

# Kinked Silicon Nanowires: Superstructures by Metal-Assisted Chemical Etching

Georgiana Sandu,<sup>†,¶</sup> Jonathan Avila Osses,<sup>†,¶</sup> Marine Luciano,<sup>‡,¶</sup> Darwin Caina,<sup>†,§</sup> Antoine Stopin,<sup>||</sup> Davide Bonifazi,<sup>||</sup> Jean-François Gohy,<sup>⊥</sup> Alejandro Silhanek,<sup>#</sup> Ileana Florea,<sup>▽</sup> Mounib Bahri,<sup>○</sup> Ovidiu Ersen,<sup>○</sup> Philippe Leclère,<sup>◆</sup> Sylvain Gabriele,<sup>‡</sup> Alexandru Vlad,<sup>⊥</sup> and Sorin Melinte<sup>\*,†,⊥</sup>

<sup>†</sup>Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

<sup>‡</sup>Interface and Complex Fluids Laboratory, Université de Mons, 7000 Mons, Belgium

<sup>§</sup>Facultad de Ingeniería, Ciencias Físicas y Matemática, Universidad Central del Ecuador, 170521 Quito, Ecuador

<sup>||</sup>School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

<sup>⊥</sup>Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

<sup>#</sup>Experimental Physics of Nanostructured Materials, Q-MAT, CESAM, Université de Liège, B-4000 Sart Tilman, Belgium

<sup>▽</sup>Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique, 91128 Palaiseau, France

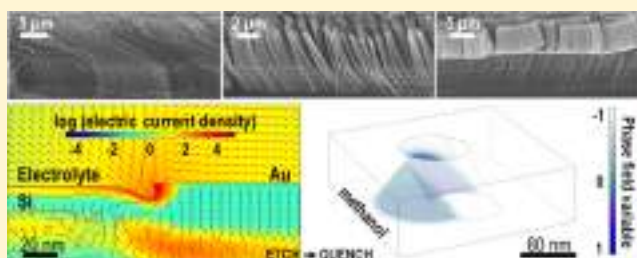
<sup>○</sup>Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS - Université de Strasbourg, 67087 Strasbourg, France

<sup>◆</sup>Laboratory for Chemistry of Novel Materials, Center for Innovation and Research in Materials and Polymers, Université de Mons, 7000 Mons, Belgium

## Supporting Information

**ABSTRACT:** We report on metal-assisted chemical etching of Si for the synthesis of mechanically stable, hybrid crystallographic orientation Si superstructures with high aspect ratio, above 200. This method sustains high etching rates and facilitates reproducible results. The protocol enables the control of the number, angle, and location of the kinks via successive etch-quench sequences. We analyzed relevant Au mask catalyst features to systematically assess their impact on a wide spectrum of etched morphologies that can be easily attained and customized by fine-tuning of the critical etching parameters. For instance, the designed kinked Si nanowires can be incorporated in biological cells without affecting their viability. An accessible numerical model is provided to explain the etch profiles and the physicochemical events at the Si/Au–electrolyte interface and offers guidelines for the development of finite-element modeling of metal-assisted Si chemical etching.

**KEYWORDS:** Finite-element modeling, metal-assisted chemical etching, silicon nanowires



Nanostructures unfold exciting avenues for the well-established Si-based semiconductor industry. Exceptional properties for novel Si-enabled nanomaterials can harness high-performance devices in the fields of electronics, photonics, energy conversion, and storage as well as biotechnology.<sup>1–11</sup> However, the synergy between these properties and their target application requires precise tuning of the characteristic parameters of the nanostructures such as morphology, size, or crystallographic orientation. In particular, controlled design of Si nanostructures, including silicon nanowires (SiNWs), is a prerequisite in order to explore their potential for biomedical purposes. Understanding SiNW–cell interaction has been identified as a subject of primary importance, and seminal work addressed the challenging mismatch between the physicochemical properties of the SiNWs, like topographic features and surface functionalization, and the biological matter.

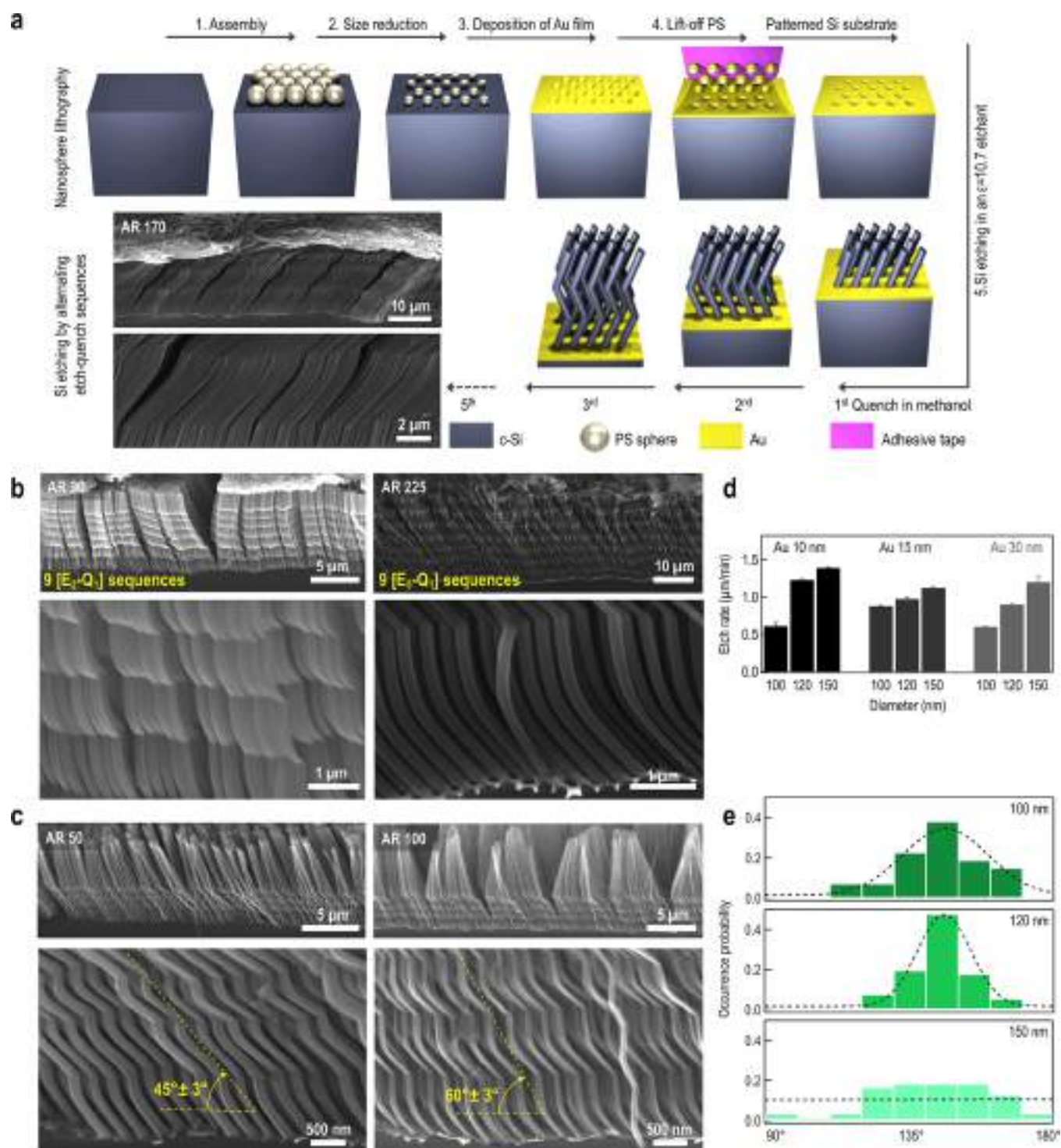
These studies offered insight into the design of substrate-free single SiNWs for integration with biotic and semibiotic systems<sup>12,13</sup> and cellular responses to SiNWs arranged in arrays and three-dimensional architectures.<sup>14–17</sup>

A plethora of techniques were proposed for the reliable fabrication of Si nanostructures and SiNWs.<sup>18–24</sup> Yet, most of these methods require specialized equipment and involve highly sensitive procedures for mass production. In contrast, metal-assisted chemical etching (MACE) associated with a nanostructured continuous catalyst profits from the simplicity of the electroless etching process while allowing for the control of

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**Figure 1.** MACE details. (a) Sketch of MACE for synthesis of k-SiNWs. First, the Si substrate is patterned with a holey Au mask by PS nanosphere lithography. Second, the nanostructuring of Si follows repetitive etch-quench [ $E - Q$ ] sequences. The SEM pictures show the k-SiNWs with  $s = 120$  nm resulted after five successive  $E_5 - Q_1$  sequences. (b) High aspect ratio k-SiNWs fabricated by 9 [ $E_2 - Q_1$ ] (left) and 9 [ $E_5 - Q_1$ ] (right) sequences for a  $t = 15$  nm,  $s = 120$  nm Au mask. (c) The longitudinal axis of the k-SiNWs deviates by different angles with respect to the Si substrate, depending on the diameter of the Au mask openings [150 (left) or 100 nm (right)]. The Au mask is 10 nm thick. (d) Etching rates associated with the geometrical parameters of the Au masks. (e) Occurrence probability for the observed kink angles as a function of  $s$ . The dashed lines in the histograms are fits of experimental data and are only intended as guides to the eye.

various parameters: morphology (solid or porous), diameter, length, and to a certain extent, crystallographic orientation.<sup>18,21,25–29</sup> MACE essentially works as a localized, short-circuited, galvanic cell comprising an intimately connected Si anode with a nanoshaped catalyst cathode in a hydrofluoric acid

(HF) and hydrogen peroxide ( $H_2O_2$ )-based electrolyte that controls both the  $H_2O_2$  reduction and Si dissolution.

Although the general understanding of MACE emphasizes on the anisotropic  $\langle 100 \rangle$ -etching predisposition as prescribed by the backbone theory, non- $\langle 100 \rangle$  SiNWs have been demon-

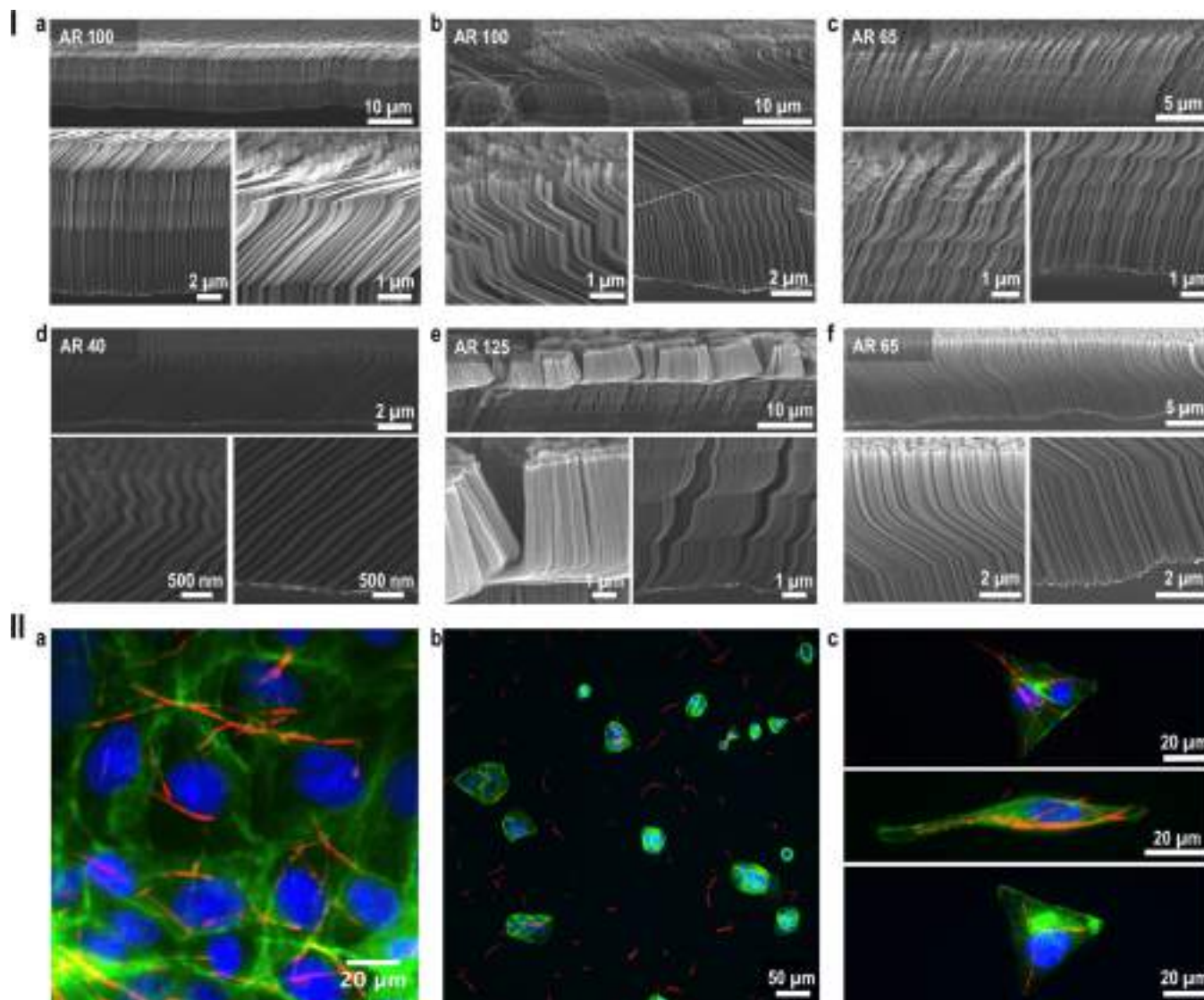
strated, regardless of the initial Si wafer orientation.<sup>25</sup> In particular, hybrid orientation SiNWs or kinked SiNWs (k-SiNWs) are extremely interesting from both theoretical and experimental standpoints considering their morphology that has a positive impact on the photon absorption, elastic properties, as well as thermal insulation.<sup>27,30–32</sup> Targeted hybrid peptide–k-SiNWs can be tailor-made from optimized directed assembly of biological matter<sup>12,33</sup> with kinks, diameter modulations, and asymmetric features adapted to the viscoelastic response of the cellular membranes. In this context, the development of simple approaches that allow for large-area, controlled fabrication of k-SiNWs is essential for exploring their physical properties and enable their use as building blocks in complex patterned environments.<sup>34–36</sup> Along this direction, several reports analyzed advanced etching schemes to control the etching direction and ultimately engineer custom crystallographic superstructures.<sup>37–40</sup> Temperature and oxidant agent concentration were identified as critical parameters for suppressing the preferred  $\langle 100 \rangle$  etching direction. For instance, temperature control of the electrolyte was used to wafer-scale, zigzag etch of the SiNWs on (111)-Si wafers.<sup>40</sup> Alternating between different etching solutions with different oxidant concentration allows the etching of orientation-modulated SiNWs on (111)-Si wafers.<sup>25</sup> The etching would follow  $\langle 100 \rangle$  etching at low oxidizing agent concentration and non- $\langle 100 \rangle$  etching at higher concentrations.

Similarly, a recent report also details the controlled fabrication of k-SiNWs via the use of various electrolytes where the etchants' availability is constrained because of additives in the etching environment.<sup>37</sup> Addition of high surface tension additives like glycerol can greatly alter the availability of etchants creating diffusion barriers for the chemical species. Indeed, the miscibility of the etchants is a critical MACE parameter in particular for etching conditions without mechanical agitation. As a matter of fact, the kinks are almost exclusively associated with static etching conditions, whereas stirring typically renders vertical  $\langle 100 \rangle$  SiNWs because the etchants are continuously replenished. However, such a procedure cannot account for reliable large-scale fabrication of high aspect ratio k-SiNWs, ubiquitously required for surface-to-volume sensitive applications, considering that the induced perturbations are local and difficult to control. Because Si MACE is a dynamic process with parameters changing as the etching advances, controlling the etching patterns to produce k-SiNWs, such as deviating the catalyst motion and turning on and off crystallographic dependencies are particularly challenging. For instance, the noble metal catalyst plays a fundamental role in MACE, accelerating the dissolution of Si in the areas where an intimate contact is preserved while exclusively dictating the features of the resulting nanostructures such as shape and crystallographic orientation. Although the motion of catalyst is uniform, it can be ruled by its shape: a metal nanoparticle has six degrees of freedom, whereas a pinned catalyst such as a rigid, contiguous mask is able to move with three degrees of freedom, two translational components and one rotational. Template-based MACE with nanopatterned Au masks is the landmark for large-scale, controlled fabrication of SiNWs and k-SiNWs. Thus, assessing the impact of the catalyst shape on the etched morphologies is critical for developing a reliable synthesis of Si superstructures.

