Supporting Information

Nanoscale-Agglomerate-Mediated Heterogeneous Nucleation

Hyeongyun Cha[1,3], Alex Wu[1], Moon-Kyung Kim[1], Kosuke Saigusa[3], Aihua Liu[1], and Nenad Miljkovic[1,2,3,*]

[1]*Department of Mechanical Science and Engineering, University of Illinois, Urbana, Illinois 61801, USA*

[2]*Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, USA*

[3]*International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan*

*Corresponding Author E-mail: nmiljkov@illinois.edu

S1. Videos

All videos were captured using a Nikon DS-Qi2 Camera. For surface fabrication and functionalization details, please see the methods section of the manuscript.

Video S1. Experimental top-view shifted-plane high speed video showing renucleation on agglomerates on a HTMS coated horizontal hydrophobic Si wafer after 100 cycles. The video is captured with a 20X objective at a rate of 10 frames/s, and exposure time of 3.5 ms. The size of the image is 500 x 332 pixels, which represents 220 x 146 µm. The lateral motion of the image was due to the thermal expansion and contraction of the sample and cold stage during experiments.

Video S2. Experimental top-view shifted-plane high speed video showing consecutive nucleation on a clean HTMS coated horizontal hydrophobic Si wafer. The video is captured with a 20X objective at a rate of 10 frames/s, and exposure time of 1.2 ms. The size of the image is 524 x 372 pixels, which represents 230 x 164 µm.

S2. Experimental Methods

Surface Fabrication. To enable observation on identical spatial locations before and after cleaning as well as between optical and atomic force microscopy, Silicon (Si) wafers were patterned using deep reactive ion etching (DRIE) to imprint low aspect ratio numbers in a grid pattern (see Supporting Information, Figure S9). The P-type (<100> orientation, 0-100 Ω-cm) Si wafers were first coated with an adhesion promoter (AP8000, Dow Chemical Co.) and positive photoresist (SPR 220-4.5, Dow Chemical Co.) after being cleaned with acetone, isopropyl alcohol (IPA), DI water, dried in a clean nitrogen (N_2) flow, and descummed with oxygen plasma (Jupiter III, March Instruments). Then, the Si wafers were soft-baked at 60°C for 2 min, followed by baking at 110°C for 1 min. Next, the wafers were exposed to ultra violet (UV) light (EVG 620, EVG) with a dose of 150 mJ/cm^2 using a chrome-soda lime mask having the numerical grid pattern design. The wafer was then immersed in a developer (AZ 917MIF, AZ Electronic Materials). Finally, the wafer was etched using DRIE (Pegasus ICP-DRIE, STS), and the remaining photoresist was removed by a stripper (Microposit Remover 1165, Dow Chemical Co.) and ultrasonicated in acetone.

Surface Functionalization. Heptadecafluorodecyltrimethoxy-silane (HTMS, CAS no. 83048-65-1, Dow Corning Co.) was deposited using vapor phase deposition. Before deposition, Si wafer was thoroughly rinsed with acetone, IPA, DI water, dried in a clean N_2 flow, and cleaned with plasma cleaner (PDC-001-HP, Harrick Plasma). Once dried, Si wafers and a 50 mL beaker containing 1 mL of HTMS toluene (C_7H_8, 98.5 %) solution (5% v/v) were sealed in a glass container and heated in an atmospheric pressure oven (Lindberg Blue M) at 80°C for 3 hours. The glass container was then allowed to naturally cool down to the room temperature for 1 hour. The HTMS vapor phase depositions allowed the development of a highly conformal (*ca*. monolayer thick) hydrophobic silane coating. Microgoniometric contact angle measurements (MCA-3, Kyowa Interface Science Ltd.) of ≈100 nL droplets on the hydrophobic Si surface showed apparent advancing and receding contact angle of $\theta_a = 111.9 \pm 0.2°/\theta_r = 102.6 \pm 1.3°$, respectively.

