Effects of Polytetrafluoroethylene or Polyimide Coating on H₂ Sensing Properties of Anodized TiO₂ Films Equipped with Pd-Pt Electrodes

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Abstract

Diode-type H₂ sensors based on anodically oxidized TiO₂ thin films equipped with Pd-Pt electrodes (Pd-Pt/T-TiO₂, T-TiO₂ represents the TiO₂ thin film fabricated by the anodization of the pre-oxidized Ti plate at 600°C for 1 h in air) have been fabricated, and the effects of the polymer coating on the Pd-Pt/T-TiO₂ sensor to humidity and oxygen partial pressure on the sensing properties to 500~8,000 ppm H₂ under dry and wet atmospheres have been investigated in this study. The films tested were polytetrafluoroethylene (PTFE), polyimide (PI) film and heterogeneously laminated layers of these two polymer films, and the sensors fabricated were referred to as P-n/Pd-Pt/T-TiO₂ or P₁-n/P₂-n/Pd-Pt/T-TiO₂ (P, P₁ and P₂: PTFE or PI, n: polymer concentration of the coating solution (wt%)). The H₂ response of almost all sensors in wet air was larger than that in dry air, while the PTFE-n/Pd-Pt/T-TiO₂ and PI-n/PTFE-n/Pd-Pt/T-TiO₂ sensors showed only a slight enhancement in the H₂ response by introduction of moisture, in comparison with the Pd-Pt/T-TiO₂ or PI-n/Pd-Pt/T-TiO₂ sensors. On the other hand, the H₂ response of all sensors in N₂ was not affected by humidity. The PI-10/Pd-Pt/T-TiO₂ sensor showed the largest H₂ response in air at 250°C as well as N₂ among the all sensors tested; the response of the sensors in dry air and dry N₂ were ca. 3.1 × 10⁻⁴ A and ca. 4.7 × 10⁻² A, respectively, where the sensor current in H₂ atmosphere was regarded as sensor response, since that in the atmosphere without H₂ was extremely small. In addition, the H₂ response of the Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂ and PI-20/Pd-Pt/T-TiO₂ sensors were almost proportional to the H₂ concentration in a lower concentration range (500~2,000 ppm) in both dry and wet air, while it tended to saturate at a higher concentration range, especially for the PI-20/Pd-Pt/T-TiO₂ sensor in wet air. On the other hand, the sensor response to H₂ is well proportional to the logarithm of H₂ concentration in both dry and wet N₂ in the whole concentration range. Thus, the direct coating of the PTFE-n film on the Pd-Pt/T-TiO₂ sensors reduced the effect of humidity on the H₂ response
and the direct coating of the PI-\( n \) film on the Pd-Pt/T-TiO\(_2\) sensors was effective for enhancing the H\(_2\) response.

**Keywords:** diode-type H\(_2\) sensor; anodized TiO\(_2\) film; polytetrafluoroethylene; polyimide; Pd; Pt

1. Introduction

To date fossil fuels such as coal, crude oil and natural gas have been main energy sources for human beings. But, the large consumption of their energy sources have caused serious environmental problems such as acid rain, large emissions of NOx and suspended particulate matter, an increase in CO\(_2\) concentration and so on. Hydrogen (H\(_2\)) has attracted much attention as an alternative clean energy source in the next generation. However, it is highly flammable and explosive in a wide concentration range (4~75% in air). Therefore, highly-sensitive and -selective H\(_2\) sensors capable of detecting H\(_2\) leakage are indispensable to ensure the safety of our future H\(_2\)-energy society. In addition, the H\(_2\) sensors operable in different oxygen concentrations are also needed in the field of industrial monitoring.

