RSC Advances

ELECTRONIC SUPPORTING INFORMATION (ESI)

Droplet Migration during Condensation on Chemically Patterned Micropillars

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ESI Movies

Movies included in the ESI show environmental scanning electron microscopy (ESEM) images captured at approximately 1 frame every 5 seconds. Movies ESI.1 and ESI.2 show all the migration events used for the analysis and to support the phenomenon reported. In addition Movies ESI.3 to ESI. 9 show enlarged images of the migration events that clearly depict the observed phenomenon, white circles emphasizes the location of the relevant pillar and droplet. The condition for all migration events are reported in Table ESI.2.

Supplementary Movie ESI.1: Droplet Migration events 1 to 11 (MovieESI1.avi).

Supplementary Movie ESI.2: Droplet migration events 12 to 26 (MovieESI2.avi).

Supplementary Movie ESI.3: Droplet migration event 17 (MovieESI3.avi).

Supplementary Movie ESI.4: Droplet migration event 1 (MovieESI4.avi).

Supplementary Movie ESI.5: Droplet migration event 3 (MovieESI5.avi).

Supplementary Movie ESI.6: Droplet migration event 4 (MovieESI6.avi).

Supplementary Movie ESI.7: Droplet migration event 10 (MovieESI7.avi).

Supplementary Movie ESI.8: Droplet migration event 11 (MovieESI8.avi).

Supplementary Movie ESI.9: Droplet migration event 9 (MovieESI9.avi).

Micropillar fabrication

Silicon micropillar arrays of 8x8 mm^2 were prepared via a standard microfabrication technique.[S1] The micropillar arrays had the following geometric configuration, which is illustrated in Figure 1 (a): pillar diameter (d) of 50 μm, inter-pillar spacing of 50 μm, and pillar height of 60 μm. To remove contaminants after fabrication, the substrates were subjected to oxygen plasma treatment (Expanded Plasma Cleaner PDC-001, Herrick Plasma, Ithaca, NY, USA) for ~10 minutes at 30 W radio-frequency (RF) power. The pillared substrates were subsequently placed in a vacuum chamber with 500 μL of 1H,1H,2H,2H-perfluorodecyldimethylcholorosilane ($PFA(Me)_2SiCl$) from Gelest Inc., PA, USA, for 24 hours at a room temperature of 23°C. This vapour reacts with the surface rendering it hydrophobic.[S2] To create hydrophilic regions and therefore patterned wettability, further treatment of the top of the pillars was performed using a 111g/100mL solution of sodium hydroxide. A ~30 μL droplet of the sodium hydroxide solution was deposited on the pillars in a Cassie-Baxter state to react only with the top surface of the pillars. Reaction of the hydrophobic surface treatment with sodium hydroxide exposes hydrophilic regions.[S2]

Substrate characterization

The base surface of the substrate and the side walls of the pillars remain hydrophobic, as later confirmed by observations of condensation behaviour under Environmental Scanning Electron Microscopy (ESEM) (Figure ESI.1):

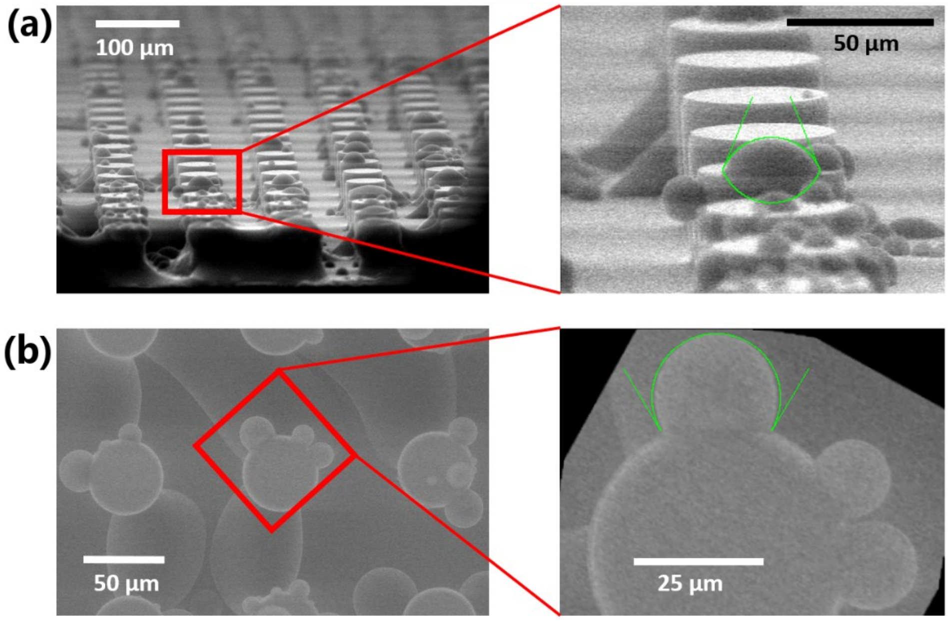

Figure ESI.1 – ESEM images of (a) condensation with a tilt angle of 80° with respect to the horizontal and (b) condensation with substrate completely horizontal (0°). Enlarged ESEM images and low bond axisymmetric drop shape analysis plugin for ImageJ (based on Laplace equation)[S3] show the expected wetting and non-wetting behaviour on the top and the sides of the pillars, respectively. It is worth noting the similarity of the contact angle observed in (b), which is 122°, with the advancing contact angle reported by Gao and McCarthy, 119°, for similar surface functionalization[S2].

