

Hydrogen Sensing Properties of an Anodized TiO₂ Film Equipped with a Pd-Pt Electrode

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An anodized TiO₂ sensor equipped with a Pd-Pt electrode was subjected to heat treatment in air (air-treated) and additionally in N₂ (N₂-treated), and then its responses to H₂ balanced with air or N₂ were investigated under dry and wet conditions. Among the conditions tested, the N₂-treated sensor showed the largest H₂ response in dry N₂ atmosphere. But, H₂ response of the air-treated sensor increased with the existence of water vapor, while that of the N₂-treated sensor decreased with the existence of water vapor. As a result, H₂ response of the air-treated sensor in wet air was quite comparable with that of the N₂-treated sensor in wet N₂. Thus, it was revealed that the existence of water vapor reduced the pretreatment- and measurement atmosphere-dependent H₂ response of the sensor.

Introduction

Our previous studies have revealed that a TiO₂ thin film having sub-micron pores could be fabricated by anodic oxidation of a Ti plate, and that the anodized TiO₂ thin film equipped with a Pd top electrode and the Ti plate bottom electrode exhibited high H₂ response in a wide range of H₂ concentration as a diode-type sensor under flowing both air and N₂ atmospheres (1-4). In addition, alloying of Pd with Pt was quite effective in improving the reproducibility of H₂ response and its long-term stability (5-7). In the present study, sensing properties of an anodized TiO₂ sensor equipped with a Pd-Pt alloy top electrode to H₂ balanced with air or N₂ were investigated under dry and wet atmospheres.

Experimental

Preparation and Characterization of an Anodized TiO₂ Thin Film

A half part of a Ti plate ($5.0 \times 10.0 \times 0.5$ mm³) 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 film was observed by scanning electron microscopy (SEM; JEOL, JSM-7500F).

Fabrication and Measurement of a Pd-Pt/TiO₂ Sensor

Figure 1 shows schematic drawing of a diode-type sensor fabricated using the anodized TiO₂ thin film and a Pd-Pt (Pd : Pt = 36 : 64 (wt%)) alloy top electrode (Pd-Pt/TiO₂

sensor). The Pd-Pt alloy electrode ($3.0 \times 3.0 \text{ mm}^2$) was fabricated on both the TiO_2 thin film and the Ti plate by radio-frequency magnetron sputtering (Shimadzu, HSR-552S, output power: 300 W(Pd) - 200 W(Pt), sputtering time: 7 min) and the electrical contact to Au lead wires was achieved by application of a Pt paste and then was ensured by subsequent firing at 600°C for 1 h in dry air (air-treated sensor). Thus, the actual electrode configuration was the Pd-Pt/ TiO_2 /Ti plate. A dc voltage of 1 or 100 mV was applied to the Pd-Pt/ TiO_2 sensor under forward bias condition (Pd-Pt(+)- TiO_2 -Ti(-)), and the H_2 sensing properties were measured at 250°C to 50~8000 ppm H_2 balanced with air or N_2 under dry and wet conditions (absolute humidity (AH) range: 0 ~ 30.4 g m^{-3}). The H_2 response properties of the sensor subjected to the additional treatment in dry N_2 at 600°C for 1 h (N_2 -treated sensor) were also measured. For easy comparison, air- and N_2 -treatments are expressed as T_{air} and T_{N_2} , respectively, and measurements in air and in N_2 atmosphere are indicated as M_{air} and M_{N_2} , respectively. Current (I)-voltage (V) characteristics of the sensor were measured in a range of -1~1 V.

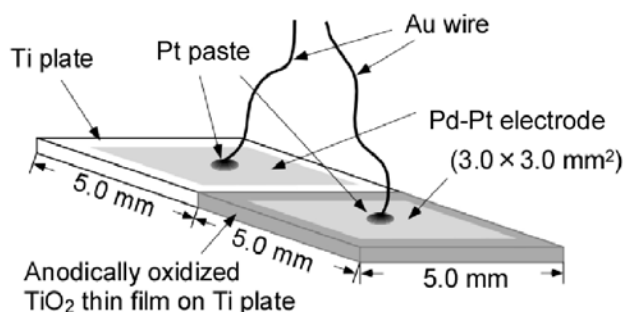


Fig. 1 Schematic drawing of a Pd-Pt/ TiO_2 sensor.

