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SnO_2–Bi_2O_3 and SnO_2–Sb_2O_3 gas sensors obtained by soft chemical method

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Abstract

In this work, SnO_2–Bi_2O_3 and SnO_2–Sb_2O_3 nanoparticles were obtained by using polymeric precursor method. Powders were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential thermal analysis and thermogravimetric analysis (DTA/TGA). Thick films were deposited on alumina substrates on which electrodes have been previously deposited by sputtering. The electric response of thick films was measured under oxygen and carbon monoxide atmospheres. It was determined that bismuth addition improves the sensor response to the oxygen presence. On the other hand, antimony addition diminishes the sample resistance due to the possible replacement of Sn^{4+} by Sb^{5+}.

Keywords: Powders-chemical preparation; Films; Electrical properties; Sensors

1. Introduction

Tin oxide, SnO_2, is a n-type semiconductor due to the existence of donor levels.[1] These levels are generally attributed to single and double ionized oxygen vacancies. This oxide has been widely used for applications, such as gas sensor[2–4] due to its low densification and high sensibility to different gases atmospheres. The SnO_2 has been prepared by a number of techniques, including coprecipitation,[5] sol–gel,[6] spray pyrolysis ,[7] microwaves,[8] microemulsion,[9] polymeric precursor,[10] solid state reaction through carbonates decomposition,[11] deposition in vapor phase[12] and hydrothermal methods.[13] However, it is known that polymeric precursor method is a low cost synthesis route that allows to obtain nanometric particles and favors the homogeneous additive distribution.[10]

Bismuth oxide is an ion conducting solid electrolyte, being the δ-phase of this oxide one of the best solid-state oxygen ion conductors known.[14] On the other hand, Leite et al. determined that antimony addition allows to control the grain size and electrical conductivity of the SnO_2 thin film, resulting in a nanostructured material.[15]

In this work, the SnO_2–Bi_2O_3 and SnO_2–Sb_2O_3 ceramic powders were prepared by polymeric precursor method. The change in the electric resistance of this device as a function of the exposition time to oxygen and carbon monoxide atmospheres was measured.

2. Experimental procedure

The ceramic powders were prepared by Pechini method, according to the following procedure. Ethylene glycol (Mallinckodt 99.5%) and citric acid (Carlo Erba 99%) were mixed maintaining the temperature system at 70 °C and continuous agitation. Antimony acetate (Aldrich 99.99%) and bismuth acetate (Aldrich 99.99%) aqueous solutions were separately prepared. Aqueous dissolution of $SnCl_2{\cdot}2H_2O$ (Mallinckrodt 95%) 0.3 M at pH 6.25 and the obtained colloidal suspension was filtered and repeatedly washed with 0.05 M diethylamine solution. Afterwards, the system was dispersed and homogenized using an Ultra-Turrax T50 turbine, and aged during 24 h. This obtained suspension and precursor solutions of Bi or Sb were added to ethylene glycol and citric acid mixture. In this study, compositions with 1 mol% Sb_2O_3 or Bi_2O_3 were analyzed. When the mixture of the precursor solutions, Ethylene glycol and the citric acid were completely homogeneous, the temperature was reduced at 25 °C and NH_4OH was introduced under constant stirring until a pH 7 was reached. The solution was dried at

