Molecular Lithography through DNA mediated etching and masking of SiO_2

Supporting Information

Sumedh P. Surwade, [†,⊥] *Shichao Zhao,* [†,‡,⊥] *and Haitao Liu* [†,*]

[‡] College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, P. R. China

[†] Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A

[⊥] These authors contributed equally

[*] To whom correspondence should be addressed: hliu@pitt.edu

1. Materials

Silicon wafer with 300 nm of oxide layer was purchased from University Wafers. Synthetic and M13mp18 DNA for preparing the origami[1] were purchased from IDT and New England Biolabs, respectively. The silicon substrate was cleaned with hot piranha solution (7:3 concentrated H_2SO_4: 35% H_2O_2). *Warning: Piranha solution presents an explosion danger and should be handled with extreme care; it is a strong oxidant and reacts violently with organic materials. All work should be performed in a fume hood. Wear proper protective equipment.* Hydrofluoric acid (HF, 48%) was purchased from Mallinckrodt, NJ, USA. *Warning: HF acid is highly corrosive, poisonous and can penetrate through tissues into bones. Symptoms of exposure*

to HF may not be evident immediately and so it must be handled with extreme care. All work should be performed in a fume hood. The relative humidity inside the etching chamber was measured using a Traceable® hygrometer (Control Company, Friendswood, TX). Tapping mode atomic force microscopy was carried out on a Veeco Dimension 3100 or on an Asylum MFP 3D in air. Ultra-sharp AFM tip (tip radius 3 ± 2 nm, model #SSS-FMR, Nanosensors) was used in acquiring some of the high resolution images.

2. Methods

2.1. Triangular DNA origami preparation

The DNA origami triangles were prepared using a previously published procedure.[2] In a typical procedure, the desired set of 253 shorts strands (16 nM) were mixed with M13mp18 (1.6 nM) in a 100 μL total volume of 1X Tris-Acetate-EDTA (TAE) buffer (400 mM Tris acetate, 10 mM EDTA, 20 mM Na^+) with 12.5 mM magnesium acetate (pH=8.3), a 10 fold excess of short strands. The sample was then annealed from 95 ºC to 20 ºC at the rate of 1 ºC/min. After the completion of annealing, excess staples were removed from the origami solution by washing at least 3 times with 300 μL of TAE/Mg^{2+} buffer in 100 kDa MW centrifuge filters (Microcon YM-100, Millipore, Billerica, MA) on a single speed bench top microcentrifuge (VWR Galaxy Ministar) for 30 – 90 seconds. It is ensured that the filter is not centrifuged to dryness and there is always 50 – 100 μL of the sample left in the filter. After filtration the origami solutions were stored at 4 ºC.

The samples for AFM imaging and etching experiments were prepared as following. The filtered origami solution (5 μL) was pipetted onto a clean silicon wafer and left undisturbed for 2 hours in a closed container with its lid covered by a moistened kimwipe to minimize evaporation.

The substrate was then immersed in 1:9 TEA buffer:ethanol solution for 5 minutes to remove the salt impurities and then dried using nitrogen gas.

2.2. Alignment of λ-DNA on the SiO_2 surface

The λ-DNA used in this study was aligned on the SiO_2 substrate using a previously published procedure.[3] A 1.5 μL drop of DNA solution (40 μg/ml) in the presence of 0.45 mM $Mg(Ac)_2$ was placed on SiO_2 substrate and compressed nitrogen gas was used to drive the drop of solution to flow in one direction resulting in stretched and parallel DNA on the SiO_2 surface. The process is repeated if dense network of DNA is desired on the surface.

2.3. Etching of SiO_2 using DNA as the catalyst

The etching reaction is carried out inside a custom build chamber that encloses a temperature-controlled metal slab and three plastic open containers each filled with concentrated hydrogen fluoride (48%), isopropanol, and water[4] (~ 5 ml each). The silicon wafer containing the DNA and a water container were placed on the metal slab and the temperature of the metal slab was maintained at 25 ºC using a heating tape and a digital temperature controller. The relative humidity inside the etching chamber was ~50%. Typical etching time was 5 minutes. After the etching, the substrate was rinsed with water and piranha solution to remove the DNA. Silicon wafer containing the DNA samples were etched immediately after the deposition of DNA to avoid possible degradation of DNA on the sample substrate.

