chemistry proceedings

MDPI

Proceedings

Semiconductor Oxide Gas Sensors: Correlation between Conduction Mechanisms and their Sensing Performances [†]

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[†] Presented at CSAC2021: 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry, online, 01-15/07/2021.

Abstract: In this work, a variety of semiconducting oxides were prepared and principally characterized by means of spectroscopic techniques (absorbance FT-IR, diffuse reflectance UV-Vis-NIR) to shed light on the electronic properties and defects involved at the roots of the gas sensing capability. The thick films were obtained by screen printing technology on which electrical characterization and gas sensing measurements were performed. From the cross analysis of the results, a description of the specific sensing mechanism is proposed for each material.

Keywords: thick film gas sensors; nanostructured semiconductor oxides; UV-Vis-NIR and FT-IR spectroscopies; electrical characterization; sensing mechanisms

Published: 1 July 2021

1. Introduction

The adsorption of a gas on the surface of a semiconducting oxide can induce a significant change in the electrical resistance of the material. This effect is at the basis of the development of chemiresistors for gas detection [1]. Due to their high sensitivity, tunable selectivity, easy production, small dimensions and low cost, they are successfully used in a broad range of applications (pollutant monitoring, food quality control, industrial system control, medical diagnosis) to detect a large number of gaseous compounds. Despite this, an increasing demand of gas sensors with high performances has been documented [2]. Many actions can be made to improve the sensing performances, such as the synthesis of nanostructures with high specific surface area, the loading with noble metals, but the first issue is to understand the sensing mechanism of the materials and their sensing properties [3,4].

The IR and the UV-Vis spectroscopies are excellent experimental tools for investigating the electronic properties and surface chemistry of a large class of metal oxides used in the fabrication of solid state devices for gas sensing [5].

This work is aimed to determine the electronic properties for a variety of semiconducting oxides (single or combined such as SnO_2 MoO_3, WO_3, ZnO, TiO_2, Ti-Sn, W-Sn, Mn-W mixed oxides, etc.) and to correlate them with the sensing mechanism and the sensor performances.

2. Materials and Methods

A selection of semiconducting oxides (single or combined such as SnO_2 MoO_3, WO_3, ZnO, TiO_2, Ti-Sn, W-Sn, Mn-W mixed oxides, etc.) were prepared by using wet chemistry methods [6,7]. The synthesis procedures were optimized to obtain nanopowders with a single phase and presenting a homogenous distribution in grain size (analyzed by X-Ray Diffraction and Scanning Electron Microscopy, respectively).

The powders were characterized by means of spectroscopic techniques with the aim to evaluate the electronic properties and defects involved in the sensing processes. Absorbance IR spectra were run on a Perkin-Elmer System 2000 FT-IR spectrophotometer equipped with a Hg-Cd-Te cryodetector, working in the range of wavenumbers 7800-580 cm^{-1}. Diffuse reflectance spectra in the UV-Vis-NIR region were run on a Varian Cary 5 spectrophotometer, working in the range of wavenumbers 53000-4000 cm^{-1}. The spectroscopic responses were studied at different temperatures both for the interaction with pure gases and for mixture gas/O_2 at different concentrations depending on the oxide.

For obtaining thick films for electrical characterization and gas sensing measurements, the functional materials were added to an organic vehicle together with a small percentage of glass frit, then they were deposited on alumina substrates with interdigitated Au contacts and a heating element and fired at 650 °C. The flow-through technique was used maintaining a flow rate of 0.5 L/min, using synthetic air as carrier gas in dry conditions for the: (i) conductance measurements vs. temperature (room temperature–650 °C) (ii) surface potential barrier height measurements to determine the intergranular energy barrier (Schottky barrier) versus temperature [8], and (iii) dynamical responses obtained in presence of mixture of different gases and operating temperature from 350 to 550 °C. The sensor response was calculated as ratio between the conductance in presence of the gas test and the conductance in air.

Finally, a sensing mechanism was proposed for each material by combining the results of spectroscopic and electrical characterization.

3. Results and Discussion

In this section, the main findings of some single (SnO_2, WO_3 and TiO_2) and mixed (Ti-Sn and W-Sn) oxides considering carbon monoxide as gas test are summarized. More detailed characterizations are reported in references [8,9].

The spectroscopic measurements on single oxides show that on one hand SnO_2 is characterized by the presence of mono-ionized oxygen vacancies (evidence in the medium IR region), on the other hand WO_3 is characterized by the presence of polarons, i.e. electrons trapped in deep levels in the band gap (evidenced in the Vis-NIR region). TiO_2 shows both mono-ionized oxygen vacancies and polarons. The amount of these defects increases upon CO interaction at increasing temperature.

As for mixed oxide $Sn_{1-x}Ti_xO_2$, the spectroscopic measurements in CO reveal two different behavior: (i) sample with $x = 0.1$ shows absorption related to the photo-ionization of mono-ionized oxygen vacancies, as SnO_2 shows; (ii) samples with $0.3 \leq x \leq 0.9$ show the increase of an absorption near to the VB-CB edge, as TiO_2 shows. Samples with $x = 0.2$ is a borderline sample, showing behavior in between those of SnO_2 and TiO_2. This behavior was confirmed by electrical measurements.

