Ion beam patterning and directed self-assembly

MICRO-724 (2022)

Advanced topics in micro- and nanomanufacturing: top-down meets bottom-up

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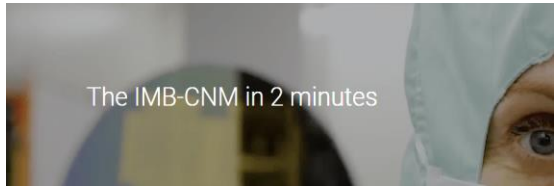

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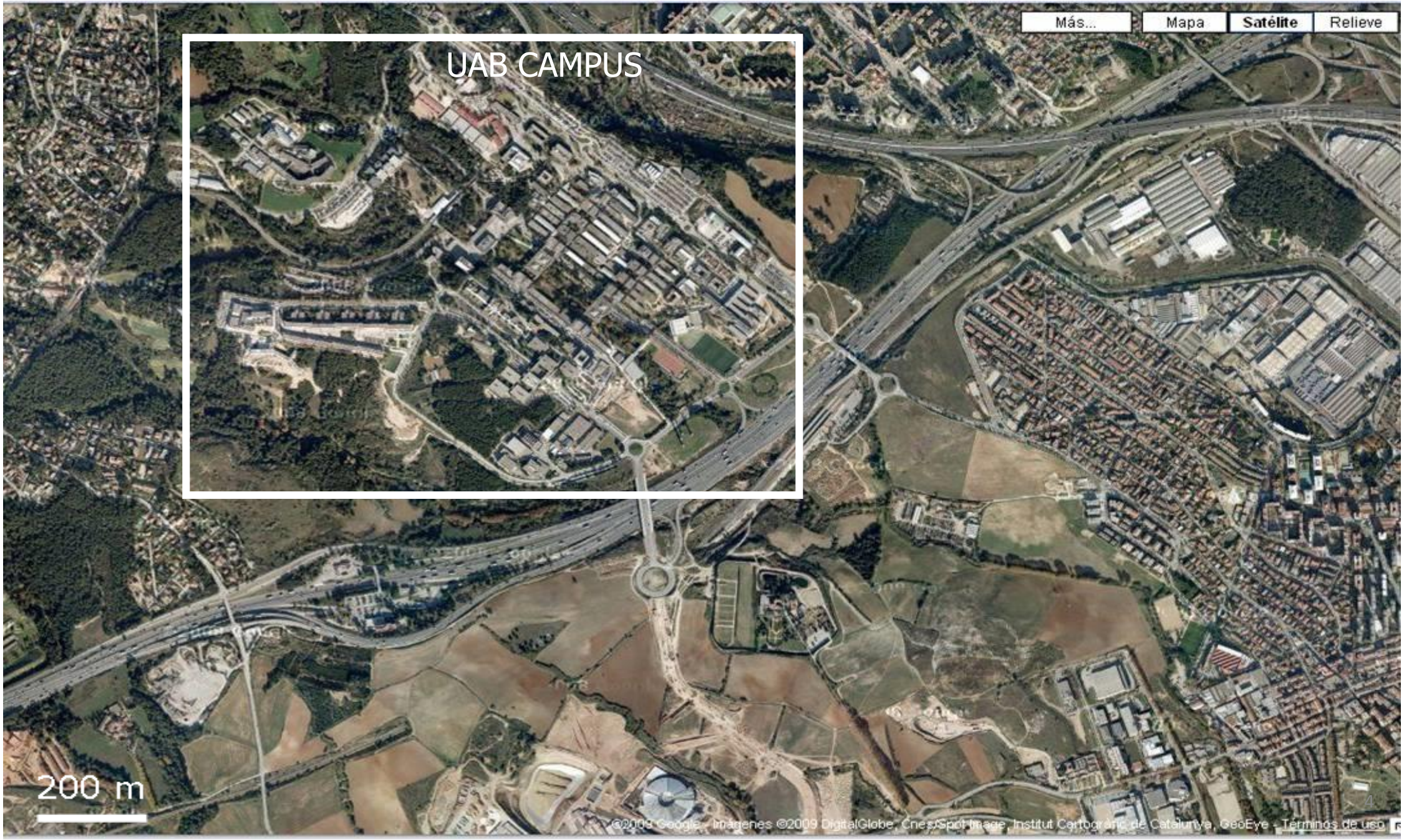
