

# Ultrathin Film Hydrogen Sensor with Self-Temperature Compensation

Shuzo Takeichi, Yuki Ushita, Ryosuke Sugai, Kenji Sakai, Toshihiko Kiwa, Keiji Tsukada

Graduate School of Natural Science and Technology, Okayama University

Okayama, Japan

e-mail: (pgrx83ea, en421411, en422426) @s.okayama-u.ac.jp

(sakai-k, kiwa, tsukada) @cc.okayama-u.ac.jp

**Abstract**—An ultrathin film sensor, consisting of two serially connected Pt/Ti films with different sensitivity to obtain the output voltage, was developed. The hydrogen sensor, based on the electrical resistance change of Pt thin films upon exposure to hydrogen gas, is operable at room temperature. However, two different Pt/Ti films showed different temperature coefficient of resistance, so the output voltage changed by temperature change. In order to solve this problem, we developed a self-temperature compensation technique by optimized combination of Pt thickness and Ti thickness. As a result, the hydrogen sensor showed good stability against temperature change.

**Keywords**-hydrogen sensor; platinum thin film; catalysis.

## I. INTRODUCTION

Hydrogen energy is attracting attention as a clean energy in fuel cells, and the number of applications is growing. However, hydrogen has a wide range of explosive concentrations (4-75% in air) and hydrogen atoms are very small. Therefore, there is a risk of leakage and a method of detecting hydrogen leakage is required. Generally, sensors for detecting hydrogen leakages in multipoint should have high sensitivity, be low cost and have low power consumption. Many types of hydrogen sensors, such as semiconductor sensors [1][2], Field-Effect Transistors (FET) sensors [3]-[7], and metallic resistance change type sensors [8]-[10] have been studied. Semiconductor sensors operated above 300 °C are conventionally used, while FET and the metallic resistance change type sensors can detect hydrogen gas by using the work function change and electrical resistance change in catalytic metals at room temperature, respectively. Moreover, the metallic resistance change type sensors that use Palladium (Pd) are simple, so this sensor is suitable for mass production. However, a serious durability problem is caused by large expansion of Pd after exposure to high concentration hydrogen gas [11]. In order to address this problem, we previously reported a metallic resistance change type hydrogen sensor using Platinum (Pt) thin films instead of Pd [12]. This sensor can detect hydrogen gas by reducing the resistance upon exposure to hydrogen gas at room temperature. However, the resistance also changed by changes in the ambient temperature. Therefore, precise detection of hydrogen gas requires temperature compensation. In this study, we developed and evaluated a hydrogen sensor with self-temperature compensation.

Section II describes experimental procedure. Section III describes the result and discussion. Section IV addresses the conclusion.

## II. EXPERIMENTAL PROCEDURE

Pt/Titanium (Ti) films (Pt thickness: 30 nm, 20 nm, 10 nm, 5 nm/Ti thickness 3 nm), were deposited on a glass substrate (0.55-mm thick) by DC sputtering to investigate the resistance change upon exposure to hydrogen gas. Generally, a Ti layer is used for improvement of poor adhesion. We previously confirmed that Ti shows no response to hydrogen gas [6]. However, the resistance change ratio, when exposed to hydrogen gas, reduced by addition of a Ti layer, because the resistance of Ti is added in parallel to that of the Pt [12]. Therefore, a thinner Ti film that has higher resistance is suitable, and a Ti (3-nm thick) layer was selected. Each Pt/Ti film on glass substrate was cut to dimensions of  $3 \times 10 \text{ mm}^2$ , respectively (Figure 1). These films were placed in a chamber that was designed to measure the response characteristics at a constant gas exchange rate. The resistance was measured by a four-terminal sensing method using pairs of separated current-carrying and voltage-sensing wires. In order to assess the basic characteristics, the sensitivities of each sample were evaluated with respect to air and hydrogen gas of 1% concentration (1%-H<sub>2</sub>) at room temperature. The gas was changed from air to 1%-H<sub>2</sub> and back to air, and the sensitivity was calculated by the following equation.

$$\Delta R / R = (R_{\text{H}_2} - R) / R \times 100 (\%) \quad (1)$$

where R and R<sub>H<sub>2</sub></sub> are the resistance of Pt/Ti film in air and hydrogen gas.