Results and Discussion

Microstructure of an Anodized TiO_2 Thin Film

Figure 2 shows SEM photographs of the surfaces of a Ti plate, an anodized TiO_2 thin film and the anodized TiO_2 thin film coated with a Pd-Pt alloy electrode. Formation of submicron-sized pores was observed at the surface after the anodic oxidation, as shown in Fig. 2(b). The pore size decreased obviously after the sputtering of the Pd-Pt alloy electrode, as shown in Fig. 2(c).

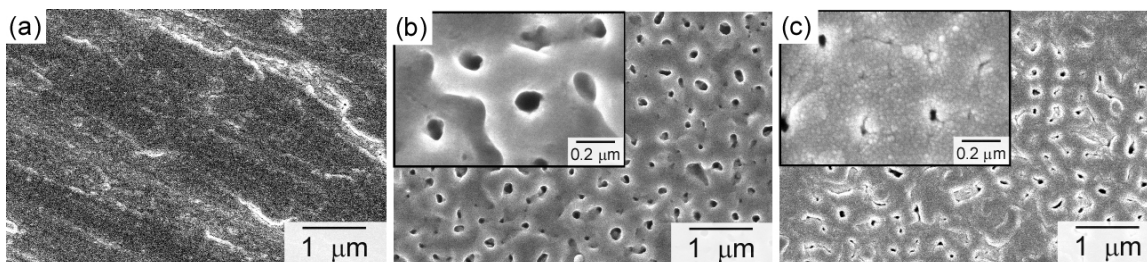


Fig. 2 SEM photographs of the surfaces of (a) a Ti plate, (b) an anodized TiO_2 thin film and (c) the anodized TiO_2 thin film coated with a Pd-Pt alloy electrode.

I-V Characteristics of a Pd-Pt/TiO₂ Sensor

Figure 3 shows *I-V* curves of the Pd-Pt/TiO₂ sensor in 8000 ppm H₂ balanced with air and N₂ at 250°C. A nonlinear *I-V* curve, which is typical for a diode-type sensor, was observed for the air-treated sensor in dry air, but it changed to an almost ohmic *I-V* curve in wet air, i.e. current values increased with the existence of water under the forward bias conditions, as shown in Fig. 3(a). On the other hand, the *I-V* curve for the N₂-treated sensor in dry N₂ showed better linearity than that in dry air, and little change in current was induced by the existence of water in N₂, as shown in Fig. 3(b). It is reasonable to consider that the surface of the Pd-Pt electrode is partially covered with chemisorbed oxygen or partially oxidized in the case of the air-treated sensor. During the H₂ response measurement in dry air (dry environment under the T_{air}-M_{air} conditions), it is anticipated that chemisorbed oxygen cannot be consumed completely by the reaction with H₂ (a small but a certain coverage of chemisorbed oxygen is maintained), but almost no oxygen chemisorption may be easily achieved under the H₂ response measurement in dry N₂ (dry environment under the T_{N₂}-M_{N₂} conditions). Thus, it is considered that the chemisorbed oxygen on the electrode contributes to the formation of the Schottky barrier at the interface between the Pd-Pt electrode and the anodized TiO₂ thin film, since the existence of chemisorbed oxygen on the electrode further promotes electron extraction from the anodized TiO₂ thin film than the level expected from the difference between the work function of the electrode and the electron affinity of the anodized TiO₂ thin film. In addition, the results shown in Fig. 3 confirm that the existence of water vapor under the T_{air}-M_{air} conditions weakens the above role of chemisorbed oxygen.

