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Invited Paper

SOLID STATE GAS SENSORS: STATE OF THE ART AND FUTURE ACTIVITIES

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This paper gives an overview about the principles and the technologies used in solid-state gas sensors. These devices work by measuring a physical property changed by adsorption/desorption processes and chemical reactions on the surface of a sensing element, i.e. a solid-state film of a gas-sensitive material. Some of the most used types of solid state gas sensors are here described together with novel sensor technologies in development for commercial exploitation in the future.

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1. Introduction

Gases are the key measurands in many industrial or domestic activities. In the last decade the specific demand for gas detection and monitoring has emerged particularly as the awareness of the need to protect the environment has grown. Gas sensors find applications in numerous fields [1,2]. Two important groups of applications are the detection of single gases (as NO_x, NH_3, O_3, CO, CH_4, H_2, SO_2, etc.) and the discrimination of odours or generally the monitoring of changes in the ambient. Single gas sensors can, for examples, be used as fire detectors, leakage detectors, controllers of ventilation in cars and planes, alarm devices warning the overcoming of threshold concentration values of hazardous gases in the work places. The detection of volatile organic compounds (VOCs) or smells generated from food or household products has also become increasingly important in food industry and in indoor air quality, and multisensor systems (often referred to as *electronic noses*) are the modern gas sensing devices designed to analyse such complex environmental mixtures [3-5]. In Table 1 examples of application for gas sensors and electronic noses are reported.

Solid state gas sensors, based on a variety of principles and materials, are the best candidates to the development of commercial gas sensors for a wide range of such applications [6-10]. The great interest of industrial and scientific world on solid state gas sensors comes from their numerous advantages, like small sizes, high sensitivities in detecting very low concentrations (at level of ppm or even ppb) of a wide range of gaseous chemical compounds, possibility of on-line operation and, due to possible bench production, low cost. On the contrary, traditional analytical instruments such as mass spectrometer, NMR, and chromatography are expensive, complex, and large in size. In addition, most analysis requires sample preparation, so that on-line, real-time analysis is difficult. Solid-state chemical sensors have been widely used, but they also suffer from limited measurement accuracy and problems of long-time stability. However, recent advances in nanotechnology, i.e. in the cluster of technologies related to the synthesis of materials with new properties by means of the controlled manipulation of their microstructure on a nanometer scale, produce novel classes of nanostructured materials with enhanced gas sensing properties providing in such a way the opportunity to dramatically increase the performances of solid state gas sensors.

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Table 1. Example of applications for gas sensors and electronic noses.

APPLICATIONS
Automobiles ▪ Car ventilation control ▪ Filter control ▪ Gasoline vapour detection ▪ Alcohol breath tests
Safety ▪ Fire detection ▪ Leak detection ▪ Toxic/flammable/explosive gas detectors ▪ Boiler control ▪ Personal gas monitor
Indoor air quality ▪ Air purifiers ▪ Ventilation control ▪ Cooking control
Environmental control ▪ Weather stations ▪ Pollution monitoring
Food ▪ Food quality control ▪ Process control ▪ Packaging quality control (off-odours)
Industrial production ▪ Fermentation control ▪ Process control
Medicine ▪ Breath analysis ▪ Disease detection

Several physical effects are used to achieve the detection of gases in solid state gas sensors. In contrast to optical processes, which employ infra-red absorption of gases, chemical processes, which detect the gas by means of a selective chemical reaction with a reagent, mainly utilize solid-state chemical detection principles. A characteristic of solid state gas sensors is the reversible interaction of the gas with the surface of a solid-state material. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction. Organic (as conducting polymers [11], porphyrins and phtalocyanines [12,61]) or inorganic (as semiconducting metal oxides [13,14]) materials, deposited in the form of thick or thin films, are used as active layers in such gas sensing devices. The read-out of the measured value is performed via electrodes, diode arrangements, transistors, surface wave components, thickness-mode transducers or optical arrangements. Indeed, although the basic principles behind solid state gas sensors are similar for all the devices, a multitude of different technologies have been developed. Hence, nowadays the number of different solid state based gas sensors is really very large. Due to the large variety of sensors, a rich fabric of interdisciplinary science ranging from solid state physics, chemistry, electronics, biology, etc., governs the modern gas-sensing devices. An incomplete list of solid state gas sensors is reported in Table 2. Solid state sensors depend strongly on the development of technologies mainly driven by other than sensor applications. A steering technology is that of micromachining which for chemical sensors has led to the development of gas sensor devices with small power consumption and short time constants, greater portability and easy integration with electronics.

The following sections are not intended to include exhaustive reviews of all available solid state gas sensors and technologies. Instead, the following sections provide a brief overview of the relevant features and applications of only some of the most important types of solid state gas sensors together with the advances in material science and technological aspects. A particular attention will be devoted to semiconducting gas sensors.

Table 2. Types of solid state gas sensors with the corresponding physical change used as gas detection principle.

