

# QUANTITATIVE STUDIES OF LONG-TERM STABLE, TOP-DOWN FABRICATED SILICON NANOWIRE SENSOR

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## ABSTRACT

We report simple and effective methods to develop long-term, stable silicon nanowire-based pH sensors and systematic studies of the performance of the developed sensors. In this work, we fabricate silicon nanowire pH sensors based on top-down fabrication processes such as E-beam lithography and conventional photolithography. In order to improve the stability of the sensor performance, the sensors are coated with a passivation layer (silicon nitride) for effective electrical insulation and ion-blocking. The stability, the pH sensitivity, and the repeatability of the sensor response are critically analyzed with regard to the physics of sensing interface between sample liquid and the sensing surface. The studies verify that the sensor with a passivation layer over critical thickness show long-term, stable sensor response without long-term drift. The studies also show the detection of pH level with silicon nanowire sensors is repeatable only after proper rinsing of sensor surfaces and there exists trade-off between the stability and the pH sensitivity of sensor response.

**KEYWORDS:** Silicon Nanowire, pH sensor, Long-term stability, Electrical insulation, Ion-blocking

## INTRODUCTION

Silicon nanowires are good sensing materials for detecting Bio-chemicals such as pH level, the concentration of DNA, and the concentration of protein because highly sensitive detection of analytes can be achieved thanks to its high surface to volume ratio. Recently, top-down fabricated silicon nanowire sensors have been developed by the combination of E-beam lithography and conventional photolithography and these sensors are highly favored in modern Integrated Circuit (IC) technology because the dimensions and the electrical properties of wires can be tuned accurately and the entire fabrication processes are CMOS (Complementary Metal-Oxide-Semiconductor) process-compatible. So far, previous works on top-down fabricated silicon nanowire sensors are primarily focused on the studies on the sensitivity, response time of sensors, or computational modeling of surface charge effect on the sensors. In order for silicon nanowire sensors to be used in industrial applications or in bio-monitoring in the long run, it is very crucial to implement reliable and systematic ways to silicon nanowire sensors to improve the stability of the sensors. Herein, we introduce a straightforward way to develop long-term and stable silicon nanowire pH sensors. We fabricate silicon nanowire pH sensors by the combination of E-beam lithography and photolithography, major techniques in top-down fabrication. A passivation layer (silicon nitride) is coated on the surface of silicon nanowire to provide superb electrical insulation and ion-blocking properties of the sensor. The stability, the pH sensitivity, and the repeatability of the sensor response are characterized and the sensing response is interpreted.

## THEORY

The detection of pH of fluid is achieved based on the principle of Field Effect Transistor (FET). The surface of silicon nanowire is deprotonated in lower pH fluid and mobile carriers (holes) are depleted due to the electrostatic interaction between the charge of nanowire at outer surface of the nanowire and the mobile carriers at inner surface of the nanowire. With the same principle, the surface of silicon nanowire is protonated in higher pH fluid and the mobile carriers are accumulated at the inner surface of silicon nanowire. A passivation layer serves a critical role to separate the surface charge at the outer surface of the nanowire from the mobile carriers at the inner surface of the nanowire and forms a field effect between two surfaces. Therefore, it is important for a passivation layer to have good properties of electrical insulation and ion-blocking to prevent electrical leakage through the passivation layer. Also, it is crucial that the passivation layer should be reactive to the change of fluid pH, otherwise, the surface is not deprotonated/protonated and the accumulation/depletion of mobile carriers in silicon nanowire is not induced. Either oxygen plasma or short, thermal oxidation is not capable of controlling the thickness of silicon dioxide layer accurately. Silicon dioxide layer does not have high dielectric constant (silicon dioxide: 3.9) compared to silicon nitride layer (silicon nitride: 7.5) and the proton-diffusivity of silicon dioxide (silicon dioxide by CVD :  $3.3 \times 10^{-16}$  cm<sup>2</sup> / sec) is much higher than those of silicon nitride (silicon nitride by CVD :  $10^{-19}$  cm<sup>2</sup> / sec). These facts imply that silicon nitride layer can be chosen as a proper passivation layer to improve electrical insulation as well as decrease the diffusion of proton ions from fluid to device layer. It was previously reported that silicon nitride layers are used as sensing membranes as well as insulators layers for pH level detection.