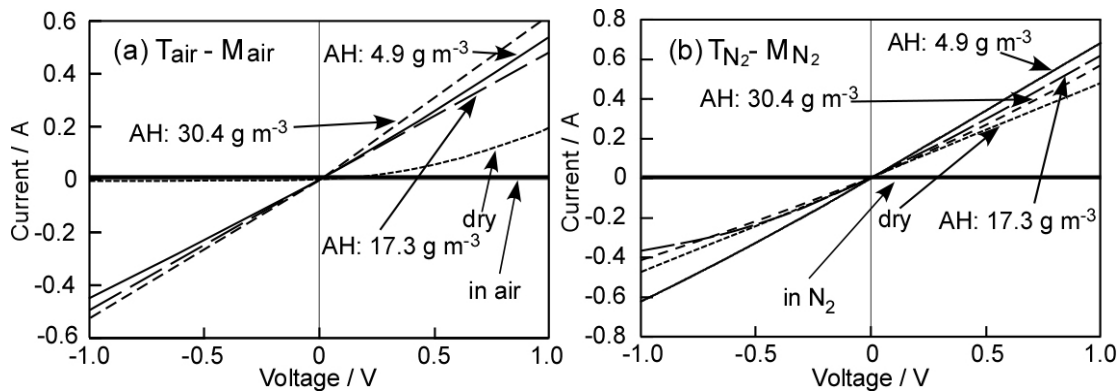


Fig. 3 *I-V* characteristics of a Pd-Pt/TiO₂ sensor in 8000 ppm H₂ balanced with (a) air or (b) N₂ at 250°C. The sensor was pretreated at 600°C for 1 h in (a) dry air and (b) dry N₂. AH: absolute humidity

H₂ Response Properties of a Pd-Pt/TiO₂ Sensor

Figure 4 shows response transients of the Pd-Pt/TiO₂ sensor to 8000 ppm H₂ at 250°C under a forward bias voltage of 1 mV. The air-treated sensor showed very small H₂ response in dry air, as shown in Fig. 4(a) and the N₂-treated sensor showed the largest H₂ response in dry N₂ among the conditions tested, as shown in Fig. 4(b). The H₂ response of the air-treated sensor was increased by the existence of water vapor. In contrast, the H₂ response of the N₂-treated sensor was decreased by the existence of water vapor in this case.

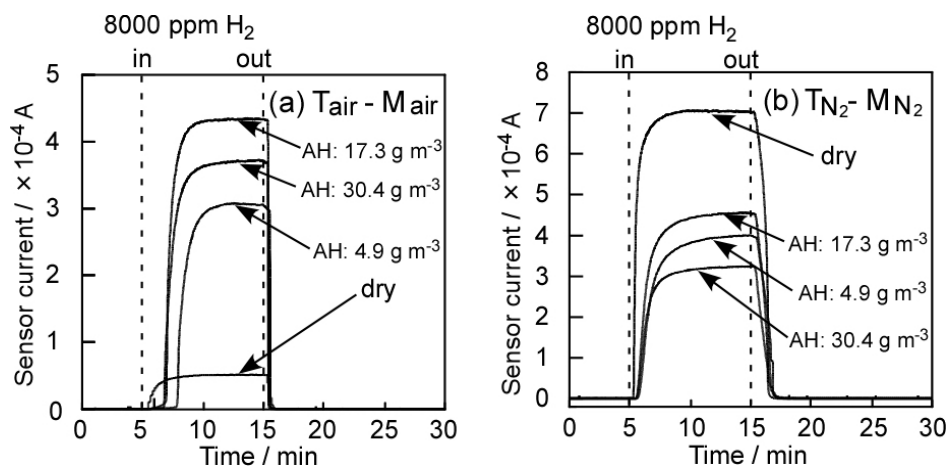


Fig. 4 Response transients of a Pd-Pt/TiO₂ sensor to 8000 ppm H₂ balanced with (a) air or (b) N₂ at 250°C. The sensor was pretreated at 600°C for 1 h in (a) dry air and (b) dry N₂ (applied voltage: 1 mV). AH: absolute humidity

