Exploration of Directed Self Assembly Polymers

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Introduction

Current Challenges to manufacturing

- Approaching limits of 193i
  - 10nm resolution has been demonstrated with multiple patterning
- EUV as an alternative is expensive with low throughput

Advantages of Directed Self Assembly

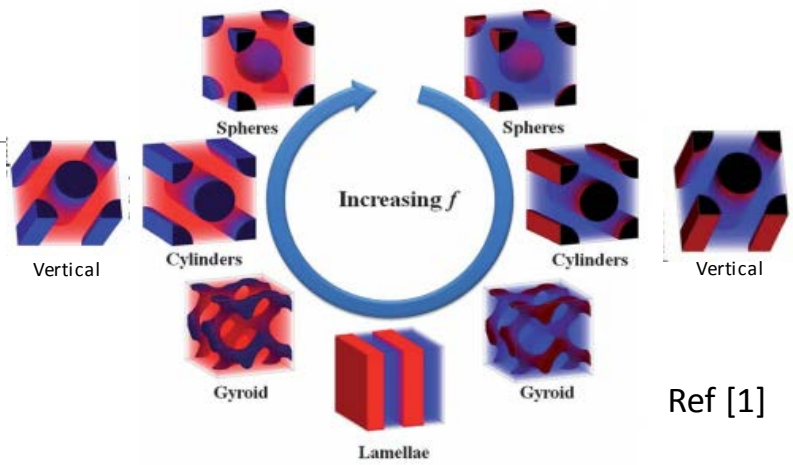
- Low resolution
  - Down to 10nm resolution and possibly smaller with multiple patterning
- Can be integrated with current patterning techniques and equipment
- Inexpensive

Disadvantages of DSA

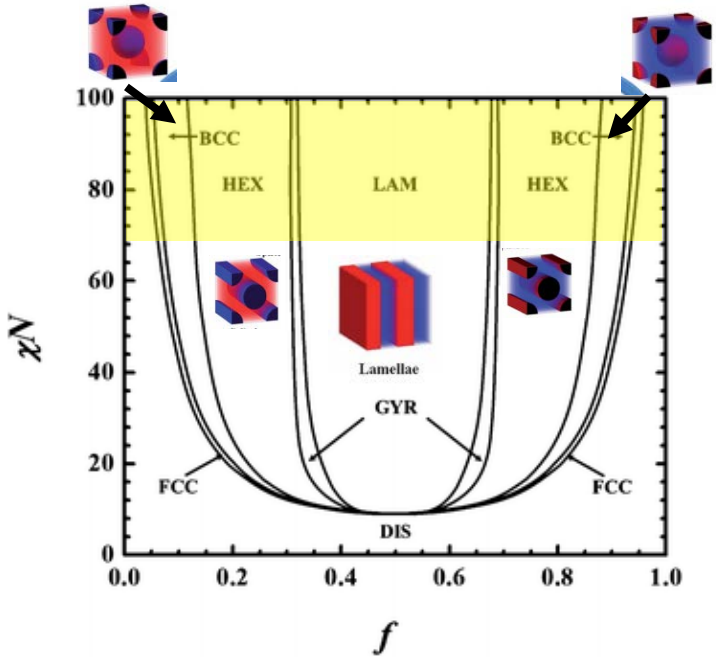
- Complex patterns can be difficult or impossible to form
- Has to be integrated into an existing lithography process
- Processing times may be long
- Defects in the directed pattern

Polymer Structure

- Polymer consists of 2 blocks
- Volume fraction of the polymer *(f)*, Flory interaction parameter *(x)*, and degree of polymerization *(N)* determine the structure
- The polymers used in the experiment were large enough to be in the highlighted region and above
- Lamellae and horizontal cylindrical used for creating lines
- Vertical cylindrical used for via holes