Here we describe a simple and efficient k-SiNWs etching scheme that facilitates the fabrication of high aspect ratio Si superstructures with hybrid crystallographic orientation. This etching mechanism relies on repetitive etch-quench sequences to induce the kinks using low surface tension ethanol cosolvent.

Multiple etching baths are no longer required as the etchant availability is modulated via the methanol quencher, and risks related to the etchant baths' imbalance at advanced etching stages are reduced. This one-pot-type synthesis facilitates the etching of mechanically stable, high aspect ratio superstructures at high etching rates. The systematic assessment of the main MACE parameters, namely Au mask thickness coupled with the opening diameter, has allowed the etching of a wide spectrum of nanostructures. We highlight that the development of well-controlled morphology k-SiNWs could help uncover cellular responses and interactions with extracellular matrix. Experimental data are coupled with a numerical model to explain the etched morphologies as well as the observed kink angles. We particularly emphasize (i) mass transport of the chemical species, (ii) Si interfaces from an electrical charge transport perspective, (iii) flow and passive mixing in microchannels delimited by k-SiNWs, and (iv) the general mechanism for the k-SiNWs formation. The knowledge provided here helps to clarify the mechanism of the kinks' formation and enables large-scale fabrication of high aspect ratio k-SiNWs, while establishing novel guidelines for the development of MACE complex numerical simulations.

**Controlled k-SiNWs Synthesis.** Figure 1a presents a route for the controlled fabrication of k-SiNWs with high aspect ratio (AR), enabled by a simple MACE scheme. The first step is the nanopatterning of the Au catalyst mask via colloidal lithography. This operation requires the self-assembly of closed-packed polystyrene (PS) spheres of 260 nm in diameter on the Si substrate. The PS spheres are further etched with reactive ion etching to the desired size representing the final diameter of the SiNWs. Subsequently, the Au catalyst is deposited on the PS-decorated Si substrate. The nanopatterned Au mask is obtained by lift-off of the PS spheres with adhesive tape. The next step is the Si etching in a solution having a molar concentration ratio  $\epsilon = 10.7$  of HF to  $\text{H}_2\text{O}_2$ , with ethanol as cosolvent, under static etching conditions. To form the kinks at the desired location, Si etching is interrupted at specific times by submersing the sample in methanol. Varying these etch-quench sequences at specific times renders superstructures of k-SiNWs;  $E_p$  is used for designating an etching step with the etching time of  $p$  minutes and  $Q_q$  for a quenching event lasting  $q$  minutes. The number of kinks  $n$  is simply controlled by the performed  $(n + 1)[E - Q]$  sequences. The cross-section scanning electron microscopy (SEM) pictures in Figure 1a show highly ordered k-SiNWs fabricated by five sequences  $E_5 - Q_1$ . On the one hand, by altering the etching time we can control the length of the etched segment and, related to this, the location of the kink. On the other hand, the geometrical parameters of the gold catalyst mask are extremely important. They will influence the porous or solid nature of the etched Si nanostructures, the etching rate as well as the mechanical stability of the Au mask during the downward movement and the gas evolution reactions associated with Si etching. As a matter of fact, catalysts greatly impact the mass transport of active species and reaction products.<sup>18</sup> For instance, as the catalyst thickness decreases, transport of reactants and byproducts is expected to occur also via small pores in the catalyst. In addition, collision and coalescence of gas bubbles can alter the Si-catalyst contact resulting in hazardous etching and, ultimately, in catalyst delamination. To get insight into the etching possibilities provided by various catalyst morphologies, we evaluated different catalyst thicknesses,  $t$  (10, 15, and 30 nm), associated with different opening



**Figure 2.** (I) A wide spectrum of morphologies can be achieved by superposing different etching times with different catalyst shapes. (a)  $t = 30$  nm,  $s = 150$  nm,  $E_p - Q_1$ ;  $p = \{5,3,3,3,5\}$ . (b)  $t = 15$  nm,  $s = 120$  nm,  $E_p - Q_1$ ;  $p = \{5,7,3,3,3\}$ . (c)  $t = 30$  nm,  $s = 120$  nm,  $E_p - Q_1$ ;  $p = \{2,2,2,3,3,3\}$ . (d)  $t = 30$  nm,  $s = 120$  nm,  $E_p - Q_1$ ;  $p = \{3,2,2,2,2\}$ . (e)  $t = 15$  nm,  $s = 120$  nm,  $E_p - Q_1$ ;  $p = \{5,3,3,3,3\}$ . (f)  $t = 30$  nm,  $s = 150$  nm,  $E_p - Q_1$ ;  $p = \{5,5\}$ . (II) Interfacing k-SiNWs with mammalian cells. (a) k-SiNWs (red) distribution and their intra- and intercellular interfaces in a dense culture media. (b) Penetration of k-SiNWs into individual cells seeded on micropatterned substrates. (c) k-SiNWs interfacing with nucleus (blue) as well as the actine cytoskeleton (green).

diameters,  $s$  (100, 120, and 150 nm). Details of the deposited Au mask morphologies are shown in Figure S1.

**Kink Physical Parameters.** Figure S2 shows the kink formation according to the number of times the reaction was quenched for a 10 nm thick Au mask and three different hole diameters. For this particular case, vertically aligned NWs are obtained for the first  $E_2$  segment. The type of the first segment is particularly intriguing: vertical NWs are obtained only for thin Au masks, whereas for larger Au thickness the etching proceeds in a non- $\langle 100 \rangle$  direction, as illustrated in Figure S3. After a 2 min quenching time, the etching proceeds in a non- $\langle 100 \rangle$  direction, leading to a kink formation. To characterize the kink, its segments' length and angle have to be considered in relation to the Au mask's geometrical parameters. For this study, to control the kink's segment length, we used etching times,  $p$ , ranging from 2 to 5 min. The k-SiNWs fabricated by nine repetitive  $E_2 - Q_1$  and  $E_5 - Q_1$  sequences are shown in Figure 1b for a  $t = 15$  nm

and  $s = 120$  nm Au mask. Figure 1c shows the k-SiNWs fabricated with a 10 nm thick Au mask with  $s$  equal to 150 and 100 nm and reveals the tilted nature of the k-SiNWs, dictated by  $s$ . Note that the length is reported as the etching depth of the Si substrate, normal to the surface. The average etching rates evaluated for various  $t$  and  $s$  are shown in Figure 1d. The highest etching rates are obtained for thin catalysts because the active species can easily diffuse along the grain boundaries. The etching rates are found to generally increase as  $s$  increases. Specifically, the highest etching rate reaches  $1.4 \mu\text{m}$  per minute for  $t = 10$  nm,  $s = 150$  nm Au masks because less Si has to be removed. Such fast etching rates are not common for MACE because aggressive gas evolution leads to Au mask delamination. The quenching step mitigates hazardous etching and maintains etching speed accuracy as discussed later.

The angles of the kinks are found to be dependent on  $s$ , as it can be observed from the statistical analysis of Figure 1e. Thus,

for small diameters there is a clear angle preference, whereas for bigger diameters a wide range of angles is possible. The dependency of the kink angle as a function of metal mask thickness was further evaluated:  $t$  does not appear to influence the distribution of the kink angles, as shown in Figure S4.

Finally, note that kinks will also form by employing a thin catalyst mask with a random pattern (Figure S5). Thus, kink generation does not require a uniformly patterned or a pinned catalyst. Nonetheless, the stability of the mask is expected to be affected by gas bubble evolution leading to the loss of Si–Au contact and eventually to Au exfoliation and the end of the etching (Figures S4 and S5).

**Customized Si Superstructures.** Our etching protocol combines the simplicity and scalability of MACE to enable functionality-driven design of Si nanostructures. Figure 2 shows the fabrication of ordered, high aspect ratio superstructures of k-SiNWs by quenching the etching at user-defined points during MACE. These results indicate that k-SiNWs and complex Si nanostructures with a large range of angles and user-defined segment lengths are possible by simply controlling the etching time and the catalyst parameters. The catalyst mask parameters are intimately coupled with the etching rates and curvature effects and will greatly influence the k-SiNWs morphology. SEM images in Figures S6 and S7 provide further information on the etching opportunities of this procedure. Zigzag SiNWs are locally observed under the studied etching conditions as shown in Figure S8. Once a SiNW segment is etched, the electrolyte concentration is altered by flushing the sample with methanol. Flushing with water renders highly porous SiNWs as displayed and further discussed in Figure S9 and Figure S10. Such versatile fabrication opens extensive research possibilities to fully explore and activate the properties of these Si superstructures.

We highlight key fabrication features of MACE strategies developed for k-SiNWs and high aspect ratio Si superstructures in Table 1. Although k-SiNWs can be formed by several MACE

High aspect ratio SiNWs and k-SiNWs as well as Si superstructures obtained by MACE enabling straightforward cell internalization experiments are essentially missing, as specific applications demand different categories of k-SiNWs.<sup>45</sup> The combination of biological cells and SiNWs has been recognized as an efficient way to control the differentiation of stem cells by modulating the activation of  $\text{Ca}^{2+}$  ion channels in response to a mechanical stimulation at the nanoscale,<sup>46</sup> and scaffolds of SiNWs could provide unique shape- and composition-controlled sensing interfaces for cells.<sup>47</sup> To address these issues, we carried out a series of experiments with epithelial cells (Supporting Information). In agreement with previous work on embryonic stem cells and human embryonic kidney cells,<sup>14</sup> our results indicate that the penetration of the as-fabricated k-SiNWs into individual epithelial cells naturally occurred during the incubation without affecting their viability. The 120 nm diameter k-SiNWs started to internalize within  $45 \pm 15$  min in epithelial cells and the number of incorporated nanowires doubled after 120 min of incubation. The surface functionalization of the nanowires with peptides or proteins that can bind to transmembrane integrins is certainly an interesting way to quicken k-SiNW cell internalization.<sup>17</sup> Such Si superstructures can be further sharpened into a compelling tool for studying intra- and intercellular biological processes and deciphering complex mechano-transduction pathways.<sup>48</sup>

Vizualization of Si superstructures was accomplished by transmission electron microscopy (TEM). Figure 3a shows results obtained for a 15 nm Au mask for all studied  $s$  values. It is clear that the initial SiNW diameters are altered by the horizontal movement of the catalyst. The deviations from the initial diameter are more important as  $s$  increases. Furthermore, the Au catalyst oscillatory motion is clearly visible in the SiNW wall close up from Figure 3b and also revealed by the 3D reconstruction of the SiNW kink (Figure 3c). The expected cylindrical shape is altered, confirming the horizontal shift of mask in addition to the downward movement associated with the Si etching. This behavior mirrors the three-directional motion expected for a weakly pinned catalyst. In addition, a closer examination of the SiNWs, Figure 3b,d, shows that their surface is decorated with Au nanoparticles, some of them reaching  $\sim 15$  nm in diameter for thick Au catalysts, as displayed in the inset to Figure 3d. This relates to energetic etching conditions that can attain rates as high as  $\sim 20$  nm/s, inducing significant mechanical stress into the metal layer, finally leading to Au disintegration. Note that the Au nanoparticles couple to the surface of SiNWs (Figure S11). The elemental mapping from Figure 3e confirms the Au decoration of k-SiNWs. This feature, as highlighted in Figure 2, is particularly interesting for biological applications where Au-decorated SiNWs are known for their distinctive photothermal response under near-infrared laser irradiation, which can potentially be used for the destruction of cancerous cells.<sup>49</sup> Porous trenches form in the Si substrate, beneath the Au, at the lithographic openings of the metal catalyst (Figure 3e, Figure S12). Such porous regions are known to facilitate diffusion of the electrolyte.<sup>50</sup> In addition, the shape of the porous trenches hints at an anisotropic kinetics or a preferential electrolyte diffusion via the lithographic openings of the Au mask. This is surprising because mass transport of reactants usually occurs via pores or cracks in thin films or discontinuous catalyst masks, therefore an isotropically expanded porous segment at the metal–Si interface is expected.<sup>51</sup> In particular, the porous region does not extend completely to the foot of the SiNW as previously reported.<sup>50</sup>

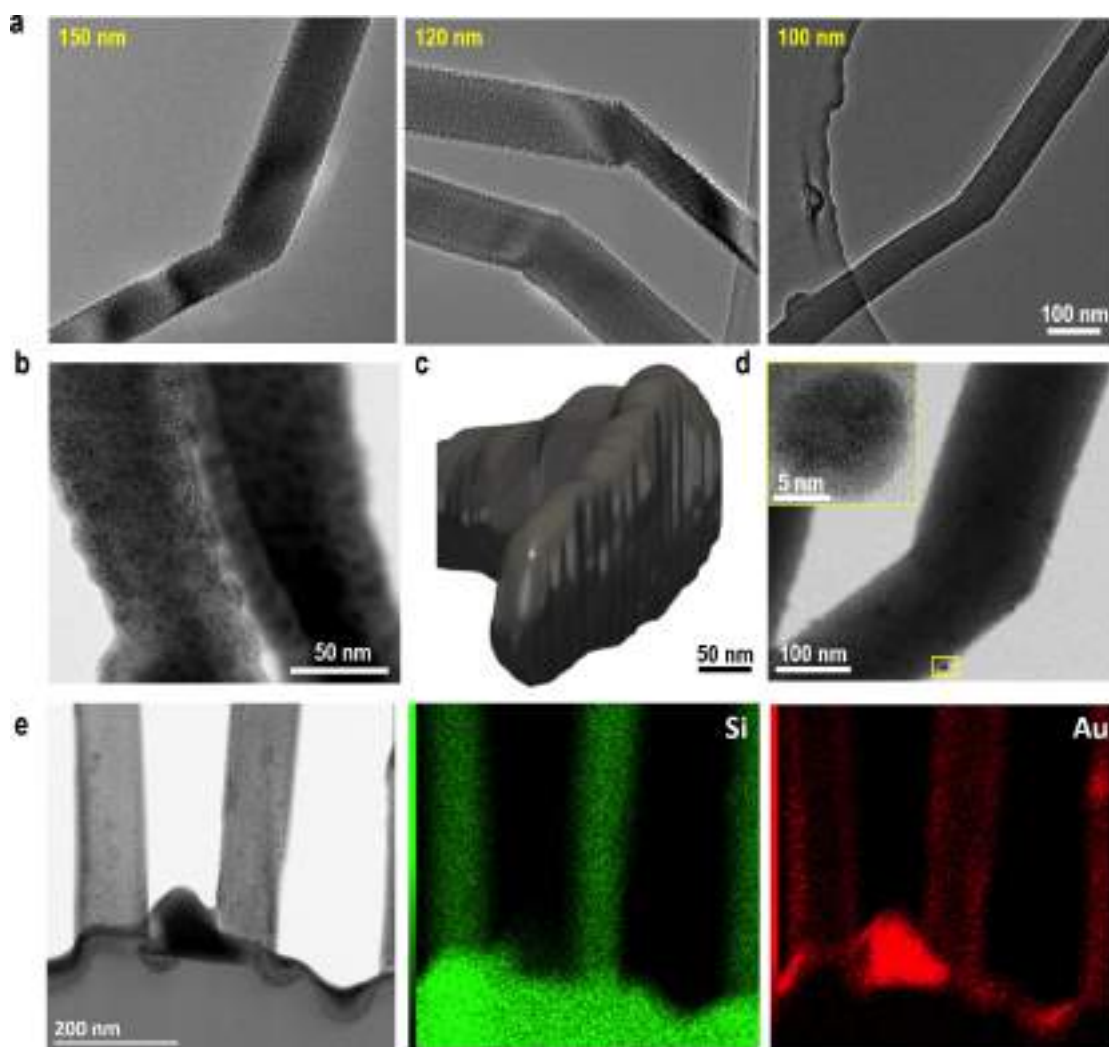
**Table 1. Overview of MACE Protocols Enabling k-SiNWs and High Aspect Ratio Si Structures**

| details                                         | type    | AR     | surface        | source           |
|-------------------------------------------------|---------|--------|----------------|------------------|
| vertical directionality-controlled <sup>a</sup> | SiNWs   | >100:1 | smooth         | ref 41           |
| nanoshaped catalyst-driven <sup>b</sup>         | k-SiNWs | >~20:1 | smooth (rough) | refs 25,38–40,44 |
| diffusion-controlled <sup>c</sup>               | k-SiNWs | >~20:1 | smooth         | ref 37           |
| one-pot synthesis                               | k-SiNWs | >200:1 | smooth (rough) | this work        |

<sup>a</sup>The catalysts are mechanically clamped during the process.

