

H₂ Sensing Properties of Diode-type Sensors Fabricated with Anodized TiO₂ Films Equipped with Polymer Coated Pd-Pt Electrodes

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Abstract

Diode-type gas sensors have been fabricated by employing anodized TiO₂ films equipped with the Pd-Pt electrodes (Pd-Pt/TiO₂) coated with a polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA) or polyimide (PI) film (P-*n*/Pd-Pt/TiO₂ (P: PTFE, PVA or PI, *n*: polymer concentration of coating solution (wt%))), and their H₂ sensing properties have been investigated under dry and wet air as well as N₂ atmospheres. The coating of a relatively-thin polymer film, except for PTFE, on the electrodes likely enhanced the H₂ response, in comparison with that of a Pd-Pt/TiO₂ sensor. However, the H₂ response tended to decrease with an increase in the thickness of these polymer films under both dry and wet air atmospheres. In addition, the H₂ responses of almost all sensors in wet air were much larger than those in dry air. On the other hand, the H₂ response of PI-*n*/Pd-Pt/TiO₂ was always larger than that of Pd-Pt/TiO₂ in both dry and wet air as well as N₂ atmospheres. The coating of PTFE on the Pd-Pt electrodes was effective in reducing the interference from humidity on the H₂ response of the Pd-Pt/TiO₂ sensor.

Key words: diode-type gas sensor, polytetrafluoroethylene, polyvinyl alcohol, polyimide, humidity, oxygen

Introduction

Recently, H₂ has been attracting much attention as an alternative next generation energy source. However, it is combustible and explosive in a wide concentration range (4~75% in air). Therefore, highly-sensitive H₂ sensors capable of detecting H₂ leakage are indispensable to ensure the safety of our future H₂-energy society. Our previous studies have revealed that a TiO₂ thin film having sub-micron pores was fabricated by anodic oxidation of a Ti plate, and that the anodized TiO₂ thin film equipped with Pd electrode exhibited high H₂ response in a wide range of H₂ concentration as a diode-type sensor under both air and N₂ atmospheres [1-4]. In addition, the alloying of Pd with Pt was quite effective in improving the reproducibility of H₂ response and its long-term stability [5, 6]. But, it was also revealed that humidity and O₂ partial pressure affected the H₂ sensing properties. Thus, we have attempted to improve H₂ sensing performance of Pd-Pt/TiO₂ sensors by the coating of polymer (polytetrafluoroethylene (PTFE), polyvinyl alcohol (PVA) or polyimide (PI)) films on the Pd-Pt alloy electrodes.

Experimental Details

Fabrication of a Pd-Pt/TiO₂ sensor

A Ti plate (5.0 mm × 10.0 mm × 0.5 mm) was thermal treated at 600°C for 1 h in air and then a half of the Ti plate was anodically oxidized in a 0.5 M H₂SO₄ aqueous solution at 20°C for 30 min at a current density of 50 mA cm⁻². Microstructure of the anodized TiO₂ film was observed by scanning electron microscopy (SEM; JOEL Ltd., JSM-7500F). Pd-Pt alloy (Pd : Pt = 58 : 42 (wt%)) electrodes were fabricated on both the TiO₂ thin film and the Ti plate by radio-frequency 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.

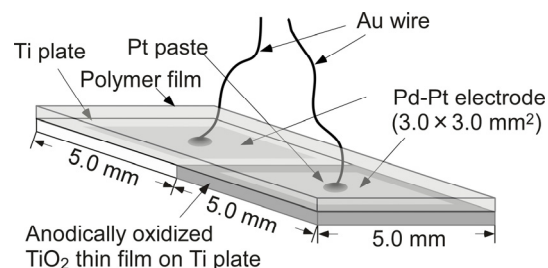


Fig. 1. Schematic drawing of a diode-type sensor.

