ADVANCED MATERIALS

DOI: 10.1002/adma.200601572

A Pyrolytic, Carbon-Stabilized, Nanoporous Pd Film for Wide-Range H_2 Sensing**

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With the increasing relevance of H_2 gas in modern industry, high-performance H_2 sensors (sensors that exhibit, e.g., a fast response, good stability, sensitivity, etc.) are becoming increasingly important in detecting and monitoring H_2. Because of its noteworthy ability to absorb a large quantity of H_2 and its highly selective response to H_2, Pd has found wide applicability in various H_2 sensors including Pd-film-based resistive sensors, metal oxide semiconductor-type sensors, Schottky-diode-type sensors, and optical sensors.[1–3] Among these H_2 sensors, resistive sensors based on dense Pd films have attracted much attention because of their simple device structure and fabrication process. However, several drawbacks, including a narrow detection range (dense-film resistive sensors are only sensitive to medium-level concentrations of H_2 gas), a slow response time, and instability in higher concentrations of H_2 usually hinder the widespread applicability of resistive sensors based on dense films.[4–7]

To improve H_2-sensing performance, nanostructured Pd materials have been developed, and they have demonstrated a much quicker response to H_2 gas. Break-junctioned Pd nanowires reported by Favier et al. have shown the fastest response because of a volume-expansion-induced resistance decrease upon the absorption of H_2.[8] However, these Pd nanowires are only sensitive to high concentrations of H_2. Based on the same sensing mechanism, Xu et al. have used self-assembled monolayers to promote the formation of break-junctioned Pd nanoclusters to realize a fast H_2 response.[9] Recently, we have fabricated nanoporous Pd film sensors by using anodic aluminum oxide (AAO) as a substrate.[10] It was shown that the nanoporous Pd film demonstrated an increased resistance upon absorption of H_2. The nanoporous Pd sensor had a quick response to low concentrations of H_2 gas (less than 1 % H_2). For higher H_2 concentrations, the nanoporous Pd films directly supported by AAOs lost their sensing stability because of stress-induced blistering of the film. Here, we report a simple but effective method to fabricate a nanoporous Pd film sensor that has a remarkable sensing performance and is able to detect both dilute and high concentrations of H_2 gas (ranging from 250 ppm to 10 % H_2) with quick response times at room temperature, through the use of pyrolytic carbon as a transition layer between the Pd film and the AAO template/substrate. A mechanism based on nanoporous structure-enhanced H_2 sensing is proposed.

Briefly, an aluminum film deposited onto a highly doped n-type Si wafer was anodized in 0.3 M oxalic acid to obtain the AAO template. A film of amorphous carbon only several nanometers thick was deposited onto the AAO template by using the chemical vapor deposition (CVD) pyrolysis of acetylene. Detailed information about the anodization and CVD processes can be found elsewhere.[11–13] A Pd film was then deposited, via sputtering, onto the upper surface of the carbon-coated AAO substrate. A resistive sensor based on a Pd film was then fabricated and tested under various concentrations of H_2 in nitrogen (Fig. 1).

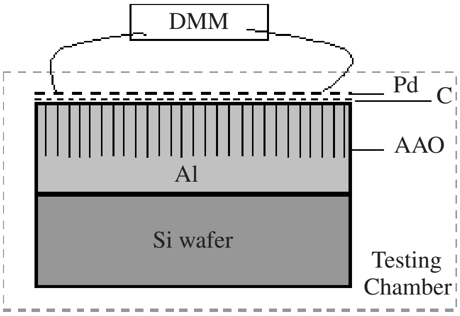

Figure 1. Resistive H_2 sensors based on a pyrolytic, carbon-supported, nanoporous Pd film.

