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Development of bridge-type hydrogen sensor using Pt ultra-thin film

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***Abstract*—We had previously demonstrated that ultra-thin Pt films exhibit a change in resistance in response to changes in the concentration of hydrogen gas in the atmosphere. However, with such resistance-type hydrogen sensors, changes in environmental temperature can interfere with measurements. Therefore, in this study, we developed a sensor that uses a bridge circuit to attain better thermal stability. This bridge circuit was composed of resistors with high and low hydrogen sensitivities; subsequently, a material with Pt surface and covered with Al_2O_3 was used as a low-sensitivity resistor. Results show that this bridge-type configuration provided good hydrogen response and temperature stability.**

***Index Terms*—hydrogen sensor, ultra-thin-Pt-film, bridge-circuit-type-sensor.**

I. INTRODUCTION

Fossil fuels such as petroleum, coal, and natural gas are being replaced with new energy sources because they emit greenhouse gases that cause global warming. Under the current social circumstances, hydrogen energy has attracted attention as one of the next-generation energy sources. Hydrogen can be easily prepared from various substances such as water, so there is no danger of depleting the resource. Further, it is a clean energy source because only water is discharged during power generation from hydrogen. In addition, since hydrogen energy has high power-generation efficiency, it is possible to regularly secure the energy. However, hydrogen is easily leaked because hydrogen molecules are very small and light in weight. In addition, hydrogen is also known to be a molecule that is difficult to handle due to its risk of explosion in air at a wide range of concentrations (4%–75%). Thus, in order to realize a safe hydrogen-based society in the future, a hydrogen sensor that detects hydrogen gas in real time is indispensable.

Several types of hydrogen sensors such as catalytic combustion-type sensors, semiconductor-type sensors, and FET-type sensors have been developed. However, these sensors require high temperature to operate or involve complicated manufacturing processes. We had previously developed a FET-type hydrogen sensor using Pt as a gate electrode. In addition, we are currently developing a hydrogen sensor that is capable of room-temperature operation and that has a simple structure involving a Pt ultra-thin film with hydrogen-sensitive resistance [1-3]. This ultra-thin-film hydrogen sensor operates based on changes in the resistance in response to changes in the hydrogen gas concentration. Therefore, the sensor requires stabilization with regard to environmental temperature changes when used in the real environments. In this study, we developed a new bridge-type hydrogen sensor with an ultra-thin Pt film to improve the thermal stability.

II. METHODS

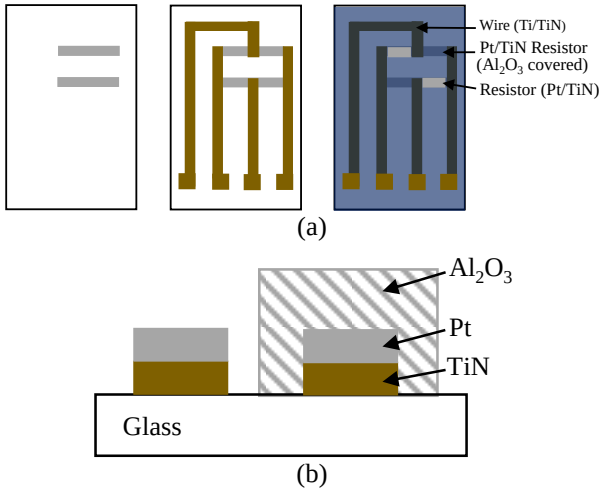

Fig.1 Hydrogen sensor chip: (a) fabrication process, (b) cross-sectional structure.

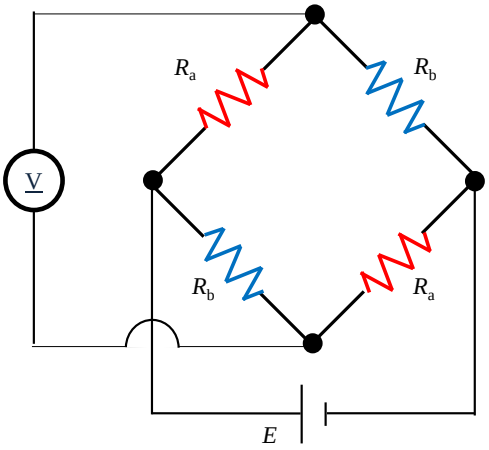

Fig.2: Equivalent circuit representing the sensor.

