NANOSTRUCTURED THICK FILM SENSORS FOR CO (g) BASED ON Al DOPED SnO_2

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Abstract

In this work, the aluminium doping of SnO_2 lattice was studied, synthesising a semiconductive nanocrystalline doped material by a gel-combustion method with citric acid as fuel, to be used for thick film sensors to detect CO (g). Aluminium concentration was varied from 1 to 5at%, nanocrystalline powders with crystallite mean size of 8-12 nm and low agglomeration were obtained. The semiconductive material was characterised with X-rays diffraction, energy dispersive electron microprobe and transmission electron microscopy. Nanocrystalline powders were used to prepare conductive pastes with suitable organic solvents employing our own formulations different from those of commercial materials. Pastes were deposited as serigraphic thick films on electronic purity alumina wafers provided with Pt electrodes. Sintering of thick sensing films was performed in a range of medium temperatures to avoid important crystallite growth since it is convenient to maintain the nanocrystalline structure in order to increase sensor sensitivity. Sensors were characterised in mixtures of [CO (g) + air] at temperatures from 300 to 400 °C. Results indicated that aluminium was incorporated in the SnO_2 lattice in low proportions leaving low concentrations of amorphous Al_2O_3 segregated. Sensors showed a high sensitivity to the target gas. In addition, it was also found that the incorporation of aluminium to SnO_2 lowers the sensor operating temperature.

Resumen

En este trabajo de investigación, se estudió el dopado con aluminio de SnO_2, sintetizando el material semiconductor dopado nanocristalino, mediante el método de gelificación-combustión empleando ácido cítrico como combustible, con el objeto de usarlo en sensores de película gruesa para detectar CO (g). La concentración de Al se varió entre 1 y 5at% y se obtuvieron polvos nanocristalinos, con tamaño promedio de cristalitas entre 8 y 12 nm y bajo grado de aglomeración. El material semiconductor fue caracterizado por difracción de rayos X, microsonda electrónica dispersiva en energías y microscopía electrónica de transmisión. Los polvos nanocristalinos fueron usados para preparar pastas conductoras con solventes orgánicos convenientes, empleando formulaciones propias diferentes de aquéllas de los materiales comerciales. Las pastas se depositaron como películas gruesas por serigrafía sobre sustratos de alúmina de pureza electrónica, provistos con electrodos de Pt. El sinterizado de las películas gruesas sensoras se realizó en un rango medio de temperaturas para evitar un crecimiento importante de las cristalitas ya que es conveniente mantener la estructura nanocristalina para aumentar la sensibilidad del sensor. Los sensores fueron caracterizados

en mezclas de [CO (g) + aire] en un rango de temperatura entre 300 y 400 °C. Los resultados indicaron que el aluminio se había incorporado a la red del SnO_2 en bajas proporciones quedando, además, muy bajas concentraciones de Al_2O_3 segregada amorfa. Los sensores mostraron una alta sensibilidad al gas a detectar. Además, se encontró que la incorporación del Al al SnO_2 permitió reducir la temperatura de operación del sensor.

Introduction

Tin dioxide (SnO_2) is one of the most studied metal oxides because of its interesting properties and applications. Perhaps the most important of them are: coatings as transparent conductors and the fabrication of sensors for reducing gases like CO, H_2 or CH_4. The sensors response is based on measurements of surface electrical resistance, in comparison with the resistance value in air, in the presence of the gas to be detected. Sensor response is defined as the ratio $S = R_{air}/R_{air+gas}$. This variation is due to the reducing gas reaction with the O^- (oxygen adsorbates on the SnO_2 surface, formed in air at the typical working temperatures, 300-500°C, which reduce the potential barrier produced by the adsorbates limiting the electrons movement).

Yamazoe et al. [1] proved that the sensors response increases significantly if the crystallite size (D) of the nanocrystalline tin dioxide is about twice the adsorption depth, 2L (L is the depth of the space-charge layer), of oxygen adsorbates. This fact means that the sensor performance improves not only when D decreases but also if L increases, since a major proportion of material takes place in the reaction of oxygen adsorbates with the target gas even if the grain size is not excessively small.

