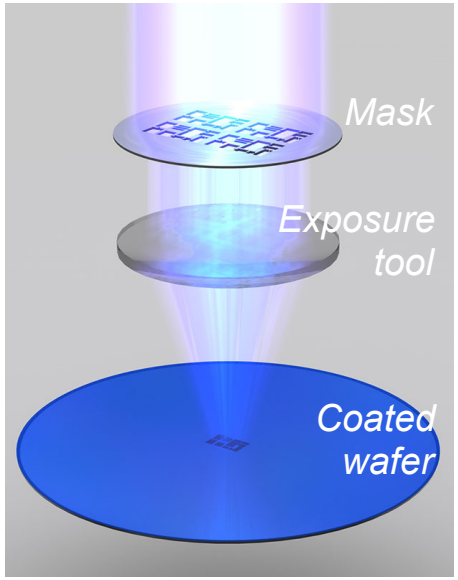
Feature processing by photo-lithography: a top-dow approach

"Photo-lithography is a process used in microfabrication to pattern parts of a thin film. It uses light to transfer a geometric pattern from a photomask to a light-sensitive chemical "photoresist" (resist) on the substrate." *(Wikipedia)*



$$\mathrm{CD} = k_1 \frac{\lambda}{\mathrm{NA}}.$$

CD: pattern resolution

λ **:** exposure wavelenght
(193nm today in production)

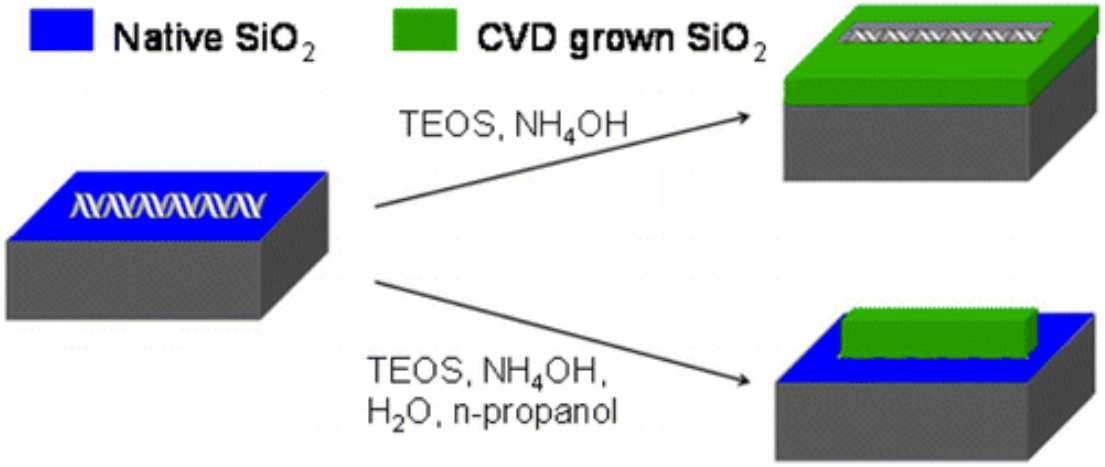
***k*$_1$, NA:** *constants*

Light wavelenght dictates patterning resolution (diffraction limits)
193 nm exposure → diffraction-limited features as small as 32 nm

Shorter wavelength: complexity of exposure optics, vaccum, cost issues… => SELF-ASSEMBLING ?

Oxide deposition (CVD) with DNA templates

When sample are exposed to a mixed vapor of $Si(OEt)_4$ (TEOS), H_2O, and NH_3, deposition of SiO_2 occurred selectively on the SiO_2 surface that was not covered by the DNA template, resulting in a negative-tone pattern of SiO_2