<sup>b</sup>Patterned metal catalysts display superior performances compared to nanoparticle based catalysts. <sup>c</sup>Zigzag SiNWs can be formed as well above a critical nanowire length of about 1  $\mu\text{m}$ .

methods, the geometrical parameters remain hard to control with kinking or NW diameter and segment modulation being randomly (or progressively<sup>37</sup>) attained. The present one-pot synthesis technique offers precise control over the segment length and aspect ratio, reaching values commonly observed in studies with mechanically clamped catalysts.<sup>41</sup> Note that the morphology of the surface plays an important role in establishing the overall mechanical properties of SiNWs. In this respect, the possibility to generate, besides diameter modulations during synthesis,<sup>42,43</sup> a catalyst-dense coating as functional layer is peculiarly appealing.



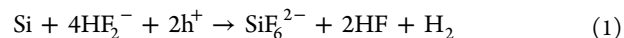
**Figure 3.** Microscopic characterization of SiNW kinks and Si–Au interface. (a) TEM images of SiNW kinks obtained from the indicated  $s$  with  $t = 15$  nm Au masks. (b) SiNW kink close up as imaged with scanning TEM (STEM) with a bright field detector for the  $s = 100$  nm,  $t = 10$  nm Au mask. (c) Three-dimensional reconstruction of a SiNW kink obtained with the  $s = 150$  nm,  $t = 30$  nm Au mask. (d) Au nanoparticles-decorated SiNW kink produced by the  $s = 100$  nm,  $t = 30$  nm Au mask. (e) Elemental mapping by energy-dispersive X-ray spectroscopy of the Au–Si interface via STEM.

**Analysis and Modeling.** The broad spectrum of the etched Si superstructures suggests a synergy between various physicochemical processes depending on the characteristic dimensions of the Au–Si system. Metal-assisted chemical etching resides on a noble metal catalyst to accelerate the dissolution of Si into a HF and  $\text{H}_2\text{O}_2$ -based electrolyte by generating instantaneous electrical currents flowing between cathodic sites where  $\text{H}_2\text{O}_2$  is reduced and the anodic sites where Si is oxidized and further dissolved. Under the current understanding, the etching proceeds with the catalytic decomposition of  $\text{H}_2\text{O}_2$  providing the holes ( $\text{h}^+$ ) that are further required for Si oxidation, facilitating its dissolution. The etching is an uninterrupted process as the catalyst protected Si is continuously etched leaving the SiNWs as residues on the Si substrate. Thus, MACE is associated with the movement of the catalyst that needs to preserve an intimate contact with the Si substrate.

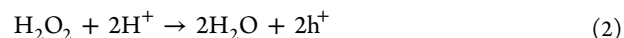
**Etching Parameters.** We performed time-dependent numerical simulations following the current understanding of MACE. The two-dimensional (2D) system used for the finite-element model is shown in Figure 4a,d and represents a projection of a Si substrate partially covered with a Au mask in contact with the

HF and  $\text{H}_2\text{O}_2$ -based electrolyte. The Si–Au interface is described by the Schottky junction model.<sup>51,52</sup> The electrolyte is modeled here as an ohmic solution with the kinetics of the electrolyte interfaces, that is, with Si and Au, governed by Butler–Volmer expressions.<sup>53</sup>

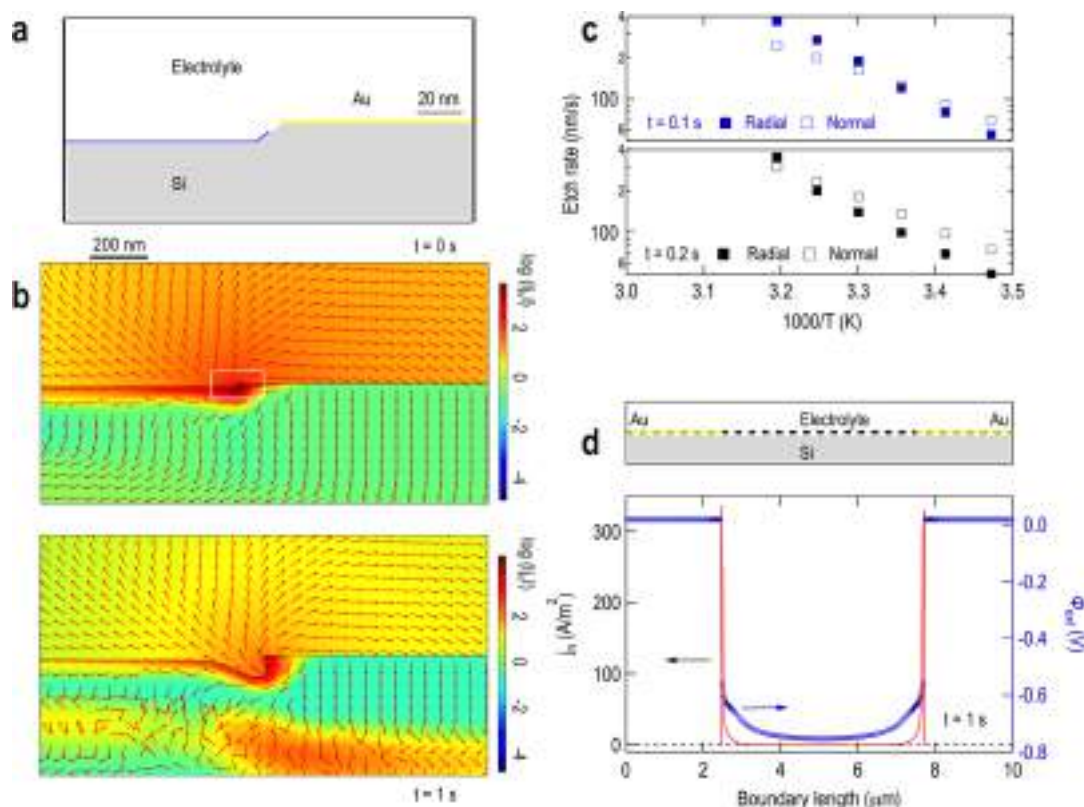
It is well-known that chemical etching of silicon in HF solutions proceeds very slowly without an external potential.<sup>52</sup> If holes are readily available, Si dissolution can proceed according to



This reaction has a potential of  $-1.24$  V (versus standard hydrogen electrode). The availability of holes will be determined by the electrical polarization and properties of the silicon. For this case, the electric polarization is provided by the positive charge generated via the Au mask by the reduction of hydrogen peroxide



This reaction has a potential of  $+1.76$  V (versus standard hydrogen electrode). Because of the Schottky barrier, not all the positive charges can be drained into the silicon, therefore, a



**Figure 4.** Time-dependent numerical calculations of Si MACE. (a) Zoom into the bidimensional domain used for the finite-element model. It includes a pre-etched line in the Si-electrolyte boundary. The blue line corresponds to the conducting Si-electrolyte boundary, whereas the yellow line to corresponds to the Si/Au-electrolyte boundary. To avoid exceedingly high electric field values, these boundaries are separated by a 10 nm gap. (b) Electric current density profiles (logarithmic scale) at  $t = 0$  and 1 s etching advancements. The highlighted rectangle corresponds to the area zoomed in panel a. (c) Temperature and time dependence of the etching rates associated with radial and normal etching directions. (d) Two-dimensional sketch representing the interfaces included in the calculation.  $\phi_{\text{ext}}$  (blue curve) and electrical current density (red curve) corresponding to  $t = 1$  s.

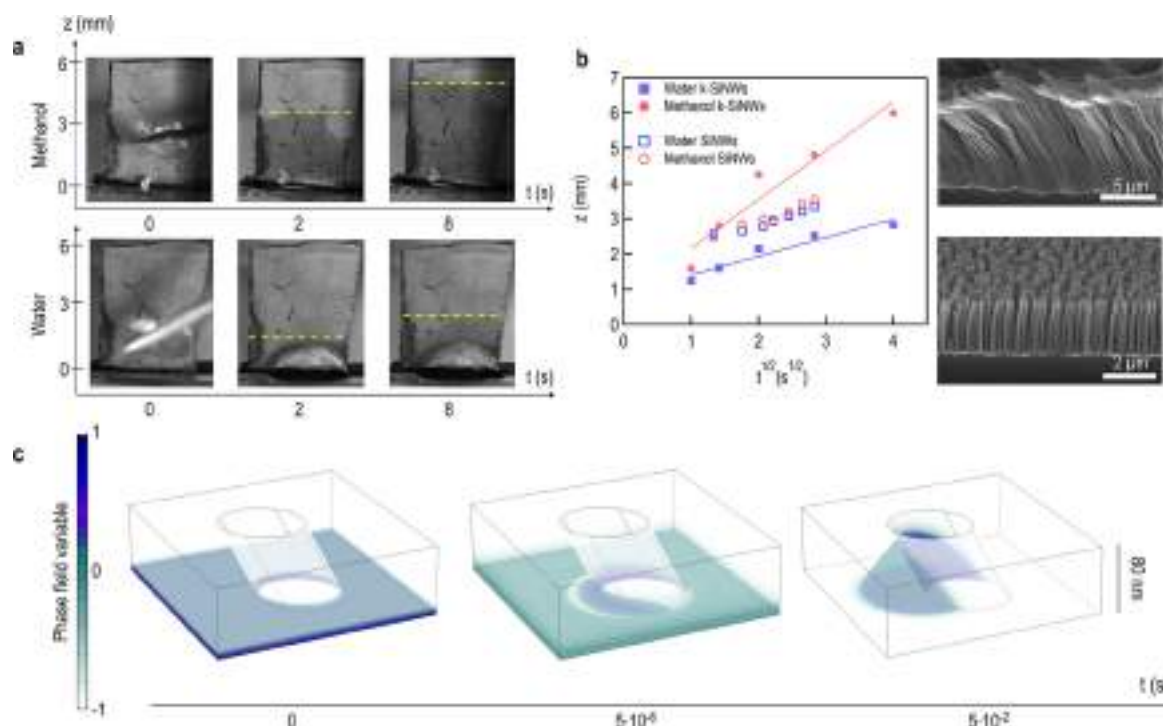
positive potential is expected on the Au side. Moreover, a positive potential buildup is also favored due to the relationship of the reduction potentials. Butler–Volmer dependences<sup>53</sup> relate the module of the outgoing, normal-to-interface, current density  $|j_n|$  to the external potential  $\phi_{\text{ext}}$ , the electrolyte potential  $\phi_b$ , and the equilibrium potential at the electrodes  $\phi_{\text{eq}}$  (see Supporting Information).

Figure 4b shows the calculated electric current density and etching profiles. The etch rate is around 100 nm/s at room temperature for both the in-plane (radial) and the out-of-plane (normal) directions with small differences due to the electrical current density variation with the distance from Au. Because the electrical current is maximum near the Au border due to the high electric field there, the highest etching rate will be close to Au (Figure 4b). These numerical profiles are in agreement with the experimental observations of Figure 3e, confirming the lithographic openings of the metal catalyst as hot spots for the Si etching. The calculated etching rates display the expected dependence with temperature (Figure 4c). For  $j_n \cong 300 \text{ A/m}^2$  at  $t = 1$  s, a normal etch rate of  $1.125 \mu\text{m}/\text{min}$  is observed, closer to the experimentally observed etch rates at large  $s$ ,  $1.25 \pm 0.15 \mu\text{m}/\text{min}$ . The reactions at the electrolyte interfaces generate an electric potential difference that is seen in Figure 4d. This electric potential difference is lower than the open circuit potential  $\phi_{\text{eqAu}} - \phi_{\text{eqSi}}$  due to the electrical current circulating in the electrolyte. The electrical current density has maxima near the Au mask border (Figure S11).

The adopted model provides insight into the experimental trends, although it relies on ideal interfaces. Although isotropic properties are assumed in the model, it is clear that the normal-to-interface etching is preferred in the realistic three-dimensional environment. The etching direction is expected to be a vector combination of both normal and radial directions. Local variations of the etching conditions such as the chemical species' availability or local heating will likely influence which component controls the etching direction. Indeed, while the experimental observations indicate that  $s$  plays a subtle role in the etching direction preference (Figure 1c), the present numerical calculations unveil the time and temperature dependencies of the radial and normal etch rates. From the numerical calculations we can estimate an electrolyte–Si Schottky barrier of  $\sim 0.45 \text{ V}$  (Figure S14). Although the SiNW kinks formation clearly implies a deviated catalyst motion, the employed model ignores the catalyst motion, because the driving force is still unknown.

**Kink Formation.** We turn next to SiNW kink formation. Figure 5a shows snapshots of the advancements of the wetting front for methanol and water in k-SiNWs relevant superstructures. For k-SiNWs morphologies, methanol completely wets the sample after 16 s, whereas water travels only half of the sample length. Liquid invasion follows a diffusion law with parameters dependent on the structural geometry of the SiNWs<sup>54</sup>

$$z = \sqrt{Dt} \quad (3)$$



**Figure 5.** Wetting properties. (a) Macroscale: Snapshots of the distance traveled by the wetting front for water and methanol in Si superstructures. (b) Plot of the distance traveled by the etching front with  $t^{1/2}$  for water and methanol wet samples [k-SiNWs (closed symbols) vs SiNWs (open symbols)]. (c) Nanoscale: Time evolution of methanol boundary around a 60° tilted SiNW, with a diameter of 100 nm, as resulted from numerical calculations with periodic boundary conditions. The color bar indicates the phase field variable. The final configuration is persistent.

where  $z$  is the displacement of the wetting front,  $t$  is the time, and  $D$  is a coefficient that captures the characteristic velocity of the liquid and the viscous forces developed according to the wetting geometry. From Figure 5b, we can conclude that 1 min quenching will remove all the electro-active species required for the etching of k-SiNWs. Furthermore, if the SiNW etched segment is tilted, there is a preferential formation of a methanol rich meniscus in the concave part of the nanowire base as shown in Figure 5c. This preferential accumulation of methanol results in the retarded action of the etchants when the etching resumes. The local concentration of species is altered, triggering a change in the etching direction.

For numerical calculations, two phases are considered, namely, methanol and air, in contact with a nanowire of 100 nm diameter and its base. A continuous phase field model based on the Cahn–Hilliard<sup>55,56</sup> equation is used, considering the surface tension  $\sigma_{ma} = 22.7 \text{ mN/m}^2$  of the methanol–air interface and  $\theta_c = 60^\circ$  contact angle for the methanol–Si interface (Figure S10). Further details can be found in the Supporting Information. In the initial configuration, the methanol is a uniform layer of 7 nm height surrounding the base of the SiNW. As time runs, the methanol rises on the inner part for a tilted SiNW with respect to the substrate, receding on the other side, as can be seen in Figure 5c. This droplet not only modifies the concentration of the etchants, it also can exert a pull up force on the underlying Au film, changing the etching conditions and contributing to the etch direction change. Note that meniscus formation along vertical SiNW segments does not show any preferential location (Figure S15). Because the the contact angle for the liquid–Si interface is expected to evolve as the etching advances, we evaluated the meniscus formation at different contact angles to account for any changes in this parameter (Figure S16, 60°-tilted SiNW). The meniscus formation around

a 45°-tilted SiNW for different contact angles is shown in Figure S17. There is a clear preferential location for the meniscus formation, except for low  $\theta_c$  where the methanol layer rather uniformly surrounds the SiNW. However, a low contact angle scenario is unlikely since the surface roughness of the SiNWs is expected to increase  $\theta_c$ .