Figure 1 shows the cross-sectional structure of the resistor and the fabrication process used to form the bridge hydrogen sensor using a Pt/TiN thin-film resistor. First, the glass substrate was cleaned by ultrasonic cleaning with acetone and ethanol. Next, a positive photoresist was applied to the cleaned glass substrate, and the pattern of the resistor formed on the substrate. Titanium nitride (TiN) was used as an adhesive layer because platinum weakly adheres to the substrate. A TiN/Ti film was used for the electrode. To operate the bridge circuit, a pair of two components with one

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having a high hydrogen sensitivity and the other having a low sensitivity is needed. Pt (5 nm)/TiN (3 nm) was applied using DC sputtering to form the high-sensitivity component and Al_2O_3, which forms a protective layer over the Pt (5 nm)/TiN(3 nm) layer, was applied using RF sputtering to form the low-sensitivity component. Finally, the sensor chip was cut to a size of 3 × 5 mm with a dicing machine, and the circuit board and the electrode pad were connected by a bonding wire.

An equivalent circuit representing the fabricated sensor is shown in Fig. 2. R_a represents the Pt/TiN thin-film resistor covered with Al_2O_3, and R_b represents the Pt/TiN thin-film resistor that was not covered with alumina. If R_a and R_b represent the respective changes in resistance in the presence of a given amount of hydrogen, the $R_a$value of the alumina-covered resistor, R_a, is equal to 0 in the presence of hydrogen. Thus, the output voltage (ΔV) of the sensor is given by equation (1).

$$\Delta V = \frac{(R_b - r_b) - (R_a - r_a)}{(R_a - r_a) + (R_b - r_b)} E = -\frac{r_a - r_b}{2R_a - (r_a + r_b)} E \quad (1)$$

Based on ΔV, it is possible to detect the presence or absence of hydrogen gas. Further, if the initial resistance values of R_a and R_b are R_{a0} and R_{b0}, respectively, and the temperature coefficients of R_a and R_b are α_a and α_b, respectively; the voltage change (ΔV) due to a temperature change can be determined using equation (2). Since all resistors of the bridge circuit are Pt-based resistors, the temperature coefficients are constant.

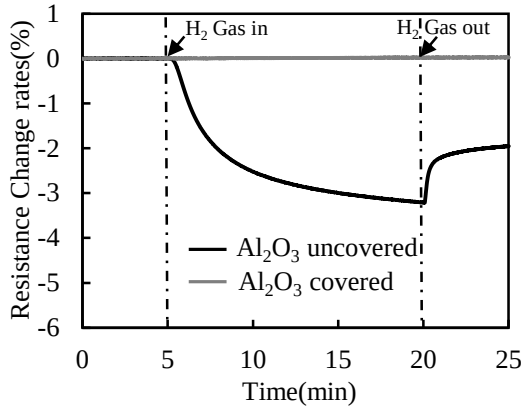
$$V' = \left(\frac{R_{b0}(1+\alpha_b t) - R_{a0}(1+\alpha_a t)}{R_{a0}(1+\alpha_a t) + R_{b0}(1+\alpha_b t)} \right) E \quad (2)$$
$$= \frac{R_{a0} - R_{b0}}{R_{a0} + R_{b0}} E$$

There is a risk of explosion at hydrogen concentrations above 4%. Therefore, the hydrogen response of the sensor was characterized using air (80% N_2 and 20% O_2) with a hydrogen concentration of 1% or less. To evaluate the selectivity of hydrogen, the response characteristics of the sensors to other gases, CH_4, C_2H_6, and CO_2, were investigated by connecting the various gas cylinders to a gas flow switching device. This device allowed the desired gas to flow into the gas chamber containing the sensor and allowed the gas composition in the chamber to be changed easily. The gas flow rate into the chamber was fixed at 0.5 L/min. The bridge-type hydrogen sensor was driven with a DC voltage of 3 V, and the sensor output voltage was measured with a digital multi-meter. In addition, to replicate the temperature changes in a real environment, the temperature of the sensor was controlled from 30°C to 100°C using an oven and with a thermocouple-type thermometer.

