Scalable Superomniphobic Surfaces
Ville Rontu, Ville Jokinen, and Sami Franssila

Abstract—Superomniphobic surfaces that repel liquids of extremely low surface tension rely on carefully fabricated doubly re-entrant topographies, typically made by silicon deep reactive ion etching technology. However, previously published processes have depended on critically timed etching steps, which are difficult to downscale. We present a scalable process that eliminates the critically timed etching steps. It is based on the use of silicon-on-insulator wafers and a silicon oxide foot of the micropillar, which makes the isotropic silicon release step non-critical. The process allows easy downscaling of pillars from 20 μm to 10 μm and 5 μm. The downscaling increases the stability of the Cassie state. Based on the process, we are able to create superomniphobic surfaces that sustain perfluorohexane (FC-72), which has the lowest surface tension of the known liquids at room temperature (γlv = 11.91 mN/m at 20 °C), in the Cassie state at droplet diameters down to 200 micrometers. These are the smallest perfluorohexane droplets repelled to date. [2019-0207]

Index Terms—Cassie Wenzel transition, microfluidics, plasma etching, self-cleaning, silicon, superhydrophobic, superoleophobic.

I. INTRODUCTION

The wettability of a material is affected by its surface chemistry, topography and the properties of the liquid. Wettability affects many natural and industrial processes such as wicking [1], protein adsorption [2], and condensation [3]. By careful design of the surface topography and chemistry, superhydrophobic, superomniphobic and superamphiphobic surfaces, which repel water, oil and both respectively, have been created. These surfaces have prospective applications in droplet control, heat exchange, antifouling, anti-icing and self-cleaning [4].

Wettability is commonly characterized by the contact angle and the Young’s equation:

\[ \gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}, \]  

(1)

where \( \theta \) is the contact angle and \( \gamma_{lv}, \gamma_{sv} \) and \( \gamma_{sl} \) are the surface and interfacial energies of the liquid vapor, solid vapor and the solid liquid interface respectively. On real surfaces, there are two characteristic contact angles: the advancing contact angle \( \theta_{adv} \) and the receding contact angle \( \theta_{rec} \). The difference between these two is called the contact angle hysteresis.

Contact angles observed on smooth surfaces range from 0° to around 120° for water and from 0° to <90° for oils, depending on the surface chemistry. However, achieving contact angles higher than those possible for smooth surfaces is highly desirable to create liquid-repellent surfaces. A suitably rough surface with a low surface energy coating will exhibit superhydrophobicity [5]–[7], which is characterized by high water contact angles, low contact angle hysteresis and low sliding angles. Superhydrophobicity is based on the Cassie-Baxter state [8] where an air pocket called the plastron limits the contact between the liquid and the solid. The contact angle of a droplet in an ideal Cassie-Baxter state (perfectly flat liquid-solid and liquid-vapor interfaces at the contact area) is often described by the equation:

\[ \cos \theta_{\text{Cassie}} = f(1 + \cos \theta) - 1, \]  

(2)

where \( \theta_{\text{Cassie}} \) is the contact angle observed on the rough surface, \( f \) is the fraction of the surface that is in contact with the liquid and \( \theta \) is the inherent contact angle of the same material as a smooth surface. Since the inherent contact angle can be >90°, simple vertical structures (Fig. 1a) create a pressure barrier that stabilizes the plastron. A suitably low solid fraction will result in surfaces with very high advancing and receding contact angles and very low adhesion of water droplets.

For oils, however, simple vertical structures are not suitable since the inherent contact angles are <90° so capillary wicking would make the plastron spontaneously fill with liquid. However, a metastable Cassie-Baxter state can be created by using re-entrant (also called overhanging) geometries (Fig. 1b) [9]–[11]. Re-entrant geometries combined with fluorinated coatings were shown to lead to superoleophobic surfaces [11] [9] that had high advancing and receding contact angles to several oils, including octane (\( \gamma_{lv} = 21.62 \text{ mN/m at 20 °C} \) [12]. Re-entrant oleophobic surfaces have been fabricated by lithography and silicon etching [11], hydrothermal ZnO.

