

A MEMS-type Micro Sensor for Hydrogen Gas Detection

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ABSTRACT

In this study, a highly sensitive hydrogen gas sensor of the multi-layer and micro-heater type was designed and fabricated using a microelectromechanical system (MEMS) process. The dimension of fabricated hydrogen gas sensor was 5 mm×4 mm and the sensing layer of palladium was deposited in the middle of the device. The sensitivity (R_s) was 0.271, 0.378 and 0.638% at the hydrogen concentrations of 500, 1,000 and 2,000 ppm, respectively. Also, the gas sensitivity showed a good positive linearity with the increase of hydrogen concentration. The effect on the insertion of anodic aluminum oxide (AAO) layer under the Pd-thin film was investigated. The sensitivity for the Pd-AAO layer was about 0.373, 0.532 and 0.783% at hydrogen concentrations of 500, 1,000 and 2,000 ppm, respectively. The sensitivity of the Pd-AAO layer improved with respect to the pure Pd-thin film due to the nanoporous nature of AAO.

Keywords: MEMS, hydrogen sensor, palladium, anodic aluminum oxide, thin film

1 INTRODUCTION

Palladium (Pd), one of the platinum group metals, has applications in hydrogen sensor, storage, generation, and catalysis [1-8]. Because hydrogen has a high solubility and diffusivity for Pd metal, it may easily penetrate into the bulk of a Pd catalyst during a surface reaction [9]. The larger surface area of Pd catalytic Pd metal may improve the available adsorption sites on the metal surface. The response times of these materials are determined by the dynamic equilibrium process between the hydrogen-containing gas and the Pd-H system. Efforts to enhance the response time of Pd-based hydrogen sensors have focused on using thinner Pd or Pd alloy films [10-12]. Therefore, a key step in the design process of these sensors is to develop an understanding of the surface-limiting interactions that will undoubtedly play a role in the response time dynamics for sensor devices exposed to ambient conditions.

In this study, highly sensitive hydrogen gas sensors were fabricated using a MEMS process. To increase the surface area of the sensing layer, the nanostructure of AAO layer was inserted on the sensor platform prior to the deposition of Pd film. The gas sensing characteristics for hydrogen gas are analyzed based on the sensing characteristics of the fabricated H₂ sensors.

2 EXPERIMENTAL

The multi-layer type H₂ sensors were designed with chip and membrane sizes of 5.0 mm × 4.0 mm and 2.1 mm × 1.5 mm, respectively. In order to improve its thermal efficiency, a sensing layer (Pd thin film) was deposited in the middle of the platform. The platform was fabricated in the following sequence: The silicon nitride (Si₃N₄) layer (2.0 μm) was deposited using low-pressure chemical vapor deposition (LPCVD) on a p-type silicon (Si) wafer for membrane formation and silicon micro machining. The Pt thin film (2,000 Å) was deposited by sputtering and patterned by reactive ion etching (RIE) to form the micro heater and sensing electrodes. A silicon dioxide (SiO₂) layer (5,000 Å) was deposited by plasma-enhanced CVD (PECVD) and patterned to form a passivation layer. Finally, the platform was fabricated through silicon bulk micromachining and wafer dicing.

The AAO layer were fabricated using pure aluminum (Al) foils (99.999 %) with a thickness of 200 μm. Prior to anodizing, Al foils were electro-polished in order to achieve a smooth surface. The electro-polishing was performed at a constant current of 1.5 A below 25°C for 30 s in a mixture solution consisting of perchloric acid (HClO₄) and ethanol (C₂H₅OH) at a volume ratio of 1:4 with magnetic stirring. The polished Al foils were cleaned with acetone and dried. The AAO layer was fabricated by two-step anodization process. The first anodization was carried out at a constant voltage of 40 V in 0.3 M oxalic acid (C₂H₂O₄) solution at 5°C for 30 min; a platinum cathode was used for the process. Then, a uniform pattern on the aluminum surface was revealed after immersing the samples in a bath of 1.8%-chromic acid (CrO₃)/6%-phosphoric acid (H₂PO₄) at 60°C for over 1 h that removed the first alumina layer. The AAO layer was developed uniformly after a second anodization using the same parameters as those used in the first anodization. Finally, a pore widening process was carried out in 0.1 M phosphoric acid at 30°C with pore diameters of around 50 nm. The sensing layer of Pd was deposited on the AAO layer by R.F. magnetron sputtering. The thickness of the deposited Pd was about 50 nm. The AAO layer coated with Pd was cut by 2,700 μm × 500 μm and attached onto the platform (Pd-AAO sensor). For comparison of sensing properties between the Pd-AAO layer and pure Pd layer, the Pd thin films with the same thickness and dimension were also deposited onto the sensor platform using a metal mask (pure Pd sensor).

