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

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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°C. The obtained films were annealed at 600°C 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.

Keywords: Tungsten oxide; tin oxide; gas sensor; pyrolysis.

Películas delgadas muy porosas de mezclas de WO_3–SnO_2 se prepararon a partir de una solución de $SnCl_4.5H_2O$ y gel polytúngstico con una relación molar de Sn/W de 0 a 1. Estas soluciones fueron pulverizadas sobre substratos de alumina a 220°C. Las películas obtenidas fueron sinterizadas a 600°C en aire por 3 h. Las películas están compuestas de una mezcla de las fases de WO_3 y SnO_2. La sensitividad a vapores de etanol y butanol es mejorada cuando la razón molar de Sn/W se incrementa en la película hasta 0.1, para mayores incrementos a esta proporción la sensibilidad decrece.

Descriptores: Oxido de tungsteno; oxido de estaño; sensor de gas; pirolisis.

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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 $\sim$ 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 $\sim$ 1.1). These solutions were sprayed on to alumina substrates at 220°C for 45 min giving a film with a thickness of $\sim 1\ \mu$m.

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 (3×2.5 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°C for 3 h, because it is well-known that the sensing effect is optimized at temperatures between 200 and 400°C.

3. 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$_\alpha$ 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°C. 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 grain size is in the namometric range.

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.

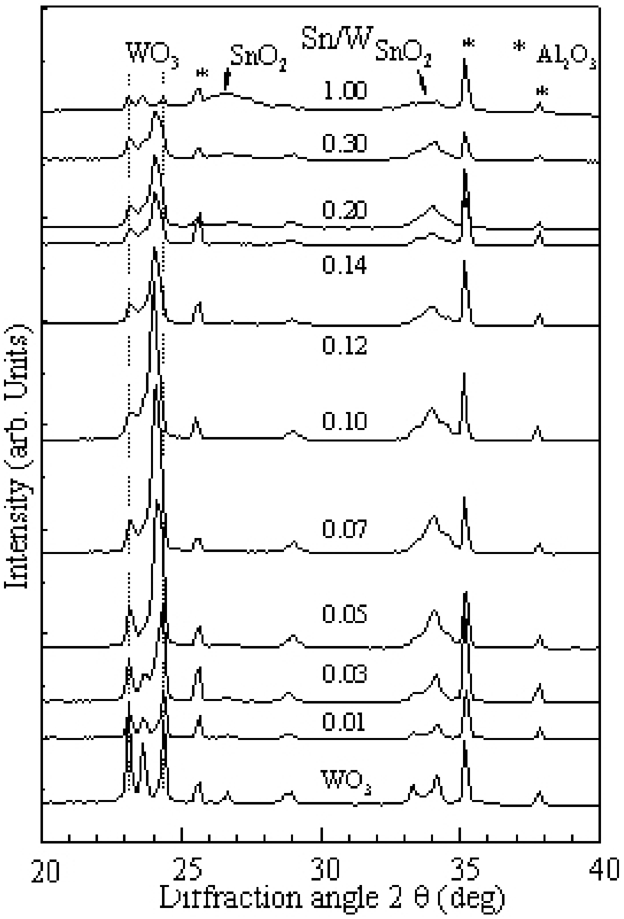

FIGURE 1. X-ray diffraction patterns for films made from a solution with a different molar ratio of Sn/W after annealing at 600°C. Asterisks denote diffraction peaks from the substrate. The broken lines indicate the stronger positions of the WO_3.