During the past few years, various H\(_2\) sensors based on anodized TiO\(_2\) films have been studied by some researchers [1-6]. For example, Varghese et al. have reported that TiO\(_2\) nanotubes films (46 nm and 17 nm in inner diameter and wall thickness of the nanotubes, respectively) were prepared by anodization of Ti foil in 0.5% HF aqueous solution followed by annealing in an oxygen atmosphere at 500°C for 6 h and the TiO\(_2\) nanotube sensor equipped with a pair of Pt electrodes showed a high response to 100 ppm to 4% H\(_2\) balanced with N\(_2\) at 290°C [1]. Mukherjee et al. have reported that the porous TiO\(_2\) thin films were prepared by anodization of Ti foil in 1 M H\(_2\)SO\(_4\) aqueous solution at 50 mA cm\(^2\) and the semiconductor-type porous TiO\(_2\) thin film sensor having a pair of Ti electrodes exhibited a
relatively large H₂ response to 500 ppm H₂ in air at 300°C [2]. We have also developed highly-sensitive diode-type H₂ sensors by employing thin TiO₂ films having sub-micron pores, which were prepared by anodic oxidation of Ti plates in 0.5 M H₂SO₄ aqueous solution, and Pd electrodes deposited by radio-frequency (rf) magnetron sputtering (Pd/TiO₂). The Pd/TiO₂ sensor exhibited non-linear current (I)-voltage (V) characteristics in air, but almost linear I-V curves in H₂ balanced with air and then high H₂ response in a wide range of H₂ concentration under flowing both air and N₂ [7-12]. These excellent H₂ sensing properties arise from much lower Schottky barrier height at the boundary between the Pd electrode and the anodized TiO₂ film in H₂ than that in air, due to dissociative adsorption of H₂ molecules and subsequent dissolution of H atoms into the Pd electrode. In addition, the alloying of Pd with Pt was found to be quite effective for improving the reproducibility of H₂ response and its long-term stability [13, 14]. But, it was also revealed that the H₂ sensing properties of the anodized TiO₂ films equipped with the Pd-Pt alloy electrodes (Pd-Pt/TiO₂) were influenced significantly by humidity and oxygen partial pressure in our previous study [15]. In order to improve the H₂ sensing properties of Pd-Pt/TiO₂ sensors, therefore, development of highly sensitive, oxygen- and moisture-independent diode-type H₂ sensors is of primary importance. Some of polymer-based materials are well-known to have considerable potentials for effective separation of gaseous species, and therefore the use of such polymer-based materials was proved to be quite effective for improving the gas selectivity of various gas sensors. For example, Li et al. have focused on the effects of polyimide (PI) coating on the H₂ selectivity of metal-insulator-semiconductor (MIS) sensors [16]. Katti et al. have reported that polytetrafluoroethylene (PTFE) coating on the pellistor-type sensors reduced the effects of other gases such as hexamethyldisilazane (HMDS) and iodine on their H₂ sensing properties [17]. Kumar et al. have reported that the coating of different types of hydrophobic polymers such as polymethylmethacrylate (PMMA), poly(perfluorobutenyl vinyl ether) and
perfluoropolyether on In$_2$O$_3$-doped SnO$_2$ sensors led to good selectivity for H$_2$ sensing, large H$_2$ response and short response and recovery times in low moisture environment (humidity level of 14%) at room temperature [18].

In this study, therefore, we have attempted to improve H$_2$ sensing performance of Pd-Pt/TiO$_2$ sensors by the coating of polymer (PTFE or PI) films on the Pd-Pt alloy electrodes.

2. Experimental

2.1 Preparation and characterization of TiO$_2$ thin film sensors

A half of a Ti plate (5.0 mm × 10.0 mm × 0.5 mm) was anodized in a 0.5 M H$_2$SO$_4$ aqueous solution at 20°C for 30 min at a current density of 50 mA cm$^{-2}$. The anodized thin film thus fabricated is referred simply to as a U-TiO$_2$ film. To improve the reproducibility of the sensors, another Ti substrate was also employed. Namely, a Ti plate was thermally treated at 600°C for 1 h in air at first and then a half of the thermally-treated Ti plate was also anodized in a manner similar to the above and the resultant film is referred to as a T-TiO$_2$ film. Thereafter, the surface of the half of the thermally-treated Ti, which was not subjected to anodic oxidation, was polished to remove the air-oxidized surface and then to ensure electrical contact to the Ti metal. Microstructure of the U-TiO$_2$ and T-TiO$_2$ films was observed by scanning electron microscopy (SEM; JOEL Ltd., JSM-7500F). Crystal phase of the films was characterized by X-ray diffraction analysis (XRD; Rigaku Corp., RINT2200) using Cu K$_\alpha$ radiation (40 kV, 40 mA). For each kind of the plate, Pd-Pt alloy (Pd : Pt = 58 : 42 (wt%), film thickness: ca. 200 nm) electrodes were fabricated on both the U-TiO$_2$ (or T-TiO$_2$) film and the Ti metal part by rf magnetron sputtering (Shimadzu Corp., HSR-552S) and electrical contact to Au lead wires was achieved by the application of Pt paste and then was ensured by subsequent firing at 600°C for 1 h in air. The sensors thus fabricated are
referred to as Pd-Pt/U-TiO$_2$ and Pd-Pt/T-TiO$_2$, depending on the kind of the Ti plates subjected to anodic oxidation.

**2.2 Polymer coating on the Pd-Pt electrodes**

A given amount of PTFE dispersion (Daikin Ind., D-1E) was mixed with deionized water, while PI (PI R&D Co., Ltd., Q-VR-FR007) was mixed with 1-methyl-2-pyrrolidone, and then the mixtures were stirred at room temperature (RT). The concentration of PTFE and PI in the mixtures was shown in Table 1. These solutions obtained were coated on the surface of the Pd-Pt alloy electrodes at RT by spin coating at 10,000 rpm. These polymer-coated sensors were heat-treated at 250°C for 30 min in air. The polymer-coated sensors were only fabricated with Pd-Pt/T-TiO$_2$, i.e., by employing the anodized TiO$_2$ film on the thermally treated Ti plate. The sensors thus fabricated are referred to as P-n/Pd-Pt/T-TiO$_2$ (P: PTFE or PI, n: polymer concentration in the coating solution (wt%)). Furthermore, heterogeneously laminated polymer layers were fabricated on Pd-Pt/T-TiO$_2$ by repeating the spin coating of different polymer precursor solution followed by heat-treatment in a similar manner as described above. These sensors are referred to as P$_1$-n/P$_2$-n/Pd-Pt/T-TiO$_2$ (P$_1$, P$_2$: PTFE or PI). Figure 1 shows a cross-sectional drawing of a typical P-n/Pd-Pt/T-TiO$_2$ sensor fabricated in this study. Thermal behavior of PTFE and PI was examined under air flowing (100 cm$^3$ min$^{-1}$) by thermogravimetry-differential thermal analysis (TG-DTA, heating rate: 5.0°C min$^{-1}$, temperature range: RT~800°C).

