Effects of Au atoms deposition on Pd film for hydrogen gas sensor using wireless and electrodeless quartz crystal resonator

Tokiya Matsukura‡, Lianjie Zhou, Akira Nagakubo*, Hirotsugu Ogi (Grad. School Eng., Osaka Univ.)

1. Introduction

Hydrogen is clean and sustainable energy source without carbon dioxide emission. Hydrogen is highly dangerous because of the wide flammability limits in air combination and the high risk of leakage. Therefore, for safe use of hydrogen, highly sensitive hydrogen gas sensors are required to detect hydrogen leakage quickly and accurately.

In hydrogen gas sensors, various materials such as ZnO[1], TiO_2[2], and Pd[3–6] are utilized. In particular, Pd is used in many hydrogen sensors because it absorbs hydrogen with high selectively, leading to the changes in its volume and electrical resistance. In the hydrogen-absorption process at Pd surfaces, the rate-limiting step is the penetration process from the surface into the subsurface region[7]. Therefore, it is expected to control the absorption rate by modifying the surface structure and atoms. In fact, it has been reported that Pt or Au deposition on Pd surface can enhance hydrogen absorption due to the special nanostructure of Pt[8] or reducing the absorption energy of Pd surface and lowering the penetration barrier by Au alloying on Pd surface[3].

We have developed a hydrogen gas sensor using wireless electrodeless quartz crystal microbalance (QCM)[4, 5, 6] which can detect 1-200 ppm hydrogen at 55°C by depositing a Pd thin film on one side of the QCM[5]. This sensor detects hydrogen from the decrease in resonance frequency caused by the tiny mass loading effect and a larger curvature change effect due to expansion of Pd with hydrogen absorption.

In this paper, we report that a Pd-based QCM gas sensor can detect hydrogen at room temperature by depositing nm-order Au atoms on the Pd surface. We also discuss the effect of the Au on the hydrogen absorption rate of Pd.

2. Experiment

We used 26 and 13.5-μm thickness AT-cut QCMs, whose fundamental resonance frequencies are 64.5 and 125 MHz, respectively. To detect hydrogen, we deposited Cr, Pd, and Au on one side by the RF (Radio Frequency) magnetron sputtering method at room temperature. Cr film is 5 nm thickness and works as a bonding layer, and the total thickness of Pd and Au film is fixed as 200 nm, where we change the Au film thickness between 0 and 2 nm

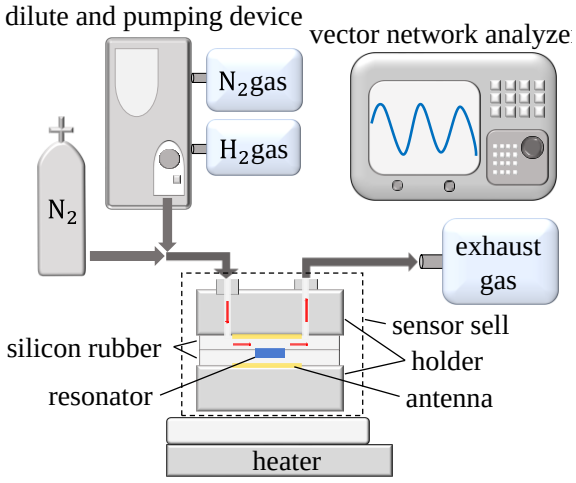

Fig. 1 Schematic diagram of hydrogen detection experimental system.

Fig. 1 shows the gas flow system, in which the QCM is sandwiched between two silicone rubbers and placed above the antenna of the sensor cell. The resonance frequency change of the QCM is measured by a vector network analyzer. We set the flow rate of 99.9999% nitrogen carrier gas as 100 mL/min, and inject 34.5 mL/min hydrogen/nitrogen gas, whose concentration is controlled by a dilution and pumping device (SHIMADZU, FDL-1). To activate the hydrogen absorption of Pd, we set the sensor cell above a heater and keep the temperature between 24 and 100℃.

We show typical frequency changes at injection of nitrogen and 250-ppm hydrogen gas at 55℃ in **Fig. 2(a) and (b)**, respectively. As shown in Fig. 2, while only carrier gas is flowing, the resonance frequency changes little. During this flow, the slopes of the resonance frequency changes are obtained as the baseline S_{Nb} and S_{Hb}. Then, at the moment of any gas injection, the resonant frequency drops steeply. This steep change would be caused by pressure change derived from the dilute and pumping device. The resonant frequency change during gas injections different for each type of gas. In the case

of nitrogen injection, the resonance frequency is hardly affected except for the effect from the pressure change. In the case of hydrogen injection, the resonance frequency linearly decreases with time, whose change ratio depends on the hydrogen concentration. Gas injections stop around 300 s, then, the resonant frequency rises and returns to the original baseline. The slope of the resonance frequency change S'_H during the gas injection is defined by Eq. (1).

$$S'_H = |(S_H - S_{Hb}) - (S_N - S_{Nb})| \quad (1)$$

Where S_H, S_{Hb}, S_N, and S_{Nb} are linear coefficients of the resonance frequency changes for hydrogen injection, before hydrogen injection, for nitrogen injection, and before nitrogen injection, respectively.

