detection has been demonstrated [7].

The facts presented above are highlighting the major developments in the evolution of the $O_2$ sensing devices and technologies, driven by the requirements to develop a more efficient fuel combustion technology, while ensuring compliance with the environmental air protection legislation. It is expected that specific legislation will continue to be the major driving force in future technological developments, with impact – not only on current industrial and domestic applications – but also on their future progress. The present paper is organized as follows. We shall firstly present the main limitations of the currently available $O_2$ sensing solutions – from the perspective of the current and envisage application requirements. Secondly, we shall review some of the emerging technologies coming from academic and industrial research – highlighting their current roadblocks; finally, we shall briefly try to envision future emerging $O_2$ sensing technologies, which may surpass the present challenges, and bring novel features, like ultimate miniaturization.

Thus, present $O_2$ sensing commercial products ($TiO_2$ resistive sensors, zirconia based-potentiometric $O_2$ sensors, planar technology potentiometric-amperometric zirconia/$NO_x$ sensors) and their fabrication technologies (thimble and planar thick films-multi ceramic tapes) will be briefly described and their major unsolved issues will be identified.

Intensive academic and industrial research for novel technologies of $O_2$ detection in harsh environment, based on semiconductor metal oxides of both *p*-type and *n*-type conductivity, large band gap semiconductors and optical principles will be briefly explored.

Finally, we shall highlight some of the major challenges for the realization of the ultra-miniaturized $O_2$ sensors based micro-heaters performed in "Silicon – on – Insulator (SOI)" - CMOS compatible technology.

## 2. Main limitations of the existing commercial solutions for $O_2$ sensing in harsh environment

As mentioned in the previous section, the first commercial potentiometric "*Bosch Oxygen Sensor*" was brought to the market in 1976 [8]. The major limitation of this thimble-type sensor made of platinum electrode and yttria-stabilized zirconia is its digital (switch-like) operation, which is able to indicate with high sensitivity only the deviation from stoichiometric ratio ($\lambda = 1$). Therefore, for fuel efficient combustion processes operating in the fuel-lean condition ($\lambda > 1$), they cannot measure with good accuracy the $\lambda$ value to be used for the closed loop control of air-fuel mixture admission at the entrance of the novel gasoline engine or diesel engine. In addition, the bulky dimensions of these potentiometric galvanic sensors and their large thermal inertia are determining a long light-off time of more than 1 minute. During this light–off time, the air-fuel mixture for the combustion process could not be controlled, as the sensor was not yet heated by the engine operation, and therefore, during this period when the engine was working in "open-loop" with fuel-rich, both fuel consumption and exhaust emissions were high.

The next generation from Bosch - "*Premium Thimble $O_2$ sensor*" - was on the market starting with 1988 [9]. An electrical heating element was embedded in this sensor and had a light-off time of about 1 minute. Due to the requirements of the USA Environment Protection Agency (EPA), starting with 1999, Bosch has commercialized the first potentiometric "*Planar $O_2$ sensor*", [9] which is made in a combined zirconia thick film–HTCC technology, allowing a much lower sensor size, while incorporating a Pt heater, and a duct for making an air reference chamber. Due to its own heater and decreased thermal inertia, this planar $O_2$ sensor has a light-off time of about 10-12 seconds, and thus the emissions during the cold start phase are reduced by more than 50%. In 2003, Bosch brought to the market the newest commercial $O_2$ sensor called "*Wideband $O_2$ Sensor*" [9], containing both a potentiometric and an amperometric sensor, which are manufactured using the same thick film HTCC technology; The "*Wideband $O_2$ sensor*" is measuring the $O_2$ concentration with a better accuracy than any of its predecessors, in a wider band for $\lambda$ (0.7 to 11). This sensor is meeting the present emissions requirements for modern gasoline direct injection (GDI) engines [1].