**2.3 Measurement of H$_2$ sensing properties**

A dc voltage of 100 mV was applied to all sensors under forward bias condition (Pd-Pt(+)-U-TiO$_2$ (or T-TiO$_2$)-Ti(-)), and transient changes in current flowing through the sensors upon exposure to 500~8,000 ppm H$_2$ balanced with air and N$_2$ under dry or wet
(absolute humidity (AH): 9.40 g m\(^{-3}\), this value is correspond to ca. 40.8% relative humidity (RH) at 25°C) atmospheres were measured in the temperature range of 150~300°C by employing a potentiostat (Bio-Logic Science Instruments, SP-150). The magnitude of sensor response was defined as the sensor current in H\(_2\) atmosphere, because the sensor current in a H\(_2\)-free environment was negligibly small.

3. Results and Discussions

3.1 Investigation on the thermal stability of PTFE and PI and the thickness of their films

To determine the operating temperature range in measuring the H\(_2\) sensing properties of polymer-coated sensors, thermal stability behavior of polymers after heat treatment at 250°C for 30 min was examined by TG-DTA. Figure 2 shows TG-DTA curves of PTFE and PI films. As for the PTFE film, an endothermic peak at ca. 338°C and exothermic peaks at ca. 535°C and ca. 567°C, which are ascribed to melting and decomposition of PTFE, respectively, were observed, and the weight drastically reduced around the decomposition temperature. On the other hand, a small exothermic peak at ca. 363°C was observed for the PI film, but the weight remained almost unchanged around the decomposition temperature. In addition, the main exothermic peak indicating the decomposition of PI was observed at 634°C. Based on these results, the maximum operation temperature of all sensors was set at 300°C.

Figure 3 shows SEM photographs of the cross sections of representative polymer films coated on the Pd-Pt electrodes. For these observations, a TiO\(_2\)-modified Si substrate, which was fabricated by the deposition of a Ti metal film on a Si substrate by rf magnetron sputtering followed by heat treatment at 600°C for 1 h, was employed as an alternative to the T-TiO\(_2\) film, since it was very difficult for us to observe the cross section of actual polymer-coated sensors fabricated on the highly ductile Ti metal plate. Morphology of these films was relatively uniform, as shown in Fig. 3. The PTFE-20 film (ca. 800 nm thick) was
relatively porous and consisted of submicron-sized particles, while the PI-20 film (ca. 160 nm thick) was much dense and thin in comparison with the PTFE-20 film. For the PI-20/PTFE-20 film, the PI film was hardly confirmed on the surface of the PTFE-20 film (ca. 460 nm thick), probably because of the penetration of the PI solution into the porous PTFE film during the second spin coating. For the PTFE-20/PI-20 film, on the other hand, the stacking structure of the PTFE film (ca. 380 nm thick) on the PI thin film (ca. 80 nm thick) was observed clearly. In addition, the morphology of the PTFE films of the PTFE-20/PI-20 and PI-20/PTFE-20 films was comparable with that of the PTFE-20 film alone. Thickness of all polymer films fabricated in this study was summarized in Table 1.

3.2 Effect of thermal treatment before anodization to H₂ sensing properties

First, the effect of the pre-thermal treatment in air of the Ti plate before anodization on the current (I)-voltage (V) characteristics of anodized TiO₂-based sensors has been investigated. Figure 4 shows I-V characteristics of Pd-Pt/U-TiO₂ and Pd-Pt/T-TiO₂ sensors in air and N₂, and also in 8,000 ppm H₂ balanced with air and N₂ under dry atmosphere at 250°C. Nonlinear I-V curves, which are typical for diode-type sensors, were observed for both the sensors in dry air and N₂. The introduction of H₂ into both dry air and N₂ drastically enhanced the magnitude of current of both the sensors especially under forward bias condition. In addition, both the sensors showed ohmic I-V curves in 8,000 ppm H₂ balanced with dry N₂. This result indicates the large contribution of the Schottky barrier at the interface Pd-Pt electrodes and anodized TiO₂ film in detecting H₂. Namely, dissociative adsorption of H₂ molecules on the electrode and subsequent dissolution of H species into the electrode can reduce the work function of the electrode and thus the height of Schottky barrier between the electrode and the TiO₂ film is decreased by the introduction of H₂ into both dry air and N₂. In addition, the magnitude of current for these sensors in 8,000 ppm H₂ balanced with dry N₂.
was much larger than that in 8,000 ppm H₂ balanced with dry air. The reason is probably because H₂ molecules are oxidized with chemisorbed oxygen on the Pd-Pt electrode surface in dry air, whereas the amount of chemisorbed oxygen on the electrode in dry N₂ is much less than that in dry air, and thus the large amount of dissociative H species dissolves into the electrode. In addition, the magnitude of current of the Pd-Pt/T-TiO₂ sensor was larger than that of the Pd-Pt/U-TiO₂ sensor in 8,000 ppm H₂ balanced with dry air and N₂. Figure 5 shows response transients of the Pd-Pt/U-TiO₂ and Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ at 250°C in air and N₂ under dry atmospheres. The response speed of both sensors in air was relatively slower than that in N₂, while the recovery speed of both sensors in air was much faster than that in N₂. The H₂ response of both sensors in air was extremely much smaller than that in N₂, and the thermal treatment before anodization improved the H₂ response of an anodized TiO₂-based sensor under both air and N₂ atmospheres, as expected from their I-V characteristics (Fig. 4). In order to get a possible reason for the higher H₂ response of the Pd-Pt/T-TiO₂ sensor than the Pd-Pt/U-TiO₂ sensor, characteristics of these two TiO₂ films were examined by SEM observation and XRD analysis.

