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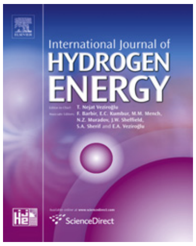

Cracked palladium films on an elastomeric substrate for use as hydrogen sensors

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ABSTRACT

We have investigated a lithography-free technique for On-Off type hydrogen sensors using a cracked palladium (Pd) film on an elastomeric substrate. Cracks were induced in a sputtered Pd film simply by undergoing hydrogen absorption and desorption processes. Compared to the same thickness of a Pd film on a Si/SiO_2 substrate that relied on the electron scattering mechanism, a cracked Pd film on an elastomeric substrate operated as a reversible On-Off hydrogen sensor based on the crack open-close mechanism when exposed to hydrogen. The thickness of a Pd film on the elastomeric substrate plays a significant role in determining the sensing mode of the cracked Pd film. The cracked Pd film with a thickness of 9–11 nm on the elastomeric substrate showed reversible and perfect On-Off responses under a wide range of hydrogen concentrations with large current variations and a fast response time of less than 1 s.

1. Introduction

The expectation of the advent of the hydrogen age has been growing since hydrogen gas (H_2) emerged as a new source of green energy. However, the safety issues associated with using H_2 must be addressed before expanding H_2-based applications because H_2 is highly explosive when its concentration exceeds 4% in air [1]. Among the many candidate materials for precisely detecting H_2, palladium (Pd) has been intensively investigated due to its distinct ability to naturally absorb and desorb hydrogen at room temperature, depending upon its environment [2]. Although many Pd-based nanostructures such as nanoparticles [3,4], nanowires [5,6], and thin films [7,8] have been reported, Pd thin films are expected to be commercialized due to their easy and cheap fabrication processes. However, the slower responses and lower sensitivities of Pd thin films compared to other types of Pd nanostructures have slowed the commercialization of H_2 sensors based on thin films. Recently, Penner et al. [9]. developed Pd mesowire-based H_2 sensors, which were fabricated by Pd electrodeposition on step edges of single-crystalline graphite and included many nanogaps in the structure. They showed very fast responses and behaved like an On-Off type H_2 sensor, igniting a wide range of research studies concerning similar H_2 sensors with On-Off responses to H_2 [10–12]. Despite their strong benefits, however, these sensors also possess drawbacks such as a complex fabrication process and limitations in detecting low H_2 concentrations. To overcome these disadvantages, we previously reported a nanogap-based sensing method that utilizes crack formation in a Pd (and PdNi) thin film generated by stretching the thin film on an elastomeric substrate, termed highly mobile

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thin films on an elastomeric substrate (MOTIFE) [13]. The MOTIFE H_2 sensors operated perfectly as On-Off sensors with high performance resulting from nanogaps on the surface of the sensors formed by mechanical stretching. Even though the MOTIFE sensors seem to resolve many shortcomings, stretching is required to create uniform nanogaps over large areas in the devices.

Here, we present a novel cracked Pd film on an elastomeric substrate (CPE) as a high-performance H_2 sensor that requires no mechanical handling procedure. Hydrogen absorption on the Pd film applies a strain to the silica-like surface of the elastomeric substrate, generating random cracks on the elastomeric substrate. Then, the random cracks propagate to the Pd film during hydrogen desorption. The easy-to-fabricate CPE shows On-Off behaviors with good repeatability, fast response, and a high sensitivity to H_2.

2. Experimental procedures

2.1. *Fabrication method for the CPE*

Polydimethylsiloxane (PDMS) elastomer (Sylgard 184, Dow Corning) substrates were prepared by mixing a base resin with a curing agent at a weight ratio of 10:1 and then by curing at 70 °C for 3 h. The thickness of the PDMS substrate was 0.75 mm. To fabricate H_2 sensors, a Pd film was deposited on the PDMS substrate under ultra-high vacuum (UHV), using direct current (DC) magnetron sputtering. Before deposition, the chamber pressure was kept in the range of

