

FULL PAPER

Effects of noble-metal loading and ultraviolet-light irradiation on gassensing properties of porous indium oxide films at room temperature

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Fundamental gas-sensing properties of porous $(pr-)In_2O_3$ powders loaded with and without 0.5 mass % noble metal $(pr-\theta.5N/In_2O_3$ and $pr-In_2O_3$, respectively, N: noble metal (Au or Pd)) to NO₂, H₂, and ethanol balanced with dry air were investigated at 30 °C under UV-light irradiation (main wavelength: 365 nm). The spherical pr- $\theta.5N/In_2O_3$ and pr- In_2O_3 powders were prepared by ultrasonic-spray pyrolysis employing polymethylmeth-acrylate microspheres with a diameter of ca. 70 nm, which were synthesized by ultrasonic-assisted emulsion polymerization. The Au loading largely improved the NO₂ response of the pr- In_2O_3 sensor, a ratio of the resistance in air. On the other hand, the Pd loading efficiently increased the difference in the conductance of the pr- In_2O_3 sensor between in NO₂ and in air under the whole UV-light irradiation range. The UV-light irradiation is effective in improving the NO₂-sensing properties of these sensors at room temperature, but the sensing performance was a little inferior to that operated at elevated temperatures under no UV-light irradiation. These sensors also responded to reducing gases, H₂ and ethanol, under UV-light irradiation, and the responses to ethanol were much larger than those to H₂. However, the responses to both the gases were much smaller than that to NO₂.

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Key-words : Semiconductor-type gas sensor, Indium oxide, Polymethylmethacrylate, Noble metal, UV-light irradiation, Nitrogen dioxide, Hydrogen, Ethanol

[Received July 5, 2021; Accepted August 23, 2021]

1. Introduction

Numerous efforts have been directed to controlling the microstructure of various ceramics to enhance their original properties as well as to add new features. Among them, the introduction of mesoporous and macroporous structures into materials have been commonly attempted by utilizing self-assembly of supramolecules^{1),2)} and polymer microspheres,^{3),4)} respectively, as a template. We have also developed various mesoporous and macroporous gassensing materials during the last two decades.^{5)–15)} Among all materials, spherical oxide powders with well-developed pores, which are prepared by ultrasonic spray pyrolysis employing polymethylmethacrylate (PMMA) microsphere templates, are quite attractive as gas-sensing materials for various types of gas sensors, because they can be easily applied onto a sensor platform by conventional techniques such as screen printing. We have thus far demonstrated that semiconductor-type gas sensors fabricated with such porous oxide powders showed excellent sensing properties to various gases at elevated temperatures.^{16)–20)} On the other hand, we have also developed semiconductor-type gas sensors operable at room temperature (RT) under UV-light irradiation.^{21),22)} Various researchers have investigated sensing properties of semiconductor-type gas sensors assisted by UV-light irradiation to various gases,^{23)–27)} and the miniaturization of these sensors by utilizing the microelectro-mechanical system technology has also been recently attempted for the practical use.^{28),29)}

In this study, porous spherical In_2O_3 (pr- In_2O_3) powders were prepared by ultrasonic spray pyrolysis employing PMMA microspheres, and the effects of noble-metal (Au or Pd) loading onto the pr- In_2O_3 powders on the gassensing properties at RT with and without UV-light irradiation were discussed, as compared with the gas-sensing properties at elevated temperatures.

2. Experimental

PMMA microspheres with a diameter of ca. 70 nm were synthesized by ultrasonic-assisted emulsion polymerization. The detailed procedure is described in our previous papers.^{18)–20)} The PMMA-microsphere aqueous dispersion obtained (37.5 cm^3) was mixed with $\ln(NO_3)_3$ aqueous

