

# Top-down Fabrication of Si Nanowire and Fully Automated Test Platform: Application to pH Sensor

Cécile Halte<sup>#1</sup>, Guillaume Delapierre<sup>#</sup>, Guillaume Costa<sup>#</sup>, Thierry Fournier<sup>†</sup>, Julien Buckley<sup>‡</sup>, Marc Gely<sup>‡</sup>, Barbara

De Salvo<sup>‡</sup>, Thierry Baron<sup>\*</sup>, Françoise Vinet<sup>#</sup>

<sup>#</sup>DRT/LETI/DTBS/SBSC/LFCM, CEA-Grenoble, FRANCE

17 rue des Martyrs, 38054 Grenoble Cedex 9, FRANCE

<sup>1</sup>cecile.halte@cea.fr

<sup>†</sup>CNRS/Institut Néel, University Joseph Fourier, FRANCE

25 rue des Martyrs, 38042 Grenoble Cedex 9, FRANCE

<sup>‡</sup>DRT/LETI/D2NT/LNDE, CEA-Grenoble, FRANCE

17 rue des Martyrs, 38054 Grenoble Cedex 9, FRANCE

<sup>\*</sup>CNRS/LTM UMR5129, University Joseph Fourier, FRANCE

17 rue des Martyrs, 38054 Grenoble Cedex 9, FRANCE

**Abstract** – Detection and quantification of very small amounts of biological species become necessary to allow an early detection of malignant disease and the development of personalized medicine. Currently, fluorescence detection or colorimetry are the most frequently used techniques. Although very sensitive, the necessary labelling step of the biotargets can alter their recognition properties and these methods have a low potential for integration. This explains the constant effort of research on label-free detection methods. One-dimensional nanostructures, such as silicon nanowires, have emerged as good candidates for ultra-sensitive electrical detection of biological species. A silicon nanowire can operate as the channel of a field-effect transistor whose conductance is modulated by the change of charge of its surface due to the binding of biological species.

A top-down fabrication process of silicon nanowire field effect transistors was developed on SOI and already tested under microfluidic environment. Measurements of the conductance of the silicon nanowire under buffer solutions at different pH were recorded; the fluidic and electronic sensing set-up being totally automated and controlled by a labview interface. A change of the conductance of the nanowire according to the pH of the solution was measured, suggesting that this device can be used to detect the presence of biological species. Measurements using bioprobes are currently under progress.

## I. INTRODUCTION

The concept of field effect transistors using a chemical gate was first introduced by Bergveld in 1972 [1]. These structures have been used to measure the activity of ions, for example H<sup>+</sup> to measure a change of the pH of the solution. In 1997, Souteyrand used field effect transistors functionalized with single strand DNA to detect the hybridization of DNA [2]. This new type of biosensors, called biological field effect transistors, presents the advantage of using a direct detection, without the need for a time-consuming labelling step, which can also alter the properties of the biological species.

However, the sensitivity and potential for integration of this detection method were quite poor until the emergence of one-dimensional nanostructures to form the channel of the field effect transistors. A large variety of nanostructures have appeared to be used in chemical or biological field effect

transistors. Currently, most of the existing studies are based on carbon nanotubes [3] or on silicon nanowires [4], [5]. The development of carbon nanotubes as chemical field effect transistor is limited because it is difficult to separate semi-conductor carbon nanotube and metallic carbon nanotube, even if this limitation can be bypassed by using 2D networks of carbon nanotubes.

Si nanowires, on the contrary, are always semi-conductive, and their dopant type and concentration can be controlled. Lieber [6] has demonstrated the possibility to use Si nanowires fabricated by Chemical Vapor Deposition (CVD) to detect a large variety of biological species with good sensitivity, comparable to the state of art of fluorescence detection, the most frequently used technique. However the fabrication of high density sensor arrays with CVD Si nanowire remains a challenge since it requires transfer and positioning of individual nanowires [7].

This explains the constant effort of research on chemical field effect transistor based on Si nanowire fabricated by ‘top-down’ semiconductor processing [8]-[10]. In this paper, the fabrication of a technological demonstrator using ‘top-down’ technology and first experimental results under fluidic environment using the demonstrator as a chemical field effect transistor are reported.

