Electronic supplementary information (ESI)

Spun-wrapped Aligned Nanofiber (SWAN) Lithography for Fabrication of Micro/Nano-Structures on 3D Objects

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Nanopatterning of silicon

A silicon wafer (University Wafer; p-type, <100> orientation, 0.01-20 Ω cm, 100 mm in diameter, 500 µm thick) was cut into 5 mm × 20 mm pieces by a diamond cutter. PS fibers of 219 nm diameter were deposited on the surface of a silicon substrate and exposed to THF vapor for 10 min using the method described earlier. The fiber-masked silicon substrate was etched in KOH solution (40% w/v) at 30 °C for 20 min. Reactive ion etching (RIE) of silicon was performed with 219 nm diameter PS fiber mask (no solvent vapor treatment) at 1800 W RF power, 80 W platen power for 2 cycles in an Alcatel AMS 100 I-SPEEDER DRIE system. Each cycle included 300 sccm SF_6 for 7 s, 150 sccm C_4F_8 for 2 s.

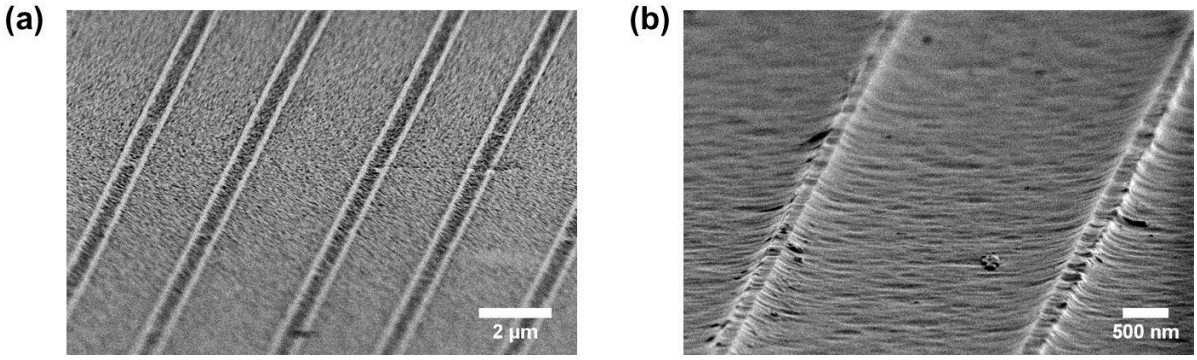

Figure S1. a) SEM image of the fiber-masked silicon substrate after wet-chemical etching. Etched feature width is 600 nm. b) SEM image of silicon after RIE. Etched feature width is 200 nm.

It is well expected that the choice of etching method influences the produced feature size. In electrochemical or wet-chemical etching processes, the maximum feature width is equal to the contact width between fiber and substrate, as the fiber mask would be surrounded by a liquid (Fig. S1a). Compared to wet-chemical etching, electrochemical etching rate can be more precisely

controlled by changing the poised potential on the electrode, but the substrate is required to be electrically conductive. If reactive ion etching (RIE) is used, the pattern width is equal to the fiber mask diameter (or deformed fiber width), due to directional (vertical) nature of the ion etching process (Fig. S1b). Moreover, dry etching methods such as RIE are conducted in absence of a liquid; thereby eliminating the strong fiber mask-substrate adhesion requirement of electrochemical and wet-chemical etching methods.

Lateral feature size

The minimum lateral dimension of continuous and uniform feature in this study is 46 nm, and can be decreased with more exact control over fiber deposition, solvent vapor treatment, and the etching processes. For instance, a 10% PS solution of molecular weight of 860K g mol^{-1} was used to form 25 nm diameter fibers, as shown in Fig. S2. The fiber appears slightly deformed due to interaction with the electron beam during the SEM. The resulting 23.8±3.5 nm feature was formed after treating the sample in THF vapor for 3 min and etching for 5 s. Substrate grain structure size was comparable to etched feature size, resulting in a less distinct etched feature. Micron-scale features can also be achieved by SWAN lithography. As a proof of concept, an 18% PS solution of molecular weight of 2,000K g mol^{-1} was used to deposit larger diameter fiber mask, followed by treatment in THF vapor for 40 min and etching for 15 min, which resulted in 2 μm wide features.

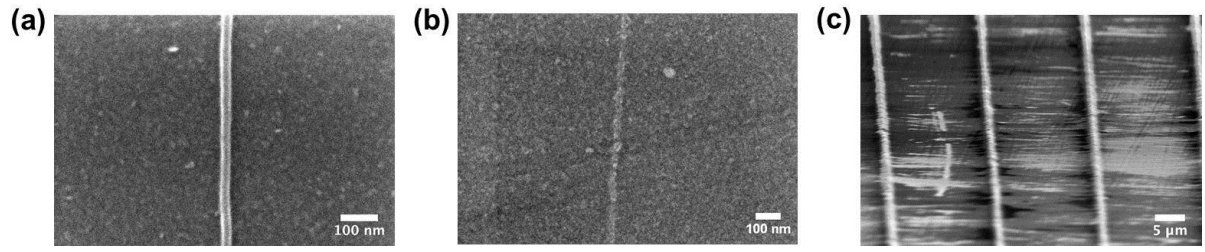

Figure S2. a) SEM image of a 25 nm diameter PS fiber on a GC substrate. b) SEM image of the resulting etched feature. c) SEM image of 2 µm wide etched features.

