

Microstructural effects of mesoporous SnO₂ powders on their H₂ sensing properties

Masahiro Hayashi¹, Takeo Hyodo², Yasuhiro Shimizu² and Makoto Egashira^{2,*}

¹Graduate School of Science and Technology, ²Faculty of Engineering
Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

*Tel: +81-95-819-2642, Fax: +81-95-819-2643, *E-mail: egashira@nagasaki-u.ac.jp

Abstract

Various mesoporous tin oxide (m-SnO₂) powders were prepared by combinations of two kinds of surfactants and tin sources. Specific surface area and pore volume of m-SnO₂ prepared from C₁₆PyCl ((C₅H₅NC₁₆H₃₃)Cl·H₂O) and Na₂SnO₃·3H₂O (m-SnO₂(1)) were larger than those of m-SnO₂ prepared from AOT (C₂₀H₃₇O₇SNa) and SnCl₄·5H₂O (m-SnO₂(2)). However, the specific surface area of m-SnO₂(1) decreased dramatically by grinding, while m-SnO₂(2) with small secondary agglomerates showed a little decrease in the specific surface area and better H₂ response with low resistance in air than m-SnO₂(1), especially at low operating temperature.

Keywords: SnO₂; mesopores; particle size; hydrogen; gas sensor

Introduction

We have so far succeeded to develop thermally stable m-SnO₂ powders. They had much larger specific surface area (> 300 m² g⁻¹ even after calcination at 600°C) than a conventional SnO₂ powder [1-3]. However, the gas sensing properties were not so high as expected, probably due to their large secondary agglomerates of powders. In the present study, therefore, attempts were made to reduce such secondary agglomerates by adjusting the preparation conditions. In addition, the response properties to H₂ of the sensors fabricated with m-SnO₂ obtained were investigated.

Experimental

Two kinds of m-SnO₂ powders were prepared under the conditions shown in Table 1. m-SnO₂(1) was prepared from a precipitate obtained by adjusting the pH of a precursor aqueous solution, which contained C₁₆PyCl, Na₂SnO₃·3H₂O and trimethylbenzene, to 10 by using 1 wt% HCl or a buffer solution (0.025 M NaHCO₃-0.025 M Na₂CO₃). On the other hand, m-SnO₂(2) was prepared from a precipitate obtained by adjusting the pH of a precursor SnCl₄ aqueous solution to 0.6~6.9 by using 25% NH₃, followed by the addition of an AOT aqueous solution. After these precipitates were aged at 20°C for 3 days in the solutions and then treated with 0.1 N H₃PO₄ for 2 h, they were calcined at 600°C for 5 h in air. The obtained powders were ground using an agate mortar. The paste of m-SnO₂ powder was applied on an alumina substrate, on which interdigitated Pt electrode had been printed, to fabricate a thick film sensor, and then they were heated at 550°C for 5 h in air. The response, R_a/R_g (R_a: the sensor resistance in air and R_g:

that in 1000 ppm H₂ balanced with air) of such thick film sensors to 1000 ppm H₂ was measured in the temperature range of 250 to 500°C.

Results and Discussions

Table 1 shows some characteristics and sensor properties of m-SnO₂(1) and (2). It is apparent that the specific surface area (SSA) of m-SnO₂(1) is larger than that of m-SnO₂(2), irrespective of grinding treatment. In addition, the SSA of m-SnO₂(1) decreased dramatically by grinding.

The centered pore diameter of each m-SnO₂ powder showed little change by grinding. On the other hand, R_a of m-SnO₂(2) was much lower than that of m-SnO₂(1), while R_a/R_g of m-SnO₂(2) was relatively higher than that of m-SnO₂(1), especially at low operating temperature. This may be attributed to easier H₂ gas diffusion into the interior part of the thick film sensor, which is the most sensitive region, owing to moderately developed mesoporous structure of m-SnO₂(2), especially at lower temperature. Figure 1 shows SEM photographs of m-SnO₂(1) and m-SnO₂(2) sensors. Secondary agglomerates of m-SnO₂(2) were extremely smaller than those of m-SnO₂(1). Therefore, in the case of m-SnO₂(2), smaller secondary agglomerates led to better contacts between the agglomerates and Pt electrode or other agglomerates, thus electron conducting paths increased in the sensing layers of m-SnO₂(2) sensors. The lower R_a of m-SnO₂(2) may be attributed to this reason. On the other hand, R_a of all the sensors fabricated with the ground powders was smaller than that of the sensors fabricated with as-prepared powders, but H₂ responses of the former sensors could not be improved largely by the introduction of the grinding process of the powder.

In this study, it became clear that m-SnO₂(2) sensors showed better response to 1000 ppm H₂, especially at lower temperature, because of moderately mesoporous structure and smaller agglomerates.

References

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Table 1. Preparation conditions, specific surface area (SSA) and centered pore diameter (CPD) of m-SnO₂ powders, and maximum response to 1000 ppm H₂ (R_a/R_g, max) and R_a at 250°C of several sensors.

m-SnO ₂	Surfactant /Sn source	pH	pH control solution	SSA /m ² g ⁻¹	CPD /nm	R _a /R _g ,max (T/°C) ¹⁾	log (R _a /Ω)		
(1)-1	a	10	1 wt% HCl	365	1.9	30(400)	8.2		
	b			209	1.9	27(400)	7.4		
(1)-2	a		buffer solution ²⁾	297	2.2	28(400)	8.2		
	b			223	2.1	26(450)	6.7		
(2)-1	a	0.6	—	145	2.0	39(350)	4.6		
	b			111	2.0	33(350)	4.3		
(2)-2	a	3.3	25% NH ₃	167	2.8	36(350)	5.2		
	b			156	2.9	37(350)	5.0		
(2)-3	a			4.7	25% NH ₃	116	1.5	37(350)	4.8
	b					114	1.0	37(350)	4.6
(2)-4	a	6.9	—	132	1.8	39(350)	4.8		
	b			122	1.8	43(350)	4.6		

a and b indicate before and after grinding, respectively.

1) Operating temperature and 2) 0.025 M NaHCO₃-0.025 M Na₂CO₃.

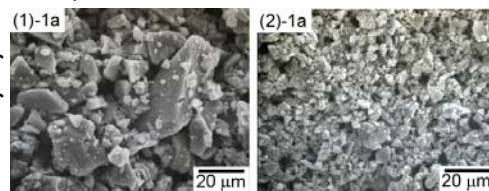


Fig. 1 SEM photographs of m-SnO₂ sensors fabricated with (1)-1a and (2)-1a.