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Reliability and selectivity of H_2 sensors composed of Pd Film nanogaps on an elastomeric substrate

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ABSTRACT

H_2 sensors composed of Pd films of 10 nm thickness were prepared on a compliant poly(dimethylsiloxane) (PDMS) substrate, using a combination of an initial H_2 concentration of 0.5% and mechanical elongation of the samples by 50% of their original length. The initial feed of hydrogen gas was controlled for the PDMS/Pd films, and then an on–off switching response was measured with H_2 concentrations ranging from 0.01% to 0.5%. The Pd films exhibited a nanogap width of less than 50 nm. The sensors exhibited slightly degraded sensing performances in humidified H_2 in a N_2 environment, whereas their performance, in terms of their saturation current, showed little variation in an ambient atmosphere. This may be the result of a retarding effect caused by water adsorption on the Pd film surface, which decreases the number of active sites available for H_2 adsorption. The sensor was exposed to several toxic gases such as CO, NO, NO_2, and NH_3, after a single cycle of H_2 exposure. The nanogaps in the multi-nanogap structure exhibited selective reactivity with H_2 but showed no response to the other gases to which they were exposed or no resulting degradation.

1. Introduction

Hydrogen (H_2) is one of the most promising clean energy resources with the potential to replace fossil fuels that generate air contaminants such as carbon and nitrogen oxides (CO_x, NO_x) through combustion [1]. H_2 is a renewable and abundant energy (generated through the electrolysis of H_2O) with zero pollutant emission; it exhibits high energy efficiency and does not contribute to the greenhouse effect. Therefore, it is ideal for use in energy transfer carriers and storage media [2]. Moreover, H_2 has a high diffusion coefficient ($0.61 \times 10^{-4}\ m^2\ s^{-1}$) and the smallest molecular size that enables the detection of leaks in a closed system [3]. However, extensive utilization of H_2 has been restricted by the fact that it is flammable above a particular concentration (4%), though it is safe to use at low densities in air, owing to its high diffusion speed that makes the safe in open space [4].

Since H_2 absorption by palladium (Pd) hydride was first noted in 1866, the compound has emerged as the simplest system to activate H_2 absorption [5]. H_2 is first adsorbed on the Pd surface and the physisorbed di-hydrogen then dissociates into the mono-hydrogen form and is chemisorbed, forming a Pd–H system [6]. This process occurs spontaneously at room temperature and atmospheric pressure. Most sensors that employ Pd as a base material and utilize H as a scattering source for n-type carriers, or for trapping p-type carriers, originated from the electron transfer resulting from Pd-H formation, which increases the overall resistance of the system [7–9]. However, we previously used another sensing mechanism that employs the volumetric expansion of Pd, a method that first introduced the on–off concept of current switching by using an electrodeposited mesowire break junction on a carbonyl substrate developed by Penner [10,11].

We previously developed hydrogen sensors that utilized the crack formation in a Pd thin film on polydimethylsiloxane (PDMS), referred to as Pd-based highly mobile palladium thin films on an elastomer (MOTIFE) [12,13]. We used only the mechanical strain present in the system to randomly produce nanogaps, without using any lithographical technique resulting in an easy fabrication process, and the sensor performance was controlled by varying the initial H_2 concentration [14]. However, certain factors still require close examination in order to establish the feasible use of this method for elastomer based devices.

In this work, we have focused on precludable effects such as humidity conditions on the performance of Pd-based MOTIFE H_2

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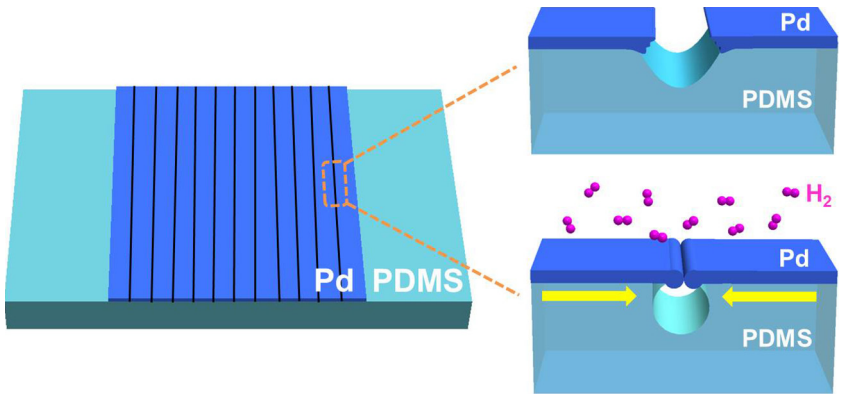

