Bridge Type Hydrogen Sensor Using Platinum Ultrathin film

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***Abstract*—The resistance of platinum thin-film was reduced by carrier density increment in the presence of hydrogen gas. The resistance change depended on the thickness of the platinum. Using these phenomena, a bridge-type hydrogen sensor, which converted this resistance change into a voltage change, was developed. The developed sensor was able to detect hydrogen at room temperature. Furthermore, we suggest a method in which the response and recovery time is accelerated by applying a pulse voltage to the sensor. The developed sensor can use DC and AC voltage as the driving power source.**

Keywords-platinum; hydrogen sensor; bridge circuit; thin-film.

I. INTRODUCTION

A large amount of energy is being consumed and fossil fuel is mainly used as the energy resource. However, the use of fossil fuel is exacerbating the greenhouse effect and there is a finite supply of fossil fuel. Therefore, a new energy resource as an alternative to fossil fuel is required. Recently, hydrogen has been attracting attention as a new source of energy. However, when the concentration of hydrogen is more than 4.1%, it is liable to explode. Therefore, the development of a hydrogen sensor that can detect low concentrations of hydrogen is required. Several types of hydrogen sensor have been reported, including those based on catalytic, thermal conductivity, electrochemical reaction, resistance change, work function change and optical change [1]-[10]. A metallic resistance change type sensor (resistance based) can operate at room temperature and the structure of this sensor is simple. Generally, this hydrogen sensor uses Palladium (Pd) as the hydrogen storage metal. While Pd has a good response toward hydrogen, its durability is weak. To address this issue, we developed a hydrogen sensor using Platinum (Pt) instead of Pd [11] and the resistance of the Pt thin-film was reduced by the carrier density increment in the presence of hydrogen gas. Moreover, it was clarified that the resistance change depended on the thickness of the Pt [12] because of the carrier density change caused at only the Pt surface. To develop a practicable hydrogen sensor made of Pt thin-film, a bridge circuit using four Pt thin-film resistances was investigated. It is advantageous that the bridge circuit sensor can reduce environmental noise and off-set signal. Moreover, it can convert resistance change to voltage change and can detect hydrogen concentration by voltage change. In this study, two bride types of sensor, which consist of one or two hydrogen sensitive thin-film resistances (Type 1 and Type 2), were developed. Then, the hydrogen response of these two sensors was evaluated. Moreover, the effect of pulse voltage applied to the sensor was investigated in order to improve the response and recovery time (time taken to achieve a 90% response to a step change). Section II describes schematic of sensing chip and experimental procedure. Section III describes the result and discussion. Section IV addresses the conclusion.

II. EXPERIMENTAL PROCEDURE

A. Schematic of sensing chip

Figure 1 shows a schematic diagram of the sensing chip. The sensing area consists of four resistances (R_1 – R_4) and these resistances can be regarded as a bridge circuit. In this study, two types of thin film having different resistances, were fabricated. When the sensor is exposed to hydrogen, the thin layer, which has high resistance, is greatly reduced and the thick layer, which has low resistance, decreases slightly.

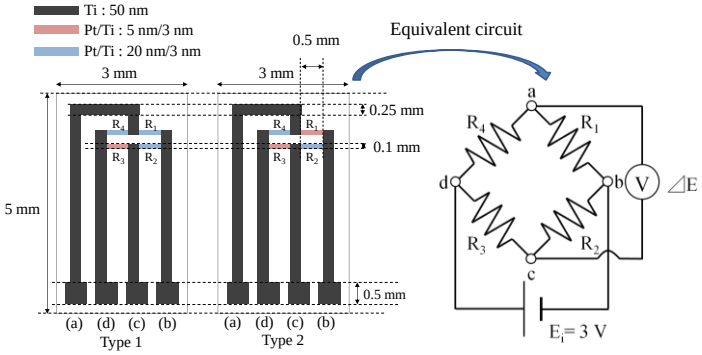

Figure 1. Schematic diagram of the hydrogen sensor.

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Therefore, the resistance change can be measured by the bridge circuit and this resistance change depends on the hydrogen concentration. The whole sensor is 3 mm × 5 mm, and each resistance size is 0.5 mm × 0.1 mm. This sensor can also reduce environmental noise using the same material.

