

# Enabling Pattern Transfer for Block Copolymer Directed Self-Assembly

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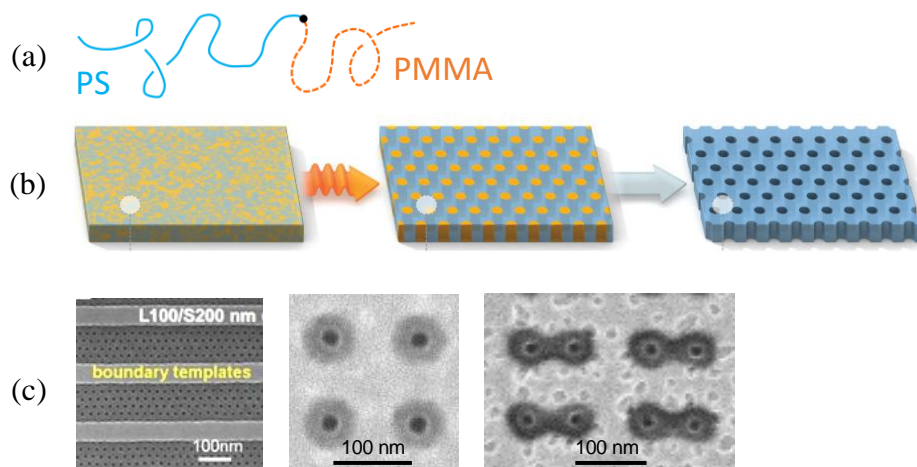
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## Introduction:

Looking ahead to patterning at the 7 nm node and beyond, a major concern of the lithography community is its continued ability to keep up with increasingly high-resolution requirements at a low cost. We are already in the realm in which traditional optical lithography has insufficient resolution to meet current patterning needs and multiple patterning is the new norm [1]. The successor to multiple patterning is expected to be extreme ultraviolet (EUV) lithography, but its high cost and downtime have left appetite for alternatives. In this context, block copolymer directed self-assembly (DSA) has emerged as a low-cost, high-throughput option to extend the resolution of more conventional lithography techniques by shrinking or multiplying the pitch of existing patterns. In industry, DSA is primarily being considered to extend the resolution of 193 nm immersion multiple patterning or EUV. However, in the context of Stanford, DSA can be considered as a complement to the ASML i-line stepper (asml\*), the Raith e-beam writer (raith), and the JEOL e-beam writer in SNSF.

Block copolymers consist of two or more chemically distinct polymers bound end-to-end. When block copolymer films are heated, the polymers self-assemble into the lowest free-energy position, forming periodic domains within the film. Although the internal structure of the self-assembled film varies greatly based on the number of blocks in the polymer and the relative proportions of those blocks, the block copolymers most heavily investigated for lithography applications are lamellae- and cylinder-forming diblock copolymers [2]. The focus of this report will focus on the industry-standard cylinder-forming block copolymer poly(styrene-block-methyl methacrylate) (PS-b-PMMA).

The cylinder-forming variant of PS-b-PMMA is composed of 70% PS and 30% PMMA. The diameter of the self-assembled cylinders is usually in the tens of nanometers and can be



*Figure 1:* Illustration of the self-assembly process using (a) PS-b-PMMA. On an unpatterned substrate, a PS-b-PMMA film will self-assemble into (b) an array of hexagonally packed cylinders. Image credit (b): [3]. In directed self-assembly, topographical wells confine the block copolymer such that (c) smaller clusters of cylinders are formed. The self-assembled cylinders can be removed to enable pattern transfer.

\* Underlined names in this report indicate names of tools in the SNF cleanroom

adjusted by changing the length of the polymer. Left unguided, a self-assembled PS-b-PMMA film will form a large-area array of hexagonally packed PMMA cylinders in a PS matrix, as shown in Figure 1-b [3]. However, for random logic, this type of long-range periodicity is a poor fit for patterning aperiodically scattered contacts and vias. For this reason, a hardmask is put over the substrate and small wells are etched into it where self-assembled cylinders are wanted. As illustrated in Figure 1-c, when a block copolymer solution is spun onto the hardmask and heated, the wells direct the self-assembly process such that the cylinders only form inside the well. From there, the PMMA cylinders can be removed and remaining PS can be used as an etch mask to transfer the cylindrical patterns into the underlying substrate. Finally, the PS/hardmask layer is removed, leaving a pattern of etched holes underneath.

