Material
Measurement
Laboratory

National Institute of Standards and Technology • U.S. Department of Commerce

Line Edge Roughness of Directed Self Assembly PS-PMMA Block Copolymers – A Possible Candidate for Future Lithography

Chengqing Wang[1], Gila Stein[2], Gus Bosse[1], Wen-li Wu[1]

[1] Polymers Division, NIST, Gaithersburg, MD
[2] Dept. Chem. & Biomol. Eng., Univ. Houston, Houston, TX

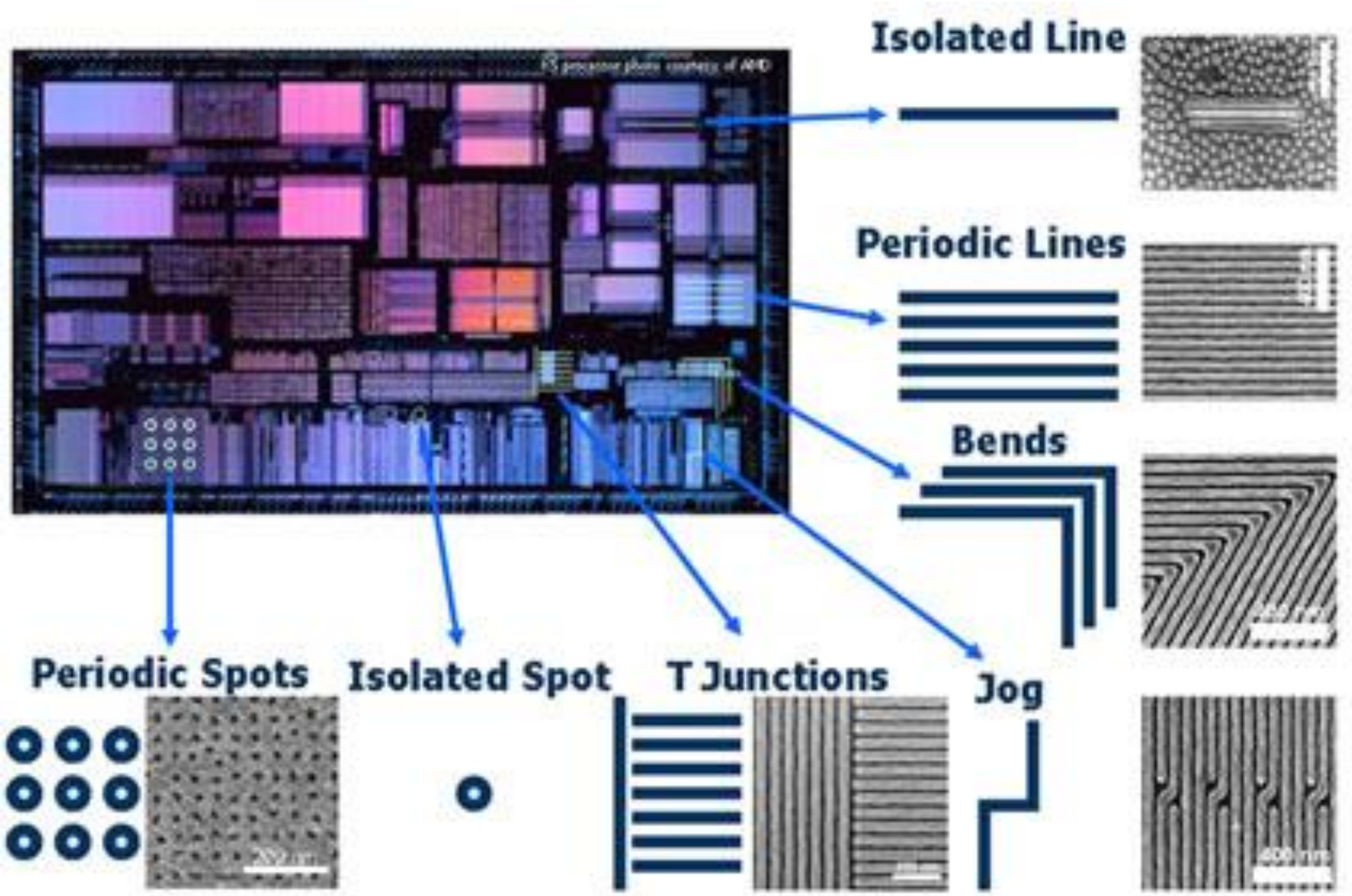
News & Analysis

Directed self-assembly grabs the spotlight at SPIE

Dylan McGrath

2/24/2010 3:04 AM EST

BCP DSA for CMOS Relevant Structures

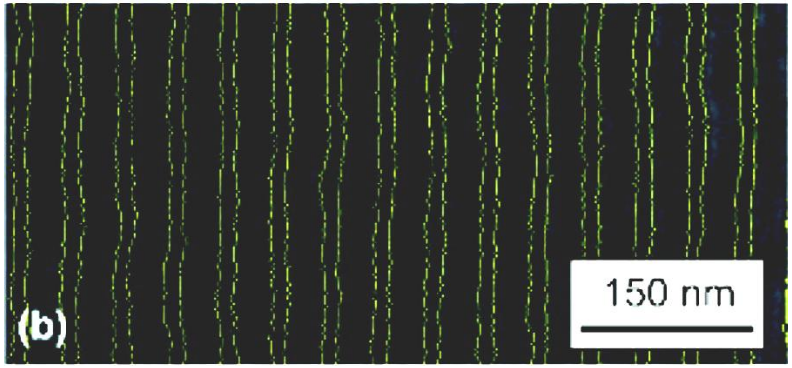


Courtesy of P. F. Nealey Research Group, Wisconsin

OBJECTIVES

- ITRS calls for a LER of ~1.3 nm at 3σ beyond 22 nm
- LER on DSA samples has only been measured with surface probes including AFM, SEM; the results are much worst than what is called for

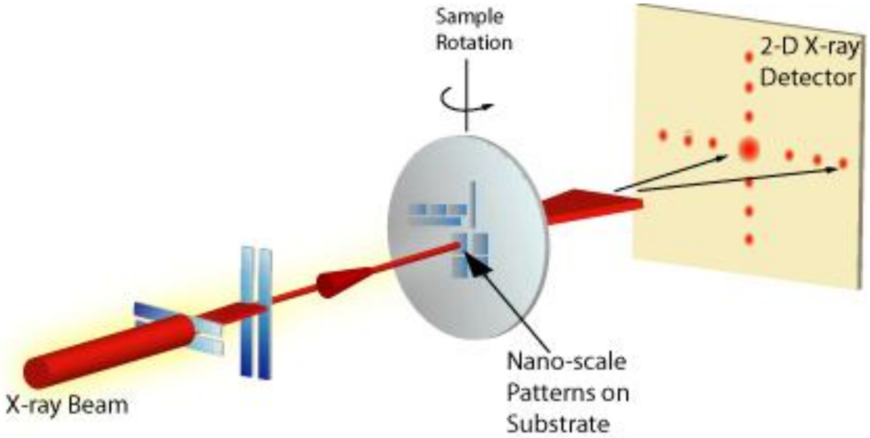
E-beam resist pattern LER = (3.5 ± 0.3) nm @3σ

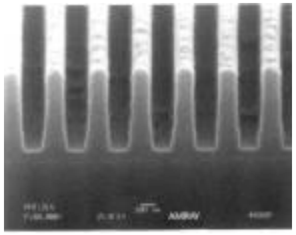


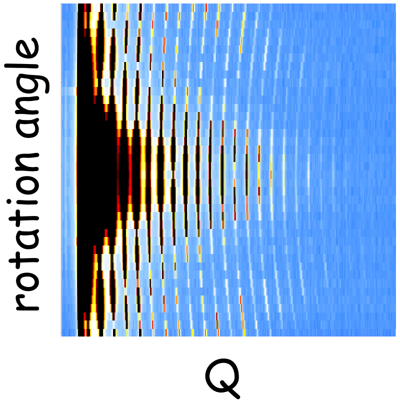
DSA pattern LER= (6.0 ± 0.6) nm @3σ

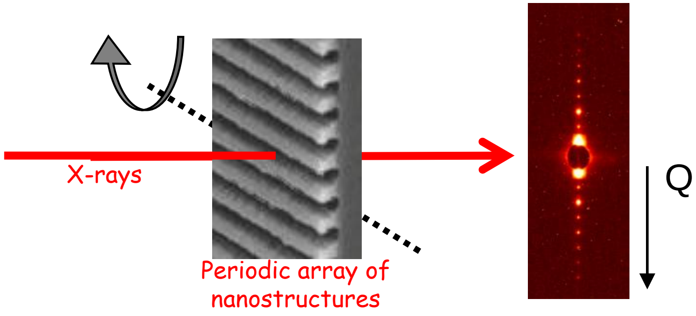
Critical Dimension Small Angle Scattering

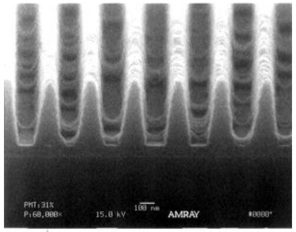
Nanostructure shape metrology with X-rays

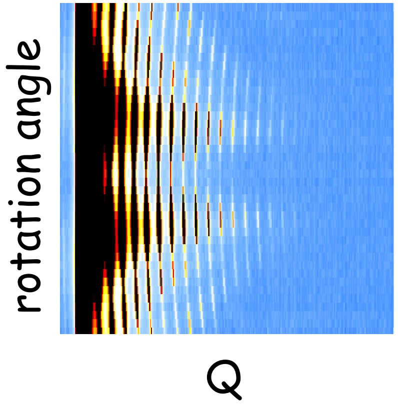








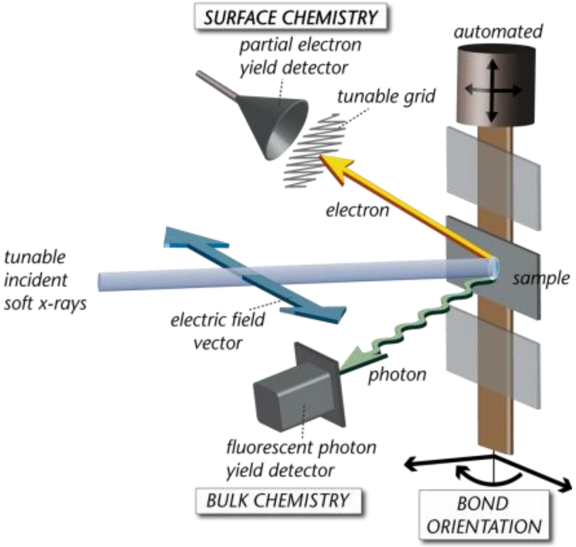




CD-SAXS was recently added to the ITRS Roadmap as a candidate next generation CD metrology

X - ray Measurements

- Transmission CD-SAXS
- Grazing incidence SAXS/WAXS
- X-ray diffraction & reflectivity
- NEXAFS / NEXAFS imaging



Applicable for Wide Range of Samples

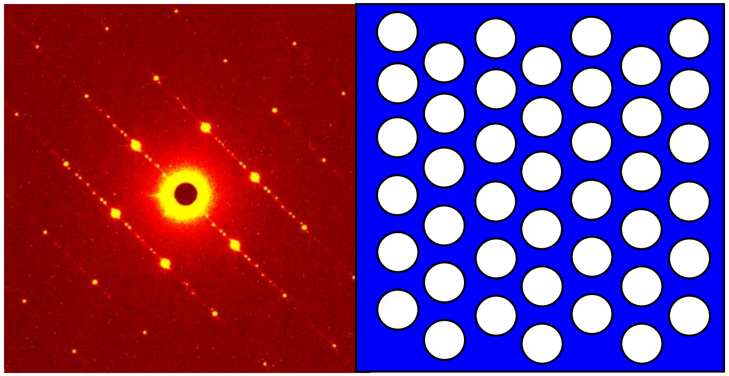
Materials measured non-destructively

- Photoresists (248 nm, 193 nm, EUV)
- Engineering Polymers (PMMA, PS)
- Oxides (SiO2)
- Nanoporous Matrices
- Barrier layers (SiN, SiCN)
- Metal Interconnects (Cu)

