Effects of Polytetrafluoroethylene or Polyimide Coating on H_2 Sensing Properties of Anodized TiO_2 Films Equipped with Pd-Pt Electrodes

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Abstract

Diode-type H_2 sensors based on anodically oxidized TiO_2 thin films equipped with Pd-Pt electrodes (Pd-Pt/T-TiO_2, T-TiO_2 represents the TiO_2 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-TiO_2 sensor to humidity and oxygen partial pressure on the sensing properties to 500~8,000 ppm H_2 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-TiO_2 or P_1-*n*/P_2-*n*/Pd-Pt/T-TiO_2 (P, P_1 and P_2: PTFE or PI, *n*: polymer concentration of the coating solution (wt%)). The H_2 response of almost all sensors in wet air was larger than that in dry air, while the PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors showed only a slight enhancement in the H_2 response by introduction of moisture, in comparison with the Pd-Pt/T-TiO_2 or PI-*n*/Pd-Pt/T-TiO_2 sensors. On the other hand, the H_2 response of all sensors in N_2 was not affected by humidity. The PI-*10*/Pd-Pt/T-TiO_2 sensor showed the largest H_2 response in air at 250°C as well as N_2 among the all sensors tested; the response of the sensors in dry air and dry N_2 were ca. 3.1×10^{-4} A and ca. 4.7×10^{-2} A, respectively, where the sensor current in H_2 atmosphere was regarded as sensor response, since that in the atmosphere without H_2 was extremely small. In addition, the H_2 response of the Pd-Pt/T-TiO_2, PTFE-*20*/Pd-Pt/T-TiO_2 and PI-*20*/Pd-Pt/T-TiO_2 sensors were almost proportional to the H_2 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-TiO_2 sensor in wet air. On the other hand, the sensor response to H_2 is well proportional to the logarithm of H_2 concentration in both dry and wet N_2 in the whole concentration range. Thus, the direct coating of the PTFE-*n* film on the Pd-Pt/T-TiO_2 sensors reduced the effect of humidity on the H_2 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_2SO_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 H_2 response to 500 ppm H_2 in air at 300°C [2]. We have also developed highly-sensitive diode-type H_2 sensors by employing thin TiO_2 films having sub-micron pores, which were prepared by anodic oxidation of Ti plates in 0.5 M H_2SO_4 aqueous solution, and Pd electrodes deposited by radio-frequency (rf) magnetron sputtering (Pd/TiO_2). The Pd/TiO_2 sensor exhibited non-linear current (*I*)-voltage (*V*) characteristics in air, but almost linear *I-V* curves in H_2 balanced with air and then high H_2 response in a wide range of H_2 concentration under flowing both air and N_2 [7-12]. These excellent H_2 sensing properties arise from much lower Schottky barrier height at the boundary between the Pd electrode and the anodized TiO_2 film in H_2 than that in air, due to dissociative adsorption of H_2 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 H_2 response and its long-term stability [13, 14]. But, it was also revealed that the H_2 sensing properties of the anodized TiO_2 films equipped with the Pd-Pt alloy electrodes (Pd-Pt/TiO_2) were influenced significantly by humidity and oxygen partial pressure in our previous study [15]. In order to improve the H_2 sensing properties of Pd-Pt/TiO_2 sensors, therefore, development of highly sensitive, oxygen- and moisture-independent diode-type H_2 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 H_2 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 H_2 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_2O_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_2SO_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 Kα 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 H_2 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 TiO_2-based sensors has been investigated. Figure 4 shows *I-V* characteristics of Pd-Pt/U-TiO_2 and Pd-Pt/T-TiO_2 sensors in air and N_2, and also in 8,000 ppm H_2 balanced with air and N_2 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 N_2. The introduction of H_2 into both dry air and N_2 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 H_2 balanced with dry N_2. This result indicates the large contribution of the Schottky barrier at the interface Pd-Pt electrodes and anodized TiO_2 film in detecting H_2. Namely, dissociative adsorption of H_2 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 TiO_2 film is decreased by the introduction of H_2 into both dry air and N_2. In addition, the magnitude of current for these sensors in 8,000 ppm H_2 balanced with dry N_2

was much larger than that in 8,000 ppm H_2 balanced with dry air. The reason is probably because H_2 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 N_2 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-TiO_2 sensor was larger than that of the Pd-Pt/U-TiO_2 sensor in 8,000 ppm H_2 balanced with dry air and N_2. Figure 5 shows response transients of the Pd-Pt/U-TiO_2 and Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 at 250°C in air and N_2 under dry atmospheres. The response speed of both sensors in air was relatively slower than that in N_2, while the recovery speed of both sensors in air was much faster than that in N_2. The H_2 response of both sensors in air was extremely much smaller than that in N_2, and the thermal treatment before anodization improved the H_2 response of an anodized TiO_2-based sensor under both air and N_2 atmospheres, as expected from their *I-V* characteristics (Fig. 4). In order to get a possible reason for the higher H_2 response of the Pd-Pt/T-TiO_2 sensor than the Pd-Pt/U-TiO_2 sensor, characteristics of these two TiO_2 films were examined by SEM observation and XRD analysis.

Figure 6 shows SEM photographs of the surface of U-TiO_2 and T-TiO_2 films. Many submicron-sized pores were formed on the surface of both TiO_2 films. The size of pores on the surface of the T-TiO_2 film was smaller than that of the U-TiO_2 film, and the number of pores per a certain unit of surface area on the T-TiO_2 film was more than that of the U-TiO_2 film. These results suggested the importance of the size of pores and the number of pores on the surface of an anodized TiO_2 film in realizing high H_2 response. But the reason for the change in surface morphology of the anodized TiO_2 film induced by the pre-thermal treatment the Ti metal plate is not clear at present. Figure 7 shows XRD patterns of U-TiO_2 and T-TiO_2 films. Both the TiO_2 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-TiO_2 film was stronger than that of the U-TiO_2 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 P_1-*n*/P_2-*n* films were coated on the electrode surface of the Pd-Pt/T-TiO_2 sensor, and the coating effects of their polymer films to the H_2 sensing properties of the Pd-Pt/T-TiO_2 sensor have been investigated.

3.3 Effects of the coating of P-*n* or P_1-*n*/P_2-*n* film on H_2 response properties of Pd-Pt/T-TiO_2 sensors

Figure 8 shows 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 air under dry and wet atmospheres. The Pd-Pt/T-TiO_2 showed relatively large response to 8,000 ppm H_2 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 form the adsorption of a relatively large amount of H_2O 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-TiO_2 sensors reduced the H_2 response at 250°C in dry air, and the coating of a PI-*n* film on the PTFE-*n*/Pd-Pt/T-TiO_2 sensors further decreased the H_2 response in dry air. On the other hand, the coating of the PI-*n* film on the Pd-Pt/T-TiO_2 sensors largely enhanced the H_2 response in dry air. This may imply the possibility of the limitation of oxygen diffusion through the film and relatively high H_2 concentration in the vicinity of the Pd-Pt electrodes. However, the coating of the PTFE-*n* film on the PI-*n*/Pd-Pt/T-TiO_2 sensors

largely decreased the H_2 response in dry air.

The H_2 response of almost all sensors in wet air was larger than that in dry air. But, the PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors showed only a slight enhancement in the H_2 response by introduction of moisture, in comparison with other sensors. Namely, the direct coating of the PTFE-*n* film on the Pd-Pt/T-TiO_2 sensors reduced the effect of humidity on the H_2 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-TiO_2 sensors was effective for enhancing the H_2 response and the PI-*10*/Pd-Pt/T-TiO_2 sensor in both dry and wet air showed the largest H_2 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-TiO_2 sensors reduced the H_2 response. In addition, the response speed of P-*n*/Pd-Pt/T-TiO_2 and P_1-*n*/P_2-*n*/Pd-Pt/T-TiO_2 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-TiO_2 sensor.

Similar measurement was also conducted with 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 dry and wet atmospheres, as shown in Fig. 9. The Pd-Pt/T-TiO_2 showed relatively large response to 8,000 ppm H_2 in both dry and wet N_2, and the response in dry N_2 (ca. 3.8×10^{-2} A) was comparable to that in wet N_2 (ca. 3.7×10^{-2} A). The addition of the moisture into N_2 is ineffective in enhancing the H_2 response of the Pd-Pt/T-TiO_2 sensor in dry N_2, because the amount of chemisorbed oxygen on the electrode surface in N_2 is extremely less than that in air. The response speed in dry N_2 (90% response time (Res): 0.84 min) was comparable to that in wet N_2 (Res: 0.98 min), and also the recovery speed in dry N_2 (90% recovery time (Rec): 2.54 min) was comparable to that in wet N_2 (Rec: 2.71 min).

The H_2 response of P-*n*/Pd-Pt/T-TiO_2 and P_1-*n*/P_2-*n*/Pd-Pt/T-TiO_2 sensors in N_2 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-TiO_2 sensor was quite effective in improving the H_2 response at 150°C~300°C in air as well as N_2 under dry and wet atmospheres.

