Preparation of Macroporous Semiconductor Gas Sensors and Their Odor Sensing Properties

Shuhei Nonaka  Non-member  (Nagasaki University, d706024k@cc.nagasaki-u.ac.jp)
Takeo Hyodo  Non-member  (Nagasaki University, hyodo@nagasaki-u.ac.jp)
Yasuhiro Shimizu  Member  (Nagasaki University, shimizu@nagasaki-u.ac.jp)
Makoto Egashira  Non-member  (Nagasaki University, egashira@nagasaki-u.ac.jp)

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Offensive odor needs to be eliminated from our living and working environment from the viewpoint of our quality of life. To realize high performance of offensive odor decomposing or eliminating systems, development of a good odor sensor or sensing system is of primary importance.

Our recent studies have revealed that gas sensing properties of conventional semiconductor metal oxides could be improved by controlling macroporous structure. In the present study, therefore, effects of introduction of ordered submicron-size pore structure on NH₃ and H₂S responses have been investigated by employing SnO₂-, WO₃- and In₂O₃-based sensors.

Non-cross-linked PMMA microspheres (d = 800 and 400 nm in diameter) were used as a template. A PMMA suspension was dip-coated on an alumina substrate, on which interdigitated Pt electrodes had been printed. Then a precursor solution, i.e. methanol dissolving SnCl₂·2H₂O, WCl₆ or In(NO₃)₃·3H₂O was impregnated into the openings of the 3-D array of PMMA in vacuum. In some cases, an appropriate amount of CuCl₂ was added to the precursor solutions, to prepare the oxide films mixed with 1 mol% CuO to the base oxide. Thereafter, the PMMA-precursor composite films were subjected to heat treatment. Each macroporous oxide thick film obtained was denoted as mp(d)-CuO/MO, in which d stands for the diameter of PMMA microsphere (4 for 400 nm and 8 for 800 nm), MO is SnO₂, WO₃ or In₂O₃. For comparative purpose, reference sensors (R-MO) without macropores were also prepared.

Gas-sensing properties of sensors to 10 ppm NH₃ or 10 ppm H₂S balanced with air were measured in the temperature range of 200-500°C. The magnitude of gas response was defined as the ratio (R_a/R_g) of sensor resistance in air (R_a) to that in a sample gas balanced with air (R_g), while the reverse ratio was used in case of R_g > R_a.

Figure 1 shows the responses of various macroporous and reference sensors to 10 ppm NH₃ as a function of operating temperature. NH₃ responses of all the mp-oxide films prepared were much lower than those of R-oxide films, probably due to less reactivity of NH₃ originating from their macroporous structure.

Figures 2 and 3 show operating temperature dependences of the responses of various macroporous and reference sensors to 10 ppm H₂S. Macroporous sensors showed much larger H₂S response than those of R-oxide films. The addition of CuO was quite effective for improving the H₂S response. Among the sensors tested, the mp(4)-CuO/In₂O₃ sensor showed the most promising H₂S sensing properties.
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Shuhei Nonaka* Non-member
Takeo Hyodo** Non-member
Yasuhiro Shimizu** Member
Makoto Egashira** Non-member

Macroporous (mp-) oxide films (SnO2, WO3 and In2O3) were fabricated by a modified sol-gel technique employing polymethylmethacrylate (PMMA) microspheres as a template. NH3 responses of all the mp-oxide films prepared were much lower than those of reference (R-) oxide films fabricated by screen printing of the sol-gel driven powder, probably due to less reactivity of NH3 originating from their macroporous structure. On the other hand, mp-oxide films, especially mp-In2O3, showed much larger H2S response than R-oxide films. Furthermore, the addition of CuO was quite effective for improving the H2S response and the recovery speed of mp-In2O3.

Keywords: semiconductor metal oxides, gas sensors, macropore, odor, NH3, H2S

1. Introduction

Offensive odor needs to be eliminated from our living and working environment from the viewpoint of our quality of life. To realize high performance of offensive odor-decomposing or -eliminating systems, development of a good odor sensor or sensing system is of primary importance(1)(2). To compensate for poor selectivity to a specific gas of one sensor, several approaches have been studied(3)-(5). Among them, a neural network technique using an array of conventional gas sensors is one of promising methods for detecting odors selectively(6)-(8). However, the performance of the sensing system is of course dependent on the properties of individual sensors used, and the further improvement of gas sensitivity and/or selectivity of each sensor is still an important target.

