Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary Information

A superhydrophobic chip based on SU-8 photoresist pillars suspended on a silicon nitride membrane

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Chip fabrication

All fabrication processes were performed in the Nanostructures Facility of Istituto Italiano di Tecnologia (IIT) in Genova (Italy). We used commercial 2 inches <100> silicon wafers covered on both sides by a 500 nm Si_3N_4 layer. Pillar patterns were generated by photolithography using two different photomasks: (i) a periodic, hexagonal pattern for pillars of 10 μm in diameter and 30 μm in pitch and (ii) a non-periodic pattern described elsewhere.[1] The photomasks consisted of chrome-coated quartz plates designed to optically transfer the patterns (**Figs.S1A,B**) to the wafer. The drawing was transferred to a laser mask writer and then printed in a layer of photoresist coated onto the photomask plate. The patterns were developed over the opaque chrome and the chrome was etched away where the resist is clear. After the completion of the etch process, the remaining photoresist was removed and the plate cleaned.

A first photolithographic step was applied to protect the membrane from the following reactive ion etch process that uncovers the silicon wafer according to the pattern of the used mask (**Fig.S1A**). The mask defines the frames for the next cutting and separation in single membrane and the area of the final membranes. The area of a single Si_3N_4 membrane (2x2 mm^2) and its thickness (500 nm) were designed to improve the mechanical stability for droplet deposition and residue formation.

First a positive photoresist (S1813) was spin-coated at 4000 rpm and then baked at 90 ^oC for 180 s over a hot plate. A UV lamp exposure of 15 seconds at 260 W was applied in soft contact modality using a Mask Aligner and the resist was developed using MF-319 developer for 1 min.

We used a DRIE (Deep Reactive Ion Etching) (Sentech 500) for the removal of the clear membrane. Plasma was induced by a radio frequency (RF) powered electromagnetic field applied to a mixture of CHF_3 (70 sccm) and O_2 (5 sccm) gases introduced in the chamber (sccm: standard cubic centimeters per minute). A separate RF bias (70 W) was applied to the substrate in order to increase anisotropic etching.

Wet etching in KOH solution (100 g of KOH in 150 ml of H_20) at 105 ^oC allowed taking away the silicon until the second Si_3N_4 layer on the other side of the wafer was reached. A new photolithographic step with a SU-8 photoresist (SU-8 25 formulation from MicroChem) was then performed on the side respect to the one in which the first photolithography was made before. The photoresist was spin-coated at 3000 rpm for 60 seconds and soft baked for 5 minutes using a heating ramp (from 65°C to 95 °C) and for 40 minutes at 95 °C.