Etching time plays an important role. Etching the sample for too long or too short a time may not result in patterns on SiO_2 due to over etching or under etching of the SiO_2 substrate. Etching time under our experimental conditions was optimized at 5 min. However, depending on

the size of the etching chamber and the reservoir, the etching time may vary and thus time optimization is very important.

2.4. Etching of SiO_2 using DNA as a protective mask

The etching reaction was similar to what that in **2.3** except that the water reservoir was removed. The silicon wafer was placed on the metal slab and the temperature was maintained at 30 ºC using a heating tape and a digital temperature controller. The relative humidity inside the etching chamber was 34%. Typical etching time was 15 minutes. After the etching, the substrate was rinsed with water and piranha solution to remove the DNA. For the kinetics study shown in Figure 4, the etching time was 5, 10, 15 and 20 minutes. As mentioned earlier, etching time plays an important role and so its optimization is a key step.

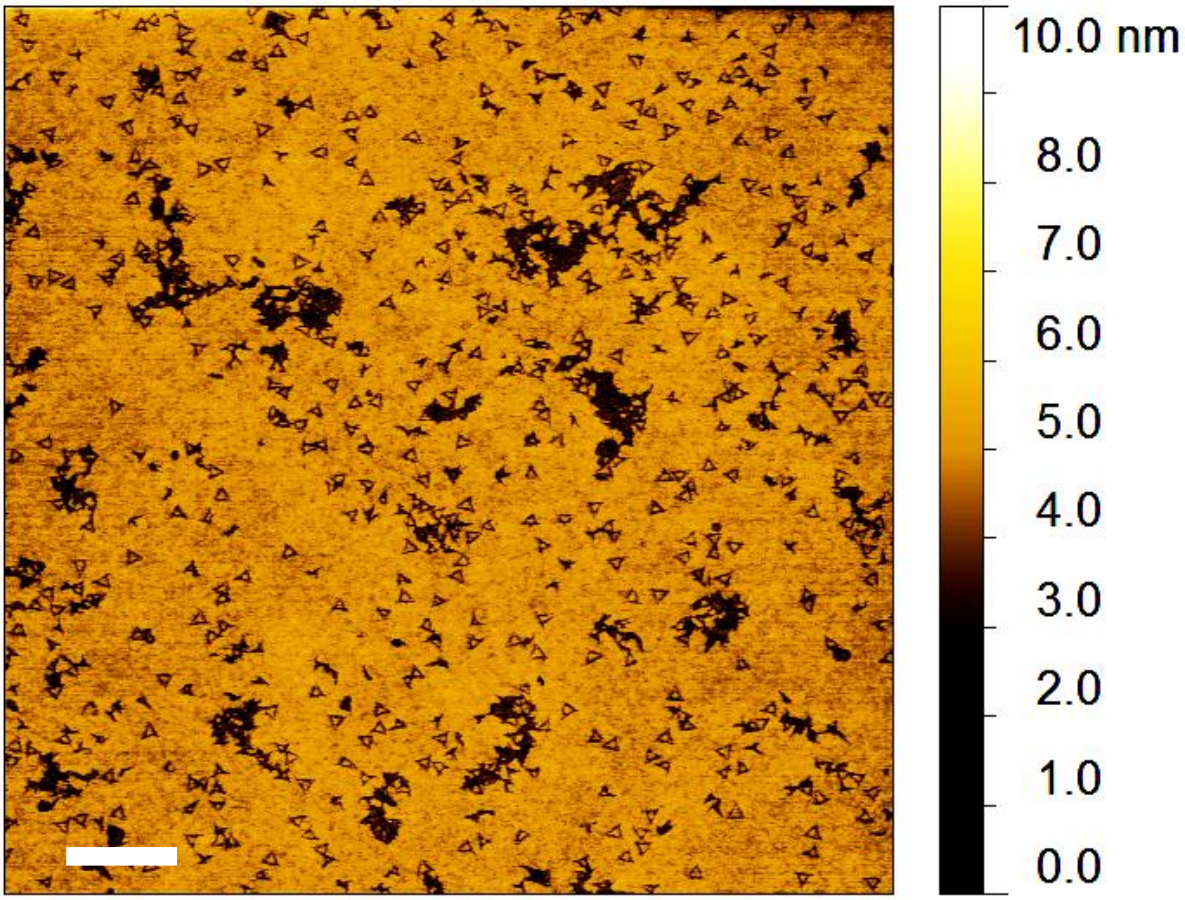

Figure S1. AFM image of triangular trenches produced upon exposure of DNA origami triangles on SiO_2 surface to HF vapor under high moisture condition. Scale bar 500 nm.

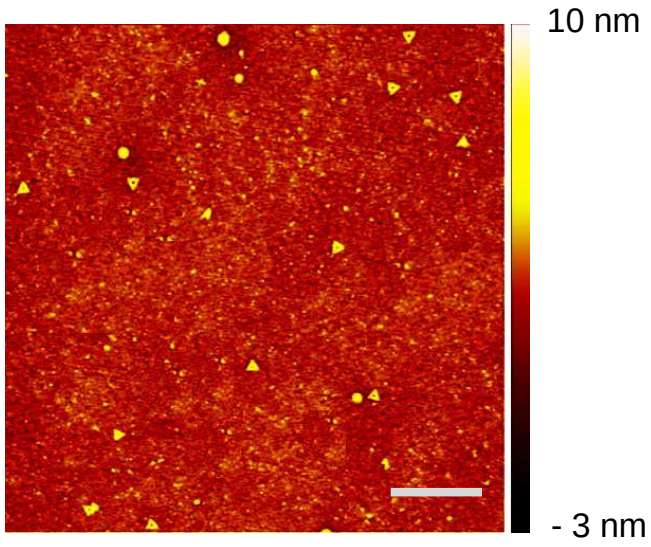

Figure S2. AFM image of triangular ridges produced upon exposure of DNA origami triangles on SiO_2 surface to HF vapor under low moisture condition. Scale bar 1 μm.

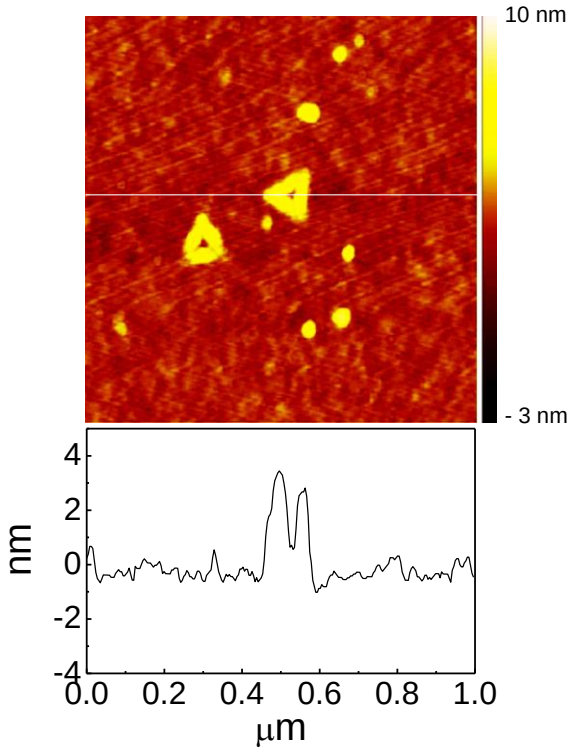

Figure S3. High magnification AFM image and cross section of triangular ridges produced upon exposure of DNA origami triangles on SiO_2 surface to HF vapor under low moisture condition.

