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Ultra-sensitive, One-time Use Hydrogen Sensors Based on Sub-10 nm Nanogaps on an Elastomeric Substrate

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ABSTRACT

Extremely narrow nanogaps with a width less than 10 nm have been achieved in Pd thin films on a PDMS substrate by the combination of tensile straining and fine control of initial hydrogen concentration. For the Pd/PDMS structures pre-elongated by 25%, the width of nanogaps was found to decrease with decreasing concentration of the initial feed of hydrogen gas. Hydrogen sensors based on the nanogaps with reduced widths resulted in a dramatic improvement in hydrogen detection limit, and the minimum detection limit obtained in this study was 10 ppm, which is the lowest ever reported for hydrogen sensors employing only a Pd thin film. These results provide an unusual opportunity to use these sensors in specific fields, where ultra-high precision hydrogen detection is required even with one-time use.

1. Introduction

The need for accurately detecting a minuscule amount of hydrogen gas (H_2) has been growing, keeping pace with the gradual expansion of H_2 use [1,2]. For example, hydrogen acts as a contaminant in major gas species such as silane gas, nitrogen, xenon, and neon used in the semiconductor and lighting industries. Furthermore, it is of significant importance to tightly monitor H_2 leakage from rocket fuel. In such fields, the H_2 concentration in a gas should be measured with a high accuracy in the range of 0.1 to 100 ppm [3]. Several research groups have reported highly sensitive H_2 detection at room temperature using various structures such as an AlGaAs-based high electron mobility transistor (HEMT) with a palladium (Pd) gate [4], multiple ZnO nanorods coated with Pd film [5], and Pd-coated rough Si nanowires [6]. In all of those structures, Pd was employed as a part of the system due to its high sensitivity to H_2 and efficient catalytic dissociation of H_2 molecules into hydrogen atoms. Although they showed a detection limit down to 4.3 ppm in air [4], the fabrication processes were rather complicated, limiting their wide-spread use. To improve the manufacturability and structure controllability of H_2 sensors, adopting a simple Pd thin film on a substrate is desirable. However, it is difficult to achieve the required high H_2 detection accuracy, using the Pd film/substrate structure.

The first demonstration of a distinctive On-Off operation in Pd mesowire break junctions provided a new direction in the use of Pd in an ideal H_2 sensor [7–9]. Notwithstanding, the smart nanostructures suffered from two issues, i.e., a complex fabrication process and low H_2 detection limit. Of the two, the first issue, associated with the complex nanogap formation process, was recently resolved by Lee et al. [10]. They successfully fabricated uniform nanogaps in a Pd thin film on an elastomeric substrate by employing a low-cost, large-scale mechanical stretching technique [10]. In the study, nanocracks were first formed in the Pd film on an elastomeric substrate by tensile straining to 25%, but closed upon strain release. When exposed to 4% H_2, the broken Pd films were swollen to be in good contact at both ends, and the swollen Pd films were contracted and recovered to their stable positions upon removal of H_2. As a consequence of this recovery to the equilibrium dimensions, nanogaps of a width of 300 nm were left behind. These nanogap-based sensors operated in a perfect on–off manner, which arose from the closing-opening mechanism of the nanogaps. However, the H_2 detection limit of H_2 sensors including such nanogaps was still very high, at 4000 ppm. From a following study performed by the same group, it was found that the H_2 detection limit is closely related to the nanogap width.

In this work, we elucidated the direct relationship between the H_2 detection limit and the nanogap width. A minimum detection limit of 10 ppm was obtained, which is the lowest reported for H_2 sensors using only a Pd thin film to the best of our knowledge. It is

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also noteworthy that such a low detection limit was not maintained after another cyclic test extending to higher H_2 concentrations. Based on these results, we propose an ultra-sensitive, one-time use H_2 sensor that can be applied to the specific areas. Although this type of sensor is the first attempt, its potential for practical use seems to be enough. Hydrogen is expanding its use in a wide range of fields such as chemical industry (hydrogenating or reducing agent), semiconductor industry (hydrogenation and surface treatment), medical diagnostics (diagnosis of bacterial infections), rocket engines (combustible fuel), fuel cells for automobiles, and petroleum transformation [11–13]. Due to the colorless and odorless nature, rapid diffusion, and the extreme flammability of H_2, its early and accurate detection is critically required [14,15]. Pd-based sensors are favored owing to their fast response (response time: a few seconds) as well as high sensitivity. However, H_2 sensors employing a Pd thin film with or without nanogaps are difficult to detect low H_2 concentrations below 1000 ppm. The easy-to-make, one-time use H_2 sensors proposed in this study will be a good candidate to meet both the fast response and accurate detection.

