Highly porous Tungsten-oxide-based films obtained by spray-gel for gas sensing applications

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Abstract

Highly porous mixed WO_3–SnO_2 films have been prepared from an aqueous solution of $SnCl_4.5H_2O$ and polytungsten gel with a molar ratio of Sn/W from 0 to 1. These solutions were sprayed on to alumina substrates at 220 ºC. The obtained films were annealing at 600 ºC in air for 3 h. The annealed films were composed of a mixture of WO_3 and SnO_2 phases. The gas sensitivity to butanol and ethanol vapors is enhanced when the Sn/W molar ratio increases in the film by up to 0.1, with further increments to this proportion the sensitivity decreases.

1. Introduction

Mixed oxides have been investigated intensively to improve or modify their gas sensing properties [1]. It has been found that most metal oxide mixtures exhibit increased surface activity. It is well-known that the conductance of simple metal oxides such as SnO_2 and WO_3 changes when the composition of the surrounding atmosphere is altered [2]. It has been concluded that the nature of the surface sites and the electron donor/acceptor properties of the gas, the adsorption, the surface reactions, and the desorption of gases are key features for the performance of semiconductor gas sensors [2]. Surface properties are expected to be influenced by grain boundaries between the grains of different chemical compositions. These phenomena will contribute to the gas-sensing properties. Mixed oxides that form distinct chemical compounds as in the systems Zn-Sn-O [3], Cd-In-O [4], and Sn-W-O [5,6] have been used successfully in gas detection.

The sol-gel technique is well suited for making mixed oxides [7]. The spray-gel technique that combines the spray pyrolysis and the sol-gel techniques has produced very porous films [8,9]. This technique is suitable for producing semiconductor metal oxides for gas-sensing applications; due to the fact that it yields a large interface between a solid and a gaseous medium.

In this work, we report the characterization and gas sensing properties of highly porous mixed WO_3–SnO_2 films obtained by spray-gel technique. The incorporation of the SnO_2 phase into WO_3 improved the gas response to ethanol and butanol with respect to pure WO_3.

2. Experimental

The spray-gel technique was used to obtain mixed tungsten oxide and tin oxide films on alumina substrates. The process basically consists of producing an aerosol from a gel, which is sprayed on a hot substrate where the film is going to grow [8]. A sol was prepared via acidification of 0.1 M sodium tungstate aqueous solution (pH ~ 7.8) through a proton exchange resin. Different quantities of an aqueous solution of $SnCl_4.5H_2O$ were added to the polytungsten sol to obtain a solution with a molar ratio of Sn/W from 0 to 1 (pH ~ 1.1). These solutions were sprayed on to alumina substrates at 220 ºC for 45 min giving a film with a thickness of ~ 1 μm.

For gas sensing studies the films were deposited onto alumina substrates using preprinted gold electrodes, 0.3 mm apart, and a Pt-heating resistor on the reverse side. Rectangular (3 x 2.5 mm^2) mixed WO_3–SnO_2 films were formed so they bridged the gold electrodes. Before the gas sensing studies the films were annealed in air at 600 ºC for 3 h, because it is well-known that the sensing effect is optimized at temperatures between 200 and 400 °C.

3. Results

3.1 Structural properties. The crystal structures of mixed WO_3–SnO_2 films obtained were characterized by x-ray diffraction (XRD). XRD was performed using a Phillips X Pert diffractometer operating with CuK_α radiation. Figure 1 shows the X-ray diffractograms for films made from different solutions with Sn/W molar ratio from 0 to 1, post-annealed at 600 ºC. Peaks belonging to WO_3 as well as SnO_2 phases are indicated in the figure, the asterisks in the figure represent the peaks due to the substrate (Al_2O_3). The incorporation of Sn into the WO_3 shows a systematic change in the peaks. The peaks corresponding to SnO_2 phase are broad indicating that their with grain size is in the namometric range.

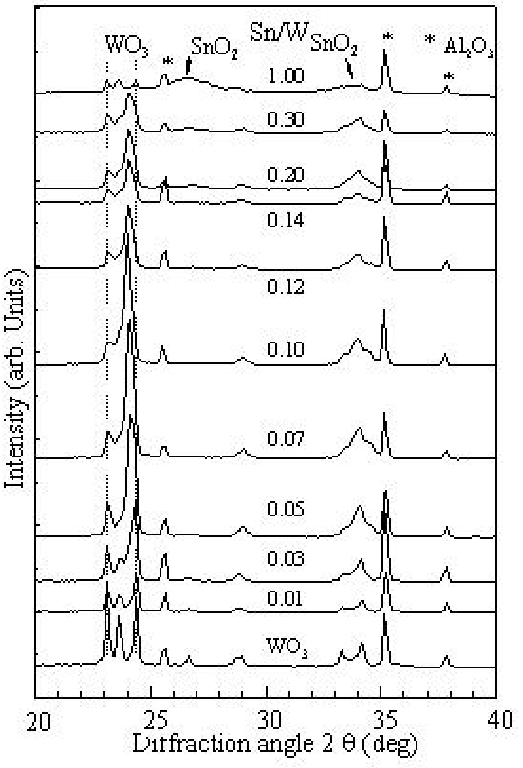
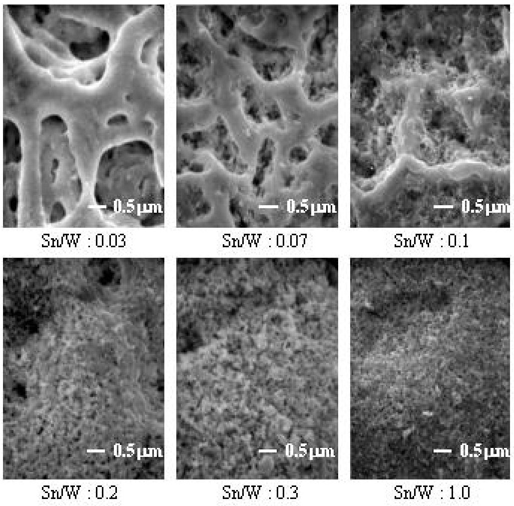


