Nanogap-based electrical hydrogen sensors fabricated from Pd-PMMA hybrid thin films

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ABSTRACT

Hybrid thin films, in which a Pd thin film was sandwiched between thin poly(methyl methacrylate) PMMA layers, were prepared on a flexible substrate using a combination of sputtering and spin coating. In real-time electrical response tests to H_2, Pd-PMMA hybrid nanogap sensors operated in an on–off manner for both air and N_2 carriers. Due to the selective penetration of H_2 and the density reduction of the cracks that formed in the trilayer of the hybrid thin films, the detection limit of the hybrid nanogap sensors (6000 ppm H_2 in air and 600 ppm H_2 in N_2) was drastically reduced compared to that of Pd nanogap sensors without PMMA layers. Hybrid thin films have great promise in realizing sensors that can be used in air without additional filter system.

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Introduction

Hydrogen gas (H_2) is an attractive alternative clean energy source because of its high efficiency, abundance, and eco-friendliness [1–4]. However, safety should be guaranteed before hydrogen energy is utilized because of the high flammability and explosiveness of H_2 above a certain concentration in air [5,6]. Therefore, the fast and reliable detection of H_2 is critically required for all energy applications that are based on H_2 [7,8]. Additionally, H_2 sensors are promising for the detection of leakage from sealed systems that use refrigerants or Freon gas. Since H_2 has a high propagation velocity (3.46 m/s), it is commonly used to detect leaks in welded systems.

The H_2-sensing techniques can be classified into several categories such as electrical, optical, strain, and chemi-mechanical methods, on the basis of the physical parameter under detection. Of those, the electrical method has more advantages over others in such aspects as the overall performance, the simplicity and the manufacturability of the sensors, and the compatibility of sensor fabrication process with the conventional IC process [9]. Palladium (Pd), the most appropriate metal for electrical H_2 detection, has a high sensitivity and selectivity to H_2 and has

the ability to function in H_2 detection systems at room temperature. Many Pd nanostructures have been developed to efficiently detect H_2 [10–12], and Pd nanogap-based sensors on flexible substrates, which were previously reported by our group, have some advantages [13–16]. In this previous work, we operated nanogap sensors in a perfect on–off manner at room temperature, and the sensors were easy to fabricate. Despite these advantages, these nanogap sensors exhibited poor H_2 detection limit (4000 ppm in N_2). Two approaches can be used to address this issue: (i) the reduction of the nanogap width and (ii) the selection of H_2 using a filter [17,18]. The second methodology has rarely been applied to H_2 sensors. Poly(methyl methacrylate) (PMMA) is a polymeric material that exhibits gas-dependent permeability; e.g., it has a much higher permeability for H_2 than other gases, such as O_2 and N_2 [19–23]. This gas separation capability of PMMA can be utilized for the selective filtration of H_2 without the use of a filtration membrane when PMMA is incorporated into a Pd-PMMA hybrid sensor system. Hybrid thin films have great promise in realizing sensors that can be used in air without additional filter system. In addition, PMMA resolves the hindering effect of the Pd thin film hydrogen sensor from O_2, improving the performance in air.

In this work, the fabrication process and H_2-sensing characteristics of hybrid sensors, in which a Pd thin film is sandwiched between thin PMMA layers on a flexible substrate, is reported. Nanogaps are later formed throughout the multilayers by mechanical stretching, and they are reproducibly closed or opened in accord with volume expansion or contraction of the Pd film, leading to

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an electrically short or open state. Due to the unique function of the PMMA layers, which permit the selective passage of H_2 molecules, the hybrid sensors can detect low concentrations of 6000 and 600 ppm of H_2 in air and N_2 environments, respectively, while maintaining the on–off operation that is characteristic of Pd nanogap sensors. Moreover, the sensors can be manufactured on a large scale using a low-cost process.

