pH driven addressing of silicon nanowires onto Si$_3$N$_4$/SiO$_2$ micro-patterned surfaces

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Abstract

pH was used as the main driving parameter for specifically immobilizing silicon nanowires onto Si$_3$N$_4$ microsquares at the surface of a SiO$_2$ substrate. Different pH values of the coating aqueous solution enabled to experimentally distribute nanowires between silicon nitride and silicon dioxide: at pH 3 nanowires were mainly anchored on Si$_3$N$_4$; they were evenly distributed between SiO$_2$ and Si$_3$N$_4$ at pH 2.8; and they were mainly anchored on SiO$_2$ at pH 2. A theoretical model based on DLVO theory and surface protonation/deprotonation equilibria was used to study how, in adequate pH conditions, Si nanowires could be anchored onto specific regions of a patterned Si$_3$N$_4$/SiO$_2$ surface. Instead of using capillary forces, or hydrophilic/hydrophobic contrast between the two types of materials, the specificity of immobilization could rely on surface electric charge contrasts between Si$_3$N$_4$ and SiO$_2$. This simple and generic method could be used for addressing a large diversity of nano-objects onto patterned substrates.

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Keywords: localization, patterned surfaces, silicon, nanowires, pH, electrostatic forces, DLVO theory

(Some figures may appear in colour only in the online journal)
way to tune interaction forces between nanowires and SiO2/Si3N4 patterned surfaces. A DLVO theory (after Derjaguin, Landau, Verwey and Overbeck (Derjaguin and Landau 1941, Verwey et al 1948) based model was used to show the diversity of possible interactions. Addressing of Si NW onto patterned substrates was experimentally performed. The influence of pH was assessed by quantifying the numbers of nanowires onto each type of material.

**Experimental methods**

**Chemicals**

Potassium chloride and reagent grade acetic acid were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Ultrapure water (18.2 MΩ) was delivered by an Elga water system.

**SiO2/Si3N4 micropatterned supports preparation**

SiO2/Si3N4 supports were provided by Laboratoire des Technologies de la Microélectronique, Grenoble. Oxidation and coatings were performed onto p type (boron, 10^{15} \text{cm}^{-3}) 8\text{"} (100) silicon wafers. Thermal silica was fabricated at 1050 °C under dry oxygen. Nitride layers were deposited by plasma enhanced chemical vapor deposition. Thicknesses of thermal SiO2 layers were measured by spectroscopic ellipsometry (9–11 nm) and complex impedance measurements (8–11 nm). Spectroscopic ellipsometry and impedance measurement both yielded a Si3N4 thickness of 42–44 nm. SiO2 substrates were covered by matrices of 23 × 23 μm² Si3N4 rounded square patterns, fabricated by optical lithography. The period of the Si3N4 patterns was P = 30 μm. Each Si3N4 zone, with its direct SiO2 surroundings, was treated as an individual feature for semi-automated image analysis (figure 1(A)). For each feature, the Si3N4 area was ~520 μm², and the SiO2 area was ~420 μm².

**Si NW synthesis**

In this study, Si NW were grown on silicon (1 1 1) substrates by reduced pressure chemical vapor deposition using the Au catalyzed vapor–liquid–solid mechanism (Rosaz et al 2011a, Rosaz et al 2011b, Serre et al 2013). The growth was performed in a CVD furnace Easy Tube™ 3000 (First Nano) at 650°C under a pressure of 3 Torr. Silane SiH₄ was used as the silicon precursor with a flow of 40 sccm. Hydrogen chloride HCl was also added during the growth in order to inhibit the gold diffusion and the lateral growth (Serre et al 2013).

Nanowires were dispersed in water by ultrasonication for 5 min. An ultrasonic bath in ethanol was used to cut/detach Si NW from their support. Aliquots of nanowire ethanol solution were left to dry. Before carrying out further experiments, nanowire samples were resuspended in fresh water/ acetic acid. The pH of water/acetic acid was controlled with a pH meter before resuspension. Solutions were mixed under 1 min of ultrasonication, and by vortexing. Vortexing was performed again just before coating onto supports.