Figure 6 shows SEM photographs of the surface of U-TiO₂ and T-TiO₂ films. Many submicron-sized pores were formed on the surface of both TiO₂ films. The size of pores on the surface of the T-TiO₂ film was smaller than that of the U-TiO₂ film, and the number of pores per a certain unit of surface area on the T-TiO₂ film was more than that of the U-TiO₂ film. These results suggested the importance of the size of pores and the number of pores on the surface of an anodized TiO₂ film in realizing high H₂ response. But the reason for the change in surface morphology of the anodized TiO₂ film induced by the pre-thermal treatment the Ti metal plate is not clear at present. Figure 7 shows XRD patterns of U-TiO₂ and T-TiO₂ films. Both the TiO₂ films were a mixture of anatase and rutile phase, and also the ratio of rutile phase was more than that of anatase phase. But, the peak intensity of rutile
phase of the T-TiO₂ film was stronger than that of the U-TiO₂ film. These results suggested that the thermal treatment before the anodization affects the amount of rutile phase and then promotes the anodization process.

In the next section, P-n and P₁-n/P₂-n films were coated on the electrode surface of the Pd-Pt/T-TiO₂ sensor, and the coating effects of their polymer films to the H₂ sensing properties of the Pd-Pt/T-TiO₂ sensor have been investigated.

3.3 Effects of the coating of P-n or P₁-n/P₂-n film on H₂ response properties of Pd-Pt/T-TiO₂ sensors

Figure 8 shows response transients of Pd-Pt/T-TiO₂, P-n/Pd-Pt/T-TiO₂ and P₁-n/P₂-n/Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ at 250°C in air under dry and wet atmospheres. The Pd-Pt/T-TiO₂ showed relatively large response to 8,000 ppm H₂ in both dry and wet air, and the response in wet air (ca. 5.1 × 10⁻⁴ A) was much larger than that in dry air (ca. 8.1 × 10⁻⁵ A). This arises probably from the adsorption of a relatively large amount of H₂O molecules on the electrode surface in wet air and therefore the disturbance of the adsorption of oxygen species, leading to a large amount of dissolved H species into the electrode. The response speed in dry air (90% response time (Res): 1.28 min) was faster than that in wet air (Res: 2.84 min), and the recovery speed in dry air (90% recovery time (Rec): 1.14 min) was comparable to that in wet air (Rec: 1.22 min). The coating of a PTFE-n film on the Pd-Pt/T-TiO₂ sensors reduced the H₂ response at 250°C in dry air, and the coating of a PI-n film on the PTFE-n/Pd-Pt/T-TiO₂ sensors further decreased the H₂ response in dry air. On the other hand, the coating of the PI-n film on the Pd-Pt/T-TiO₂ sensors largely enhanced the H₂ response in dry air. This may imply the possibility of the limitation of oxygen diffusion through the film and relatively high H₂ concentration in the vicinity of the Pd-Pt electrodes. However, the coating of the PTFE-n film on the PI-n/Pd-Pt/T-TiO₂ sensors
largely decreased the H₂ response in dry air.

The H₂ response of almost all sensors in wet air was larger than that in dry air. But, the PTFE-\( n \)/Pd-Pt/T-TiO₂ and PI-\( n \)/PTFE-\( n \)/Pd-Pt/T-TiO₂ sensors showed only a slight enhancement in the H₂ response by introduction of moisture, in comparison with other sensors. Namely, the direct coating of the PTFE-\( n \) film on the Pd-Pt/T-TiO₂ sensors reduced the effect of humidity on the H₂ response, probably because of the waterproof property of PTFE. On the other hand, the direct coating of PI-\( n \) film on the Pd-Pt/T-TiO₂ sensors was effective for enhancing the H₂ response and the PI-10/Pd-Pt/T-TiO₂ sensor in both dry and wet air showed the largest H₂ response among the all sensors tested; the response of the sensors in dry air and wet air were ca. 3.1 × 10⁻⁴ A and ca. 9.0 × 10⁻⁴ A, respectively. However, the coating of the PTFE-\( n \) film on the PI-\( n \)/Pd-Pt/T-TiO₂ sensors reduced the H₂ response. In addition, the response speed of P-\( n \)/Pd-Pt/T-TiO₂ and P₁-\( n \)/P₂-\( n \)/Pd-Pt/T-TiO₂ sensors in wet air was slower than that in dry air, while their recovery speed in wet air was comparable to that in dry air, as were observed for the Pd-Pt/T-TiO₂ sensor.

