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Metal Oxide Nanowire Gas Sensors: Application of Conductometric and Surface Ionization Architectures

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The present work reports on conductometric gas sensors based on metal oxide nanostructures developed in our laboratory in Brescia (Italy) showing their potentialities in term of sensitivity, selectivity and stability toward different molecules, including odorous compounds such as ammonia and hydrogen sulfide. The capability of these devices to discriminate different odors is further reported integrating these devices into an electronic nose system, and applying it to food quality control, in particular, to identify coffee samples contaminated with mold. Finally, preliminary results obtained with surface ionization gas sensors are reported, discussing their working principle and differences with respect to conductometric gas sensors, suited to further address selectivity.

1. Introduction

Metal oxide gas sensors have been widely studied in literature and exploited at industrial level thanks to their high sensitivity to a broad range of chemical compounds, the cheap methods of fabrication and the compatibility with silicon technology. Furthermore, their reduced weight, size and power consumption, which allows the development of portable instrumentation and/or the use in sensor networks.

The sensing mechanism relies on the modulation of the space charge layer (SCL) at the oxide surface due to redox interactions with gases. Therefore, the application of nanomaterials, with crystallite size comparable with the SCL, strongly enhances the gas sensitivity.

Metal oxide nanowires are single crystalline materials with nanosized cross-section and high aspect ratio. Moreover, they can be integrated in functional device both as single nanowire and as bundles of nanowires, featuring different functional properties suited for a variety of applications. For example Strelcov et al. (2008) demonstrated that single nanowire devices allows the exploitation of the self-heating effect for extreme power consumption reduction, while Zhang et al. (2004) showed that bundles feature an open and porous structure, suited for high sensitivity.

In this work, we will report the results obtained in our laboratory using metal oxide nanowire gas sensors, working with a wide range of chemicals, including odorous molecules such as ammonia and

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hydrogen sulphide. In particular, we will address the potentialities of nanowires according to the main functional parameters of gas sensors, namely sensitivity, selectivity and stability. We further show the results obtained integrating nanowires into an electronic nose (EN) system to exploit their potentialities to identify the odour (molecular fingerprint) of a given atmosphere, with emphasis on food quality control. Finally we show our latest results on the development of gas sensors working on new, largely unexplored, sensing mechanisms such as surface ionization, which can be further exploited to enhance the selectivity of sensor arrays.

2. Experimental

The sensing layers have been fabricated over 2 mm x 2 mm x 0.75 mm alumina substrates. Thin films have been deposited by rheotaxial growth and thermal oxidation (RGTO) technique developed by Sberveglieri (1995), which allows obtaining a monolayer of oxidized droplets featuring a high surface to volume ratio.
Nanowires have been synthesized evaporating MOX powders in a tubular furnace, vapours condense via a Vapour-Liquid-Solid (VLS) process over Pt-catalyzed substrates located on colder regions, where proper thermodynamic conditions promote the growth of nanowires. Selective growth of nanowires on desired areas has been achieved by means of lift-off technique developed by Vomiero et al. (2010). Briefly the method is based on the application of a sacrificial SiO_x layer for selective patterning of the substrate before nanowires growth. After condensation of nanowires, SiO_x is removed in a diluted HF solution, leaving clean areas over the substrate, where Pt electrodes and heater can be deposited with good adhesion.
Pt structures, namely electrodes and a Pt meander (that acts both as heater and temperature probe) are finally sputtered on substrates provided by the oxide layer (both thin film and nanowire). The SEM images of nanowire and thin film layers are shown in Figure 1 together with the final device.
Measurements have been carried out by flow through technique in a temperature-stabilized sealed chamber (volume of 1 L) at 20 °C under controlled humidity, working with a constant flux of 300 mL/min. The atmosphere composition was controlled by means of mass-flow controllers, mixing flows coming from certified bottles containing a given amount of the analyte gas diluted in synthetic air. The background atmosphere was generated thorough a dry air certified bottle and a humidity system, working with constant relative humidity (RH = 30 % at 20 °C).
Gas sensors have been further integrated in an electronic nose system, in particular in the commercial EOS835 developed by SACMI IMOLA scarl, Imola, Italy. A description of EOS835 system is provided by Pardo and Sberveglieri (2004). Data have been further analyzed through the Exploratory Data Analysis (EDA), a written-in-house software package based on MATLAB described by Vezzoli et al. (2008).

