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Sensing properties for a microhydrogen sensor with modified palladium film

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ABSTRACT

A microhydrogen gas sensor platform was fabricated by a MEMS process. A nano-bumpy structure was produced using a polystyrene aqueous suspension to develop the surface areas of the sensing area (palladium thin film). The palladium film was deposited on a fabricated platform by a radio frequency magnetron sputtering. A cross section of each AFM image was analyzed to determine the mean surface roughness. The root-mean square roughness of the 1-layer nano-bumpy Pd structure and 2-layers nano-bumpy Pd structure were 9.07 nm and 13.1 nm, respectively, whereas that of the Pd thin film was 0.98 nm. The sensitivities of the Pd thin film sensor, mono-layer nano-bumpy sensor and double-layers nano-bumpy sensor at hydrogen gas concentrations of 2000 ppm was 0.638%, 1.045% and 1.511%, respectively.

1. Introduction

Hydrogen fuel cells [1] are electrochemical devices that convert chemical energy directly to electrical energy and emit no greenhouse gases. The use of hydrogen fuel cells, however, has raised many safety issues including the consequent detection of potentially hazardous concentrations of hydrogen gas.

Among hydrogen sensitive materials, palladium (Pd) has the unique property of interacting with hydrogen gas. A change in the partial pressure of hydrogen gas determines the physical properties of Pd, such as the mass, volume and electrical resistance, due to the formation of Pd–H hydride. Nanostructures are expected to play important roles in sensor technologies. Surface effects, small-size effects and even quantum effects severely affect the physical and chemical properties of nano-sized materials. Recently, a nanoscale hydrogen sensor was proposed. Many studies have developed sensitive nanostructured materials for hydrogen gas sensor applications [2–8] over a wide concentration detection region with short response times (less than a few min). The detection of low hydrogen concentrations (parts per million (ppm)) is essential for hydrogen sensors with the dynamic range of the sensor range extending to the explosion limit. Nanostructured Pd can have a lower hydrogen detection limit, owing to its very high surface-to-volume ratio.

There have been many researches about gas sensors with nano-structured films utilizing nano-porous templates such as di-block copolymers [9], anodized aluminum oxide (AAO) [10–13], and poly-styrene (PS) nano-beads [14–16]. In this study, a multi-layered microhydrogen gas sensor platform was fabricated using a MEMS process. A nano-bumpy Pd structure was fabricated using polystyrene (PS) nano-beads to increase the surface areas of Pd film, which had been deposited on the fabricated platform by radio frequency (R.F.) magnetron sputtering. Surface morphologies of the nano-bumpy Pd films were investigated and a hydrogen sensing measurement was performed for the fabricated sensor.

2. Experimental

The multi-layered microhydrogen sensor platform was designed as a dimension of 5.0 mm × 4.0 mm and fabricated using a MEMS process for reducing the power consumption [17]. To improve its thermal efficiency, a sensing layer was deposited in the middle of the platform, and a platinum (Pt) thin film was patterned for the sensing electrodes and micro heater. The entire fabrication process was accomplished using three masks for the photolithography steps. These were to develop the gas sensor fabrication process for mask micro-heater/electrode, passivation layer, and bulk micromachining pattern. The electro-thermal characteristics of the fabricated micro sensor platform were evaluated by the temperature coefficient of resistance (TCR) value of micro-heater. After the heater voltage was applied, the operating temperature of the H_2 sensor was calculated with the TCR value. The operating temperature of the micro heater was positively correlated with the heater voltage [17].

An aqueous suspension of 100 nm diameter polystyrene beads (Fluka Analytical) was used to fabricate the nano-bumpy Pd structure. A drop of the suspension was placed on the MEMS platform using a pipette. Before spin-coating the suspension on the platform, the platform was treated with O_2 plasma using a microwave plasma etcher (KVET-i2000L, KVT). The O_2 plasma pretreatment at an RF

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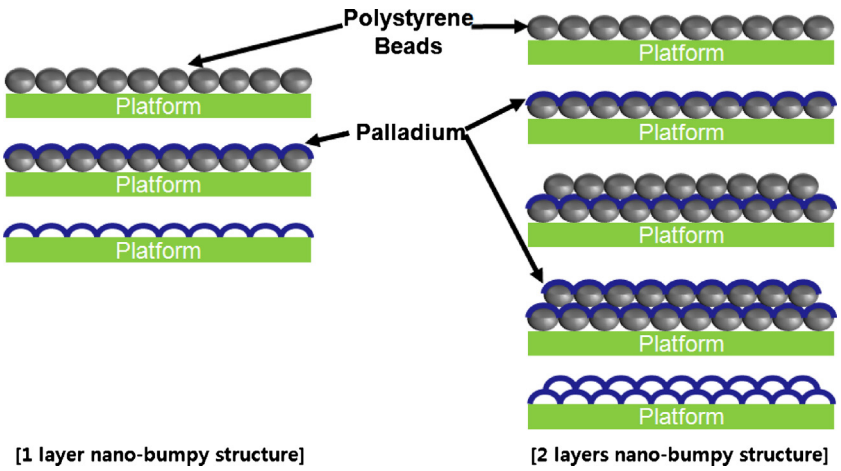

Fig. 1. Flow chart for fabrication of the nano-bumpy Pd structure.

power of 100 W for 5 min made the substrate surface hydrophilic. To deposit a monolayer, the sample was spun by a spin coater at a speed of 1500 rpm for 30 s. The samples were then dried for 6 h in a dry box at room temperature.

