A highly sensitive oxygen sensor operating at room temperature based on platinum-doped In_2O_3 nanocrystals

Giovanni Neri,[a] Anna Bonavita,[a] Giuseppe Micali,*[a] Giuseppe Rizzo,[a] Signorino Galvagno,[a] Markus Niederberger[b] and Nicola Pinna[c]

Received (in Cambridge, UK) 29th July 2005, Accepted 11th October 2005
First published as an Advance Article on the web 8th November 2005
DOI: 10.1039/b510832b

Semiconducting In_2O_3 nanocrystals, synthesised *via* a nonaqueous sol–gel method and doped with 1 wt% of platinum, have shown to possess a unique high sensitivity to oxygen at room temperature (RT). Consequently, a Pt/In_2O_3-based oxygen sensor for room temperature operation has been developed showing higher performance compared to the state-of-the-art devices.

Semiconducting metal oxides have received great attention in the past few years as sensing materials for resistive gas sensors. In an n-type semiconductor, the adsorption of atmospheric oxygen produces a depletion of electrons, which are the majority charge carriers, and hence the conductivity of the semiconductor decreases as the oxygen concentration increases. Therefore, in principle, they are able to detect oxygen in a wide range of oxygen concentrations. Resistive oxygen sensors find wide use in industrial, environmental, medical, and domestic fields.[1]

However, resistive oxygen sensors based on both n- and p-type semiconducting metal oxides require high operating temperature and many efforts are currently in progress in developing oxygen sensors operating at lower temperature. Recently a nanostructured $SrTiO_3$-based sensor has been reported to be very effective for near ambient temperature oxygen sensing.[2] On the other hand, this perovskite material is highly insulating and this complicates the reading of electrical signal with conventional instruments. It should be mentioned that smaller particle sizes and lower operating temperatures strongly decrease the conductivity of semiconducting materials. Therefore many sensing materials cannot be used for practical applications at room temperature.

In this communication we present an oxygen gas sensor based on Pt/In_2O_3 nanoparticles and operating at room temperature. The sensor shows a significant enhancement of performance with respect to the state-of-the-art n-type semiconducting sensors.[3,4] In_2O_3 is a wide band-gap material, Eg ~3.70 eV, whose microstructural, electrical and sensing characteristics have been well studied.[5] Its electrical properties vary largely depending on stoichiometry. When prepared in oxygen-deficient form, it reaches n-type doping level due to oxygen vacancies. Further, in order to enhance the sensitivity and to get a lower operating temperature, In_2O_3 can be opportunely prepared in a nanostructured form and/or doped with suitable metallic promoters.[6]

We synthesised In_2O_3 nanopowders *via* a nonaqueous sol–gel method involving the solvothermal reaction of indium(III) isopropoxide with benzyl alcohol. The experimental details are reported elsewhere.[7] According to XRD and HRTEM investigations, the nanopowders are composed of highly crystalline nanoparticles with an average diameter of about 20 nm.

These In_2O_3 nanopowders have been further activated by addition of 1 wt% of platinum. The dopant has been dispersed on the surface of the semiconducting metal oxide by wetness impregnation, contacting the In_2O_3 nanopowders with the proper amount of an aqueous solution of H_2PtCl_6. The nanopowders have been finally dried and fired at controlled temperature (between 150 and 450 °C) to promote the decomposition of the platinum precursor into metallic platinum.

An oxygen gas sensor has then been realised by dispersing first the Pt/In_2O_3 semiconducting particles in a suitable solvent to obtain an ink with appropriate viscosity, which has been successively printed as a film of around 1 μm thickness on a ceramic substrate (dimensions 6 × 3 mm^2) supplied with interdigited (spacing 200 μm) comb-like Pt electrodes and heater. For transient measurement, the oxygen sensor was placed in a flow stainless-steel test chamber having a volume of about 5 ml, and tests carried out maintaining the chamber for 20 min. in a nitrogen flow (200 ml min^{-1}) followed by different O_2 concentration pulses supplied for 30 min. by varying the partial pressure of the air in the range 0.1–20 kPa. Throughout all experiments a dry environment (RH = 0) was maintained within the chamber.

A preliminary electrical characterization has shown that Pt/In_2O_3 nanoparticles deposited on a ceramic substrate present a low electrical resistance (around 20–30 kΩ, in dry air at RT) which can be easily monitored by conventional instruments. It has also shown that the sensor response, expressed here as $\Delta R/R_b$ (%) where $\Delta R = R_g - R_b$ with R_g the resistance in N_2–O_2 mixture and R_b the baseline resistance in nitrogen, is strongly dependent on the annealing temperature of the printed film, showing a volcano curve with a maximum around 350 °C (see Fig. 1).

