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Original

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WO₃-Doped Indium Oxide Thick Films for Ozone Detection at Low Temperature [†]

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Abstract: Ozone, a strong oxidizing gas, has dramatically increased its concentration in the troposphere during the last decades. Since high O₃ concentrations are hazardous to human health, the development of effective methods and economic devices to detect this gas is an urgent need. In this frame, In₂O₃ is well known as an n-type ozone sensitive and selective material, generally displaying its optimal sensing capability in the temperature range 200–350 °C. To enhance the sensing capability of In₂O₃ and to decrease its operative temperature, in this work, commercial In₂O₃ powders were doped with 2.5 wt. % WO₃. Pure and doped-In₂O₃ materials were used to develop sensing devices by screen-printing technology. Resistance measurements were performed in the temperature range 25 °C–150 °C under 200–500 ppb O₃. Best results were obtained at 75 °C with sensor's responses as high as 40 under 200 ppb of ozone.

Keywords: ozone detection; W-doped indium oxide; thick film

1. Introduction

Ozone is known to be the most reactive form of oxygen, being less stable with respect to O₂. It is produced in the troposphere in a chain of chemical reactions involving nitrogen and hydrocarbon gases as well. However, during the last decades, the level of ozone has dramatically increased in the troposphere, due to the interaction between sunlight and a wide range of chemicals emitted by anthropogenic activities, like automobiles and industry [1]. This is a critical issue, since high concentrations of this powerful oxidizing gas are hazardous to the human respiratory system, causing inflammation and congestion of the respiratory apparatus [2,3]. Thus, monitoring the concentration of ozone in atmosphere appears of the highest importance. In 2015, EPA (United States Environmental Protection Agency) revised guideline for ozone standard levels recommending not to exceed 70 parts per billion (ppb) to improve public health protection [4,5].

Among a wide range of analytical techniques able to measure ozone concentration, gas-sensitive semiconductors evidence tremendous potential, compared with traditional ozone measurements methods, because of their low cost, ease of operation, high long-term stability, low power dissipation and high reliability. In this frame, indium oxide (In₂O₃) has been described to be particularly sensitive towards ozone [6–8], even if its optimal response is generally observed in the range 200–350 °C [9]. Only few papers report a maximum response to ozone in temperature range below 100 °C [10,11], without a UV illumination.

Many experiments have assessed that bulk-doping of semiconductor metal oxides is an efficient method to enhance sensor sensitivity, modifying not only the surface reactivity but also the bulk electrophysical features, defect chemistry and porosity of the matrix. WO₃, a n-type ozone sensitive oxide [12], improves sensitivity of the metal oxide film, creating adsorption centers with higher affinity for oxygen species, since unusual valence states (W⁶⁺) are produced [13].

In this work, a 2.5 wt. % of WO₃-doped commercial In₂O₃ nano-powder (W-In₂O₃) was used to prepare an ozone sensing device by screen printing technique and its properties are compared with those of an un-doped In₂O₃ reference material.

2. Materials and Methods

A commercial In₂O₃ powder (Sigma Aldrich, 99.9% purity, particle size < 100 nm) was doped with 2.5 wt. % WO₃ via an impregnation method, starting from WCl₆ (Sigma Aldrich, ≥99.9% purity) as precursor. The powders were mixed in dichloromethane (Alfa Aesar, ACS, 99.5+%) under magnetic stirring for 3 h. After drying at 40 °C, the powder was washed twice in distilled water and centrifuged. The powder was then dried in air at 80 °C overnight, and finally annealed at 400 °C for 3 h with a heating rate of 2 °C /min. Pure In₂O₃ was used as a reference material. Both powders were characterized by nitrogen adsorption (BET technique) and Field Emission-Scanning Electron Microscopy (FE-SEM) with elementary analysis (EDX). Sensors were prepared by screen printing the sensing materials onto commercial α-alumina substrates (Coorstek ADS-R 96) with platinum interdigitated electrodes (Electroscience 5545). The inks for screen printing were prepared by dispersing ceramic powders in a mixture of terpenols (Emflow, Emca Remex), in order to achieve the proper rheological characteristics, and polyvinyl butyral (PVB, Sigma Aldrich) as a temporary binder. After drying overnight, all sensors were fired at 600 °C in air for 1 h. Once fabricated, sensors were tested in a home-made system, where ozone was generated by a UV lamp (UVP, SOG-01, UK) from a constant air flow of compressed air. Ozone concentration was modulated by varying the length of lamp exposed and was determined by means of calibration curves given by the lamp manufacturer.