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growth [13], electrospinning [14], and spray coating [15]. Tuteja et al. [16] showed that the robustness of the oil-repellent state depends on the ability of the topography to resist liquid penetration either by sagging or by bypassing the energy barrier created by the re-entrant geometry and that downscaling leads to an increase in the robustness for micropillar surfaces. The limitation of these surfaces is that in practice they still require the inherent contact angle to be clearly higher than 0°, since otherwise the surface is unstable against any external pressure that is inevitably present (such as hydrostatic or Laplace pressure). Therefore, liquids with extremely low surface tension, including fluorinated solvents, could not be repelled.

This problem was addressed by Liu and Kim [17] who designed doubly re-entrant surface geometries (Fig. 1c). These surfaces were repellent to liquids even in cases where the inherent contact angle is 0°, as demonstrated by the ability of the surfaces to repel fluorinated solvents including perfluorohexane ($\gamma_{lv} = 11.91 \text{ mN/m at } 20^\circ \text{C}$) [12]. Since the surfaces work with any inherent contact angle, surface chemistry modification is not needed, but fabrication of the doubly re-entrant geometry is a challenge. The main method so far has been to utilize lithography and silicon etching [17]–[19] although 2-photon polymerization based 3D printing has also been reported [20], [21]. The problem with random structures, which would be easier to fabricate than lithographic, is that it is not enough to have the surface doubly re-entrant in most places, it needs to be doubly re-entrant everywhere as otherwise the non-doubly re-entrant areas will initiate a lateral capillary filling process. Domingues et al. [18], [19] addressed the problem of lateral capillary filling by using doubly re-entrant cavities that prevent spreading of the liquids in case of a collapsed Cassie-Baxter state. However, this requires wide spacing between the cavity walls to satisfy the low solid fraction requirement for superomniphobicity leading to low breakthrough pressure. A second problem is that the overall stability of the Cassie state on the doubly re-entrant surfaces can still be low due to the low surface tension. To address this issue, it would be beneficial to fabricate the features at smaller size scales to scale up the breakthrough pressure. However, the silicon etching process presented by Liu and Kim depends on a critically timed etching step that will become more and more challenging as the features are downscaled. Furthermore, while 3D printing by 2-photon polymerization can produce even submicron structures [22], the process is extremely slow and is limited to millimeter scale areas.

Here we present a scalable lithography and silicon etching process that can produce doubly re-entrant surfaces for liquid repellency without critically timed etching steps. We show how the surfaces repel low surface tension liquids and how the stability of the Cassie state improves as the feature size is downscaled between 20 $\mu$m and 5 $\mu$m.

II. EXPERIMENTAL

A. Doubly Re-Entrant Pillar Fabrication

The pillars were fabricated on the 25-$\mu$m thick (100) oriented n-type (1-20 $\Omega \cdot \text{cm}$, phosphorus doped) device layer of a 150-mm silicon-on-insulator (SOI) wafer (Ultrasil), which is separated from 600-$\mu$m thick n-type (1-20 $\Omega \cdot \text{cm}$, phosphorus doped) handle wafer by a 1-$\mu$m thick buried oxide, by the process shown in Fig. 2.

The wafers (Fig. 2a) were cleaned in 5:1:1 $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{O}_2$ (H$_2$O de-ionized (18 MΩ $\cdot$ cm), NH$_3$ min. 25 % VLSI grade (Honeywell), H$_2$O$_2$ 30 w-% VLSI grade (Honeywell)) solution according to SC-1 cleaning protocol. Then photolithography with Süss MA-6 at 365-nm wavelength was done to pattern 2-$\mu$m holes on AZ5214E photoresist (Microchemistry) (Fig. 2b–c). It was used as an
ethic mask in the following DRIE step through the device layer (Fig. 2d) using Bosch type process in Aviza Omega i2L etcher using parameters shown in Table I creating 2-μm diameter and 25-μm deep holes in silicon.

