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

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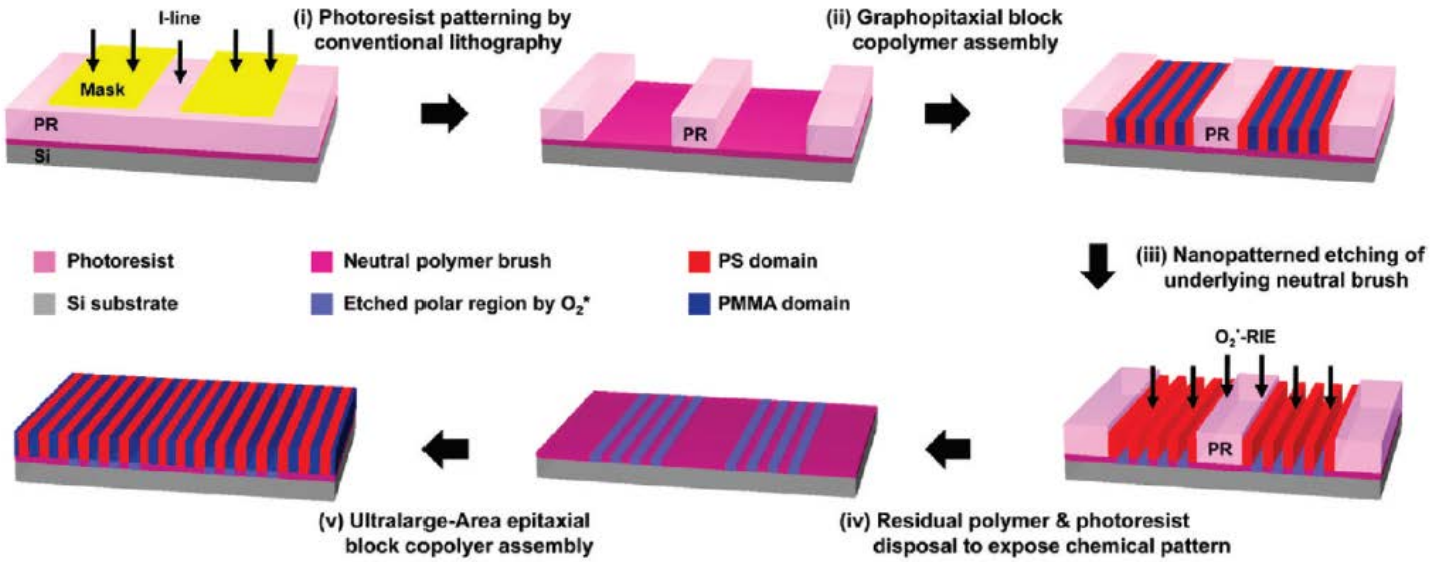
Purpose

- Goal: Develop a sub-lithographic Directed Self-Assembly (DSA) process at RIT to enable teaching and research opportunities.
- Objective: Achieve lamellar (line/space) structure formation using a Polystyrene-block-PMMA (PS-b-PMMA) Block Copolymer (BCP)
- The process flow for this experiment was based on work published by S.J. Jeong. [1]

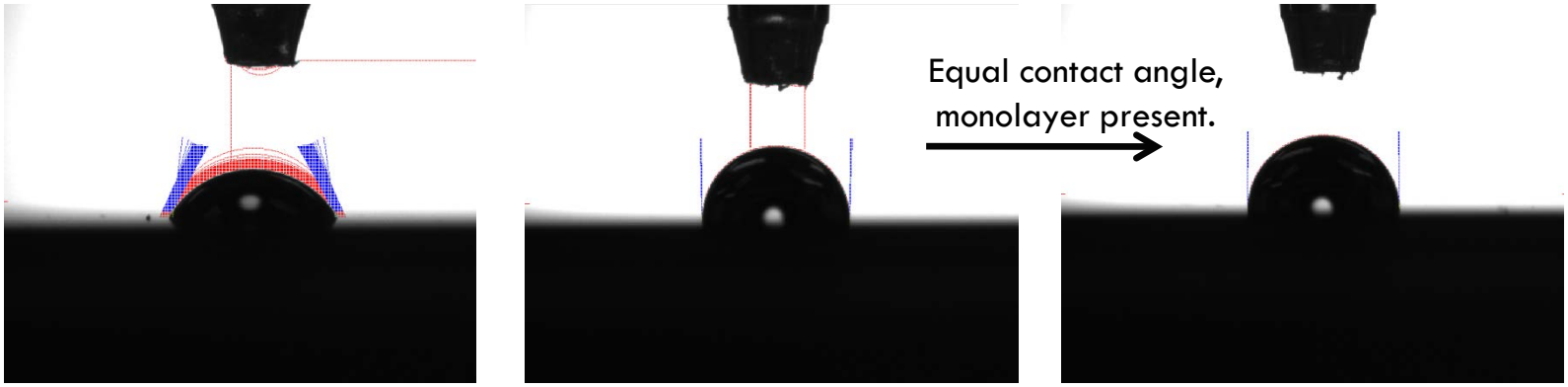
Process Flow



High-level process flow overview [1]