Sensor's response (R_g/R_o) is defined as the ratio between sensor's resistance under ozone flow (R_g) and under air measured at the equilibrium (R_o). The sensor responses were measured in the range 25 °C–150 °C by means of a LCR meter (Hioki 3533-01), performing all measurements under a constant flow rate of 1 L/min of dry air and 200–500 ppb O₃. Response and recovery time were determined, together with cross-sensitivity test towards NH₃, CH₄, humidity, CO₂ and N₂O performed using the same working conditions. Target gas was diluted with air utilizing flow meters (Teledyne Hastings Instruments HFM 300, HFC 302). Sensors were heated using a DC power supply (Peak Tech, DE), by a Ni-Cr wire located underneath the sensor. A thermocouple in contact with the sensor was used to determine the operating temperature.

3. Results and Discussion

3.1. Materials Characterization

Specific surface area of powders were rather similar: 13.3 m²/g for pure In₂O₃ and 15.2 m²/g for W-In₂O₃, indicating that doping didn't modify significantly the porosity of the pristine commercial powder. FE-SEM observations of both powders and of heat treated sensors (Figure 1) confirmed BET results. Moreover, only a slight increase of grain size was observed on both powders, before and after thermal treatment. EDX analysis confirmed a 2.5 wt. % content of WO₃ respect to the whole material.

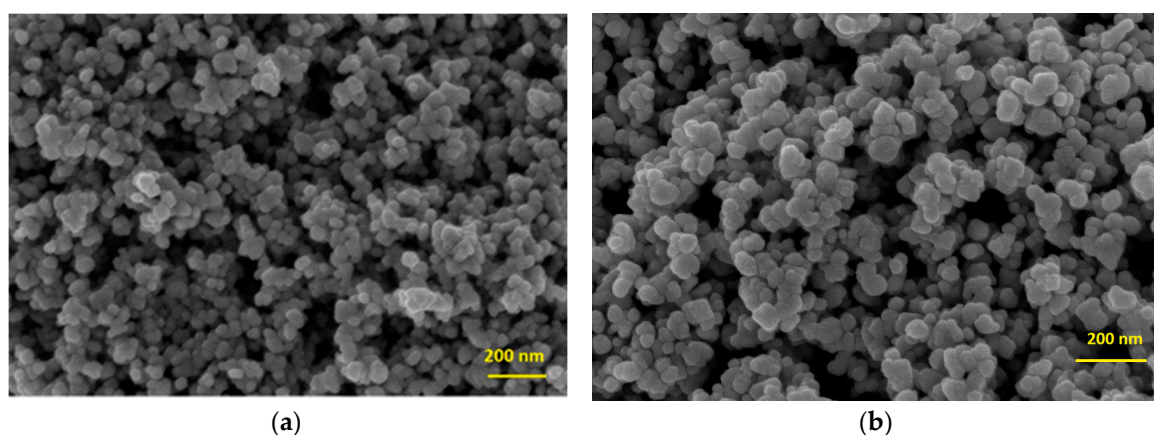


Figure 1. FE-SEM micrographs of sensors: In_2O_3 (a); $\text{W-In}_2\text{O}_3$ (b).

3.2. Sensor Characterization

The sensors' response showed an optimum at 75 °C. Furthermore, the response was enhanced 7 times under 500 ppb of ozone in $\text{W-In}_2\text{O}_3$ sensor respect to pristine In_2O_3 (Figure 2).

