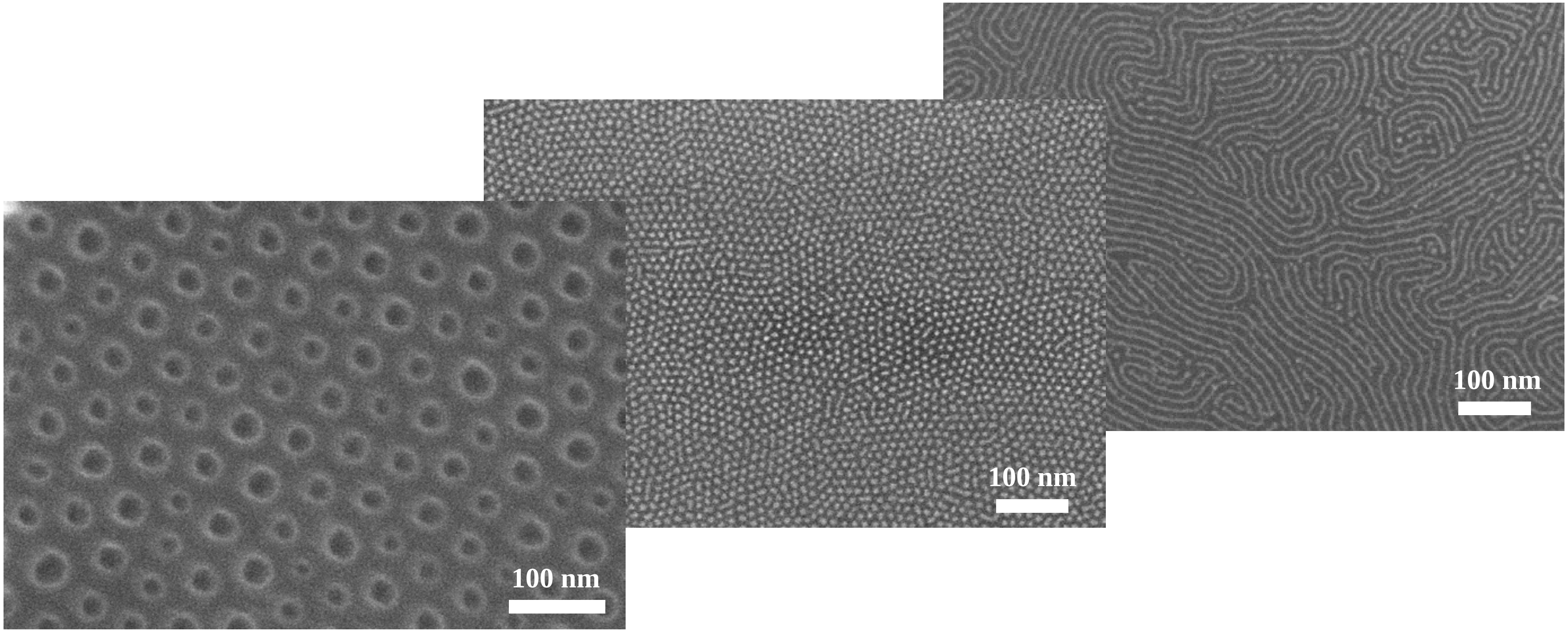


Block Copolymer Nanolithography (Basic)

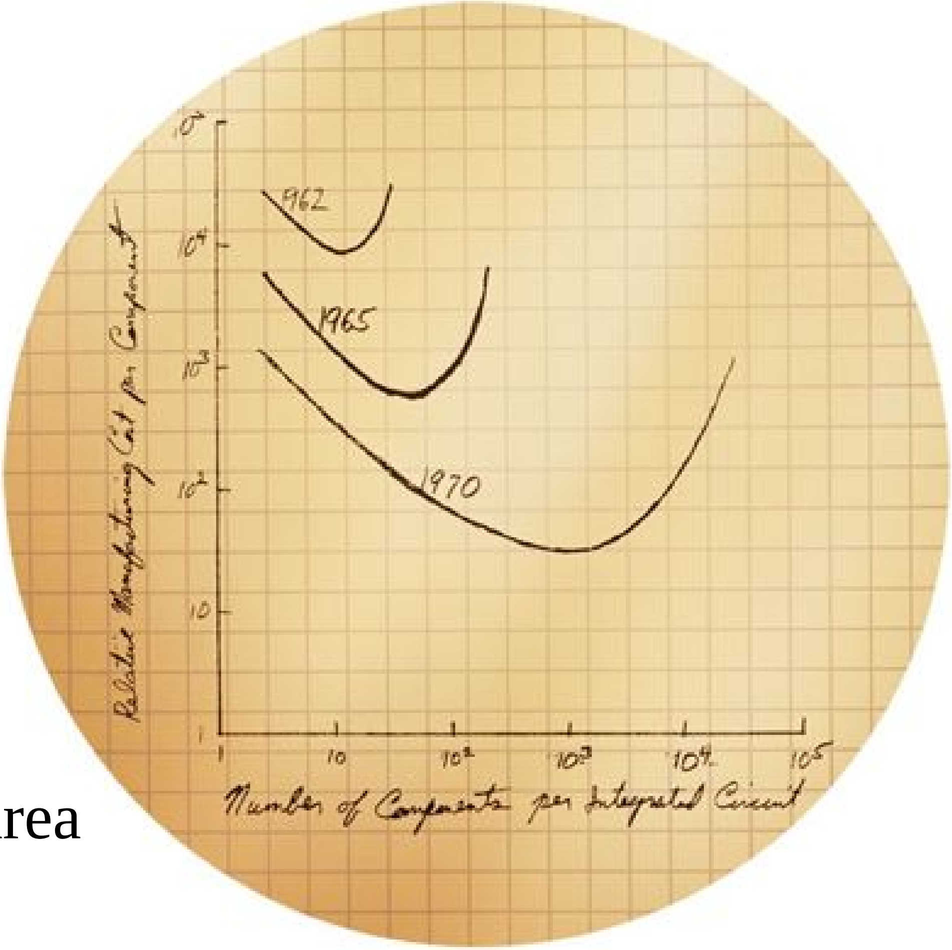
Anette Löfstrand,
Solid State Physics and NanoLund, Lund University, Sweden
anette.lofstrand@ftf.lth.se

Outline

- Motivation
- Basic principle
  - Self-assembly
  - Annealing methods
  - Directed self-assembly
- Lithography
  - Surface reconstruction
  - Block modification
  - Selective infiltration synthesis
- Pattern transfer
- Applications
- Challenges

Motivation – Devices

- Device functionality
- Trend to downscale devices
  - Moore’s law
- Downscale lithography
  - Pattern dimensions
  - Pattern pitch
- Trend to increase patterned area



From Gordon Moore’s 1964 notebook.
Moore, Gordon. "Cramming More Components onto Integrated Circuits”, Electronics Magazine Vol. 38, No. 8 (April 19, 1965).

