Highly Mobile Palladium Thin Films on an Elastic Substrate: Nanogap-Based Hydrogen Gas Sensors

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The design of chemical sensors for commercial applications needs to be improved to meet the requirement of mass production, yet many current strategies in sensor design are increasingly complicated and less accessible to manufacturers. These designs mostly rely on making nanoporous gaps in a material of interest, which allow enhancements in performance and miniaturization. In hydrogen gas (H₂) sensors, nanoporous gaps in palladium nanowires have been widely used to study sensor mechanisms and to develop reversible gas sensing capabilities, which is an important step forward in rational sensor design. However, integrating these nanoporous gaps into a large-scale device has been a significant challenge, and as a consequence, it has been difficult to realize a commercially viable device. Approaches that overcome the problem inherent to scalability have been developed in Pd thin-film H₂ sensors, but they suffer from low sensitivity, low speed, and poor reliability. Herein, we present a novel, low-cost, scalable, and lithography-free nanogap-based sensing method. This highly mobile thin film on elastomer (MOTIE) utilizes crack formation in a Pd (and PdNi) thin film generated by stretching the film on an elastomeric substrate to reliably and reproducibly provide highly sensitive H₂ sensors. Not only do we demonstrate that stretching a Pd thin film on an elastomer creates uniform nanogaps over large areas, the size of which can be controlled down to 300 nm at 25% strain, but we also show that these structures may be used for a high-performance H₂ sensor.

Nanogaps in Pd are extensively used to effectively detect hydrogen gas (H₂). The first demonstration of this concept was carried out with nanogaps, known as break junctions, in electrochemically synthesized Pd nanowires. It was shown that these nanogaps could be used as a core component to increase the sensitivity, response speed, and selectivity to H₂ gas. In the following years, attempts to increase the sensing capabilities of Pd-based structures through the use of nanogaps have been extensive, and various fabrication routes for making nanogaps have been developed. These include 1) bottom-up approaches, in which Pd nanoparticles and nanowires are synthesized electrochemically; 2) top-down approaches, in which a single nanotrench on a Pd microwire is formed lithographically and 3) hybrid strategies, in which Pd islands with nanoscale gap separations are grown electrochemically on a lithographically patterned surface. In the context of forming nanogaps, new techniques based on the mechanical breakage of metals in the field of molecular electronics and lithography have also been described. However, none of these approaches are amenable to the fabrication of nanogaps over large areas for practical applications.

Another issue that the break junctions have suffered is that Pd thin films peel off from the surface after repeated H₂/N₂ cycles. This defect originates from high mechanical strain (on the order of several GPa) at the incoherent interface between the Pd and surface (for example SiO₂) during the Pd to PdH₄ conversion with its accompanying volume change. To address this problem, a flexible polymer substrate could be used with Pd on top if the substrate was mechanically coupled to the Pd to effectively eliminate the origin of the strain at the interface during cycling. Previous studies have shown the possibility that a stretchable form of a solid material supported by an elastomeric substrate accommodates large levels of strain without damaging the solid material. In principle, it would be possible to use a soft support under a metal of interest as a means of creating cracks (or nanogaps) in a metal by stretching the support while simultaneously providing a coherent interface between the metal and support during a volume change that reduces the strain at the interface. Herein, we describe a new method for making nanogaps in Pd and PdNi on an elastomeric substrate over large areas using lithography-free approach where the elastomeric substrate acts as a mobile support for forming nanogaps and for eliminating the strain at the interface during Pd and PdNi volumetric changes. Moreover, the highly mobile thin film supported by an elastomeric substrate described herein enables the detection of lower levels of H₂ concentration compared to other types of on-off sensors based on the Pd expansion mechanism.