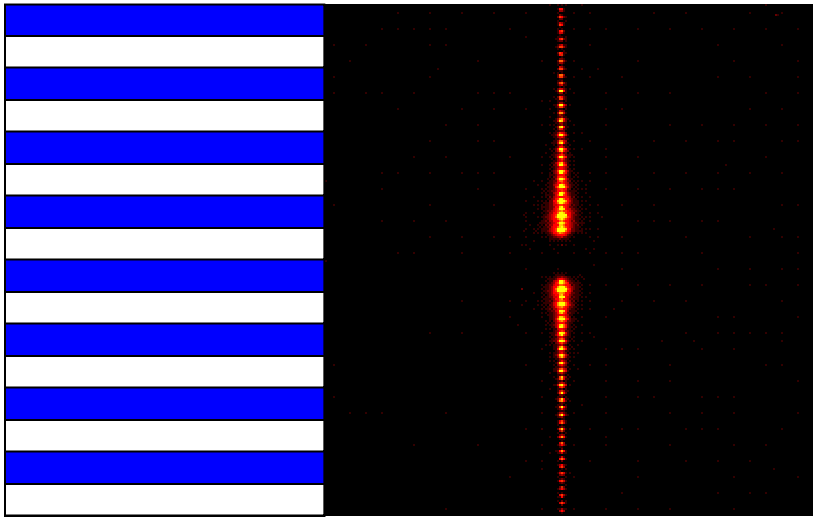
Pattern Geometries

- Line/Space patterns (gratings)
- Arrays of columns
- Arrays of holes (vias)