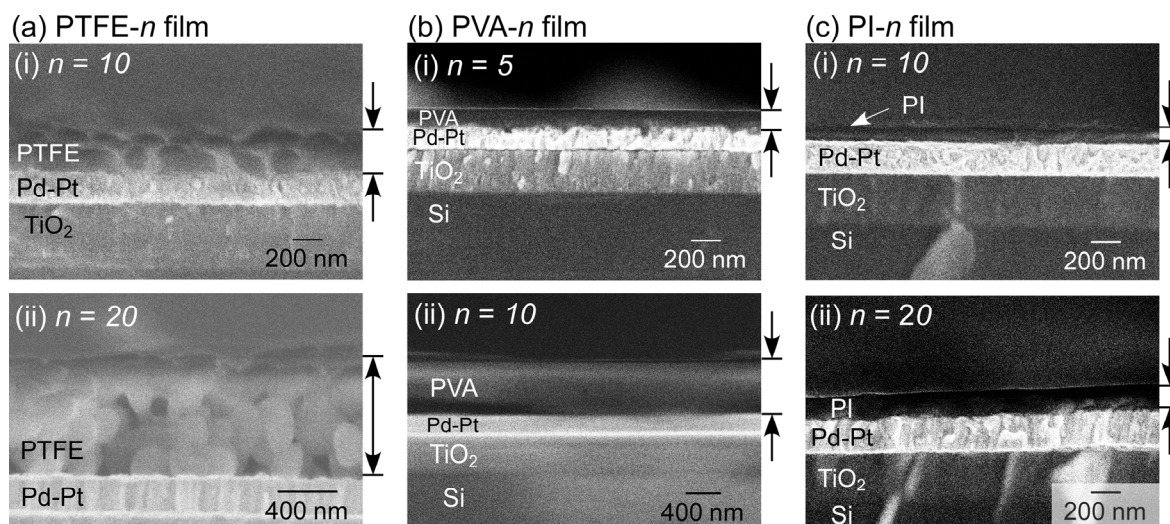


Fig. 2. SEM photographs of the cross section of (a) PTFE, (b) PVA and (c) PI films.

This sensor is referred to as Pd-Pt/TiO₂.

Polymer coating

A given amount of PTFE dispersion (Daikin Ind., D-1E) or PVA (Wako Pure Chemical Ind., 163-03045) was mixed with deionized water, but in the case of PI (PI R&D Co., Ltd., Q-VR-FR007), it was dissolved in 1-methyl-2-pyrrolidone. Thereafter, the mixtures were stirred at room temperature. These solutions obtained were coated on the Pd-Pt alloy electrodes surface at room temperature by spin coating at 10,000 rpm. These polymer-coated sensors were heat-treated in air for 30 min at 250°C (PTFE and PI) and 120°C (PVA). The sensors thus fabricated are referred to as P-*n*/Pd-Pt/TiO₂ (P: PTFE, PVA or PI, *n*: polymer concentration in the coating solution (wt%)). Figure 1 shows a schematic drawing of a P-*n*/Pd-Pt/TiO₂ sensor. Thermal behavior of PTFE, PVA and PI was examined under air flowing (100 cm³ min⁻¹), by thermogravimetry-differential thermal analysis (TG-DTA, heating rate: 1.0 deg min⁻¹, temperature range: RT~800°C).

Measurement of sensor properties

A dc voltage of 100 mV was applied to the all sensors under forward bias condition (Pd-Pt(+)-TiO₂-Ti(-)), and the H₂ sensing properties measured to 8000 ppm H₂ balanced with air and N₂ under dry or wet (absolute humidity (AH): 9.40 g m⁻³) conditions.

