

# Lamellar Directed Self-Assembly using PS-b-PMMA Block Copolymers

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**Abstract**—The goal of this senior design project was to develop a DSA process for the RIT SMFL and enable further research and teaching opportunities. The objective of this project was to achieve lamellar structure formation using a PS-b-PMMA BCP annealed thermally and in solvent vapor. Thermal annealing of the samples resulted in destructive film oxidation. SVA was carried out on the samples using both toluene and THF and the pattern was revealed using an oxygen RIE. No significant changes in pattern morphology were noted when comparing the toluene and THF SVA processes. Final patterns were observed using the RIT Nano-Imaging Lab SEM. Dense polystyrene pillar morphologies were observed for both blanket and resist patterned samples instead of the expected lamellar morphologies. The polystyrene pillars were observed to form with a mean diameter of 16.8nm and a standard deviation of 2.3nm from a random sampling of 50 pillars from three separate SEM images. A histogram analysis of the pillar diameter shows a right-sided distribution of the diameters of the pillars.

**Index Terms**— Directed Self Assembly, Block Copolymers, Solvent Vapor Annealing.

## I. INTRODUCTION

PHOTOLITHOGRAPHY has historically been the primary method through which patterns are transferred into substrates for semiconductor processing; by the transfer of a pattern directly using patterned photoresist. As technology nodes advance and critical dimensions shrink, direct patterning has posed a serious threat to the cost-effective manufacturing of semiconductor devices. Increasingly stringent edge placement, overlay, line edge roughness, and critical dimension (CD) specifications have necessitated the creation and use of extremely costly lithography tools. As semiconductor fabrication facilities attempt to integrate sub-10nm CD integrated circuits, Extreme-Ultraviolet (EUV) technology becomes necessary in order to enable these technologies via direct-pattern transfer lithography. The feasibility of manufacturing with EUV photolithography has yet to be demonstrated, and alternative patterning methods have been proposed to realize a cost-effective patterning solution for the advancement of semiconductor technology. One such method functions via the deposition and direction of self-assembling compounds, to create structures on a substrate which can then be used for pattern transfer.

These directed self-assembly (DSA) processes utilize

polymer compounds referred to as block copolymers (BCPs) which, when deposited, separate phases to create patterns that have been demonstrated at the Rochester Institute of Technology (RIT) Semiconductor and Microsystems Fabrication Laboratory (SMFL) to have the ability to form contact holes with a diameter of 30nm [1]. It is the goal of this design project to further explore and characterize DSA processes through the use of photolithographic direction at the RIT SMFL. The objective of this design project is to achieve a low-cost patterning solution for advanced technology nodes, which will enable sub-lithographic patterning using existing lithography technology (248nm, 193nm dry, and 193nm-immersion). Various BCP materials and patterning test masks will be used to evaluate potential DSA process candidates to achieve the goal of this design project.

## II. THEORY

### A. Surface Brush

In this report, references will be made to a material or process called a "brush." A brush is a monolayer which has chemically bonded to the substrate material in order to form a uniform surface energy which Directed Self-Assembly can occur on. It is important for this brush to be continuous and uniform across the surface of the material to avoid the formation of defects.

For this design project, a brush material of Hydroxyl-terminated Polystyrene (OH-t-PS) with a molecular weight of 20k g/mol was used. The molecular weight was matched to that found in the polystyrene block of the BCP. The brush material was spincoated at a speed of 3000RPM for 120s, and then baked at 120°C for 24 hours, achieving a final thickness of approximately 40nm.

The brush material at this point is too thickly coated, however the 24 hour anneal at 120°C has chemically bonded a monolayer of the material to the Silicon Dioxide underneath. Stripping the excess material in Toluene will leave behind the monolayer brush, and the substrate is now ready to be coated with the BCP.

### B. Directed Self-Assembly

DSA is fundamentally the molecular arrangement which occurs when two polymers which do not mix are deposited and annealed. Like oil and water, the two polymer domains

will separate. Annealing the substrates, either at elevated temperatures or in a solvent vapor, will speed up the self assembly process to a speed which is practical for research and manufacturing.

Block Copolymers are essentially macromolecules composed of two separate polymers joined by a functional block. The compound used in this experiment is PS-b-PMMA [20.5k-20.5k] g/mol. A 20.5k molecular weight [MW] PS polymer is joined to a 20.5k MW PMMA polymer by the functional block. Using a BCP for DSA processes allows a single material to be spincast.

