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Self-assembled monolayer-enhanced hydrogen sensing with ultrathin palladium films

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(Received 28 January 2005; accepted 30 March 2005; published online 11 May 2005)

Resistive-type palladium structures for hydrogen sensing remains as a research focus for their simplicity in device construction. We demonstrate that a siloxane self-assembled monolayer placed between a substrate and an evaporated ultrathin Pd film promotes the formation of small Pd nanoclusters and reduces the stiction between the palladium and the substrate. The resulting Pd nanocluster film can detect 2% H_2 with a rapid response time of ~70 ms and is sensitive to 25 ppm hydrogen, detectable by a 2% increase in conductance due to the hydrogen-induced palladium lattice expansion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1929075]

The utilization of effective hydrogen sensors to quickly and sensitively respond to hydrogen gas leaks and to monitor manufacturing and distribution will be crucial for the safe deployment of all hydrogen-based applications. In particular, resistive sensor elements that change their values in the presence of hydrogen are the focus of many research groups[1–5] due to their simple fabrication methods, compact packaging and relatively straightforward signal detection. For example, palladium increases its resistivity in the presence of hydrogen due to the formation of Pd hydride[6,7] and has been used as a sensing element in hydrogen sensors.[8–10] However, the response time and sensitivity of the currently available resistive-type sensors are not adequate for many hydrogen applications such as hydrogen leak detectors in hydrogen-powered vehicles. Some progress has been made to improve both the response time and the sensitivity through the discovery of new sensing materials[1–3] and the exploitation of the nanostructures of known sensing materials.[4,5] Among the latter, Pd nanobead chains fabricated by electrodeposition on single crystal graphite step edges showed a response time as short as 70–75 ms for a 5% hydrogen/nitrogen mixture.[5] This is the fastest response to hydrogen ever reported. The sensing mechanism is based on the hydrogen-induced lattice expansion (HILE) in Pd,[11,12] which causes the swelling of the Pd nanobeads thus narrowing/closing the gaps between the beads in the Pd chains. Inspired by the short response time achievable through HILE, Dankert *et al.* proposed a more practical way to apply this mechanism by fabricating Pd discontinuous films close to the percolation threshold.[13] The resistance of such a film is expected to decrease in the presence of hydrogen due to the HILE in Pd film that increases the number of conducting percolation pathways. They also made a film consisting of Pd agglomerates of 2–5 μm in size by Joule heating a 10 nm thick continuous film on a sapphire substrate and demonstrated the expected resistance decrease in the presence of concentrated deuterium (at a pressure of $5–9\times10^4$ Pa). One problem that can hinder practical applications is the drift in the film resistance after each hydrogen loading/unloading cycle. No detailed studies on hydrogen response times of these Joule heating produced Pd agglomerates were reported. As reported earlier,[12,14] HILE-based hydrogen sensing using ultrathin Pd films could have response times as long as minutes. The slow response times based on this mechanism may be due to the in-plane strain of Pd attached directly to the supporting substrate,[13] because of the strong adhesion at the metal–oxide interface.[15] A large portion of the Pd atoms in an ultrathin film resides at the interface thus slowing the film's HILE response.

Siloxane self-assembled monolayers (SAM) are widely used as a lubricating layer to reduce the adhesion at the interface between different components in microelectromechanical systems.[16] Here, we show that enhanced hydrogen sensing performance can be achieved for ultrathin Pd films deposited on siloxane SAM resulting in rapid response times, high sensitivity and reversibility upon each H_2 loading/unloading cycle.

The SAM supported Pd film preparation involves two steps. First, sanitized microscope slide cover glass slips were immersed in 1 mM N-octyldimethylchlorosilane in toluene or in commercial windshield rain repellant (Prestone) for 24 h for the formation of siloxane SAM coated glass (SCG) and rinsed with isopropanol. Ultrathin Pd was then evaporated onto the SCG (Polaron E6700 evaporator, base pressure of the vacuum chamber is $\sim10^{-6}$ Torr and evaporating rate is 0.1 Å/s). For the purpose of comparison, a cleaned bare glass (BG) was placed beside the SCG as a reference. In order to obtain information for optimal thickness, we conducted *in situ* monitoring of the film conductivity as a function of its nominal thickness during film deposition.