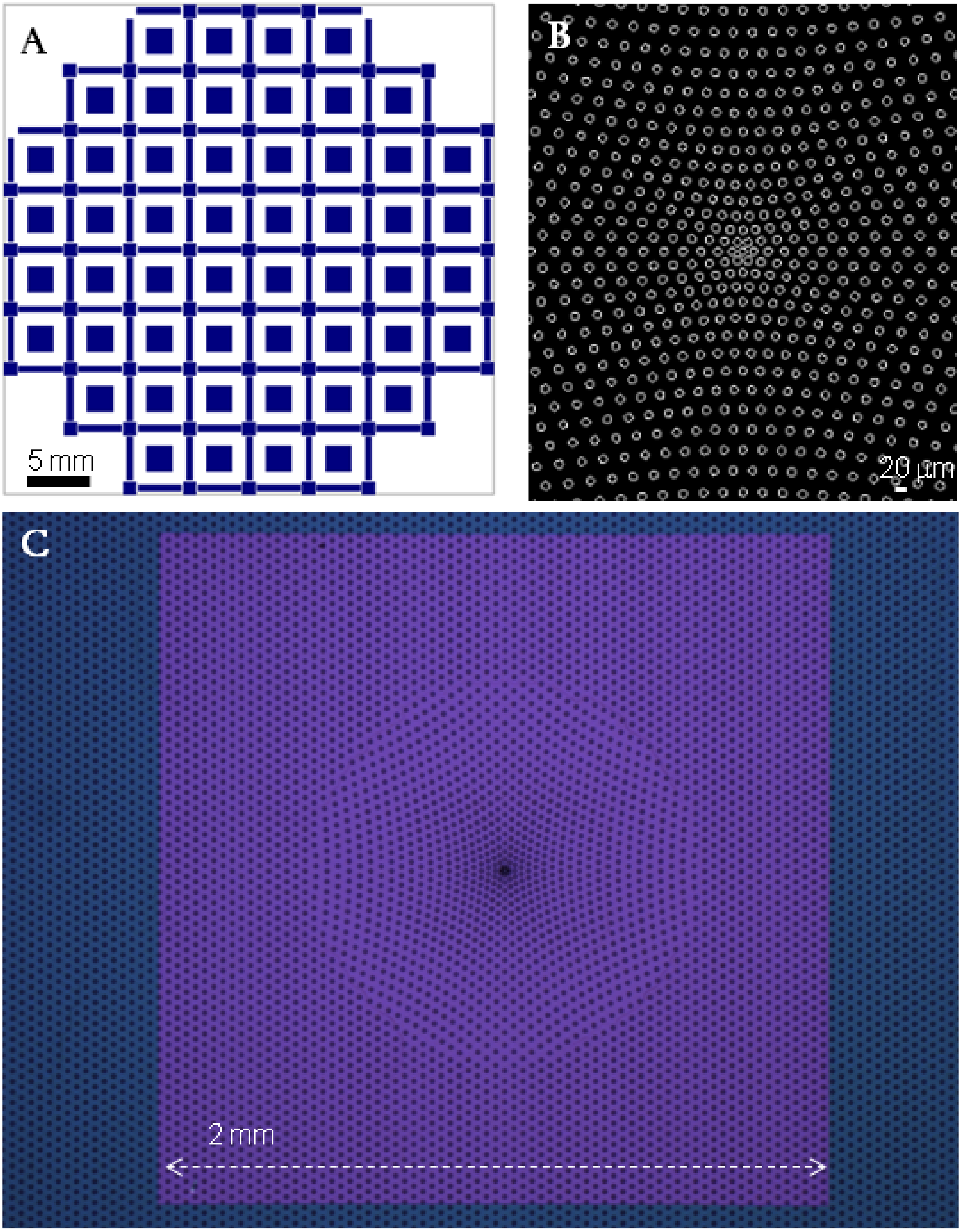

Fig.S1 A: Schematic design of the Si wafer-map showing patterned chips. The blue squares represent the 2x2 mm^2 Si_3N_4 membranes within 5x5 mm^2 Si-frames. **B**: CAD drawing of central part of mask with non-periodic pillar pattern. The distance between the pillars decreases from 20 μm at the outside to about 1 μm at the center. The pillar-diameter is 10 μm for the periodic and non-periodic masks. **C**: Optical image of Si_3N_4 membrane and non-periodic SU-8 pillars surrounded by a Si frame.

The distance between pillars was designed to have two different types of geometries. This new mask was designed to be coupled with the previous one. The regions of circles were centered to the membranes using a mask Aligner (both periodic and non periodic pattern) and after a UV exposure of 15 seconds at 260 W the substrates were post-exposure-baked (2 step of 5 and 10 minutes, respectively at 65 ^{o}C and 95 ^{o}C) and developed in SU-8 developer for 5 minutes. A piranha solution was finally used to clean the surfaces from all organic traces of resist. An image of a single chip is shown in **Fig.S1C**. Due to the thin Si_3N_4 membrane the chip is fragile but can be manipulated at the silicon frame, preferably by tweezers. It could be made more rigid by increasing the thickness of the membrane.

The membranes related to the periodic pattern have SU-8 circular pillars disposed in a hexagonal lattice with a constant step. We determined a contact angle of Θ=151.2^{o} for a water droplet by using a Kruss DSA100 instrument. (**Fig.S2**) The non-periodic pattern is characterized by a step defined by a function decreasing towards the center of the membrane (**Figs.S1B,C**). Due to variation of pillar step-size along the surface, a gradient in wettability is developed.[1] The region where the pillars show a high density is less hydrophobic according the Cassie state.

