

W-Sn Mixed Oxides and ZnO to Detect NO_x and Ozone in Atmosphere †

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Abstract: Thick films of zinc oxide (ZnO) in form of nanospheres or hexagonal prisms and of tungsten-tin (W-Sn) mixed oxides at nominal Sn molar fraction (0.1, 0.3 and 0.5) were prepared. The functional materials were synthesized and characterized by SEM and TEM, X-ray diffraction, specific surface area measurements, UV-Vis-NIR and IR spectroscopies. The gas sensing measurements highlighted that ZnO is more performant in form of nanoprisms, while W-Sn sensors offer a better response towards NO_x and ozone with respect to pure WO₃.

Keywords: W-Sn mixed oxides; ZnO nanomorphologies; NO_x and ozone detection; thick film gas sensors; UV-Vis-NIR and FT-IR spectroscopies

1. Introduction

Road traffic and fuel combustion utilities strongly influence the air quality in urban atmosphere, above all NO_x and ozone in addition to particulate matter. Thereby, the monitoring of the atmospheric pollutants is necessary, but particularly interesting through portable and versatile devices based on thick film gas sensors, having low requirements in terms of power, consumables, maintenance and installation costs. Taking advantage of previous experiences of some of the authors in this area, this work has been aimed to prepare and study materials and sensors based on semiconductor metal oxides specifically devoted to detect NO_x and ozone [1–4]. For this work, W-Sn solid solutions and nanoforms of ZnO have been considered. For W-Sn materials, the aim was to join advantages of high sensitivity toward oxidizing gases of WO₃ and Sn addition to reduce WO₃ grain growth with temperature. For ZnO, the aim was to compare nanoparticle aggregates with 2D-nanocrystals for detecting oxidizing gases.

2. Materials and Methods

The single oxides WO₃ and SnO₂, W-Sn mixed oxides and nanoforms of ZnO were successfully synthesized and used to prepare thick film gas sensors. W-Sn mixed oxides (nominal Sn molar fraction of 0.1, 0.3 and 0.5) were obtained by sol-gel co-precipitation method using required stoichiometric proportions of Tin(II) 2-ethylhexanoate in a proper amount of 1-butanol and WCl₆ dissolved in absolute ethanol. Diluted HNO₃ solution was added to catalyze the hydrolysis process and the resulting yellowish green powder was calcined at 550 °C for 2 h. Both ZnO nanoforms were

synthesized through sol–gel processes, starting from a water solution of zinc nitrate hexahydrate. ZnO nanospheres were prepared adding to the solution a proper amount of ammonium hydroxide, the precipitate then washed, dried and calcined at 450 °C, whereas ZnO hexagonal prisms were directly obtained keeping the mixture in oven at temperatures lower than 100 °C for several hours. All materials were characterized through FE-SEM and TEM electron microscopy, BET and XRD analysis. Diffuse reflectance UV-Vis-NIR and absorbance FT-IR spectroscopies, in situ conditions, were employed to characterize the electronic properties of the materials. Screen printing technique was used to deposit the sensing layers and the corresponding thick films (all fired at 650 °C in this work) were tested for sensing in a sealed test chamber using the flow-through technique. In order to correlate the spectroscopic analysis with electrical characterizations, Schottky barriers versus temperature in dry air as well as in 100 ppm of CO and 10 ppm of NO₂ have been measured. Dynamical responses in presence of the target gases have been carried out, as well.

3. Results

XRD patterns of pure WO₃, W-Sn(0.1), W-Sn(0.3) and W-Sn(0.5) powders correspond to monoclinic crystal structure (space group P21/n) of polycrystalline WO₃ without any other phases (Figure 1), the crystallite size of the above powders, evaluated by Scherrer's formula, being 85, 25, 24 and 19 nm, respectively. XRD analysis, performed onto ZnO samples, attributes a hexagonal wurtzite structure, space group P6₃mc, for both nanofoms. Further characterizations onto ZnO samples can be found in [1].