### **Project Goal:**

The purpose of this project is to develop a functional DSA process to the SNF community. Currently, we have a well-established DSA process [4, 5] that uses guiding wells etched into bare silicon. However, these wells do not allow for pattern transfer, as there is no hardmask that can be lifted off once the block copolymer pattern is etched into the substrate. This report will detail the fabrication process for SiO<sub>2</sub>/TiN guiding wells and the DSA results using PS-b-PMMA.

### **Materials and Surface Modifications:**

*Block copolymer:* The block copolymer used for this project is poly(styrene-*block*-methyl methacrylate) (PS-b-PMMA) with majority block PS. After thermal anneal, this block copolymer will form PMMA cylinders in a matrix of PS. Although a wide range of block copolymer materials are available, PS-b-PMMA was chosen because it is the current industry standard and is well-documented in literature [6, 7]. For this project, the block copolymer P2400P-SMMA with 46k-21k molecular weight was purchased from Polymer Source. At this molecular weight, the block copolymer has a natural pitch ( $L_0$ ) of 40 nm, indicating that it forms PMMA cylinders with a 20 nm diameter and 40 nm pitch. The block copolymer was dissolved in propylene glycol monomethyl ether acetate (PGMEA) to create a 1 wt% solution.

*Guiding wells:* Usually, the guiding wells are composed a hardmask bilayer with the top layer acting as the sidewalls and the bottom layer as the base. Because the block copolymer film is usually too thin (50-100 nm) to withstand a long etch, the bottom layer of the well is frequently used as an intermediate hardmask between the block copolymer film and the underlying substrate. This enables higher aspect ratio holes to be etched into the material underneath. At the same time, the bottom layer is also an etch stop for the top layer, so the two layers should have some etch contrast. The primary function of the top layer of the well is to block off areas of the substrate where DSA cylinders are not wanted. Therefore, it must be able to withstand the etch used to transfer the block copolymer pattern into the base of the well. Both materials also must be able to withstand a 200 °C anneal and be cleanly removed from the substrate after pattern transfer. One final consideration in choosing the guiding well materials is that the surface chemistry of the well is very important aspect to the morphology of the self-assembled cylinders. For this reason, materials with a high density of grafting sites are preferable to allow for easier surface modification.

Given these constraints, the most common approach is to use spin-on carbon (SOC) for the sidewalls and SiN or SiO<sub>2</sub> for the base of the guiding wells [8, 9]. However, because SOC is not readily available at SNF, we chose a different structure demonstrated by Gharbi *et al.* [10] with the well sidewalls made of SiO<sub>2</sub> and base made of TiN. Gharbi *et al.* explain that SiO<sub>2</sub> was chosen for its thermal stability up to very high temperatures and dense grafting sites. As for the base material, TiN was selected because it is a good etch stop for SiO<sub>2</sub> and is relatively common use in semiconductor manufacturing. Labmembers should not feel limited to TiN, though, as almost any metal [11] can be used for as the base for the guiding well.

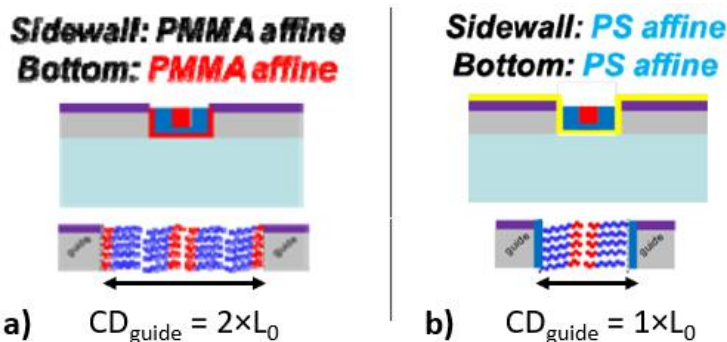


Figure 2: Illustration of DSA using (a) a PMMA-affinitive well and (b) a PS-affinitive well. The PMMA domain is drawn in red and the PS domain in blue. The top images show a cross-section of a single DSA cylinder in a well. In the bottom images, the orientation of the block copolymers inside the well is drawn. Image credit: [12].

schemes are discussed: (1) PMMA-affinitive all-over and (2) PS-affinitive all-over. As illustrated in Figure 2-a, the PMMA-affinitive scheme causes there to be a thin (~5 nm) PMMA wetting layer on the well surface. On top of the wetting layer, there is a thick layer of PS surrounding the PMMA cylinder. In contrast, the PS-affinitive wells do not have the initial PMMA wetting layer. As illustrated in Figure 2-b, the PS wets directly to the base and sidewalls of the well and the PMMA cylinder forms in the center.

