Optimization of Pt ultrathin film pattern for hydrogen sensor

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Abstract— Hydrogen gas poses risks of gas leakage and explosion owing to the very small size of the hydrogen molecule and its wide range of inflammability (4–75% in air). Therefore, high-performance hydrogen sensors are indispensable for leak detection as well as the widespread safe use of hydrogen energy. We previously reported several types of sensors. Out of those, ultrathin film sensors can be easily manufactured because they have a simple structure and can be operated at ambient temperature. However, the sensitivity, the response and recovery times of these hydrogen sensors need to be improved. Therefore, a Pt ultrathin film pattern was optimized for improving hydrogen sensitivity as well as response and recovery times. The line length and width of the ultrathin film were effective layout parameters for hydrogen sensitivity. The hydrogen sensor with a longer line length and narrower line width showed larger resistance ratio change. In addition, hydrogen response and recovery times were improved by heat treatment with a pulsed current. Moreover, we evaluated the detection limit and gas selectivity of the sensor. As a result, it was observed that this sensor can detect concentrations as low as 10 ppm and has good selectivity to the inference gasses.

Index Terms—hydrogen sensor, Pt ultrathin film.

I. INTRODUCTION

In recent years, depletion of fossil fuels has become a global problem, and the necessity for new energy resources has been increasing. Hydrogen energy is attracting notable attention amongst the available options. The hydrogen gas, which is used for fuel cell vehicles [1], has high power generation efficiency and is known as one of the clean energy sources [2] [3]. However, since hydrogen gas poses risks of gas leakage and explosion owing to the very small size of its molecule and wide range of inflammability (4–75% in air), high-performance hydrogen sensors are indispensable for leak detection and the widespread safe use of hydrogen energy.

We previously reported several types of sensors that can be operated at ambient temperature, such as FET type sensor or resistance change type sensor, using Pt ultrathin films [4]-[6]. Although ultrathin film sensors can be easily manufactured because of their simple structure and ability to operate at ambient temperatures, their sensitivity, response and recovery times need to be improved. In this study, we attempted to improve the hydrogen response characteristic of Pt ultrathin film sensors by optimizing the thin film pattern.

II. METHODS AND MEASUREMENTS

In this study, a resistance change type sensor was fabricated using catalysis of Pt. Figure 1 shows a hydrogen response mechanism of the Pt thin film. When the hydrogen adheres to the surface of Pt, the hydrogen molecules resolve into hydrogen ions and electrons. These electrons become free electrons and diffuse into the platinum thin film. Therefore, the electric resistance decreases and hydrogen can be detected. Also, when returning to a no-hydrogen air condition, the oxygen molecules in the air and hydrogen ions diffused in Pt react, and get desorbed as water molecules. Therefore, the resistance value is recovered [5] [7]. Five patterns with different sizes of the sensor sensitive part were fabricated and the sensitivity and recovery characteristics were compared. Table 1 shows the dimensions of the Pt pattern lines. Figure 2 shows a photograph of No. 1 and No. 2 Pt ultrathin films. The sensor chip consisted of Al electrodes and a Pt ultrathin film on TiN film as the hydrogen sensing part on a Si substrate. The film thicknesses of the sensing parts were 10 nm of Pt film and 20 nm of TiN. The TiN film was used as an adhesive layer between the Pt film and Si substrate. Figure 3 shows a cross sectional diagram of the hydrogen sensing part and the connection with the Al electrode.

Table 1. Dimensions of the Pt lines.

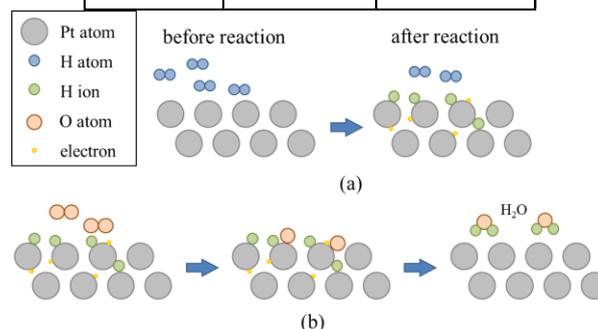| No.	width (μm)	length (μm)
1	20	100
2	20	440
3	20	440
4	100	4400
5	150	4300

