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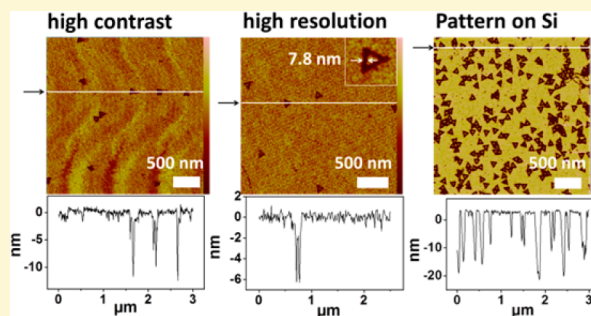
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S Supporting Information

ABSTRACT: We report a mechanistic study of a DNA-mediated vapor phase HF etching of SiO₂. The kinetics of SiO₂ etching was studied as a function of the reaction temperature, time, and partial pressures of H₂O, HF, and 2-propanol. Our results show that DNA locally increases the etching rate of SiO₂ by promoting the adsorption of water and that the enhancement effect mostly originates from the organic components of DNA. On the basis of the mechanistic studies, we identified conditions for high-contrast (>10 nm deep), high-resolution (~10 nm) pattern transfers to SiO₂ from DNA nanostructures as well as individual double-stranded DNA. These SiO₂ patterns were used as a hard mask for plasma etching of Si to produce even higher-contrast patterns that are comparable to those obtained by electron-beam lithography.



INTRODUCTION

In recent years, research in DNA nanostructures has developed to a stage in which arbitrarily shaped and mechanically robust nanostructure can be constructed^{1–8} with a theoretical precision of <5 nm at a cost as low as \$6/m².⁹ The deposition of DNA nanostructures on the substrates has been demonstrated with precise control over their location and orientation, making them ideal templates for high-resolution, low-cost nanofabrication.^{10–12} However, the pattern transfer from DNA nanostructures to inorganic substrates remains a bottleneck of this area of research. Tremendous efforts were dedicated to overcome the lack of chemical stability of DNA and the inadequate adhesion interaction between DNA and the substrate.¹³

Metallization is the most widely used approach to DNA-based nanofabrication. Solution phase metallization of λ-DNA was first demonstrated by Sivan and co-workers.¹⁴ Recently, the metallization of different metals, such as Ag, Cu, Ni, and Au, on DNA strands and DNA nanostructures has been demonstrated.^{2,15–17} In addition to the deposition of metal onto the whole nanostructure, site-specific metallization was also made possible by modifying DNA nanostructure with binding sites that accept DNA-modified Au or Ag nanoparticles.^{18–20} In addition to these solution phases approaches, vapor phase deposition of metals onto DNA has also been reported by the groups of Mao and Woolley. They used DNA to pattern vapor phase deposited metal, and the resulting metal film can be used as a hard mask for patterning the underlying substrate.^{21–23}

Our group recently showed that DNA nanostructures can modulate certain surface reactions to produce a faithful pattern

transfer from the DNA nanostructures to an inorganic substrate.^{24,25} In one of the studies, DNA was shown to have a local effect on the vapor phase HF etching, which resulted in direct negative-tone and positive-tone pattern transfers from DNA to SiO₂.²⁴ The fact that DNA can be used to directly pattern SiO₂ carries significant technological significance because SiO₂ is one of the most important hard mask materials for semiconductor nanofabrication.²⁶

Although our early study established vapor phase HF etching as a promising approach to pattern transfer to SiO₂, several important scientific and technical questions were left unanswered. Specifically, the mechanism of the modulation effect of DNA has not been firmly established, although it was hypothesized that adsorption of water vapor on the surface plays an important role.²⁴ In addition, the kinetic behavior of the reaction has not been extensively explored, and consequently, the reaction conditions for pattern transfer have not been optimized for high resolution and contrast. As a result, the pattern transfer typically produced trenches (ridges) that are only 2–3 nm in depth (height).²⁴ For practical applications, a much higher vertical contrast is needed. In a similar vein, the lateral resolution of the pattern transfer was limited to ~17 nm. Although this is an impressive resolution, it is on par or worse than that of the state-of-the-art photolithography and electron-beam lithography.

