Sensors and Actuators B 140 (2009) 190–195

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Properties and mechanism study of SnO_2 nanocrystals for H_2S thick-film sensors

H. Liu [a], S.P. Gong [a], Y.X. Hu [a,b], J.Q. Liu [a], D.X. Zhou [a,*]

[a] Engineering Research Center for Functional Ceramics of the Ministry of Education, Department of Electronic Science & Technology, Huazhong University of Science & Technology, No. 1037 Luoyu Road, Hongshan District, Wuhan City 430074, PR China
[b] Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan City 430062, PR China

ARTICLE INFO

Article history:
Received 8 January 2009
Received in revised form 15 March 2009
Accepted 13 April 2009
Available online 3 May 2009

Keywords:
Tin oxide
Nanocrystals
Gas sensors
H_2S
Thick film

ABSTRACT

Two different laboratory-synthesized SnO_2 nanocrystals using gel combustion method and hydrothermal method were used for the fabrication of nanocrystalline thick-film sensor samples through screen-printing technique. Their sensitive properties toward low concentrations of H_2S gas in air (0.7–100 ppm) at 25–250 °C and microstructure features were examined for comparison. Interestingly, both of the two different samples showed maximum response at about 150 °C, and the response (S) as a function of H_2S concentration (P_{H_2S}) was approximately fit to $S \propto P_{H_2S}^{0.6}$. Theoretical calculation based on the surface chemistry suggests that at 150 °C, oxygen might be ionosorbed on SnO_2 surfaces predominantly as O_2^- and O^- with the proportion ratio of 1:2. It was found that the sensor sample based on SnO_2 nanocrystals produced by gel combustion method had higher response and shorter response time, which might be attributed to the more porous nanocrystalline (about 50 nm in size) microstructure than the one prepared from hydrothermal-synthesized SnO_2 nanocrystals, where smaller SnO_2 nanocrystals (about 12–13 nm) are densely packed and agglomerate into large entities of about 2–3 μm in size.

1. Introduction

Metal oxides are emerging as important materials for their versatile properties such as high-temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity and semiconductivity [1–3]. Semiconducting oxides such as SnO_2, ZnO, WO_3 and In_2O_3 are frequently used in gas sensors for the detection of reducing or oxidizing gases owing to the high sensitivity, fast response, simple design and low cost. In this field, much effort has been made to improve the sensing properties toward low concentrations of pollutant gases especially at lower temperatures through structural and/or chemical modification of metal oxides [4]. For this purpose, metal oxide nanocrystals, both in thin- and thick-film forms, attract increasing attention due to the larger surface-to-volume ratio as well as crystal (grain) size effect [5–8].

For instance, SnO_2 nanocrystals produced via both chemical and physical routes such as sol–gel process [9–11], laser ablation techniques [12–14], mechanochemical milling [15,16], have been deposited in thick films and showed enhanced response behavior toward pollutant gases like NO_2, Cl_2, O_3, H_2S and CO at ppm or sub-ppm level, which also benefits from the addition of noble metals like Pd, Pt, Au and Ag or specific "sensitizer" like CuO for H_2S gas. 3 at.% Cu-doped nanocrystalline SnO_2 (25 nm in size) thin films fabricated by sol–gel dip coating technique in our previous study [17] were highly sensitive to H_2S gas at room temperature and the response was 3648 toward 68.5 ppm of H_2S. Vaishampayan et al. [18] reported 1 at.% Fe-doped SnO_2 nanocrystals synthesized by the modified Pechini citrate route capable of detecting 10 ppm of H_2S at room temperature, and the peak response toward 200 ppm of H_2S occurred at about 200 °C.