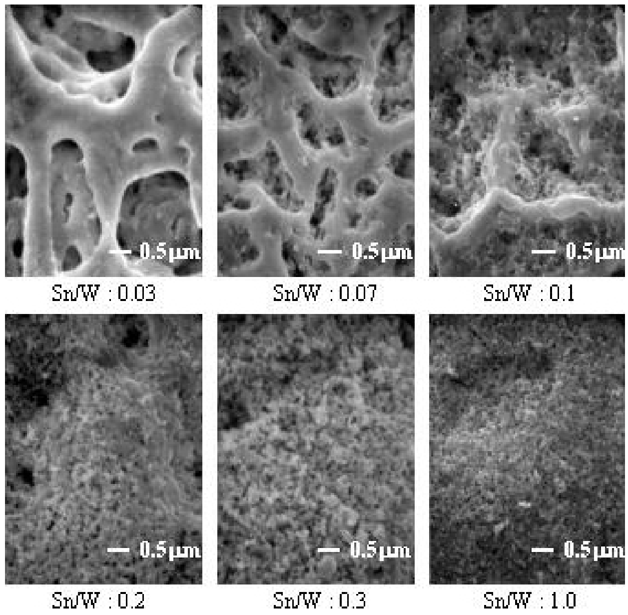

FIGURE 2. SEM micrographs for mixed WO_3–SnO_2 films after annealing at 600°C obtained from solutions with the shown molar ratio of Sn/W.

4. 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°C 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.

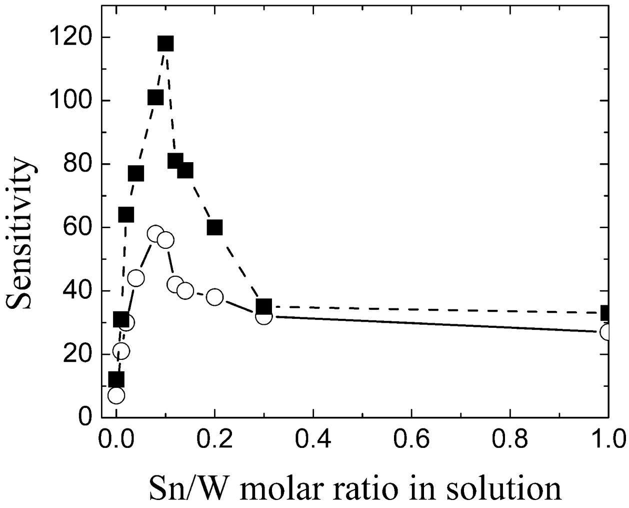

FIGURE 3. Sensitivity vs molar ratio Sn/W from the solution used to obtain mixed WO_3–SnO_2 films after annealing at 600°C, and being exposed to 5 ppm of ethanol (○) and butanol (■) in air. The operating temperature is 400°C.

5. 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) of SnO_2 improves the detection sensitivity of both butanol and ethanol, probably due to the change of acid-based properties of the surface in the films [11]. However, with higher proportions diminishes the gas sensitivity.

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1. K. Zakrzewska, *Thin Solid Films* **391** (2001) 229.
2. M.J. Madou and S.R. Morrison, *Chemical Sensing with Solid State Devices*, (Academic Press, San Diego, 1989).
3. Y.-S. Shen and T.-S. Zhang, *Sens. Actuators B* **12** (1993) 5.
4. Z. Szklarski, K. Zakrzewska, and M. Rekas, *Thin Solid Films* **174** (1989) 269.
5. J.L. Solis and V. Lantto, *Sens. Actuators B* **48** (1998) 322.
6. J.L. Solis *et al.*, *Sens. Actuators B* **68** (2000) 286.
7. M. Macek, B. Orel, and T. Meden, *J. Sol-Gel Sci. Technol.* **8** (1997) 771.
8. M.A. Damian, Y. Rodriguez, J.L. Solis, and W. Estrada, *Thin Solid Films* **444** (2003) 104.
9. A. Medina, J.L. Solis, J. Rodríguez, and W. Estrada, *Sol. Energy Mater. Sol. Cells* **80** (2003) 473.
10. C.V. Gopal Reddy, W. Cao, O.K. Tan, and W. Zhu, *Sens. Actuators B* **81** (2002) 170.
11. T. Jinkawa, G. Sakai, J. Tamaki, N. Miura, and N. Yamazoe, *J. Mol. Catal. A: Chem.* **155** (2000) 193.
12. F. Hellegouar'h, F. Arefi-Khonsari, R. Planade, and J. Amouroux, *Sens. Actuators B* **73** (2001) 27.