

Fabrication of a Hydrogen Sensor using Palladium-coated Silver Dendrites Formed Electrochemically

Shin-Bok Lee¹, Ho-Young Lee¹, Eunsongyi Lee², Wooyoung Lee², and Young-Chang Joo^{1,*}

¹Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

²Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

(received date: 24 November 2009 / accepted date: 22 July 2010)

Here, we report a cost-effective method for making palladium-coated silver (Ag) dendrites for hydrogen sensing. Ag dendrites, 50–150 nm in diameter, are made through electrochemical migration in a micro-electrochemical cell. They are then coated with a 200-nm-thick palladium (Pd) thin film. The hydrogen sensor made of palladium-coated Ag dendrites showed better hydrogen sensing characteristics than ones made of a pure Pd film. This is due to the large surface area of the Ag dendrites. Heat-treatment made the hydrogen sensing curve more stable, which is attributable to an alloying effect between Pd and Ag.

Keywords: nanostructured materials, hydrogen absorbing materials, coating, electro chemistry, electrical conductivity/resistivity

1. INTRODUCTION

Hydrogen has been regarded as a source of clean energy and is the most attractive as an energy source in the future. For the safe use of hydrogen, it is necessary to develop reliable hydrogen gas sensors that work at room temperature and are smaller size, have high sensitivity, real-time detection, a simple control system and ultra-low power consumption. Many studies of this topic employed metal palladium (Pd) as the active sensing material due to its unique property of hydrogen absorption. Metal Pd, however, has some undesirable properties. To be specific, the phase transition from the palladium phase to the β -phase (palladium hydride) occurs at low H_2 partial pressure (down to 7 Torr) at 300 K, which is an irreversible process [1]. In addition, since metal Pd can easily absorb H_2 , absorption saturation occurs even at low H_2 pressure, around several tens of Torr [2]. Pd films are likely to peel off under repeated exposure to hydrogen because of the large internal stress exerted on the film due to volume expansion from hydrogen absorption.

To overcome these drawbacks, Pd alloys like Pd-Au, Pd-Ni and Pd-Ag are being considered to replace metal Pd. Pd-Ag alloy has drawn much interest because of its faster response time and lower detection limit [2]. It is reported that Ag can form an alloy with Pd at various atomic ratios, and the H_2 absorption capacity of Pd-Ag alloy is generally lower than

that of pure Pd [2]. Pd-Ag alloy has better mechanical strength than Pd metal, which can help it overcome the peel-off problem of pure Pd [3].

The magnitude of response and response time of gas sensors can be enhanced by controlling the morphology of their sensing material, giving it a large surface area on the nano-scale. For this reason, many kinds of structures are considered. MEMS structures, silicon nanowires, nanowire using AAO (anodized aluminum oxide), carbon nanotubes, nano electrodes [4] and nano fibers are investigated to improve the performance of hydrogen sensors. However, the fabrication methods are sophisticated and expensive.

We developed a cost-effective method for fabricating of a hydrogen sensor at room-temperature using Ag dendrites formed by electrochemical migration phenomenon. Electrochemical migration is the growth of conductive metal filaments by the migration of metal ions [5–7]. When DC bias is applied to metal electrodes under high humidity, the anode electrode becomes ionized metal ions. The ions diffuse from the anode to cathode through the electrolyte under the induced electric field. The ions are reduced to form a metal dendritic filament that grows from the cathode toward the anode. Electrochemical migration is well known as the cause of failure in electronic packaging when it is exposed to a humid environment. We first demonstrate that this method can be used to make the hydrogen sensing material Pd-Ag alloy dendrite. Ag dendrites can grow easily just in a few minutes under a water-dropped condition using the electrochemical migration phenomenon. Then, the Pd is coated for

*Corresponding author: ycjoo@snu.ac.kr

Pd-Ag alloying, and hydrogen sensing performance is evaluated.