Similar measurement was also conducted with Pd-Pt/T-TiO₂, P-\( n \)/Pd-Pt/T-TiO₂ and P₁-\( n \)/P₂-\( n \)/Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ at 250°C in N₂ under dry and wet atmospheres, as shown in Fig. 9. The Pd-Pt/T-TiO₂ showed relatively large response to 8,000 ppm H₂ in both dry and wet N₂, and the response in dry N₂ (ca. 3.8 × 10⁻² A) was comparable to that in wet N₂ (ca. 3.7 × 10⁻² A). The addition of the moisture into N₂ is ineffective in enhancing the H₂ response of the Pd-Pt/T-TiO₂ sensor in dry N₂, because the amount of chemisorbed oxygen on the electrode surface in N₂ is extremely less than that in air. The response speed in dry N₂ (90% response time (Res): 0.84 min) was comparable to that in wet N₂ (Res: 0.98 min), and also the recovery speed in dry N₂ (90% recovery time (Rec): 2.54 min) was comparable to that in wet N₂ (Rec: 2.71 min).

The H₂ response of P-\( n \)/Pd-Pt/T-TiO₂ and P₁-\( n \)/P₂-\( n \)/Pd-Pt/T-TiO₂ sensors in N₂ was also
much larger than that in air, and their H$_2$ response in N$_2$ increased by about 2~3 orders of magnitude, in comparison with that in air. In addition, all sensors except for the PI-20/Pd-Pt/T-TiO$_2$ sensor showed relatively fast response speed in both dry and wet N$_2$, in comparison with those in both dry and wet air, probably because it is unnecessary to remove oxygen adsorbates and/or oxide layers on the electrode surface before the dissociative adsorption of H$_2$ and subsequent dissolution of H atoms into the electrode. But, they showed relatively slow recovery speed in both dry and wet N$_2$, in comparison with those in both dry and wet air, probably because the existence of gaseous oxygen in the environment is essential for achieving fast extraction of H species dissolved in the electrodes.

The coating of the PTFE-$n$ and PI-$n$/PTFE-$n$ films except for the PTFE-20 film, tended to decrease the H$_2$ response of the Pd-Pt/T-TiO$_2$ sensor in both dry and wet N$_2$. On the other hand, the H$_2$ response of the PI-$n$/Pd-Pt/T-TiO$_2$ sensors in dry and wet N$_2$ was larger than that of the Pd-Pt/T-TiO$_2$ sensor, while the coating of the PTFE-$n$ film of the PI-$n$/Pd-Pt/T-TiO$_2$ sensors reduced their H$_2$ response. Among them, PI-10/Pd-Pt/T-TiO$_2$ sensors in dry and wet N$_2$ showed the largest H$_2$ response (ca. 4.7 × 10$^{-2}$ A and ca. 4.6 × 10$^{-2}$ A, respectively). In addition, the H$_2$ response of all sensors in N$_2$ was found to be not affected by humidity.

Figures 10 and 11 show operating temperature dependence of sensor current of Pd-Pt/T-TiO$_2$, P-$n$/Pd-Pt/T-TiO$_2$ and P$_{1-n}$/P$_{2-n}$/Pd-Pt/T-TiO$_2$ sensors to 8,000 ppm H$_2$ in air and N$_2$ under both dry and wet atmospheres. The H$_2$ response of all sensors in N$_2$ was much larger than that in air, under both dry and wet atmospheres in the whole temperature range (500~8,000 ppm) studied. In addition, the H$_2$ response of almost all sensors in air tended to show smaller H$_2$ response in lower operating temperature under both dry and wet atmospheres. In contrast, almost all sensors in N$_2$ showed relatively high and operating temperature-independent H$_2$ response in the temperature range of 150°C~300°C, except for PTFE-$n$/Pd-Pt/T-TiO$_2$ sensors at 150°C. Thus, it was revealed that the coating of the PI-$n$
film on the Pd-Pt/T-TiO₂ sensor was quite effective in improving the H₂ response at 150°C~300°C in air as well as N₂ under dry and wet atmospheres.

To clarify the effect of humidity and oxygen partial pressure on the H₂ response of Pd-Pt/T-TiO₂, P-n/Pd-Pt/T-TiO₂ and P₁-n/P₂-n/Pd-Pt/T-TiO₂ sensors, temperature dependence of the ratio of H₂ response under wet atmosphere to that under dry atmosphere in air as well as N₂ and the ratio of H₂ response in N₂ to that in air under wet as well as dry atmospheres were plotted in Figs. 12 and 13, where each H₂ response was expressed as wIo (w: wet or dry atmosphere, o: in air or N₂). The magnitude of wet/air of the PTFE-n/Pd-Pt/T-TiO₂ sensors was smaller than that of the Pd-Pt/T-TiO₂ sensor (Fig. 12(a)(i)), indicating the reduction of the effect of humidity on the H₂ response. Therefore, this result indicated that the waterproof property of PTFE was effective in reducing the H₂ response in wet air in the whole temperature range. However, especially in the case of PI-10/PTFE-10/Pd-Pt/T-TiO₂ sensor, the additional coating of PI-10 on the PTFE-10 increases the magnitude of wet/air at temperatures lower than 200°C, in comparison with that of Pd-Pt/T-TiO₂, leading to the enhancement of the interference from humidity on the H₂ response. In contrast, the magnitude of wet/N₂ was almost unity in N₂ for all the sensors, except for those of PTFE-20/Pd-Pt/T-TiO₂ sensors at 150°C (Fig. 12(a)(ii)). In addition, the magnitude of wet/N₂ of almost all sensors was larger than that of Pd-Pt/T-TiO₂ sensor (Fig. 12(b)), showing an increase in the effect of oxygen concentration on the H₂ response by the PTFE-n coating on the Pd-Pt electrodes. The coating of the PI-n film on the PTFE-n/Pd-Pt/T-TiO₂ sensors slightly reduced the effect of oxygen partial pressure on their H₂ response under wet atmosphere, but the magnitude of wet/N₂ was still larger than that of the Pd-Pt/T-TiO₂ sensor.