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solution $(0.05 \text{ mol dm}^{-3}, 62.5 \text{ cm}^3)$, and an appropriate amount of HAuCl₄ or Pd(NO₃)₂ aqueous solution (0.1 mol dm^{-3}) was added to the precursor solution to load Au or Pd onto In₂O₃, respectively, in some cases. Figure S1 shows a specially designed mist-supplier for the ultrasonic spray pyrolysis. The precursor solution was poured into a plastic container with a bottom made of polystyrene film (thickness: ca. 10 µm), and then it was nebulized by an ultrasonic vibrator (Honda Electric Co., Ltd., HM-303N, 2.4 MHz). The obtained mists were fed into an electric furnace heated at 1000 °C, to prepare porous spherical In2O3 powders loaded with or without noble metal $(pr-nN/In_2O_3)$ or pr-In₂O₃, respectively, N: noble metal (Au or Pd), n: the amount of N loading onto pr-In₂O₃ [mass %], 0.5 in this study). The microstructure of these powders was observed by scanning electron microscopy (SEM; JEOL Ltd., JSM-7500F). The pore-size distribution and specific surface area (SSA) of these powders were measured by Barrett-Joyner-Halenda and Brunauer-Emmett-Teller methods using N₂ adsorption/desorption isotherms (Micromeritics Inst. Corp., Tristar3000), respectively. The crystal phase of these powders was characterized by X-ray diffraction analysis (XRD; Rigaku Corp., RINT2200) using Cu Kα radiation, and their crystallite size (CS) was calculated from the (222) diffraction peak using the Scherrer equation.

The pr-In₂O₃ or pr-0.5N/In₂O₃ powder was mixed with an appropriate amount of α -terpineol, and the paste obtained was screen printed onto an alumina substrate equipped with a pair of interdigitated Pt electrodes (gap size: ca. 200 µm). After drying at 100 °C, they were heattreated at 550 °C for 5 h in ambient air. The responses of these sensors to $1-20 \text{ ppm NO}_2$, 6,000 ppm H₂, and 50 ppm ethanol balanced with dry air were measured at 30 °C at a flow rate of 100 cm³ min⁻¹ under UV-light irradiation using a light-emitting diode (UV-LED, ARK TECH Co., Ltd., LS-4A1-1, main wavelength: 365 nm), after preheat treatment at 200 °C for several tens of minutes in dry air. The volume containing the gas-flow pathway and the rectangular container (V), in which the sensors are set, is ca. 106 cm³.²²) In addition, the response of these sensors to 5 ppm NO₂ balanced with dry air at elevated temperatures (200-500 °C) was also measured at a flow rate of 100 cm³ min⁻¹ under no UV-light irradiation. The cylindrical container used (V: ca. 106 cm³) was heated in an electric furnace.16)-18)

Results and discussion

Figure S2 shows XRD spectra of all the powders. All the peaks of these powders were assigned to cubic In_2O_3 (JCPDF No. 6-416), and no peaks derived from Au and Pd were in the spectra of the pr-0.5Au/In₂O₃ and pr-0.5Pd/ In₂O₃ powders, respectively, because of the small amount and/or small size of Au and Pd nanoparticles loaded onto the In₂O₃ powders. In addition, the loading of Au or Pd onto In₂O₃ had little influence on their CSs, but the CSs of the pr-0.5Au/In₂O₃ and pr-0.5Pd/In₂O₃ powders (ca. 14.2 nm and ca. 14.3 nm, respectively) were slightly smaller than that of pr-In₂O₃, (ca. 14.5 nm). Figure S3 shows

nitrogen adsorption/desorption isotherms and pore-size distributions of these powders, together with their SSAs. All the powders had well-developed porous structures with centered diameters of ca. 67-81 nm and ca. 30 nm, which were calculated from nitrogen adsorption and desorption isotherms, respectively, because they had a hysteresis loop in the nitrogen adsorption/desorption isotherms in the relatively high-pressure range. These results indicate that their well-developed porous structure mainly consists of well-developed ink-bottle pores with narrow necks (ca. 30 nm) and wide bodies (ca. 67-81 nm). In addition, these powders had a large number of mesopores with a diameter of less than 10 nm, and the pore-size distribution and the pore volume were largely dependent on the amounts and the kinds of N loaded onto pr-In2O3. Namely, the Au loading mainly decreased the amounts of pores with a diameter of ca. 2-10 nm, while the Pd loading increased the amounts of pores with a diameter of less than 2 nm. They are the reasons why the Au and Pd loading decreased and increased SSA of the pr-In₂O₃ powder, respectively. Figure S4 shows SEM photographs of the pr-In₂O₃ and pr-0.5Au/In₂O₃ powders. The morphology of these powders obtained was spherical, and a large number of circular pores were confirmed on the surface. The size of these circular pores was almost correspondent to the centered diameter, ca. 30 nm which was estimated from their N₂ desorption isotherms.