There is an optimal guiding well critical dimension (CD) to isolate a single DSA cylinder, and notably, the elimination of the PMMA wetting layer reduces that optimal CD for the PS-wetting case relative to the PMMA-wetting case. In the case of the  $L_0 = 40$  nm block copolymer used in this report, the CD to form a single PMMA cylinder should be ~80 nm ( $2 \times L_0$ ) for the PMMA-wetting wells and ~40 nm ( $1 \times L_0$ ) for the PS-wetting wells. The reduction in guiding well CD comes with a couple of benefits, namely an improvement in cylinder CD uniformity and placement accuracy. That is, with less polymer squishing around inside the well, the PMMA cylinders are more consistently sized and positioned at the center of the well [13]. Furthermore, the thinner amount of polymer at the bottom of the well in the PS-wetting case enables the self-assembled patterns to be etched more easily into the underlying substrate. For this reason, a secondary goal of this project was to implement a PS-wetting scheme for the guiding wells.

#### Well surface affinity:

Modifying the surface affinity of the guiding wells is a powerful tool for controlling how the block copolymer interacts with the well.

Depending on a given material's surface chemistry, it will either attract the PS block of the block copolymer or the PMMA block. This causes the polymer chains to orient themselves differently within the guiding wells based on the well surface affinity. In this report, two primary wetting

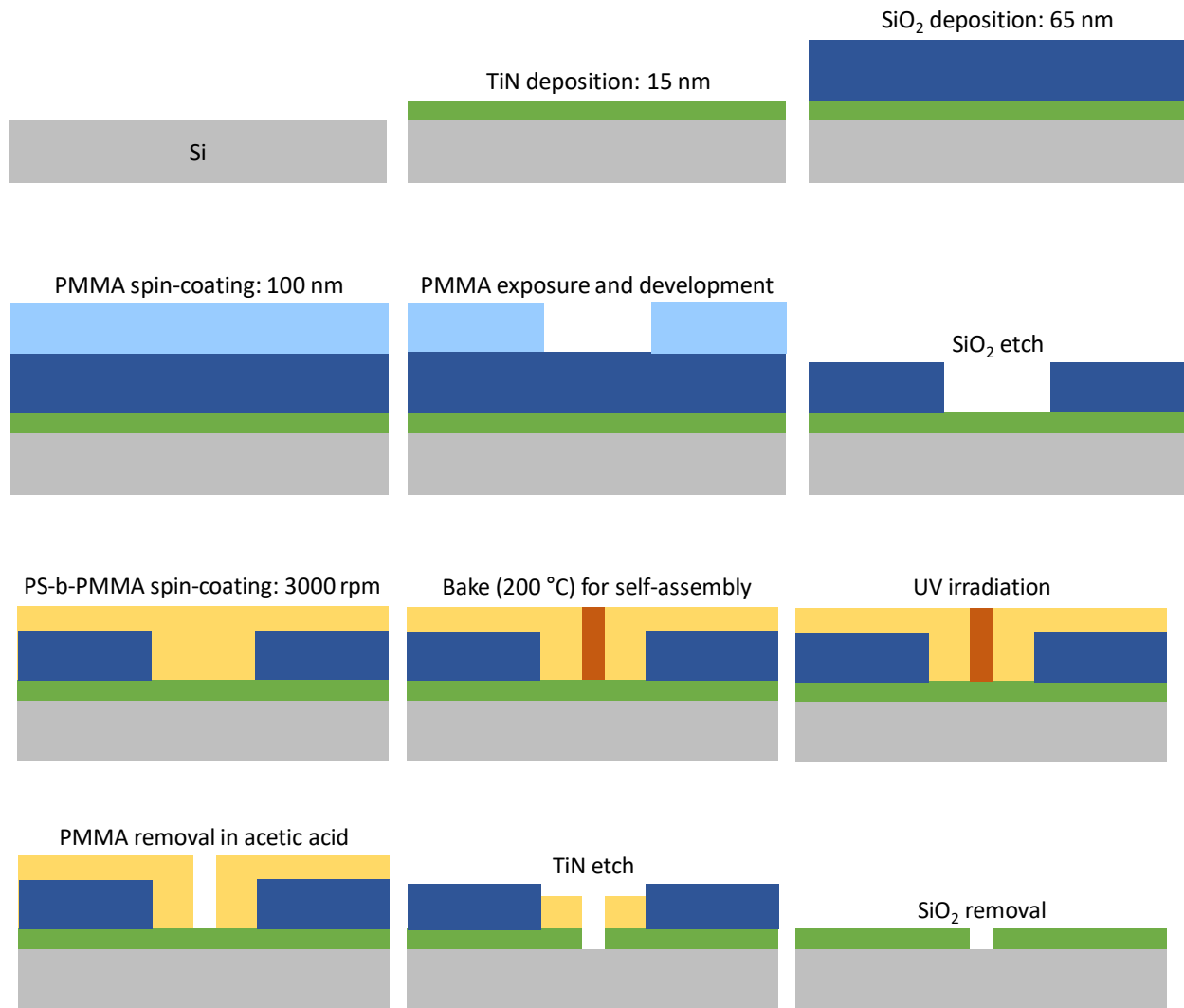


Figure 3: Diagram of experimental flow for SiO<sub>2</sub>/TiN guiding well fabrication, directed self-assembly, and pattern transfer. This project describes the process until the TiN etch step.