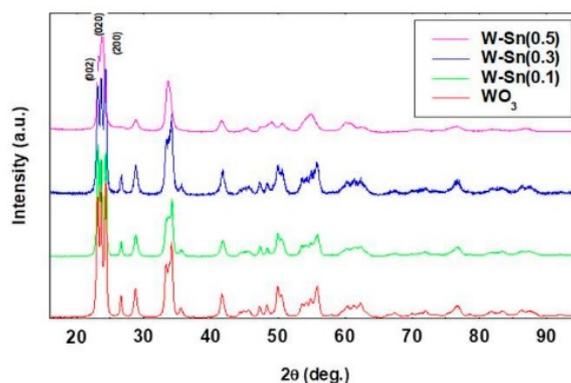
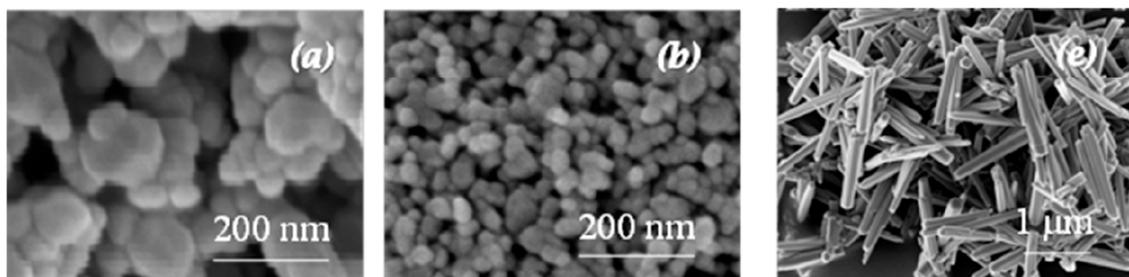


Figure 1. XRD pattern of pure WO₃ and W-Sn powders (nominal Sn molar fraction of 0.1, 0.3 and 0.5).

In agreement with XRD analysis, FE-SEM observations confirmed that the addition of Sn to WO₃ successfully reduced the coalescence of WO₃ grains as shown in Figure 2a–d in which the images of calcined materials are reported. Figure 2e,f shows ZnO powders shaped into nanoparticles or hexagonal prisms.



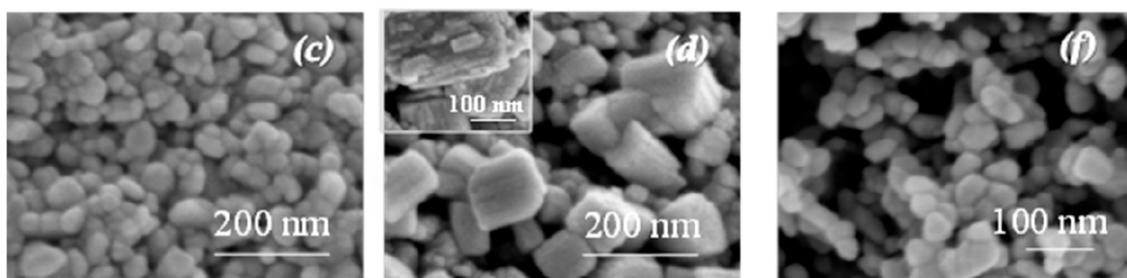


Figure 2. FE-SEM images of the calcined powders: (a) WO_3 ; (b) $\text{W-Sn}(0.1)$; (c) $\text{W-Sn}(0.3)$; (d) $\text{W-Sn}(0.5)$; (e) ZnO nanoprisms; (f) ZnO nanospheres.

From the electrical point of view, all studied materials behave as n-type semiconductors because of lattice defects as highlighted in the Arrhenius plots (not shown here for sake of brevity) in which the semiconductor behavior was modulated by the Schottky barrier formation at gas–semiconductor interface. With respect to W-Sn materials, UV-Vis-NIR and FT-IR spectroscopies (see Figure 3) highlighted the predominant electronic defects. In particular, in reducing atmosphere, WO_3 shows polaron formation (band in the near IR region, deepness in the band gap = 0.55 eV), while SnO_2 shows the increase of mono-ionized oxygen vacancies (band in the medium IR, deepness in the band gap = 0.19 eV). The mixed oxides $\text{W-Sn}(0.1)$, $\text{W-Sn}(0.3)$ and $\text{W-Sn}(0.5)$ show polaron formation as observed for WO_3 .

