

# Exploration of Directed Self Assembly Polymers

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PAUL BISCHOFF

33<sup>RD</sup> ANNUAL MICROELECTRONIC ENGINEERING CONFERENCE  
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# Introduction

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## 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

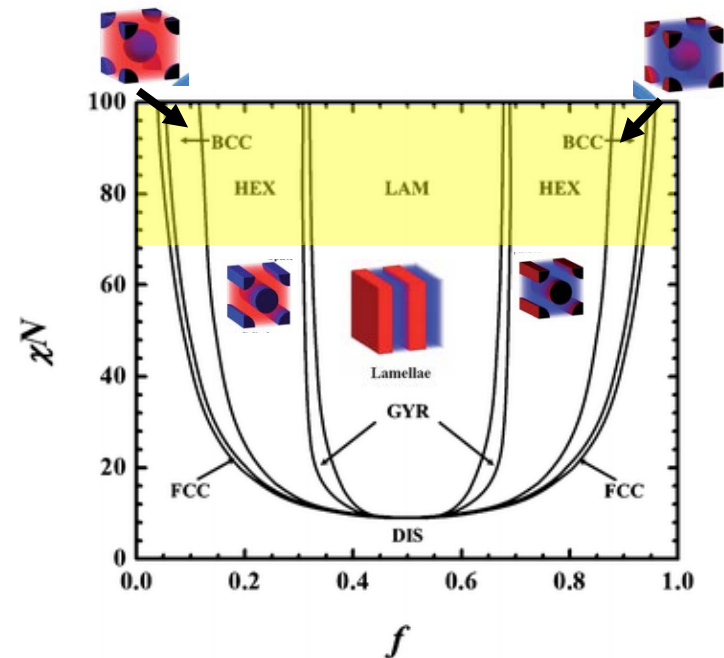
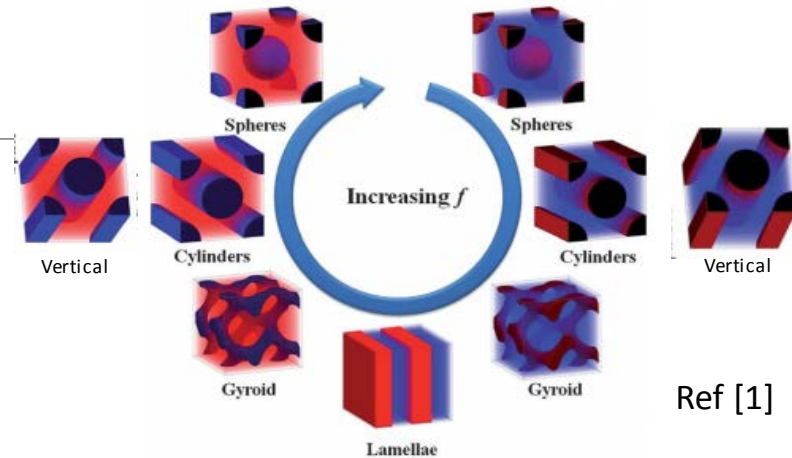
- Low resolution
  - Down to 10nm resolution and possibly smaller with multiple patterning
- Can be integrated with current patterning techniques and equipment
- Inexpensive