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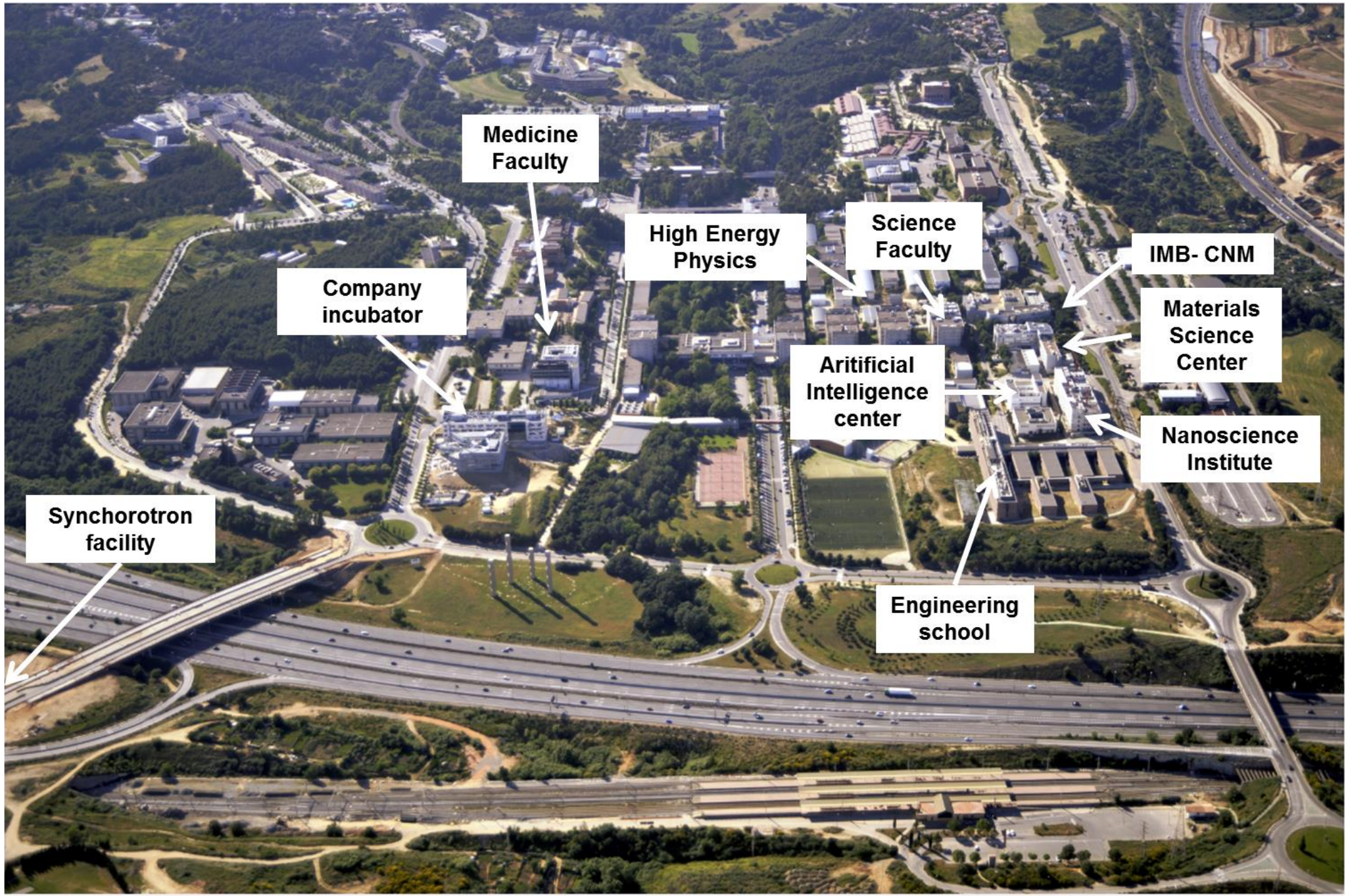
Medicine Faculty
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Company incubator
Materials Science Center
Aritificial Intelligence center
Nanoscience Institute
Synchorotron facility
Engineering school