## EXPERIMENTAL

**Materials.** Silicon on insulator (SOI) wafer (top layer: silicon, 100 nm; buried layer: oxide, 400 nm; base layer: silicon, 600  $\mu$ m; Soitec) is used as a substrate and device structure. Leaded chip carriers (LDCC) (40 leads, Spectrum Semiconductor Materials Inc.) and plastic leaded chip carriers (PLCC) package (Spectrum Semiconductor Materials Inc.) are used as packaging platforms for electrical connection. PDMS (Alfa Aesar) is used as microfluidic material for

containing sample liquid. Ag/AgCl reference electrode (Microelectrode Inc.) is used to maintain the electrical potential between fluid and device.

**Fabrication of Silicon Nanowire pH Sensors.** The SOI wafer is oxidized to form a thin SiO<sub>2</sub> of 110 nm via dry thermal oxidation. It results in the decrease of top Si layer thickness from 100 nm to 50 nm. Then, the Si device layer is doped with boron (B) by ion implantation (dose =  $3.63 \times 10^{13}$  cm<sup>-2</sup>; ion energy = 18 KeV; tilt angle = 7°) and rapid thermal annealing at 984°C for 20 sec in nitrogen environment is followed for dopant activation. The effective doping concentration is measured to be equivalent to  $2\sim 3 \times 10^{18}$  cm<sup>-3</sup> at the Si device layer. Afterward, the top SiO<sub>2</sub> layer is thinned down to 50 nm by wet etching in 10:1 buffered oxide etchant (BOE) and E-beam lithography is carried out on PMMA-coated substrate to define the dimension of silicon nanowires (width: 100 nm; length: 60 μm). The sample is developed in the PMMA developer (isopropyl alcohol (IPA): methyl isobutylketone (MIBK) = 3:1) for 2 min and this is followed by soaking in IPA for 1 min and finally rinsing with DI water. After the development, 15 nm chromium (Cr) is deposited on the sample and nanopattern is generated by following a lift-off process. The Cr layer is used as an etching mask for SiO<sub>2</sub> layer. The SiO<sub>2</sub> layer is etched by Reactive Ion Etching (RIE) processes in a CF<sub>4</sub> + O<sub>2</sub> environment and the etching of Cr etching mask with wet Cr etchant is followed. For the etching of Si device layer, a RIE process with CF<sub>4</sub> + O<sub>2</sub> gases is used. Then, the top remaining SiO<sub>2</sub> layer is removed by 10:1 BOE. After the etching process, a passivation layer, silicon nitride layer is deposited on the entire substrate by PECVD. The Aluminum interconnection is photolithographically defined and aluminum is deposited after wet etching of passivation layers through the patterned openings with a followed lift-off process. Then, the sample is thermally annealed in forming gas (10% H<sub>2</sub> / 90 % N<sub>2</sub>) at 400 °C for 30 min to form ohmic contact between silicon layer and aluminum pads.

**Packaging of Silicon Nanowire pH Sensors.** A PDMS microfluidic channel (width = 50 μm; height = 50 μm) is bonded to a 1 cm × 1 cm chip where silicon nanowire pH sensors are fabricated via oxygen plasma treatment. The PDMS channel is aligned accurately so that the aluminum patterns of the sensor chip are perfectly passivated from liquid to avoid electrical leakage between electrodes in the electrical measurement. A PDMS bonded chip is bonded to a LDDC by conductive carbon tape (Ted Pella Inc.) and wirebonding is achieved between the electrodes of the sensor chip and the electrical pads in the LDDC. Then, the LDDC with a PDMS microfluidic channel is inserted to a PLCC package and the package is mounted on an electrical breadboard.

