Etching Block Copolymer Directed Self-Assembly Holes

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Introduction:

As chipmakers contemplate patterning at the 5 nm node and beyond, finding costeffective lithography solutions for high-resolution patterning is increasingly challenging. Already, multiple patterning with 193 nm immersion lithography is the norm [1], and extreme ultraviolet (EUV) lithography is expected to be implemented by foundries at the 7 nm node [2]. Even so, the high costs of these technologies have left room in the lithography ecosystem for low-cost alternatives, such as block copolymer directed self-assembly (DSA). A block copolymer is composed of two distinct polymer blocks bonded end-to-end. When a block copolymer film is heated, the polymers self-assemble into their minimum free energy position. For the industry-standard PS-*b*-PMMA block copolymer [3] composed of 70% PS and 30% PMMA, free energy is minimized through self-assembly into an array of hexagonally packed PMMA cylinders in a PS matrix (see Figure 1-b). After self-assembly, the PMMA cylinders can be selectively removed, leaving a porous PS film that can be used for etching or lift-off.

While periodic holes are useful for some applications, most IC-related processes require patterning holes in a more arbitrary arrangement. For these cases, a process called graphoepitaxy can be used to produce smaller clusters of PMMA cylinders by confining the block copolymer in topographical wells (see Figure 1-c). These guiding wells can be placed at will, enabling flexible placement of DSA holes. Because the guiding wells can be patterned using a lower-resolution lithography system, DSA effectively extends the resolution of the other patterning technique. The industry focus on DSA is primarily as a complement to multiple patterning with 193 nm immersion [4] or EUV lithography [5]. However, in the context of the Stanford Nanofabrication Facility (SNF), DSA can be seen a complement to the ASML i-line stepper (<u>asml</u>*), the Raith 150 e-beam writer (raith), or possibly the Heidelberg MLA 150 direct-write tool (heidelberg).



Figure 1: Illustration of the self-assembly process using (a) PS-*b*-PMMA. On an unpatterned substrate, the block copolymer film can self-assemble into (b) an array of hexagonally packed cylinders. Image credit (b): [6]. In directed self-assembly, guiding wells isolate (c) smaller clusters of cylinders. Image credit (c-left): [7]. The self-assembled cylinders can be removed to enable pattern transfer.

* Underlined names in this report refer to equipment names in SNF/ExFab or SNSF, as indicated

Project Objective:

The goal of this project is to develop a process at SNF for etching DSA holes into a hard mask layer. We focus on a DSA process that uses a poly(styrene-block-methylmethacrylate) (PS-*b*-PMMA) block copolymer with $L_0 = 40$ nm, meaning that the DSA cylinders are 20 nm in diameter and spaced at a 40 nm pitch. Previously [8], we reported on an SiO₂/TiN guiding well structure to enable DSA pattern transfer and the fabrication of said structure at SNF. Here, we describe improvements to our process and the initial DSA pattern transfer results into the TiN at the base of the well that doubles as a hard mask. The full process flow, from guiding well fabrication to DSA to pattern transfer into TiN, is illustrated in Figure 2.



Figure 2: Diagram of full experimental flow for SiO₂/TiN guiding well fabrication, directed self-assembly, and pattern transfer into TiN.

<i>Table 1:</i> TiN Sputtering Conditions		
Pressure	5 mTorr	
Power	150 W	
Ar Flow	10 sccm	
N ₂ Flow	20 sccm	

<i>Table 2:</i> SiO ₂ CVD		
Conditions		
Pressure	1100 mTorr	
Power	200 W	
Temp	350 °C	
SiH ₄ Flow	250 sccm	
He Flow	800 sccm	
N ₂ O Flow	1700 sccm	

Table 3: Guiding Well		
Etch Conditions		
Pressure	30 mTorr	
Power	100 W	
CHF ₃ Flow	20 sccm	
CF ₄ Flow	5 sccm	
Ar Flow	10 sccm	

Table 4: Etch Rates for		
Guiding Well Materials		
SiO ₂	27.5 nm/min	
PMMA	16.3 nm/min	
TiN	19.8 nm/min	



Figure 3: Etch rates for blanket (a) SiO_2 and (b) PMMA in the etch conditions given in Table 3. The etched thickness is measured using ellipsometry plotted against time. The slope of the fitted line gives the etch rate for each material.