Surface Characterization. Contact angle measurements of ≈100 nL droplets on all samples were performed using a microgoniometer (MCA-3, Kyowa Interface Science). Field emission scanning electron microscopy and energy dispersive X-ray spectroscopy (S-4800 and S-4700, Hitachi) were

performed on all samples at an imaging voltage range of 5.0 to 15.0 kV. To prevent the sample charging, gold/palladium alloy (Au/Pd) was sputter-coated at 20 mA for 30 seconds (K575, Emitech). Atomic force microscopy (MFP-3D, Asylum Research) was performed in tapping mode on all samples using a cantilever with a tip radius <10 nm (Tap300AL-G, TED PELLA, INC.).

Condensation Experimental Set-up. Water vapor condensation cycle experiments were performed using customized top-view optical light microscopy setup. A monochrome microscope camera (DS-Qi2, Nikon) was attached to the upright microscope (Eclipse LV100, Nikon) for top view analysis. Samples were horizontally placed on a cold stage (TP104SC-mK2000A, Instec) using a thin layer of thermal grease (Omegatherm, Omega, thermal conductivity of 2.2 W/m·K) and reduced the sample temperature of $T_w = 1 \pm 0.5°C$ for 100 seconds to induce water droplet condensation and $T_w = 30 \pm 0.5°C$ for 150 seconds to induce evaporation in a laboratory environment condition having an air temperature $T_{air} = 22 \pm 0.5°C$ and a relative humidity $\Phi \approx 50 \pm 1\%$ (RO120, Roscid Technologies). Illumination was supplied by an LED light source (SOLA SM II Light Engine, Lumencor). The LED light source was specifically chosen for its high-intensity, low power consumption (2.5W) and narrow spectral range (380-680 nm) in order to minimize heat generation at the surface due to light absorption. Furthermore, by manually reducing the condenser aperture diaphragm opening size and increasing the camera exposure time, we were able to minimize the amount of light energy needed for illumination and hence minimize local heating effects during condensation experiments. Imaging was performed with 20× (TU Plan Fluor EPI, Nikon) or 50× (TU Plan ELWD EPI, Nikon) objectives.