## 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

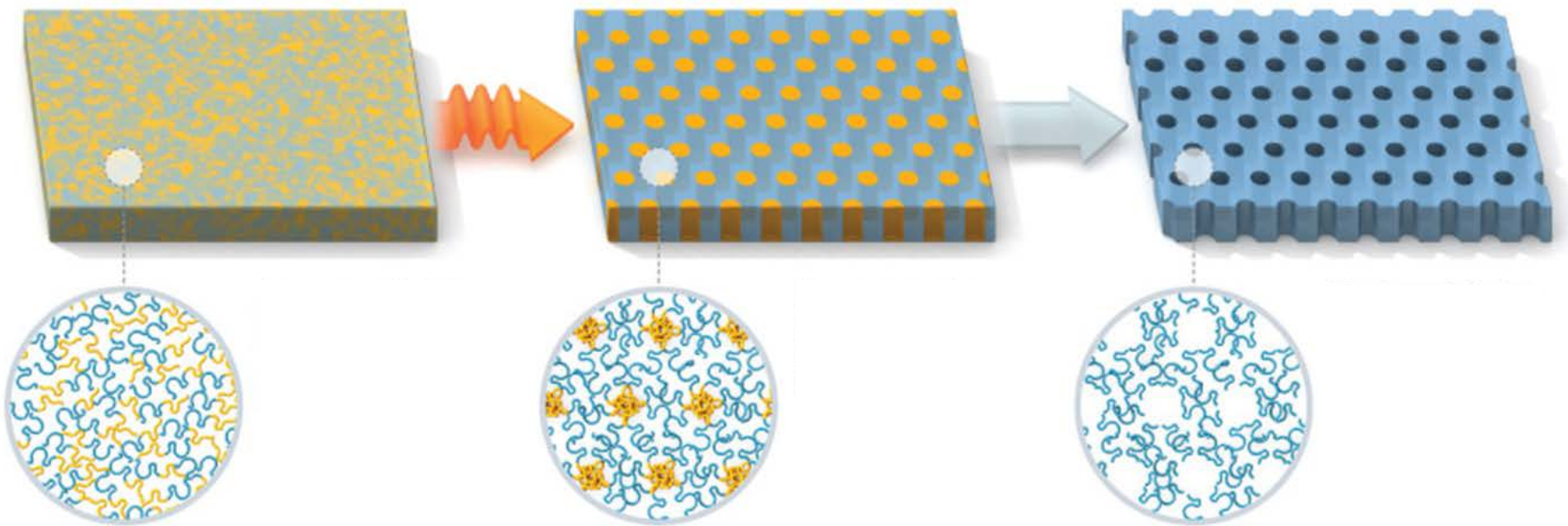
# Polymer Structure

- Polymer consists of 2 blocks
- Volume fraction of the polymer ( $f$ ), Flory interaction parameter ( $\chi$ ), 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



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]

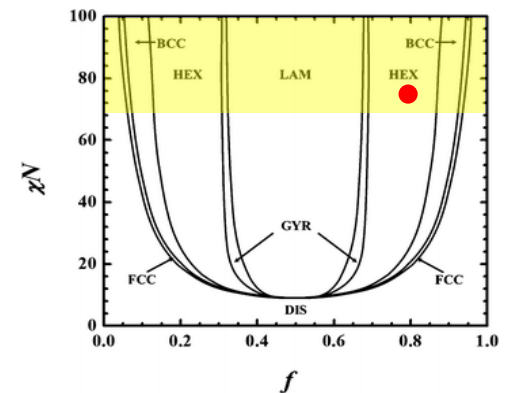
# Polymers Used in This Work

## PS-PDMS

- Di-block of polystyrene and polydimethylsiloxane
- PDMS contains silicon that becomes SiO<sub>2</sub> 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

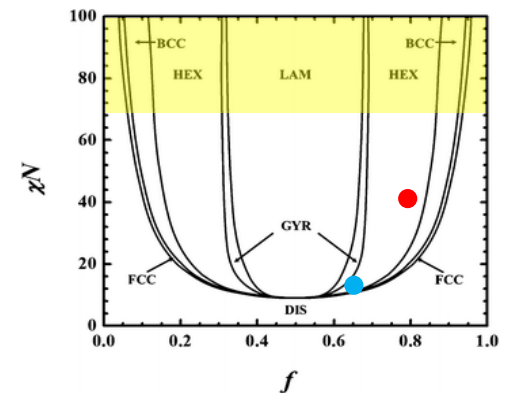
# Reference Research

"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

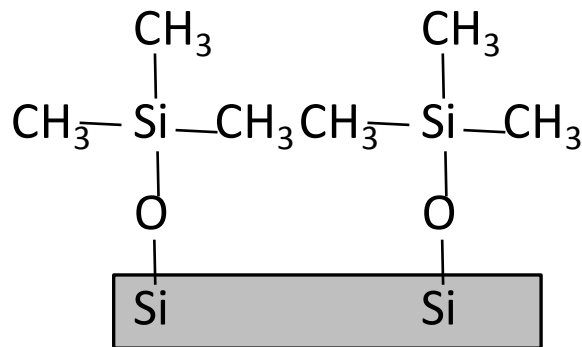


Locations of reference research. PS-b-PEO shown in red and PS-b-PDMS shown in blue

