Focused Ion Beam Engineered Nanogap in a Palladium Microwire as a Mechanical Switch for Hydrogen Detection

T. Kiefer [a], F. Favier [b], O. Vázquez-Mena [a], G. Villanueva [a], J. Brugger [a]

[a] Microsystems Laboratory, Station 17, École Polytéchnique Fédérale de Lausanne (EPFL),
Lausanne, 1015 Switzerland
phone: +41 – (0)21 – 6930925 e-mail: thomas.kiefer@epfl.ch
[b] ICG - AIME, UMR 5253 CNRS Université Montpellier 2, cc015, Montpellier cedex 5,
34095 France

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In recent years, hydrogen has become of increasing interest with the development of fuel cell applications. Since hydrogen gas has a large flammability range and is quite difficult to contain, sensors are needed to ensure that potential permeating hydrogen does not exceed required flammability limits. The use of nanogaps in palladium (Pd) as chemically actuated electrical switches has proven to be a promising approach for such sensors. However, existing fabrication methods exclusively make use of bottom-up techniques like electrodeposition [1] or ultra-thin evaporated films which inherently feature disordered nanogaps [2]. However, no top-down approaches for the reproducible fabrication of nanogaps in hydrogen sensors have been reported so far.

In this work, we investigate a top-down approach for the fabrication of nanogap based hydrogen detectors in evaporated Pd. In particular, focused ion beam (FIB) being a well-known rapid prototyping nanofabrication tool is used to mill one single nanogap into a microwire. In air, this gap electrically interrupts the wire. Under a hydrogen gas atmosphere, the two opposing parts increase their volume due to the phase transition from pure palladium to palladium hydride [3]. The narrowing of the gap eventually connects the two interfaces and forms an electrical contact.

By analyzing various conditions which have an influence on the behaviour of the sensor as the underlying substrate, adhesion layers and different FIB milling times, we studied the functionality of the switching mechanism. The possibility and the limitations to realize such an electrical switch by a top-down method are investigated.

Pd microwires with different thicknesses of 10 nm, 25 nm 50 nm and 100 nm have been fabricated by evaporation and a lift-off process. As substrates, two different options have been tried: silicon wafers with a 200 nm thick thermal oxide and a 2 µm thick layer of polyimide (PI). Either no or thin titanium layers have been evaporated on top, serving as adhesion layers. A single nanogap has then been milled into the wire using a focused ion beam (30kV, 1pA). An initial analysis of the gap size in dependence of the milling time helped to optimize the FIB parameters and wire dimensions (see Fig. 1 and 2). Electrical measurements under hydrogen have been performed using a setup comprising a fluidic flow cell, calibrated mass flow meters and a potentiostat.

Wires which have been deposited on SiO_2 did not show the desired effect. Only 25 nm and 50 nm thin wires on polyimide showed reversible electrical switching. For a layer thickness of 100 nm, the necessary aspect ratio for a complete cut has been too large, for a thickness of 10 nm the effect of adhesion was assumed to be too strong to allow the closing of the gaps. A typical result of the electrical measurements under hydrogen is shown in Fig. 3 for a 25 nm thin Pd wire. These and in situ AFM measurements under hydrogen (see Fig. 4) were used to study the closing mechanism of the gaps.

In the presentation we will show details on FIB as a top-down method for the prototyping of a nanogap based hydrogen sensor and its response characteristics. FIB showed to be useful for the study of various parameters having an influence on the closing of a nanoswitch in PVD palladium under hydrogen, giving indications for a further sensor design.

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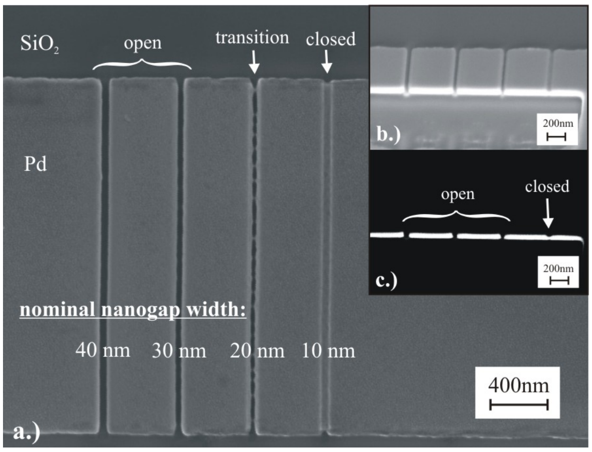