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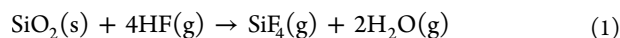
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This work aims to address these challenges by characterizing the detailed kinetic behavior of the DNA-mediated HF etching reaction. In addition to probing the mechanism of DNA-mediated HF etching, the kinetic studies also produce a set of design rules that can be used to guide the optimization of reaction conditions for high-resolution, high-contrast pattern transfer. Our result shows that DNA promotes vapor phase HF etching of SiO₂ by enhancing the adsorption of water near itself; the organic moieties of DNA make the major contribution to the enhancement effect. On the basis of these results, we identified optimized pattern transfer conditions that produce high-resolution (~10 nm), high-contrast (>10 nm) pattern transfer to SiO₂. The SiO₂ patterns generated by DNA can be used as a hard mask for plasma etching of Si to produce high-contrast, high-resolution features that are comparable to those produced by electron-beam lithography.

RESULTS AND DISCUSSION

The overall reaction of vapor phase HF etching of SiO₂ is shown in eq 1:



Several mechanisms have been proposed for this reaction.^{27–29} It is generally accepted that this reaction is initiated by condensation of HF and water vapors on the SiO₂ surface. Water is both a catalyst and a reaction product, which makes the overall reaction autocatalytic.³⁰ Therefore, the reaction rate will depend on the concentrations of adsorbed water and HF on the surface, both of which are ultimately determined by the vapor pressure of water ($p^{\text{H}_2\text{O}}$), the vapor pressure of HF (p^{HF}), the reaction time (t), and the temperature (T) of the sample. In addition to these four parameters, we are also interested in the effect of the vapor pressure of 2-propanol (p^{IPA}). An alcohol additive is known to decrease the surface roughness of SiO₂ in a HF vapor etching reaction and has been extensively used in such reactions; however, its impact on the etching kinetics and quality of pattern transfer has not been studied.³¹ Finally, DNA nanostructures are anchored onto SiO₂ via electrostatic interaction mediated by surface-adsorbed Mg²⁺. The presence of Mg²⁺ ion and other ionic species near the DNA may also affect the etching rate by directly promoting the ionization of HF or indirectly through changing water adsorption.³²

In this study, we chose the triangular-shaped DNA nanostructure as a model to study the effect of the aforementioned parameters on pattern transfer. The triangular-shaped DNA nanostructure was used because it does not aggregate and offers several structural features (e.g., linear sides, central void, sharp tips, and presence of a double-strand tail) that are useful in assessing the quality of the pattern transfer.³³

In a typical experiment, the triangular-shaped DNA nanostructures were deposited onto a silicon wafer that has a 300 nm thick thermally grown SiO₂ layer. The silicon wafer with deposited DNA was then etched using a home-built etching setup. In this setup, vapors of HF, H₂O, and 2-propanol were supplied by passing N₂ through the respective bubblers. The N₂ streams were then combined, and the flow rate of the N₂ carrier gas determines the partial pressure of each reagent. A detailed description of the setup can be found in the Supporting Information (Figure S1).

In this study, we will focus on reaction conditions that produce the negative-tone pattern transfer, i.e., cases in which DNA increases the etching rate. During the vapor phase etching process, the entire SiO₂ surface, regardless of the presence of

the DNA nanostructures, was etched (Figure 1). The DNA nanostructure, however, increases the etching rate of SiO₂ near

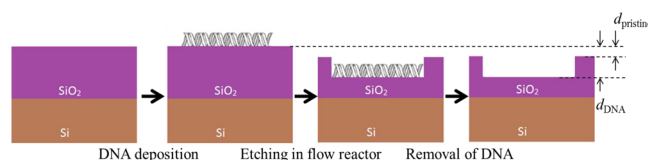


Figure 1. Change in geometry during the DNA-mediated HF etching of SiO₂.

its immediate vicinity. It was hypothesized that the enhancement effect is due to its ability to promote water adsorption near itself.²⁴ However, direct measurement of a monolayer amount of water on a SiO₂ surface with sub-10 nm resolution is extremely challenging, if not impossible. To overcome this challenge, we extract the magnitude and spatial extent of the enhancement effect of DNA from the vertical contrast and lateral resolution of the resulting pattern, respectively. The width of the trench was typically measured at the center of the sides. The depth measurement, however, could be limited by the narrow width and may not reflect the true topography (see below). For this reason, we perform depth measurement at the apexes of the triangle instead.