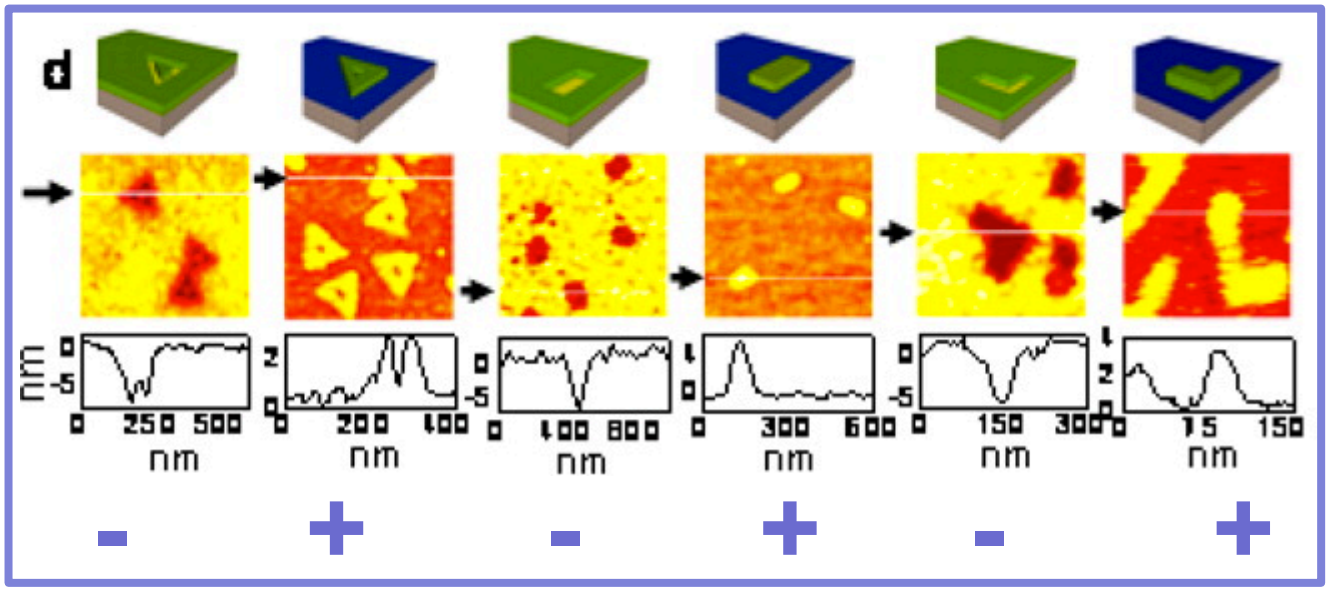


To reverse the area selectivity of the CVD, propanol vapor was introduced and the relative humidity of the reaction chamber was increased. In this case, the CVD reaction selectively deposited SiO_2 onto the DNA nanostructures to produce a positive-tone pattern

J. Am. Chem. Soc., 2013, 135, 6778–6781
DOI: 10.1021/ja401785h

Oxide deposition (CVD) with DNA templates

selective deposition of inorganic oxide onto a DNA nanostructure in the presence of a SiO2 substrate