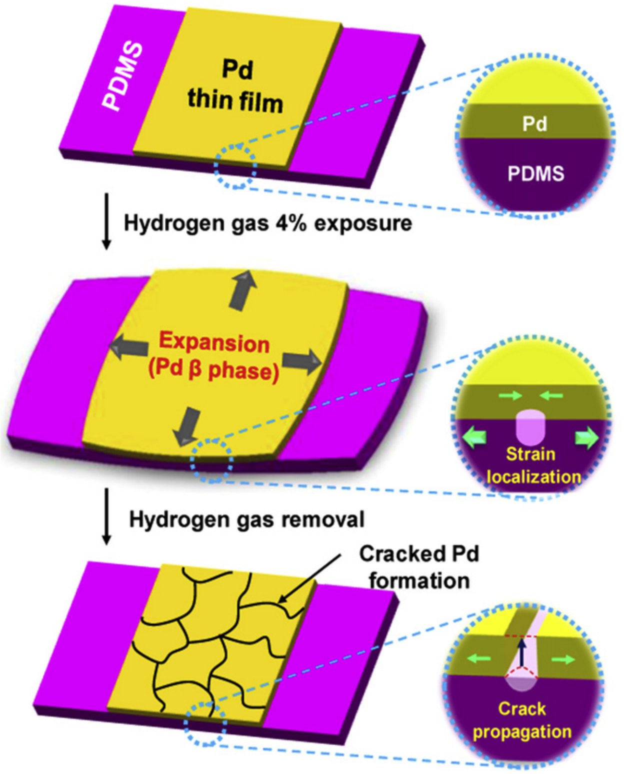

Fig. 1 – Schematic of the fabrication process used for the CPE. (Step 1) Deposition of a Pd thin film onto a PDMS substrate using ultra high-vacuum DC magnetron sputtering. (Step 2) Expansion of the Pd thin film caused by the absorption of hydrogen atoms. (Step 3) Formation of random cracks on the retracted Pd thin film upon desorption of H_2 from the film.

