様式①

【研究成果の要約】

氏　名	加藤 史仁
1.研究題目	能動的欠陥導入合金膜を使用した爆発性ガス微小リーク検出センサーの開発

2.研究内容

現在、モビリティや発電、樹脂製品製造で使用される主な燃料の多くは、原油由来のものであり、温室効果ガスの二酸化炭素（CO_2）が大量に排出されている。そのため、地球温暖化に起因した気候変動の問題が顕在化しており、カーボンニュートラルに向けた取り組みが検討されている。CO2 排出量の問題は、地球規模の異常気象の誘発など、気候変動に与える影響は大きく、環境に優しい代替燃料が求められている。こうした課題を鑑みて、化石燃料に代わる次世代燃料の一つとして、水素が注目されている。水素は、利用過程における CO_2 の排出が無く、大気汚染物質の要因となるガスの排出も無い。水素は、環境に優しい 2 次エネルギであり、太陽光や水力、風力などの再生可能な 1 次エネルギに由来する水素を使用することで、環境負荷を大幅に低減できる。そのため、水素は、カーボンニュートラルの実現に大きく貢献しうる有望なエネルギの一つとして考えられている。但し、水素は、低い爆発下限界と着火エネルギを有し、拡散係数が高いため、ガスリークを生じた場合、大災害に直結しうる極めて危険なガスである。また、リーク量が極微量であっても、質量の軽い水素は、密閉空間において、局所的に高濃度滞留することもあるため、取り扱いの際、細心の注意を払う必要がある。

本研究では、爆発の危険性が高い水素の微小リークを高感度に検出できる水素センサーの開発を目指す。その際、水素吸蔵材料のパラジウム（Pd）の特性に着目し、Pd よりも原子半径が大きい金（Au）を添加することで、単一の Pd に比べて結晶格子定数を拡大した金パラジウム（PdAu）合金を水素感応膜として用いる。また、PdAu 合金の薄膜に対して、面内方向の強い圧縮力を与え、膜内部に結晶欠陥を積極的に形成する。格子定数拡大による結晶中の空隙や圧縮応力印加による薄膜中の欠陥は、水素化物の析出サイトとなるため（図 1）、水素吸蔵性能などの諸特性の向上が期待できる。この PdAu 合金薄膜を薄板水晶振動子の片面に形成した無線駆動水晶振動子水素センサーを開発し、水素センサーとしての基本特性を評価した。

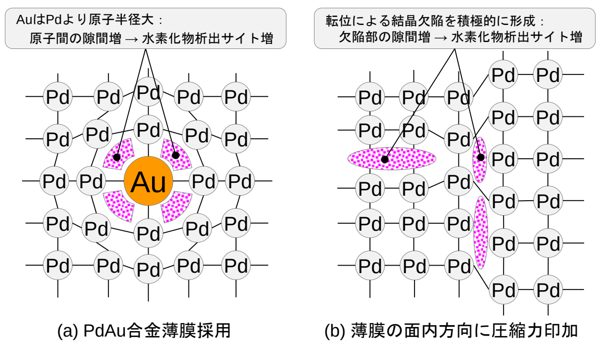

図1 水素化物析出サイト形成手法

3.研究成果

水素感応膜となる PdAu 薄膜を成膜する基板として、薄板水晶振動子を採用し、水晶の限界破壊応力を考慮した設計を通じて、PdAu 薄膜成膜用曲率ジグを製作した。高周波スパッタリング装置を使用して、Pd と Au のターゲットを設置したカソードの電源出力を最適化することで、Pd リッチとなる所望の組成比を有する PdAu 薄膜の成膜手法を構築した。PdAu 薄膜の熱処理検討を通じて、常温成膜したアズデポ膜がより良いことを明らかにした。PdAu 合金薄膜を感応膜とする水素センサーを試作し、Pd 薄膜に比べて検出感度が向上することを立証した（図 2：圧縮応力印加無し）。

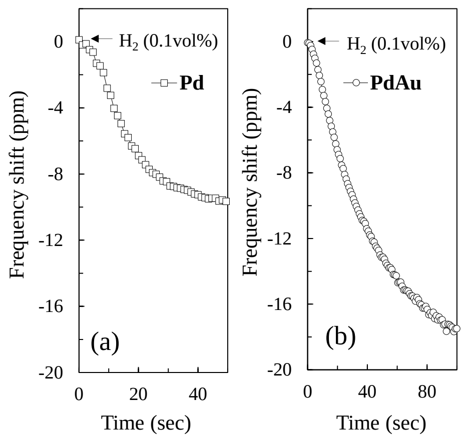

図2 水素ガス注入時の周波数変化

参考：　国際会議論文　https://doi.org/10.24492/use.45.0_3P3-2

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

Takato Otake[1†], Manabu Suzuki[1], Fumihito Kato[1*], and Hirotsugu Ogi[2] ([1]Dept. Mech. Eng., Nippon Inst. Of Tech.; [2]Grad. Sch. Eng., Osaka Univ.)

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.

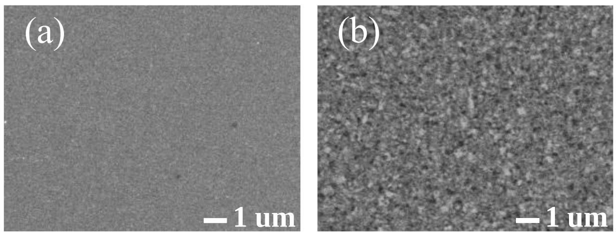

Fig. 1 SEM images: (a) Surface of simultaneous deposition, (b) multilayer deposition and annealing.

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

E-mail: †t.otake.eng@gmail.com, *kato.fumihito@nit.ac.jp

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.

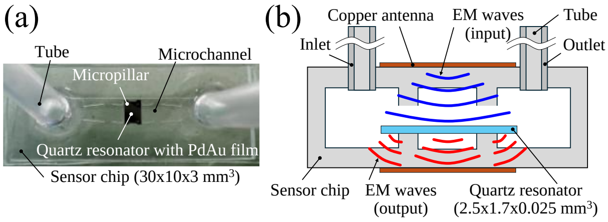

Fig.2 (a) Photographic image of a sensor chip, (b) Principle of wireless operation using EM waves.

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.

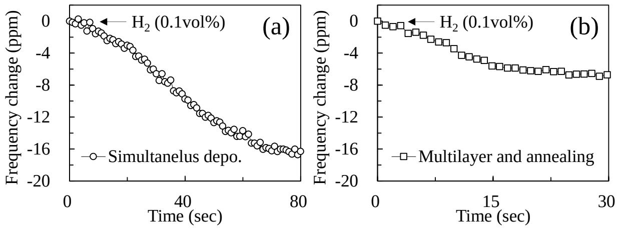

Fig.3 Frequency changes while detecting H_2 gas by each PdAu alloy film: (a)Simultaneous deposition, (b)multilayer deposition and annealing.

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

This study was partially supported by the Paloma Environmental Technology Development Foundation Research Grant (2024) and JSPS KAKENHI Grant Number 24K08262.

References

1) H. Ogi, Jpn. J. Appl. Phys. 63, 040802 (2024).
2) F. kato et al., Jpn. J. Appl. Phys. 57, 07LD14 (2018).
3) F. kato et al., Jpn. J. Appl. Phys. 61, 126501 (2022).