**Contact angle measurements**

Static contact angle measurements were performed on separate SiO2 and Si3N4 supports, using the sessile drop method with a Digidrop apparatus from GBS scientific instrument apparatus. Droplets of 0.8 μl were deposited onto a support with a syringe equipped by a Teflon tip. Photographs of the droplet on the support was analyzed by the software, in order to calculate the contact angles of the liquid onto the support (Barhoumi et al). Pure water, and fresh water:acetic acid mixtures (yielding pH from 1.5 to 5) were coated onto the
surfaces. The pH of each source solution was monitored with a pH-meter before and after experiments. All measurements were performed in a saturated atmosphere of the liquid vapor. Before measurements, a small quantity of liquid was placed on an absorbing paper in the measurement chamber, in order to saturate the atmosphere of the chamber with the vapor of the tested liquid. At least three measurements for each pH and each support were recorded.

Electrochemical impedance measurements on Si/SiO₂ and Si/ SiO₂/Si₃N₄ substrates

Si/SiO₂ and Si/SiO₂/Si₃N₄ substrates with an In/Ga ohmic contact on the back side were used as working electrodes in a three electrode potentiostatic measurement set-up. A platinum electrode was used as a counter electrode, while an Ag/AgCl electrode was used as reference electrode. Supports were characterized by impedance measurements using a Voltalab 40 (Radiometer Analytical, Villeurbanne). Briefly, impedance measurements were performed at a fixed frequency of 100 kHz, by applying a DC potential ranging from 0 to 2 V with respect to the Ag/AgCl reference electrode. Out-of-phase and in-phase impedances were then acquired using complex Ohm’s law, as already described (Souteyrand et al 1997, Cloarec et al 2002).

Impedances were measured using an aqueous 40 mM KCl electrolyte, with pH ranging from 2 to 4. The pH of each solution was adjusted using acetic acid final concentration. A pH-meter was used before and after each impedance measurement, in order to verify the pH stability of the tested solution. Mott–Schottky plots were constructed in order to monitor the effect of pH on the silicon flat band potential (Cloarec et al 1999) of Si/SiO₂ and Si/SiO₂/Si₃N₄ substrates.

Results and discussion

Principle of pH driven addressing of SiNW onto patterned surfaces

Our approach for addressing nanowires onto patterned substrates relies on the fact that materials such as silicon dioxide and silicon nitride exhibit silylamine and/or silanol amphoteric surface moieties (figure 2(A) and table 1). These chemical functions can drastically change their electric charge, depending on the H₂O⁻ concentration in their vicinity. Silanols can either be deprotonated (a), neutral (b) or protonated (c). In the pH range we explored, silylamines can either be neutral (d) or protonated (e). The different protonated, neutral and deprotonated species coexist on a same material. Their relative proportions only depend on acid–base equilibria driven by pH. Choosing adequate surface materials and pH value, it is theoretically possible to tune the interaction forces between nano-objects and patterned surfaces (figure 2(B)).

When free nano-objects are dispersed in a liquid onto a surface, several type of forces can contribute to their interactions. We explain below how experimental conditions were chosen for maximizing electrostatic interactions, among the other possible forces:

- van der Waals and electrostatic forces take place in the bulk and at the liquid/solid interfaces (nanowire/nanowire interactions, nanowire/support interactions).
- Water composition was only modified by adding acetic acid. In our work, water was used as the liquid medium; pH was adjusted using acetic acid (CH₃–COOH). No other salts were added in the electrolyte. This minimized the Debye length in the solution, thus maximizing the electrostatic interactions. In addition, contrary to mineral acids such as HCl or H₂SO₄, acetic acid easily evaporates at room temperature. This avoids residual salt deposits onto the surfaces, and considerably simplifies microscopy image acquisition.