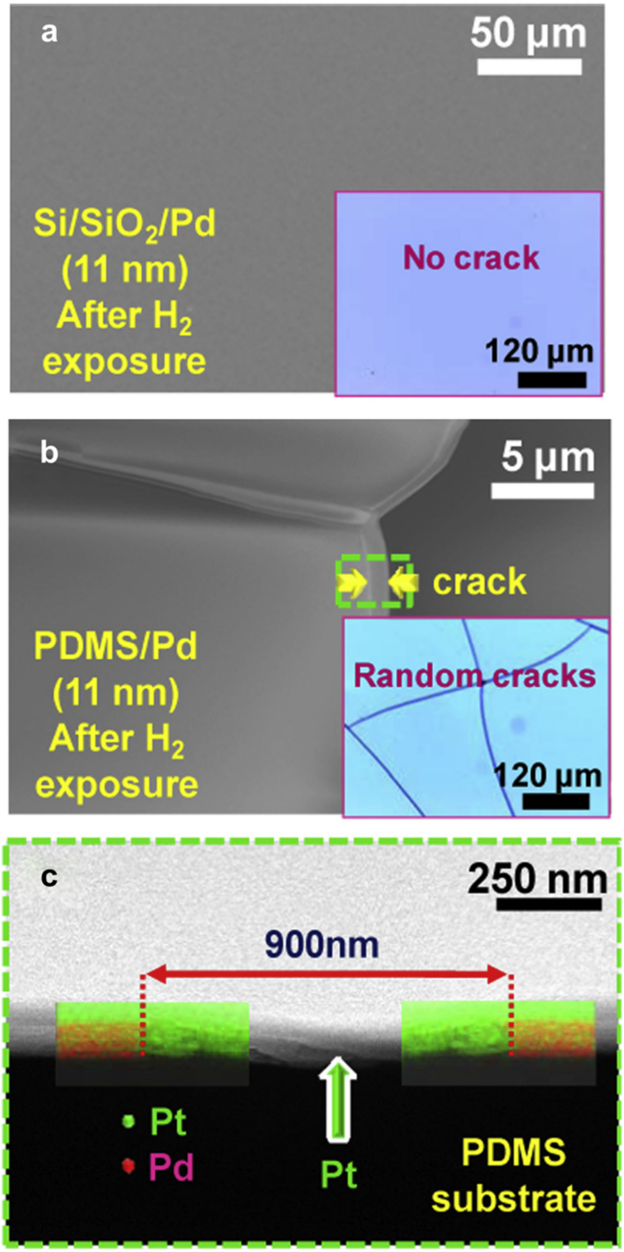

Fig. 2 – (a) An SEM image of a Pd thin film on a Si/SiO_2 substrate. There are no cracks on the surface of the film after exposure to H_2. The inset shows an optical microscope image of the film. (b) An SEM image of a Pd thin film on a PDMS substrate. Unlike the film in (a), there are random cracks on the surface of the film after exposure to H_2. The optical microscope image in the inset clearly shows the random cracks. (c) A cross-sectional TEM image of the crack. The crack formed on the top surface of PDMS was measured to be ~900 nm wide. Pt was used for the FIB milling.

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4×10^{-8} Torr in the pre-baking step. Pd sputtering was carried out under an Ar flow of 14 sccm at a DC power of 20 W, employing a highly pure Pd target (purity: 99.99%) and Ar gas with a purity of 99.9999%. The thicknesses of the Pd films were 6–20 nm.

2.2. *Analysis of the surface characteristics*

High resolution transmission electron microscopy (HR-TEM, JEOL Ltd., JEM-4010) was utilized to investigate the nanostructures of the Pd films on the PDMS. The surface morphologies of the films were examined by scanning electron microscopy (SEM, JEOL Ltd., JSM-6500F) and optical microscopy (OM, Olympus Co.). Examination of the cross-sectional structures of the CPF was performed by transmission electron microscopy (TEM, JEOL Ltd., JEM-2100F). For the TEM and STEM experiments, the samples were sliced into pieces thinner than 100 nm using a focused ion-beam (FIB, FEI Co., Nova600 Dual Beam). TEM observations were performed at 300 kV.

2.3. *Hydrogen gas sensing measurement system*

The system for the H_2 sensing test consisted of a sealed gas chamber with a volume of ~250 ml and H_2 and N_2 mass flow controllers. The gas chamber has a gas inlet and an outlet. The gas mixture of H_2 and N_2 was fed into the chamber through the inlet after being intermixed to produce the desired composition. A check valve opens at pressures higher than ambient pressure so that the chamber is maintained nearly constant at atmospheric pressure. The purities of the N_2 and H_2 gases were 99.9%. A personal computer was connected to a current source-measure unit (Keithley 236) and a nano-voltmeter (Keithley 2182). The real-time electrical resistance or current response to H_2 was measured at room temperature.

3. Results and discussion

3.1. *Fabrication method and structures*

Figure 1 shows the simple and practical process used to fabricate the CPE. This fabrication process consists of three steps. First, a Pd thin film (10 mm (width) × 10 mm (length) × 9–11 nm (thickness); Supporting Information, Fig. S1)) was deposited by UHV DC magnetron sputtering on a PDMS substrate (20 mm (width) × 10 mm (length) × 0.75 mm (thickness)), which was prepared by an established method [14]. Next, the PDMS/Pd was exposed to 4% H_2 so that the Pd film absorbs H_2 and expands due to the phase transition from the α to β phase triggered by absorbed hydrogen atoms, corresponding to a lattice expansion of 3.5% [9]. In the middle of the H_2 absorption, a strain in the Pd film is transferred down to PDMS and generates random cracks. In the last step, the H_2 flow was disconnected to produce random cracks on the Pd film. The removal of hydrogen atoms from the Pd film results in the film retracting to its equilibrium dimensions, leading to crack propagation initiated from the crack contours at the Pd/PDMS interface. The details of this mechanism are discussed further below.