Two sets of data are especially relevant to understanding the kinetic behavior of the etching reaction. As shown in Figure 1, the first is the thickness (d_{pristine}) of SiO₂ removed in the absence of DNA and the corresponding average etching rate (v_{pristine}). The second is the thickness of SiO₂ removed (d_{DNA}) and the corresponding average etching rate in the presence of DNA (v_{DNA}). We note that the etching rate of SiO₂ is likely to be time-dependent because of the autocatalytic nature of the reaction. In our experiments, we used ellipsometry and atomic force microscopy (AFM) to measure the average thickness of SiO₂ and the depth of the trench, respectively. The surface coverage of the trenches is usually <8%, and therefore, the change in the SiO₂ thickness reported by ellipsometry should reflect d_{pristine} . The depth of the trench reflects the difference between d_{pristine} and d_{DNA} .

Kinetics Behavior of the DNA-Mediated HF Etching of SiO₂. *Effect of the Reaction Time.* Figure 2A shows the change in the overall thickness of the SiO₂ layer (i.e., d_{pristine}) as a function of reaction time while keeping all other parameters fixed ($p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 2096$ Pa, and $T = 30$ °C). The related AFM images are shown in Figure S2 of the Supporting Information. The thickness change shows a superlinear increase over time. This is consistent with the hypothesis that the etching reaction is autocatalytic: as the reaction progresses, more water is produced and the reaction rate will increase until the formation and desorption of water reach equilibrium. At long reaction times, we also noticed an increase of surface roughness (Figure S2 of the Supporting Information) and a significant deterioration of the quality of the transferred pattern.

The trench depth showed a more complex time dependence. Figure 2F shows the time evolution of the trench depth for two reactions conducted at 35 and 30 °C; in both series, all other reaction conditions were fixed ($p^{\text{HF}} = 178$ Pa, $p^{\text{H}_2\text{O}} = 1118$ Pa, and $p^{\text{IPA}} = 293$ Pa). The corresponding AFM images are shown in Figures S3 and S4 of the Supporting Information. Although the difference in the reaction temperature was only 5 °C, the two reactions showed very different behavior. At 35 °C, we observed a continuous, almost linear increase in the trench