After DRIE and removing the photoresist (Fig. 2e), the holes were filled by growing a 1-μm thick SiO₂ (Fig. 2f) by CVD method at 710 °C and 250 mTorr pressure in Centrotherm E1200 HT 260-4 using a tetraethyl orthosilicate (TEOS) (99.99 %, Versum Materials) based process. After this, another lithography (Fig. 2g–h) was performed to define 5-, 10- and 20-μm diameter caps on AZ5214E photoresist, which were aligned with the former 2-μm holes. This photoresist was used as an ethic mask in the subsequent anisotropic SiO₂ RIE (Fig. 2i) using Surface Technology Systems Advanced Oxide Etcher (STS-AOE) and C₄F₈ and H₂ chemistry. The etch time was 4 min 10 s with C₄F₈ flow of 10 sccm, H₂ flow of 8 sccm, coil power of 1150 W and platen power of 250 W. The base pressure was 0.5 Pa, but pressure spike to 3.3 Pa was used. After etching through the SiO₂, anisotropic Si etching was continued (Fig. 2j) in STS Advanced Silicon Etcher (STS-AOE) and C₄F₈ and H₂ chemistry. The etch time was 3 s with RF power at 100 W and purge time of 1 min in STS-AOE using the same process as before for oxide etching leaving only ALD SiO₂ in the vertical sidewalls (Fig. 2k).

**TABLE I**

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tbody>
<tr>
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<td>1.7</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Pressure (mT)</td>
<td>40</td>
<td>60</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Source (W)</td>
<td>1500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>Platen (W)</td>
<td>0</td>
<td>160</td>
<td>450 to 700</td>
<td>240 to 360</td>
</tr>
<tr>
<td>C₄F₈ (sccm)</td>
<td>270</td>
<td>330 to 270</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SF₆ (sccm)</td>
<td>1</td>
<td>390</td>
<td>390</td>
<td>390</td>
</tr>
<tr>
<td>O₂ (sccm)</td>
<td>1</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

Number of loops used were 110.

B. Surface Characterization

The contact angle measurements, drop height experiments and the Laplace breakthrough pressure experiments were performed using a goniometer (Theta, Biolin Scientific) in an ISO 6 cleanroom at 21 ± 0.5 °C temperature and 45 ± 5 % relative humidity. Prior to all experiments, the surfaces were cleaned by 1 min O₂ plasma treatment in Oxford Instruments PRS900 to ensure a clean silica surface chemistry. De-ionized water (18 MΩ·cm) was obtained from the in-house water purification system. Acetone and 2-propanol (isopropanol) were VLSI grade (VLSI Puranal) from Honeywell. Hexadecane (99%), perfluorooctane (98%) and perfluorohexane (99%), were from Sigma-Aldrich.

C. Contact Angle Measurements

Advancing and receding contact angles were measured by the sessile droplet needle method. A gauge 30 steel needle (0.311 mm outer diameter) was inserted into the droplet and the volume of the droplet was increased or decreased at the rate of 0.1 µl/s to measure the advancing and receding contact angles respectively. The measurements were carried out between droplet volumes 2 µl and 7 µl. For perfluorohexane, instead a gauge 22 steel needle (0.718 mm outer diameter) and 0.2 µl/s drop rate were used for the advancing angle, while the receding angle was recorded from an evaporating droplet. All reported values are the averages and standard deviations of three measurements.

D. Drop Height Experiments

Hexadecane and perfluorohexane droplets were dropped on the surfaces from different heights and Cassie state or collapse into a Wenzel state was observed. The height is calculated from the tip of the needle to the surface. The volume of the droplet was increased with a rate of 0.5 µl/s until the force balance between gravity and surface tensions led to the droplet detaching. A gauge 30 and 22 steel needle was used for hexadecane and perfluorohexane respectively. The volumes of the droplets were measured from the images as an average of 5 measurements to be 3.84 µl ± 0.25 µl for hexadecane and 1.59 µl ± 0.04 µl for perfluorohexane. For each surface, the dropping height was increased using a z-stage until the threshold for Wenzel collapse was found. The reported values are the averages of the highest measured height that still led to the droplet staying in the Cassie state and the lowest height that caused a Wenzel state collapse. The reported ± values are half the difference between the highest Cassie and the lowest Wenzel height. Three experiments at each height for each surface were performed. Most experiments had a clear 3-0 result, but in some cases 2-1 (e.g. twice Cassie and once Wenzel) were obtained, and these were counted for the majority.