Figure 1 shows cross-sectional SEM photographs of all the sensors. The oxide-film thicknesses of the pr-In₂O₃, pr- $0.5 \text{Au}/\text{In}_2\text{O}_3$, and pr- $0.5 \text{Pd}/\text{In}_2\text{O}_3$ sensors were ca. 15 µm, ca. 20 μ m, and ca. 17 μ m, respectively, and there was little difference in the stacking state of their spherical particles among these sensors. This fact indicates that the loading of Au or Pd onto In₂O₃ has little impact on the microstructure of the films and thus that the gas-sensing properties of these sensors can be clearly evaluated without respect to the geometric characteristics of the oxide films. Figure 2 shows response transients of all the sensors to 5 ppm NO₂ at 30 °C in dry air under UV-light irradiation of 0-129 mW cm⁻², and the variations in the magnitude of their NO₂ responses with UV-light intensity were summarized in Fig. 3. Here, the NO₂ response (R_g/R_a) was defined as a ratio of the resistance in NO₂ balanced with dry air (R_g) to that in dry air (R_a) . The loading of Au or Pd onto In₂O₃ reduced the resistance of the pr-In₂O₃ sensor in dry air under no UV-light irradiation. Figure S5 shows energyband diagrams of interfaces between loaded materials (PdO, Pd, and Au) and In₂O₃. Generally, the work function (φ) of Au (ca. 5.1 eV)³⁰ and Pd (4.8 eV)³¹ [or PdO (ca. $(5.5 \text{ eV})^{31}$ bulks is larger than that of In_2O_3 bulk (ca. 4.3) eV).³²⁾ On the basis of these values, the resistance of the pr-0.5Au/In₂O₃ and pr-0.5Pd/In₂O₃ sensors should be larger than that of the pr-In₂O₃ sensor. Actually, the resistance of In₂O₃ loaded with Au by general impregnation was larger than that of pristine In₂O₃.^{33)–35)} However, Zhang et al. clarified that the work function of Au nanoparticles monotonically decreased with a decrease in the particle size by Kelvin probe force microscopy and that the



Fig. 1. Cross-sectional SEM photographs of all sensors.

work function of a Au nanoparticle with a diameter of 10 nm reached only $\sim 3.6 \text{ eV}.^{30}$ In this case, electrons transfer from the Au nanoparticle to In₂O₃, and thus the energy-band diagram of the interface is shown in Fig. S5(c)(ii). This is considered to be the reason why the resistance of the pr-0.5Au/In₂O₃ sensor was lower than that of the pr-In₂O₃ sensor. It is expected that Au components are highly dispersed in the pr-0.5Au/In₂O₃ powder, because it is prepared by instantaneous heating of aqueous precursor mists containing HAuCl₄ as well as In(NO₃)₃. Actually, Au nanoparticles cannot be observed even by transmission electron microscope.³⁶ In addition, the resistance of the

pr-*n*Au/In₂O₃ decreased with an increase in *n* in the range of 0–1.5 mass %.³⁶⁾ This behavior indicates that the number of Au nanoparticles with work function smaller than that of pr-In₂O₃ increased with an increase in *n*. On the other hand, the resistance of the pr-*n*Au/In₂O₃ increased with an increase in *n* in the range of more than 1.5 mass %,³⁶⁾ because the number of large Au nanoparticles with work function larger than that of pr-In₂O₃ increased with an increase in *n*. We do not have findings on the size dependence on the work function concerning Pd and PdO nanoparticles, but the loading of Pd and/or PdO by general impregnation technique also increased the resistance of various oxide films.^{22),34)} Therefore, it is expected that the work function of Pd and/or PdO nanoparticles would decrease with a decrease in size.²⁰⁾