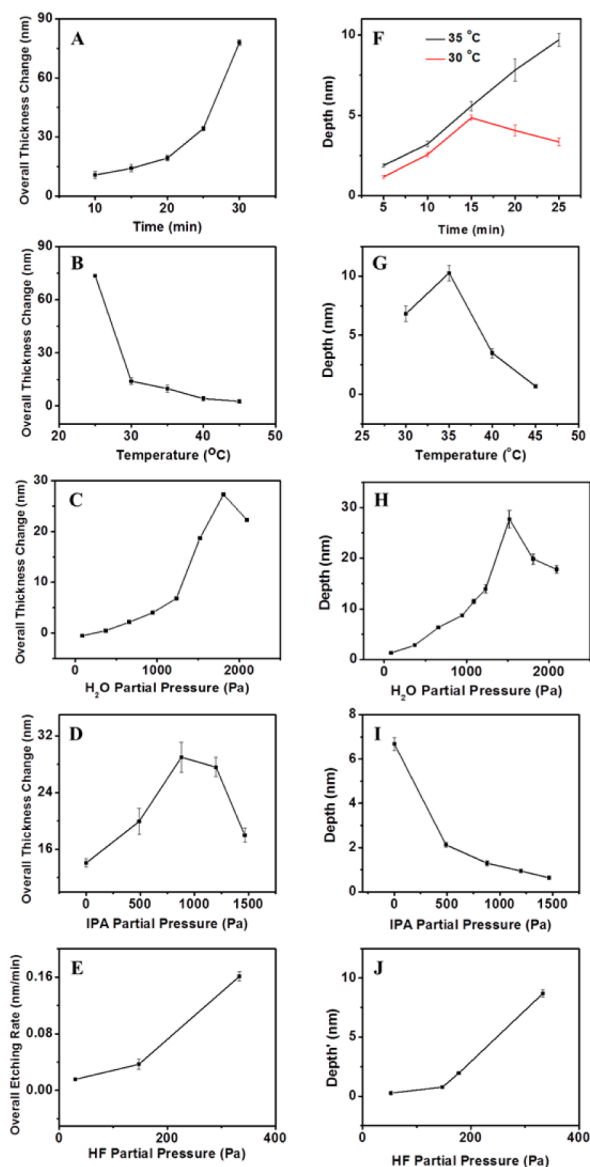


Figure 2. Kinetics of vapor phase HF etching of SiO₂. (A) $p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 2096$ Pa, $T = 30$ °C, and t varied from 10 to 30 min. (B and G) $p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 2096$ Pa, $t = 15$ min, and T varied from 25 to 45 °C. (C and H) $p^{\text{HF}} = 333$ Pa, $T = 35$ °C, $t = 20$ min, and $p^{\text{H}_2\text{O}}$ varied from 83 to 2096 Pa. (D and I) p^{IPA} varied from 0 to 1467 Pa (see the Supporting Information for details). (E and J) $p^{\text{H}_2\text{O}} = 946$ Pa, $T = 35$ °C, and p^{HF} varied from 30 to 333 Pa. The etching time was adjusted to obtain comparable contrast in the AFM image. The depth shown here is the expected value for the same etching duration (20 min), assuming the etching rate is independent of time. See the Supporting Information for details. (F) $p^{\text{HF}} = 178$ Pa, $p^{\text{H}_2\text{O}} = 1118$ Pa, $p^{\text{IPA}} = 293$ Pa, and t varied from 5 to 25 min.

depth, indicating that the difference in the two etching rates (i.e., v_{pristine} and v_{DNA}) is a constant during this reaction. In contrast, the reaction conducted at 30 °C showed an initial increase in the trench depth that peaked at 15 min, followed by an eventual decrease.

These results can be explained if we assume that enough water was produced at 15 min and 30 °C to saturate the entire surface. At an even longer etching time, the etching becomes nonselective as DNA cannot further enhance water adsorption. At 35 °C, it takes longer to saturate the surface with water because of the faster desorption of water; as a result, the etching

remains selective, and the trench depth showed a more persistent increase. However, even at 35 °C, the surface roughness still increased significantly after reaction for 20 min, and the quality of the pattern transfer deteriorated as a result. The optimal etching time is 15 or 20 min under these conditions.

Effect of the Reaction Temperature. To study the effect of temperature on the pattern transfer, we conducted the etching experiment between 25 and 45 °C while keeping all other parameters fixed ($p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 2096$ Pa, and $t = 15$ min). Figure 2B shows the change in SiO₂ thickness measured by ellipsometry (i.e., $\Delta d_{\text{pristine}}$) as a function of substrate temperature. It can be seen that v_{pristine} decreased drastically as the temperature was increased. This observation is consistent with the idea that the adsorption of water and/or HF is inhibited at high temperature and therefore the etching rate decreases as temperature increases.

Interestingly, the depth of the trench showed a very different response to a change in temperature. As shown in Figure 2G and Figure S5 of the Supporting Information, when the reaction temperature was increased from 30 to 45 °C, the trench depth initially increased and then decreased. To understand this observation, we again note that water is a reaction product and, if not removed by desorption, will eventually saturate the surface. If the temperature is too low, the water produced by the etching reaction will quickly saturate the entire surface, regardless of the presence of DNA. As a result, the DNA will not selectively increase the etching rate. The opposite situation will occur if the temperature is too high, in which case, water desorbs from the entire surface, regardless of the presence of DNA. The effect of DNA in modulating water adsorption will be most pronounced in the intermediate temperature range.

Effect of the Partial Pressure of Water. The effect of $p^{\text{H}_2\text{O}}$ was studied by adjusting the flow rate of wet and dry N₂ while keeping the overall flow rate constant. We assumed that the N₂ is fully saturated with water after passing through the water bubbler and also took into account the water vapor from the HF/H₂O reservoir to calculate $p^{\text{H}_2\text{O}}$ in the etching chamber.

Figure 2C shows the change in SiO₂ thickness when $p^{\text{H}_2\text{O}}$ was varied from 83 to 2096 Pa while all other parameters were kept fixed ($p^{\text{HF}} = 333$ Pa, $T = 35$ °C, and $t = 20$ min). It is clear that increasing $p^{\text{H}_2\text{O}}$ resulted in an increase in v_{pristine} , presumably because of an increase in the adsorption of H₂O. There is a slight decrease in the etching rate at a very high $p^{\text{H}_2\text{O}}$ that we attributed to the dilution of adsorbed HF on the surface. Figure 2H shows that the trench depth increased drastically as $p^{\text{H}_2\text{O}}$ increased, indicating that at higher humidity, the H₂O absorption is favored near the DNA. The small decrease at a very high $p^{\text{H}_2\text{O}}$ may be due to water saturation on the entire surface, as we discussed previously. Overall, data in Figure 2H are consistent with the fact that water adsorption on DNA is much more sensitive to the increase in relative humidity than that on SiO₂: the amount of absorbed water on SiO₂ increases by only 40% when the relative humidity increases from 0 to 85%.³⁴ In contrast, DNA shows an increase of 2800% in water adsorption when the relative humidity increases from 0 to 98%.³⁵