To clarify the effect of humidity and oxygen partial pressure on the H_2 response 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, temperature dependence of the ratio of H_2 response under wet atmosphere to that under dry atmosphere in air as well as N_2 and the ratio of H_2 response in N_2 to that in air under wet as well as dry atmospheres were plotted in Figs. 12 and 13, where each H_2 response was expressed as ${}_wI_o$ (w: wet or dry atmosphere, o: in air or N_2). The magnitude of ${}_{wet}I_{air}/{}_{dry}I_{air}$ of the PTFE-*n*/Pd-Pt/T-TiO_2 sensors was smaller than that of the Pd-Pt/T-TiO_2 sensor (Fig. 12(a)(i)), indicating the reduction of the effect of humidity on the H_2 response. Therefore, this result indicated that the waterproof property of PTFE was effective in reducing the H_2 response in wet air in the whole temperature range. However, especially in the case of PI-*10*/PTFE-*10*/Pd-Pt/T-TiO_2 sensor, the additional coating of PI-*10* on the PTFE-*10* increases the magnitude of ${}_{wet}I_{air}/{}_{dry}I_{air}$ at temperatures lower than 200°C, in comparison with that of Pd-Pt/T-TiO_2, leading to the enhancement of the interference from humidity on the H_2 response. In contrast, the magnitude of ${}_{wet}I_{N_2}/{}_{dry}I_{N_2}$ was almost unity in N_2 for all the sensors, except for those of PTFE-*20*/Pd-Pt/T-TiO_2 sensors at 150°C (Fig. 12(a)(ii)). In addition, the magnitude of ${}_wI_{N_2}/{}_wI_{air}$ of almost all sensors was larger than that of Pd-Pt/T-TiO_2 sensor (Fig. 12(b)), showing an increase in the effect of oxygen concentration on the H_2 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-TiO_2 sensors slightly reduced the effect of oxygen partial pressure on their H_2 response under wet atmosphere, but the magnitude of ${}_{wet}I_{N_2}/{}_{wet}I_{air}$ was still larger than that of the Pd-Pt/T-TiO_2 sensor.

The magnitude of ${}_{wet}I_{air}/{}_{dry}I_{air}$ of the PI-*20*/Pd-Pt/T-TiO_2 sensor was comparable with that of the Pd-Pt/T-TiO_2 sensor, but the magnitude of ${}_{wet}I_{air}/{}_{dry}I_{air}$ of the PI-*10*/Pd-Pt/T-TiO_2 sensor

was smaller than that of the Pd-Pt/T-TiO_2 sensor in the whole temperature range and the effect of humidity on the H_2 response was decreased with an increase in operating temperature and was almost negligible ($_{wet}I_{air}/_{dry}I_{air} \approx 1$) at 300°C (Fig. 13(a)(i)). The magnitude of $_{wet}I_{N_2}/_{dry}I_{N_2}$ of the PI-*n*/Pd-Pt/T-TiO_2 and PTFE-*n*/PI-*n*/Pd-Pt/T-TiO_2 sensors was almost unity (Fig. 13(a)(ii)), as was observed in the cases of the PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors (Fig. 12(a)(ii)). In addition, the magnitude of $_{dry}I_{N_2}/_{dry}I_{air}$ of PTFE-*n*/PI-*n*/Pd-Pt/T-TiO_2 sensors was larger than that of the Pd-Pt/T-TiO_2 sensor. However, the magnitude of $_{w}I_{N_2}/_{w}I_{air}$ of only the PI-*10*/Pd-Pt/T-TiO_2 sensor was smaller than that of the Pd-Pt/T-TiO_2 sensor, especially at 300°C under dry atmosphere, showing the certain reduction of the interference from oxygen partial pressure on the H_2 response. The coating of the PTFE-*10*/PI-*10* film on the Pd-Pt/T-TiO_2 sensor also reduced the interference from oxygen partial pressure under wet atmosphere on the H_2 response of the Pd-Pt/T-TiO_2 sensor at lower temperatures (especially at 150°C) (Fig. 13(b)(ii)).

3.4 H_2 concentration dependence of H_2 response of representative sensors

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 H_2 balanced with dry and wet air are shown in Fig. 14(a). The sensor current decreased steadily with a decrease in H_2 concentration in both dry and wet air, and then the sensor current in 500 ppm H_2 became extremely small. In addition, the H_2 responses of all sensors to 500~8,000 ppm H_2 in wet air were larger than those in dry air. The sensor current in 500 ppm H_2 of the Pd-Pt/T-TiO_2 and PTFE-*20*/Pd-Pt/T-TiO_2 sensors was rather noisy and small, but the PI-*20*/Pd-Pt/T-TiO_2 sensor showed the largest response even to 500 ppm H_2 in both dry and wet air. Figure 14(b) shows the relationship between the sensor current and H_2 concentration in dry and wet air measured for three kinds of sensors. The sensor current in H_2 was almost proportional to the H_2

concentration in a lower concentration range, while it tended to saturate in higher concentration range, especially in wet air. On the other hand, the 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°C. For instance, the responses in 500 ppm H_2 balanced with dry and wet air of the PI-*20*/Pd-Pt/T-TiO_2 sensor were ca. 1.65×10^{-5} A and 3.23×10^{-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 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 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 H_2 in both dry and wet N_2. Thus, the H_2 response in N_2 was much larger than that in air, especially in lower H_2 concentrations. Figure 15(b) shows the relationship between the sensor current and H_2 concentration in dry and wet N_2 measured for three kinds of sensors. It was found that the sensor current in H_2 is well proportional to the logarithm of H_2 concentration in both dry and wet N_2. On the other hand, the 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°C. For instance, the responses in 500 ppm H_2 balanced with dry and wet N_2 of the PI-*20*/Pd-Pt/T-TiO_2 sensor were ca. 4.22×10^{-2} A and 3.80×10^{-2} A, respectively. Among them, the PI-*20*/Pd-Pt/TiO_2 sensor showed the most improved H_2 response in all atmospheres, i.e. in air both dry and wet, air as well as N_2 atmospheres.

The H_2 concentration dependence of ${}_{wet}I_o/{}_{dry}I_o$ and ${}_{w}I_{N_2}/{}_{w}I_{air}$ 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 ${}_{wet}I_{air}/{}_{dry}I_{air}$ 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 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 ${}_{wet}I_{N_2}/{}_{dry}I_{N_2}$ was almost unity for all the sensors in the whole H_2 concentration range. On the other hand, the magnitude of ${}_wI_{N_2}/{}_wI_{air}$ 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 ${}_wI_{N_2}/{}_wI_{air}$ 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 ${}_wI_{N_2}/{}_wI_{air}$ 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 ${}_wI_{N_2}/{}_wI_{air}$ 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. 3.1×10^{-4} A) was smaller than that in wet air (ca. 9.0×10^{-4} A), while the H_2 response in dry N_2 (ca. 4.7×10^{-2} A) was comparable to that in wet N_2 (ca. 4.6×10^{-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

1. O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, C. A. Grimes, Hydrogen sensing using titania nanotubes, Sens. Actuators B 93 (2003) 338-344.
2. G. K. Mor, O. K. Varghese, M. Paulose, K. G. Ong, C. A. Grimes, Fabrication of hydrogen sensors with transparent titanium oxide nanotube-array thin films as sensing elements, Thin Solid Films 496 (2006) 42-48.
3. T. Mukherjee, S. K. Hfazer, S. Basu, Porous titania thin films grown by anodic oxidation for hydrogen sensors, Mater. Manuf. Proc. 21 (2006) 247-251.
4. C. Lu, Z. Chen, High-temperature resistive hydrogen sensor based on thin nanoporous rutile TiO_2 film on anodic aluminum oxide, Sens. Actuators B 140 (2009) 109-115.
5. E. Sennik, Z. Colak, N. Kilinc, Z. Z. Öztürk, Synthesis of highly-ordered TiO_2 nanotubes for a hydrogen sensor, Int. J. Hydrogen Energy 35 (2010) 4420–4427.
6. J. Moon, M. Kemell, J. Kukkola, R. Punkkinen, H-P. Hedman, A. Suominen, E. Makila, M. Tenho, A. Tuominen, H. Kim, Gas sensor using anodic TiO_2 thin film for monitoring hydrogen, Proc. Eng. 47 (2012) 791-794.
7. T. Hyodo, H. Shibata, Y. Shimizu, M. Egashira, H_2 sensing properties of diode-type gas sensors fabricated with Ti- and/or Nb-based materials, Sens. Actuators B 142 (2009)

97-104.

8. Y. Shimizu, N. Kuwano, T. Hyodo, M. Egashira, High H_2 sensing performance of anodically oxidized TiO_2 films contacted with Pd, Sens. Actuators B 83 (2002) 195–201.
9. T. Iwanaga, T. Hyodo, Y. Shimizu, M. Egashira, H_2 sensing properties and mechanism of anodically oxidized TiO_2 film contacted with Pd electrode, Sens. Actuators B 93 (2003) 519–525.
10. T. Hyodo, T. Iwanaga, Y. Shimizu, M. Egashira, Effects of electrode materials and oxygen partial pressure on the hydrogen sensing properties of anodically oxidized titanium dioxide films, ITE Lett. 4 (2003) 594–597.
11. H. Miyazaki, T. Iwanaga, Y. Shimizu, M. Egashira, Hydrogen-sensing properties of anodically oxidized TiO_2 film sensors Effects of preparation and pretreatment conditions, Sens. Actuators B 108 (2005) 467–472.
12. Y. Shimizu, T. Hyodo, M. Egashira, H_2 sensing performance of anodically oxidized TiO_2 thin films equipped with Pd electrode, Sens. Actuators B 121 (2007) 219-230.
13. Y. Shimizu, K. Sakamoto, M. Nakaoka, T. Hyodo, M. Egashira, H_2 sensing performance of TiO_2-based diode-type sensors, Adv. Mater. Res. 47-50 (Multi-functional Materials and Structures), (2008) 1510–1513.
14. T. Hyodo, M. Nakaoka, Y. Shimizu, M. Egashira, Diode-type H_2 sensors using anodized TiO_2 films-structural and compositional controls of noble metal sensing electrodes, Sens. Lett. 9 (2011) 641–645.
15. T. Hyodo, M. Nakaoka, K. Kaneyasu, H. Kato, H. Yanagi, Y. Shimizu, Diode-type gas sensors fabricated with a titania film on a Ti plate and Pd-Pt electrodes –Effects of polymer coating on the hydrogen-sensing properties–, Mater. Sci. Eng. 18 (2011) 212006.
16. D. Li, A. H. McDaniel, R. Bastasz, J. W. Medlin, Effects of a polyimide coating on the hydrogen selectivity of MIS sensors, Sens. Actuators B 115 (2006) 86–92.