2. EXPERIMENTAL

Micro-electrochemical cells consisting of an anode (Ag), deionized water, and a cathode (Ag) were used for this experiment. Figure 1 is the schematic diagram of the fabrication procedure. One micron thick Ag electrodes, 1 μm thickness, were formed on an oxidized Si wafer using hard-mask patterning through thermal evaporation. The spacing between the two electrodes was 100 μm . A drop (1 μl) of deionized (D.I.) water was supplied to the space between the two electrodes using a micro-pipette. Then, the two electrodes were covered with a glass-chip to complete a micro-electrochemical cell. A DC bias voltage of 0.8 V was applied between the two electrodes for 2-3 minutes to form Ag dendrites. After the formation of the Ag dendrites, a 200 nm Pd film was deposited by evaporation on the area where Ag dendrites were formed.

The hydrogen sensing performance was monitored using a test system consisted of three subsystems: the chamber, gas supply unit, and data acquisition equipment. A 500 sccm constant flow of nitrogen was used as the carrier gas to achieve a baseline. Constant flow of nitrogen-hydrogen gas mixture with different concentrations and 500 sccm was used as the test gas. All feed flow rates were measured and controlled with mass flow controllers (MFCs). To achieve a real-time measurement of electrical resistance with respect to hydrogen concentration, constant current was applied to

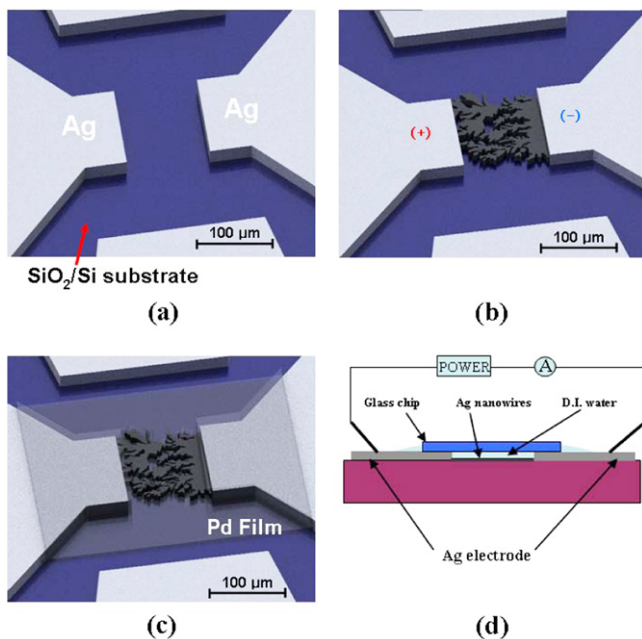


Fig. 1. Schematic diagram of the fabrication procedure (a) to (c), and cross-section view of micro-electrochemical cell (d).

the device and the voltage change was recorded by a data acquisition system every second. The magnitude of response (S) to hydrogen gas can be described by, $S = (R - R_0)/R_0$, where R_0 is the initial resistance before inducing hydrogen gas. S was calculated by measuring electrical resistance (R) change when nitrogen gas flow was switched to the nitrogen-hydrogen gas mixture. The time needed for the sensor to reach 90 % of the total resistance change is defined as the response time.

The samples were annealed at 300 $^{\circ}\text{C}$ for 10 h under high vacuum to investigate the influence of alloying on the hydrogen sensing performance. An H_2 sensor with a pure 200 nm thick Pd film without Ag dendrites was also fabricated with the same structure to compare sensing characteristics.