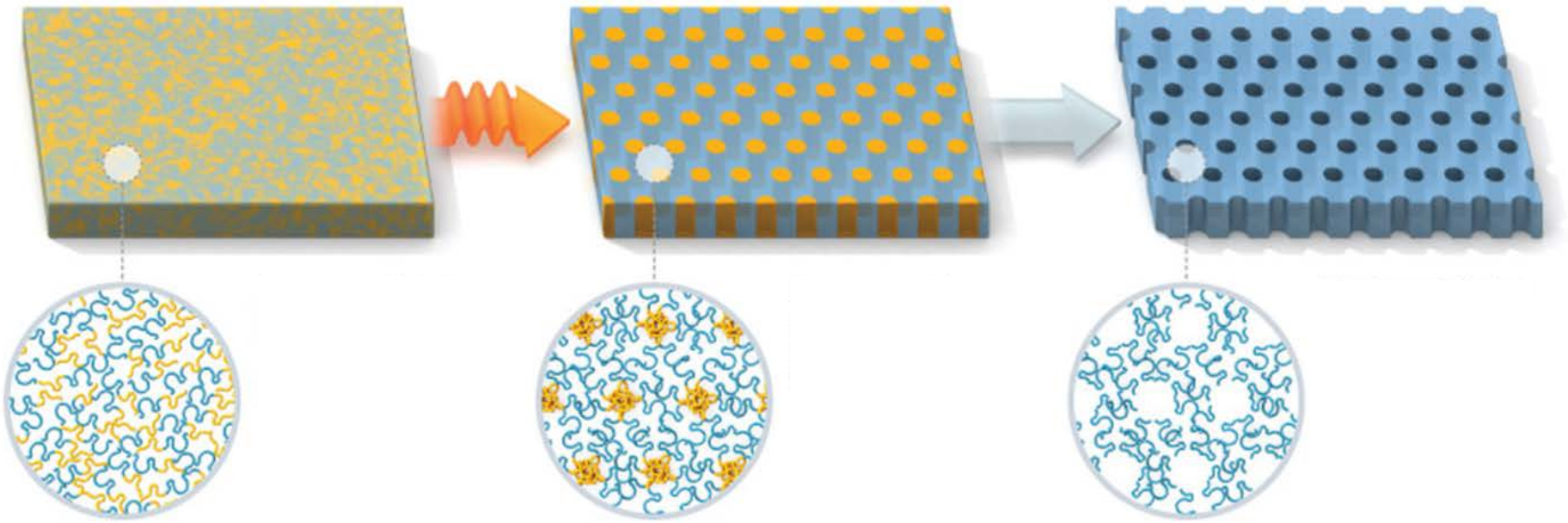


Ref [1]



Phase diagram of di-block co-polymer, Ref [4]

Via Hole Formation



A) The block co-polymer is coated with random orientation.
B) Annealing causes the polymer to orient so that one of the blocks forms vertical cylinders
C) The vertical cylinders are etched leaving via hole structures

Ref [3]

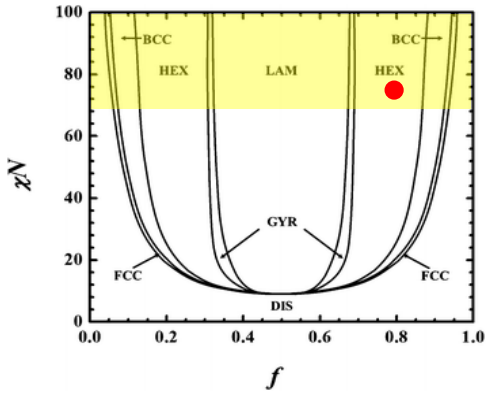
Polymers Used in This Work

PS-PDMS

- Di-block of polystyrene and polydimethylsiloxane
- PDMS contains silicon that becomes SiO2 when etched
- PDMS will form features while PS is etched away
- Molecular weight of the polymer was 67k-b-22k g/mole
  - This will create cylindrical structures

