

A Perfectly Hydrophobic Surface ($\theta_A/\theta_R = 180^\circ/180^\circ$)

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Inspired by the extraordinary hydrophobic behavior of plant and animal surfaces (the lotus leaf in particular), researchers have made impressive efforts to prepare similarly hydrophobic artificial materials.^{1–11} During the present decade, an extensive literature has been written that demonstrates that simultaneous control of surface chemistry and topography can form extremely water-repellent surfaces; water contact angles ranging from ~ 150 to $\sim 175^\circ$ have been reported, and the surfaces have been termed “superhydrophobic.” We pointed out¹² that this field has a long history that has been neglected, in fact what is now called the “lotus effect” was described in the 1940s.^{13,14} We report here preparation of the first perfectly hydrophobic surface that exhibits advancing and receding water contact angles of 180° . To obtain convincing evidence that the contact angles of this surface are indeed 180° and to distinguish them from 179° , a new technique for testing extreme hydrophobicity was devised.

The history of organosilane use to impart hydrophobicity to normally hydrophilic objects (which is central to the majority of recent studies of superhydrophobicity) is not widely known (nor cited) because key discoveries were never appropriately published due to World War II. The copper-catalyzed synthesis of mixtures of methylchlorosilanes from chloromethane and elemental silicon was discovered in 1940 at the General Electric Company by Rochow.¹⁵ These mixtures of $\text{Me}_n\text{SiCl}_{4-n}$ were used¹⁶ initially to hydrophobize aircraft parts for the war effort. Separating the mixtures was difficult because each of the compounds reacts with glass distillation equipment, rendering it lyophobic and ineffective in separation as the liquids do not wet it.

Pure reactive organosilanes are now available, and their vapor phase and solution phase reactions with hydrated silica surfaces under controlled conditions are fairly well understood.^{17,18} Under different conditions, organosilanes can (1) react by self-assembly to form monolayers (horizontal polymerization), (2) react with surface silanols to form covalently attached monolayers, or (3) condense with water as well as surface silanols to form covalently attached, cross-linked polymeric layers (vertical polymerization).¹⁸ The reaction conditions, alkyl group structure, and water content determine which of these processes dominates.

We began to study reactions of silicon wafer surfaces with controlled composition mixtures of $\text{Me}_n\text{SiCl}_{4-n}$ ($n = 0–3$) to try to reproduce surfaces that must have been prepared in the 1940s and to make new surfaces. We envisioned that co-condensation of mono-, di-, tri-, and tetrafunctional silanes would form branched structures that may yield controllable topographies and flexibilities that reduce or eliminate contact angle hysteresis.^{19,20} Me_3SiCl , Me_2SiCl_2 , and MeSiCl_3 , when reacted individually with silicon wafers as pure silanes under a variety of conditions, create surfaces with unexceptional water contact angles that are never higher than 108° ; SiCl_4 forms silica from the vapor phase.²¹ We began with binary mixtures of these four compounds and studied both vapor and solution reactions. Under certain conditions, mixtures of high content MeSiCl_3 yielded surprising results: advancing and receding

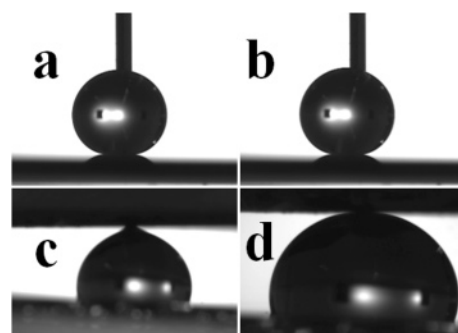


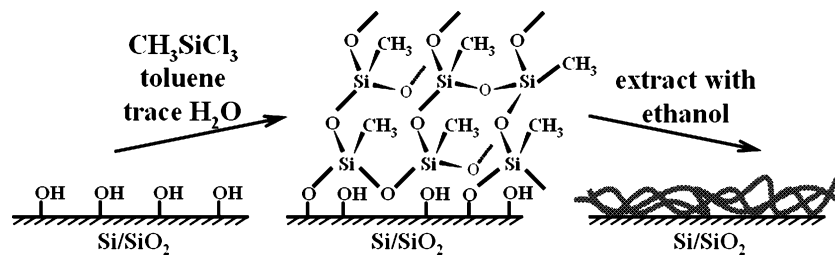
Figure 1. Advancing (a) and receding (b) water droplets on a silicon wafer modified with MeSiCl_3 . (c) A surface with θ_A and $\theta_R < 180^\circ$ being detached from a droplet supported on a $\theta_A/\theta_R = 120^\circ/110^\circ$ surface. (d) A perfectly hydrophobic surface in contact with a supported droplet.

water contact angles of $>170^\circ$. This led us to focus on MeSiCl_3 itself, and we report here a reproducible procedure to prepare what we call “Lichao’s Surface” that exhibits $\theta_A/\theta_R = 180^\circ/180^\circ$.

