

ION-STEP METHOD FOR SURFACE POTENTIAL SENSING OF SILICON NANOWIRES

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ABSTRACT

This paper presents a stimulus-response method for surface potential sensing of silicon nanowire field-effect transistors (Si-NW FETs). When an ‘ion-step’ from low to high ionic strength is given as stimulus to the surface, a change of current through the Si-NWs is measured. When the surface potential is changed from negative for a bare SiO₂ surface to neutral/positive when there is poly-L-lysine adsorption, this change is measured by a change in current variation at the ion-step.

KEYWORDS: Ion-step method, silicon nanowires, surface potential

INTRODUCTION

Silicon nanowire (Si-NWs) are used widely as field-effect transistors for application of pH sensing[1], flow velocity sensing[2], biosensing[3] and so on. The sensing mechanism is based on the conductivity change of the NW due to a surface potential modulation on the gate oxide, which can result from pH changes, streaming potential changes or charged biomolecule binding. Surface potential ϕ_0 is linearly related to surface charge density as $\sigma = C_{dl}\phi_0$, with C_{dl} the double layer capacitance which is constant at constant ionic strength. Steady-state measurements of the Si-NW surface potential are quite sensitive to drift, decreasing the sensitivity. Stimulus-response measurements on the other hand make the measurement less sensitive to baseline drift, as the system response to an actuation step is measured.

THEORY

A stimulus-response method to measure the surface potential of ion-selective FETs was introduced in 1990[4,5], namely by performing a transient ionic strength change (‘ion step’). An ‘ion-step’ from low to high ionic strength gives a sudden increase of C_{dl} , which causes a drop in ϕ_0 that is linearly proportional to σ . At Nernstian surfaces, ϕ_0 then returns to its original value due to a subsequent increase in σ . At sub-Nernstian surfaces, a steady-state ϕ_0 decrease remains. In this paper, we demonstrate that the latter new variant of the ion-step method can be applied to nanowire sensing. As proof of principle we demonstrate the measurement of poly-L-lysine adsorption to the Si-NW.

EXPERIMENTAL

Si-NW arrays with height of ~100 nm are fabricated as previously reported[6]. One Si-NW array has either 100 (length 50 μm) or 200 NWs (length 100 μm). Details on sample delivery and lab-on-a-chip (LOC) system can be found in [7]. Si-NW chips are cleaned with acetone and IPA, then treated with UV/ozone (UV/Ozone ProCleaner Plus, Bioforce nanoscience) for 5 min. PDMS microfluidic chips with microchannels of 200 μm width and 50 μm height are used to deliver solutions. An Ag/AgCl wire is inserted into the microchannel as reference electrode for controlling the solution potential, and therefore the Cl⁻ concentration for the salt solution is kept constant during all the measurements. poly-L-lysine (PLL) coating is realized by immersing the chip in 0.2 mg/ml PLL solution in 5 mM PBS 10 mM NaCl solution at pH 7.0 for 2 h. Then the chip is washed with PBS solution and DI water, then dried with N₂ flow. Figures 1 (a) and (b) show the schematic diagram and microscope image of Si-NW LOC system, respectively. An ion-step from 10 mM K⁺ (10 mM KCl + 1 mM buffer) to 50 mM K⁺ (10 mM KCl + 40 mM KNO₃ + 1 mM buffer) is applied to the sensor. The buffer used is a mixture of citric acid and Tris.