Fig. 1. Hydrogen response mechanism of the ultrathin Pt film: (a) dissociation of hydrogen gas at the surface, (b) desorption.
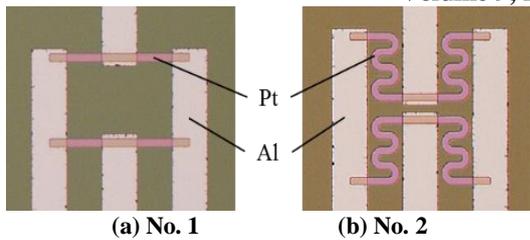
(a) No. 1   (b) No. 2

Fig. 2. Photographs of the hydrogen sensing parts with different Pt film pattern.

First, heating of the sensitive part using a pulsed current was carried out for the purpose of improving the response and recovery times. Second, in order to investigate the Pt pattern dependence of the hydrogen response, hydrogen gases with concentrations of 1% and 0% in air were controlled by a gas switching device, and the hydrogen responses were compared. Figure 4 shows a schematic diagram of the measurement system. The flow rate of the gas was maintained constant using a gas flow meter. The source meter was controlled by the PC, the sensor was driven by constant current, and the resistance was calculated from the output voltage. Then, the hydrogen response characteristic was measured by changing the hydrogen concentration to confirm the detection limit of the sensor. In addition, response characteristics to interference gases, NH_3, CO_2, C_2H_6, and CH_4 were investigated to evaluate the selectivity.

III. RESULT

A. Improvement of response time by heating using pulsed current

In this study, we tried to improve the sensitivity, response time and recovery time of the hydrogen sensor by heating the sensor by a pulsed current. From the Arrhenius' equation, the following relation holds between the reaction rate k and the absolute temperature T:

$$ln\,k = A - \frac{E_a}{RT} \qquad (1)$$

Where, k, A, R, Ea, and T are reaction rate, frequency factor, gas constant, revitalize energy, and absolute temperature, respectively. As the temperature T is increased, the reaction rate k also increased. Therefore, the sensor was heated by Joule heat of the pulsed current to accelerate the response and recovery times.
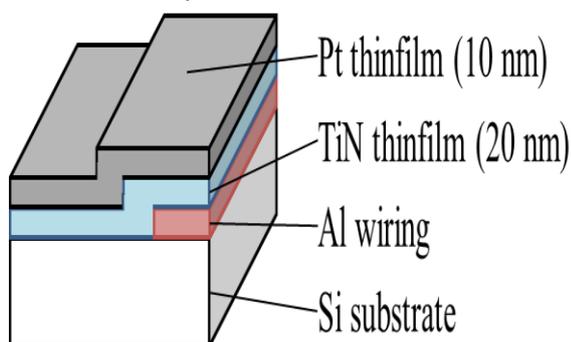

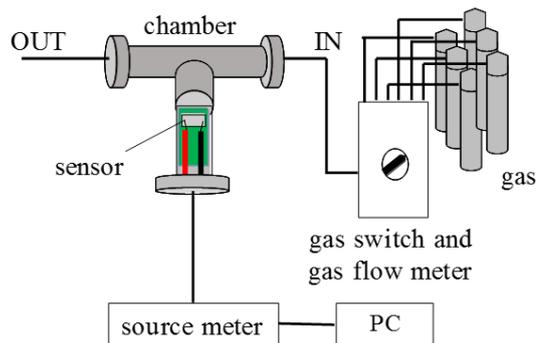**Fig. 3. Cross sectional diagram of the sensor.**

Fig. 4. Schematic diagram of the measurement system.

Figure 5 shows the hydrogen response with and without pulsed current for No. 1 hydrogen sensor. The resistance change rate is defined by Eq. (2).

$$\Delta R = \frac{R - R_0}{R_0} \times 100 \quad (\%) \qquad (2)$$

Where, R and R_0 are resistance value and initial resistance value. Table 2 shows the value of the drive current and the sensor temperature during normal operation and heating treatment. During normal operation, the hydrogen sensor was driven at 1 mA, and heating was applied at 30 mA and 5 seconds. These operation treatments made sure that the sensor temperature was about 20°C during normal operation and approximately 150°C during heat treatment. When the pulsed current was not applied, the resistance of the Pt did not recover to the original value. On the other hand, the output voltage recovered to the original value after heating using the pulsed current. In addition, the sensitivity and response speed were improved by applying the pulsed current before reacting to the hydrogen. When the pulsed current was not applied, the resistance value did not recover due to which the hydrogen diffused in Pt remained. On the other hand, heating using the pulsed current accelerated the hydrogen movement to the surface and the reaction with the oxygen in the air. Consequently, the recovery time improved.

