

# 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-

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**Abstract.** H<sub>2</sub> responses of a diode-type gas sensor fabricated with a TiO<sub>2</sub> film prepared by anodization of a Ti plate and Pd-Pt electrodes (Pd-Pt/TiO<sub>2</sub>) and the effects of polymer coating on the Pd-Pt/TiO<sub>2</sub> sensor were investigated in this study. The H<sub>2</sub> response of the Pd-Pt/TiO<sub>2</sub> sensor in dry N<sub>2</sub> was larger than that in dry air at 250°C, but the addition of moisture into the atmosphere reduced O<sub>2</sub> concentration dependence of H<sub>2</sub> response. The responses decreased drastically at lower temperature (50°C), but the responses in N<sub>2</sub> were larger than those in air under both dry and wet conditions. The coating of polymer on the Pd-Pt/TiO<sub>2</sub> sensor increased the H<sub>2</sub> responses in wet air and N<sub>2</sub> and reduced O<sub>2</sub> concentration dependence of H<sub>2</sub> responses.

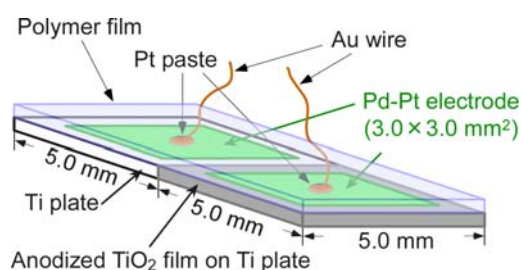
## 1. Introduction

H<sub>2</sub> sensors have already been used in some application fields such as fire alarms and gas leakage detectors, but the additional improvements in their H<sub>2</sub> sensing properties are indispensable for the use of the sensors in the operation of various hydrogen-energy devices such as fuel cells and hydrogen engines. We have revealed that a diode-type gas sensor which was fabricated with a TiO<sub>2</sub> thin film prepared by anodization of a Ti plate and Pd-based electrodes exhibited high H<sub>2</sub> responses in both air and N<sub>2</sub>, because of the reduction in the height of Schottky barrier formed at the interface between the TiO<sub>2</sub> and the Pd-based metal by the decrease in the work function of the Pd-based metal with the adsorption and subsequent dissolution of H-species [1-6]. In the present study, H<sub>2</sub> sensing properties of the diode-type gas sensor at lower temperatures and effects of a coating with different polyolefin elastomers on the Pd-Pt electrodes on the H<sub>2</sub> sensing properties have been investigated.

## 2. Experimental

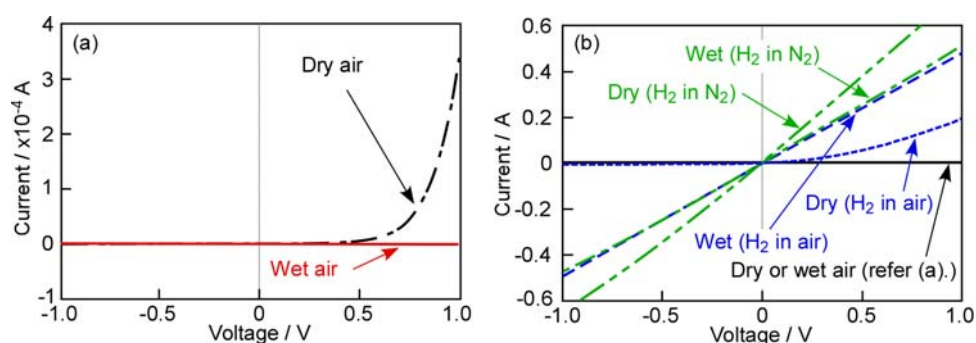
Figure 1 shows schematic drawing of a polymer-coated diode-type gas sensor with a TiO<sub>2</sub> thin film and Pd-Pt electrodes, which was fabricated as follows. A half part of a Ti plate (5.0 × 10.0 × 0.5 mm<sup>3</sup>) was anodized in a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at 20°C for 30 min at a current density of 50 mA cm<sup>-2</sup> [1-6]. A pair of Pd-Pt electrodes (3.0 × 3.0 mm<sup>2</sup>) was fabricated on both the TiO<sub>2</sub> thin film and the Ti plate by

