

Supplementary Information for

Control of Superhydrophilicity/Superhydrophobicity using Silicon Nanowires via Electroless Etching Method and Fluorine Carbon Coatings

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Wettability characterization

Based on the analytical approach by Bico et al.,¹ they explained that it is impossible to obtain contact angles of 0 degree in actual solid surfaces. They also suggested that superhydrophilic surfaces could be obtained when the hemi-wicking or super-wetting phenomenon is caused by additional rough surface geometries on a hydrophilic surface (e.g. a general Si surface is hydrophilic with contact angle below 90 degree). The super-wetting, which causes superhydrophilicity could be realized by introducing highly porous or rough structures on a flat substrate.² The contact angle near 0 degrees could be obtained only after a few seconds from the moment of sitting of liquid droplet on a rough solid surface that is capable of accompanying the wicking phenomenon. In our experiments, we confirmed that the super-wetting or superhydrophilic behavior near 0 degree could be obtained on the modified surfaces with silicon nanowire arrays. We present additional images for the super-wetting phenomenon on the surface.

e.g.) Si surface with SiNWs

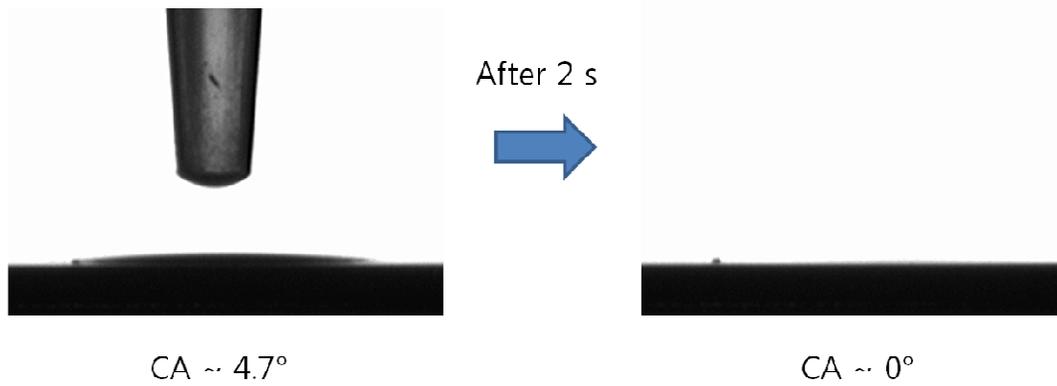


Figure S1. CA images by high speed camera with 2 ms time interval on a Si surface with SiNWs.

In Table 1, we list the apparent contact angles for all of the fabricated surfaces, using standard deviation as the measurement error. The surface roughness factors are also included to explain the relationship between the apparent contact angles and the critical contact angles.

Table S1. Roughness factors, critical contact angles, and apparent contact angles for the SiNWs.

Etching time	h [μm]	r	θ_c [$^\circ$]	θ [$^\circ$]	θ_{c,C_4F_8} [$^\circ$]	$\theta_{C_4F_8}$ [$^\circ$]
0 s	-	-	-	43.6 ± 1.4	-	105.8 ± 2.7
2 s	0.01	1.03	15.6	40.2 ± 1.2	164.4	108.9 ± 2.0
5 s	0.03	1.10	26.2	38.7 ± 2.2	153.8	112.8 ± 2.6
10 s	0.04	1.14	29.9	36.3 ± 2.6	150.2	116.5 ± 3.7
30 s	0.05	1.17	32.9	34.8 ± 2.5	147.1	130.7 ± 2.9
1 min	0.91	1.35	43.7	14.9 ± 2.0	136.3	142.7 ± 1.4
5 min	1.00	4.18	77.1	9.5 ± 1.7	102.9	164.4 ± 0.4
10 min	2.01	8.02	83.4	8.5 ± 1.4	96.6	164.6 ± 3.3
15 min	4.01	15.0	86.5	8.7 ± 1.6	93.5	168.6 ± 4.9
30 min	8.68	31.3	88.3	9.1 ± 0.8	91.7	166.3 ± 3.6
70 min	15.94	56.6	89.1	6.6 ± 2.5	90.9	173.5 ± 2.9

