Experimental Methods

Preparation of Silicon Oxide Surfaces. Thermally grown silicon oxide surfaces on a polished silicon wafer were chosen as the substrate for evaluating microwave assisted formation of SAMs. This substrate was chosen in part for the high density and purity of its oxide. Four inch, p-type, single-side polished, <1 0 0> silicon wafers with a 100 nm dry oxide film were purchased from the Nanofabrication Facility in 4D LABS at Simon Fraser University. These oxide coated wafers were cut into 1 cm by 1 cm squares, and cleaned with a piranha solution. Piranha cleaning was performed prior to the formation of SAMs to minimize contamination on the surfaces of the wafer. A 7:2 (v/v) mixture of concentrated sulfuric acid (Anachemia Canada, Inc.) and 30% (v/v) hydrogen peroxide (VWR International) was used to prepare the piranha solution. CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care. The wafer pieces were immersed in the piranha solution for ~15 min followed by immersion into 18 MΩ·cm deionized water (Barnsted NANOpure DIamond water filtration system) for 5 min. These substrates were subsequently rinsed under a stream of 18 MΩ·cm deionized water for 1 min with an approximate
flow rate of 25 mL per second. These cleaned wafer pieces were dried under a stream of nitrogen gas filtered with a PTFE membrane containing <0.2 micron pores. To further dry these substrates, they were baked in an oven at 120°C for 3 min.

**Microwave Assisted Preparation of SAMs.** Monolayers of monoreactive perfluoroalkylsilanes were assembled on the clean silicon oxide surfaces by immersing these substrates into a toluene solution. In order to prepare a 30 mM perfluoroalkylsilane solution, 1H,1H,2H,2H-perfluorodecyltrimethylcholorosilane (FDDCS, product #L16582, 90% purity Alfa Aesar) was added to 25 mL of toluene (ACS Reagent grade, purity > 99.5%; purchased from Fisher Scientific, catalog No. T324-4) in a 25 mL volumetric flask. Solutions containing FDDCS of different concentrations (i.e. 3 mM and 0.3 mM) were prepared from this stock solution by serial dilution. A 3 mL aliquot of the desired perfluoroalkylsilane solution was added to a glass tube (Part no. 908035, CEM Discover) for the microwave reaction.

Silicon substrates were put into the glass tubes containing the desired silane solution. Each silicon substrate was immersed in this solution at room temperature for 5 min before microwave treatment for consistency between experiments (e.g., eliminating significant variations in the immersion time during preparations for microwave treatment). The solution was exposed to microwaves at a constant power of 300 W in a CEM Discover microwave reactor for increments of 1 min. Because the glass tube potentially reaches high temperatures and high pressures, these glass tubes were kept at room temperature without microwave radiation for at least another 5 min. The silicon substrates were immersed in their silane solution for a total immersion time of 18 min. A consistent immersion time was used to evaluate the influence of microwave radiation on the formation of SAMs without being significantly influenced by
variations in contact with the solution. The samples were washed with a fresh solution of toluene and placed into a Soxhlet extractor with refluxing toluene for 1 h as per a previously described procedure (see: Y. Gong, M. C. P. Wang, X. Zhang, H. W. Ng and B. D. Gates, *Langmuir*, 2012, **28**, 11790-11801).

**Water Contact Angle (WCA) Measurements.** Hydrophobicity and uniformity of the SAMs were evaluated by static water contact angle (WCA) measurements. A 2 µL droplet of 18 MΩ·cm deionized water was dispensed onto the substrate for each measurement. The WCA was measured as the angle between the air-water interface of the droplet and the interface of the water and substrate. Five advancing contact angle measurements were obtained for each sample by adding 2 µL for each subsequent measurement. Four receding WCA measurements were obtained after removing the water in 2 µL increments from the resulting droplet. The average contact angle was determined by taking the average of the advancing contact angle measurements. Hysteresis of these measurements was estimated by comparing the average of the advancing contact angles with the average of the receding contact angles.

**Atomic Force Microscopy (AFM) Measurements.** In order to characterize the surface topography of the samples, AFM images were acquired using an MFP 3D AFM (Asylum Research) in AC mode using silicon cantilevers from BudgetSensors (Tap150-G, resonant frequency of 150 kHz, force constant 5 N/m). Images were acquired from scan areas of 5 µm by 5 µm with a scan speed of 0.5 Hz and a resolution of 512 by 512. The AFM images were analyzed using Igor Pro 6.22.
**X-ray Photoelectron Spectroscopy (XPS) Measurements.** Chemical composition and density of the self-assembled monolayers were investigated by XPS. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (AlKα of 1486.7 eV) operating at 150 W. Survey scans (0 to 1200 eV) were acquired using a pass energy of 160 eV and a dwell time of 200 ms. High resolution scans (0.05 eV spectral resolution) were obtained using a pass energy of 20 eV and a dwell time of 1000 ms. An area of 700 µm by 300 µm was analyzed in three separate regions of each sample to check the uniformity of the surface modification.
Fig. S1  Atomic force microscope (AFM) images (A and B) of piranha cleaned silicon oxide surfaces. Cross sectional profile (C) plotted for the region indicated in the image (A) by a white dotted line. This sample had a roughness of 0.15 nm as measured by the root mean square (RMS) method.
Fig. S2  X-ray photoelectron spectrum of a silicon oxide coated substrate after preparation of 1H,1H,2H,2H-perfluorodecyldimethylchlorosilane based self-assembled monolayers by 6 min of microwave treatment followed by 1 h of extraction in refluxing toluene.