The weak UV-light irradiation of $0.57 \,\mathrm{mW \, cm^{-2}}$ decreased the resistance of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors in dry air, since electrons were excited from the valence band to the conduction band to increase the carrier density. By contrast, the weak UV-light irradiation increased the resistance of the pr-0.5Au/In₂O₃ in dry air. This is probably because the number of oxygen adsorbates increased on the Au surface and/or at the boundary between Au and In₂O₃ through the activated adsorption by the weak UV-light irradiation [Eq. (1)], and the number of electrons trapped by the oxygen adsorbates was larger than the number of electrons produced by the UV-light irradiation.

$$O_2 + e^- \to O_2^- \tag{1}$$

Degler et al. also suggested that the number of negatively charged oxygen adsorbates was increased by the loading of Au onto SnO_2 surface.³⁷⁾ Most Pd nanoparticles loaded on pr-In₂O₃ are originally oxidized to form PdO,^{20),22)} and thus the number of oxygen adsorbates which is increased by the weak UV-light irradiation is much smaller than that of electrons excited. This is likely to be the reason why the weak UV-light irradiation decreased the resistance of the pr-0.5Pd/In₂O₃ sensor. Further increase in the intensity of the UV-light irradiation monotonically decreased the resistance of all the sensors.

The introduction of NO_2 into dry air increased the resistance of all the sensors, both with and without UV irradiation, because the adsorption of NO_2 molecules on the surface decreased the concentration of free electrons in the oxide films [Eq. (2)] and its effect was much larger than that of oxygen adsorbates.

$$NO_2 + e^- \to NO_2^- \tag{2}$$

These sensors all showed the largest responses to 5 ppm NO₂ under no UV-light irradiation. However, their response and recovery speeds under no UV-light irradiation were much slower than those under UV-light irradiation. The adsorption of NO₂ is commonly dominant over that of O₂ on the oxide surface from the viewpoint of equilibrium. Besides, NO₂ molecules form deeper acceptor levels on the oxide surface than the negatively charged oxygen adsorbates (O₂⁻).³⁸⁾ They are the main reasons of



Fig. 2. Response transients of all sensors to 5 ppm NO₂ at 30 °C in dry air under UV-light irradiation of $0-129 \text{ mW cm}^{-2}$.



Fig. 3. Variations in (a) responses and (b) ΔG of all sensors to 5 ppm NO₂ at 30 °C in dry air with UV-light intensity. *Values under no UV-light irradiation in parentheses.

the large resistance of the sensors in NO₂ balanced with air. However, the behavior of these sensors indicates that the rates of adsorption and desorption of NO₂ molecules onto and from the oxide surface are quite slow from the viewpoint of kinetics, because of the shortage of driving energy at 30 °C. The weak UV-light irradiation even accelerated the response and recovery speeds of all the sensors, whereas it decreased the responses of all sensors. Among them, the pr-0.5Au/In₂O₃ sensor showed the largest NO₂ response under the smallest UV-light irradiation (0.57 $mW cm^{-2}$) and its response to 5 ppm NO₂ obviously decreased with an increase in the intensity of UV-light irradiation. On the other hand, the responses of pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors were drastically decreased even by the small UV-light irradiation and they tended to decrease gradually with an increase in the intensity of UV-light irradiation, as shown in Fig. 3(a). The response and recovery speeds of all the sensors were hardly dependent on the intensity of UV-light irradiation. Figure 3(b) shows the dependences of the difference in conductance between in air and in NO₂ (ΔG) on the intensity of UV-light irradiation. It has been confirmed that the temperature of all the sensors was 30 °C under operation with and without UV-light irradiation. Given that the electron mobility (μ) was not dependent on the UV-light intensity at all, therefore, ΔG is proportional to the difference in carrier (electron) concentration between in air and in NO₂ (Δn_e ($n_{e,a}-n_{e,g}$), $n_{e,a}$ and $n_{e,g}$: carrier concentration in dry air and in target gas, respectively), as shown in the following equation,

$$\Delta G = \frac{1}{R_{\rm a}} - \frac{1}{R_{\rm g}} = Ae\mu\Delta n_{\rm e} \tag{3}$$