- Capillary forces drive the organization of nano-objects at the liquid/solid/air interface. In order to avoid the contribution of capillary forces, nanowire solutions were not left to dry. Fresh homogeneous aqueous nanowire solutions with controlled pH was first left to incubate onto the surface. This concentrated nanowires on the surface via simple sedimentation. After nanowire deposition, the surface was gently flushed with water at the exact same pH, without any drying. Nanowires strongly interacting with the surface were thus maintained on the support,
while other nanowires were eluted. This approach is similar to the principles of ion exchange chromatography, the nanowires behaving as rigid polyelectrolytes on charged surfaces.

**Theoretical relationship between solution pH and surface potentials**

We summarize below an approximated theoretical description of silicon dioxide and silicon nitride surfaces used for

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Table 1. Summary of Brønsted acid–base equilibria on the tested surfaces, and calculation chosen parameters.

| Material name                  | Type of surface functions | Acid–base equilibria for the surface functions | Parameters used for theoretical calculations of surface charge density and surface potential. |
|--------------------------------|---------------------------|-----------------------------------------------|-----------------------------------------------------------------------------------------|
| Silicon dioxide surface (SiO₂) | Silanols                  | Si–OH⁺ + H₂O ↔ Si–OH + H₂O⁺                    | pKa₁ = 0.2; pKa₂ = 5.4                                                                 |
|                                |                           | Si–OH + H₂O ↔ Si–O⁻ + H₂O⁺                     | Density of chemical functions (silanols): d_{Si-OH} = 0.5 μmol m⁻² (Dugas and Chevalier 2003) |
| Silicon nitride surface (Si₃N₄ + SiO₂) | Silanols and silylamines | Si–OH⁺ + H₂O ↔ Si–OH + H₂O⁺                    | pKa₁ = 0.1; pKa₄ = 4.75; pKa₅ = 11                                                                 |
|                                |                           | Si–OH + H₂O ↔ Si–O⁻ + H₂O⁺                     | Density of chemical functions (silanols + silylamines) is d_{Si-OH+Si-NH₂} = 0.5 μmol m⁻² (value arbitrarily equal to the density of SiO₂) |
|                                |                           | Si–NH₃⁺ + H₂O ↔ Si–NH₂ + H₂O⁺                   | Ratio silanol/total amount of functions: d_{Si-OH}/d_{Si-OH+Si-NH₂} = 0.958 (Hoh et al 1992) |
| Silicon nanowire (native oxide SiO₂) | Silanols                | Si–OH⁺ + H₂O ↔ Si–OH + H₂O⁺                    | pKa₆ = 1.3; pKa₇ = 4.5; Density of chemical functions (silanols) d_{Si-NW} = 0.5 μmol m⁻² (Dugas and Chevalier 2003) |
|                                |                           | Si–OH + H₂O ↔ Si–O⁻ + H₂O⁺                     | Considering the method of fabrication of SiNW, the point of zero charge (PZC) (Carré et al 2003) of native superficial oxide is considered to be approximately ~2.9 in the theoretical calculations. |
calculating the influence of pH on surface potential in our work. SiO2 surfaces bear silanol amphoteric groups, protonated or deprotonated depending on the pH of the liquid medium. The silanol (de)protonation state is described by three equations, characterized by their dissociation constants Ka1, Ka2 and Ka3 (Carré et al 2003, Barhoumi et al 2010). Each material exhibits a specific protonation behavior, depending on the density of chemical functions.

The constants N\textsubscript{Si\(\text{OH}\)\textsubscript{silanol}}, N\textsubscript{Si\(\text{OH}\)\textsubscript{silanol}}, N\textsubscript{Si\(\text{NH}\)\textsubscript{silanol}} and N\textsubscript{Si\(\text{NW}\)\textsubscript{silanol}} describe the surfacic densities (number of function per surface unit) of silanols and/or silylamines for SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4} and SiNW surfaces. Table 1 summarizes the chemical moieties involved in acid–base equilibria for the three materials, in the pH range (2.00–3.50) tested in the present work. C is defined as the total surfacic concentration of all silanols (neutral Si–OH; protonated Si – OH\textsuperscript{+}; deprotonated Si–O\textsuperscript{−}).: C = [Si–OH] + [Si–OH\textsuperscript{+}] + [Si–O\textsuperscript{−}].