SWAN lithography throughput

Depositing nanofiber mask takes the majority of the time for SWAN lithography process; thus, it is the limiting factor of the throughput rate. To calculate a representative throughput, a 10 mm diameter (D) cylindrical substrate is used as an example. To deposit nanofibers with 0.2 µm diameter (d) and 1.8 µm spacing (S), the substrate is spun at a rotational speed (ω) of 360 rpm and the motorized stage is moved at a linear speed of $V = (d + S)\frac{\omega}{2\pi} = 0.012\ mm/s$. The areal coverage rate ($\dot{A}$) by nanofiber mask is $\dot{A} = \pi \times D \times V = 3.8 \times 10^{-7}$ m²/s. Increasing the substrate cross-section size or spin-wrapping multiple substrates in parallel can further improve the throughput. Compared to the commonly used nanopatterning techniques, SWAN lithography has much higher throughput than electron beam lithography (EBL) and focused ion beam (FIB) milling, and similar throughput to nanoskiving.[1–4] It has lower throughput than soft lithography and nanoimprint lithography, but it does not require a nanostructured master that is typically fabricated by the aforementioned lower throughput nanopatterning techniques.

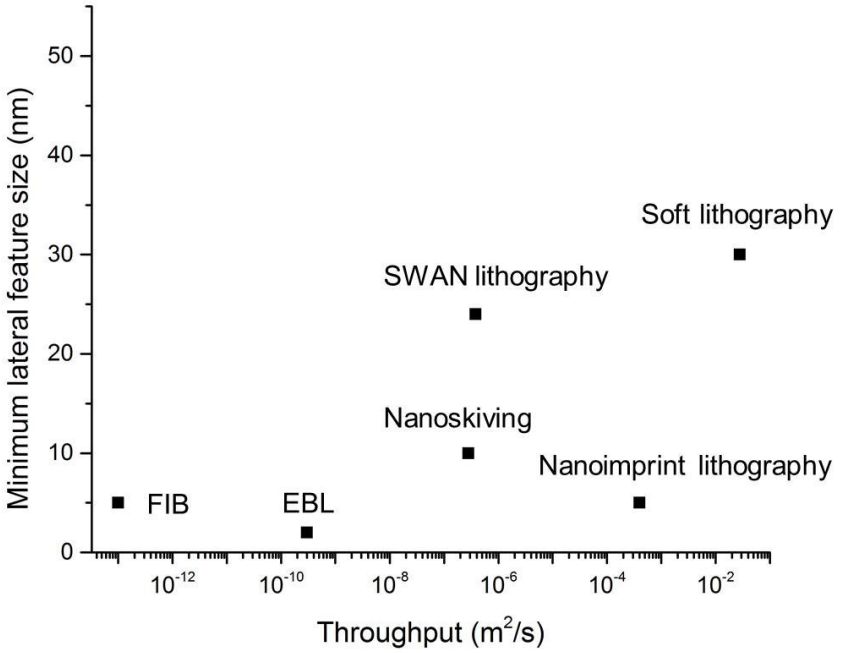

Figure S3. Minimum lateral feature size vs. areal throughput for SWAN lithography and commonly used nanopatterning methods.

Replica molding

Sylgard® 184 silicone elastomer (Dow Corning) base and curing agent were mixed at 3:1 ratio. The resulting Polydimethylsiloxane (PDMS) prepolymer was cast onto a patterned GC surface, cured at 90 °C for 1 h and then at 150 °C for additional 3 h. After PDMS was completely cured, it was peeled off the GC template. The PDMS sheet and a no. 1 glass coverslip were pressed together after being treated in air plasma for 45 s (200 mTorr, 18 W). A 200 µM F1300 fluorescein (Life Technologies) solution was flowed into the nanochannels. Fluorescence microscopy image was taken using an Axio Observer.Z1 inverted microscope (Zeiss Microscopy) with a Plan-Apochromat 63×/1.40 oil objective (Zeiss Microscopy) and an AxioCam MRm camera (Zeiss

Microscopy). A post scan of the original template confirmed no damage to original features after repeated replica molding.