17. V. R. Katti, A.K. Debnath, S.C. Gadkari, S.K. Gupta, V.C. Sahni, Passivated thick film catalytic type H_2 sensor operating at low temperature, Sens. Actuators B 84 (2002) 219–225.
18. A. Kumar, P. Zhang, A. Vincent, R. McCormack, R. Kalyanaraman, H. J. Cho, S. Seal, Hydrogen selective gas sensor in humid environment based on polymer coated nanostructured-doped tin oxide, Sens. Actuators B 155 (2011) 884-892.

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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-TiO_2 and (ii) Pd-Pt/T-TiO_2 sensors in air and N_2, and also in 8,000 ppm H_2 balanced with air and N_2 under dry atmosphere at 250°C.

Fig. 5 Response transients of (i) Pd-Pt/U-TiO_2 and (ii) Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 in (a) air and (b) N_2 under dry atmosphere at 250°C.

Fig. 6 SEM photographs of the surface of (i) U-TiO_2 and (ii) T-TiO_2 films.

Fig. 7 XRD patterns of (i) U-TiO_2 and (ii) T-TiO_2 films.

Fig. 8 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 8000 ppm H_2 at 250°C in air under (a) dry and (b) wet atmospheres.

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.

Fig. 10 Operating temperature dependence of sensor current of Pd-Pt/T-TiO_2, PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 in (a) air and (b) N_2 under (i) dry and (ii) wet atmospheres.

Fig. 11 Operating temperature dependence of sensor current of Pd-Pt/T-TiO_2, PI-*n*/Pd-Pt/T-TiO_2 and PTFE-*n*/PI-*n*/Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 in (a) air and (b) N_2 under (i) dry and (ii) wet atmospheres.

Fig. 12 Operating temperature dependence of (a) ${}_{wet}I_o/{}_{dry}I_o$ and (b) ${}_wI_{N2}/{}_wI_{air}$ of Pd-Pt/T-TiO_2, PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors.

Fig. 13 Operating temperature dependence of (a) ${}_{wet}I_o/{}_{dry}I_o$ and (b) ${}_wI_{N2}/{}_wI_{air}$ of Pd-Pt/T-TiO_2, PI-*n*/Pd-Pt/T-TiO_2 and PTFE-*n*/PI-*n*/Pd-Pt/T-TiO_2 sensors.

Fig. 14 (a) Response transients to 500~8,000 ppm H_2 and (b) variation in sensor current of Pd-Pt/T-TiO_2, PTFE-*20*/Pd-Pt/T-TiO_2 and PI-*20*/Pd-Pt/T-TiO_2 sensors with H_2 concentration (C_{H_2}) in (i) dry and (ii) wet air at 250°C.

Fig. 15 (a) Response transients to 500~8,000 ppm H_2 and (b) variation in sensor current of Pd-Pt/T-TiO_2, PTFE-*20*/Pd-Pt/T-TiO_2 and PI-*20*/Pd-Pt/T-TiO_2 sensors with H_2 concentration (C_{H_2}) in (i) dry and (ii) wet N_2 at 250°C.

Fig. 16 H_2 concentration dependence of (a) ${}_{wet}I_o/{}_{dry}I_o$ and (b) ${}_wI_{N_2}/{}_wI_{air}$ of Pd-Pt/T-TiO_2, PTFE-*20*/Pd-Pt/T-TiO_2 and PI-*20*/Pd-Pt/T-TiO_2 sensors.

Table 1 Fabrication conditions and thickness of polymer films coated on the Pd-Pt electrodes.

Sample	Polymer film	Polymer concentration (wt%)		Film thickness (nm)	
		PTFE	PI	PTFE	PI
PTFE-*5*	PTFE	5	–	200	–
PTFE-*10*		10	–	282	–
PTFE-*20*		20	–	800	–
PI-*10*	PI	–	10	–	95
PI-*20*		–	20	–	164
PI-*10*/PTFE-*10*	PI/PTFE	10	10	–	377
PI-*20*/PTFE-*20*		20	20	–	463
PTFE-*10*/PI-*10*	PTFE/PI	10	10	245	49
PTFE-*20*/PI-*20*		20	20	380	77

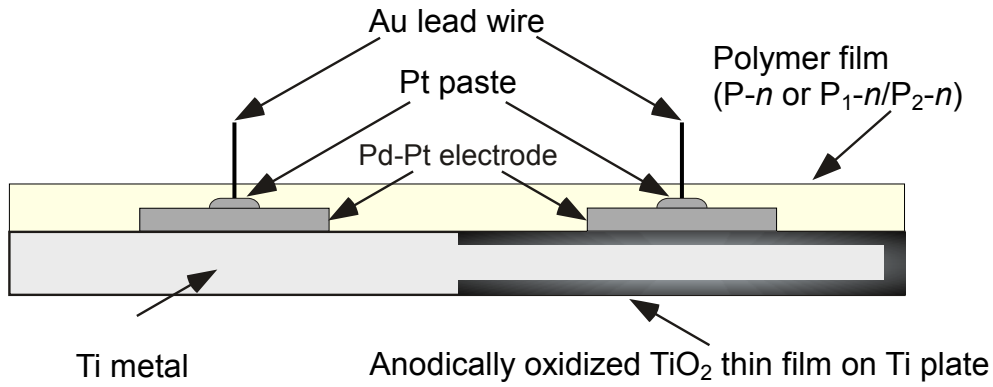


Fig. 1 Schematic drawing of a diode-type sensor.

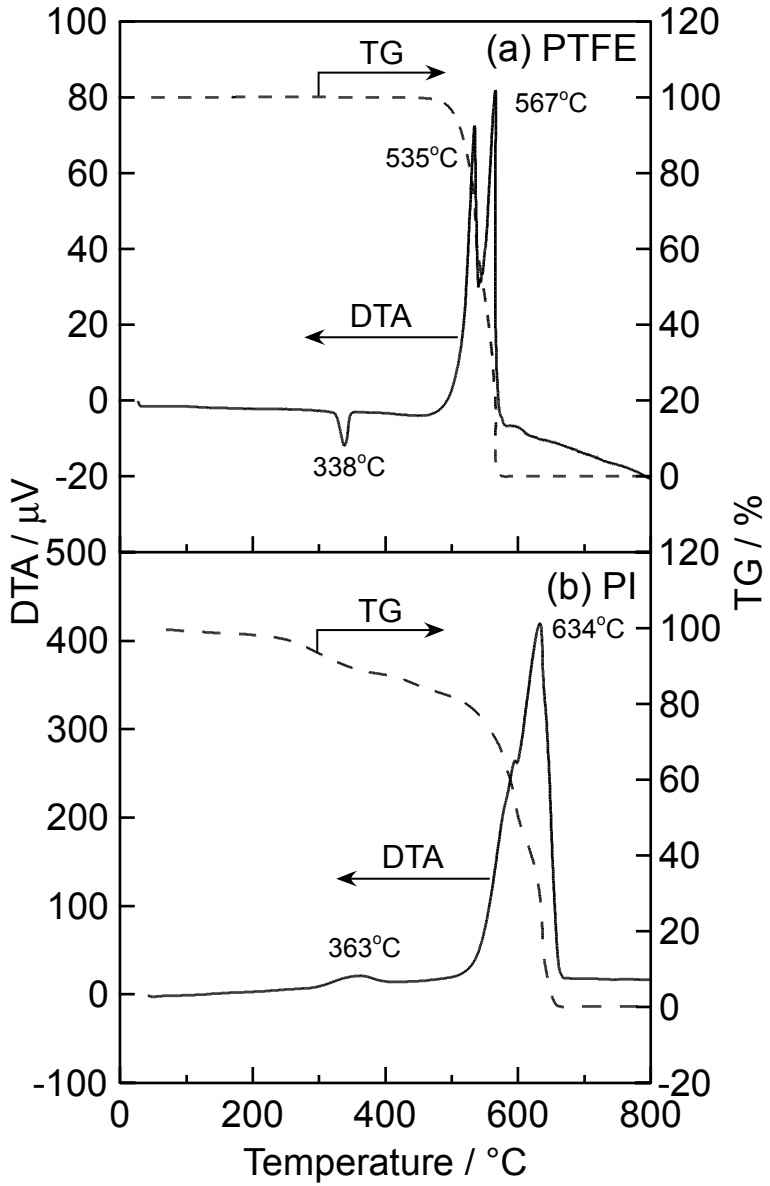


Fig. 2 TG-DTA curves of (a) PTFE and (b) PI films with a heating rate of 5.0°C min^{-1} under air flowing.