Methods and materials

Nanogap sensor fabrication

The procedure for Pd-PMMA hybrid nanogap sensor fabrication is schematically shown in Fig. 1. As a flexible substrate, poly(dimethylsiloxane) (PDMS) was first prepared in accordance with a previously published method [13,14]. The PDMS substrate was cut into $2 \times 1\,cm^2$ samples, which were etched for 3 min at 53 W using an O_2 plasma physical etcher (Model CUTE-MP, Femto Science). PMMA and benzene were mixed at a weight-to-weight ratio of 0.02:99.98, and the mixture was coated onto the etched PDMS by spin coating. A thin Pd film (11–14 nm thick) was then deposited on the PMMA-coated PDMS using a direct current (DC) magnetron sputtering method under a 34 sccm Ar flow. The base pressure was maintained at 1.62×10^{-7} Torr before sputtering. The prepared PMMA-benzene solution was again coated onto the sample to form a PMMA/Pd/PMMA trilayer on the substrate, as shown in Fig. 1. The trilayer film on PDMS was elongated by 25% using a mechanical stretcher. Due to this mechanical elongation, nanocracks were produced in the trilayer (the last panel and the inset of Fig. 1). The nanocracks formed in this manner were closed once the applied stress was removed, due to the elastomeric nature of PDMS. These nanocracks were converted to more stable nanogaps, after going through a cycle of exposure to H_2 gas flow. Through this cyclic exposure, the nanocracks were completely closed in the presence of H_2 and then recovered to their equilibrium dimensions on the removal of the gas, leading to stable nanogaps.

Electrical measurement

The cracked trilayer sample was loaded onto a printed circuit board (PCB), and silver paste was used to wire the sample to the PCB. The PCB with the sample was then placed in a test chamber, in which electrical measurements were performed at room temperature under controlled gas conditions. Detailed specifications of the chamber and the test methods are described elsewhere [15,16]. Air was used as the primary gas both as a carrier for H_2 and for venting the system.

PDMS preparation

The elastomeric substrate, poly(dimethylsiloxane) (PDMS) was synthesized with a monomer purchased by Dow Corning (Sylgard 184 Silicon elastomer base). The monomer was mixed with a curing agent at the ratio of 10:1 and incubated for 16 h at room temperature for solidification. After that, heat treatment was performed on a hotplate at 75 °C for 4 h. The substrate was cut into 20 mm × 10 mm, 0.75 mm thickness.

Microscopy

Nanocracks or nanogaps were observed on the surfaces of the PMMA/Pd/PMMA films on the PDMS substrate using field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL Ltd.). Cross-sectional images of the samples were also obtained around the nanogaps using transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd.). The samples were sliced and thinned by a dual beam focused ion beam (FIB, Nova 600, FEI Co.).

Results and discussion

Fig. 2a shows an SEM image of the cracks that were formed on the surface of a sample after mechanical stretching followed by a cycle of exposure to H_2. Linear cracks appear almost parallel to one another but perpendicular to the elongation direction. The average distance between neighboring cracks was estimated to be
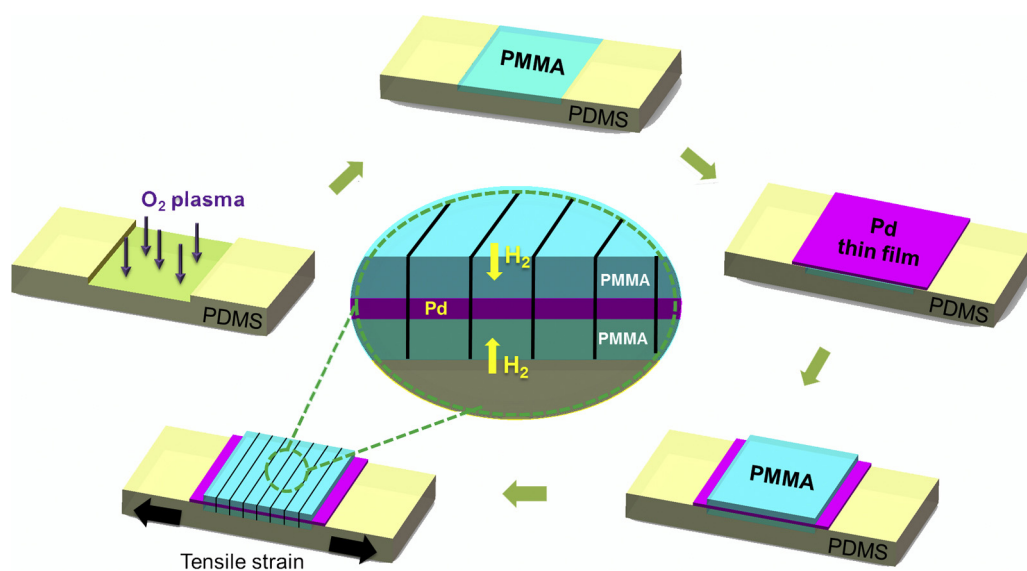