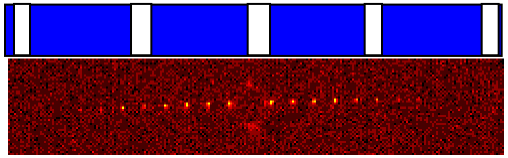
Hexagonal Close Packed 60 nm vias

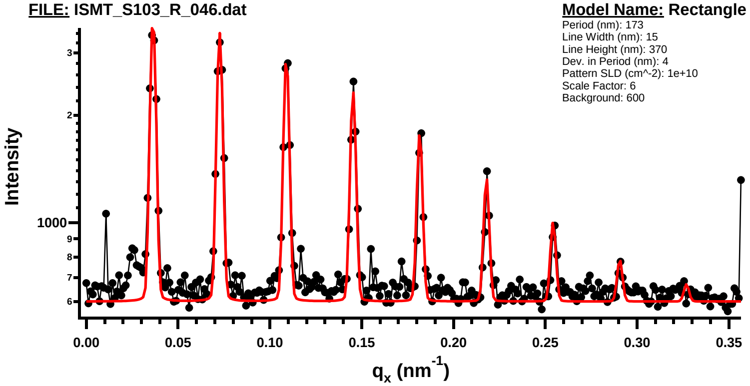


Dense (1:1 spacing) 550 nm lines

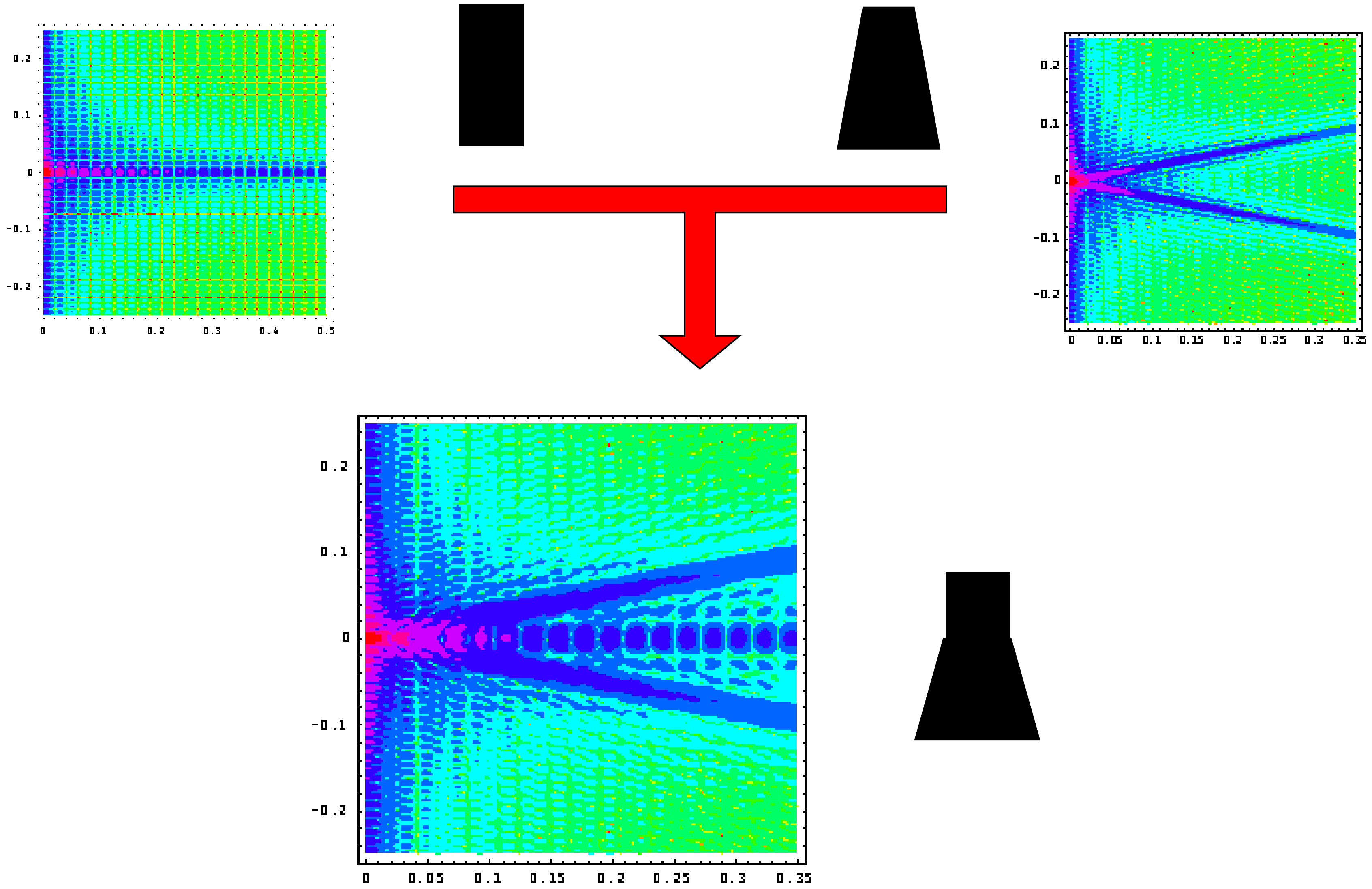


Sparse (1:10 spacing) 15nm lines



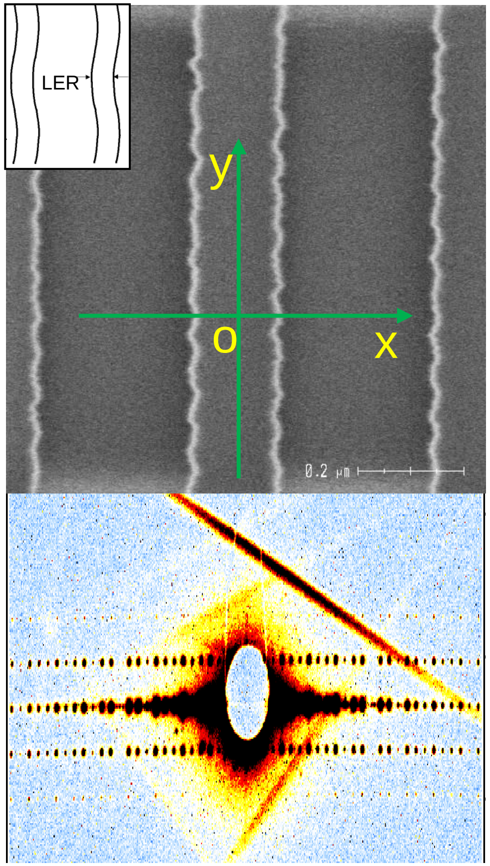


More Complicated Structures

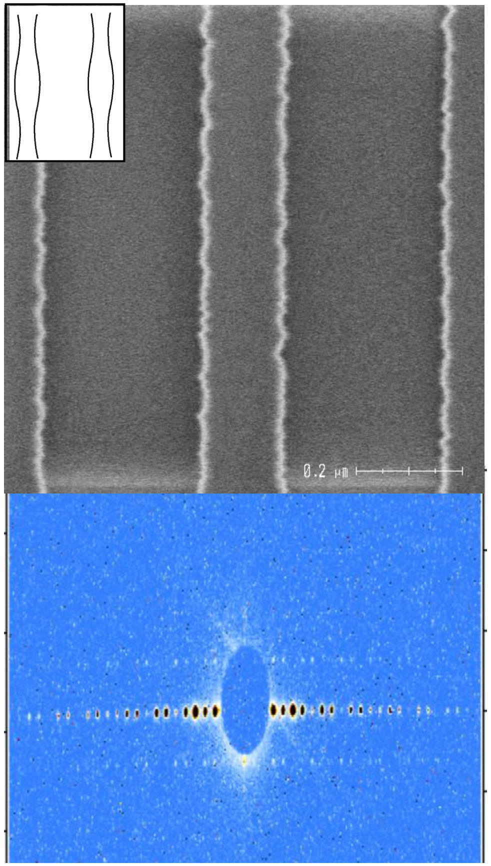


Designed LER with a fixed wavelength

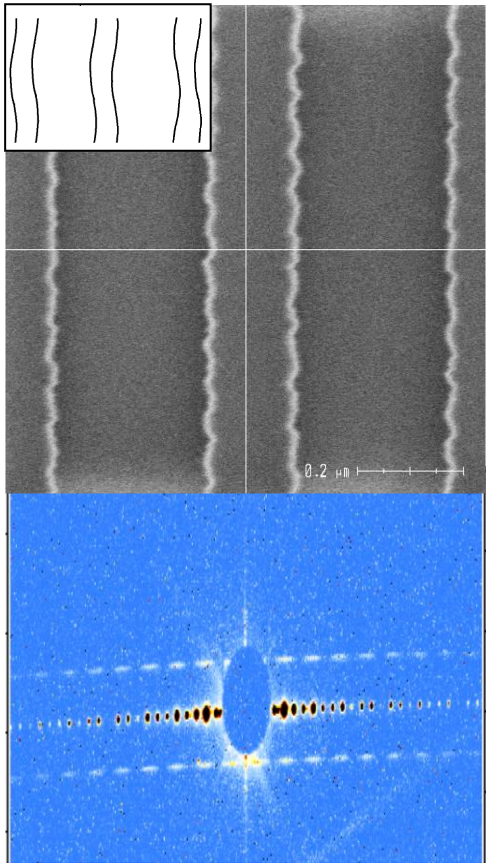
NIST-Intel-Sematech



$$f_L = -w + A\sin(2\pi f y + \phi_0)$$
$$f_R = w + A\sin(2\pi f y + \phi_0)$$



$$f_L = -w - A\sin(2\pi f y + \phi_0)$$
$$f_R = w + A\sin(2\pi f y + \phi_0)$$



$$f_L = -w + A\sin(2\pi f y + \phi_L)$$
$$f_R = w + A\sin(2\pi f y + \phi_R)$$

CD-SAXS Dimensional Metrology References

1. Wu, W.; Lin, E. K.; Lin, Q. H.; Angelopolous, M., Small angle neutron scattering measurements of nanoscale lithographic features. *J. Appl. Phys.* **2000,** *88* (12), 7298-7303.
2. Jones, R. L.; Hu, T.; Lin, E. K.; Wu, W. L.; Kolb, R.; Casa, D. M.; Bolton, P. J.; Barclay, G. G., Small angle x-ray scattering for sub-100 nm pattern characterization. *Appl. Phys. Lett.* **2003,** *83* (19), 4059-4061.
3. Hartschuh, R.; Ding, Y.; Roh, J. H.; Kisliuk, A.; Sokolov, A. P.; Soles, C. L.; Jones, R. L.; Hu, T. J.; Wu, W. L.; Mahorowala, A. P., Brillouin scattering studies of polymeric nanostructures. *J. Polym. Sci. Pt. B-Polym. Phys.* **2004,** *42* (6), 1106-1113.
4. Hu, T. J.; Jones, R. L.; Wu, W. L.; Lin, E. K.; Lin, Q. H.; Keane, D.; Weigand, S.; Quintana, J., Small angle x-ray scattering metrology for sidewall angle and cross section of nanometer scale line gratings. *J. Appl. Phys.* **2004,** *96* (4), 1983-1987.
5. Jones, R. L.; Hu, T.; Soles, C. L.; Lin, E. K.; Wu, W.; Casa, D. M.; Mahorowala, A., Preliminary evaluation of line-edge roughness metrology based on CD-SAXS. *Metrology, Inspection, and Process Control for Microlithography Xviii, Pts 1 and 2* **2004,** *5375*, 191-198.
6. Jones, R. L.; Lin, E. K.; Lin, Q. H.; Weigand, S. J.; Keane, D. T.; Quintana, J. P.; Wu, W. L., Cross section and critical dimension metrology in dense high aspect ratio patterns with CD-SAXS. *Characterization and Metrology for ULSI Technology 2005* **2005,** *788*, 403-406.
7. Jones, R. L.; Lin, E. K.; Qinghuan, L.; Weigand, S. J.; Keane, D. T.; Quintana, J. P.; Wen-li, W., Cross section and critical dimension metrology in dense high aspect ratio patterns with CD-SAXS. *AIP Conference Proceedings* **2005,** (788), 403-6.
8. Jones, R. L.; Lin, E. K.; Wu, W. L.; Weigand, S. J.; Keane, D. T.; Quintana, J. M., Cross sectional measurements of dense high aspect ratio patterns using CD-SAXS. *Metrology, Inspection, and Process Control for Microlithography XIX, Pts 1-3* **2005,** *5752*, 404-411.
9. Jones, R. L.; Soles, C. L.; Lin, E. K.; Hu, W.; Reano, R. M.; Pang, S. W.; Weigand, S. J.; Keane, D. T.; Quintana, J. P., Pattern fidelity in nanoimprinted films using CD-SAXS. *Emerging Lithographic Technologies IX, Pts 1 and 2* **2005,** *5751*, 415-422.
10. Jones, R. L.; Hu, T. J.; Soles, C. L.; Lin, E. K.; Reano, R. M.; Casa, D. M., Real-time shape evolution of nanoimprinted polymer structures during thermal annealing. *Nano Letters* **2006,** *6* (8), 1723-1728.
11. Jones, R. L.; Soles, C. L.; Lin, E. K.; Hu, W.; Reano, R. M.; Pang, S. W.; Weigand, S. J.; Keane, D. T.; Quintana, J. P., Pattern fidelity in nanoimprinted films using critical dimension small angle x-ray scattering. *Journal of Microlithography Microfabrication and Microsystems* **2006,** *5* (1).
12. Jones, R. L.; Wu, W. L.; Wang, C. Q.; Lin, E. K.; Kwang-Woo, C.; Rice, B. J.; Thompson, G. M.; Weigand, S. J.; Keane, D. T., Characterization of line edge roughness using CD-SAXS - art. no. 61520N. *Metrology, Inspection, and Process Control for Microlithography XX, Pts 1 and 2* **2006,** *6152*, N1520-N1520.
13. Knight, S.; Dixson, R.; Jones, R. L.; Lin, E. K.; Orji, N. G.; Silver, R.; Villarrubia, J. S.; Vladar, A. E.; Wu, W. L., Advanced metrology needs for nanoelectronics lithography. *Comptes Rendus Physique* **2006,** *7* (8), 931-941.
14. Chengqing, W.; Jones, R. L.; Lin, E. K.; Wen-li, W.; Villarrubia, J. S.; Kwang-Woo, C.; Clarke, J. S.; Rice, B. J.; Leeson, M. J.; Roberts, J.; Bristol, R.; Bunday, B., Line edge roughness characterization of sub-50 nm structures using CD-SAXS: round-robin benchmark results. *Proceedings of the SPIE - The International Society for Optical Engineering* **2007**, 65181O (9 pp.).
15. Ho, D. L.; Wang, C. Q.; Lin, E. K.; Jones, R. L.; Wu, W. L., A laboratory scale critical-dimension small-angle x-ray scattering instrument. *Frontiers of Characterization and Metrology for Nanoelectronics: 2007* **2007,** *931*, 382-386.
16. Ro, H. W.; Jones, R. L.; Peng, H.; Hines, D. R.; Lee, H. J.; Lin, E. K.; Karim, A.; Yoon, D. Y.; Gidley, D. W.; Soles, C. L., The direct patterning of nanoporous interlayer dielectric insulator films by nanoimprint lithography. *Adv. Mater.* **2007,** *19* (19), 2919-+.
17. Wang, C. Q.; Jones, R. L.; Lin, E. K.; Wu, W. L.; Ho, D. L.; Villarrubia, J. S.; Choi, K. W.; Clarke, J. S.; Roberts, J.; Bristol, R.; Bunday, B., Line edge roughness and cross sectional characterization of sub-50 nm structures using critical dimension small angle x-ray scattering. *Frontiers of Characterization and Metrology for Nanoelectronics: 2007* **2007,** *931*, 402-406.
18. Wang, C. Q.; Jones, R. L.; Lin, E. K.; Wu, W. L.; Villarrubia, J. S.; Choi, K. W.; Clarke, J. S.; Rice, B. J.; Leeson, M.; Roberts, J.; Bristol, R.; Bunday, B., Line edge roughness characterization of sub-50nm structures using CD-SAXS: Round-robin benchmark results - art. no. 65181O. *Metrology, Inspection, and Process Control for Microlithography XXI, Pts 1-3* **2007,** *6518*, O5181-O5181.
19. Chengqing, W.; Kwang-Woo, C.; Jones, R. L.; Soles, C.; Lin, E. K.; Wen-li, W.; Clarke, J. S.; Villarrubia, J. S.; Bunday, B., Linewidth roughness and cross-sectional measurements of sub-50 nm structures with CD-SAXS and CD-SEM. *Proceedings of the SPIE - The International Society for Optical Engineering* **2008**, 69221Z-1-8.
20. Chengqing, W.; Kwang-Woo, C.; Wei-En, F.; Ho, D. L.; Jones, R. L.; Soles, C.; Lin, E. K.; Wen-Li, W.; Clarke, J. S.; Bunday, B., CD-SAXS measurements using laboratory-based and synchrotron-based instruments. *Proceedings of the SPIE - The International Society for Optical Engineering* **2008**, 69222E-1-7.

CD-SAXS Dimensional Metrology References

21. Chengqing, W.; Kwang-Woo, C.; Wei-En, F.; Jones, R. L.; Ho, D. L.; Soles, C.; Lin, E. K.; Wen-li, W.; Clarke, J. S.; Villarrubia, J. S.; Bunday, B., Linewidth roughness and cross-sectional measurements of sub-50 nm structures using CD- SAXS and CD-SEM. *2008 IEEE/SEMI Advanced Semiconductor Manufacturing Conference* **2008**, 142-7.
22. Hyun Wook, R.; Jones, R. L.; Huagen, P.; Hae-Jeong, L.; Lin, E. K.; Karim, A.; Yoon, D. Y.; Gidley, D. W.; Soles, C. L., Porosity characteristics of ultra-low dielectric insulator films directly patterned by nanoimprint lithography. *Proceedings of the SPIE - The International Society for Optical Engineering* **2008**, 69211M-1-11.
23. Ro, H. W.; Jones, R. L.; Peng, H.; Lee, H. J.; Lin, E. K.; Karim, A.; Yoon, D. Y.; Gidley, D. W.; Soles, C. L., Porosity characteristics of ultra-low dielectric insulator films directly patterned by nanoimprint lithography - art. no. 69211M. *Emerging Lithographic Technologies Xii, Pts 1 and 2* **2008,** *6921*, M9211-M9211.
24. Ro, H. W.; Peng, H.; Niihara, K. I.; Lee, H. J.; Lin, E. K.; Karim, A.; Gidley, D. W.; Jinnai, H.; Yoon, D. Y.; Soles, C. L., Self-sealing of nanoporous low dielectric constant patterns fabricated by nanoimprint lithography. *Adv. Mater.* **2008,** *20* (10), 1934-+.
25. Wang, C.; Choi, K. W.; Jones, R. L.; Soles, C.; Lin, E. K.; Wu, W. L.; Clarke, J. S.; Villarrubia, J. S.; Bunday, B., Linewidth roughness and cross-sectional measurements of sub-50 nm structures with CD-SAXS and CD-SEM - art. no. 69221Z. *Metrology, Inspection, and Process Control for Microlithography Xxii, Pts 1 and 2* **2008,** *6922* (1-2), Z9221-Z9221.
26. Wang, C. Q.; Choi, K. W.; Fu, W. E.; Ho, D. L.; Jones, R. L.; Soles, C.; Lin, E. K.; Wu, W. L.; Clarke, J. S.; Bunday, B., CD-SAXS measurements using laboratory-based and synchrotron-based instruments - art. no. 69222E. *Metrology, Inspection, and Process Control for Microlithography Xxii, Pts 1 and 2* **2008,** *6922* (1-2), E9222-E9222.
27. Wang, C. Q.; Choi, K. W.; Fu, W. E.; Jones, R. L.; Ho, D. L.; Soles, C.; Lin, E. K.; Wu, W. L.; Clarke, J. S.; Villarrubia, J. S.; Bunday, B., Linewidth roughness and cross-sectional measurements of sub-50 nm structures using CD-SAXS and CD-SEM. *2008 IEEE/SEMI Advanced Semiconductor Manufacturing Conference* **2008**, 142-147.
28. Chengqing, W.; Kwang-Woo, C.; Yi-Ching, C.; Price, J.; Ho, D. L.; Jones, R. L.; Soles, C.; Lin, E. K.; Wen-Li, W.; Bunday, B. D., Nonplanar high-k dielectric thickness measurements using CD- SAXS. *Proceedings of the SPIE - The International Society for Optical Engineering* **2009**, 72722M (8 pp.).
29. Wang, C. Q.; Fu, W. E.; Li, B.; Huang, H.; Soles, C.; Lin, E. K.; Wu, W. L.; Ho, P. S.; Cresswell, M. W., Small angle X-ray scattering measurements of spatial dependent linewidth in dense nanoline gratings. *Thin Solid Films* **2009,** *517* (20), 5844-5847.
30. Yokhin, B.; Krokhmal, A.; Dikopoltsev, A.; Berman, D.; Mazor, I.; Lee, B. H.; Ihm, D. C.; Kim, K. H., Compact X-ray Tool For Critical-Dimension Metrology. *Frontiers of Characterization and Metrology for Nanoelectronics: 2009* **2009,** *1173*, 364-368.

diblock copolymers

- The ratio of the molecular weights between these two blocks dictates the phase

- The magnitude of the molecular weight dictates the size of the domain

Challenges: (1) defect density (2) resolution (3) LER

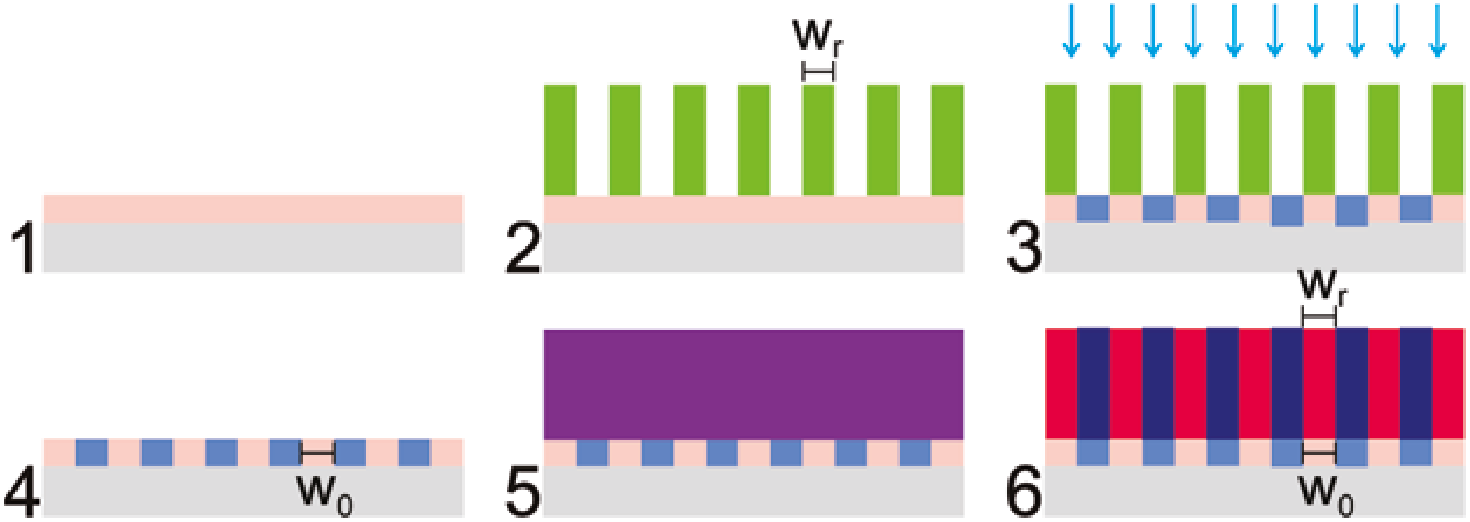
Sample Preparation

Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 433–441
DOI: 10.1021/ma901914b

Measuring the Structure of Epitaxially Assembled Block Copolymer Domains with Soft X-ray Diffraction

Gila E. Stein,[*,†,§] J. Alexander Liddle,[†] Andrew L. Aquila,[‡] and Eric M. Gullikson[‖]



Overview of PS-PMMA assembly on chemical patterns. (1) Start with a hydrophobic PS surface. (2) Pattern with EBL (ZEP resist) and develop grating. (3) Oxidize to generate hydrophilic stripes. (4) Strip the ZEP resist. (5) Coat with PS-PMMA film. (6) Heat the film above the glass transition to order the PS-PMMA lamellae. The structures measured with SoXRD and SEM are depicted in steps 2 and 6.