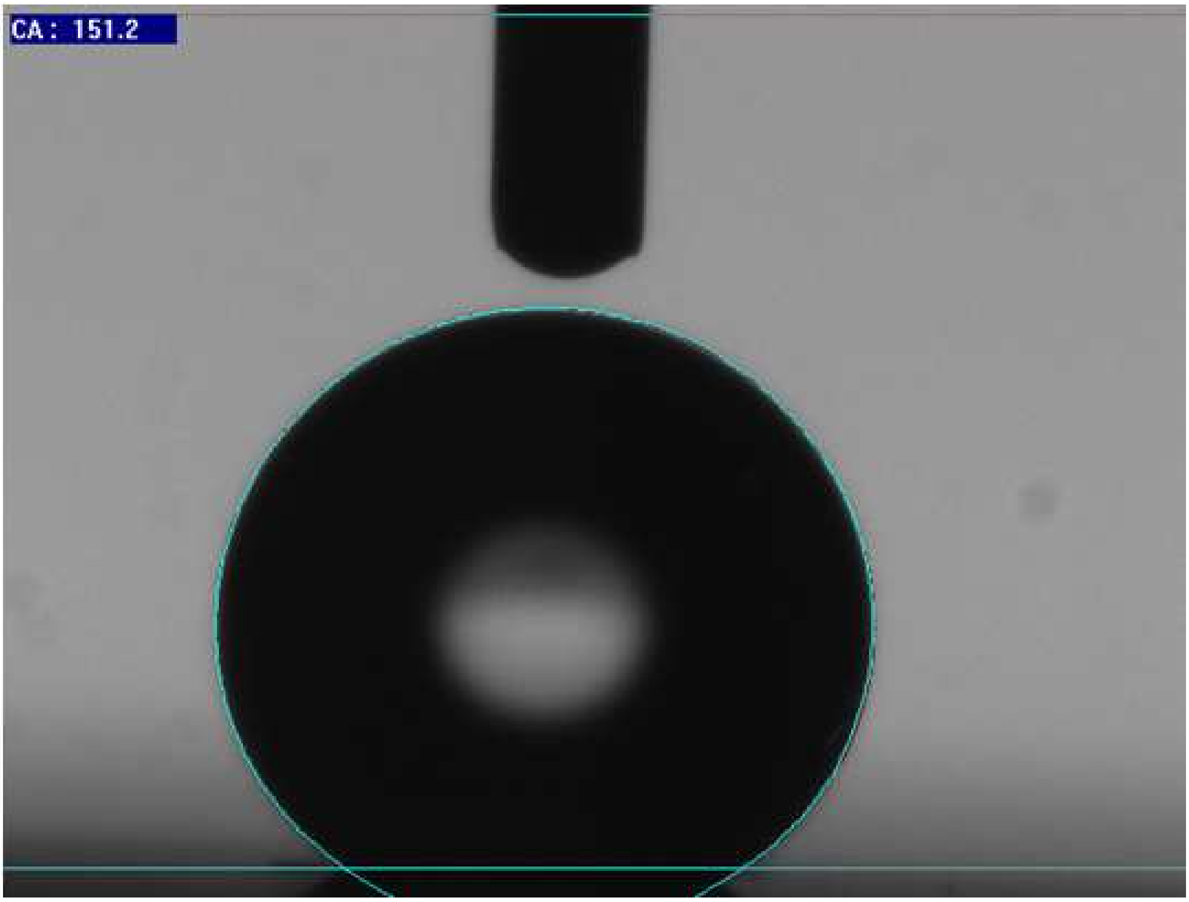

Fig.S2 A: Contact-angle determination of a water droplet.

Au_{71}NP composition: The average number gold of atoms in the cores was extrapolated based on the correlation of cluster dimensions with the number of atoms in gas phase gold clusters.[2]

Synchrotron radiation diffraction experiments. The pink beam from an ESRF undulator was monochromated to a wavelength of λ=0.083201 Å and focused by refractive lenses to ~0.170(h)x130 (v) nm^2 at the sample position.[3] Diffraction experiments were performed at room temperature in transmission-geometry without sample rotation. The SHS-chip with the residue was placed on a PI x/y/z piezo-stage on top of a PI hexapod goniometer. The ~4 μL droplet was deposited on the chip by a manual pipette. The droplet evaporation time was about 1 hour.[4] XRD patterns were collected in transmission-geometry using a FRELON camera[5] (2Kx2K pixels, 16-bit readout with 4x4 or 2x2 binning) at a distance of 309.5 mm from the sample. We performed systematic radiation damage tests for the strongest equatorial reflections. A typical exposure time/pattern was 0.5 s. Distance calibration was performed using an Ag-behenate sample. XRF data were collected using of a Vortex® Silicon Drift X-ray detector. Positions on the sample were chosen using an on-axis optical Olympus microscope aligned with the focal spot of the nano-beam.

Data correction and analysis. XRD and XRF data were collected using the SPEC (Certified Scientific Software, Cambridge, MA) environment. Dark current and detector distortion correction were applied to the XRD data with ESRF proprietary software. The patterns were examined, analyzed and displayed as C-XRD plots using the FIT2D software.[6] Set aside diffuse scattering streaks observed at the very edge of the pillars, scattering from the substrate including pillars was very weak and did generally not require background corrections. Analysis of XRF data and extraction of XRD orientation vectors from equatorial streaks was performed using a proprietary software[7]. The display of the XRF profile (**Fig.3D**) was done by Origin (OriginLab). Parameter errors derived from Gaussian fits are indicated as: (σ).

References

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