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Hydrogen Sensing with a Single Palladium Nanowire

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We describe the properties of single nanocrystalline palladium (Pd) nanowires for the resistance-based detection of hydrogen gas (H_2). These Pd nanowires were prepared on glass surfaces using the Lithographically Patterned Nanowire Electrodeposition (LPNE) method. Pd nanowires had a mean grain size of 15 (±3) nm and a height and width in the range from 11 to 48 nm and 36–93 nm, respectively. Sensors consisting of a single Pd nanowire and an evaporated gold electrical contact demonstrated a limit-of-detection for H_2 of 2 ppm and withstood repeated exposures to 10% H_2 without fracturing. Response and recovery times for nanowires were directly correlated with their lateral dimensions. The reproducibility of the resistance response to H_2 and the stability of the resistance baseline were both excellent.

Keywords: Palladium Nanowires, Hydrogen, Sensor, Electrodeposition.

1. INTRODUCTION

Leaked hydrogen gas from devices such as fuel cells must be detected rapidly and reliably to insure their safety. The lower explosion limit for H_2 in air is 4%, so a limit of detection well below this—near 0.4%—is required for such sensors. Palladium (Pd) resistors provide a simple basis for the detection of hydrogen. Pd absorbs hydrogen to form a hydride (PdH_x) with x saturating at 0.67, with the resistance of the hydride increases linearly with x by a factor of 1.8 over the range from $x = 0$ to $x = 0.67$.[1] But Pd resistors consisting of evaporated thin films exhibit a response time that is far too slow for this application.[2–6] The origin of this sluggish response is the diffusion of protons in palladium which occurs with a diffusion coefficient of just $D = 3.8 \times 10^{-7}$ cm^2/s (at 298 K).[1]

In 2001, we postulated that a more rapid response might be obtained by substituting Pd nanowires for evaporated films.[7] Indeed, sensors based upon arrays of 200 nm diameter Pd wires showed a rapid response time of <1 s, but the limit-of-detection (LOD_{H_2}) was in the 2% range necessary to induce the α to β phase transition—far too high to be of use for H_2 safety sensors. The reason for this poor sensitivity was that Pd nanowires reproducibly fractured upon exposure to H_2 at concentrations exceeding 2%. After fracture occurred, the α to β phase transition induced the swelling of the nanowires, restoring their conductivity as wire fracture faces were forced together by the strain induced by the phase transition. As already indicated, this 2% LOD_{H_2} is far too high for H_2 safety sensors.

In spite of much excellent work,[8–15] Pd nanowires that do not fracture and which also exhibit a rapid response time have not been demonstrated up until now. In this paper, we report on single Pd nanowire hydrogen sensors.[16] These sensors demonstrate superior H_2 sensing performance, including response time in the 1–5 s range at high H_2 concentration and a LOD_{H_2} of 2 ppm at room temperature.

2. EXPERIMENTAL DETAILS

The Pd nanowires used in the study were prepared using lithographically patterned nanowire electrodeposition (LPNE).[17, 18] The nanowires were prepared by electrodepositing at a potential of −0.80 V versus saturated calomel electrode (SCE) from an aqueous electrolyte (0.2 mM $PdCl_2$, 0.22 mM EDTA (ethylenediaminetetraacetic acid) and 0.1 M KCl). LPNE produces nanowires that have a rectangular cross section with a well-defined height and width that are independently adjustable over a wide range. In this study we probed nanowires ranging in height from 11 (±1) to 48 (±3) nm and in width from 36 (±2) to 93 (±5) nm.