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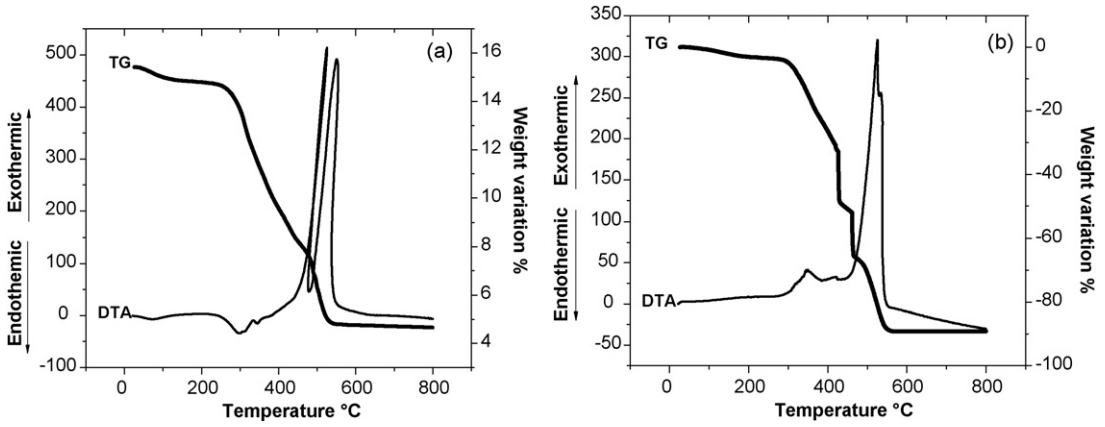

Fig. 1. TGA and DTA curves of samples with bismuth (a) and antimony (b) addition.

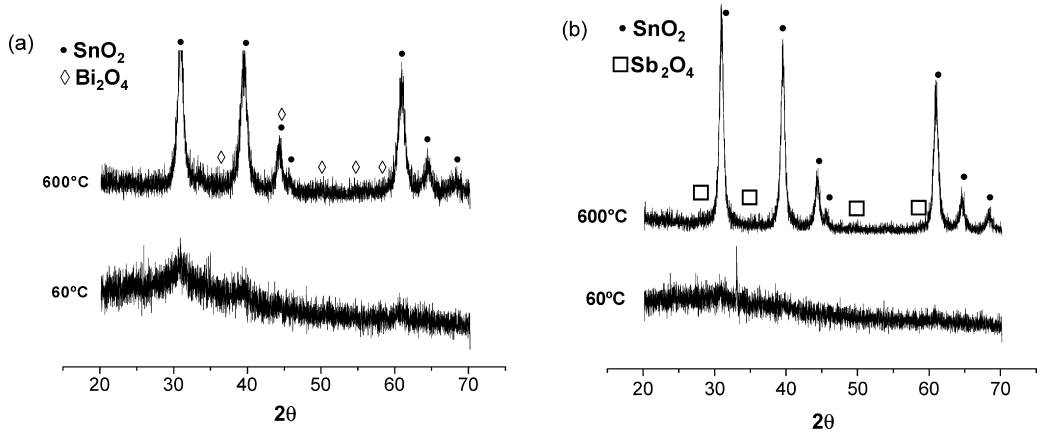

Fig. 2. XRD spectra of the samples with bismuth (a) and antimony (b) addition, thermally treated at 60 °C or 600 °C.

140 °C and a black resin was obtained. The resin was heated at 350 °C for 12 h and the remaining solid was milled. The obtained powders were characterized through differential thermal analysis and thermogravimetric analysis, DTA/TGA in air atmospheres (DTA-50, TGA-50 Shimadzu), and X-ray diffraction, XRD (Philips PW 1830/40 diffractometer running with Co radiation ($\lambda = 1.790$ Å)).

Resulting powders were thermally treated at 600 °C for 2 h and after that they were milled during 2 h in an attrition milling. Powders were characterized by transmission electron microscopy, TEM (Jeol JEM-1200 FORMER) and XRD. Then, a paste was prepared with an organic binder (glycerol) and the obtained powders. The used solid/organic binder ratio was 1/2. Thick, porous film samples were made by painting onto insulating alumina substrate with interdigit shape gold electrodes deposited by sputtering. Finally, doped and undoped samples were treated during 2 h in air at 500 °C. The electric resistance variation was measured at 350 °C when the atmosphere was changed from vacuum (10^{-4} mmHg) to oxygen (44 mmHg) and from vacuum (10^{-4} mmHg) to CO gas atmosphere (44 mmHg).

3. Results and discussion

Fig. 1 shows the DTA/TGA curves obtained for the SnO_2–Bi_2O_3 and SnO_2–Sb_2O_3 systems (Fig. 1(a and b), respectively). These curves show a weight loss located between 270 and 600 °C, which is associated to two exothermic peaks above 400 °C. These peaks are related to the decomposition of the organic compounds and tin oxide crystallization.