Motivation – Lithography Techniques

- **EBL**: High definition, small area, long exposure time, high cost.
- **EUV**: High definition, high cost.
- **Classical UV**: Low definition, large area, low cost.
- **NIL**: Definition from mold, residual layer, large area.

- **BCP**: High definition, large area, low cost. Directed self-assembly.

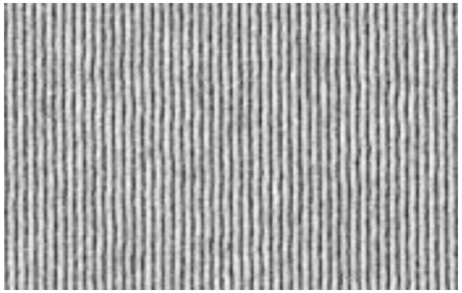
Motivation – Block Copolymer

- Self-assembly of polymers.
- Typically 10-50 nm pattern period.
- Small pattern dimensions.

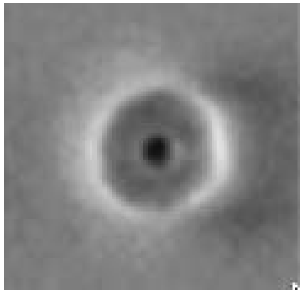
<u>Typical applications use</u>

- High density hexagonal dot pattern
- High density line pattern
- Pattern shrink

Hellwig et al. (2010)



Kim et al. (2003)



Kato et al. (2013)

Basic Principle

- Diblock Copolymer: A-*b*-B
- The blocks A and B can be designed to repell each other

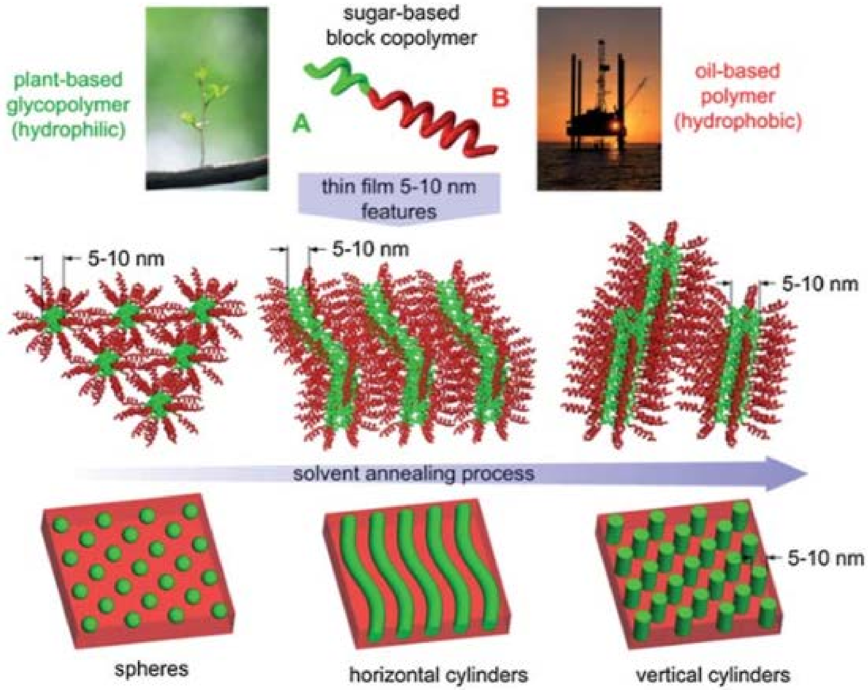
  → micro phase separation.

- Heat or solvent vapor

  → Increased mobility.

- By finding the state of most favourable energy

  → self-assembly.



Borsali et al, Nanoscale, 2013, 5, 2637.

Hashimoto and Fukunaga, Nanostructured Soft Matter, Nanofabrication of Block Copolymer Bulk and Thin Films, Microdomain Structures as Templates, 2007, pp 45-97.