The magnitude of wet/air of the PI-20/Pd-Pt/T-TiO₂ sensor was comparable with that of the Pd-Pt/T-TiO₂ sensor, but the magnitude of wet/air of the PI-10/Pd-Pt/T-TiO₂ sensor
was smaller than that of the Pd-Pt/T-TiO₂ sensor in the whole temperature range and the effect of humidity on the H₂ response was decreased with an increase in operating temperature and was almost negligible \( \frac{\text{wet}_\text{air}}{\text{dry}_\text{air}} \approx 1 \) at 300°C (Fig. 13(a)(i)). The magnitude of \( \frac{\text{wet}_\text{N}_2}{\text{dry}_\text{N}_2} \) of the PI-n/Pd-Pt/T-TiO₂ and PTFE-n/PI-n/Pd-Pt/T-TiO₂ sensors was almost unity (Fig. 13(a)(ii)), as was observed in the cases of the PTFE-n/Pd-Pt/T-TiO₂ and PI-n/PTFE-n/Pd-Pt/T-TiO₂ sensors (Fig. 12(a)(ii)). In addition, the magnitude of \( \frac{\text{dry}_\text{N}_2}{\text{dry}_\text{air}} \) of PTFE-n/PI-n/Pd-Pt/T-TiO₂ sensors was larger than that of the Pd-Pt/T-TiO₂ sensor. However, the magnitude of \( \frac{\text{w}_\text{N}_2}{\text{w}_\text{air}} \) of only the PI-10/Pd-Pt/T-TiO₂ sensor was smaller than that of the Pd-Pt/T-TiO₂ sensor, especially at 300°C under dry atmosphere, showing the certain reduction of the interference from oxygen partial pressure on the H₂ response. The coating of the PTFE-10/PI-10 film on the Pd-Pt/T-TiO₂ sensor also reduced the interference from oxygen partial pressure under wet atmosphere on the H₂ response of the Pd-Pt/T-TiO₂ sensor at lower temperatures (especially at 150°C) (Fig. 13(b)(ii)).

### 3.4 H₂ concentration dependence of H₂ response of representative sensors

The response transients of the Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂ and PI-20/Pd-Pt/T-TiO₂ sensors to 500~8,000 ppm H₂ balanced with dry and wet air are shown in Fig. 14(a). The sensor current decreased steadily with a decrease in H₂ concentration in both dry and wet air, and then the sensor current in 500 ppm H₂ became extremely small. In addition, the H₂ responses of all sensors to 500~8,000 ppm H₂ in wet air were larger than those in dry air. The sensor current in 500 ppm H₂ of the Pd-Pt/T-TiO₂ and PTFE-20/Pd-Pt/T-TiO₂ sensors was rather noisy and small, but the PI-20/Pd-Pt/T-TiO₂ sensor showed the largest response even to 500 ppm H₂ in both dry and wet air. Figure 14(b) shows the relationship between the sensor current and H₂ concentration in dry and wet air measured for three kinds of sensors. The sensor current in H₂ was almost proportional to the H₂
concentration in a lower concentration range, while it tended to saturate in higher concentration range, especially in wet air. On the other hand, the $\text{H}_2$ response of the PI-20/Pd-Pt/T-TiO$_2$ sensor was higher than that of the Pd-Pt/T-TiO$_2$ and PTFE-20/Pd-Pt/T-TiO$_2$ sensors at 250$^\circ$C. For instance, the responses in 500 ppm $\text{H}_2$ balanced with dry and wet air of the PI-20/Pd-Pt/T-TiO$_2$ sensor were ca. $1.65 \times 10^{-5}$ A and $3.23 \times 10^{-5}$ A, respectively.

The response transients of the Pd-Pt/T-TiO$_2$, PTFE-20/Pd-Pt/T-TiO$_2$ and PI-20/Pd-Pt/T-TiO$_2$ sensors to 500~8,000 ppm $\text{H}_2$ balanced with dry and wet N$_2$ are also shown in Fig. 15(a). The sensor current gradually decreased with a decrease in $\text{H}_2$ concentration in both dry and wet N$_2$, but all sensors showed stable and relatively large response even to a concentration of 500 ppm $\text{H}_2$ in both dry and wet N$_2$. Thus, the $\text{H}_2$ response in N$_2$ was much larger than that in air, especially in lower $\text{H}_2$ concentrations. Figure 15(b) shows the relationship between the sensor current and $\text{H}_2$ concentration in dry and wet N$_2$ measured for three kinds of sensors. It was found that the sensor current in $\text{H}_2$ is well proportional to the logarithm of $\text{H}_2$ concentration in both dry and wet N$_2$. On the other hand, the $\text{H}_2$ response of the PI-20/Pd-Pt/T-TiO$_2$ sensor was higher than that of the Pd-Pt/T-TiO$_2$ and PTFE-20/Pd-Pt/T-TiO$_2$ sensors at 250$^\circ$C. For instance, the responses in 500 ppm $\text{H}_2$ balanced with dry and wet N$_2$ of the PI-20/Pd-Pt/T-TiO$_2$ sensor were ca. $4.22 \times 10^{-2}$ A and $3.80 \times 10^{-2}$ A, respectively. Among them, the PI-20/Pd-Pt/TiO$_2$ sensor showed the most improved $\text{H}_2$ response in all atmospheres, i.e. in air both dry and wet, air as well as N$_2$ atmospheres.