Figure 4: Measurement of TiN etch rate in the etch conditions given in Table 3. (a) Gratings were patterned in PMMA e-beam resist on a blanket TiN film, following which the sample was etched for 30 s and the PMMA was stripped. The sample was then imaged in AFM (b) and the step height measured in Gwyddion (c).

Experimental Methods:

TiN deposition: Titanium nitride was deposited onto a bare Si wafer with magnetron sputtering (lesker-sputter). The deposition rate of TiN was previously measured by x-ray reflectance [8] to be 31.4 nm/hr under the sputtering conditions given in Table 1. Using this recipe, we used a deposition time of 30 min to obtain a 15.7 nm film.

 SiO_2 deposition: Silicon dioxide was deposited onto the TiN layer with plasma-enhanced chemical vapor deposition (ccp-dep). Using the standard Si350-0 recipe (see Table 2), the

deposition rate was measured [8] with ellipsometry (woollam) to be 62.4 nm/min. Targeting 100 nm of deposited SiO₂, we used a deposition time of 96 s.

Guiding well patterning: Guiding wells at various CDs were patterned in the JEOL ebeam lithography tool (JEOL Ebeam, SNSF). Prior to exposure, 950K PMMA A3 e-beam resist was spun onto the wafer at 2000 rpm to target a film thickness of ~150 nm [9] and baked on a hot plate at 180 °C for 90 s. Next, the wafer was exposed at a dose of 1500 μ C/cm² and developed in 1:3 MIBK:IPA for 30 s. The e-beam pattern used to expose the wafer contained 3.5 × 3.5 µm arrays of circles ranging from 36 nm to 100 nm in CD. To adjust the local block copolymer film thickness, these arrays also varied in well density.

Guiding well etch: Reactive ion etching (oxford-rie) was used to etch the SiO₂ layer with the recipe given in Table 3. Figure 3 gives the etch rates of blanket PECVD SiO₂ and 950K PMMA e-beam resist, as measured by ellipsometry (woollam). Due to poor ellipsometry model fitting, the etch rate of TiN in 2.5 μ m × 50 μ m gratings was measured by atomic force microscopy (AFM; XE-70, SNSF) using Gwyddion [10] step height fitting, as shown in Figure 4. Table 4 summarizes the etch rates for these materials, indicating a selectivity of 1.7 for SiO₂ to PMMA and a selectivity of 1.4 for SiO₂ to TiN. Due to reactive ion etching (RIE) lag [11], an etch time of 5 min was required to etch through the SiO₂ to reach the TiN layer. To remove any remaining PMMA resist from the substrate, the sample is cleaned with O₂ plasma (oxford-rie, O₂ flow: 15 sccm, pressure: 100 mTorr, power: 50 W) for 2 min.

Block copolymer DSA: The PS-b-PMMA block copolymer P2400P-SMMA with a PS majority block was purchased from Polymer Source, Inc. Given its molecular weight (46.1-*b*-21.0 kg/mol), the block copolymer has a natural pitch (L_0) of 40 nm and thus self-assembles into 20 nm cylinders at a 40 nm pitch. A solution of 1 wt% PS-*b*-PMMA in propylene glycol monomethyl ether acetate (PGMEA) was mixed outside of SNF and approved by the SNF Process or Materials Review Requests (PROM) committee for storage in ExFab. Using a manual resist spinner (headway3), the block copolymer solution was spun onto the patterned SiO₂/TiN substrate at 2500 rpm and baked at 200 °C for 15 min in an oven (white-oven). Next, the sample was exposed (Oriel lamp, ExFab Venice) for 3 s to deep UV radiation with an intensity of 6.0 mW/cm² at $\lambda = 220$ nm. Irradiation induces cross-linking in the PS block and



Figure 5: Diagram of DSA process for PS-*b*-PMMA in SiO₂/TiN guiding wells.



Figure 6: Measurement of TiN etch rate under the etch conditions in Table 5. (a) Using the same method as described in Figure 4, AFM is used to image a set of gratings after a 45 s etch. (b) The step height is estimated in Gwyddion to determine the etch rate.

chain-scission in the PMMA block [12], allowing the PMMA to be removed with better selectivity. Finally, the PMMA cylinder is dissolved in acetic acid by soaking for 10 min (<u>wbflexcorr</u>), leaving behind the porous PS film. The DSA process is drawn in Figure 5 for reference.

