Dew Tolerant Hydrogen Sensor for Fuel Cell Applications

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Abstract: This paper describes the technology to passively remove condensed water droplets from a heat transfer type H_2 sensor. In this study, three methods were investigated: (1) water-repellent coating, (2) absorption of repelled water into a suspended porous membrane over the sensor surface and (3) water droplet elimination driven by wettability gradient. A developing H_2 sensor was used as a platform for water-droplet-removal structures. By preliminary evaluations, it was found that method (2) is more effective for water droplet removal than method (1). For method (3), photochromic compound film on the super-water-repellent undercoat, which changes its wettability by UV exposure, was used. It was confirmed that contact angle could be controlled by the UV light dose.

Key words: water droplet, hydrogen sensor, fuel cell, wettability gradient

1. INTRODUCTION

A H_2 sensor is required in the anode side exhaust channel of a fuel cell stack to monitor the operating state of the fuel cell system. For this application, a heat transfer type H_2 sensor is suitable, because it works from 0 % to 100 % H_2 concentration. The measurement principle is based on the heat dissipation of a microheater by H_2, which has a higher heat transfer coefficient than the other gases present in a fuel cell, i.e. N_2 and water vapor.

The humidity of the place where the H_2 sensor is placed is almost 100 % due to both humidification of supplied H_2 and back-diffusion of generated water within the fuel cell. For fuel cell applications, therefore, dew tolerance is one of important requirements to the H_2 sensor. Even if a water-proof porous PTFE membrane is placed ahead of the H_2 sensor, water vapor can pass through the membrane and then condenses on the surface of the H_2 sensor while the system is low-temperature. This causes a malfunction of the sensor. Continuously heating the whole sensor system to prevent water vapor from condensing is not preferred from the viewpoint of standby power consumption and sensor lifetime.

Thus, we started to develop passive water-droplet-removal structures for the H_2 sensor. In this study, we investigated the combination of a water-repellant material and a water-absorbing porous material, and water droplet actuation driven by wettability gradient.

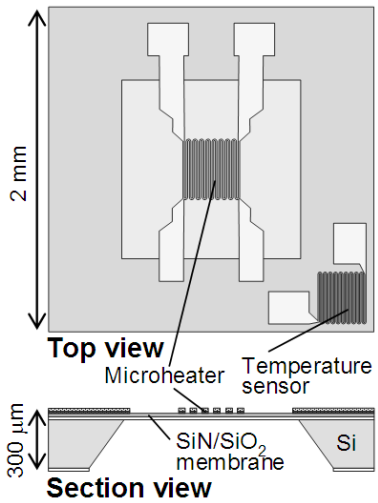

Fig. 1: Structure of heat transfer type H_2 sensor.

2. STRUCTURE AND FABRICATION PROCESS

2.1 H_2 sensor

The structure of the heat transfer type H_2 sensor is shown in Fig. 1. On a Si wafer, a 100/200 nm thick SiN/SiO_2 thin insulation film is deposited and a Pt/Cr microheater is formed. To minimize thermal loss due to heat conduction to the sensor body, Si on the backside of the microheater is removed by anisotropic wet etching using aqueous TMAH solution to form a SiN/SiO_2 diaphragm structure. The sensor is operated by DC constant current. H_2 concentration is measured by monitoring the variation of voltage involved in that of resistance based on the heat dissipation of a microheater by H_2.

2.2 Water-droplet-removal structure 1

Water-droplet-removal structure 1 is shown in Fig. 2. The center and surrounding areas of the H_2 sensor are coated with water-repellent polymer and water-absorbing porous ceramics, respectively.

The fabrication method is to simply coat the center area of the sensor surface with water-repellent polymer

and the surrounding area with water-absorbing porous ceramics. As the water-repellent polymer, Cytop (Asahi Glass Co.) is spin-deposited on the H_2 sensor before backside Si etching to release the diaphragm. The thickness of the Cytop film is 500 nm. Cytop can be patterned by plasma etching. To remove unnecessary Cytop on the surrounding area, the inner area of the H_2 sensor is masked by photoresist, and then O_2 plasma etching is performed.