**Measurement of Stability of Silicon Nanowire pH Sensors.** Four-points method is used to monitor the change of the resistance of silicon nanowire over 3 hours. AC power supply is used and the applied voltage is 100 mV and the frequency is 30 Hz. The output signal is acquired and saved by LabVIEW software. Two parameters, average noise level and drift level, are defined to quantify the measurement results. Average noise level is calculated by averaging the deviation of response signal from the absolute average and normalizing it with the absolute average. Drift level is calculated by subtracting the average response signal of last 30 minute measurement from the average response signal of initial 30 minute measurement. The response plot is obtained by normalizing real-time response with initial sensor response.

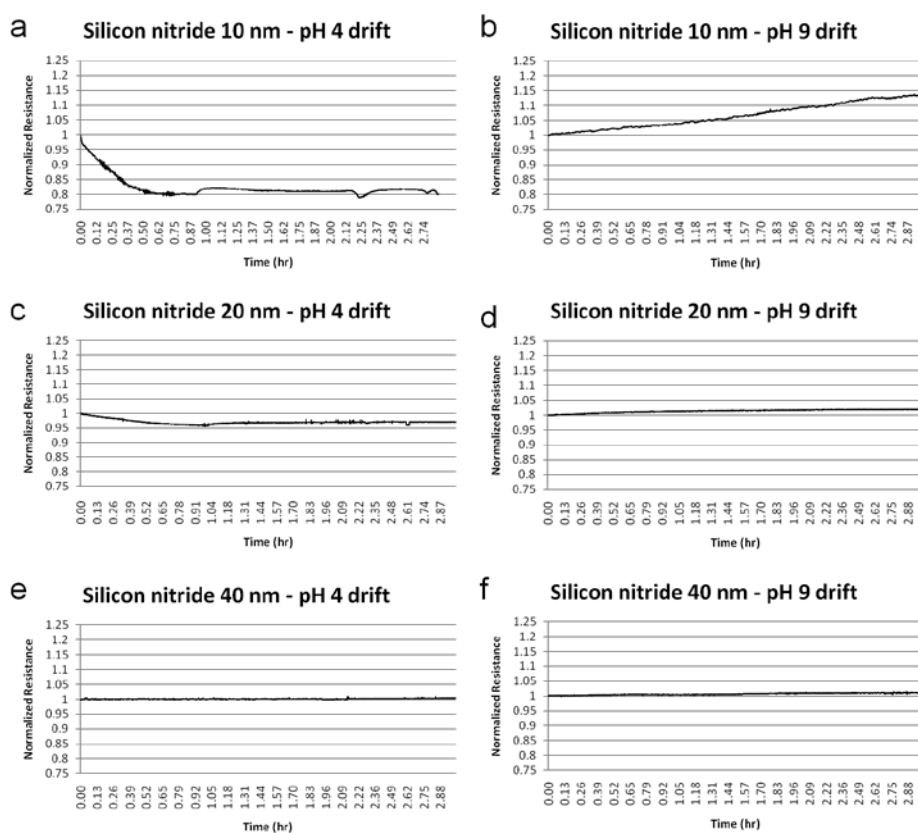
**Measurement of pH Sensitivity of Silicon Nanowire pH Sensors.** In order to characterize the conductance of silicon nanowires, current-voltage (I-V) curve is obtained in the voltage range from -0.1 V to 0.1 V and the slope of the curve which is equivalent to the conductance of silicon nanowire is calculated via least squares fitting. The pH scanning is performed three times and averaged. The error bars are included in each pH scanning graph. Most of error bars are too short to be visible in the graph, however, it is included in the graph.

For both measurements, the scanning is performed at 5 min after the fluid is injected to PDMS channel to wait for the fluid to be stabilized in order to eliminate the flow rate effect to the sensor response. The fluid is desired to be static during the measurement period in order to observe the pure contribution of pH level to the sensor response. Also, Ag / AgCl reference electrode is implemented to the fluid in order to maintain electrical potential between the fluid and the device.