	Type of devices	Physical change
1	Semiconductor gas sensors	Electrical conductivity
2	Field effect gas sensors: diodes, transistors, capacitors	Work function (electrical polarisation)
3	Piezoelectric sensors : Quartz crystal microbalances (QMB), surface acoustic wave (SAW), microcantilevers	Mass
4	Optical sensors (fibre optic or thin film)	Optical parameters: SPR, reflection, interferometry, absorption, fluorescence, refractive index or optical path length
5	Catalytic gas sensors: Seebeck effect, pellistors, semistors	Heat or temperature
6	Electrochemical gas sensors (potentiometric or amperometric)	Electromotive force or electrical current in a solid state electrochemical cell

2. Review of solid state gas sensors

2.1 Semiconductor gas sensors

Semiconductor gas sensors (SGS), known also as chemoresistive gas sensors, are typically based on metal oxides (e.g. SnO_2, TiO_2, In_2O_3, WO_3, NiO, etc.). In the field of this type of gas sensors, recent applied studies and products releases have shown some significant trends on Nanotechnologies and gas-sensing layers to be employed. One of these trends aims to implement low cost, low-power consumption, reliable, smart and miniaturized sensing devices and it shows the decisive advantage of using micromachined silicon platform as substrates for the sensitive layers [15-16]. On the other hand, several theoretical and applied articles have shown the advantage of reducing the metal oxide grain size down to nanometer scale in order to improve the sensing properties (mainly sensitivity and selectivity) as well as stability over time of the oxide layer [17-21]. Nanocrystalline semiconducting metal oxides with controlled composition are indeed of increasing interest in gas sensing and constitute also a new and exciting subject of fundamental research [22].

The gas/semiconductor surface interactions on which is based the gas-sensing mechanism of SGS occur at the grain boundaries of the polycrystalline oxide film. They generally include reduction/oxidation processes of the semiconductor, adsorption of the chemical species directly on the semiconductor and/or adsorption by reaction with surface states associated with pre-adsorbed ambient oxygen, electronic transfer of delocalized conduction-band electrons to localized surface states and vice versa, catalytic effects and in general complex surface chemical reactions between the different adsorbed chemical species. The effect of these surface phenomena is a reversible and significant change in electrical resistance (i.e. a resistance increase or decrease under exposure to oxidizing respectively reducing gases referring as example to an *n*-type semiconductor oxide). This resistance variation can be easily observed and used to detect chemical species in the ambient. The influence of these surface chemistry phenomena on the sensor response may be understood on the base of the charge-transfer model (CTM) and the modified band model of semiconducting metal oxide sensor devices that take into account also the effects of additives, dopants, grain size as well as contacts [14]. According to this model, the changes in the electrical resistance of the sensor are described by the formation of depletion space-charge layers at the surface and around the grains, with upwards bending of the energy bands. Surface energy barriers for conduction electrons result, whose height and width is variable, depending on the occupancy of surface states related to adsorbed species.

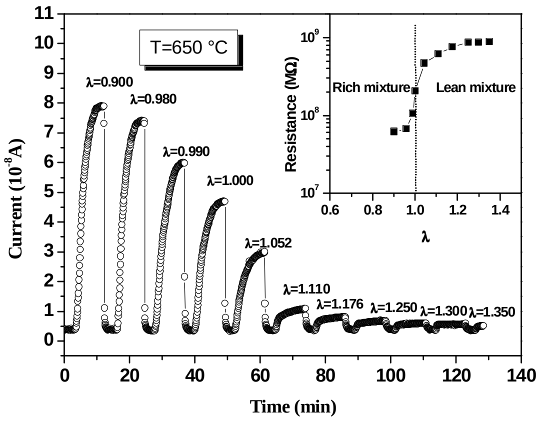


Fig. 1. Sensor response to nitrogen/oxygen mixtures correspondent at different λ lambda values at 650 °C. In the insert the electrical resistance of the sensor at different oxygen concentration versus the corresponding λ values. It's evident a jump of about two orders of magnitude, switching from rich (λ<1) to lean (λ >1) mixture.

The gas/solid interactions exploited in SGS can involve changes in the surface conductance or changes in the bulk conductance; correspondingly two principal types of metal oxide-based gas sensors can be distinguished [6,7]. Since a semiconductor oxide is in general non-stoichiometric and the oxygen vacancies are the main bulk defects, changes in bulk conductance are due to changes in oxygen partial pressure at operating temperatures so high (600-1000 °C) that the oxygen vacancies can quickly diffuse from the interior of the grains to the surface and vice versa and the bulk of the oxide has to reach an equilibrium state with ambient oxygen. The main application of this first kind of sensors is the measurement of oxygen partial pressure as required in combustion control systems, in particular in the feedback control of the air/fuel ratio of automobile engine exhaust gases near the λ point in order to improve the fuel economy efficiency and to reduce the harmful emission of gases as CO, NO_x and hydrocarbons [23,24]. Normally, electrochemical cells based on solid state electrolytes as ZrO_2 are used as λ-sensors. Recently, *Francioso et al.* proposed the use of TiO_2 thin-film deposited by the sol-gel technique in chemoresistive gas sensors for application in λ measurement [25] In Fig. 1 the dynamic response of the a TiO_2-based sensor to different nitrogen/oxygen mixtures is reported together to sigmoid plot of the sensor resistance vs the λ values.