Surface free energy characterization by the van-Oss method ³⁻⁷

The surface free energy of an interfacial interaction is expressed as the sum of two terms (an apolar dispersive term and a polar interactive term), as follows:

$$\Delta G = \Delta G^{LW} + \Delta G^{AB} \quad (S1)$$

where G is the free energy of interaction, and the superscript LW and AB represent the apolar dispersive (Lifshitz-van der Waals) and polar (acid-base) components, respectively. The surface free energy can also be expressed in terms of the surface tensions of the substances, and (S1) is then alternatively rewritten in the following form:

$$\gamma_i \equiv -\frac{1}{2}\Delta G_{ii}, \quad \gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (S2)$$

where the subscript i represents the component for substance i . In particular, van-Oss discovered that for most substances, the acid-base polar component is composed of electron-acceptor (γ^+) and electron-donor (γ^-) parameters:

$$\Delta G_{ij}^{AB} = -2\sqrt{\gamma_i^+ \gamma_j^-} - 2\sqrt{\gamma_i^- \gamma_j^+} \quad (S3)$$

The free energy term is given by

$$\Delta G_{ij}^{LW} = -2\sqrt{\gamma_i^{LW} \gamma_j^{LW}}, \quad \Delta G_{ij}^{AB} = -2\sqrt{\gamma_i^{AB} \gamma_j^{AB}} \quad (S4)$$

Young's equation which describes the basic relationship between the surface tension and the contact angle of a liquid droplet on a solid surface, and Dupre's equation, which describes the work of adhesion between a solid and a liquid, are as follows:

$$\gamma_L \cos \theta = \gamma_s - \gamma_{SL} \quad (\text{S5})$$

$$\Delta G_{SL} = \gamma_{SL} - \gamma_s - \gamma_L \quad (\text{S6})$$

These two equations yield the Young-Dupre equation, and the interfacial interaction between a solid and a liquid can then be written as follows:

$$-\Delta G_{SL} = \gamma_L (1 + \cos \theta) = 2 \left(\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + \sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_s^- \gamma_L^+} \right) \quad (\text{S7})$$

Using (S7), we can derive the values for a solid surface, $\gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-}$ by measuring the contact angles θ with three different kinds of liquid (one being apolar, and the others polar) to obtain three unknowns, γ_s^{LW} , γ_s^+ , and γ_s^- . In this study, to determine the surface free energy of bare and C₄F₈-coated silicon surfaces, we measured the contact angles with diiodomethane (CH₂I₂, 99%), DI water (H₂O), and glycerol (C₃H₅(OH)₃, 99%) under ambient conditions. In Table S2, we list the interfacial tensions of these liquids at room temperature. The surface free energy was averaged, using results obtained from more than three evaluations, and the values for the bare and coated silicon were 52.96±1.26 mJ/m² and 13.52±0.62 mJ/m², respectively.

Table S2. Interfacial surface tension components for the liquids.

Liquid	γ_L^{LW} (mJ/m ²)	γ_L^+ (mJ/m ²)	γ_L^- (mJ/m ²)	γ_L (mJ/m ²)
Diiodomethane	50.80	0	0	50.80
DI water	21.80	25.50	25.50	72.80
Glycerol	34.00	3.92	57.40	64.00

Robustness of superhydrophobic surfaces

For the robustness of a superhydrophobic surface, which depends on the applied pressure on a liquid droplet, we conducted additional experiments by pressing a droplet on the sample surface using micro-pipette attached on an automatically controlled traverse. In experiments, we controlled the micro-pipette along z-axis (upward/downward direction) by about 1 mm/sec in order to press the droplet on the hydrophobic/superhydrophobic surfaces. Based on the Laplace estimation equation ($\Delta P = 2\gamma|\cos\theta|/x$, where γ , θ and x represent liquid surface tension (for DI water=72 mN/m)^{8, 9, 10}, apparent contact angle, and gap between bottom surface and the end of micro-pipette, respectively) on the superhydrophobic surfaces, applied pressure is about from 74.03 Pa to 164.6 Pa. As we can