## RESULTS AND DISCUSSION

Stability of the silicon nanowire devices with various thicknesses (10 nm, 20 nm, 40 nm) of silicon nitride are measured at low pH (pH 4) and high (pH 9) for three hours. The responses are shown in Figure 1. The resistance of the device tends to decrease in low pH while it tends to increase in high pH according to the principle of silicon nanowire sensors described in the earlier section. The response of the sensors with 20 and 40 nm nitride passivation layers show asymptotic behavior and it is well-understood by theoretical model of silicon nanowire sensors in the previous literature<sup>1</sup>. In this model, the response of silicon nanowire sensors with respect to time is numerically simulated by coupling and solving various governing equations of mass transport. The simulation shows that the sensor response evolves in three phases. Phase I is reaction limited and occurs at very short time as the sensors begin to capture the analyte available very close to the surface and the response varies linearly with time. Once the region near the surface is depleted of analyte, the diffusion-limited transport of analyte through water molecules dictates sensor response in phase II which varies as  $t$  for sensors of cylindrical geometry, which is equivalent to nanowire-geometry. Finally, in phase III, the response of the sensor saturates due to the detailed balance of forward and backward reactions, therefore, the response of the sensors is stabilized.<sup>1</sup> Three-hour time window is long enough to observe these three phases. However, the response of the devices with 10 nm silicon nitride passivation layers do not show asymptotic behavior and show continuous decrease in low pH and increase in high pH as time passes. It is speculated that proton ions in fluid are not blocked by 10 nm silicon nitride layer and those ions are embedded at Si / Insulator interface. It is mainly attributed to the defects such as pin holes or

interstitial atoms generated during PECVD processes of silicon nitride. If the thickness is comparable to 20 nm, proton ions are still blocked, however, a 10 nm silicon nitride layer may not be thick enough to block proton ions. In ISFET-based pH sensors, it is a well known fact that proton diffusion through insulation layer causes the change of the surface state density at the interface between Si / Insulator and this change leads to a drift of sensor response.<sup>2</sup> Likewise, in silicon nanowire sensors, constant supply of proton ions from fluid through thin insulation layer changes the surface state density at Si / Insulator interface and affect the mobile carrier density which is influenced by the surface state density at the interface. In low pH, proton ions diffuse out to Si / Insulator interface from the fluid and increase the electrostatic force the charges between outer surface of silicon nanowire and inner surface of silicon nanowire. As a result, the depletion of the mobile carrier is enhanced and conductance of the nanowire decreases. On the other hand, in high pH, inherent proton ions which are originally present by Si / Insulator interfacial defects are diffused out from the device to the fluid and decrease the electrostatic force across the insulation layer, thus, increase the conductance of silicon nanowire. It is crucial to separate the long-term drift of response signal caused by poor ion-blocking from slow response caused by inherent physics to differentiate the effect of pH level to the response from the effect of ion-diffusion to the response. For example, the resistance of the nanowire sensor with a 20 nm silicon nitride layer at low pH starts decreasing significantly at the beginning of the measurement, however, the response finally shows asymptotic behavior and reaches to steady state, stable level. This trend is caused by the slow response of silicon nitride surface to pH change (From air to pH 4), not by the diffusion of proton ions through insulator. However, the response of nanowire sensor with a 10 nm silicon nitride layer, continuous decrease / increase of the response, can be interpreted by coupling slow pH response of surface with drift caused by proton diffusion and it arises complication of the analysis.

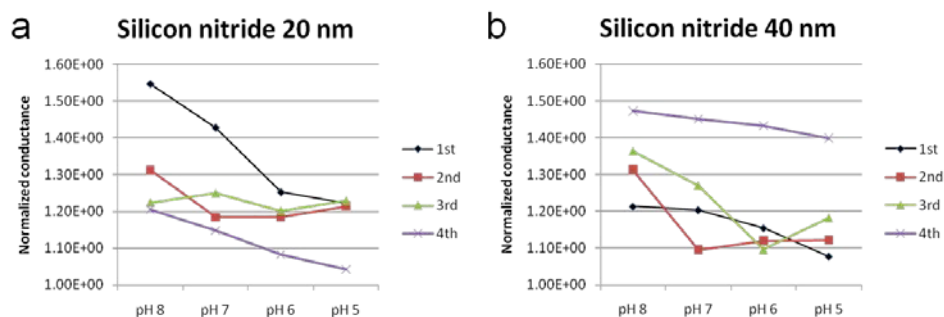


**Figure 1.** Long-term (~ 3 hrs), electrical measurement of silicon nanowire-based pH sensor with a passivation layer of silicon nitride at low pH (pH 4) and high pH (pH 9). (a) Normalized resistance of the device with a 10 nm silicon nitride at pH 4 (b) Normalized resistance of the device with a 10 nm silicon nitride at water at pH 9 (c) Normalized resistance of the device with a 20 nm silicon nitride at pH 4 (d) Normalized resistance of the device with a 20 nm silicon nitride at pH 9 (e) Normalized resistance of the device with a 40 nm silicon nitride at pH 4 (f) Normalized resistance of the device with a 40 nm silicon nitride at pH 9

