Journal of Solid State Chemistry 144, 86–90 (1999)
Article ID jssc.1998.8122, available online at http://www.idealibrary.com on IDEAL®

Application of a Modified Ultrasonic Aerosol Device to the Synthesis of SnO_2 and Pt/SnO_2 for Gas Sensors

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Received July 10, 1998; in revised form November 23, 1998; accepted November 25, 1998

SnO_2 and Pt/SnO_2 powders were synthesized with a modified ultrasonic aerosol pyrolysis device. The advantages of this new method were tested by comparison of pure SnO_2 powders synthesized by conventional and modified aerosol methods. Then, the synthesis of SnO_2 with Pt was carried out by this new method. The droplet evaporation and pyrolysis processes induce the formation of materials with a fine microstructure that exhibit, after annealing, a high sensitivity to ethanol or CO in air. In the Pt/SnO_2 powders, platinum aggregates dispersed onto the SnO_2 grains improve the sensitivity of SnO_2 powders when the sample is annealed at 700°C. Therefore, a Pt/SnO_2 sample submitted to such thermal treatment is a good candidate for CO and C_2H_5OH detection due to its sensitivity to both gases. © 1999 Academic Press

INTRODUCTION

At present thin films and ceramics based on nanocrystalline tin oxide are widely used as materials for solid-state gas sensors (1, 2). SnO_2 is used as an active element for flammable and toxic gas detection since its near-surface-region conductivity is very sensitive to the atmosphere. It interacts with reducing gases by surface adsorption, leading to a modification of the free electron density on the surface. A small amount of catalytic metal, such as Pt, Pd, Cu, and Ag, dispersed on the surface of SnO_2, increases sensitivity and selectivity toward specific gases (3–5), probably due to the catalytic effect and to the induced microstructural changes (6). The material is held at a constant temperature and its resistance is monitored and correlated with specific gas concentrations. Conductivity variation of these materials depends largely on their morphological features and the trend is to control the synthesis of these materials. In this sense, new methods for the preparation of nanoscale tin oxide particles are being developed today (7). The main challenge is to control the size and shape of the SnO_2 grains and to obtain a fine and homogeneous dispersion of the catalytic metallic aggregates onto the SnO_2 grains.

We present, in this paper, the synthesis, microstructural characterization, and electrical properties of SnO_2 and Pt/SnO_2 powders prepared by a modified ultrasonic aerosol pyrolysis process. As a first step, the potential advantages of this modified procedure have been assessed by comparison of pure SnO_2 powders synthesized by both conventional and modified aerosol processes. Then, the synthesis of Pt/SnO_2 powders by this new method was carried out.

EXPERIMENTAL

The pyrolysis of an aerosol produced by ultrasonic excitation of a precursor solution has been widely used in the preparation of oxides (8–10). The synthesis method described in this work is similar to conventional ultrasonic aerosol pyrolysis used in SnO_2 preparation (11, 12), but slight modifications are introduced in the aerosol generation zone. Figure 1 is a schematic diagram of the new ultrasonic aerosol pyrolysis device. In this device the liquid solution to be sprayed is contained in a glass conic vessel, which is introduced into another vessel filled with water. The bottom of this last vessel is fitted with a piezoelectric transducer with a resonance frequency of 850 kHz. By this method we have synthesized pure SnO_2 and Pt/SnO_2 powders. In the case of pure SnO_2, the precursor solution was obtained from $SnSO_4$ dissolved with citric acid in distilled water. Complete dissolution was reached by addition of a very small amount of H_2SO_4. The solution was diluted up to 0.04 M. One percent Pt-doped tin oxide powders were synthesized, adding the necessary amount of a solution of platinum acetylacetonate [$Pt(acac)_2$] dissolved in acetylacetone (0.01 M) to the tin solution. The two solvents are not miscible but the ultrasonic shaking allows us to obtain a very fine emulsion between platinum and tin solutions. In both cases, the aerosol so generated was conveyed by purified air ($Q_g = 7$ liters/min) to the tubular furnace at 900°C. Thus, the solvent evaporated, leading to the formation of