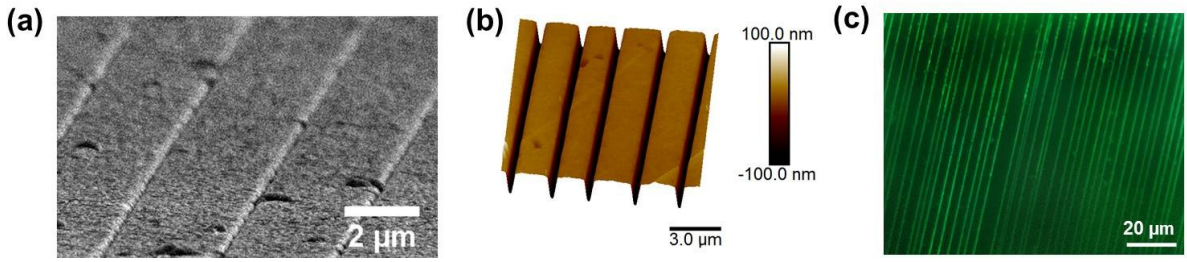

Figure S4. a) SEM image of the PDMS nanochannels created by replica molding. b) AFM image of the PDMS nanochannels. c) fluorescence microscopy image of fluorescein solution flowing through a functional PDMS nanofluidic device.

Gold nanopattern characterization

To confirm that the gold features (as shown in Fig. 3 of the manuscript) are indeed continuous, experimental measurements were conducted and the results were compared with theoretical predictions.

Experimental Measurements: We measured the conductance (G) of the unpatterned gold (Au) film, the adhesion promoting titanium (Ti) film (deposited beneath the Au film), and arrays of 300 nm wide Au nanowires at 1.8 µm spacing, all on the 2 mm diameter and 5 mm long sections of the 3D hyperbola-shaped substrate (see figure below). All measurements were performed in triplicates. The conductance of the 100 nm Au film, $G(Au\ film)_{exp}$, and the 10 nm Ti film, $G(Ti\ film)_{exp}$, were measured to be 0.124±0.014 S, and 2×10^{-4} S, respectively. The conductance of the Au nanowire array, $G(Au\ nanowires)_{exp}$, was measured to be 0.016±0.004

S. Since our measurements indicated that $G(Au\ film)_{exp} \gg G(Ti\ film)_{exp}$, we neglected the contribution of the Ti adhesion layer in our theoretical analysis below.

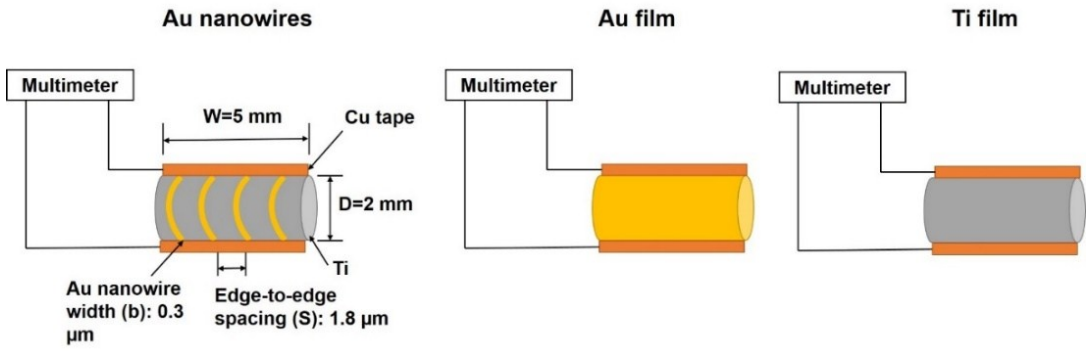

Figure S5. Schematics of Au nanowires, Au film and Ti film conductance measurements.

Theoretical Predications: Conductance is defined as $G = \sigma\ (A/l)$, where σ is the conductivity, A is the cross-sectional area perpendicular to the direction of the electric current, and l is the length of the conductor. For the nanowire array, $A = Nbh$, where N is the number of nanowires in the 5 mm wide section of the cylinder, $b = 300\ nm$ is the width of each nanowire, and $h = 100\ nm$ is the thickness of each nanowire. For the Au film, $A = Wh = N(b + S)h$, where $W = 5\ mm$ is the width of the Au film, and $S = 1.8\ \mu m$ is the edge-to-edge spacing between the nanowires. In both cases, the length of the conductor, $l = \pi D/2$, where $D = 2\ mm$ is the diameter of the cylindrical section. Given that σ, l and h are the same for the Au nanowire array and the Au film, if the Au nanowires are continuous, the conductance ratio can be calculated from:

$$\frac{G(Au\ nanowires)_{theroy}}{G(Au\ film)_{theory}} = \frac{A(Au\ nanowires)}{A(Au\ film)} =$$

$$\frac{W(Au\ nanowires)}{W(Au\ film)} = \frac{Nb}{N(b+S)} = \frac{0.3\ \mu m}{0.3\ \mu m + 1.8\ \mu m} = \frac{1}{7} = 0.143$$

The theoretical conductance ratio is in agreement with the experimentally measured ratio:

$$\frac{G(Au\ nanowires)_{exp}}{G(Au\ film)_{exp}} = \frac{0.016 \pm 0.004}{0.124 \pm 0.014} = 0.129 \pm 0.035$$

The variations in the conductance measurement data is attributed to contact resistances between the probes and the film/nanowire array. The close match between the theoretical and experimental ratios suggests that the features are continuous and free of major defects.

References:

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