PS-PEO

- Di-block of polystyrene and polyethylene oxide
- PEO etches faster than PS
- PS will form the features
- Two sets of molecular weights were used
  - 52.5k-b-35.6k g/mole PS-b-PEO 26.9%mole PEO to create cylindrical structures
  - 40%mole PEO to create lamellae structures



Locations of project polymers. PS-b-PEO shown in red and PS-b-PDMS shown in blue

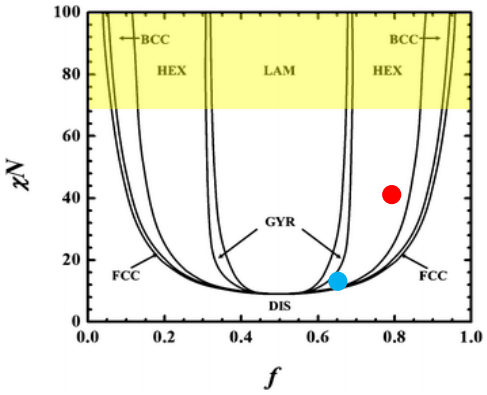
Reference Research

"Formation of Long-Range Stripe Patterns with Sub-10-nm Half-Pitch from Directed Self-Assembly of Block Copolymer" by M. Takenaka, et al. [2]

- Molecular weight of PS-b-PDMS was 1.03k-b-0.74k g/mole
- Coated on both native oxide surface and PDMS brush coated wafers
- Annealed at 170C for 24h in vacuum
- Both resulted in block separation and horizontal (cylindrical) lines

"Defect Analysis and Alignment Quantification of Line Arrays Prepared by Directed Self-assembly of a Block Copolymer" by C. Simao, et al. [5]

- Molecular weight of PS-PEO was 42k-b-11.5k g/mole
- Polymer was coated on native SI, Trimethoxy silane treated, and PS brush wafers
- Coated from 1% solution in toluene at 3000rpm for 30 seconds
- Annealed in chloroform vapor for 3 hours
- Horizontal (cylindrical) lines were observed on all surfaces

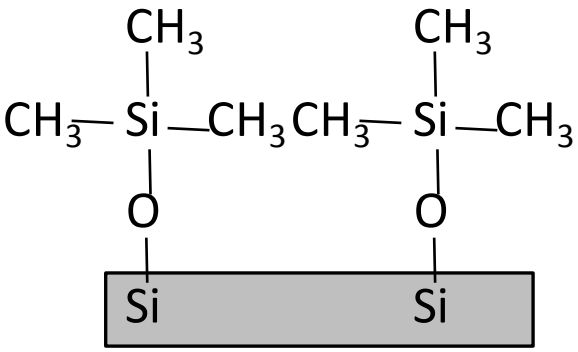


Locations of reference research. PS-b-PEO shown in red and PS-b-PDMS shown in blue

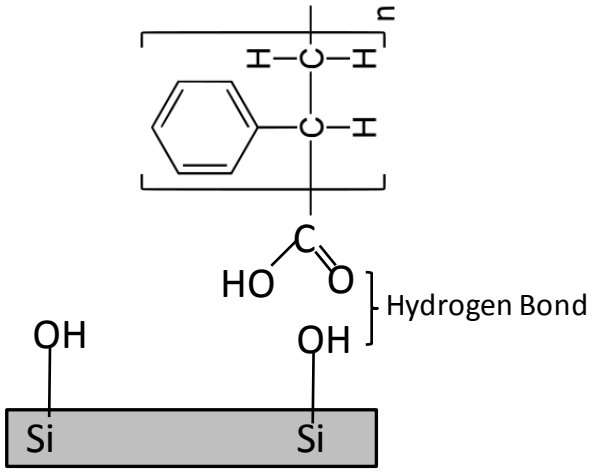
Surface Treatment

Polymers were coated on 2 different wafer surfaces

- HMDS (Hexamethyldisilazane) treated surface
  - Treated with vapor
  - Similar to the Trimethoxy silane used in the reference research [5]
- Carboxylic terminated PS layer
  - PS was spin coated, baked, then remaining polymer was washed in toluene and ethanol
  - Carboxylic group hydrogen bonds to the surface making it resistant to solvent removal