B. Production procedure of sensing chip

Figure 2 shows the production procedure of this sensor. First, glass substrate is cleaned by ultrasonic cleaning in acetone and ethanol alternately. Next, the surface of the glass substrate is coated by photoresist using a spin coating machine and baked for 90 s at 110 °C. After that, the glass substrate is irradiated with ultraviolet rays through a mask pattern of the circuit and immersed in a developer solution. Subsequently, the glass substrate is baked in 5 min at 60 °C and a metal film is deposited on glass substrate by sputtering. Finally, the fabricated circuit is cleaned by ultrasonic cleaning. From the above procedure, only metal remains on the circuit (Figure 1 (a) ~ (f)).These processes are repeated three times. In the first process, an electrode layer is formed by titanium (Ti) (50 nm) (Figure 1 (1)). Next, the reaction layer is formed by Pt (5 nm) on Ti (3 nm) (Figure 1 (2), (3)). Finally, the low reaction layer is formed by Pt (20 nm) (Figure 1 (4)). In this study, two types of bridge sensor, Type 1 and 2, were fabricated as shown in Table 1.

TABLE I. THE THICKNESS OF EACH RESISTANCE

	R*₁ *(Pt/Ti)	***R*₂ *(Pt/Ti)***	***R*₃ *(Pt/Ti)***	***R*₄ *(Pt/Ti)***
Type 1	20 nm/3 nm	20 nm/3 nm	5 nm/3 nm	20 nm/3 nm
Type 2	5 nm/3 nm	20 nm/3 nm	5 nm/3 nm	20 nm/3 nm

C. Measurement condition

The hydrogen sensor must be able to detect a hydrogen concentration of less than 4.1% because the hydrogen concentration range of explosion is between 4.1% and 74.2%. In this study, gases of air (80%-nitrogen and 20% oxygen) and 1%-H_2 (1%-hydrogen and 99%-air gas) were prepared in order to evaluate the hydrogen response. Three volts are applied to input terminals (Figure 1 (b)-(d)) of the sensor as the driving power source. Then, when gases are injected into the chamber for 5 minutes alternately, the voltage between the output terminals (Figure 1 (a)-(c)) is measured. When DC voltage is applied to the sensor as the driving power source, the wiring affects the output. To reduce the effect of the wiring, AC voltage ($6V_{p\text{-}p}$, 1Hz) is applied to two terminals (Figure 1 (b)-(d)) of the sensor as the driving power source. In this case, the terminal voltage of the other two terminals (Figure 1 (a)-(c)) is measured as well as the DC measurement.

D. Improvement of response time

The conventional hydrogen sensor has the problem of slow response time. In this study, in order to accelerate the response time, it was attempted to accelerate the reaction by increasing the temperature of the sensor. Therefore, pulse voltage (40 V) was applied to the sensor for 3 s. As mentioned above, the gas is changed from air gas to 1%-H_2 gas to fill the chamber with 1%-H_2 and the pulse voltage is applied to the sensor to reduce the response time by 30 s after changing the gas (waiting time to fill gas). In the same way, the pulse voltage is also applied to the sensor to reduce the recovery time as well as the response time by 30 s after changing the switch from H_2-1% gas to the air gas to fill the chamber with the air gas.

III. RESULT AND DISCUSSION

Figure 3 shows the hydrogen response of the developed sensor using DC measurement. Output of Type 1 and Type 2 increased in the presence of hydrogen gas. Here, R_1, R_2 and R_4 of Type 1 are the same because the film thickness is the same. Therefore, the output of ΔE is given by (1).

$$\Delta E = [E_i (R_2 - R_3)] / [2(R_2 + R_3)] \quad (1)$$

Moreover, in the case of Type 2, R_1 is equal to R_3, and R_2 is equal to R_4 because the film thickness is the same. Consequently, the output voltage is given by (2)

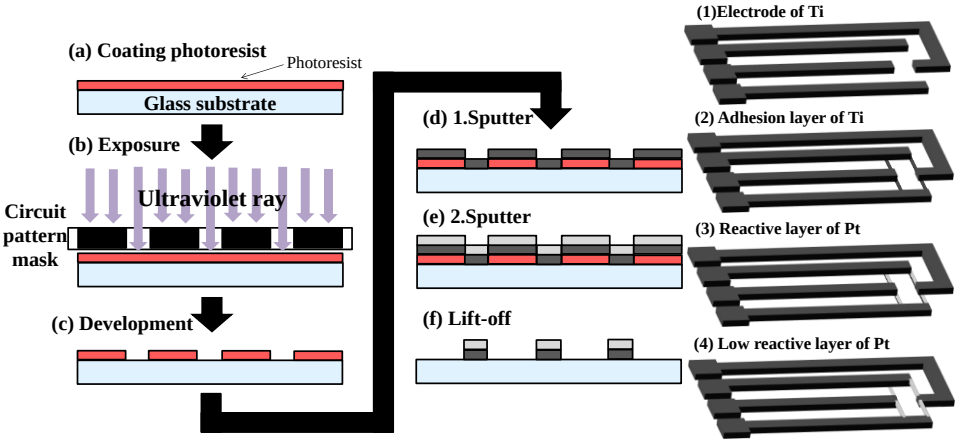

Figure 2. Schematic diagram of fabrication process for the hydrogen sensor.