The curvature of the SiNW kink segments is an intriguing phenomenon and the etching of curved SiNWs has been associated with cosolvent etchants such as methanol, ethanol, or glycerol.<sup>37,57,58</sup> While experimental observations sustain the curvature dependence with the cosolvent concentration, curved segments are typically linked to large thicknesses and large diameter openings of the Au mask. MACE begins as a thermodynamically favored process, however, as the etching advances other forces interfere with the reactions. First, methanol meniscus formation will alter the concentration of species at the Si–electrolyte interface. Once the etchant concentration is re-established, the etching resumes. Second, the etched geometry is expected to impact both the electrolyte flow as well as the quenching agent flow as the etching advances, giving rise to parasite capillarity and viscous forces. The curvature formation has to be associated with the development of directional forces related to the NW geometry. As the etched geometry develops into opened zigzag nanochannels, it is well-known that these are prone for developing turbulent flow, providing efficient mixing of electrolyte and quenching agent. This explains the fact that the SiNW kink angles are increasing with the etched length.

In summary, we described the versatility of MACE to fabricate high aspect ratio and orientation-customized k-SiNWs based on successive etch-quench sequences. We found that the parameters of the catalyst Au mask greatly influence the geometry and porosity of the etched Si superstructures. On the

one hand, the opening diameter impacts the etching rate and the overall kink angle distribution. On the other hand, the thickness of the Au mask has a pronounced effect on the porosity of the produced nanostructures and small catalyst thicknesses are not suitable for long etching times. Fine tuning of these parameters have allowed the etching of functionally designed, complex Si nanostructures with high aspect ratio. Focusing on the quenching step, we propose a simple mechanism for kink formation through preferential formation of an alcohol-rich meniscus in the concave region of the etched Si segment. Our time-dependent calculations corroborate the current understanding of the mechanisms involved in MACE of Si and represent another step toward more complex finite-element models for Si superstructures corrosion. The numerical computing approach could be extended to other electrochemical systems requiring modeling of the semiconductor electrode–electrolyte interfaces. Although we used the fabricated k-SiNWs in a substrate-free approach to address cell internalization, the Si superstructures can be employed, for example, in frustrated phagocytosis experiments to shuttle biomolecular cargo once the density and diameter are matched to the cell size and the aspect ratio is tuned for cellular adhesion and penetration. Our findings open extensive opportunities for Si superstructures tailored for enhanced functionalities and encourage numerical investigations for understanding the MACE fundamentals.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.nanolett.9b02568](https://doi.org/10.1021/acs.nanolett.9b02568).

Insight into the experimental procedures and details of the numerical calculations (PDF)

Representative movie of the electric current density evolution at the Si–Au interface during initial stages of metal-assisted chemical etching. Frame rate is 16 images/s and total length is 6 s (AVI)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [sorin.melinte@uclouvain.be](mailto:sorin.melinte@uclouvain.be).

### ORCID

Davide Bonifazi: 0000-0001-5717-0121

Jean-François Gohy: 0000-0003-4169-1883

Ovidiu Ersen: 0000-0002-1553-0915

Alexandru Vlad: 0000-0002-0059-9119

Sorin Melinte: 0000-0003-2176-554X

### Author Contributions

<sup>†</sup>G.S., J.A.O. and M.L. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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# Kinked silicon nanowires: Superstructures by metal assisted chemical etching

Georgiana Sandu,<sup>†,∇</sup> Jonathan Avila Osses,<sup>†,∇</sup> Marine Luciano,<sup>‡,∇</sup> Darwin Caina,<sup>†,¶</sup> Antoine Stopin,<sup>§</sup> Davide Bonifazi,<sup>§</sup> Jean-François Gohy,<sup>||</sup> Alejandro Silhanek,<sup>⊥</sup> Ileana Florea,<sup>#</sup> Mounib Bahri,<sup>@</sup> Ovidiu Ersen,<sup>@</sup> Philippe Leclère,<sup>△</sup> Sylvain Gabriele,<sup>‡</sup> Alexandru Vlad,<sup>||</sup> and Sorin Melinte<sup>\*,†</sup>

<sup>†</sup>*Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium*

<sup>‡</sup>*Interface and Complex Fluids Laboratory, Université de Mons, 7000 Mons, Belgium*

<sup>¶</sup>*Facultad de Ingeniería, Ciencias Físicas y Matemática, Universidad Central del Ecuador, 170521 Quito, Ecuador*

<sup>§</sup>*School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom*

<sup>||</sup>*Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium*

<sup>⊥</sup>*Experimental Physics of Nanostructured Materials, Q-MAT, CESAM, Université de Liège, B-4000 Sart Tilman, Belgium*

<sup>#</sup>*Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique, 91128 Palaiseau, France*

<sup>@</sup>*Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS - Université de Strasbourg, 67087 Strasbourg, France*

<sup>△</sup>*Laboratory for Chemistry of Novel Materials, Center for Innovation and Research in Materials and Polymers, Université de Mons, 7000 Mons, Belgium*

<sup>∇</sup>*Contributed equally to this work*

E-mail: sorin.melinte@uclouvain.be

# Materials and methods. I

*Colloidal lithography.* Silicon substrates (p-type,  $\langle 100 \rangle$ , resistivity 10-25  $\Omega\text{cm}$ ) have been used after 10 minutes ultrasonic treatment in methanol. Next, a short oxygen plasma treatment was performed to render their surface hydrophilic for the colloidal processing. Typically, a monolayer of 260 nm nominal diameter polystyrene (PS) spheres (Microparticles GmbH) was assembled, well-ordered or not, on the pre-treated Si substrate. Depending on the protocol, in the next step, reactive ion etching was used to reduce the PS sphere diameter to the desired size. Next, the metallic layer is subsequently deposited on the PS-decorated Si substrate by physical vapor deposition. Adhesive tape followed by an overnight stay in dichloromethane was employed for the lift-off of the PS spheres.

*Transmission electron microscopy (TEM) analysis.* TEM analysis and electron tomography were performed on a Jeol JEM-2100F electron microscope operated at 200 kV. TEM images for electron tomography were collected over a tilt range of  $\pm 65^\circ$  with tilt increments of  $5^\circ$ , at a nominal magnification of 35000 - 60000 using the SerialEM software. The 3D reconstructions of the aligned tilt series were obtained using the simultaneous iterative reconstruction technique. Image filtering and alignment was done using Tomviz and the reconstruction performed using BrightfieldGui. Final image rendering was then done in Tomviz.

*Scanning TEM analysis.* Scanning transmission electron microscopy (STEM) measurements were performed on a Cs corrected (probe corrected) JEOL JEM-2100F electron microscope operating at 200 kV. Energy dispersive X-ray (EDS) spectroscopy mapping was performed in STEM using a JEOL Silicon Drift Detector (DrySD60GV, sensor size 60  $\text{mm}^2$ ) with a solid angle of 0.5 sr.

*Focused ion beam preparation.* Cross section lamella were prepared using a Scios tool displaying a combination of a scanning electron microscope (SEM) operating at 30 kV and a focused ion beam (FIB) containing a Ga source. For the lamella preparation, high Ga beam

energy has been used in a first step in order to isolate an area of interest within the sample and stick it to the TEM grid substrate. Then, in order to reduce the Ga implantation within the sample and the damage produced by the Ga impact during preparation, we decreased the Ga beam energy from 30 to 2 kV for the thinning process.

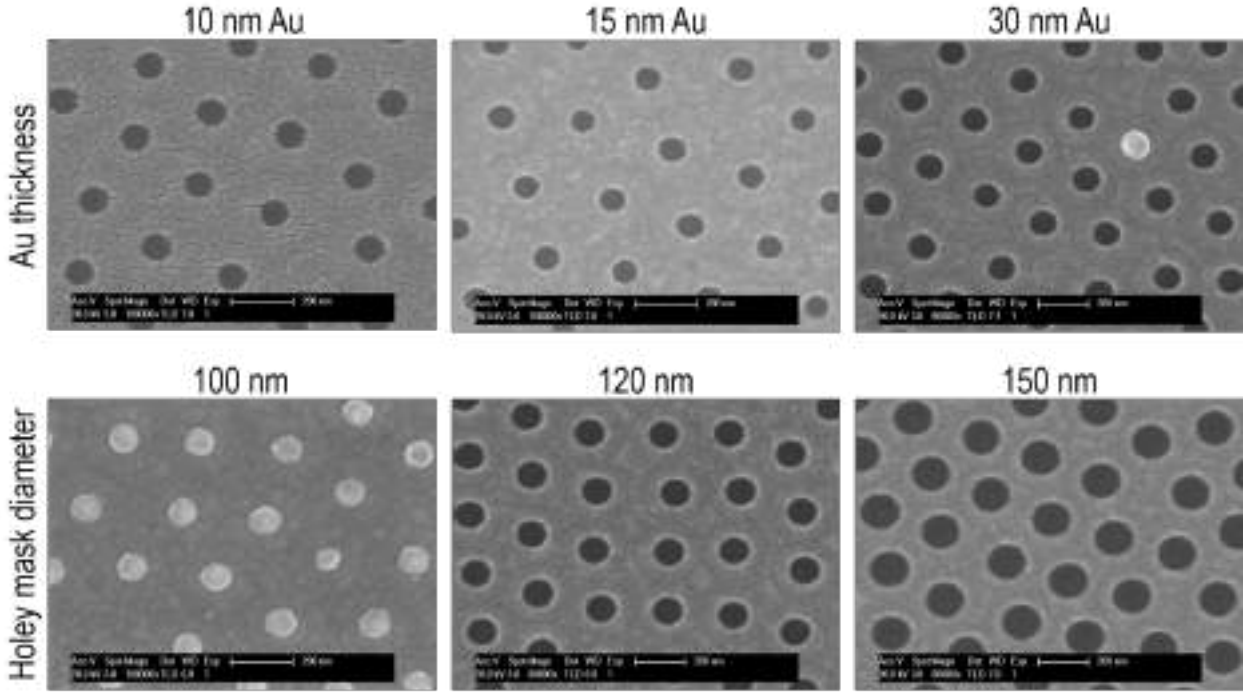


Figure 1: Physical parameters of the processed Au masks (SEM images). Since Si etching is catalyzed by Au, the geometrical parameters of the Au mask were investigated. This study includes three thicknesses  $t$ : 10, 15 and 30 nm, as well as three opening diameters  $s$ : 100, 120 and 150 nm. For the thickest mask, a 1 nm Ti adhesion layer was included to allow for the lift-off of the polystyrene spheres and to avoid any Au delamination. As evaporated, the 10 nm-thick Au mask is not continuous; thicker films are required for a uniform catalyst layer.

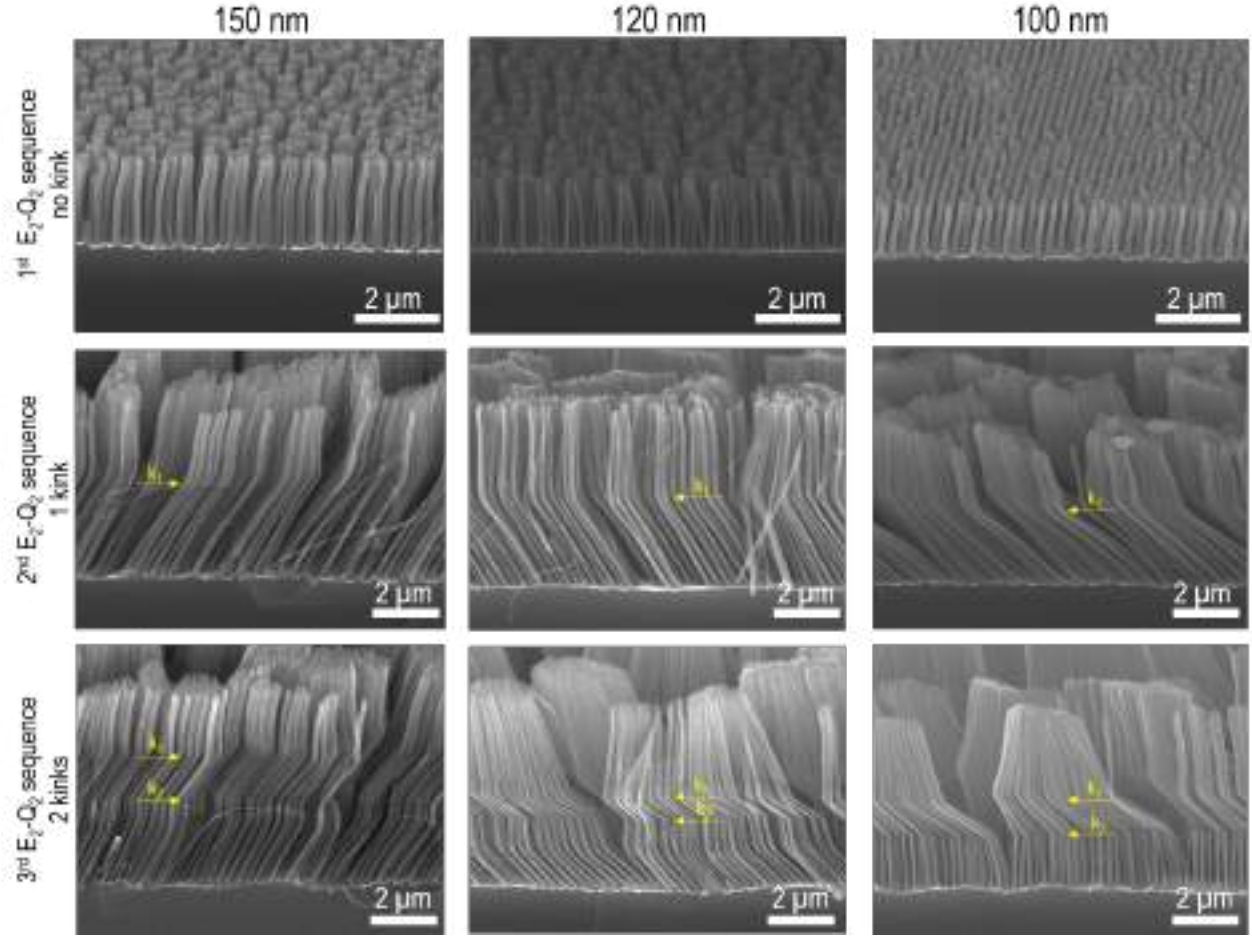


Figure 2: Kinks generation in SiNWs for 10 nm-thick Au masks with different diameters of openings, 150, 120, and 100 nm (SEM images). From top to bottom, images for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> E<sub>2</sub> – Q<sub>2</sub> sequences are displayed for single ( $k_1$ ) and double ( $k_1, k_2$ ) kinks.