Nordic Nanolab Network

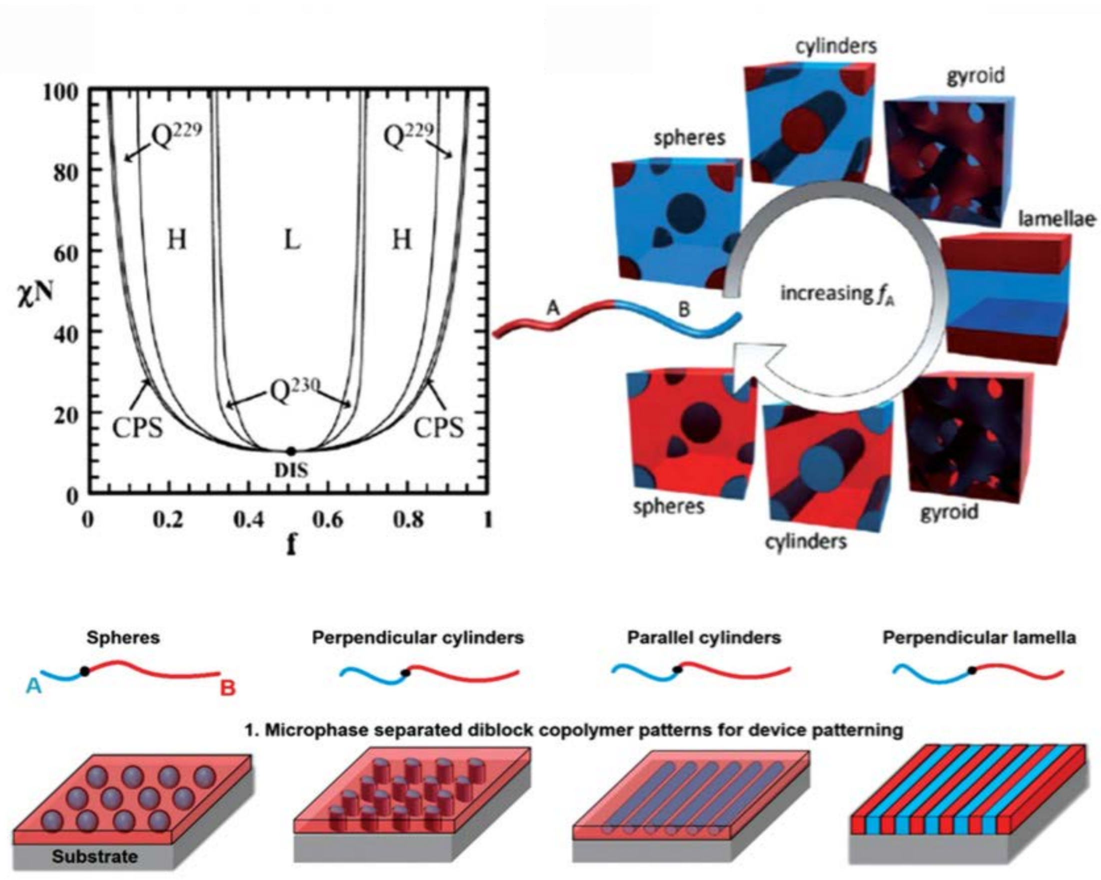
Basic Principle – Self-Assembly

- Relative volume f
- Interaction parameter χ
- Chain length N

Smaller pitch →

Smaller N

Higher χ

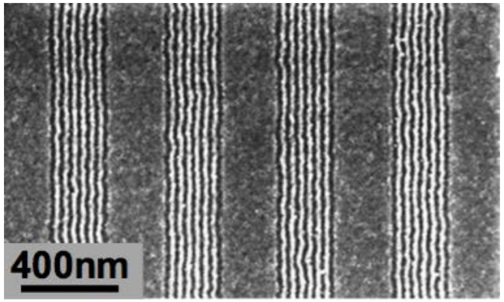


Morris et al., Adv. Mater. 28, 5586–618.

Basic Principle – Annealing Methods
Thermal Annealing

- Adding heat → Increased mobility → Self-Assembly.
- Above glass transition temperature T_g.

- Example: PS-*b*-PMMA
  - Poly(styrene)-*block*-Poly(methyl methacrylate)
  - T_g of 91-128°C and 38-122°C resp.
  - 230°C for 5 minutes in a high nitrogen flow.
  - Lund NanoLab: Rapid Thermal Processing (RTP) system, RTP-1200-100 from UniTemp GmbH (dmitry.suyatin@ftf.lth.se).



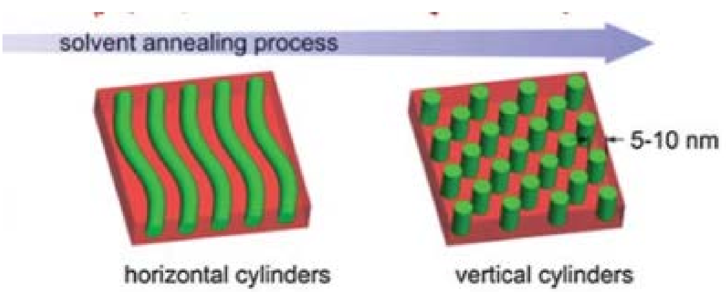
polymerdatabase.com

Oria et al., Microelectronic Engineering 110 (2013), pp 234-240.

Nordic Nanolab Network

Basic Principle – Annealing Methods
Solvent Vapor Annealing

- Adding solvent → Increased mobility → Self-Assembly.
- Often mixture of solvents selective to each block.

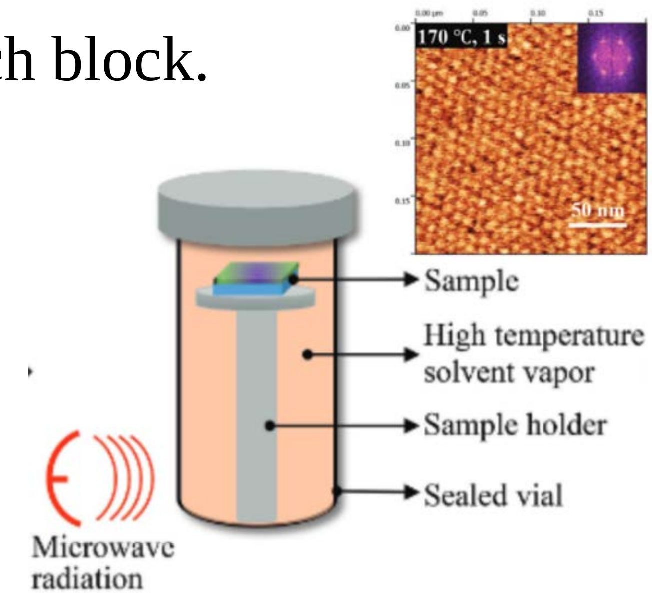


- Example: PS-*b*-MH
  - Poly(styrene)-*block*-Maltoheptaose
  - Tetrahydrofuran and Water resp.
  - Ratio 1:1 (w/w) for horizontal cylinders, 4:1 (w/w) for vertical.
  - Sample in sealed container with solvent vapor mixture at RT for 1-24 h.
  - Lund NanoLab: Solvent wet bench (maria.huffman@ftf.lth.se).

Borsali et al, Nanoscale, 2013, 5, 2637.

Basic Principle – Annealing Methods
Microwave Annealing

- Adding heat and solvent → Increased mobility → Self-Assembly.
- Often mixture of solvents selective to each block.



