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Investigation of the film thickness influence on the sensor response of In₂O₃-based sensors for O₃ detection at low temperature and operando DRIFT study / Ziegler, Daniele; Palmero, Paola; Tulliani, Jean Marc Christian; Staerz, Anna; Oprea, Alexandru; Weimar, Udo; Barsan, Nicolae. - ELETTRONICO. - 14(2019), pp. 45-47. ((Intervento presentato al convegno 8th GOSPEL workshop. Gas sensors based on semiconducting metal oxides: basic understanding & application fields tenutosi a Ferrara nel 20-21 Giugno 2019.

Availability:

This version is available at: 11583/2738252 since: 2019-06-29T14:15:26Z

Publisher:

MDPI

Published

DOI:10.3390/proceedings2019014045

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Extended Abstract

Investigation of the Film Thickness Influence on the Sensor Response of In₂O₃-Based Sensors for O₃ Detection at Low Temperature and Operando DRIFT Study [†]

Daniele Ziegler ^{1,*}, Paola Palmero ¹, Jean-Marc Tulliani ¹, Anna Staerz ², Alexandru Oprea ², Udo Weimar ² and Nicolae Barsan ²

¹ Politecnico di Torino, Department of Applied Science and Technology, INSTM R.U PoliTO-LINCE Laboratory, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy; paola.palmero@polito.it (P.P.); jeanmarc.tulliani@polito.it (J.-M.T.)

² Institute of Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Auf der Morgenstelle 15, D-72076 Tuebingen, Germany; anna.staerz@ipc.uni-tuebingen.de (A.S.); alexandru.oprea@ipc.uni-tuebingen.de (A.O.); upw@ipc.uni-tuebingen.de (U.W.); nb@ipc.uni-tuebingen.de (N.B.)

* Correspondence: daniele.ziegler@polito.it

[†] Presented at the 8th GOSPEL Workshop. Gas Sensors Based on Semiconducting Metal Oxides: Basic Understanding & Application Fields, Ferrara, Italy, 20–21 June 2019.

Published: 19 June 2019

Industrial pollution and traffic emissions emit dangerous amounts of O₃, NO₂, VOCs and PM into environment, bringing higher incidence of morbidity and mortality in respiratory sicknesses [1]. Among tropospheric pollutant species, monitoring the O₃ concentration is remarkably important for its toxicity. The aftereffects of O₃ exposure indeed are upper respiratory irritation, rhinitis, cough, headache, occasional nausea, and vomiting [2]. In 2015, the United States Environmental Protection Agency (EPA), reinforced the National Ambient Air Quality Standards (NAAQS) for O₃ at ground-level not to exceed 70 ppb to improve the protection of human health [3].

This work presents n-type In₂O₃ as sensitive material to detect O₃ between 0.1 and 1 ppm at low temperatures (75 °C–150 °C). In₂O₃ powders were synthesized by hydrothermal route [4], with the goal to achieve a finer crystallite size, higher specific surface area and lower degree of agglomeration compared to commercial In₂O₃ (Sigma Aldrich, St. Louis, MO, USA). Those characteristics are essential to enhance the sensor performances [5].

In the synthesis, In₂O₃ nanostructures were realized by hydrothermal method using indium nitrate as indium precursor, soda as mineralizer and CTAB as capping agent, according to previous literature [6]. The mixture was maintained for 24 h at 70 °C and then for 12 h at 120 °C. Subsequently, powders were calcined at 400 °C for 30 min obtaining In₂O₃ [4].

In₂O₃ powders were characterized by laser granulometry, Thermal Analysis, X-ray Diffraction, N₂ adsorption, Field Emission-Scanning Electron Microscopy and High-Resolution Transmission Electron Microscopy.

Sensors were fabricated by screen-printing technique onto α -alumina substrates with Pt electrodes and a backside Pt heater. Inks for screen-printing were realized by mixing In₂O₃ powders with ethylene glycol monobutyl ether (Emflow), as organic vehicle and polyvinyl butyral (PVB) acting as temporary binder. After screen-printing deposition sensors were dried at 80 °C overnight and fired at 500 °C for 1 h in air. For obtaining different layer thicknesses in the range 10–100 μ m, the first layer was dried and then a new layer was printed onto it.