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0022-4596/99 $30.00

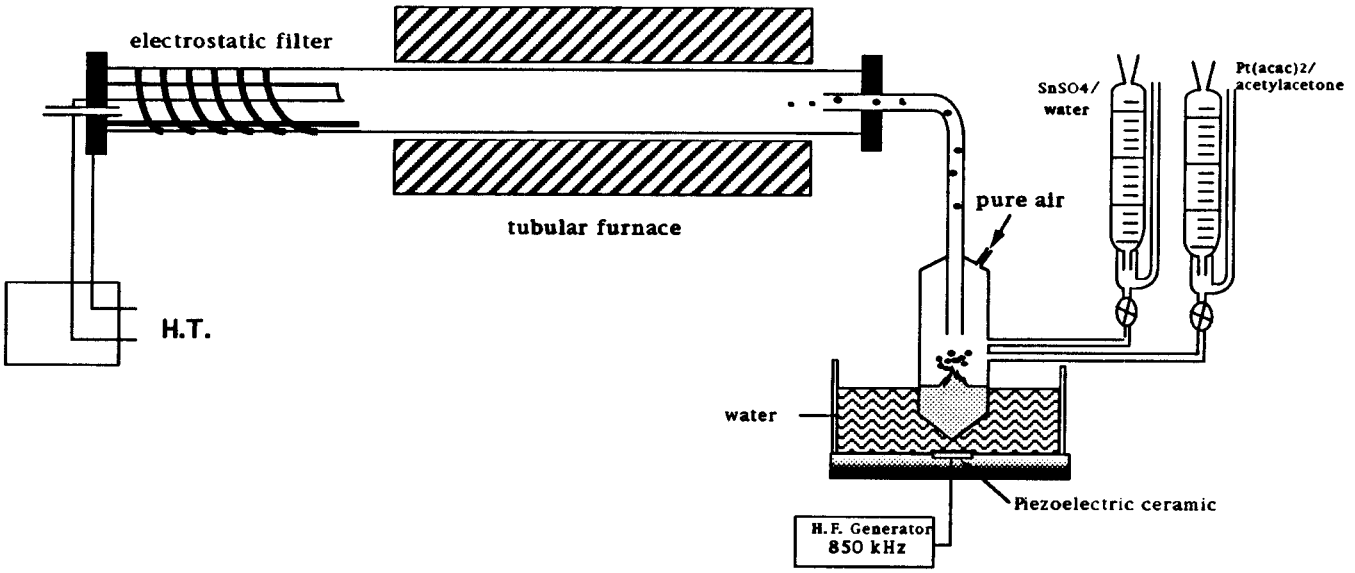

FIG. 1. Schematic diagram of the new ultrasonic aerosol pyrolysis device.

submicrometer oxide particles which are collected outside the furnace with an electrostatic filter (*in situ* samples).

Pellets of *in situ* samples, obtained by cold pressing (3000 kg/cm^2), were annealed for 4 h at 700 or 800°C in air, to stabilize the microstructure and to study the influence of annealing on the electric properties.

Samples were characterized by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer (Cu$K\alpha$ radiation) and by energy-dispersive spectroscopy (EDS) on a Link AN 10000 system. The crystallite average size was deduced from the width of XRD maxima by applying the classic Scherrer equation. Morphology and particle size were analyzed by both scanning electron microscopy (SEM) on a JEOL JSM 6400 microscope and transmission electron microscopy (TEM) on a JEOL 2000 FX microscope.

Electrical measurements were performed on annealed samples. Gold electrodes were deposited by vacuum evaporation. The conductance was measured as a function of both temperature (100–500°C) and surrounding atmosphere (pure air, air/80 ppm C_2H_5OH, and air/300 ppm CO). Several alternate thermal cycles were performed by increasing and decreasing the temperature for each sample and gas mixture. The conductance measurements were carried out by decreasing the temperature from 500 to 100°C (5°C/min). The sensitivity S was determined according to the following expression: $S = (G - G_0)/G_0$, where G and G_0 stand for the conductance under polluted and pure air, respectively.