From X-ray diffraction spectra the presence of cassiterite as the main crystalline phase, in all the systems, is observed (Fig. 2).

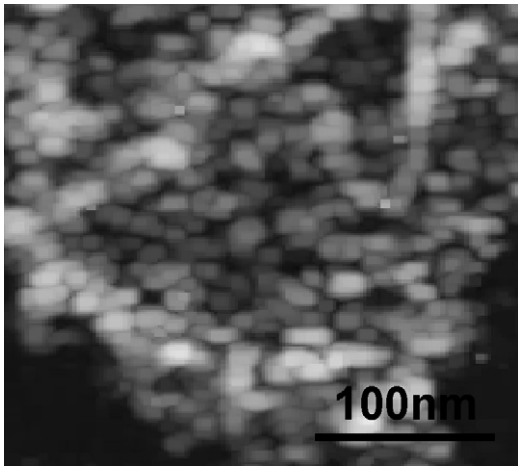

Fig. 3. TEM micrographs of the SnO_2 powders with bismuth addition thermally treated at 600 °C during 2 h and milled.

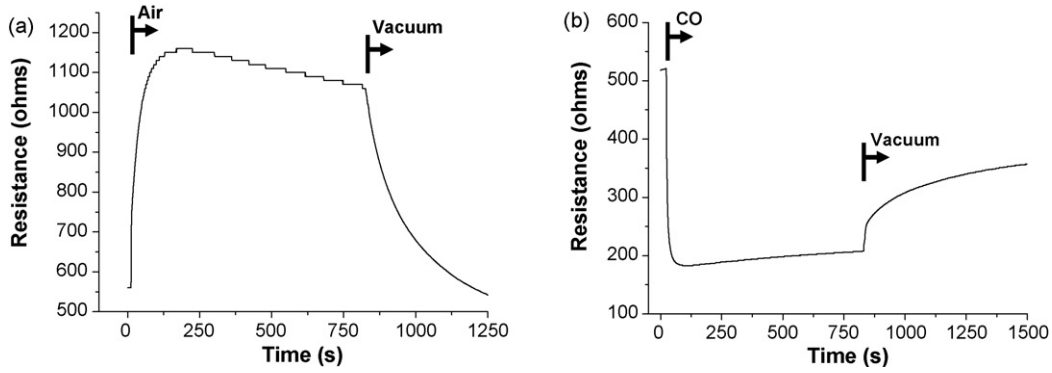

Fig. 4. Resistance curve of the thick film with pure SnO_2, as a function of the exposition time to an oxygen (a) and carbon monoxide (b) atmosphere, measured at 350 °C.

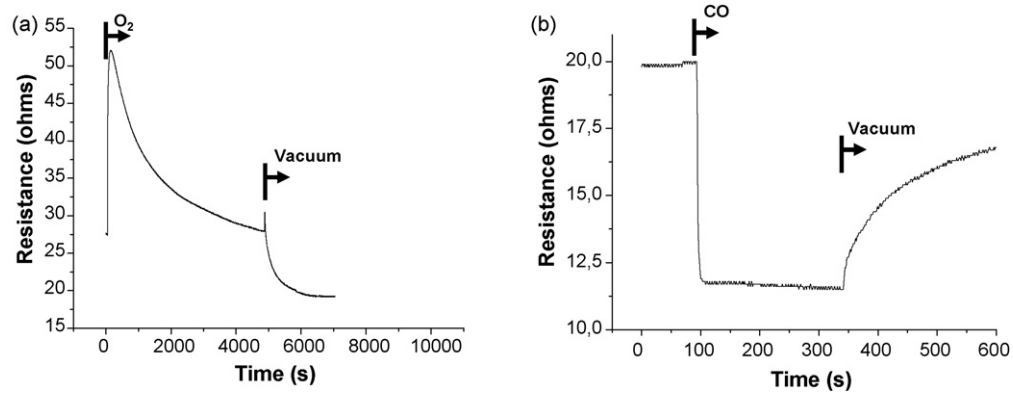

Fig. 5. Resistance curve of the thick film with 1 mol% Sb as a function of the exposition time to an oxygen (a) and carbon monoxide (b) atmosphere, measured at 350 °C.