To cross-check the uniqueness of the random cracks on the PDMS/Pd structure, we also fabricated a Pd thin film on a Si/SiO_2 substrate with the same thickness as the CPE. The Pd thin film on the Si/SiO_2 substrate showed no cracks on the surface of the film after exposure to H_2 (Fig. 2(a)). In contrast, random cracks appeared on the surface of the CPE, as shown in Fig. 2(b). The width of the cracks ranged from 0.5 to 2 μm and the center-to-center distance between cracks was about 300 ± 100 μm. The details of the cracks were examined by cross-sectional TEM. The TEM image in Fig. 2(c) clearly shows the feature characteristics of the cracks including a clear gap with a width of

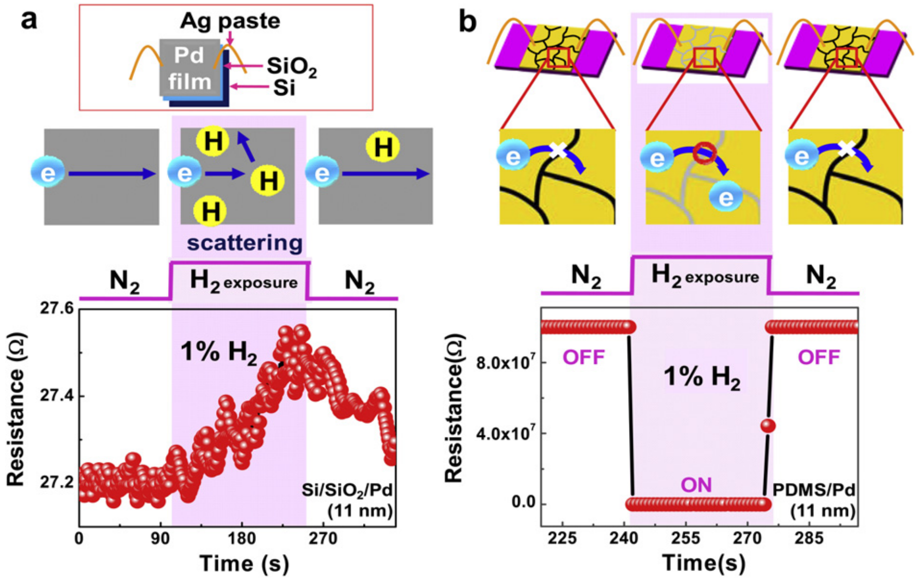

Fig. 3 – The real-time electrical responses of (a) a Pd thin film on a Si/SiO_2 substrate and (b) a CPE to 1% H_2 at room temperature. Schematic illustrations of the respective mechanisms ((a) changes in electron scattering frequencies and (b) On-Off switching by the crack open-close) are also presented.

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900 nm between cracked Pd films on the PDMS substrate. The cracks originate from the PDMS substrate, whose surface was modified by Ar plasma during the Pd sputtering. This is made possible because the surface of the elastomeric PDMS easily changes to a silica-like brittle surface when it is exposed to plasmas of Ar, O_2, and N_2 [15]. The silica-like surface is vulnerable to various sources of strain such as constriction, elongation, and torsion. Expansion of the Pd film due to H_2 absorption can apply a tensile strain onto the surface of PDMS, resulting in random cracks on the PDMS surface. Then, removal of H_2 forces compressive stress to the Pd film and thereby, the cracks on the surface of PDMS propagate through the Pd film, leading to a CPE.

3.2. *Sensing mechanisms and H_2 response properties*

In order to compare the H_2-sensing mechanisms of a normal Pd film and the CPE, the real-time electrical responses of a Pd thin film on a Si/SiO_2 substrate and a CPE were monitored upon exposure to 1% H_2. Fig. 3 shows the results along with schematics of the mechanisms. For the Pd thin film on a Si/SiO_2 substrate, the increase in resistance is attributed to electron scattering by hydrogen atoms incorporated in the Pd layer [2]. On the other hand, the CPE operates as an On-Off switch. The cracks are in the open state (OFF stage) without H_2. Once the CPE is exposed to H_2, the broken pieces of the Pd film swell and connect to each other, bringing about an electrical short circuit (ON stage). This On-Off mechanism enables large sensing signals compared to those from a carrier scattering mechanism.