HMDS Treated



Carboxylic terminated PS

Process

- Coated with thin layers
  - Polymers dissolved in 1% solution with Toluene
  - Spun at 3000 rpm for 2 minutes
- Anneal to allow polymer to flow into shape
  - Can be done thermally, in solvent atmosphere, or combination of the two
  - PS-b-PDMS was annealed for 24 hours in Nitrogen ambient at 170C
  - PS-b-PEO was annealed in chloroform ambient for 3 hours at room temperature
- Measurements were taken on Atomic Force Microscope (AFM)
  - Thickness determined from topography map using tapping mode
  - Possible structure determined from phase imaging

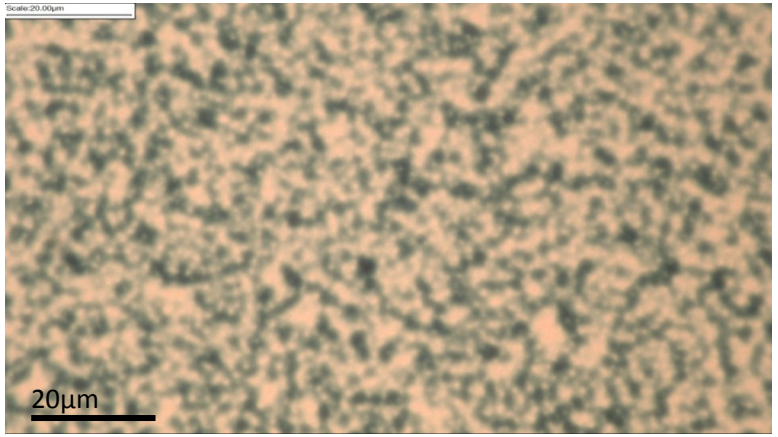
Blue oven thermocouple

SMFL SCS spin coater

PS-b-PDMS (Cylindrical)

- PS-b-PDMS originally coated on native Si showed de-wetting
- Filtering did not improve the coating
- Flooding the wafer did not improve coating quality
- Coating with a different solvent (THF) still resulted in de-wetting
- HMDS showed the same de-wetting problem
- Coating on a PS under-layer showed significant improvement
  - There was still enough film non uniformity to prevent accurate measurement