simultaneous radio-frequency magnetron sputtering of Pd (output power (OP): 300 W) and Pt (OP: 200 W) (Shimadzu, HSR-552S) for 7 min. The composition in the electrodes (Pd : Pt) was 49 : 51 (at%), which was measured with energy-dispersive X-ray spectroscopy attached to scanning electron microscope (JEOL, JSM-7500F). After the electrical contact to Au lead wires was attached to the electrodes with a Pt paste and then they were annealed at 600°C for 1 h in dry air, a diode-type gas sensor, Pd-Pt/TiO<sub>2</sub>, was obtained. The sensor was coated with a polymer film. In this study, three kinds of polyolefin elastomers supplied by Tokuyama Corporation, general non-ionic hydrocarbon polymer (N-HC), cation-conductive HC polymer with sulfonic acid group (C-HC) and anion-conductive HC polymer with quaternary ammonium group (A-HC) were used as the polymer. These polymers were dissolved in toluene (N-HC) or 1-propanol (C-HC and A-HC), and the polymer film was coated on the surface of the sensor by dipping the sensor in the solution and subsequent drying at 60°C for 1 h. In some cases, the dip-coating process was repeated several times (n: 1, 3 and 5 times) to obtain a thicker polymer film. Polymer-coated sensors were expressed as M-HC(n) (M-HC: the kind of polymer (N-HC, C-HC and A-HC), n: the number of dipping (1, 3 and 5)).



**Figure 1.** Schematic drawing of a polymer-coated diode-type gas sensor fabricated with a TiO<sub>2</sub> thin film and Pd-Pt electrodes.

Current (*I*)-voltage (*V*) characteristics of the sensor were also measured in a range of -1~1 V. A dc voltage (Δ*V*) of +1 or +100 mV was applied to Pd-Pt/TiO<sub>2</sub> and M-HC(n) sensors under forward bias condition (Pd-Pt(+)-TiO<sub>2</sub>-Ti(-)) at 250°C or 50°C, respectively, and the gas sensing properties to 8000 ppm H<sub>2</sub> balanced with air or N<sub>2</sub> were measured at these temperatures under dry and wet conditions (absolute humidity (AH) under the wet condition: 17.4 g m<sup>-3</sup>). A sensor current value at 10 min later after H<sub>2</sub> injection to air or N<sub>2</sub> was regarded as H<sub>2</sub> response, since a base current in air or N<sub>2</sub> was negligibly small.