### Processes:

Figure 3 above shows the process flow used to generate the guiding wells in this project. The details of the various processes are given below.

*TiN deposition:* Titanium nitride was deposited by RF magnetron sputtering in the Lesker (lesker-sputter). Based on the work of Rincon-Delgado *et al.* [9], the thickness for the TiN layer was targeted at 15-20 nm. Given the sputtering conditions in Table 1, the deposited TiN film thickness was confirmed via x-ray reflectivity (XRR) to be 31.6 nm after one hour and 15.6 nm after

Pressure	5 mTorr
Power	150 W
Ar Flow	10 sccm
N <sub>2</sub> Flow	20 sccm

thirty minutes (see Figure 4). For this reason, a sputtering time of thirty minutes was used for this bottom layer of the guiding well.

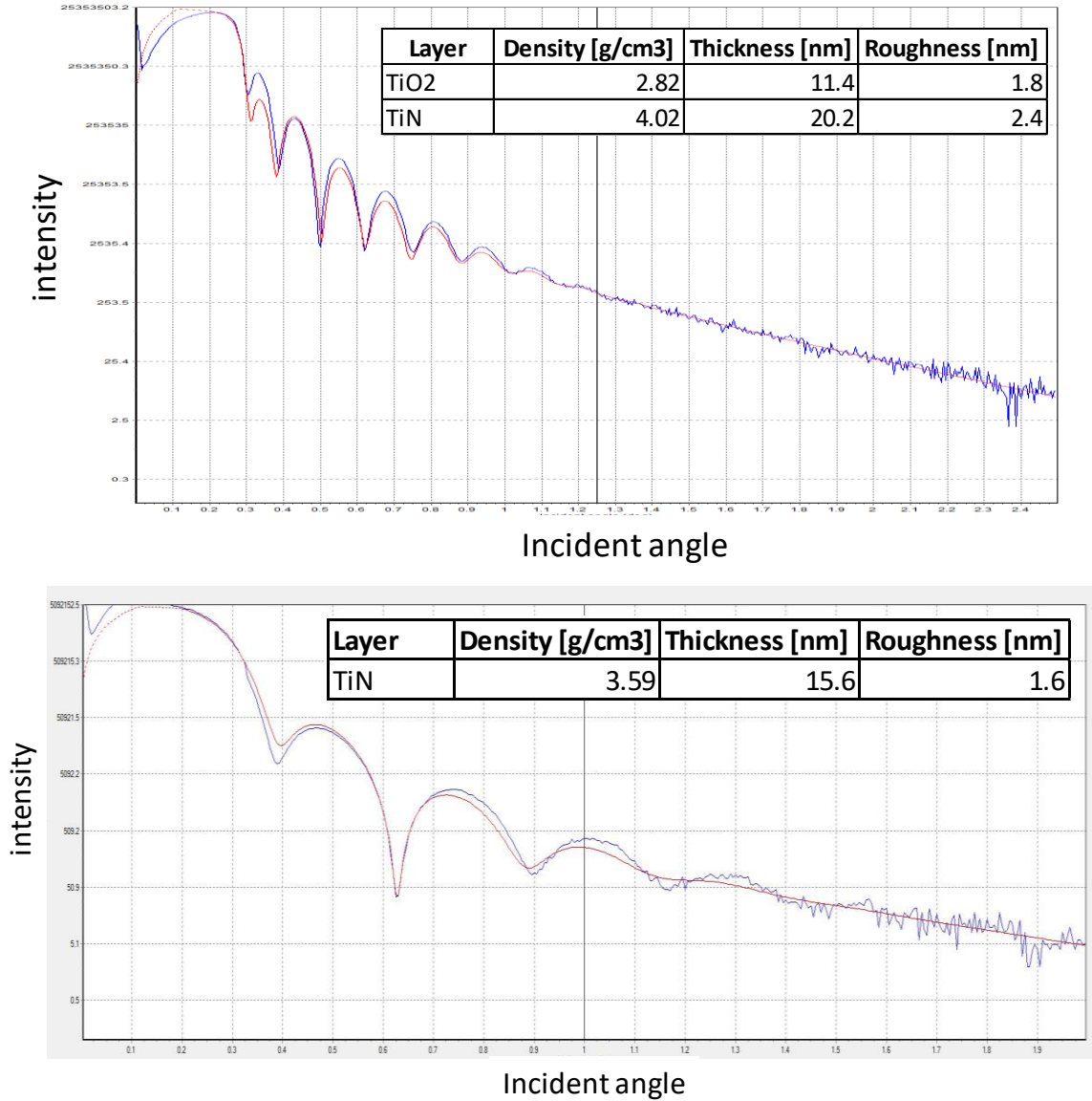


Figure 4: XRR measurements of as-deposited TiN films after (top) one hour and (bottom) thirty minutes. The measured data are given in blue and the fitted curves are given in red. In the top measurement, a TiO<sub>2</sub>/TiN bilayer was used to fit the measured data better, pointing to more of a titanium oxynitride film.

*SiO<sub>2</sub> deposition:* Silicon dioxide was deposited by plasma-enhanced chemical vapor deposition in PlasmaTherm Shuttlelock (ccp-dep). Based on a DSA process flow previously developed at Stanford for etched silicon guiding wells [5], the thickness for the SiO<sub>2</sub> layer was targeted at 65 nm. Using the standard SiO350-0 recipe (see Table 2), the deposited SiO<sub>2</sub> film thickness was measured via ellipsometry (woollam) to be 63 nm after 60 sec and 93 nm after 90