Characterization of these nanowires involved X-ray diffraction (data not shown), atomic force microscopy, and transmission and scanning electron microscopy (Fig. 1). Briefly, intermittent contact mode atomic force microscopy

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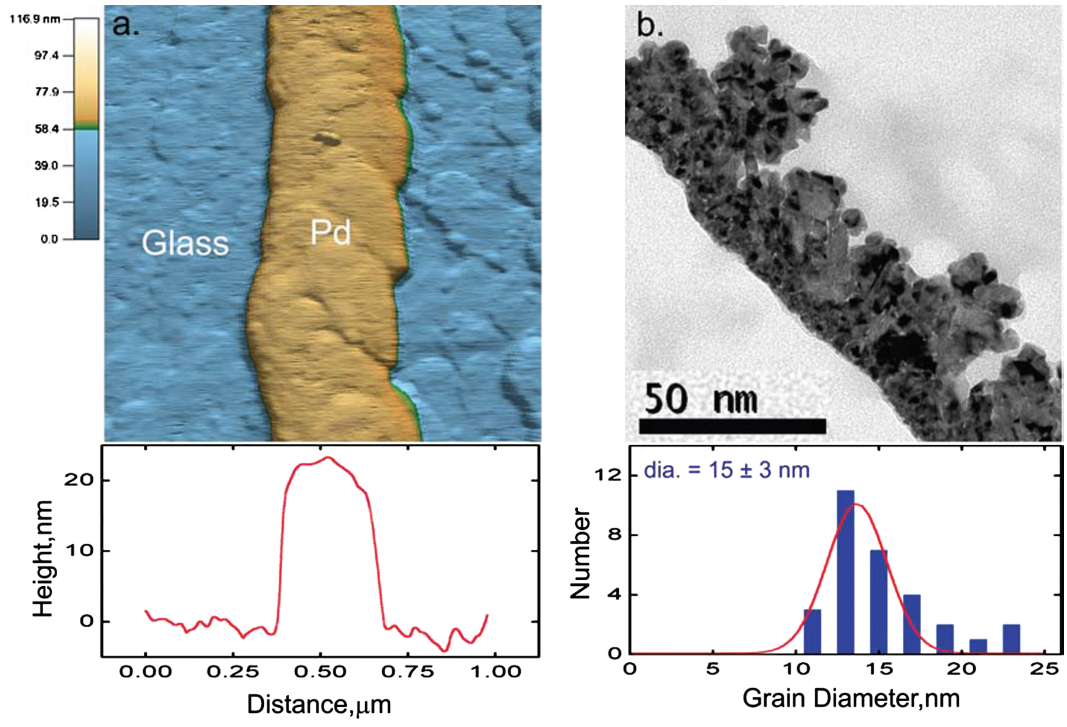

Fig. 1. Pd nanowire characterization. (a) Atomic force microscopy (AFM) image of a single palladium nanowire prepared by LPNE, showing the approximately rectangular cross-section. (b) Transmission electron micrograph (TEM) of a typical Pd nanowire showing a mean grain size (bottom) of 15 (±3) nm.

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(AFM) imaging was performed in air at ambient pressure and humidity using an AutoProbe CP-Research (Park Scientific Instruments, Sunnyvale, CA; now Veeco Instruments, Santa Barbara, CA) scanning probe microscope. Transmission electron microscopy (TEM) was performed on nanowires that were released from the surfaces on which they were synthesized and transferred to TEM grids as free-standing wires. This was accomplished as following: linear Pd nanowires, deposited onto glass by LPNE at either 5 μm or 2 μm inter-wire pitch, were released from the glass by etching in 2% hydrofluoric acid solution for 5 minutes. A stream of water was then directed onto these surfaces and the nanowires were washed onto carbon-coated copper grids (Ted Pella, Inc). All the grids were dried overnight before TEM measurements. Images were obtained using a Philips CM20 TEM at an operating voltage of 200 KeV.

A four-probe gold electrode of 60 nm thickness was evaporated onto a single Pd nanowire using a shadow contact mask. Copper wires were attached to these gold contacts using silver paste. A typical device is shown in the scanning electron microscope (SEM) images of Figure 2. These evaporated contacts isolated a 100 μm length of each nanowire and the electrical resistance of this nanowire was measured by applying a bias voltage of 5 mV as a function of time during the exposure to pulses of hydrogen of predetermined concentration, which involved the computer-controlled mixing pure H_2 and pure N_2 using mass flow controllers.