IMB-CNM

Applied research center in the are of micro/nano engineering (Devices, circuits and systems)

200 staff **10** research groups

Micro/Nano fabrication Clean room

1,500 m²
total area

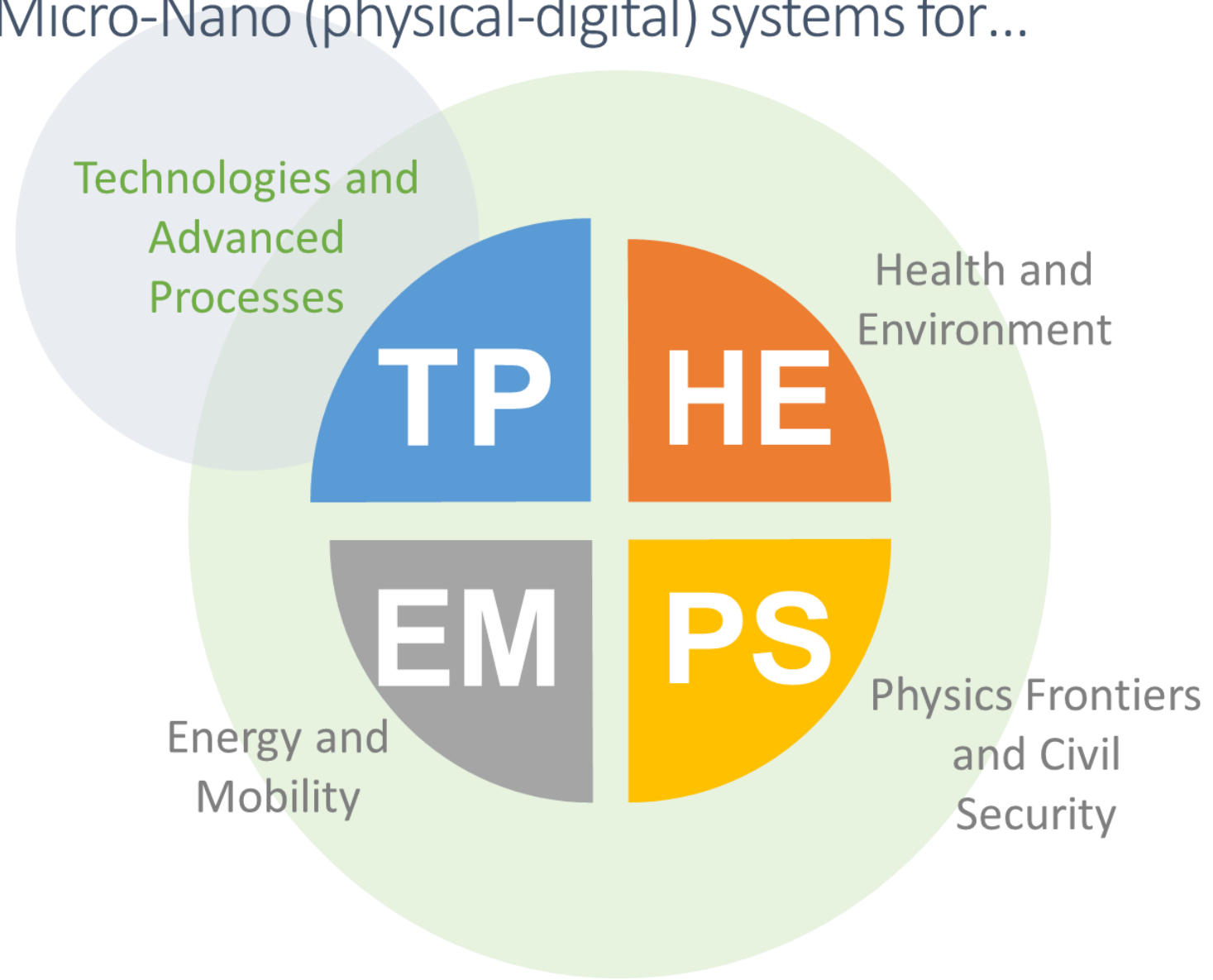
40
staff

190
equipment units

3000
Wafers/year

1
tech unit

3
thematic axes



Smart integrated micro/nano Systems for solving social challenges

Smart Intracellular electronic chips

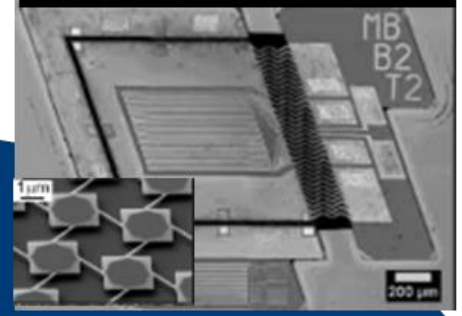
Enabling micro&nano technologies

Personalized medicine

Environment and security

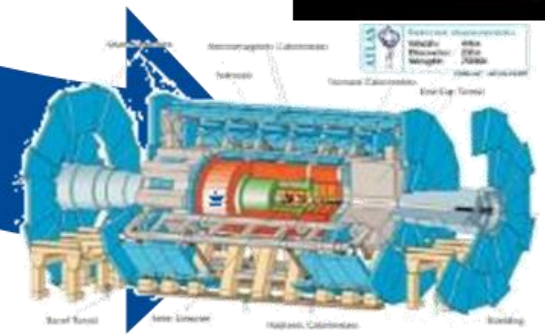
Energy Efficiency and harvesting

Nanostructures into smart systems

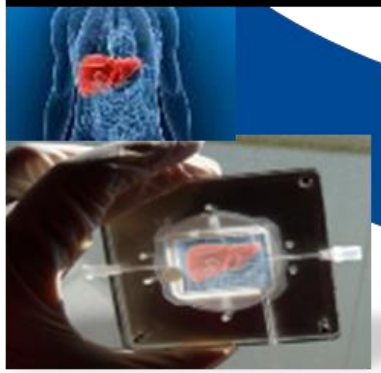


Single use and self-powered engineered devices

radiation detectors for harsh environments



Organ on a chip



STRUCTURE

Introductory lectures

A. Electron and ion beam lithography

- Recap on principles and limitations
- Relevant examples of ion-beam patterning

B. Directed self-assembly (DSA)

- Bottom-up vs top down fabrication
- DSA for high volume manufacturing
- Principles of DSA of block co-polymers

Advanced lessons

- Ion beam patterning for the fabrication of Nanoelectronic and nanomechanical devices

Advanced DSA aspects: Creation of guiding paterns and applications

Recommended bibliography