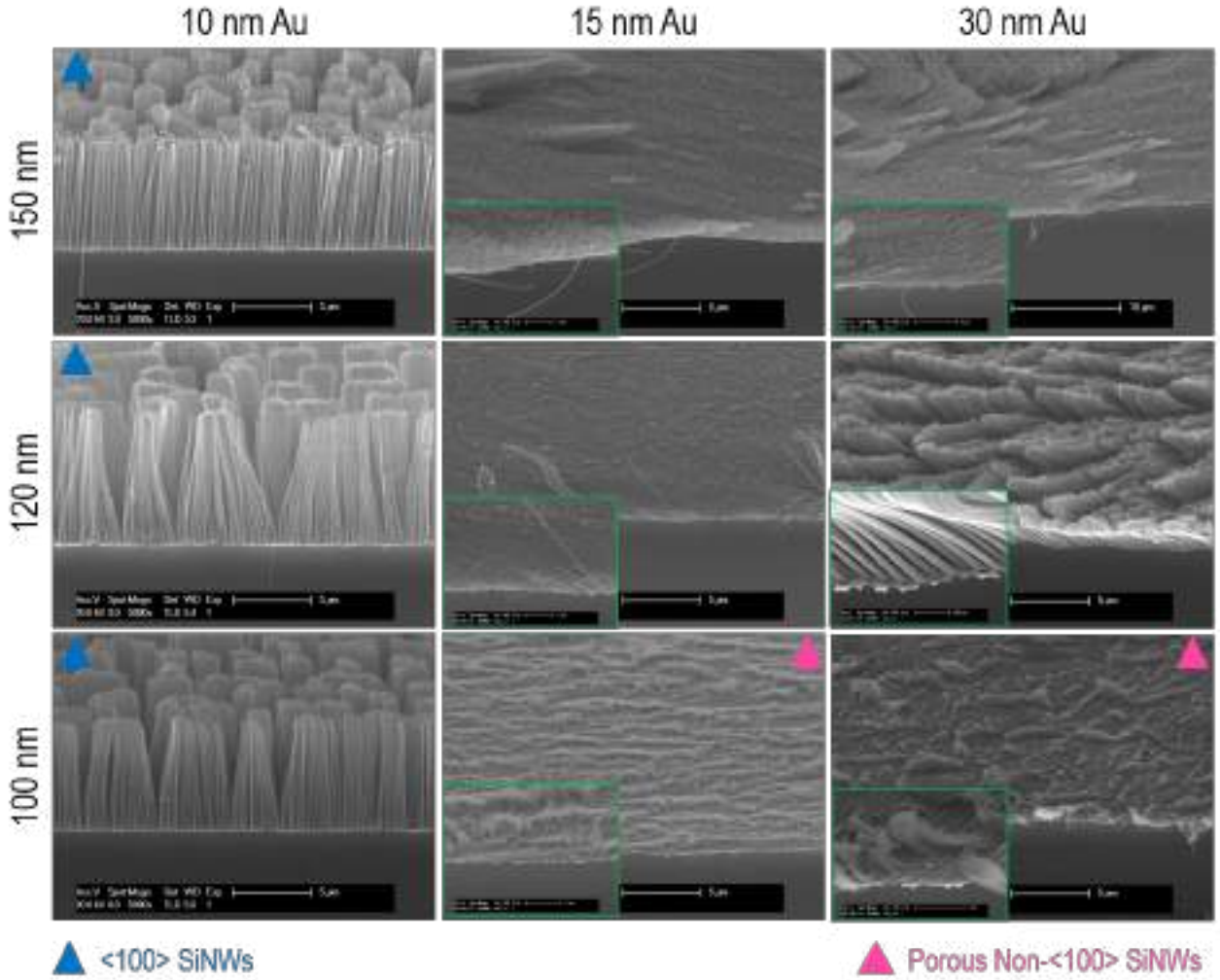


Figure 3: The first etched segment (5 minutes etching time) for all the investigated Au catalyst masks (SEM images). For the thinnest catalyst layer, the etching proceeds in a  $\langle 100 \rangle$  direction resulting in uniform, vertically aligned SiNWs. For thicker Au masks, the etching follows a non- $\langle 100 \rangle$  direction. The diameter of the openings greatly influences the porosity of the etched nanostructures.

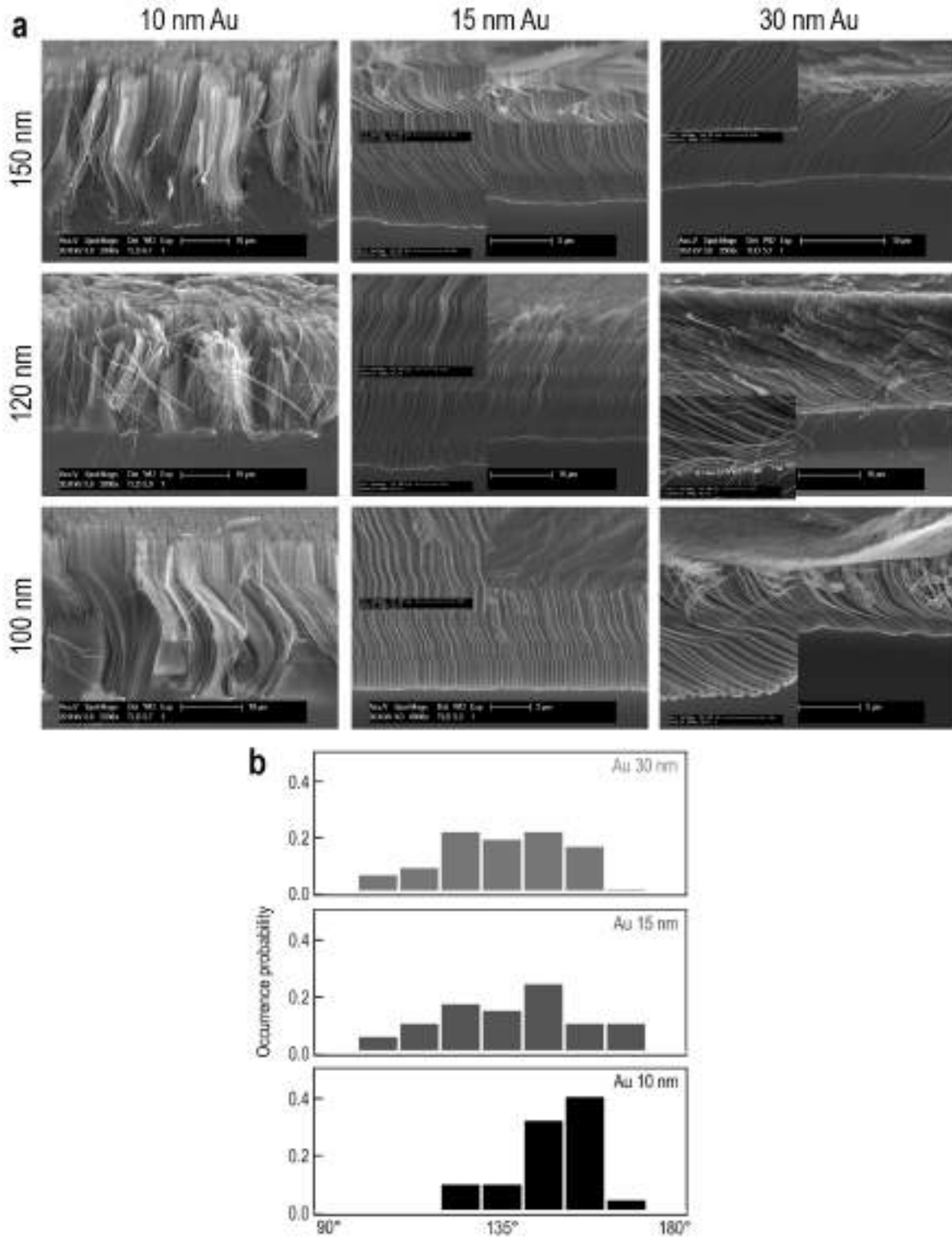


Figure 4: a. Kinked superstructures etched following  $E_p - Q_1$  ;  $p = \{5, 5, 3, 5, 3\}$  for all evaluated thicknesses,  $t$ , and hole diameters,  $s$ . A thin catalyst will not resist the energetic etching conditions and results in hazardous etching. b. Kink angles occurrence probability as evaluated according to the catalyst thickness (all hole diameters were considered).

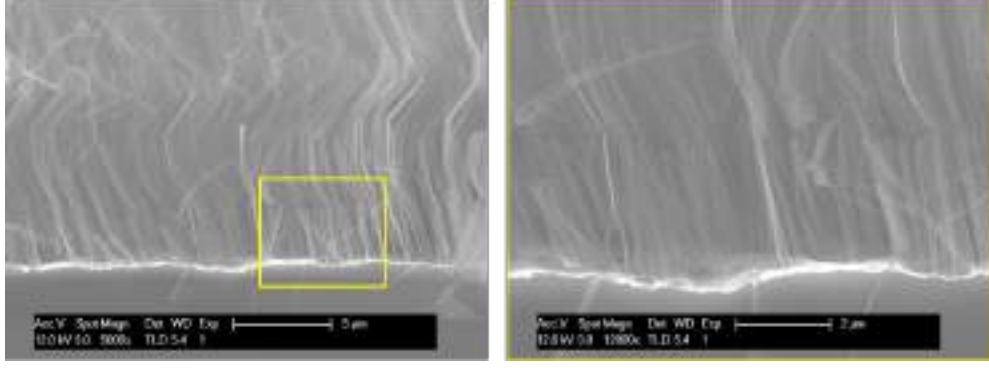


Figure 5: Si MACE using Au masks with random opening patterns (i.e. not close-packed configurations of the polystyrene colloidal particles). The displayed superstructures were obtained with a 10 nm-thick Au catalyst mask, large hole diameters and  $[E_2 - Q_1]$  sequences (SEM images). The result clearly shows that the kinks formation does not require a uniform catalyst or an ordered assembly of the polystyrene spheres. This is crucial in understanding the driving force responsible for the catalyst motion, since such nanostructures are the result of a continuous Au layer movement despite the presence defects. The defects in the Au catalyst will render whiskers-type k-SiNWs.<sup>12-14</sup>

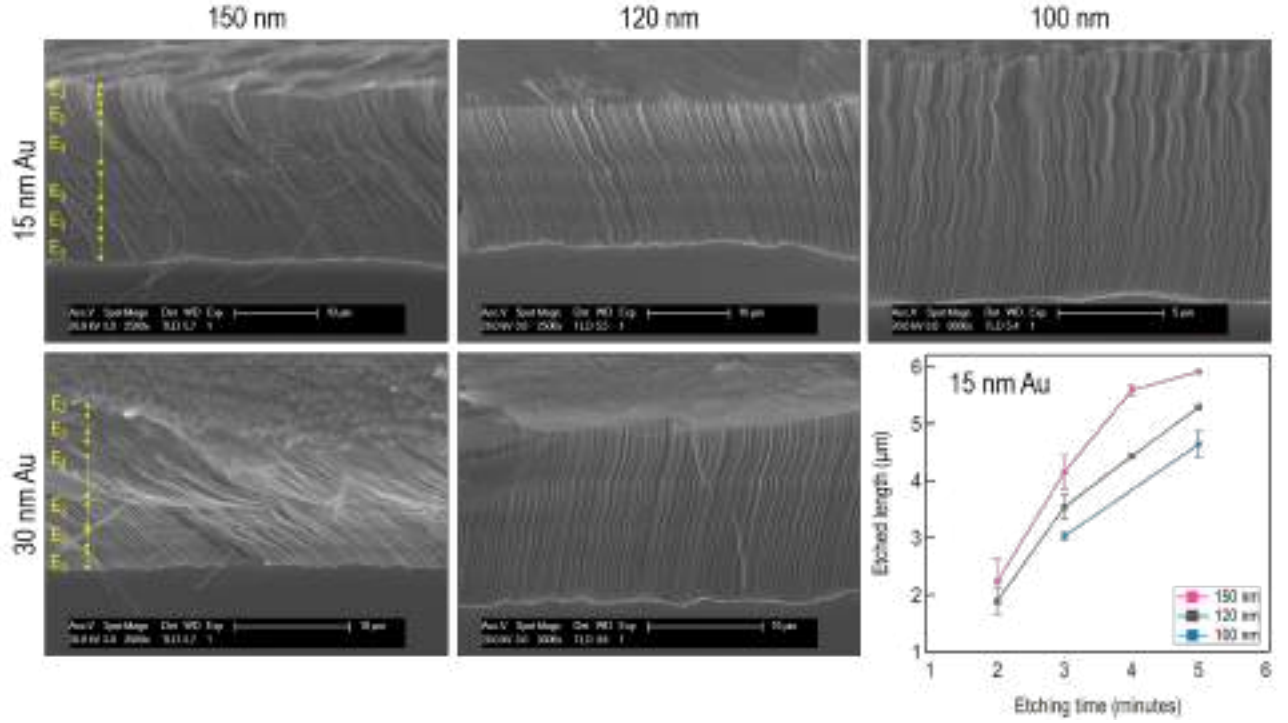


Figure 6: The impact of the Au catalyst on the Si superstructures morphology following  $E_p - Q_q$  sequences with  $p = \{2, 2, 4, 3, 3, 3\}$  and  $q = \{1\}$  (SEM images). First, depending on the Au masks parameters ( $t$  and  $s$ ), the nature of the first Si etched segment will greatly vary and, in some cases, it will be sacrificed in the etching process (for instance, for the 15 nm-thick Au mask associated with the 120 nm hole diameter). Second, the curvature of the Si etched segments does not appear to be influenced by the diameter of the Au mask openings, but rather by the Au mask thickness. Finally, the overall tilting of the k-SiNWs with respect to the Si substrate varies with both the Au mask thickness and the hole diameter through altered etching rates.

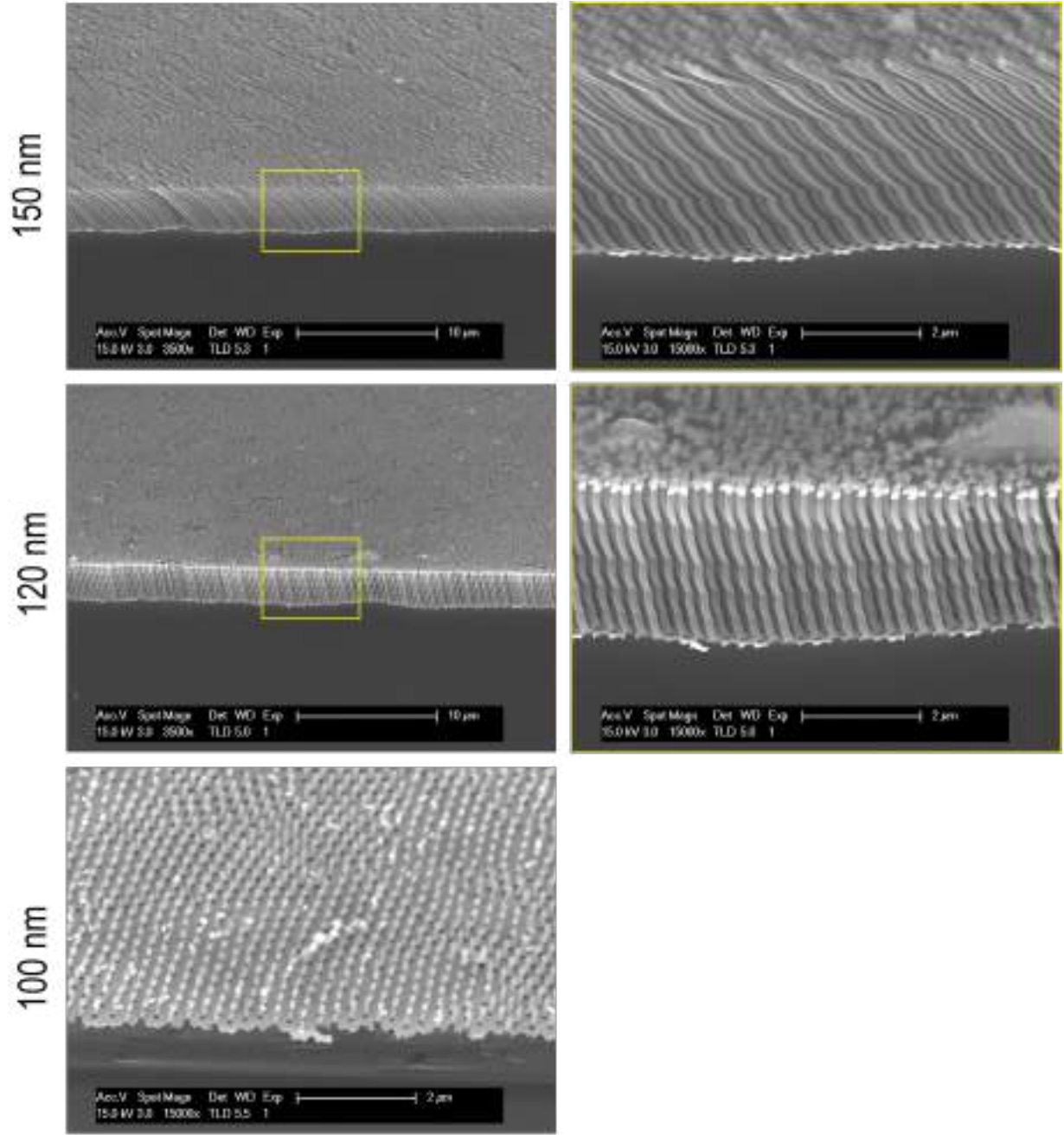


Figure 7: Etching following  $E_p - Q_q$  sequences with  $p = \{5, 2, 2, 2, 2, 2\}$  for  $t = 30$  nm for all the studied diameters. For  $s = 100$  nm, following this scheme will not render any nanowires. The first etched segment was sacrificed during etching.