Figure 1. X-ray diffraction patterns for films made from a solution with a different molar ratio of Sn/W after annealing at 600 ºC. Asterisks denote diffraction peaks from the substrate. The broken lines indicate the stronger positions of the WO_3.

The microstructure of the films was analyzed by a scanning electron microscope (SEM), a Hitachi S500 instrument. From micrographs (Fig. 2) one can follow the porosity variation of the mixed WO_3-SnO_2 films as a function of the molar ratio. The films obtained from solutions of Sn/W with a molar ratio of less than 0.10 are highly porous, whereas the films made from a molar ratio of Sn/W higher than 0.10 are compact. The porous structure of the films is related to the WO_3 [8] and the small particles appearing with the incorporation of Sn in the film could be related to SnO_2.



Sn/W : 0.03 Sn/W : 0.07 Sn/W : 0.1

Sn/W : 0.2 Sn/W : 0.3 Sn/W : 1.0

Figure 2. SEM micrographs for mixed WO_3–SnO_2 films after annealing at 600 ºC obtained from solutions with the shown molar ratio of Sn/W.

3.2 Gas sensing properties. Pt-wire contacts were attached with a low-temperature gold paste to the two gold electrodes on the alumina substrate for electrical conductance measurements. The samples to be tested were placed in a stainless steel chamber (4.4 L) and exposed to different butanol and ethanol vapor concentrations. The films were connected in series with both a known resistor and a 5V source. The conductance of the films was obtained by measuring the voltage drops across the resistor. Gas-sensing properties of the films were studied at 400 °C, using a computer-controlled measuring system. The gas sensitivity is defined here, as the conductance ratio G_{gas}/G_{air}, where G_{gas} denotes the conductance after 1 min in the test gas and G_{air} is the conductance in air.

Figure 3 shows the results of a detailed study on the gas sensitivity of mixed WO_3-SnO_2 films obtained from different solutions with a molar ratio of Sn/W from 0 to 1 after annealing at 600 ºC in 5 ppm of ethanol and butanol. The gas sensitivity of the mixed WO_3-SnO_2 to butanol and ethanol vapors is higher than that of pure WO_3. It was found that the optimal molar ratio of Sn/W for the solutions used to prepare the films was 0.1 with high gas sensitivity to butanol and ethanol, respectively. Similar results were reported with 10 wt.% of SnO_2 or ZrO in Fe_2O_3 [10]. The high sensitivity of these sensors was explained on the basis of SnO_2 or ZrO inducing the acid-based properties of the sensing materials so that the sensitivity to detection of ethanol vapor in air was increased [11]. The mechanism of the ethanol sensing is well described by

Hellegouar´h et al. [12], and is in agreement with our results.

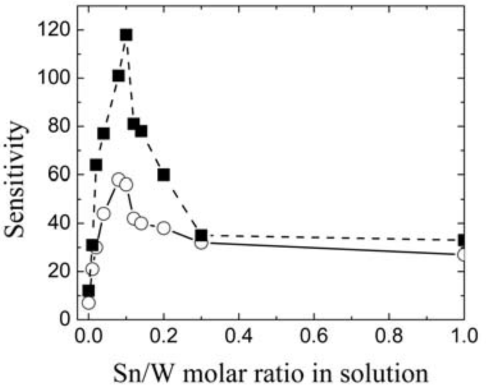


Figure 3. Sensitivity vs molar ratio Sn/W from the solution used to obtain mixed WO_3–SnO_2 films after annealing at 600 ºC, and being exposed to 5 ppm of ethanol (○) and butanol (■) in air. The operating temperature is 400 ºC.

4. Discussion and conclusions

The annealed films obtained from a solution with a molar ratio of Sn/W lower than 0.01 were mainly monoclinic WO_3, whereas those obtained from solutions with higher Sn/W molar ratios were composed of a mixture of SnO_2 and WO_3 phases, the relative intensity of the WO_3 peaks at 2θ in the 22 – 25° range change, it could be that the Sn produces a distortion of the WO_3 unit cell. The film obtained from a solution with a molar ratio of Sn/W of 1.0 has a mixture of nanocrystalline SnO_2 and WO_3. The films obtained from solutions of Sn/W with a molar ratio of up to 1.0 keep some porosity, but an agglomerate of grains is formed when films are deposited from solutions with a higher Sn/W molar ratio than 0.07.

Gas sensitivity to butanol and ethanol vapors is enhanced when both WO_3 and SnO_2 phases are present in the films. It was found that the optimal Sn/W molar ratios for spraying solutions were 0.10 to get high gas sensitivity to butanol and ethanol, respectively. Therefore, the presence of small amounts (less than 0.10).

Acknowledgements

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