The crystalline structure of the Pd thin film was characterized using X-ray diffraction (XRD) with Cu-K_α

radiation (RIGAKU DMAX-III A). The surface and cross-section morphology of the deposited Pd was acquired using field emission scanning electron microscopy (FE-SEM, Hitachi S-4300) and transmission electron microscopy (TEM, Tecnai G2 F30), respectively.

The sensing properties of fabricated sensors were tested in a flow chamber designed for hydrogen gas response. Nitrogen gas was injected continuously and the sensor was exposed to a hydrogen gas flow. After the gas test, the hydrogen gas injection was stopped and cleared by the nitrogen gas. Mass flow controllers were used to set the hydrogen gas and nitrogen gas flow rates. All data acquisition was controlled by a PC equipped with a digital multimeter (Keithley 2100). The sensitivity was defined as shown in Eq. (1):

$$\text{Sensitivity} = \frac{R_g - R_0}{R_0} \times 100(\%) \quad (1)$$

where R_0 and R_g are the H_2 sensor resistances in nitrogen and after hydrogen gas injection, respectively. The hydrogen gas concentration was set in the range of 500 ppm ~ 5000 ppm

3 RESULTS AND DISCUSSION

The crystalline structure of the deposited Pd was confirmed by XRD. Figure 1 shows the XRD peaks of the deposited Pd. The diffraction angles at $2\theta = 40.13^\circ$ and 46.37° corresponded well to the (111) and (200) planes in the cubic structure of the Pd. The diffraction patterns of the Pd showed good conformity with the diffraction data from JCPDS 46-1043.

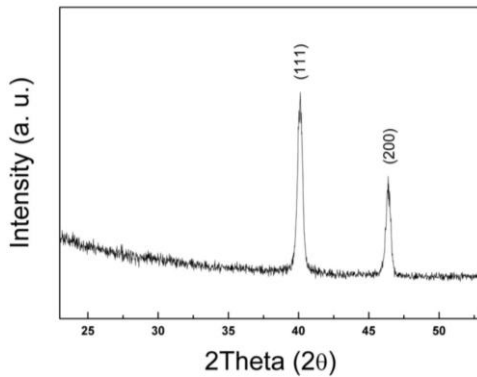


Figure 1. The X-ray diffraction pattern of the deposited Pd film.

Figure 2 shows a cross-sectional TEM image of the deposited Pd. The thickness of the deposited Pd was approximately 50 nm. Figure 3 (a) shows the surface image of Pd film deposited on the AAO layer. The AAO layer had pore diameters of about 50 nm with 80 nm interpore distances. Also, the morphology of the deposited Pd with 50 nm thickness on the AAO layer is almost the same as that of the AAO layer. Figure 3 (b) shows the surface image of the Pd film on the Si wafer. The image indicates a densely packed columnar structure with a grain size of

about 20 nm that had a smooth surface. Compared with the Pd thin films on Si wafer, the surface area of Pd film on the AAO layer is very high with a nanoporous structure.