Fig. 1. Schematic of the Pd nanogap sensors on an elastomeric substrate with perpendicularly formed random nanogaps on the Pd surface (left) and its on–off switching mechanism of off (top right) and on (bottom right).

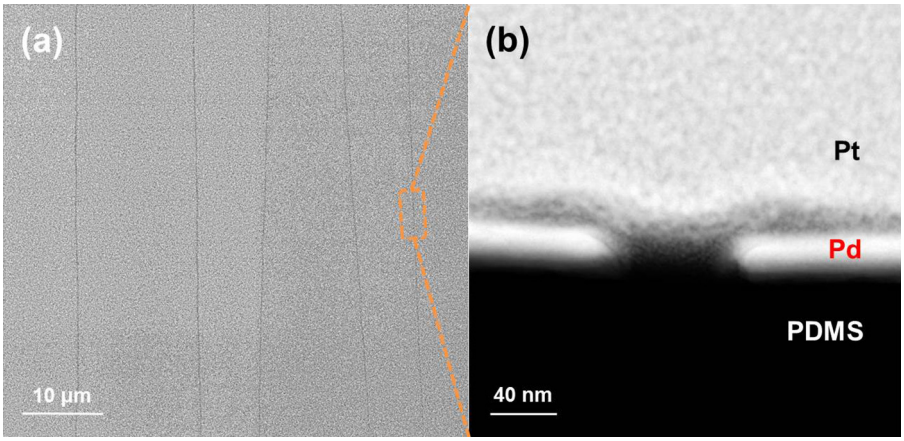

Fig. 2. (a) Surface morphological SEM image of the randomly cracked surface of a PDMS/Pd sensor, and (b) cross-sectional TEM image of a single nanogap with a width of 50 nm.

sensors, fabricated using an initial H_2 concentration of 0.5%. Pd films with a controlled nanogap width of less than 50 nm exhibit on–off current switching that is dependent on H_2 concentration. The sensors were slightly degraded with humidified H_2, whereas the performance in each same concentration has seldom changed at dry atmosphere. Based on multi-nanogaps structure, the sensor was tested with various other gases to confirm the selective response to H_2.

2. Experimental details

2.1. Preparation of the Pd MOTIFE sensors

The elastomer resin, a PDMS monomer (Sylgard 184, Dow Corning Corp.), was mixed using a curing agent for 15 min at a ratio of 10:1, and baked on a hot-plate at 75 °C for 4 h. The cured substrates were prepared with dimensions of 20 mm × 10 mm,