- Example: PS-*b*-MH
  - Poly(styrene)-*block*-Maltoheptaose
  - Tetrahydrofuran and Water resp.
  - Ratio 3:1 (w/w) for vertical cylinders.
  - Sample in sealed container in Microwave with solvent vapor mixture at 170°C for 1 s.

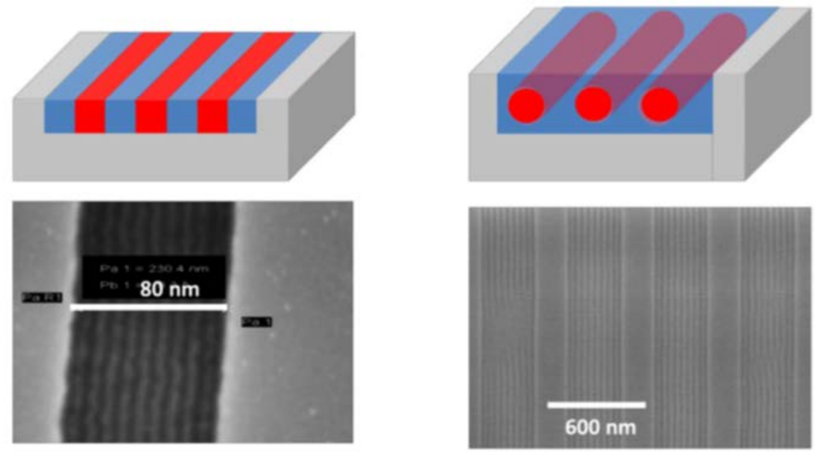
Liao et al., Advanced Materials 29(35):1701645

Basic Principle – Directed Self-Assembly Grapho-Epitaxy

- Directing the self-assembly
  - → Increased long range order
  - → Enables more advanced pattern designs.

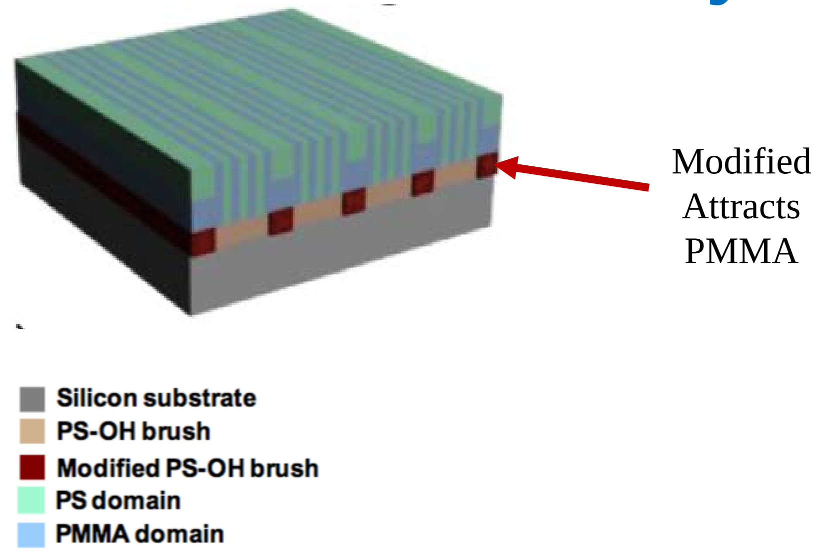
- Edges have different surface energy than planar surface.
  - → Attracts blocks unequally
  - → Structures align along trenches

- <u>Example</u>: PS-*b*-PDMS on trenches.



Morris, Microelectronic Engineering 132 (2015) 207–217
(Ndoni, DTU)

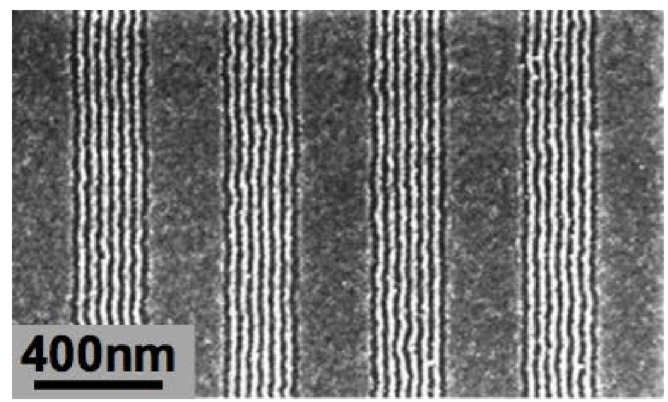
Basic Principle – Directed Self-Assembly Chemo-Epitaxy



- <u>Example</u>: PS-b-PMMA on PS-OH brush.

- Non-modified brush layer
  → Attracts PS and PMMA equally
  → Vertical lamellae structure.

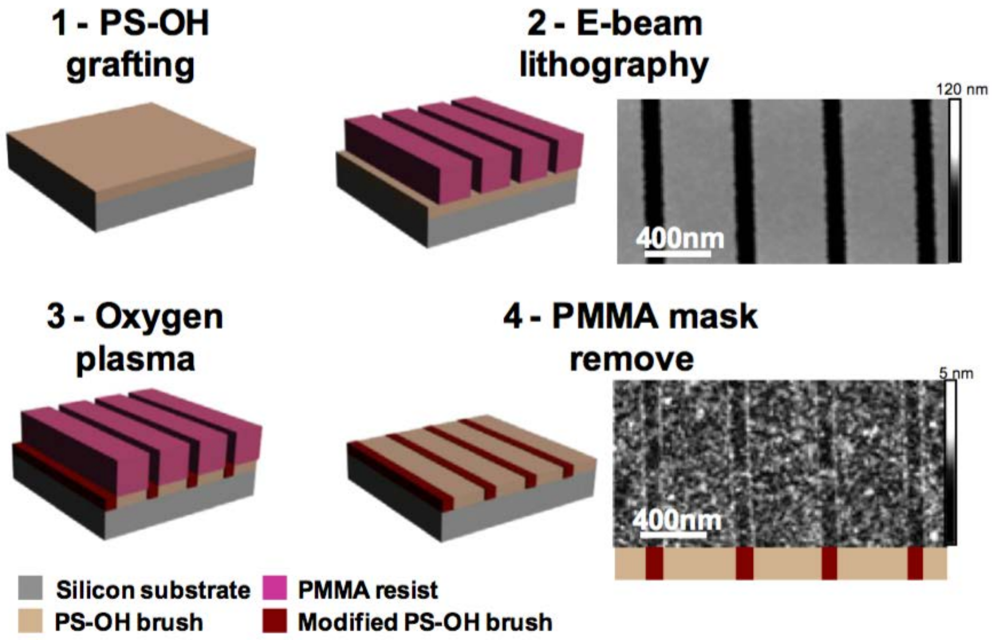
- Modified brush – more hydrophilic
  → Attracts PMMA
  → Horizontal lamellae structure.