3. RESULTS and DISCUSSION

When a DC bias is applied between two Ag electrodes in a micro-electrochemical cell, the anode (Ag) becomes unstable and ionized, forming Ag^+ ions at the anode/ H_2O interface. The Ag^+ ions migrate through the D.I. water to the cathode due to the potential difference between the anode and the cathode. At the cathode $\text{Ag}/\text{H}_2\text{O}$ interface, Ag^+ ions are reduced back to metallic Ag and as a consequence, form Ag dendrites. It was observed by real-time monitoring that Ag dendrites easily grow in a few minutes using this electrochemical migration method [5-8]. Figure 2(a) shows an SEM image of the Ag dendrites exhibiting dendritic character. In addition, Figure 2(b) demonstrates a typical SEM image of Ag dendrites, exhibiting a single morphology with uniform featherlike branches. The individual dendrite width is about 70 nm and is composed of symmetrical branches and leaves.

Initial resistance of the specimen is increased by forming an Ag dendrite from 0.10 to 0.28 Ω . The Pd film on the Ag dendrite shows discontinuous morphology. This discontinuous morphology increases the resistance of the specimen. After heat treatment of Pd-Ag dendrite, the resistance increased to 0.71 Ω because of the alloy effect. The surface roughness of the fabricated specimen was measured by atomic force microscopy (AFM). It increased by forming Ag dendrites

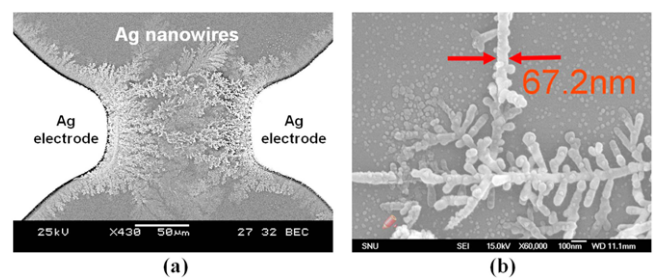


Fig. 2. (a) SEM image of Ag nano-sized dendrites exhibiting a fractal character, (b) SEM image of dendrites formed by electrochemical method.

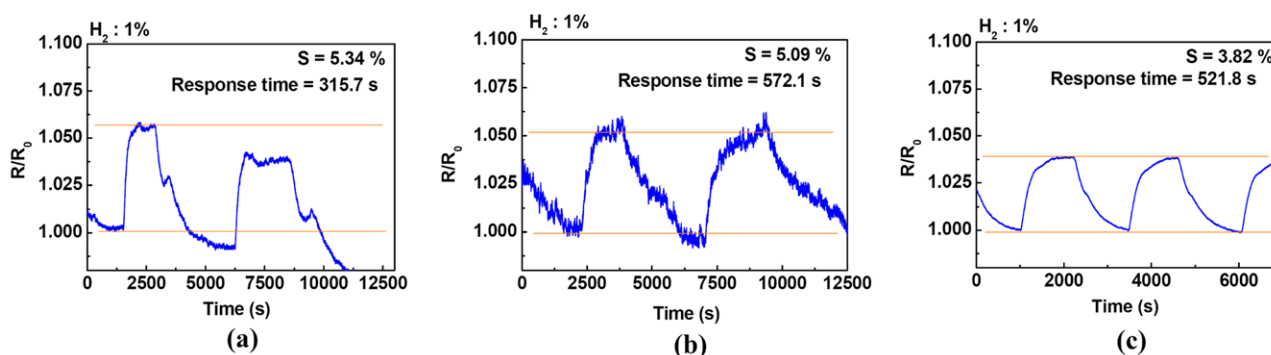


Fig. 3. (a) Hydrogen sensing response curve of Pd-coated Ag dendrites to 1 % hydrogen gas concentration, (b) Hydrogen sensing response curve of metal Pd film to 1 % hydrogen gas concentration, (c) Hydrogen sensing response curve of Pd-coated Ag dendrites heat-treated at 300 °C for 10 h under high vacuum ambient.

(2.51 to 25.7 nm), but the roughness of the Pd-Ag dendrite decreased after heat treatment (34.0 to 25.3 nm).