B. Dependence of Pt pattern on the response time

The hydrogen response of each pattern was compared. Figure 6 shows the hydrogen responses of sensor No. 1–5. The No. 1, 2, and 3 hydrogen sensors have different line length with the same width, 20 μm. The No. 4 and 5 have different line width with almost same line length. According to the increment of the line length, the hydrogen sensitivity improved. The No. 4 and No. 5 have almost the same line length, 4400 μm and 4300 μm, respectively; however, No. 4 has a narrower line width of 100 μm as compared to 150 μm of No. 5. By comparing these two responses, No. 4 showed higher sensitivity. As per these results, long length and narrow width was effective in obtaining high sensitivity. When the line length is long, the ratio of the edge part to the surface area of the sensitive part increases as shown in Fig. 1. In the edge part, the amount of reaction with hydrogen increased and the sensitivity improved due to the electric field distribution being more concentrated here than in the other parts, and the carrier density in Pt increased

accordingly. It was observed that similar phenomena also occurred about the line width, due to the ratio between the surface area and the edge part. These phenomena seem to have confirmed the pattern dependence of the change amount on the line length and the line width. Thus, the hydrogen response was improved by optimizing the line length and the line width of Pt pattern.
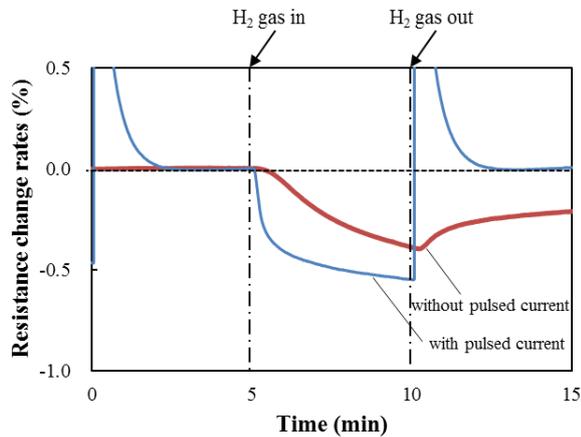

Fig. 5. Comparison of response times of the hydrogen sensor with and without pulse current treatment.

Table 2. Drive current and sensor temperature.

	drive current (mA)	sensor temperature (°C)
normal	1	20
heated	30	150

C. Dependence of hydrogen concentration

The hydrogen concentration dependence of the No. 4 hydrogen sensor was evaluated because it had the highest sensitivity. The hydrogen gases with different concentration of Air, H_2-1%, H_2-0.1%, H_2-100 ppm, H_2-10 ppm were used. The hydrogen response was observed from 10 ppm (0.001%) (Fig. 7). As the combustion range of hydrogen gas is 4 to 75% in air, the detection limit was a value sufficient to detect early stage of hydrogen leakage.
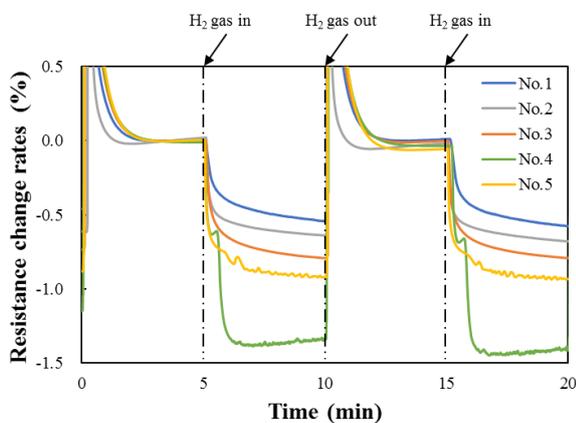
D. Selectivity of gas

Fig. 6. Hydrogen response differences of the hydrogen sensors with different pattern dimension.

