# Chapter 27
# Single Palladium Nanowire: Morphology and its Correlation with Sensing Mechanism

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**Abstract** In this work devices based on single palladium nanowire are realized by combining dielectrophoresis and focused ion beam (FIB) and characterized as hydrogen sensor at room temperature. Fixing the geometry of the electrodes, patterned by FIB, several devices are fabricated by varying the frequency of the applied field (DEP), to assess the effect on the shape of nanowire. Different kind of nanowire structures are, then, observed by means of SEM and AFM. The sensing mechanisms in presence of hydrogen are investigated and compared for each, finding that electrical current decreases because of palladium hydride formation.

## 27.1 Introduction

Grow in place approach is one of the techniques used to fabricate miniaturized devices. It allows to grow, position and align a single nanowire between the contacting electrodes, without any manipulation [1]. Among the *grow in place* techniques, dielectrophoresis (DEP) is receiving an increasing interest. It uses a non-uniform electric field to polarize small particles, suspended in solution, forcing them to move in a well controllable way up to assemble nanowires [2]. The geometry of the electrodes plays a very important part in the realization of

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G. Neri et al. (eds.), *Sensors and Microsystems*,
Lecture Notes in Electrical Engineering 91, DOI: 10.1007/978-94-007-1324-6_27,

nanostructured materials through DEP. Focused ion beam (FIB) is the useful tool for patterning microelectrodes creating suitable nucleation points for nanowire growth [3].

In this work, Pd nanowires with different morphologies have been realized, applying an alternating electric field to a palladium electrolyte solution dropped between Pt microelectrodes deposited by FIB. Branched nanowire have been obtained at high electric field frequency while plain nanowire has been assembled at lower frequency. Devices based on single branched and plain nanowires have been electrically characterized in hydrogen environment at RT and their responses have been compared.

## 27.2 Experimental

A crystalline silicon wafer coated with 100 nm of $Si_3N_4$ has been used as starting substrate. FIB column, integrated in a FEI Quanta 200 3D dual beam system, has been used for platinum nanoelectrodes patterning. Highly focused gallium ion beam interacts with the platinum organometallic precursor gas. Metal–organic compounds are dissociated and the non volatile part of the compound is deposited onto the sample surface to form electrodes. Using 30 kV as accelerating voltage and 10 pA as emission current for ion beam emission, platinum nanoelectrodes about 8 μm spaced are deposited onto the substrate. The feed solution for DEP processing has been prepared dissolving crystalline Pd(acetate)2 in 10 mM HEPES buffer solution. A function generator and an oscilloscope have been used as the alternating current (AC) source and for monitoring the applied electrical signal, respectively. 2 μl of saturated solution have been deposited by casting onto the substrate, previously washed in isopropyl alcohol, deionised water and dried in a nitrogen flow.

Two series of single Palladium nanowire-based devices have been grown between the electrodes by applying a 10 $V_{pp}$ ($V_{peak\text{-}peak}$) sinusoidal electric field at two different frequency, 300 kHz and 300 Hz. The process stops when the opposite electrodes are short-circuited by the grown nanowire.

The single palladium nanowire-based devices have been tested as hydrogen sensor. The device has been first characterized in direct current (DC) condition at room temperature and in ambient air, showing an ohmic current–voltage (I–V) characteristic between –1 and 1 V, with a typical electrical resistance of about 15–70 kΩ.

A volt-amperometric technique, at constant bias, has been then employed for sensor DC electrical characterization in a controlled gas-flow environment, pre-mixed with dry carrier in the desired percentage by mass flow meters and continuously controlled by means of an on-line Fourier transform infrared spectrometer. All the tested devices have been biased at 5 mV. Total gas flow has been set at 500 sccm.

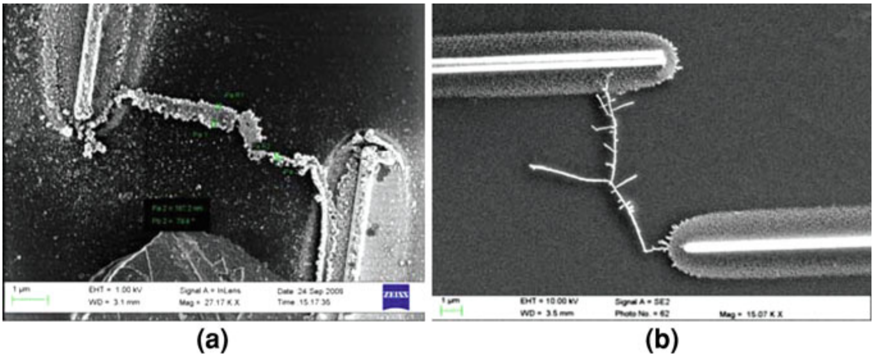

**Fig. 27.1** SEM images of Pd nanowires made at 300 Hz (**a**) and at 300 kHz frequency (**b**)

## 27.3 Results and Discussion

Fixing FIB electrode pattern with 6-µm gap size and no overlapping, two devices have been realized changing the electric field frequency.