We performed cyclic measurements under various H_2 concentrations to further investigate the response behaviors of the two types of Pd films. Fig. 4(a) and (b) show representative electrical responses of a Pd thin film on a Si/SiO_2 substrate and a CPE, respectively, to 4% H_2 at room temperature. As displayed in Fig. 3, the CPE operates as a reversible and perfect On-Off switch after the first reaction, which is required to make cracks, while the Pd film on a Si/SiO_2 substrate undergoes relatively small resistance changes based on the carrier

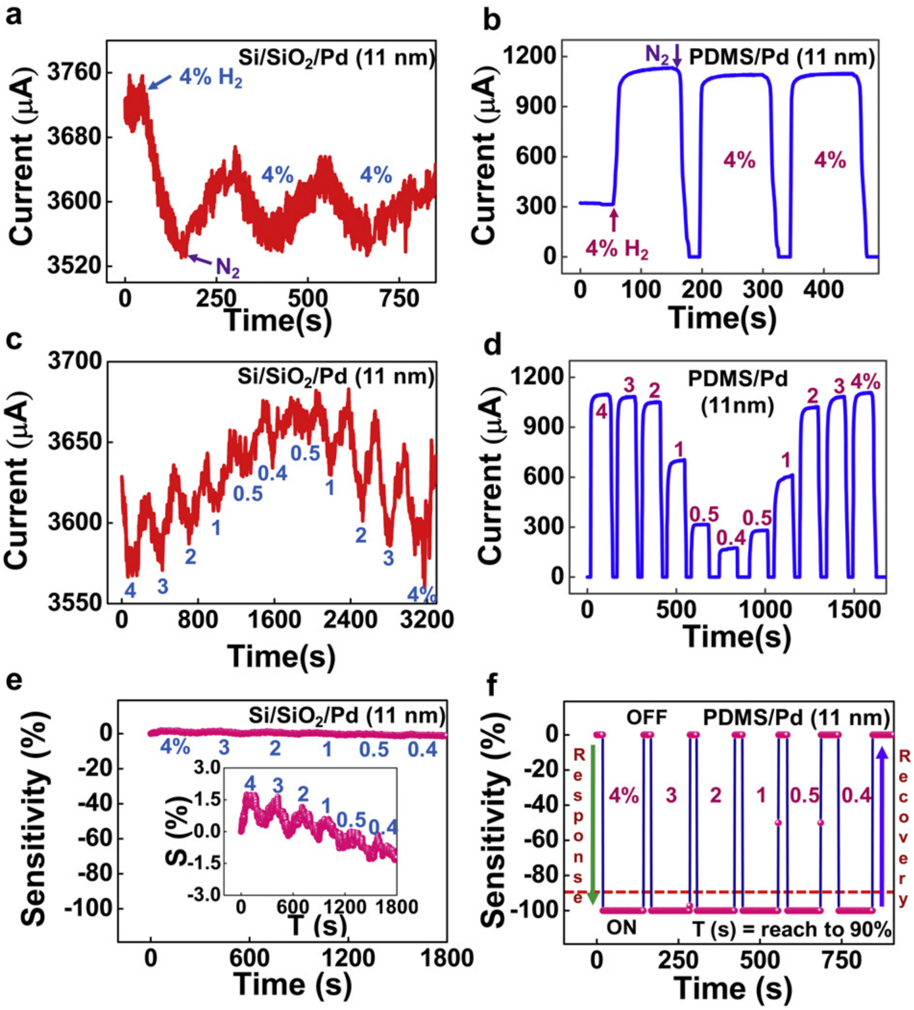

Fig. 4 – Representative electrical responses of (a) a Pd thin film on a Si/SiO_2 substrate and (b) a CPE to 4% H_2 at room temperature. From (b), the CPE was found to operate as a nearly perfect reversible On-Off switch. The real-time cyclic responses of (c) the Pd thin film on the Si/SiO_2 substrate and (d) the CPE to varying concentrations of H_2 in the range of 0.4–4%. The sensitivity vs. time curves for (e) the Pd thin film on the Si/SiO_2 substrate and (f) the CPE, as determined from the electrical resistances. The inset of (e) shows the zoomed in sensitivity vs. time curve. In (f), the average response time is less than 1 s to 0.4–4% H_2 (the time interval between data points is 1 s).