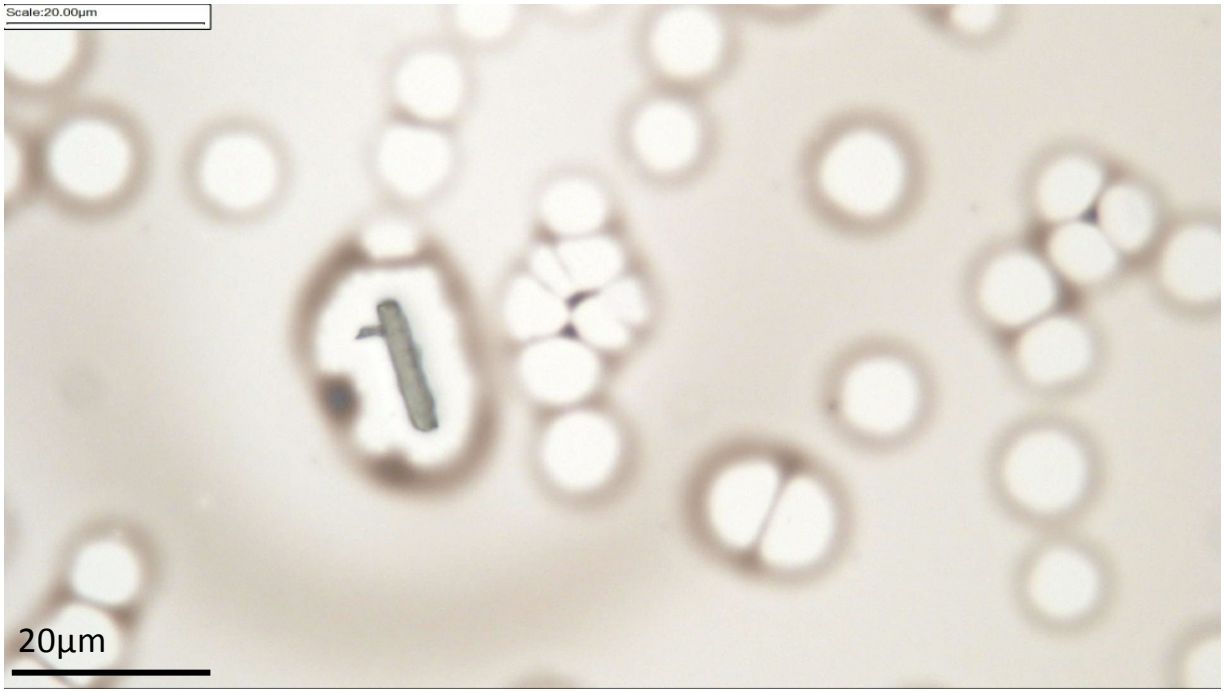
PDMS de-wetting on HMDS treated wafer



PDMS film non-uniformity on PS under-layer

40%mole PEO (Lamellae)

- Once coated the PEO crystallized
  - This is undesirable as the PEO clumps preventing phase separation
- A bake at 200C for 5 min did not remove crystals
  - Both melting point of PEO and glass transition temperature for PS are below 200C



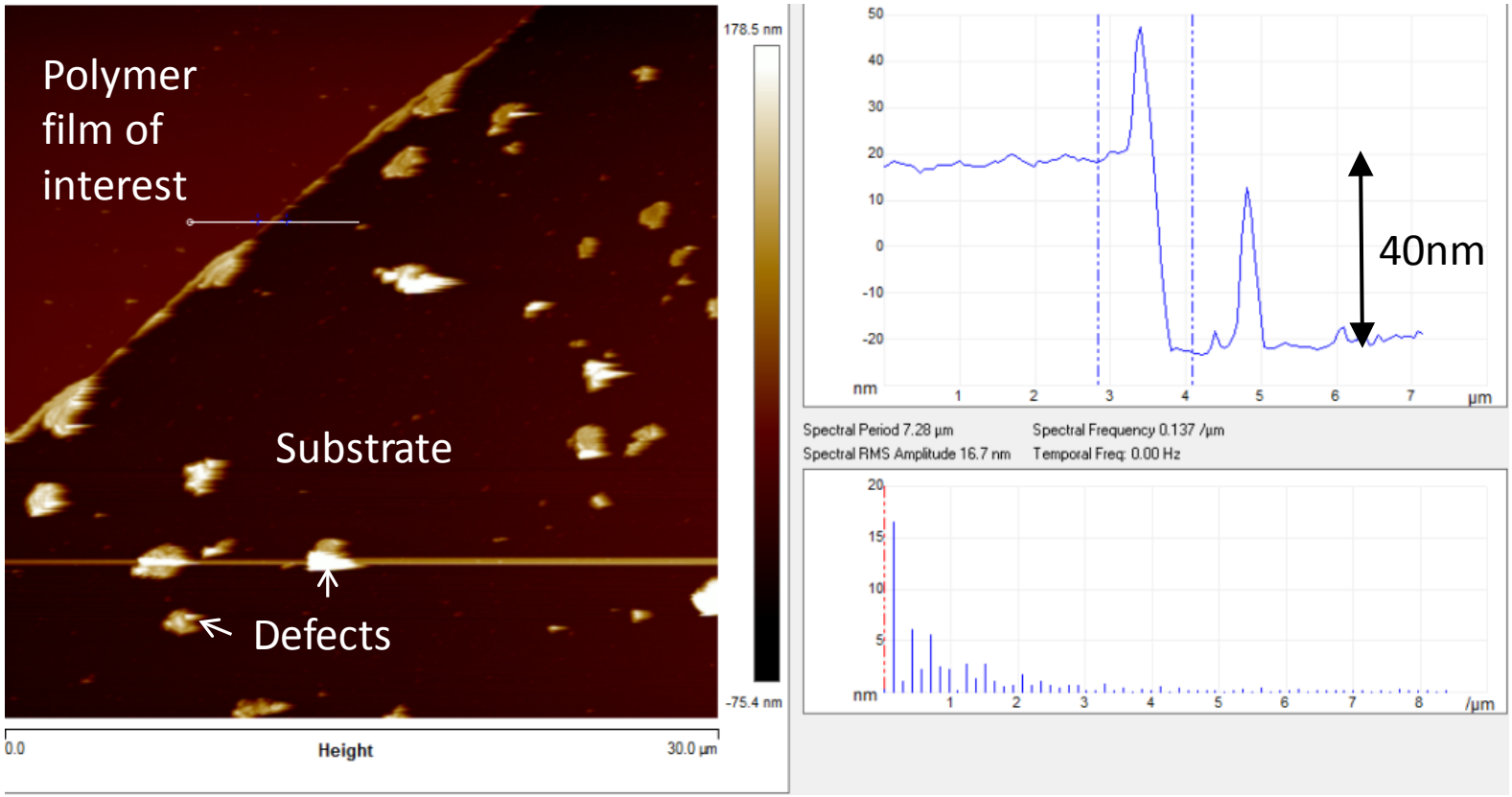
PEO crystallization on HMDS treated wafer