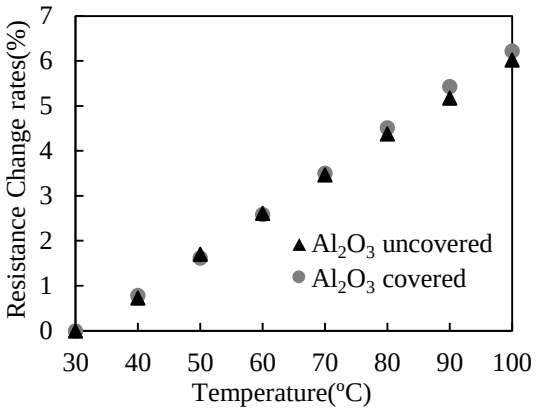
III. RESULTS AND DISCUSSION

A. *Hydrogen response characteristics of Pt.*

Figure 3 shows a comparison of the hydrogen response



(a)

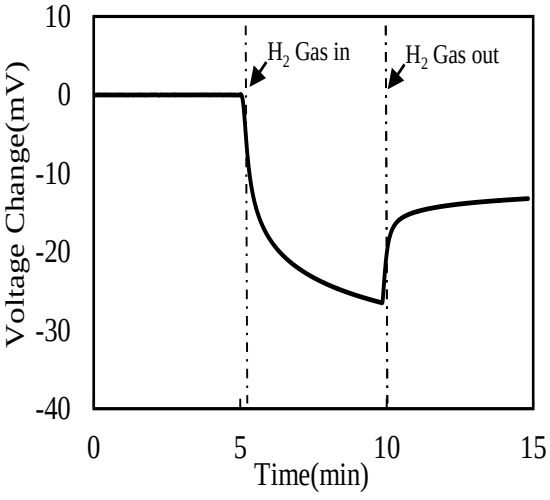


(b)

Fig.3 Effect ofAl_2O_3 film. (a) The hydrogen response and (b) the temperature dependence of the Pt/TiN resistors.

characteristics of the Pt (5 nm)/TiN (3 nm) resistors with and without the Al_2O_3 film. In this study, the Pt/TiN thin-film resistor was exposed to 1% H_2 (1% hydrogen and 99% air) for 15 minutes, and the rate of change in the resistance (ΔR) was measured.

$$R = \frac{R - R_0}{R_0} \times 100 \quad (3)$$



(a)

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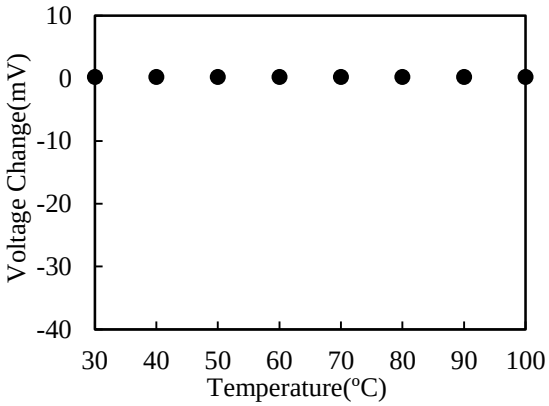


(b)

Fig.4 (a) Hydrogen response and (b) temperature dependence of the bridge-type sensor.

The resistance of the Pt/TiN resistors protected with Al_2O_3 decreased by 0.04%, indicating low hydrogen sensitivity, while that of the Pt resistors without Al_2O_3 protection decreased by 3.21%, indicating higher hydrogen sensitivity. Figure 3(b) shows the temperature dependence of both the resistors' resistances. As the temperature increased from 30°C to 100°C, both the resistors had almost the same temperature coefficient: the resistance of the resistor covered with the Al_2O_3 film increased at a rate of 6.22% and that of the sensor without the Al_2O_3 film increased at a rate of 6.09%. Therefore, these two resistors could be effectively used in the bridge circuit.

B. Bridge circuit type sensor

Next, the bridge-type sensor was characterized. Figure 4(a) shows the hydrogen response of the bridge-type sensor when exposed to 1% H_2 (1% hydrogen and 99% air) for 5 min. The change in the output voltage reached a maximum of 27.5 mV. Figure 4(b) shows the temperature dependence of the voltage in the bridge-type sensor. As the temperature increased from 30°C to 100°C, the output voltage changed by 17 µV. Because all of the resistors of the bridge-type sensor were made of Pt/TiN, their temperature coefficients were equal; therefore, there was no significant change in the sensor output due to changes in the temperatures.