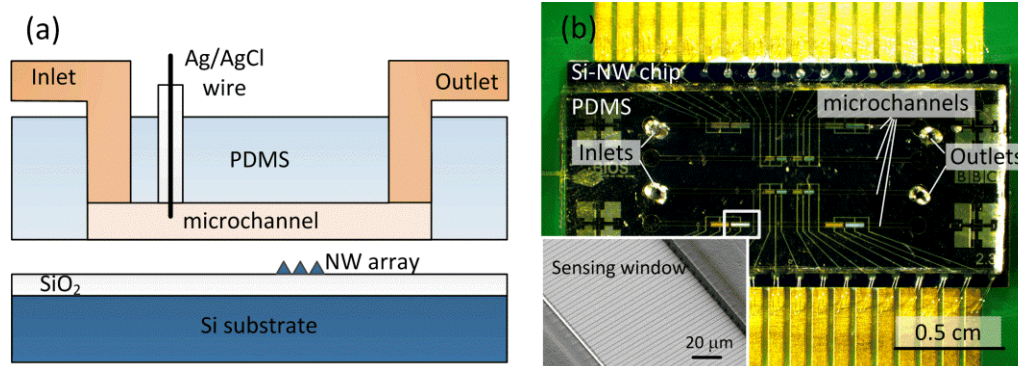


Figure 1: (a) Schematic and (b) microscope image of the Si-NW LOC. The inset on (b) shows a high resolution scanning electron microscope image of Si-NW sensing array in a sensing window.

Samples are delivered by pressure source (MFCS-8C, Fluigent) and the solution switch is realized with an injection valve (Cheminert nanovolume 10-port valve, Valco Instruments Co. Inc.). A flow speed of 24 mm/sec is estimated. A driven ac voltage of 10 mV is applied to the Si-NW array at frequency of 30 Hz by a lock-in-amplifier (SR 830, Stanford Research Systems).

RESULTS AND DISCUSSION

The ion step response for a SiO₂ gate oxide at different pH values is shown in Fig. 2, expressed as a change of the current through the wires. Due to the negative charge of the oxide surface, a reduction of surface potential ϕ_0 when increasing the salt concentration reduces the current in the Si-NW sensor. The current change increases from pH5 to 9 due to the increase of surface potential in negative direction. However, unexpectedly we observe a strong change at pH 3.2 even when we stabilize the surface in that solution for over 1 h before the measurements. Here more investigation is needed.

Figure 3(a) shows the pH response $\Delta\phi$ with and without PLL coating, expressed as the surface potential change with respect to the value at pH4.0. We see that $\Delta\phi$ becomes linearized with pH change due to the introduction of amine groups at the surface. Figure 3(b) demonstrates the feasibility of the ion-step approach, showing ion-step measurements before and after incubation of Si-NWs with PLL. A reduction of the ion-step response from 2nA to almost zero at pH 5.0 is observed, which corresponds to $\Delta\phi \sim 12$ mV. We interpret this reduction as the result of the reduction of the surface potential of the gate surface from strongly negative to neutral at pH 5.0 due to the electrostatic adsorption of PLL (positively charged below pH 9.0) on the oxide surface. This method can be used for applications such as biosensing.

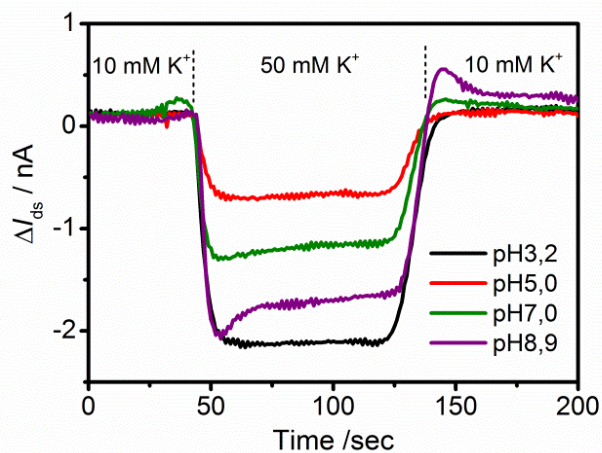


Figure 2: Ion-step response of a SiO₂ NW surface at different pH.