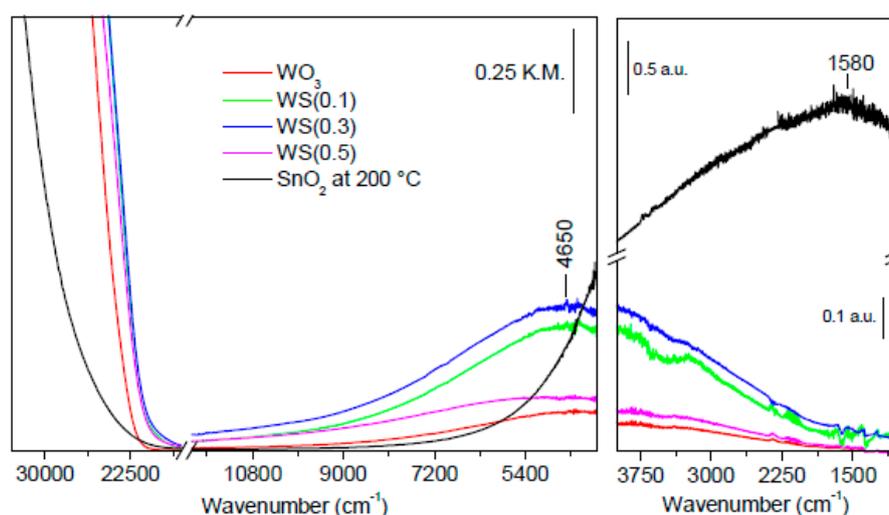


Figure 3. FT-IR spectra of W-Sn samples during interaction with CO/O_2 (1:5, $p_{\text{CO}} = 5$ mbar) at the temperature of the maximum absorption intensity.

The behavior of the energy barriers versus temperature is a powerful tool to characterize the various sensing materials toward the different gases. Indeed, if the testing gas is reducing and the semiconductor is of type n, it will turn out that the Schottky barrier will decrease because a certain quantity of electrons pass to the conduction band, vice versa if the testing gas is oxidizing or the semiconductor is of type p. It can be observed that the only material, among those here characterized, really effective toward CO was SnO_2 for which the barrier in CO (see Figure 4a) was strongly decreased than the one in air, meaning that a large amount of electrons was able to cross the barrier due to surface chemical reaction between the gas and surface adsorbed oxygen ions. On the contrary, SnO_2 was poorly responsive toward NO_2 except at very low temperatures, while all other materials examined were almost insensitive to CO , but exhibited high responses to NO_2 . In particular, the sensor with nominal Sn molar fraction of 0.3 exhibited the highest difference between the energy barrier in NO_2 and in air (see Figure 4b) as well as it offered the highest response in the dynamical measurement toward 1 ppm of NO_2 (see Figure 5a).