The second principal type of semiconductors gas sensors is based only on changes in surface conductivity at lower temperatures (<600 °C) and at quasi-constant oxygen partial pressure. In this condition the sensor detects small concentrations of reactive gases in air by a displacement from the constant oxygen pressure equilibrium state, induced by gas interfering effects at the surface of the sensor. Here we will discuss about this latter class of resistive-type gas sensors.

The working temperature, at which these devices work, varies depending on the specific target gas in the ambient and on the selected sensor material in conjunction with its properties in every case. As this working temperature ranges usually from 200 to 400 °C, it is necessary to implement a heating element in sensor device. A simple SGS is thus basically composed of a substrate in alumina or silicon (on which the sensing layer is deposited), the electrodes (to measure the resistance changes of the sensing film) and the heater (commonly a Pt resistive type heater) to reach the optimum sensing temperature. An image of a sensor on allumina substrate is shown in Fig. 2. A semiconductor gas sensor can work in different *operation mode*, the most used is based on the monitoring of the sensor resistance at constant temperature operation. Other operation modes are the modulated operation temperature [26], the single and/or simultaneous measurement of sensor resistance and thermovoltage [27], the single and/or simultaneous measurement of sensor resistance and temperature [28].

The semiconductor gas sensors offer low cost, high sensitivity and a real simplicity in function, advantages that should work in their favour as new applications emerge. Moreover, the possibility of easily combining in the same device the functions of a sensitive element and signal converter and control electronics markedly simplifies the design of a sensor and constitutes the main advantage of chemoresistive-type sensors over biochemical, optical, acoustic, and other gas sensing devices.

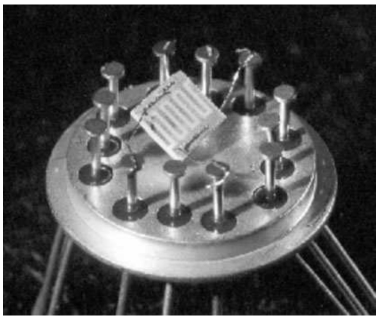


Fig. 2. Image of the sensor on alumina substrate bounded on a TO-8 socket.

In spite of the numerous advantages of resistive-type gas sensors, they show different disadvantages as poor reproducibility and long-time instability due to aging. There are two undesired aging effects that may appear when the sensor works for a long period: a *drift* of the baseline signal (defined as the conductance in air or in a reference gas) or a *drift* in the sensor response. Metal oxides sensors are also non-linear devices; the change in sensor response due to a defined change in gas concentration depends generally on the concentration of the gas to be monitored and also on the concentration of other gases (cross sensitivity effect). In this case more than one sensor or more than one operation modes of the same sensor are required to determine the concentration level. In the worst case, the partial sensitivity varies with the aging of the sensor due to drifts or contamination effects.
Long-time instabilities are of considerable importance for the practical use of the sensor; pre-aging thermal treatments and cycle calibration checks have to be carried out in order to avoid the wrong use of the device. The causes of instabilities are mainly microstructural and morphological changes (change in size, number and distribution of grains and intergranular boundaries) of the sensing elements, but also irreversible reactions with chemical species in the ambient, modifications of the sensor heating element or of the electrodes have to be taken into account.

Other important disadvantages are the sensitivity to water vapour and the lack of selectivity. Metal oxide-based gas sensors are normally sensitive to more than one chemical species in air and usually show cross-sensitivities. This non-specificity of the response to chemical species whose presence, identity and concentration in air have to be determined is by now considered an intrinsic property of metal oxide-based gas sensors. It's easy to understand how this disadvantage represents a real problem when different reactive gases are present simultaneously in the same atmosphere and interference effects between them can occur. Unselectivity cannot be eliminated completely but it can be improved in different ways, like: (i) the use of filters [29] or chromatographic columns to discriminate between gases on the basis of their molecular size or other physical properties [30], (ii) the use of catalysts and promoters or more specific surface additives [31,32], (iii) the selection of the material for the sensing layer [13,33] and its physical preparation, (iv) the analysis of the transient sensor response [34], (v) the selection of a fixed temperature to maximize sensitivity to a particular analyte gas [35] or (vi) the use of temperature modulated operation mode [26]. A different approach to the problem of unselectivity is based on the development of the above mentioned *electronic nose*, that consists in an array of different sensing elements with partially overlapping sensitivity and a *pattern recognition* system [3-5]. Basically the idea of an electronic nose is to exploit the unavoidable cross-sensitivity of the sensors instead of trying to eliminate it, by linking the sensors in an array configuration and by analyzing the responses of the sensors in a subsequent data processing step in order to perform a qualitative and/or quantitative analysis of the ambient under examination.

