



Title	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–
Author(s)	Hyodo, Takeo; Nakaoka, M; Kaneyasu, K; Kato, H; Yanagi, H; Shimizu, Y
Citation	IOP Conference Series, 18(21), 212006; 2011
Issue Date	2011-10-29
URL	http://hdl.handle.net/10069/26154
Right	© 2011 Ceramic Society of Japan.; This is an author-created, un-copyedited version of an article accepted for publication in IOP Conference Series: Materials Science and Engineering. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The definitive publisher authenticated version is available online at http://dx.doi.org/10.1088/1757-899X/18/21/212006 .

This document is downloaded at: 2020-10-30T08:38:53Z

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-

T Hyodo¹, M Nakaoka², K Kaneyasu³, H Kato⁴, H Yanagi⁴ and Y Shimizu¹

¹Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

²Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

³Figaro Engineering, 1-5-11 Senbanishi, Minoo, Osaka 562-8505, Japan

⁴Tokuyama Corporation, 40 Wadai, Tsukuba, Ibaraki 300-4247, Japan

E-mail: hyodo@nagasaki-u.ac.jp

Abstract. H₂ responses of a diode-type gas sensor fabricated with a TiO₂ film prepared by anodization of a Ti plate and Pd-Pt electrodes (Pd-Pt/TiO₂) and the effects of polymer coating on the Pd-Pt/TiO₂ sensor were investigated in this study. The H₂ response of the Pd-Pt/TiO₂ sensor in dry N₂ was larger than that in dry air at 250°C, but the addition of moisture into the atmosphere reduced O₂ concentration dependence of H₂ response. The responses decreased drastically at lower temperature (50°C), but the responses in N₂ were larger than those in air under both dry and wet conditions. The coating of polymer on the Pd-Pt/TiO₂ sensor increased the H₂ responses in wet air and N₂ and reduced O₂ concentration dependence of H₂ responses.

1. Introduction

H₂ sensors have already been used in some application fields such as fire alarms and gas leakage detectors, but the additional improvements in their H₂ 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 TiO₂ thin film prepared by anodization of a Ti plate and Pd-based electrodes exhibited high H₂ responses in both air and N₂, because of the reduction in the height of Schottky barrier formed at the interface between the TiO₂ 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, H₂ 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 H₂ sensing properties have been investigated.

2. Experimental

Figure 1 shows schematic drawing of a polymer-coated diode-type gas sensor with a TiO₂ thin film and Pd-Pt electrodes, which was fabricated as follows. A half part of a Ti plate (5.0 × 10.0 × 0.5 mm³) was anodized in a 0.5 M H₂SO₄ aqueous solution at 20°C for 30 min at a current density of 50 mA cm⁻² [1-6]. A pair of Pd-Pt electrodes (3.0 × 3.0 mm²) was fabricated on both the TiO₂ 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/TiO₂, 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)).

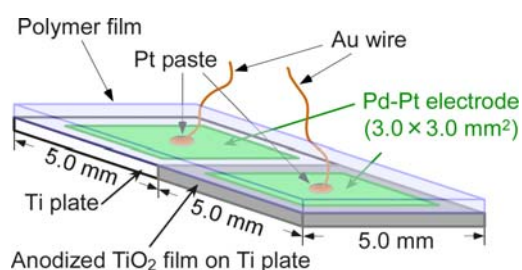


Figure 1. Schematic drawing of a polymer-coated diode-type gas sensor fabricated with a TiO₂ thin film and Pd-Pt electrodes.

Current (*I*)-voltage (*V*) characteristics of the sensor were also measured in a range of -1~1 V. A dc voltage (AV) of +1 or +100 mV was applied to Pd-Pt/TiO₂ and M-HC(n) sensors under forward bias condition (Pd-Pt(+)-TiO₂-Ti(-)) at 250°C or 50°C, respectively, and the gas sensing properties to 8000 ppm H₂ balanced with air or N₂ were measured at these temperatures under dry and wet conditions (absolute humidity (AH) under the wet condition: 17.4 g m⁻³). A sensor current value at 10 min later after H₂ injection to air or N₂ was regarded as H₂ response, since a base current in air or N₂ was negligibly small.