TiN etch: An inductively coupled plasma (ICP) etch tool (<u>pt-mtl</u>) was used in RIE mode to break through the residual PS layer and etch the underlying TiN. Under the etch conditions in

Table 5: TiN Etch		
Conditions		
Pressure	10 mTorr	
Bias Power	50 W	
Cl ₂ Flow	30 sccm	
BCl ₃ Flow	5 sccm	
Ar Flow	10 sccm	

Table 5, the etch rate of TiN in 2.5 μ m × 50 μ m gratings was measured with AFM (<u>XE-70</u>) as 17.9 nm/min. A sample fitting of the etched step height from Gwyddion [10] is given in Figure 6. To account for RIE lag and the breakthrough etch of the PS residual layer at the base of the well, an initial etch time of 70 s was used to etch the TiN. The remaining PS was removed from the wells in a plasma asher (<u>drytek2</u>) using the standard descum recipe (O₂ flow: 100 sccm, pressure: 150 mTorr, power: 500 W) for 5 min.

Results and Discussion:

Surface affinity: To understand the self-assembly results for a guiding well made of a given set of materials, it is first essential to understand the materials interact with the block copolymer film. For a PS-*b*-PMMA block copolymer, there are three possible surface affinities for the sidewalls and bases of the guiding wells: (1) PS-wetting, (2) PMMA-wetting, and (3) neutral-wetting. As the names suggest, PS and PMMA are preferentially attracted to the surfaces in the PS- and PMMA-wetting schemes, respectively, and both blocks are equally attracted to the surfaces in the neutral-wetting scheme.

The surface affinity of the guiding wells has major implications for the expected selfassembly result, as demonstrated by the three common wetting schemes drawn in Figure 7. One notable difference between the wetting schemes is the guiding well CD required to produce a single-hole pattern. According to work done by Tiron *et al.* [13], a single-hole pattern will be produced in a well with $CD \approx L_0 = 40$ nm for a PS-wetting scheme and in a well with $CD \approx 2 \times$ $L_0 = 80$ nm for a PMMA-wetting scheme. While this means that greater hole shrink can be achieved using a PMMA-wetting scheme, Doise *et al.* [14] have also shown that after the



Figure 7: Illustration of DSA using (a) a PMMA-affinitive well, (b) a PS-affinitive well, and (c) a PMMA/neutral-affinitive well. The PMMA block is drawn in red and the PS block in blue. For each affinity scheme, the orientation of the polymer inside a well containing a single PMMA cylinder is drawn and the well size needed to produce a single DSA hole is given. Image adapted from [13].

PMMA cylinder is removed, a much thicker PS residual layer will remain in the well in the PMMA-wetting flow than in the other flows.

In this project, we continue to work with the SiO₂/TiN guiding wells described in our previous report [8]. Unmodified, the SiO₂ and TiN are both hydrophilic and, as such, attract PMMA. Although we expect a thicker residual PS layer (~20 nm [14, 15]), the PMMA-wetting flow has the benefit of being easy to implement, as no chemical modification of the guiding wells surfaces is necessary. Given the block copolymer's natural pitch ($L_0 = 40$ nm) and the well affinity to PMMA, we expect to see single-hole formation in guiding wells with CD \approx 80 nm.

Guiding well etch characterization: Due to RIE lag, it is hard to know how long to etch the SiO₂ wells to ensure that the SiO₂ is etched through to the TiN layer. For this reason, we used AFM (<u>XE-70</u>) and focused ion beam (FIB; <u>FEI Helios</u>, SNSF) to check the etch depth. Although the resolution of standard AFM tips is not as high as FIB for high aspect ratio features, AFM is a cheaper and higher throughput tool. To take advantage of this, we used AFM to measure the step height of a set of wider (200-500 nm × 50 µm) gratings patterned next to the guiding wells, as the AFM tips could not reach the bottom of the wells to measure them directly. Because the gratings have a larger CD than the guiding wells, RIE lag [11] indicates that the wells will take more time to etch through than the gratings. As such, we ensured that the gratings were etched through in AFM (i.e. gratings depth \geq SiO₂ thickness of 100 nm) before



Figure 8: Example of the underetched SiO_2 layer, as imaged in (a) AFM and (c) FIB. Characterization of the gratings in AFM shows an etch depth of (b) 68 nm, indicating that they are not etched through. As expected, FIB shows that the guiding wells are also not etched through.