The basic part of efforts made nowadays by scientific research community in SGS field are devoted both to optimize the performances of gas sensors by improving their sensitivity, selectivity and stability for the detection of single gases and the development of electronic noses for application mainly in environmental control and in food industry.

An important trend of research in solid state gas sensors is devoted to the seek for novel materials suited to gas sensing. These efforts have lead the scientific community working in the field to consider a new concept design for gas sensors based on the use of nanostructured mixed oxides and heterojunctions. The idea originated from some observations related to the working principles of metal oxide-based gas sensors. As it is well known, the resistance variation of the sensing layer involves two important functions, i.e. the recognition and the transducer functions. Gas/solid interactions phenomena are involved in the receptor function, while the microstructure of the oxide determines the trasduction of the chemical stimulus in air into an electrical signal. Generally speaking, if a single oxide system is adopted, these two functions cannot be optimized independently. Instead, by introducing in the system a foreign material, which is very reactive to a target gas and act as an 'antenna' material, both functions may be optimized simultaneously and the sensor may become more sensitive even to low reactive gas concentrations. In these cases, the material acting as a unique receptor (antenna material) should be interfaced electronically to the transducer material and its chemical change should sensitively modulate the semiconducting properties of the transducer oxide through the hetero-junction [40-45]. Layered-type sensors and composite-type sensors containing hetero-contacts between the two phases fulfill this novel concept of gas sensors. They constitute a promising class of gas sensors with enhanced gas-sensing properties.

2.1.1 Application examples

A huge literature on the characterization and use of semiconducting oxides as gas sensors has been produced. Just as example, we mention some results reported by the authors and related to examples of metal oxide gas sensors for applications in an electronic nose [35]. The application of a multisensor system to the analysis of binary gas mixtures of carbon monoxide and methane (CO/CH_4) in air at different relative humidity levels (0 %, 30 % and 50 % R.H.) have been considered by *Capone et al.* [35,36]. The sensor array consisted of eight Pd doped SnO_2 based sensors deposited by drop-coating onto Si-micro-machined hotplates were used for this experimental work. They selected CO and CH_4 as target gases because both are toxic and hazardous gases which may be present in a domestic and/or industrial environment. The sensing elements of the array were diversified by varying the Pd-doping content (0.2, 2 % wt. of Pd) and the geometry of the Pt contact electrodes in comb-like and gap configuration with differently spaced fingers. The sensors resulted very sensitive both to CO and CH_4. Humidity enhances the response to CO and decreases the response to CH_4, however, in humid air there is always an enhancement of the response of the SnO_2/Pd sensors when carbon monoxide and methane are present simultaneously. Principal Component Analysis (PCA) gave good discrimination results for the different binary CO/CH_4 mixtures. In particular we found that data are distributed in PCs space according to a well-defined geometric structure with data clusters oriented along preferential directions (Fig. 3).

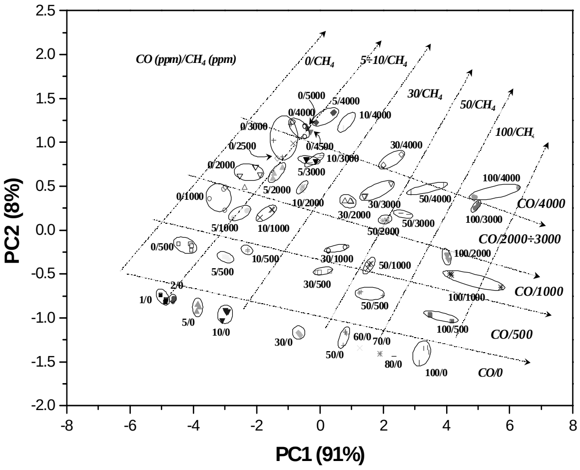


Fig. 3. PCA results in the plane of the first two principal components for the data set related to 30 % R.H.

A.M. Taurino et al. studied the gas sensing properties of TiO_2 thin films grown by seeded supersonic beam of cluster oxides [37]. Different TiO_2-based sensors prepared by using different deposition parameters, have been tested in a gas sensor array and they showed good responses to some alcohols (ethanol, methanol and propanol). Fig. 4 shows, as an example, the dynamic response of the sensor array towards ethanol, at the operating temperature of 260 °C.