This behaviour suggests that metallic platinum, formed by decomposition of the H_2PtCl_6 precursor, is the active species for oxygen chemisorption at RT. Indeed, the undoped In_2O_3 is insensitive towards oxygen at RT. Moreover, the decomposition of H_2PtCl_6 precursor starts at 160 °C and can be considered complete above 300 °C. The different degree of decomposition was confirmed by the darker aspect of the sensing films annealed at high temperature. However, at the temperature of 450 °C, sintering

[a]*Dept. of Industrial Chemistry and Materials Engineering, University of Messina, Clda di Dio, Vill. S.Agata, 98166 Messina, Italy. E-mail: neri@ingegneria.unime.it; Fax: +390903977464; Tel: +390903977241*
[b]*Max-Planck-Institute of Colloids and Interfaces, 14424 Potsdam, Germany*
[c]*Martin-Luther-Universität Halle-Wittenberg, Institut für Anorganische Chemie, Kurt-Mothes-Strasse 2, 06120 Halle (Saale), Germany*

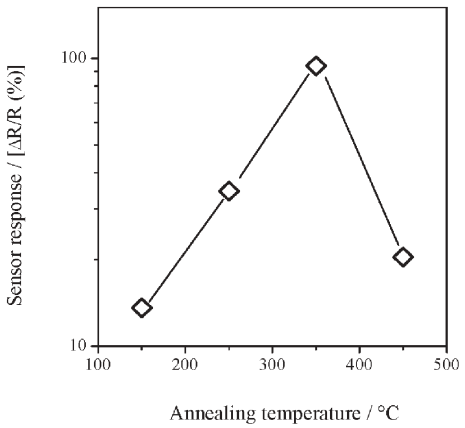

Fig. 1 Sensor response *vs* annealing temperature of the printed film.

phenomena can cause the growth of metallic platinum particles and/or the coalescence of the In_2O_3 nanoparticles, decreasing the surface area and the number of chemisorption centers and consequently also the sensitivity.

Fig. 2 shows the transient response to different O_2 concentrations at RT of the sensor annealed at 350 °C. Allowing the sensor response and recovery to reach the equilibrium (see insert in Fig. 2) a fully reversible behaviour is observed. The response time, τ_{res}, and recovery time, τ_{rec}, defined as the time necessary to reach 90% of the final value of resistance, are 18 and 35 min., respectively, quite fast considering the low operating temperature.

The response to 20% of oxygen in nitrogen was about 95, which is very high for a n-type sensor at this low temperature. For comparison, Table 1 shows the response of various oxygen sensors at room temperature so far reported. The sensitivity of our device is about one order of magnitude higher than previous sensors and comparable with the p-type $SrTiO_3$ sensor.

The sensor response follows a linear trend in the wide range of oxygen partial pressure investigated as shown in Fig. 3. Oxygen detection by this sensor is due to electrical conductivity variations induced by adsorption of gas molecule on the semiconductor surface. When oxygen adsorbs on a semiconductor, negatively charged oxygen species are formed. At room temperature, O_2^- species are predominantly formed on the semiconductor surface as

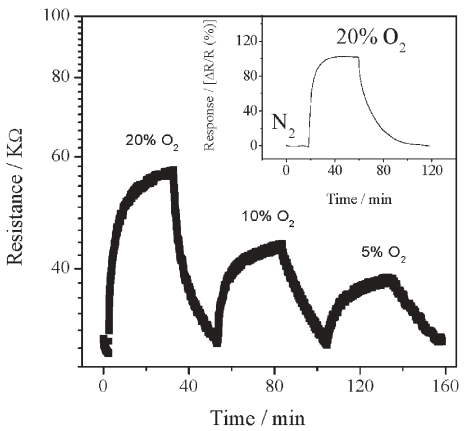

Fig. 2 Transient response at RT of the sensor annealed at 350 °C.

Table 1 Features of RT O_2 sensors based on n- and p-type semiconductors

Semiconductor	Type	Response to 20% O_2 [$\Delta R/R$ (%)]	Reference
Pt/In_2O_3	n	95	This work
SnO_2	n	13	3
ZnO	n	9.5	4
$CuAlS_2$	p	15	9
TiS_2	p	5	10
$CuFeTe_2$	p	1.2	10
$SrTiO_3$	p	120	2

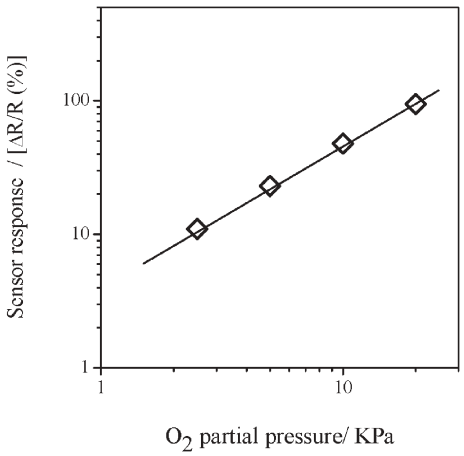

Fig. 3 Log–log calibration curve at RT of the Pt/In_2O_3 sensor.

a result of O_2 adsorption. The oxygen ionosorption causes electron transfer from the surface of the grain to the adsorbed species, thus leading to the formation of an electron-depleted surface layer. As a result, the electrical conductivity decreases.