Figure 1(a) shows the evolution of the film conductivity during the Pd evaporation on both a SCG and a BG. Below 5 nm, the Pd film conductivity on both types of substrates is strongly thickness dependent. Specifically, between 3.3 and 3.4 nm, the conductivity of the Pd film on SCG increased by a factor of ~5 within 0.1 nm (the resolution of our thickness

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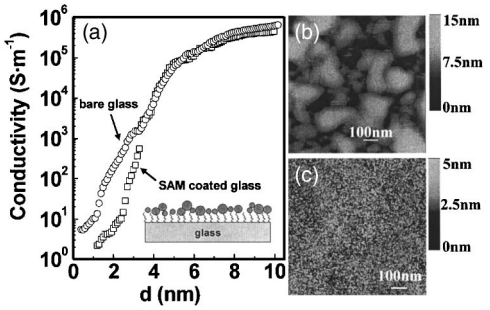

FIG. 1. (a) Thickness dependent conductivity of Pd films deposited on BG (◯) and on SCG (□). The inset shows a schematic of an ultrathin Pd film consisting of nanoclusters on a SAM coated substrate; (b) and (c) are AFM images of nominal 3.3 nm thick Pd films on BG and SCG, respectively.

monitor). In contrast, the Pd film on BG exhibits a more gradual increase in this range. Above 5 nm, the incremental percentage increase in conductivity for both films becomes less thickness dependent and it is assumed that the films are becoming coalescent.[17] The surface morphology for both types of samples at a thickness of 3.3 nm was investigated by atomic force microscopy (AFM). Evaporated Pd on BG surface forms randomly connected Pd domains with an averaged size of 1200 nm^2, about 6 nm in height, and ~100 nm apart from each other [Fig. 1(b)]. In contrast, the Pd film on SCG [Fig. 1(c)] consists of much smaller Pd clusters, similar to the morphology of ultrathin gold films on alkylthiol SAMs.[18] The application of siloxane SAM lowers the surface free energy and results in the formation of smaller Pd nanoclusters, leading to intercluster gaps of less than 10 nm wide versus an average of 100 nm for the films on BG. As discussed later, the smaller Pd clusters and the narrower gaps between them are crucial for increasing the film's sensitivity to hydrogen gas detection.

The kink at ~3.3 nm for the Pd film on SCG indicates that a large amount of nanoclusters are at the percolation threshold. Thus, further addition of a very small amount of Pd will enable the formation of large numbers of new conducting pathways and significantly enhance the conductivity of the film. Likewise, swelling of the Pd clusters due to HILE will also induce a large increase in conductance at the threshold of percolation. Therefore, a film with a thickness of ~3.3 nm is ideal for detection of hydrogen gas. As shown in Fig. 2(a), a 3.3 nm thick Pd film on SCG showed a conductance increase ($\Delta\sigma/\sigma_0$ with $\Delta\sigma=\sigma_H-\sigma_0$) as high as 68% when exposed to 2% H_2 (the background gas is nitrogen). The response time, defined as the rise time to reach 90% of $\Delta\sigma$, is about 68 ms and the conductance returns to the baseline without any significant drift when the hydrogen content is removed. As shown Fig. 2(b), this reversibility is stable for many loading/unloading cycles. In contrast, Fig. 3(c) shows that the conductance of the 3.3 nm thick reference film on BG first undergoes a decrease. This decrease is offset and eventually outpaced by an increase in conductance, leading to only a small conductance increase in response to hydrogen. Moreover, the conductance of these ultrathin Pd films on BG drifts with each H_2 loading/unloading cycle, which was also observed for Pd microclusters on sapphire substrates.[13] As pointed out in Refs. 12 and 14, the adsorption of hydrogen by Pd can have two opposing effects on the electrical transport properties of discontinuous ultrathin Pd films: (a) the conductance decreases with the formation of