2. Experimental details

Cured polydimethylsiloxane (PDMS) was used as an elastomeric substrate. The elastomeric substrates were prepared by a method reported previously [16]. The substrate size was 20 mm × 10 mm with a thickness of 0.75 mm. After cleaning the PDMS substrates, a Pd film was deposited from a Pd target (2 inch 99.99% purity) at room temperature, using direct current (DC) magnetron sputtering. The base pressure was 4×10^{-8} Torr and the process pressure was set at 1.2×10^{-3} Torr under 14 sccm Ar flow. The Pd film deposition rate was adjusted to be 3.7 Å/s at a sputtering power of 20 W and the film thickness was set to be 10 nm through the sputtering time control. The Pd film was sized into 10 mm × 10 mm squares.

Nanogaps were formed in these Pd film/PDMS substrates following the procedure schematically shown in Fig. 1. The samples were loaded onto a custom-made stretching machine and strained by 25%. Here, the strain was defined as $(L - L_0)/L_0 \times 100$ (%), where L_0 and L are the initial length and the length under a tensile stress, respectively. Uniaxially elongating a sample in this way, nanocracks are initiated on the silica-like surface of the PDMS substrate and propagate through the Pd film [10,17]. Upon relieving the mechanical stress, the extended Pd films are recovered to their stable positions, leading to overlaps of broken Pd films. The broken Pd films expand when they are exposed to a certain concentration of H_2 flow, and an internal stress is stored inside the films during the film expansion. The magnitudes of the film expansion and the accumulated stress depend on the amount of absorbed hydrogen atoms, which increases with increasing H_2 concentration. Since nanogaps are produced as a result of Pd film contraction and internal stress relief after H_2 removal, their widths vary in accord with the first-fed H_2 concentration.

The nanogap-including Pd film/PDMS substrate sample was put onto a printed circuit board (PCB), electrically connected to it using silver paste, and was then loaded into a gas chamber to evaluate its H_2-sensing characteristics. All H_2-sensing measurements were performed at room temperature using N_2 as a carrier and vent gas. Real-time current (or resistance) was measured in the gas flow of varying H_2 concentrations, using a current source-measure unit (Keithley 236). In this study, the initial H_2 concentration fed into the gas chamber was varied over a broad range: 0.1 (1000 ppm), 0.5 (5000 ppm), 1, 1.3, 1,5, 1.8, 2, 3, 4, and 5%. After feeding various initial concentrations, the H_2 concentration was decreased in a stepwise manner until a detection limit was reached. In addition, actual nanogap images corresponding to the respective detection limits were obtained using transmission electron microscopy (TEM, JEM-2100F) to determine a correlation between the detection limit and the nanogap width. For TEM measurements, a Pt film was first deposited onto a Pd/PDMS sample for sample protection and sliced in a direction perpendicular to the nanogap using focused ion beam (FIB, Quanta 3D FEG-FEI).