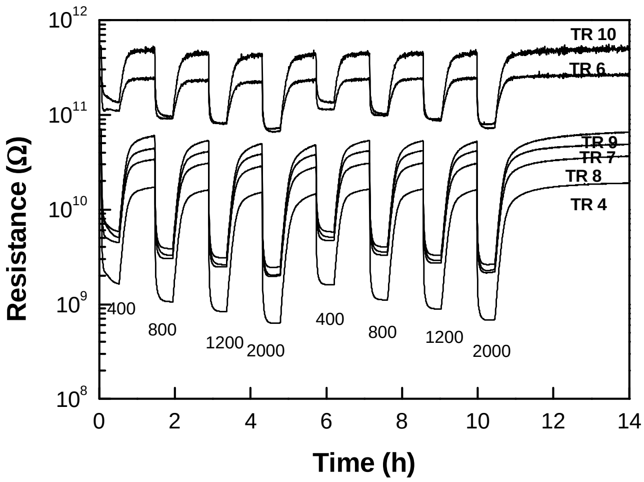


Fig. 4. Typical dynamic responses of six different TiO_2 based microsensors towards ethanol at a working temperature of 260 °C (concentration expressed in ppm).

An important field of application of electronic nose is also the food industry. Since the European Community has defined strict standards for food quality, significant efforts have been devoted to the development of new techniques that could complement the traditional sensorial and analytical analysis of foodstuffs. The attention has been turned to Electronic Noses which in mimicking human nose offer an objective way of detecting aromatic fingerprints. In particular, due to the fundamental importance of olive oil in the 'mediterranean diet' and in market, there is a great interest towards all the techniques able to provide an analysis of olive oil quality. Olive oil was the first foodstuff to be classified by both chemical and sensorial analysis according to the EU Normative. It means that an olive oil can be labelled as extra-virgin only if both its chemical and sensorial characteristics are within certain standards established by law. Thus, market requires urgently reproducible, reliable, inexpensive, easy to train and to use, objective 'sniffing' electronic device dedicated to olive oil for different applications, the mainly being classification and degradation studies. Authenticity is an issue of major concern across the oil industry. Olive oil is marketed based on acidity grade in 'olive-husk oil, olive-oil, virgin olive oil, extra-virgin olive'. Olive oil is also marketed based upon country and region of production and upon olive type. There is a very large difference in price between, for example an Italian and a Spanish or Greek olive-oil

The authors developed an Electronic Nose developed at the Institute IME-CNR for testing a number of different commercial olive oils of various quality produced in different areas in Italy [35,38,39]. Furthermore, the analysed olive-oils were compared with local oils of the *Salento* region in *Apulia (Italy)*. Indeed, one of the most important goal in the field of olive-oil characterisation is the classification of them on the basis of their arising region. This is most important for the regions that have the so called D.O.P. (Protect Origin Denomination) label which is an index of the quality of the product.

A significant result was obtained by analysing the array response to the volatile compounds of some commercial and non-commercial local olive oils from *Salento* by PCA. In the score plot we can clearly distinguish all the different classes of olive oils and a discrimination between the commercial and non-commercial local olive oils (Fig. 5).

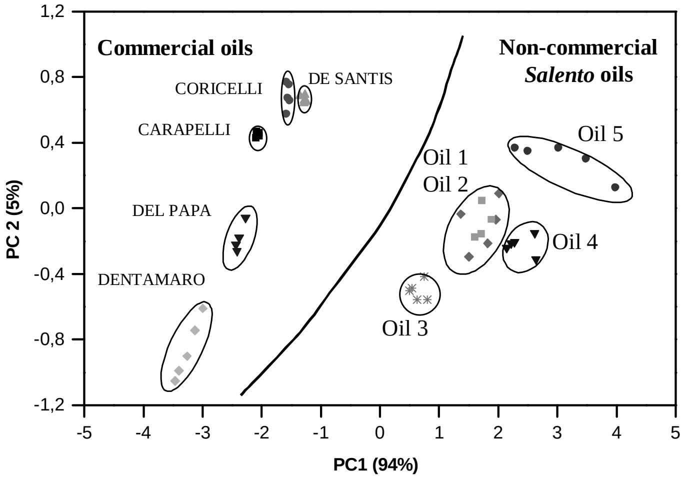


Fig. 5. PCA plot related to commercial and non-commercial olive oils from Salento (Italy). The commercial olive oils are labelled with the name of the trade-mark.

2.2 Optical gas sensors

The optical gas sensors play an important role in sensing field for the measurements of chemical and biological quantities. First optical chemical sensors were based on the measurement of changes in absorption spectrum. At present a large variety of optical methods are used in chemical sensors and biosensors including ellipsometry, spectroscopy (luminescence, phosphorescence, fluorescence, Raman), interferometry (white light interferometry, modal interferometry in optical waveguide structures), spectroscopy of guided modes in optical waveguide structures (grating coupler, resonant mirror), and a surface plasmon resonance (SPR). In these sensors a desired quantity is determined by measuring the refractive index, absorbance and fluorescence properties of the analyte molecules or a chemo-optical transducing element [46-49]. This type of gas sensors are not treated in detailed in this contribution. This is not due to any judgement of the their relative importance but simply for practical reasons. Hence, we referee to the mentioned literature for a complete discussion.