E. Laplace Breakthrough Pressure Experiments

2-propanol and perfluorohexane droplets of 2–3 µl volume were placed on a surface and their evaporation was recorded on the camera at 1 fps. The radius of the droplet in the last
frame in which the droplet remained in the Cassie state before the Wenzel collapse was recorded. The reported values are the averages and standard deviations of three measurements.

III. RESULTS AND DISCUSSION

A. Fabrication

Doubly re-entrant pillars were fabricated with a scalable process consisting of two lithography steps and no critical timed etching steps. The process consists of first etching holes for the pillar stem through the device layer of an SOI-wafer. The buried oxide (BOX) layer in the SOI-wafer acts as an etch stop for the hole etching. The holes are then filled with conformal-deposited SiO2. The second lithography, which defines the 5, 10 and 20-μm diameter pillar caps, requires alignment with the pillar stems, but it is otherwise very simple. Fig. 3a and b shows small misalignment in the alignment, which does not affect wetting performance. It is enough to align the pillar stem and cap so that a gap exists between the vertical overhang and pillar stem. Two etch steps are performed using the same resist mask from the second lithography step: oxide by reactive ion etching (RIE) and 1 μm of silicon by deep reactive ion etching (DRIE). This creates vertical walls into which vertical overhang material is deposited by highly conformal ALD. The ALD SiO2 used here is a low-temperature process (120 °C) giving low stress SiO2 at high growth per cycle (1.77 Å/cycle). Anisotropic oxide etch without a mask is carried out to create sidewall spacers of SiO2. Oxide on horizontal surfaces is removed in the process. Since the doubly re-entrant pillar is completely made of SiO2, the final isotropic silicon etching is non-critical and all the silicon can be easily etched away. Non-critical etching is important since large etchable area processes tend to have poor uniformity. The etchable area is approximately 90–95 % with superomniphobic surfaces.

Samples with three different pitches were fabricated for each pillar cap diameter labeled as 5-μm S, M or L, 10-μm S, M or L and 20-μm S, M or L. The S pitch is 4 times the pillar cap diameter, M pitch is 5 times and L 6 times. The size of the pillar and the pitch affect both the solid fraction and the stability of the Cassie state, so it is important to have a fabrication process with robust control over both of these. Fig. 3 shows SEM micrographs of a 10-μm pillar (Fig 3a) and 5-μm S pillar array (Fig. 3b and c). These samples were all fitted on a single 150-mm SOI-wafer in square arrays of 5, 10, and 20 mm covering the entire wafer surface. Dividing the surface into arrays prevented spreading of the liquids in case of a loss of Cassie-Baxter state. Non-criticality of the final isotropic etching, which is visual in Fig. 3d) allowed etching away the silicon completely even though lateral etch depth between 5 and 20 um pillar caps is 4 times larger. This is not possible with the processes previously used to create doubly re-entrant pillars [17], [18] where small over etching in final isotropic etch could be catastrophic.

The process that we have described can be further down-scaled. The first lithography could be efficiently done with an optical stepper or nanoimprint lithography (NIL) enabling sub-micron stem. The second lithography’s alignment becomes
slightly more challenging with smaller features. Here we have used high-temperature TEOS CVD oxide process for the hole filling. With decreased dimensions, the hole filling could be realized with a low temperature ALD process decreasing the temperature budget of the whole fabrication process to $<120\,^\circ\text{C}$. An ALD process for the sidewall spacer also enables easy downsizing of the spacer thickness. With downscaling, the processing time would also decrease as etch and deposition steps would become shorter. The materials could also be changed. Instead of the BOX, another etch stop material could be used. Silicon on the device layer could be changed to another material that can be etched both anisotropically and isotropically with good selectivity to the etch stop layer and the doubly re-entrant pillar material. The doubly re-entrant pillar can be made from practically any material that can be deposited with ALD. It could also be possible to realize surfaces on polymer substrates using similar fabrication strategy. In addition to pillars, the same process can be used to make doubly re-entrant cavities shown in [18] or gradient lines used for droplet manipulation [23].