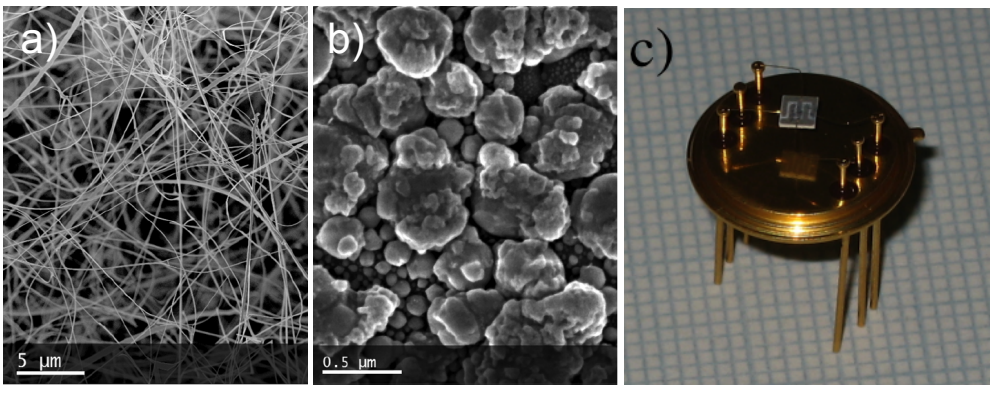

Figure 1:Secondary electron SEM image of tin oxide nanowires (a) and RGTO thin film (b). The final device is shown in (c).

3. Results and discussion

3.1 Conductometric gas sensors

The performance of gas sensors were first screened with basic chemicals, including, CO, ethanol, acetone, NO_2, NH_3, H_2S, in order to acquire a database concerning, the sensor optimal working temperature for each compound and, for a given temperature, the response spectra shown by each sensor. AS an example, the temperature effect on the response amplitude of gas sensors based on SnO2 nanowires and RGTO thin films toward NH_3 and H_2S are shown in Figure 2, (a) and (b) respectively. It is evident, for example, that at low temperature (T < 300 °C) the RGTO response to H_2S is higher than the response exhibited by the nanowire counterpart, while increasing the sensor temperature above 350-400 °C, strongly suppress the RGTO response, while keeping almost unaltered the nanowire response. As a consequence, at the sensor temperature of 350 °C, the RGTO film shows a response to H_2S about 250 times higher than the response to NH_3, while increasing the sensor temperature to 450 °C, the H_2S response is about 5 times the response to NH_3. At the same temperature (450 °C), the nanowire sensor shows a response to H_2S about 20 times the response to NH_3. These differences are useful features that can be exploited in an electronic nose instrument to gain selectivity.

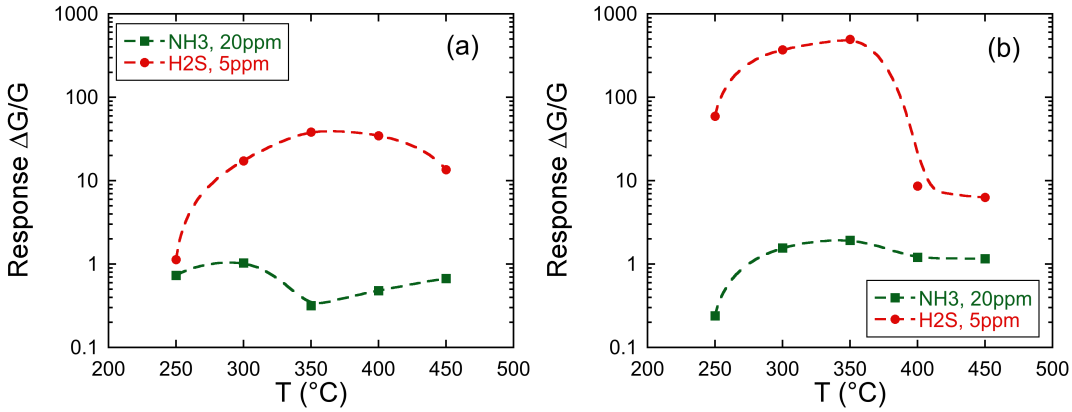

Figure 2: Effect of the working temperature on the response amplitude of gas sensors based on SnO_2 nanowires a) and RGTO thin films b) toward NH_3 and H_2S.