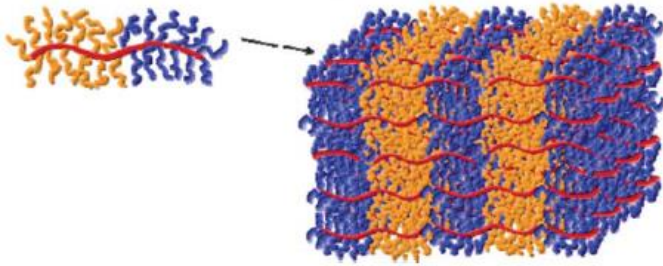


Figure 1: Pattern formation via BCP self-assembly. [2]

Note that after spincoating, the BCPs will have a random orientation on the wafer. The assembly of the structures occurs as the molecules arrange themselves into the lowest-energy state, with polymer molecules forming groups with other like molecules. Since there is insufficient energy to separate the bonds between the functional block group and the polymer groups, periodic structures are formed.

Fig. 1 is a representation of how BCP molecules arrange to form patterned domains on the substrate. The domains forming the lamellar structures can be typically have different etch selectivities, allowing the pattern to be revealed via plasma etching.

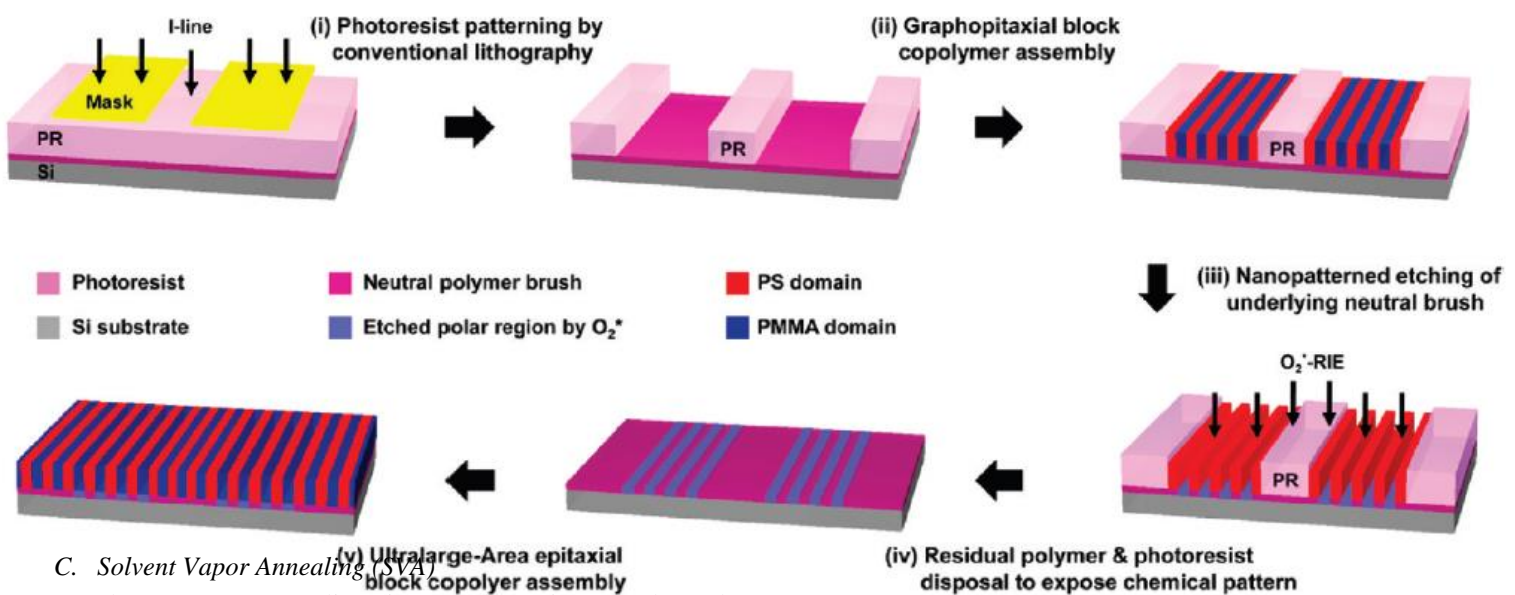
in an aluminum boat inside of a beaker containing a small amount of solvent. The aluminum boat prevented the solvent from contacting the sample directly while still allowing the vapors to contact the sample. A watch glass was placed over the beaker and solvent vapor annealing times from 10 to 15 minutes were evaluated. The solvent vapor absorbs into the BCP film, swelling and plasticizing it, similar to how the BCP film would plasticize under elevated temperatures during a thermal anneal [4]. Due to the fact that SVA can be done at room temperature, film oxidation issues can be avoided and thermal budget for the process can be reduced, increasing the viability of DSA for CMOS processes with tight thermal budgets.