29%mole PEO (Cylindrical)

- Coatings were a success on both HMDS and PS under-layer
  - For the first samples surface uniformity was good enough for AFM measurement
- Step was made using X-acto knife to find thickness of the film
- 30um x 30um section containing the step was measured on the AFM
- The film height was found to be around 40nm
  - This is expected for a single polymer layer

Thickness Results

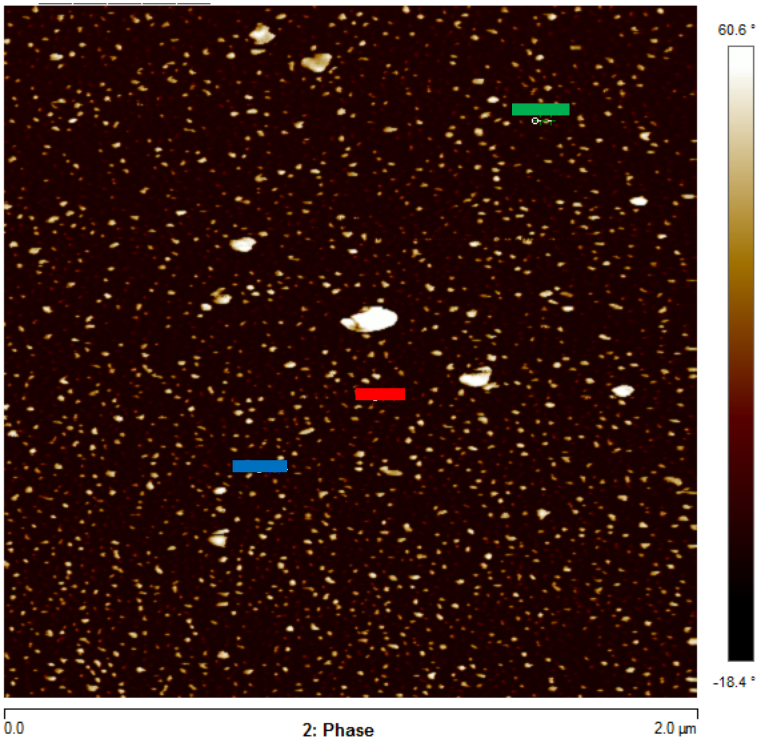
29%mole PEO cylindrical structure on PS under-layer