As a robust and insulating substrate, the AAOs are a uniform nanotemplate for shaping nanoporous carbon and the subsequent nanoporous Pd film. As shown in Figure 2, the deposition of thin films of C and Pd did not change the nanoporous features of the surface morphology even thought the average diameter of the nanopores decreased a little. The nanoporous Pd film sensor is sensitive to both dilute and high concentrations of H_2 gas. Upon absorption of H_2, the resistance of the nanoporous film increases as a result of H_2-induced lattice or volume expansion. As reported earlier,[10] the variation in the resistance of a nanoporous Pd film (upon absorption of H_2) is different from Pd nanowires or monolayer-promoted Pd films, although break-junctions often exist in the nanoporous Pd films shaped by AAOs. There are two competitive processes that affect the final variations in nanoporous

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[**] This work was supported by National Science Foundation (EPS0447479), Department of Energy (DE-FG26-04NT42171), and Army Research Laboratory (W911NF-04-2-0023).

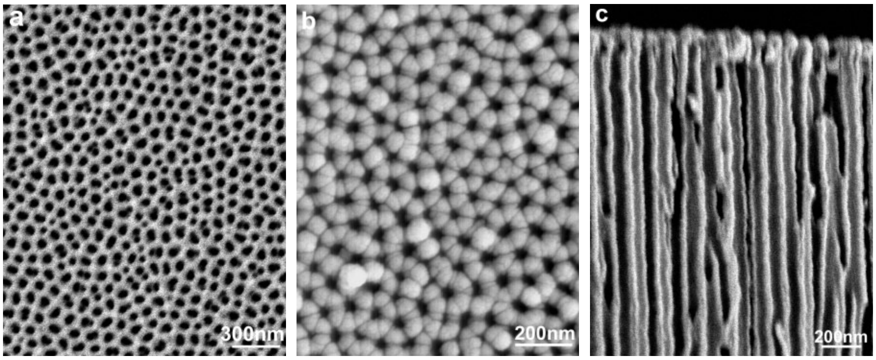

Figure 2. a) Scanning electron microscopy (SEM) image of an AAO template. b) SEM image of a nanoporous Pd film on top of a pyrolytic, carbon-coated AAO template. c) SEM image of a cross section of a fractured Pd/C/AAO film (prepared by vertically cutting the wafer-supported sample with a diamond cutter) showing deformed Pd deposition below the top edge of the carbon-coated AAO nanoholes.

Pd film resistance. One is a H_2-induced increase in film resistance, which is similar to the features of a traditional dense Pd film, and the other is a break-junction-induced decrease in film resistance that results from volume expansion, which has been found in break-junction Pd nanowires. For the nanoporous Pd film prepared here, the film resistance always increased after H_2 absorption. This increase indicates that the break-junction effect has been minimized to such a degree (through appropriate selection of the film thickness) that it does not dominate the H_2-sensing process.

The steady-state response (relative resistance change, $\Delta R/R_0$) increases with increasing H_2 concentration (Figs. 3 and 4). At lower H_2 concentrations (less than 1000 ppm), the steady-state response value of the nanoporous, carbon-supported, Pd film sensor is 0.4 % at 250 ppm H_2 and up to 1.0 % at 1000 ppm H_2. At higher H_2 concentrations (less than 10 %), a steady-state response value up to 15.6 % at 10 % H_2 can be found in the nanoporous, carbon-supported, Pd film sensor. On the other hand, a dense Pd film sensor directly supported by a thermally oxidized Si wafer can only detect a medium-level concentration of H_2 (concentrations between 1000 ppm and 1 % H_2). A nanoporous Pd film sensor directly supported by the AAO template could have a slightly wider detection range (from 1 % H_2 to dilute levels of H_2). At H_2 concentrations above 1 %, unstable responses and very slow recovery (or even no recovery, which is a symptom of volume-expansion-induced blistering or film damage) could be found for the dense Pd film sensor and the nanoporous Pd film sensor directly supported by the AAO template. Thus, to have a sound sensor, the upper detection limit for the above two sensors should be less than 1 % H_2.