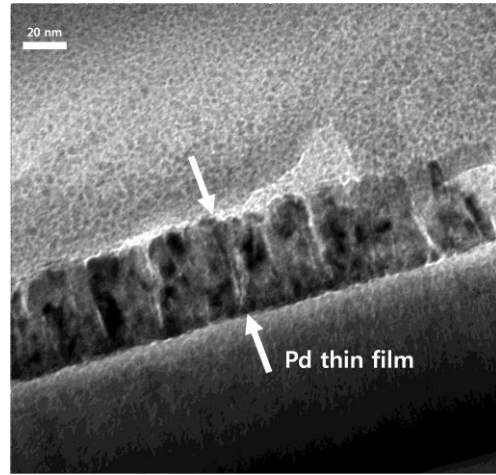
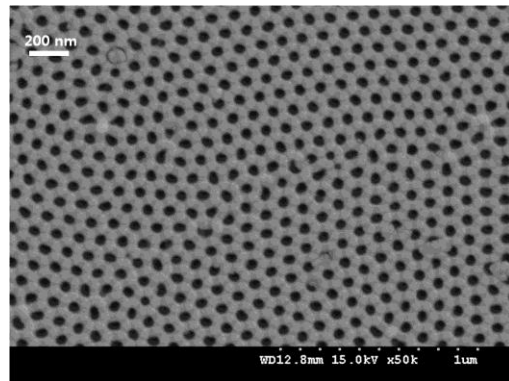
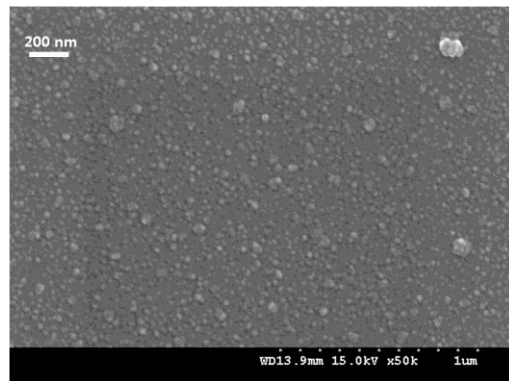


Figure 2. The cross-sectional TEM image of Pd thin film ($\times 200,000$).



(a)



(b)

Figure 3. The FE-SEM images of (a) the Pd deposited on AAO template and (b) the Pd film on the Si wafer ($\times 50,000$).

Figure 4 shows the transient response of the pure Pd sensor as a gas exposure time at hydrogen concentrations ranging from 500 to 2,000 ppm at a heater voltage of 4.0 V. At hydrogen concentrations of 500, 1,000 and 2,000 ppm, the R_s of the H_2 sensor was 0.271, 0.378 and 0.638 %, the response time was 35 seconds at 1,000 ppm, and the recovery time (defined as that required for 90 % of the full signal change) was 82 seconds. The sensitivity, R_s of the pure Pd sensor at an applied heater voltage of 4.0 V and at various hydrogen gas concentrations is shown in Figure 5. The sensor showed a very high sensitivity and good positive linearity with concentration.

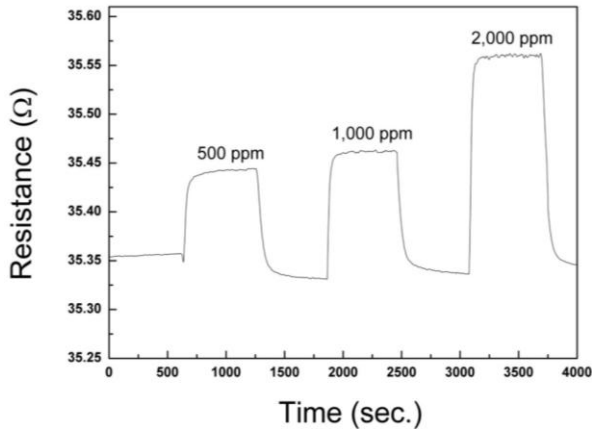


Figure 4. The transient response of pure Pd sensor at various H_2 concentrations.

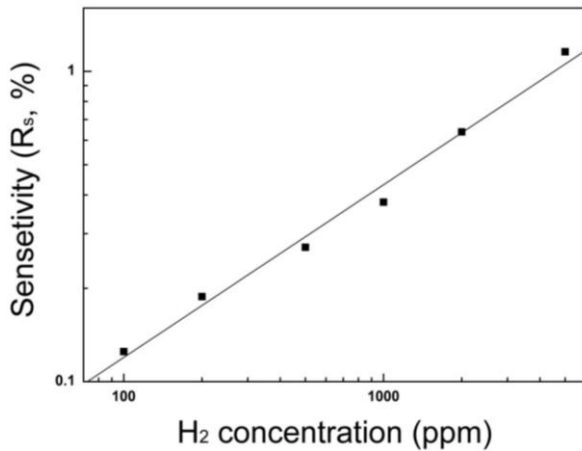


Figure 5. The sensitivity (R_s) of pure Pd sensor with H_2 concentration.