Chemical Composition Measurement Procedure. To study the chemical composition of agglomerate molecules, a wide band EDS point analysis was performed on a single agglomerate and its peripheral hydrophobic surface area (see Supporting Information, Figure S2). Once the EDS results revealed the existence of significantly higher concentrations of specific chemical elements on the agglomerate when compared to the adjacent hydrophobic area, an EDS line scan analysis was performed for each element along the line trace across the nanoscale agglomerates (Figure 3a). The beam voltage was 10.0 kV at a beam current of 10 µA.
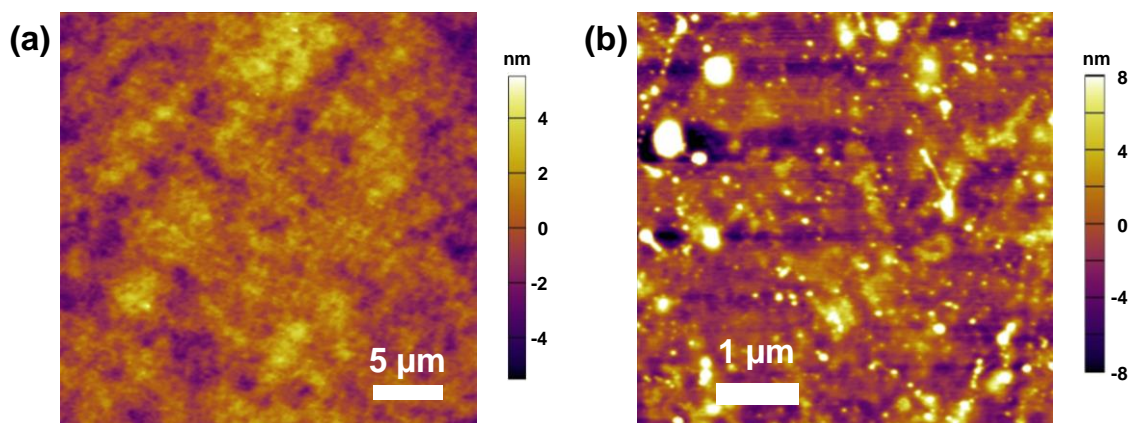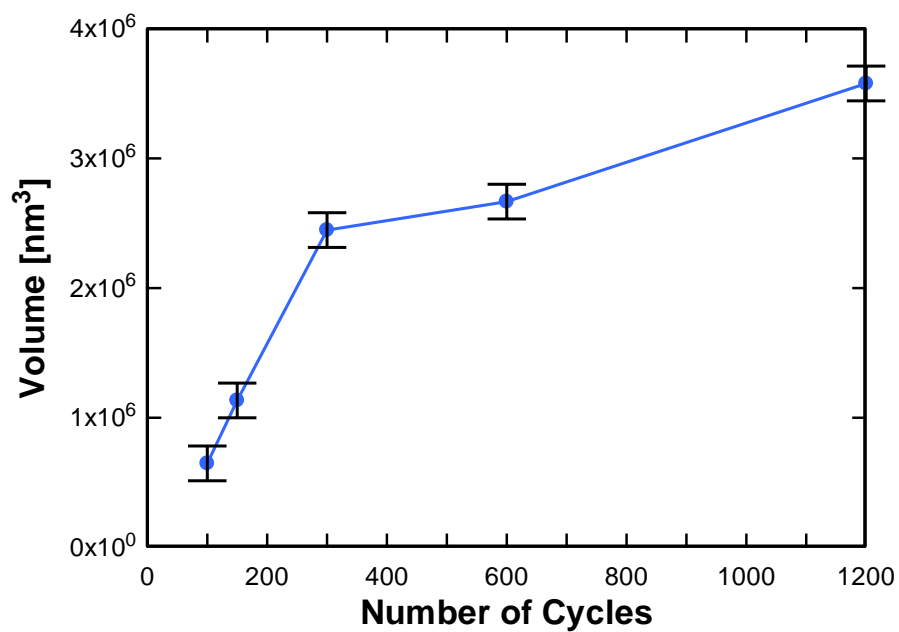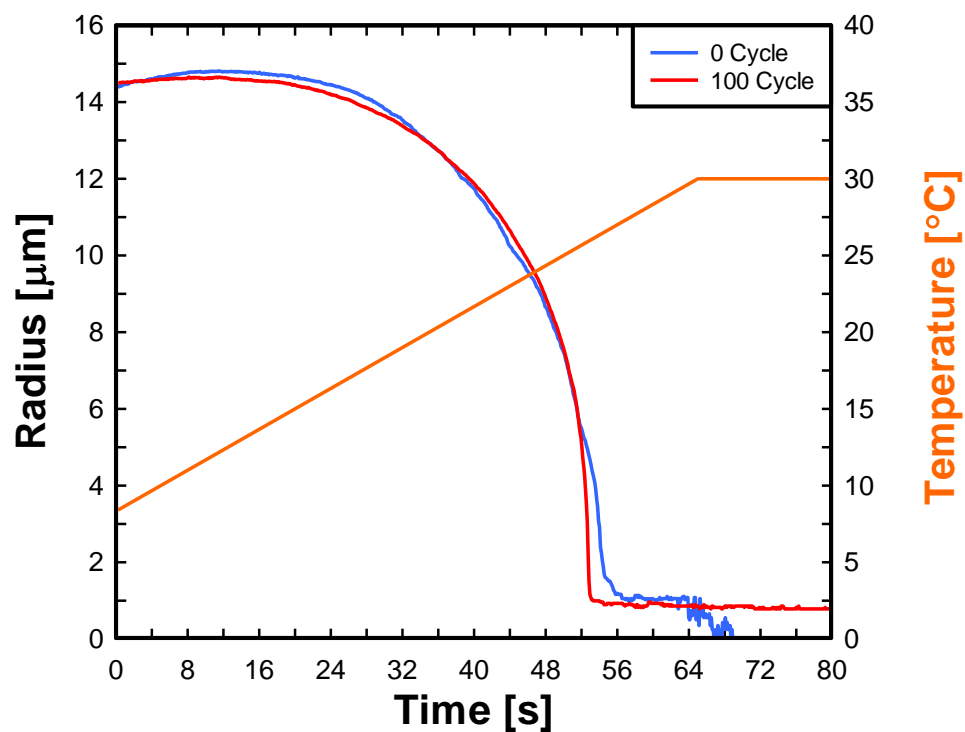
S3. Figures