### III. EXPERIMENTAL PROCEDURE

n-type Silicon wafers are used as the starting substrates for the experiment. 1000 Angstroms of Silicon Dioxide was grown on the surface of the wafers. The surface brush material, OH-t-PS, was spincast at 3000RPM for 120 seconds, then annealed at 120°C for 24 hours. The wafer was then dipped into Toluene for 60 seconds and dried in air. Photoresist [NLOF-2020:PGMEA 1:1] was spincast on the substrate to a thickness of approximately 130nm. Lithography was done using the ASML ETM and was developed using 0.36M TMAH developer solution for 60s. The nLOF was then hardbaked at 140C for 60seconds.

The BCP PS-b-PMMA was then spincast at 3000RPM for 120 seconds. The wafers were then annealed in solvent vapor using toluene for 10 to 15 minutes. Longer SVA times resulted in film dewetting.

Characterization of the substrates was performed using contact angle measurements, optical micrographs, SEM imaging, and AFM measurements. Figure 2, shown at the bottom of this page, shows cross sectional views of the main steps in this process flow.



C. Solvent Vapor Annealing (SVA)  
Solvent vapor annealing is an alternative to thermal annealing, to allow graphoepitaxial grow pattern. For this project the BCP coated sam

Figure 2: High-level process flow overview [1].

#### IV. RESULTS AND ANALYSIS

Contact angle measurements were taken to confirm that the surface brush process had been successful. Figure 3, below, shows the images captured during contact angle verification for the bare oxide sample (left) OH-t-PS un-annealed (center), and the surface after toluene strip (right).

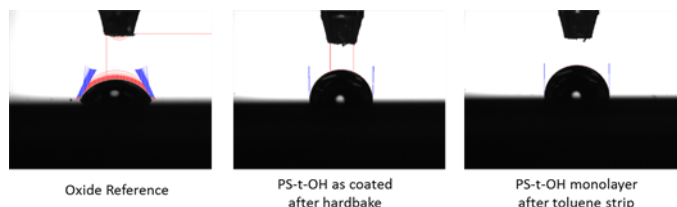


Figure 3: Contact angle characterization of surface brush process.

contact angle of 62.6 degrees. After coating with the brush material, the contact angle was measured to be 91.0 degrees. After annealing and stripping the OH-t-PS, the contact angle was measured to be 89.6 degrees, confirming the presence of a PS monolayer present at the oxide-air interface.

Dummy samples were then prepared to evaluate the spincoating thickness for the BCP and brush materials. Both polymers are dissolved 2% by weight in Toluene, and after being spincoated at 3000RPM for 120 seconds, both films were 42nm in thickness, measured via ellipsometry in the SMFL.

A sample coated with BCP was then annealed under Argon for 2 hours at 250°C on a hotplate. Due to the insufficient annealing time compared to the 24 hour anneal performed in the primary reference paper [3], no self-assembly was expected to occur. Shown below in Figure 3 is a 20x magnification optical micrograph of the surface of this sample.

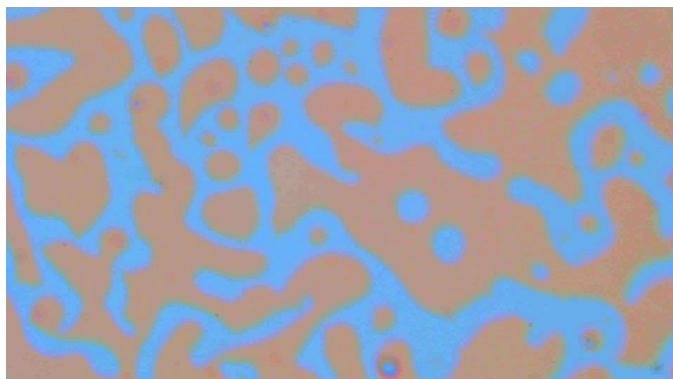


Figure 4: Optical Micrograph of BCP [orange] and Oxide [blue] dewetting.