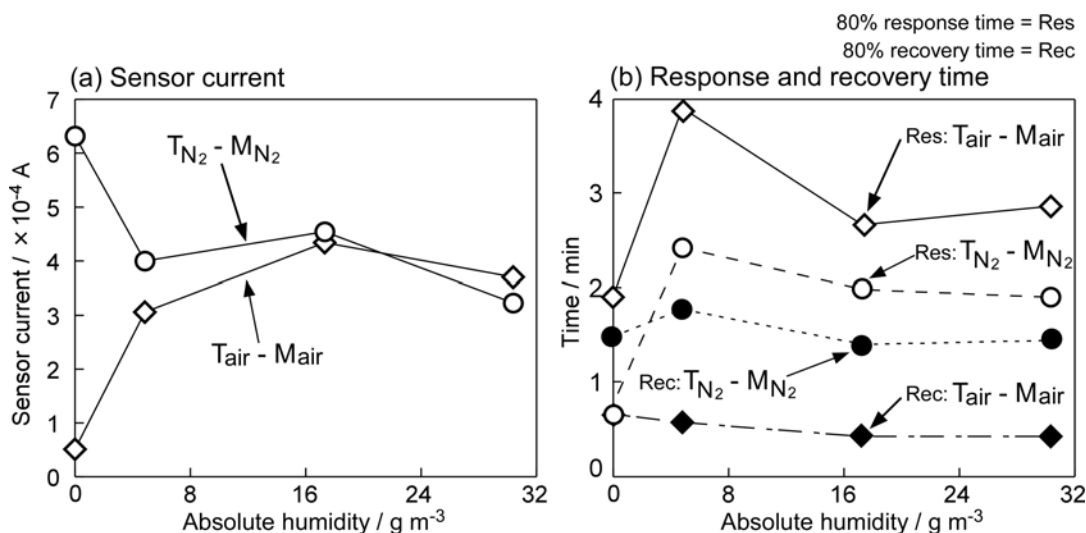


Fig. 5 Variations in (a) sensor current and (b) response and recovery times of a Pd-Pt/TiO₂ sensor in 8000 ppm H₂ operated at 250°C under a forward bias voltage of 1 mV with absolute humidity.

Figure 5(a) depicts the variations in H₂ response of the sensor with absolute humidity in the measurement atmosphere. The magnitude of the H₂ response of the air-treated sensor in wet air was quite comparable to that of the N₂-treated sensor in wet N₂ (a response current range of $3.0\sim 4.5\times 10^{-4}$ A), and it showed little absolute humidity dependence. Thus, it was revealed that the existence of water vapor reduced the pretreatment- and measurement atmosphere-dependent H₂ response of the sensor. Figure 5(b) shows the variations in response and recovery times of the sensor with absolute humidity in the measurement atmosphere. In dry atmosphere, a longer response time was observed under the T_{air}-M_{air} conditions, in comparison with that under the T_{N₂}-M_{N₂} conditions. This is because the response time under the T_{air}-M_{air} conditions contains the time necessary to remove chemisorbed oxygen to a certain level before the dissociative adsorption of H₂ and subsequent dissolution of H atoms into the electrode which is the main sensing mechanism of this type sensor. On the other hand, the T_{air}-M_{air} conditions

offered a shorter recovery time than the T_{N_2} - M_{N_2} conditions, implying that the gaseous oxygen accelerates release of H atoms from the electrode. The response time became longer with the existence of water vapor on the whole under both the T_{air} - M_{air} and T_{N_2} - M_{N_2} conditions. Thus, it is obvious that water vapor and/or chemisorbed water molecules on the electrode interferes the dissociative adsorption of H_2 and subsequent dissolution of H atoms into the electrode from the view point of response time. However, the recovery time remained almost unchanged with the existence of water vapor under both the T_{air} - M_{air} and T_{N_2} - M_{N_2} conditions.

H_2 Concentration Dependence of Response of a Pd-Pt/ TiO_2 Sensor

The response transients of the Pd-Pt/ TiO_2 sensor to 50~8000 ppm H_2 balanced with dry air and dry N_2 under a forward bias voltage of 100 mV are shown in Fig. 6(a). The sensor current decreased drastically with decreasing H_2 concentration under the T_{air} - M_{air} conditions. And then the sensor current in 50~500 ppm H_2 became extremely small. In contrast, much larger responses to 50~8000 ppm H_2 were observed under the T_{N_2} - M_{N_2} conditions than the T_{air} - M_{air} conditions, especially in the H_2 concentration range (C_{H_2}) less than 500 ppm. In addition, the sensor current in H_2 is directly proportional to the H_2 concentration under the T_{air} - M_{air} conditions, while it is proportional to the logarithm of H_2 concentration under the T_{N_2} - M_{N_2} conditions, as shown in Fig. 6(b). From these results, it was confirmed that oxygen in the measurement atmosphere lowered the H_2 response, especially in the low concentration range less than 500 ppm.