However, Pt/Ti film also changed by temperature change, so hydrogen detection was severely affected. Generally, hydrogen sensor with a robustness to temperature in the range of -30 to 80 °C is required for detecting hydrogen gas [13], and it is necessary to detect hydrogen gas precisely in the temperature range. Therefore, we developed the hydrogen sensor with self-temperature compensation, which has two different Pt/Ti films were serially connected (Figure 2). This sensor, utilizing resistance change of Pt/Ti film, can detect hydrogen gas as output voltage change. In this sensor, hydrogen response and temperature dependence were measured. As samples, Pt (5 nm thick) on Ti (3 nm thick) and Pt (30 nm thick) on Ti (3 nm thick) were prepared, and

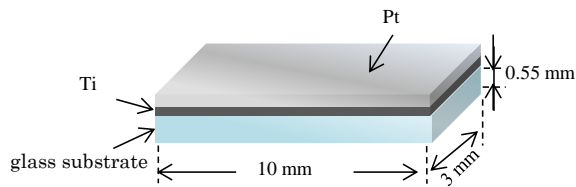


Figure 1. Schematic diagram of Pt/Ti thin film.

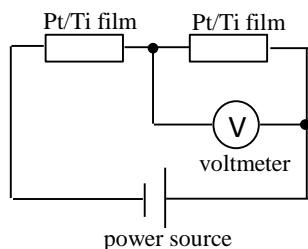


Figure 2. Schematic diagram of serially connected hydrogen sensor with different Pt/Ti thickness.

the output voltage of Pt (5 nm thick) on Ti (3 nm thick) was measured in air and 1%-H<sub>2</sub>. The temperature dependence in air was also evaluated in the temperature range from 50 °C to 80 °C in steps of 10 °C. Moreover, to eliminate temperature effect more precisely, combination of Pt thickness and Ti thickness was optimized. First, resistance temperature coefficient of samples, which are Pt films (thickness: 30 nm, 20 nm, 10 nm and 5 nm) on Ti films (thickness: 0 nm, 3 nm and 20 nm), was measured in the range from 50°C to 100°C in the steps of 10 °C. Then, based on the results of temperature dependence, a hydrogen sensor with two Pt/Ti films, which was optimized to have the same temperature coefficient of resistance, was fabricated. The hydrogen response and temperature dependence of the optimized hydrogen sensor was also evaluated under the same conditions as previously mentioned.

### III. RESULTS AND DISCUSSION

The measured resistances of Pt/Ti films when exposed to hydrogen gas are shown in Figure 3. The results show the resistances of Pt/Ti films decreased for all measured samples when gas was switched from air to 1%-H<sub>2</sub>. This decrease was caused by the catalytic action of Pt. When hydrogen molecule is adsorbed on the Pt surface, the hydrogen molecule is decomposed into hydrogen ions and electrons by the catalytic action of Pt as expressed in (2). Basically, the decomposed electrons diffuse into the platinum as the carriers, and platinum electrical resistance decreases.

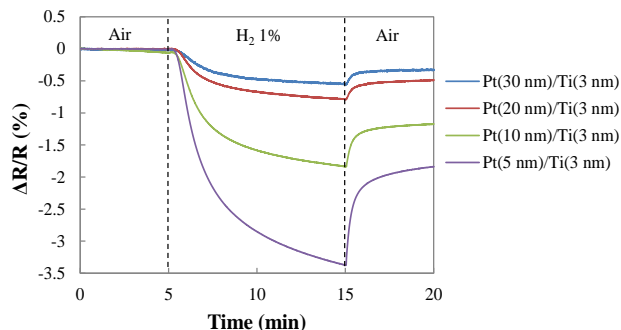


Figure 3. Hydrogen response curve of Pt/Ti thin films with different thickness.

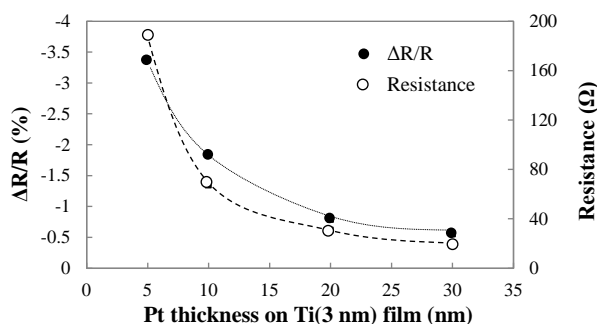


Figure 4. Pt thickness (5, 10, 20 and 30 nm on Ti(3 nm)) dependence for sensitivities to hydrogen gas when exposed to 1% concentration and the resistance in air.