AFM imaging showed that the quality of the transferred patterns was high (e.g., narrow outlines with a preserved central island feature) when $p^{\text{H}_2\text{O}}$ was <1090 Pa (Figure S6A–E of the Supporting Information). However, at higher $p^{\text{H}_2\text{O}}$ values, the central island features were not preserved and instead became

triangular-shaped holes (Figure S6F–I of the Supporting Information). These observations suggest that as water saturates the DNA, the etching reaction loses its spatial selectivity. In addition, the surface roughness also became worse at high $p^{\text{H}_2\text{O}}$ values, because of the high overall etching rate (also see below). For these reasons, a low $p^{\text{H}_2\text{O}}$ (~ 946 Pa) provides the best balance between the contrast and the quality of the pattern transfer.

Effect of the Partial Pressure of 2-Propanol. A smooth surface is essential to obtain high-quality and faithful pattern transfer. For this reason, we previously introduced alcohol vapor into the etching reaction mixture because it is known to reduce the surface roughness of the HF vapor phase etching.²⁴ However, its effect on the kinetics and selectivity of DNA-mediated etching has not been reported. Here we investigate the effect of 2-propanol on the surface roughness and etching kinetics.

In this set of experiments, we fixed the flow rates of HF and H_2O carrier gases and adjusted the flow rate of 2-propanol carrier gas to change p^{IPA} . With an increasing p^{IPA} , the overall SiO_2 thickness change initially increased and then decreased (Figure 2D). It was proposed by Novak and co-workers that at low p^{IPA} values, a 2-propanol monolayer was formed on SiO_2 ; this monolayer could trap water and lead to an increase in the etching rate at low p^{IPA} values.³⁶ It is not clear what caused the decrease in the etching rate at high p^{IPA} values. One possibility is that 2-propanol and water could form a low-boiling point azeotrope mixture (bp 80.79°C) on the surface, facilitating the desorption of water.³⁷ We also note that this behavior is similar to that observed at high $p^{\text{H}_2\text{O}}$ values, suggesting the dilution of adsorbed HF may be another contributing factor.

Figure 2I shows the trench depth for the same set of experiment. We find that the introduction of 2-propanol reduced the trench depth, indicating that it reduces the selectivity of SiO_2 etching between pristine and DNA-covered SiO_2 (Figure S7 of the Supporting Information). Although the roughness indeed decreased at high p^{IPA} values (Figure S8 of the Supporting Information), this benefit does not justify its use in our reaction.

Effect of the Partial Pressure of HF. Figure 2E shows the average etching rate of SiO_2 in the absence of DNA as a function of p^{HF} . A monotonic increase in the etching rate was observed. This behavior is expected because increasing the partial pressure of HF (p^{HF}) should increase the adsorption of HF and thereby increase the SiO_2 etching rate. When all other conditions were fixed ($p^{\text{H}_2\text{O}} = 946$ Pa, and $T = 35^\circ\text{C}$), increasing p^{HF} (Figure 2J and Figure S9 of the Supporting Information) resulted in an increase in the trench depth, which indicates that the etching selectivity ($v_{\text{DNA}}/v_{\text{pristine}}$) also increased with an increasing p^{HF} . However, a very high p^{HF} is not desirable because the surface roughness increases significantly under these conditions (Figure S9 of the Supporting Information and also below).

Correlation between the Overall Etching Thickness and Roughness. In Figure S10 of the Supporting Information, we plot the surface roughness as a function of the overall thickness change (d_{pristine}) for the experiments shown in Figures S2–S6 of the Supporting Information. Although these experiments were conducted under very different conditions, a consistent trend is that a larger thickness change is correlated with a larger surface roughness. Because the quality of transferred pattern will be negatively impacted by a large surface roughness, an optimized condition should produce a small d_{pristine} .