Poly(dimethylsiloxane) (PDMS) was chosen as an elastomeric substrate because of its 1) compatibility with Pd (no interdiffusion); 2) chemical inertness to H₂; and 3) mechanical flexibility. The PDMS substrate (20 mm wide × 10 mm long × 0.75 mm thick) was prepared according to established literature methods. A Pd film (10 mm wide × 10 mm long × 6–10 nm thick; Figure S1 and Supporting Information, Figure S1) was deposited on the PDMS substrate using ultrahigh-
vacuum (UHV) DC magnetron sputtering at a base pressure of $4 \times 10^{-8}$ Torr. During the Pd sputtering process, the PDMS surface was converted into silica owing to the Ar plasma that easily forms cracks in the PDMS/Pd and increases adhesion between the PDMS and Pd, thereby circumventing the need to conduct an additional surface modification. After the Pd deposition, the PDMS/Pd was mounted onto a stretching machine and cracks were intentionally generated by stretching the PDMS/Pd sample to a tensile strain of 25% (Figure 1b). The tensile strain in this case is defined as $\varepsilon = \left( \frac{L - L_0}{L_0} \right) \times 100$ %, where $L_0$ is the initial length of PDMS/Pd and $L$ the length of PDMS/Pd in the presence of tensile strain. Depending on the intended use, the width of the cracks (that is, gaps) can be deliberately controlled by the magnitude of the strain applied to the PDMS/Pd. After the tensile strain was released, the PDMS/Pd rebounded to its original position, closing the gaps between the cracked Pd (Figure 1c). To create nanogaps in the Pd film from these closed cracks, we utilized the volumetric change of Pd that occurs after it is exposed to H$_2$ gas (Figure 1d). This aspect is discussed in further detail below. Finally, for H$_2$ sensing measurements, the Pd film on the PDMS substrate was electrically connected to a printed circuit board using an Ag paste.

Scanning electron microscopy (SEM) analysis of the resulting cracked Pd thin film confirms that the fabrication method does yield nanogaps in a Pd thin film on a PDMS substrate (Figure 2 and Supporting Information, Figure S3). An applied tensile strain of 25\% along the $x$ direction created linear cracks in the $y$ direction perpendicular to the elongation of the 10 nm Pd film on the PDMS substrate. An SEM image showed the cracks had a circa 20 \(\mu\)m center-to-center separation, that the Pd film was broken into pieces through the cracking process (Figure 2a), and the Pd film adhered well to the PDMS surface as a result of the surface modification of the PDMS during the Pd sputtering in an Ar atmosphere. Although most of the cracks were found to have similar width of (2 ± 0.5) \(\mu\)m (Figure 2b), in principle, the crack width can be controlled by the magnitude of the tensile strain applied to the PDMS substrate and the thickness of the Pd film. Furthermore, buckling patterns in the $x$ direction (parallel to the direction of stretching) were observed on the Pd films when the PDMS/Pd was strained (Figure 2a), but these buckling patterns resolved after the stress was released. Note that the cracks and buckling patterns were formed periodically across the 1 cm$^2$ area simply by stretching the PDMS/Pd (Figure 2c).
After the tensile strain on the PDMS/Pd is released, the cracks are still observable, but they are not as clear as before the strain is released (Figure 2d). On the other hand, the buckling patterns disappear. The average spacing between cracks was about 15 μm. A HR-TEM image of a cross-section of a crack revealed that the broken Pd films overlap inside PDMS cracks underneath (a Pt layer was deposited for a TEM sampling; Figure 2e). As a result, the Pd film on the PDMS is electrically conductive after the strain is released as there is no gap in the cracks. Thus, stretching a PDMS/Pd to 25% and then releasing it results in cracks but no nanogaps on the Pd film (Figure 2f). To create nanogaps, we utilized the mechanism that Pd grains swell upon exposure to H₂ and, after the removal of H₂ (insertion of N₂), the grains return to their initial volume but not their initial positions. Indeed, previous studies have shown that this volume contraction creates nanogaps in Pd nanowires.[6,21]