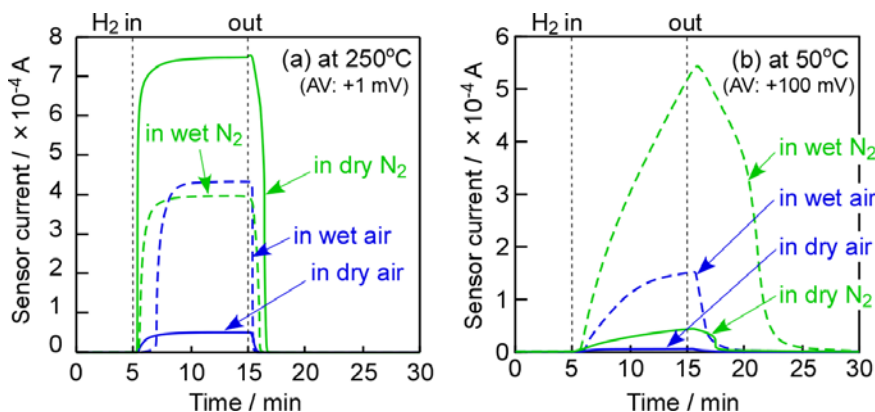


**Figure 2.** *I-V* curves of a Pd-Pt/TiO<sub>2</sub> sensor in different gaseous conditions at 250°C.

### 3. Results and Discussions

Figure 2 shows *I-V* curves of a Pd-Pt/TiO<sub>2</sub> sensor under different gaseous conditions at 250°C. A nonlinear *I-V* curve which was typical for a diode-type sensor was observed in dry air, but introduction of moisture in dry air extremely reduced the magnitude of the current. On the contrary, introduction of 8000 ppm H<sub>2</sub> in dry air drastically increased the magnitude of the current, but the *I-V* curve was still nonlinear. The simultaneous addition of moisture and H<sub>2</sub> into the atmosphere changed the nonlinear *I-V* curve to an almost ohmic one with an additional increase in the magnitude of the current. Also in 8000

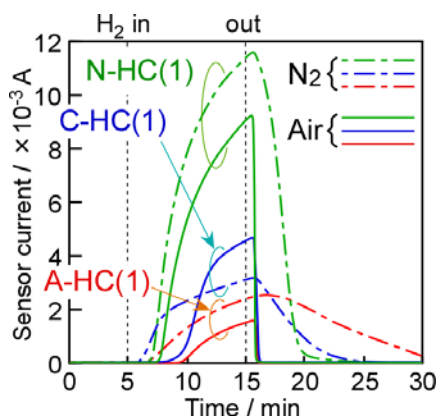
ppm H<sub>2</sub> balanced with dry N<sub>2</sub> (i.e., when O<sub>2</sub> was removed from dry air), the almost linear *I-V* curve was obtained, but the magnitude of the current was the largest among all conditions. On the other hand, the introduction of moisture into the dry N<sub>2</sub> containing 8000 ppm H<sub>2</sub> reduced the magnitude of the current to the similar level of that in the wet air. These *I-V* characteristics easily promise that the Pd-Pt/TiO<sub>2</sub> sensor is very sensitive to the change of gaseous compositions at 250°C.



**Figure 3.** Response transients of a Pd-Pt/TiO<sub>2</sub> sensor to 8000 ppm H<sub>2</sub> in air and N<sub>2</sub> under dry and wet conditions at 250°C and 50°C (AV: applied voltage).

Figure 3(a) shows response transients to 8000 ppm H<sub>2</sub> in air and N<sub>2</sub> under dry and wet conditions at 250°C (AV: +1 mV). The sensor showed H<sub>2</sub> response properties as expected from the *I-V* characteristics. Namely, it showed small H<sub>2</sub> response in dry air, but the response largely increased by the introduction of moisture and the response speed slowed down. In addition, it showed very large H<sub>2</sub> response in dry N<sub>2</sub>, whereas the response decreased by the introduction of moisture and the H<sub>2</sub> response in N<sub>2</sub> was similar to that in air under wet conditions. The little dependence of H<sub>2</sub> response on O<sub>2</sub> concentration under wet conditions is very favorable from the viewpoints of practical application.

The sensor showed clear responses to 8000 ppm H<sub>2</sub> also at much lower temperature (50°C) under all conditions at an applied voltage of +100 mV as shown in Figure 3(b), but the magnitude of H<sub>2</sub> response at 50°C was smaller than that at 250°C, irrespective of the larger applied voltage. In addition, the removal of O<sub>2</sub> and/or the addition of moisture in the base gas largely enhanced the H<sub>2</sub> response at 50°C. On the other hand, the response and recovery speeds at 50°C were slower than those at 250°C, and they tended to become faster with an increase in O<sub>2</sub> concentration and a decrease in humidity.