Figure 4 shows dewetting of the BCP film on the brush treated Oxide film. For reference, the PMMA glass transition temperature is approximately 110°C and the PS glass transition temperature is approximately 104°C.

AFM scans of the surface showed that the orange areas were very smooth and no self-assembly had occurred within them. Further exploration will be done to solve the issue of film dewetting during anneal. Several experiments are

currently planned for next week in order to attempt solvent vapor annealing, a low temperature alternative.

Thermal annealing was then attempted using the Heraeus Oven in the SMFL. A new thermal controller was installed and offsets were determined using a thermocouple at +25 i.e. the setpoint on the thermal controller needed to be 25C higher to achieve the desired temperature. The full 24 hour anneal was then carried out at .9 Torr for 24 hours at 250C, with a small amount of nitrogen leaking in to the chamber to reduce atmospheric leaks. After the anneal was completed, destructive film oxidation was observed and the BCP film was destroyed. This is likely due to the presence of oxygen during the anneal, either in the N<sub>2</sub> gas flow or through vacuum leaks in the oven. SEM images of these samples were unable to resolve any pattern.

Solvent vapor annealing (SVA) was then carried out on new samples. Samples were annealed in both Toluene and Tetrahydrofuran (THF). First, an anneal was carried out overnight which resulted in complete film dewetting. Anneals were then done for 10 and 15 minutes in both Toluene and THF. In order to decorate the pattern so it could be viewed under a SEM, a 10 second decorating etch was done in the Drytek Quad in the SMFL at 50W power, with 40sccm O<sub>2</sub> flow and at 70mTorr pressure. SEM micrographs were then taken of these samples using the RIT Nano-Imaging Lab field emission SEM. Shown below in Figure 5 shows a SEM comparison of the Toluene and THF samples annealed for 10 minutes.

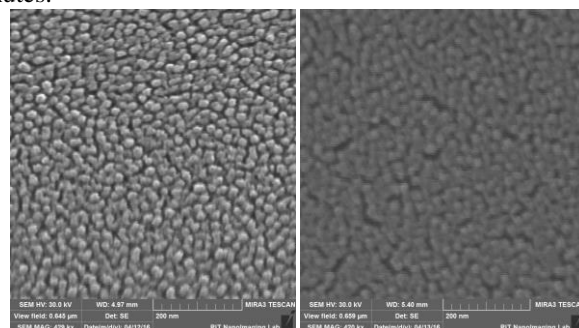


Figure 5: Comparison of DSA pattern for Toluene (left) and THF (right) SVAs taken at 429kX magnification.

No significant differences are observed in the pattern morphologies for the toluene and THF annealed samples. Evaluation of the dry develop etch moved forward with the toluene SVA, and samples were then etched using the same recipe for 30 seconds. Figure 6 shows the DSA pattern in polystyrene after the etch.

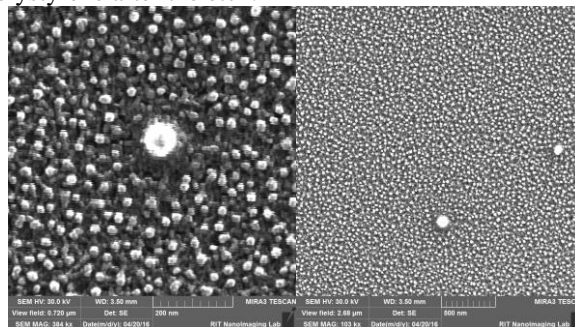




Figure 6: SEM Images of final DSA pattern at 384kX (left) and 103kX (right).

Figure 6 shows a noticeable increase in pattern contrast, with slightly smaller pillar diameters due to etch bias during the dry develop. As the PMMA is ashed away, some polystyrene is also ashed, reducing the diameter and height of the pillars slightly.