B. Omniphobic Characterization

In order to validate that the omniphobic performance of the surfaces is at least as good as the previously reported, we performed droplet contact angle and stability characterization.

The obtained surfaces were able to repel water, hexadecane, acetone, 2-propanol and perfluorohexane as shown in Fig. 4a and Table II. The surface chemistry in all of these cases was freshly plasma-cleaned SiO$_2$. All the test liquids would completely wet a planar SiO$_2$ surface, so the doubly re-entrant geometry is purely responsible for the stability of the Cassie state. The droplets were in a non-sticky Cassie state characterized by high contact angles (Fig. 4b) and low sliding angles. Fig. 4c–d show a 2-$\mu$m perfluorohexane droplet sliding on the 5-$\mu$m M surface with a tilting angle of $6^\circ$.

Table II shows the results of the advancing and receding contact angle measurements. For the range of solid fractions present on our surfaces, the Cassie contact angles varied between $144^\circ$ and $161^\circ$. Since the inherent contact angle is $\approx 0^\circ$ for all liquids, we do not expect the surface tension of the liquid to affect the contact angle on the omniphobic surface. Nevertheless, we note that there is a downward trend in both the advancing and receding contact angles as the surface tension becomes smaller.

The advancing and the receding contact angles in Table II get lower as the solid fraction of the samples increases (the 10-$\mu$m M sample with hexadecane is the only exception) as is predicted by the Cassie equation (2), although within the studied solid fraction range ($2.7$–$9.6\%$) the effect on the contact angles is quite modest. It is worth recognizing that there is significant uncertainty in the measured values of very high contact angles [24], especially on low surface tension liquids [25], [26]. To achieve similar solid fractions using the doubly re-entrant cavity approach presented by Domingues et al. [18], the spacing between cavity walls would need to be approximately ten times larger than our pillar spacing. This can cause a problem when the repelled droplets (diameter 100 $\mu$m–1 mm in our case) are of similar size as the cavities to achieve the same ratio. It is also known that the wavelength of roughness should be small enough, possibly up to 3 orders of magnitude smaller, compared to the droplet size [27].

1) The Effect of Scaling on the Stability of the Cassie State:
The size of the pillar and the spacing between the pillars both had a clear effect on the stability of the Cassie state. The stability for doubly re-entrant pillars is characterized by the breakthrough pressure ($\Delta P_{\text{max}}$) given by

$$\Delta P_{\text{max}} = \frac{\gamma \pi D'}{p^2 - \pi D'^2/4} \quad [17],$$

where $p$ is the pitch and $D'$ is the diameter of a pillar minus twice the width of the vertical part overhang ($w$), which in our case is close to the diameter of the pillar since the width of the overhang is only 200 nm. The internal pressure of a spherical droplet is given by the Laplace pressure:

$$P_{\text{Laplace}} = \frac{2\gamma}{R},$$

where $R$ is the radius of the droplet.

Two types of experiments were performed to characterize the effect of the size of the pillar and the spacing on the breakthrough pressure. The Laplace pressure test is shown in Fig. 5a–e and the drop height test is shown in Fig. 5f–g. Both tests showed that scaling down the pillar size is beneficial as big differences were observed between 20-$\mu$m pillars, 10-$\mu$m pillars and 5-$\mu$m pillars. Fig. 4a shows an evaporating perfluorohexane droplet on the 5-$\mu$m S surface just before the Laplace pressure becomes too high for the surface to sustain, after which it collapsed to the Wenzel state as shown in Fig. 5b.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid fraction (%)</th>
<th>Liquid</th>
<th>Surface tension at 20°C (mN/m)</th>
<th>Advancing contact angle (°)</th>
<th>Receding contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-$\mu$m M</td>
<td>4.6</td>
<td>water</td>
<td>72.75 [28]</td>
<td>171 ± 1</td>
<td>158 ± 4</td>
</tr>
<tr>
<td>10-$\mu$m M</td>
<td>4.6</td>
<td>hexadecane</td>
<td>27.47 [12]</td>
<td>172 ± 2</td>
<td>153 ± 3</td>
</tr>
<tr>
<td>10-$\mu$m M</td>
<td>4.6</td>
<td>acetone</td>
<td>22.80 [29]</td>
<td>168 ± 1</td>
<td>152 ± 3</td>
</tr>
<tr>
<td>10-$\mu$m M</td>
<td>4.6</td>
<td>2-propanol</td>
<td>21.74 [28]</td>
<td>167 ± 1</td>
<td>146 ± 4</td>
</tr>
<tr>
<td>10-$\mu$m M</td>
<td>4.6</td>
<td>perfluorohexane</td>
<td>11.91 [12]</td>
<td>161 ± 1</td>
<td>144 ± 1</td>
</tr>
</tbody>
</table>