In 2008, "NGK INSULATORS LTD" and Continental have jointly brought to the market the first (planar) $NO_x$ sensor, called "*High precision $NO_x$ sensor*" [10]; this achievement allowed a more than 30% improvement in the accuracy of $NO_x$ detection, when compared to the approximate, indirect methods used before, in which the $O_2$ concentration from exhaust gas after the SRC systems was correlated to the $NO_x$ concentration from the exhaust gas.

They have used the same thick film HTCC technology, but a novel concept, where, initially, the $O_2$ gas from exhaust was pumped to outside in the first sensor chamber, while the $NO_x$ only reached the second chamber, where the $NO_x$ was reduced to $N_2$ and $O_2$. The resulted $O_2$ was pumped out, and its pumping current was a quantitative measure of the released $NO_X$ from the combustion process.

Besides λ sensors based on potentiometric and amperometric principles, resistive $O_2$ sensors based on *n*-type semiconductor metal oxides were developed - starting from 1988 - by the Japanese company "NGK Spark Plugs-NTK Technical Ceramics". These sensors are based on chemoresistors based on titania ($TiO_2$) thick films and they also incorporate a heater [11].

Actually, the research of planar $TiO_2$ sensors for $O_2$ sensing was started by "Ford Motor Company", before 1975 [12, 13]. In their approach, they used titania ($TiO_2$) pellets doped with donors metals aiming at the extension of the monotonic dependence of its electrical resistance on the $O_2$ partial pressure up to 0.2 bar. However, as the electrical resistance of the $TiO_2$ sensor varied for about 3 decades, when the air-fuel mixture passed through the stoichiometric point, at $\lambda = 1$, these titania sensors were also considered quasi-digital sensors, or low band $O_2$ sensors.

These results were further developed by the NGK-NTK approach, which developed its commercial thick film-HTCC technology titania sensor for $O_2$ detection.

The biggest limitation of these $TiO_2$ resistive sensors is the strong temperature dependence of the electrical conductivity. This is an intrinsic behaviour of any semiconductor material, where conductivity is exponentially increasing as a function of temperature due to thermal generation of pairs of mobile charge carriers, electrons (in the conduction band) and holes (in the valence band). Therefore, such a sensor will respond not only to $O_2$ concentration, but also to any temperature variation.

For this reason, its temperature should be kept constant during operation, which may require an electronic feed-back loop for the heating power applied to the sensor.

A classical structure of a lambda sensor is depicted in Fig. 1.

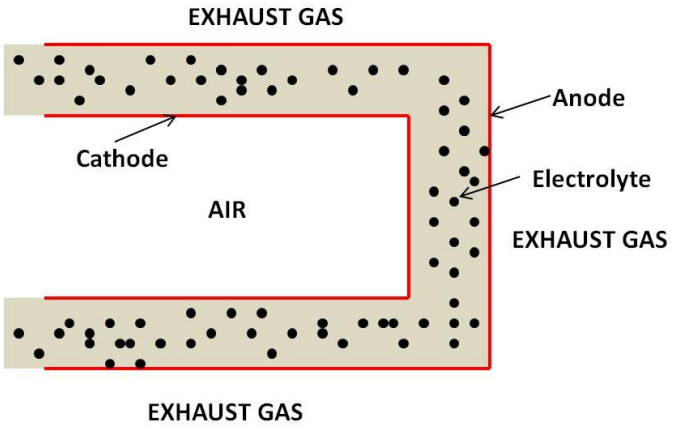


**Fig. 1.** Classical structure of a lambda $O_2$ sensor with ion-conducting electrolyte, placed in the exhaust pipe of a vehicle.

A general characteristic and limitation of all these commercial, robust $O_2$ ceramic sensors is the fact that they do require a power consumption of minimum 7 watts [3], while the heating time is still much longer (8-10 s). These figures should be compared to the MEMS micro-heater capabilities, for which the power consumption is in the range of a hundred of mW's and the heating time for reaching the operation temperature is in the range of milliseconds. In addition, the cost and miniaturization of the existing commercial Lambda sensor, made by either potentiometric or planar technologies, cannot decrease below a certain threshold, due to the fabrication process (either thimble or planar) which has certain strong limitations when compared to the integrated circuit batch technologies, where many thousands of sensor chips can be made on a single wafer, and many wafers are processed in parallel. Therefore, there is a challenging interest towards $O_2$ sensor fabrication by IC compatible technology, despite the high technological and conceptual efforts that may be needed to reach such a high-risk target, and preserve or even further improve the technical performances of the existing commercial lambda sensors. Some of the research stages that may need to be reached and passed for achieving an initial proof of concept for an integrated $O_2$ sensor will be described in a separate section of this study.