Figure S1. Atomic force microscopy image of (a) a clean HTMS coated Si wafer and (b) after deposited-water evaporation. Vapor phase deposition of HTMS molecules resulted in the development of a highly conformal, ultra-thin, ultra-smooth, and covalently bonded coating. Deionized water (17.44 MΩ·cm) was deposited using a 25 gauge dispensing needle and a gravity bag.
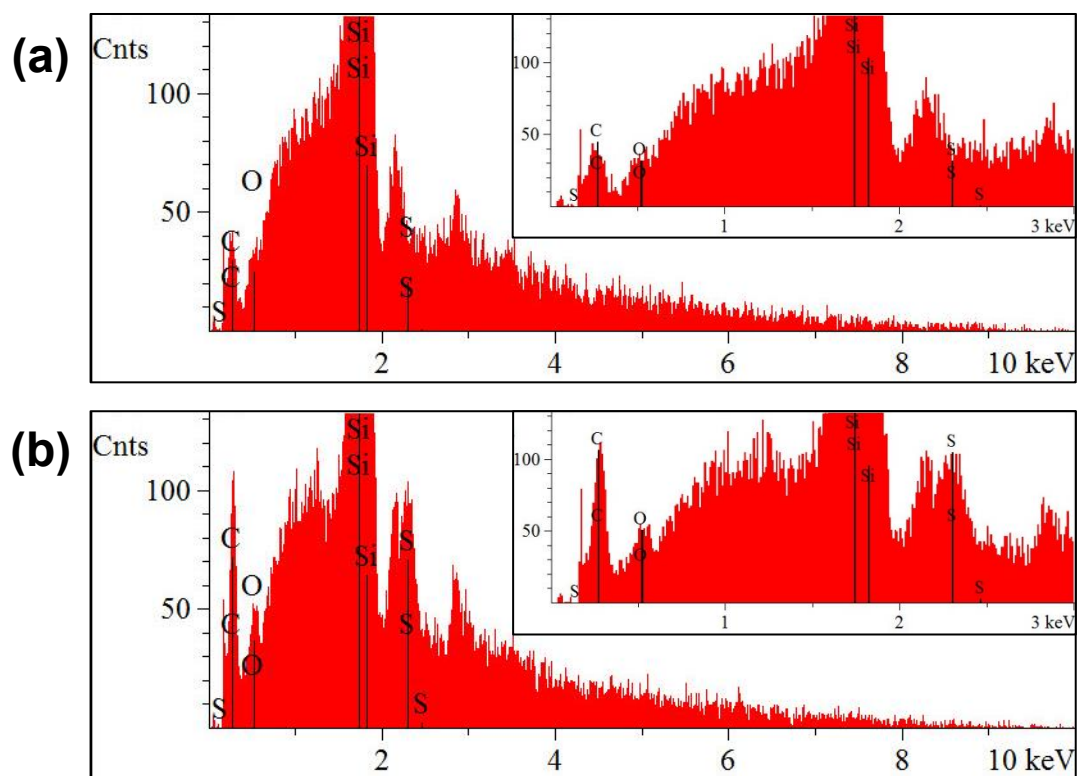
Figure S2. Energy dispersive X-ray spectroscopy (EDS) point analysis on a (a) hydrophobic surface and (b) single agglomerate (insets: expanded spectra). The results show significantly higher concentrations of carbon (C), oxygen (O), and sulfur (S) on the agglomerates when compared to the adjacent hydrophobic area.