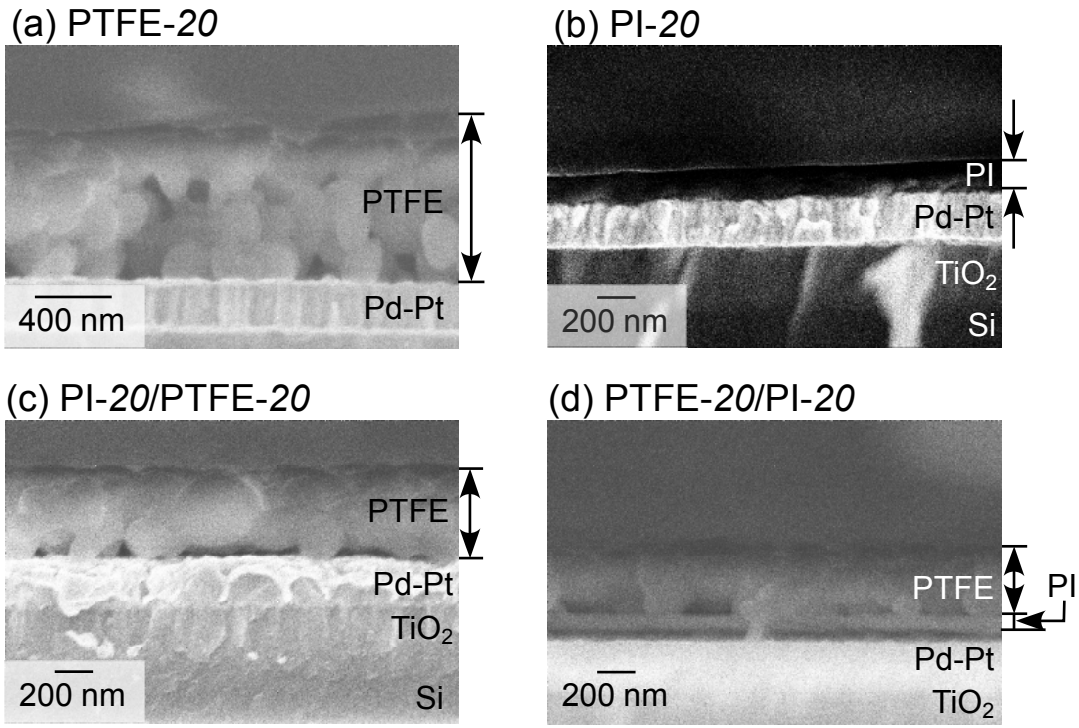


Fig. 3 SEM photographs of the cross section of representative polymer films.

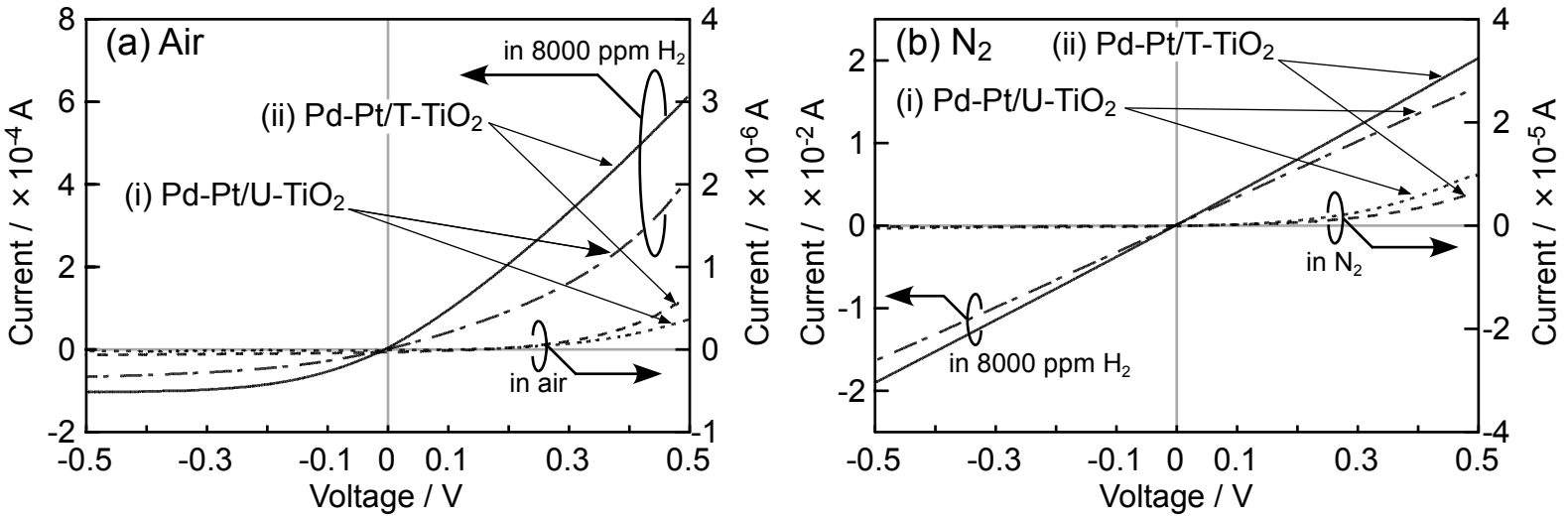


Fig. 4 *I-V* characteristics of (i) Pd-Pt/U-TiO_2 and (ii) Pd-Pt/T-TiO_2 sensors in air and N_2, and also in 8,000 ppm H_2 balanced with air and N_2 under dry atmosphere at 250°C.

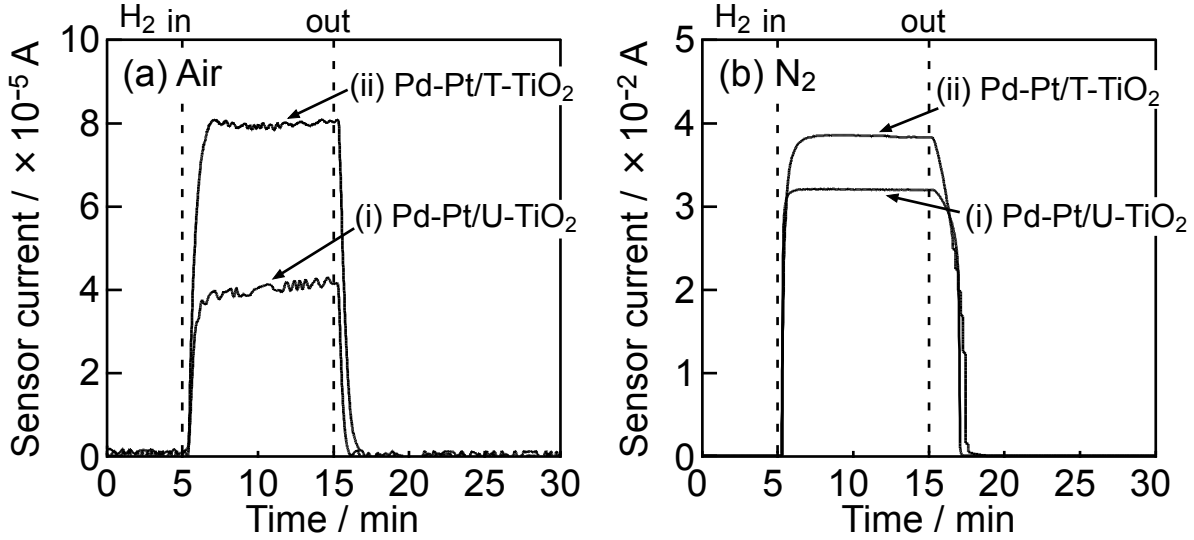


Fig. 5 Response transients of (i) Pd-Pt/U-TiO_2 and (ii) Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 in (a) air and (b) N_2 under dry atmosphere at 250°C.

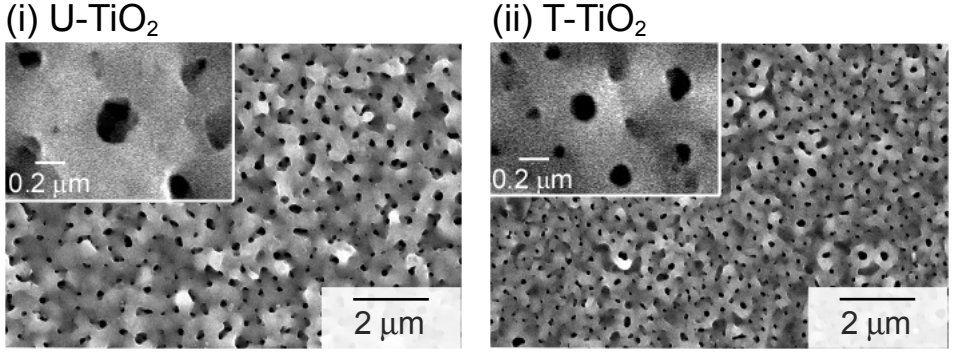


Fig. 6 SEM photographs of the surface of (i) U-TiO_2 and (ii) T-TiO_2 films.

