Preparation of macroporous SnO₂ films using PMMA microspheres and their sensing properties to NO_x and H_2

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Abstract

Macroporous SnO₂ (mp-SnO₂(P-n); P means polymethylmethacrylate (PMMA) and n = diameter of PMMA microsphere) thick film gas sensors were fabricated by a modified sol-gel method by employing PMMA microspheres (n = 800, 400, 250 and 150 nm) as a template and SnCl₂ as a tin source. Morphology of mp-SnO₂ films was markedly dependent on the SnCl₂ concentration and the diameter of PMMA microspheres. Especially, the ratio of the thickness of the SnO₂ wall to the diameter of the hollow SnO₂ microsphere seems to increase with decreasing the diameter of PMMA microspheres used.

Among the films prepared, mp-SnO₂(P-250) exhibited the largest response to NO and NO₂ in air at 225 °C, whereas its response transients were relatively slow, indicating low adsorption and desorption speeds of negatively charged chemisorbed NO_x species on the SnO₂ surface. On the other hand, mp-SnO₂(P-800) showed the largest H₂ response among the sensors at temperatures higher than 400 °C. It has been revealed that the thickness and porous structure of the SnO₂ thick films are important factors to determine the sensing properties to NO₂ and H₂.
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1. Introduction

Strict optimization of gas reactivity and diffusivity of semiconductor gas sensors is enormously essential for improving their gas sensitivity and selectivity. Loading of a noble metal and/or an oxide on sensor materials, which is well known as a typical technique for controlling gas reactivity on the sensor surface, largely improved the sensing performance to a target gas [1–4]. However, the loading effect seems to become more pronounced only when the nano- and micro-structure of the semiconductor gas sensor materials is optimized suitable for a gas reaction region as well as a gas-diffusion pathway. Therefore, numerous efforts have recently been directed to constructing the most suitable structure to control gas reactivity and diffusivity in the sensing layer and then to improve gas sensitivity and selectivity. Those include

stacking of a catalyst or gas-diffusion layer on the sensing layer by sputtering [5], chemical vapor deposition [6], spin-coating [7] and slide-off transfer printing [8–11]. Chemical surface modification of SnO₂ powders with ethoxysilanes, which resulted in changes in gas-diffusion speed of both O₂ and a target gas as well as in potential barrier height at grain boundaries among SnO₂ particles, also improved significantly the gas-sensing properties [12–15]. In addition, the importance of the gas-diffusion dynamics in the SnO₂ sensing layers in determining gas-sensing properties has been proved mathematically [16,17].

Besides these important studies, we have demonstrated that mesoporous SnO₂ and semiconductor oxides modified with mesoporous SnO₂ are promising as sensor materials for H₂ and NO_x [18–22]. The SnO₂ powders with hexagonally ordered mesopores of a diameter range around 3 nm and high specific surface area (374 m² g⁻¹ even after calcination at 600 °C) exhibited excellent H₂ response and large NO response comparable to NO₂ sensitivity. To fully utilize

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their mesoporous structure and active sites on the surface of the mesoporous frameworks, however, simultaneous control of macroporous structure in the sensing layers is suggested to be another important subject.

We have recently developed a diode-type Pd/TiO$_2$ sensor equipped with macropores in the TiO$_2$ film as a gas-diffusion pathway fabricated by anodic oxidation of a Ti metal [23–25]. The number of macropores in the TiO$_2$ film that was much less than that of anodically oxidized alumina with many uni-axially ordered macropores (alumite), largely improved response and recovery speed to H$_2$ as well as the magnitude of the response. On the basis of these results, our particular attention has been paid to fabrication of macroporous materials by utilizing polymer microspheres as a template [26–31]. Macroporous materials with three-dimensionally (3-D) ordered arrays of pores with diameters from tens to hundreds of nanometers have commanded interest in a wide range of application: e.g. as photonic crystals for optical communication devices, supports for catalytic agents and electronic and electrochemical industry materials for sensor devices and electrodes. Especially the application of macroporous SnO$_2$ films with opal- and inverted opal-structure to gas sensors by Scott et al. [32] is worth noting. A colloidal crystal templating method with a well-ordered packed structure of silica or polystyrene (PS) microspheres have been used conventionally to develop highly ordered macroporous structures, in these studies. However, we believe that spherical polymethylmethacrylate (PMMA) can be utilized as an alternative template material, from the viewpoint of easy removal of the template without any fracture of the 3-D ordered macroporous frameworks, i.e. easy thermal decomposition of polymeric templates [33–36]. Then, we have demonstrated that macroporous SnO$_2$, TiO$_2$ or MgO thick films with relatively ordered 3-D arrays of macropores were fabricated by a modified sol-gel method employing PMMA microspheres as a template [37,38].