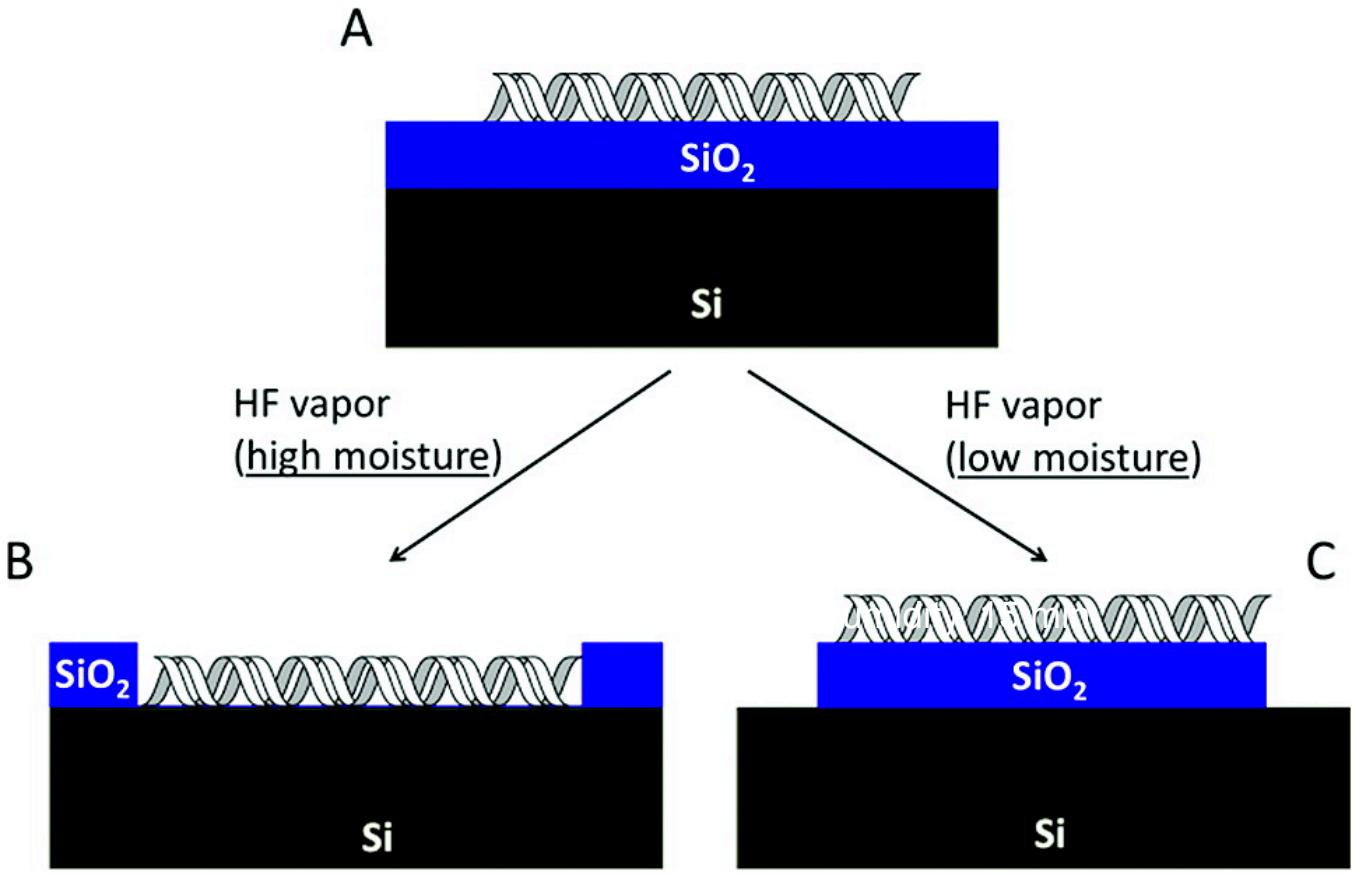
+/- presence of water/n-propanol

Oxide deposition on different substrates with <20nm lateral resolution

J. Am. Chem. Soc., 2013, 135, 6778–6781
DOI: 10.1021/ja401785h

HF « dry » etching of SiO_2 on DNA nanostructures

HF induced pattern transfer from DNA nanostructures



J. Am. Chem. Soc., 2011, 133 (31), pp 11868–11871

HF « dry » etching of SiO_2 on DNA nanostructures

HF induced pattern transfer from DNA nanostructures

$SiO_2(s) + 4\ HF(g) \rightarrow SiF_4(g) + 2\ H_2O(g)$

$6\ HF + 3\ H_2O \rightarrow 3\ HF_2^- + 3\ H_3O^+$ (deprotonation)