RESULTS AND DISCUSSION

The characterization of samples by EDS shows that the *in situ* samples contain residual sulfur. It suggests that, although the synthesis temperature is high enough (900°C), the sulfate does not decompose totally, because the precursor remains at such temperature for only 2 s. Thus, a S/Sn atomic ratio of 0.04 is observed on *in situ* samples, which decreases to 0.01 when the samples are annealed at 700°C. No sulfur is detected in samples annealed at 800°C. On the other hand, the Pt/SnO_2 system shows a 1.3 at.% Pt as detected by EDS, similar to the concentration present in the precursor solution.

The X-ray diffraction patterns of *in situ* and annealed samples showed clear maxima which can be assigned to the cassiterite phase (13). Maxima corresponding to metallic Pt are not observed, probably due to the small amount of Pt present in the samples. The crystallite sizes deduced from the XRD maxima for cassiterite are collected in Table 1. The crystallite size increases from 10 nm for *in situ* samples to 12–20 nm when the sample is annealed at the different temperatures. Similar results were obtained in Pt-doped an undoped SnO_2 samples (Table 1). The SnO_2 crystallite growth is not affected by the presence of a small amount of Pt. It is worth mentioning that, in the case of Pt/SnO_2 thin films (14) or Pd/SnO_2 powders (15) synthesized by the conventional pyrosol method, a decrease in crystal size is observed as Pt or Pd is introduced, although the metal concentration employed by these authors is higher than that used in the present work. On the other hand, the formation process of the material in our case is quite different from such thin film preparation (14). After evaporation of the solvent in the aerosol droplets, tin sulfate decomposes directly, without passing through a gaseous phase, to SnO_2, whereas Pt aggregates are formed from a gaseous phase (evaporation of the platinum acetylacetonate, due to its high

TABLE 1
Crystallite Average Size (from XRD) and Electrical Properties of the Synthesized Samples

			Conductance maximum				
	Crystallite size (nm)		Under C_2H_5OH		Under CO		Pure air
Sample	(110)	(101)	T(°C)	S	T (°C)	S	E_a (eV)
SnO_2 *in situ*	10	11					
SnO_2 A700	13	14	150	1105	150	980	0.37
SnO_2 A800	18	20	150	2198	300	172	0.28
SO[a]		24	220	390	360	18	0.54
Pt/SnO_2 *in situ*	10	10					
Pt/SnO_2 A700	12	13	130	17860	200	6300	0.45
Pt/SnO_2 A800	18	20	170	634	No peak		0.34

[a]Sample synthesized by the conventional ultrasonic aerosol pyrosol under the same conditions used in this work for the synthesis of SnO_2 A800 sample. Data taken from Ref. (12).

vapor pressure) which leads to the deposition of Pt onto the SnO_2 grains.

Figure 2 shows the morphology of SnO_2 *in situ* powders and after the sintering of a pellet at 800°C for 4 h. Although not pictured here, the morphology of Pt/SnO_2 powders, both *in situ* and after annealing, is very similar to that depicted in Figs. 2a and b. As can be seen in Fig. 2a the *in situ* samples are constituted by hollow spherical particles (average size 1–5 μm) that undergo a drastic change after pellet formation and ulterior annealing (Fig. 2b). The hollow spherical particles are transformed into fine and homogeneous microstructures with an average grain size of 30 nm. Such change is perhaps due to the crushing of these hollow particles during pellet formation.

We must emphasize that the microstructure obtained for the SnO_2 *in situ* sample using the new device is very different from that obtained when the conventional pyrosol is used (Fig. 2c). In the latter case and using the same preparation conditions (precursor solution, carrier gas, pyrolysis temperature), slightly elongated quasi-spherical grain agglomerates, with an average diameter of around 1 μm, are observed. Inside the agglomerates, the grains (average size 100 nm) show poor cohesion, leading to appreciable porosity (12). This different microstructure can be related to the different resonance frequencies of both systems. In conventional ultrasonic aerosol pyrolysis, a 850-kHz frequency is generated directly inside the precursor solution. However, in the new ultrasonic device, the same frequency is applied to the vessel filled with water, which acts as transmission medium to the little glass conic vessel containing the precursor solution, where the aerosol is probably formed at a higher frequency which results in smaller-diameter aerosol droplets (16). Then, the evaporation and pyrolysis processes lead to quite different results. They produce hollow spherical particles with a thin shell in which the amount of material is smaller than for the particles obtained with the conventional ultrasonic aerosol.