Optimized Pattern Transfer Conditions. Our kinetic studies suggest the following design rules for achieving high-quality pattern transfers. (1) An intermediate reaction time is preferred. At short reaction times, the contrast is not fully developed; however, long reaction times may lead to nonselective etching because of the saturation of water on the entire surface. (2) An intermediate reaction temperature is preferred. A very low reaction temperature results in fast etching even in the absence of DNA; an overly high temperature is detrimental because water adsorption is inhibited regardless of the presence of DNA. (3) Intermediate water and HF partial pressures are preferred. An increase in the partial pressure of water and HF results in an increase in the overall etching rate and the contrast of the transferred pattern. However, surface roughness also increases at high etching rates, and the pattern transfer deteriorates as a result. (4) 2-Propanol is not desirable, as its presence will generally decrease etching selectivity.

On the basis of these results, we identified two conditions for high-resolution, high-contrast pattern transfer: condition A, $p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 1090$ Pa, $T = 35^\circ\text{C}$, and $t = 20$ min; condition B, $p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 658$ Pa, $T = 35^\circ\text{C}$, and $t = 20$ min. Under condition A, the triangular trenches obtained on SiO_2 were 11.8 ± 0.3 nm in depth (measured at the apexes of the triangle) and the full width at half-maximum (fwhm) of the edges was 14 ± 1 nm (Figure 3A). Compared to our previous

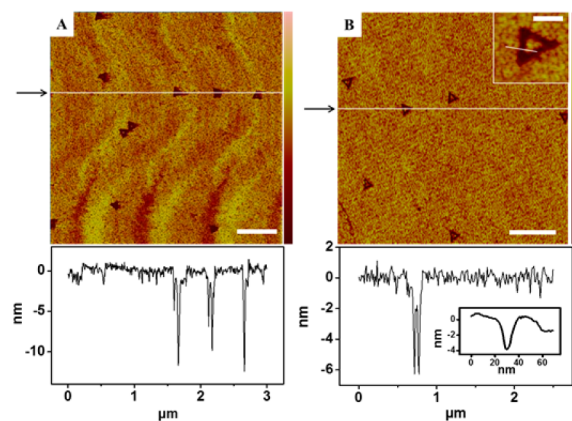


Figure 3. AFM images and cross sections of the deepest (A) and narrowest (B) trenches of the triangular patterns produced by optimized pattern transfer conditions A and B, respectively. The white line in the top inset of panel B indicates the location of the cross section shown in the bottom inset. The wavy lines with $\sim 1\ \mu\text{m}$ periodicity in panel A were artifacts. The color scale bars represent 10 nm in both images. The white scale bars represent 500 nm, and the scale bar in the inset represents 100 nm.

work, this study improved the trench depth by ~ 5 times. The surface roughness was 0.404 nm, which is only 3.5% of the depth of the trench. The overall thickness change of the SiO_2 layer was 6.82 ± 0.32 nm, which translates to an etching selectivity ($v_{\text{DNA}}/v_{\text{pristine}}$) of 2.73. These results could be reproduced on both 300 nm SiO_2 grown on a $\text{Si}[100]$ wafer and 15 nm SiO_2 grown on a $\text{Si}[110]$ wafer in a period of 2 months. Under condition B, an even higher resolution can be obtained at the expense of a reduced contrast. The fwhm of the trenches was reduced to 11 ± 1 nm, while the depth was 6.0 ± 1.5 nm (both measured on the sides of the triangle). The inset of Figure 3B shows a pattern that is 7.8 nm in width (fwhm), which is smaller than that of the DNA template (28.6 nm).

Although we do not know the detailed reason behind this observation, we speculate that the center of the origami arm is more effective in catalyzing the etching reaction, likely because water is least likely to desorb from these locations. However, we also note that the tip deconvolution effect will make the trenches appear to be narrower and additional work is needed to quantify this contribution.

Mechanistic Studies and Lithography Enabled by the Optimized Pattern Transfer Condition. Compared to our previous results,²⁴ the new pattern transfer condition offers an up to 5-fold increase in the depth and a 50% reduction in the width of the trench. These improvements make it possible to answer additional mechanistic questions and also allow further patterning approaches, as detailed below.