Figure S3. Agglomerate volume as a function of number of condensation/evaporation cycles. The agglomerate growth rate decreased substantially after 300 cycles, indicating solubility limit of VOCs and aerosol particles inside the condensing droplet was reached.

Figure S4. Droplet radius as a function of time during evaporation on clean surface (0 cycle) and on an agglomerate (100 cycle). The result shows that contaminants did not hinder the evaporation rate, indicating that VOC molecules or particles are not substantially covering the liquid-vapor interface.
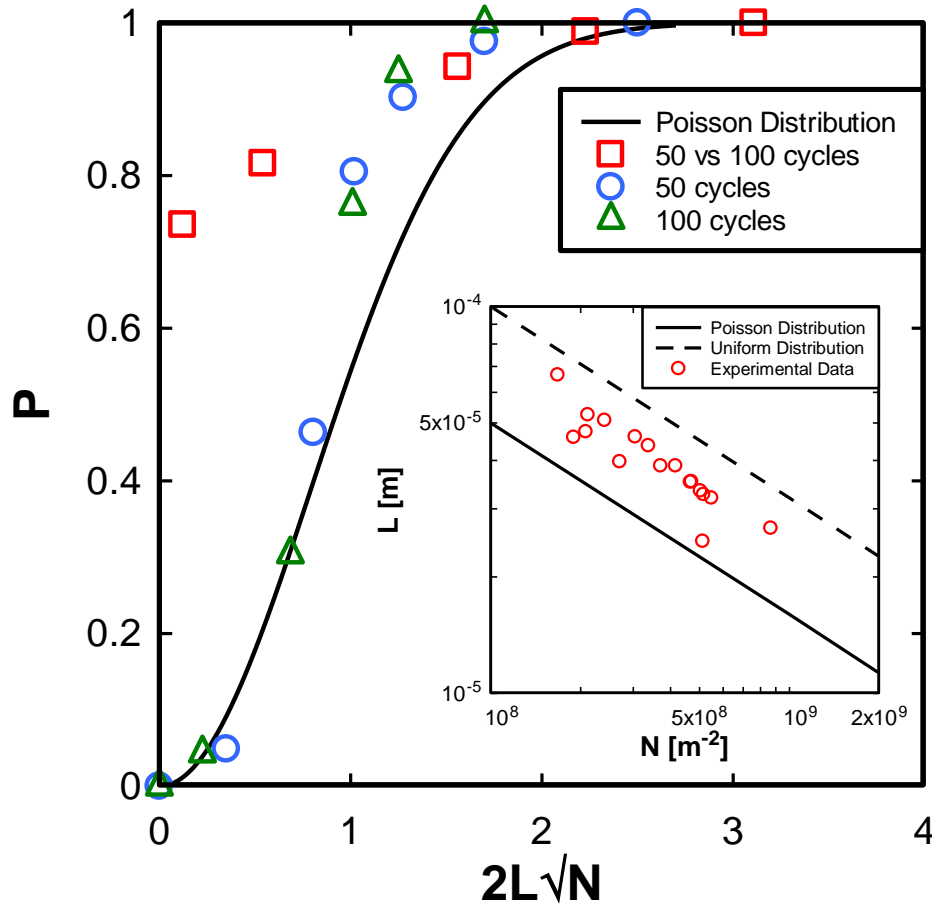
Figure S5. Nucleation behavior on a HTMS coated Si wafer after 50 (blue circle) and 100 (green triangle) condensation/evaporation cycles. Inset: measured mean separation distances. The nucleation sites after 50 and 