Figure 9: The results after 5 min etch. Characterization of the gratings in (a) AFM shows an etch depth of (b) 116 nm, indicating that the SiO_2 is overetched. Characterization of the wells in (c) FIB show that the SiO_2 is completely etched through.

checking the etch of the guiding wells in FIB. For example, Figure 8-a shows an AFM image of some gratings with a depth measured at \sim 70 nm, indicating that the SiO₂ is underetched. This is confirmed in the corresponding FIB image (Figure 8-b), in which a thick layer of SiO₂ is seen at the bottom of the wells. For the 5 min etch time, we verified the etch depth with the same method. From the AFM image of the gratings in Figure 9-a, the etch depth is measured to be 115.9 nm, meaning that the SiO₂ in the gratings is overetched. As verified in the FIB image in Figure 9-b, the guiding wells resulting from the 5 min etch are etched all the way through to the TiN layer without overetch.

Increased guiding well depth: In our previous report [8], we targeted an SiO₂ well depth of 65 nm to match that of the all-Si guiding wells that we fabricated in earlier experiments [16]. Assuming this well depth and the ~20 nm residual layer, we expect the thickness of the PS along the sidewalls to be at most 45 nm thick after etching through the residual layer. Given that the block copolymer etch is not perfectly unidirectional, it is likely that the PS thickness left after the breakthrough etch will be less than 45 nm thick and, therefore, could be insufficient to withstand the pattern transfer into the TiN layer. To give more leeway on the block copolymer etch, we increased the SiO₂ thickness from 65 nm to 100 nm. Since the PS residual layer is fixed at 20 nm, the additional well height could nearly double the thickness of PS along the sidewalls of the guiding well after the breakthrough etch. Figure 10 compares scanning electron microscope (SEM; FEI Magellan, SNSF) images of the DSA results from the wells with a depth of 65 nm to the wells with a depth of 100 nm. In both cases, good self-assembly results are obtained for guiding wells with CD ~ 80 nm, as is consistent with a PMMA-wetting flow.



Figure 10: DSA results for (a) 65 nm well depth and (b) 100 nm well depth. Guiding well CD = 76 nm.

UV lamp for DSA: One of the goals of this project is to bring a DSA process to SNF, meaning that the entire DSA process should be performed on tools available to all labmembers. Previously [8], we were using a UV lamp belonging to Prof. H.-S. Philip Wong's research group to expose the block copolymer film before removing the PMMA block. The critical parameter for a UV lamp suitable for exposing the block copolymer is wavelength. As shown in the PMMA absorption spectrum in Figure 11, nonzero absorption occurs for $\lambda < 280$ nm. For lamps within this deep UV range, the PMMA block of the block copolymer absorbs the UV radiation and breaks down such that it can be easily removed from the PS block. The poor results achieved by UV lamps outside of the PMMA absorption range can be seen in Figure 12 after exposing a block copolymer film in the ultraviolet photoresist cure tool (uvcure, $\lambda \approx 400$ nm) for 25 min. Here, the PMMA cylinders appear to be only partially removed and the excess heating of the sample due to unabsorbed UV radiation appears to have caused the block copolymer film within the wells to pull away from the sidewalls.

Of the UV lamps available at SNF, we chose the Oriel lamp in ExFab Venice to expose the block copolymer film. In comparison to the Wong group lamp with $\lambda = 254$ nm, the Oriel lamp has $\lambda = 220$ nm and, therefore, a PMMA absorption coefficient 46 times that of the Wong group lamp. Furthermore, the UV intensity of the Oriel lamp at $\lambda = 220$ nm was measured to be 6.0 mW/cm². Because of the high absorption coefficient and high intensity of the UV radiation produced by the Oriel lamp, the time needed to expose the block copolymer film was expected to drop significantly. Figure 13 shows SEM images of DSA samples after varying exposure times, revealing that even at exposure times as low as 1 s, the PMMA block is still able to be cleanly removed from the PS block. Ultimately, an exposure time of 3 s was chosen to ensure that the process was closer to the center of the process window.



Figure 11: UV absorption spectrum for PMMA, as expressed through the extinction coefficient as a function of a wavelength. Image adapted from [17]. DSA results obtained the $\lambda \approx 400$ nm UV lamp.

