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Enhancement of sensitivity of Pd-based hydrogen sensor by repeated hydrogen flow confirmed by wireless QCM

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1. Introduction

Hydrogen is a promising alternative energy carrier. Development of sensitive, fast, and reliable hydrogen sensor remains important because of drastic increase in hydrogen usage. In existing hydrogen sensors, palladium or its alloy has been used as the hydrogen sensing material, owing to its high selectivity and absorption ability for hydrogen gas. The sensing mechanisms of most palladium-based hydrogen sensors rely on changes in physical properties (electric conductivity, volume, elastic stiffness, and so on) when hydrogen atoms occupy the interstitial sites in palladium lattice. When palladium is exposed to hydrogen gas, hydrogen molecules are first attached on palladium surface and dissociated into hydrogen atoms, and then they migrate into the bulk lattice through the subsurface state to cause the bulk diffusion [1]. The first surface-attachment process is expected to be completed in a short time because it proceeds spontaneously [2]. Therefore, the sensitivity of palladium-based hydrogen sensor is fundamentally determined by the hydrogen atom content on palladium surface and the speed of hydrogen diffusion from surface to palladium bulk. As have been reported [3,4], as-deposited palladium shows poor hydrogen absorption performance, limiting the sensitivity of palladium-based hydrogen sensor. However, its mechanism remains unknown.

In this study, we reveal a method to significantly improve the hydrogen absorption of palladium by repeated hydrogen exposure, causing several hydrogen absorption-desorption cycles. The enhancement of hydrogen sensitivity compared with that of as-deposited palladium film is confirmed by our high-frequency wireless-electrodeless quartz crystal resonator.

2. Hydrogen detection method

The hydrogen detection sensitivity with palladium thin film is evaluated using wireless-electrodeless quartz crystal resonator. We first deposit 5 nm chromium and then 200 nm palladium on one surface of an AT-cut quartz crystal resonator with a rectangular parallelepiped area of 2.5×1.7 mm^2. Its thickness is 13.5 μm, showing the fundamental through-thickness shear-mode resonant frequency of 125 MHz. Because the vibration excitation and detection are realized using antennas in a wireless manner, the other surface of the resonator is remained uncoated. When the resonator is exposed to hydrogen gas, palladium film expansion occurs because of hydrogen absorption, causing the geometry change of the resonator. The resonant frequency of an AT-cut resonator decreases as the curvature increases. Thus, the sensitivity in hydrogen detection can be evaluated through the frequency decrease.

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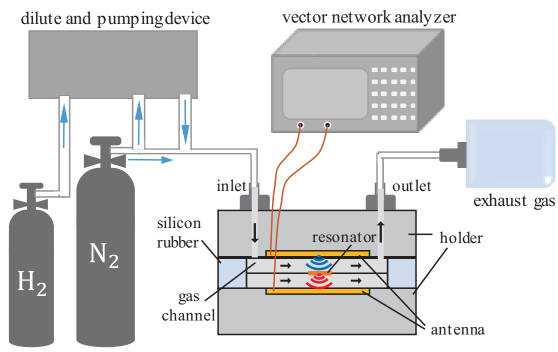

Fig. 1 Schematic of experiment system.

3. Experiment

Fig. 1 illustrates the homemade experiment system. The resonator with as-deposited palladium film was lightly sandwiched by two silicon-rubber gaskets in the sensor cell. The sensor cell was placed on a heater to keep the temperature steady at 55 ℃. We flow high purity nitrogen gas (99.9999%) to the sensor cell channel as carrier at flow rate of 100 mL/min. Diluted hydrogen joins the carrier-nitrogen flow, reaching the sensor cell with an intended concentration. The resonant frequency is monitored by the transmission coefficient (S_{12} parameter) by a vector network analyzer. We first measured the sensitivity of our hydrogen sensor to hydrogen gas with concentration of 200 ppm. Then we flowed high concentration hydrogen gas (1100 ppm) to the sensor cell. The exposure duration time is 140 seconds, then, the absorbed hydrogen atoms in palladium are slowly discharged by changing the hydrogen flow to high purity nitrogen gas. We performed the absorption-desorption cycles 8 times, after which, the frequency response to the 200-ppm hydrogen gas was measured again to evaluate the enhancement effect on the sensitivity. Note that the high concentration hydrogen exposure time in each cycle should be carefully controlled to avoid possible detachment of palladium film.

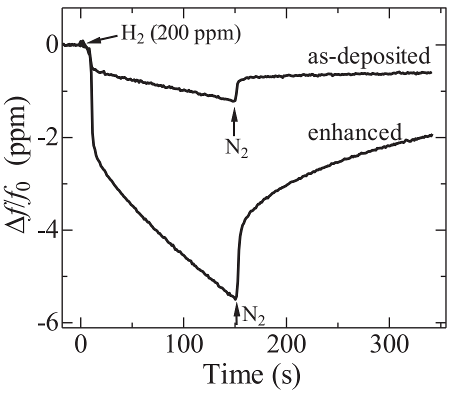

Fig. 2 Frequency responses of palladium-coated quartz-crystal resonator upon hydrogen exposure before and after the palladium-film activation.

4. Results and Discussion

Fig. 2 shows the sensitivity change of hydrogen detection using palladium-coated quartz resonator. At first, the quartz resonator with as-deposited palladium film shows lower sensitivity to 200 ppm hydrogen. After sensitivity enhancement by exposing the resonator to repeated high concentration hydrogen flow, the amount of frequency change increases significantly. The sensitivity is improved by a factor of about 6 when we focus the frequency-change rate. The steep frequency drop just after gas injection as observed in **Fig. 2** will be attributed to the hydrogen attachment on the palladium surface, although a part of this drop is also caused by the baseline shift at the gas injection. This steep frequency drop is also remarkably enlarged after the enhance process, indicating that the surface status of palladium may has been changed by the absorption-desorption cycles. The morphology of palladium thin film strongly influences the absorption speed of palladium [5]. Moreover, the hydrogen absorption initially proceeds from the active site (point defects and buckles) on palladium surface and successive hydrogen absorption-desorption leads to formation of more active sites [6]. Therefore, the mechanism of sensitivity enhancement in our experiment should attribute to the morphology change of palladium surface. We find that after the activation of the palladium surface we proposed here, the limit of the detectable hydrogen gas concentration is less than 1 ppm.

5. Conclusion

We present a method to improve the sensitivity of palladium based hydrogen sensor by repeated high concentration hydrogen exposure. The sensitivity enhancement was confirmed using quartz crystal resonator. Palladium thin film was deposited on single surface of quartz crystal resonator. The frequency decrease of resonator caused by geometry change was utilized to evaluate the sensitivity of hydrogen detection. Compared with quartz resonator with as-deposited palladium film, the hydrogen detection sensitivity is improved by a factor of 6 by repeated hydrogen flow. Through the analysis of frequency response change, we attribute the detection sensitivity enhancement to the morphology change of palladium film surface induced by repeated high concentration hydrogen absorption-desorption process.

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