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High-Sensitive Wireless QCM Sensor for Hydrogen Gas Detection with PdAu Alloy Film

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1. Introduction

Fossil fuels support most of the current social infrastructure in Japan, such as transportation and power generation. However, these fuels emit greenhouse gases and air pollutants. Therefore, there is a demand for alternative clean energy sources from the perspective of environmental protection. In response to these societal demands, hydrogen (H_2) energy has attracted attention, and the H_2 market is expected to grow rapidly in the future. Compared to methane, H_2 has a wider explosion range, lower minimum ignition energy, and larger diffusion coefficient. Therefore, increasing demand for sensors with higher sensitivity and faster response times. The commercial H_2 sensors require continuous heating to promote chemical reactions. In addition, they are difficult to use for detecting in an oxygen-free atmosphere, which results in severe restrictions on their application. One H_2 sensor that does not have the above problems is the quartz crystal microbalance (QCM) H_2 sensor. This QCM sensor has a thin quartz resonator with a hydrogen-sensitive film deposited on the surface. It detects changes in the mass loading and shape of the quartz plate due to H_2 adsorption as changes in the resonant frequency. In recent years, wireless QCM H_2 sensors that operate wirelessly using electromagnetic (EM) waves have been developed[1, 2]. The wireless QCM H_2 sensor uses palladium (Pd), which is a H_2 storage material, as the sensing film. This chip can detect H_2 at low concentrations of 10 ppm or less and has a 90 % response time of less than 20 seconds[2, 3]. However, management for the H_2 society, which is expected to grow in the future, will require H_2 sensors with higher detection sensitivity and faster response performance. In this study, wireless QCM H_2 sensors that use the PdAu alloy as the sensitive film were developed. And then, their effects on improving H_2 detection characteristics were investigated.

2. Formation of Dislocations in PdAu Film

When a H_2 molecule contacts the Pd material, it separates into atoms, and they then occupy vacancies in the Pd crystal lattice. Furthermore, if there are defects such as dislocations in the Pd crystal, they become precipitation sites for hydrides, which effectively absorb the H_2. Therefore, a thin film with defects in the Pd crystal can be useful as a H_2 gas sensitive film[3]. In this study, focusing on these characteristics, we investigated the deposition methods for the PdAu alloy film with interstitial and substitutional defects introduced by adding Au, which has a larger atomic size than Pd, into Pd crystals. Two methods were investigated for the deposition of PdAu alloy films using the radio-frequency sputtering apparatus (KSP-231NS, Kenix). One method is the simultaneous deposition of the PdAu alloy film (Pd 70 wt%: Au 30 wt%). The other method involves depositing four alternating layers of Pd and Au films (with a total thickness of 30 nm) and then annealing them (at 400°C for 4 hrs.) to promote the thermal diffusion of atoms and the mixture of crystal grains, finally forming the PdAu alloy film. **Figure 1** shows scanning electron microscope (SEM) images of each PdAu alloy film. Fig. 1(a) shows the surface of the simultaneously deposited PdAu alloy film, where extremely small and dense crystal grains were observed. On the other hand, Fig. 1(b) shows the surface of the PdAu alloy film with annealing after multilayer deposition, and coarse crystal grains due to the diffusion of each atom were observed throughout the film. It is considered that the PdAu alloy film obtained by thermal diffusion of the Au/Pd multilayer film contains numerous voids because Pd and Au atoms move randomly during the annealing process.

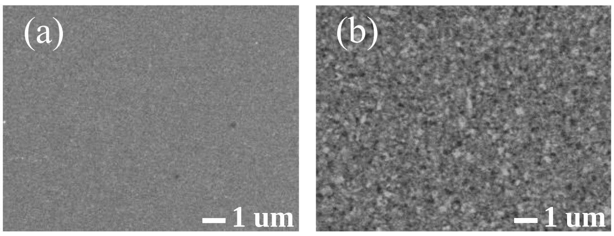

Fig. 1 SEM images: (a) Surface of simultaneous deposition, (b) multilayer deposition and annealing.