Macroscopic Contact Angles

Droplet macroscopic contact angles on a hydrophobic (chemically treated) and on a hydrophilic (hydrophobic coating removed by further treatment with NaOH) flat silicon substrate were measured using a drop shape analyser, DSA100 from Krüss (Krüss GmbH, Hamburg, Germany), in a controlled environment (25°C and 45% relative humidity). A 3μLdroplet of water was gently deposited on the flat substrate and base diameter, droplet volume and contact angle were extracted using DSA1 software. The macroscopic contact angles on the hydrophilic and the hydrophobic surfaces were 50° and 110°, respectively. The uncertainty of three independent measurements was ±2°. The advancing and receding contact angles obtained by injecting and withdrawing water to and from a sessile drop were also measured by using a custom-made contact angle measurement system. The advancing and receding contact angles were found to be 86° and 50° and 116° and 92° on the hydrophilic and hydrophobic surfaces, respectively, which are consistent with previously reported values.[S2]

Experimental observations

Condensation experiments were carried out using an Environmental Scanning Electron Microscope (ESEM) Versa 3D from FEI (Hillsboro, Oregon, USA). The ESEM insert (5x aperture, O-ring), standard Gas Scanning Electron Detector (GSED), and Peltier stage were mounted inside the environmental chamber prior to experiments. The xT Microscope Control software allowed for the fine control of the stage temperature, the system pressure and/or the system humidity, and imaging of condensation phenomena. The electron beam voltage was set to 20 kV and the current was kept below 23 pA by selecting a spot size parameter of 4. In order to avoid droplet heating, probe currents were at least one order of magnitude smaller than those previously reported in literature.[S4] To minimize current effects, the field of view was also kept above 400 μm x 300 μm. After mounting the micropillar array onto the Peltier stage, the chamber was closed to achieve vacuum inside the chamber. Next, the stage was tilted 30° and approached to the electron beam. Vacuum mode was subsequently changed from high-vacuum to ESEM mode and the system pressure was set at 200 Pa. To ensure a uniform temperature between the cooling stage and that of the sample, the substrate temperature was kept at 0 °C for 10 minutes prior to starting condensation experiments. Thereafter, the pressure inside the chamber was gradually increased at 20 Pa/min until the first droplets of condensate were observed on the micropillar substrate. Droplet migration events were observed at several environmental pressures ranging from 560 to 760 Pa with a substrate temperature at all times close to the liquid-vapour saturation temperature. The environmental pressure and temperature values reported by the ESEM showed typical deviations of ±30 Pa and ±0.5°C when compared to the water liquid-vapour saturation curve. Table ESI.1 shows the environmental conditions of pressure and temperature for each of the independent droplet migrations events observed and the deviations when compared to the liquid-vapour saturation curve for water. The size of captured images was 1536 by 1024 pixels, and the dwell time per pixel was ~3 μs. Therefore, one frame was captured approximately every 5 seconds with the xT Microscope Control software.

Table ESI.1 – Pressure (Pa), temperature (°C), and deviation from the pressure (Pa) and temperature (°C) reported by ESEM when compared to the water liquid-vapour saturation curve for the different independent droplet migrations events observed. All the droplet migrations reported in Table ESI.1 are included in Supplementary Movies ESI.1 and ESI.2.

Droplet Migration Event	Pressure (Pa)	Temperature (°C)	Pressure Deviation (Pa)	Temperature Deviation (°C)	L_a/R_c	$2R_c/d$
1 (Movie ESI.4)	649	1.3	17	0.35	1.57	0.84
2	757	3.3	11	0.21	1.71	0.82
3 (Movie ESI.5)	641	1.3	25	0.52	1.66	0.82
4 (Movie ESI.6)	627	0.8	15	0.32	1.57	0.74
5	599	0.1	11	0.25	2	0.66
6	607	0.2	7	0.17	2.24	0.68
7	615	0.3	4	0.09	1.35	1.1
8	630	0.8	12	0.26	2.5	0.64
9	667	1.6	13	0.27	2.72	0.5
10 (Movie ESI.7)	699	2.3	16	0.32	1.84	0.74
11 (Movie ESI.8)	700	2.3	15	0.3	1.85	0.78
12	700	2.3	15	0.3	2.4	0.6
13	700	2.3	15	0.3	1.43	0.84
14	594	0.1	16	0.36	1.5	0.96
15	594	0.1	16	0.36	2	0.78
16 (Movie ESI.9)	599	0	7	0.15	2.44	0.54
17 (Movie ESI.3)	599	0.4	26	0.55	1.16	1.1
18	599	0.2	16	0.35	1.78	0.9
19	599	0.3	20	0.4	1.56	1
20	599	0.3	20	0.45	1.94	0..7
21	599	0.4	25	0.55	2.16	0.74
22	599	0.2	16	0.35	2.16	0.74
23	567	-0.2	30	0.7	1.64	1.1
24	594	0	12	0.26	1.92	1
25	620	0.5	8	0.18	2.26	0.78
26	720	2.8	21	0.41	2.47	0.6

References

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