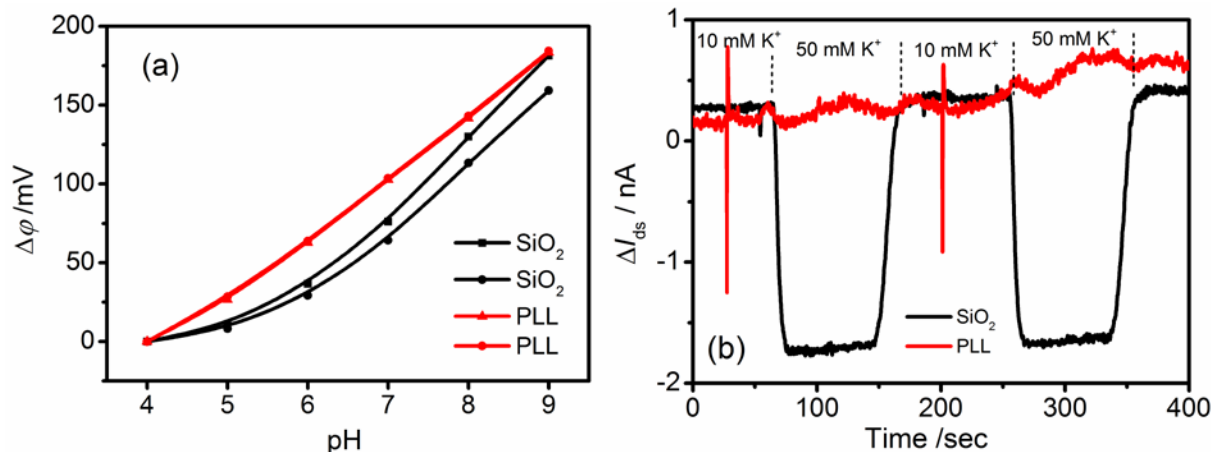


Figure 3: (a) pH responses of Si-NWs with bare SiO_2 gate or PLL coating. (b) Ion-step responses of a bare SiO_2 surface (black) and of a SiO_2 surface with adsorbed PLL (red) at pH 5.0, indicating the sensing of PLL adsorption.

CONCLUSIONS

We demonstrated that the surface potential change due to PLL adsorption to Si-NWs can be measured with the ion-step method. By increasing the ionic strength from 10 mM to 50 mM, a current reduction is observed for a negatively charged surface while after PLL adsorption, due to the reduction of the surface potential, the current change reduces to almost zero. This stimulus-response method can be used as an alternative method for surface potential sensing with less sensitivity to baseline drift.

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REFERENCES

1. S. Chen, J.G. Bomer, E.T. Carlen, A. van den Berg, "Al₂O₃/silicon nanoISFET with near ideal Nernstian response," *Nano Lett.*, 11, 2334–2341, 2011.
2. D.P. Kim, C.H. Lee, X. Zheng, "Probing flow velocity with silicon nanowire sensors", *Nano Lett.*, 9, 1984-1988, 2009.
3. Y. Cui, Q. Wei, H. Park, C.M. Lieber, "Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species," *Science*, 293, 1289–1292, 2001.
4. R.B.M. Schasfoort, R.P.H. Kooyman, P. Bergveld, J. Greve, "A new approach to immunoFET operation," *Biosensors & Bioelectronics*, 5, 103-124, 1990.
5. J.C. van Kerkhof, J.C.T. Eijkel, P. Bergveld, "ISFET responses on a stepwise change in electrolyte concentration at constant pH", *Sensors Actuators B*, 18-19, 56-59, 1994.
6. S. Chen, J.G. Bomer, W.G. van der Wiel, E.T. Carlen, A. van den Berg, "Top-down fabrication of sub-30 nm monocrystalline silicon nanowires using conventional microfabrication," *ACS Nano*, 3, 3485-3492, 2009.
7. A. De, J. van Nieuwkastele, E.T. Carlen, A. van den Berg, "Integrated label-free silicon nanowire sensor arrays for (bio)chemical analysis," *Analyst*, 138, 3221–3229, 2013.

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