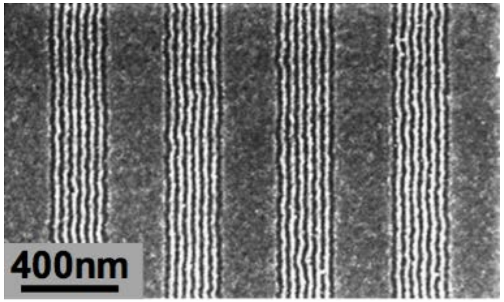


Oria et al., Microelectronic Engineering 110 (2013), pp 234-240.

Basic Principle – Directed Self-Assembly Chemo-Epitaxy

- Grafting PS-OH brush layer.
- PMMA e-beam exposure and development of DSA pattern.
- Modifying open brush in O_2 plasma 150 W RIE.
- Removing PMMA.
- Spinning PS-*b*-PMMA.
- Thermal annealing.





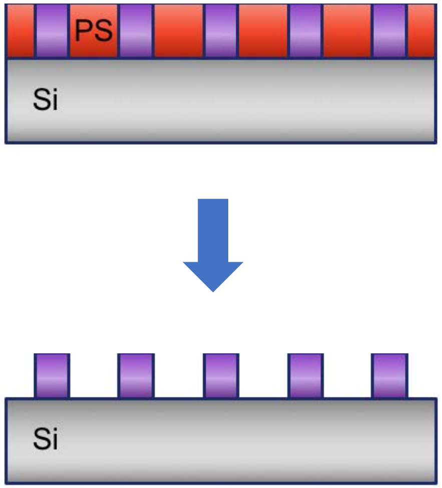
Oria et al., Microelectronic Engineering 110 (2013), pp 234-240.

Lithography

• Removal or modification of one block

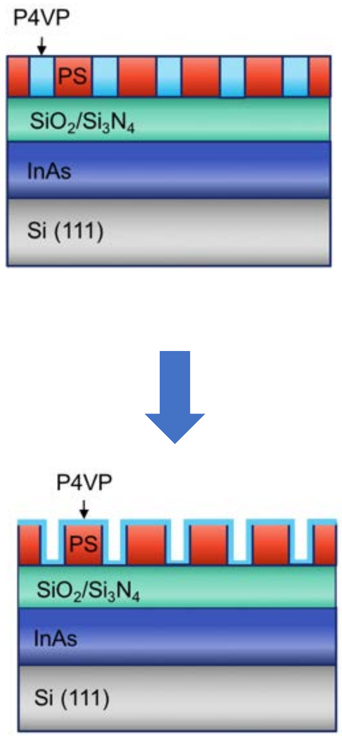
→ Pattern topography

→ Enables pattern transfer

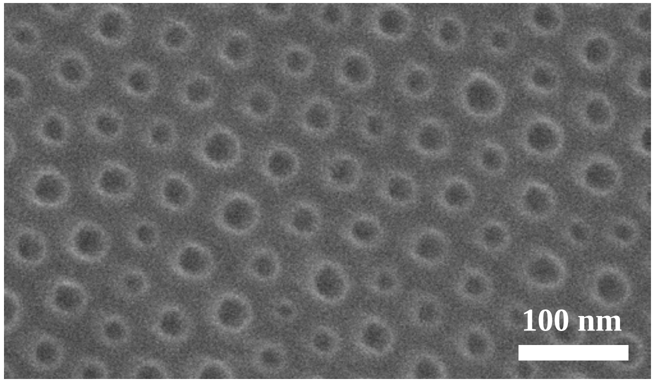


Lithography – Surface Reconstruction

- Preferential solvent for minority block
  → Extracts minority block to surface
  → Pore opening.



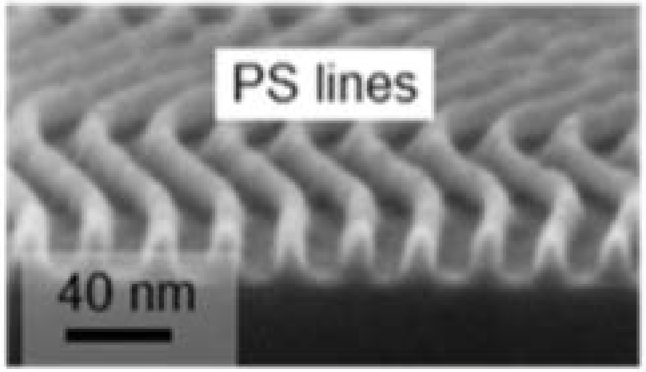
- <u>Example</u>: PS-*b*-P4VP in Ethanol.
  - Immersion 60 minutes in 60°C Ethanol.
  - P4VP extracted to the surface.



Löfstrand et al., unpublished

Lithography – Block Modification
Dry etch selectivity

- Dry etch selectivity between blocks
  → Etches one block faster
  → Pattern topography.



- Example: PS-*b*-PMMA in O_2 plasma RIE.
  - Poly(styrene)-*block*-Poly(methyl methacrylate)
  - 60 W, 2 mTorr, 20-25 s.
  - PMMA is removed, as it etches faster than PS.