After that, a suspension including the water-absorbing porous ceramics powder is spin-deposited on top of the photoresist. The suspension is prepared by mixing TiO_2 powder, surfactant and water. After evaporating the solvent of the suspension at 145 °C, the thick photoresist is removed by lift off. Finally, the porous ceramics is cured at 300 °C in air. The thickness of the porous ceramics is 6 μm. Fig. 3 shows the fabricated device.

2.3 Water-droplet-removal structure 2

Water-droplet-removal structure 2 is shown in Fig. 4. This structure also uses the combination of the water-repellent polymer and the water-absorbing porous ceramics. The porous ceramics is placed above the water-repellent polymer on the inner area of the H_2 sensor, with a microgap in between. Any water droplets larger than the microgap will be wicked into the porous ceramics. The microgap was formed by etching a sacrificial Ti layer through the porous ceramics [1].

The fabrication process is as follows: After spin-coating of Cytop, a 3 μm thick Ti film was sputtered on top of the Cytop layer and patterned by photolithography and dilute HF etching. Using the same mask, Cytop was also patterned by O_2 plasma etching. After removing the photoresist, a second Cytop layer is spin-deposited and structured by photolithography and O_2 plasma etching. After removing the photoresist, alumina cement paste served as the water-absorbing material is applied to the sensor substrate by dip-coating. The substrate is dipped in the cement paste and raised soon. Because the aqueous cement paste is repelled by Cytop, it is only deposited on Cytop-free areas of the substrate. After drying the cement paste, the second Cytop layer is removed by O_2 plasma etching. Finally, the Ti layer was removed by sacrificial XeF_2 etching to form a microgap between the Cytop layer and the porous alumina ceramics cover.

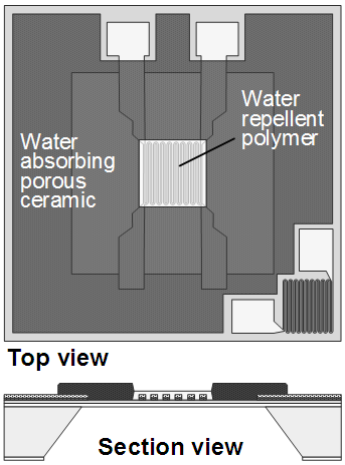

Fig. 2: Water-droplet-removal structure 1: The center and surrounding areas of the H_2 sensor are coated with water-repellent polymer and water-absorbing porous ceramics, respectively.

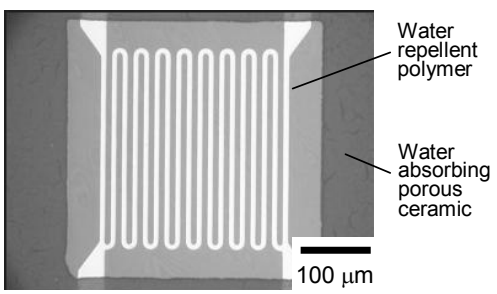

Fig. 3: Microheater covered with water-repellent polymer and surrounded by water-absorbing porous ceramics.

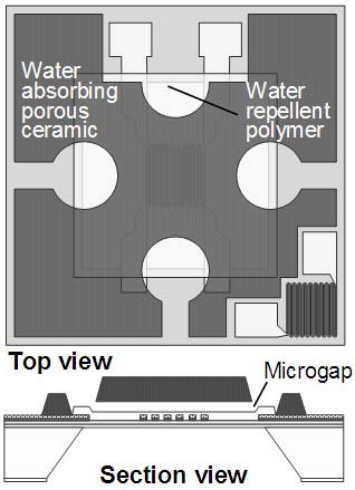

Fig. 4: Water-droplet-removal structure 2: The porous ceramics is placed above the water-repellent polymer on the inner area of the H_2 sensor, with a microgap in between.