where e and A stand for elementary charge and geometric coefficient, respectively. Even the smallest UV-light irradiation of $0.57 \,\mathrm{mW \, cm^{-2}}$ increased $\Delta n_{\rm e}$ of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors, which indicates the increase in the number of NO2 adsorbates on the surface. However, the responses of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors decreased even though the number of NO2 adsorbates was increased by the UV-light irradiation. This tendency originates from a decrease in the resistance (an increase in $n_{e,a}$) in air. On the other hand, $n_{e,a}$ of the pr-0.5Au/In₂O₃ sensor was decreased by the smallest UV-light irradiation of $0.57 \,\mathrm{mW \, cm^{-2}}$, and thus it was smaller than those of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors. Nevertheless, the response of the pr-0.5Au/In₂O₃ sensor was much larger than those of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors. That is because $n_{e,a}$ of the pr-0.5Au/In₂O₃ sensor in air, which is much smaller than those of the pr-In₂O₃ and pr-0.5Pd/In₂O₃ sensors, increased the relative ratio of $n_{e,g}$ to $n_{\rm e,a}$ $(n_{\rm e,g}/n_{\rm e,a})$. Furthermore, $\Delta n_{\rm e}$ of all the sensors increased with an increase in the UV-light intensity to a greater or lesser, and thus their responses decreased with an increase in the intensity of the UV-light irradiation.

Figure 4 shows response transients of the pr-0.5Au/ In₂O₃ sensor to 1–20 ppm NO₂ at 30 °C in dry air and the NO₂-concentration dependence on the magnitude of the NO₂ response, under the UV-light irradiation of 0.7 mW cm⁻². The NO₂ response simply increased with an increase in concentration. The response to less than 1 ppm NO_2 was not measured in this study, but it should abruptly rise in the range of sub-ppm concentration of NO₂, as shown by the dashed line. On the other hand, the responses to higher concentrations of NO₂ (\geq 15 ppm) increased without attaining saturation. The relationship between the response and the concentration is similar to those of the N₂ adsorption/desorption isotherms at -196 °C under the low relative pressure region of 0-0.5 (see Fig. S3). As mentioned below, the interaction between negatively adsorbed NO₂ molecules and the oxide surface is quite large. In addition, it is also well-known that various types of nitrogen oxides such as nitrate species (NO_3^-) are on the oxide surface.³⁹⁾⁻⁴¹⁾ The interaction among these NOx-based adsorbates as well as between the NOx-based adsorbates and the oxide surface under UV-light irradiation may



Fig. 4. (a) Response transients of pr-0.5Au/In₂O₃ sensor to 1–20 ppm NO₂ at 30 °C in dry air and (b) NO₂-concentration dependence on NO₂ response, under UV-light irradiation of 0.7 mW cm^{-2} .

promote the number and/or the adsorption strength of their NOx-based adsorbates. Moreover, a certain amount of NO₂ molecules was easily converted to NO and atomic oxygen under UV-light irradiation and they reacted one another, as shown below.⁴²⁾

$$NO_2 + h\nu \rightarrow NO + O$$
 (4)

$$O + O_2 \to O_3 \tag{5}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{6}$$

These reactions must also complicatedly influence the concentration dependence on the NO_2 response. Hereafter, we should spectroscopically investigate these phenomena in detail.

The effects of operating temperatures (200-500 °C) on the NO₂ response of all the sensors were compared with those of UV-light irradiation. Figure 5 shows response transients of pr-In₂O₃, pr-0.5Au/In₂O₃, and pr-0.5Pd/ In_2O_3 sensors to 5 ppm NO₂ at elevated temperatures in dry air under no UV-light irradiation. The resistance of the pr-In2O3 sensor monotonically decreased with an increase in temperature, whereas that of the pr-0.5Pd/In₂O₃ sensor was hardly dependent on temperature. The variation in resistance of the pr-0.5Au/In₂O₃ sensor with temperature was quite complicated. Namely, the resistance of the pr-0.5Au/In₂O₃ sensor decreased with an increase in temperature at least to 200 °C, but it increased with an increase in temperature between 200 and 400 °C. This dependence of the resistance in air on the operating temperature under no UV-light irradiation is different from that on the intensity of the UV-light irradiation at 30 °C, probably because the rise in operating temperature increased the number of oxygen adsorbates on the pr-In₂O₃ surface by the spillover effect from Au nanoparticles loaded³⁷⁾ and changed the species of oxygen adsorbates from O_2^- to O^- and O^{2-} in the temperature range. In addition, the Au loading onto the pr-In2O3 surface was slightly effective in enhancing the NO₂ response only at 200 °C. The responses of all the sensors at elevated temperatures under no UV-light irradiation were relatively larger than those at 30 °C under UV-light irradiation. The largest NO₂ responses of all the sensors were attained at 200 °C and they decreased with an increase in temperature. This tendency is similar to the