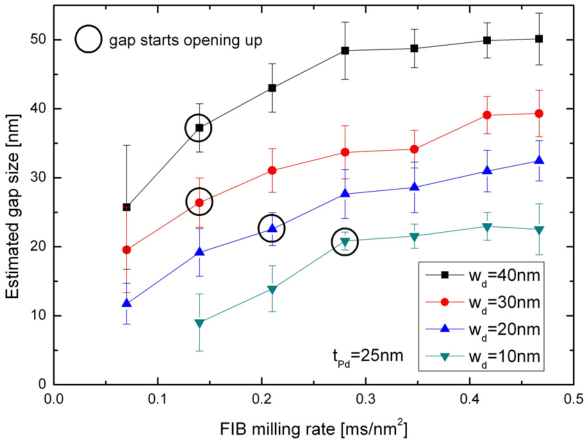

Fig.1: *SEM images for nanogap analysis of a.) FIB cuts (30kV,1pA) with different widths in a 50nm thin palladium (Pd) wire on* SiO_2 *b.) FIB milled cross sections of the gaps c.) Image with enhanced contrast*

Fig.2: *Gap size estimation by SEM as a function of the milling rate. The parameter* w_d *indicates the nominal gap width. This enables to determine when the gap is completely open (here: Pd wire of 25 nm thickness).*

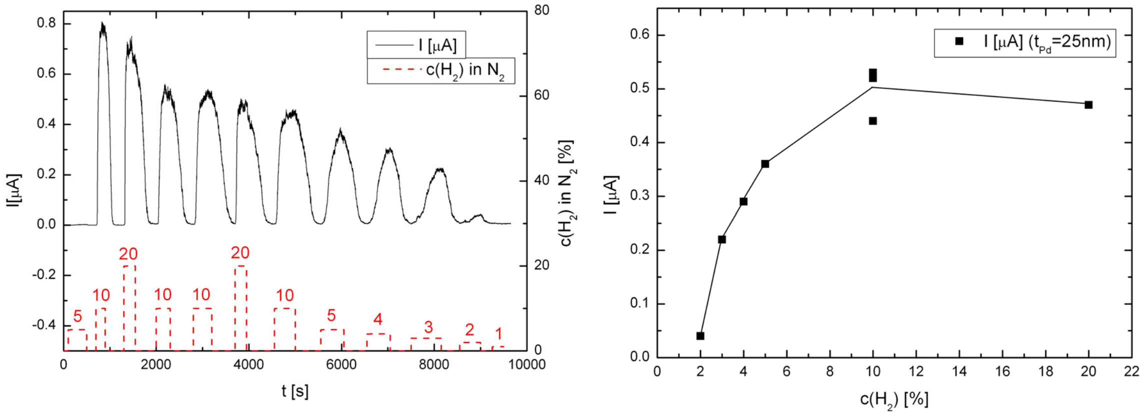

Fig.3: (Left): *Electrical current through a 25nm thin Pd wire with a 1nm thin Ti adhesion layer on polyimide (PI) for* H_2*/air cycles. Measured for a ~50nm wide gap in under different hydrogen concentrations (room temperature, U=20mV). In air, the resulting current is 0A.* ***(Right):*** *Electrical current in dependence of the* H_2 *concentration. The comparison with continuous wires showed, which fraction of the gap is effectively closing.*

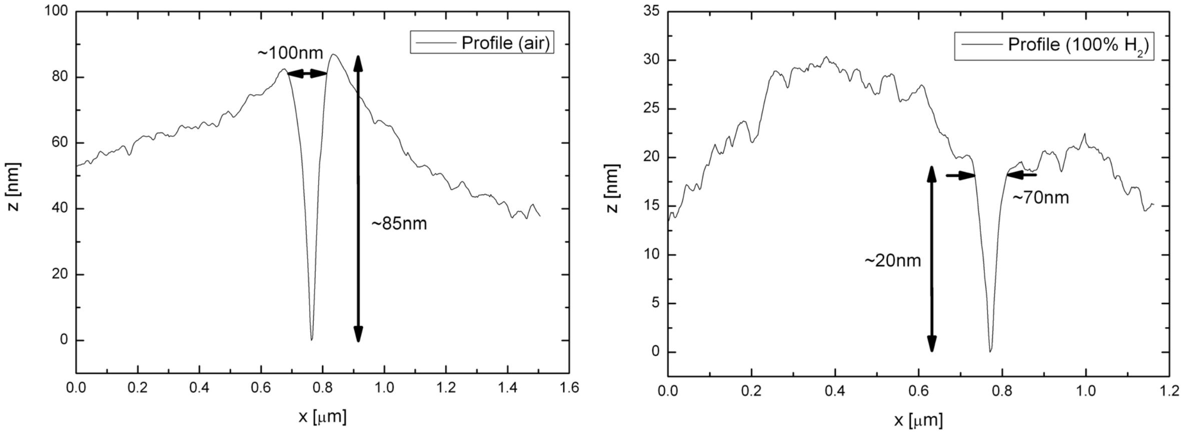

Fig.4: *In situ AFM measurement of a typical nanogap in a 50nm thin Pd wire in air* ***(left)*** *and hydrogen* ***(right)****. This gap is closing by ~30 nm in height. Reversible closing/opening of the nanogaps has been observed.*