## 3. State of the art in academic and industrial research of $O_2$ sensing for combustion control

As mentioned above, oxygen detection for combustion control requires a careful selection of the sensing principles and materials to be used, due to the harsh environment where these devices have to work. In this section, we shall briefly describe some emerging technologies for $O_2$ sensing in harsh environment, technologies based on: optical measurements, wide-band gap semiconductors and chemoresistive metal oxide semiconductors principles.

In medical applications, oxygen optical sensing by fluorescence quenching (FQ) generated in organic layers subject to exposure in the $O_2$ gas to be detected, is an important research topic. Due to the organic polymer dye which is used as sensing layer, this approach is valid only at low temperatures, below 60 °C.

As an extension of the FQ principle, a fibre optic oxygen sensor based on fluorescence quenching in hexanuclear molybdenum chloride ($Mo_6Cl_{12}$) cluster was proposed, more than a decade ago, by a group from Michigan State University for high temperature applications [14].

The fluorescent clusters of molybdenum chloride are deposited at the sensing end of the silica fibre. The FQ sensor works as follows: the fibre is pumped at the input with an UV-325 nm light beam from a HeCd gas laser and the fluorescent molybdenum chloride clusters from the other end are reflecting a red light, whose signal power is decreasing when the oxygen concentration is increasing.

The dynamic range of the sensor is high, and thus the variation of oxygen concentration specific to fuel combustion can be monitored by this FQ based sensor. Reaching commercial (i.e., real life) compatible operation will require further studies of the long term stability of the fluorescence in the sensing film.

Another important research direction in the optical sensing of oxygen is based on the use of Tunable Diode Laser Absorption Spectroscopy (TDLAS), where the single absorption line of the gas to be detected is fitted with the wavelength of the light source (laser beam) and the absorption band of the detector (photodiode), which is finally collecting the transmitted laser beam.

The difference between the intensity of the emitted light and detected light will provide the information about the gas concentration the gas to be detected (which is equal to the gas concentration absorbed in the optical path of the sensor). Such an approach is made by "Zollo Technologies", which have developed "Zollo Boiler Optimization Spectroscopy Sensor-BOSS", which is using a Vertical-Cavity Surface-Emitting Laser (VCSEL) laser diode as a light source for monitoring $O_2$, $H_2O$, and CO in the combustion chamber of the coal power plant boilers.

Such systems occupy a high volume and cannot be easily integrated in other applications.

Similarly, General Electric has patented its own fibre optic based-technology for monitoring multi-parameters like $NO_x$, CO, $O_2$ and $H_2$ in harsh environment [15].

The FP6 "OPTO-EMI-SENSE" project [16] proposed an optical fibre sensor network for the monitoring of exhaust emissions; within this optical fibre network, the UV gas Absorption Spectroscopy was proposed for the detection of NO and $NO_2$, while the near infrared (NIR) spectroscopy is to be used for the CO detection.

The use of wide band gap semiconductors, like silicon carbide (SiC: 2.36-3.05 eV), gallium nitride (3.4 eV) or aluminium nitride (6.2 eV) (AlN) and C-diamond (5.46-5.60) eV, represents a viable alternative for oxygen gas sensing; this is due to their low intrinsic concentration of mobile charge carrier at higher temperatures, needed for oxygen detection. Thus, SiC-based micro-heaters were used as a hot substrate for thermal activation of the chemoresistive sensing layers aiming at the detection of a large family of gases like $H_2$, $C_xH_y$, $H_2S$, and $O_2$. In addition, promising $H_2$, $C_xH_y$ gas sensor structures were obtained in SiC, GaN and diamond based Schottky diode, MIS, MOS capacitors, and MOSFET devices [17-19] by means of work function modification due to the gas to be detected. However, the commercial wide band gap semiconductor technology and associated sensing field are still at the early stages, while the oxygen detection is bringing additional challenges of compatibility between the $O_2$ sensing layers and the standard processes specific to the semiconductor technology.