TEM characterization was performed on all samples. Brightfield images in Fig. 3 show the evolution of crystallite size as a function of annealing temperature. The material includes well-defined crystallites, the mean size of which varies from 10 to 20 nm for samples annealing at 700°C (Fig. 3a) to 20 to 30 nm for samples annealing at 800°C (Fig. 3b). Similar crystallite sizes were obtained in Pt/SnO_2 samples, although it was not possible to observe the Pt nanoparticles on the grain surface of SnO_2. In samples obtained by conventional ultrasonic aerosol pyrolysis (12) and annealing at 800°C, the size distribution range is higher; the mean size varies from 25 to 40 nm.

The conductance of pure and Pt-doped SnO_2 systems, after annealing at 700 and 800°C, was measured at steady state successively under different surrounding atmospheres (Fig. 4). As shown in Table 1, the sensitivity of pure SnO_2, annealed at 700 and 800°C, to ethanol and CO is better than that obtained by using conventional pyrolysis (SO sample). Modification of the conventional ultrasonic Aerosol Pyrosol allows us to obtain, after cold pressing and annealing, a finer microstructure and thus better sensitivity.

Although no significant change is observed in SnO_2 crystallite sizes, the introduction of Pt aggregates strongly improves the sensitivity after annealing at 700°C compared with pure SnO_2 ($S = 1105 \rightarrow 17860$ under C_2H_5OH/air; $S = 980 \rightarrow 6300$ under CO/air). Nevertheless, after annealing at 800°C a change can be seen in the response under CO and ethanol. The sensitivity is strongly damaged in both cases and no sensitivity peak appears under CO (Fig. 4). It is worth mentioning that the smaller the Pt aggregates are, the better is their role as catalyst, particularly for CO oxidation (17, 18). Although we have not been able to observe an increase in Pt aggregate size when annealing at 800°C, due