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scattering frequencies. The superior H_2-sensing performance of the CPE compared to that of a normal Pd film is remarkable in regard to its cyclic responses to varying H_2 concentrations in the range of 0.4–4% (Fig. 4(c) and (d)). The Pd thin film on Si/SiO_2 exhibits a baseline shift and relatively small and noisy signals, whereas the CPE shows clear, reversible On-Off responses that are also scalable with H_2 concentration. The real-time electrical responses of the CPE with a thickness of 11 nm are also shown in Fig. S2(a) to stepwise increases then decreases in H_2 concentrations without a cut-off of H_2 flow between adjacent data points. The current gradually increases with increasing H_2 in the concentration range of 0.4–1%, but it drastically changes between 1 and 2% H_2 due to a full phase transition to the β phase [2]. In addition, current vs. H_2 concentration curves in Fig. S2(b) confirm that the CPE shows only a slight hysteresis. The resistances of the CPE at H_2 concentrations of 4, 3, 2, 1, 0.5, and 0.4% were 91.0, 92.3, 95.2, 143.3, 316.7, and 572.1 Ω, respectively, which indicate higher resistances at lower H_2 concentrations and are all negligible compared to the initial resistance (~100 MΩ). For this reason, the sensitivities of the CPE are 100% irrespective of the H_2 concentration, as shown in Fig. 4(f), where the sensitivity is defined as the % resistance change in the presence of H_2 to the initial resistance. As a comparison, it is seen in the inset of Fig. 4(e) that the sensitivities of the Pd film on a Si/SiO_2 are less than 2% under all measured H_2 concentrations. The CPE also outperforms the normal Pd film in terms of the response time defined as the time to reach 90% of the total resistance change. In contrast to the slow response (~80 s) of the Pd film on Si/SiO_2, the response time of the CPE is less than 1 s over the measured H_2 concentration range of 0.4–4%. From these, it is obvious that the PDMS substrate plays a key role in easing expansion and contraction processes of broken Pd pieces, via lateral motions synchronous to those in the Pd film for relieving a stress accumulation.

3.3. *Thickness-dependent of Pd and H_2 sensing modes*

Fig. 5 shows schematic illustrations of the operation modes (Fig. 5(a)) and the corresponding proof-of-concept response cycles of the CPE to 4% H_2 (Fig. 5(b)–(d); see also the Supporting Information Fig. S3 and Fig. S4) depending on the Pd film thickness (6–20 nm). The aforementioned On-Off behavior of the CPE appears in the thickness range of 9–11 nm. For the Pd thickness less than 8 nm, the CPE loses its functionality as an H_2 sensor (always Off mode) after a couple of H_2 cycling, while it operates as a normally On-sensors above 12 nm with Off mode disappeared. This might be due to the different level of recovery of the respective Pd film to equilibrium dimensions upon disconnecting H_2 feed. The recovery level and total volume expansion of the Pd film are important with respect to the crack width on the PDMS substrate [9,13]. In the Pd film thickness of 9–11 nm, the CPE acts as an On-Off sensor because the broken Pd pieces recovered to their stable positions generate cracks on the CPE and the total volume expansion of the Pd pieces is enough to close the cracks in the following exposure to H_2 (see the Fig. 5(c)). In contrast, the CPE exhibits only local cracks when the Pd thickness is larger than 11 nm and the cracks disappear for even thicker Pd (see the Supporting Information Fig. S7). This is believed to be the result of insufficient crack propagation from the PDMS to the Pd film that is restrained by the top portion of the thick Pd film. Because of this, the current of the CPE with a Pd thickness of 12 nm does not fall to zero to the cyclic exposure to 4% H_2, as shown in Fig. 5(b). On the other side, however, the performance of the CPE with a Pd film thinner than 8 nm degrades as the number of H_2 cycling increases, as confirmed from Fig. 5(d). In this case, the CPE still functions in an On-Off mode until it finally loses its functionality (becomes an Off sensor). This performance degradation may be accounted based on the gradual crack widening and insufficient volume expansion of the Pd film. The cracks on the PDMS likely widen within a certain extent in proportion to the number of H_2 absorption/desorption cycles, causing the subsequent widening of Pd cracks after recovery to equilibrium dimensions. As a consequence, the CPE cannot return to the On state after several H_2 cycling since a small volume expansion produced by H_2 uptake of the thin Pd is not enough to close the widened cracks. Therefore, the thickness of the Pd film is a key factor to