Figure 5 shows the hydrogen-dependent change in the voltage of the bridge-type sensor. The sensor was exposed to hydrogen gas concentrations of 10, 100, 1000 or 10000 ppm for 15 minutes and the corresponding changes in the output of the sensor were measured. A sensor output of 226 µV was measured in the presence of the lowest concentration of 10 ppm hydrogen gas; this represents the limit of detection.

Figure 6(a) shows the interference of other gases with the bridge-type sensor; an enlarged view is shown in Fig. 6(b).

The responses to 1% concentrations of H_2, CH_4, C_2H_6, and CO_2 were measured. The sensor output during exposure to hydrogen gas was 27.5 mV, and it changed by less than 25 µV in the presence of the other gases. This finding indicates good hydrogen selectivity of the bridge-type sensor.

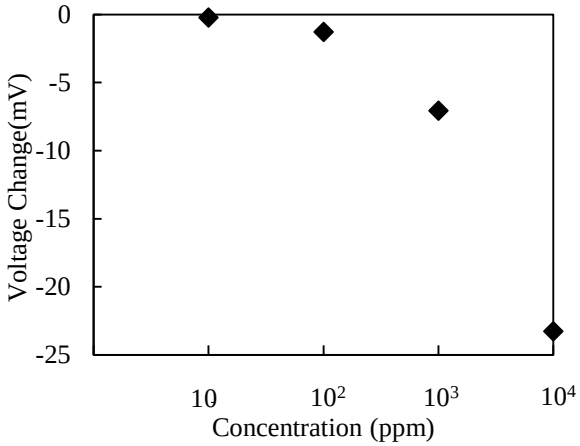
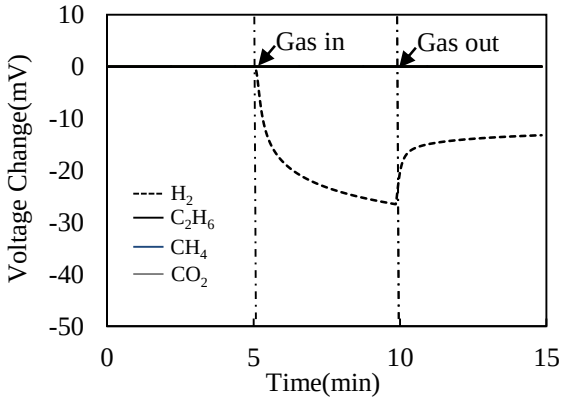
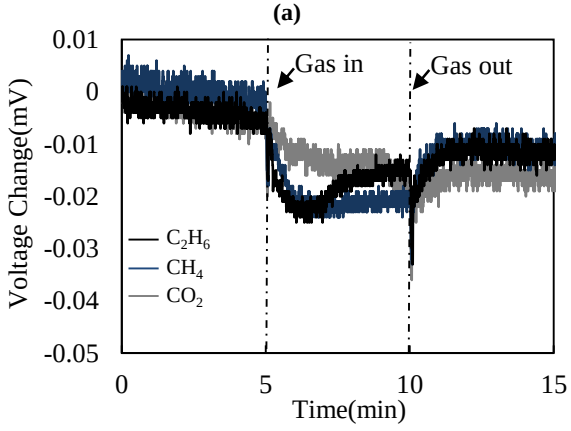


Fig.5 Hydrogen-dependent response characteristics of the sensor.



(a)



(b)

Fig. 6 Selectivity of the bridge-type sensor (a) time-response of the voltage and an (b) enlarged view.

IV. CONCLUSION

To reduce the resistance variation of Pt/TiN ultra-thin film caused by the characteristics of the metal in response to temperature changes, a bridge-type hydrogen sensor with Pt/TiN thin-film resistors with and without protective Al_2O_3 films was developed. The hydrogen response and temperature dependence of the proposed sensor were measured over a range of temperatures and in the presence of various interfering gases. The results indicated that the

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developed sensor has a good hydrogen response, can be operated at room temperature, and is highly robust against temperature changes.However,the response and recovery of the sensor output was slow. Therefore, it is necessary to improve the response and recovery speed of the sensor.

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