Nevertheless, we mention only some results obtained by our research group regarding optochemical gas sensors based on organic thin films. In fact, since about five years at the Institute for Microelectronics and Microsystems of National Council of Researches (IMM-CNR) - Unity of Lecce, in collaboration with the University of Lecce, extensive researches on the characterization and the gas sensing properties of organic thin layers (metallophthalocyanines, metalloporphyrins and conducting polymers) for applications in chemical gas sensors have been carried out [58-60,62,65-67]. In particular, some works regarding the detection of nitrogen dioxide by metallophthalocyanine have been published by our group [60]. Here, we mention recent results obtained with four different MPc synthesized and deposited as thin films by spin-coating onto quartz substrates. Their utilization as sensing layers in chemical gas sensors based on an a change of optical Vis-NIR absorption curves is reported in Ref.[58], where the optical responses of the MPc thin films towards five different volatile vapour organic compounds (VOCs) of interest in food analysis have been analysed. The sensors have been arranged in an array configuration and used as chemo-optical nose for the discrimination of the considered VOC vapours by considering both the optical Q bands in data analysis. Fig. 6 shows the Principal Component Analysis (PCA) based on the Q_1 and the Q_2 bands.

Our group is also involved in the development of optical gas sensors whose trasduction principle is based on the surface plasmon resonance technique. Thin films of organic molecoles (metallophtacyanines, metalloporhyrins, pyrroles, etc.) are used in this type of gas sensors. SPR is one of the most sensitive detection methods for changes of thickness and refractive index in ultra-thin films. It is a convenient optical trasduction technique in molecular recognition and it has been already applied to sensor systems, above all for biological purposes [49]. As example, we report the optical recognition (based on SPR trasduction method) of alcohol vapours as ethanol and methanol through ultrathin calyx[4]pyrrole films deposited by Langmuir-Blodgett technique [59]. SPR measurements were performed with attenuated total reflection (ATR) method by using the Kretschmann–Raether configuration. In this case, the reflectivity of 1 mW p-polarised (i.e. polarised parallel to the plane of incidence) He–Ne laser (632.8 nm) is measured as a function of incident angle from a prism-sample assembly.

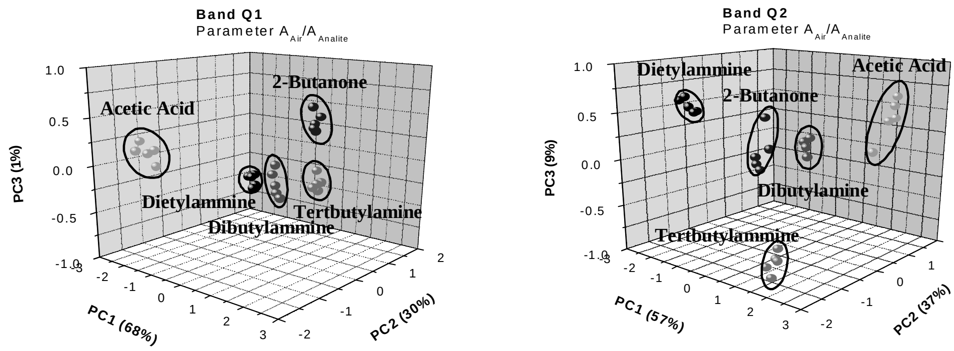
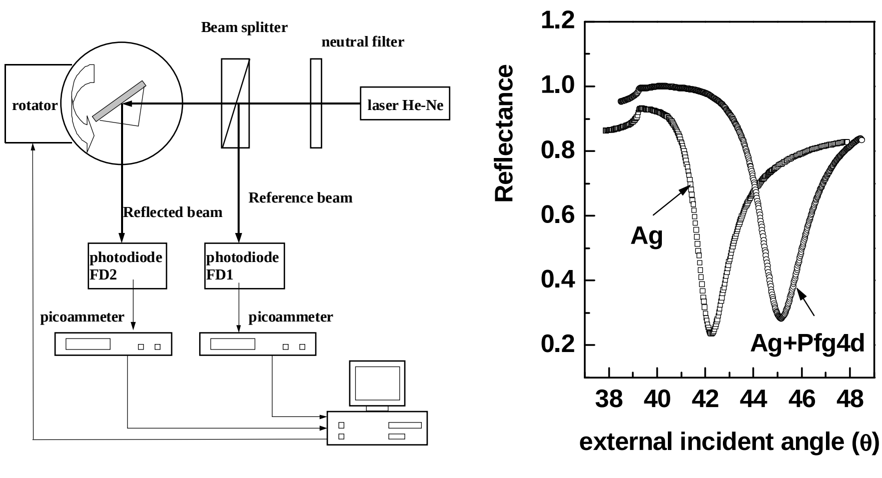


Fig. 6. PCA 3D score plot related to the responses of the array optical sensors corresponding to the Q_1 absorption band (a) and the Q_2 absorption band (b) respectively.