## II. EXPERIMENTAL METHODS

### A. Si nanowire fabrication

The silicon nanowires were fabricated using silicon-on-insulator (SOI) wafers. The SOI wafers initially had a 200-nm silicon layer on a 402-nm thick SiO<sub>2</sub> insulating layer (Fig. 1.a). The silicon top layer was first reduced by several steps of silicon thermal oxidation / desoxidation to obtain a 50-nm silicon top layer. The wafers were doped by ion implantation with boron or phosphorous to obtain doping concentrations of 10<sup>16</sup> cm<sup>-3</sup> and 5\*10<sup>18</sup> cm<sup>-3</sup>; implantation was followed by annealing at 950°C during 15s (Fig. 1.b). The SOI wafers were cut into chips of 2\*2.5cm<sup>2</sup> and further technological

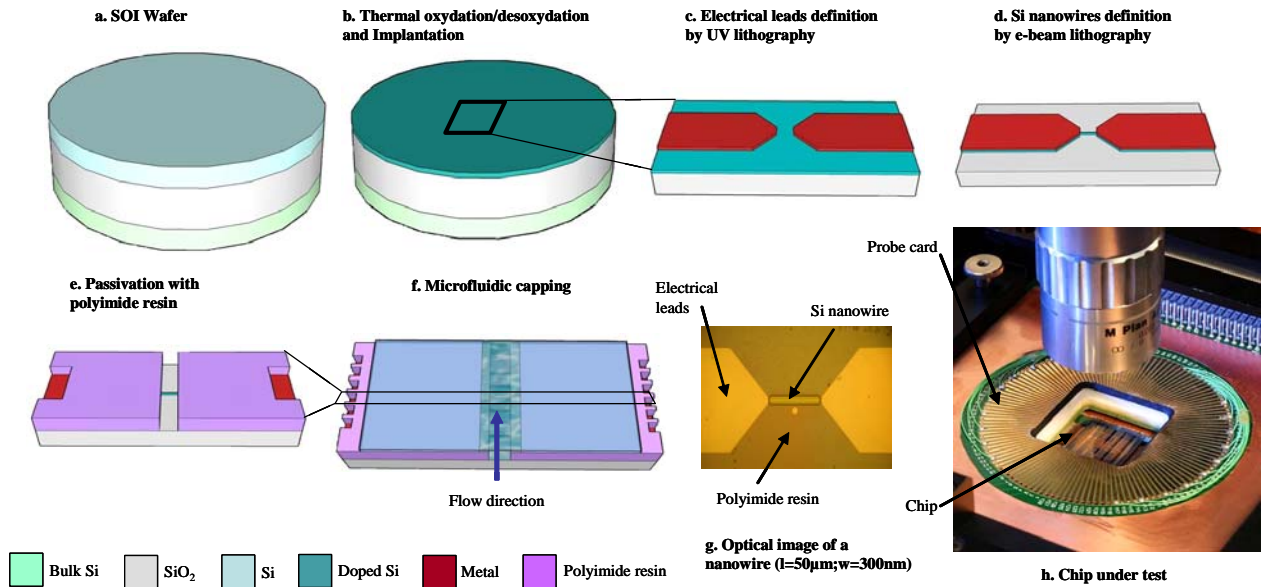


Fig. 1 Si Nanowire fabrication

steps were performed on individual chips. Electrical leads (for the source and drain electrodes) were defined using optical lithography and deposition of a thin layer of titanium and 50nm of gold by electron gun evaporation followed by lift-off in acetone (Fig. 1.c). The Si nanowires were defined using e-beam lithography and reactive ion etching (RIE). A two step annealing (30s at 350°C followed by 5min at 450°C under  $N_2H_2$ ) was performed to form a reliable ohmic contact between the nanowire and the electrical leads (Fig. 1.d). The electrical leads were finally coated by a photosensitive polyimide resin which was opened by optical lithography on the nanowires and at the ends of the electrical leads. The polyimide resin was heated at 300°C during 1 hour to improve its chemical resistance (Fig. 1.e and 1.g). Silicon nanowires with widths comprised between 50 and 800nm were fabricated, with each chip containing 30 Si nanowires of 25 or 50µm long.

### B. Si nanowire functionalization

All reactants were purchased from Sigma-Aldrich. Surface-functionalized SiNW devices were cleaned and activated in an oxygen plasma (0.16 Torr, 600 W power for 2 min). Devices were then immersed in 0.1% toluene solution of 3-aminopropyltriethoxysilane (APTES) for 17h at 80°C, rinsed with acetone, ethanol and deionised water, and dried by centrifugation. Chemical functionalization was finally stabilized by thermal heating at 110°C for 3h.

### C. Device test procedure

Electrical devices characterizations were performed on a probe station PA200 (Suss Microtec) equipped with a dedicated probe card (Fig. 1.h).

Dry electrical tests were performed using a Keithley 2400 and a Keithley 2602 to excite and measure independently the source, drain and back gate electrodes.

A lock-in SR830 was used to perform the electrical tests under fluidic environment. A 1V source-drain voltage was applied to the nanowire at a frequency lower than 100 Hz. The current of the nanowires was amplified by a Keithley 428 before being measured by the lock-in. Up to 40 nanowires could be multiplexed thanks to a Keithley 2700 and a 7702 multiplexer module.