However, some recent studies on the sensing properties of pure nanocrystalline SnO_2 thin films toward H_2S [19] and H_2 [4,20] seemed to contradict the general trend that higher sensitivity is to be expected for smaller crystals, and it was therefore concluded that small size of crystals was an essential but not sufficient condition for the achievement of maximum gas sensitivity and fast response. While for more porous thick films, where the starting oxide nanocrystals are usually dispersed in a paste and have to undergo heating treatment higher than 500 °C, the higher tendency of nanocrystals to grow and/or agglomerate is an important issue deserving ongoing discussion, but so far its influence on the properties of nanocrystalline thick-film sensors has rarely been reported.

On the other hand, the sensing mechanism of semiconductor gas sensors remains far from being understood satisfactorily. For example, the power law dependence of the response on gas concentration has long been known empirically without theoretical understanding, where the exponent value for SnO_2 gas sensors were reported to be 0.5 for H_2 at 350 °C [20], 0.5 and 0.75 for CO at 445 °C [21] and 200 °C [22] respectively. Kolmakov et al. [23] also found that the exponent value ranges between 0.48 and 0.58 for individual SnO_2 nanowire upon CO exposure at 200–280 °C. Obviously, careful study of the surface reaction underlying the sensing mechanism

* Corresponding author. Tel.: +86 27 87557447; fax: +86 27 87545167.
E-mail address: huan@mail.hust.edu.cn (D.X. Zhou).

0925-4005/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2009.04.027

is needed for further improvements of nanocrystalline gas sensors, where the variances in material composition, fabrication process and testing condition should be reduced to the minimum.

In this context, we investigated the H_2S-sensing behaviors of thick-film gas sensors prepared from two laboratory-synthesized SnO_2 nanocrystals using gel combustion method and hydrothermal method respectively. The similarities and differences between the properties of the samples were interpreted in view of sensing mechanism and microstructure features, so as to provide both experimental data and theoretical basis for the development of high-performance nanocrystalline gas sensors.

2. Experimental

Thick-film sensor samples were fabricated through screen-printing technique with two different kinds of SnO_2 nanocrystals previously synthesized in the laboratory by gel combustion method [24] and hydrothermal method [25], the average crystal size being 27.9 and 4.1 nm respectively. The starting nanocrystals were slightly ground and mixed with terpineol-based vehicle consisting of ethyl cellulose and dibutyl phthalate to form a viscous paste. A small amount of glass frit was also added in order to improve the film strength and the adhesion to the substrate. The paste was printed on planar 96%-alumina ceramic substrates bearing interdigited Ag–Pd electrode, dried at 120 °C and then fired in air at 700 °C for 1 h.

The response of the thick-film sensor samples toward H_2S gas in air in the range 0.7–100 ppm at 25–250 °C was measured by a gas-sensing characterization instrumentation (QMCS-I, HUST, China) where the samples were connected in series with a signal resistor (R_o) and mounted over the test-board in a chamber of 0.7 L volume with controlled temperature and humidity. The static method was employed where the gas concentration was determined by the volume ratio. For the electrical measurement, the voltage of 5 V was applied in the circuit and the signal voltage (V_o) of the signal resistor was continuously recorded when the sensor sample was upon gas exposure. The resistance (R) of the sample can be calculated by

$$R = \frac{5 - V_o}{V_o} \times R_o \quad (1)$$

The gas response (S) is defined as

$$S = \frac{R_a}{R_g} \quad (2)$$

where R_a is the sensor resistance in clean air and R_g the resistance in the test gas at the operation temperature at steady state.

The Brunauer–Emmett–Teller (BET) specific surface area of the thick films were calculated using N_2 adsorption/desorption measurements taken with an auto-adsorption analyzer (ASAP 2020, Micromertitics, USA). Both the surface and cross-section morphologies of the thick films were observed by scanning electron microscope (SEM) (Sirion 200, FEI, Holland).