To demonstrate the concept of creating nanogaps, a cracked Pd film on a PDMS substrate was exposed to H₂, converting it into PdHₓ, followed by the removal of H₂, the conversion of the PdHₓ back to Pd, and film contraction. An SEM image subsequently confirmed that the contraction of the overlapped Pd films yields nanogaps (Figure 2g) that are more clearly observable than those before exposure to H₂ (Figure 2d). The gap in the Pd film over the cracked PDMS surface can be seen in a tilted cross-sectional TEM image (Figure 2h). The Pd film was only observed outside the crack on the PDMS substrate (300 nm gap and 50 nm deep). From the elemental mapping analysis (inset of Figure 2h), no Pd is found inside the crack. This is confirmed by EDX data (Supporting Information, Figure S4) that were obtained from outside (spectrum 1) and inside the crack (spectrum 2). The spectra showed that Pd exists only outside the crack, thereby creating a nanogap in the Pd film. This observation indicates that the Pd ends were relocated relative to the PDMS crack owing to the H₂ exposure and subsequent removal (Figure 2i).

In a proof-of-concept demonstration of the H₂ sensing capability of this Pd-based MOTIFE, a nanogapped Pd film on PDMS substrate was put through cycles of H₂ exposure (Figure 3a). The Pd film for the H₂ sensing experiments (8 nm thick) was prepared by the aforementioned procedure (Figure 3b). Provided that the Pd film is exposed to H₂ gas, dissolved hydrogen atoms on the Pd surface penetrate into the Pd film and subsequently increase the interatomic distances, resulting in Pd film swelling on each side of the cracks and contact between the ends of the broken Pd pieces (Figure 3c). Saturated current was obtained from an 8 nm thick Pd film exposed to 4% H₂, representing the "on" state (marked with green-dotted boxes in Figure 3a).

The absorbed hydrogen atoms rapidly desorbed upon removal of H₂ gas, resulting in Pd atoms returning to their stable positions with reduced interatomic distances (recovery to equilibrium dimensions; Figure 3d). This hydrogen-desorption process leads to a sudden drop to zero in the current level, namely the "off" state (marked with red-dotted boxes in Figure 3a). More details of gap-closing and opening operation were provided by in situ optical observation (Figure 3e; see also videos in the Supporting Information). The optical images taken in a consecutive time series reveal that the film was mobile upon exposure to H₂, and the
operation was clearly reversible without causing mechanical damage to the film. Note that the images at the time of 2.5–8.5 s show darker contrast at the junction between the two Pd films. This effect is not due to opening of the nanogap, but rather to the Pd films folding downward as they press against each other. The PDMS substrate plays a role of caging the relative lateral motion of broken Pd pieces, transferring a strain in the Pd film to a flexible layer, which synchronizes its motion with that of the Pd film.

The capability that distinguishes the Pd-based MOTIFE H₂ sensor from others in terms of high sensitivity, low detection limit, device reliability, and high response speed (time) was demonstrated (Supporting Information, Table 1), while maintaining the cost advantage of the large-scale thin film process. The H₂ sensing sensitivity, detection limit, and reliability of the Pd-based MOTIFE were evaluated in the context of repeated exposure to H₂ gas of different concentrations, ranging from 0.05% to 10%. A representative electrical response of the Pd-based MOTIFE (10 nm thick Pd, 300 nm gaps in a 1 cm² film) to H₂ gas (in an N₂ carrier gas) shows the notable on–off behavior (Figure 4a). The amplitude of the current correlated with the H₂ concentration; a higher concentration results in a greater Pd volume expansion that bridges the gaps, and as a consequence, a larger current crosses the Pd film. When the Pd-based MOTIFE is exposed to a higher H₂ concentration, the nanogaps appear wider after hydrogen desorption because of a greater volume contraction owing to more hydrogen desorption from the PdHₓ. For this reason, the detection limit of the Pd-based MOTIFE was 0.4% H₂ after its reaction with 10% H₂, and subsequently the sensor was capable of reversibly sensing up to 10% H₂ over 29 on–off cycles at atmospheric pressure and room temperature. Note that this highly sensitive and perfect on–off sensing over many cycles without the degradation of the Pd film was implemented by forming nanogaps over large areas in a Pd film by stretching a flexible PDMS substrate. In contrast, normal Pd films on hard Si/SiO₂ substrates operate as “normally on”, and resistance-based sensors show much lower sensitivity (3.92%, 10 nm Pd film upon exposure to 2% H₂) and shifted baseline resistance (Supporting Information, Figure S5). Furthermore, the response time, defined as the time to reach 90% of the total change in electrical resistance change [4] was also evaluated. The average response time of the Pd-based MOTIFE was 0.67 s upon exposure to 2% H₂ (Figure 4b), which is fast compared to typical film-type sensors on a hard surface (ca. 64 s, 10 nm Pd films on Si/SiO₂ substrate; Supporting Information, Figure S5). This is due to the facile Pd film movement that opens and closes the gaps upon exposure to H₂, which is assisted by the flexible PDMS substrate.