Nanofabrication

Nanolithography techniques and their applications

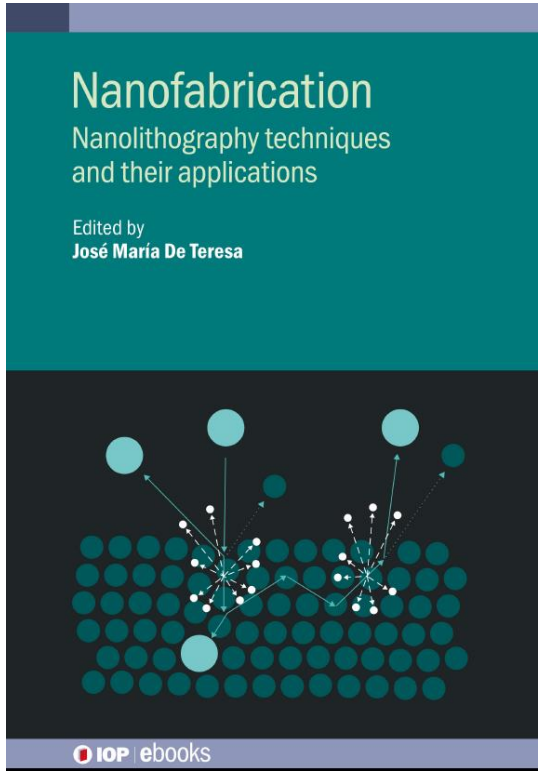
Edited by JoséMaría De Teresa

ISBN 978-0-7503-2608-7 (ebook)

ISBN 978-0-7503-2606-3 (print)

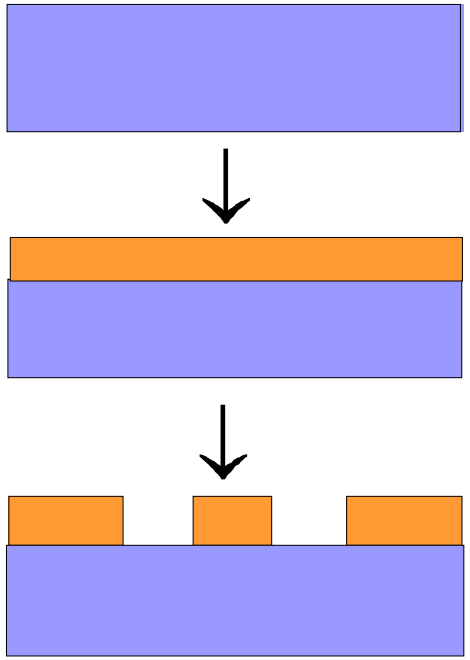
ISBN 978-0-7503-2609-4 (myPrint)

ISBN 978-0-7503-2607-0 (mobi)



- J. E. E. Baglin, “Ion beam enabled nanoscale fabrication, surface patterning, and self-assembly” Applied Physics Reviews 7, 011601 (2020). https://doi.org/10.1063/1.5143650
- P. Li, et al. “Recent advances in focused ion beam nanofabrication for nanostructures and devices: fundamentals and applications,” Nanoscale 13, 1529–1565 (2021), http://dx.doi.org/10.1039/D0NR07539F
- Ji S, Wan et al. Directed self-assembly of block copolymers on chemical patterns: A platform for nanofabrication Prog. Polym. Sci. 54–55 76–127 (2016) ttps://doi.org/10.1016/j.progpolymsci.2015.10.006

Lithography based fabrication



Resolution is the main figure of merit to describe the performance of lithography

Resolution is defined as the minimum feature that can be printed in the resist

Improving resolution without degrading other parameters (throughput, reliability, etc) has been the battle horse of nanofabrication

Question:

- What it limits resolution in optical lithography?