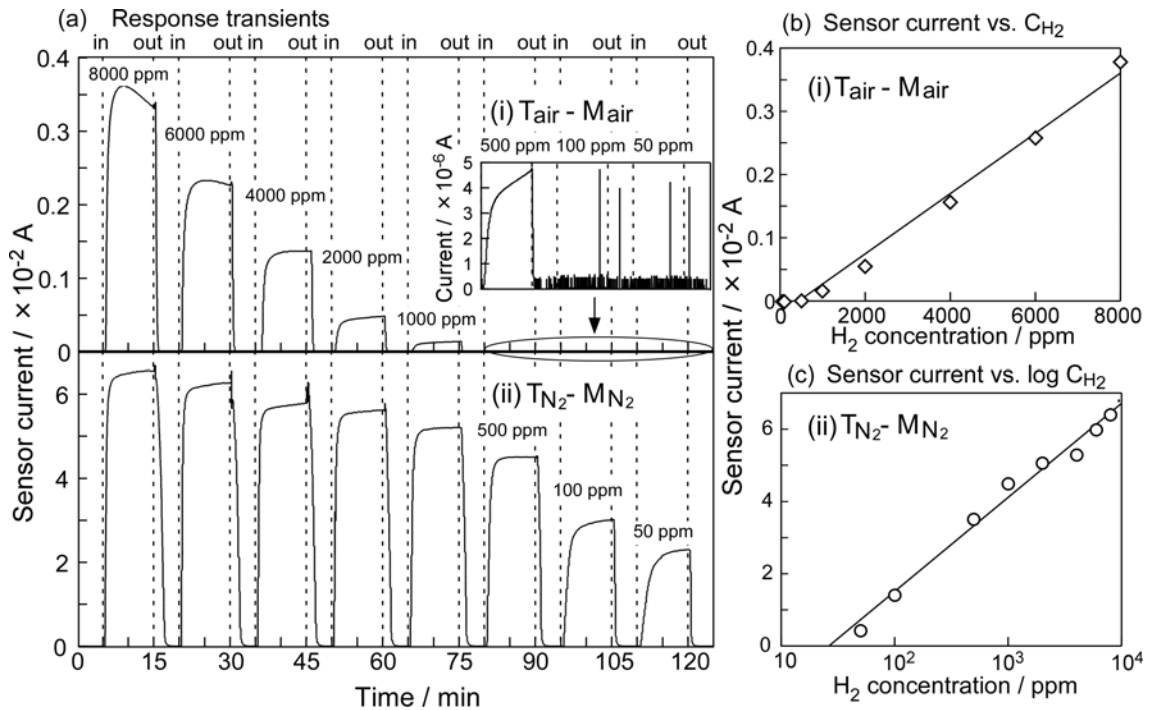


Fig. 6 (a) Response transients to 50~8000 ppm H_2 and (b, c) variations in sensor current of a Pd-Pt/ TiO_2 sensor to 50~8000 ppm H_2 (C_{H_2}) in (i) dry air and (ii) dry N_2 at 250°C (applied voltage: 100 mV).

Similar measurements were also conducted with the Pd-Pt/TiO₂ sensor to 50~8000 ppm H₂ in wet atmosphere (AH: 17.3 g m⁻³), as shown in Fig. 7(a). The sensor current decreased drastically with decreasing H₂ concentration in wet atmosphere under both the T_{air}-M_{air} and T_{N₂}-M_{N₂} conditions. Especially, the H₂ response in the H₂ concentration range less than 500 ppm became very small. From the comparison between Figs. 6 and 7, we could confirm the effects of water vapor on the H₂ response explained by referring to the results shown in Figs. 5(a) and 5(b), i.e. water vapor enhances the H₂ response under the T_{air}-M_{air} conditions, but reduce the H₂ response under the T_{N₂}-M_{N₂} conditions, over the whole H₂ concentration range studied. In addition, it was found that the sensor current in wet H₂ atmosphere was well proportional to the logarithm of H₂ concentration under the T_{air}-M_{air} conditions (1000~8000 ppm) and the T_{N₂}-M_{N₂} conditions (500~8000 ppm), as shown in Fig. 7(b). This behavior is similar to that observed under the dry T_{N₂}-M_{N₂} conditions shown in Fig. 6(c) in all the H₂ concentration range, but the slope of the current in H₂ under the wet T_{air}-M_{air} conditions is apparently smaller than that under the T_{N₂}-M_{N₂} conditions in the H₂ concentration range higher than 1000 ppm. Under both T_{air}-M_{air} and T_{N₂}-M_{N₂} conditions the sensor showed very small H₂ responses in the H₂ concentration range less than 500 ppm H₂. Poor linearities were observed between the sensor current and the H₂ concentration under both the T_{air}-M_{air} and T_{N₂}-M_{N₂} conditions, as shown in Fig. 7(c). Thus, water vapor may induce a similar effect to that of oxygen from a view point of H₂ sensing mechanism, more precisely the H₂ concentration dependence of response, though the details are not clarified yet.