We report below the calculations used for describing SiO2 acid–base behavior. Similar calculations were performed for formalizing Si\textsubscript{3}N\textsubscript{4} and SiNW surfaces acid–base equilibria. The acid dissociation constants Ka1 and Ka2 of SiO\textsubscript{2} silanols are defined by:

\[
\begin{align*}
Ka_1 &= \frac{[\text{Si} – \text{OH}][\text{H}_2\text{O}^+]}{[\text{Si} – \text{OH}_2^+]}, \\
Ka_2 &= \frac{[\text{Si} – \text{O}^-][\text{H}_2\text{O}^+]}{[\text{Si} – \text{OH}]}.
\end{align*}
\]

Ka\textsubscript{pK}a is defined by pKa = −log(Ka).

At a given pH, the effective surfacic concentration of protonated silanols of SiO\textsubscript{2} is given by

\[
[\text{Si} – \text{OH}_2^+] = N\textsubscript{silanols} \times \% (\text{Si} – \text{OH}_2^+),
\]

where N\textsubscript{silanols} is the total number of silanols per surface area, and \% (Si–OH\textsuperscript{2+}) is the fraction of protonated silanols at a given pH.

The fraction Si – OH\textsuperscript{2+} is

\[
\% (\text{Si} – \text{OH}_2^+) = \frac{[\text{Si} – \text{OH}_2^+]}{[\text{Si} – \text{OH}_2^+] + [\text{Si} – \text{OH}] + [\text{Si} – \text{O}^-]},
\]

\[
\% (\text{Si} – \text{OH}_2^-) = \frac{1}{1 + \frac{[\text{Si} – \text{OH}]}{[\text{Si} – \text{OH}_2^+] + [\text{Si} – \text{O}^-]}}.
\]

\[
\% (\text{Si} – \text{OH}^2^-) = \frac{1}{1 + \frac{\text{Ka}_1}{[\text{H}_2\text{O}^+] + \frac{\text{Ka}_1}{[\text{H}_2\text{O}^+]}}}.
\]

\[
\% (\text{Si} – \text{OH}^2-) = \frac{1}{1 + 10^{\text{pK}_a_1} + 10^{2\text{pK}_a_1 – \text{pK}_a_2}}.
\]

Combining equations (2)–(4) yields an expression of the surfacic concentration of protonated silanols

\[
[\text{Si} – \text{OH}_2^+] = N\textsubscript{silanols} \times \frac{1}{1 + 10^{\text{pK}_a_1} + 10^{2\text{pK}_a_1 – \text{pK}_a_2}}.
\]

Similarly, the surfacic concentrations of Si–O\textsuperscript{−} and Si–OH for SiO\textsubscript{2} are

\[
[\text{Si} – \text{OH}] = N\textsubscript{silanols} \times \frac{1}{1 + 10^{-\text{pK}_a_1} + 10^{2\text{pK}_a_1 – \text{pK}_a_2}},
\]

\[
[\text{Si} – \text{O}^-] = N\textsubscript{silanols} \times \frac{1}{1 + 10^{-2\text{pK}_a_1 – \text{pK}_a_2} + 10^{-\text{pK}_a_2}}.
\]

At a given pH, the net charge per surface area of the SiO\textsubscript{2} surface is

\[
\text{charge}_{\text{SiO}_2} = [\text{Si} – \text{OH}_2^+] – [\text{Si} – \text{O}^-].
\]

This corresponds to

\[
\text{charge}_{\text{SiO}_2} = N\textsubscript{silanols} \times \frac{1}{1 + 10^{-\text{pK}_a_1} + 10^{2\text{pK}_a_1 – \text{pK}_a_2}} \frac{1}{1 + 10^{-2\text{pK}_a_1 – \text{pK}_a_2} + 10^{-\text{pK}_a_2}}.
\]