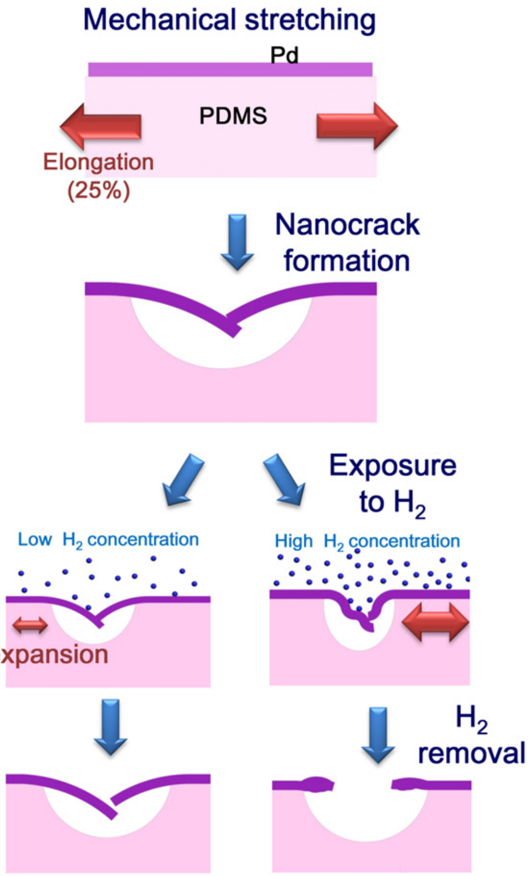

Fig. 1. Schematic process for fabrication of nanogaps with controllable widths in Pd films on a PDMS substrate. Steps 1 and 2: Nanocrack formation on the Pd/PDMS structure by 25% elongation followed by strain relief. Step 3: Expansion of broken Pd films under various initial concentrations of H_2. Step 4: Formation of nanogaps with variable widths after recovery to stable positions upon removing H_2.

3. Results and discussion

Fig. 2 shows cross-sectional TEM images of nanogaps in four Pd film/PDMS substrate samples, which have undergone H_2 cyclic tests starting from different initial concentrations ((a) 0.1%, (b) 1.3%, (c) 1.5%, and (d) 2%) down to their respective H_2 detection limits. The nanogap width was measured to be 8, 10, 40, and 53 nm in the order of (a) through (d), indicating that it increases with an increase in the initial H_2 concentration. As shown in Fig. 2(a), one piece of Pd film sinks below another piece, and in this regard, the Pd film configuration is similar to that observed before exposure to H_2 (see Ref. [10]). On the other hand, broken Pd films are clearly separated by nanoscale gaps of varying distances. This can be accounted for on the basis of Pd film expansion caused by hydrogen atom absorption in the initial H_2 environment. When a Pd film is put under a low concentration of H_2, hydrogen atoms penetrate into interstitial sites of the Pd matrix, and the Pd–H system is in the α phase. In this phase, the film expands by less than 0.13% in the lattice parameter, and the tensile stress accumulated in the Pd films is small, leading to narrow nanogaps after film recovery on H_2 removal. When the Pd film is in a higher concentration of H_2, it is transformed into the β Pd hydride, where the lattice expansion reaches 3.47%