Besides, Yamazoe et al. have found that doping with trivalent cations enables to increase the response since the carriers concentration is reduced and consequently, L increases [1]. As an example of this phenomenon, they showed Al_2O_3 doped SnO_2 sensors which were built for H_2 detection but they did not report data on CO(g) sensing. It is important to point out that these authors have prepared sensors material by coprecipitation, followed by calcination at high temperature. They could not evaluate the Al solubility in the SnO_2 lattice, in spite of reporting that it had to be lower than 1% as determined by resistivity measurements.

The aim of this work was to study the possibility of increasing the Al solubility in the SnO_2 lattice because this fact could improve the gas sensor sensitivity since carriers concentration could decrease even more. Nanocrystalline SnO_2 was synthesised by the nitrate-citrate gel-combustion method [2, 3] since the employment of similar routes in other systems made possible to increase the solubility limit of the dopant, in a metastable condition, while retaining the homogeneity in composition of materials [4, 5]. This is due to the fact that the powder is obtained by the rapid disintegration of the homogeneous gel, so the system cannot evolve towards its equilibrium state.

Even though Al can be introduced in SnO_2 lattice in low proportions, results of the present work show that the solubility limit of Al in SnO_2 can be extend by the use of the gel-combustion method in comparison with coprecipitation. Crystallite sizes were considerably small, between 8 and 12 nm. Sensors showed a high sensitivity, between 8 and 10 for 200 ppm of CO in air. It has also been found that the incorporation of Al to SnO_2 enables to decrease the working temperature.

Experimental Procedure

1. Powders and thick films preparation

SnO_2 with 0, 2 and 5 at% Al powders have been obtained by the nitrate-citrate gel-combustion method [2,3]. The employed raw materials were pure metallic Sn and Al, dissolved in diluted HNO_3. The use of chlorides of both metals has been avoided because Cl^- ions, if retained, can damage the sensors performance. Citric acid was added in a proportion of six acid moles per metal mole and neutrality was attained with NH_4OH. The solution was then thermally concentrated at a temperature of 80°C on a heating plate until a dark gel was obtained. Finally, at temperature above 250°C, the dried gel burned due to a vigorous exothermic reaction between nitric and citric acids. The ashes produced by combustion were calcined for 1 hour at 700°C.

Pastes were prepared with the synthesised powders and organic solvents to get thick films for sensors, painted on electronic purity Al_2O_3 substrates, provided with Pt contacts, dried at 100°C with a final sintering for an hour at 700°C.

2. Powders and thick films characterisation

Powders and films were studied by X-Ray diffraction (XRD) with a Philips PW 3710 diffractometer, employing Cu-Kα radiation to identify phases and to determine the crystallites size. For this last evaluation the Scherrer equation: $D = 0.9\ \lambda / \beta \cos\theta$ was used, where D is the crystallite size, λ is the wave length of the incident radiation (1.5418 Å for Cu-Kα radiation), β is the half maximum peak width and θ is the peak position. The instrument width, necessary to correct β, was evaluated employing a Al_2O_3 with a mean crystallite size of 25 μm.

Powders morphology was studied by Transmission Electron Microscopy (TEM) with a Philips CM200 electron microscope. Chemical composition and Al distribution were evaluated by energy dispersive electron microprobe (EDS) using a EDAX CM20 microprobe.

3. Sensors characterisation

To evaluate the sensors performance, the electrical resistance in synthetic air and in a diluted solution of 200 ppm of CO in synthetic air was measured with a 617 Keithley electrometer between 300 and 400°C. In both measurements the gas flow was 200 ml/min.