AFM step height

AFM Phase Measurement

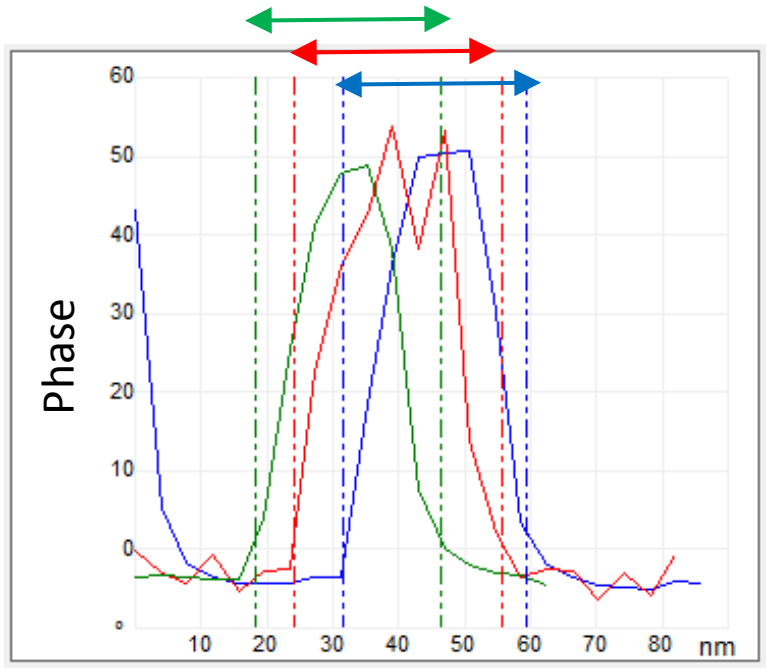
- 2um x 2um section of the film was measured
- Phase measurement used to measure elasticity of a material
- There is a significant difference between the block polymers to form image
- HMDS treated wafers did not form structures
- Width of three random dots were taken
  - Measurement locations shown with colored lines
- Indication of via hole structures



AFM Phase Image

AFM Phase Measurement

- The increase in phase represents the areas where PEO is present
- The PEO needs to be etched in order to form the via holes
- All widths were around 30nm