Fig. 5. Response transients of all sensors to 5 ppm NO_2 at elevated temperatures in dry air under no UV-light irradiation.

behavior under UV-light irradiation, which indicates that further reduction in the intensity of the UV-light irradiation enhanced the NO₂ responses of these sensors. On the other hand, the difference in response and recovery speeds between at 30 °C under UV-light irradiation and at elevated temperatures under no UV-light irradiation cannot be discussed because the shape of the test chambers and their dead volume were different between these measurement conditions.

Figure S6 shows response transients of pr-In₂O₃, 0.5Au/ pr-In₂O₃, and 0.5Pd/pr-In₂O₃ sensors to 6,000 ppm H₂ and 50 ppm ethanol at 30 °C in dry air under UV-light irradiation, and the variations in the magnitude of their responses to $6,000 \text{ ppm H}_2$ and 50 ppm ethanol with the intensity of UV-light irradiation were summarized in Fig. S7(a). Here, the responses to these reducing gases $(R_{\rm a}/R_{\rm g})$ were defined as a ratio of the resistance in dry air (R_a) to that in H₂ or ethanol balanced with dry air (R_g) . The $pr-In_2O_3$ sensor showed a slight response to 6,000 ppm H₂, which decreased with an increase in the intensity of UVlight irradiation. In addition, the response and recovery speeds of the pr-In₂O₃ sensor were quite slow under every UV-light irradiation. On the other hand, the response of the pr-In₂O₃ sensor to 50 ppm ethanol was larger than that to $6,000 \text{ ppm H}_2$, and the magnitude of its ethanol response increased and its response and recovery speeds gradually accelerated with an increase in the intensity of UV-light irradiation. The N loading increased the H₂ response of the pr-In₂O₃ sensor, especially under small UV-light irradiation, while it was not so effective in improving the response and recovery speeds. On the other hand, the Pd loading enhanced the ethanol response especially under large UV-light irradiation, while the Au loading was ineffective in improving the ethanol response. Figure S7(b) shows the dependences of the difference in conductance between in target gases (6000 ppm H₂ or 50 ppm ethanol) and in air (ΔG) on the intensity of UV-light irradiation. Considering ΔG of all the sensors to 6000 ppm H₂ are relatively small and not dependent on the intensity of UVlight irradiation, the oxidation of H₂ with oxygen adsorbates on the surface does not proceed efficiently under UVlight irradiation even by the N loading, and thus the H₂ responses of all the sensors were smaller than we expected. As ΔG of all the sensors to 50 ppm ethanol simply increased with an increase in the intensity of UV-light irradiation, the UV-light irradiation was effective in enhancing the oxidation of ethanol with oxygen adsorbates on the surface. The Pd loading is the most effective way to enhance the oxidation of ethanol as well as to improve the ethanol response on the pr-In₂O₃ surface.