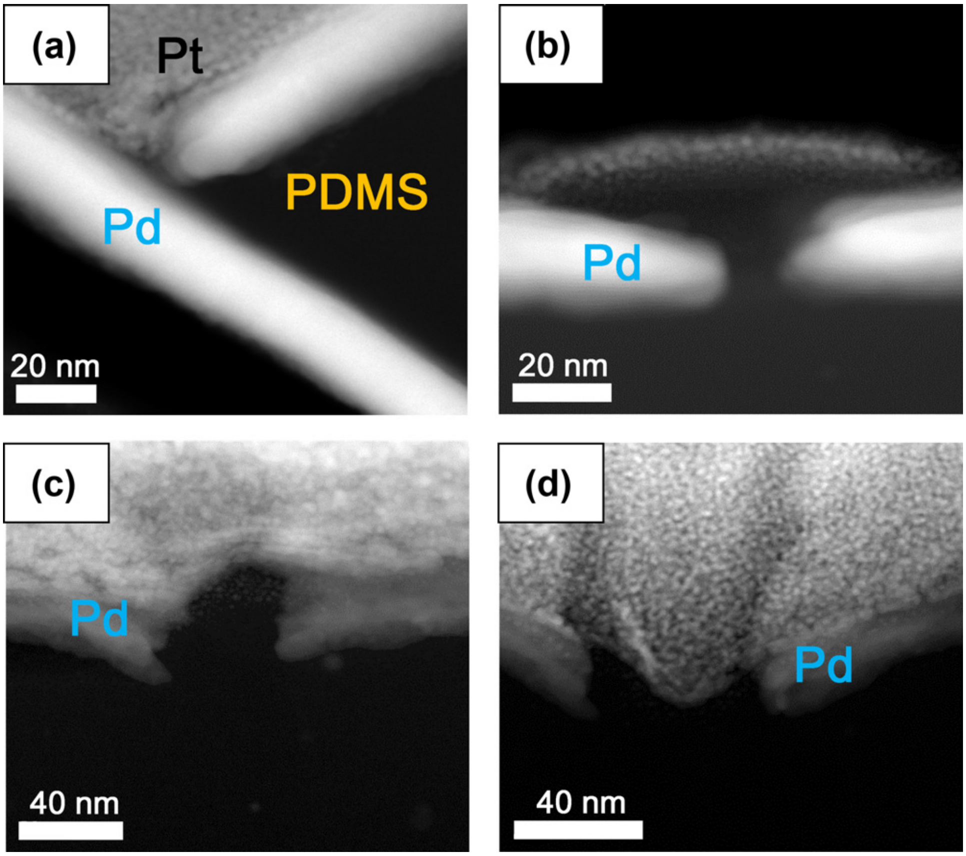

Fig. 2. Cross-sectional TEM images of nanogaps in Pd/PDMS structures exposed to an initial H_2 concentration of (a) 0.1%, (b) 1.3%, (c) 1.5%, and (d) 2%. The nanogap width decreases with a decrease in the initial H_2 concentration.

[18,19]. Due to this large volume expansion of Pd films, a large tensile stress accumulates in the film, which is transferred to the brittle surface of the PDMS substrate. In addition, strong superposition of the broken Pd films at their both ends exerts a repulsive force to each other, which plays as another stress. These large stresses accumulated under high H_2 concentrations result in an enlargement in both nanocracks on the PDMS surface and nanogaps in the Pd film.

Real-time response tests were conducted by varying the initial H_2 concentration to examine the correlation between the nanogap width and the H_2-sensing properties. Fig. 3(a) shows representative cyclic response curves measured at room temperature for three samples that were exposed to 3, 1.5 and 0.1% H_2 (from top to bottom), respectively, in the first cycle. The H_2 concentration was kept at these initial values for three or four cycles in the beginning stage to form solid nanogaps of definite sizes, and then the concentration was lowered in a step-by-step manner until the detection limits were identified. To completely desorb the absorbed hydrogen atoms before changing H_2 concentration, the samples were kept under N_2 gas flow for 20 s even after full recovery of current to its lowest level (in this case, zero current). For all the samples, the current levels stay almost unchanged for multiple cycles with identical H_2 concentrations, indicating the nanogap width and the extent of Pd film expansion remain intact regardless of the number of cycles only if the H_2 concentration is constant. Over the measured H_2 concentration range, the samples operate in an On-Off mode, which arises from a nanogap closing–opening mechanism triggered by the expansion and contraction of broken Pd films. However, the completeness of the nanogap closure depends on the magnitude of Pd film expansion, leading to a higher current at a higher H_2 concentration, as shown in Fig. 3(a). This scalability of the response to H_2 concentration is a desirable feature for an ideal H_2 sensor. The H_2 detection limit of importance appears to decrease as the initially fed H_2 concentration decreases. This trend is in good agreement with that of nanogap width previously observed by TEM, confirming that a smaller nanogap results in a lower detection limit. Under this simple principle, the surprisingly low H_2 detection limit of 10 ppm was obtained from the initial H_2 concentration of 1000 ppm that corresponds to 8-nm-wide nanogaps. This detection limit is the lowest value ever reported for H_2 sensors based on a simple Pd thin film on a substrate.