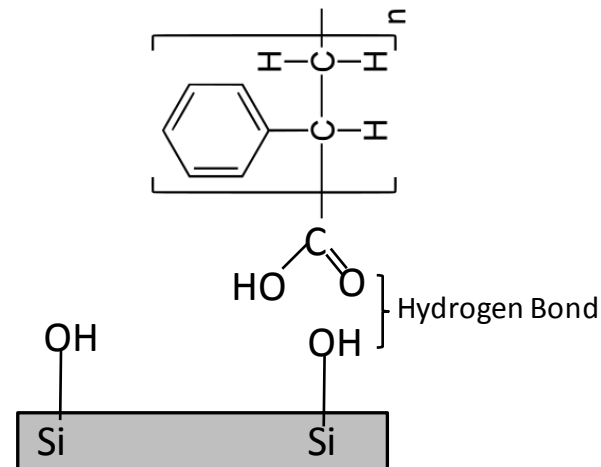
# Surface Treatment

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



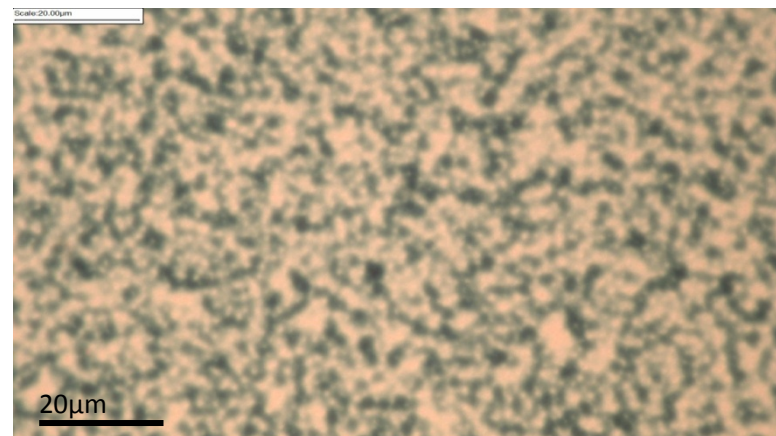
# PS-b-PDMS (Cylindrical)

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- 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)

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- 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

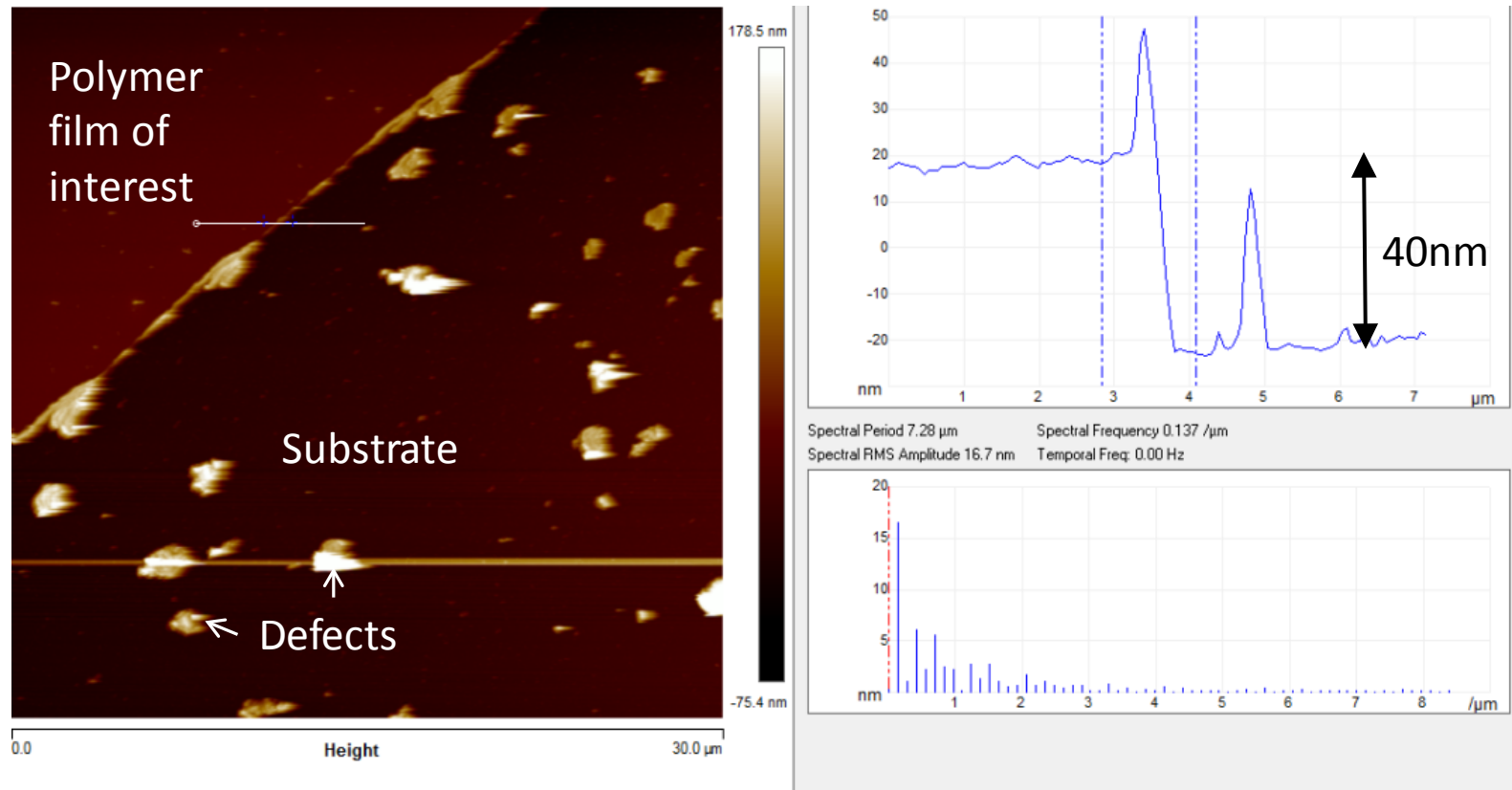
# 29% mole PEO (Cylindrical)