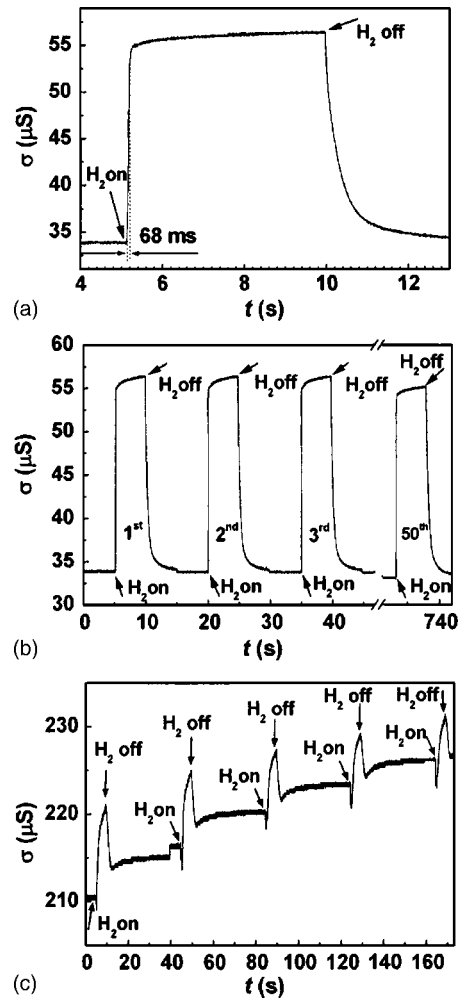

FIG. 2. (a) Conductance response of a 3.3 nm thick Pd film on SCG to 2% H_2. The flow of H_2 is controlled by a solenoid valve with a switching time of 25 ms; (b) repeated cycling of H_2 loading and unloading onto the same sample; (c) response of a 3.3 nm thick Pd film on BG to 2% H_2.

PdH_x and (b) the conductance increases due to HILE, thereby narrowing the gaps between the Pd nanoclusters. The initial decrease in conductance in Fig. 3(c) can be ascribed to the formation of PdH_x hydride. The subsequent increase in conductance is due to the HILE-induced dilation of Pd clusters forming more conductive pathways. This result is consistent with our previous assumption of the slow motion of Pd clusters on BG due to the strong adhesion between the Pd atoms and the substrate.[13] The comparison between thin Pd films on SCG and on BG proves that the SAM layer between Pd and glass contributes to faster and reversible responses of the ultrathin Pd films to hydrogen.

At room temperature, bulk PdH_x ($x<0.8$) undergoes an α to β phase transition starting at 1–2 kPa of H_2 pressure (i.e., 1%–2% in concentration of one atmospheric pressure), leading to a change in the lattice constant from 3.895 Å (the maximal for α phase) to 4.025 Å (minimal for the β phase), an increase of 3.5%, corresponding to an 11% increase in volume.[19,20] Because most of the increase in lattice constant occurs in this α-to-β transitional phase, HILE-based hydrogen sensing at room temperature suffers from a detection limit of 1%–2% H_2 if the gaps between clusters/beads are too wide to be closed by HILE. In fact, this limitation is observed in the hydrogen response of Pd mesowires which consist of coarse Pd grains of 50–150 nm in diameter and

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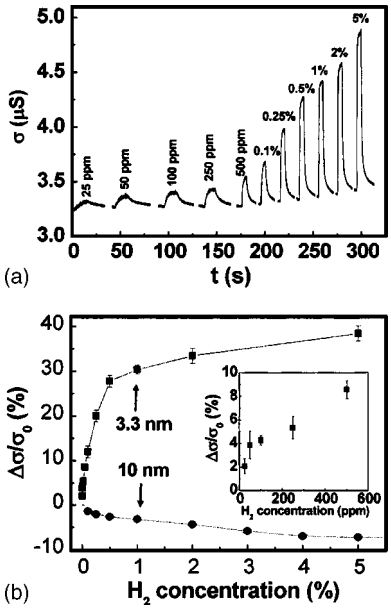

FIG. 3. (a) Conductance responses of a 3.3 nm thick Pd film on SCG to various concentrations of H_2. Data were acquired for each concentration and collected to be drawn in the same plot, (b) conductance change vs H_2 concentration for the same sample (—■—). The inset is a magnified view of the data in the low concentration region. Data obtained for a continuous Pd film (10 nm thick) on SCG is also given (···●···) for comparison.

