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Resistance change of nanogap Au/Pd nanoparticles under hydrogen atmosphere

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1. Introduction

Hydrogen is attracting attention as an important alternative energy source to fossil fuels because of its excellent combustion properties, lack of carbon dioxide emissions, and abundance of resources. However, hydrogen is the lightest of all gases, diffuses and leaks easily, embrittles metallic materials, and explodes when its concentration in air exceeds 4%, so it must be handled with care. Therefore, a hydrogen gas sensor with fast response, high sensitivity, and high reliability is needed for safe use, and several types of hydrogen gas sensers have been investigated[1-3].

Sensors using palladium (Pd) nanoparticles (clusters) have been studied for their excellent hydrogen selectivity[4,5]. The sensor consists of Pd nanoparticles dispersed on an insulator substrate. When the nanoparticles are exposed to an atmosphere containing hydrogen gas, they absorb the hydrogen, and volume expansion occurs. The nanoparticles then come into contact, and the surface resistance of the substrate decreases. Therefore, hydrogen gas is detectable by measuring the resistance change. Sensitivity of this sensor can be improved by narrowing the gap between nanoparticles. This is because a small volume expansion can lead to contact between the nanoparticles and hydrogen gas at low concentrations can be detected. In a previous study[6], nanogap Pd nanoparticles, in which gap size was reduced to a few atoms, were fabricated, and a resistance change of 53% was achieved for 100 ppm hydrogen gas. However, the respose time was not so short, and further improvement was required.

To improve the response time, in this study, we investigate resistance change of nanogap Au/Pd nanoparitlces under hydrogen atmosphere. In a previous study[7] on the hydrogen absorption rate of Pd, it was experimentally observed that the hydrogen absorption rate increased more than 40 times when about one atomic layer of Au was attached to the Pd surface. Based on this study, we investigate whether attachment of Au on the surface of nanogap Pd nanoparticles improves the hydrogen absorption rate and improves the response time. Nanogap Au/Pd nanoparticles with about one atomic layer of Au on the surface of Pd are fabricated by sputtering, and the resistance change under hydrogen atmosphere is measured. The experimental results are compared with those of nanogap Pd nanoparticles and we discuss for the development of a hydrogen gas sensor with fast response and high sensitivity.

2 Experimental

2.1 Nanogap nanoparticle fabrication

Au/Pd nanoparticles were fabricated by sputtering Pd and Au on a cover glasses (thickness of 0.08 ~ 0.12 mm) that were ultrasonically cleaned with distilled water, acetone, and ethanol. The RF magnetron sputtering system used in this study is shown in **Fig. 1**. Two cathodes are attached to the sputtering chamber, and shutters are located under the targets, allowing sequential sputtering of two metals. The sputtering power was 15 W for Pd and 20 W for Au.

A piezoelectric material is placed below the substrate, and the resonance spectrum of the piezoelectric material is repeatedly measured during sputtering. The attenuation of the resonant vibration of the piezoelectric material changes depending on the gap size between of the nanoparticles, and it shows a maximum when the gap closes and nanoparticles contact each other. Therefore, by interruping the sputtering when the maximum

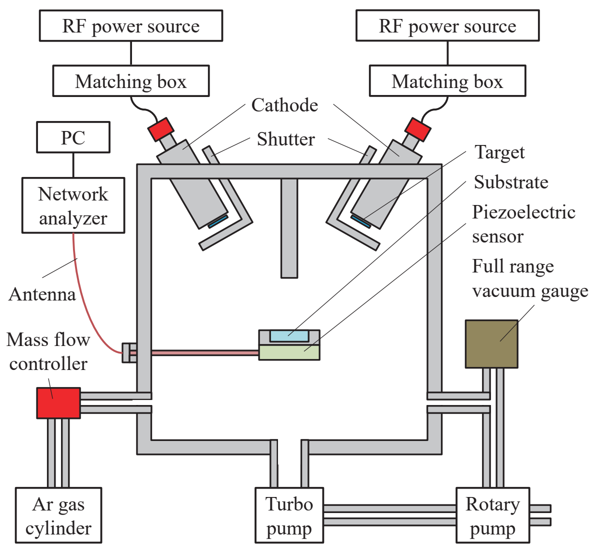

Fig. 1 Schematic drawing of RF magnetron sputtering system.