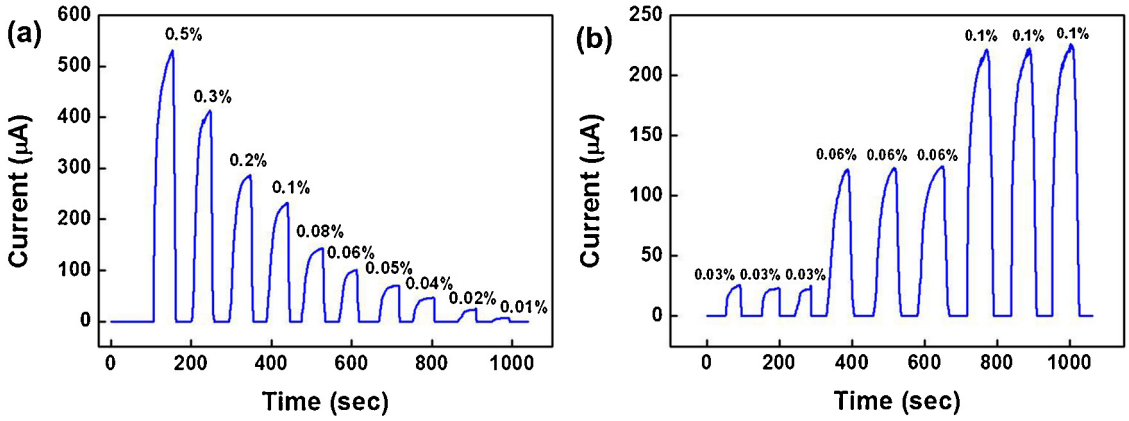

Fig. 3. (a) Real-time electrical responses of the Pd MOTIFE sensors fabricated using initial concentrations of 0.5% H_2 in N_2, and (b) their repeated H_2 exposure cycles at varying concentrations.

and a thickness of 0.75 mm. A Pd film of 10 nm thickness was sputtered onto the PDMS substrate, using a power of 20 W and ultrahigh vacuum (UHV) direct current (DC) magnetron sputtering. The chamber pressure was 4.2×10^{-7} Torr and the working pressure was 2.28 mTorr, under 34 sccm of Ar flow. The deposited film dimensions were 10 mm × 10 mm. In order to create the nanogaps on the Pd layer, specimens were mechanically stretched along the uniaxial direction to an elongation of 50% of its original length, using in-house stretching equipment. H_2 exposure was performed at an initial concentration of 0.5%. The total H_2 exposure time was 50 s. After an initial cycle of H_2, the samples were tested at various H_2 concentrations based on humid environment.

2.2. Sample characterization

The surface morphology of the MOTIFE nanogap sensors were observed using field-emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL Ltd.), and cross-sectional images of the samples were obtained in the vicinity of the nanogaps using transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd.). The samples were sliced and thinned using a dual-beam focused ion beam (FIB, Nova 600, FEI Co.). The sample MOTIFE nanogap sensors were loaded onto a printed circuit board (PCB) and electrically connected with a contact pad using silver paste. The electrical measurements of the H_2 sensing properties were carried out under controlled gas conditions using a Keithley 236 current source measurement unit (Keithley Instruments, Inc., Ohio, USA) and a gas sensing system consisting of a furnace (Korea Vacuum Tech., Korea; 250 mL), a mass flow controller (MFC), and gas cylinders containing the target gas (H_2) and the base gas (N_2). All experiments were performed at room temperature and N_2 was used for venting the chamber.

3. Results and discussion

Fig. 1 depicts the structure of the Pd thin film on the elastomer substrate, containing randomly formed nanogaps. These cracks were formed on the silica-like surface of the PDMS substrate, and propagated through the Pd film during the process of uniaxial mechanical elongation and releasing [15,16]. When the elongated Pd film was returned to its original dimensions, the cracks overlapped each other, and the broken Pd films expanded depending on the H_2 concentration [12]. The magnitude of the film expansion and the accumulated stress on the Pd film depended on the amount of absorbed H_2 atoms regulating the gap size of the Pd film, as the expanded film contracted with the removal of H_2 [14]. In a previous report, we confirmed the detection limits (given in parentheses) of PDMS/Pd systems using initial H_2 concentrations of 0.35% (3%), 0.2% (1.5%), 0.001% (0.1%) [14]. These results implied that initial H_2 concentration is crucial in defining the gap sizes of a Pd film. In this report, we exposed the sensors to initial H_2 concentrations below 0.5%. This concentration in a Pd–H system is on the border of a phase change from α to β. When Pd is in the α phase, the film expands by less than 0.13% of the lattice parameter (3.90 Å), whereas the Pd hydride film undergoes a lattice expansion of 3.47% in the β phase. In order to reduce the size of the nanogap and obtain a sufficient detection range, the β phase should be avoided because of the large volume expansion in the Pd film, as this enlarges the nanogaps and leads to an increase in the detection limit.