The same liquid on different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid fraction (%)</th>
<th>Liquid</th>
<th>Surface tension at 20°C (mN/m)</th>
<th>Advancing contact angle (°)</th>
<th>Receding contact angle (°)</th>
</tr>
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<tbody>
<tr>
<td>5-$\mu$m S</td>
<td>9.6</td>
<td>hexadecane</td>
<td>27.47</td>
<td>166 ± 1</td>
<td>141 ± 10</td>
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<td>5-$\mu$m M</td>
<td>6.1</td>
<td>hexadecane</td>
<td>27.47</td>
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<td>151 ± 8</td>
</tr>
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<td>5-$\mu$m L</td>
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<td>27.47</td>
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<td>153 ± 3</td>
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<td>27.47</td>
<td>159 ± 5</td>
<td>141 ± 8</td>
</tr>
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<td>hexadecane</td>
<td>27.47</td>
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</tr>
<tr>
<td>10-$\mu$m M</td>
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<td>27.47</td>
<td>157 ± 4</td>
<td>148 ± 5</td>
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<tr>
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<td>170 ± 3</td>
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</table>
Fig. 4. Omniphobic surfaces. a) Digital photos of water, hexadecane, acetone, 2-propanol and perfluorohexane droplets. Water, acetone and perfluorohexane are on the 5-μm S surface. Hexadecane and 2-propanol are on the 5-μm M surface. b) The advancing contact angle of perfluorohexane on the 10-μm M surface. d) A 2-μl perfluorohexane droplet sliding with 6° sliding angle on the 5-μm M surface. The white arrows point to the same position in both images. The scalebar (bottom right) is 2 mm in all figures.

Fig. 5. Effect of the pillar size to the stability of the Cassie state of low surface tension liquids. a) An evaporating perfluorohexane droplet on the surface just before the Wenzel collapse on a 5-μm S surface. b) The same droplet just after Wenzel collapse. c) An evaporating perfluorohexane droplet on the surface just before the Wenzel collapse on a 10-μm S surface. d) An evaporating 2-propanol droplet on the surface just before the Wenzel collapse on a 5-μm M surface. e) An evaporating 2-propanol droplet on the surface just before the Wenzel collapse on a 10-μm M surface. f) A perfluorohexane droplet (1.6 μl) dropped on the 5-μm S surface from the height of 3.3 mm. g) A hexadecane droplet (3.8 μl) dropped on the 5-μm M surface from the height of 8 mm. The scale bar (bottom right) is 500 μm in all figures.

See also supplementary Video S1. In this case, the diameter of the droplet was 199 μm at the point of Wenzel collapse, corresponding to a Laplace pressure of 240 Pa. In contrast, Fig. 5c shows the perfluorohexane droplet just before collapse on the 10-μm S surface, which has the pillar diameter and the pitch doubled. The diameter of the droplet just before the collapse was 629 μm, corresponding to a Laplace pressure of 76 Pa. Fig. 5d–e show a corresponding difference between the size of a 2-propanol droplet just before collapse on the 5-μm M and 10-μm M surfaces. The results of the Laplace pressure stability test are summarized in Table III.