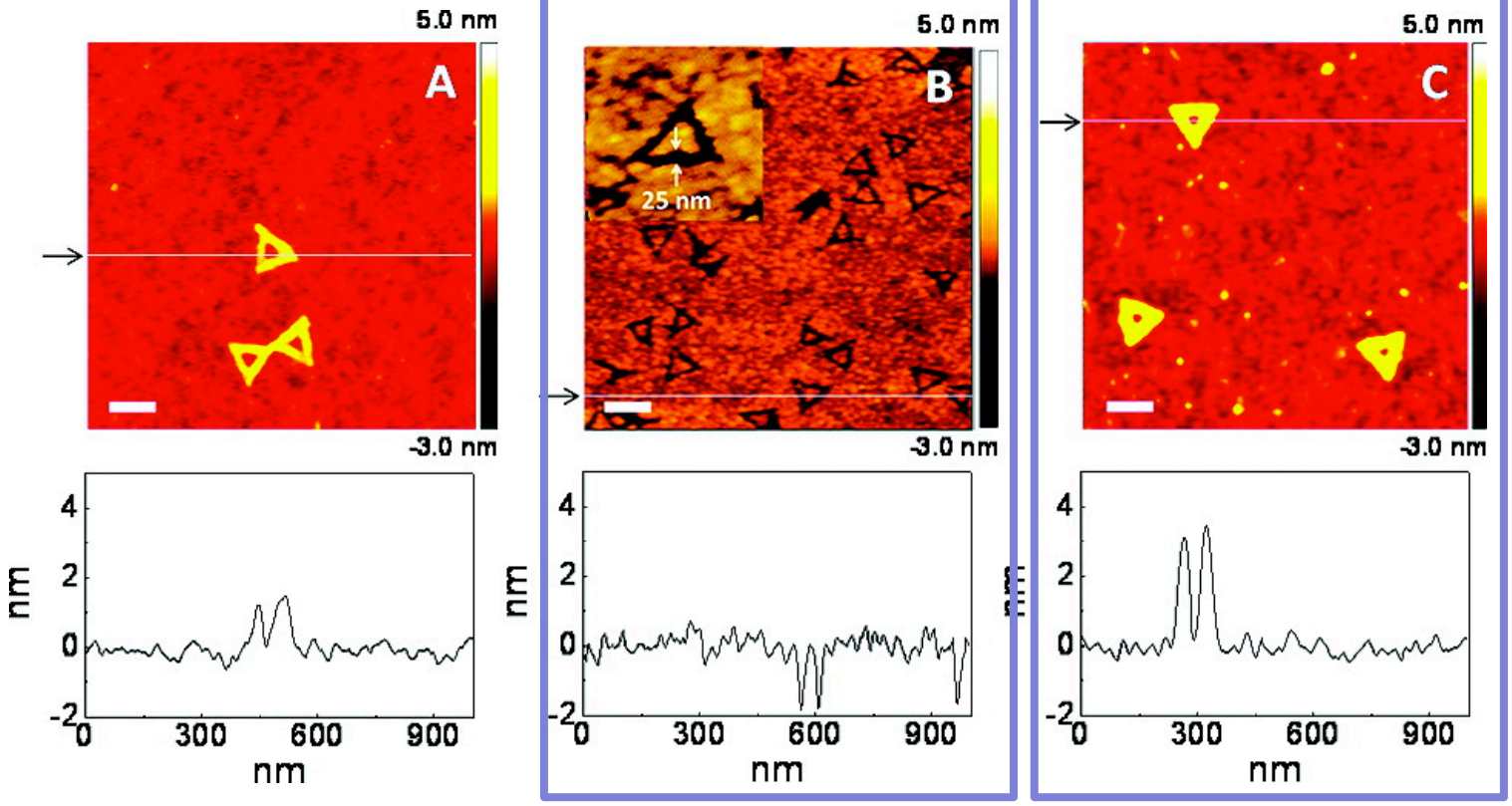
$3\ HF_2^- + 3\ H_3O^+ + SiO_2 \rightarrow 2\ HF + SiF_4 + 5\ H_2O$ (etching)

- DNA may absorb water (up to +100% w/w!) (phosphate groups)
- but DNA may also serve as a diffusion barrier after deposition on SiO_2…
- ... then H_2O content in SiO_2 adsorbed DNA may favor or inhibit **HF dry etching**

J. Am. Chem. Soc., 2011, 133 (31), pp 11868–11871

HF induced pattern transfer from DNA nanostructures

Triangular DNA origami on a SiO_2 surface

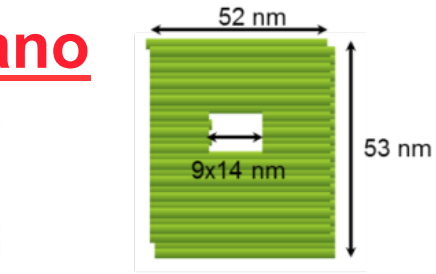


Scale bars represent 100 nm.

J. Am. Chem. Soc., 2011, 133 (31), pp 11868–11871

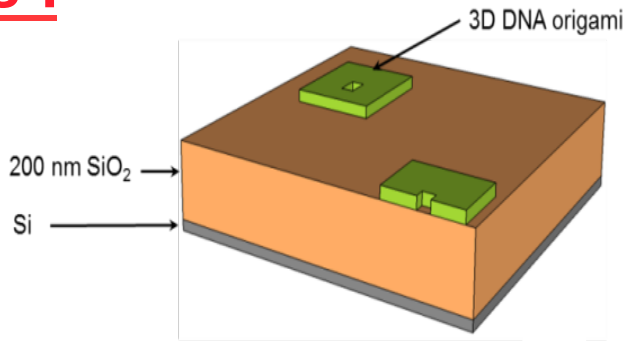
DNA Origami Mask for sub-10 nm lithography

