Hydrogen Sensors from Electrodeposited Palladium Mesowires

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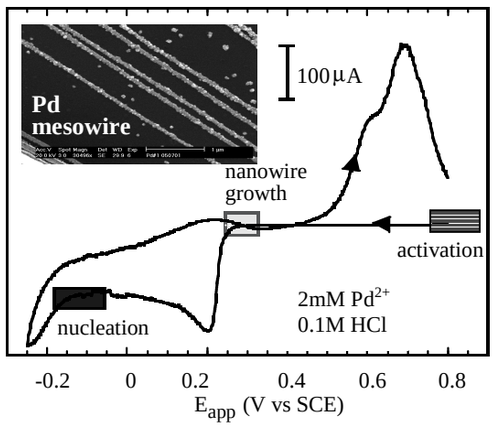
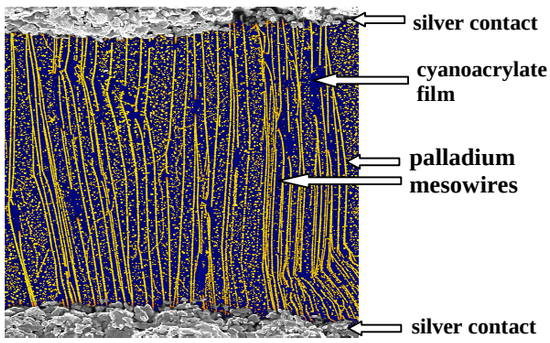
Chemical sensing is about surface and interface interactions between the analyte molecules and the sensing material. In that sense, nanoparticles and nanowires, are potentially very efficient chemical sensors. The mechanism envisioned involves the adsorption (and eventually diffusion) of the analyte molecule at the surface that induces a change, for example in the electrical resistance of the nano-object: sensing is then measuring these conductivity changes. The most convenient way to measure conductivity changes in such devices is to obtain the specific material as nano or mesowires. A few results were recently presented on chemically selective sensors operating on this principle showing changes in the conductivity of gold nanowires upon exposure to thiols or amines. In the same way, single walled carbon nanotubes exhibit resistance changes upon exposure to gaseous oxygen, water and amines. Surface functionalized silicon nanowires were also recently included in various devices for pH measurement, Ca^{2+} or proteins specific detection.



We describe in this paper, an electrochemical method for the preparation of palladium meso and nanowires. The method proceeds by the selective electrodeposition of metal at step edges. Nanowire growth was accomplished on highly oriented pyrolytic graphite surfaces (HOPG) by applying three voltage pulses in succession: An "activation" pulse, optimized to oxidize step edges on HOPG surface just prior to deposition; a reducing "nucleation" pulse with a large overpotential for metal deposition (-200mV to -500mV) and a duration of 5-10 ms; and a reducing "growth" with a small deposition overpotential of less than -100 mV. The nanowire radius was controlled by the deposition time.

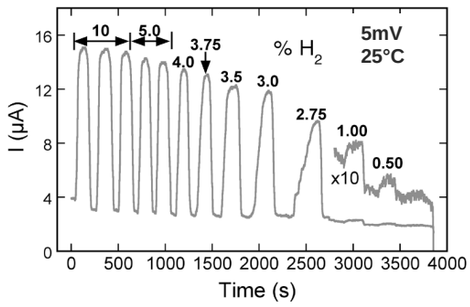
We also show how to manipulate these objects to build chemical sensors. As an example, we describe the way we built hydrogen sensors and hydrogen-actuated switches from arrays of mesoscopic Pd wires. The performance for these sensors are given in detail.

Hydrogen sensors and hydrogen-actuated switches were constructed by transferring the Pd mesowire arrays onto a cyanoacrylate film.

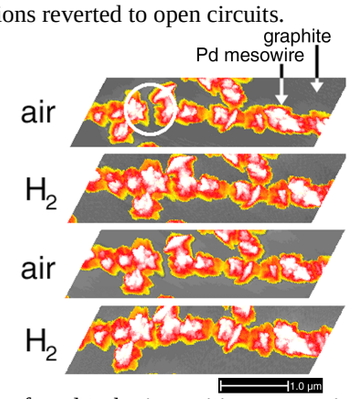


10 to 100 mesowires were then arrayed electronically in parallel by contacting them using silver paint.

These sensors exhibit, at room temperature, a rapid (as fast as 40ms) and reversible decrease in the electrical resistance upon exposure to hydrogen gas (or D_2). This conductivity change was correlated with the hydrogen concentration over a range from 1 to 10% of H_2 in air.



In contrast to all existing H_2 sensors based on macroscopic Pd resistors which become more resistive in presence of hydrogen (because of the higher resistance of PdH_x, with $0<x<0.7$, compare to Pd metal), however, the resistance of the presented Pd mesowire arrays decreases under H_2. By the aim of AFM and SEM observations, we propose a unique mechanism of operation that account for this "inverse" response: The sensor response involves the closing of nanoscopic gaps or "break junctions" caused by the dilation of wire grains undergoing the conversion of palladium to palladium hydride. As hydrogen is reversibly occluded by palladium grains, in its absence each gap reopens and wire arrays in which all wires possessed such break-junctions reverted to open circuits.



Sensors were found to be insensitive to a variety of other gas than H_2, including Ar, He, N_2, water vapor… and showed a good resistance to poisoning by O_2, CO, and CH_4.

References:

F. Favier, E.C. Walter, M.P. Zach, T. Benter, R.M. Penner, *Science* **293**, 2227-2231, 09/21/2001.

E.C. Walter, F. Favier, R.M. Penner, *Anal. Chem.*, 2002 **74**, 1546-1553