Moreover, when hydrogen concentration is decreased, the resistance recovers, because the absorbed hydrogen desorbs and the carrier concentration decreases. Figure 4 shows the sensitivities and the resistances to 1%-H<sub>2</sub> as a function of Pt thickness. With decreasing the thickness of Pt film, sensitivity increased. This is because the surface-to-volume ratio of platinum increases with reducing the thickness. In brief, the number of carriers, generated by the catalytic reaction, increases in relation to the thinness of the Pt film, because the catalytic reaction occurs primarily on the surface without depending on film thickness. Also, the sensitivity as a function of Pt thickness is inversely proportional, similar to the resistance. The sensitivity depends on resistance and carrier caused by catalytic reaction. In this measurement, generated carrier is constant regardless of Pt thickness, so it is considered that the relationship of the sensitivity and Pt thickness is similar to the resistance. From these results, the sensitivity was increased with decreasing Pt thickness. However, the resistance did not completely recover when the gas was switched from 1%-H<sub>2</sub> to air. This indicates that all absorbed hydrogen ions and electrons were not desorbed, and a long time is needed for complete desorption. To solve this problem, we reported hydrogen desorption using instantaneous large pulsed heating in a previous study [12].

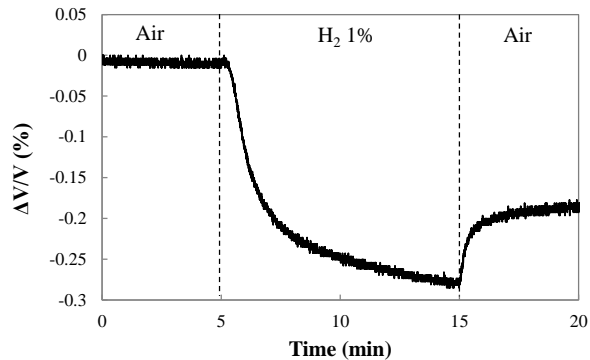


Figure 5. Hydrogen response curve of the hydrogen sensor that was serially connected Pt (5 nm)/Ti (3 nm) and Pt (30 nm)/Ti (3 nm) films.

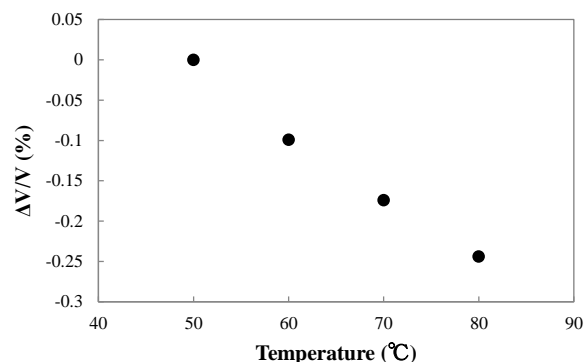


Figure 6. Temperature dependence for output voltage change of the serially connected Pt (5 nm)/Ti (3 nm) and Pt (30 nm)/Ti (3 nm) films.

$|\Delta R/R|$  in Pt (5 nm)/Ti (3 nm) film was about 3.4% after exposure to hydrogen gas. However,  $|\Delta R/R|$  of 3% occurred by temperature change in the range from 50°C to 80°C, so the temperature effect cannot be ignored. To compensate for this temperature effect, a sensor consisting of two different serially connected Pt/Ti films, which are Pt (5-nm thick) on Ti (3-nm thick) and Pt (30-nm thick) on Ti (3-nm thick), was fabricated. The time response curve of the hydrogen sensor when exposed to air and 1%-H<sub>2</sub> is shown in Fig. 5. This sensor utilizes the difference in sensitivities of the two Pt/Ti films, and the rate of voltage change ( $|\Delta V/V|$ ) when exposed to 1%-H<sub>2</sub> was about 0.28%. Next, the temperature dependence in the range of temperature from 50°C to 80°C in increments of 10 °C was evaluated (Fig. 6) and  $|\Delta V/V|$  was about 0.24%. This result shows the temperature effect is reduced compared with the single Pt/Ti film. However,  $|\Delta V/V|$  with respect to 1%-H<sub>2</sub> also reduced, so it did not improve the temperature effect compared with the hydrogen reaction.