I/ Design: cadnano



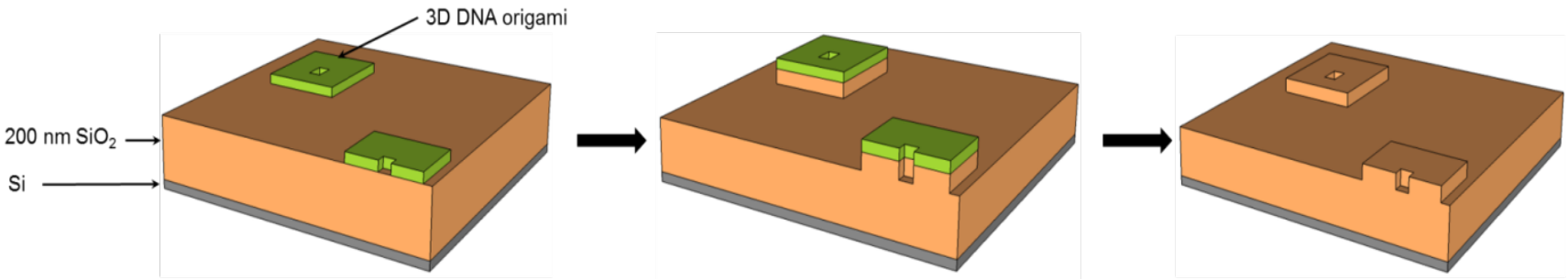
II/ Synthesis:

III/ Process :



Results from the A3DN project carried in Grenoble (R. Tiron & D. Gasparutto)

DNA Origami Mask for sub-10 nm lithography



1- DNA adsorption on Si-SiO_2 (wafer silanols and Mg^{2+} bridging of DNA origamis)

2- DNA pattern transfer by HF vapor etching (etching rate of 0.2 nm/s under mixed ethanol vapor and anhydrous HF gas at 45 °C)

3- DNA mask removal

- Process based on the ionization of HF vapor by low pressurized **alcohol** vapor, which acts as a catalyst:

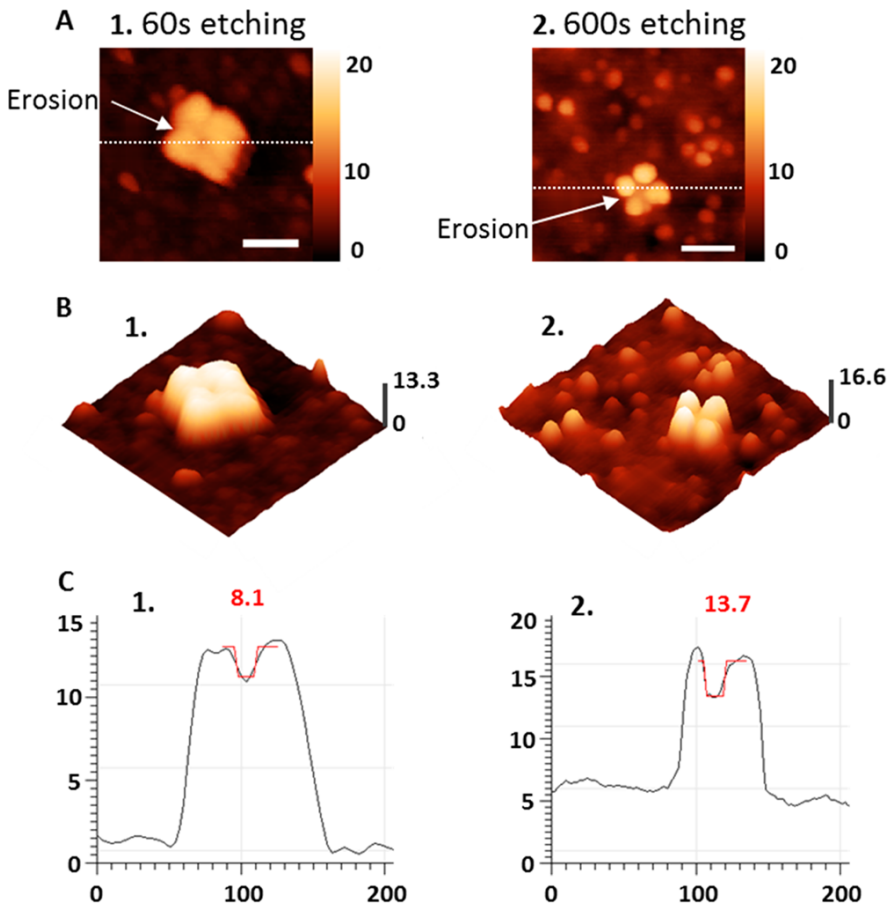
$$2HF(ads) + A(ads) \rightarrow HF_2^-(ads) + AH^+(ads)$$