Fig. 3(b) exhibits a full correlation chart between the H_2 detection limit and the initial H_2 concentration. Although the data points look scattered, particularly in H_2 concentrations larger than 2%, they follow a general trend line (curve fitted to data). The trend line can be divided into three sub-segments, as indicated in the figure. The respective segments are supposed to be related to a phase of the Pd–H system. In the first segment of H_2 concentrations lower than about 1%, the Pd–H is in the α phase, where the Pd volume expansion caused by hydrogen atoms absorbed in interstitial sites is relatively small and increases weakly with an increase in absorbed hydrogen atoms. As a consequence, both the nanogap width and its dependency on H_2 concentration are small, resulting in low H_2 detection limits and their small rate of change in this segment. Once the initial H_2 concentration exceeds 1%, the β Pd hydride phase starts to form in the α phase matrix and rapidly encroaches on the α phase as the initial H_2 concentration increases. In this α–β mixed segment, the nanogap width significantly enlarges with increasing H_2 concentration, bringing about a rapid increase in the detection limit. From a previous study, the α to β phase transition is completed at around 2% H_2 [20,21]. Coincidently, the third segment appears beyond a critical point of about 2% in this study. In this segment, the nanogap width does not change appreciably since the

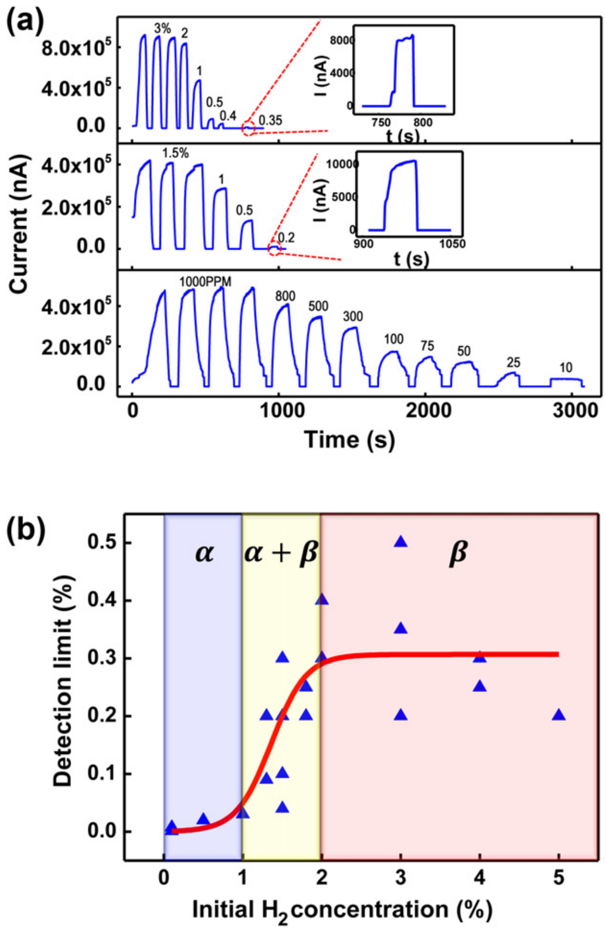

Fig. 3. (a) Real-time current responses of the Pd/PDMS structures at room temperature. The value above each peak represents the H_2 concentration in an N_2 carrier. Cyclic tests begin with 3, 1.5, and 0.1% H_2, respectively, from top to bottom. The insets in the upper and middle panels show the response curves at the respective H_2 detection limit. (b) A full chart between the H_2 detection limit and the initial H_2 concentration. The solid line is drawn to show the general trend.

maximum amounts of Pd film expansion and H_2 in-take are limited. Consequently, the H_2 detection limit remains almost constant at 3000 ppm, which is close to the value (4000 ppm) reported in the literature [10].

Even though a minimum detection limit of 10 ppm has been achieved for Pd nanogap-based On-Off sensors, it was not reproducible when the sensors underwent another H_2 cycle test beginning with a high H_2 concentration. Fig. 4 shows the second cyclic responses of a sample, from which the 10 ppm detection limit was obtained in the first cycle beginning with 0.1%, in the H_2 concentration range of 10% to a detection limit. The H_2 detection limit obtained from this second cycle is 0.1%, 100 times larger than that from the first cycle. A similar increase in the detection limit was also observed in another sample that showed a detection limit of 0.2% at the first cycle beginning with 1.5% H_2, although it was increased by only 2.5-fold in this case. These results originate from the fact that the widths of both the nanocracks on the PDMS surface and the nanogaps in the Pd film become wider due to the larger amount of stress accumulated during the larger Pd expansion at the second cycle spanning over a H_2 concentration range much broader than the first one. This suggests that the ultra-sensitive H_2 sensors with an extremely low detection limit are suitable for one-time detection of a trace amount of H_2.