100 condensation/evaporation cycles were repeatable, as shown by the deviation of the cumulative probability distribution of overlay (red square) of 50 and 100 condensation/evaporation cycles from the predicted Poisson distribution, $P = 1 - \exp(-N\pi L^2)$.
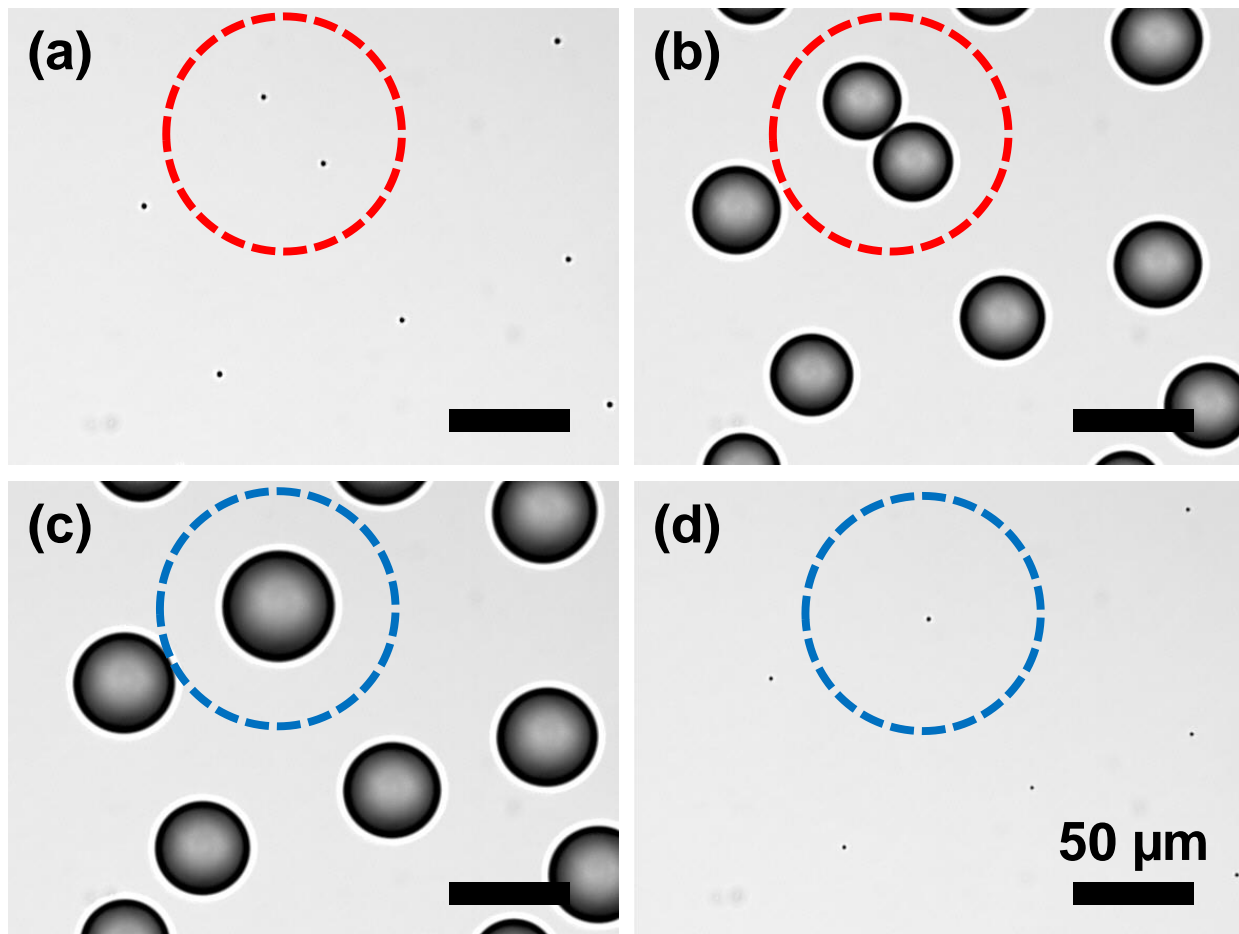
Figure S6. Top-view optical microscopy of (a) the distribution of nanoscale agglomerates on the surface after 25 condensation/evaporation cycles, and (b) water droplet condensation during the 26th cycle showing preferential heterogeneous nucleation on the nanoscale agglomerates, (c) coalescence of condensing water droplets, and (d) subsequent evaporation showing that water droplet coalescence also resulted in the coalescence of nanoscale agglomerates. The coalescence of agglomerates indicate either agglomerate