Our recent studies have revealed that gas sensing properties of conventional semiconductor metal oxides could be improved by controlling macroporous structure(9)(10). For example, macroporous SnO2 and In2O3 sensors with submicron-sized ordered pores developed by employing polymethylmethacrylate (PMMA) microspheres as a template showed much higher H2 or NOx responses than a SnO2 sensor fabricated with conventionally prepared SnO2 powder and therefore having no ordered pore structure(9)(10). The improved gas sensing properties are thought to arise from the modified gas diffusivity as well as an increase in effective surface area of the sensor materials.

In the present study, therefore, effects of introduction of submicron-sized ordered pore structure on the NH3 and H2S responses have been investigated by employing SnO2-, WO3- and In2O3-based sensors.

2. Experimental

2.1 Preparation of Macroporous Films

Macroporous microspheres with different particle size (d = 800 and 400 nm in diameter, Soken Chem. & Eng. Co., Ltd.) were used as a template. First, a PMMA suspension was prepared by adding 3.0 g of PMMA microspheres and 0.05 g of triblockcopolymer (P123, (EO)20(PO)70(EO)20, EO: ethylene oxide, PO: propylene oxide, BASF Corp.) as a dispersant into 5.0 g ultra pure water (resistivity higher than 18.2 MΩ cm). After the suspension was treated with ultrasonic irradiation for 30 min to achieve homogeneous dispersion, it was dip-coated on an alumina substrate, on which interdigitated Pt electrodes had been printed. Thereafter, the substrate was air-dried at room temperature (RT), and then a precursor solution, i.e. methanol (99.5 vol%, Wako Pure Chem. Ind., Ltd.) dissolving SnCl2·2H2O (97%, Kishida Chem. Co., Ltd.), WCl6 (99%, Kishida Chem. Co., Ltd.) or In(NO3)3·3H2O (98%, Kishida Chem. Co., Ltd.) at a concentration of 0.5, 0.3 or 0.5 mol dm⁻³, respectively, was impregnated into the openings of the 3-D array of PMMA microspheres in vacuo, and then was air-dried at RT. In some cases, an appropriate amount of CuO (99%, Kishida Chem. Co., Ltd.) was added to the precursor solutions, to prepare the oxide films mixed with 1 mol% CuO to the base oxide. Thereafter, the PMMA-precursor composite films were 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 the oxide framework. To form pore structure reflecting the 3-D array of PMMA microspheres, the following heating process was adopted: slow heating at a rate of 1 °C min⁻¹ up to 250°C, fast heating at a rate of 10 °C min⁻¹ up to 400°C and 2 h holding at the same temperature, again slow heating at a rate of 1 °C min⁻¹ up to 600°C and 2 h holding at the same temperature. Each macroporous oxide thick film obtained was denoted as mp(d)-CuO/MO, in which d stands for the diameter of PMMA microsphere (4 for 400 nm and 8 for 800 nm), MO is SnO2, WO3 or In2O3.

Thick film oxide sensors without macropores (R-MO) were also prepared SnO2 powder and therefore having no ordered pore structure(9)(10). The improved gas sensing properties are thought to arise from the modified gas diffusivity as well as an increase in effective surface area of the sensor materials.
prepared for reference. Oxide powders were prepared by hydrolysis of the raw materials used for the precursor solutions at RT, followed by firing at 600°C for 2 h. Then the powder was mixed with an appropriate amount of organic lacquer (Goo Chemical Co., Ltd., OS-4530), and the mixture was screen-printed on an alumina substrate with interdigitated Pt electrodes. These sensors were subjected to firing at 550°C for 5 h.

2.2 Characterization of Sensors Morphology of macroporous films was observed by a scanning electron microscope (SEM, Hitachi, S-2250N). Crystal phases of the films were characterized by X-ray diffraction (XRD, Rigaku, RINT-2200) using CuKα radiation (40 kV, 40 mA).