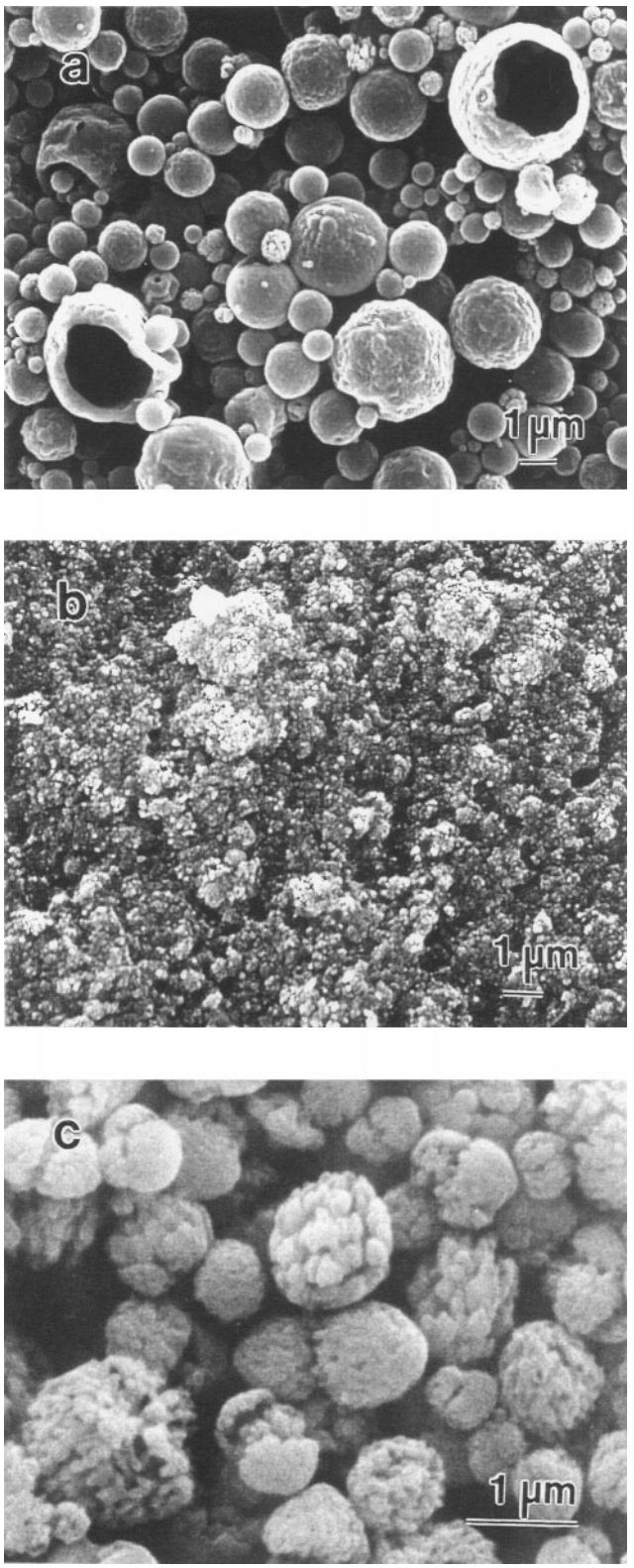

FIG. 2. Scanning electron micrographs of SnO_2 (a) *in situ* obtained by the new ultrasonic aerosol pyrosol, (b) after the sintering of a pellet at 800°C for 4 h, and (c) *in situ* obtained by the conventional ultrasonic aerosol pyrosol.

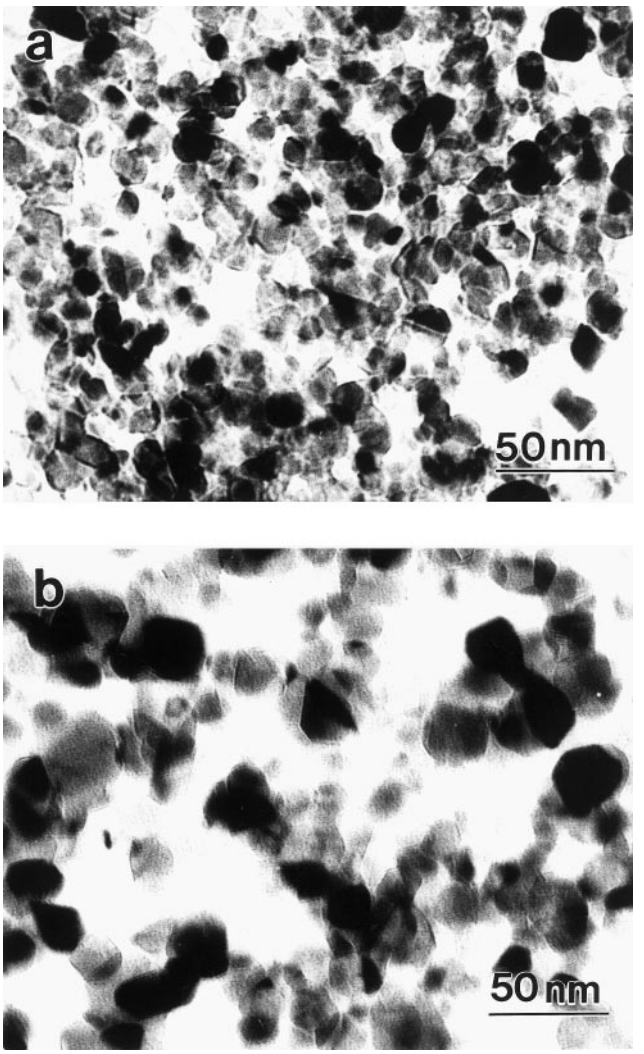

FIG. 3. Brightfield electron micrographs of (a) SnO_2 A700 sample and (b) SnO_2 A800 sample.

to the small amount of Pt present, it can be expected that such annealing drastically increases the Pt aggregate size and thus reduces the sensitivity, whereas annealing at 700°C affects the microstructure slightly. The Pt/SnO_2 sample, when annealed at 700°C, is a good candidate for CO and C_2H_5OH detection due to its sensitivity to both gases.