$$SiO_2(s) + 2HF_2^-(ads) + 2AH^+(ads) \rightarrow SiF_4(ads) + 2H_2O(ads) + 2A(ads)$$

- Low pressure in the chamber helps in desorbing the water released upon etching

Diagne C et al.
ACS Nano. 2016 Jul 26;10(7):6458-63

Sub 10 nm-large patterns transferred onto SiO_2



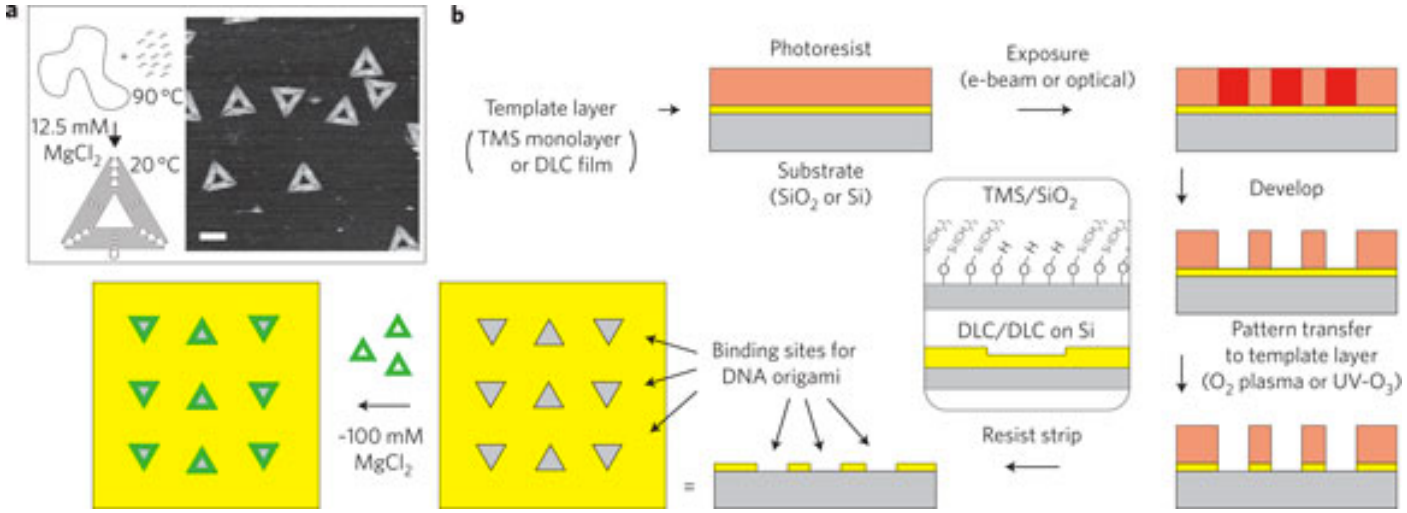
- The longer HF exposition, the deeper etching…
- Nevertheless, some erosion is observed, and motif height is 7 times lower than expected
- Blocking of the etching reaction could be explained by the reaction of magnesium (initial DNA buffer) with the hot water vapors produced during the etching reaction to form magnesium hydroxide $Mg(OH)_2$.

Diagne C et al.
ACS Nano. 2016;10(7):6458-63

Sub 10 nm-resolution using HF vapor etching
From 30 to 60 s at an etching rate of 0.2 nm/s
SiO_2 etching limited to 20nm depth (MgF_2 adlayer?)

Placement and orientation of individual DNA shapes on lithographically patterned surfaces

The problem of random DNA nanostructure deposition and lithographic scheme for addressing it:



Rothemund & al.
Nature Nanotechnology 4, 557 - 561 (2009)
doi:10.1038/nnano.2009.220