Wan et al., *ACS Nano* 2015, 9, 7, 7506-7514

Lithography – Block Modification Increased Etch Selectivity

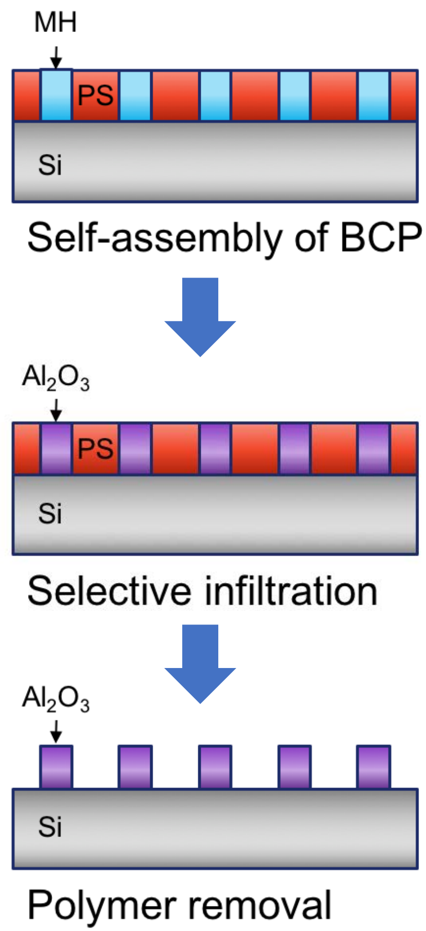
- Etch selectivity between blocks
  → Etches one block faster
  → Pattern topography.

- Example: PS-*b*-PMMA in O_2 plasma RIE.
  - UV exposure breaks bonds in PMMA
    → Higher etch rate

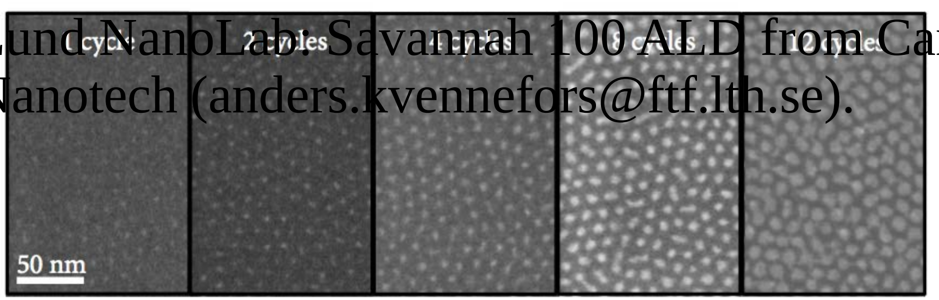
  - UV exposure creates bonds in PS
    → Lower etch rate

Lithography – Block modification
Selective Infiltration Synthesis

- Infiltration of Alumina selectively into one block
  → High etch selectivity
  → Pattern topography.



- Example: PS-*b*-MH in TMA and Water.
  - ALD tool with cycling precursor pulses in N_2 flow.
    → Alumina in MH
  - Lund NanoLab: Savannah 100 ALD from Cambridge Nanotech (anders.kvennefors@ftf.lth.se).



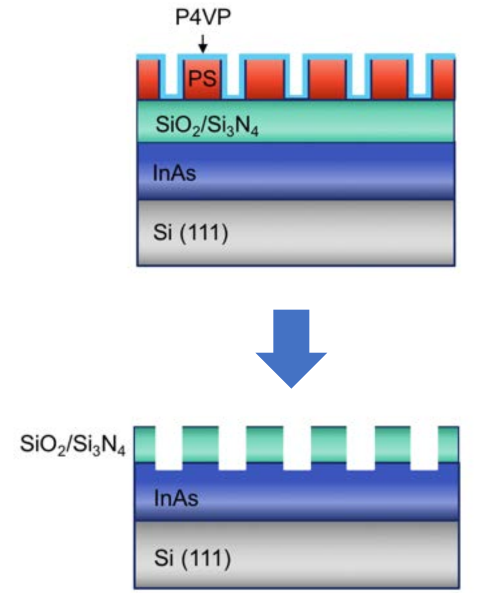
Löfstrand et al., unpublished

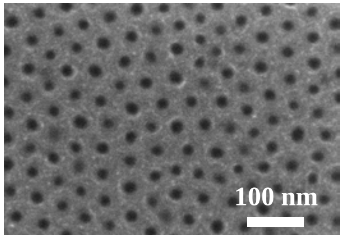
Pattern Transfer

- BCP topography pattern

  → Polymer etch mask.

- Example: PS-*b*-P4VP on Silicon Nitride
  - Poly(styrene)-*block*-Poly(4-vinyl pyridine)
  - Surface reconstruction
  - Oxygen plasma ICP-RIE residual ashing.
  - N_2:CHF_3 plasma ICP-RIE Silicon Nitride etching.
  - Oxygen plasma ICP-RIE polymer stripping.
  - Lund NanoLab: Apex SLR ICP-RIE from Advanced Vacuum Systems AB (dmitry.suyatin@ftf.lth.se).