3.2 Electronic Nose

The different response spectra of the nanowire and RGTO thin film at the sensor temperature of 450 °C toward some basic chemicals, namely CO, ethanol, NH_3 and H_2S are shown in Figure 3a a. A temperature as high as 450 °C is chosen since it fasten the response and recovery kinetics of metal oxide gas sensors. These differences in the response spectra have been exploited, for example, by Ponzoni et al. (2008) to discriminate chemical warfare agents simulants from chemicals of common use that may induce false alarms. On the other hand, the non-specificity of these devices and their different specific sensitivities, can be further exploited in odour application such as food quality control, where the large amount of molecules participating to define a given smell make it extremely hard a full identification of its chemical composition.

Odor is one of the most significant parameters among the sensory properties of foods. The representative flavor of volatile compounds, so-called fingerprint, may provide knowledge about safety and particular characteristic of food, acting sometimes as an indicator of process mistake as well.

Certainly, some volatile compounds can create from biochemical process of the foodstuff, as a consequence of technological treatments or product storage.

Off-flavors may include substances originating from the metabolism of spoilage microorganisms, bacteria and fungi; which may naturally or accidentally contaminate the products prior of during its production.
Electronic noses (ENs) have been applied in various food contexts, chemical and biochemical technologies have recently emerged as valuable candidates for food quality control, due to their simplicity of use, low cost, rapidity and good correlation with sensory panels.
Such as process monitoring, freshness evaluation, shelf-life investigation, authenticity determination, and product traceability. ENs has been given until now to microbiology applications of chemical sensor devices, for instance, the screening of foodborne pathogens contamination (Alicyclobacillus spp. Spoilage of fruit juice; early detection of microbial contamination in processed tomatoes; screening of fungal and fumonisin contamination of maize grains; fungal contamination on green coffee beans; geographical discrimination of coffee before and after roasting).
For example, the commercial EOS835 was used to analyze the coffee contamination from mold, observing that it was able to identify the contaminated status after five/six days of growth, Figure 3b .

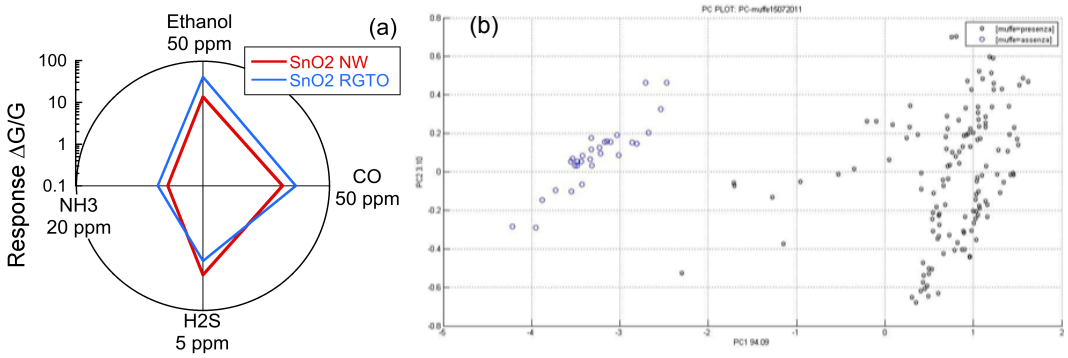

Figure 3: a) Response spectra of gas sensors based on SnO_2 nanowires and RGTO thin films heated at the working temperature of 450 °C. b) PCA score PLOT obtained with electronic nose about coffee contamination of mold: black star samples with contamination of mold, blue circle samples without contamination.

3.3 Surface ionization gas sensors

Different materials are used in an electronic nose to increase the selectivity of the sensing system. Beside this, novel approaches and transduction mechanism leading to diverse response spectra are welcomed to enhance the performances of ENs.
Recently, Hackner et al. (2009) proposed gas sensors based on surface ionization mechanism. Briefly, this kind of device exploits the capability of metals and metal oxides heated at high temperature (600 - 900 °C) to ionize gaseous molecules impinging over the material surface. Applying a high electric field (of the order of 10^4 V/cm) between the material (metal or metal oxides) and a suspended counter electrode, ionized molecules fly toward the counter-electrode where are then neutralized generating the ionization current. This sensing mechanism is highly dependent on the ionization energy of the molecule and their proton affinity. The marked dependence from these parameters induces a very selective response in surface ionization device to those molecules featuring the presence of ammine groups, which show a high proton affinity and low ionization energy. On the contrary, molecules such as oxygen, carbon mono- and di-oxide as well as humidity, which are strongly interfering gases for conductometric devices, induce almost null surface ionization responses.
In the same work, Hackner et al. (2009) at al. demonstrated that single crystalline nanowires, thanks to their high crystalline quality, nanosized cross-section and high aspect ratio, are materials particularly efficient to develop these devices.