As explained above, the response of the commercial resistive sensors based on titania ($TiO_2$) is affected by both oxygen partial pressure and the operating temperature. This situation is demanding a complex temperature control electronics in order to eliminate the effect of temperature from the sensor response, and thus to avoid ambiguity in sensor operation. An extensive academic and industrial research has been performed in the last two decades for the discovery of new metal oxide semiconductor materials which will allow temperature independent detection of oxygen in chemoresistive sensors. This principle will also eliminate the need for an air reference chamber, and thus may be more easily manufactured, with respect to potentiometric λ sensors. The latest results of this research can be summarized as follows [13].

In the case of *p*-type MOS ceramic materials, it was discovered that the electrical conductivity of the mixed electronic ionic conducting $SrTi_{1-x}Fe_xO_{3-y}$ (STFOx) solid solution (x = 0.3-0.4) will depend only on the partial pressure of oxygen when the $O_2$ pressure is higher than about 10 Pa, and will not depend on temperature in the 750 °C to 950 °C range [20]. Thus, for example, STFO35 (strontium titanate ferrite with $x$ = 0.35) when used as a sensing layer in a resistive $O_2$ sensor will respond only to oxygen partial pressure variations and not to temperature variations in the range from 750 °C to 950 °C. Therefore, the above temperature ambiguity of the sensor response is eliminated by iron addition to such a stoichimetry, where 35% of the titanium atoms will be replaced by iron atoms. This temperature independent behaviour, obtained for $x$ = 0.35 (rather unexpected for a *p*-type semiconductor), can be simply explained by the compensation effect between the decreasing mobility and the increasing mobile charge carrier concentration as a function of temperature, when increasing the iron doping concentration (bearing in mind that the STFO band gap is reduced from 3.3 eV at $x$ = 0 to 1.8 eV at $x$ = 0.35 [21]).

During their operation, the oxygen sensors for combustion control in automotive applications are exposed to a chemically and thermally harsh environment, where both high temperatures around 900 °C and reactive gases like $NO_x$, $SO_2$ are also present. In order to obtain a stable sensor operation in the field, the STFO35 sensing layer should be treated - during sensor fabrication - at temperatures higher than the operation temperature, so that the crystalline structure of the film (described by characteristics such as the average grain size and crystalline orientation) be preserved for the duration of the sensor's lifetime. Some of the major concerns of the above mentioned STFO35 ceramic layer are the composition stability during high temperature sintering and its potential surface poisoning during film exposure to $SO_2$, due to sulphates formation.

In order to avoid any chemical reactions between the STFO35 layer and the ceramic substrate during high sintering temperatures, a buffer layer (acting as a diffusion barrier) is deposited above the substrate (in most of the cases this is alumina), and thus deterring the composition deterioration of the STFO35 layer [22]. A typical buffer material to be used for this purpose is the $SrAl_2O_4$ layer, which is deposited on the alumina substrate. The poisoning of the substrate in the presence of $SO_2$ is still a major challenge, which has not yet been solved by means of the deposition methods from different slurries.