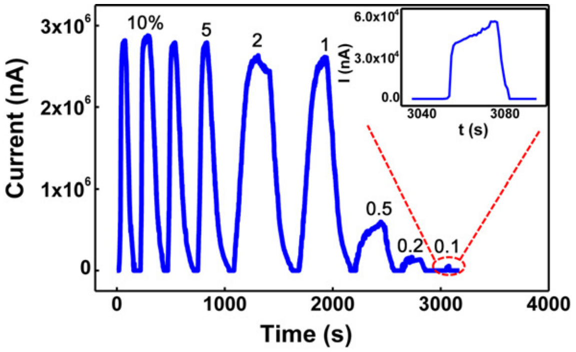

Fig. 4. The second cyclic responses of a Pd/PDMS that showed a detection limit of 10 ppm in Fig. 3(a). The second cycles began with 10% H_2, and the detection limit was 0.1% in this case (see the inset).

4. Summary

We have achieved extremely narrow nanogaps with a sub-10 nm width in Pd thin films on a PDMS substrate. For control of the nanogap width, the Pd/PDMS structures (including nanocracks) that were preformed by mechanical stretching were put under H_2 flow with varying concentrations. The nanogap width appeared to decrease with decreasing initial H_2 concentration because the magnitude of stress accumulated in the film during Pd film expansion becomes smaller at a lower H_2 concentration. The reduced nanogap width directly led to a drastic improvement in H_2 detection limit of the nanogap-based H_2 sensors. A surprisingly low detection limit of 10 ppm, which is the lowest ever reported for H_2 sensors employing only a Pd thin film, was obtained from a sample exposed to 1000 ppm in the first cycle. However, this detection limit was not reproducible when the sample went through another cyclic test extending to higher H_2 concentrations. These results provide an interesting concept of a new type of H_2 sensor, i.e., ultra-sensitive, one-time use H_2 sensors for fast and accurate detection of H_2 leak.

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Hwaebong Jung was born in 1986 in Yesan, Republic of Korea. He received a B.E. in Material Science and Engineering at Yonsei University in 2012. He is currently studying MOTIFE sensors and hydrogen storage using Mg as a step toward his M.E. degree in hydrogen storage and sensor devices at Yonsei University.

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Jin-Seo Noh is a professor of Department of Nano-Physics at Gachon University. He earned his bachelor's degree in 1991 and Master's degree in 1993 from Korea University, Korea. He earned his Ph. D. degree in Materials Science in 2003 from the University of Wisconsin-Madison. He has been with the Samsung Advanced Institute of Technology (SAIT) as a member of research staff in 2003–2008, where he performed research on next-generation memories and logic devices. He spent another year working on 28 nm technology development at the System LSI Division of Samsung Electronics. In 2009, he was appointed as a Research Professor to the Institute of Nanoscience and Nanotechnology of Yonsei University. His current research interests include nanomaterials-based thermoelectric energy conversion, nano electronics/spintronics, nanostructures-utilizing hydrogen gas and toxic gas sensors, and technology fusion crossing the borders. He has been appointed a faculty member of the Department of Nano-Physics at Gachon University.

Wooyoung Lee is a professor of Department of Materials Science and Engineering, the chairman of Yonsei Institute of Convergence Technology and the Head of Institute of Nanoscience and Nanotechnology at Yonsei University in Korea. He received a BS degree in metallurgical engineering in 1986, a MS degree in metallurgical engineering from the Yonsei University in 1988. He received a Ph.D. degree in physics from University of Cambridge, England in 2000. He is also the director in Korea-Israel Industrial R&D Foundation and the advisor in National Assembly Research Service. In recent years, his research interests have centered on thermoelectric devices, spintronics, hydrogen sensors and hydrogen storage materials. He has received a number of awards in nano-related research areas and a Service Merit Medal (2008) from the Korean Governments due to contribution on the development of intellectual properties. He has authored and co-authored over 150 publications, and has edited a few of special books on nano-structured materials and devices.