- Hydroxyl-terminated-Polystyrene was chosen for the surface brush material.
- nLOF-2020 was chosen as the photoresist to assist in graphoepitaxy.

Process Verification – Surface Brush



Oxide Reference

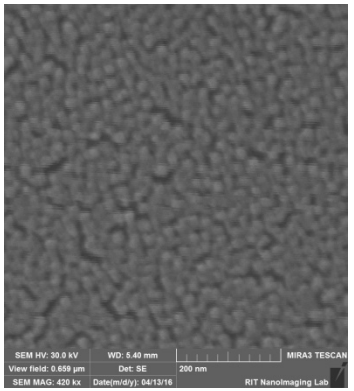
PS-t-OH as coated
after hardbake

PS-t-OH monolayer
after toluene strip

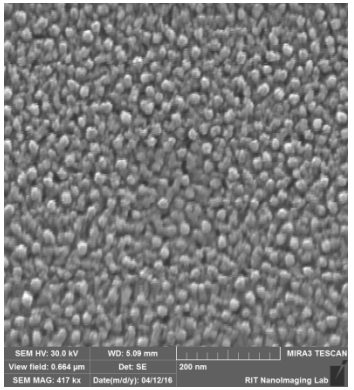
- Purpose: Create a neutral underlayer for DSA.
- OH-t-PS is spincast at 45nm thickness, then thermally reacted with SiO2 surface at 120C for 24hrs.
- After toluene strip, surface remains hydrophobic, indicating the presence of an OH-t-PS monolayer.

Block Copolymer Annealing – Thermal vs. Solvent Vapor

- Thermal annealing of the BCP must be carried out in an oxygen free environment, and typically takes 2 to 12 hours.
- Solvent Vapor Annealing [SVA] can be done at room temperature in approximately 10 minutes [4]
- Thermal annealing attempts resulted in destructive film oxidation.
- SVA splits determined that DSA morphology was not significantly affected by chosen solvent or annealing conditions.



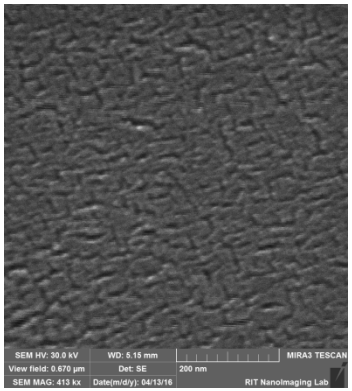
Tetrahydrofuran SVA SEM



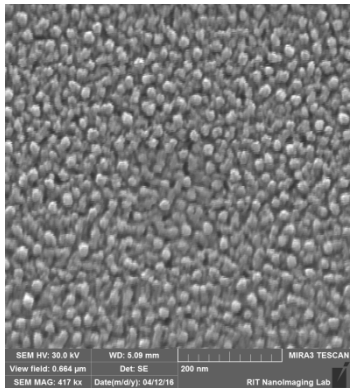
Toluene SVA SEM

Oxygen RIE Process Development

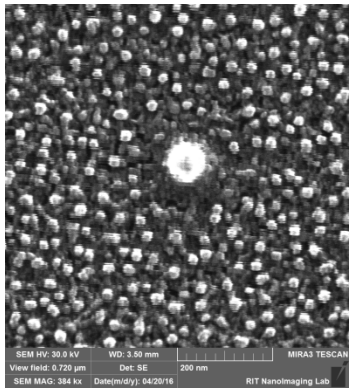
- The oxygen RIE is essentially a "dry develop," etching the PMMA compounds and leaving the PS behind.
- As the BCP film thickness was only 42nm, a low power RIE needed to be developed.
- Etches were stopped at 15 second increments to verify complete etching of the PMMA domains.