The $\text{H}_2$ concentration dependence of $w_{\text{N}_2}/d_{\text{air}}I_0$ and $w_{\text{N}_2}/w_{\text{air}}I_0$ of Pd-Pt/T-TiO$_2$, PTFE-20/Pd-Pt/T-TiO$_2$ and PI-20/Pd-Pt/T-TiO$_2$ sensors were plotted in Fig. 16. The magnitude of $w_{\text{N}_2}/d_{\text{air}}I_0$ of the PTFE-20/Pd-Pt/T-TiO$_2$ sensor was smaller than that of the Pd-Pt/T-TiO$_2$ sensor in the whole $\text{H}_2$ concentration range tested, and it was almost equal to
unity at lower \( H_2 \) concentrations (less than 1,000 ppm \( H_2 \)), indicating the reduction of the effect of humidity on the \( H_2 \) response (Fig. 16(a)(i)). In addition, the magnitude of \( w_{NI_2}/d_{dryNI_2} \) was almost unity for all the sensors in the whole \( H_2 \) concentration range. On the other hand, the magnitude of \( w_{NI_2}/w_{I_{air}} \) of the PTFE-20/Pd-Pt/T-TiO\(_2\) sensor was larger than that of the Pd-Pt/T-TiO\(_2\) sensor, while the magnitude of \( w_{NI_2}/w_{I_{air}} \) of the PI-20/Pd-Pt/T-TiO\(_2\) sensor was smaller than that of the Pd-Pt/T-TiO\(_2\) sensor, showing a decrease in the effect of oxygen partial pressure on the \( H_2 \) response in the case of the PI-20/Pd-Pt/T-TiO\(_2\) sensor (Fig. 16(b)). However, the magnitude of \( w_{NI_2}/w_{I_{air}} \) under both dry and wet atmospheres increased with a decrease in the \( H_2 \) concentration, especially in the lower concentration range (less than 2,000 ppm). In air environment, the percentage of \( H_2 \) oxidized at the electrode surface is considered to be increased with decreasing \( H_2 \) concentration, leading to a smaller \( H_2 \) response in low \( H_2 \) concentration range. But, such phenomenon can be neglected in \( N_2 \) environment. Such a difference in \( H_2 \) oxidation behavior at the surface of the electrode is considered to be responsible for the change in \( w_{NI_2}/w_{I_{air}} \) with \( H_2 \) concentration.

4. Conclusions

Effects of PTFE or PI film coating on the \( H_2 \) sensing properties of Pd-Pt/T-TiO\(_2\) sensors have been investigated in this study. The coating of a PTFE film on the Pd-Pt electrodes was effective in reducing the interference from humidity on the \( H_2 \) response of the Pd-Pt/T-TiO\(_2\) sensor in air. In addition, the \( H_2 \) response of all sensors in \( N_2 \) was much larger than that in air and the interference from humidity was negligible in \( N_2 \). Among the sensors tested, the PI-10/Pd-Pt/T-TiO\(_2\) sensor showed the most improved \( H_2 \) response in air as well as \( N_2 \) under both dry and wet atmospheres; the \( H_2 \) response in dry air (ca. \( 3.1 \times 10^{-4} \) A) was smaller than that in wet air (ca. \( 9.0 \times 10^{-4} \) A), while the \( H_2 \) response in dry \( N_2 \) (ca. \( 4.7 \times 10^{-2} \) A) was comparable to that in wet \( N_2 \) (ca. \( 4.6 \times 10^{-2} \) A). The coating of the heterogeneously
laminated polymer (P$_1$-n/P$_2$-n) layer on the Pd-Pt/T-TiO$_2$ sensors was not effective for enhancing the H$_2$ response. The optimization of thickness and/or porosity of these polymer films are probably essential for further improving the H$_2$ response properties. The response of the Pd-Pt/T-TiO$_2$ and PTFE-20/Pd-Pt/T-TiO$_2$ sensors to 500 ppm H$_2$ in both dry and wet air was extremely small, while the PI-20/Pd-Pt/T-TiO$_2$ sensor showed large response even to 500 ppm H$_2$ in both dry and wet air. In addition, all the sensors showed stable and relatively large response even to a concentration of 500 ppm H$_2$ in both dry and wet N$_2$.

References


Biographies

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Figure Captions

Fig. 1 Schematic drawing of a diode-type sensor.