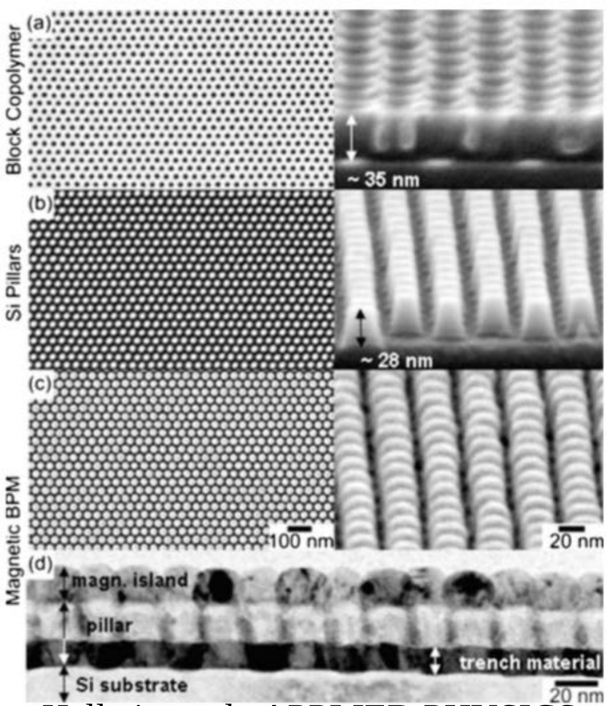




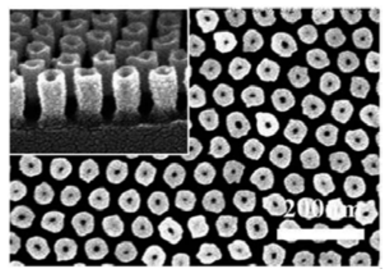
Löfstrand et al., unpublished

Applications

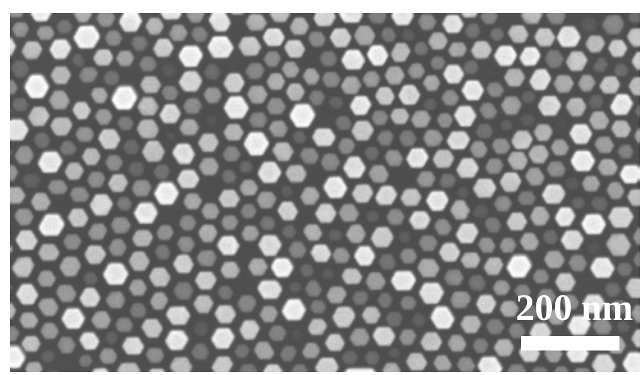
- High density hexagonal dot pattern
  - Sensors
  - Bit patterned media
  - Epitaxy templates



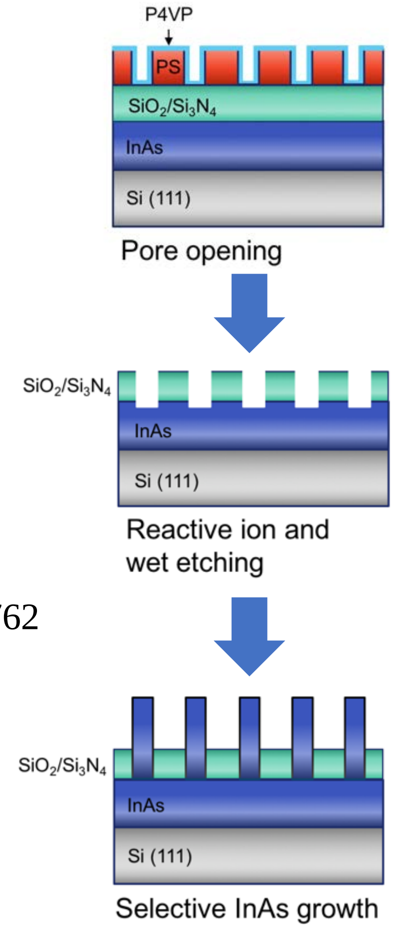
Hellwig et al., APPLIED PHYSICS LETTERS **96**, 052511 2010