Silicon nitride bears both silanol and silylamine sites. The silylamine protonation state can be described by one equation, characterized by its dissociation constant Ka\textsubscript{5}

\[
\text{Si} – \text{NH}_2^+ + \text{H}_2\text{O} \leftrightarrow \text{Si} – \text{NH}_2 + \text{H}_2\text{O}^+
\]

with Ka\textsubscript{5} = \frac{[\text{Si} – \text{NH}_2][\text{H}^+]}{[\text{Si} – \text{NH}_2^+]} = 10^{\text{pK}_a_5}.

pKa\textsubscript{5} of the Si – NH\textsubscript{3}+ / Si–NH\textsubscript{2} couple is approximately 10 to 11 [Tsukruk and Bliznyuk 1998 #25]. At a pH inferior to 7, all the silylamines Si–NH\textsubscript{2} can therefore be considered as protonated in their form. The percentage of silylamines is considered as approximately 1% of the total number of chemical functions (silylamines + silanols, whatever their protonation state) (Hoh et al 1992). The contribution of the silylamines to the net surfacic charge therefore corresponds, in our pH range, to a positive charge.

The description of the materials used in our equations (1)–(10) is approximated as follows: only individual silanols and silylamines were included in the calculation. We did not include geminal silanols and siloxane bonds in silicon dioxide, or silazanes for silicon nitride. Indeed siloxanes and silazanes are considered as too stable to be involved in acid–base equilibria at room temperature. Additionally, we assumed that every silanol (or silylamine) of a given material is equivalent to another, for a same material. Acid–base dissociation constants have therefore been used as effective constants, potentially gathering different contributions of several type of silanols (silylamines) on silicon dioxide (silicon nitride). Indeed surface behaviors of materials as commonly used as silicon dioxide and silicon nitride still need to be investigated and understood (Ong et al 1992, Leung et al 2009, Sulpizi et al 2012).
Modeling nanowire/surface interactions

DLVO theory was used to calculate the order of magnitude of forces between nanowires and SiO$_2$ and Si$_3$N$_4$ for different pH. Details are given in supplementary data and are described elsewhere (Martines et al 2008). Briefly, the assumptions used for the calculations were the following:

(1) Van der Waals and electrostatic interactions were calculated as follows

\[ U_{VDW}(H) = -\frac{A_H}{12\pi H^2}, \]  
\[ U_{EDL}(H) = -\frac{\varepsilon\varepsilon_0K_H}{2}(\psi_{01}^2 + \psi_{02}^2)[1 - \coth(\kappa H)] \]
\[ + 2\frac{(\psi_{01} - \psi_{02})}{(\psi_{01}^2 + \psi_{02}^2)} \cosech(\kappa H). \]
\[ U(D) = \sum_{\text{sphere}} [U_{\text{plane}}(H^+) + U_{\text{plane}}(H^-)]. \]

(2) Protonation/deprotonation equilibria (predominance diagrams) of SiO$_2$, Si$_3$N$_4$ and Si nanowires allows to calculate the respective charge densities $\sigma$ of surfaces. Gouy–Chapman theory provides a relationship between the surface charges $\sigma$ and the surface potential $\psi_0$

\[ \sigma = (8k_B N_A T \varepsilon \varepsilon_0 C_0)^{1/2} \sinh \left( \frac{e\psi_0}{k_B T} \right) \text{(C m}^{-2}) \]

with

\[ e \] is the elementary charge (1.6 $\times$ 10$^{-19}$ C),
\[ k_B \] is the Boltzmann constant (1.38 $\times$ 10$^{-23}$ J K$^{-1}$),
\[ N_A \] is the Avogadro number (6.02 $\times$ 10$^{23}$ mol$^{-1}$),
\[ T \] is the temperature (K),
\[ \varepsilon \] is the dielectric constant of water (78.2 @298 K),
\[ \varepsilon_0 \] is the dielectric permittivity of vacuum (8.8541 $\times$ 10$^{-12}$ F m$^{-1}$, or 8.8541 $\times$ 10$^{-12}$ C$^2$ J$^{-1}$ m$^{-1}$),
\[ C_0 \] is the concentration of the electrolyte (mol$^{-1}$),
\[ z \] is the ion valence (Ahmed et al 2014),
\[ \kappa \] is the Debye screening length (Ahmed et al 2014).