Hernandez-Ramirez et al. (2011) studied horizontal configurations exploiting a single metal oxide nanowire as ionizing material and the counter-electrode laying on the same substrate. This layout allows a simpler preparation thanks to its compatibility with in-plane deposition techniques and to obtain surface ionization currents at lower temperatures (300 – 500 °C) and lower electric fields (of the order of 100 V/cm) with respect to the vertical layout. Nevertheless, the exploitation of such structures requires expensive and time consuming fabrication techniques, such as Focused Ion Beam (FIB) for the proper manipulation of the single nanowire, which makes the device appealing but difficult to prepare and exploit in practice. To overcome this drawback, we have recently started to work on surface ionization devices based on planar layout, exploiting bundles of nanowires instead of a single nanowire. The device layout is shown in Figure 4a, where one of the two L-shaped electrodes is used to bias the metal oxide (MOX) layer, while the Pt meander is grounded and used as counterelectrode to collect the ionization current. The same technology used to prepare conductometric gas sensors is used also to prepare surface ionization devices, just adapting the sensor layout to the different sensing mechanism. This strategy would lead to surface ionization devices with cost comparable with those of conductometric gas sensors, The dynamic response of the device to ethanol is shown in Figure 4b. The integration of these gas sensors together with chemiresistors (based both on nanowires and thin films) can further improve the selectivity capability of the sensor array due to the integration of different transduction principles.

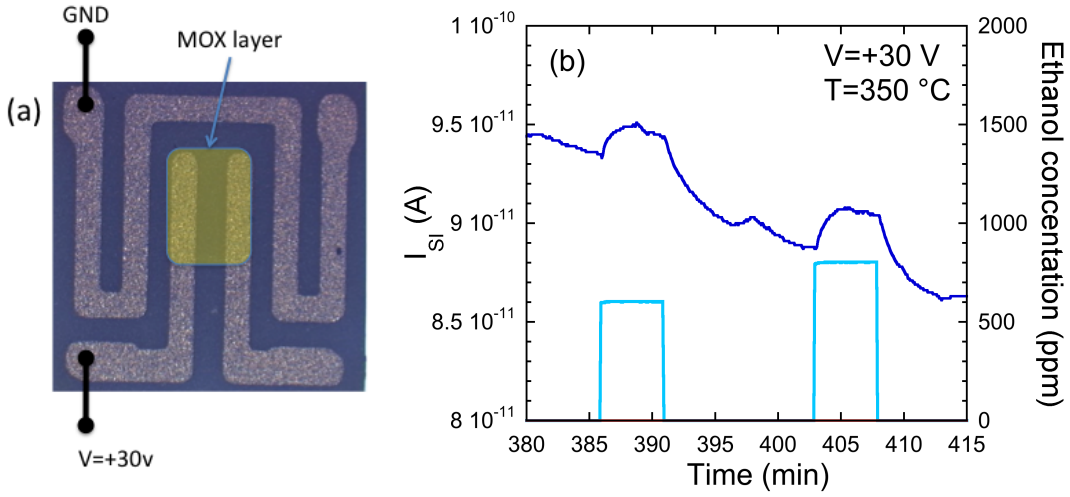

Figure 4: a) Layout of a surface ionization device based on nanowire bundle and horizontal configuration; b) dynamic response of the surface ionization device based on a layer of CuO nanowires to ethanol.

4. Conclusions

In this work we have presented the technology of metal oxide nanowire based gas sensors, describing the preparation method and comparing these devices with thin film gas sensor typically used in the field. We focused in particular on basic chemicals including odorous molecules such as NH_3 and H_2S, showing that nanowires and thin films exhibit different response spectra that can be usefully exploited in electronic nose systems to address selectivity. We further report the identification of mold contaminated coffee through the EOS835 electronic nose as a remarkable application. We further introduced our latest results on the development of novel configurations and sensing mechanism

aimed to increase the selectivity of sensor arrays, namely surface ionization gas sensors exploiting the horizontal layout.
As far as preparation costs are concerned, the use of cheap evaporation and condensation methods to prepare nanowires and the exploitation of nanowire bundles (without the use of expensive nanomanipulation and nanolithography techniques to manipulate/contact single nanowires), keeps this technology in line with the costs of preparation of commercial conductomteric sensors based on thin or thick film technology. The same is for surface ionization devices, which exploit the same nanowire technology.

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