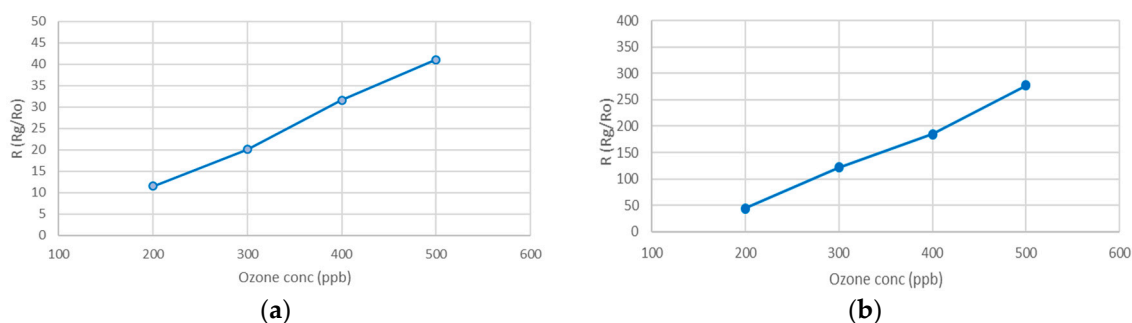


Figure 2. Sensor response as a function of ozone concentration: pure In_2O_3 (a); $\text{W-In}_2\text{O}_3$ (b).

This phenomenon can be probably attributed to more active sites and oxygen vacancies induced by n-n heterojunction between WO_3 and In_2O_3 nanoclusters. Resistance variations under different ozone concentration (200–500 ppb) for $\text{W-In}_2\text{O}_3$ are plotted in Figure 3.

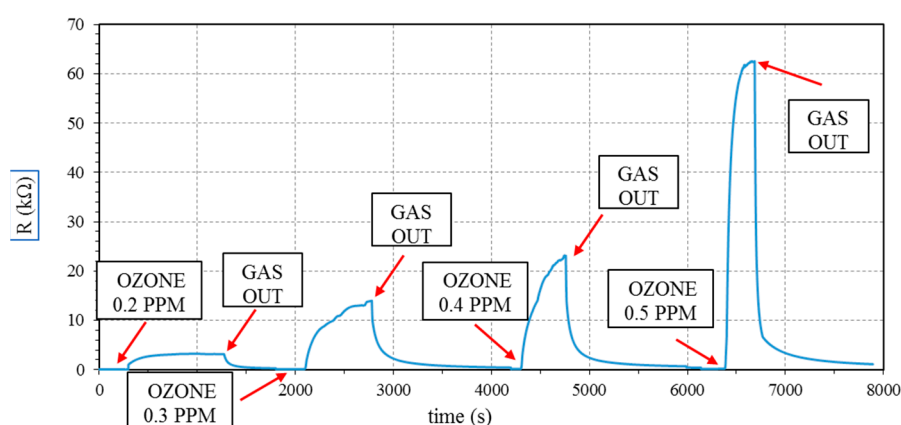


Figure 3. Resistance variation of $\text{W-In}_2\text{O}_3$ sensor under 200–500 ppb ozone concentration at 75 °C.

Cross sensitivity results for both sensors are reported in Table 1. The maximum interferences were observed with water vapor under high relative humidity values (90% RH).

Both materials exhibited acceptable response and recovery time (the time taken to reach 90% of the sensor response when increasing or decreasing O_3 concentration, respectively; in the order of 1–2 min). Finally, putting in comparison other studies employing indium oxide thick films, maximum

response is ordinarily achieved in the 200–350 °C range. Only Starke et al. [10] obtained the maximum response at 85 °C (sensor response around 300 under 250 ppb of ozone), although the deposition technique was different (drop coating), as well as film thickness (2 µm instead of 20 µm) and grain size (12 nm vs. about 80 nm).

Table 1. Results of cross sensitivity tests for In₂O₃ and W-In₂O₃ sensors at 75 °C.

Sensor	In ₂ O ₃	W-In ₂ O ₃
Gas	(R _g /R _o)	(R _g /R _o)
NH ₃ 50 ppm	1.00	0.86
CH ₄ 50 ppm	1.00	1.00
Air + RH 90%	0.59	0.55
CO ₂ 50 ppm	1.00	1.00
N ₂ O 15 ppm	1.00	1.00

4. Conclusions

To conclude, this work has confirmed the exploitation of W-In₂O₃ thick films as sensitive and selective material for ozone detection at sub-ppm level. W⁶⁺ ions probably create adsorption centers with higher affinity for oxygen adsorption, resulting in a higher sensitivity of indium oxide for a strong oxidant gas as ozone. Thus, these results are extremely promising and support the exploitation of tungsten-doped indium oxide as a low-temperature ozone sensor. However, humidity interference should be reduced in the future. To the best of our knowledge, up to now, no other works has investigated the sensor response towards ozone of tungsten-doped indium oxide film.

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

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