molecule solubility inside condensate droplets or self-assembly on the liquid-vapor interface. Red and blue dotted-circle indicate the agglomerate and water droplet before and after coalescence, respectively.
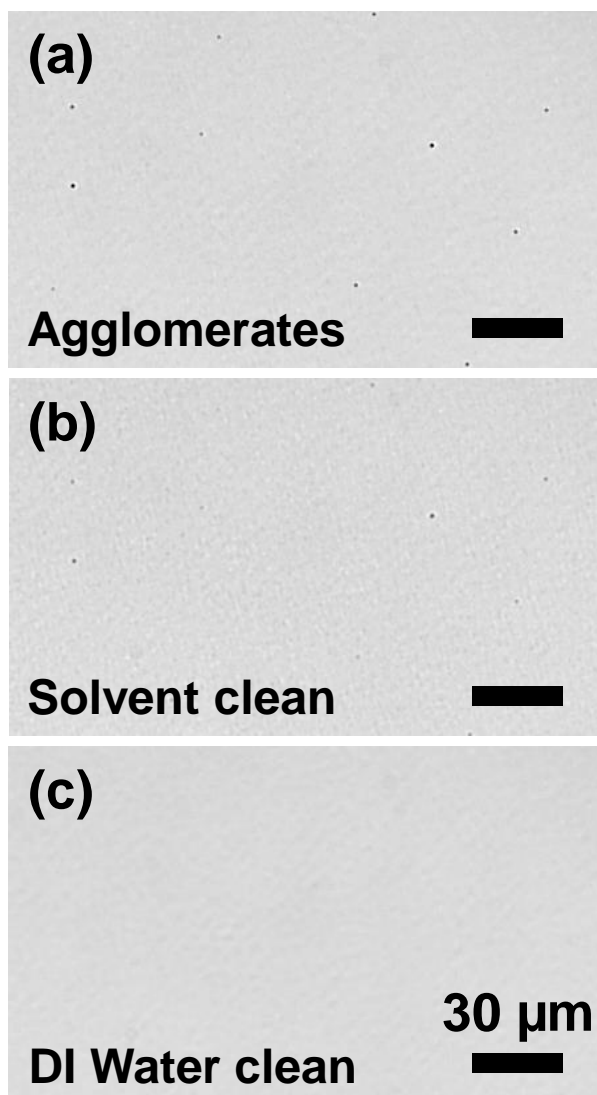
Figure S7. Top-view optical microscopy images of an HTMS coated Si wafer (a) with agglomerate deposition after 100 condensation/evaporation cycles, (b) after rinsing for 5 seconds with solvents (IPA and acetone), and (c) after rinsing for 5 seconds with DI water. The results show that cleaning the surface with DI water after agglomerate deposition resulted in removal of all agglomerates, while cleaning the surface with solvents such as IPA and acetone did not remove agglomerates.
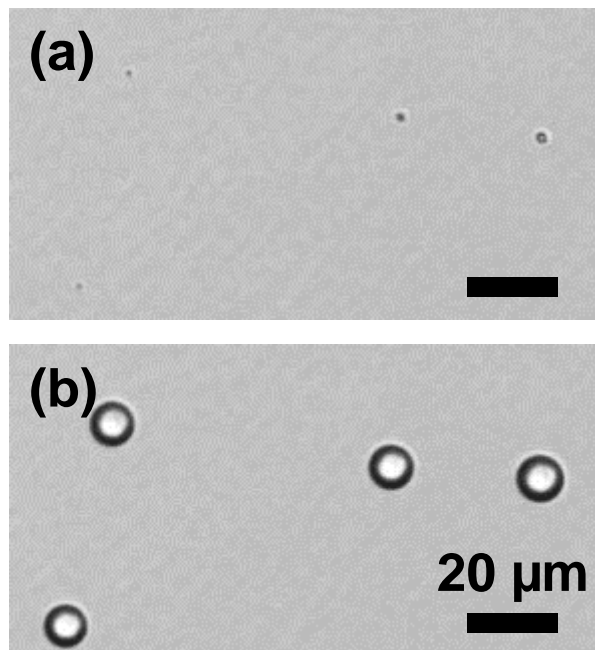