Results and Discussion

XRD patterns of the studied materials did not present any shift lattice parameters with increasing doping concentration, suggesting that aluminium solubility in SnO_2 was low. In spite of that, Al_2O_3 peaks were not observed.This fact was assigned to the low doping concentration but, experiments with high Al concentrations suggested that it was more probable that this phase had remained amorphous. The powders crystallite size resulted between 8 and 12 nm, considerably smaller than that obtained for coprecipitated material, Yamazoe et al. [1]. As an example, Figure 1 shows the diffractogram corre-

sponding to undoped SnO_2 powder exhibiting a crystallite mean size of 12 nm. It was also found that the crystallite size was slightly reduced by an increasing of aluminium content. The thick films exhibited similar crystallite size to that of powders because the calcination temperature was relatively low.

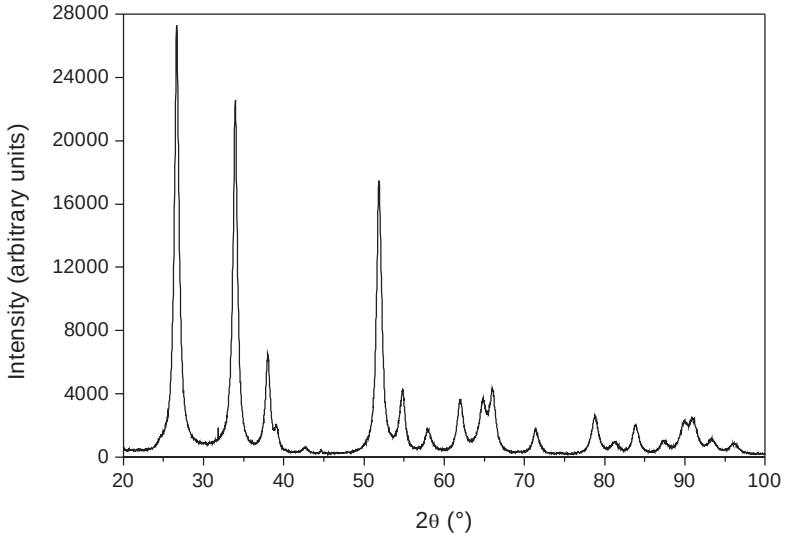

Figure 1: *Diffractogram corresponding to non-doped SnO_2 powder.*

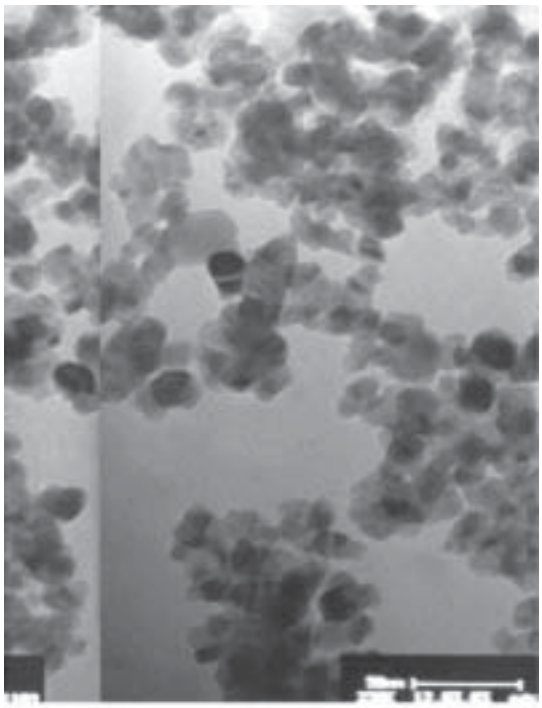

Figure 2. *TEM micrograph of nanocrystalline 5 at% Al doped SnO_2 powders (bright field).*

TEM studies enabled to confirm the crystallite size as determined by XRD. For example, the Figure 2 shows a TEM bright field image of SnO_2 – 5 at% Al powder with a crystallite size of 10 nm. Besides, it is important to point out that powders are formed by spherical particles, characteristic of powders obtained by gel-combustion method with a very low state of agglomeration. The EDS study of powder demonstrated that a part of the Al is not incorporated into the SnO_2 lattice since small segregated Al-riched regions were observed as well.