Results and Discussion

Morphology of all polymer films coated to the Pd-Pt electrodes on a TiO₂-modified Si substrate was observed by SEM, as shown in Fig. 2, because it was very difficult for us to observe the cross-section of actual P-*n*/Pd-Pt/TiO₂ sensors fabricated on a ductile Ti metal

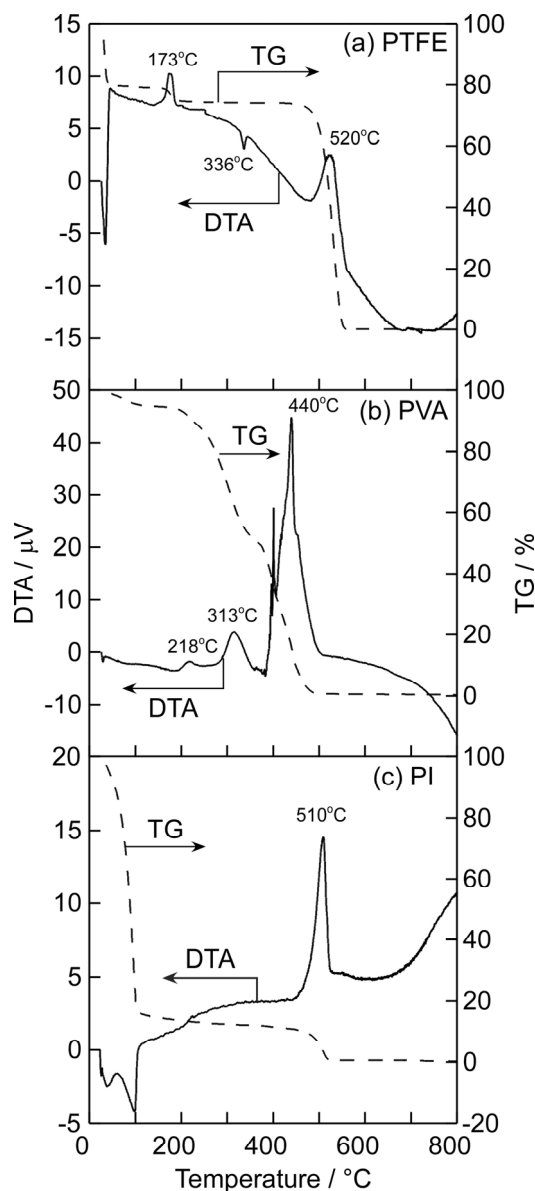


Fig. 3. TG-DTA curves of (a) PTFE, (b) PVA and (c) PI.

plate. It was confirmed that the thickness of polymer films decreased with a decrease in the polymer concentration in the solution and morphology of almost all polymer films was relatively uniform and the PTFE-20 film was the thickest among the all films fabricated. In addition, the PTFE-*n* films were relatively porous and they consisted of submicron-ordered particles, while the PVA-*n* and PI-*n* films were much dense in comparison with the PTFE-*n* films.

Figure 3 shows TG-DTA curves of PTFE, PVA and PI. For the PTFE, an exothermic peak at ca. 173°C was observed, probably because of decomposition of poly(oxyethylene)alkyl ether in the PTFE dispersion. In addition, an endothermic peak at ca. 336°C and an exothermic peak at ca. 520°C, which are ascribed to melting and decomposition of PTFE, respectively, were also observed, and the weight drastically reduced around the decomposition temperature. On the other hand, the lowest exothermic peak originating from the partial decomposition of PVA was observed at 218°C, and the main exothermic peak indicating the decomposition of PI was observed at 510°C. Based on these results, the maximum operation temperature of PTFE-*n*/Pd-Pt/TiO₂, PVA-*n*/Pd-Pt/TiO₂ and PI-*n*/Pd-Pt/TiO₂ sensors were set at 300°C, 200°C and 300°C, respectively.