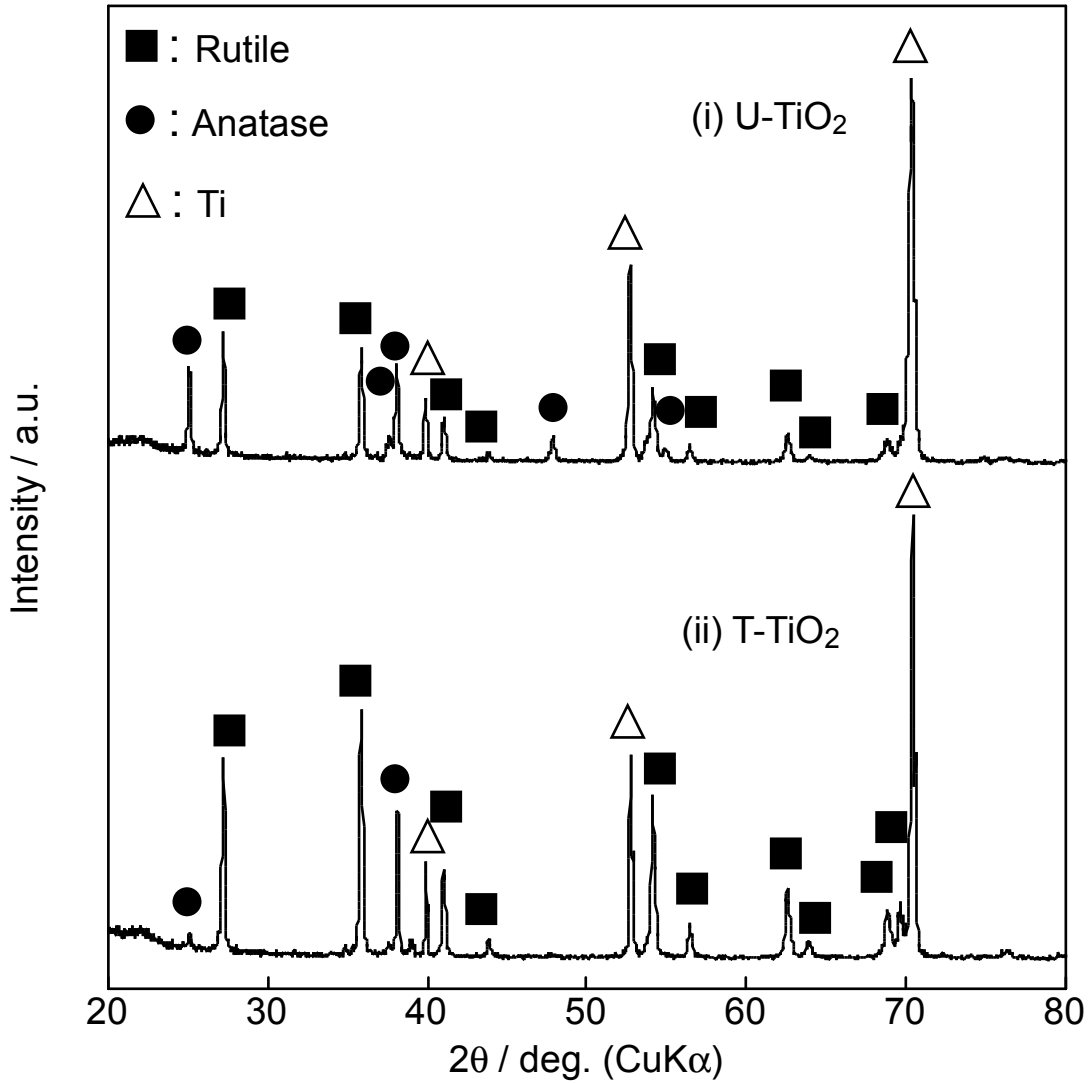


Fig. 7 XRD patterns of (i) U-TiO_2 and (ii) T-TiO_2 films.

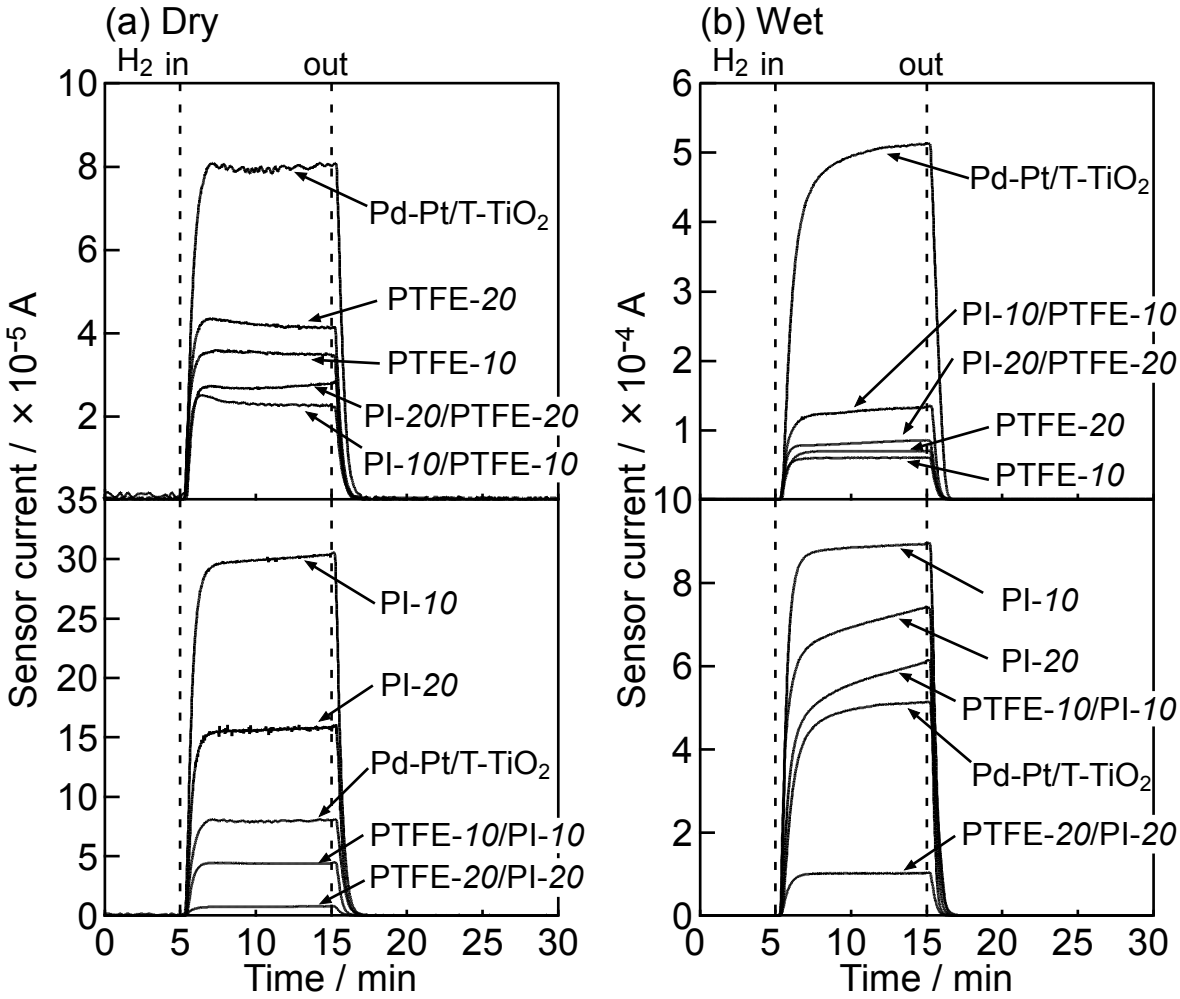


Fig. 8 Response transients of Pd-Pt/T-TiO_2, P-*n*/Pd-Pt/T-TiO_2 and P_1-*n*/P_2-*n*/Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 at 250°C in air under (a) dry and (b) wet atmospheres.

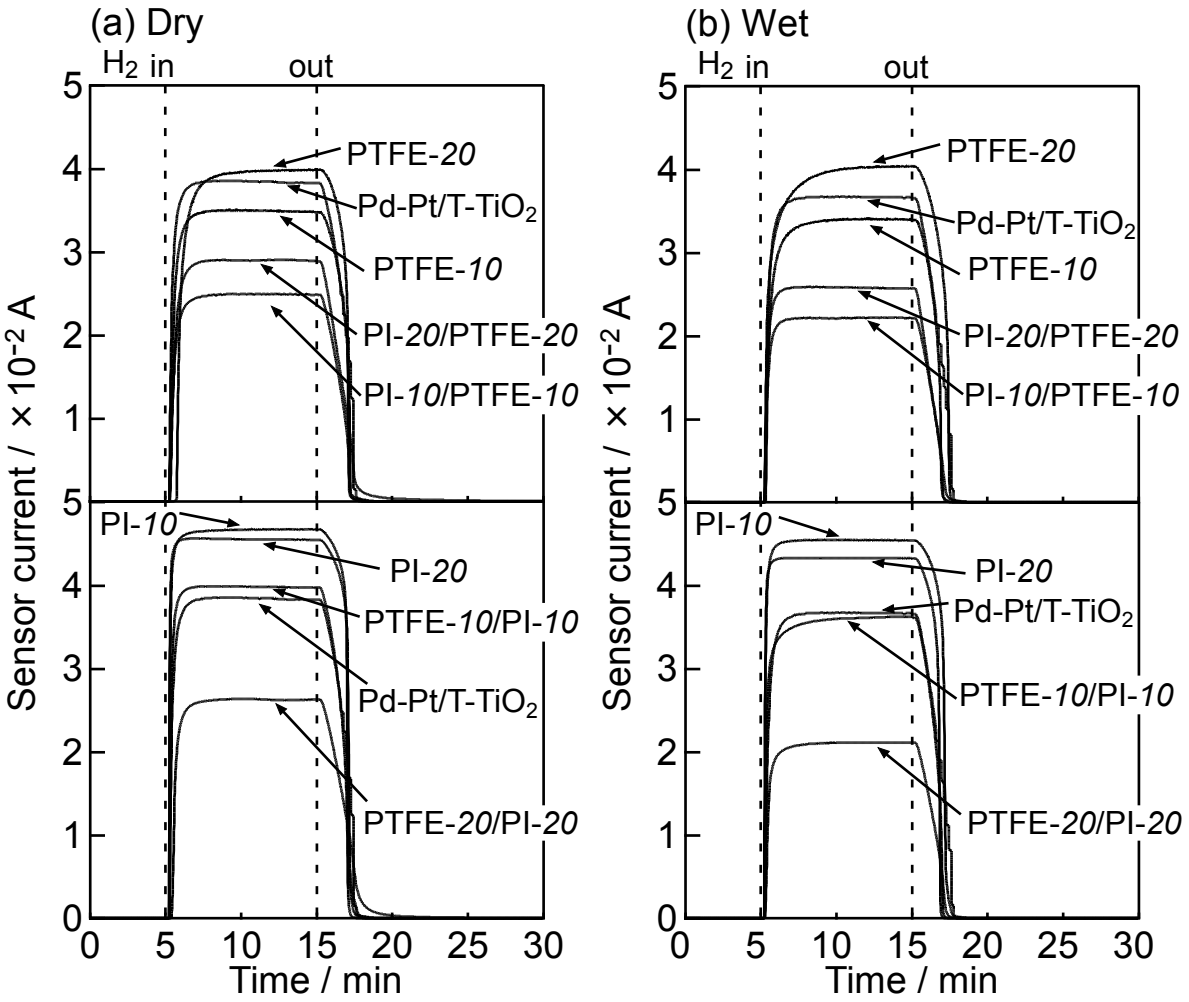


Fig. 9 Response transients of Pd-Pt/T-TiO_2, P-*n*/Pd-Pt/T-TiO_2 and P_1-*n*/P_2-*n*/Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 at 250°C in N_2 under (a) dry and (b) wet atmospheres.