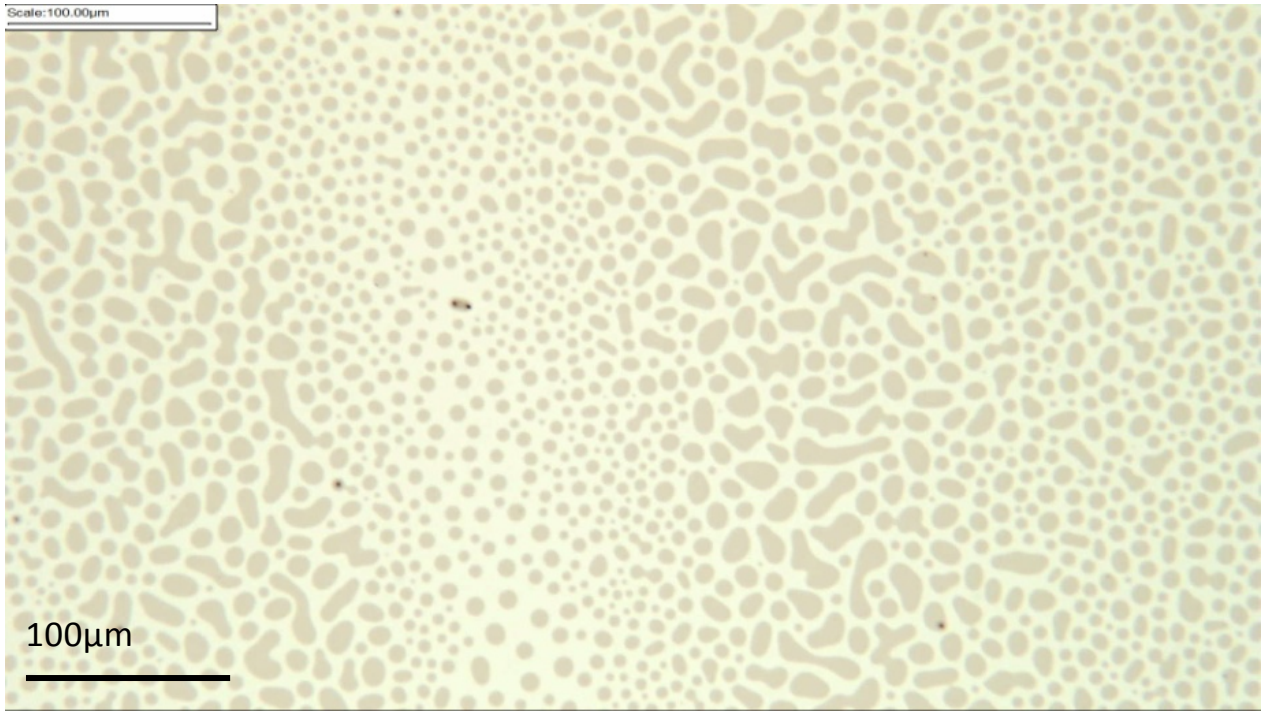
AFM Phase Measurement

29%mole PEO Etching

- Etching was attempted on the sample with via holes but the entire film was etched
  - A shorter time or lower power will be needed to prevent the entire film from etching away
- The limited number of samples prevented full etch rate characterization

29%mole PEO wafer re-work

- Repeat trials met with film de-wetting issues
  - De-wetting occurred during annealing
  - Surface cleanliness may disrupt PS adhesion



PEO de-wetting

Results Summary

Polymer	HMDS treated	PS under-layer
PS-b-PDMS	De-wetted	Non-uniform film
PS-b-PEO 29%mole	No structure formed	Via holes
PS-b-PEO 40%mole	Crystallized	Crystallized

Conclusions and Future Work

Conclusions

- De-wetting was the main source of error
- Too high of a PEO ratio will result in crystallization
- Surface cleanliness may impact the hydrogen bonding for the PS under-layer
- 30nm via holes can be achieved with the 29%mole PEO on PS under-layer
- DSA is very sensitive to the surface

Future Work

- Use a lower weight, smaller polymer
- Use a patterned surface to direct the pattern
- Have a more rigorous cleaning procedure for samples before processing
- Use different brush polymers
- Take AFM images before annealing to see the effects of annealing on separation of the blocks

References

[1] J. Y. Cheng, *et al.*, "Simple and Versatile Methods To Integrate Directed Self-Assembly with Optical Lithography Using a Polarity-Switched Photoresist," *ACS Nano,* vol. 4, pp. 4815-4823, Aug 2010.

[2] M. Takenaka, *et al.*, "Formation of Long-Range Stripe Patterns with Sub-10-nm Half-Pitch from Directed Self-Assembly of Block Copolymer," *Journal of Polymer Science Part B-Polymer Physics,* vol. 48, pp. 2297-2301, Nov 2010.

[3] Courtland, Rachel. "Self-Assembly Takes Shape." *IEEE Spectrum*. IEEE, 31 Jan. 2012. Web. 07 May 2015.

[4] Koo, Kyosung, Hyungju Ahn, Sang-Woo Kim, Du Yeol Ryu, and Thomas P. Russell. "Directed Self-assembly of Block Copolymers in the Extreme: Guiding Microdomains from the Small to the Large." Royal Society of Chemistry, 27 June 2013. Web. 7 May 2015.

[5] C. Simao, D. Tuchapsky, W. Khunsin, A. Amann, M. A. Morris, and C. M. S. Torres, "Defect Analysis and Alignment Quantification of Line Arrays Prepared by Directed Self-assembly of a Block Copolymer," in *Conference on Metrology, Inspection, and Process Control for Microlithography XXVIII*, San Jose, CA, 2014.

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