Fig. 1. Schematic diagram of the fabrication of nanogap sensors using PMMA/Pd/PMMA trilayer films on a PDMS substrate. First, the PDMS substrate is prepared and O_2-plasma etched. Second, a bottom PMMA layer is spin-coated onto the etched substrate. Third, a Pd thin film is sputter-deposited. Fourth, a top PMMA layer is coated onto the Pd film similarly to the bottom PMMA layer. Finally, cracks are introduced into the trilayer by 25% mechanical stretching. The inset shows a magnified representation of the cracked trilayer.
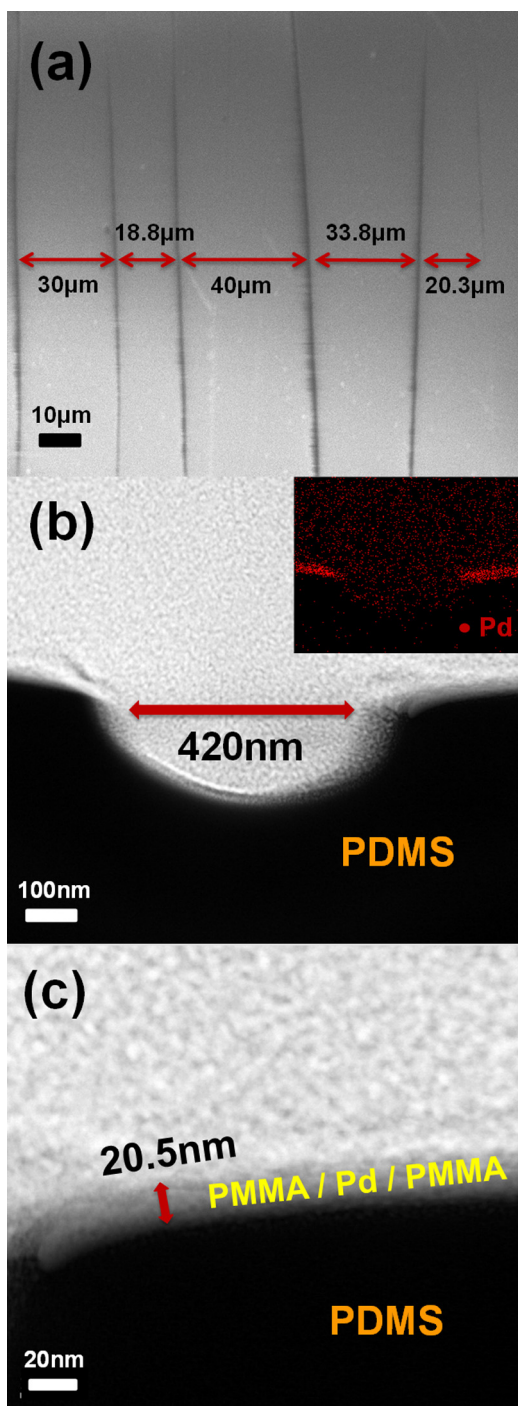
Fig. 2. (a) SEM image of the cracks formed in PMMA-Pd-PMMA/PDMS after the sample underwent mechanical stretching and consecutive cycle of exposure to air with and without H_2. (b) A cross-sectional TEM image of portion of a crack. From the Pd EDX map in the inset, it was observed that the Pd film is broken around the crack. (c) A magnified TEM image of the right side of the crack.

mapping, shown in the inset of Fig. 2b, revealed that the Pd films exist only outside of the crack, supporting the breakdown of the trilayer around the cracks. It was difficult to map the PMMA layers due to the similarities in the major elements of PMMA and PDMS. The width of the crack was measured to be 420 nm, similar to that in the Pd film on PDMS [13]. Based on this length scale, the cracks are termed nanogaps. Fig. 2c shows a magnified image of the trilayer on one side of the nanogap. Although the interfaces between Pd and PMMA are indistinct, the trilayer uniformly covers the PDMS substrate. Moreover, no observable defects are present in the trilayer, indicating that Pd and PMMA layers adhere well to each other. Based on the total thickness of 20–21 nm (Pd thickness of 11–14 nm), the thickness of each PMMA layer was estimated to be 3–5 nm.