Finally, the ability to achieve a detection limit below 0.1% H₂ using a different material-based MOTIFE rather than Pd was also evaluated. For example, a sensor using PdNi alloy films was used to suppress the α–β-phase transition upon exposure to H₂ [12,13] and thus quantify electrical signals above 2% H₂, a level at which the Pd-based MOTIFE cannot distinguish (Figure 4a; Supporting Information, Figure S6). A PdNi-based MOTIFE was prepared by the same procedure with the Pd-based MOTIFE (Supporting Information, Figure S7). A representative electrical response of the PdNi-based MOTIFE (6 nm thick PdNi) to H₂ gas (in an N₂ carrier gas) shows the notable on–off behavior with the detection limit of 0.08% H₂ after its reaction with 10% H₂ (Figure 4c). The electrical response above 2% H₂ was easily discernible and accurately quantified H₂ concentrations, and without the rapid phase transition that takes place in pure Pd. This different response behavior between the Pd- and PdNi-based MOTIFEs was clearly seen upon exposure to H₂ (Figure 4d), showing that the Pd-based MOTIFE exhibited sudden current change around 1.5% of H₂ owing to the phase transition α to β, while the PdNi-based MOTIFE showed near linear current change. Importantly, the average response time of the PdNi-based MOTIFE upon exposure to 2% H₂ was

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**Figure 4.** a) The real-time electrical response of a Pd-based MOTIFE to H₂ in N₂ carrier at room temperature. The hydrogen concentrations are shown in percentages on top of the electrical response. b) The sensitivity versus time curve for the Pd-based MOTIFE. The sensitivity was converted from the electrical resistance response. The average response times are 0.67 to 2% H₂ (the time interval between data points is 0.42 s). c) The real-time electrical response of a PdNi-based MOTIFE to H₂ at room temperature. d) The current variation versus H₂ concentration range for pure Pd-based and PdNi-based MOTIFE during 0–4% H₂. e) A sensitivity versus time curve for the PdNi-based MOTIFE. The average response times are 0.50 to 2% H₂ (the time interval between data points is 0.42 s).
0.50 s (Figure 4c), which is sufficient for commercial applications.

In summary, MOTIFE is a new lithography-free nanogap-based sensing method that uses crack formation over large areas in a metal thin film. Pd- and PdNi-based MOTIFEs can be readily used for highly sensitive and reliable H₂ sensors that show nearly perfect reversible on-off behavior. This novel method is general and can be applied to the creation of nanogaps over large areas on many flat metal surfaces. It is not restricted solely to Pd and PdNi alloys for sensing H₂ because the method is general and can be applied to other metals (see the Supporting Information, Figure S8 for Ti and S9 for Bi) that can utilize nanogaps to specifically sense other chemicals. This new set of capabilities will allow researchers and manufacturers to produce low-cost and scalable sensors that are a step towards the realization of high-volume production.

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