After the 200 nm thick Pd film was deposited onto the Ag dendrites, we observed the H₂ sensing characteristics of the device. Figure 3(a) shows the hydrogen sensing response curve of Pd-coated Ag dendrites between 1 % hydrogen gas and the baseline gas (99.999 % N₂) at room temperature. This hydrogen concentration is known from the condition of phase transition between α -phase and β -phase in Pd. To investigate the transition concentration of Pd-coated Ag dendrites and Pd, this condition was applied. The resistance of the sensor increases with increasing concentration of hydrogen. The magnitude of response and the response time of the Pd-coated Ag dendrites were 5.34 % and 315.7 s, respectively. But the hydrogen sensing curve shows decreasing behavior with time. At the start of the test, the base resistance decreased. After that, it saturated.

Figure 3(b) shows a typical sensing result of a 200 nm thick Pd film on a Si substrate. It is notable that the Pd thin film showed a longer response time (572.1 s) and somewhat lower magnitude of response (5.09 %) than those of Pd-coated Ag dendrites (315.7 s, 5.34 %), which is probably caused by their difference in surface area. It has been reported that a better hydrogen sensor with a faster response time could be achieved with a nano scale structure, because of the larger surface area [9].

Figure 3(c) shows the hydrogen sensing response curve of Pd-coated Ag dendrites that were heat-treated at 300 °C for 10 h under a high vacuum ambient (10⁻⁶ Torr). It was observed that the magnitude of response to hydrogen became smaller (3.82 %) and the response time became longer (521.8 s), but good reversibility and stability were achieved. It has been reported that heat treatment at 300 °C can make separated thin films of Pd and Ag into an alloy [10]. Because the H₂ absorption capacity of Pd-Ag alloy is generally lower than that of pure Pd [2], the magnitude of response (S) of the Pd-Ag alloy is lower than that of metal Pd under the same

hydrogen partial pressure (1 % hydrogen concentration).

It was reported that at low hydrogen pressures, the equilibrium hydrogen content in Pd increases with increasing hydrogen partial pressure [11]. But a subsequent region of pressure invariance, or plateau region is seen as hydrogen content increases. At this hydrogen pressure, the α -phase structure of Pd reaches maximum hydrogen solubility and the hydride phase (β -phase) begins to nucleate. After the α -phase has fully transformed into the β -phase, the hydrogen content in Pd increases with increasing hydrogen pressure again [11]. In case of Pd-Ag alloy, there is a complementary decrease in the hydrogen pressure over the plateau region with increasing silver content. The hydrogen content of the β -phase over the region of the α -phase to β -phase transformation also exhibits a complementary decrease [11].

Figure 4 shows the responses of Pd-Ag dendrite with heat treatment to 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5 % H₂ concentration. It was found that as the H₂ concentration increases, the magnitude of the response increases. Pd-Ag dendrite with heat treatment shows an increase in response time at 1.5% H₂ concentration.

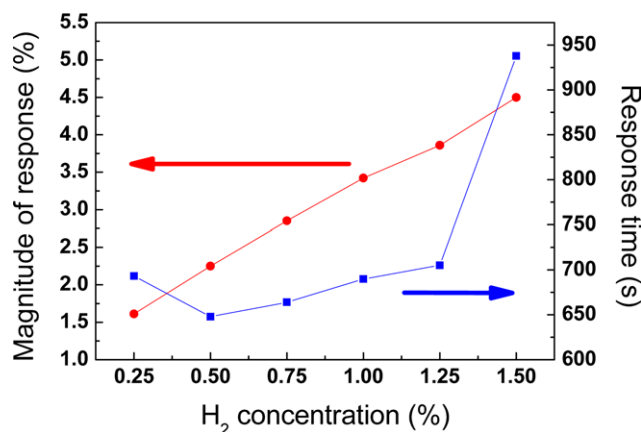


Fig. 4. Magnitude of response and response time (s) of Pd-Ag dendrite with heat treatment to 0.25 % to 1.5 % H₂ concentration.