Role of the Salt Residue in the Etching Reaction. DNA has both organic (i.e., bases and sugar) and inorganic components (i.e., phosphate backbone and counterions), and each may play a different role in the pattern transfer. To decompose their effect, we have investigated the effect of inorganic salt on the HF etching reaction. In addition to the phosphate backbone and counterion, salt may also accumulate on a deposited DNA nanostructure from the buffer solution, either through selective adsorption or as a result of solvent evaporation. For example, it is known that Mg^{2+} ions adsorb on the SiO_2 surface and play a critical role in anchoring the DNA nanostructure onto the surface.¹² The salt residues could impact the etching rate either by directly promoting the ionization of HF or by indirectly changing the thermodynamics of water adsorption.

To remove all organic components from the DNA, we performed UV/ozone treatment on DNA samples deposited on SiO_2 .³⁸ UV/ozone treatment is a well-established method for oxidatively removing organic species on a surface.³⁹ The SiO_2 surface was characterized by AFM before and after the treatment, and the data are shown in Figure 4. Surprisingly,

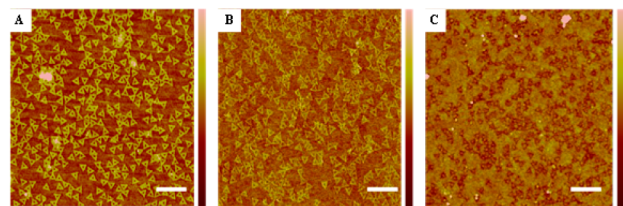


Figure 4. AFM images of (A) DNA nanostructures on the SiO_2 substrate, (B) the salt residue on the surface after UV/ozone treatment for 3 h, and (C) the triangular trench produced by HF vapor etching ($p^{\text{HF}} = 333 \text{ Pa}$, $p^{\text{H}_2\text{O}} = 1090 \text{ Pa}$, $T = 35^\circ\text{C}$, and $t = 20 \text{ min}$). The height bars represent 5 nm. The scale bars represent 500 nm.

we found that the triangular patterns persisted even after UV/ozone treatment for 3 h, although their height did show a significant decrease from 1.59 ± 0.19 to $0.93 \pm 0.26 \text{ nm}$. X-ray photoelectron spectroscopy (XPS) confirmed the elimination of nitrogen in DNA and the preservation of Mg^{2+} on the surface (Figure S11 of the Supporting Information). The absence of nitrogen suggests that the organic components were completely removed, and therefore, we attribute the triangular pattern to the inorganic salt residues associated with DNA nanostructures (Figure 4B).

We found that the inorganic residue can produce shallow trenches ($0.94 \pm 0.29 \text{ nm}$, measured at the apexes of the triangle) when it is subjected to HF vapor phase etching [$p^{\text{HF}} = 333 \text{ Pa}$, $p^{\text{H}_2\text{O}} = 1090 \text{ Pa}$, $T = 35^\circ\text{C}$, and $t = 20 \text{ min}$ (Figure

4C)]. Although we do not know the mechanistic details, it is clear that the salt could enhance the HF vapor etching of SiO_2 .⁴⁰ However, the depth of the trench is significantly smaller than those obtained under the same condition using the DNA nanostructure template ($11.8 \pm 0.3 \text{ nm}$, measured at the apexes of the triangle), suggesting that the organic component of DNA plays a major role in the enhanced etching.

Pattern Transfer from Individual DNA Strands. An intriguing question about DNA-mediated HF etching is its resolution limit and, in particular, whether the pattern transfer can be achieved with a single DNA strand. We previously showed that λ -DNA, when stretched and deposited onto a SiO_2 , can enhance the HF etching rate to produce trenches.²⁴ However, the presence of DNA bundles makes it difficult to definitively conclude if the resulting patterns were from an individual double-stranded DNA.

In this study, we observed that many triangular-shaped trenches were accompanied by a small tail ($2.0 \pm 0.4 \text{ nm}$ in depth and $7 \pm 1 \text{ nm}$ in width), located in the middle of one of the sides (Figure 5). We believe that this tail is produced by the

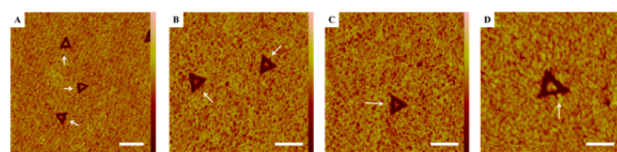


Figure 5. High-magnification AFM images of etching results to show the presence of a tail, as indicated by the arrow. The height bar represents 5 nm in panels A–D. The scale bar represents 250 nm in panels A–C and 100 nm in panel D.