Fluidic channels were fabricated using Gene Frame and a Pyrex cap was used to encapsulate the chip (Fig. 1.f). Capillaries were bonded at the entry and at the outlet of the fluidic channel.

A 6-way selection valve with a peristaltic pump (Upchurch) were used to put the nanowire in contact with different chemical solutions at a constant flow rate of 10µL/min.

The fluidic and electronic sensing set-up was totally automated and controlled by a labview interface.

## III. RESULTS AND DISCUSSIONS

### A. Dry electrical tests

The silicon nanowires were characterized electrically in air before chemical functionalization. Fig. 3.a represents typical  $I_{DS}/V_{DS}$  curves at different  $V_{GATE}$  for a n-type nanowire (50µm length, 200nm width): these curves are linear and the maximum of current between source and drain increases when  $V_{GATE}$  increases, as expected for a n-type MOSFET with ohmic contacts.

Actually, if the channel is n-doped, and the source and drain are also n-doped (called a normally-on n-type MOSFET), by applying a positive gate voltage, more electrons will be

attracted in the channel, there will be an increase of the number of charge carriers in the channel and its conductance will increase. By applying a negative gate voltage, holes will be attracted in the channel, there will be recombination between holes and electrons and the conductance of the channel will decrease. Fig. 2 illustrates the principle of a n-type MOSFET, the principle of a p-type device can be deduced by the reversal of polarity of the applied voltages.

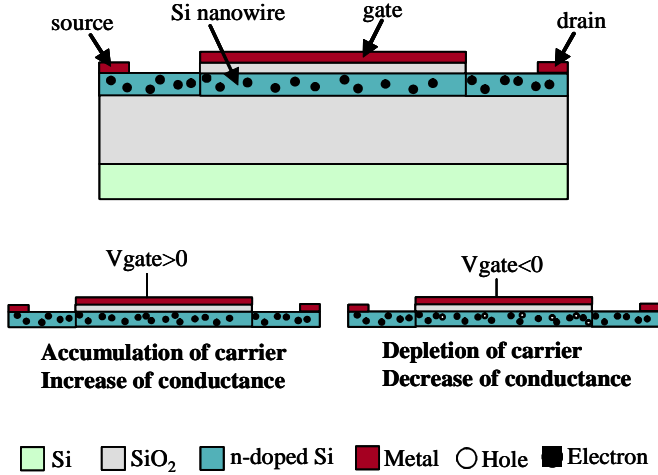


Fig. 2 Principle of a n-type MOSFET

Fig. 3.b confirms that the two-step heating improves the contact between the silicon nanowire and the metallic electrical leads since there is approximately a 42% increase in the measured conductance of the nanowire at  $V_{GATE}=0V$ .

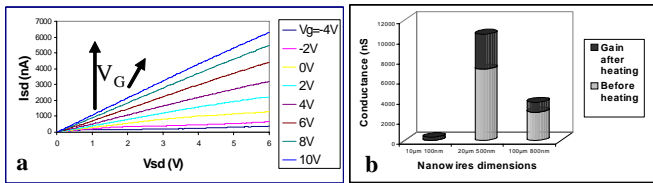


Fig. 3 Electrical characterization of Si Nanowire

In Table 1 the measured conductance of nanowires of 6 different dimensions (length of 24 or 50 $\mu$ m; width of 200, 300 or 500nm) is reported. 8 nanowires of each dimension were characterised and the obtained values prove the good reproducibility of the fabricated Si nanowires. The calculated theoretical conductance of each nanowire is also reported. The measured and theoretical conductance are clearly proportional which gives a second proof that the contact between the nanowire and the electrical leads is ohmic. The 1.45 proportionality factor can be explained by a real doping concentration lightly different from that expected by the simulation. It is also possible that the dimensions of the nanowires (especially the width and thickness) differ from that expected.

TABLE I  
REPRODUCIBILITY OF SI NANOWIRE CONDUCTANCE

Si NW length width	Measured mean conductance (nS)	Theoretical conductance (nS)	Theoretical / Measured Conductance
24 $\mu$ m 200 nm	3033 $\pm$ 422	4504	1.41
24 $\mu$ m 300 nm	4716 $\pm$ 440	6757	1.43
24 $\mu$ m 500 nm	7884 $\pm$ 511	11261	1.43
50 $\mu$ m 200 nm	1429 $\pm$ 181	2162	1.51
50 $\mu$ m 300 nm	2256 $\pm$ 206	3243	1.44
50 $\mu$ m 500 nm	3829 $\pm$ 246	5405	1.41

### B. pH sensor model

To fabricate a chemical field effect transistor, the metallic gate must be replaced by a layer of chemical functionalization. The source and drain electrodes were coated with a passivation layer (in our case a polyimide resin) so that the chemical functionalization could be in contact with conductive electrolyte without creating a short circuit. The ions present in the conductive electrolyte will change the charge distribution at the surface of the channel and act as the applied gate voltage. The presence of a specific chemical species in the solution will be detected by a change of conductance of the semiconductor channel.