Combining the results of spectroscopic and electrical characterization, two detection mechanisms emerge depending of the kind of chemical reaction involved. The first occurs between ionosorbed oxygen atoms and CO, with a consequent electron transfer from surface to bulk, resulting in a conductance increase and a consequent barrier height decrease. The second occurs between surface lattice oxygen atoms and CO: the bond electrons of the surface lattice oxygen atoms do not contribute to the formation of the spatial charge region as well as of the Schottky barrier. For concluding, the prevalent gas detection mechanism in the materials with $x < 0.3$, is the usual through Schottky barrier modification, whilst for $x \geq 0.3$ is based on bond electrons which, after the reaction, enter the conduction band without affecting the barrier height, but only bulk conductance.

Concerning the CO responses, the Ti-Sn solid solutions offer higher responses than those of pristine oxides and the solution with $x = 0.25$ resulted the best material to detect carbon monoxide.

The spectroscopic characterization of W-Sn mixed oxides put in evidence the presence of polaron levels, with a position not affected by the Sn content, for mixed oxides with Sn molar content up to 33% (as for WO_3) and mono-ionized oxygen vacancies for the mixed oxide with Sn molar content of 89% (as for SnO_2).

The different positions of the defect levels in the band gap cause the formation of surface potential barriers significantly lower for WO_3, and the mixed oxides with Sn molar content up to 33% (WO_3-like samples) than for SnO_2 and the mixed oxide with Sn molar content of 89% (SnO_2-like sample). This result allows defining the correlation between the electronic levels associated to the defects and the surface potential barriers in air and in reducing atmospheres. In particular, the electrical measurements indicate that the changes in the already low barriers of WO_3 and WO_3-like samples are almost negligible in the presence of a reducing gas like CO; otherwise, CO significantly decreases the barriers of SnO_2 and SnO_2-like sample. These results are completely in agreement with the low CO sensitivity of WO_3 and WO_3-like samples, and with the better CO sensitivity of SnO_2 and SnO_2-like sample.

4. Conclusions

In the electrical characterization, the main parameter typically measured is the conductance. All the operating characteristics of the sensors are derived from this measurement and it could be considered the strength and the weakness of semiconductor sensors. On one hand it is simple and easily measured, but it is a second-order parameter that, although very sensitive to some reactions at the solid surface, is not a direct indicator of the exact processes taking place. For this reason, we investigated the behavior of different oxide materials by means of IR and UV-Vis spectroscopies to enlighten surface reactions and electronic properties and coupling the results to those of electrical characterization. We demonstrate the possibility to describe the processes involved in the detection mechanism with a method which can be applied to every functional material characterized towards every gas of interest.

Author Contributions: Conceptualization, characterizations, experiments conduction and data analysis A.F., S.M., and M.C.C.; writing—original draft preparation A.F.. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: "The authors declare no conflict of interest."

References

1. Neri, G. First fifty years of chemoresistive gas sensors. *Chemosensors* **2015**, *3*, 1–20, doi:10.3390/chemosensors3010001.
2. Fioravanti, A.; Carotta, M.C. Year 2020: A snapshot of the last progress in flexible printed gas sensors. *Appl. Sci.* **2020**, *10*, doi:10.3390/app10051741.
3. Galstyan, V. "Quantum dots: Perspectives in next-generation chemical gas sensors" – A Review. *Anal. Chim. Acta* **2021**, doi:10.1016/j.aca.2020.12.067.
4. Dey, A. Semiconductor metal oxide gas sensors: A review. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2018**, *229*, 206–217, doi:10.1016/j.mseb.2017.12.036.
5. Barhoum, A. *Optical Spectroscopy for Characterization of Metal Oxide Nanofibers*; 2019; ISBN 9783319536545.
6. Nikam, A. V.; Prasad, B.L.V.; Kulkarni, A.A. Wet chemical synthesis of metal oxide nanoparticles: A review. *CrystEngComm* **2018**, *20*, 5091–5107, doi:10.1039/C8CE00487K.
7. Fioravanti, A.; Marani, P.; Massarotti, G.P.; Lettieri, S.; Morandi, S.; Carotta, M.C. (Ti,Sn) solid solution-based gas sensors for new monitoring of hydraulic oil degradation. *Materials (Basel).* **2021**, *14*, 1–13, doi:10.3390/ma14030605.
8. Carotta, M.C.; Fioravanti, A.; Gherardi, S.; Malagù, C.; Sacerdoti, M.; Ghiotti, G.; Morandi, S. (Ti,Sn) solid solutions as functional materials for gas sensing. *Sensors Actuators, B Chem.* **2014**, *194*, doi:10.1016/j.snb.2013.12.021.
9. Morandi, S.; Amodio, A.; Fioravanti, A.; Giacomino, A.; Mazzocchi, M.; Sacerdoti, M.; Carotta, M.C.; Skouloudis, A.N. Operational functionalities of air-quality W–Sn metal-oxide sensors correlating semiconductor defect levels and surface potential barriers. *Sci. Total Environ.* **2020**, *706*, 135731, doi:10.1016/j.scitotenv.2019.135731.