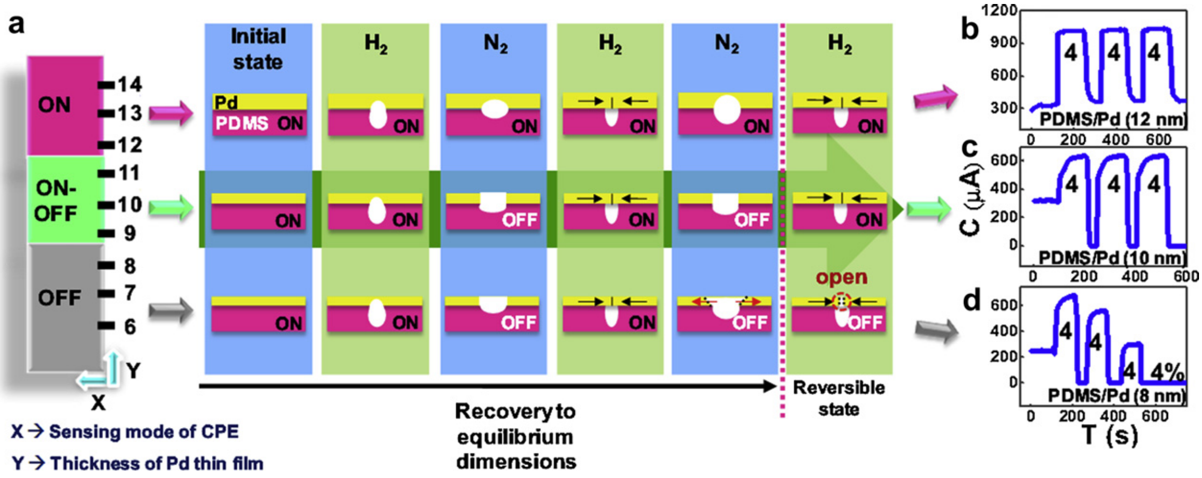

Fig. 5 – (a) Schematic illustrations of the Pd-thickness-dependent H_2 sensing modes and step-by-step morphological changes of the CPE. Representative electrical responses of the CPE with a Pd of (b) 12, (c) 10, and (d) 8 nm in thickness in the presence of 4% H_2 at room temperature. The thicknesses were selected to represent the respective sensing modes shown in (a).

determine the On-Off sensing mode, which enables high performance H_2 sensors.

4. Conclusions

A cracked Pd thin film on an elastomeric substrate (CPE) is a novel, low cost, scalable, and lithography-free method that uses cracking of a sputtered Pd film over large area simply by undergoing hydrogen absorption and desorption processes. Unlike a Pd film on a Si/SiO_2 substrate, the CPE behaved as a reversible On-Off hydrogen sensor based on the crack open-close mechanism during the absorption and desorption of H_2. Depending on the thickness of a Pd film on the elastomeric substrate, the H_2 sensing modes of the CPE were divided into three distinct categories; Off, On-Off, and On mode in the order of increasing thickness. The CPE could be readily used for a perfect On-Off mode in the specific Pd thickness range of 9–11 nm, in which the width of the generated cracks ranged from 0.5 to 2 μm and the center-to-center distance between cracks with 300 ± 100 μm. The performance of the CPE in this optimum thickness range was excellent and could be characterized by good reversibility, huge sensing signals, and fast response (less than 1 s) in H_2 concentrations of 4 to 0.4%, while maintaining the cost benefit of the large-scale thin film process. All these attributes make the CPE a promising candidate for practical H_2 sensors.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.ijhydene.2012.01.067.

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