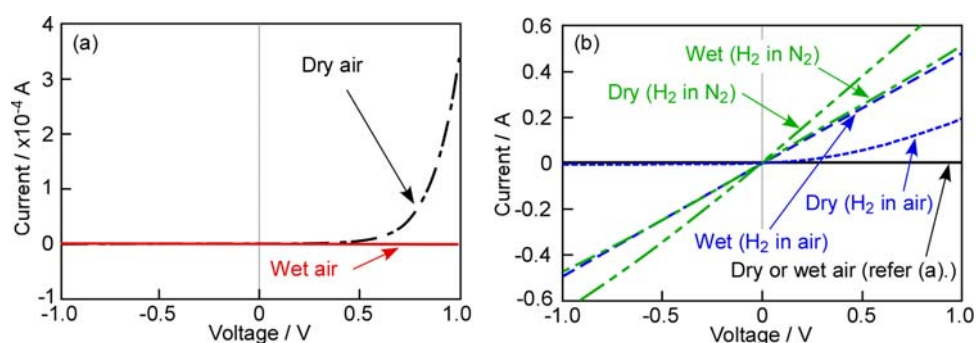


Figure 2. *I*-*V* curves of a Pd-Pt/TiO₂ sensor in different gaseous conditions at 250°C.

3. Results and Discussions

Figure 2 shows *I*-*V* curves of a Pd-Pt/TiO₂ 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 H₂ in dry air drastically increased the magnitude of the current, but the *I*-*V* curve was still nonlinear. The simultaneous addition of moisture and H₂ 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 H₂ balanced with dry N₂ (i.e., when O₂ 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 N₂ containing 8000 ppm H₂ 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/TiO₂ sensor is very sensitive to the change of gaseous compositions at 250°C.

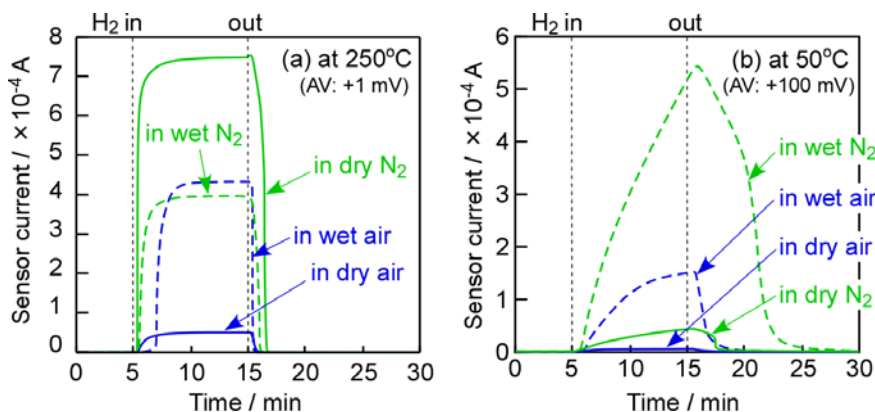


Figure 3. Response transients of a Pd-Pt/TiO₂ sensor to 8000 ppm H₂ in air and N₂ under dry and wet conditions at 250°C and 50°C (AV: applied voltage).

Figure 3(a) shows response transients to 8000 ppm H₂ in air and N₂ under dry and wet conditions at 250°C (AV: +1 mV). The sensor showed H₂ response properties as expected from the *I-V* characteristics. Namely, it showed small H₂ 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 H₂ response in dry N₂, whereas the response decreased by the introduction of moisture and the H₂ response in N₂ was similar to that in air under wet conditions. The little dependence of H₂ response on O₂ concentration under wet conditions is very favorable from the viewpoints of practical application.

The sensor showed clear responses to 8000 ppm H₂ 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 H₂ response at 50°C was smaller than that at 250°C, irrespective of the larger applied voltage. In addition, the removal of O₂ and/or the addition of moisture in the base gas largely enhanced the H₂ 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 O₂ concentration and a decrease in humidity.

