Supporting Information for:

Immobilizing a Drop of Water - The Fabrication of Highly Hydrophobic Surfaces that Pin Water Droplets

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Experimental:

Photolithography: Silicon wafers (test grade, <100>, p-type, University Wafers, Boston, MA) were used as the substrates for all experiments. Either SU-8 2002 (MicroChem, Newton, MA) or SPR-700 (Rohm and Haas, Marlborough, MA) was applied by a spin-coater (model PWM32, Headway Research Inc., Garland, TX) onto each wafer in a two step process: 500 rpm for 5 sec. with a ramp of 250 rpm/s followed by 3500 rpm for 30 sec. with a ramp of 1000 rpm/s. The SPR-700 required the application of an adhesion layer of hexamethyldisilazane applied under the same spin-conditions and baked at 115° for 1 min. The resists were pre-baked for 1 minute at 95° and 115°, respectively. Using a mask aligner (6mW/cm^2, Karl Suss MA6/BA6, Garching, Germany), the samples were exposed for 16 and 14 seconds, respectively, through the same chrome mask with features of crossed lines 2.5 μm x 2.5 μm in each direction. The samples were post baked for 1 minutes at 115° and developed in their respective solvents; propylene glycol monomethyl ether acetate (PGMEA, PM Acetate, Air Products, Allentown, PA) for the SU-8 and tetramethylammonium hydroxide (~2.25% in water, RD6, Futurrex, Inc., Franklin, NJ) for the SPR-700.

Reactive Ion Etching: An Advanced Silicon Etch ICP-RIE (Surface Technology Systems, New Port, England) was used for all etching. The conditions for both negative and positive samples were similar. The system was run with only SF_6 with a flow rate of 80 sccm, at 10 mT, with 2000 W applied to the 13.56 MHz RF coil. The etching time was between 52-64 sec. for the negative samples and 294-308 seconds for the positive samples. After etching, the samples were sonicated and rinsed in acetone and isopropanol to remove any remaining photoresist or broken silicon pieces. In both positive and negative samples, no power was applied to the platen; this was done to decrease the anisotropic nature of RIE. The posts were made using an alternating passivation/etching process. The conditions for these samples were: 15

mT, SF_6 flow rate of 80 sccm, O_2 flow rate of 8 sccm, 600 W to the coil and 50 W to the platen for the etching step; and 15 mT, C_4F_8 flow rate of 50 sccm, 400 W to the coil and 0 W to the platen for the passivation step. Each step was 3 sec. in duration and total etching process was 20 cycles.

Silanization: All samples were cleaned prior to silanization by boiling in acetone and isopropanol for 10 min each followed by UV/ozone oxidation (UVOCS) for 20 min. Octadecyltrichlorosilane (90+%, Aldrich) monolayers were formed by dipping samples into a 1 mM solution in dry toluene for 10 seconds followed by sonicating the sample in toluene two times for 30 seconds each. This process of dipping and sonicating was repeated a second time to ensure full monolayer coverage. PF monolayers were formed by placing the samples and 5 μL of trichloro(1H, 1H, 2H, 2H-perfluoroctyl)silane (97%, Aldrich) in a desiccator for 12 hours under house vacuum (~ mT).

Microscopy: High-resolution scanning electron microscope (HRSEM) secondary electron (SE) imaging was carried out (at 45°) with a LEO-Supra 55 VP HRSEM.

Contact angle: All measurements were done at ambient conditions (~20 C and % RH). Measurements were taken in under 1 minute and the time for evaporation was greater than 45 minutes. All contact angles were obtained using an NRL C.A. Goniometer and Imaging System (model 100-00, Ramé-hart Inc., Mountain Lakes, NJ). The images were analyzed using ImageJ (a freeware program available at rsb.info.nih.gov/ij).

Figure 1S: A set of SEM images under non-optimal conditions for the ICP-RIE for a positive substrate. A) Insufficient etching time yielded under-etched structures with a flat top and an hour-glass shape. The nm-tips do not form at the original silicon surface but the etching creates a neck that breaks ~1 micron below the resist. B) An over-etched substrate yielded a topographically diverse substrate. Excessive pitting, complete removal of the nm-tips, and structures that are not normal to the original substrate are common features observed. C) Higher magnification image (from a different substrate than (B)) illustrates etched tunnels between the neighboring nadir regions between a pair of nm-tips, regions containing these tunnels are often observed in our over-etched substrates.

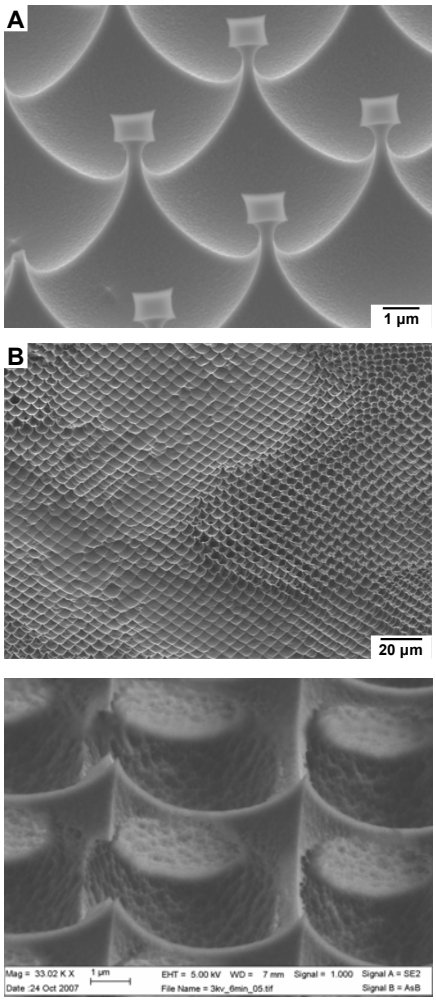

Figure 2S: A set of SEM images of a substrate from a positive photoresist mask illustrating the non-uniform etching on the mm-scale. Differences in color correspond to differences in etching depth and the presence of pitting; dark regions are deeper than light regions and the darkest regions are pitted. A) A large-area image showing that the surface is a patch-work of different etching depths. The regions are randomly interdispersed and average size of a region is tens to hundreds of microns across. B) An image of two pitted regions containing four defect sites. These sites are unetched, raised plateaus in the silicon due to defects in the mask. The pitted regions (the darkest regions) always have a defect in the center. C) A higher magnification of the pitted region from the upper left corner in (B). At the center, there exist a single square that was not developed in the photomask. The pitted regions are the dark circles that reside in the nadir region between four tips. The extent and degree of pitting decreased radially from the defect site.

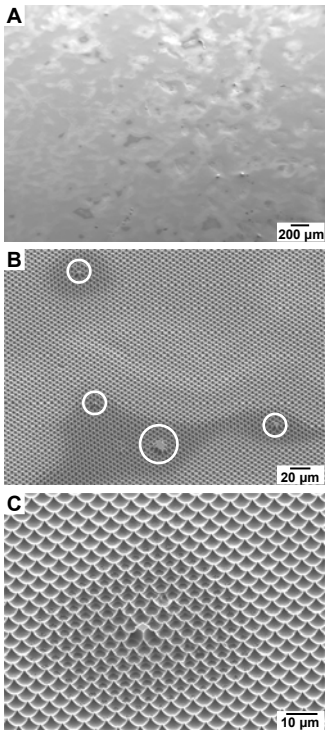

Figure 3S: A-B) SEM images of posts etched in silicon using the negative resist and same photomask. These images illustrate that all surfaces are less rough than those with the nm-tips.