(3) The Debye screening length $\lambda_D$ is directly influenced by the proton concentration (Tadmor et al 2002)

\[ \lambda_D = \sqrt{\frac{\varepsilon\varepsilon_0 e^2}{(2k_B T)^{1/2}}} \] (nm)

with $C_0$ concentration in monovalent ions in (millimol$^{-1}$) or (mol m$^{-3}$).

We formalized the behavior of our materials’ surface charges, taking into account the Debye screening length, and the influence of pH on surface charge densities (hence surface potentials). The calculation was performed for solutions of methanoic acid, and no other additional salts were used. In these conditions, methanoic acid concentration drives bulk proton concentration, which influences Debye screening length. Equations were implemented with Matlab. Figure 3 shows an example of surface charge density and surface potential plausible pKa values of SiO$_2$, Si$_3$N$_4$ and Si nanowires, according to literature. The inset in the right graph also shows how Debye length varies with pH values in our conditions.

This example of theoretical calculations, based on arbitrarily chosen (but plausible) pKa values, yields points of zero charge (PZC) of 2.8, 3.4 and 2.9 for SiO$_2$, Si$_3$N$_4$, and Si nanowires, respectively. These values are consistent with our experimental PZC determination for SiO$_2$ and Si$_3$N$_4$, as presented in the next section.
DLVO theory was used to infer theoretical values of interaction energy between nanowires, and silicon dioxide and silicon nitride surfaces. Calculations were based on Debye length, charge densities and surface potentials described before.

**Discussion on the theoretical model**

Depending on the chosen pKa values—which depend mainly on structural organization, and material fabrication processes (Gaigeot et al)—several complex and nonlinear behaviors of interactions can be obtained. In our calculations, forces were calculated for a distance of 0.5 nm between nanowires and flat surfaces. Nanowires were considered to be positioned parallel to the surface for the calculations. Theoritical curve in figure 7 provides results of example calculations illustrating the possibility to select a pH for which nanowires are mainly attracted towards Si\textsubscript{3}N\textsubscript{4} surfaces, and easily eluted from SiO\textsubscript{2} surfaces. The right Y axis indicate (\(U_{DLVO} \text{ Si}_3\text{N}_4\))/\(U_{DLVO} \text{ SiO}_2\)), namely the ratio between the energy of interaction of nanowires with Si\textsubscript{3}N\textsubscript{4} surface (\(U_{DLVO} \text{ Si}_3\text{N}_4\)), and the energy of interaction of nanowires with SiO\textsubscript{2} surface (\(U_{DLVO} \text{ SiO}_2\)). Indeed, the ratio between the interaction forces of respectively Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} reaches a maximum for a pH of approximately 3.15. It is to be noticed that the absolute value of the (\(U_{DLVO} \text{ Si}_3\text{N}_4\))/\(U_{DLVO} \text{ SiO}_2\)) ratio is not meaningful in our calculations, since this value depends on the chosen distance between nanowires and the surface used for calculations. It is therefore much more important to consider and analyze the shape of the curve (presence of maxima and minima). In the conditions used in our calculations, a pH \(\sim 3.15\) yields the best selectivity for capturing Si NW onto silicon nitride, while nanowires should interact poorly with silica. On the contrary, when the ratio (\(U_{DLVO} \text{ Si}_3\text{N}_4\))/\(U_{DLVO} \text{ SiO}_2\)) is approximately equal to 0.5 (along the dashed horizontal line in figure 7, for pH values around 2.8 and 3.5), the interactions of nanowires with silicon dioxide and silicon nitride should be equivalent. If the ratio (\(U_{DLVO} \text{ Si}_3\text{N}_4\))/\(U_{DLVO} \text{ SiO}_2\)) is inferior to 0.5, interactions with silicon dioxide should be favored. This example is to be compared with our experimental data in the final section. The main interest of our theoretical model is to show that there is a possibility to use pH as the main driving force for tuning the affinity of Si NW onto patterned heterogeneous surfaces, with a simple implementation. However, we cannot say that the chosen parameters correctly describe the actual surfaces used in our experiments. Indeed, several sets of parameter values may yield a similar behavior. We therefore only propose our set of parameter values as a plausible example, in adequacy with the experimental data presented below.