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appears, nanogap nanoparticles can be fabricated. This technique is called the non-contact piezoelectric resonance method[8]. In this study, two resonant modes arouond 1.23 MHz and 26.8 MHz were measured alternately, and the gap size was controlled referring to the changes in their attenuation.

2.2 Resistance measurement under hydrogen atmosphere

The electrical resistance was measured using a laboratory-made measurement cell. Contact probes were attached to the substrate surface, and using a nanovoltmeter and a DC power supply, the resistance was measured. A carrier gas (N_2, 99.9999%) was supplied to the cell at a constant flow quantity, and a sample gas (H_2, 0.1% / N_2, 99.9%) was added to the carrier gas using a syringe pump for hydrogen gas detection experiments. The flow quantity of the carrier gas was 117 ml/min and that of the sample gas was 13 ml/min, resulting in a hydrogen concentration of 100 ppm in the measurement cell.

3. Results and Discussion

Nanogap Au/Pd nanoparticles were fabricated by sputtering Pd for 238 s followed by Au for 10 s, and nanogap Pd nanoparticles were fabricated by sputtering Pd for 450 s. Their gap sizes were equalized using a non-contact piezoelectric resonance method. **Figure 2** shows their resistance change under the hydrogen atmosphere. Sensitivity was defined as the change ratio of the resistance after 200 s hydrogen gas flow. The response time was defined as the time at which 90% of the resistance change at 200 s was reached, as indicated by the dots in Fig. 2.

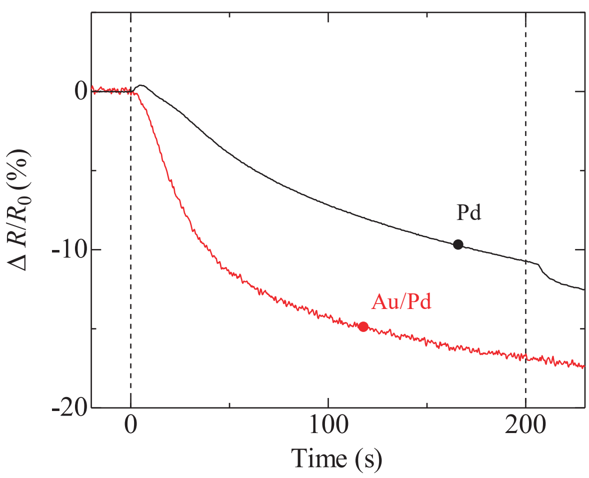

Fig. 2 Resistance change and response time during first H_2 gas flow.

During the hydrogen gas flow, the resistance decreased monotonically. This result indicates that nanogaps are closed by hydrogen absorption. The sensitivity of the Au/Pd nanoparticles was 16.7%, and it was higher than that of Pd nanoparticles (10.8%). Response time of Au/Pd nanoparticles was 118 s, and it was shorter than that of Pd nanoparticles (166 s). From these results, it was observed that the sensitivity and response time are improved by attaching Au on Pd nanoparticles. In the previous study[7], it was reported that attaching only one atomic layer of Au to the Pd surface decreases the permeation barrier and accelerates the hydrogen absorption. The same phenomenon might have occurred in the Au/Pd nanoparticles. In addition, the present study implies that attachment of Au on Pd nanoparticles may also contribute the improvement of the sensitivity.

4. Conclusion

In this study, nanogap Au/Pd nanoparticles were fabricated using a piezoelectric resonance method, and their resistance change under hydrogen atmosphere was measured. The results showed that the maximum resistance change was larger, and the response time was shorter than that of nanogap Pd nanoparticles. These results are expected to lead to the development of hydrogen gas sensors with fast response and high sensitivity.

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