These experimental results show that Pd and Pd-coated Ag dendrites without heat treatment have similar magnitude of response values, which are higher than that of Pd-coated Ag dendrites with heat treatment under 1 % hydrogen concentration. The reason why the magnitude of response of the Pd-Ag alloy is lower than others can be explained by the following: The magnitude of response is related to hydrogen absorption capacity. Most of the α -phase transformed into the β -phase at 1 % hydrogen concentration in both pure Pd and Pd-coated Ag dendrite, and the magnitude of response (hydrogen absorption capacity) of pure Pd is always higher than Pd-Ag alloy in the plateau region (1 % hydrogen concentration in this experiment) [11]. Moreover, since the Ag atoms in the Pd-Ag alloy does not react with hydrogen [2], the Ag atoms disturb hydrogen diffusion in the Pd-Ag alloy [12,13], which makes the diffusion rate slower, and consequently, makes the response time longer than Pd-coated Ag dendrites without heat treatment.

The Pd-coated Ag dendrites fabricated by the electrochemical method at room temperature with proper heat treatment are suitable as a hydrogen sensing material because their hydrogen sensing performance is excellent (high magnitude of response and good repeatability). Finally, they are cost-effective due to their easy processibility and short process time. It is expected that the optimization of Pd film thickness and heat treatment condition will enhance their hydrogen sensing performance even further.

4. CONCLUSION

A fabrication method for hydrogen sensors using Pd-coated Ag dendrites formed by an electrochemical method have been introduced for the first time. The produced sensors have a good magnitude of response, fast response time, high durability, and an especially low-cost/easy fabrication process. Pd-coated Ag dendrites showed shorter response times (315.7 s) and somewhat higher magnitudes of response

(5.34 %) than those of metal Pd thin films (response time: 572.1 s, magnitude of response: 5.09 %). This is due to the large surface area for hydrogen sensing, providing more surface reaction sites between the sensing material and hydrogen gas. Heat-treated Pd-coated Ag dendrites showed a more stable response curve at the change of hydrogen concentration. However, they showed a smaller magnitude of response (3.82 %) and a longer response time (521.8 s) than the untreated ones, which is probably due to the alloying effect.

REFERENCES

1. R. C. Hughes, W. K. Schubert, T. E. Zipperian, J. L. Rodriguez, and T. A. Plut, *J. Appl. Phys.* **62**, 1074 (1987).
2. M. Wang, and Y. Feng, *Sens. Actuator B-Chem.* **123**, 101 (2007).
3. J. Shu, B. P. A. Grandjean, A. Van Neste, and S. Kaliaguine, *Can. J. Chem. Eng.* **69**, 1036 (1991).
4. S. Mubeen, B. Yoo, and N. V. Myung, *Appl. Phys. Lett.* **93**, 133111 (2008).
5. W. Ready and L. Turbini, *J. Electron. Mater.* **31**, 1208 (2002).
6. B. Rudra and D. Jennings, *IEEE Trans. Reliab.* **43**, 354 (1994).
7. S.-B. Lee, Y.-R. Yoo, J.-Y. Jung, Y.-B. Park, Y.-S. Kim, and Y.-C. Joo, *Thin Solid Films* **504**, 294 (2006).
8. Y.-R. Yoo and Y.-S. Kim, *Met. Mater. Int.* **13**, 129 (2007).
9. S. K. Hazra, and S. Basu, *Sens. Actuator B-Chem.* **115**, 403 (2006).
10. T.-C. Huang, M.-C. Wei, and H.-I. Chen, *Sep. Purif. Technol.* **32**, 239 (2003).
11. F. A. Lewis, *The Palladium Hydrogen System*, Academic Press, London (1967).
12. H. Kurokawa, K. Bada, M. Koyama, M. Kubo, and A. Miyamoto, *Appl. Surf. Sci.* **244**, 636 (2005).
13. H. Barlag, L. Opara, and H. Zuhner, *J. Alloy. Compd.* **330-332**, 434 (2002).