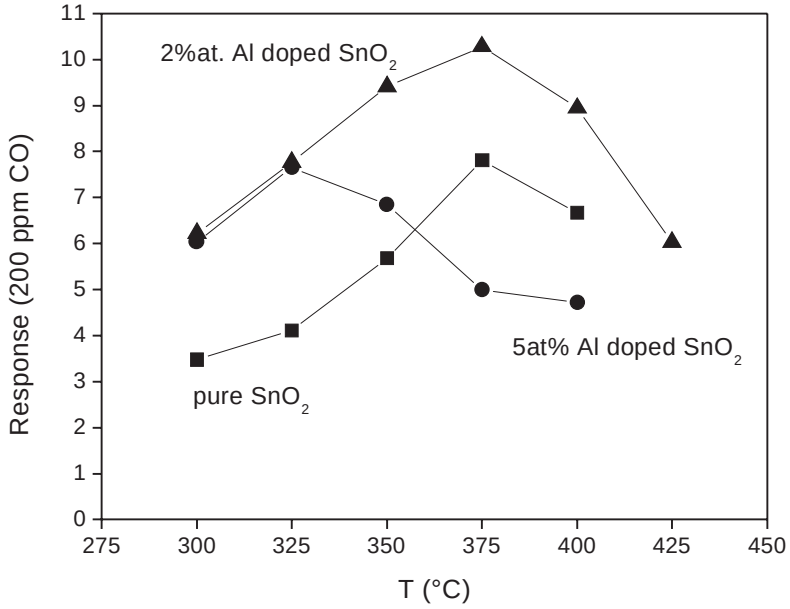

Figure 3*. Response (for 200ppm CO + air) of thick film pure SnO_2 and of doped - 2 and 5 at% Al doped SnO_2 sensors.*

To evaluate the Al solubility in SnO_2 lattice, the variation of the electrical resistance with the Al concentration was measured. The resistance of undoped SnO_2 films was about 10^7 Ω. The resistance of 0.2 at% Al doped SnO_2 films resulted within the same magnitude order but ~3 times more resistive while the 5 at% Al doped SnO_2 films exhibited a difference of more than one order of magnitude higher. This continuos increase of resistance is consistent with the decrease of the carriers concentration and with the increase of L (which is possible if Al is incorporated into the SnO_2 lattice). Yamazoe et al. [1] reported a higher resistance variation for coprecipitated powders. These authors found a resistance change three orders of magnitude higher for 1 at% Al doped SnO_2 but they did not observe an important resistance increase with higher doping concentration. This fact was associated to Al_2O_3 segregation even for very low Al concentrations, concluding that the Al solubility limit in SnO_2 was lower than 1at%. The considerable difference in the behaviour of materials according to their synthesis (coprecipitation or gel-combustion) suggests that the gel-combustion method enables to increase significantly the Al solubility in SnO_2.

In Figure 3**,** the response of pure, 2 at% and 5 at% Al doped SnO_2 is plotted versus temperature (°C) for 200 ppm CO in air. If pure SnO_2 sensors were compared with 2 at%

Al doped SnO_2 sensors, it was observed that the latter exhibited a higher sensitivity for the whole considered temperature range. The maximal sensitivity resulted: ~8 for non-doped SnO_2 and 10 for 2 at% Al doped SnO_2. The optimal working temperature (T_w) resulted ~375ºC for both types of sensors. However, 5 at% Al doped SnO_2 sensors exhibited a lower optimal working temperature: 325ºC and their sensitivity resulted of 8. This decrease of T_w may be assigned to a shift of the formation temperature characteristic of adsorbates O^- by the incorporation of Al in the SnO_2 lattice. This phenomenon has been reported in the technical literature for doping with trivalent elements like Bi [6].

Conclusions

Results indicate that the gel-combustion method enables to increase the Al solubility in SnO_2 in comparison with the coprecipitation method and, at the same time, it reduces the crystallite size. Both facts improve the sensitivity of the sensors built with the gel-combustion synthesised materials as it was proved with the obtained thick films sensors. The response of the sensors reported in this work was considerably high, between 8 and 10 for 200ppm CO in synthetic air. Furthermore, it is possible to reduce the temperature of operation of sensors by increasing the Al concentration.

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