Wireless QCM Hydrogen Sensor with PDMS-microchannel Fabricated by Nanoimprint Lithography

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1. Introduction

Fossil fuels are main fuels used in the fields of automobiles and power generation that support the social infrastructure. Fossil fuels emit carbon dioxide (CO_2), which is a greenhouse gas, and nitrogen oxides (NO_x), and sulfur oxides (SO_x), which are air pollutants. Therefore, more environmentally friendly alternative fuels are required. Hydrogen energy is attracting attention as one of the candidates. It does not emit CO_2, NO_x, or SO_x in the process of using it. Against this background, the hydrogen infrastructure market is expected to grow rapidly in the future, and fuel cell vehicles are expected to drive the market significantly thereafter. Hydrogen sensors that allow high-speed response and high sensitivity are required for the management and conservation of hydrogen energy. Conventional hydrogen sensors utilize chemical reactions on the device surface, and therefore a steady heating up to several hundred degrees Celsius to induce chemical reactions is required. Furthermore, it is difficult to use them in an oxygen-free atmosphere because they utilize reactions with oxygen. The quartz crystal microbalance (QCM) sensor is a sensor that can detect substances with small masses, such as gases or biomolecules[1)]. The QCM sensor is a resonance device in which the metal electrodes are formed on both sides of a thin quartz plate, which is cut from the bulk quartz at a specific angle. It is a mass-sensitive sensor which detects the mass loading due to the adsorption of target substances on the surface of the quartz resonator as a change in the resonance frequency. In this study, palladium (Pd) that can occlude hydrogen about 1,000 times its own volume is used as a hydrogen sensitive film[2)]. By applying this sensitive film to the wireless QCM sensor, a novel hydrogen sensor, which does not require heating and can be used in an oxygen-free atmosphere, is investigated. When using Pd as a hydrogen sensitive film, its film is often deposited on the surface of a quartz resonator using the sputtering method, and the sensing ability of the Pd film is significantly affected by the sputtering condition (e.g., degree of vacuum, temperature of substrate etc.). In this study, we investigate the effect of the sputtering condition in forming the Pd film on hydrogen the detection sensitivity.

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2. PDMS-microchannel based QCM sensor

The sensor chip to evaluate hydrogen detection sensitivity of Pd thin films was fabricated using a MEMS process in this study (**Fig. 1**). This sensor chip was fabricated with poly(dimethylsiloxane) (PDMS), which is a silicone resin, as the base material using nanoimprint lithography that can transfer or duplicate micropatterns on the order of several tens of nm. It is composed of upper and lower microchannel substrates, which are made of PDMS, embedded electrodes, and the AT-cut quartz resonator which has a length of 2.5 mm, a width of 1.7 mm, and a thickness of 0.025 mm, and the quartz resonator is supported by four micropillars and placed in the microchannel[3)]. The quartz resonator is excited via the inverse piezoelectric effect of the quartz crystal by applying electromagnetic waves from the copper-foil antenna attached to the top of the sensor chip. At the same time, the electric charges generated by the piezoelectric effect of the vibrating quartz crystal are detected by the antenna attached to the bottom of the sensor chip. Using electromagnetic waves makes it possible to drive a sensor chip wirelessly.

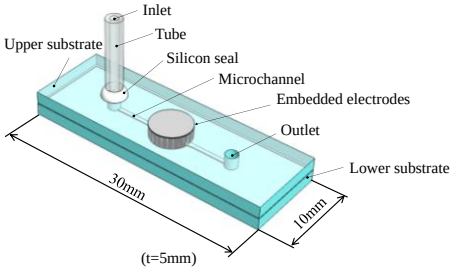

Fig. 1 Appearance of evaluation sensor chip made of PDMS.

3. Pd film deposition and detection sensitivity evaluation

The quartz resonator with a fundamental resonance frequency of 66.8 MHz was attached to the dedicated fixture for sputtering. Thereafter, a chromium (Cr) film of 3 nm as the adhesion layer and them a the Pd film of 30 nm were deposited using the radio frequency (RF) sputtering apparatus (KSP-231NS, Kenix). At this time, the vacuum degree of the spatter chamber was set to 5×10^{-4} Pa or less, and the RF power was set to 100 W. As a

condition for depositing the Pd film, we focused on the vacuum degree; the film quality was investigated for vacuum degrees of 0.4 Pa and 5 Pa. **Figure 2** shows the configuration of the measurement setup used to evaluate the detection sensitivity of hydrogen. Each gas was controlled using a mass flow controller (FCC4000, Kofloc) so that the flow rate was constant (50 ml/min). At first, nitrogen gas was fed, a stable frequency change as a baseline was obtained, and then hydrogen gas with a concentration of 1 vol% (nitrogen buffer 99 vol%) was fed.

