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H_2S-Sensing Properties of Nanocrystalline SnO_2 Powder Produced by Mechanochemical Milling

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Abstract Nanocrystalline tin dioxide powders have been produced by mechanochemical milling followed by heat treatment and subsequent preparation of SnO_2 thick-films. X-Ray powder diffraction was used to investigate the structure of the materials. Crystallite sizes in the range from 15 to 20 nm (determined from XRD line broadening) were obtained. Heat treatment of the milled powder resulted in the formation of tetragonal and orthorhombic SnO_2 phases, which was confirmed by XRD analysis. The optimal parameters for the milling time, rotation speed and heat treatment were determined before this work and used in the current work. The gas-sensing properties of tin dioxide can be modified by adding of La_2O_3 as surface catalyst. La_2O_3 was added by dipping sintered tin dioxide films into varying concentrations of $La(NO_3)_3 \cdot 6H_2O$ solution. The response of the prepared thick-films to H_2S, in the concentration range from 0.5 to 20 ppm in air, revealed that at a temperature of 250 °C, undoped SnO_2 sensors respond to H_2S much stronger than La_2O_3-doped SnO_2 sensors do.

Introduction

Nanocrystalline powders can be used for the preparation of semiconductor gas sensors, if they have a grain size of less than 20 nm. In gas sensing surface reactions are of importance, requiring a high surface of the sensor material. The synthesis of ceramic powders with a high surface area by mechanical milling and subsequent heat treatment comprise the content of mechanochemical processing (MCP) [1]. Metastable nanocrystalline structures can be obtained in powder form during the mechanical milling process, where the powder particles are periodically trapped between colliding balls and plastically deformed or fractured [2]. A chemical reaction can take place either during the milling process or in the furnace during the heat treatment. The main advantage of the MCP method is that the synthesized powder has a large surface area and it is possible to control the grain size.

The important factor, associated with the sensing properties, is the grain size and geometry of connection [3]. For the most conventional tin dioxide sensors, the grain size is considerably greater than the depth of the space charge region and electrical conduction is governed by the grain boundaries. If the grain size is much less than 15 nm, the sensitivity to a reducing gas may be significantly increased.

Most of the reports, related to a La_2O_3-doped SnO_2 sensor, have described a gas response either to the chlorinated methanes [4], trimethylamine [5], or H_2 [6], but the sensing properties to hydrogen sulfide have not been sufficiently studied. Therefore, one aim of investigation was to measure the sensing properties of SnO_2 thick film with added La_2O_3 oxide as catalyst on the surface.

Experimental

Nanosized SnO_2 powder particles were produced by mechanochemical synthesis, where the milling process was performed at room temperature in a centrifugal type mill. The starting materials (2.3 g of $SnCl_2$, 0.9 g of $Ca(OH)_2$ and 15.5 g of $CaCl_2$) were sealed in a non-metal vial and milled for 1h with a rotation speed of 175 rpm. The ball-to-powder mass ratio was 9:1. The chemical reaction induced was

$$SnCl_2 + Ca(OH)_2 \rightarrow SnO + CaCl_2 + H_2O. \quad (1)$$

The milled powder was subsequently heat treated at 400 °C for 1h in air, to induce the reaction

$$SnO + 1/2(O)_2(g) \rightarrow SnO_2. \quad (2)$$

Removal of the $CaCl_2$ by-product was carried out with deionised water. The washed powder was dried in a furnace at 65 °C for 8h and characterized by the total pore volume of 0.22 ml/g for a measured BET particle size of 78 m^2/g. No contamination of the powder during milling was found.

A Philips PW 1830 X-ray powder diffractometer with Cu-K_α radiation was used to follow the crystallisation of the powder. The SnO_2 crystallite size was determined using Scherrer's equation [7]. The specific surface area and porosity of the synthesized powders were measured with a Coulter Omnisorp 100 CX, using a N_2 gas adsorption method at 77K.

Thick-film gas sensors were prepared by hand coating of a paste, the SnO_2 powder mixed with an α-terpineol-based solvent, over the Au sensing electrodes on the Al_2O_3 substrate. Subsequently the substrates were sintered at 700°C for 2h in air. The surface modification of the sensor was performed by dipping the coated substrates in a lanthanum nitrate solution followed by decomposition at 700°C for 1h in air. To get the compositions of 0.1 and 1 at % La_2O_3 on the surface, 8.6 mg and 86 mg of $La(NO_3)_3 \cdot 6H_2O$ powder were added respectively to the 25 ml of distilled water. The mass of La_2O_3 powder was accounted per 1 g of SnO_2. Pt wires were attached on the pads of the heater and sensing electrodes by using an Au-paste and heat treatment. The gas response tests were carried out with a PC-controlled measuring system. The test gas concentrations were in the range from 0.5 to 25 ppm, using a gas flow controller unit with an air flow rate of 0.5 l min^{-1}. Sensitivity, S, to gas is defined as

$$S = (R_{air} - R_{gas})/ (R_{air}) \cdot 100\%, \quad (3)$$

where R_{air} is the sensor resistance in clean air and R_{gas} is the resistance in the test gas.

