Studies of Resistive-type Hydrogen-Sensitive Sensors Using Pd-Based Thin Films

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***Abstract*—Zigzag-shaped Pd-based thin films (pure Pd and Pd-SiO_2 mixture with thickness ranged from 10 nm to 100 nm deposited on cover-glass substrates were used to fabricate resistive-type hydrogen sensors. It is found that relative sensitivities are independent of the thin-film thickness and are 10%, 7.4%, 6.1%, and 5% for the pure-Pd sensor in 2%, 1.5%, 1%, and 0.5% H_2/N_2, respectively. However, its response time (t_a) is substantially influenced by the thin-film thickness for pure-Pd resistive-type sensor. t_a is measured with a thickness coefficient of 0.14 s/nm in 2% H_2/N_2 while it is 0.5 s/nm in 1% H_2/N_2. Compared to the pure-Pd sensor, the Pd-SiO_2 sensor has a shorter response time (20 s to 33 s) and a higher relative sensitivity (8.7% to 6.1%) in 1% H_2/N_2. In 3% H_2/N_2, relative sensitivity is even as high as 15.2% with a response time of 10 s.**

Keywords-hydrogen; resistive-type; sensitivity; sensorr

I. INTRODUCTION

Hydrogen has attracted attention as a clean energy carrier. However, it is volatile and explosive. Thus, a lot of efforts have been made to search for high performance hydrogen sensors to monitor hydrogen leak. This is required not only for better control of hydrogen-involved processes but also for health and safety. Various types of semiconductor hydrogen sensors have been reported [1]-[6]. Among them, resistive-type sensors with Pd thin film have been reported to give good H_2 sensitivity. Previous studies reveal that the sensing behavior is of two types, depending on whether the electric resistance is increased or decreased upon exposure to H_2. Our previous work [6] also concluded that the resistive-type sensor with the Pd-SiO_2 thin-film mixture exhibits much better sensing performance than that with the pure-Pd thin film did. However, the sensor reversibility was evaluated using testing gases with hydrogen concentration below 1% in N_2. In addition, a fixed 30 nm Pd-SiO_2 thin-film mixture or pure-Pd thin film was employed. No further effect of thin-film thickness on sensitivity and response time was investigated. In this work, the Pd-SiO_2 thin-film mixture was again successfully deposited upon a robust and low-cost cover-glass substrate. Various hydrogen-containing gases with concentration up to 3% in N_2 were used to study its sensing properties that will be compared to those of the pure-Pd thin-film. Besides, thin films with thickness ranged from 10 nm to 100 nm were also employed in the fabrication of resistive-type sensors. Effects of thin-film thickness on sensitivity and response time were then investigated. It is found from experimental results that the Pd-SiO_2 thin-film mixture really exhibits better sensing performance than that of the pure-Pd thin film. Experiments and measurements about the proposed resistive-type hydrogen sensor are described in following section. In Section III, experimental results including key merits, such as sensitivity and response time, are addressed. Finally, conclusions are drawn in Section IV.

II. EXPERIMENTS

Thin films of a pure Pd and a Pd-SiO_2 mixture were deposited on 18 mm × 18 mm × 0.17 mm cover-glass substrates by a thermal evaporator equipped with multiple tungsten boats. The background pressure of the thermal evaporator for deposition was 2×10^{-7} torr. The pure-Pd thin film was deposited at the rate of 72 nm /min. The Pd-SiO_2 mixture was deposited by co-evaporating Pd and SiO_2 at the rate of 80 nm /min. The thickness of the deposited thin film was monitored by a quartz crystal head real time. Fig. 1 shows geometric dimension of the resistive-type sensor fabricated in a zigzag-shaped microstructure with a total length of 53 mm. The cross-sectional area which the current flows through is 50 μm × t nm where t is the thickness of the deposited thin film. The sensing area of the resistive-type sensor is 53 mm × 50 μm. Since no other metals are required, our Pd-SiO_2 resistive-type sensor could be fabricated in a simple manner and at low cost. Besides, we found that surface morphologies between the pure-Pd and the Pd-SiO_2 thin films are quite different. That is, the Pd-SiO_2 thin film is indicative of porous-like morphology [7]-[8]. Hydrogen

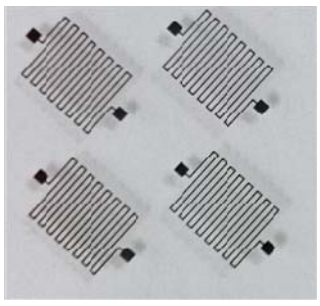

Figure 1. Schematic image of the Pd-based thin film used as a resistive-type hydrogen sensor with a sensing area of 53 mm × 50 μm.

 ISBN: 978-1-61208-543-2

detection was carried out using a custom-made flow-through test chamber made from stainless steel. A 500 ml/min constant flow N_2 was used as the carrier gas to achieve a baseline. It allows controlling the gas flow from N_2 to gas mixtures with various concentrations of 100 ppm to 3% H_2/N_2. The use of H_2 in N_2 is to realize the role of oxygen species on absorbing H atoms. Current-transient responses were measured by mounting the resistive-type sensors on a test fixture and using a semiconductor parameter analyzer. Then the dynamic current at a constant voltage and hence the electric resistance change recorded every 5 s were obtained as sensing signals.