A wafer was then lithographically patterned using the ASML stepper in the SMFL. First, the wafer was coated with the surface brush process. Then, nLOF-2020 photoresist diluted 1:1 in PGMEA was spincoated at a speed of 3500RPM for 60 seconds. This resulted in a photoresist thickness of 132nm measured on the Nanospec and Spectramap. The ASML FEM mask was used, and 31x31 matrix sizes were used with a nominal dose of 60mJ/cm<sup>2</sup> with no focus offset. A dose step of 2mJ/cm<sup>2</sup> was used, with a focus step of .1um. Shown below in Figure 7 are SEM images taken of the lithographic sample.

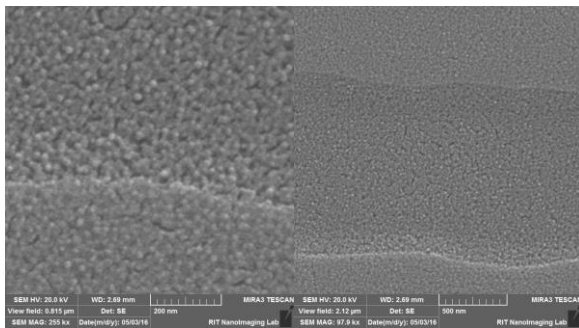


Figure 7: SEM images taken at 255kX (left) and 98kX (right) of the lithographically directed samples.

Note that there is no effect of the resist edge on the DSA pattern as was expected. This is potentially due to the large CD of the trench feature compared to the process flow reference paper [3]. A loss of contrast was also observed for the lithographically patterned samples due to the presence of the photoresist coating. Acceleration voltage was decreased so that the FEM pattern could be observed to locate the trenches, which complicated SEM imaging significantly. Lamellar structures did not form within the trenches, instead, polystyrene pillars resulted from the DSA annealing and patterning process. Analysis of the size of the pillars yielded a mean diameter of 16.8nm with a standard deviation of 2.3nm. Shown below in Figure 8 is a histogram of the pillar diameter in 1.5nm bins.

Normalized Pillar Diameter

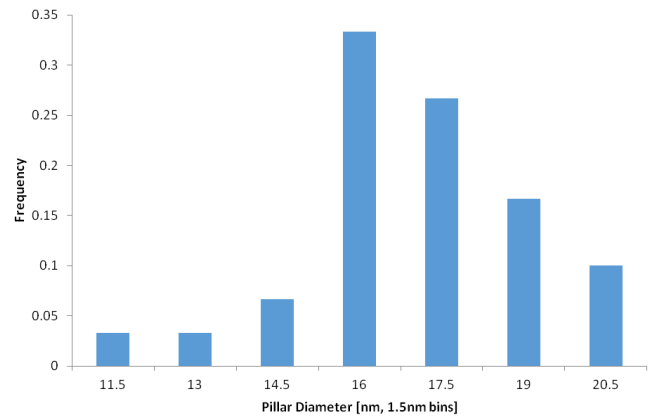


Figure 7 was generated using software by 1. The distribution of the pillar diameter is right-sided. There is possible concern

## V. CONCLUSIONS

The anticipated lamellar morphology was not observed in this project. A pattern of dense polystyrene pillars of mean diameter 16.8nm was observed after DSA pattern formation, with the pattern morphology not being significantly affected by SVA solvent type or lithographic direction as was expected. To best utilize this pattern, a tone reversal process could be carried out to form contact holes. An example of one such tone reversal process would be an oxide fill with CMP followed by another oxide RIE to clear the pillars and form contact holes in a hardmask.

## VI. FUTURE WORK

This project developed a repeatable process flow for DSA pattern development. In the future, experiments could be carried out using alternative BCPs to explore the final pattern morphologies of those materials. Reduction of trench CD using e-beam lithography will test the hypothesis that the polystyrene pillar morphology seen in this experiment was due to the surface effects dominating final pattern formation. There is also potential to explore the effects of more evenly matching BCP film height and the photoresist thickness, as the BCP is only 42nm thick while the photoresist is ~130nm thick. A randomly polymerized PS neutralization layer can also be used in place of an OH-t-PS surface brush layer. This would reduce sample preparation time significantly by cutting out the 120C 24 hour surface brush anneal. The thermal annealing can be investigated further to see if lower temperature/shorter anneals are feasible to achieve DSA pattern formation, or to attempt to diagnose the issues encountered using the Heraeus oven in the SMFL.

## VII. REFERENCES

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