The microstructure and grain size were examined using a Field Emission Scanning Microscope JSM-633 OF (FESEM).

Results and discussion

As it was noted earlier, large quantities of $CaCl_2$ were used during the milling process. The purpose of the present investigation was to encapsulate the separated SnO particles by salt stopping their further growth.

The XRD pattern of a milled powder after heat treatment is shown in Fig. 1. Heat treatment below 300 °C did not cause the appearance of any diffraction peaks. There is clear evidence that chemical reactions were completed: two peaks of tetragonal SnO_2 can be seen at 26.6 and 33.9 (2Θ°) respectively. The third tetragonal peak is not seen at 51.8 (2Θ°), because very probably all the particles are surrounded by a thick layer of $CaCl_2$.

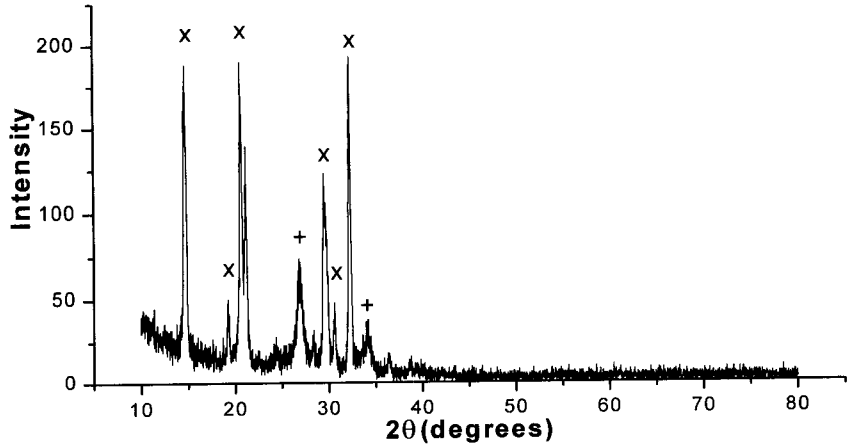

Fig. 1 X-ray diffraction pattern of the powder milled for 1h and heated at 400 °C (1 h) in air. The distribution of (+) SnO_2 tetragonal and (-) $CaCl_2$ peaks is shown.

After removal of the $CaCl_2$ mass and drying, the synthesized powder has the XRD pattern presented in Fig. 2. The stable tetragonal phase is clearly present in the larger proportion while much less of the orthorhombic phase is found. It may be concluded that the crystallization has succeeded at this low temperature of 400 °C. The three main peaks are located at 26.6, 33.9, and 51.8 (2Θ°) respectively and they show a high degree of crystallinity. The crystallite size, D, was calculated according to the Scherrer equation,

$$\Delta(2\Theta) = K\alpha/(D\cos\Theta), \quad (4)$$

where $\Delta(2\Theta)$ is the width at half-maximum intensity (in radians) and Θ is the Bragg angle of the (110) diffraction peak, K is constant, depending on the line shape profile, (currently K=1), α is the wavelength of the X-ray source and D the crystallite size.

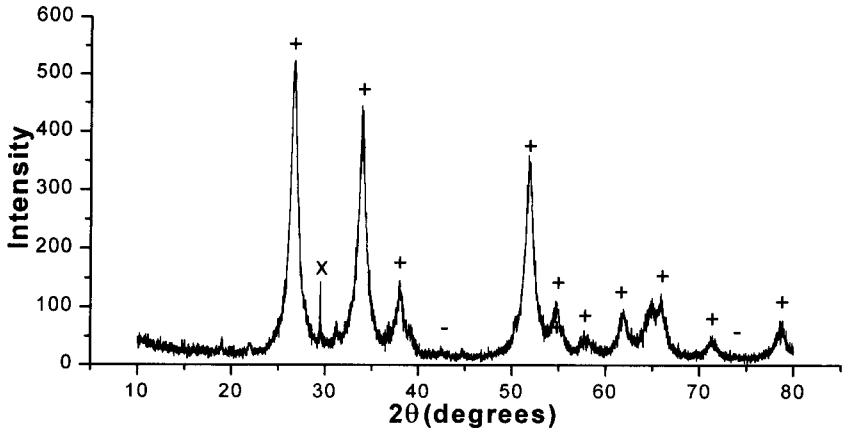

Fig. 2 X-ray diffraction pattern of the milled (for 4 h), heat treated (at 400 °C for 1 h) and washed powder with the typical distribution of (+) tetragonal, and (-) orthorhombic SnO_2 phases. The sharp peak (x) at 29.4 ($2\Theta°$) indicates residual $CaCl_2$.