Real-time electrical measurements were conducted to evaluate the H_2-sensing performance of the nanogap sensors based on Pd-PMMA hybrid thin films on a PDMS substrate. For comparison, the response behaviors of the nanogap-based H_2 sensor that was made from pure Pd thin film (12 nm thick) on the same PDMS substrate were investigated in an air environment. The representative result is shown in Fig. 3a. The cracks that formed under tensile straining closed after strain release because the ends of the broken Pd films overlap [13,16]. This phenomenon explains why the sensors are highly conductive prior to exposure to H_2. When the sensor is supplied with 2% H_2 (20,000 ppm), the Pd film expands and the cracks close completely, leading to a higher current level. The sensor then becomes non-conductive when the H_2 flow is stopped due to the gap openings that arise from the contraction of the Pd film to its stable dimensions. The gap closure-opening mechanism that is caused by the expansion–contraction of the Pd film enables the on–off operation of a Pd-film-based nanogap sensor. However, it should be noted that the H_2 detection limit of this sensor is relatively poor, at 1.2% in air (see the inset in Fig. 3a). This limit of detection is much worse than that in a N_2 environment, probably because of the hindering effect of O_2 in air [24–27]. The O_2 molecules in air can possibly form a PdO layer on the surface of Pd film, and the PdO layer controls the adsorption rate of H_2 and may emit H_2O vapors during its transformation to PdH, both of which make the H_2 adsorption more difficult [27].

The Pd-PMMA hybrid nanogap sensors also exhibited on–off sensing behaviors, as shown in Fig. 3b. This result demonstrates that the top and bottom of the PMMA layers that adhere to the Pd film do not interrupt the expansion–contraction cycles of the central Pd film. The current response to a 2% H_2 is 2–3 times higher than that of a pure Pd nanogap sensor, presumably arising from the larger inter-crack distance in Pd-PMMA hybrid nanogap sensors. The larger inter-crack distance or the lower crack density generally leads to a higher current through the more complete overlap of broken Pd film edges. Surprisingly, the H_2 low detection limit of this hybrid nanogap sensor was found to be 6000 ppm in air, which has been enhanced as compared to that of the aforementioned limit for the Pd-film-based nanogap sensor. This limit is similar to the detection limit (4000 ppm) of Pd nanogap sensors measured in a N_2 environment [13]. One of the major reasons for this significant improvement is the selective permeation capability of thin PMMA layers for H_2 gas. A more detailed explanation is provided later in this paper. Furthermore, the changes in the current level with changes in the H_2 concentration over the measured concentration range reinforce the advantage of the reported sensor. The performance of the hybrid nanogap device for H_2-sensing in a N_2 environment was investigated, and the result is presented in Fig. 3c. Similar to the air conditions, the sensor operates in an on–off mode for the cyclic test with N_2 as a carrier and vent gas. However, the H_2 detection limit was significantly reduced to 600 ppm, which is 7-fold less than that of nanogap sensors that are based on pure Pd