Clearly, the sensor with a 10 nm silicon nitride layer do not show stable response since average noise level is higher than the response change by a pH step change and drift level is comparable to 10 %. However, the rest of the sensors show relatively low noise level and drift level. Compared to previously reported data<sup>3</sup> (5~6 % conductance change in pH 4 and pH 10) where the drift level was measured from the silicon nanowire sensor with silicon dioxide insulator by short thermal oxidation, the drift level of the sensors except the sensor with a 10 nm silicon nitride layer show much smaller drift.

Figure 2 shows that pH sensitivity of the silicon nanowire with a 20 nm silicon nitride layer is 10.85 %/pH at the 1<sup>st</sup> scanning, however, this pH sensitivity is not reproduced in followed two scannings when the interval of each scanning is

5 minute. After the nanowire sensor is immersed in DI water overnight (~12 hours), the pH sensitivity is reproduced at the fourth scanning, however, the sensitivity decreases to 5.44 %/pH. This tendency is repeated in the silicon nanowire with 40 nm silicon nitride layer; the pH sensitivity of the 1<sup>st</sup> scanning is 4.51 % / pH and it decreases to 2.45 % / pH. Decrease of pH sensitivity with thicker insulator is well understood by the decrease of the field-effect across the insulator at fixed chemical bias. Poor reproducibility of pH sensitivity of the sensors with short intervals is mainly attributed to hysteresis (memory) effect which is caused by a time lag response as stated previously. Even after a pH step change, the response change from previous pH step change still remains and interfere the measurement of pH response from the latest pH step change. Based on the previous theoretical study,<sup>4</sup> the width of a hysteresis loop is a function of the amplitude, time constant of the slow response, and of the loop time. If the sweep time is smaller, the sensitivity decreases and a hysteresis loop increases. This theory explains the poor reproducibility shown in the 2<sup>nd</sup> and 3<sup>rd</sup> scanning. Rinsing the sensor with water for long time eliminates the hysteresis effect and the sensitivity is recovered at the 4<sup>th</sup> scanning. The decrease of the pH sensitivity after rinsing is caused by the surface oxidation of silicon nitride surface<sup>4</sup> and this oxidation is increased with increasing time between pH change and pH measurement and leads to decrease the pH sensitivity of silicon nanowire sensor.



**Figure 2.** pH sensitivity measurement of silicon nanowire-based pH sensor with a passivation layer of silicon nitride with a short interval (5 min). 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> scanning are performed in serial without water-rinsing step. 4<sup>th</sup> scanning is performed after incubation of the sensor in water for 24 hrs, (a) pH sensitivity measurement of the sensor with a 20 nm silicon nitride layer (b) pH sensitivity measurement of the sensor with a 40 nm silicon nitride layer

## CONCLUSION

In this study, we developed long-term, stable silicon nanowire-based pH sensors by coating nanowire with a passivation layer (PECVD-silicon nitride) for effective electrical insulation and ion-blocking. The stability, the pH sensitivity, and the repeatability of the sensor response are systematically studied in terms of the physics of Liquid / Insulator interface and Si / Insulator interface. The studies demonstrate that the sensors with a passivation layer over critical thickness show long-term, stable sensor response without long-term drift. The studies also show that there exists clear trade-off between long-term stability and pH sensitivity in silicon nanowire-based pH sensors. The sensors with thicker passivation layers over critical thickness give more long-term, stable response, however, the pH sensitivity decreases. It is crucial to choose a passivation layer of proper material and thickness for silicon nanowire-based pH sensors to show good performance in long-term pH measurement.

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