The free space of the glass substrate is brought into optical contact with the prism using a thin layer of an index-matching fluid (n = 1.517). In Fig. 7 the scheme of the experimental apparatus and, as example, the SPR reflectivity curves for the Ag/glass and the porphyrinogen (4 LB layers)/Ag/glass structures are reported. The shift in the minimum of external incident angle θ_{spr} is equal to 2.9° (from 42.7 to 45.6°). This is attributable to the change in the effective refractive index for the Ag surface covered with porphyrinogen LB film.



(a) (b)

Fig. 7. (a) Experimental configuration of SPR apparatus; (b) Surface Plasmon Resonance (λ= 632.8 nm) curves for 52 nm Ag layer and Ag+4 LB layers of porphyrinogen.

Advances in the research of our group involved the development of a novel SPR imaging system particularly suitable to characterise patterned organic monolayers and develop biochemical sensors arrays.

2.3 Electrochemical gas sensors

Chemical species reacting at an electronic conductor/ionic conductor interface exchange electric charges, then resulting in an electric signal. Electrochemical gas sensors employ an electrochemical cell consisting of a casing that contains a collection of chemical reactants (electrolytes or gels) in contact with the surroundings through two terminals (an anode and a cathode) of identical composition. For gas sensors, the top of the casing has a membrane which can be permeated by the gas sample. Oxidization takes place at the anode and reduction occurs at the cathode. A current is created as the positive ions flow to the cathode and the negative ions flow to the anode. Gases such as oxygen, nitrogen oxides, and chlorine, which are electrochemically reducible, are sensed at the cathode while electrochemically oxidizable gases such as carbon monoxide, nitrogen dioxide, and hydrogen sulfide are sensed at the anode [50].

The output of the electrochemical cell is directly related to the concentration or partial pressure of the gaseous species. Depending on whether the output is an electromotive force (namely an open circuit voltage) or an electrical current, the electrochemical gas sensors can be classified in potentiometric or amperometric. Potentiometric measurements are performed under conditions of near-zero current. Amperometric sensors are usually operated by imposing an external cell voltage sufficiently high to maintain a zero oxygen concentration at the cathodic surface; therefore, the sensor current response is diffusion controlled.

Solid state electrochemical devices are the most used sensor type for the measurement of oxygen for automotive market where legislation has restricted the permitted emissions levels of carbon monoxide, hydrocarbons and nitrogen oxides. Potentiometric sensors based on YSZ (yttria-stabilized zirconia) together with three-way catalyst system (TWC) represents the most used system for emission control at this time. The TWC system oxidizes carbon monoxide and unburned hydrocarbons and reduce nitrogen oxides. In order for the catalyst to function the input air to fuel ratio to the engine must be maintained close to the equilibrium balance between fuel and oxygen at the so-called lambda point. The air/fuel ratio is maintained most effectively at this value by a closed-loop control system that measures the oxygen content of the exhaust gas [51].

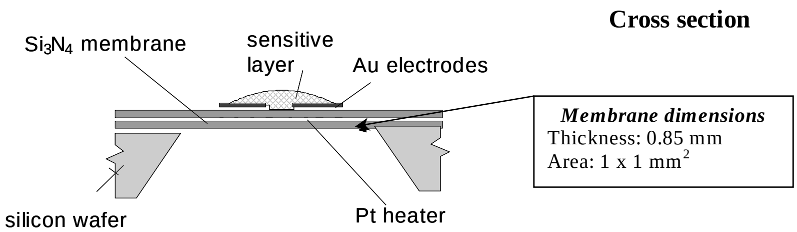


Fig. 8. Scheme of a closed-membrane type gas sensor. In particular, the model of microhotplates is fabricated at the Institute of Microtechnology (IMT) of Neuchâtel in Switzerland.

At present, these sensors are commonly produced as macroscopic ceramic devices or, more recently, as miniature thick film devices. The next miniaturization step is application of thin film technology and micromachining. Especially production on silicon substrates offers new possibilities including integration of sensors with microelectronic circuitry, combination with other sensors to multisensors, and batch-fabrication on wafers. An additional reason to apply micromachining to solid electrolyte sensors is the possibility to produce microhotplates by anisotropic etching of silicon. Most solid electrolyte require operation at elevated temperatures, typically higher than 600 K, and micro hotplates allow both a drastic reducion of energy consumption and faster thermal cycling. In the case of gas sensors based on semiconducting oxide thin films, microhotplate devices are already well known and industrially produced. For the current status of electrochemical micro gas sensors based on ionic conduction we refer to Ref. [52].

Since micromachining technology are becoming a fundamental tool is solid state gas sensors we devoted the next paragraph to a brief description of micromachined substrates and their important role in solid state gas sensors.

3. Micromachined substrates for solid state gas sensors

Micro-technologies have been developed for the production of silicon semiconductors. Thanks you to the batch production, the growing size of silicon wafers and the miniaturization of each micro-device, an ever increasing number of elements can be processed in parallel resulting in a considerable reduction of costs. The silicon revolution has enabled us to produce small, reliable processors in the form of Integrated circuits (ICs) using microelectronics technology. Silicon processing technology is no doubt the most advanced technology in the world and may not easily surpassed by other technologies.