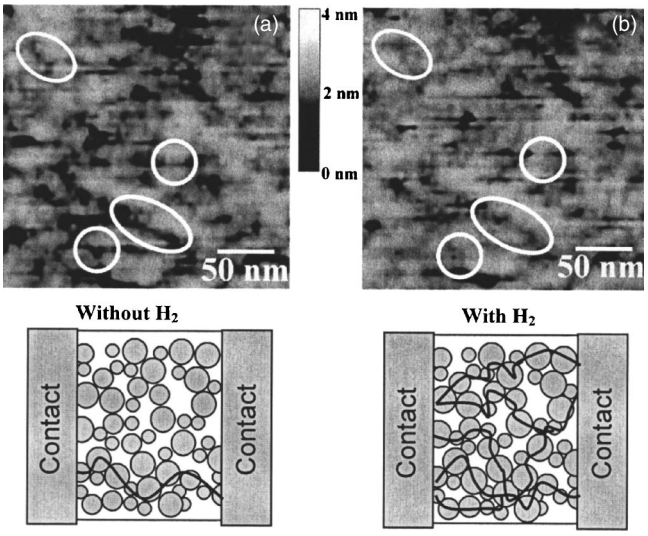

FIG. 4. *In situ* AFM image of a 3.3 nm thick Pd film on SCG acquired (a) before and (b) during exposure to H_2 gas. Several hydrogen-induced gap narrowings or closings are highlighted within the white circles. The corresponding schematics in the lower panels illustrate the formation of increased conducting pathways due to HILE in Pd nanoclusters.

intergrain gaps of tens of nanometers wide.[5] Unlike bulk PdH_x, the lattice constant-pressure isotherms of Pd nanocrystalline and small nanoclusters, measured by *in situ* x-ray diffraction exhibits an even increase in the lattice constant as a function of hydrogen gas pressure.[21,22] Siloxane SAM promotes the formation of Pd nanoclusters with intercluster gaps in the nanometer range. Thus, narrowing of the intercluster gaps is still achievable through HILE at low H_2 concentration for thin nanocluster Pd films on SCG. A slight narrowing of the intercluster gaps can still produce an appreciable increase in film conductance since the electron tunneling current between the intercluster gaps[11,14] depends exponentially on the gap spacing. Figures 3(a) and 3(b) demonstrate that 3.3 nm Pd films on SCG can overcome the detection limit of 1%–2% H_2 at room temperature. A H_2 concentration of as small as 25 ppm can generate a detectable 2% increase in film conductance. For comparison, the results from a 10 nm Pd film on SCG are shown in Fig. 3(b). At this thickness, the film is continuous and behaves similar to bulk Pd, i.e., the conductivity decreases in the presence of hydrogen due to the formation of Pd hydride.

The HILE of 3.3 nm Pd film on SCG was directly observed in *in situ* atomic force microscopy (AFM) images acquired before [Fig. 4(a)] and during [Fig. 4(b)] the films's exposure to a stream of hydrogen gas. Gap narrowing between Pd nanoclusters can be identified in the denoted area in Fig. 4(b). The HILE as it pertains to the sensing films is denoted schematically in the lower portion of Figs. 4(a) and 4(b).

In conclusion, siloxane SAMs were used as a functional layer between Pd films and glass substrates to promote the formation of Pd nanoclusters and to reduce stiction during dilation upon HILE. We identified the optimal thickness for the Pd ultrathin film on SCG and the sensing mechanism for which a large and fast conductivity change occurs in the presence of hydrogen. The hydrogen-induced conductivity change is reversible and stable.

This work was supported by the U.S. Department of Energy, BES-Materials Science, Contract No. W-31-109-ENG-38. One of the authors (Z.L.X.) also acknowledges support from the U.S. Department of Education, and the State of Illinois under HECA.

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