SiO2 Control 45s



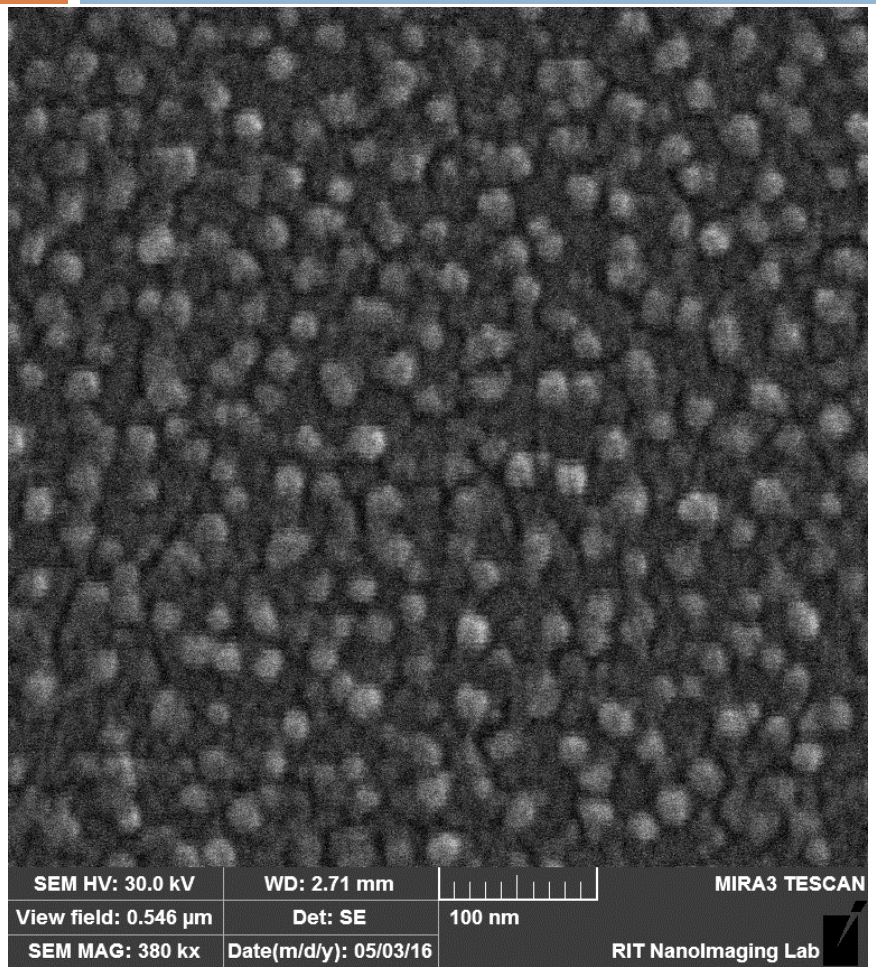
15s RIE SEM



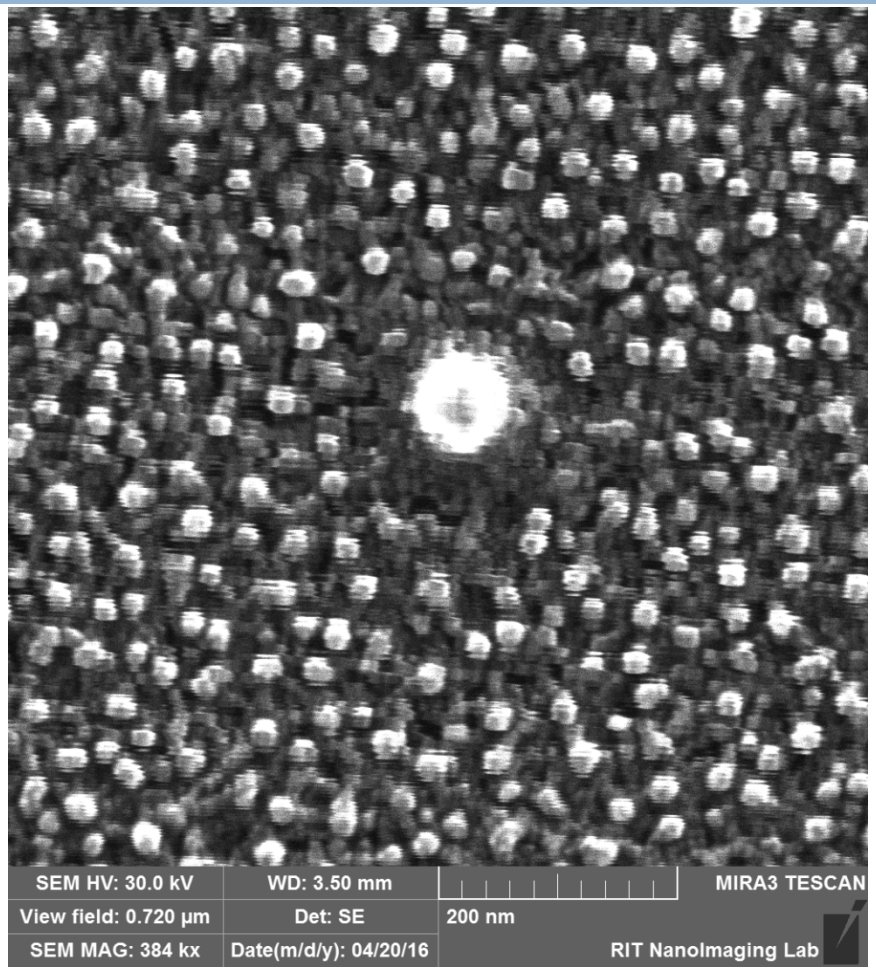
45s RIE SEM

FESEM Images

30s Etch – nLOF-2020 Patterned Wafer

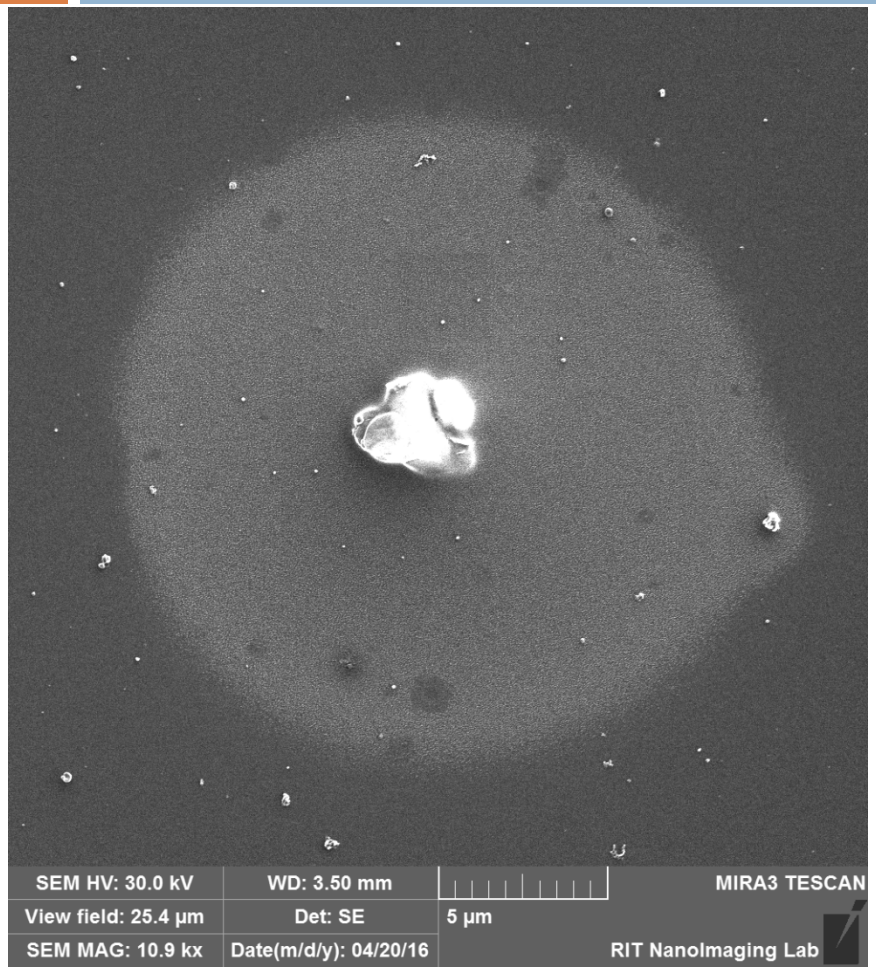


30s Etch – Unpatterned Wafer

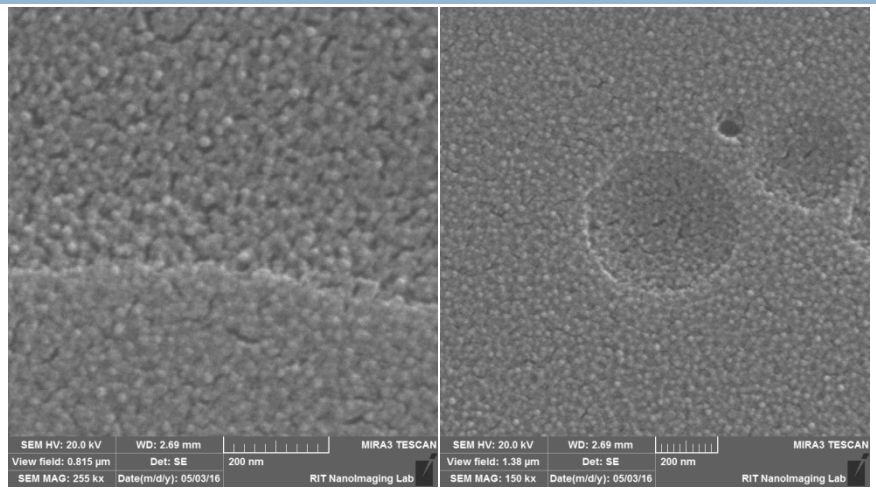


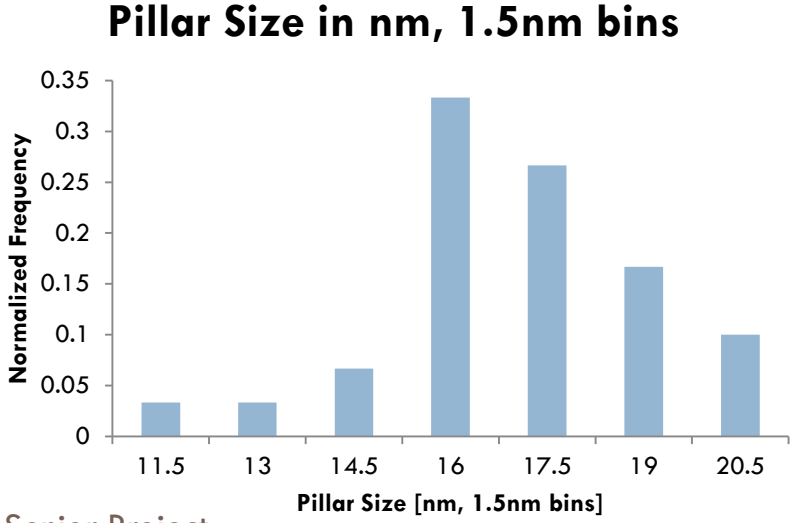
FESEM Images

30s Etch – Near Defect (Unpatterned)



30s Etch – Patterned on Resist Edge





Conclusions

- Anticipated lamellar morphology was not observed.
  - A dense “pillar” morphology of mean size 16.8nm formed.
  - Trench CDs may have been too large to induce graphoepitaxy.
- Contact hole patterning could be done using a tone-reversal mask, (e.g. oxide fill with CMP.)