Sample Preparation

- Neutral polymer brush: random copolymer of PS and PMMA (Mn = 8.9 kg/mol

- PDI = 1.47, 59% PS prepared by grafting from the melt (a 30 nm thick film) while ramping the temperature from 140 to 250 °C over 24 h under high vacuum (10-5 Pa/10^{-7} Torr)

- E-beam pattern pitch, d = 46 nm

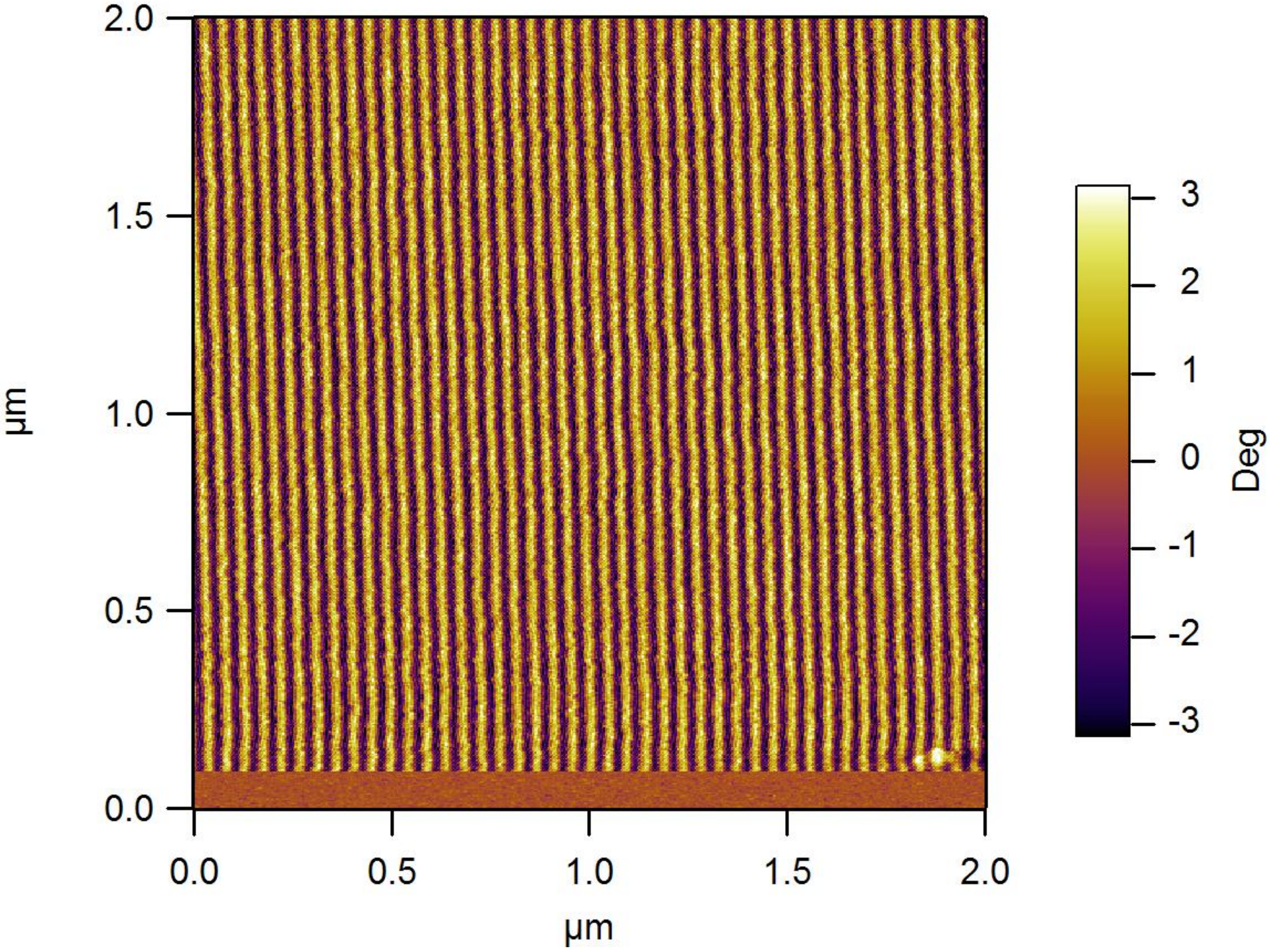
- Width of the hydrophobic ~ 0.55d at an e-beam dose of 1130 µC/cm^2

- PS-PMMA (Mn =100 kg/mol, PDI = 1.12, 50% PS by volume) annealing in air for 5 to 7 min at 240 °C

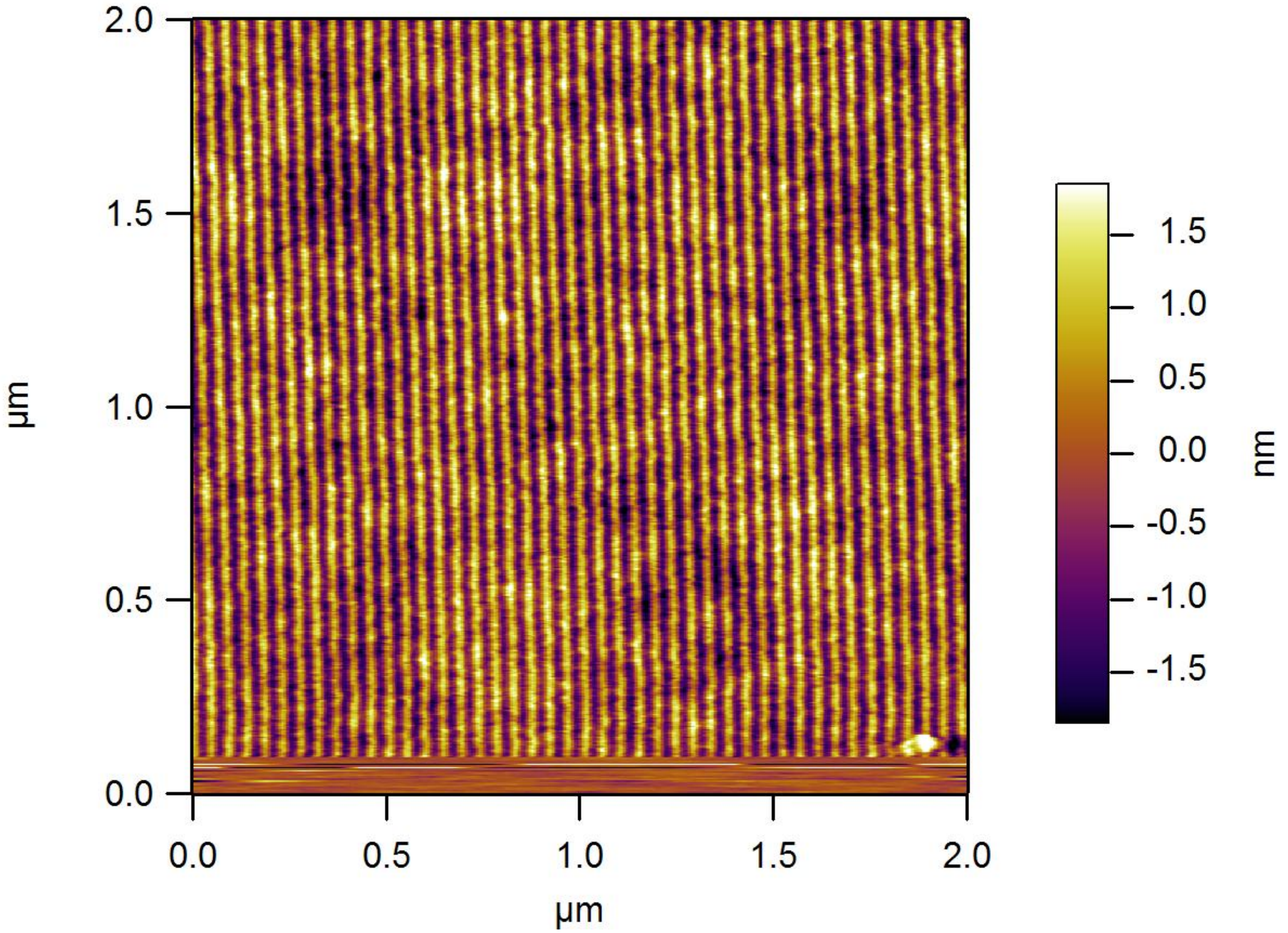
- PS-PMMA BCP with a lamellar periodicity, L0 =(46 ± 1) nm