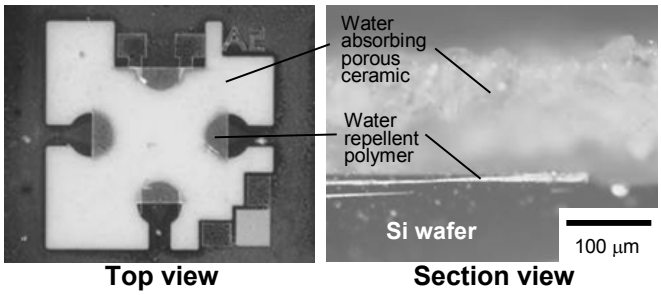

Fig. 5: Water-absorbing porous ceramics structure on water-repellent polymer coating with a microgap.

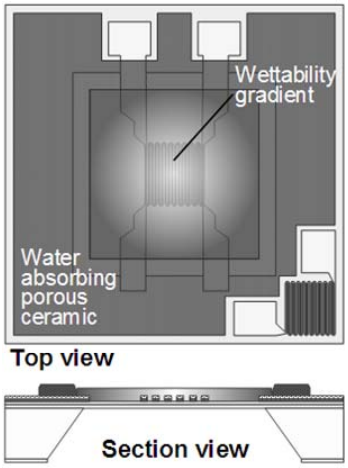

Fig. 6: Water-droplet-removal structure 3: Wettability gradient between the inner (hydrophobic) and outer (hydrophilic) area eliminates water droplets from the sensing area.

Fig. 5 shows the fabricated device. A microgap of 8 μm was confirmed under a 120 μm thick porous ceramics cover. The formed microgap is larger than the thickness of sacrificial Ti layer. This may be caused by the deformation of the porous ceramics during drying at 300 ºC.

2.4 Water-droplet-removal structure 3

Water-droplet-removal structure 3 is shown in Fig. 6. This structure uses wettability gradient between the inner (hydrophobic) and outer (hydrophilic) area of the H_2 sensor to eliminate water droplets from the sensing area. If there is a sufficient wettability gradient, water droplets move toward a more hydrophilic area.

To generate the wettability gradient, a photochromic compound is deposited on a super-water-repellent surface. The photochromic compound (malachite green carbinol base, i.e. 4,4'-bis (dimethylamino) triphenylmethane leucohydroxide) is synthesized as follows [3]: Phenyl lithium is added to a THF solution of Michler's ketone in a water-free atmosphere. Then, water is added to stop the reaction of phenyl lithium with Michler's ketone and substitute lithium with hydrogen. The product solution is separated from the water phase and purified by dehydration and recrystallization. The chemical structure of the product is confirmed by ^{1}H-NMR.

As the undercoat of the photochromic compound, a super-water-repellent surface is prepared by coating the sensor surface with a mixture of Cytop and SiO_2 particles. Subsequently, the substrate is dipped in a dichloromethane solution of 2 wt% photochromic compound for 10 s, and then raised at 2 mm/sec. The substrate is dried in the dark at room temperature, and then exposed to gray-scale UV light to generate the wettability gradient.

3. EVALUATION

3.1 Water-droplet-removal structure 1

The effect of the water-droplet-removal structures was confirmed by exposing the fabricated devices to a highly humid air generated from hot bubbling water or by directly dropping water to the devices. The behavior of the water droplets was observed with an optical microscope.

Fig. 7 shows the optical micrograph of the water-droplet-removal structure 1 under evaluation. The surrounding area was filled with water, whereas the inner area repelled the water. The maximum diameter of the water droplets on the inner area was smaller than 100 μm. Larger water droplets were absorbed by the porous ceramics. This structure has some effect of removing water droplets from the inner sensing area, but is not effective to small water droplets.

3.2 Water-droplet-removal structure 2

Fig. 8 shows the optical micrograph of the water-droplet-removal structure 2 under during evaluation. Water droplets were injected into the gap directly by a micro pipet. Any water droplet is not observed with the optical microscope. Water can be absorbed quickly by the porous ceramics without leaving behind visible residual water. Because the gap between the water-repellant polymer and the porous ceramics is as small as 8 μm, this structure can remove any water droplets larger than 8 μm in height.