The prepared thick films revealed moderately good response and recovery times. Fig. 3 represents a typical response of a SnO_2 thick film sensor operating at 250 °C. As it can be noticed, the response time (at the level of 0.9) is about 10 min.

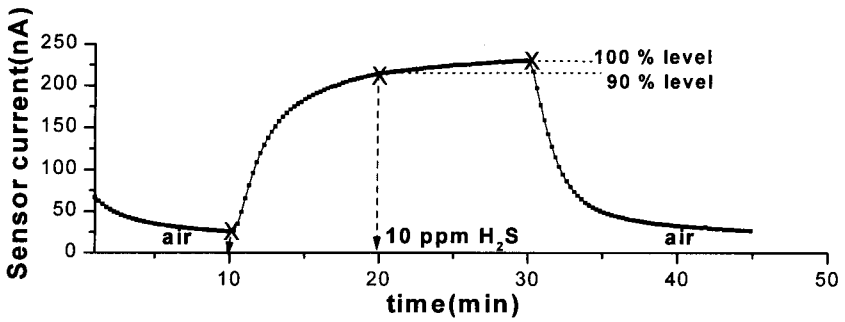

Fig. 3 Response of SnO_2 thick film sintered at 700 °C for 1 h to 10 ppm of H_2S gas in air.

The maximum sensitivity to H_2S was achieved, with S = 300, upon exposure to 20 ppm of H_2S (Fig. 4). The response of an SnO_2 sensor that was doped with 1.0 at % La_2O_3 was not so high (S = 30).

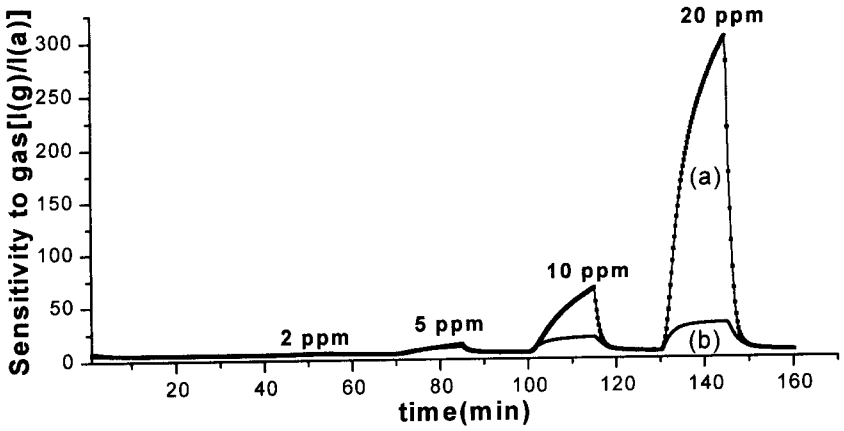

Fig. 4 Dynamic response of undoped SnO_2 (a), and 1.0 at % La_2O_3-doped SnO_2 (b) thick films to increasing H_2S concentrations in air.

Very likely neither the undoped nor the doped sensors have sufficient porosity and consequently the gas response time is long. The milling process itself contributes to creation of surface hydroxyl groups and after the subsequent heat treatment, even at high 400 °C, nevertheless, there remains a considerable surface hydroxyl concentration [8]. Thus, another possible factor, affecting the sensitivity to gas, is the formation of strong Sn-O-Sn bonds and their influence on the H_2S adsorption.

Conclusions

Mechanochemical processing of predetermined stoichiometric amounts of $SnCl_2$ and $Ca(OH)_2$ in an excess of $CaCl_2$ resulted in the formation of the desired mass of SnO. After separation, moderately agglomerated particles were oxidised to SnO_2 powder with the tetragonal phase. The results obtained in the present work suggest that the response of SnO_2 thick film sensors to H_2S gas may be improved by 1) synthesising powder grains much smaller than 15 nm, 2) using such type of chemical reactions, which does not produce water, and 3) removing the salt matrix by a non-aqueous solvent instead of distilled water.

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