- Sample size = 1 mm x 1 mm

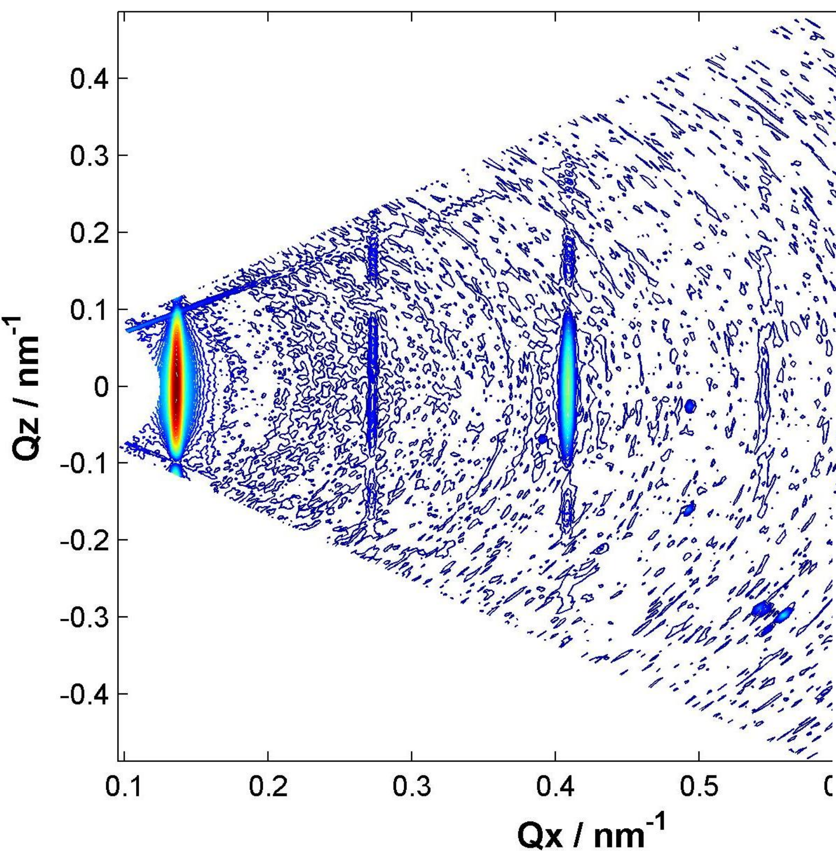
AFM BCP Pattern - Phase



AFM BCP Pattern - Height

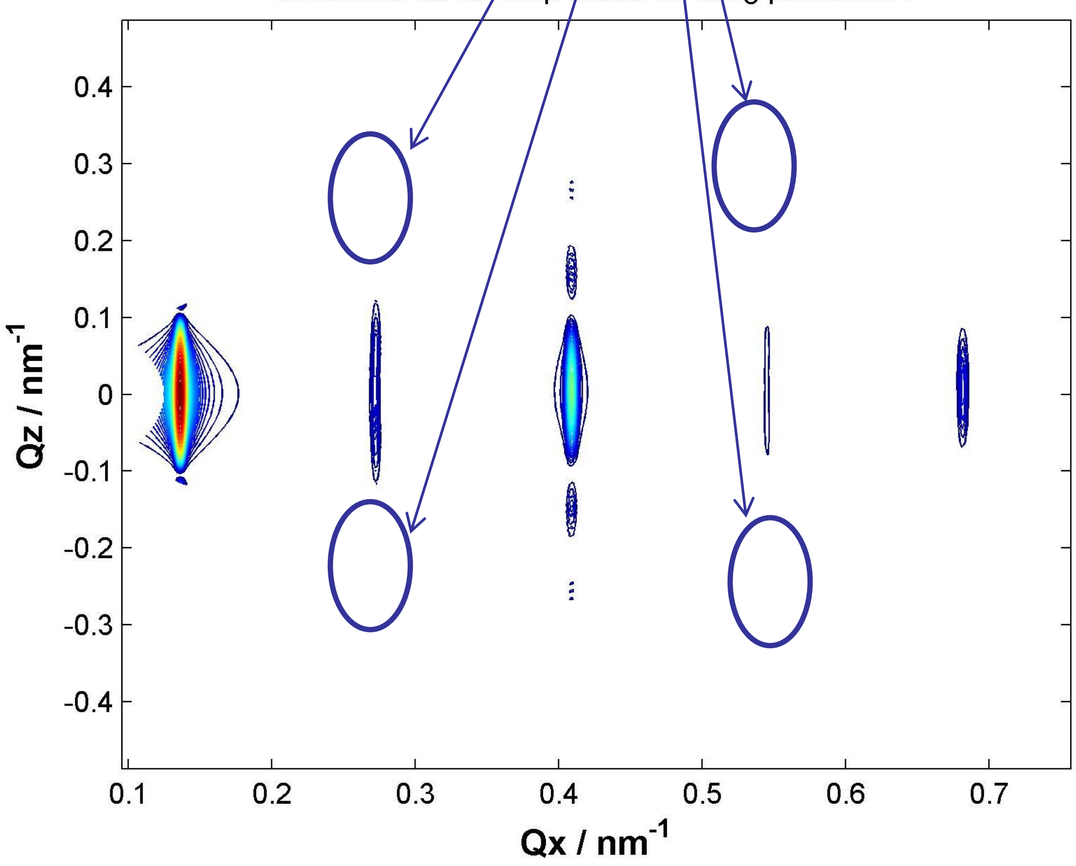


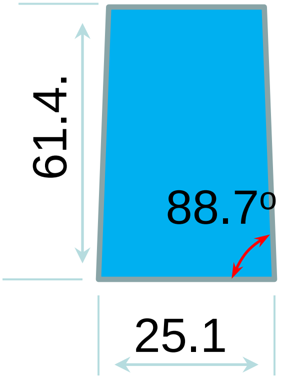
Experimental Qx-Qz map



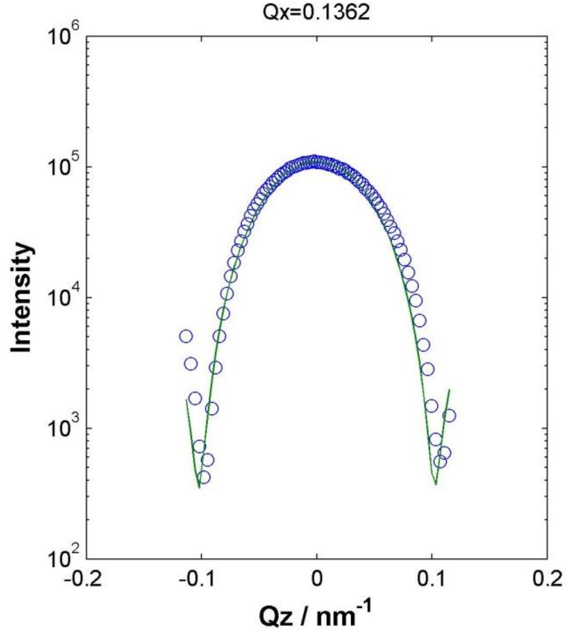
Missing intensities

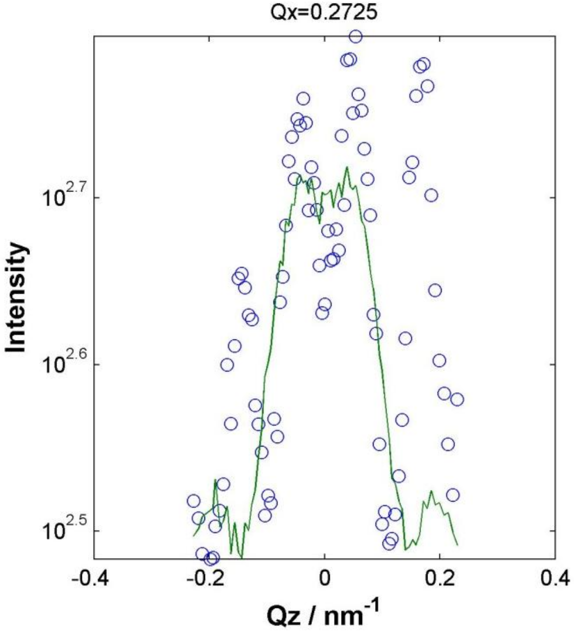
Simulated Qx-Qz map based on fitting parameters