Obviously, through the use of nanoporous Pd structures, the improvement in the response to low H_2 concentrations is quite clear in comparison to dense Pd films. Furthermore, there is little difference in the response to low H_2 concentrations between the Pd/C/AAO sensor and the Pd/AAO sensor. But with the aid of pyrolytic carbon, a great improvement in the response to high H_2 concentrations can be achieved. This result suggests that film damage from excess volume expansion or stress induced by the absorption of H_2 in the C-supported nanoporous Pd film have not occurred for H_2 concentrations as high as 10 %. Thus, with regard to the detection limit, the carbon-supported, nanoporous Pd film sensor demonstrates a great advantage in sensing over a wide range (from 250 ppm to 10 % H_2) compared to traditional dense Pd film sensors, AAO-supported Pd film sensors, and even the break-junction Pd nanowires.

As shown in Figures 5 and 6a, a typical response time (i.e., the time for reaching a 90 % variation in film resistance after the introduction of H_2 gas) for the carbon-supported nanopo-

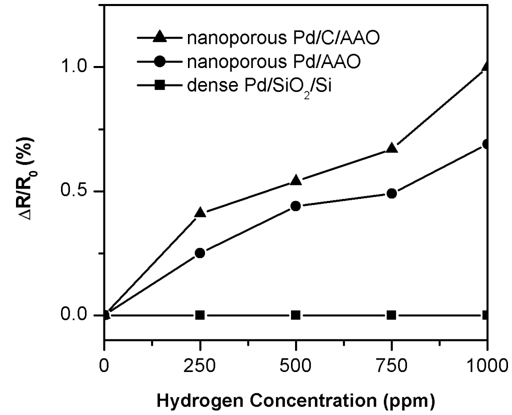

Figure 3. Steady-state response of a nanoporous carbon-supported sensor at dilute H_2 concentrations. Response curves for an AAO-supported sensor and a dense film sensor supported by an oxidized wafer are also presented.

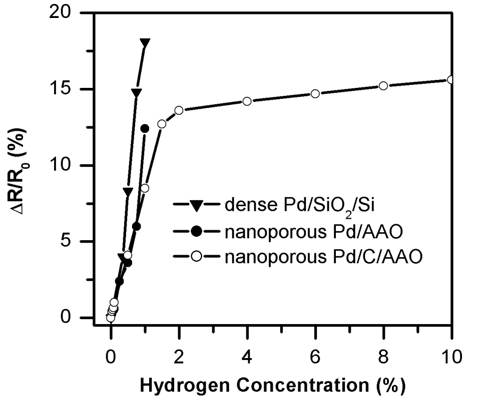

Figure 4. Steady-state response of a nanoporous carbon-supported sensor at various H_2 concentrations. Response curves of an AAO-supported sensor and a dense film sensor supported by an oxidized wafer are also presented.

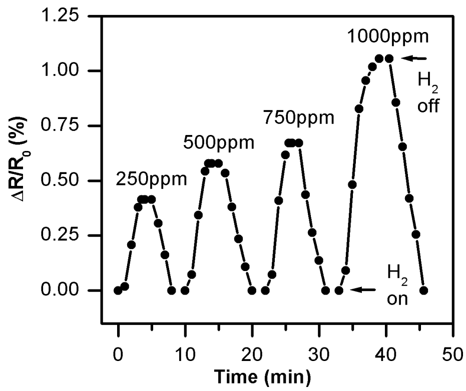

Figure 5. Response of a nanoporous carbon-supported Pd sensor at dilute H_2 concentrations.

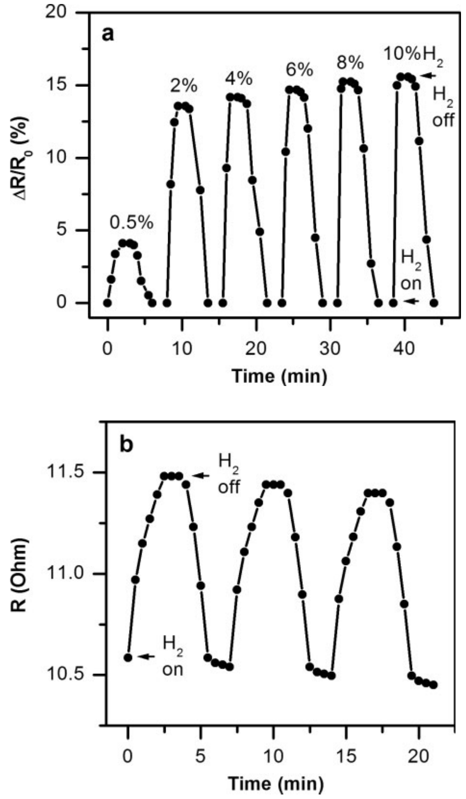

Figure 6. a) Response of a nanoporous carbon-supported Pd sensor at high H_2 concentrations. b) Typical variation in the resistance under repeated testing between nitrogen and 1 % H_2 balanced with nitrogen.