3. H_2 gas storage experiment

A QCM H_2 gas sensor chip was fabricated using nanoimprint lithography (NIL) (**Fig. 2(a)**), and H_2 absorption experiments were conducted. The detailed fabrication method of this sensor chip was described in the previous study[2]. The AT-cut quartz resonator (2.5x1.7x0.025 mm3) used in H_2 absorption experiments had a fundamental resonance

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frequency of 66.8 MHz. After the deposition of a 3 nm chromium (Cr) adhesion layer on one side, each PdAu alloy film was deposited. The simultaneously deposited PdAu alloy film was used without annealing after depositing to a total thickness of 40 nm. The PdAu alloy film was formed by alternately depositing thin layers of Au (3 nm) and Pd (7 nm) four times, resulting in a total thickness of 40 nm. The film was then heat-treated at 400 °C for 6 hrs. in vacuum and slowly cooled. The AT-cut quartz resonators deposited each PdAu alloy film were sticked and fixed on four micropillars (φ0.1 mm) in the microchannel. EM waves were propagated from the copper (Cu) foil antenna attached to the top of a sensor chip to excite the quartz resonator via the inverse piezoelectric effect. At the same time, EM waves excited by vibrating the quartz resonator were received by the other Cu foil antenna attached to the bottom (Fig. 2(b)). The flow rates of H_2 gas, which is a concentration of 0.1 vol% with nitrogen gas, and buffer gas, which is pure nitrogen, were controlled at 50 ml/min using a mass flow controller (FCC-4000, Kofloc). The fundamental resonant frequency was continuously measured while the gases were flowing, and sensor characteristics were evaluated from frequency changes.

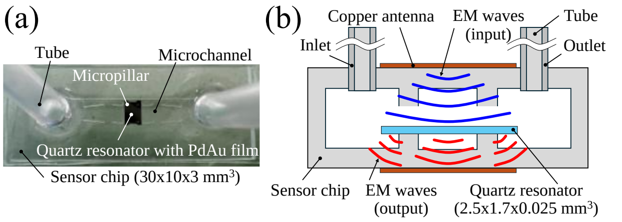

Fig.2 (a) Photographic image of a sensor chip, (b) Principle of wireless operation using EM waves.

4. Results/Discussion

Figure 3 shows frequency changes when each PdAu alloy film absorbed H_2 gas (0.1 wt%). In the sensor chip with the simultaneously deposited PdAu alloy film, a frequency change of approximately 16 ppm was observed, and high detection sensitivity was achieved. On the other hand, the multilayer-deposited and annealed PdAu alloy film had a sensitivity of about 6 ppm, which was about 40 % of the sensitivity of that with the simultaneously deposited film. In comparison of 90 % response time, the chip with the simultaneously deposited PdAu alloy film was about 60 sec. On the other hand, the multilayer-deposited and annealed PdAu alloy film had a response time of about 15 sec. In comparing detection sensitivity, it was found that the chip with the simultaneously deposited PdAu alloy film was superior. This is thought to be because the simultaneously deposited PdAu alloy film has fine and numerous crystal grains, allowing hydrogen atoms to easily penetrate deep into the PdAu alloy film through the fine grain boundaries and voids. This is thought to be because the simultaneously deposited PdAu alloy film has fine and numerous crystal grains, allowing hydrogen atoms to easily penetrate deep into the PdAu alloy film through the fine grain boundaries and voids. In comparing response time, the multilayer-deposited and annealed PdAu alloy film was superior. The multilayer-deposited and annealed PdAu alloy film has coarse crystal grains. Therefore, when large Pd crystal grains absorb H_2, they cause a volume expansion accompanied by a greater force compared to smaller crystal grains. As a result, it is considered that a fast response time was achieved. On the other hand, the simultaneously deposited PdAu alloy film has extremely small and dense crystal grains of Pd and Au, and they are close to each other. Therefore, it is considered that when Pd crystal grains expanded in volume due to the H_2 absorption, the nearby Au crystal grains inhibited this expansion, resulting in slow warping of the quartz plate and an increased response time.

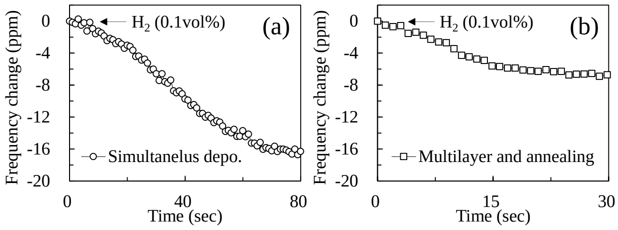

Fig.3 Frequency changes while detecting H_2 gas by each PdAu alloy film: (a)Simultaneous deposition, (b)multilayer deposition and annealing.

5. Conclusion

It was revealed that simultaneous deposition increased the sensitivity, and that the response time was improved by the multilayer deposition and annealing. In the future, we will develop hydrogen-sensitive films which can archive higher sensitivity and faster response times.

Acknowledgments

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