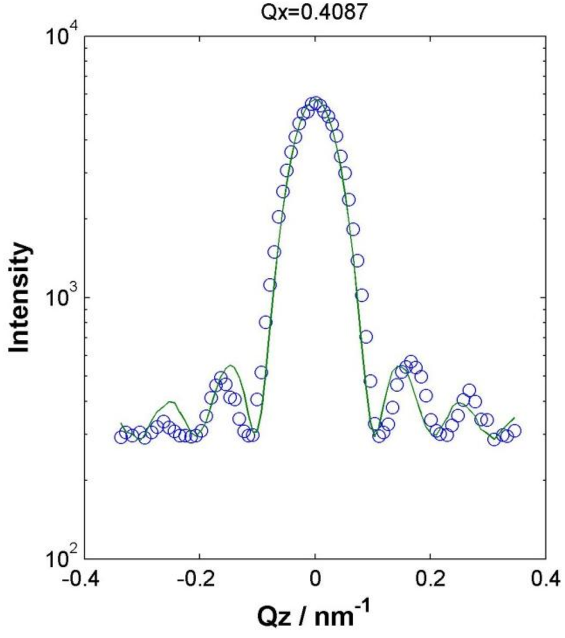


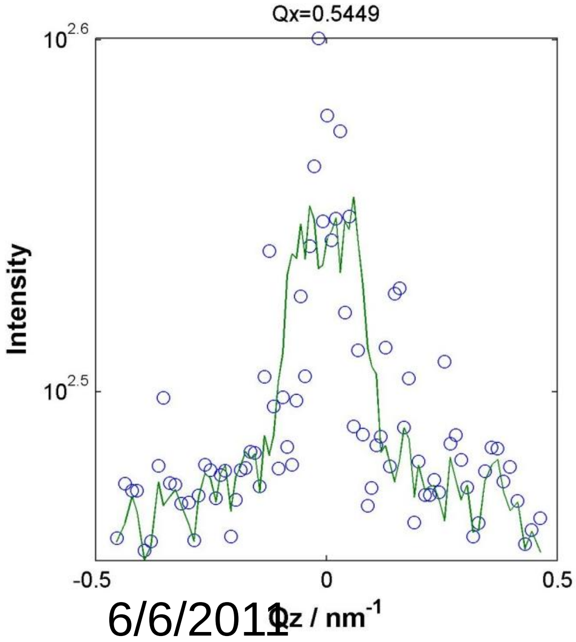


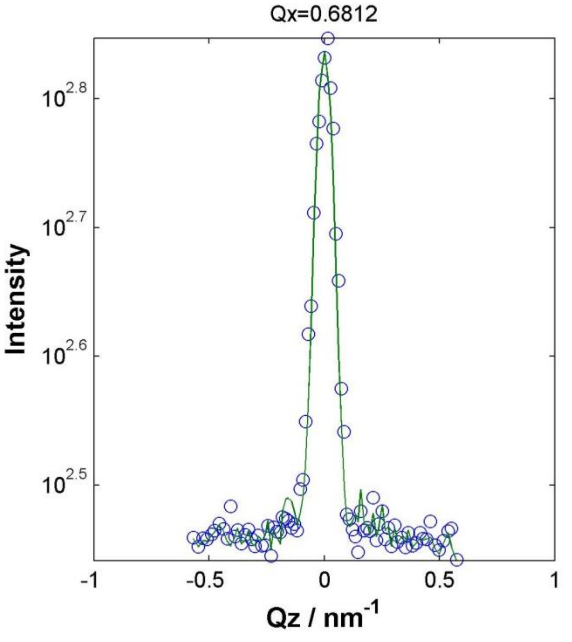
σ = 2. 2 7nm



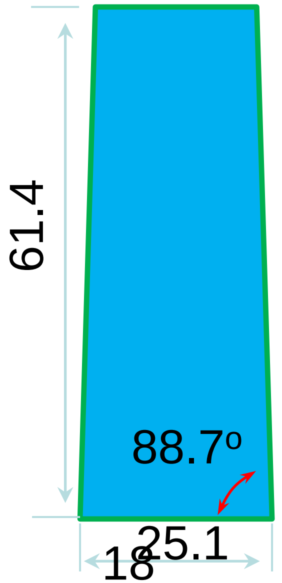




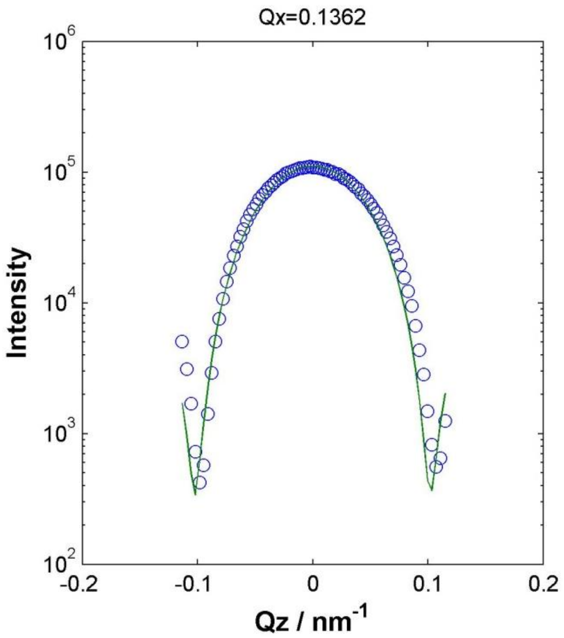


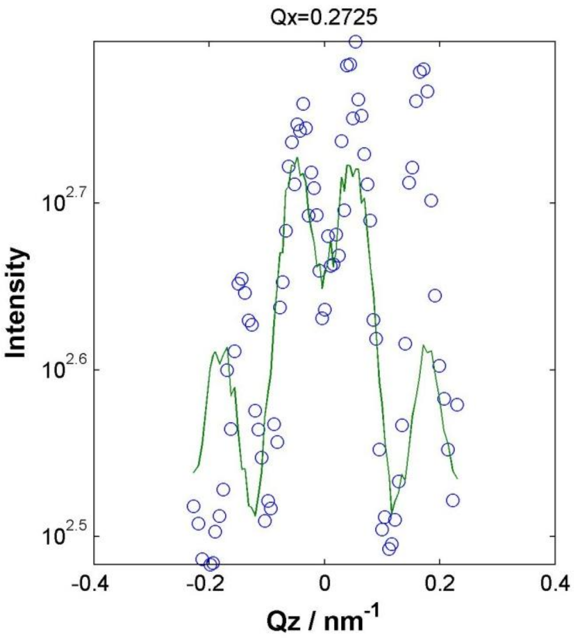


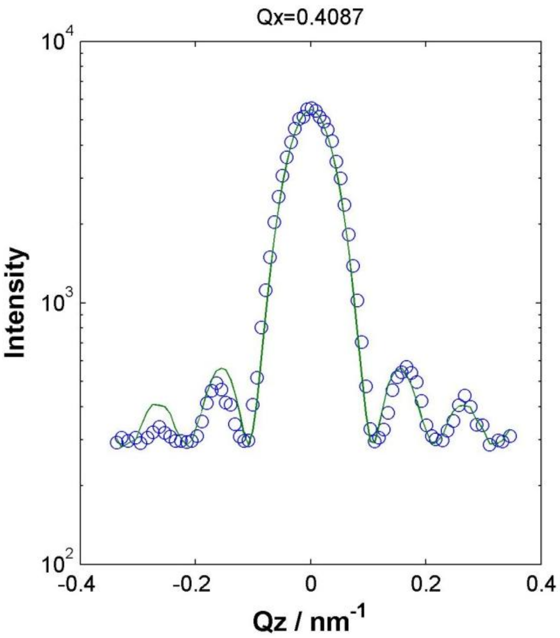
χ^2=13.92

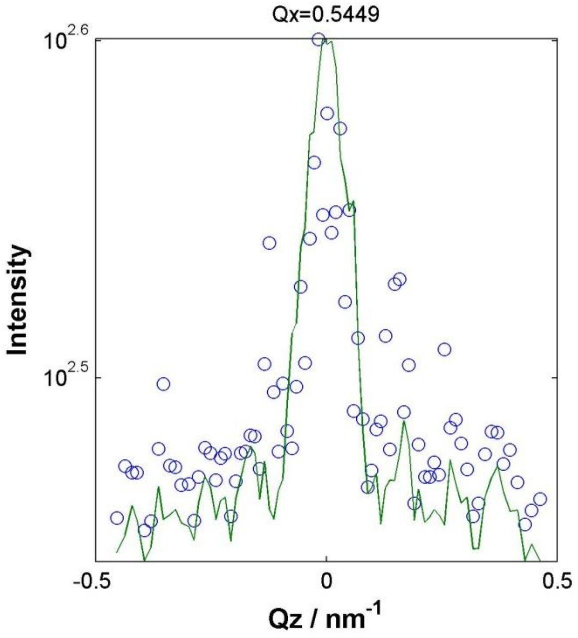


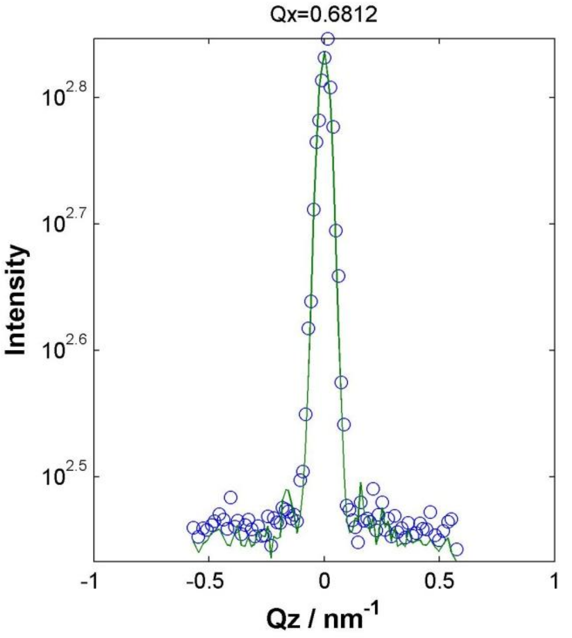
σ = 2. 27 nm

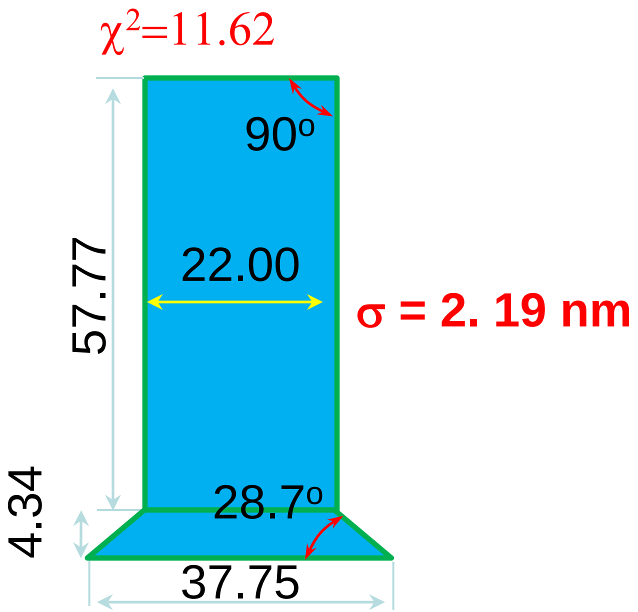

Qx=0.1362

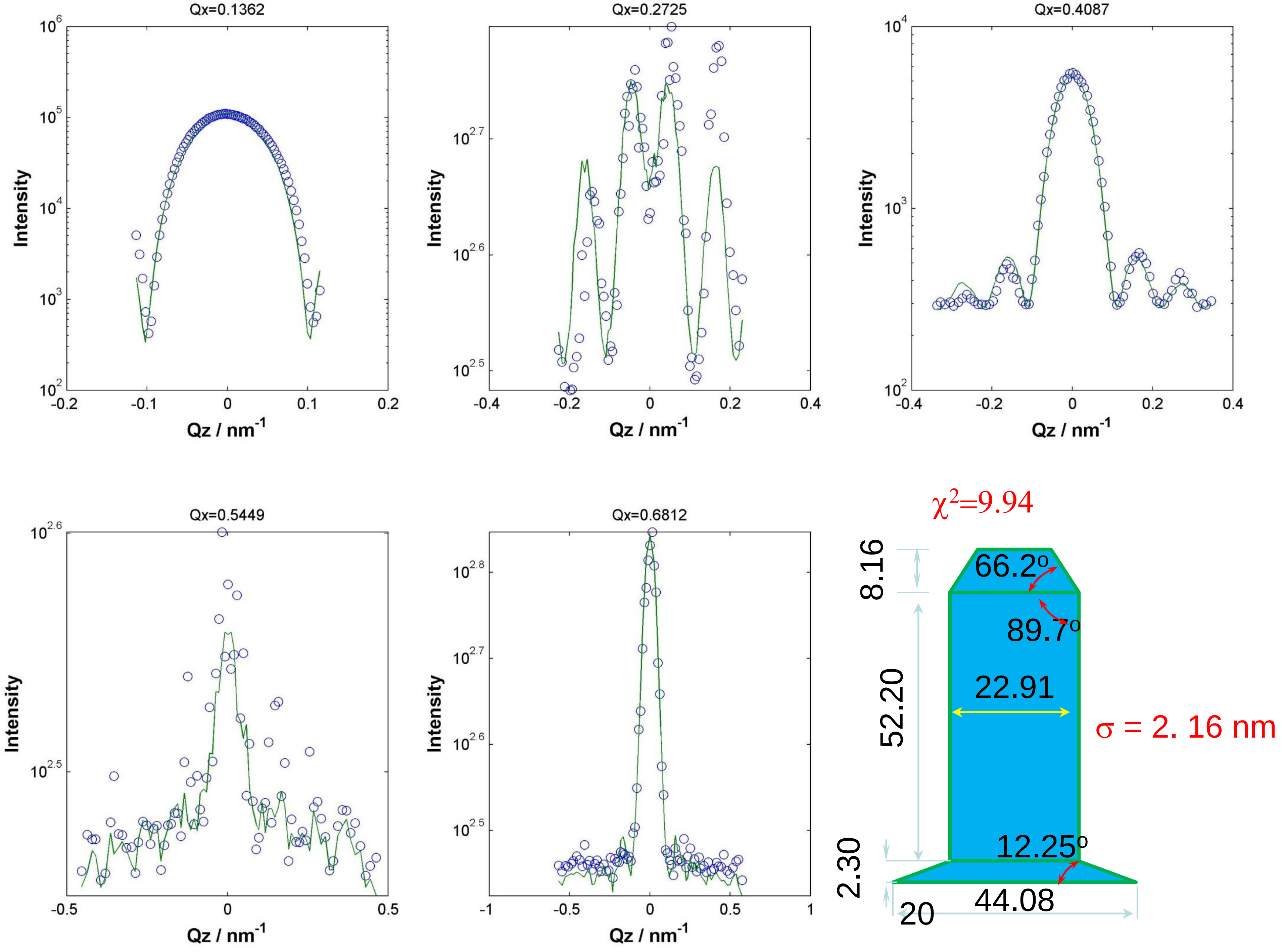

Qx=0.2725

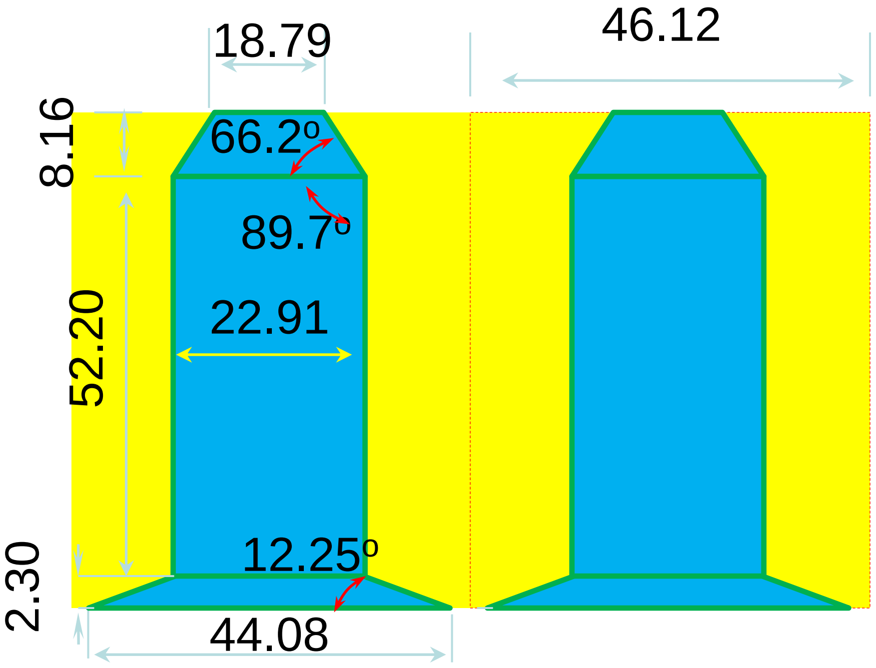

Qx=0.4087


Qx=0.5449


Qx=0.6812




Qx=0.1362
Qx=0.2725
Qx=0.4087
Qx=0.5449
Qx=0.6812
Intensity
Qz / nm^{-1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
$10^{2.5}$
$10^{2.6}$
$10^{2.7}$
$10^{2.8}$
-1
-0.5
-0.4
-0.2
-0.1
0
0.1
0.2
0.4
0.5
1
χ^2=9.94
8.16
66.2°
89.7°
52.20
22.91
σ = 2. 16 nm
2.30
12.25°
44.08
20