3.3 Water-droplet-removal structure 3

First, the photochromic compound film on the super-water-repellent undercoat was exposed to UV light from a high pressure mercury lamp at different doses, and the change of wettability was observed. Fig. 7 shows water droplets on the coating before and after UV exposure. The dose of UV light is 4000 mJ/cm^2 at a wavelength of 365 nm. The contact angle changed from 157.9 ° to 72.8 ° by UV exposure. Fig. 8 shows the relationship between UV light dose and water contact angle. It was found that the contact angle could be controlled by the UV light dose, suggesting possibility to make the wettability gradient by gray-scale UV exposure.

Next, the effect of the water-droplet-removal structure was confirmed by a similar method as mentioned in Section 3.1. However, the condensed droplets did not move outside, and the whole surface rather seemed to be hydrophilic. This indicates that the wettability gradient was scarcely created. We will investigate an appropriate dose and gradient of UV light to create the wettability gradient sufficient to drive water droplets.

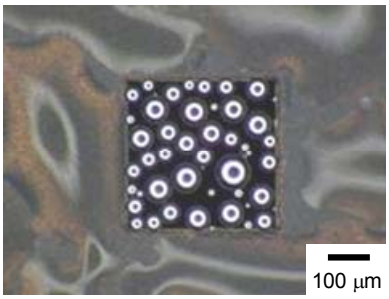

Fig. 7: Remaining water droplets on water-droplet-removal structure 1.

Fig. 8: No visible residual water droplet in the microgap on water-droplet-removal structure 2 just after injection of water droplets.

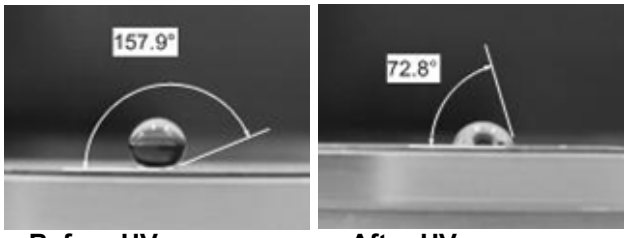

Fig. 9: Water droplets on photochromic compound deposited on super-water-repellent undercoat before and after UV exposure.

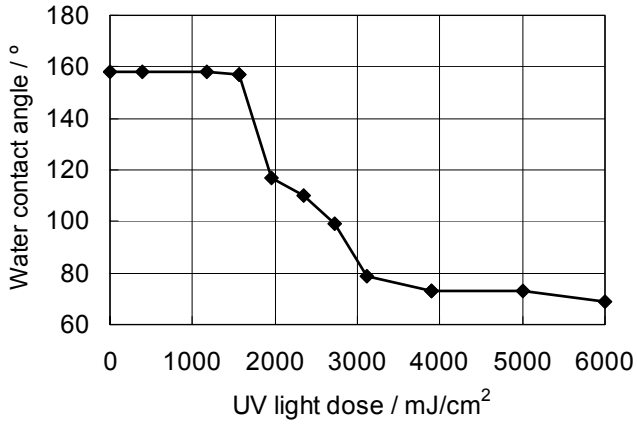

Fig. 10: UV light dose dependency of water contact angle on the photochromic compound coating.

4. CONCLUSION

This study aimed at the development of technology to passively remove condensed water droplets from a heat transfer type H_2 sensor. Three methods were investigated: (1) water-repellent coating, (2) water absorption into a suspended porous membrane over the sensor surface and (3) water droplet elimination driven by wettability gradient. A developing H_2 sensor was used as a platform for water-droplet-removal structures.

By preliminary evaluations, it was found that water droplets smaller than ca. 100 μm cannot be completely eliminated by method (1), whereas no visible water droplet was left by method (2). Method (2) is more effective for water droplet removal than method (1). For method (3), photochromic compound film on the super-water-repellent undercoat, which changes its wettability by UV exposure, was used. We confirmed that contact angle could be controlled by the UV light dose, but could not confirm the actuation of a water droplet by wettability gradient. Further work on the modification of the wettability gradient by using a photochromic compound is in progress.

ACKNOWLEDGEMENT

This study was partly performed within the New Regional Consortium R&D Program supported by the Japanese Ministry of Economy, Trade and Industry. The synthesis of malachite green carbinol base was conducted through Center for Integrated Nanotechnology Support, Tohoku University. We appreciate Dr. Shoji and Prof. Ueda for their substantial cooperation in the synthesis.

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