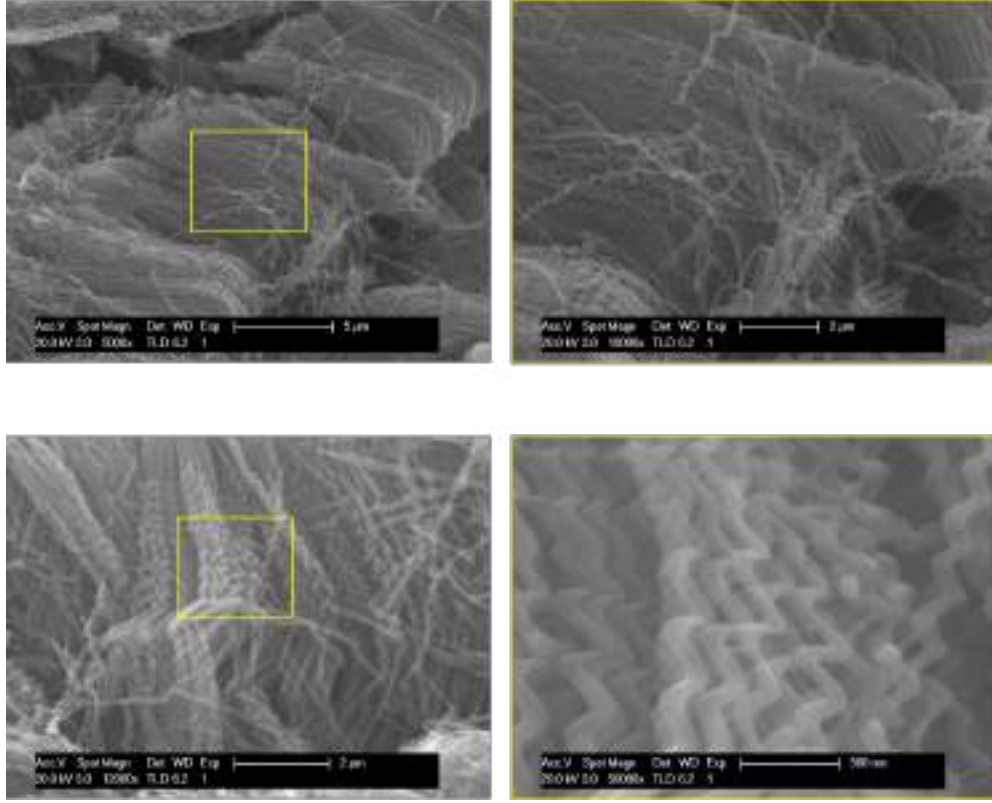


Figure 8: Zigzag SiNWs observed locally under the studied etching conditions. Such nanostructures, unfortunately, cannot be fabricated as k-SiNWs at large scale with the presented method.

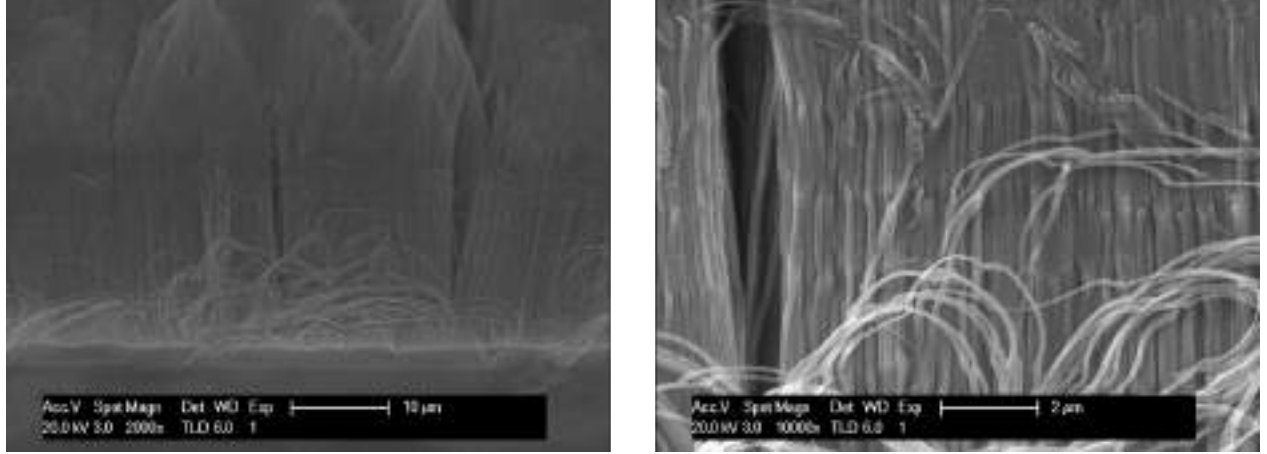


Figure 9: Metal assisted chemical etching of Si following  $[E_2 - Q_1]$  sequences using de-ionized water as quenching medium. The periodical quenching is clearly visible, however, it results in defects rather than kinks. The resulting SiNWs are vertical and highly porous and do not present a curvature.

Table 1: Measured contact angles.

|                                | 15 nm Au         | 30 nm Au         | Si               |
|--------------------------------|------------------|------------------|------------------|
| Water                          | $65.23 \pm 2.19$ | $70 \pm 3.41$    | $85.97 \pm 2.65$ |
| Methanol                       | $23.82 \pm 2.31$ | $34.57 \pm 3.11$ | $40.74 \pm 2.73$ |
| Water-based etching solution   | $49.18 \pm 0.88$ | $53.85 \pm 2.98$ |                  |
| Ethanol-based etching solution | $23.10 \pm 2.10$ | $29.21 \pm 1.79$ |                  |

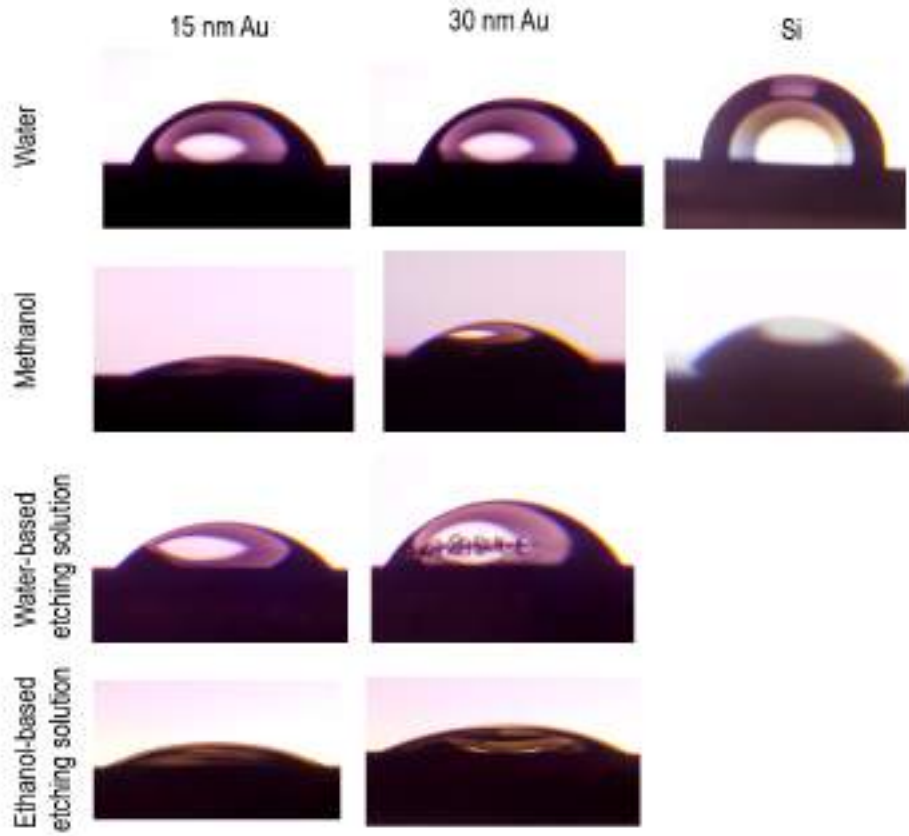


Figure 10: Experimentally determined contact angles for the liquid-Si or Au-air interfaces involved in etching. While the contact angle at the methanol-Si interface was evaluated experimentally at  $40.74^\circ \pm 2.73^\circ$ , a  $60^\circ$  contact angle was used in the simulations to account for the expected increase in surface roughness of the SiNWs as the etching advances.

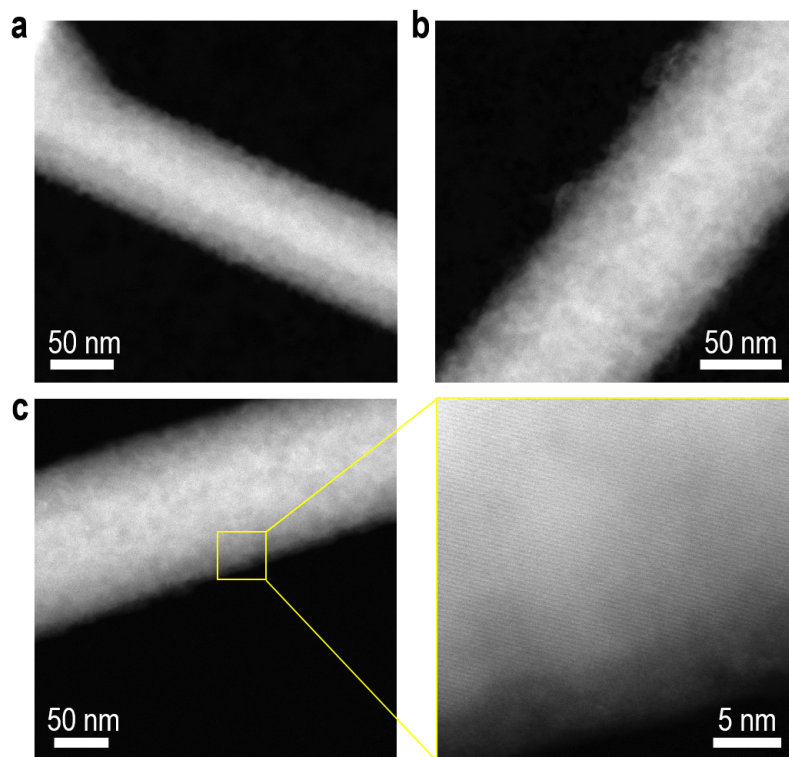


Figure 11: (a-c) High-angle annular dark-field (HAADF) STEM images illustrating the gold particles distribution on the external surface of SiNWs and the SiNW-Au interface.

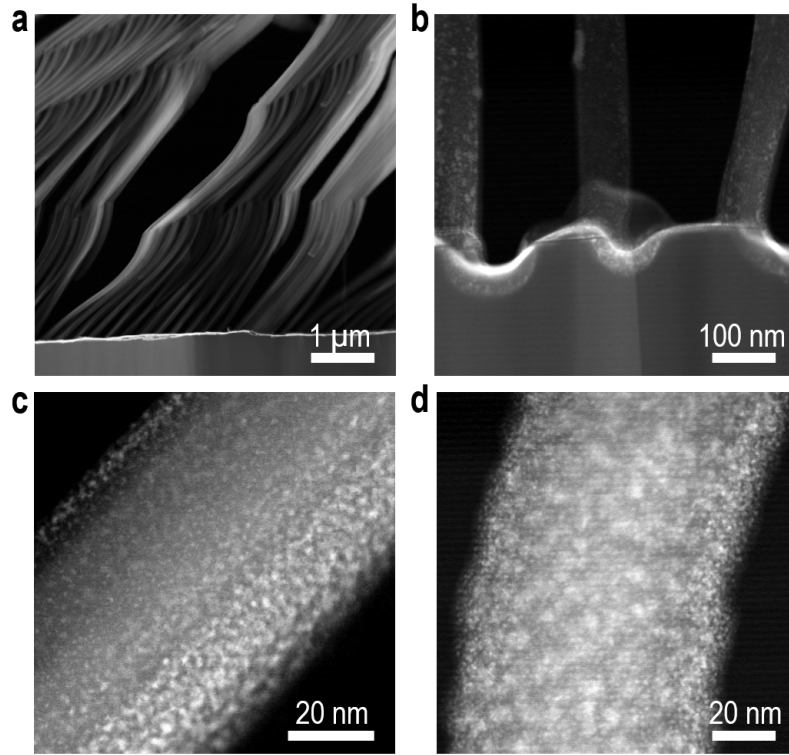


Figure 12: HAADF STEM images showing both the SiNWs and the substrate (a, b) and the distribution of gold particles on the studied SiNWs (c,d).

# Numerical simulations

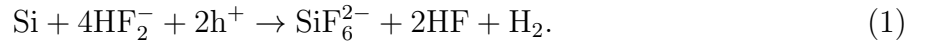
## Metal assisted chemical etching

In the metal assisted chemical etching (MACE) of silicon,<sup>1,2</sup> a metal in close proximity with the silicon in a solution of HF and oxidant facilitates the transport of charge carriers to enable the etching reactions. The positive charge generated via the metal (gold) electrode by the catalytic reduction of the oxidant hydrogen peroxide is conducted through the gold-silicon interface into the silicon. Then, at the electrolyte-silicon interface takes place the dissolution of the silicon.

Accordingly, the electrolyte is modeled as an ohmic solution, while the kinetics of the electrolyte interfaces with the Si and Au is modeled by Butler-Volmer expressions.<sup>3</sup> Drift and diffusion of electrons and holes are considered for the silicon,<sup>4</sup> and ideal Schottky barriers are considered for the gold-silicon and electrolyte-silicon interfaces.

## Chemical reactions

The chemical etching of silicon in HF solutions proceeds very slowly in silicon without an external potential. If holes are readily available at the silicon surface, however, several reactions with resulting dissolved silicon can proceed, and among them<sup>5,6</sup>



This reaction has a reduction potential of  $-1.24 \text{ V}_{\text{SHE}}$ . The availability of holes, or the same, outgoing positive current, will be determined by the electric polarization and electrical properties of the silicon. The electrical polarization is in this case provided by the positive charge generated via the gold mask by the reduction of hydrogen peroxide:



This reaction has a reduction potential of +1.76 V<sub>SHE</sub>. Due to the gold-silicon Schottky barrier, not all the available holes can be drained into the silicon, and a positive potential is expected on the Au side.