rous Pd film sensor is less than 4 min for dilute H_2 gas. At H_2 concentrations of 2 %, the response time is 90 s, and it only takes less than 30 s to have an 8 % variation in film resistance. With an increase in H_2 concentration to 10 %, the response time is less than 30 s. This performance is an improvement over traditional thick-film-type sensors but is still much longer than the reported break-junction-type sensors with 100 ms or slower response times. Quicker responses for the nanoporous Pd-film sensor may be achieved by further optimizing film thickness. It should be mentioned that in a balancing atmosphere of nitrogen there is always a slight drift in the film resistance for our nanoporous Pd film sensors. Such a drift to lower resistances (after a full recovery of the starting resistance) is depicted in Figure 6b, which shows a nearly reproducible response of the pyrolytic carbon-supported Pd film sensor under repeated sensing tests with 1 % H_2 in nitrogen. The drift in film resistance in an inert atmosphere was so small that it could not affect normal sensing performance (increased resistance from the absorption of H_2 in the nanoporous Pd film).

The wide-range sensing ability of the nanoporous carbon-supported H_2 sensor described here is mainly attributed to the nanoporous structure of the Pd film. As the specific area of the nanoporous Pd film is much larger than for a dense Pd film, H_2 gas tends to dissociate easily on the surface of the nanoporous Pd film. The nanoscale thickness (45 nm) and patterned morphology aids the diffusion of H_2 into the Pd lattice. Thus, during a H_2-sensing process, rapid absorption and desorption of H_2 can occur, accompanied with noticeable resistance variation, which results in enhanced H_2 sensing for dilute H_2 gas levels as low as 250 ppm.

It has been established that lattice or volume expansion of a dense Pd film upon absorption of high concentrations of H_2 can cause considerable stressing in the dense Pd film or stress mismatch at the film/substrate interface, which finally leads to blistering of dense Pd films. As a result, the sensor loses sensing stability (i.e., reversibility, durability, etc.).[7] Stressing was also a problem in our previous nanoporous Pd film sensors.[10] Therefore, any effort to alleviate such stress will help to stabilize the Pd deposition and obtain an improved H_2-sensing performance (higher upper detection limit). Compared to the AAO-supported Pd films that can only detect up to 1 % H_2; the nanoporous Pd film supported by the carbon-coated AAO template can detect a high concentration of H_2 without fail. This result suggests that the pyrolyzed carbon layer helps to minimize the strain between Pd and the aluminum oxide substrate and thus remarkably enhances the film stability upon the absorption of high H_2 concentrations.

Moreover, we believe that a volume-expansion-enhanced pinning also helps to stabilize the nanoporous film because the regular array of holes has the effect of minimizing the stress when H_2 expands the lattice. Upon the absorption of H_2, volume expansion occurs in the entire Pd film, including the Pd deposited slightly below the upper edge of the AAO nanoholes. As a result, a favorable volume-expansion-induced pinning force forms around the inner part of the AAO nanoholes. The pinning force increases with an increase in the absorbed H_2 or the H_2 concentration. Such local pinning, together with the transition layer of pyrolytic carbon, makes it possible to detect a high concentration of H_2.

In summary, a nanoporous Pd film sensor fabricated on a carbon-coated AAO template has been found to have remarkable H_2-sensing performance compared to traditional, dense Pd film sensors. In contrast to traditional dense Pd films that can only detect average concentrations of H_2, the pyrolytic, carbon-supported, nanoporous Pd film sensor is effective in detecting both dilute and high concentrations of H_2 gas because of its nanoporous, structure-enhanced, H_2-sensing ability. Various nanoporous H_2 sensors based on H_2-sensitive materials like Pd, Pt, Ni, and their alloys are expected to work based on the nanoporous-structure-enhanced H_2-sensing mechanism.