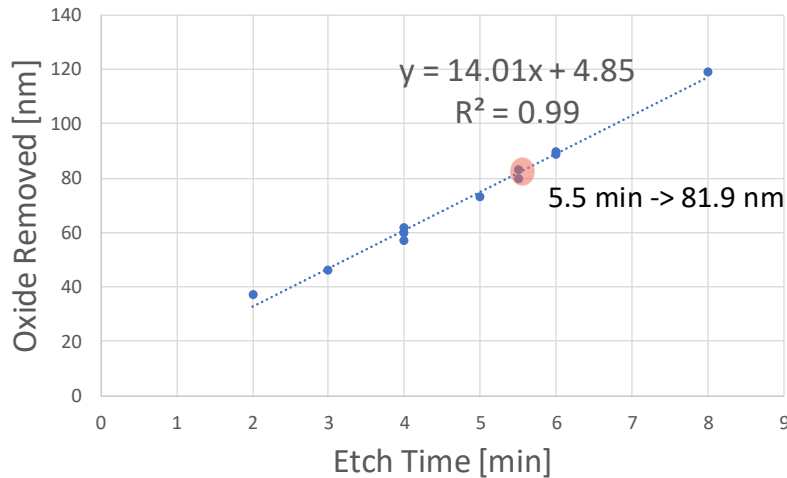
sec. Given these deposition rates, a deposition time of 62 sec was used to deposit 65 nm of SiO<sub>2</sub> on top of the underlying TiN layer.

*Guiding well patterning:* The guiding wells were patterned using the JEOL JBX-6300FS e-beam lithography system in SNSF. In this process, PMMA 950K A2 was spun at 1500 rpm onto the SiO<sub>2</sub>/TiN bilayer to give a PMMA film thickness of 96 nm. After e-beam exposure, the PMMA was developed in 1:3 MIBK:IPA for 30 sec. Arrays (3.5 × 3.5 μm) of wells were patterned at a range of CDs (36 - 100 nm) to cover the optimal single-cylinder well CDs for single-cylinder PS- and PMMA-wetting flows. To tune local block copolymer film thickness, the wells were also patterned at a range of densities.

*SiO<sub>2</sub> etch:* Etching of the SiO<sub>2</sub> layer to form the guiding wells was performed in the Oxford reactive ion etcher (oxford-rie). Using the etch conditions given in Table 3, the etch rate was confirmed via ellipsometry (woollam) to be 14.0 nm/min, as shown in Figure 5. To ensure that the SiO<sub>2</sub> was completely etched through, a 5.5 min etch time was used to open the guiding wells. After the etch was complete, the remaining resist was stripped in a piranha solution.