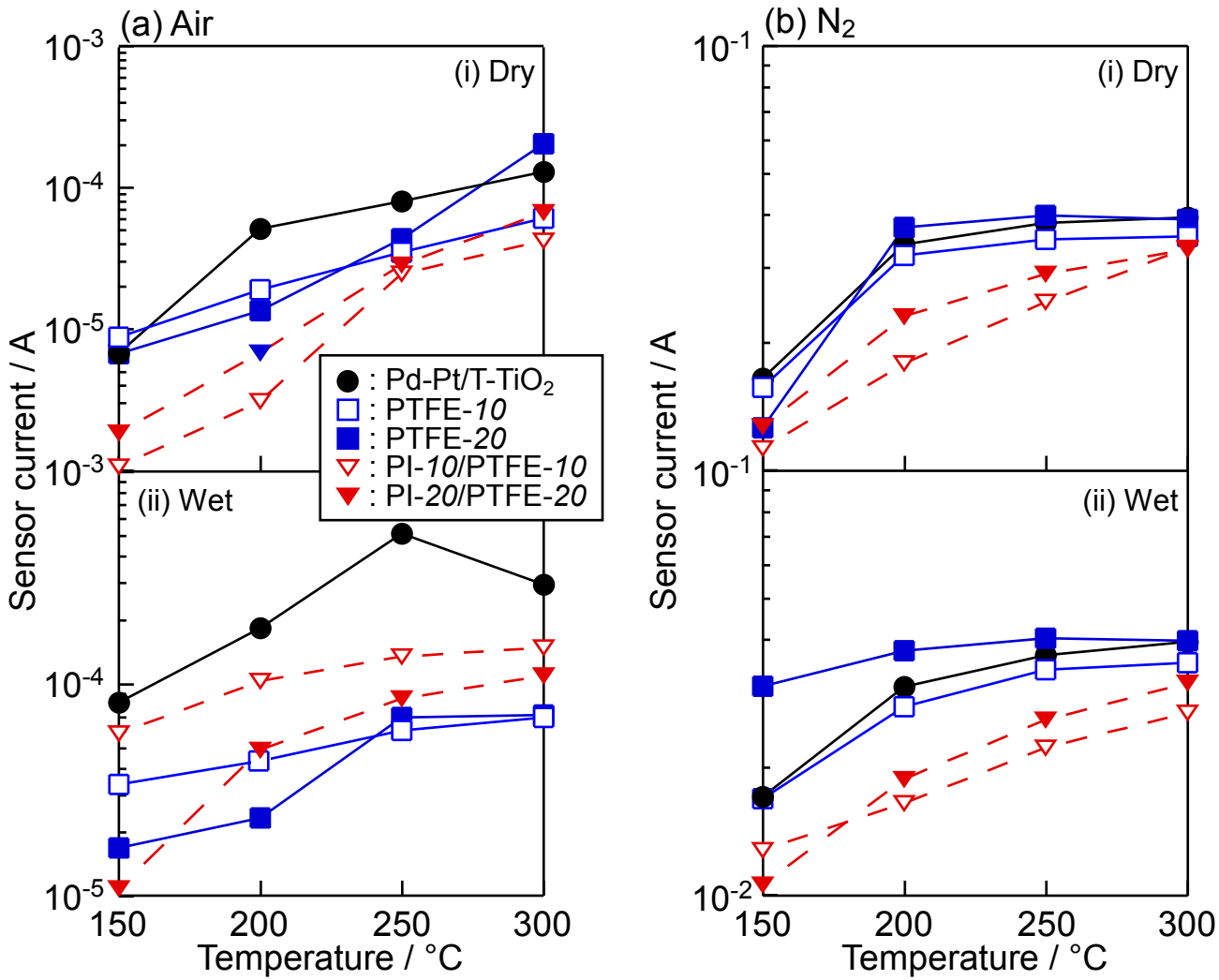
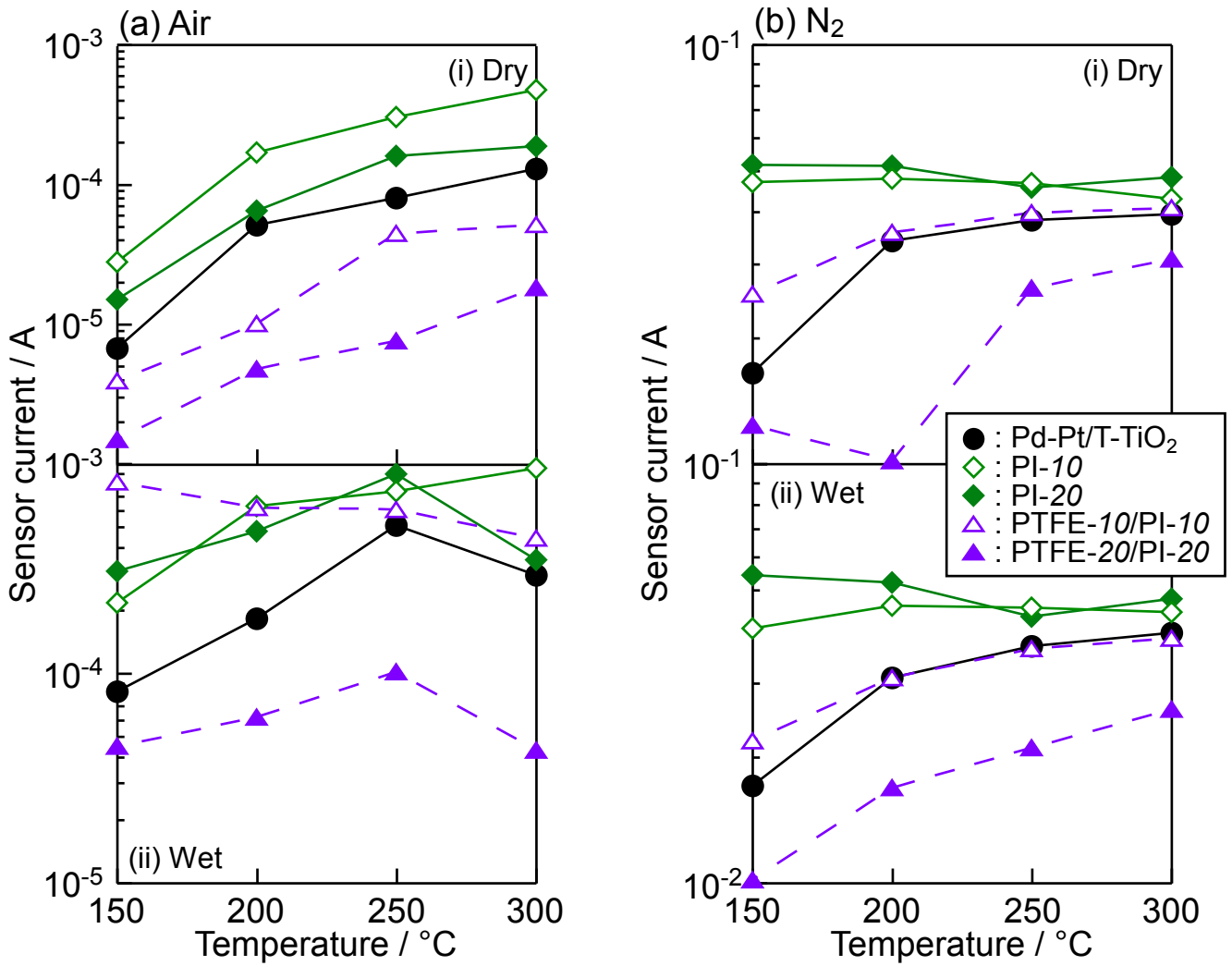


Fig. 10 Operating temperature dependence of sensor current of Pd-Pt/T-TiO_2, PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors to 8,000 ppm H_2 in (a) air and (b) N_2 under (i) dry and (ii) wet atmospheres.