- SVA showed larger than anticipated process latitude and did not significantly affect DSA pattern morphology.
- Lithographic pattern direction did not significantly affect DSA pattern morphology.

Future Work

- A randomly polymerized Polystyrene underlayer could be used to cut out the lengthy surface brush anneal. [1]
- Matching of the BCP/photoresist thicknesses may assist in graphoepitaxy.
- Thermal annealing of the BCP film can also be explored, if oxidation can be prevented.
- Additional analysis to determine etch bias and final polystyrene structure height.

Acknowledgements + References

- Dr. Thomas Smith
- Dr. Richard Hailstone
- SMFL Staff
- Dr. Robert Pearson and Dr. Dale Ewbank
- Dr. Surendra Gupta

- References:

  - *[1]S. Jeong and S. Kim, "Ultralarge-area block copolymer lithography via soft graphoepitaxy", Journal of Materials Chemistry, vol. 21, no. 16, p. 5856, 2011.*
  - [2]K. Koo, H. Ahn, S. Kim, D. Ryu and T. Russell, "Directed self-assembly of block copolymers in the extreme: guiding microdomains from the small to the large", *Soft Matter, vol. 9, no. 38, p. 9059, 2013.*
  - [3]S. Jeong, H. Moon, B. Kim, J. Kim, J. Yu, S. Lee, M. Lee, H. Choi and S. Kim, "Ultralarge-Area Block Copolymer Lithography Enabled by Disposable Photoresist Prepatterning", *ACS Nano, vol. 4, no. 9, pp. 5181-5186, 2010.*
  - *[4]* C. Sinturel, M. Vayer, M. Morris, and M. A. Hillmyer, "Solvent Vapor Annealing of Block Polymer Thin Films," Macromolecules, vol. 46, pp. 53995415, Jul 2013.