Fig. 2 TG-DTA curves of (a) PTFE and (b) PI films with a heating rate of 5.0°C min⁻¹ under air flowing.

Fig. 3 SEM photographs of the cross section of representative polymer films.

Fig. 4 I-V characteristics of (i) Pd-Pt/U-TiO₂ and (ii) Pd-Pt/T-TiO₂ sensors in air and N₂, and also in 8,000 ppm H₂ balanced with air and N₂ under dry atmosphere at 250°C.

Fig. 5 Response transients of (i) Pd-Pt/U-TiO₂ and (ii) Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ in (a) air and (b) N₂ under dry atmosphere at 250°C.

Fig. 6 SEM photographs of the surface of (i) U-TiO₂ and (ii) T-TiO₂ films.

Fig. 7 XRD patterns of (i) U-TiO₂ and (ii) T-TiO₂ films.

Fig. 8 Response transients of Pd-Pt/T-TiO₂, P-n/Pd-Pt/T-TiO₂ and P₁-n/P₂-n/Pd-Pt/T-TiO₂ sensors to 8000 ppm H₂ at 250°C in air under (a) dry and (b) wet atmospheres.

Fig. 9 Response transients of Pd-Pt/T-TiO₂, P-n/Pd-Pt/T-TiO₂ and P₁-n/P₂-n/Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ at 250°C in N₂ under (a) dry and (b) wet atmospheres.

Fig. 10 Operating temperature dependence of sensor current of Pd-Pt/T-TiO₂, PTFE-n/Pd-Pt/T-TiO₂ and PI-n/PTFE-n/Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ in (a) air and (b) N₂ under (i) dry and (ii) wet atmospheres.

Fig. 11 Operating temperature dependence of sensor current of Pd-Pt/T-TiO₂, PI-n/Pd-Pt/T-TiO₂ and PTFE-n/PI-n/Pd-Pt/T-TiO₂ sensors to 8,000 ppm H₂ in (a) air and (b) N₂ under (i) dry and (ii) wet atmospheres.

Fig. 12 Operating temperature dependence of (a) wetIo/dryIo and (b) wIN₂/wIair of Pd-Pt/T-TiO₂, PTFE-n/Pd-Pt/T-TiO₂ and PI-n/PTFE-n/Pd-Pt/T-TiO₂ sensors.

Fig. 13 Operating temperature dependence of (a) wetIo/dryIo and (b) wIN₂/wIair of Pd-Pt/T-TiO₂, PI-n/Pd-Pt/T-TiO₂ and PTFE-n/PI-n/Pd-Pt/T-TiO₂ sensors.
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Fig. 15  (a) Response transients to 500~8,000 ppm H₂ and (b) variation in sensor current of Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂ and PI-20/Pd-Pt/T-TiO₂ sensors with H₂ concentration (C_H₂) in (i) dry and (ii) wet N₂ at 250°C.

Fig. 16  H₂ concentration dependence of (a) wetIo/dryIo and (b) wetN₂/wetair of Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂ and PI-20/Pd-Pt/T-TiO₂ sensors.
Table 1  Fabrication conditions and thickness of polymer films coated on the Pd-Pt electrodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer film</th>
<th>Polymer concentration (wt%)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PTFE</td>
<td>PI</td>
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</tr>
<tr>
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</tr>
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<td>PI-20</td>
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</table>
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Fig. 7 XRD patterns of (i) U-TiO$_2$ and (ii) T-TiO$_2$ films.
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Fig. 9 Response transients of Pd-Pt/T-TiO$_2$, P-n/Pd-Pt/T-TiO$_2$ and P$_1$-n/P$_2$-n/Pd-Pt/T-TiO$_2$ sensors to 8,000 ppm H$_2$ at 250°C in N$_2$ under (a) dry and (b) wet atmospheres.
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Fig. 13 Operating temperature dependence of (a) wet $I_0$/dry $I_0$ and (b) wet $I_{N_2}$/wet $I_{air}$ of Pd-Pt/T-TiO$_2$, PI-$n$/Pd-Pt/T-TiO$_2$ and PTFE-$n$/PI-$n$/Pd-Pt/T-TiO$_2$ sensors.
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(a) Response transients

![Graph showing response transients to 500-8,000 ppm H₂ and variation in sensor current of Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂, and PI-20/Pd-Pt/T-TiO₂ sensors with H₂ concentration (C₇₂) in (i) dry and (ii) wet N₂ at 250°C.](image)

(b) Sensor current vs. log C₇₂

![Graph showing sensor current vs. logarithm of H₂ concentration.](image)

Fig. 15 (a) Response transients to 500-8,000 ppm H₂ and (b) variation in sensor current of Pd-Pt/T-TiO₂, PTFE-20/Pd-Pt/T-TiO₂, and PI-20/Pd-Pt/T-TiO₂ sensors with H₂ concentration (C₇₂) in (i) dry and (ii) wet N₂ at 250°C.
Fig. 16 \( \text{H}_2 \) concentration dependence of (a) \( \frac{I_{\text{wet}}}{I_{\text{dry}}} \) and (b) \( \frac{I_{\text{N}_2}}{I_{\text{air}}} \) of Pd-Pt/T-TiO\(_2\), PTFE-20/Pd-Pt/T-TiO\(_2\) and PI-20/Pd-Pt/T-TiO\(_2\) sensors.