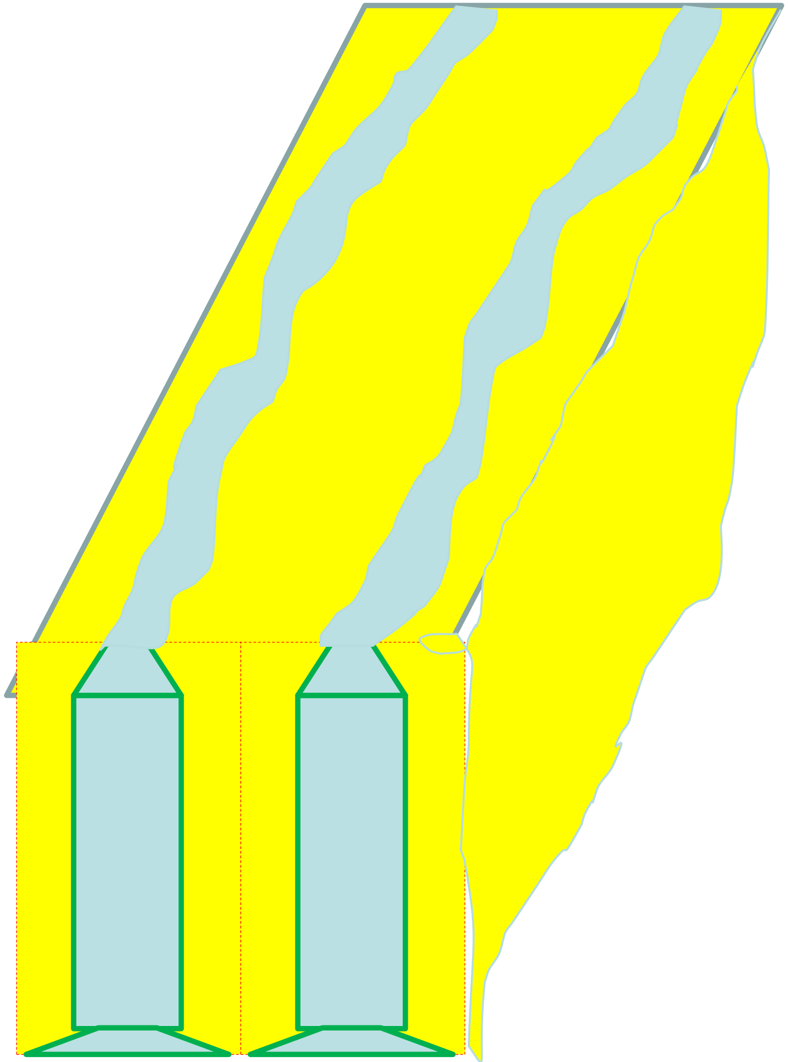


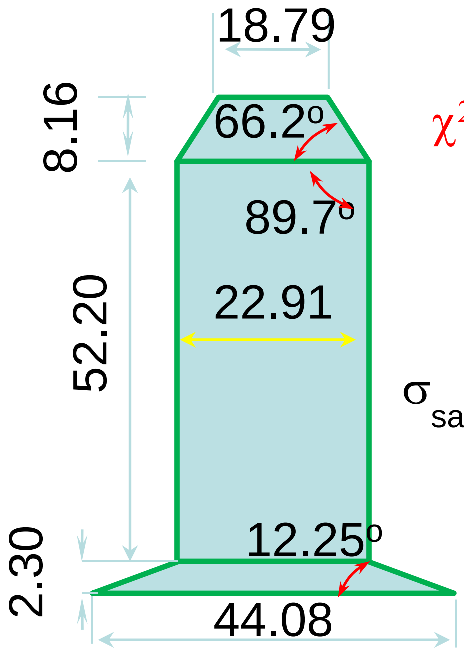
Debye Waller factor
σ = 2. 16 nm

Area:
Blue part: 1.4126×10^3
Yellow part: 1.4770×10^3

The fitting is physically reasonable except the sharp corner regions

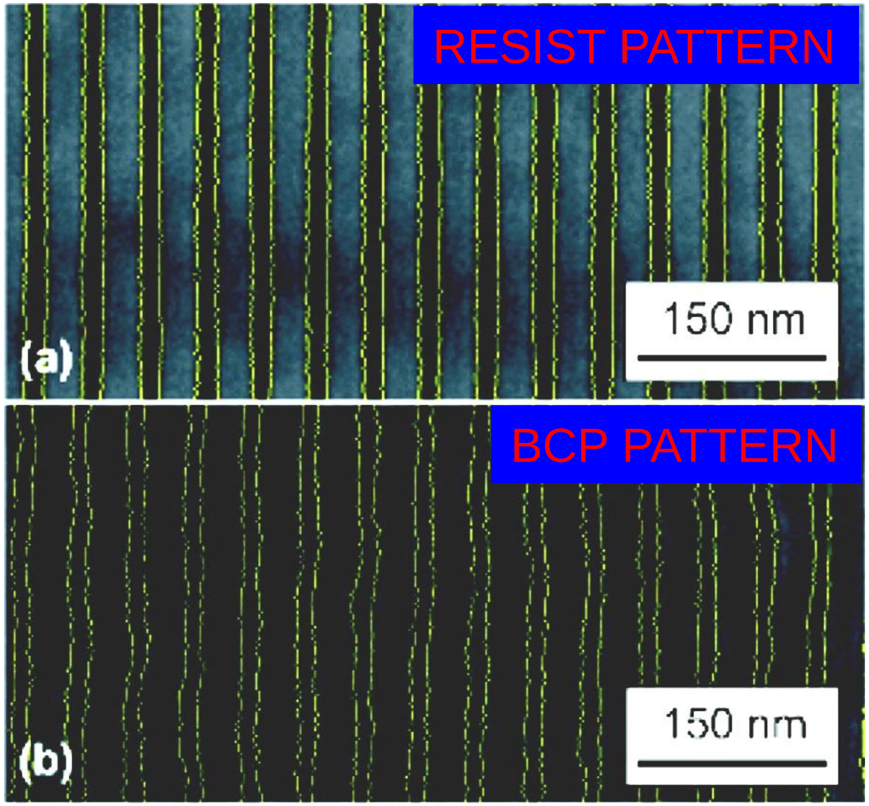
The view of AFM/SEM





$\chi^2=9.94$

σ_{saxs} = 2. 16 nm



w_0/d = 18.79 /46.12 =0.41- quantitatively verified by NEXAFS

Published in: Gila E. Stein; J. Alexander Liddle; Andrew L. Aquila; Eric M. Gullikson; *Macromolecules* **2010,** 43, 433-441.
DOI: 10.1021/ma901914b

The meaning of Debye Waller factor

σ = 2. 16 nm

If one accepts a hyperbolic tangent composition profile with a interface width of 4 nm between PS and PMMA, the interface roughness is **1.3 nm or a 3σ = 3.9 nm**

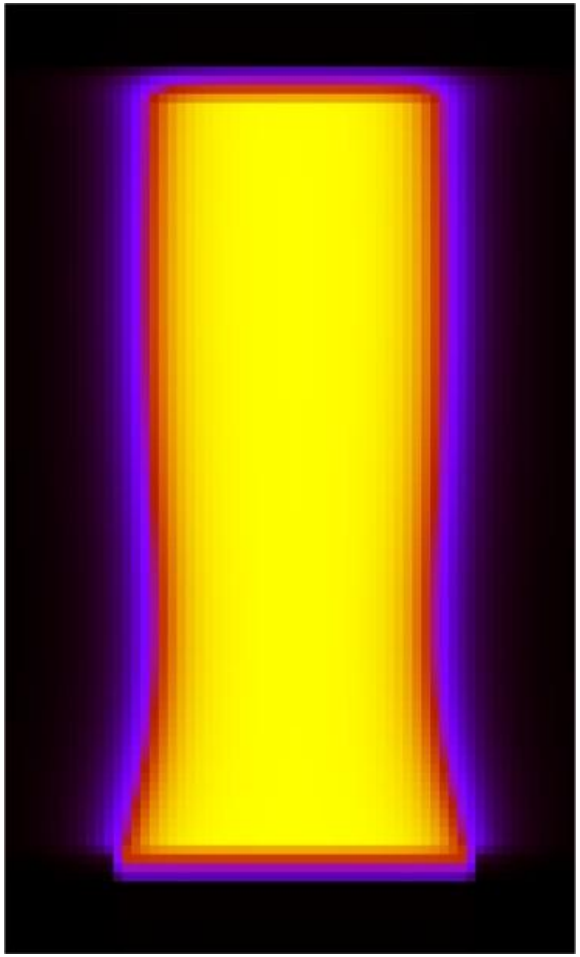
Roughness **does** exist in the DSA sample studied since the diffuse scattering exists at $q_y \neq 0$, i.e. the value of **σ can't** completely caused by a compositional gradient at interface

3.9 nm 3σ exceeds ITRS roadmap requirements for 22 nm node (3σ = 1.3 nm!)

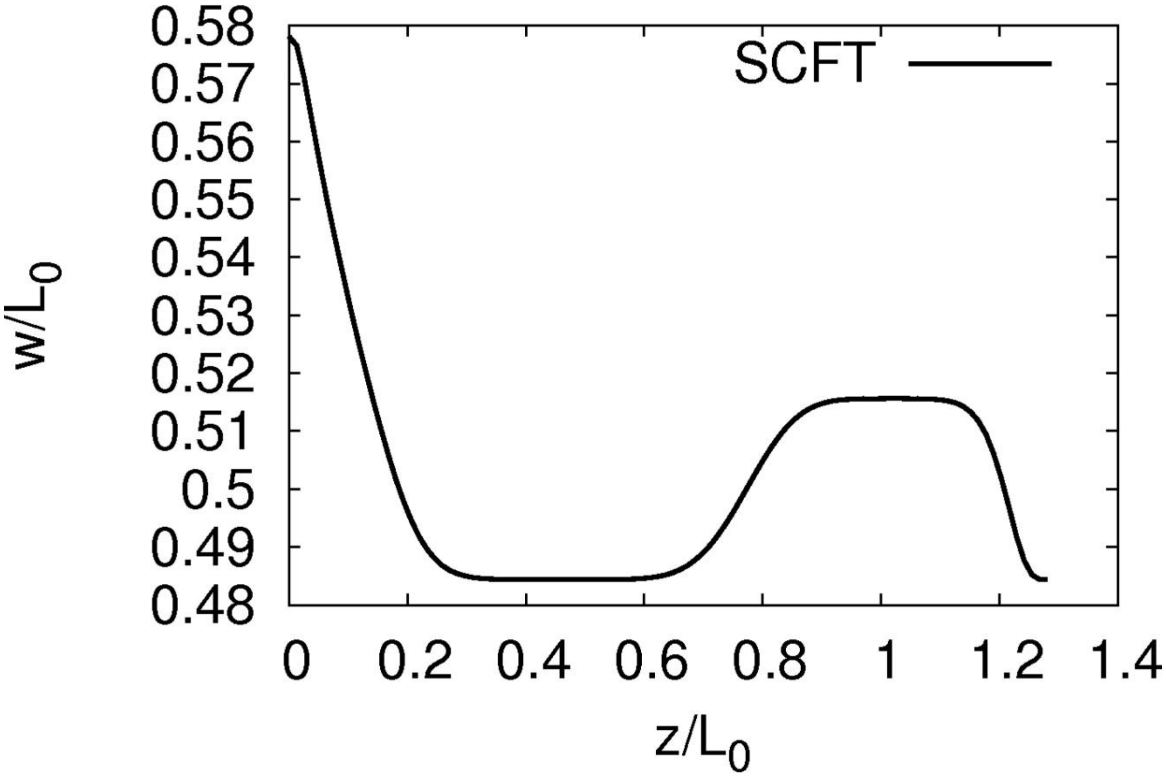
Simulations of Diblock Block Copolymer Gratings

- In an effort to better understand the CD-SAXS data, we performed a series of simulations of the diblock copolymer grating shape.
- Two simulations methodologies were employed:
  - Self-consistent field theory (SCFT),
  - Continuum partial saddle point Monte Carlo (PSPMC).
- SCFT is fast, efficient, and accurate in many cases (e.g., for large molecular weight); however, it does not capture thermal fluctuations.
- PSPMC is more computational demanding, but it allows one to explore the effects of thermal *composition* fluctuations at finite molecular weight.
- Use simulations to refine line shape profiles (done)
- Use theory to estimate BCP-DSA chi requirements (done)
- Use simulation models to quantify LER (in progress)

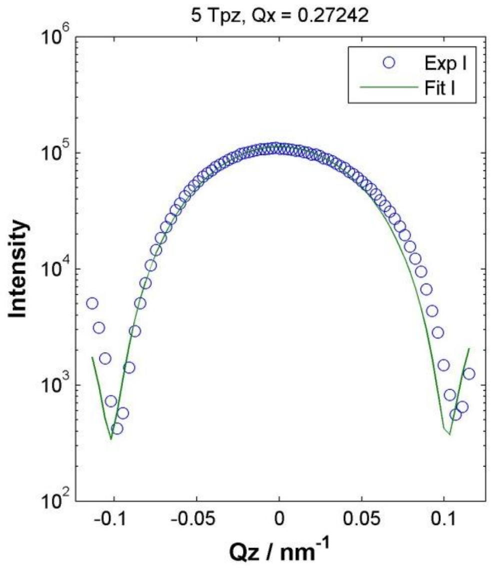
SCFT Results

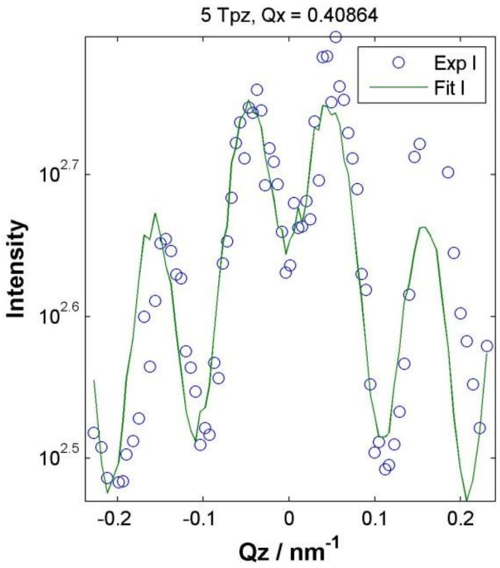


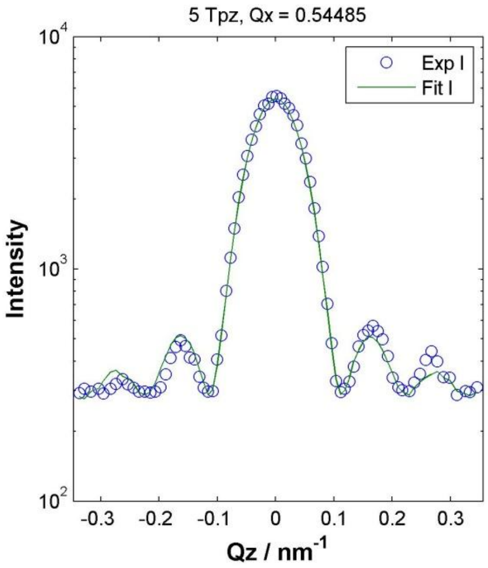
SCFT Composition Snapshot
f = 0.5, χN = 38