An SEM image of several nanogaps on the PDMS/Pd film surface after mechanical stretching and cycling of H_2 and N_2 is given in Fig. 2(a). The nanogaps were randomly formed on the surface of the Pd, and each nanogap was oriented approximately perpendicular to the stretching direction. The average spacing between adjacent nanogaps was approximately 15 μm, which is the same as that of the Pd cracks that routinely occur on PDMS [12]. The cross-sectional TEM image in Fig. 2(b) shows an individual Pd nanogap width of 50 nm. This nanogap width is 6 times smaller than those found on Pd-based MOTIFE sensors fabricated using an initial H_2 concentration of 10% [12]. The Pt layer is showed on top of the Pd layer as seen in Fig. 2(b). This was deposited before slicing to minimize the sample damage during FIB milling procedure.

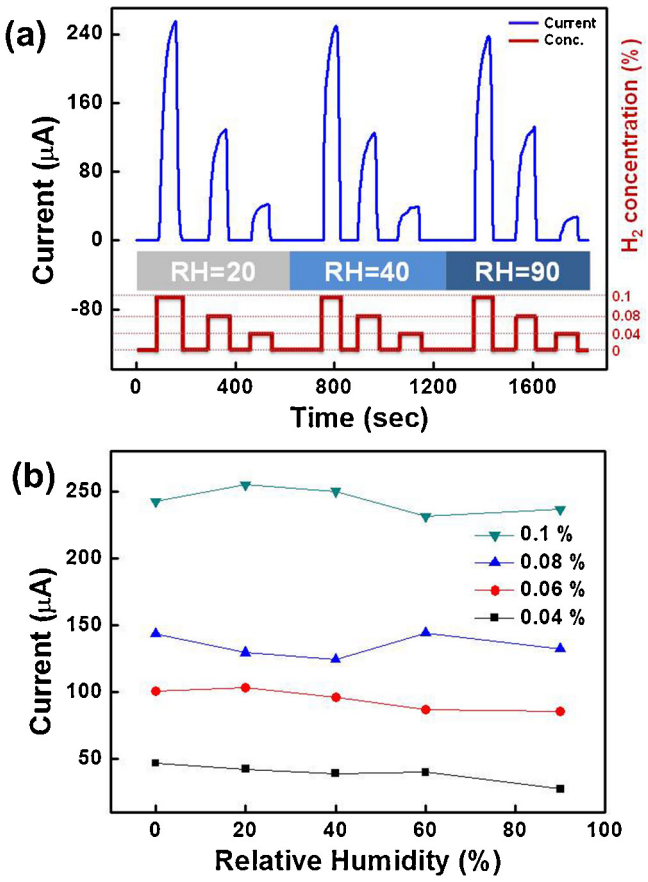

Fig. 4. (a) Real-time electrical responses of the Pd MOTIFE sensors at various relative humidity (RH), and (b) their humidity dependent responses from 0% to 90% RH, for different H_2 concentrations.

Real-time electrical measurements were performed in order to confirm the properties of Pd-based MOTIFE sensors fabricated using an initial H_2 cycle concentration of 0.5%. The dependence of the on–off switching behavior on H_2 cycle concentration was determined by varying the H_2 concentration for repeated cycles from 0.01 to 0.5%, as shown in Fig. 3(a). The detection limit was 0.01% and the recovery times for all the detection range did not exceed 1 s. Real-time current measurements for repeated cycles with the same H_2 concentrations were also tested, with the results given in Fig. 3(b). The same H_2 cycle concentrations of 0.03%, 0.06%, and 0.1% were used three times, and the real-time current results were recorded. The measured current was at nearly the same level for each repeated cycle for each H_2 concentration, demonstrating that PDMS/Pd systems made using initially controlled H_2 concentrations exhibit a high mechanical stability.