Also, samples with bismuth addition presented peaks corresponding to the Bi_2O_4 phase (Fig. 2a) whereas samples with antimony showed peaks assigned to the Sb_2O_4 phase (Fig. 2b). Savala et al. found the $Bi_2Sn_2O_7$ phase above 800 °C, which seems to be acting as a molecular sieve allowing only CO gas to react with the sensor surface, imparting selectivity to the sensor.[16] In these samples, this phase was not found because samples were treated at lower temperature.

Fig. 3 shows the TEM photograph of the sample with bismuth oxide. From the figure a medium particle size of 12 nm can be determined. On the other hand, the presence of particles agglomerates was not registered.

Figs. 4–6 show the electric response of pure SnO_2, and Sb_2O_3 or Bi_2O_3 doped SnO_2 thick films, during the oxygen and carbon monoxide exposition at 350 °C. From the curves an important increasing in the resistance of the samples with the oxygen exposition was registered. This behavior is related to the increasing of the intergranular potential barrier height due to the oxygen adsorption. Also, a disminution in the resistance of the sample at large exposition times is related to the possible overlapping of the depletion regions.[17] Bismuth addition favored oxygen diffusion and the sensing response to this gas. On the other hand, when antimony oxide is added, the resistance decreases due to free electrons injected during the Sb^{5+}–Sn^{4+} replacement. A similar

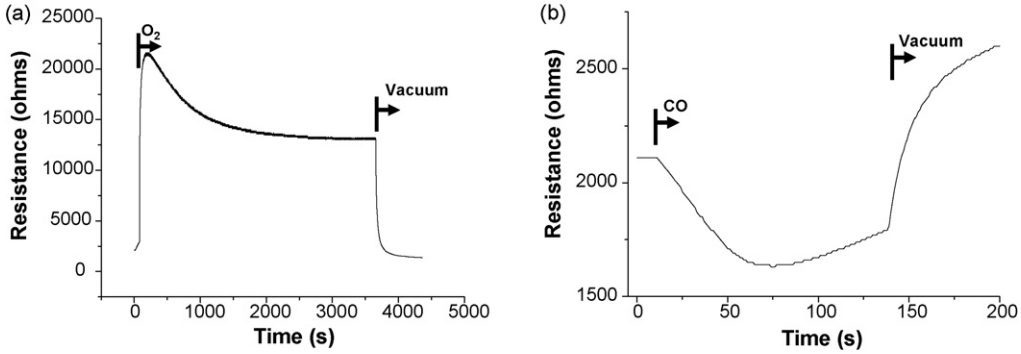

Fig. 6. Resistance curve of the thick film with 1 mol% Bi as a function of the exposition time to an oxygen (a) and carbon monoxide (b) atmosphere, measured at 350 °C.

behavior was also observed by other authors.[15,18] This behavior would justify the lower resistance value observed in the systems with antimony. Also, a notable resistance diminution at large exposition times was registered.

When the films were exposed to reducing gases, such as CO, Figs. 4–6(b), the electrical resistance decreases due to the gas reaction with the previously adsorbed oxygen, reducing the potential barrier height. Undoped samples were more sensitive than doped oxide samples to CO atmospheres.

4. Conclusions

Tin oxide powders doped with antimony and bismuth have been prepared by the polymeric precursor method. Nanoparticles free of agglomerates were obtained after a milling step. Both systems were sensitive to changes in the oxygen and carbon monoxide atmospheres. However, samples with bismuth addition showed a better performance under oxygen atmospheres. The lower resistance of the antimony-doped samples with can be justified considering that the Sb^{5+} occupies a Sn^{4+} position injecting free electrons in the bulk. The apparition of the Sb_2O_4 crystalline phase was confirmed by XRD.

Acknowledgements

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