It is clear from the results that making the pillars smaller increased the maximum Laplace pressure that the surface could tolerate before the droplet collapsed into Wenzel state. In fact, the perfluorohexane droplets on our 5-μm S surfaces (200 μm diameter) are smaller than the perfluorohexane (FC-72) droplets (300 μm diameter) reported by Liu and Kim [17] and the smallest (highest Laplace pressure) perfluorohexane droplets reported to date. The four pairs of surfaces that could be directly compared were 5-μm S/M to 10-μm S/M with perfluorohexane and 5-μm M/L to 10-μm M/L with 2-propanol, for which the
increase in maximum pressure varied between 3.2 fold and 6.2 fold.

Theoretically, approximately two-fold increase would be expected for scaling between 10 μm and 5 μm (approximately, since the width of the overhang was not varied). One partial explanation is that any additional pressure, e.g. from vibrations, would tend to increase the ratio above two. This is supported by the fact that the experimentally observed Wenzel collapses mostly occurred earlier than expected from the theoretical predictions given by (3). The 20-μm samples did not reliably sustain droplets in the Cassie state and were therefore excluded from the quantitative analysis. Finally, the case with 2-propanol on the 5-μm S samples was unclear, with seemingly no clear point of collapse into Wenzel state (see supplementary Fig. S1).

The results from the drop height experiments are summarized in Table IV. Fig. 5f shows a perfluorohexane droplet dropped on the 5-μm S surface from the height of 3.3 mm and remaining in the Cassie state. Fig. 5g shows a hexadecane droplet dropped on the 5-μm M surface from the height of 8 mm bouncing off, before settling in the Cassie state. For perfluorohexane, the clearest result is that the 5-μm S sample sustained drops from clearly greater heights than the other samples. Compared to its counterpart, the 10-μm S sample, the maximum drop heights were 3.8 mm ± 0.4 mm and 2.7 mm ± 0.3 mm, respectively. The 10-μm L and all the 20-μm samples did not remain in Cassie state even when dropped from 2 mm, at which point the droplet starts to touch the surface before detaching from the pipette. The beneficial effect of scaling on the stability of the Cassie state is very clear from the hexadecane results. The maximum drop heights increase monotonously when downscaling from the 20-μm to 10-μm and to 5-μm. For example, for the M samples, the maximum drop heights were 3.8 mm ± 0.8 mm, 7.2 mm ± 0.8 mm and 8.8 mm ± 0.8 mm for the 20-μm, 10-μm and 5-μm sized samples, respectively.

One additional observation that we made was that the fluorinated oil perfluorooctane was seemingly more difficult to repel than perfluorohexane, although it has a higher surface tension of ∼14 mN/m at 20 °C [30] compared to the 11.91 mN/m of perfluorohexane [12]. It was possible to obtain a Cassie state with perfluorooctane as well, but it commonly underwent an unexplained transition into Wenzel state after short residence time on the surface, especially when the droplet was stationary (rolling droplets were more stable). A possible explanation is that the much higher vapor pressure of perfluorohexane (23 kPa at 20 °C) [31] compared to perfluorooctane (3 kPa at 20 °C) [31] helps to stabilize the Cassie state due to pressure buildup under the droplet.

### IV. Conclusion

We have presented a scalable process for fabricating doubly re-entrant silicon oxide microstructures in a process that does not require a critically timed etching step. The process utilizes standard microfabrication steps and can produce surfaces in the wafer scale, 150-mm wafers in this study. Further, we showed how scaling down the pillar dimensions leads to an increase in the stability of the Cassie state, as predicted by theory. There are two principal ways to increase the stability of a given liquid on an omniphobic surface of a given overall geometry. First, it is possible to attempt to increase the upward surface tension force by decreasing the pitch. However, that approach has a clear drawback in that the solid fraction of the surface will then increase, which at some point renders the droplets immobile, which is contrary to the purpose of omniphobic surfaces. The second option, which was investigated in this work, is to downscale the geometry.
Contrary to the first approach, there is no increase of the solid fraction, and thus no drawback for reducing the performance. The main drawback of downsizing is that the processing becomes more difficult, which can be addressed by having a microfabrication process that is easy to scale down, such as the one presented in this work.

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REFERENCES