Parameter	Value
Pressure	1100 mTorr
Power	200 W
Temperature	350 °C
SiH <sub>4</sub> Flow	250 sccm
He Flow	800 sccm
N <sub>2</sub> O Flow	1700 sccm

Parameter	Value
Pressure	10 mTorr
Power	50 W
CHF <sub>3</sub> Flow	20 sccm
CF <sub>4</sub> Flow	5 sccm
Ar Flow	10 sccm



*Figure 5:* Thickness of SiO<sub>2</sub> removed at various etch times. By fitting a line to the data, the etch rate for the etch conditions in Table 3 is given by the slope of the line. To ensure that the SiO<sub>2</sub> is completely etched through, an overetch of 82 nm was targeted, yielding an etch time of 5.5 min, as highlighted in pink.

*Block copolymer DSA:* A solution of 1 wt% PS-*b*-PMMA in PGMEA was spun (headway2) onto patterned SiO<sub>2</sub>/TiN pieces at 3000 rpm. The pieces were then heated in an oven (white-oven) at 200C for 10 min to induce self-assembly and exposed to UV radiation (254 nm) for 25 min to break down the PMMA block. For this project, a personal UV lamp was used to irradiate the block copolymer film, but labmembers can use any UV lamp that produces wavelengths absorbed by PMMA. Some options in SNSF are the Samco Ozone Cleaner and the Loctite UV Exposure Tool. Finally, the pieces were immersed in acetic acid (wbflexcorr) for 10 min to dissolve the PMMA cylinders out of the PS matrix. See Figure 6 for illustrated DSA process flow.

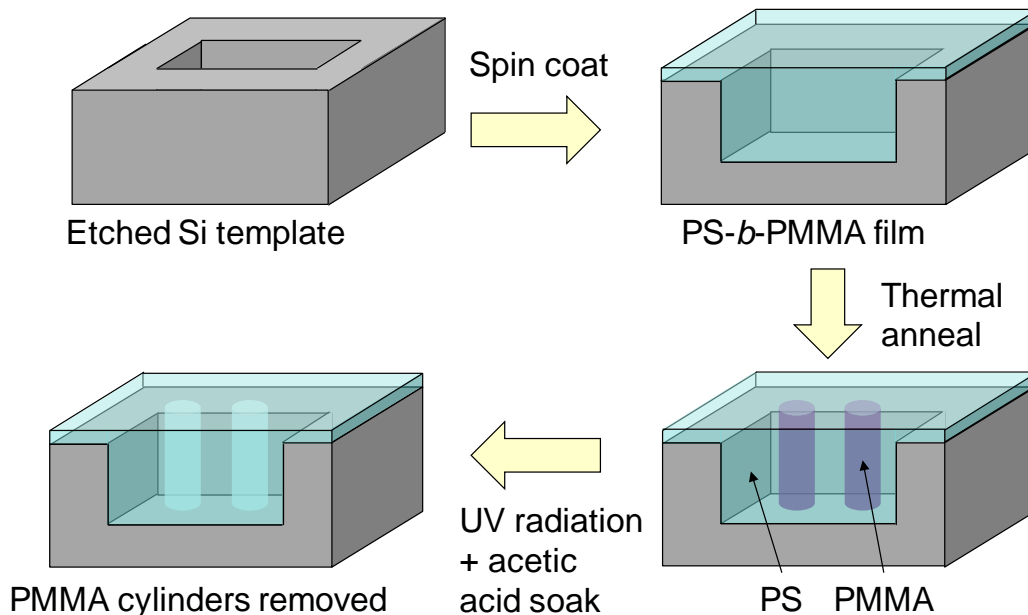


Figure 6: DSA flow using PS-*b*-PMMA block copolymer in etched guiding wells.

## Experimental Results:

*Guiding wells:* Scanning electron microscopy was used to image the guiding wells before and after DSA. As shown in Figure 7, the guiding wells appear to have significant surface roughness from the SiO<sub>2</sub> deposition. Although the surface roughness is undesirable, it is still tolerable for the DSA process, as the SiO<sub>2</sub> layer only needs to withstand the block copolymer pattern transfer. The water contact angle the SiO<sub>2</sub> surface was measured to be 16°, indicating a hydrophilic surface that should attract PMMA.

*DSA results:* Figure 8 shows the DSA results for guiding wells at a range of CDs. As expected for PMMA-affinitive wells, good PMMA cylinder formation was found in wells with  $CD \approx 75 \text{ nm} \approx 2 \times L_0$ . In keeping with simulations by Latypov et al. [14], shallow PMMA cylinders were found in wells smaller than  $2 \times L_0$  and multi-hole patterns were found in wells larger than  $2 \times L_0$ . These results indicate that the as-fabricated SiO<sub>2</sub>/TiN wells successfully functioned as PMMA-affinitive guides for PS-*b*-PMMA.