After spin coating, Pd was deposited on the coated platform (nano-bumpy sensor) by R.F. magnetron sputtering. At the same time, Pd thin films were deposited on an uncoated platform (thin film sensor). The sputtering conditions were at a pressure and input power of 1.2×10^{-2} Torr and 25 W, respectively. The deposited Pd film was patterned through a metal mask. The area of the patterned Pd was 2700 μm × 500 μm with a thickness of approximately 50 nm. To improve the sensor characteristics, a double-layer nano-bumpy structure was fabricated by depositing 25 nm of palladium on the PS beads, re-coating with PS beads, and depositing another 25 nm of palladium. After patterning the Pd film, the nano-bumpy sensor was heated in air at 550 °C for 60 min to burn out the polymer nano-spheres. The fabricated H_2 sensors were a Pd thin film sensor (T–H_2 sensor), a mono-layer Pd nano-bumpy sensor (N1–H_2 sensor) and a double-layers Pd nano-bumpy sensor (N2–H_2 sensor). Fig. 1 shows a flow chart for the fabrication of the nano-bumpy Pd structure.

The surface morphology of the nano-bumpy Pd structure was observed by field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi). Atomic force microscopy (AFM, Autoprobe CP, PSI) was used to estimate the surface morphology and root-mean square roughness (RMS) over a $1.0 \times 1.0\ \mu m^2$ area. The microhydrogen sensors were tested in a flow chamber designed for gas response testing. All data acquisition was controlled using a PC equipped with a digital multimeter (Keithley 2100). The sensitivity was defined by Eq. (1):

$$R_s = \frac{\Delta R}{R_0} \times 100\,(\%) = \frac{R_g - R_0}{R_0} \times 100\,(\%) \quad (1)$$

where R_0 and R_g are the H_2 sensor resistances in nitrogen and after hydrogen gas injection, respectively. The hydrogen gas concentration ranged from 25 to 5000 ppm.

3. Results and discussion

Fig. 2 shows the coated polystyrene beads on the micro-platform. The coated polystyrene beads consisted of closed packing nanospheres. The coated platform is a monolayer of nanospheres. Fig. 3 shows the 40° tilt view images of the mono-layer nano-bumpy Pd structure on the platform before and after heat treatment. The nano-bumpy Pd structure with closed packing was observed on the platform (a) and the shape of the structure was retained after heat treatment (b). The figure showed no holes in the nano-bumpy Pd structure. Each cell was connected to its neighbors with open channels. Fig. 4 shows a 40° tilt and plan view images of the double-layers nano-bumpy Pd structure on the platform. A nano-bumpy Pd structure with closed packing was observed at the bottom layer. The shape was maintained in the top layer of the nano-bumpy Pd structure.

AFM was performed to examine the surface morphology and measure the RMS roughness of the Pd thin film, the nanoporous Pd, mono-layer and double-layers nano-bumpy Pd structure. Fig. 5

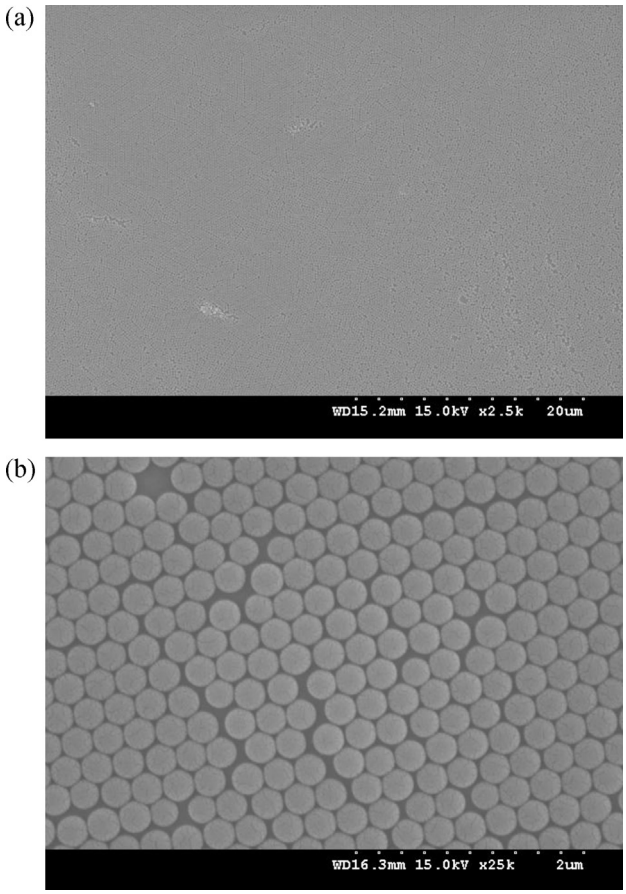

Fig. 2. The coated polystyrene beads on the sensor platform: (a) 2500× and (b) 25,000×.

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