Films were characterized by Scanning Electron Microscopy, electrical measurements and *operando* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

Sensors were tested towards different amounts of O₃, NO₂ and H₂ under 0, 30% and 60% of RH (relative humidity) to study the selectivity of the as-realized chemical sensors for O₃ detection. Best results were achieved at 150 °C towards O₃, with the sensor selectivity for O₃ increasing by increasing the working temperature from 75 °C to 150 °C. Both oxidant gases (O₃ and NO₂) showed best performance at higher RH amounts, whereas for H₂ the trend was opposite, probably due to the competition between H₂ and H₂O for the same adsorption sites on the In₂O₃ surface. At 150 °C, under 1 ppm O₃, the variation of film resistance is 5 orders of magnitude, while it was only equal to 2 orders of magnitude under 1 ppm of NO₂. Under 30% RH, the influence of sensor thickness is much higher under O₃ compared to NO₂ and a logical trend was noticed in which by changing one order of magnitude the sensor thickness, the sensor response varies of more than 3 orders of magnitude under 1 ppm O₃. Under NO₂, only a small influence of the sensing film thickness on the sensor response was detected. Finally, the interference with H₂ is negligible as the sensor response towards H₂ is independent from the film thickness, as expected. Calibration curves of In₂O₃ sensor towards O₃, NO₂ and H₂ at 150 °C and 30% RH in the range 10–100 μm of thickness are displayed in Figure 1.

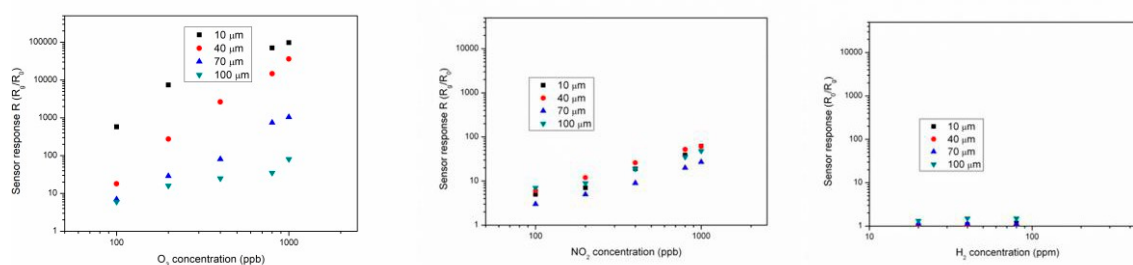


Figure 1. Comparison between 10, 40, 70 and 100 μm thick In₂O₃ sensor response towards O₃ (left), NO₂ (center) and H₂ (right) at 150 °C and 30% RH.

By DRIFTS, the aim is to clarify the interaction of NO₂ and O₃ with In₂O₃ surface establishing tightly the relationship between surface structure and adsorbed species with the gas sensing response.

Considering the NO₂-In₂O₃ interaction, the OH groups, most likely due to adsorbed water on the In₂O₃ surface, play a key role in the NO₂ adsorption. NO₂ withdraw more electrons from In₂O₃ in the presence of water forming nitrites and resulting in the measured increased in electrical resistance. This is confirmed by the higher increase in electrical resistance under humid atmospheres. OH groups are consumed when NO₂ is adsorbed onto the surface in the form of nitrites and in this process, H bonds are broken.

In the interaction of O₃ with In₂O₃ surface, signals related to peroxide formation during O₃ adsorption and decomposition were detected as well as peaks due to physisorbed O₃ still present at 150 °C. Furthermore, bands generated by carbonate-like species formed through reactions of O₃ with residual carbonaceous impurities from the synthesis route were recognized.

To conclude, in this work the role of the film thickness under O₃, NO₂ and H₂ exposure was studied for In₂O₃ sensor realized by screen printing technique. Finally, by *operando* DRIFT a complex sensing mechanism has been evidenced for In₂O₃ sensors, involving OH groups and adsorbed water in the mechanism of NO₂ adsorption and peroxide formation and O₃ physisorption during O₃ exposure.

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