3. H_2S gas response

Fig. 1 shows the response of the two thick-film sensor samples toward H_2S gas at different temperatures. It can be seen that both of the two different samples showed maximum response at about 150 °C (that is the optimal operation temperature). The response is higher for the sensors based on SnO_2 nanocrystals synthesized by gel combustion method. The response curves of the two samples toward 20 ppm of H_2S in air when operated at 150 °C are given in Fig. 2, where the whole testing-cycle time was set to be 400 s. Obviously, the sample prepared from SnO_2 nanocrystals produced by gel combustion method has shorter response time as well as higher response than the one based on hydrothermal-synthesized SnO_2 nanocrystals.

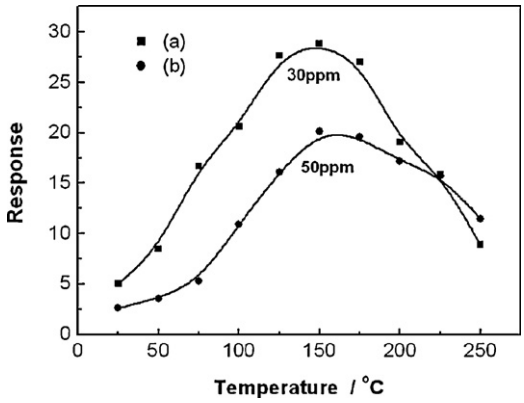

Fig. 1. Response toward H_2S gas at different temperatures: (a) SnO_2 nanocrystals produced by gel combustion method and (b) hydrothermal-synthesized SnO_2 nanocrystals.

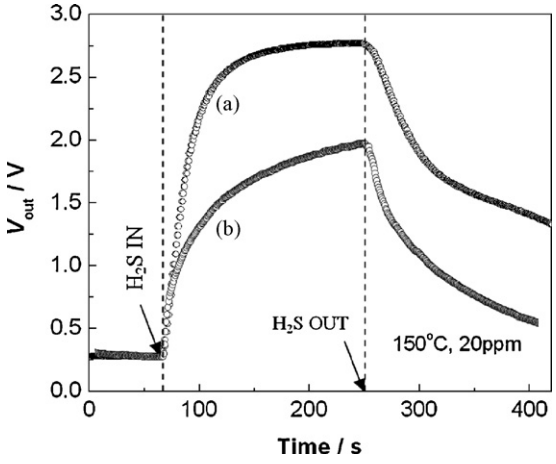

Fig. 2. Response curves toward 20 ppm of H_2S at 150 °C: (a) SnO_2 nanocrystals produced by gel combustion method and (b) hydrothermal-synthesized SnO_2 nanocrystals.

Dependence of the response on H_2S concentration is plotted on a log–log scale as shown in Fig. 3. Over a wide range of H_2S concentration, the sample based on SnO_2 nanocrystals synthesized by gel combustion method has higher response and is able to detect H_2S as low as 0.7 ppm. Interestingly, when the response (S) as a function

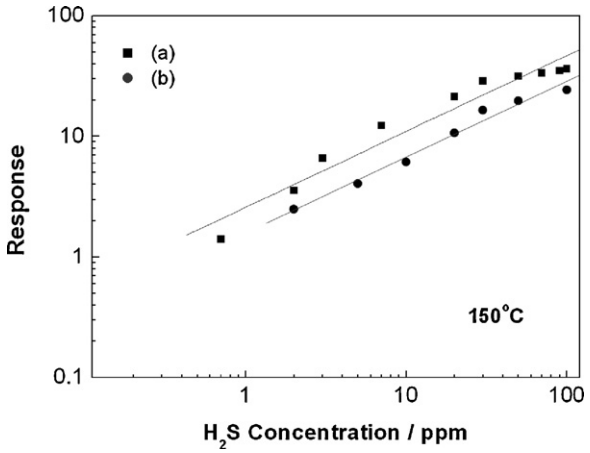

Fig. 3. Dependence of the response on H_2S concentration: (a) SnO_2 nanocrystals produced by gel combustion method and (b) hydrothermal-synthesized SnO_2 nanocrystals.