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- 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

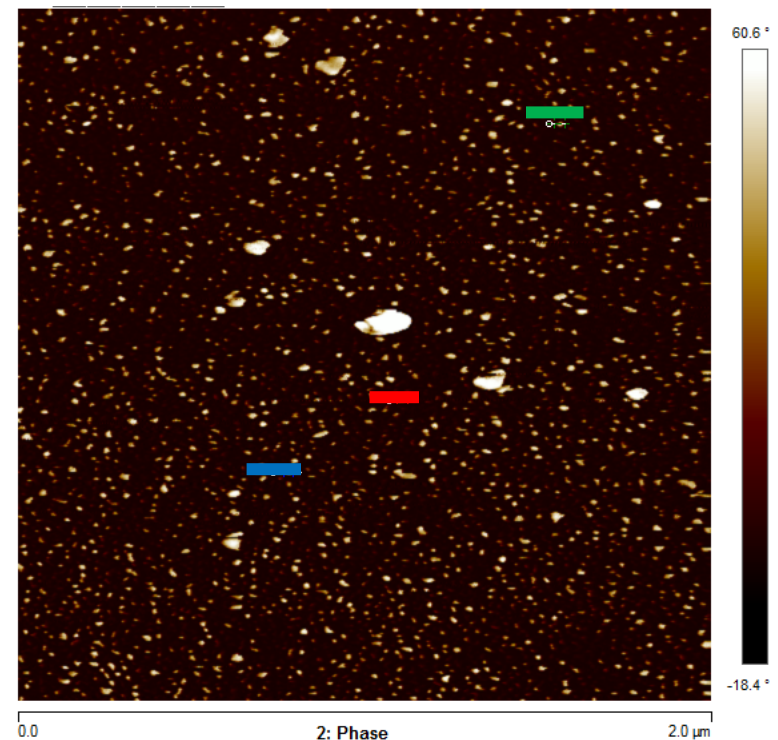
29% mole PEO cylindrical structure on PS under-layer