A schematic view of a macroporous and reference sensor is shown in Fig. 1. Gas-sensing properties of sensors to 10 ppm NH₃ or 10 ppm H₂S balanced with air were measured in the temperature range of 200-500°C. The magnitude of gas response was defined as the ratio (Rₛ/Rₐ) of sensor resistance in air (Rₐ) to that in a sample gas balanced with air (Rₛ), while the reverse ratio was used in case of Rₛ > Rₐ.

3. Result and Discussion

3.1 Microstructural Analysis X-Ray diffraction analysis revealed that the resulting macroporous and reference sensors without CuO addition were all desired single phase oxide films. When CuO was added, macroporous and reference sensors showed the mixed phase of CuO and mother oxide, and formation of no new mixed metal oxides was confirmed.

Figure 2 shows SEM photographs of the surface of typical PMMA template films fabricated on an alumina substrate. Close-packed structure of PMMA microspheres was observed in some regions of both films. The thickness of both template films was controlled to be the same and was 8.4 µm.

SEM photographs of the surfaces of mp(4)-SnO₂ and mp(8)-SnO₂ sensors are shown in Fig. 3. Formation of a lot of voids left behind after the decomposition of the PMMA microspheres is obvious at both sensor surfaces. But, the diameter of the voids was not exactly the same as that of PMMA, and a shrinking of ca. 35% was observed for both sensors. An average value of wall thickness of the skelton of mp(4)-SnO₂ and mp(8)-SnO₂ was 80 and 113 nm, respectively. The thickness of the sensor film decreased to 7.1 µm for both sensors from that of PMMA.

The thickness of each sensor is summarized in Table 1. Note that the response is plotted as Rₛ/Rₐ for the macroporous sensors, but as Rₛ/Rₐ for the reference sensors. Since the response of both series of sensors was beyond unity, exposure to NH₃ resulted in an opposite resistance change, i.e. a resistance decrease for the macroporous sensors, but a resistance increase for the reference sensors. If NH₃ would react with oxygen adsorbates on the surface of n-type semiconductor metal oxide powder, which is a constituent of sensors and then reduce the surface coverage of oxygen adsorbates at the steady-state, we can observe a resistance decrease of the sensors. Such a resistance change would be observed, if the formation amounts and then the chemisorbed amounts of NOₓ, which is oxidation products of NH₃, would be small, especially in the vicinity of sensor electrodes (an interior part of the sensor film). However, when influence of chemisorbed NOₓ cannot be neglected during the oxidation of NH₃, a decrease in sensor resistance is weakened. This is the case for the NH₃ response of the macroporous sensors, due to relatively low oxidation activity.)
Fig. 4. Temperature dependences of responses to 10 ppm NH₃ of (a) macroporous and (b) reference sensors.

Fig. 5. Temperature dependences of responses to 10 ppm H₂S of macroporous and reference sensors.

Fig. 6. Temperature dependences of responses to 10 ppm H₂S of CuO-added macroporous and reference sensors.

originating from their porous structure and thinner sensor material, in comparison with the reference sensors. Therefore, the NH₃ response of these macroporous sensors was very low and 1.6 at most at 400°C observed with the mp(4)-SnO₂ sensor, as shown in Fig. 4(a). In contrast, all the reference sensors showed a large resistance increase upon exposure to NH₃ and then a large response, especially for the R-WO₃ sensor, probably due to higher oxidation activity of the sensor materials originating from dense and thicker sensors.

3.3 Gas-Sensing Properties of Macroporous Sensors to 10 ppm H₂S Figure 5 shows operating temperature dependences of the responses to 10 ppm H₂S of various macroporous and reference sensors. Unlike the NH₃ response properties shown in Fig. 4, all the macroporous sensors showed higher H₂S response than the reference sensors with only one exception of mp(4)-WO₃. In the case of the mp(4)-WO₃ sensor, its resistance in air was too high to be measured practically, and therefore it showed apparently no response to H₂S.