3. RESULTS AND DISCUSSION

The rectangular cross-section of the Pd nanowire investigated here is apparent in the AFM image shown in Figure 1(a). TEM images of the Pd nanowires (Fig. 1(b)) prepared from plating solutions containing EDTA reveal a mean grain size of 15 (±3) nm—significantly larger than the 5 (±1) nm grain size seen in the absence of added EDTA.[16] The mechanical properties of these two types of nanowires were different in one important respect: in contrast to Pd nanowires prepared in EDTA-free solutions, the nanowires shown in Figure 1(b) did not facture upon exposure to H_2. The origin of this disparity in

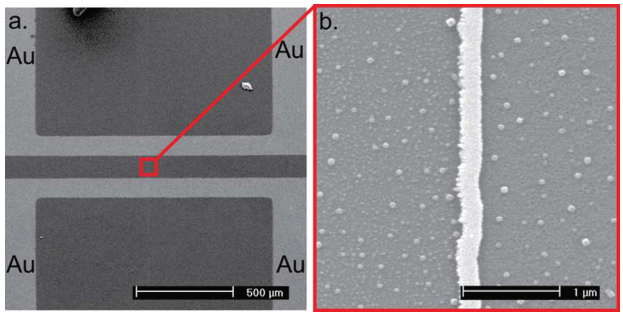

Fig. 2. Single Pd nanowire based H_2 sensor. (a) Scanning electron microscope (SEM) image at low magnification of a H_2 sensor consisting of a single Pd nanowire with evaporated 60 nm gold film as contacts. (b) Higher magnification SEM image of a 40 nm (height) × 180 nm (width) Pd nanowire.

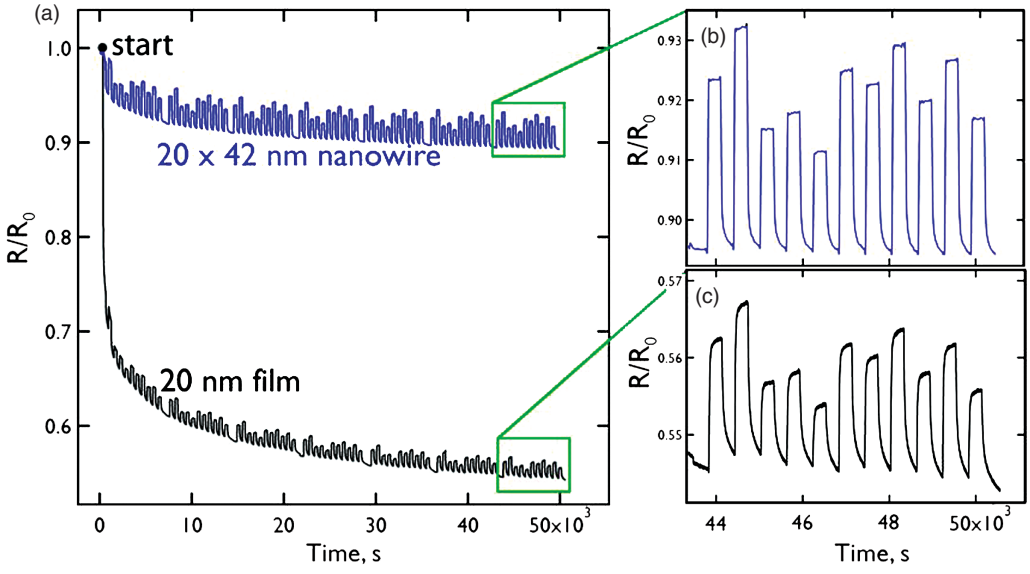

Fig. 3. Initial exposures of a Pd nanowire and a Pd film of 20 nm to H_2. (a) R/R_0 versus time for the exposure to 77 pulses of H_2 ranging from 0.2% to 1%. (b) R/R_0 versus time for the final sequence of 11 H_2 exposures of a 20 nm (height) × 42 nm (width) Pd nanowire. (c) R/R_0 versus time for the final sequence of 11 H_2 exposures of the Pd film of 20 nm thickness.

mechanical properties is not fully understood at this time, but in the remainder of this paper we report the remarkable properties of single nanowires prepared from the EDTA-containing electrolyte for detecting H_2.