97-base loop of the DNA nanostructure (Figure S13A of the Supporting Information); secondary structure analysis suggests that this loop likely exists in a linear structure (Figure S13B of the Supporting Information).⁴¹ This result clearly indicates that even a single double-stranded DNA is capable of enhancing the local etching rate of SiO_2 .

Pattern Transfer on the Si Surface Using Plasma Etching.

The newly developed pattern transfer conditions offer much higher contrast and therefore the possibility to etch through a thin ($\sim 10 \text{ nm}$) SiO_2 film. The SiO_2 pattern thus produced could then be used as a hard mask for patterning the underlying substrate, such as Si. To demonstrate this possibility, we used a silicon wafer with 15 nm of thermal oxide to conduct the DNA-mediated HF etching. After the vapor HF etching and removal of DNA templates using UV/ozone treatment, AFM imaging showed that the trenches have a depth (measured at the apexes of the triangle) of $6.8 \pm 0.5 \text{ nm}$ and a width (measured at the sides of the triangle) of $12 \pm 2 \text{ nm}$ (Figure 6A and Figure S14 of the Supporting Information). The wafer was then subjected to a SF_6/O_2 plasma that preferentially etches Si ($\text{Si}:\text{SiO}_2$ etching selectivity ratio of 50:1).⁴² After the plasma etching, the depth of the trench (measured at the apexes of the triangle) increased from 6.8 ± 0.5 to $10.3 \pm 2.1 \text{ nm}$ (Figure 6B and Figure S14 of the Supporting Information); the surface roughness also increased by almost 4 times from 0.20 ± 0.01 to $0.76 \pm 0.05 \text{ nm}$. We then selectively removed the top SiO_2 layer by etching with a solution of 5% HF and observed triangular trenches on the underlying Si substrate. As shown in Figure 6C and Figure S14 of the Supporting Information, the depth of the trenches increased to $18.4 \pm 2.7 \text{ nm}$ (measured at the apexes of the triangle) while the fwhm is $19 \pm 4 \text{ nm}$

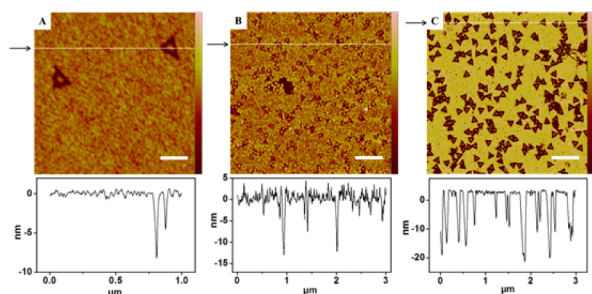


Figure 6. AFM images and cross sections of (A) triangular trenches produced by HF etching ($p^{\text{HF}} = 333$ Pa, $p^{\text{H}_2\text{O}} = 946$ Pa, $T = 35$ °C, and $t = 20$ min), (B) the same sample after it had been subjected to SF_6/O_2 plasma etching for 5 s, and (C) triangular patterns on the same sample after removal of the top SiO_2 film by immersion in a 5% HF solution for 30 min. Arrows indicate lines of cross section. The color scale bar represents 5 nm in panel A and 10 nm in panels B and C. The scale bar represents 200 nm in panel A and 500 nm in panels B and C.

(measured at the sides of the triangle). The surface roughness was 0.27 ± 0.01 nm. It is interesting to note that the depth of the trench increases after removing the top SiO_2 layer. Noting that the width of the trench also increased after removing SiO_2 , we believe that the depth measurement before removing SiO_2 was limited by the narrow trench (i.e., the AFM tip is unable to probe the bottom of the trench) and did not reflect the true geometry of the trench.

CONCLUSIONS

In conclusion, we have studied the kinetic behavior of the DNA-mediated HF etching of SiO_2 . Our result is consistent with the idea that DNA promotes the HF etching of SiO_2 by enhancing the adsorption of water in its vicinity. We identified two optimized pattern transfer conditions that can reproducibly produce patterns with 11 nm resolution and high contrast. The as-patterned SiO_2 layer was used as a hard mask for plasma etching to produce sub-20 nm features in the Si substrate. These results highlight the potential of DNA nanostructure as a template for general-purpose nanofabrication.

ASSOCIATED CONTENT

Supporting Information

Experimental details and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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