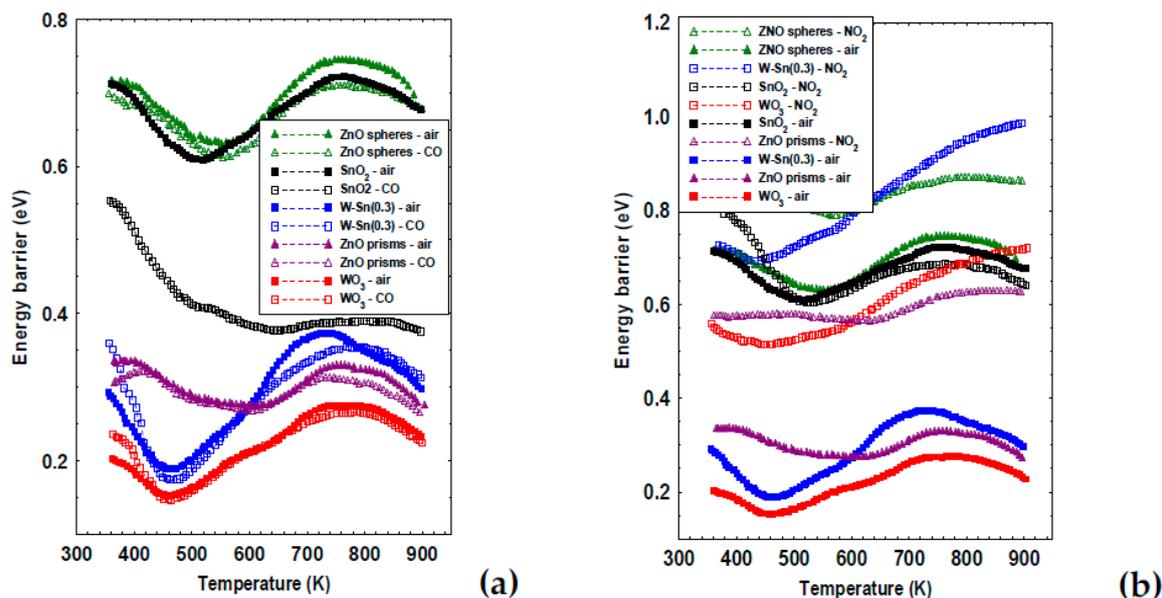


Figure 4. (a) Comparison between the energy barriers in dry air and in 100 ppm of CO; (b) in dry air and in 10 ppm of NO₂.

In Table 1, the electrical responses to 50 ppm of carbon monoxide obtained at different working temperatures for all samples are reported. Except SnO₂, all other sensors exhibited poor responses. It can be also noted that ZnO spheres better performed with respect to ZnO prisms. Indeed, as typical for reducing gases, spherical geometry is favored with respect to bi-dimensional one, while, for oxidizing gases, the relation between the response and the grain dimension must be still completely understood. However, the Figure 5 b shows that, in the case of ozone and ZnO sensors, the bi-dimensional morphology is more performant than the spherical one.

Table 1. Responses of all sensors to 50 ppm of CO reported as G_{gas}/G_{air} obtained at different temperatures.

Sample	Temperature (°C)			
	350	400	450	500
WO ₃	1.06	1.06	1.06	1.02
W-S(0.1)	1.13	1.15	1.09	1.12
W-S(0.3)	1.14	1.12	1.08	1.08
W-S(0.5)	1.28	1.3	1.23	1.02
SnO ₂	6.36	4.71	3.70	2.90
ZnO spheres	1.81	1.54	1.63	1.57
ZnO prisms	1.06	1.06	1.06	1.02

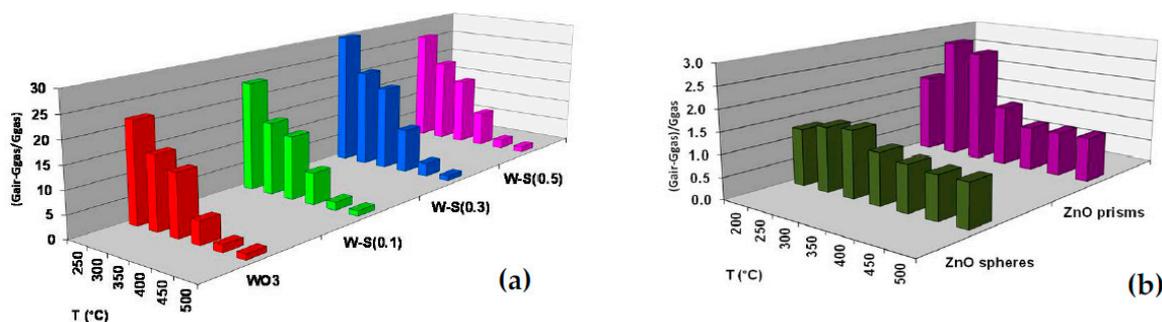


Figure 5. (a) Responses of W-Sn sensors to 1 ppm of NO₂ reported as $(G_{air}-G_{gas})/G_{gas}$ obtained at different working temperatures; (b) responses to 100 ppb of O₃ for ZnO spheres and prisms both fired at 650 °C.

Author Contributions: A.F. and M.C.C. conceived the work, synthesized the materials, prepared the sensors and performed the electrical characterizations, S.M. and A.A. carried out the XRD, BET and spectroscopic characterizations, S.M. collaborated with A.F. and M.C.C. to the analysis of all data and to write the paper, M.M. performed the FE-SEM characterizations and M.S. analyzed all crystallographic data.

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

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