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$$\Delta E = [E_i (R_2 - R_3)] / (R_2 + R_3) \quad (2)$$

When the sensor is exposed to the hydrogen gas, R_2 (Pt/Ti =20 nm/3 nm) and R_3 (Pt/Ti = 5 nm/3 nm) are reduced by carrier density increment. Moreover, the resistance change depends on the thickness of the platinum. The results of reference [12] show that Pt/Ti (20 nm/3 nm) decreased 0.14 Ω and Pt/Ti (5 nm/3 nm) decreased 5.8 Ω. Therefore, the output increased because the change of R_2 and R_3 is different. Compared with Type 1, output of Type 2 is larger. Type 2 is useful as a sensor. As for the response time, the 90% response time in the case of no pulse voltage was about 210 s. When the pulse voltage is applied, the total response time and waiting time (30 s) is about 50 s. After pulse voltage is applied, the output becomes saturated in 20 s because high voltage was applied to the sensor and the temperature of the sensor increased by joule heat. Moreover, the recovery time is more than 12 h when the pulse voltage is not applied. However, when the pulse voltage is applied, total recovery time and waiting time (30 s) is about 50 s. After the pulse voltage is applied, the output became about 0 V and was saturated in 20 s. The reason for accelerating the response and recovery time is described below.

This sensor uses the chemical change of (3), (4).

$$H_2 \rightleftarrows 2H^+ + 2e^- \quad (3)$$

$$4H^+ + O^{2-} + 2e^- \rightleftarrows 2H_2O \quad (4)$$

Therefore, heating a sensor is a simple method of increasing the speed of the reaction rate. The Arrhenius equation (5) shows the reason for this,

$$k = A \times \exp(-E_a/RT) \quad (5)$$

where k, A, E_a, R, T are the rate constant, constant, activation energy, gas constant, and absolute temperature, respectively. The more T is increased by heating and the k of (5) is increased, the greater the reaction of (3), (4) is accelerated. For these reasons, the response and recovery times are accelerated. Therefore, the pulse voltage application is useful for accelerating the response. Moreover, in this study, the sensor is heated by pulse voltage only when the heating is required. In such a way, power consumption can be reduced. Figure 4 (a) shows the hydrogen response of the developed sensor using AC measurement. As shown in Figure 4 (a), it is difficult to show the hydrogen response because of the offset effect. To solve this problem, the instrumentation amplifier (AD627AN) was used. The offset is canceled by the antiphase of the sensor output. The gain of instrumentation amplifier is 5. Figure 4 (b) shows the hydrogen response of AC measurement using the instrumentation amplifier. The output increased by the presence of hydrogen gas and the hydrogen response could be detected clearly. Moreover, the response and recovery time is accelerated, as well as the use of DC voltage as the driving power source.

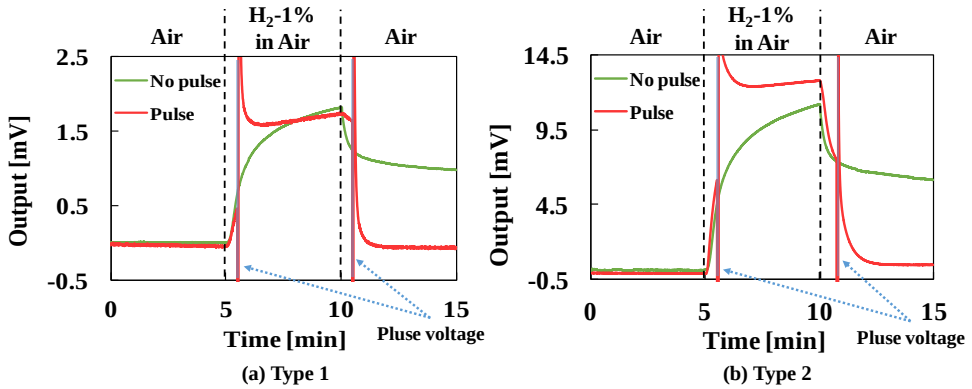

Figure 3. Hydrogen response characteristics of Type 1 and Type 2 operated with DC power supply.