**Experimental determination of PZC of Si\textsubscript{3}N\textsubscript{4} and thermal SiO\textsubscript{2} by contact angle measurements**

PZC of our Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} surfaces were experimentally determined as described by Carré et al (2003). Briefly, at the point of zero charge, the surface charge density is considered to be equal to zero. At this point:

\[
\frac{d \left( \cos \theta \right)}{d \left( \text{pH} \right)} = 0.
\]

\(\theta\) being the contact angle of a solution with a given pH (figure 4). Consequently, a maximum or a minimum of contact angle \(q\) is expected at pH \(= \text{PZC}\), as the pH of the water is scanned (Chau and Porter 1991, Vittoz et al 1998, Mccafferty and Wightman 1999).

**Experimental determination of PZC of SiO\textsubscript{2} surface by impedance measurements**

Impedance measurements were used to measure the variation of flat band potential versus pH for Si/SiO\textsubscript{2} supports. The extremum of flat band potential corresponds to an inversion of sign of the surface charge. This corresponds to the point of zero charge (figure 5).

Contact angle measurements and impedancemetry allowed to evaluate SiO\textsubscript{2} PZC values of 2.8 \(\pm 0.2\) pH units and 2.7 \(\pm 0.2\) pH units, respectively. These two evaluations are therefore consistent. Contact angle measurements yielded a PZC value for Si\textsubscript{3}N\textsubscript{4} of 3.5 \(\pm 0.3\) pH units. These experimental data are plausible by comparison to the literature. They were taken into account in our model: theoretical calculations were performed using pKa values of Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} surfaces generating PZC fitting with the experimental data.

**Selective capture of nanowires. Influence of pH on selectivity**

The affinity of Si nanowires for SiO\textsubscript{2} or Si\textsubscript{3}N\textsubscript{4} could be experimentally tuned by changing the pH of the nanowire coating solution.

Figure 6 shows an optical microscope image of nanowires partitioned onto a Si\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2} heterogeneous substrate.
The substrate was soaked in a nanowire aqueous solution with acetic acid at pH 3.25, then rinsed with acetic acid aqueous solution at pH 3.25. Nanowires were mainly captured on Si$_3$N$_4$ zones. The few nanowires present on the SiO$_2$ region are all connected to Si$_3$N$_4$ zones, and we suspect that these wires are captured by silicon nitride regions. More typical optical microscope images and scanning electron microscope images are available in supplementary data.

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Figure 7 shows experimental data points (red squares, left Y scale) indicating how the distribution of nanowires for SiO$_2$ and Si$_3$N$_4$ varies with pH. The term ‘distribution coefficient’ is used herein in a similar meaning to the ‘distribution constant’ used in chromatography (http://iupac.org/publications/analytical_comp/Chat09sec239.pdf). For each Si$_3$N$_4$/SiO$_2$ feature (as defined in figure 1), the distribution yield is defined as the ratio between the coverage yield of nanowires on Si$_3$N$_4$ ($\Gamma_{\text{Si}_3\text{N}_4}$), and the coverage yield on the total feature ($\Gamma_{\text{Si}_3\text{N}_4+\text{SiO}_2} = \Gamma_{\text{Si}_3\text{N}_4} + \Gamma_{\text{SiO}_2}$). Semi-automated image analysis leads to an evaluation of the coverage yields of individual features, by counting the number of pixels of nanowires per surface area of Si$_3$N$_4$ and SiO$_2$ for each feature. The experimental data of figure 7 corresponds to the following distribution yield calculation:

$$\frac{\text{median} (\Gamma_{\text{Si}_3\text{N}_4})}{\text{median} (\Gamma_{\text{Si}_3\text{N}_4}) + \text{median} (\Gamma_{\text{SiO}_2})}.$$

A distribution yield close to 1 indicates that nanowires were mainly captured on silicon nitride zones; nanowires on silicon dioxide were eluted during the washing step. Inversely, a distribution yield close to 0 indicates that nanowires were mainly captured onto silicon dioxide of features. Nanowires on silicon nitride were eluted during a washing step.