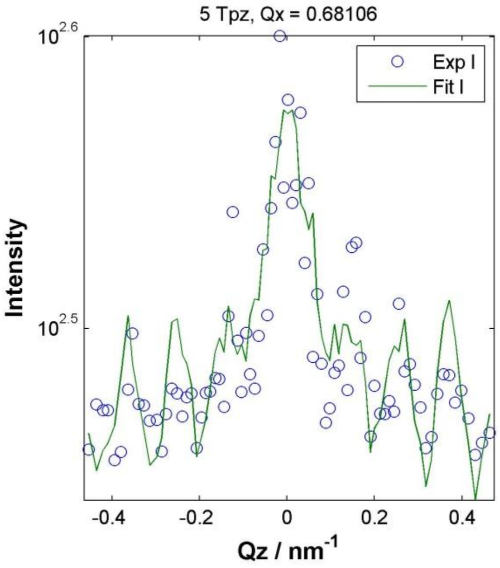


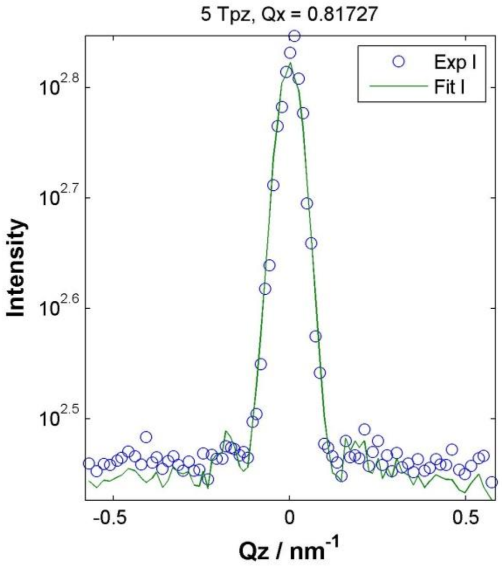
w is the grating width (i.e., the local critical dimension [CD]), L_0 is the grating pitch, and *z* is the vertical direction. We can see that the “foot” results in the *A*-*B* interface overshooting the bulk value of w/L_0 = 0.5. SCFT predicts that the gating will have an “hourglass” shape with a clear shoulder. i.e., SCFT predicts that the grating shape is *not* a simple trapezoid.


5 Tpz, Qx = 0.27242
Intensity
10^6
10^5
10^4
10^3
10^2
Qz / nm^{-1}
-0.1
-0.05
0
0.05
0.1
Exp I
Fit I

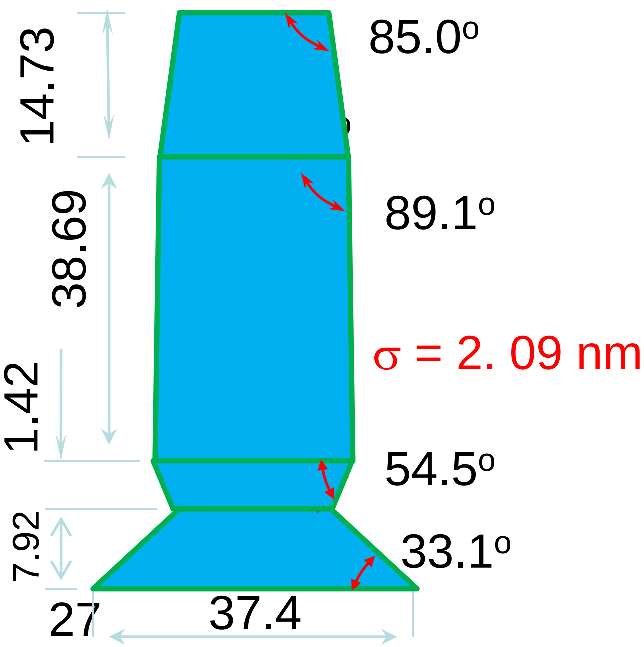

5 Tpz, Qx = 0.40864
Intensity
$10^{2.7}$
$10^{2.6}$
$10^{2.5}$
Qz / nm^{-1}
-0.2
-0.1
0
0.1
0.2
Exp I
Fit I


5 Tpz, Qx = 0.54485
Intensity
10^4
10^3
10^2
Qz / nm^{-1}
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
Exp I
Fit I

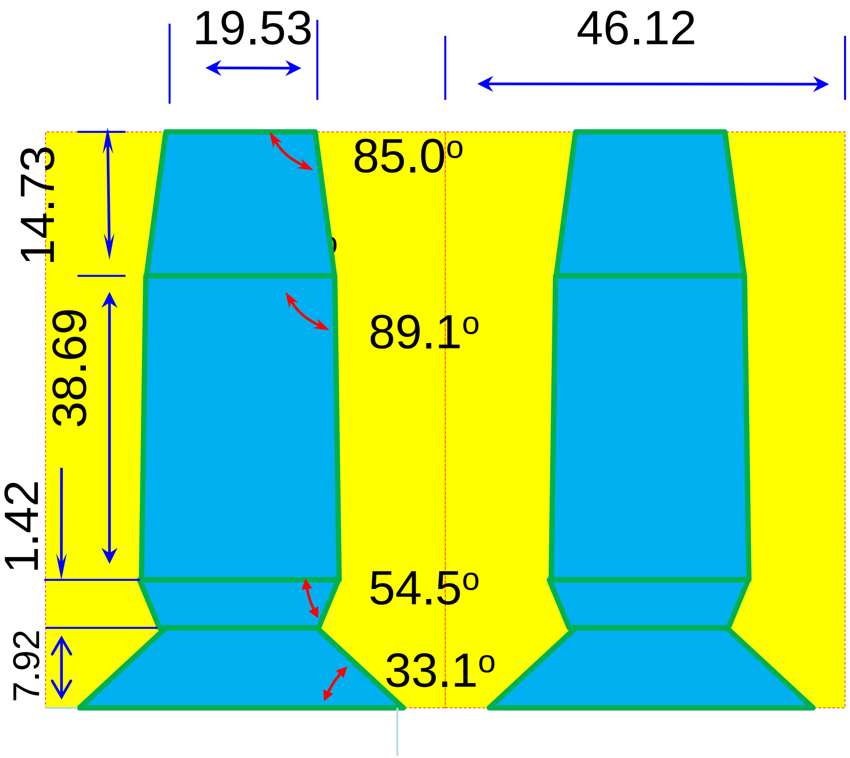

5 Tpz, Qx = 0.68106
Intensity
$10^{2.6}$
$10^{2.5}$
Qz / nm^{-1}
-0.4
-0.2
0
0.2
0.4
Exp I
Fit I


5 Tpz, Qx = 0.81727
Intensity
$10^{2.8}$
$10^{2.7}$
$10^{2.6}$
$10^{2.5}$
Qz / nm^{-1}
-0.5
0
0.5
Exp I
Fit I

$\chi^2 = 9.51$


14.73
85.0°
38.69
89.1°
σ = 2. 09 nm
1.42
54.5°
7.92
33.1°
37.4

SCFT Refined Modeling of CD-SAXS Data



σ = 2. 09 nm

Negligible change
in LER estimates

Areas:
Blue part: 1.41 x 10^3
Yellow part: 1.48 x 10^3

Consistent with block composition

Can BCPs Satisfy the ITRS LER Requirement?

- For an *AB* BCP, we can use a relatively simple formula from BCP strong segregation theory to examine LER:

$$\sigma^2 \approx \log(k_{max}/k_{min})/(2\pi\gamma),$$

γ - interface tension

where σ is the 1σ LER; k_{max} and k_{min} are the high- and low-wavenumber cutoffs, respectively; and γ is the interfacial tension:

$$\gamma = b\chi^{1/2}/(\nu 6^{1/2}),$$

where b is the statistical segment length, χ is the Flory “chi” parameter, and ν is the volume occupied by a statistical segment.

Can BCPs Satisfy the ITRS LER Requirement?

- Following Semenov (Macromolecules **1993**, *26*, 6617), we set $k_{max} \approx 2\pi/\Delta$ and $k_{min} \approx 2\pi/L_0$, where $\Delta = 2b/(6\chi)^{1/2}$ is the interfacial width, and L_0 is the BCP pattern pitch.
- Combining these expressions and simplifying gives

$$\sigma^2 \approx 0.39\nu \log(1.22L_0\chi^{1/2}/b)/(b\chi^{1/2})$$

- We can further simply by relating b and ν. Specifically, if we assume that the segments occupy a spherical volume, then

$$\nu \geq 4\pi(b/2)^3/3 \approx 0.52\, b^3,$$

and

$$\sigma^2 \geq 0.20b^2 \log(1.22L_0\chi^{1/2}/b)/\chi^{1/2}$$

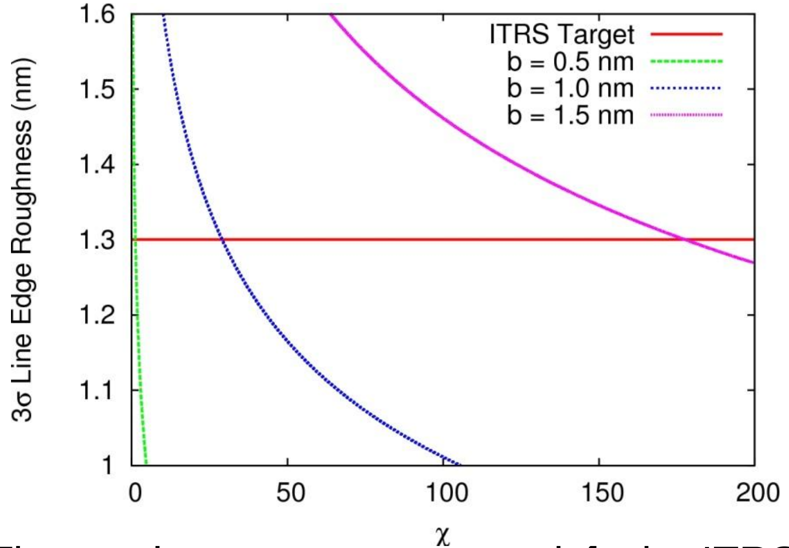
- In order to satisfy the ITRS *CD* requirement, we set $L_0 \approx 2\, CD = 24$ nm. We can then view χ and b as “adjustable” parameters determined by the BCP chemistry.

Can BCPs Satisfy the ITRS LER Requirement?

- We fix the value of *b* to be between 0.5 nm and 1.5 nm, and then we ask

> "What value of χ will satisfy the ITRS LER requirement of $3\sigma \leq 1.3$ nm?"

- In the following figure we plot the 3σ LER given by the above equation vs. χ for *b* = 0.5 nm, 1.0 nm, and 1.5 nm:



$\chi \approx 0.037$ for PS-PMMA

$\chi \approx 0.2$ for PS-PDMS

b = 0.68 nm for PS or PMMA

The χ values necessary to satisfy the ITRS Target range from $\chi \approx 1.2$ (for *b* = 0.5 nm) to well in excess of $\chi = 150$ (for *b* = 1.5 nm)! These values of χ are exceptionally large, and, in fact, they represent a conservative, low estimate.

It is not clear if there are "well-behaved" copolymers with χ values in this range.

Summary - CD-SAXS of BCP DSA Patterns

- The cross section of DSA block copolymers can be complicate, this renders the interpretation of AFM and SEM results difficult especially for LER
- CD-SAXS can provide quantitative picture of full cross-section
- For PS-PMMA samples their LER is 3.9 nm (3σ), a value depends on the exact value of interface width
- Not sure if ITRS 22 nm node 3σ targets can be met
- New block copolymers with their χ parameters significant greater than PS-PMMA and PS-PDMS are needed to meet resolution & LER requirement at sub-20nm nodes
- Work in progress to determine LER from scattering data without information of interface width (power spectra of diffuse scattering)