AFM step height

# AFM Phase Measurement

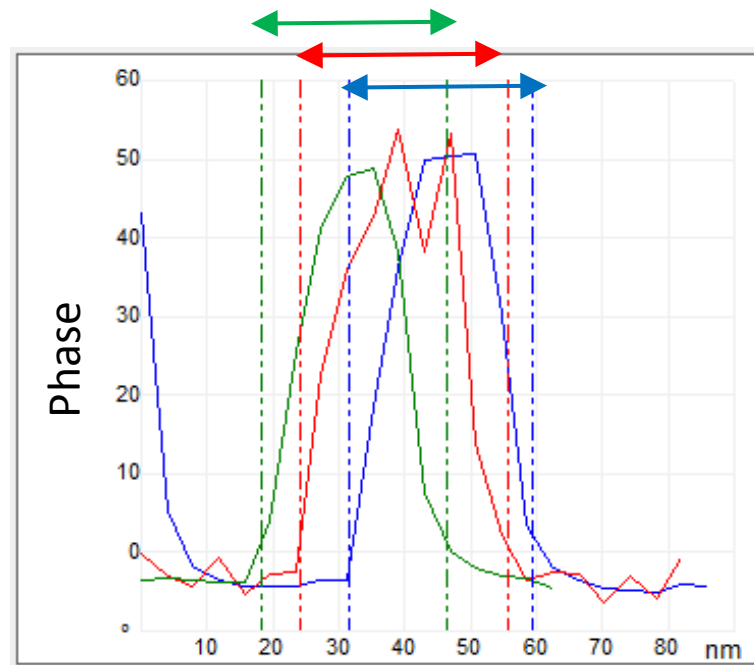
- 2um x 2um section of the film was measured
- Phase measurement used to measure elasticity of a material
- There is a significant difference between the block polymers to form image
- HMDS treated wafers did not form structures
- Width of three random dots were taken
  - Measurement locations shown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



Lateral distance

AFM Phase Measurement

# 29% mole PEO Etching

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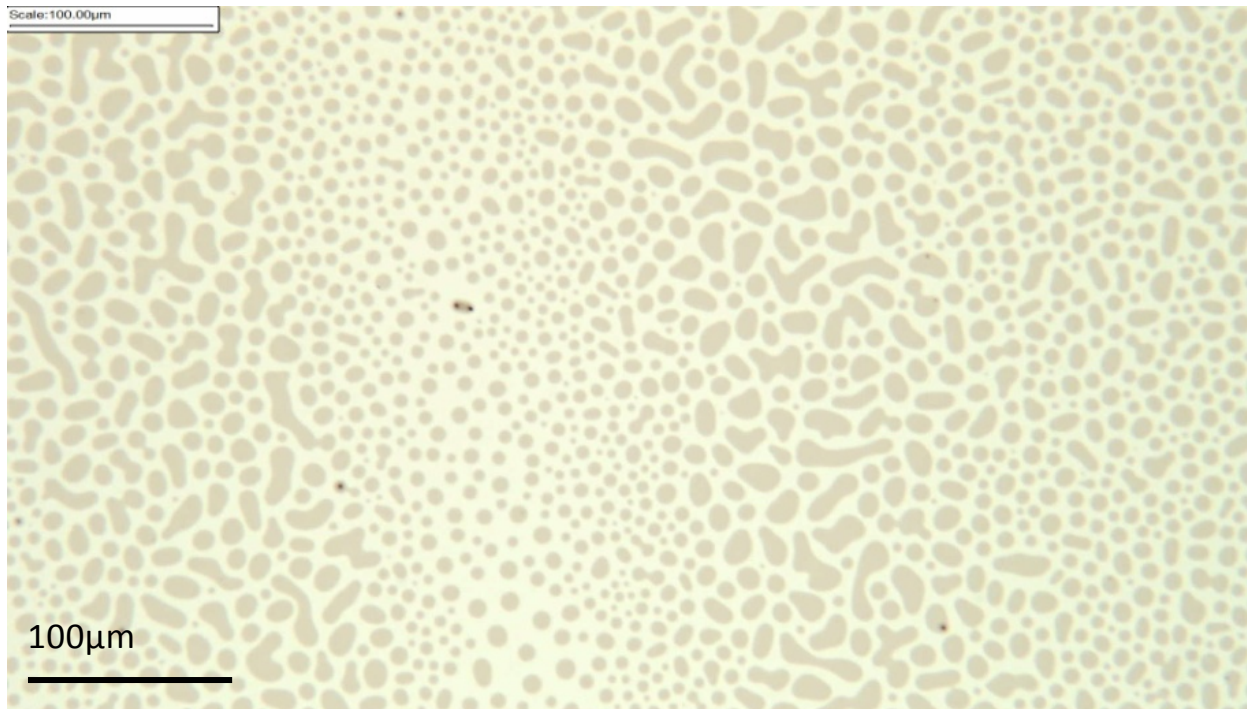
- Etching was attempted on the sample with via holes but the entire film was etched
  - A shorter time or lower power will be needed to prevent the entire film from etching away
- The limited number of samples prevented full etch rate characterization



# 29% mole PEO wafer re-work

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



PEO de-wetting



# Results Summary

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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

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## 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

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- [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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