III. RESULTS AND DISCUSSION

Fig. 2 shows the transient current response of the pure-Pd sensor to the introduction and removal of various hydrogen-containing gases biased at 2 V. In a N_2 ambience, a resistivity of 1.66×10^{-5} Ω·cm was measured according to a thin-film thickness of 16 nm together with the zigzag-shaped dimension. When the pure-Pd thin film is exposed to a hydrogen-containing gas, hydrogen molecules are dissociated into hydrogen atoms, which are absorbed in the interstitial sites of the Pd lattice. The electric-resistance increment and hence the increase in resistivity can be attributed to carrier scattering due to the incorporated hydrogen atoms. On the contrary, by replacing the hydrogen-containing gas with N_2, desorption of hydrogen atoms gives rise to the reduction of the resistivity of the pure-Pd thin film. Then, the relative sensitivity (S_H) is obtained according to experimental results shown in Fig. 2. It is found that S_H are

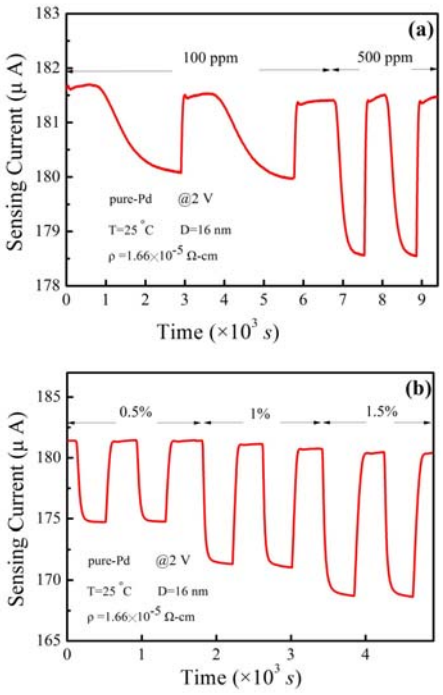

Figure 2. Transient current response of the pure-Pd sensor.

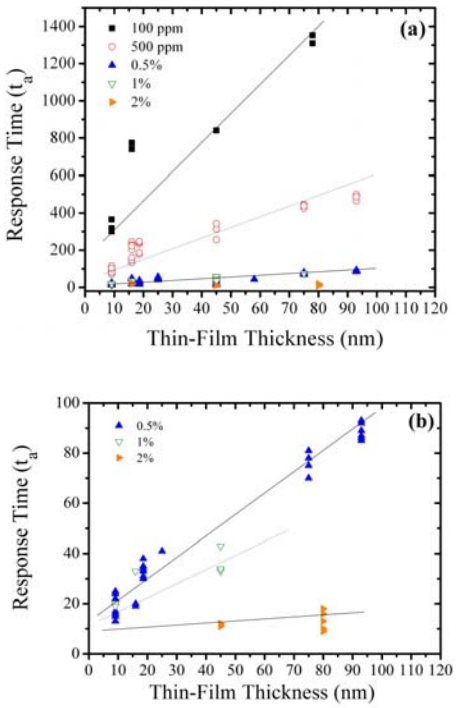

Figure 3. Reponse time versus thin-film thickness for a pure-Pd sensor.

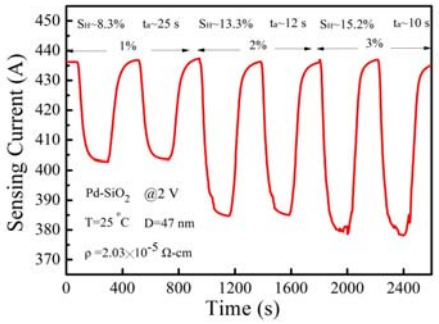

Figure 4. Transient current response of the Pd-SiO_2 sensor.

7.4% and 6.1% for the pure-Pd sensor in 1.5% and 1% H_2/N_2, respectively. No clear correlation was found between the relative sensitivity and the thin-film thickness. However, as shown in Fig. 3, the response time (t_a) as a function of thin-film thickness for a pure-Pd sensor subjected to 100 ppm to 2% H_2/N_2, we find it is substantially dependent on the thin-film thickness. For example, t_a with a thickness coefficient of 0.14 s/nm in 2% H_2/N_2 was obtained while it is 0.5 s/nm in 1% H_2/N_2. Fig. 4 shows sensing characteristics of the Pd-SiO_2 sensor. The baseline current in N_2 is 436.2 μA responding to a resistivity of 2.03×10^{-5} Ω·cm. The high resistivity is due to incorporation of insulating SiO_2. The current variation is more substantial when the gas with a higher hydrogen concentration is introduced to the Pd-SiO_2 sensor. This is because that the resistivity increased in the

 ISBN: 978-1-61208-543-2

sensing film is proportional to the H_2 concentration in the sensing film. Since more hydrogen molecules coming to the sensing film can be dissociated into hydrogen atoms, more hydrogen atoms can diffuse into and locate inside the sensing film. It is thus easily demonstrated that the hydrogen concentration in the sensing film is enhanced by introducing hydrogen-containing gas with a high concentration. A typical response time of 12 s and $S_H \approx 13.3\%$ is obtained for the Pd-SiO_2 resistive-type hydrogen sensor in 2% H_2/N_2. We measured the high hydrogen concentrations 3% H_2/N_2. There is a better performance of $S_H \approx 15.2\%$ and $t_a \approx 10$ s.

IV. CONCLUSIONS

Pd-based resistive-type hydrogen sensors were reported with new findings include at least that (i) response time is substantially dependent on the thin-film thickness and (ii) SiO_2 incorporated into Pd thin film is useful for increasing sensitivity and shortening response time. However, studies of effects of the mole fraction of SiO_2 incorporated into the Pd film on the sensor's sensitivity and response time are undergoing to obtain low-cost and high-performance hydrogen sensors.

ACKNOWLEDGMENT

This work was financially supported by the Ministry of Science and Technology under contract no. MOST 104-2221-E-019-021-MY2.

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