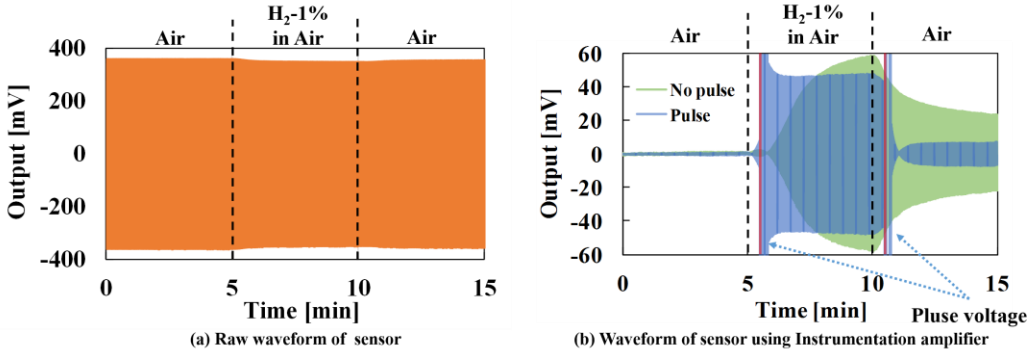

Figure 4. Hydrogen response characteristic of Type 1 and Type 2 operated with AC power supply, and pulse heating effect.

IV. CONCLUSION

A bridge circuit type hydrogen sensor was developed utilizing the principle of electrical resistance change in Pt thin-film. This sensor can detect hydrogen concentration at room temperature. In addition, DC and AC voltage was used as the driving power source and the voltage change caused by the hydrogen sensor was detected when using AC voltage, which can reduce the effect of the wiring. Moreover, the response and recovery times became shorter by applying pulse voltage to the sensor. In future research, the developed sensor will be evaluated under various condition to apply to practical use such as hydrogen station and fuel cell vehicles.

REFERENCES

[1] T. Hubert, L. Boon-Brett, G. Black and U. Banach, "Hydrogen sensor - A Review" Sensors and Actuators B, Chemical, Volume 157 , Issue 2, pp. 329-352, 2011.

[2] M. Matsumiya, W. Shin, N. Izu and N. Murayama, "Nano-structured thin-film Pt catalyst for thermoelectric hydrogen gas sensor" Sensors and Actuators B, Chemical Volume 93, Issues 1–3, pp. 309–315, 2003.

[3] M. Lang, *et al*., "Long-term stability of a MEIS low energy hydrogen sensor" Sensors and Actuators B, Chemical Volume 187, pp. 395–400, 2013.

[4] S. Horch, *et al*., "Enhancement of surface self-diffusion of platinum atoms by adsorbed hydrogen" nature 398, pp. 134-136, 1999.

[5] C. Liewhiran, N. Tamaekong, A. Wisitsoraat, A. Tuantranont and S. Phanichphant, "Ultra-sensitive H_2 sensors based on flame-spray-made Pd-loaded SnO_2 sensing films" Sensors and Actuators B 176, pp. 893– 905, 2013.

[6] M. Nishibori, *et al*., "Robust hydrogen detection system with a thermoelectric hydrogen sensor for hydrogen station application" international journal of hydrogen energy 34, pp. 2834–2841, 2009.

[7] I. Simon and M. Amdt, "Thermal and gas-sensing properties of a micromachined thermal conductivity sensor for the detection of hydrogen in automotive applications", Sensors and Actuators A 97-98, pp. 104-108, 2002.

[8] G. Korotcenkov, S. D. Han and J. R. Stetter, "Review of Electrochemical Hydrogen Sensors" Chem. Rev. 109, pp. 1402–1433, 2009.

[9] T. Xua, M. P. Zach, Z. L. Xiao, D. Rosenmann, U. Welp, W. K. Kwok, and G. W. Crabtree, "Self-assembled monolayer-enhanced hydrogen sensing with ultrathin palladium films" Applied Physics Letters 86, p. 203104 , 2005.

[10] X. Wang, Y. Tang, C. Zhou and B. Liao, "Design and optimization of the optical fiber surface plasmon resonance hydrogen sensor based on wavelength modulation" Optics Communications 298–299, pp. 88–94, 2013.

[11] K. Tsukada, H. Inoue, F. Katayama, K. Sakai and T. Kiwa, "Changes in Work Function and Electrical Resistance of Pt Thin Films in the Presence of Hydrogen Gas", Japanese Journal of Applied Physics, 51, p. 015701, 2012.

[12] K. Tsukada, S. Takeichi, K. Sakai and T. Kiwa, "Ultrathin-film hydrogen gas sensor with nanostructurally modified surface" Japanese Journal of Applied Physics 53, p. 076701, 2014.

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