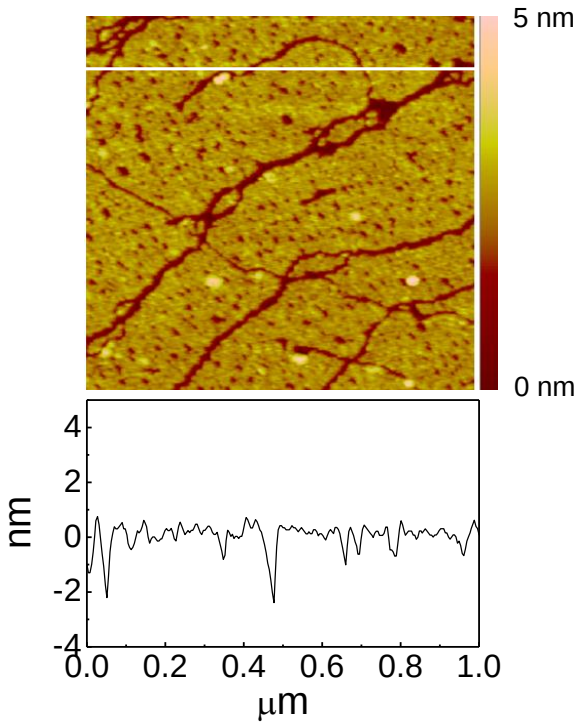

Figure S4. High magnification AFM image and cross section of trenches produced upon exposure of λ-DNA aligned on SiO_2 surface to HF vapor under high moisture conditions.

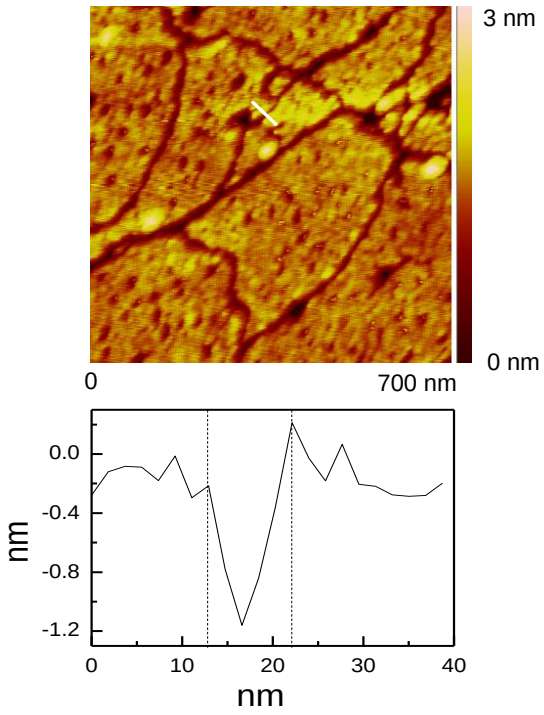

Figure S5. High magnification AFM image and the cross section of a trench showing width of ~ 5 nm (FWHM). The white line in the figure indicates location of the cross section.

	Figure 3B		Figure 3C		Figure S1		Figure S2	
	Depth	Width	Height	Width	Depth	Width	Height	Width
Average (nm)	2.57	23.4	2.83	79.4	2.13	16.7	3.16	27.0
Standard deviation (nm)	0.68	4.2	0.35	7.3	0.13	2.8	0.24	3.5

Table S1: Averages and standard deviations of the dimensions of the trenches and ridges. Data obtained from Figure 3B and Figure 3C of main manuscript and Figure S1 and Figure S2 of supplementary section. All values are full width at half max (FWHM).

References

1 Rothemund, P. W. K. Folding DNA to create nanoscale shapes and patterns. *Nature* **440**, 297-302 (2006).

2 Hung, A. M. *et al.* Large-area spatially ordered arrays of gold nanoparticles directed by lithographically confined DNA origami. *Nature Nanotech.* **5**, 121-126 (2010).

3 Deng, Z. & Mao, C. DNA-Templated Fabrication of 1D Parallel and 2D Crossed Metallic Nanowire Arrays. *Nano Lett.* **3**, 1545-1548 (2003).

4 Reinhardt, K. A. & Kern, W. Handbook of Silicon wafer Cleaning Technology (William Andrew Publishing, Norwich, NY, 2008).