Figure 6 shows the R_s and response time for the Pd-AAO sensor at various heater voltages at a hydrogen gas injection of 2000 ppm. After heater voltages of 0 ~ 5 V were applied, the sensitivity of the H_2 sensor was 0.783, 0.738, 0.526, 0.392, 0.318 and 0.258 % and the response time was 42, 40, 39, 41, 46 and 50 seconds, respectively. With increasing applied voltage, the sensitivity of the A- H_2 sensor was decreased. The response time was shorter than that of other heater voltages at a heater voltage of 2.0 V (i.e. 70°C). Because of improved surface area, the Pd-AAO

sensor at 0 V showed the higher sensitivity and longer response time than the pure Pd sensor. With increasing the operating temperature of Pd-AAO sensor, the adsorption energy decreased and the adsorption rate increased. Therefore, the response time became fast. In addition, the desorption energy also decreased with increasing operating temperature and the desorption rate was efficiently high at above 2 V. Because the adsorption and desorption of hydrogen on a Pd surface at high temperatures (> 2 V) occurs at the same time, the response time would be expected to be longer than at 2 V.

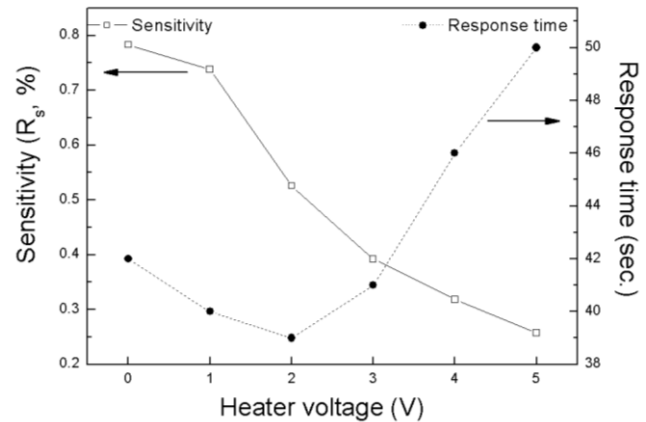


Figure 7. The sensitivity and response time of Pd-AAO sensor with heater voltage at 2,000 ppm hydrogen gas injection.

The sensitivity of Pd-AAO sensor at various hydrogen gas concentrations is shown in Figure 8. For comparison, the sensitivity for a pure Pd sensor was superimposed. At hydrogen gas concentrations of 500, 1,000, 2,000 and 5,000 ppm, the sensitivities of Pd-AAO sensor were 0.373, 0.532, 0.783 and 1.507%, respectively, and higher than those of pure Pd sensor. The increased sensitivity for Pd-AAO layer was attributed to the increased active surface area between the H_2 gas molecules and nanoporous Pd surface.

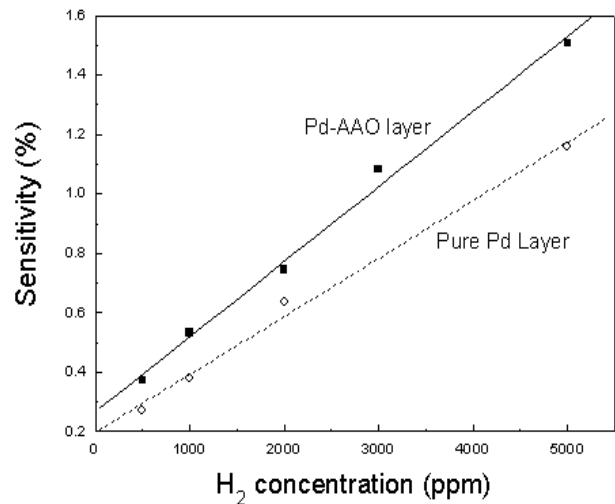


Figure 8. Sensitivity variations of H₂ sensors with hydrogen concentration.

4 CONCLUSION

Highly sensitive hydrogen gas sensors were fabricated using a MEMS and an AAO process. The observations by a TEM, FE-SEM and AFM confirmed the uniform nanocrystalline structure of the deposited Pd thin film and nanoporous Pd structure of Pd-AAO layer. The Pd-based sensor showed a very high sensitivity and good positive linearity with hydrogen concentration. The gas sensitivity and response properties showed different behaviors for the palladium film deposited on the AAO layer. At hydrogen concentrations of 500, 1,000 and 2,000 ppm, the sensitivity was about 0.373, 0.532 and 0.783 %, respectively. It was concluded that the sensitivity of the Pd-AAO layer increased with respect to the pure Pd-thin film due to the nanoporous nature of AAO.

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