The selectivity to interference gases was evaluated using

various interference gasses. The responses to 1% concentrations of H_2, CH_4, C_2H_6, and CO_2 were compared. Figure 8 shows the time-response curves of these gasses. The hydrogen gas sensor showed good selectivity that favored only the hydrogen gas.
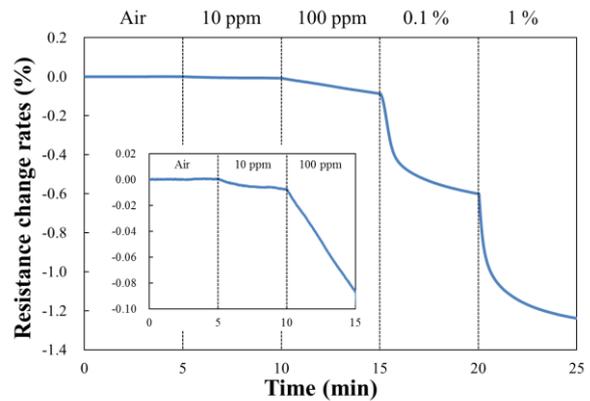

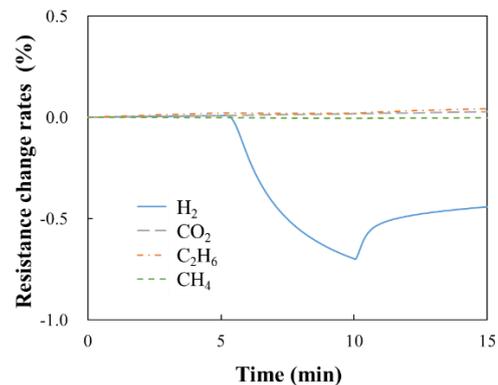**Fig. 7. Hydrogen concentration dependence of the hydrogen sensor.**

Fig. 8. Selectivity of the hydrogen sensor to the inference gasses.
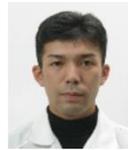
IV. CONCLUSION

The line length and width of the Pt ultrathin film were effective layout parameters for hydrogen sensitivity. The long line length and narrow line width increased the sensitivity to hydrogen. The hydrogen detection limit of the layout optimized hydrogen sensor at 10 ppm, and also showed good selectivity to the various interference gases. In addition, the hydrogen response and recovery time were improved by heating with pulsed current treatment.

REFERENCES

[1] K. Tokimatsu, B. McLellan, M. Höök, S. Murakami, R. Yasuoka, M. Nishio, "Energy modeling approach to the global energy-mineral nexus: A case of fuel cell vehicle," Energy Procedia, 142, 2361-2364, 2017.

[2] Alvin G. Stern, "A new sustainable hydrogen clean energy paradigm," Int. J. Hydrogen Energy, Vol. 43, Issue 9, 4244-4255, 2018.

[3] M. Pourbaba, S. Zirakkar, "Utilization of renewable energy to produce electrical energy (Hydrogen Energy)," Procedia Eng., Vol. 21, 1088-1095, 2011.

[4] K. Tsukada, S. Takeichi, K. Sakai, T. Kiwa, "Ultrathin-film hydrogen gas sensor with nanostructurally modified surface," Jpn. J. Appl. Phys., 53, 076701, 2014.

[5] K. Tsukada, H. Inoue, F. Katayama, K. Sakai, T. Kiwa, "Changes in work function and electrical resistance of Pt thin films in the presence of hydrogen gas," J. Appl. Phys., 51, 015701, 2012.

[6] K. Tsukada, M. Kariya, T. Yamaguchi, T. Kiwa, H. Yamada, T. Maehara, T. Yamamoto, S. Kunitsugu, "Dual-Gate Field-Effect Transistor Hydrogen Gas Sensor with Thermal Compensation," Jpn. J. Appl. Phys., 49, 024206, 2010.

[7] B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L. G. M. Pettersson, A. Nilsson, "Structure and Bonding of Water on Pt(111)," Phys. Rev. Lett. Vol. 89, Number 27, 276102, 2002.

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