In Fig. 27.1a, a SEM image of a device made at 300 Hz frequency is shown (series A). From the movie, recorded during the assembly, a very rapid nanowire formation between the two electrodes has been observed and so the deposition has been stopped after 2 s. The nanowire morphology shows no ramifications, with a thickness varying from 180 to 350 nm. This morphology has been called "plain".

In Fig. 27.1b, it is shown a single Pd nanowire, grown applying a 300 kHz frequency between electrodes (series B). Nanowire is branched with average diameter of about 60 nm.

At low frequencies a thick single palladium nanowire, with no branches, is assembled while at high frequencies a thinner and branched single nanowire is obtained. Under high frequency fields are applied, branched structures may result by Pd ions diffusion towards secondary sites, different from the main nucleating tip, bringing out to the formation of new nucleating points.

Single palladium nanowire morphologies have been analysed using an atomic force microscope (AFM) in tapping mode with the aim to investigate the Pd nanowire morphology obtained at different field frequency.

AFM images (Fig. 27.2) confirm that single nanowires consist of palladium continuous aggregates. As shown in the figures, for both series A and series B the clusters are closely interconnected, settling in overlaid layers, so as to leave no void spaces and creating a continuous structure.

The recorded electrical responses, when devices are under hydrogen gas, are shown in Fig. 27.3. Devices based on single palladium nanowire have been maintained, for 30 min, in a dry air flow for the zero current (baseline) monitoring. Hydrogen concentrations ranging from 0.5 to 4% have been then introduced in the test chamber and the device electrical responses have been recorded.

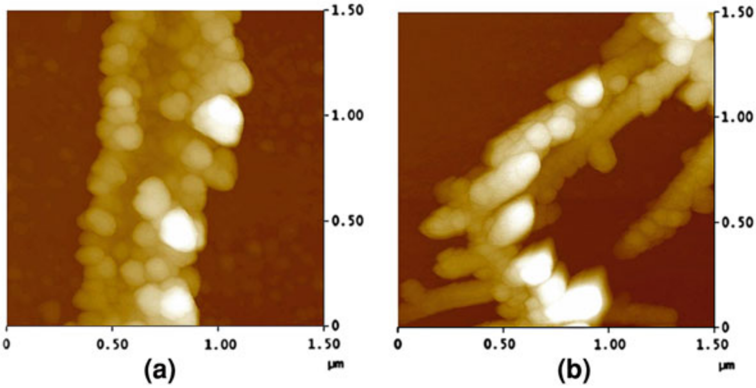

**Fig. 27.2** AFM image of palladium nanowire made at 300 Hz, series A (**a**) and 300 kHz, series B (**b**)

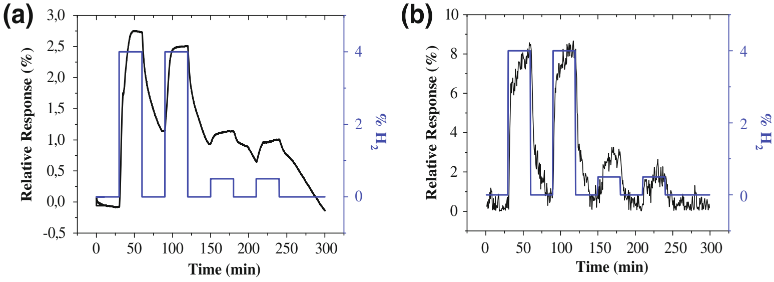

**Fig. 27.3** Relative response versus time, recorded at room temperature and at 4 and 0.5% $H_2$ concentrations in dry air for series A (**a**) and B (**b**). $H_2$ concentrations are drawn with straight lines

Devices show a current decreasing in presence of hydrogen. Upon exposure to hydrogen, palladium reacts to form the more resistive palladium hydride (PdHx where x is the atomic ratio H/Pd), as a consequence the electric current decreases.

Series B shows a higher relative response as compared with series A, because of the higher Surface/Volume ratio for several ramifications. Series B follows more closely the concentration change and when hydrogen is removed from the test chamber, it shows a lower drift current and greater stability than the series A.

## 27.4 Conclusions

We have shown how devices based on a single palladium nanowire can be fabricated in well controllable conditions using FIB and DEP combination and how, fixing the electrode geometry, it is possible to change the morphology of nanowires.

**Acknowledgment** The authors gratefully acknowledge the Ministry of Universities and Research (MIUR) for financial support as part of Public–Private Laboratory TRIPODE (Technologies and Research for the application of polymers in electronics devices).

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