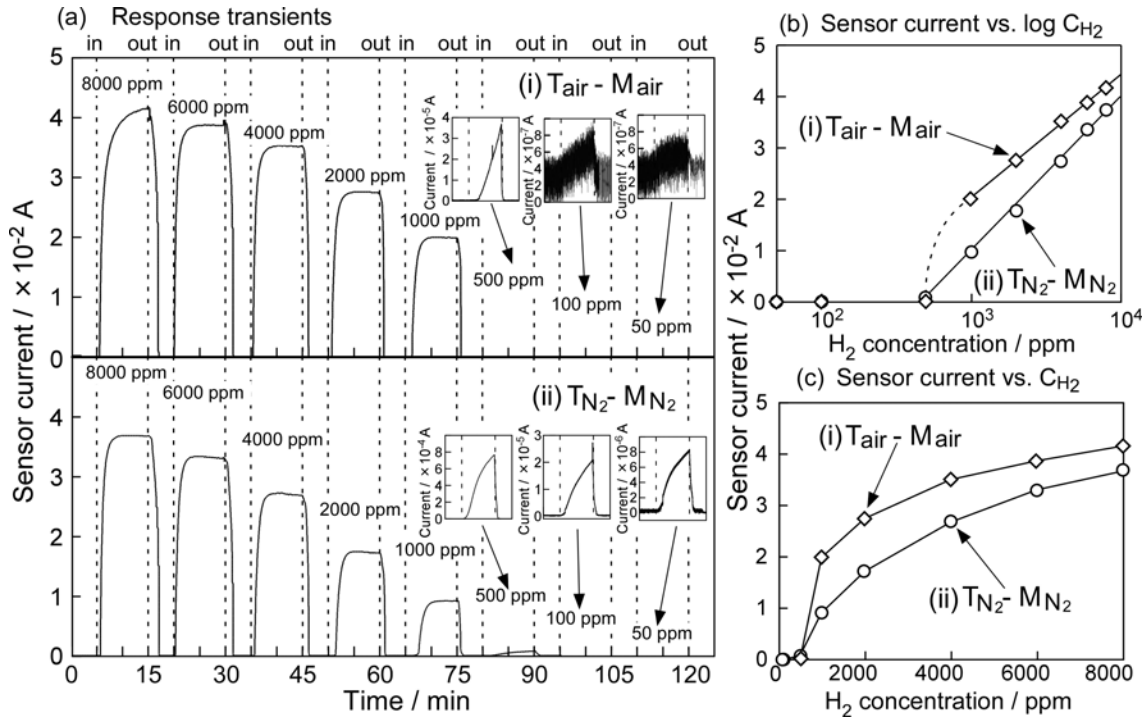


Fig. 7 (a) Response transients and (b~c) variations in sensor current of a Pd-Pt/TiO₂ sensor to 50~8000 ppm H₂ (CH₂) in (i) wet air and (ii) wet N₂ (AH: 17.3 g m⁻³) at 250°C (applied voltage: 100 mV).

Conclusions

H₂ sensing properties of an anodized TiO₂ sensor equipped with a Pd-Pt alloy top electrode were investigated in air and N₂ under dry and wet conditions. It was revealed that the existence of water vapor reduced the influence of pretreatment- and measurement atmosphere-dependent H₂ sensing properties of the anodized Pd-Pt/TiO₂ sensor. It is also suggested that the H₂ sensing mechanism is affected by oxygen as well as water vapor.

Acknowledgments

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