The resistance of a freshly prepared Pd nanowire is shown in Figure 3(a) as it is repeatedly exposed to a sequence of H_2 pulses ranging in the concentration from 0.2% to 1% over 14 hours. Significant drift of the baseline resistance is seen in the data, but the drift decreases progressively over the 14 hours experiment until at the end it is reduced to $\Delta R/R_0 \approx 0.09\%$/hour as in Figure 3(b). We believe that the decrease in baseline drift seen here derives from the progressive cleaning of the palladium surface of water and organic residues by repeated exposures to H_2. We preconditioned each device using this procedure.

Raw sensing data for two different sizes of Pd nanowires and an evaporated Pd film of the same height show rapid and reversible increases in resistance for H_2 ranging from 0.02% to 0.1% (Fig. 4(a)), 0.2% to 1% (Fig. 4(b)), 1.2% to 2% (Fig. 4(c)), 4% to 10% (Fig. 4(d)). Calibration plot for three different sizes of Pd nanowires (Fig. 5(a)) shows great reproducibility of the $\Delta R/R_0$ at each concentration from 2 ppm to 10%. It also reveals that $\Delta R/R_0$ is insensitive to the dimension of the nanowire. The response time (defined as the time to reach 90% of the steady-state response) and recovery times (defined as the time to reach 10% of the baseline resistance), on the other hand, were strongly dependent on the wire cross-sectional dimensions. Both the response time (Fig. 5(b)) and recovery time (Fig. 5(c)) decrease when the height of the

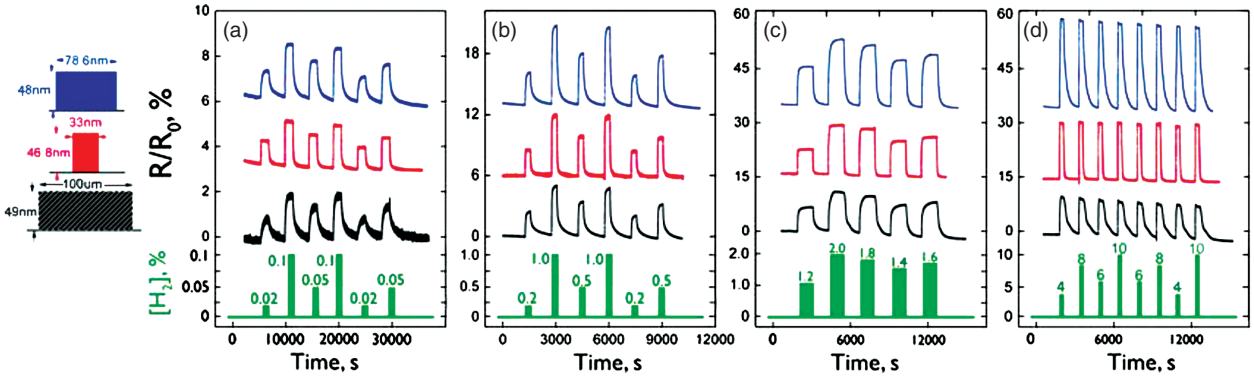

Fig. 4. $\Delta R/R_0$ response of two different Pd nanowire sensors (inlet) over a wide H_2 range, comparing with an evaporated Pd film of the same height. (a) 0.02–0.1% H_2 pulses with a duration of 9 h. (b) 0.2–1% H_2 pulses with a duration of 3 h. (c) 1.2–2% H_2 pulses with a duration of 3.5 h. (d) 4–10% H_2 pulses with a duration of 3.5 h.