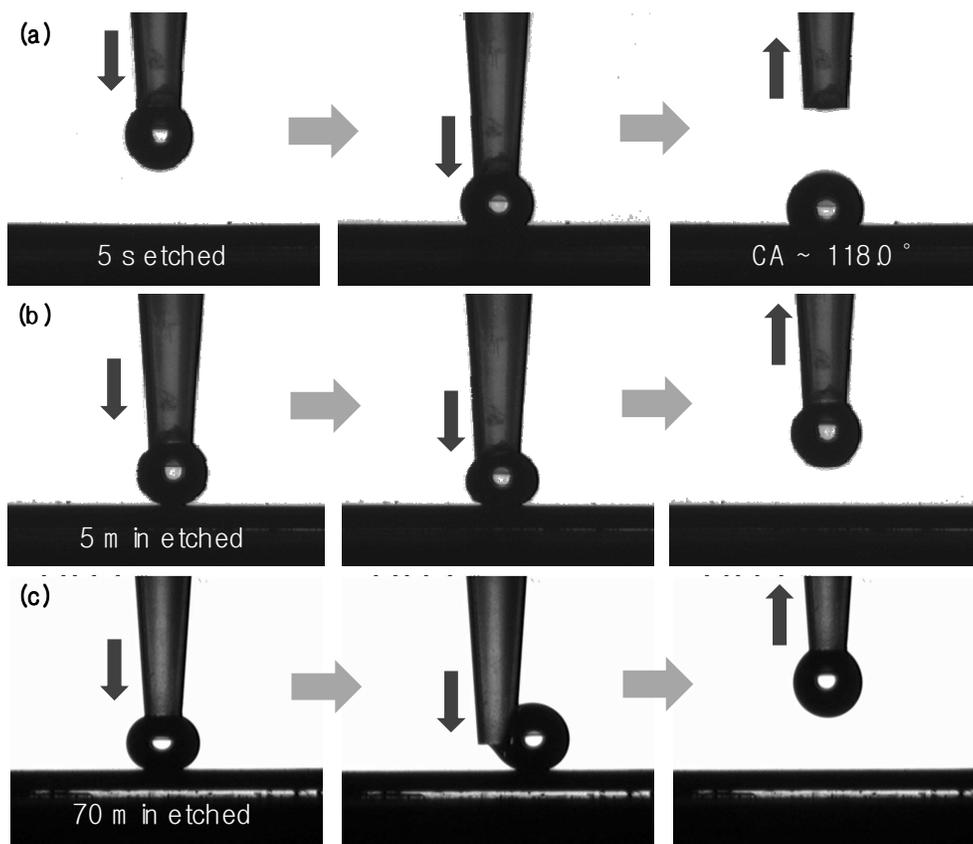


Figure S2. Sequence images from a movie about a liquid droplet behavior on hydrophobic and superhydrophobic surfaces: (a) with 5 s-etched SiNWs; (b) with 5 min-etched SiNWs; (c) with 70 min-etched SiNWs (movie files are attached as Supplementary Information).

see from Fig. S2 and movie files attached in Supplementary Information, when we apply pressure by moving the pipette downward with liquid droplet, on hydrophobic surface with 10 s-etched SiNWs (Fig. S2 (a)), the droplet easily sticks to the surface showing just hydrophobic but not superhydrophobic characteristics. By contrast, the droplets are not attached on the surface but even maintain with distorted feature momentarily due to the robust superhydrophobicity, which prevents contact angle transition from Cassie-state to Wenzel state, with sufficiently long SiNWs (Fig. S2 (b) for 5 min-etched and Fig. S2 (c) for 70 min-etched case).^{11, 12}

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