approximately 30.7 μm, which is about twice as long as that of Pd thin films on a PDMS substrate [13]. The larger inter-crack distance in the Pd layer is thought to arise from the division of the applied mechanical stress to three layers of the hybrid thin film. To closely examine the features of individual cracks, a cross-sectional TEM image was obtained from a part of the crack, as shown in Fig. 2b. This image clearly shows that the cracks are formed throughout the PMMA/Pd/PMMA trilayer down to the surface of the PDMS substrate. Energy-dispersive X-ray spectroscopy (EDX) elements
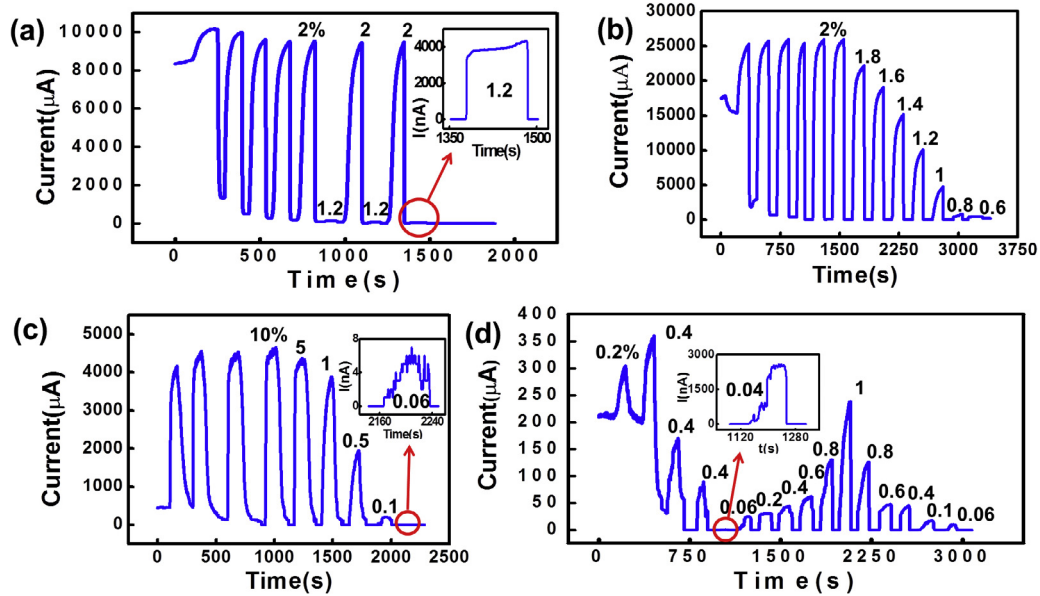
Fig. 3. The real-time electrical responses at room temperature: (a) a Pd nanogap sensor in air, (b) a PMMA/Pd/PMMA hybrid nanogap sensor in air, (c) the same hybrid nanogap sensor in N_2, and (d) the same hybrid nanogap sensor in air with an initial H_2 concentration of 0.2%. The insets in (a), (c), and (d) show the response curves for the lowest detectable H_2 concentrations.

films (see the inset in Fig. 3c). This findings support the selective permeability of H_2 molecules through the PMMA layers [19,23].

In a previous study, it was demonstrated that the detection limit of a Pd nanogap sensor is closely related to the H_2 concentration to which the sensor was exposed during the initial cycle [16]. To determine whether a similar effect occurs in Pd-PMMA hybrid nanogap sensors, cyclic response tests were performed starting with 0.2% H_2 in air. For this condition, a very low detection limit of 400 ppm H_2 was obtained for this sensor (inset of Fig. 3d). This limit is more than an order of magnitude less than the value that was obtained from the cyclic measurements initiated using 2% H_2 in air (Fig. 3b). This drastic reduction in the H_2 detection limit is attributed to the nanogap width shrinkage, which is dependent on the initial H_2 concentration. A previous study revealed that this effect is not reproducible once a sample is brought under H_2 gas with a concentration higher than that of the initial level. However, the almost symmetric sweep-up (0.04–1% H_2) and sweep-down (1–0.06% H_2) response of the signals as well as the low detection limit (600 ppm), which is similar to the first limit, indicate that the degradation of the detection limit is retarded in this Pd-PMMA hybrid nanogap sensor,

possibly due to the strain-buffering effect of the PMMA layers (see Fig. 3d) [28–30].

In order to investigate the response time of Pd-PMMA hybrid films, samples were exposed to 2% hydrogen for several times and operated as on–off mode. Fig. 4a and b shows the sensitivity versus time curve for Nitrogen and Oxygen atmosphere, respectively, where the time interval between each data points is 0.4 s. The sensitivity is defined as $\Delta R/R_0 \times 100(\%)$ where ΔR is the resistance change and R_0 is the initial resistance, and the response time is defined as the time required to reach at least 90% of the maximum sensitivity. Fig. 4a shows the fast response time behavior of 10 nm Pd-PMMA hybrid film based on N_2. The average response and recovery time was not exactly constant, but similar to be approximately 0.38 and 0.7 s. Fig. 4b shows the rapid response and recovery time within 0.4 s of the 12 nm Pd-PMMA hybrid film in ambient atmosphere. The results were observed probably because of hindering effect of O_2 in air [24–27].