Figure 12: SEM images of (a) good DSA results obtained by the Wong group UV lamp and (b) poor



Figure 13: Exposure of PS-*b*-PMMA in the SNF Oriel Lamp at varying times. For reference, (a) shows the baseline DSA result with exposure in the Wong group lamp for 25 min. For (b) 1 s and (c) 5 s, the exposure produces good results. However, for (d) 75 s and (e) 150 s, the block copolymer film is overexposed and appears to be pulling away from the guiding well sidewalls. Scale bars: 500 nm.

Block copolymer pattern transfer results: After verifying the tweaks to the guiding well depth and the UV exposure step, the block copolymer film was used to etch the TiN underlayer and the remaining PS was removed in O₂ plasma. Top-down SEM (FEI Magellan) images of the etching results are given in Figure 14-a. Due to the good directionality of the SEM electron beam and the relatively low aspect ratio of the guiding wells, we expected to see a DSA hole in the middle of each well, assuming the pattern transfer was successful. Instead, there do not appear to be any patterns at the bottom of the guiding wells.



Figure 14: SEM images of the guiding wells after TiN etch of 70 s. The yellow highlights demarcate the boundaries of a single guiding well. For guiding wells with $CD \approx 85$ nm, we see that (a) before etching in BOE, the holes in the TiN are not visible. However, (b) after BOE etch, the holes in the TiN can be readily found. For guiding wells with CD < 75 nm, the block copolymer does not self-assemble into deep cylinders. As expected, (c) we observe very little pattern transfer in the TiN for wells with $CD \approx 55$ nm.

To check if the apparent lack of pattern was indeed due to pattern transfer failure, the sample was etched in 20:1 BOE for 1 min. While BOE will etch TiN films, especially ones as oxidized the one in this structure, the selectivity of SiO₂ to TiN is expected to be very high [18]. The effect of the BOE etch on the SiO₂/TiN bilayer was examined in SEM (<u>FEI Magellan</u>). As shown in Figure 14-b, the SiO₂ is not completely removed, but it is removed sufficiently to reveal the holes in the underlying TiN layer. Although the holes etched into the TiN are larger (CD \approx 38 nm) than the initial DSA holes, the larger CD is consistent with an isotropic BOE etch, which would enlarge smaller DSA holes etched into TiN.

To confirm the holes in the TiN are indeed from the block copolymer film, we checked the etching results for undersized guiding wells. For a PMMA-wetting flow, simulations [19] indicate that guiding wells with CD \approx 55 nm are too small to yield a transferrable DSA pattern. Our previous [8] experiments also suggest that the PMMA vacancies in wells with CD \approx 55 nm are shallower than those produced in wells with larger CDs. As is consistent with these observations, we observe close to no pattern transfer in the TiN for guiding wells with CD \approx 55 nm (see Figure 14-c). For this reason, we can conclude that the holes in the TiN film are indeed etched with the block copolymer film, indicating that the DSA holes were successfully transferred into the TiN.

Conclusions and Future Work:

In this report, we discuss the etching of block copolymer DSA holes (CD = 20 nm) into a TiN hard mask. To make the DSA process fully available to the SNF community, we performed the DSA process on tools that can be accessed by all labmembers. In the process of finding a deep UV lamp in the SNF ecosystem, we discovered that the use of the high-intensity, short-wavelength Oriel deep UV lamp in ExFab can reduce the UV exposure time from 25 min to 3 s.

To enable more margin in the etch of the DSA holes, we also successfully fabricated deeper guiding wells and confirmed that they yield good self-assembly results. Finally, we demonstrated the successful etch of the DSA holes into a TiN hard mask layer. Although we confirmed that the holes in the TiN originated from the block copolymer etch, the process we used to etch away the SiO₂ such that the TiN holes could be imaged also etched the TiN. As such, we currently do not have critical information about the size or profile of the original etched holes. To complete this study, the pattern transferred from the block copolymer into TiN needs to be accurately characterized. One possible route for characterization is cross-sectional imaging in FIB, which would use a low ion-beam current to slowly mill through a row of guiding wells and take frequent images of the cross-section. Another possible route for characterization is to further transfer the DSA holes from the TiN into the Si substrate. Because the TiN can be easily removed from Si in piranha without etching the Si, this would allow us to indirectly verify the TiN hole profile. Ultimately, we plan to explore how DSA can more elegantly complement lower-resolution lithography tools, such as the <u>asml</u> and <u>heidelberg</u>, and fit into the SNF lithography ecosystem.

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