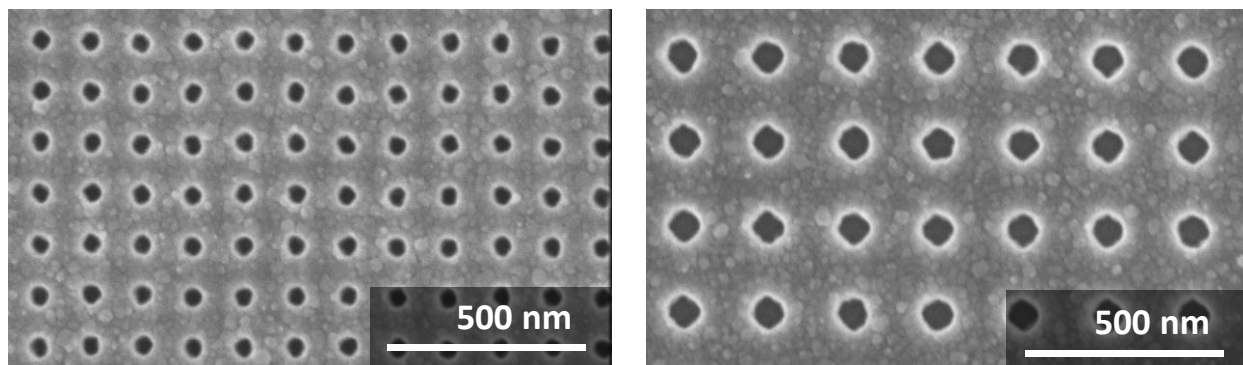


Figure 7: Scanning electron microscope images of the etched SiO<sub>2</sub>/TiN guiding wells. The wells on the left have CD  $\approx$  60 nm, while the wells on the right have CD  $\approx$  100 nm.

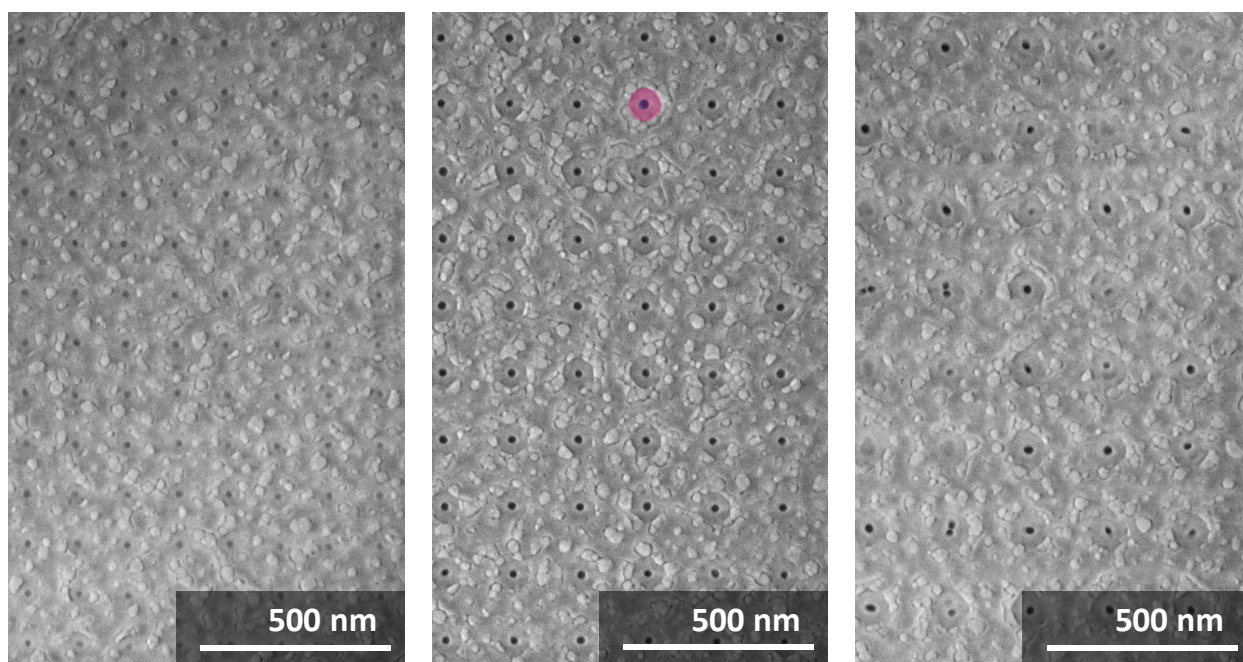
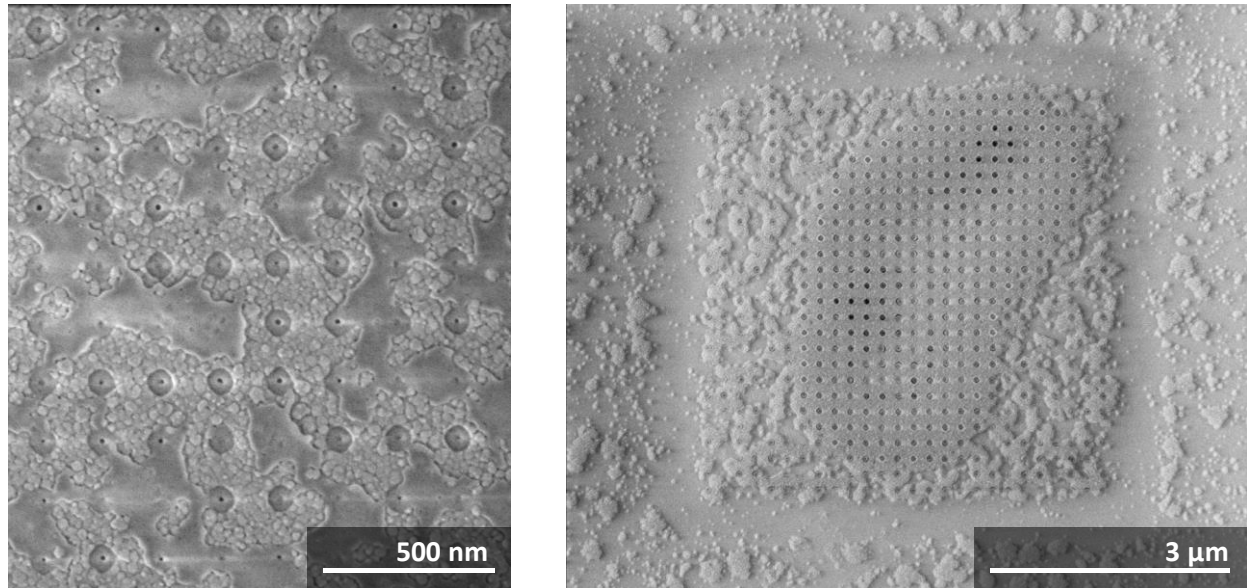