Recently, it has been demonstrated that by employing the "aerosol deposition method" (ADM) at room temperature, a dense and good quality layer of STFO35 has been obtained, which did not need any further sintering step for reaching the appropriate grain size specific to a sensitive layer [23]. The STFO35 thick layers deposited by this method have shown good sensing properties and simplified the sensor fabrication process, by eliminating the need for a buffer layer. In addition, based on previous results obtained on dense films [24], it may be expected that due to the dense film morphology, the amount of sites for $SO_2$ adsorption to be reduced and thus the chemical resistance of the STFO35 deposited by the ADM method is expected to be significantly higher. Therefore the poisoning effects due to $SO_2$ may be thus reduced. However, it seems that the performance "price" paid by dense films is the slow response time of the sensor due to the longer time needed by the oxygen equilibration process between the film body and outside the film, in the gas ambient, which is the core of the sensor operation. Such an approach may not be suitable for the exhaust gas monitoring in automotive applications, where response times close to 0.1 ms are needed for real-time control of the air-fuel mixture at the input of the engine, at any moment.

Recently, it has been demonstrated that a temperature-independent oxygen sensing structure can be obtained by employing layers of $STFO_x$ with $x = 0.6$ (STFO60) [25]. The used sensing layer preparation method generated nano-structured STFO60, which is responsible not only for the temperature

independence, but also for the enhanced oxygen response. Oxygen detection performed with STFO60 resistive sensors, during run tests on diesel engines, have showed no cross sensitivity to $NO_2$, $C_3H_8$, CO, and $CO_2$. This is a result better than those previously reported on $TiO_2$ resistive sensors which were shown to be sensitive to $NO_2$ [26]. However, the long-term reliability of these STFO60 sensors, as well as their lifetime in the presence exhaust gas contaminated with $SO_2$ have not yet been tested.

In parallel with the research work carried out on *p*-type semiconductor ceramic films, an intensive effort was done for the realization of the $O_2$ resistive sensors based on *n*-type metal oxide semiconductors. The results are briefly described below. One direction consisted in further research on titania sensors, for improving the chemical film stability at the interface with alumina, reducing the operation temperature; the objective of reducing the $SO_2$ poisoning effects was addressed through the use of novel deposition methods, like AMD (as described above) or sol-gel technology [27].

Another research direction focused on the elimination of the temperature variation effects during oxygen partial pressure measurement with *n*-type MOS ceramic resistive films. Unfortunately, for these *n*-type layers, no material composition was found for which the temperature response of the electric conductivity to remain constant as a function of temperature, as it was the case of *p*-type STFO35 and STFO60. Recently, it has been shown that the temperature dependence on the electrical conductivities of 10% zirconia-doped-ceria ($Ce_{0.9}Zr_{0.1}O_2$) and 50% yttria-doped-ceria ($Ce_{0.5}Y_{0.5}O_{2-\delta}$) are very similar, but the yttria doped ceria has no sensitivity to oxygen [28].

Under these circumstances, a "ratiometric" sensor construction was suggested in [28], where a resistive divider is implemented between the resistors made of the two ceramic films from above, while the sensor response to be measured on 10% zirconia-doped-ceria. Ceria has also the capability of oxygen storage by changing its oxidation state from $^{+}3$ in $Ce_2O_3$ to $^{+}4$ in $CeO_2$, by further oxidation reaction. While exhibiting these features, this material is of interest as three way catalyst and oxygen sensor, a topic which is still to be studied [29]. Other *n*-type semiconductors ceramic films, like $Ga_2O_3$, are under research these days. The effect of nanostructuring on the response time and sensitivity is evaluated.

Finally, it is worth mentioning that with the exception of the titania resistive sensors (commercially available) which are on the market, there is no other resistive ceramic sensor ready to be commercialized. This situation may be due to the market requirements for these sensors, where lifetime, response time, cross sensitivity and chemical stability of the sensor to $SO_2$ poisoning effect, should be all fulfilled on the same device.

## 4. Towards SOI-based CMOS-compatible oxygen sensors for harsh environment

As described above, a major step forward towards the miniaturization of oxygen sensors for combustion control was represented by the realization of ceramic planar sensor, for which thick film-HTCC technology was employed. The feature size of this meso-technology is determined by the specific properties of the screen printing technology and by the thickness of the deposited films. For combustion control in gasoline or diesel engines, the above mentioned sensors should withstand temperatures up to 1000 °C. At such high operation temperatures, wide band gap semiconductors could be taken into consideration, due to their inherent much lower thermal generation of free carriers compared to silicon. However, as explained above, the technologies based on wide band gap semiconductors are still in their early stages for sensing applications purposes.