The high sensitivity observed can be explained by the large surface area of the sensing film, due to the small size of indium oxide particles. In conventional sensing materials the average grain size considerably exceeds the depth of the sub-surface space charge layers, which means that electrical conduction is controlled by the transport of carriers across potential barriers at the grain boundary contacts. On the other hand, on nano-crystalline materials with grain sizes comparable to the depth of the sub-surface depletion layers oxygen adsorption causes the individual grains to become fully depleted from the conduction electrons. The addition of a small amount of metallic Pt has further and effectively enhanced O_2 sensing characteristics. The role of platinum is likely to act as a catalytic promoter, enhancing the oxygen adsorption on the surface of In_2O_3 and favouring oxygen spillover,[8] even if other factors such as the increase of Schottky barrier or the reduction of the interfacial resistivity between the metal oxide layer and the Pt electrodes, cannot be excluded.

The results reported here clearly prove that films based on Pt–In_2O_3 nanopowders can be used in oxygen sensor devices offering advantages such as operation at RT, low electrical resistance, high sensitivity, and good linearity in a wide range of O_2 concentrations. However, some drawbacks have yet to be overcome. For example, cross-sensitivity to water vapour can affect the electrical behaviour of the sensing layer, representing the main limitation to the practical application of devices operating at low temperature. Preliminary experiments have shown that the sensor responds to

oxygen over a range of humidity levels, but further experiments are necessary to verify the repeatability of the response and the long-term stability under these conditions.

In conclusion, the features reported above underline the possibility of employing these films as sensitive layers in gas sensors for low power and low cost applications such as a portable oxygen detector.

Notes and references

1 J. W. Fergus, *J. Mater. Sci.*, 2003, **38**, 4259; Y. Xu, X. Zhou and O. Toft Sorensen, *Sens. Actuators, B*, 2000, **65**, 2.
2 Y. Hu, O. K. Tan, J. S. Pan and X. Yao, *J. Phys. Chem. B*, 2004, **108**, 11214.
3 J. Atkinson, A. Cranny and C. S. de Cloke, *Sens. Actuators, B*, 1998, **47**, 171.
4 F. Chaabouni, M. Abaab and B. Rezig, *Sens. Actuators, B*, 2004, **100**, 200.
5 M. Bender, N. Katsarakis, E. Gagaoudakis, E. Hourdakis, E. Douloufakis, V. Cimalla and G. Kiriakidis, *J. Appl. Phys.*, 2001, **90**, 5382; A. Gurlo, M. Ivanovskaya, N. Barsan, M. Schweizer-Berberich, U. Weimar, W. Gopel and A. Dieguez, *Sens. Actuators, B*, 1997, **44**, 327; E. Comini, M. Ferroni, V. Guidi, G. Faglia, G. Martinelli and G. Sberveglieri, *Sens. Actuators, B*, 2002, **84**, 26; K. Zakrzewska, *Thin Solid Film*, 2001, **391**, 229; G. Korotcenkov, A. Cerneavschi, V. Brinzari, A. Cornet, J. Morante, A. Cabot and J. Arbiol, *Sens. Actuators, B*, 2002, **84**, 37.
6 M.-I. Baraton, in *Nanostructured Materials: Science and Technology*, Nato Advanced Study Institute, Kluwer Academic Publisher, Dordrecht, 1998, p. 303.
7 N. Pinna, G. Neri, M. Antonietti and M. Niederberger, *Angew. Chem., Int. Ed.*, 2004, **43**, 4345.
8 N. Yamazoe, Y. Kurokawa and T. Seiyama, *Sens. Actuators*, 1973, **4**, 283.
9 M. Abaab, A. S. Bouazzi and B. Rezig, *Microelectron. Eng.*, 2000, **51**, 343.
10 K. Kishiro, S. Takemoto, K. Kuriyaki and K. Hirakawa, *Jpn. J. Appl. Phys., Part 1*, 1994, **33**, 1069; K. Kishiro, K. Kuriyaki and K. Hirakawa, *Jpn. J. Appl. Phys., Part 2*, 1993, **32**, L674.