3. Result and Discussion

We investigate the effects of deposited nm-order Au atoms on the Pd surface by changing Au film thickness. We inject 1–200 ppm hydrogen at 55℃ and evaluate the detection limit. By depositing ~0.5 nm Au atoms, the detection limit is enhanced, however, it becomes worse by depositing further Au atoms. The slope for different concentration hydrogen can be expressed by Eq. (2)[5],

$$S_H = -A(k_a C_{H2} + k_d) \quad (2)$$

A is an arbitrary constant, C_{H2} is the hydrogen concentration, and k_a and k_d are the reaction rate constants for hydrogen absorption and hydrogen desorption, respectively. The reaction rate k_a also takes maximum by depositing ~0.5 nm Au, and decreases as the increase in Au thickness above it. These results indicate that monolayer-order Au atoms enhance hydrogen decomposition on the Pd film surface and its absorption into it. However, further deposited Au atoms reduce Pd sites for hydrogen decomposition and adsorption, leading to an optimal Au thickness.

To evaluate the effect of the optimal thickness Au deposition for activation energy, we measured the slope dependence on hydrogen concentration and temperature. The activation energy was determined by Arrhenius's low of Eq. (3).

$$k_a = A_0 \, exp(-E/k_b T) \quad (3)$$

where A_0 is an arbitrary constant, E is the activation energy, k_b is Boltzmann constant, and T is temperature. Au deposition decreases the activation energy by ~20%, which enables us to detect ~10 ppm hydrogen at room temperature.

We will further investigate and discuss the life time of the sensor and the enhancement mechanism by depositing Au.

4. Conclusion

We have achieved high sensitivity and room temperature operation of the Pd-based QCM hydrogen gas sensor by depositing nm-order Au atoms. Au deposition improves the hydrogen gas sensor performance, but there is an optimal thickness, which will contribute to new hydrogen sensors and understanding for hydrogen-Au-Pd reactions.

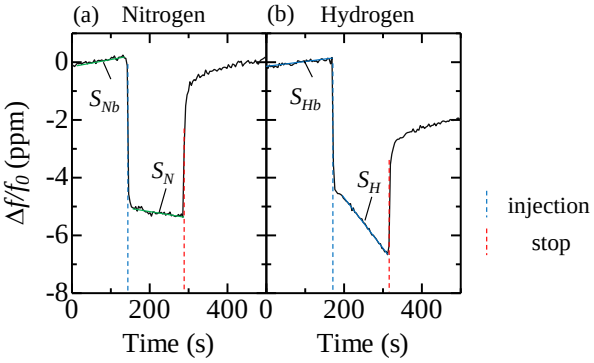

Fig. 2 Typical resonance frequency change during injection of hydrogen gas and nitrogen gas. S_H, S_{Hb}, S_N, and S_{Nb} are linear coefficients of the resonance frequency changes.

References

1. J. Kim, A. Mirzaei, H.W. Kim, P. Wu, S.S. Kim: Sens. Actuators B **293** (2019) 210.
2. T. Hyodo, H. Shibata, Y. Shimizu, M. Egashira: Sens. Actuators B **142** (2009) 97–104.
3. N. Namda, S. Ogura, S. Ohno, W. Di, M. Wilde, P. Pervan, M. Milun, and K.Fukutani: PNAS **31** (2018) 7896.
4. L. Zhou, N. Nakamura, A. Nagakubo, and H. Ogi: Jpn. J. Appl. Phys. **59** (2020) SKKB02.
5. L. Zhou, N. Nakamura, A. Nagakubo, and H. Ogi: Appl. Phys. Lett. **115**, (2019) 171901.
6. L. Zhou, F. Kato, N. Nakamura, Y Oshikane, A Nagakubo, H. Ogi: Sens. Actuators B Chem.334, 129651 (2021).
7. T. L. Ward and T. Dao, J. Membr: Sci. **153**, (1999) 211.
8. K. Hassan, A.S.M I. Uddin, G. Chung: Sens. Actuators B **234** (2016) 435.