For combustion control optimization in domestic boilers, the maximum ambient temperature an $O_2$ sensor needs to withstand is 225 °C. For this temperature level, the state-of-the-art bulk silicon IC technology for producing the required sensors and the associated electronics may not have the required degree of reliability.

On the other hand, the Silicon-on-Insulator (SOI) micro-hotplate CMOS-compatible technology looks like a more reliable solution (Fig. 2) [30]. In this case, the major challenges come from combining the SOI-based micro-hotplates with novel sensing layers (like STFO60), from the associated metallization technology, and from the relatively high operating temperatures required by $O_2$ resistive detection. Such high operating temperatures are requested as the equilibrium between the oxygen concentration in the sensing layer and the oxygen concentration coming from outside should be reached in a relatively short amount of time, in order to obtain a sensor with short response time.

The results of experimental kinetics of oxygen incorporation in STFO layers have shown, in good correlation with defect chemistry, that at temperatures around 400 °C and for small STFO thicknesses, the $O_2$ incorporation (removal) is surface-controlled, while at higher temperatures (above 500 °C) it is diffusion-controlled [31]. However, in these experiments, iron doping was used only as an indicator for monitoring optical absorption in STO films, so some changes in the temperature ranges quoted above may occur. These ranges depend on the iron concentration and on the STFO layer preparation method.

At this stage, it is important to mention that the SOI micro-hotplate [32] is able to maintain on the poly-Silicon heater a maximum temperature of 650 °C, for a few months, which is a very good result for relatively fast oxygen incorporation/removal, and, hopefully, for a short response time. Assuming that the state-of-the-art STFO30-60 sensing layers will be employed, one of the

remaining challenges will be the use of either subtractive or additive sensing layer deposition IC-compatible methods. Additive methods may be preferred. At the same time, the compatibility between the thickness, morphology, and (nano)structural properties of the sensing film, the sensor requirements and the mechanical capability of the suspended SOI micro-hotplate should also be considered.

Special attention should be paid to avoiding breaking or bending the SOI micro-hotplate during the processing and annealing of the STFO film.