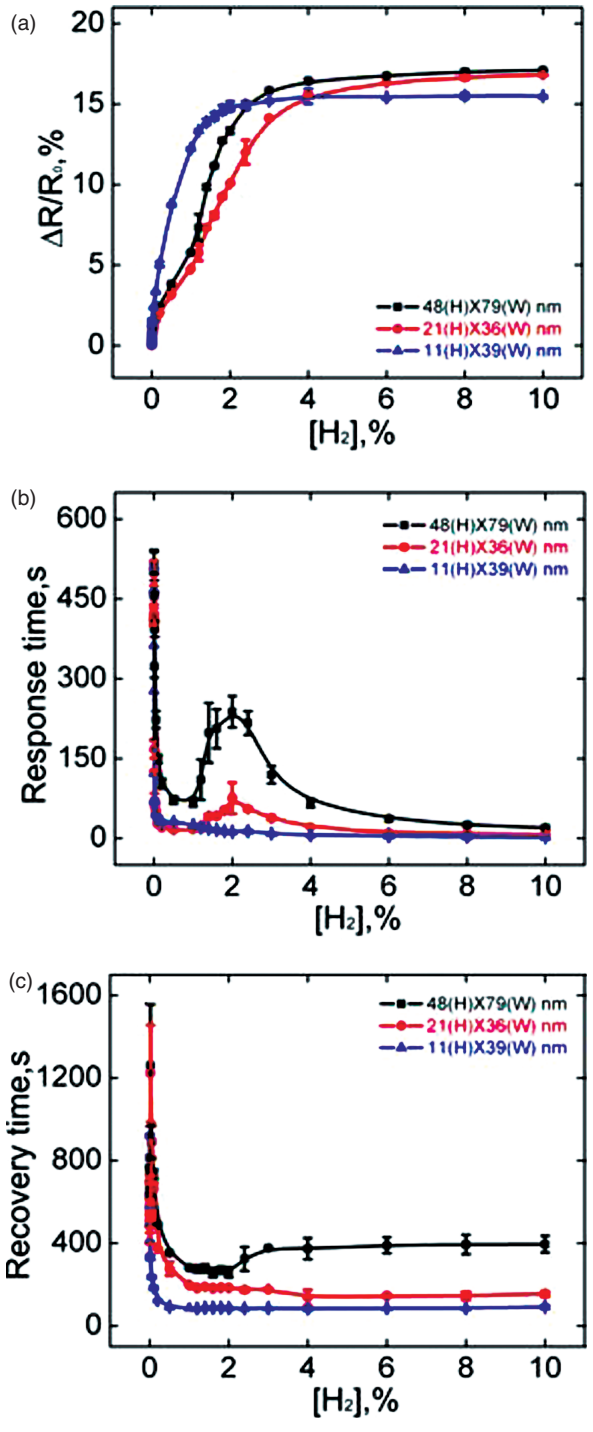

Fig. 5. Calibration plots for three different sizes of Pd nanowires. (a) $\Delta R/R_0$ versus H_2 concentration response. (b) Summary of response time as a function of H_2 concentration for three Pd nanowires. (c) Summary of recovery time as a function of H_2 concentration for three Pd nanowires.

nanowire decreases. Thus, the wire height is the main predictor of the temporal response and recovery times for Pd nanowires, especially at higher concentrations. Furthermore, for the nanowires with width of 21 (±2) nm and 48 (±3) nm, the response time is retarded in the H_2 concentration range from 1% to 2%, which coincides with the α to β phase transition. So it is likely that this phase transition is the origin of this slowed response seen as the peaks in Figure 5(b). The existence of this peak suggests that the α to β phase transition prevents Pd nanowire from rapidly equilibrating with the hydrogen. However, for the nanowire with height of 11 (±1) nm, this peak is not seen. We infer that the slowing of the sensor response depends strongly on the cross-sectional dimensions of the nanowire and a smaller nanowire is able to more rapidly accommodate the strain imposed by the phase transition.

4. CONCLUSIONS

Here we have demonstrated that single electrodeposited Pd nanowires prepared using the LPNE process are able to rapidly and reversibly detect hydrogen as a resistance increase down to 2 ppm with excellent reproducibility and baseline stability at room temperature. This study highlights the importance of microstructure in terms of the mechanical properties of polycrystalline nanowires. In this case, the resistance of Pd nanowires to fracture makes possible a dramatic improvement in the sensitivity, culminating in an improvement in the LOD_{H_2} from 2% to 2 ppm. In our future work, we will seek an understanding of the relationship between microstructure and the mechanical properties of nanoscopic metal wires.

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