Figure S8. Top-view optical microscopy images of agglomerate deposition (a) after 100 condensation/evaporation cycles and (b) acting as a preferential sites for heterogeneous nucleation during subsequent condensation cycles on a ≈150 nm thick layer of C_4F_8 coated Si wafer. The results show that agglomerate deposition phenomena is not unique to SAM surfaces.
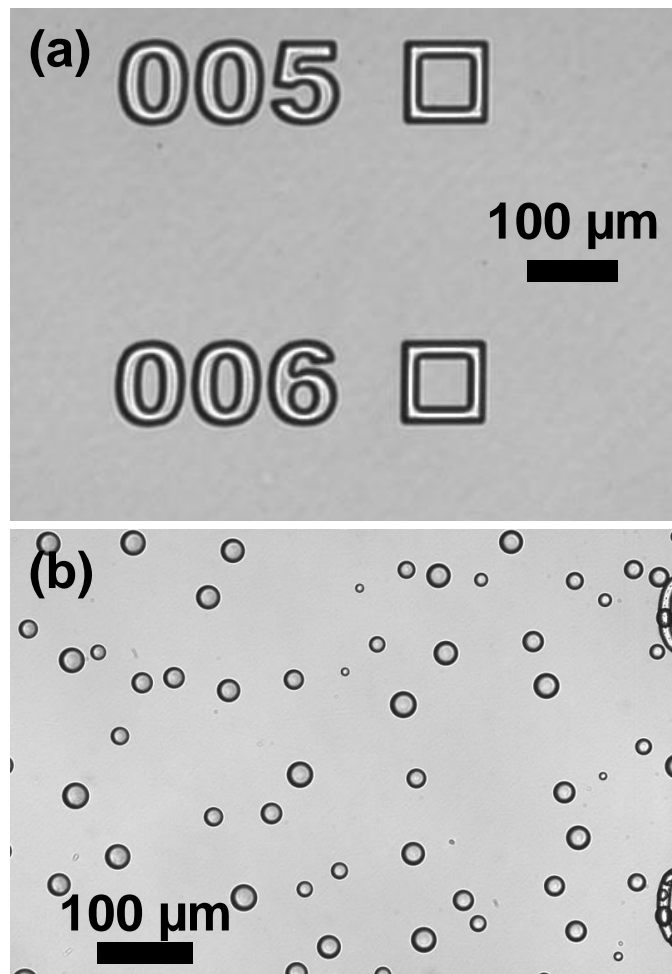
Figure S9. (a) Patterned Si wafer using DRIE and (b) condensation on a clean hydrophobic area adjacent to the pattern. Si wafer was patterned to enable observation on identical spatial location before and after cleaning process as well as among different experiments including optical microscopy, FESEM, and AFM. Heterogeneous nucleation was studied only on the homogeneous area of the Si wafer and was not affected by the imprinted pattern during our experiments.