Experimental

By using a titanium film (100 nm in thickness) as a primer, an aluminum film (2.5 µm thick) was deposited onto a highly doped n-type Si wafer by using electron-beam (e-beam) evaporation. The aluminum film was anodized in 0.3 M oxalic acid through a two-step method and pore-widened in a 5 wt % H_3PO_4 solution to obtain AAO templates with pore diameters averaging 60–70 nm and pore lengths of ca. 2 µm. A thin film of amorphous carbon (several nanometers thick) [12] was deposited onto the AAO template through CVD pyrolysis of 10 % acetylene at 650 °C for 10 min. As there was no catalyst particles deposited at the bottom of the AAO nanopores, the AAO template itself could only induce a limited catalytic pyrolysis of the acetylene, and thus only a very thin layer of carbon film formed on top of the AAO template. A Pd film with a nominal thickness of 45 nm (measured with quartz crystal thickness monitors during the sputtering process) was then deposited, via sputtering, onto the upper surface of the samples. A robust resistive sensor was fabricated through copper wire connections (via conductive clips) at two ends on top of the surface of the Pd films. For comparison, nanoporous Pd film sensors directly supported by an AAO template and a dense Pd film sensor directly supported by a thermally oxidized n-type Si wafer were also prepared.

The sensor was then put into a flask chamber where various concentrations of H_2 in nitrogen (100 ppm–10 % with a flow rate of 100–1000 standard cubic centimeters per minute (sccm)) were introduced. A scanning electron microscope (Hitachi S-900) was used to examine surface morphology of the Pd films and vertically fractured parts (cross-sectional surfaces) of the Pd/C/AAO/Si system. A DC multimeter (DMM, Keithley 2000) was used for resistive testing of the above sensors at room temperature (23 °C).

Received: July 23, 2006
Revised: January 4, 2007

[1] I. Lundström, M. S. Shivaraman, C. M. Svenson, I. Lundkvist, *Appl. Phys. Lett.* **1975**, *26*, 55.
[2] C. Christofides, A. Mandelis, *J. Appl. Phys.* **1990**, *68*, R1.
[3] K. Luongo, A. Sine, S. Bhansali, *Sens. Actuators B: Chem.* **2005**, *111–112*, 125.
[4] H. H. Lin, T. Gao, J. Fantini, M. J. Sailor, *Langmuir* **2004**, *20*, 5104.
[5] J. Villatoro, D. Monzón-Hernández, *Opt. Express* **2005**, *27*, 5087.
[6] F. Rahimi, A. Iraji, F. Razi, *J. Phys. D: Appl. Phys.* **2005**, *38*, 36.
[7] M. Armgarth, C. Nylander, *IEEE Electron Device Lett.* **1982**, *EDL-3*, 384.
[8] F. Favier, E. C. Walter, M. P. Zach, T. Benter, R. M. Penner, *Science* **2001**, *293*, 2227.
[9] T. Xu, M. P. Zach, Z. L. Xiao, D. Rosenmann, U. Welp, W. K. Kwok, G. W. Crabtree, *Appl. Phys. Lett.* **2005**, *86*, 203 104-1.
[10] D. Ding, Z. Chen, C. Lu, *Sens. Actuators B: Chem.* **2006**, *120*, 182.
[11] W. C. Hu, D. W. Gong, Z. Chen, L. M. Yuan, K. Saito, P. Kichambare, C. A. Grimes, *Appl. Phys. Lett.* **2001**, *79*, 3083.
[12] K. B. Shelimov, D. N. Davydov, M. Moskovits, *Appl. Phys. Lett.* **2000**, *77*, 1722.
[13] J. Li, C. Papadopoulos, J. M. Xu, M. Moskovits, *Appl. Phys. Lett.* **1999**, *75*, 367.