Shin et al., RSC Adv., 2016, 6, 70756–70762



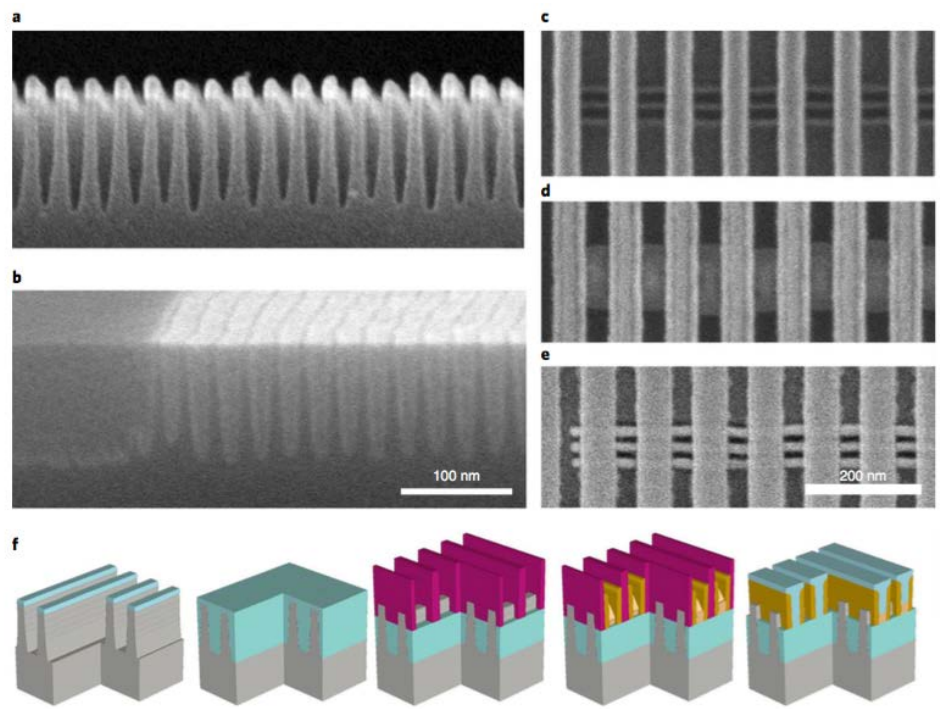
Löfstrand et al., unpublished



Nordic Nanolab Network

Applications

- High density line pattern
  - Wire grid polarizers
  - FinFETs



Liu *et al.*, *Nature Electronics*, vol. 1, no. 10, pp. 562-569, 2018

Applications

- Pattern shrink
  - Via holes

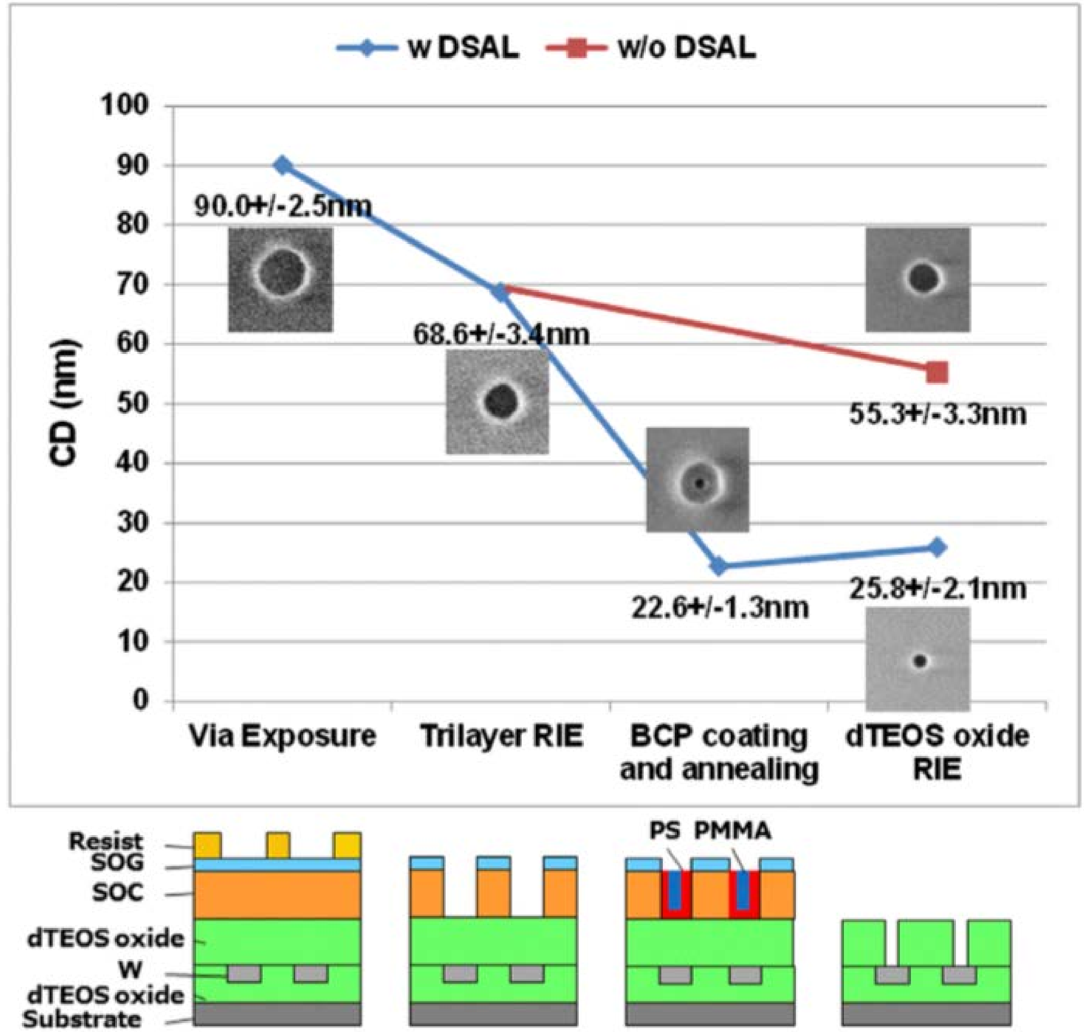


Fig. 2. CD and intra-wafer CD uniformity on each process step.

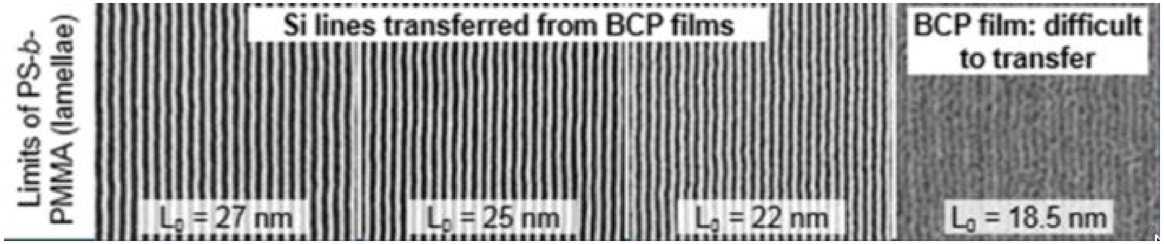
Kato et al., Microelectronic Engineering 110 (2013) 152–155

Challenges

- Defectivity
  - Line Edge Roughness
  - Polymer quality
  - Pattern defects

- Pattern Design
  - Local patterning
  - Surface energy sensitivity

- Sub-10 nm Pattern Transfer
  - Interface length between blocks



Wan et al., *ACS Nano* 2015, 9, 7, 7506-7514

Equipment

- RTP
  - Lund NanoLab: Rapid Thermal Processing (RTP) system, RTP-1200-100 from UniTemp GmbH (dmitry.suyatin@ftf.lth.se).
  - Chalmers: Rapid Thermal Processor (RTP) JIPELEC Jet First 200 (mats.hagberg@chalmers.se).
    Electrum: RTA, Mattson 100 RTP Systems (pereh@kth.se).
  - NTNU: RTP, Jetfirst 200 mm (Svenn Ove Linde).

Nordic Nanolab Network

Equipment

- ALD
  - Lund NanoLab: Savannah 100 ALD from Cambridge Nanotech (anders.kvennefors@ftf.lth.se).
  - Chalmers: Oxford FlexAl (karin.hedsten@chalmers.se).
  - Electrum: ALD, BENEQ TFS 200 (ybw@kth.se).
  - Ångström: Picosun R200 (carl.hagglund@angstrom.uu.se).
  - Micronova: ALD reactor ALD-2, Beneq TFS-500 (Ville Vähänissi).
  - NTNU: ALD Savannah S200, Veeco (Mark Chiappa).
  - UiO: ALD, Beneq TFS 200 (Kristin Bergum).

Equipment

- ICP-RIE
  - Lund NanoLab: Apex SLR ICP-RIE from Advanced Vacuum Systems AB (dmitry.suyatin@ftf.lth.se).
  - Chalmers: PlasmaPro 100 Cobra ICP 180 from Oxford Instruments (marcus.rommel@chalmers.se).
  - Electrum: Cryo RIE Albanova, Oxford Plasmalab 100 (anders@biox.kth.se).
  - Micronova: Oxford Instruments Plasmalab System100 - ICP 180 (Toni Pasanen).
  - NTNU: ICP-RIE Cryo, PlasmaLab System 100-ICP180 (Svenn Ove Linde).

Thank you
for your attention!