Figure 4 shows response transients of all sensors to 8000 ppm H₂ in air at 200°C and 250°C under dry and wet conditions. Here, the

magnitude of sensor current in H₂ atmosphere can be regarded as H₂ response, since the sensor current in the H₂-free environment was extremely low. The coating of a relatively-thin polymer film, except for PTFE, on the electrodes likely enhanced the H₂ response, in comparison with that of a Pd-Pt/TiO₂ sensor. However, the H₂ response tended to decrease with an increase in the thickness of every kind of films under both dry and wet air atmospheres. This may imply the possibility of the consumption of H₂ during its diffusion into the interior region through the film and lower H₂ concentration in the vicinity of the Pd-Pt electrodes. But, the reasons for this phenomenon not clear at present. Among them, the coating of PI films on the electrodes was the most effective in improving the H₂ response in both dry and wet air atmospheres. The H₂ response of almost all sensors in wet air was much larger than those in dry air.

The H₂ response of all sensors to 8000 ppm H₂ balanced with dry and wet N₂ was also measured in this study. It was also revealed that the H₂ response of PI-*n*/Pd-Pt/TiO₂ was always larger than that of Pd-Pt/TiO₂ in both dry and wet N₂ atmospheres. In addition, the H₂ response remained unchanged irrespective of the variations in film thickness under dry and wet N₂ atmospheres in the cases of PTFE-*n*/Pd-Pt/TiO₂ and PVA-*n*/Pd-Pt/TiO₂ sensors. To clarify the effect of humidity and O₂ partial pressure on the H₂ response of P-*n*/Pd-

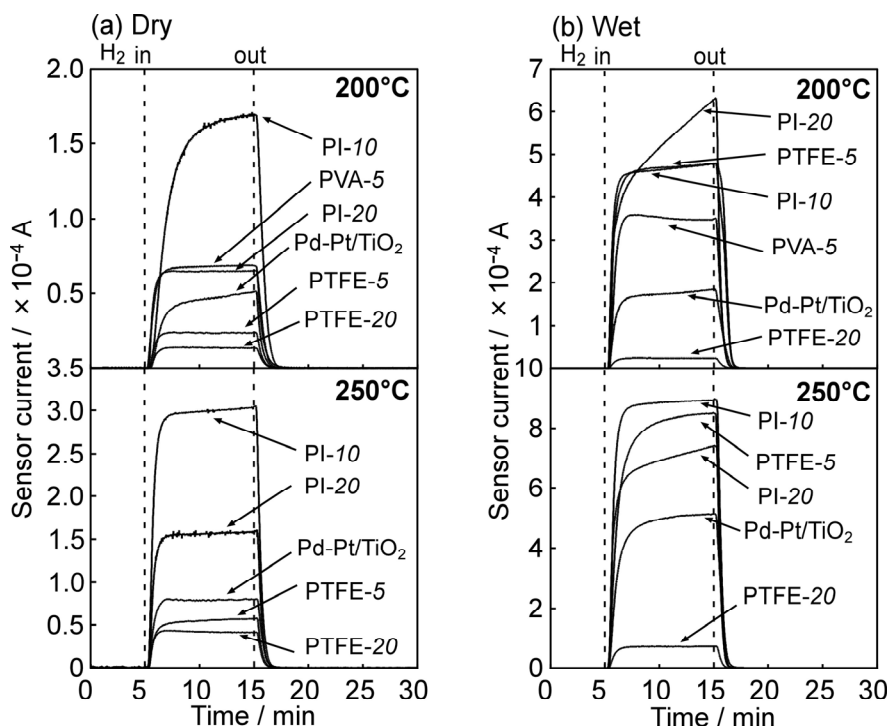


Fig. 4. Response transients of representative sensors to 8000 ppm H₂ in air at 200°C and 250°C under (a) dry and (b) wet atmospheres.