We use Butler-Volmer dependencies<sup>7</sup> to model the kinetics of the surfaces facing the electrolyte, that relate the module of the outgoing current density  $|j_n|$ , the external potential  $\phi_{ext}$ , the electrolyte potential  $\phi_l$  and the equilibrium potential at the electrodes  $\phi_{eq}$ . For the gold-electrolyte interface, we use the linearised expression:

$$|j_n| = j_{exAu}(\alpha_c + \alpha_a) \frac{F}{RT} \eta, \quad (3)$$

where  $j_{exAu}$  is the exchange current,  $\alpha_c$  and  $\alpha_a$  are the cathodic and anodic coefficients of the contacts,  $F$  is the Faraday constant,  $R$  the gas constant,  $T$  the temperature, and  $\eta$  the overpotential  $\eta = \phi_{ext} - \phi_l - \phi_{eq}$ , with values  $j_{exAu} = 0.114$  A/m<sup>2</sup>,  $\alpha_c = 1$ ,  $\alpha_a = 0$ , and  $\phi_{eq} = \phi_{eqAu} = 1.79$  V. For the silicon-electrolyte interface, we use

$$|j_n| = j_{exSi} \left( e^{\alpha_a \frac{F}{RT} \eta} - e^{-\alpha_c \frac{F}{RT} \eta} \right), \quad (4)$$

with  $j_{exSi} = 5 \times 10^{-7}$  A/m<sup>2</sup>,  $\alpha_c = 0$ ,  $\alpha_a = 1$ , and  $\phi_{eq} = \phi_{eqSi} = -1.11$  V. The value of  $\phi_{ext}$  is obtained by imposing current conservation at the boundaries. The electrolyte potential is calculated by assuming an ohmic behaviour, with a uniform electrical conductivity  $\sigma = 5$  S/m, by solving Poisson's equation  $\nabla^2 \phi_l = 0$ , and by imposing continuity of the boundary-normal component of the current density  $-\sigma \nabla \phi_l$  at the silicon-electrolyte interface, and total current continuity at the gold-electrolyte interface.

## Silicon model

The Nernst Plack equations apply to the silicon,<sup>8</sup> with both electron and hole charge carriers:

$$\nabla \cdot (-\epsilon \nabla \phi) = q(p - n + N_d^+ - N_a^-), \quad (5)$$

$$q \frac{\partial n}{\partial t} - \nabla \cdot \mathbf{J}_n = -qU_n, \quad (6)$$

$$q \frac{\partial p}{\partial t} + \nabla \cdot \mathbf{J}_p = qU_p, \quad (7)$$

$$\mathbf{J}_n = qn\mu_n \nabla E_c + \mu_n k_b T \nabla n + qnD_n \nabla \ln T, \quad (8)$$

$$\mathbf{J}_p = qp\mu_p \nabla E_v - \mu_p k_b T \nabla p - qpD_p \nabla \ln T, \quad (9)$$

$$E_c = -(\phi + \chi_0), \quad (10)$$

$$E_v = -(\phi + \chi_0 + E_g), \quad (11)$$

where  $t$  is the time,  $T$  is the temperature,  $q$  is the electrical charge,  $k_b$  is the Boltzmann constant,  $\epsilon$  is the electrical permittivity,  $\chi_0$  is the electron affinity,  $E_g$  is the band gap potential,  $E_c$  is the conduction band edge and  $E_v$  is the valence band edge. Here  $\phi$  is the electric potential,  $n$  and  $p$  correspond to the electron and hole concentrations,  $N_d^+$  and  $N_a^-$  to the donor and acceptor concentrations,  $\mathbf{J}_n$  and  $\mathbf{J}_p$  to the electron and hole currents,  $\mu_n$  and  $\mu_p$  to the mobilities of electrons and holes,  $U_n$  and  $U_p$  to the rate reactions of electrons and holes,  $D_n$  and  $D_p$  to the diffusion coefficients of electrons and holes. The Eq. (5) corresponds to Poisson's equation, relating the total charge to the electric potential. The Eqs. (6) and (7) are the current conservation equations, with  $U_n=U_p=0$ , while Eqs. (8) and (9) give the drift diffusion contributions to the current. An ideal Schottky barrier<sup>9</sup> is considered between the silicon and gold, and Si has a  $p$ -doping of value  $10^{16}$  atoms/cm<sup>3</sup>.

## Etching

Assuming that for two holes going out of the silicon surface one silicon atom is removed, the etching speed of the boundary with coordinates  $X, Y$ , will be given by

$$\frac{dX}{dt} = -r_x j_x / |d(zq)/dV| / 2, \quad (12)$$

$$\frac{dY}{dt} = -r_y j_y / |d(zq)/dV| / 2, \quad (13)$$

where  $\mathbf{j} = (j_x, j_y)$  is the current density and  $d(zq)/dV$  is the species charge per unit volume, with value  $8 \times 10^9$  C/m<sup>3</sup> used here for silicon. The reaction rate numbers  $r_x$  and  $r_y$  are introduced here to take into account anisotropic etching, but taken both equal to 1.

## Domain

A bidimensional geometry of  $10 \mu\text{m}$  width  $\times$   $4 \mu\text{m}$  height containing the silicon in the lower part, the electrolyte in the upper part, and two gold contacts  $2.5 \mu\text{m}$  wide and zero thickness as shown in Figure 4. A pre-etch profile of  $10 \text{ nm}$  depth is added to the silicon boundary to enhance conditioning of the mesh deformation as seen in Figure 4. The height of the gold film is kept constant, the etching is allowed at the electrolyte-exposed silicon surface, and the gold border is permitted to recede due to the etching. The above equations were solved in Comsol with the Semiconductor module, using the built-in models for silicon parameters and Schottky barriers, besides the Secondary Current Distribution (Corrosion), Deformed Geometry and Coefficient Form Boundary PDE modules, and solved fully coupled.

## Analysis of the current shape near the Au-Si interface

To highlight the electrical current profile near the metal-silicon interface, we consider an ohmic semiconductor covered by gold for  $-a < x < 0$  and  $y = 0$  as shown in Fig. 13. We consider only majority positive charge carriers in the semiconductor and look for a quasi-neutral solution with  $p = N_a^-$ . Under this assumption, we have  $\nabla^2 \phi = 0$ . We consider the

domain  $-a < x < a \wedge -\infty < y < 0$ , and look for a solution  $\phi(x, y)$  periodic in  $x$  such that  $\phi(x, 0) = V_0/2$  for  $-a < x < 0$  and  $\phi(x, 0) = -V_0/2$  for  $0 < x < a$ . This solution is given by:

$$\phi(x, y) = -\frac{V_0}{\pi} \arctan \left( \frac{\sin(\pi x/a)}{\sinh(-\pi y/a)} \right). \quad (14)$$

The electrical current for this solution is, however, not bounded due to the singularity of the electric field at the origin and  $x = \pm a$ , so we shift the solution in  $y \rightarrow y - y_d$ . We also shift the potential by  $\phi_d$  to fit the boundary conditions:

$$\phi(x, y) = -\frac{V_0}{\pi} \arctan \left( \frac{\sin(\pi x/a)}{\sinh(-\pi(y - y_d)/a)} \right) - \phi_d. \quad (15)$$

This potential, although not exact for the realistic semiconductor, highlights the dependence of the electrical current near  $x = 0$  where a sudden voltage change takes place due to the gold-silicon and electrolyte-silicon Schottky barriers, which are forward and reverse polarized. The potential expressed by Eq. 15 is continuous at  $x = 0$  and the partial derivative  $\partial\phi/\partial y$  is bounded everywhere. Moreover, the semiconductor behaves near the gold and electrolyte interfaces mostly as intrinsic under the screened electrostatic potential  $\phi(x, y)$ , given by Eq. 15. Indeed, the surface potential decays within the Debye length, so we can assume in this depleted region that the charge carrier concentration is the intrinsic concentration  $n_i$  and the charge carrier mobility is  $\mu$ . The normal current at the interface is  $j_n = -qn_i\mu \frac{\partial\phi}{\partial y}|_{y=0}$ :

$$j_n = j_y = qn_i\mu \frac{V_0}{a} \frac{\sin(\pi x/a) \cosh(\pi y_d/a)}{\sin(\pi x/a)^2 + \sinh(\pi y_d/a)^2}. \quad (16)$$

This electrical current is very peaked around  $x = 0$  with a profile  $j_n \propto x/(x^2 + y_d^2)$  as seen in Fig. 13 and its profile is similar to that observed in the numerical calculations.

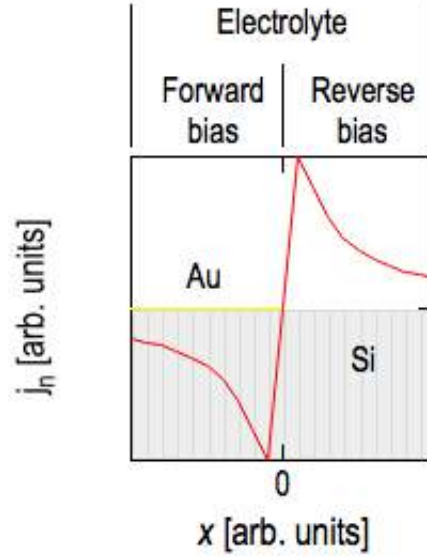


Figure 13: Schematics of the electrolyte boundaries facing silicon ( $x > 0$ ) and gold ( $x < 0$ ) and the normal electrical current profile near  $x = 0$ .

The electrical current dictating the etching process is the one passing through the electrolyte-silicon Schottky barrier:

$$j_S = A_G T_l^2 e^{-q\varphi_b/k_b T} \left( e^{q(\phi_{ext} - \varphi_b)/k_b T} - 1 \right), \quad (17)$$

where  $A_G$  corresponds to the effective Richardson constant,  $T_l$  to the lattice temperature and  $\varphi_b$  to the Schottky barrier height. In the reverse bias region the current will saturate to  $j_0 = A_G T_l^2 e^{-q\varphi_b/k_b T}$ . This is the maximum electrical current that can be expected in the electrolyte-silicon region. The maximum etching rate can be calculated with the aid of Eqs. 12 and 13 ( $j_0 = j_x = j_y$ ). By using  $A_G = 1.1 \times 10^6$  A/K<sup>2</sup>m<sup>2</sup>,  $\varphi_b = 0.450$  or  $0.475$  V we estimate the etching rates as a function of temperature for two values of the Schottky barrier and compare them to the numerical obtained ones in Fig. 14.

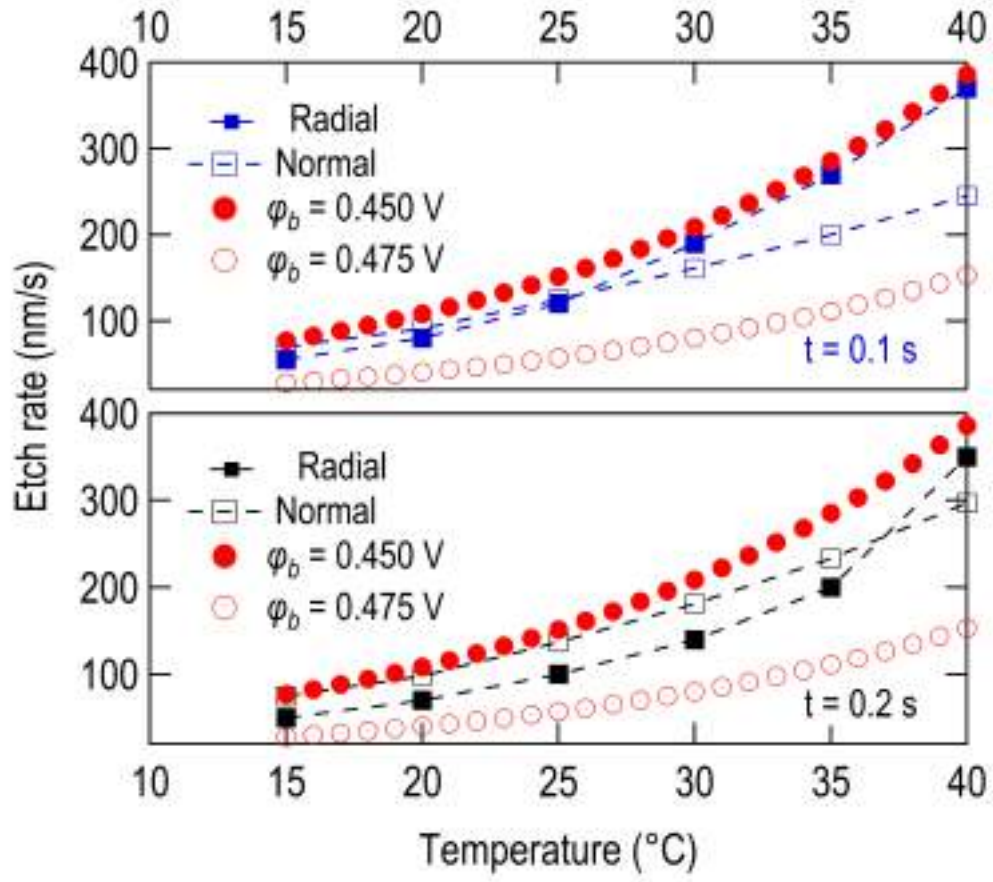


Figure 14: Etch rates as a function of temperature estimated for two values of the electrolyte-silicon Schottky barrier (circles) and computed numerically (squares) at indicated etching times.

## Meniscus formation during the methanol quench step

The considered methanol and air volumes are represented by a phase variable  $\phi_p$ , from which the volume fraction of the methanol is obtained by  $V_m = \frac{1}{2}(\phi_p + 1)$  and that of the air by  $V_a = \frac{1}{2}(-\phi_p + 1)$ , with starting values of  $\phi_p = 1$  and  $\phi_p = -1$ , respectively. The Cahn-Hilliard equation<sup>11</sup> is

$$\frac{\partial \phi_p}{\partial t} + \mathbf{u} \cdot \nabla \phi_p = \nabla \cdot \frac{\gamma \lambda}{\epsilon_{pf}^2} \nabla \psi, \quad (18)$$

with

$$\psi = -\nabla \cdot \epsilon_{pf}^2 \nabla \phi_p + (\phi_p^2 - 1)\phi_p + \frac{\epsilon_{pf}^2}{\lambda} \frac{\partial f}{\partial \phi_p}, \quad (19)$$

$$\lambda = \frac{3\epsilon_{pf}\sigma_{ma}}{\sqrt{8}}, \quad \gamma = \chi\epsilon_{pf}^2, \quad (20)$$

where  $t$  is the time,  $\sigma_{ma} = 22.7 \text{ mN/m}^2$  is the surface tension of the methanol-air interface,  $\epsilon_{pf}$  is the interface thickness of the order of 3 nm,  $\chi$  is a tuning parameter taken here as unity and  $f$  the external free energy. In this case the gravity is introduced by  $f = V_m^2 \rho_m g z$ , where  $\rho_m$  is the density of the methanol,  $g$  the gravitational acceleration and  $z$  the height. The fluid velocity is neglected ( $\mathbf{u} = 0$ ). The boundary conditions for the methanol-air interface, with  $\mathbf{n}$  the normal vector and  $\theta_c$  the methanol-silicon contact angle, are given by

$$\mathbf{n} \cdot \frac{\gamma \lambda}{\epsilon_{pf}^2} \nabla \psi = 0, \quad (21)$$

$$\mathbf{n} \cdot \epsilon_{pf}^2 \nabla \phi_p = \epsilon_{pf}^2 \cos(\theta_c) |\nabla \phi_p|. \quad (22)$$

Typical periodic boundary conditions were set for the domain boundaries. The above equations are solved with the Phase Field Module of Comsol. In the initial configuration, the methanol consists of a uniform layer of 7 nm height covering the base by surrounding the SiNW of 100 nm diameter. As time runs, the methanol rises on the inner part of the nanowire, receding on the other side, as it can be seen in Figs. 15, 16, and 17. This drop

not only could change locally the concentration of the etchant, but also can exert a pull up force on the underlying gold film, changing the etching conditions and contributing to the etching direction change.<sup>10</sup>