Samples were analyzed for surfaces on which no drying took place during nanowire coating. The influence of capillary forces were therefore minimized in our results. Besides, contact angle measurements of SiO$_2$ and Si$_3$N$_4$ were evaluated to be between 20° and 50°. This indicated that our surfaces had similar behaviors in terms of hydrophobicity/hydrophilicity. This order of magnitude of contact angles is likely to be caused by adsorption of atmospheric organic aerosols onto surfaces. Contact angle variations with pH showed that surface charges were influenced by acidity. This proved that a significant amount of the surface chemical functions (silanols or silylamines) correctly responded to protonation/deprotonation. Such behavior would not take place if the surface was mainly covered with adsorbed amorphous carbon. We therefore choose to test our coating procedures without further intense washings (e.g. H$_2$SO$_4$/H$_2$O$_2$ treatment) just before nanowire deposition. Our approach was therefore kept as simple as possible.

In our experimental conditions, fluidic transport of nanowires was managed in a simple way, only involving natural diffusion, convection and sedimentation processes to
Figure 8. Statistical distribution of distribution yields of nanowires on SiO2 and Si3N4 surfaces. For each pH, box indicates key percentiles about (Γ_Si,N4/(Γ_Si,N4 + Γ_SiO2)): quartiles 25%, 50% (median) and 75%, mean (E), 1% and 99% (×), minimum and maximum (–). The numbers of Si3N4/SiO2 features involved for calculations were respectively 80, 80, 56, 80 and 70 for pH 2.00, 2.75, 3.00, 3.25, and 3.50, respectively.

Conclusion

We designed a theoretical model, mainly based on Brønsted acid–base equilibria and DLVO theory. This model was used to evaluate the intensity of interaction forces between Si NW, and silicon dioxide and silicon nitride, respectively. This model indicates a possibility to tune the affinity of Si NW towards Si3N4 and SiO2 simply by using pH as the driving parameter. Si NW (50 nm × 5 μm) were coated on patterned mixed Si3N4 and SiO2 surfaces at different pH in acetic acid solutions. Experimental conditions were chosen to minimize the influence of capillary forces and hydrophobic interactions. Distribution yields of nanowires between Si3N4 and SiO2 zones were evaluated by semi-automated image analysis. Experimental results confirm that a simple pH adjustment enables selective capture of nanowires on silicon nitride, with a median distribution yield of ~95% and an interquartile range of ~16%. In the future, an upgrade of the fluidic transport system is expected to improve the dispersion of experimental data. Interaction of nanowires with nanometric patterns of different aspect ratios should also be tested. Additionally, the theoretical model can be improved by a more accurate description of surface charges (Hiemstra and van Riemsdijk 1996, Behrens and Grier 2001, Gaigeot et al 2012, Tian and Teplyakov 2012) and an improved description of interaction forces (Ninham 1999). Finally, elaboration of patterned surface materials and nanowires can also be adjusted for enhancing effects of electrostatic contrasts between adjacent zones. The use of pH as a driving parameter for selectively address nanowires onto a patterned substrate is expected to be effective for various other surface materials, and a large diversity of nanomaterials, for instance carboxyl functionalized carbon nanotubes, II–VI and III–V nanowires. PZC of large sets of materials are already documented for materials such as Al2O3 or TiO2 (Kosmulska 2004, Kosmulska 2009). Adequate choices of surface materials (therefore choice of their PZC) and pH lead to a variety of situations for selectively capturing nanowires onto surfaces. This could be used for nanowires addressing as well as nanowires selection.

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