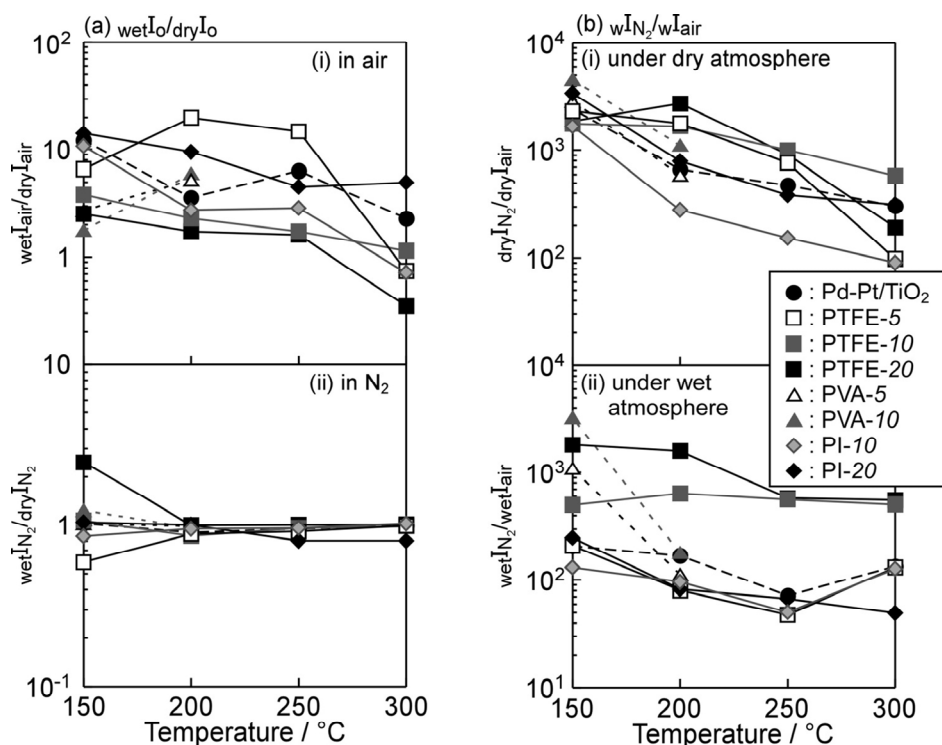


Fig. 5. Temperature dependence of (a) $wet I_o / dry I_o$ and (b) $w I_{N_2} / w I_{air}$.

Pd/TiO₂ sensors, temperature dependence of the ratio of the 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 Fig. 5, where each H₂ response was expressed as $w I_o$ (w : wet or dry atmosphere, o : in air or N₂). The magnitude of $wet I_{air} / dry I_{air}$ of PTFE- n /Pd-Pt/TiO₂ sensors was smaller than that of Pd-Pt/TiO₂ sensor, except for that of PTFE-5/Pd-Pt/TiO₂ sensor at 200 and 250 °C (Fig. 5(a)(i)), indicating the reduction of the effect of humidity on the H₂ response, probably because of the waterproof property of PTFE. In addition, the magnitude of $wet I_{N_2} / dry I_{N_2}$ was almost 1 in N₂ for all the sensors, except for those of PTFE- n /Pd-Pt/TiO₂ sensors ($n = 5$ and 20) at 150 °C (Fig. 5(a)(ii)). On the other hand, the magnitude of $w I_{N_2} / w I_{air}$ of almost all P- n /Pd-Pt/TiO₂ sensors was larger than that of Pd-Pt/TiO₂ sensor (Fig. 5(b)), showing an increase in the effect of O₂ concentration on the H₂ response by the polymer coating to Pd-Pt electrodes. However, $w I_{N_2} / w I_{air}$ of the only PI-10/Pd-Pt/TiO₂ sensor was smaller than that of Pd-Pt/TiO₂, especially under dry atmosphere, showing the certain reduction of interference from O₂ on the H₂ response.

In summary, the PI- n /Pd-Pt/TiO₂ sensors showed the most improved H₂ response in both dry and wet air atmospheres. In addition, the coating of PTFE on the Pd-Pt electrodes was effective in reducing the interference from

humidity on the H₂ response of the Pd-Pt/TiO₂ sensor, but the optimization of the morphology (thickness and/or porosity) of these polymer films was essential for further improving the H₂ response properties.

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