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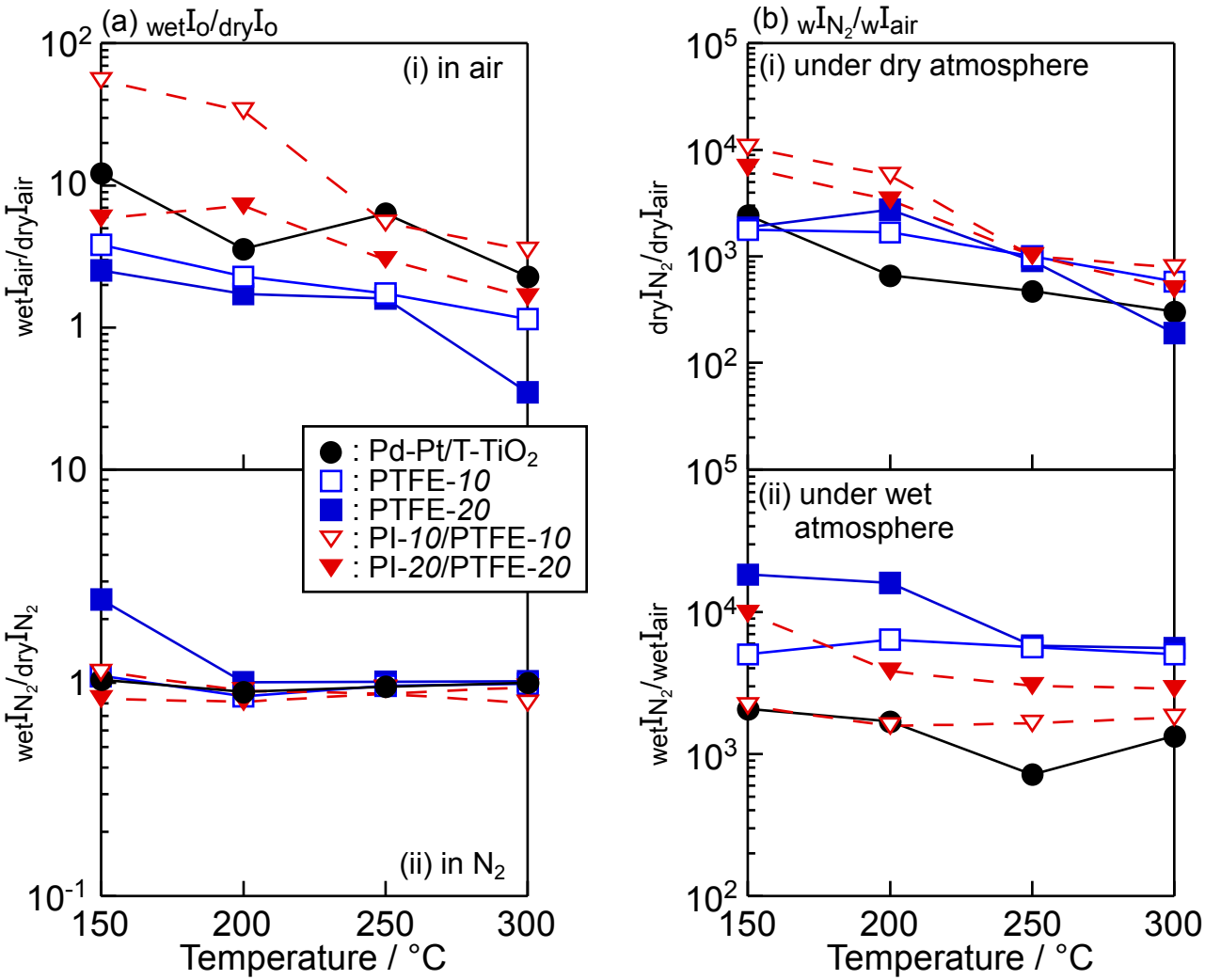


Fig. 12 Operating temperature dependence of (a) ${}_{wet}I_o/{}_{dry}I_o$ and (b) ${}_{w}I_{N_2}/{}_{w}I_{air}$ of Pd-Pt/T-TiO_2, PTFE-*n*/Pd-Pt/T-TiO_2 and PI-*n*/PTFE-*n*/Pd-Pt/T-TiO_2 sensors.

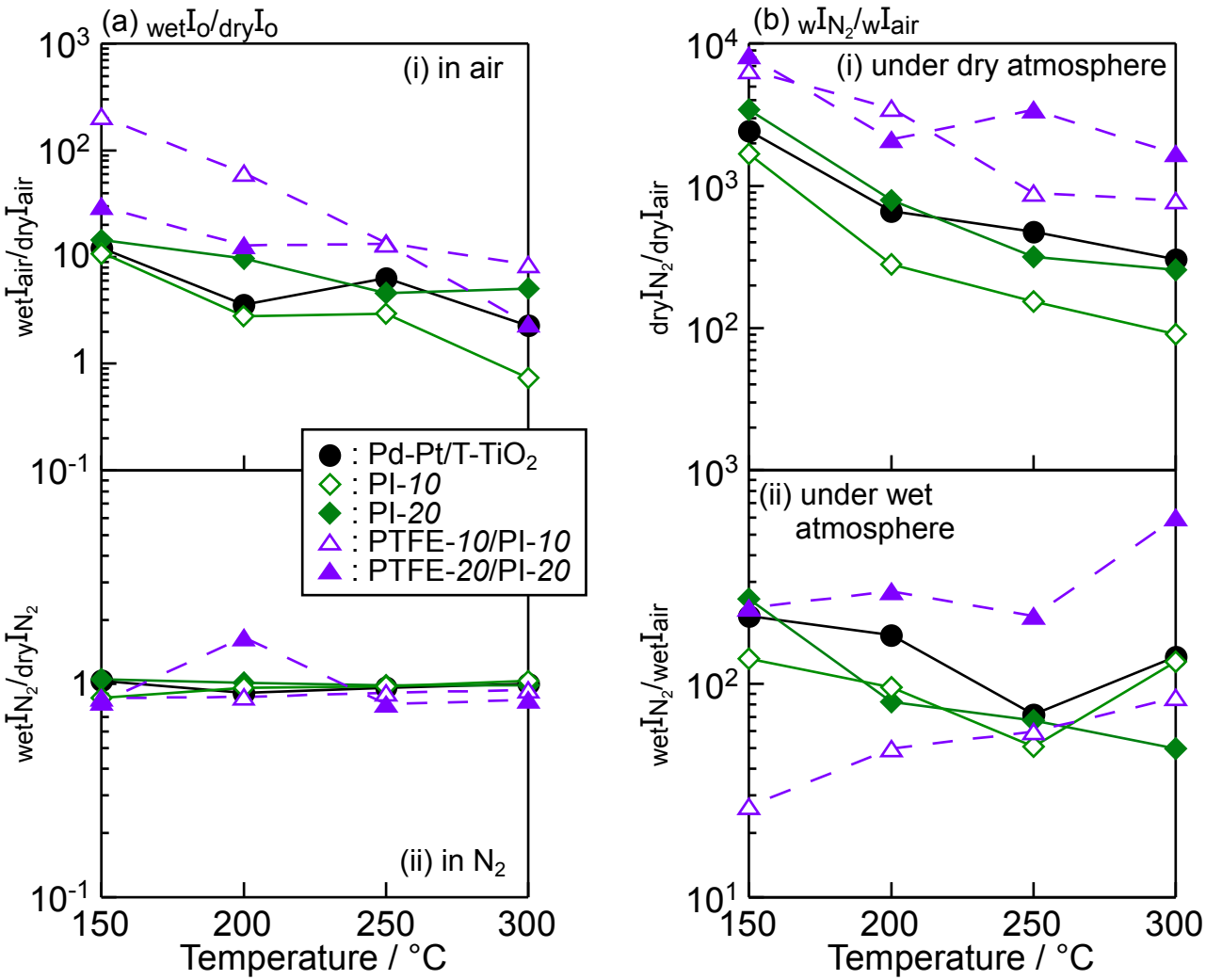
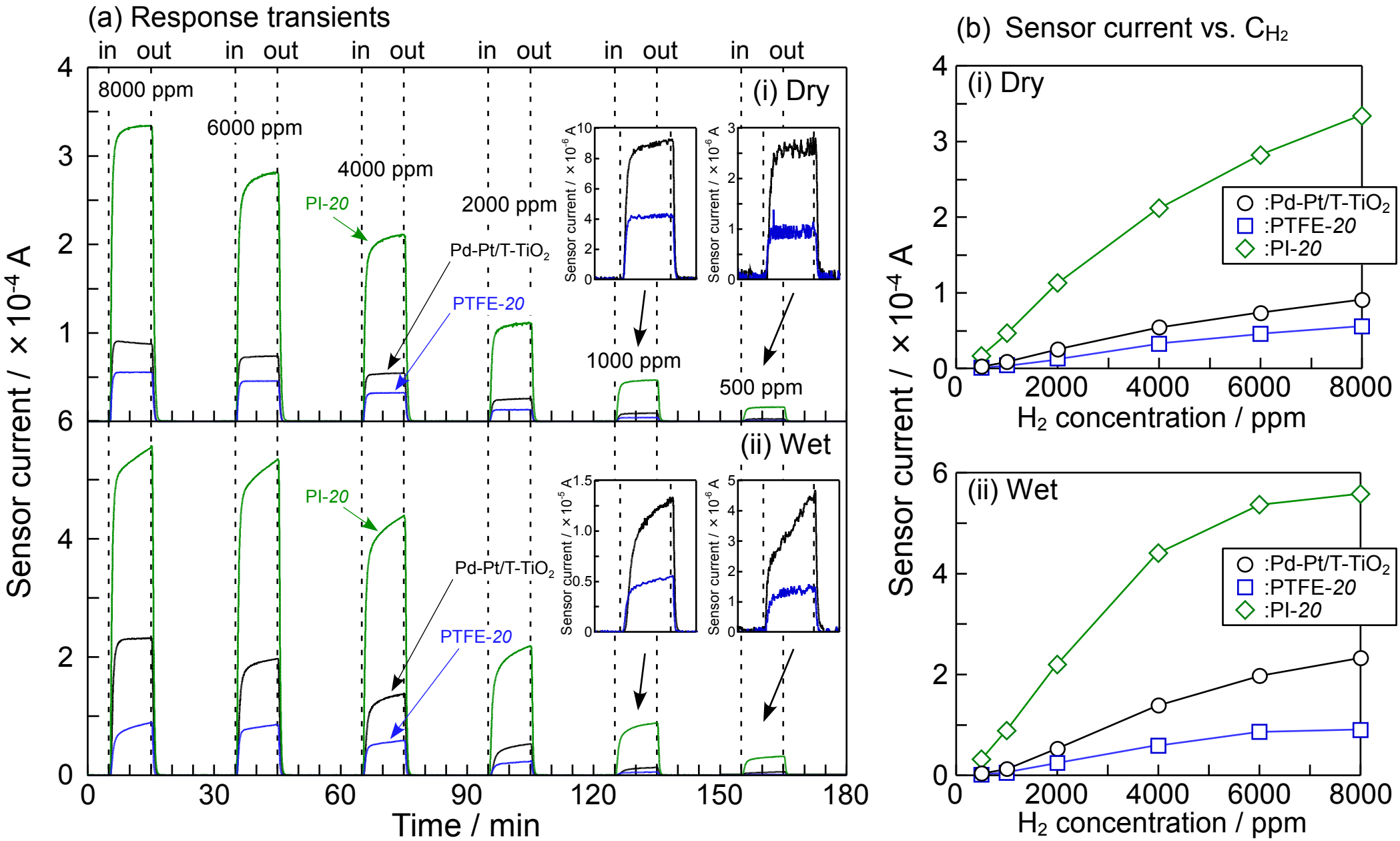