The dependence on RH of the electrical response of Pd MOTIFE systems made using different H_2 concentrations is given in Fig. 4(a). The humidity measurements were conducted using H_2 mixtures containing wet N_2 at ambient temperatures, with humidity levels ranging from 0% to 90% RH. The only difference in the measured real-time currents at the different humidity levels for each H_2 concentration was that of a slight decrease in the currents with increasing RH. The saturated current points at particular

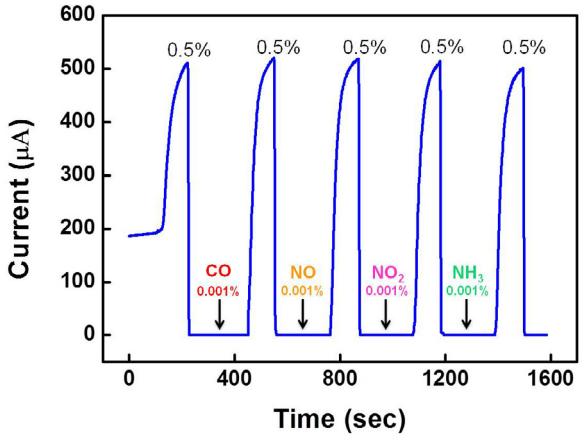

Fig. 5. Real-time electrical responses of the selective H_2 response, compared with responses to other retarding gases.

concentrations were also measured at various points in the RH range, as shown in Fig. 4(b). Increasing RH led to a slight decrease in the measured saturated current points for all the H_2 concentrations apart from that of 0.08%, which showed a slight increase with increasing RH. These results indicate a slightly degraded response to H_2, but little dependence on humidity. This may be attributed to a retarding effect, owing to water adsorption on the Pd film surface that decreased the number of active sites available for H_2 adsorption [17]. This obstruction of the Pd adsorption sites may have been more apparent at low H_2 concentrations, with low amounts of H_2 molecules on the surface. Although the elastomer substrate is generally known to be vulnerable to humidity, we did not observe a serious degradation in sensor performance when the H_2 concentration was above 0.08%. The dependence of the current of the sensor response on humidity is investigated in dry H_2 compared to that of humid H_2 with 90% RH condition. The saturated current values for dry H_2showed little drift (within 4 μA), whereas the values for humid H_2 had a tendency to drift downwards and exhibited larger variations (within 20 μA). However, the effect of humidity on the PDMS/Pd system appears to be insignificant at H_2 concentrations of 0.1%.

A measurement of the selective reactivity of Pd-based MOTIFE sensors based on the on–off mechanism was conducted using several toxic gases (CO, NO, NO_2, and NH_3). A sensor was continuously exposed to these target gases individually, after a single cycle of H_2, as shown in Fig. 5. The concentration of all the harmful gases was 10 ppm, and the real-time electrical response of the sensor was recorded. The current levels, when compared with other sensors made using the same H_2 concentration, did not exhibit any degrading effect or response to the other N_2-based gases. As mentioned previously, Pd nanogap films on PDMS only react with H_2, because H absorption on the interstitial site of fcc Pd, together with the resulting volumetric expansion, closes the nanogap. The kinetics of the on–off switching behaviors examined in this study demonstrate that Pd-based MOTIFE sensors exhibit selective on–off responses, and their Pd nanogaps experience no degradation effects.

4. Conclusions

We fabricated Pd-based MOTIFE H_2 sensors using an initial H_2 concentration of 0.5%, and measured their on–off switching responses over repeated cycles of H_2 exposure at concentrations between 0.01% and 0.5%. The Pd films contained nanogaps with a width of less than 50 nm. The sensors exhibited slightly degraded sensing performances when exposed to humidified H_2 in N_2, whereas their performance in an ambient atmosphere showed little variations in signal. The nanogaps contained in the multi-nanogap structure exhibited selective reactivity only with the H_2 gas, and exhibited no response to the other gases to which they were exposed (NO, NO_2, CO or NH_3) and no resulting degradation.

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Biographies

Wonkyung Kim was born in 1976 in Mokpo, Republic of Korea. He received a BE in Material Science and Engineering at Yonsei University in 2007. He has been a High school teacher since 2002. He is currently studying MOTIFE sensors using Pd as a step toward his PhD degree in hydrogen sensor devices at Yonsei University.

Byungjin Jang was born in 1987 in Seoul, Republic of Korea. He received a BS degree in Material Science and Engineering at Yonsei University in 2012. He is currently studying MOTIFE sensors using Pd as a step toward his PhD degree in hydrogen sensor devices at Yonsei University.

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