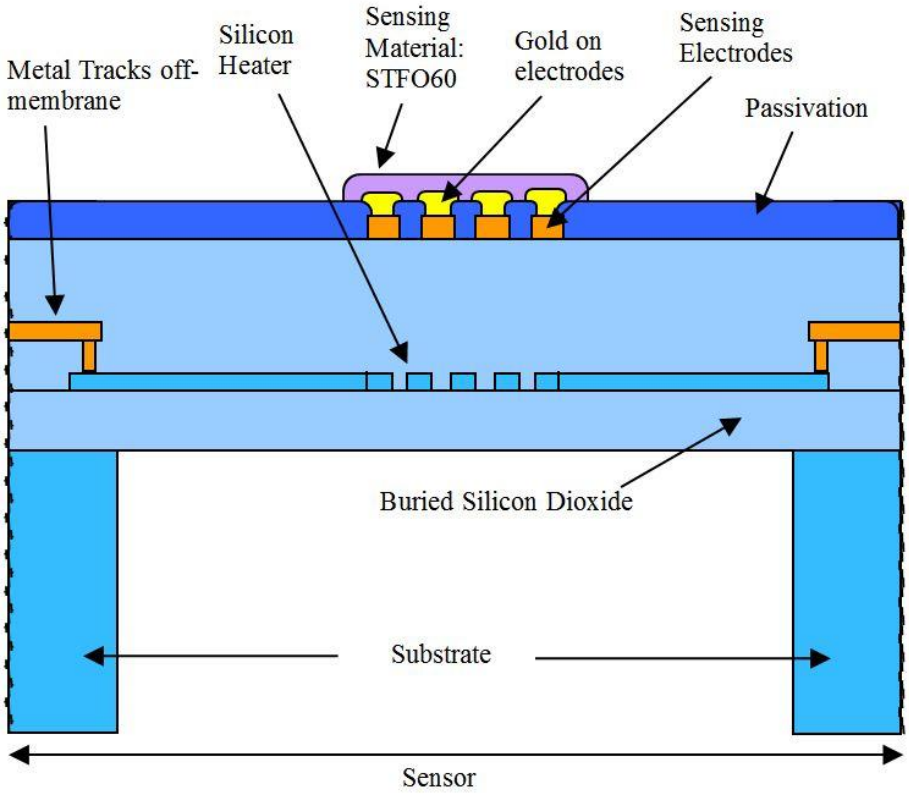


**Fig. 2.** $O_2$ resistive sensing structure employing STFO60 as sensing layer and SOI CMOS-compatible micro-hotplate membrane as substrate.

Another important research topic is the realization of a reliable metallization for the SOI-based MEMS CMOS-compatible resistive $O_2$ sensor, employing STFO60 as sensing layer. For obtaining a relatively fast $O_2$ chemoresistive sensor (with a response time in the range of a few seconds), the sensor operation temperature should be around 600 °C. This being the case, the metallization for the interdigitated electrodes (IDEs) of the sensor should not contain an aluminum layer, as Al is not able to withstand this operating temperature level for very long times due to its relatively low melting point (660 °C).

Therefore, for reliability purposes, if employing the state-of-the-art metallization solutions which comprise an Al layer, one may need to limit the STFO60 layer annealing temperature and the sensor operating temperature at about 500 °C.

This is below the optimum value required by the thermal consolidation of STFO60. This needs to be performed at 650 °C, in order to preserve the grain size of the sensing film.

In addition, the potential solid state reactions between the STFO60 film and the aluminum layer should be considered. Such reactions may deteriorate the chemical composition of the STFO60 film, since phase separations like $Al_2O_3$, or $Fe_2O_3$ might occur. In this context, a buffer (diffusion barrier) layer as in the case the planar ceramic $O_2$ sensing technology might be employed.

Employing Al for metallization will also have an adverse effect on the $O_2$ sensor response time. By imposing a maximum operating temperature of only 500 °C, Al prohibits STFO60 to reach its fully $O_2$ sensing capabilities, which require an operating temperature of at least 600 °C.

All the above mentioned factors indicate the need for employing a noble metal-based metallization in the fabrication process of a reliable $O_2$ resistive sensor based on the SOI micro-hotplate technology. Such a noble metal, like platinum, will allow higher STFO60 annealing temperature levels and higher operating temperature. Both temperature levels will be limited only by the capability of the SOI membrane.

Another important research topic for the realization of an integrated $O_2$ sensor in the SOI-based MEMS CMOS-compatible technology is the sensing film deposition method on the suspended membrane.

A deposition method such as screen printing is not compatible with the IC technology and the associated feature size. At the same time, the fragility of the suspended membrane, which can be easily broken during screen printing, should also be considered.

Intensive research activity on depositing sensing layers by direct printing, additive methods have been reported [33].

The key process requirement is the correct formulation of the ink, which should have a low tendency for sedimentation and an appropriate particle size inside the slurry.

Overall, the envisioned advantages of a miniaturized, SOI-based CMOS-compatible oxygen resistive sensor in terms of low power consumption, low cost, high reproducibility, high volume capacity, sensor and electronics integration, build a major driving force able to surpass the challenges and concerns described above.

## 5. Conclusions

The present paper has shown the evolution of the oxygen sensing technology for industrial applications of combustion control, with a main focus on the devices for the automotive industry.

The state-of-the-art potentiometric and resistive $O_2$ sensors suitable for the above mentioned applications were described in detail.

The main limitations of the existing commercial solutions for $O_2$ sensing in harsh environment were also described.

The main optical principles for oxygen sensing were extensively discussed, especially their use in medical applications.

Emerging technologies employing SOI-based CMOS-compatible micro-hotplates as substrate and iron-doped strontium titanate as sensing layer were also presented and their technological challenges were briefly discussed.

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