Fig. 13 Operating temperature dependence of (a) $_{wet}I_o/_{dry}I_o$ and (b) $_wI_{N_2}/_wI_{air}$ of Pd-Pt/T-TiO_2, PI-*n*/Pd-Pt/T-TiO_2 and PTFE-*n*/PI-*n*/Pd-Pt/T-TiO_2 sensors.



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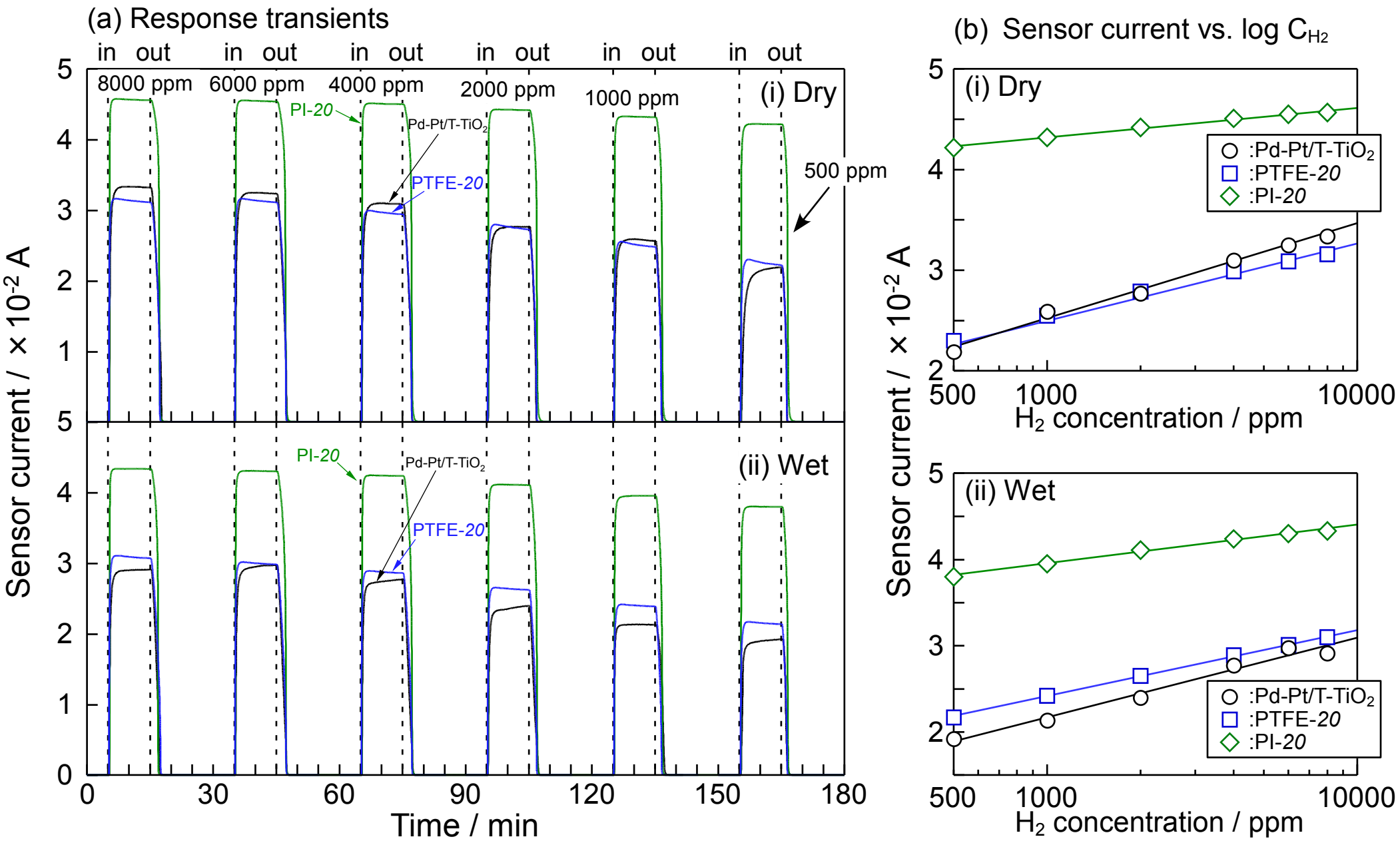

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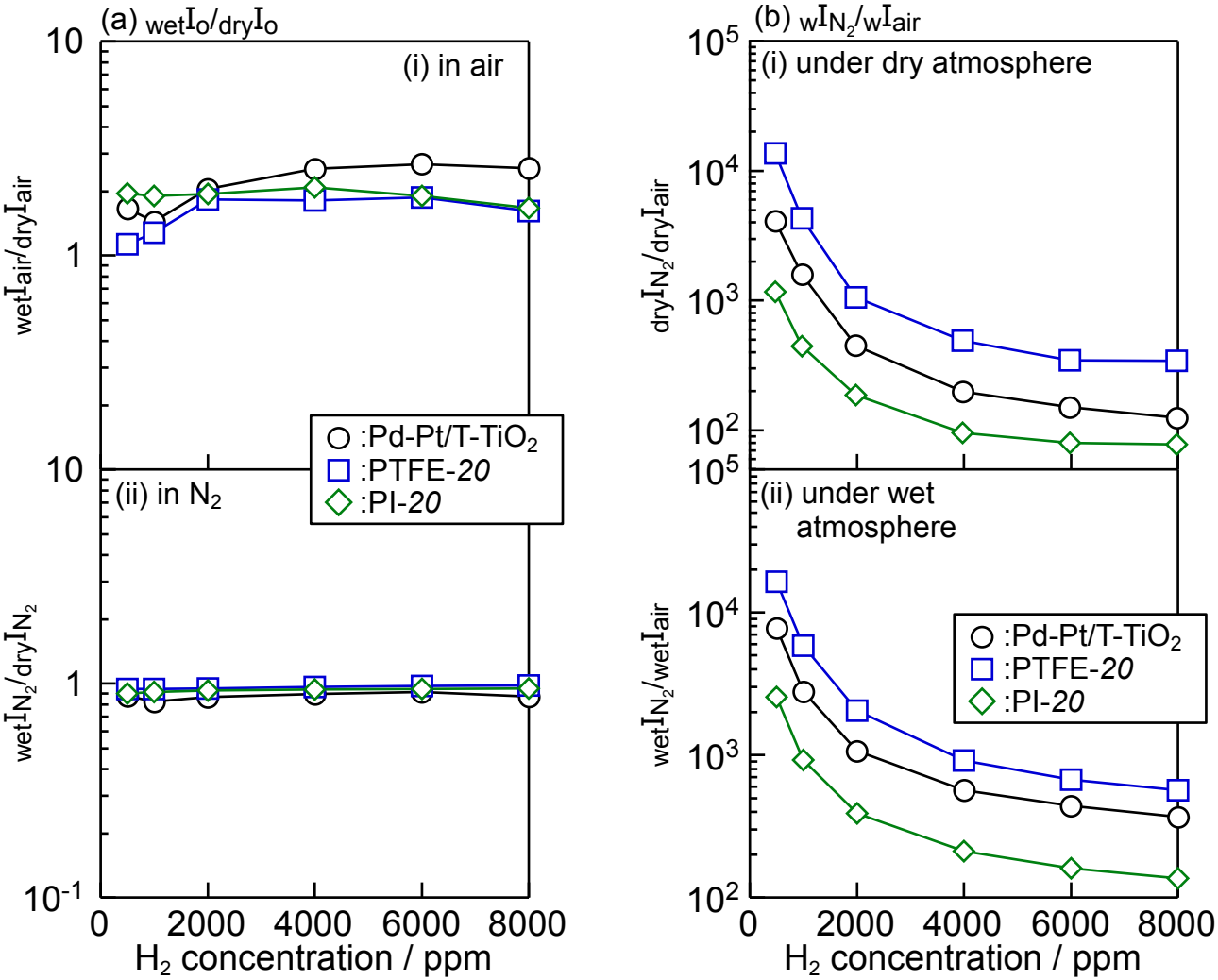

Fig. 16 H_2 concentration dependence of (a) ${}_{wet}I_o/{}_{dry}I_o$ and (b) ${}_wI_{N_2}/{}_wI_{air}$ of Pd-Pt/T-TiO_2, PTFE-*20*/Pd-Pt/T-TiO_2 and PI-*20*/Pd-Pt/T-TiO_2 sensors.