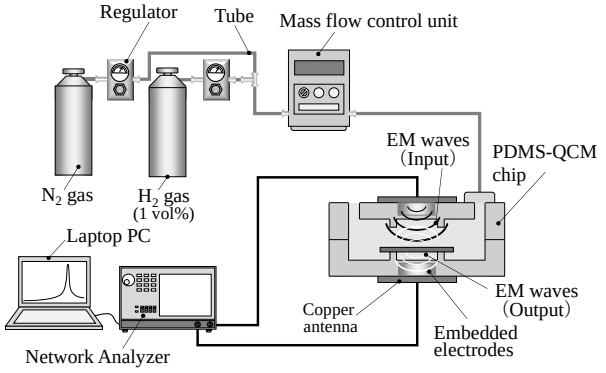

Fig. 2 The configuration of measurement setup used to evaluate the detection sensitivity of hydrogen

As a result, the frequency change occurred due to the hydrogen absorption of the Pd film. After a steep frequency change was obtained, a gentle frequency change was observed. Subsequently, when nitrogen gas was fed, the frequency change due to the hydrogen desorption from the Pd film nearly returned to the baseline (**Fig. 3(a)**). **Figure 3(b)** shows the hydrogen absorption curves of the sensor chip with the Pd film deposited at vacuum degrees of 0.5 Pa and 5 Pa, respectively.

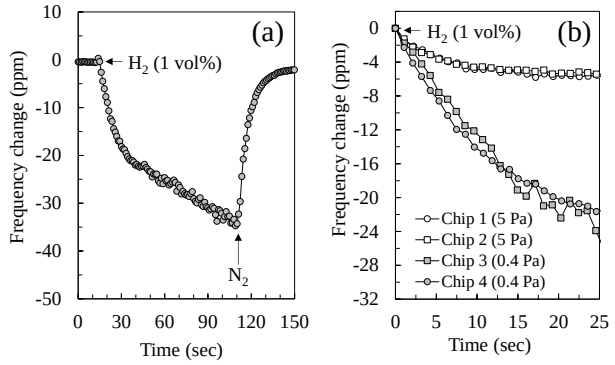

Fig. 3 (a) Response of hydrogen absorption and desorption and (b) absorption curves due to differences in film deposition pressure.

4. Results and Discussion

As shown in Fig. 2(b), the sensor chips with the quartz resonator on which the Pd film was deposited at 0.4 Pa had frequency changes of about 22 ppm due to hydrogen absorption for 25 seconds, while the sensor chips at 5 Pa had frequency changes of about 4 ppm. When hydrogen is regarded as an ideal gas and the hydrogen absorption amounts are calculated from the obtained frequency changes, they correspond to 600 and 110 times the volume of the Pd film, respectively. These values are appropriate considering the hydrogen absorption characteristics of the Pd film. Due to changes in the resonance frequency, it was found that the sensor chips with the quartz resonator deposited the Pd film at 0.4 Pa had higher hydrogen detection sensitivity than those of 5 Pa. This result is presumed to be due to the difference in the mean free path during Pd film deposition. When the vacuum degree is 0.4 Pa while sputtering, the dense Pd film can be deposited because the mean free path is longer than that of 5 Pa. It was considered that the absorption amount of hydrogen improved because the density of the Pd film increased relatively as the mean free path became longer. There were no significant differences in the slope of the initial velocity between reaction curves; therefore, there was no almost difference in response speed between sensors with the Pd film deposited at 0.4 Pa and 5 Pa. This means that there is no marked difference in the solubility of hydrogen atoms in the Pd film deposited at each pressure. These results indicate that the hydrogen detection sensitivity can be improved by depositing the Pd film in a high degree of vacuum to form a high-density film.

5. Conclusion

In this study, we focused on Pd as a hydrogen absorption material, and the wireless QCM sensor chip for evaluating hydrogen detection sensitivity of the Pd film was fabricated. As a result of investigating deposition conditions of the Pd film using the sputtering method, it was found that the hydrogen adsorption sensitivity improves when the degree of vacuum is higher. The proper pressures for Pd film deposition will be investigated in the future.

Acknowledgment

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References

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