Figure 8: Scanning electron microscope images of the SiO<sub>2</sub>/TiN guiding wells after DSA processing and PMMA cylinder removal. The wells on the left have CD  $\approx$  55 nm, in the center have CD  $\approx$  75 nm, and on the right have CD  $\approx$  90 nm. In the center image, one of the guiding wells is highlighted in pink and the DSA cylinder in the middle is highlighted in purple for reference.

*Surface modification results:* To implement a PS-affinitive well, our hypothesis was that PS would wet the surface if the existing SiO<sub>2</sub>/TiN wells could be made hydrophobic. For this reason, hexamethyldisilazane (HMDS) was grafted to the empty SiO<sub>2</sub>/TiN wells (yes-oven) to make the surface more hydrophobic, as was confirmed by the increased water contact angle (66°). Although the water contact angle is large relative to the pre-HMDS case (16°), a water contact angle of 66° indicates that the surface is still hydrophilic. Figure 9 shows the DSA results in the SiO<sub>2</sub>/TiN wells with HMDS coating. Good PMMA cylinder formation is still found for wells with CD  $\approx$  75 nm, indicating that the sidewalls are not hydrophobic enough to attract the PS effectively. More notable, however, is the extremely uneven block copolymer film thickness on the HMDS-coated wells. This is shown vividly in left-hand side of Figure 9, where



the block copolymer film can be seen beading up and forming islands on the substrate. Further investigation is required to find a solution to this problem.



*Figure 9:* Scanning electron microscope images of the HMDS-coated  $\text{SiO}_2/\text{TiN}$  guiding wells after DSA processing and PMMA cylinder removal. The wells on the left have  $\text{CD} \approx 75$ . Unevenness in the film thickness is visible both at high-magnification (left) and low-magnification (right).

### **Conclusion:**

In this project, a PMMA-wetting flow for PS-b-PMMA using  $\text{SiO}_2/\text{TiN}$  guiding wells has been successfully demonstrated. While an attempt was made to develop a PS-wetting flow by modifying the wells with HMDS, it was ultimately unsuccessful in making the wells affinitive to the PS block. Furthermore, the HMDS coating resulted in a very unevenly thick block copolymer film, which has yet to be resolved. In addition to testing other strategies for implementing a PS-wetting DSA flow, future work will include etching the block copolymer patterns into the TiN underlayer such that a complete DSA flow can be made available to the SNF community.

### **Acknowledgements:**

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