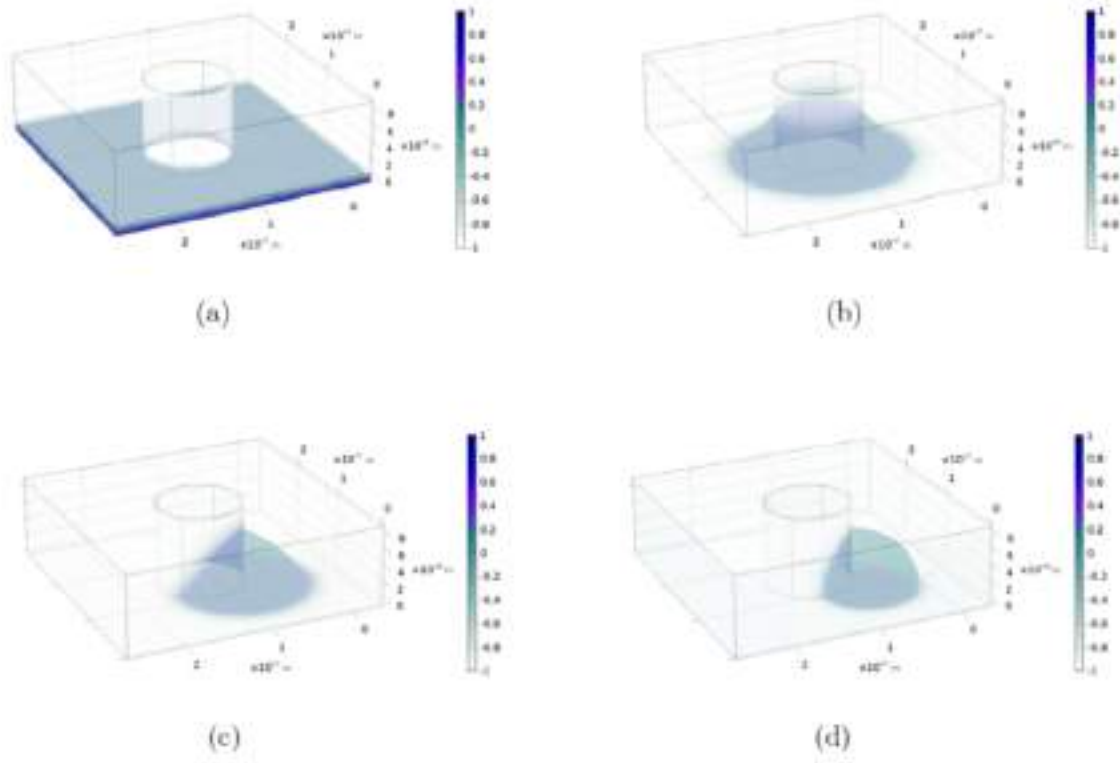


Figure 15: 100 nm diameter and 90°-oriented SiNWs with respect to the substrate. a. Initial condition with a 7 nm thick methanol layer surrounding the base of the NW. b. Final state for 35° contact angle. c. Final state for 60° contact angle. d. Final state for 90° contact angle. The contact angle refers to the methanol-silicon interface. For this contact angle the initial condition is already a solution, however under perturbations it will likely take other configurations, so another initial condition was taken, namely the final state of 60° contact angle given in panel (c). Colour scale indicates the phase field variable.

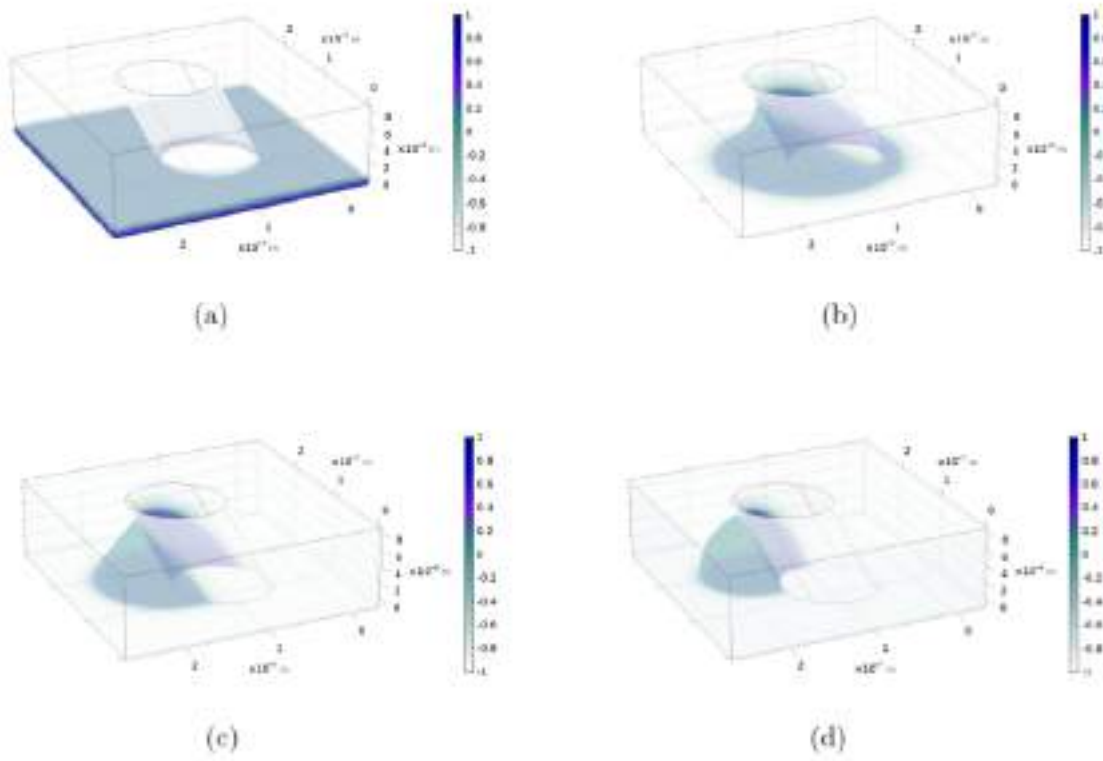


Figure 16: 100 nm diameter and 60°-tilted SiNWs with respect to the substrate. a. Initial condition with a 7 nm thick methanol layer surrounding the base of the NW. b. Final state for 35° contact angle. c. Final state for 60° contact angle. d. Final state for 90° contact angle. The contact angle refers to the methanol-silicon interface. Colour scale indicates the phase field variable.

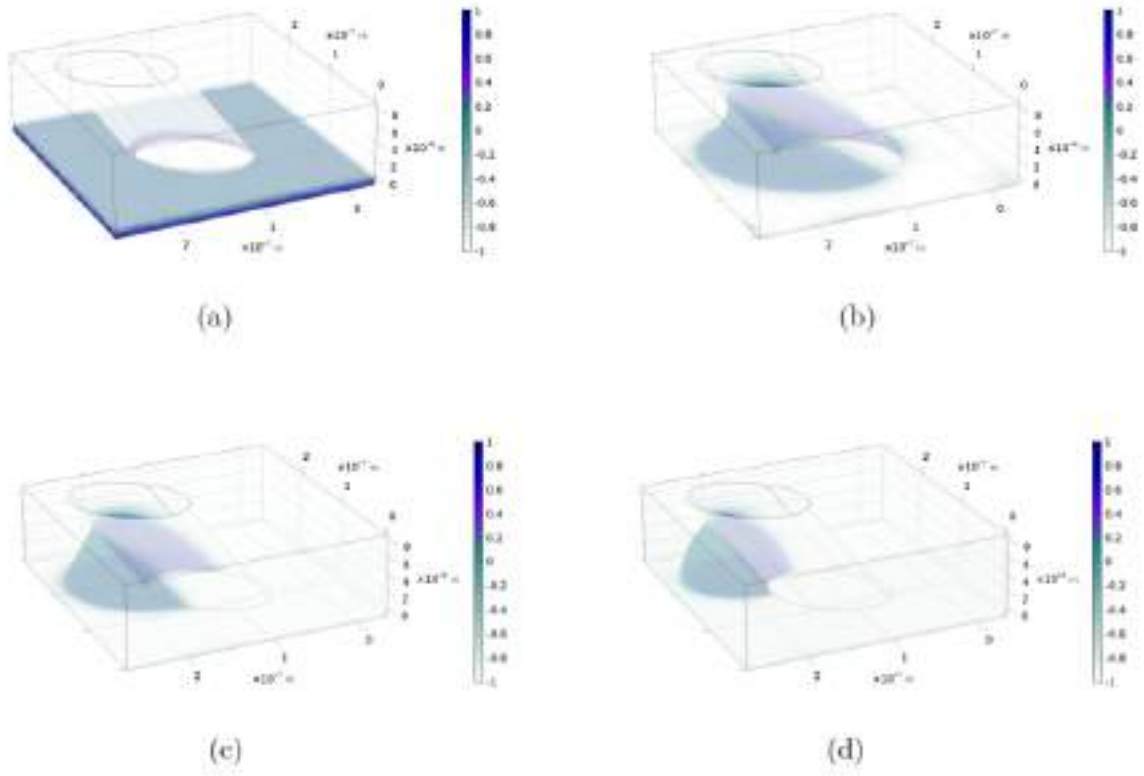


Figure 17: 100 nm diameter and 45°-tilted SiNWs with respected to the substrate. a. Initial condition with a 7 nm thick methanol layer surrounding the base of the NW. b. final state for 35° contact angle. c. Final state for 60° contact angle. d. Final state for 90° contact angle. The contact angle refers to the methanol-silicon interface. Colour scale indicates the phase field variable.

## Materials and methods. II

### Substrates for microcontact printing.

In a first series of experiments, a polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) mixture of 10:1 monomer:crosslinker ratio was spin-coated on glass coverslips previously washed in a 70:30 ethanol:water solution. The PDMS was then cured at 60°C for 4 hours to obtain a membrane of  $\sim 60 \mu\text{m}$  thick and 3 MPa in stiffness.<sup>15</sup> Microstructured silicon wafers were molded with a PDMS mixture of 10:1 monomer:crosslinker ratio and PDMS was cured at 65°C for 4 hours. The PDMS membrane was gently peeled off and cut in stamps of 1.5 x 1.5 cm<sup>2</sup>. The PDMS stamps were washed in an ultrasonic bath for 15 minutes using in a 1.5% solution of detergent (Decon 90, Decon Laboratories Limited), then were rinsed three times with demineralized water and finally washed with a 70% ethanol aqueous solution. The microstructured surface of PDMS stamps was made hydrophilic with ultraviolet/ozone expositions of 8 minutes. A solution of fibronectin (Human FN, Millipore) was deposited on the structured side of the PDMS stamps and incubated for 1 hour under a sterile hood. The PDMS stamps were gently dried with a nitrogen flow and placed into contact of PDMS coated glass coverslips to form protein micropatterns of two different geometries: rectangle of triangles with a surface area of 2000  $\mu\text{m}^2$  and 1600  $\mu\text{m}^2$ , respectively. Microprinted PDMS substrates were passivated with a pluronic F-127 solution (BASF) to avoid cell spreading out of the patterns.

### I. Cell culture on k-SiNWs dispersion-modified PDMS substrates.

We used 120 nm diameter k-SiNWs processed with a 15 nm thick Au catalyst mask and six consecutive [E<sub>5</sub> – Q<sub>1</sub>] sequences. The k-SiNWs were dispersed in 1 ml of methanol followed by ultrasounds for 30 s. Then, 10  $\mu\text{l}$  of k-SiNWs solution was deposited on microprinted PDMS substrates followed by cell culture. Madin-Darby Canine Kidney (MDCK) epithelial cells were maintained in polystyrene flasks in an incubator at 37°C and 5% CO<sub>2</sub>. The MDCK

cells were cultured in proliferation medium composed of Dulbecco's Modified Eagle Medium (DMEM), high glucose (4.5 g/l) and L-glutamine (BE12-604F, Lonza), supplemented with 10% fetal bovine serum (FBS, AE Scientific) and 1% antibiotic (penicillin, streptomycin, AE Scientific). The MDCK cells were seeded on the micropatterned substrates at a density of 10000 cells/cm<sup>2</sup>.<sup>16</sup>

## **II. Cell culture followed by exposition to k-SiNWs dispersion.**

In a second series of experiments, MDCK epithelial cells were maintained in polystyrene flasks in a incubator at 37°C and 5% CO<sub>2</sub>. The MDCK cells were cultured in proliferation medium composed of DMEM, high glucose (4.5 g/l) and L-glutamine (BE12-604F, Lonza), supplemented with 10% FBS (AE Scientific) and 1% antibiotic (penicillin, streptomycin, AE Scientific). The MDCK cells were seeded on standard glass substrates at a density of 10000 cells/cm<sup>2</sup>.<sup>16</sup> Then, the k-SiNWs were added (10  $\mu$ l) in the culture medium for 48 hours. We used 120 nm diameter k-SiNWs processed with a 15 nm thick Au catalyst mask and six consecutive [E<sub>5</sub> – Q<sub>1</sub>] sequences. The k-SiNWs were dispersed in 1 ml of methanol followed by ultrasounds for 30 s.

## **Immunostaining and imaging.**

The k-SiNWs exposed MDCK epithelial cells were fixed with 4% paraformaldehyde (PFA, Electron Microcopy Sciences) and 0.05% Triton X-100 (Sigma) in phosphate buffered saline (PBS 1X, Capricorn Scientific) for 12 minutes at room temperature. Then, the cells were rinsed three times in PBS and incubated 30 minutes with a blocking solution containing 1% bovine serum albumine (BSA, GE Healthcare) and 5% FBS in PBS. The MDCK cells were labeled for F-actin with phalloidin (Alexa Fluor 488 Phalloidin, 1:200, Molecular Probes) and DNA with 4,6-diamidino-2-phenylindole (DAPI, 1:200, ThermoFisher Scientific) for 45 minutes at 37°C. Immunostained cells were mounted on microscope slides with SlowFade Gold Antifade (Molecular Probes). The MDCK cells were observed in epifluorescence mode

with a Nikon Eclipse Ti-E motorized inverted microscope equipped with  $\times 60$  and  $\times 100$  Plan Apo (NA 1.45, oil immersion) objectives, two lasers (Ar ion - 488 nm, HeNe - 543 nm) and a modulable diode (408 nm) and recorded with a Roper QuantEM:512SC EMCCD camera (Photometrics Tucson) using NIS Elements Advanced Research 4.0 software (Nikon).

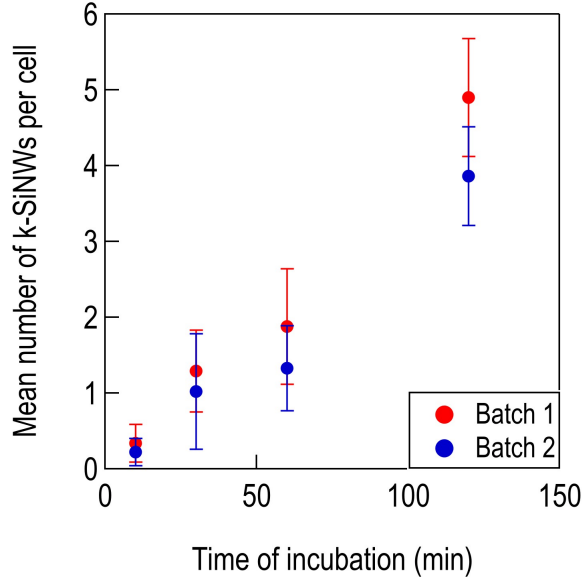


Figure 18: For evaluating the internalization of 120 nm diameter k-SiNWs, the MDCK epithelial cells were plated on PDMS-coated glass substrates covered with fibronectin micropatterns as described above. The cells were cultured for 24 hours in a culture medium previously detailed. Then, MDCK cells were rinsed in warm PBS and incubated from 10 to 120 minutes with a new DMEM-based culture medium containing a k-SiNWs dispersion at the same concentration given above. After incubation at 10, 30, 60 and 120 minutes, the cells were fixed in PFA, stained for F-actin with phalloidin and for DNA with DAPI as aforesaid. We used a  $\times 60$  magnification objective to determine the mean number of internalized nanowires per cell. Two different batches were processed. Our results indicate that the as-fabricated nanowires started to internalize as soon as 30 minutes in epithelial cells. The amount of k-SiNWs after 120 minutes of incubation was nearly the double of that observed after 60 minutes of incubation.

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