4. Conclusion

Sensing properties of pr-In₂O₃ and pr-0.5N/In₂O₃ sensors (N: Au or Pd) to NO₂, H₂, and ethanol balanced with dry air were investigated at 30 °C under UV-light irradiation (main wavelength: 365 nm). The weak UV-light irradiation increased the resistance of the pr-0.5Au/In₂O₃ sensor in dry air, probably because of an increase in the

number of oxygen adsorbates. Thus, the NO₂ response of the pr-0.5Au/In₂O₃ sensor was much larger than that of the pr-In₂O₃ sensor under weak UV-light irradiation. On the other hand, the pr-0.5Pd/In₂O₃ sensor showed the largest ΔG to NO₂ under every UV-light irradiation range. This indicates that the amount of NO2 adsorbed on the surface of the pr-0.5Pd/In₂O₃ sensor was much larger than that of other sensors. The operation of these sensors at elevated temperatures especially at 200-250 °C was effective in improving the NO₂-sensing properties of these sensors under no UV-light irradiation, in comparison with the mild operation at 30 °C under UV-light irradiation. Hereafter, the optimization of the operating condition as well as the compositional and microstructural controls of the pr-nN/In₂O₃ sensor are essential in improving their NO₂-sensing properties at RT under UV-light irradiation. In addition, these sensors also responded to $6,000 \text{ ppm H}_2$ and 50 ppmethanol at 30 °C in dry air under UV-light irradiation. Especially, the strong UV-light irradiation to pr-0.5Pd/ In_2O_3 sensor efficiently enhanced the ethanol response.

References

- T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, B. Chem. Soc. Jpn., 63, 988–992 (1990).
- J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonawicz, C. T. Kreage, K. D. Schmitt, D. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 114, 10834–10854 (1992).
- 3) A. Imhof and D. J. Pine, Nature, 389, 948-951 (1997).
- B. T. Holland, C. F. Blanford and A. Stein, *Science*, 281, 538–540 (1998).
- T. Hyodo, N. Nishida, Y. Shimizu and M. Egashira, J. Ceram. Soc. Jpn., 109, 481–483 (2001).
- T. Hyodo, N. Nishida, Y. Shimizu and M. Egashira, Sensor. Actuat. B-Chem., 83, 209–215 (2002).
- T. Hyodo, S. Abe, Y. Shimizu and M. Egashira, Sensor: Actuat. B-Chem., 93, 590–600 (2003).
- M. Hayashi, T. Hyodo, Y. Shimizu and M. Egashira, Sensor. Actuat. B-Chem., 141, 465–470 (2009).
- Y. Yuzuriha, T. Hyodo, T. Sasahara, Y. Shimizu and M. Egashira, *Sens. Lett.*, 9, 409–413 (2011).
- K. Sasahara, T. Hyodo, Y. Shimizu and M. Egashira, J. Eur. Ceram. Soc., 24, 1961–1967 (2004).
- T. Hyodo, K. Sasahara, Y. Shimizu and M. Egashira, Sensor: Actuat. B-Chem., 106, 580–590 (2005).
- H. Seh, T. Hyodo and H. L. Tuller, Sensor. Actuat. B-Chem., 108, 547–552 (2005).
- I.-D. Kim, A. Rothschild, T. Hyodo and H. L. Tuller, *Nano Lett.*, 6, 193–198 (2006).
- M. Morio, T. Hyodo, Y. Shimizu and M. Egashira, Sensor. Actuat. B-Chem., 139, 563–569 (2009).
- T. Hyodo, Y. Takakura, K. Kuroiwa, K. Tsuchiya and Y. Shimizu, J. Nanosci. Nanotechno., 19, 5351–5360 (2019).
- K. Hieda, T. Hyodo, Y. Shimizu and M. Egashira, Sensor. Actuat. B-Chem., 133, 144–150 (2008).
- T. Hyodo, H. Inoue, H. Motomura, K. Matsuo, T. Hashishin, J. Tamaki, Y. Shimizu and M. Egashira, *Sensor. Actuat. B-Chem.*, 151, 265–273 (2010).
- 18) T. Hyodo, E. Fujii, K. Ishida, T. Ueda, Y. Shimizu and