A notable finding in the present study is that the macroporous sensors were more sensitive to H₂S than the reference sensors. Higher resistance in air of the macroporous sensors than the reference sensors is anticipated to be one of the reasons for their higher H₂S responses. Other factors may also be responsible for higher H₂S response observed for macroporous sensors, in comparison with reference sensors, but, they are still unidentified and then are major subjects in our future work. In addition, the macroporous sensors fabricated with 400 nm PMMA showed large responses, in comparison with those fabricated with 800 nm PMMA, both for SnO₂- and In₂O₃-based sensors. These results offer the potential that the response of conventional sensor materials may be further improved by controlling their macroporous structure.

In the next step, the effect of CuO addition on the H₂S response of both the macroporous and the reference sensors was investigated. Characterization data for these sensors are also summarized in Table 1. Figure 6 shows operating temperature dependences responses to 10 ppm H₂S of CuO-added macroporous and reference sensors. CuO-added macroporous and reference WO₃ sensors were not fabricated in this study, because the resistance of the mp(4)-WO₃ sensor had already reached the level which was beyond practical measurement in air. The CuO addition was effective to enhance the H₂S response of both the macroporous and reference SnO₂ and In₂O₃ sensors. The mechanism of the H₂S response enhancement induced by CuO addition has already been discussed elsewhere (11)-(14). A pronounced finding in the present study is that the CuO addition was more effective for the macroporous sensors than for the reference sensors, both for SnO₂ and In₂O₃-based sensors. In addition, CuO-added macroporous sensors fabricated with 400 nm PMMA were superior to those fabricated with 800 nm PMMA. This phenomenon is quite interesting for further improvement of H₂S response as well as for design of other odor sensors, though its reason is not clear at present.

Figure 7 shows response transients of the macroporous and reference CuO-added In₂O₃ sensors at 200°C. Both the macroporous sensors showed faster response and recovery behavior than the reference sensor. Such superior response and recovery behavior arose undoubtedly from easier diffusion of H₂S to and diffusion of oxidation products from the interior region of the sensor (near the electrode) owing to their macroporous structure.

Figure 8 shows responses to H₂S of several CuO-added sensors at 200°C as a function of the concentration in the range of 0.6-10 ppm. A good linearity was obtained for all the sensors in the concentration range tested. From the slopes of these lines in Fig. 8, we can get the sensitivity to H₂S to be 1.73, 14.6, 91.6 and 614
Fig. 7. Response transients to 10 ppm H$_2$S of CuO-added In$_2$O$_3$ sensors.

Fig. 8. Variations in response at 200ºC of several CuO-added sensors with H$_2$S concentration.

4. Conclusion

Introduction of macroporous structure was not effective for improving the NH$_3$ responses of SnO$_2$, WO$_3$ and In$_2$O$_3$ sensors, probably due to a decrease in oxidation activity of NH$_3$ originating from their macroporous structure. In contrast, H$_2$S responses could be improved by the introduction of macroporous structure into the mother sensor metal oxides. The same phenomenon was observed for the CuO-added sensors. Among the sensors tested, the mp(4)-CuO/In$_2$O$_3$ sensor showed the most promising H$_2$S sensing properties.

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Shuhei Nonaka (Non-member) received his B. Eng. Degree from Nagasaki University in 2006. He is now a student in Graduate School of Science and Technology, Nagasaki University, and is currently engaged in research and development of macroporous odor sensors.

Takeo Hyodo (Non-member) received his B. Eng. Degree in applied chemistry and M. Eng. Degree in materials science and technology in 1992 and 1994, respectively, and Dr. Eng. Degree in 1997 from Kyushu University. He has been a Research Associate at Nagasaki University since 1997. His research interests are development of electrochemical devices such as chemical sensors and lithium batteries and morphological control of both ceramics and electrodes.

Yasuhiro Shimizu (Member) received his B. Eng. Degree in applied chemistry in 1980 and Dr. Eng. Degree in 1987 from Kyushu University. He has been an Associate Professor at Nagasaki University since 1987. His current research concentrates on meso- and macro-structural control of semiconductor gas sensors to improve their sensing properties.

Makoto Egashira (Non-member) received his B. Eng. Degree and M. Eng. Degree in applied chemistry in 1966 and 1968, respectively, and Dr. Eng. Degree in 1974 from Kyushu University. He has been a Professor at Nagasaki University since 1985. His current interests include development of new chemical sensors, surface modification and morphological control of ceramics.