All the facilities offered by silicon micro-technology make it an excellent tool for the production of microsensors [53,54]. Additionally, since the electrical sensor signals have to be acquired, amplified and evaluated, the sensor technology has to be compatible with modern electronics. Thus, another cost reduction may be achieved by the integration of the sensing part and electronic circuitry on the same chip and this provide a second argument for second fabrication by microelectronic technologies.

In this context micro-machined gas sensing device are acquiring an ever-growing importance in the field of gas sensors [56]. The heart-piece of this structure is the active area that comprises of a heater, sensor electrodes and the gas sensitive layer situated in the centre of a thin membrane which itself is supported by an outer frame of silicon. Basically there are two different structures for micromachined gas sensors: the *closed-membrane-type* and the *suspended-membrane-type* gas sensors. The latters are called also *spider-type* gas sensors. This resistively heated dielectric membrane (a-SiON or LPCVD Si_3N_4) provides the thermal insulation between the active area heated up to high temperature and the silicon frame that remains at room temperature.

Numerous are the attractive features and advantages offered by using such membranes in gas sensing devices:

- they can be handled easily in electronic industry and enables integration with electronics; in particular, they need voltage source both for resistance measurement and for the necessary heater compatible with standard digital electronics (e.g. CMOS);
- they allow a low power consumption not exceeding 100 mW for operation. This small amount of heating power is caused by the reduction in the heated surface area as well as by the excellent thermal isolation provided by the thin dielectric membranes.
- they allow the production of tiny sensor device of small size and lower weight (greater portability;
- they allow the reduction of manufacturing cost;
- they can be easily grouped into battery-operated arrays (i.e. sensor array integrated on sensing-chip).

Fig. 12 shows schematically a top view (a) and a cross-section of a single micromachined structure drop-coated by the sensing layer (b). In particular this model of micro-hot plates are fabricated at the Institute of Microtechnology (IMT) of Neuchâtel in Switzerland [57].

4. Conclusions

The essentially positive outlook for the gas sensors industry stems from the undeniable fact that gas sensors are indispensable to numerous, key industries, since they provide vital information about the gaseous composition of the ambient. Moreover, driven by the continued proliferation of more advanced electronic control systems to increase efficiencies, users of gas sensors require ongoing advances in sensor accuracy, reliability, response time, robustness, miniaturization, and/or communications capability. Such requirements drive the trends of R&D in gas sensors industry, which in turn fuels opportunities for technology advancements that can open up new applications gas sensors. While many different approaches to gas detection are available, the R&D of solid state gas sensors have enormously advanced in recent years. Of course, due to the variety of solid state gas sensors, it’s impossible to deal with all the different types of solid state gas sensors. Hence, in this review we focused on the principles of some of the main solid state gas sensors, discussing the state of art and the future trends of the scientific research. In particular, metal oxide gas sensors discussed in more detailed way respect to the other types of solid state gas sensors due to their low cost and relative simplicity, advantages that should work in their favour as new types of applications and technologies emerge.

In the future there is no doubt that nanocrystalline metal oxides will constitute the key for the development of semiconducting gas sensors with improved gas-sensing properties. Not only in chemoresistive gas sensors, but in general in solid state gas sensors, nanostructured material will play a fundamental and determinant role in the gas sensors of new generation. Nanoscience and NanoTechnology are, in fact, devoting great efforts to the development of novel materials for gas sensor applications. We mention, just as example, the interest in inorganic-organic hybrid nanocomposite containing conducting polymers as organic part and metal oxides as inorganic part [63] and in ribbon-like nanobelts made of semiconducting metal oxides. The latters are chemical pure, structurally uniform and largely defect-free, with clean surfaces not requiring protection against oxidation; each nanobelt is made up of a single crystal with specific surface planes and shape. This new class of nanostructures offer a great potential for applications in ultra-small sensors because the conductivity of these materials changes dramatically when a gas or liquid molecules attach their surfaces [64]. Driving elements in gas sensor field are also the miniaturization of the devices, the use of silicon microfabrication techniques in sensor production, the development of specific electronic noses trained for specific applications and the optimization of smarter pattern recognition techniques.

In addition, with the development of standard wireless communication protocols optimised for sensors, wireless sensor network are expected to gain a wide acceptance in such applications as homeland security, food monitoring process monitoring and medical instrumentation.

Current status and future prospects in research and development of metal oxide-based gas sensors are a special topic of many conferences and workshops in gas-sensing field:

·EUROSENSORS – European Conference on Solid-State Transducers
·SGS - International Seminar on Semiconductor Gas Sensors
·IMCS – International Meeting on Chemical Sensors
·ISOEN - International Symposium "Olfaction & Electronic Nose"
·IEEE SENSORS- International conference on sensors
·TRANSDUCERS - International Conference on Solid-State Sensors and Actuators
·EACCS - East Asian Conference on Chemical Sensors

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