M. Egashira, Sensor. Actuat. B-Chem., 244, 992–1003 (2017).

- T. Ueda, I. Boehme, T. Hyodo, Y. Shimizu, U. Weimar and N. Barsan, *Chemosensors*, 8, 72 (2020).
- N. Tammanoon, T. Iwamoto, T. Ueda, T. Hyodo, A. Wisitsoraat, C. Liewhiran and Y. Shimizu, ACS Appl. Mater. Inter., 12, 41728–41739 (2020).
- F. H. Saboor, T. Ueda, K. Kamada, T. Hyodo, Y. Mortazavi, A. Ali Khodadadi and Y. Shimizu, *Sensor*. *Actuat. B-Chem.*, 223, 429–439 (2016).
- 22) T. Hyodo, K. Urata, K. Kamada, T. Ueda and Y. Shimizu, *Sensor. Actuat. B-Chem.*, 253, 630–640 (2017).
- E. Comini, A. Cristalli, G. Faglia and G. Sberveglieri, Sensor. Actuat. B-Chem., 65, 260–263 (2000).
- 24) T. Wagner, J. Hemmemann, C.-D. Kohl and M. Tiemann, *Thin Solid Films*, 520, 918–921 (2011).
- 25) H. Jin and H. Haick, Sensor. Actuat. B-Chem., 237, 30– 40 (2016).
- 26) F. Xu and H.-P. Ho, *Micromachines-Basel*, 8, 333 (2017).
- 27) A. Chizkov, M. Rumyantseva and A. Gaskov, *Nanomaterial*, 11, 892 (2021).
- 28) I. Cho, Y. C. Sim, M. Cho, Y.-H. Cho and I. Park, ACS Sensors, 5, 563–570 (2020).
- 29) M. T. Vijjapu, S. G. Surya, S. Yuvaraja, X. Zhang, H. N. Alshareef and K. N. Salama, ACS Sensors, 5, 984–993 (2020).
- Y. Zhang, O. Pluchery, L. Caillard, A.-F. Lamic-Humblot, S. Casale, Y. J. Chabal and M. Salmeron, *Nano Lett.*, 15, 51–55 (2015).
- 31) S. Matsushima, T. Maekawa, J. Tamaki, N. Miura and

N. Yamazoe, J. Chem. Soc. Jpn., 12, 1677–1683 (1991).

- O. Lang, C. Pettenkofer, J. F. Sánchez-Royo, A. Segura, A. Klein and W. Jaegermann, J. Appl. Phys., 86, 5687– 5691 (1999).
- Y. Takao, M. Nakanishi, T. Kawaguchi, Y. Shimizu and M. Egashira, *Sensor. Actuat. B-Chem.*, 24–25, 375–379 (1995).
- M. Egashira, Y. Shimizu, Y. Takao and Y. Fukuyama, Sensor. Actuat. B-Chem., 33, 89–95 (1996).
- T. Hyodo, Y. Tominaga, T. Yamaguchi, A. Kawahara, H. Katsuki, Y. Shimizu and M. Egashira, *Electrochemistry*, 71, 481–484 (2003).
- T. Ueda, K. Ishida, K. Kamada, T. Hyodo and Y. Shimizu, *Front. Mater.*, 6, 81 (2019).
- 37) D. Degler, S. Rank, S. Müller, H. W. Pereira de Carvalho, J.-D. Grunwaldt, U. Weimar and N. Barsan, ACS Sensors, 1, 1322–1329 (2016).
- B. Ruhland, T. Becker and G. Müller, *Sensor: Actuat. B-Chem.*, 50, 85–94 (1998).
- J. Baltrusaitis, P. M. Jayaweera and V. H. Grassian, *Phys. Chem. Chem. Phys.*, 11, 8295–8305 (2009).
- 40) F. Zasada, P. V. B. Pinho, W. Piskorz, C. Hudy, J. Janas, J. Gryboś, K. Góra-Marek and Z. Sojka, *J. Phys. Chem. C*, 124, 19681–19697 (2020).
- 41) X. Han, H. G. W. Godfrey, L. Briggs, A. J. Davies, Y. Cheng, L. L. Daemen, A. M. Sheveleva, F. Tuna, E. J. L. McInnes, J. Sun, C. Drathen, M. W. George, A. J. Ramirez-Cuesta, K. M. Thomas, S. Yang and M. Schröder, *Nat. Mater.*, **17**, 691–696 (2018).
- 42) K. L. Kenty, N. D. Poor, K. G. Kronmiller, W. McClenny, C. King, T. Atkeson and S. W. Cambell, *Atmos. Environ.*, 41, 4270–4280 (2007).