To compensate for the temperature effect more precisely, the resistance temperature coefficient of Pt/Ti films, having a combination of different Pt thickness and Ti thickness, was measured in the temperature range from 50°C to 100°C and the temperature coefficient  $\alpha$  was derived from (3) as follows.

TABLE I. TEMPERATURE COEFFICIENT OF Pt/Ti FILMS

Pt \ Ti	0 (nm)	3 (nm)	20 (nm)
5 (nm)	0.00065	0.00102	0.00064
10 (nm)	0.00098	0.00154	0.00094
20 (nm)	0.00132	0.00193	0.0017
30 (nm)	0.00171	0.00201	0.00181

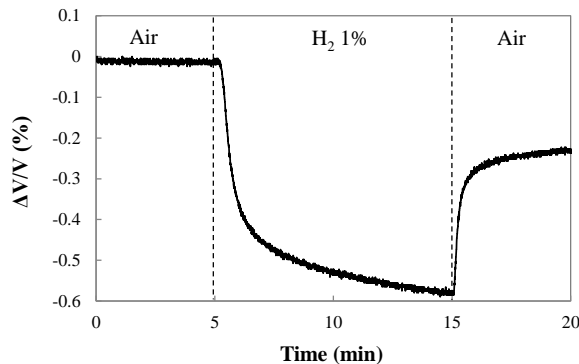


Figure 7. Hydrogen response curve of the serially connected Pt (5 nm)/Ti (3 nm) and Pt (10 nm)/Ti (20 nm) films.

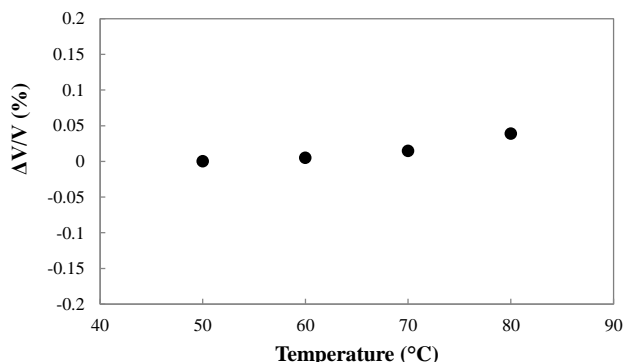


Figure 8. Temperature dependence for output voltage change of the serially connected Pt (5 nm)/Ti (3 nm) and Pt (10 nm)/Ti (20 nm) films.

$$\alpha = (R_{T2} / R_{T1} - 1) / \Delta T \tag{3}$$

where  $R_{T1}$ , and  $R_{T2}$  are the resistance of Pt/Ti film at temperature of  $T_1$  and  $T_2$  respectively, and  $\Delta T$  is the temperature difference. As shown in Table I, it was found that the temperature coefficient of Pt (10 nm thick)/Ti (20 nm thick) film is almost the same as that of Pt (5 nm thick)/Ti (3 nm thick) film. Therefore, Pt (5 nm thick)/Ti (3 nm thick) film and Pt (10 nm thick)/Ti (20 nm thick) film were suitable for obtaining a sensor that is highly stable to temperature change. The hydrogen sensitivity and temperature dependence of the hydrogen sensor with optimized thickness were evaluated (Figures 7, 8).  $|\Delta V/V|$  when exposed to 1%-H<sub>2</sub> was 0.58%. On the other hand,  $|\Delta V/V|$  in the temperature range from 50°C to 80°C was 0.039%. Therefore, it was found that the developed

hydrogen sensor can detect hydrogen without the influence of the temperature.

#### IV. CONCLUSION

A hydrogen sensor of two serially connected Pt/Ti films having different hydrogen sensitivity was developed to measure the output voltage with self-temperature compensation. The developed sensor can detect hydrogen by utilizing the electrical resistance change of Pt thin films, and is operable at room temperature. It was found that the sensitivity of Pt/Ti film to hydrogen mainly depends on the film thickness, because the catalytic reaction occurs primarily on the surface. The temperature coefficient of resistance in Pt/Ti films was evaluated to reduce the temperature effect in the sensor. As a result, the temperature coefficient of Pt (5 nm thick)/Ti (3 nm thick) was found to be almost the same as that of Pt (10 nm thick)/Ti (20 nm thick). By using the combination of the optimized thickness, the new type of hydrogen gas sensor was able to measure the output voltage with stable operation against changes in temperature.

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