CONCLUSIONS

We have successfully modified a conventional ultrasonic aerosol pyrosol for the fabrication of submicrometer grain powders. SnO_2 and Pt/SnO_2 with a fine microstructure and optimum sensitivity were synthesized by this method. By a judicious choice of the precursors for the pyrolysis it was possible to obtain a homogeneous and fine dispersion of catalytic platinum aggregates onto the SnO_2 grains. The

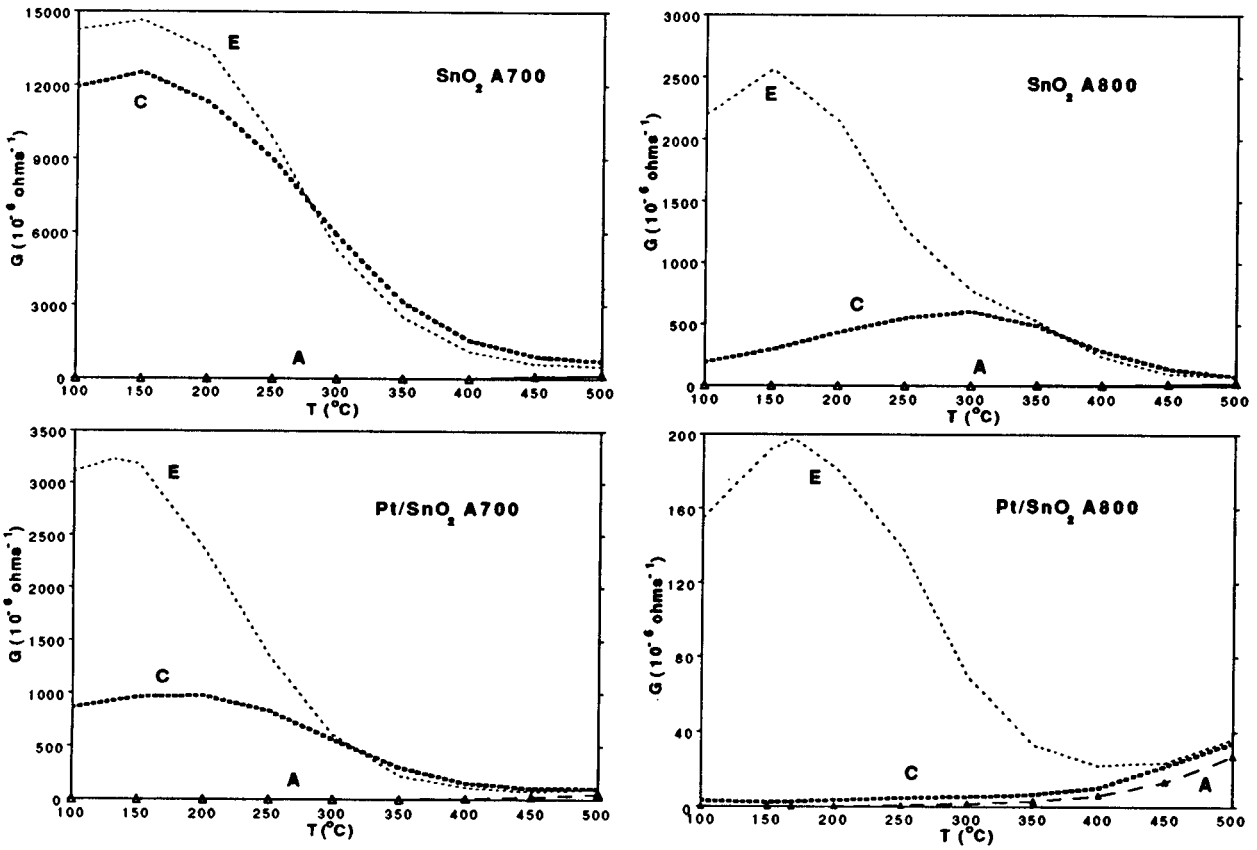

FIG. 4. Evolution of the conductance G as a function of temperature under pure air (A), under air/80 ppm C_2H_5OH (E), and under air/300 ppm CO (C).

materials annealed at 700°C show high sensitivity to ethanol and CO in air, which is improved by the presence of Pt nanoparticles on the grain surface of SnO_2.

ACKNOWLEDGMENTS

The authors are grateful to S. Nicolopoulos for valuable technical assistance. Financial support was provided by the International Association (INTAS) and CICYT (Spain) through Research Project MAT96-0919.

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