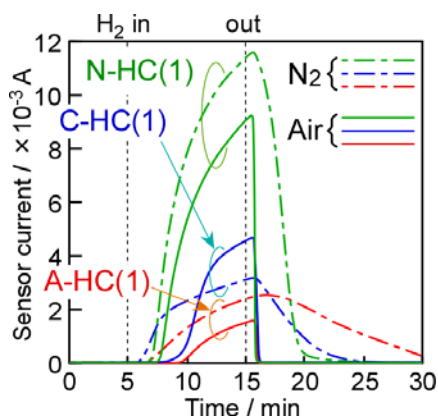


Figure 4. Response transients of M-HC(1) sensors to 8000 ppm H₂ in wet air and N₂ at 50°C (AV: +100 mV). The film thickness of N-HC(1), C-HC(1) and A-HC(1) was 1.38 μm, 2.18 μm and 2.35 μm, respectively.

Figure 4 shows response transients of M-HC(1) sensors to 8000 ppm H₂ in wet air and N₂ at 50°C. The responses of the Pd-Pt/TiO₂ sensor in wet air and N₂ increased with a coating of all polymers. Since

the Pd-Pt/TiO₂ sensor showed larger H₂ 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 H₂ responses of the polymer-coated sensors might be enhanced. Interestingly, O₂ concentration dependence of the H₂ response seems to reduce by the coating of polymers.

Variations in sensor currents in H₂ (i.e., H₂ responses) of Pd-Pt/TiO₂ and M-HC(n) sensors with the thickness of polymer films in air and N₂ under dry and wet conditions at 50°C were plotted in Figure 5. Under wet condition, H₂ 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 H₂ 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 H₂ responses in both air and N₂ 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 H₂ response of the sensor. On the other hand, the H₂ responses under dry condition reduced by the coating of N-HC and A-HC, probably because of little permeation of H₂ in these polymers. However, the H₂ 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 N₂ 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.

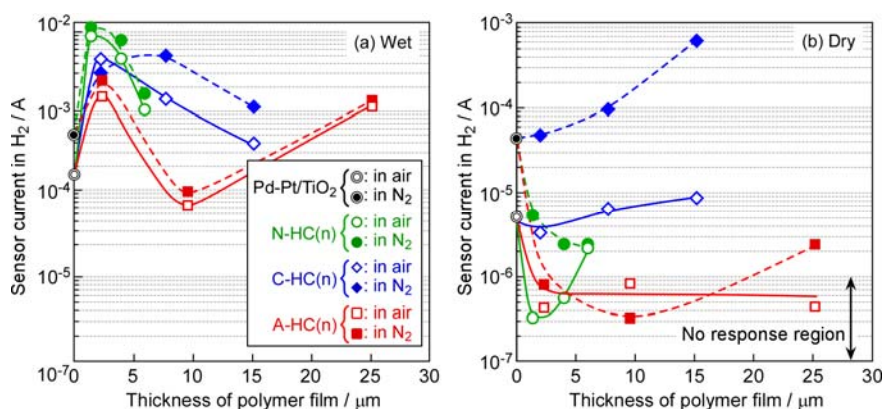


Figure 5. Variations in sensor currents in H₂ of Pd-Pt/TiO₂ and M-HC(n) sensors with the thickness of polymer films at 50°C (AV: +100 mV).

4. Conclusions

The H₂ response of the Pd-Pt/TiO₂ sensor in dry N₂ 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 N₂, and thus the response in wet air was quite comparable with that in wet N₂. The Pd-Pt/TiO₂ sensor showed low H₂ responses at 50°C, and the H₂ responses in N₂ were larger than those in air under both dry and wet conditions. The coating of polymer on the Pd-Pt/TiO₂ sensor reduced O₂ concentration dependence of H₂ responses.

References

- [1] Shimizu Y, Kuwano N, Hyodo T and Egashira M 2002 *Sens. Actuators B* **83** 195
- [2] Iwanaga T, Hyodo T, Shimizu Y and Egashira M 2003 *Sens. Actuators B* **93** 519
- [3] Hyodo T, Iwanaga T, Shimizu Y and Egashira M 2003 *ITE Lett.* **4** 594
- [4] Miyazaki H, Hyodo T, Shimizu Y and Egashira M 2005 *Sens. Actuators B* **108** 467
- [5] Shimizu Y, Sakamoto K, Nakaoka M, Hyodo T and Egashira M 2008 *Adv. Mater. Res.* **47-50** 1510
- [6] Nakaoka M, Hyodo T, Shimizu Y and Egashira M 2008 *ECS Trans.* **16(11)** 317