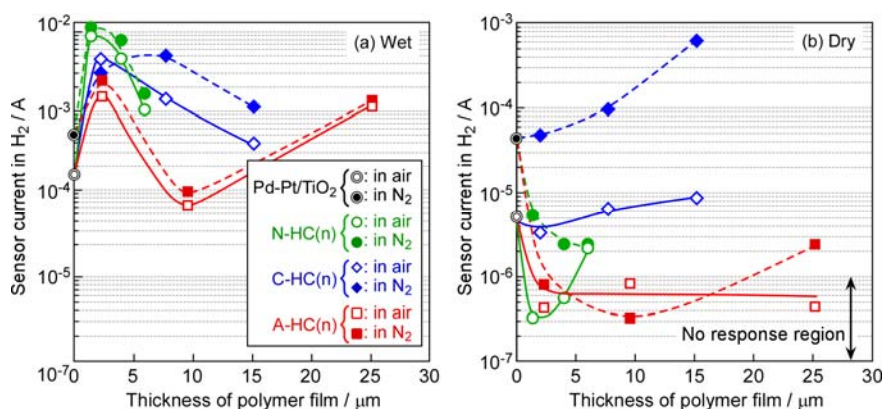


**Figure 4.** Response transients of M-HC(1) sensors to 8000 ppm H<sub>2</sub> in wet air and N<sub>2</sub> at 50°C (AV: +100 mV). The film thickness of N-HC(1), C-HC(1) and A-HC(1) was 1.38 μm, 2.18 μm and 2.35 μm, respectively.

Figure 4 shows response transients of M-HC(1) sensors to 8000 ppm H<sub>2</sub> in wet air and N<sub>2</sub> at 50°C. The responses of the Pd-Pt/TiO<sub>2</sub> sensor in wet air and N<sub>2</sub> increased with a coating of all polymers. Since

the Pd-Pt/TiO<sub>2</sub> sensor showed larger H<sub>2</sub> responses under wet condition than those under dry condition, all polymers used in this study might play an important role for absorption and retention of water molecules on the electrode surface and thus the H<sub>2</sub> responses of the polymer-coated sensors might be enhanced. Interestingly, O<sub>2</sub> concentration dependence of the H<sub>2</sub> response seems to reduce by the coating of polymers.

Variations in sensor currents in H<sub>2</sub> (i.e., H<sub>2</sub> responses) of Pd-Pt/TiO<sub>2</sub> and M-HC(n) sensors with the thickness of polymer films in air and N<sub>2</sub> under dry and wet conditions at 50°C were plotted in Figure 5. Under wet condition, H<sub>2</sub> responses of all sensors tended to decrease with an increase in the thickness of polymer films except for the A-HC(3) sensor, probably because the amount of permeable H<sub>2</sub> decreased with an increase in the thickness of polymer films. Therefore, the N-HC(1) sensor with the thinnest polymer film may show the largest H<sub>2</sub> responses in both air and N<sub>2</sub> under wet condition among them. Unfortunately, the existence of sulfonic acid group of C-HC and quaternary ammonium group of A-HC may be less effective in improving H<sub>2</sub> response of the sensor. On the other hand, the H<sub>2</sub> responses under dry condition reduced by the coating of N-HC and A-HC, probably because of little permeation of H<sub>2</sub> in these polymers. However, the H<sub>2</sub> response of C-HC(n) sensors increased with an increase in the film thickness. In addition, the responses of C-HC(n) sensor in dry N<sub>2</sub> were much larger than those in dry air. The strange behavior may arise from the properties of sulfonic acid group in C-HC film. The reason for these phenomena will be studied in our future work.



**Figure 5.** Variations in sensor currents in H<sub>2</sub> of Pd-Pt/TiO<sub>2</sub> and M-HC(n) sensors with the thickness of polymer films at 50°C (AV: +100 mV).

#### 4. Conclusions

The H<sub>2</sub> response of the Pd-Pt/TiO<sub>2</sub> sensor in dry N<sub>2</sub> was larger than that in dry air at 250°C. The introduction of moisture into the atmosphere increased the response in air and decreased the response in N<sub>2</sub>, and thus the response in wet air was quite comparable with that in wet N<sub>2</sub>. The Pd-Pt/TiO<sub>2</sub> sensor showed low H<sub>2</sub> responses at 50°C, and the H<sub>2</sub> responses in N<sub>2</sub> were larger than those in air under both dry and wet conditions. The coating of polymer on the Pd-Pt/TiO<sub>2</sub> sensor reduced O<sub>2</sub> concentration dependence of H<sub>2</sub> responses.

#### References

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