Focused ion beam patterning to dielectrophoretically assemble single nanowire based devices

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Abstract. Direct-write processing is increasingly taking place in nanodevice fabrication. In this work, Focused Ion Beam (FIB), a powerful tool in maskless micromachining, is used for electrode patterning onto a silicon/silicon nitride substrate. Then a single palladium nanowire is assembled between electrodes by means of dielectrophoresis (DEP). The nanowire morphology depends on the electrode pattern when DEP conditions are fixed. FIB/DEP combination overcomes the problem of nanowire electrical contamination due to gallium ion bombardment and the as-grown nanowire retains its basic electrical properties. Single nanowire based devices have been fabricated with this novel approach and have been tested as hydrogen sensors, confirming the reliability of this technology.

1. Introduction

Direct patterning of electrodes is a promising route for the fabrication of complex nanoelectronic circuits. Generally, device electrodes are realized using electron beam or optical lithography, metallisation and lift-off. Direct-write processes avoid these multi-step procedures and fabricate devices with electrical pads defined directly onto the substrate. Focused Ion Beam (FIB), a well known direct-write tool in nanodevice processing, is often used for electrode patterning in nanodevices. Its operating mechanism relies on a highly focused and energetic gallium ion beam that interacts with the platinum organometallic precursor to deposit platinum nanocontacts. In particular, FIB is often employed to make electrical contacts at the nanowire end after its positioning onto the substrate [1]. Recently we have demonstrated the feasibility of a process to realize a single Pd nanowire hydrogen sensor grown by dielectrophoresis (DEP) using electrodes previously deposited by FIB [2]. This procedure overcomes gallium ion contamination, which creates defects and gallium impurities along the length of the nanowire, and modifies the actual resistivity.

In this paper, we show how it is possible to vary the single palladium nanowire morphology by changing the FIB electrode pattern at fixed DEP working conditions. Finally the electrical characterization of the sensors based on a single Pd nanowire is discussed.

2. Experimental

A crystalline silicon wafer coated with 100 nm of Si$_3$N$_4$ was used as starting substrate. A FIB column, integrated in a FEI Quanta 200 3D dual beam system, was used for platinum nanoelectrode patterning. The 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 are deposited onto the substrate. Each platinum electrode, 300 nm in width and 500 nm in height, has a length of about 100 µm, ending in 0.25 cm² Cr/Au pads, previously deposited by electron beam-assisted evaporation.

The feed solution for DEP processing was prepared by dissolving crystalline Pd(acetate)₂ ((C₂H₃O₂)₂Pd, Sigma Aldrich) in 10 mM HEPES (C₈H₁₈N₂O₄S, Sigma Aldrich) buffer solution, with a pH of 6.5. To ensure complete and homogeneous dissolution, the solution was maintained hermetically closed and in the dark, on a magnetic stirrer for three hours and then centrifuged at 13000 rpm to separate the precipitate. A function generator (AGILENT 33220A) and an oscilloscope (LECROY LC684D) were used as the alternating current source and for monitoring the applied electrical signal, respectively. 2 µl of saturated solution were deposited by casting onto the substrate, previously washed in isopropyl alcohol, deionised water and dried in a nitrogen flow.

Palladium nanowires were grown between the electrodes by applying a 10 Vpp (Vpeak-peak) sinusoidal electric field at 300 kHz. The process stops when the opposite electrodes are short-circuited by the forming nanowire. The single palladium nanowire based devices work as a hydrogen sensor.

Devices were first characterized in direct current (DC) condition at room temperature and in ambient air. A volt-amperometric technique, at constant bias, was then employed for sensor DC electrical characterization in a controlled gas-flow environment, pre-mixed with dry carrier gas in the desired percentage by mass flow meters and continuously controlled by means of an on-line Fourier transform infrared spectrometer [3]. All the tested devices were biased at 5 mV. The total gas flow was set at 500 sccm.

3. Results and discussion

Platinum patterns with different lengths of electrode overlap were fabricated keeping a fixed gap size of about 6 µm and fixed DEP working conditions. Electrode geometry affects the electric field gradient and consequently the shape and the number of nanowires and the growth sites.

In figure 1 we report three different electrode patterns which show how it is possible to obtain either one or two palladium nanowires if the electrodes are more or less overlapped. In figure 1a the two electrodes are not overlapped and a single main (M) palladium nanowire is formed. It is branched, thin, and maintains the same morphology along the wire. Its diameter is about 60 nm. In figure 1b the electrodes partly overlap each other and a single main (M) nanowire is still formed, although the growth of a secondary shorter nanowire (S) with a different nucleation site is observed. This wire cannot complete its growth by connecting the opposite electrode, because the growth of the main nanowire is faster and the process stops when it reaches the opposite electrode. The main nanowire presents an unusual morphology composed of two shapes: the topside consists of aggregated grains ranging from 100 to 200 nm while the underside shows a central trunk with many branches, which is thin and has a width of 60 nm. The electric field generated by this electrode pattern favours the growth of aggregated grains. As the nanowire grows close to the other electrode, more intense electric fields are produced at the edge of the palladium growth [4] and the trunk-structure growth appears dominant. For increased electrode overlap, about 80 µm, the growth of two main and secondary palladium nanowires is evident (figure 1c). The presence of the nanowires, described above, are also predicted by software simulation, modelling the electric field streamlines when pattern and working conditions are defined [2].

Any of the fabricated devices present gallium contamination in agreement with what has been already reported [2]. A Pt halo around each electrode is clearly visible. It is generated by the large spread in the interaction of the gallium ion beam with the organometallic platinum precursor gas [5]. Halos do not overlap, preserving electrical insulation of the transducer, but they reduce the gap size modifying the electric field gradient and consequently the single nanowire growth.
Figure 1. SEM images of palladium nanowires are shown: (a) single Pd nanowire has grown using an electrode pattern with no overlap; (b) a main nanowire (M) and a secondary nanowire (S) are formed when the electrode pattern is partly overlapped; (c) two main (M1 and M2) palladium nanowires originate between each electrode tip and the opposite one. Also in this case, secondary (S1 and S2) shorter, non short-circuiting Pd nanowires are formed. The electrode overlap is about 80 µm.

Devices based on single palladium nanowires are conductive showing an ohmic current-voltage (I-V) characteristic between −1V and +1V, with electrical resistance ranging from 40 kΩ to 120 kΩ. A typical electrical response, when the device is under hydrogen gas, is shown in figure 2. The device was maintained, for 30 minutes, in a dry air flow for zero current (baseline) monitoring. Hydrogen concentrations ranging from 1% to 0.1% were then introduced in the test chamber and the electrical response of the device was recorded.
Figure 2. Sensor resistance (left axis) vs time, recorded at room temperature ranging from 1% to 0.1% H₂ concentration in dry air (right axis).

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 electrical resistance increases. The permeation of hydrogen through the palladium nanowire is in fact a reversible dissociative chemisorption process, and when dry air is introduced into the test chamber, the device presents a quite reversible behaviour [6].

4. Conclusions
We have shown how single Pd nanowire based hydrogen sensor devices can be realized without any manipulation of the wire itself, using a combination of DEP and FIB for the fabrication process. Nanowire morphology can be tuned by changing the electrode pattern. Moreover, the deposition of FIB platinum electrodes, before nanowire fabrication, avoids gallium contamination, preserving the electrical properties of the nanowires. The device operates as a hydrogen sensor at room temperature. Within the testing range, the sensor is sensitive and quite reversible.

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