To detect a change of the pH of the solution in contact with the nanowires, the Si nanowire surface was functionalized with APTES. At pH<10 the amino groups were protonated, bringing positive charges at the nanowire surface and acting as a positive gate voltage; whereas at pH>7 the silanol groups were deprotonated, bringing negative charges at the nanowire surface and acting as a negative gate voltage (Fig. 4)

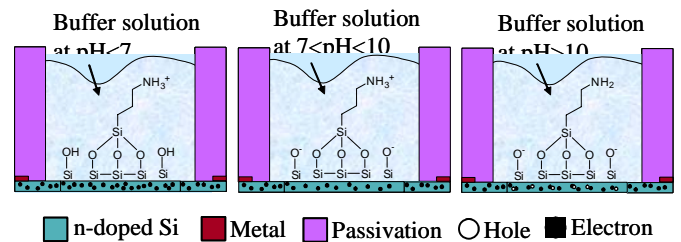


Fig. 4 Principle of pH sensor using CHEMFET

Tests with the model of pH sensor were realized. Different pH buffer solutions were prepared from phosphate buffer solution and 0.1M NaCl solution and were put in contact successively with nanowires functionalized with APTES. The conductance of the nanowire was measured and reported in Fig. 5 for a n-type Si nanowire.

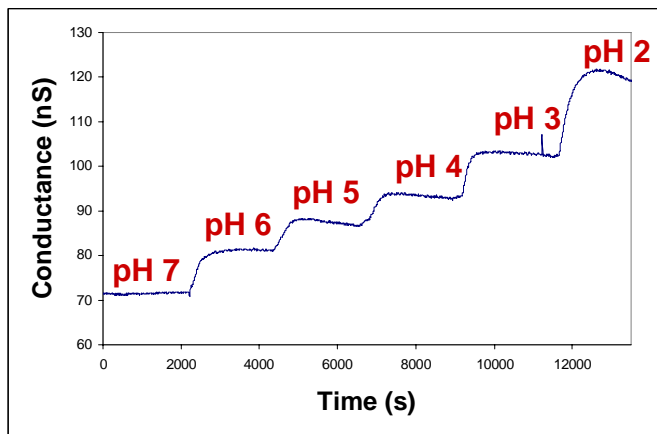


Fig. 5 Change of Si nanowire conductance according to pH

The nanowire being n-doped, the conductance increased when the pH decreased, since the amino groups acted as a positive gate voltage. The signal/noise ratio for a change of pH of 1 unity was evaluated at 50 (S/N ratio was calculated by dividing the change of the conductance by the standard deviation of the baseline). We also checked that the change of conductance according to the pH was reversible. Fig. 6 shows the variation of conductance for a p-doped nanowire between pH 4 and 7.

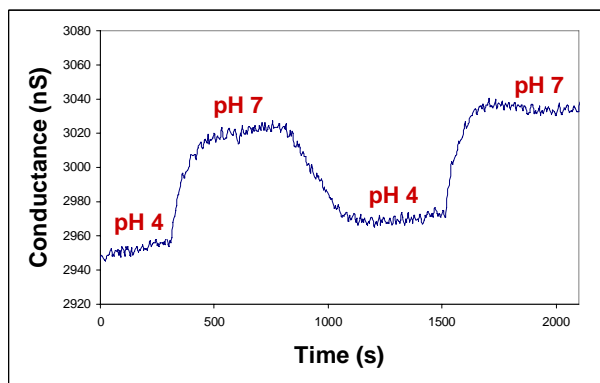


Fig. 6 Reversibility of the change of conductance according to pH

#### IV. CONCLUSION

We demonstrated the fabrication of n-type and p-type Si nanowires that operate as field-effect transistors in the air, as well as the change of the response in the conductance of the Si nanowire versus the pH of the surrounding solution. This simple model of pH sensor allowed us to validate our electronic and fluidic sensing set-up.

Chemical functionalization of the nanowire to covalently attach biological probes on its surface in order to detect a change of conductance indicating a bio-affinity is under progress. Study of the fabrication of chemical field effect nanowires by a totally CMOS compatible technology is also

under progress to demonstrate the potential for electronic integration.

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