Silicon wafers were simply submerged in toluene solutions of MeSiCl_3 at room temperature, rinsed with toluene, ethanol, and water, and dried. Vessels were closed to the air during reaction but exposed (RH = 40–65%) during solution and sample introduction. A detailed procedure for this reaction is included as Supporting Information. Water droplets do not come to rest on horizontal surfaces treated with this procedure. Figure 1a,b shows photographs taken of advancing and receding water droplets as water is added and removed from the droplet. The measured receding contact angle is higher than the measured advancing contact angle using this method of analysis (video taping and recording many advancing and receding angles). A receding angle of 180° can be measured (and photographed) just before the droplet detaches from the surface ($\theta_R = 180^\circ$). The droplet is “pushed onto” the surface during advancing, and finite advancing contact angles ($\theta_A = 175–178^\circ$) can be measured.

We recently reported²² contact angles of a surface as $\theta_A/\theta_R = >176^\circ/>176^\circ$ and commented that we could not accurately measure these high contact angles with this technique. A method for measuring extreme hydrophobicity was devised that can distinguish between surfaces with a slight affinity for water ($\theta_A/\theta_R = 175–179^\circ/175–179^\circ$) and those with no affinity ($\theta_A/\theta_R = 180^\circ/180^\circ$): surfaces to be examined were lowered onto a supported droplet, and repetitive contact, compression, and release of the droplet were recorded by video. Surfaces with contact angles $<180^\circ$ exhibit affinity for the droplet during attachment and release (Figure 1c). This surface is not perfectly hydrophobic, but exhibits contact angles of $\theta_A/\theta_R = >176^\circ/>176^\circ$. Figure 1d shows Lichao’s Surface in contact with a water droplet. The droplet shows no affinity for this surface during contact or release after compression; the work of adhesion is apparently zero.

MeSiCl_3 -derived surfaces are indistinguishable by eye from unmodified wafers (contain no micron-scale topography). SEM (Figure 2) indicates the presence of a network of cylindrical fibers

Scheme 1. Formation of and Extraction of Toluene from the Methylsilicone Network

with diameters of ~ 40 nm. The conditions used for this modification promote “vertical polymerization”¹⁸ of MeSiCl₃ into a covalently attached toluene-swollen 3-D methylsiloxane network. Rapid extraction of toluene by ethanol induces the phase separation observed (Scheme 1). The silicone is not swollen by ethanol. This procedure has been reproduced over 100 times, and extremely hydrophobic surfaces are always formed. “Perfectly hydrophobic” ($\theta_A/\theta_R = 180^\circ/180^\circ$) samples are formed in $\sim 70\%$ of the cases. When the humidity is not sufficiently high or the reaction is not allowed to proceed for a sufficient length of time, smoother surfaces with lower contact angles form. When the humidity is too high, phase separation causes spherical-shaped particles and these surfaces exhibit lower contact angles. The lower magnification micrograph shown in Figure 2 was chosen because one spherical particle is present in the lower right portion.

Water does not touch these surfaces (this is the extreme of Cassie behavior), and droplets placed on them remain spherical. Defects

in nonperfect surfaces cause contact line pinning. These defects can be removed, in most cases, by reaction with trimethylsilyl iodide. A vessel with its inner surface treated in this fashion would hold, but not touch water.

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Supporting Information Available: Experimental details for preparation of the perfectly hydrophobic surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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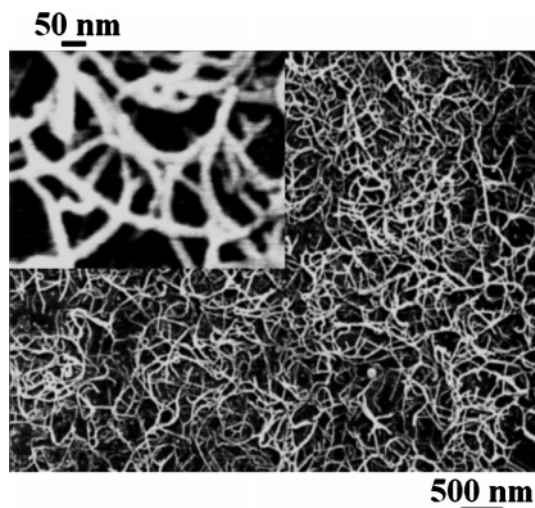


Figure 2. SEM images of a Lichao's Surface.