The schematic representation of the mechanisms leading to the reduced detection limit of the Pd-PMMA hybrid nanogap sensor compared to that of pure-Pd-based nanogap sensors is shown in
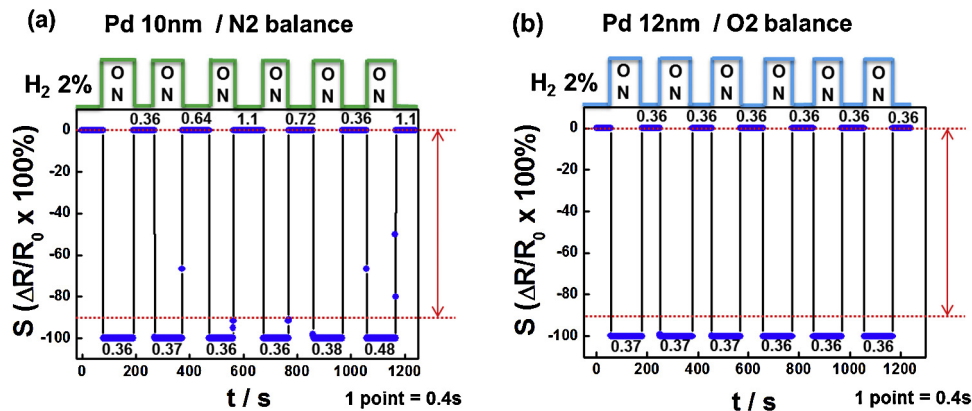

Fig. 4. Sensitivity versus time curve to 2% uniform hydrogen concentration for (a) 10 nm Pd hybrid thin films in nitrogen atmosphere and (b) 12 nm films in ambient air.
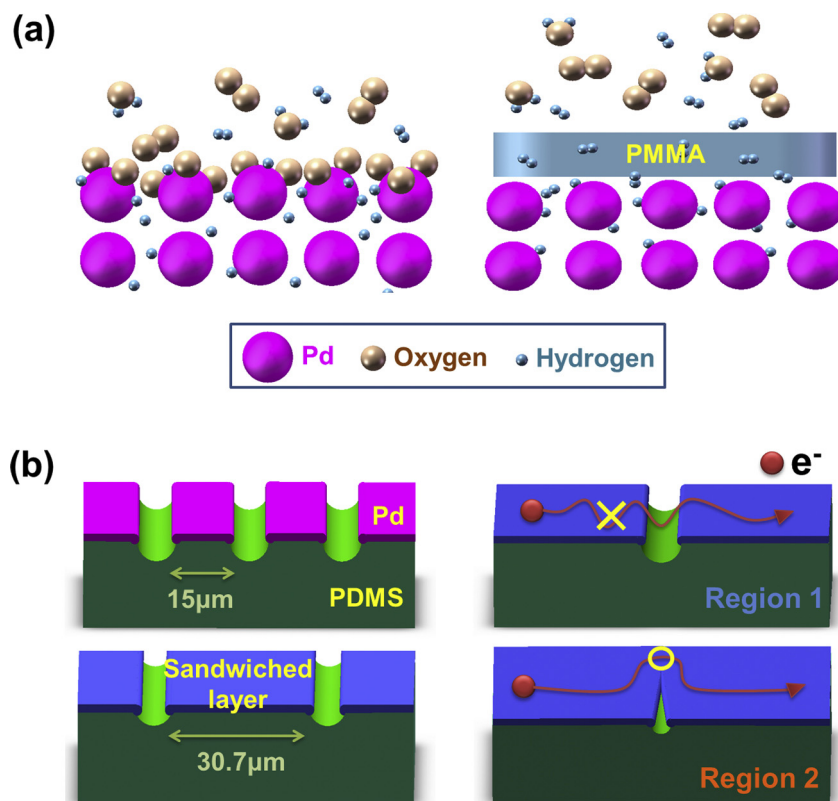
Fig. 5. Schematic diagrams indicating the origins of the difference between the H_2 detection limits of the Pd nanogap sensor and the PMMA/Pd/PMMA hybrid nanogap sensor. (a) Left: interaction of the Pd film with various gas species in an air environment; right: H_2 filtration through the PMMA layer and the consequent effective interaction between the Pd film and H_2. (b) The difference between the average inter-crack distances of the Pd nanogap sensor and the PMMA/Pd/PMMA hybrid nanogap sensor, and the states of the respective gaps after being exposed to moderate concentrations of H_2: the gaps in the hybrid nanogap sensor are closed (bottom), while the gaps in the Pd nanogap sensor are only slightly closed (top).