The aim of the present study is to establish further suitable fabrication conditions of macroporous SnO$_2$ thick films by a modified sol-gel method employing different kinds of PMMA microspheres and SnCl$_2$ methanol solution as a Sn source and then to investigate sensing properties of the macroporous SnO$_2$ thick films to NO$_x$ and H$_2$.

2. Experimental

2.1. Preparation of macroporous SnO$_2$ films

Four kinds of non-cross-linked PMMA microspheres (P-n, n = 800, 400, 250 and 150 nm in diameter, Soken Chem. & Eng. Co., Ltd.) were used as a template. After 1.0 g of the PMMA microspheres was dispersed in 5.0 g ultra pure water (resistivity higher than 18.2 MΩ cm) with 0.05 g ammonium polycarboxylic acid as a dispersant, the suspension was treated ultrasonically for 30 min to achieve high dispersion of PMMA microspheres. The suspension was then dip-coated

on the silicon substrate pre-oxidized at 1000 °C for 1 h or an alumina substrate with interdigitated Pt electrodes. Thereafter, they were air-dried at room temperature (RT), allowing PMMA microspheres to self-assemble into a 3-D array by sedimentation.

The precursor solution, SnCl$_2$·2H$_2$O (97%, Kishida Chem. Co., Ltd.) dissolved in methanol (99.5 vol.%, Wako Pure Chem. Ind., Ltd.) (SnCl$_2$ concentration: 0.1–2.0 mol dm^{-3}), was permeated into the openings of the 3-D array of PMMA microspheres in vacuo, and then were air-dried at RT. Thereafter, the composite film of the 3-D array of PMMA and the 3-D framework of the source material was subjected to heat treatment in flowing air, in order to remove the core PMMA microspheres by thermal decomposition and then to oxidize the source material to SnO$_2$ framework. Thermal decomposition behavior of the PMMA microspheres was investigated by thermaogravimetric and differential thermal analysis (TG-DTA, Shimadzu Co., Ltd., DTG-50) up to 600 °C at a heating rate of 10 °C min^{-1}, in order to determine calcination conditions. Based on the results described in Section 3.1, the composite films fabricated were fired in an appropriate heating process (slow heating at a rate of 1 °C min^{-1} up to 250 °C, fast heating at 10 °C min^{-1} up to 400 °C, slow heating at 1 °C min^{-1} up to 600 °C and holding for 2 h at 600 °C). Each macroporous SnO$_2$ thick film obtained was denoted as mp-SnO$_2$(P-n) in this study; P means PMMA and n represents diameter of PMMA microsphere.

2.2. Characterization of macroporous SnO$_2$ film

Morphology of macroporous SnO$_2$ films was observed by a scanning electron microscope (SEM, Hitachi, S-2250N) and a transmission electron microscope (TEM, JEOL, JEM2010-HT). Crystal phase and crystallite size of the SnO$_2$ films were characterized by X-ray diffraction (XRD, Rigaku, RINT-2200) using Cu Kα radiation (30 kV, 16 mA). The crystallite size was calculated by the Scherrer's equation. Specific surface area and pore size distribution were measured by a BET method using a N$_2$ sorption isotherm (Micromeritics, TriStar 3000). However, the specific surface area of the macroporous SnO$_2$ films was hard to be measured due to their small volume. Therefore, a macroporous SnO$_2$ disc (ca. 1 mm thick and 10 mm in diameter) was prepared, as described below. At first, a disc of PMMA microspheres was prepared by uniaxial pressing (ca. 1 kgf cm^{-2}). A small amount of a SnCl$_2$ methanol solution was permeated into the 3-D array of the PMMA disc in vacuo, and then was air-dried at room temperature. They were calcined under the conditions described above.

2.3. Measurement of sensing properties

Gas-sensing properties of the macroporous SnO$_2$ films fabricated on an alumina substrate equipped with interdigitated Pt electrodes were measured to 10–100 ppm NO and NO$_2$ (specific velocity: 1.55×10^{-3} m s^{-1}) and 1000 ppm H$_2$