Optimization of Pt ultrathin film pattern for hydrogen sensor

Yuto Goda\(^a\), Tetsuro Hirata\(^a\), Kenji Sakai\(^a\), Toshihiko Kiwa\(^a\)
Kenji Kondo\(^b\), Takuya Takahashi\(^b\), Naohiro Ueda\(^b\), Keiji Tsukada\(^a\)
\(^a\)Okayama University, Japan
\(^b\)RICOH Electronic Devices Co., Ltd., Japan

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>
<thead>
<tr>
<th>No.</th>
<th>width (μm)</th>
<th>length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>440</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>440</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>4400</td>
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<tr>
<td>5</td>
<td>150</td>
<td>4300</td>
</tr>
</tbody>
</table>

Fig. 1. Hydrogen response mechanism of the ultrathin Pt film: (a) dissociation of hydrogen gas at the surface, (b) desorption.
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, NH₃, CO₂, C₂H₆, and CH₄ 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 $T$:

$$\ln k = A - \frac{E_a}{RT}$$

Where, $k$, $A$, $R$, $E_a$, 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.

$\Delta R = \frac{R - R_0}{R_0} \times 100 \%$ (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.

<table>
<thead>
<tr>
<th>drive current (mA)</th>
<th>sensor temperature (°C)</th>
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<tbody>
<tr>
<td>normal</td>
<td>1</td>
</tr>
<tr>
<td>heated</td>
<td>30</td>
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</table>

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, H₂-1%, H₂-0.1%, H₂-100 ppm, H₂-10 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

The selectivity to interference gases was evaluated using various interference gases. The responses to 1% concentrations of H₂, CH₄, C₂H₆, and CO₂ were compared. Figure 8 shows the time-response curves of these gases. 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 interference gases.

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


AUTHOR BIOGRAPHY

Yuto Goda received the B.S. degree from Okayama University in 2018. He is currently a graduate student in the Graduate School of Interdisciplinary Science and Engineering in Health Systems, Okayama University, Japan. His subject includes hydrogen sensor and magnetic measurement system.

Tetsuro Hirata received the M.S. degree from graduate student in the Graduate School of Natural Science and Technology, Okayama University in 2019. His subject included hydrogen sensor and magnetic measurement system.

Kenji Sakai received Dr. Eng. degree from Doshisha University in 2010. After that, he was a Research Fellow of the JSPS at Doshisha University. He is currently an assistant professor of Graduate school of Interdisciplinary Science and Engineering in Health Systems, Okayama University. He is now involved in the research of magnetic sensor and SQUID devices and their applications, non-destructive evaluation system, and gas sensor.

Toshihiko Kiwa received Dr. Eng. degree from Osaka University in 2003. After that he worked for one year as a JSPS fellow at the Research Center for Superconductor Photonics, Osaka University, where he was involved in the development of terahertz and superconductor devices. Currently, he is an associate professor of Graduate school of Interdisciplinary Science and Engineering in Health Systems, Okayama University. His research interests include chemical sensors, magneto metric sensors, and terahertz devices.

Kenji Kondo received the B.S. degrees in electronic and control systems engineering from Shimane University, Shimane, Japan, in 2001. In 2015, he joined RICOH Electronic Devices Co. Ltd., Osaka, Japan. He has been working in the field of CMOS devices, and he is currently in charge of the development of advanced process integration for analog devices with RICOH Electronic Devices Co. Ltd., Osaka, Japan.

Takuya Takahashi received the B.S. and M.S. degrees in department of Applied Physics from Tokyo Institute of Technology, Tokyo, Japan, in 1997 and 1999, respectively. In 1999, he joined Ricoh Co. Ltd., Tokyo, Japan. He has been working in the field of CMOS devices, and he is currently in charge of the development of advanced process integration for analog devices with RICOH Electronic Devices Co. Ltd., Osaka, Japan.

Naohiro Ueda received the B.S. and M.S. degrees in electrical engineering from Yokohama National University, Yokohama, Japan, in 1987 and 1989, respectively. In 1989, he joined Ricoh Co. Ltd., Tokyo, Japan. He has been working in the field of CMOS devices and non-volatile memory, and he is currently in charge of the development of advanced process integration for digital/analog devices with RICOH Electronic Devices Co. Ltd., Osaka, Japan. He is a member of Institute of Electrical and Electronics Engineers, and a member of Institute of Electrical Engineers of Japan.

Keiji Tsukada received Dr. Eng. and the Ph. Dr. degrees from Tsukuba University in 1990, and 2001, respectively. He joined the Central Research Laboratory, Hitachi Ltd. in 1982, where he was involved in the study of integrated solid-state chemical sensor for blood analyses. He was with the Superconducting Sensor Laboratory from 1991-1996. He was involved in the research and development of SQUID’s and multichannel SQUID system. He was with the Central Research Laboratory, Hitachi Ltd. from 1996-2003. He was a Project Leader of the SQUID application research group. He is presently a Professor of Graduate school of Interdisciplinary Science and Engineering in Health Systems, Okayama University. He is involved in the research of chemical sensor, magnetic sensor and superconducting sensor devices, and their applications.