Fig. 5. In this mechanism, gaseous species other than H_2, such as O_2 and H_2O, frequently interact with the film surface when a pure Pd film is exposed to air (Fig. 5a). This interaction may cause byproducts such as oxides, hydroxides, and water vapors at the surface, which hinder the absorption of H_2 molecules onto the surface [20–33]. This phenomenon leads to the deterioration of the capability to detect low concentrations of H_2 [13,32]. In contrast, when a Pd film is sandwiched between PMMA layers, it is difficult for bulky molecules, such as O_2 and H_2O, to penetrate through PMMA, whereas H_2 molecules easily permeate the PMMA layer (Fig. 5a) [19,23]. This selective permeability of the PMMA layers with respect to H_2 gas enables the Pd-PMMA hybrid nanogap sensors to detect relatively low concentrations of H_2 in air.

Another possible reason for the reduction in the detection limit originates from the strain-buffering effect of the PMMA layers [28–30]. A portion of the stress that is applied to induce cracks in the PMMA/Pd/PMMA trilayer is consumed by the PMMA layers. Thus, the density of the cracks that forms in the trilayer is smaller than that in a pure Pd film, even under the same magnitude of mechanical strain (25%). Accordingly, the average inter-crack distance of the trilayer is approximately 2-fold larger than that of a pure Pd film [13], as schematically shown in Fig. 5b and measured in Fig. 2a. This result indicates that trilayer-based nanogaps have the potential to detect H_2 gas with a concentration as low as half that detected by Pd-based nanogaps because the maximum nanogap width that can be closed by H_2 absorption is the average inter-crack distance multiplied by the ratio of lattice expansion. Nanogaps of up to 1.07 μm can be closed for PMMA/Pd/PMMA trilayers with an average inter-crack distance of 30.7 μm when assuming a 3.5% lattice expansion (the lower boundary of the β PdH_x) [34–36]. The detectable H_2 concentration can be further reduced because the actual nanogap width was approximately 420 nm in our case.

Conclusions

PMMA/Pd/PMMA hybrid trilayer films on a flexible substrate were fabricated using alternate spin coating and sputtering. Nanogaps were formed in the hybrid films by simple mechanical stretching followed by exposure to gas with and without H_2. The average distance between neighboring nanogaps was 31 μm, approximately 2-fold larger than that of pure-Pd-based nanogaps. Based on the real-time responses to H_2 at room temperature, it was confirmed that the Pd-PMMA hybrid nanogap sensors operated in an on–off mode in both air and N_2 environments. Most notably, the H_2 detection limits of the sensors were very low (6000 and 600 ppm in air and N_2, respectively) and represented a substantial reduction relative to the detection limits of Pd nanogap sensors. This effect is attributed to the selective H_2 permeation through the PMMA layers and the larger average distance between the nanogaps compared with that in pure Pd film. These results demonstrate that the hybridization of a Pd film with PMMA layers is an easy and practical way to improve the performance of the Pd nanogap sensors, especially in air.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.11.080.

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Biographies

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

Kang Yeol Lee was born in 1978 in Sacheon, Korea. He received a B.S. degree from Gyeongsang National University, Korea in 2003. He also received a Ph.D. degree in physical chemistry from Gyeongsang National University, Korea in 2008. 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, fuel cell, and nanotectonics.

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 gassensors, 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 B.S. 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.