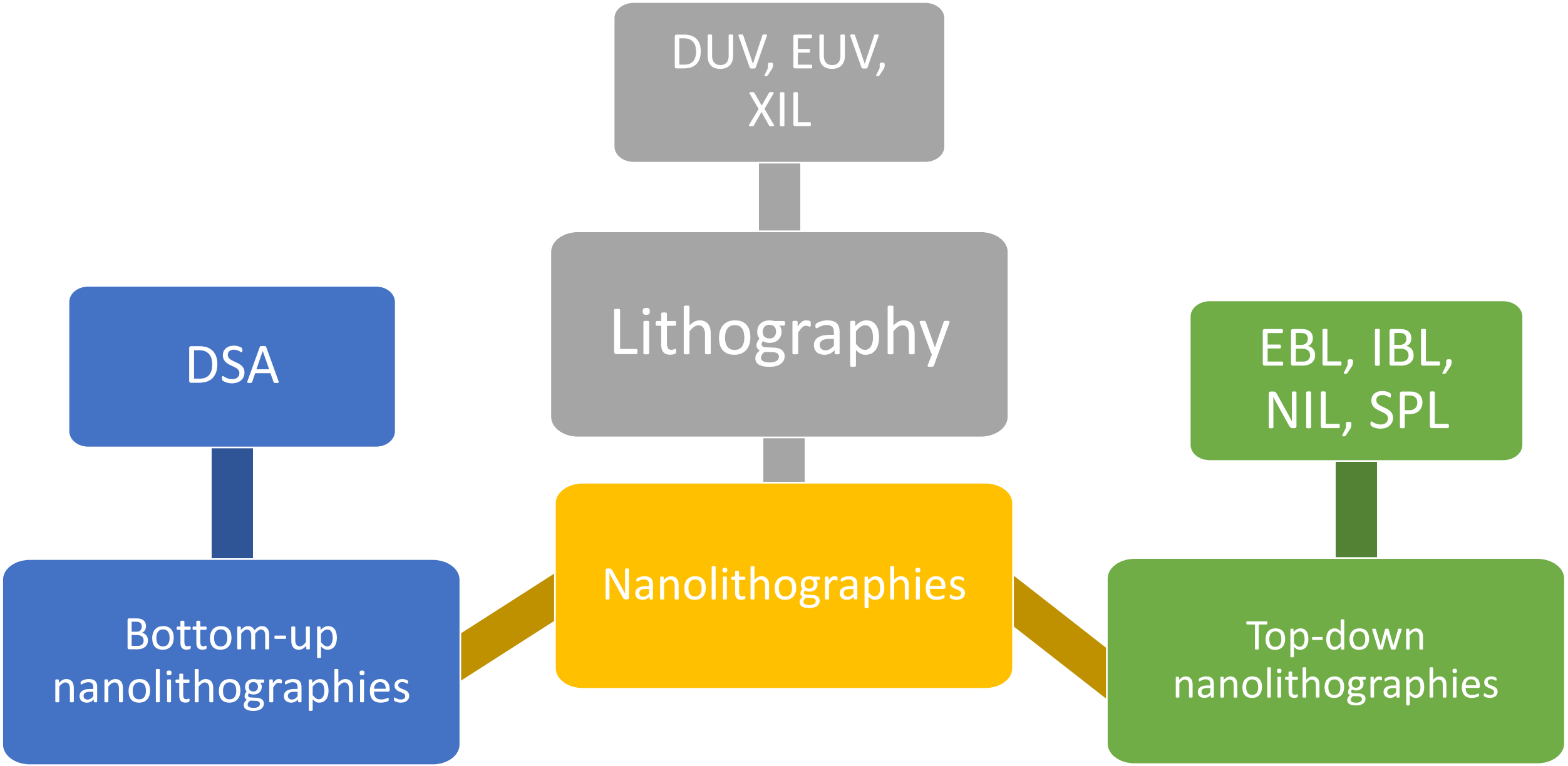
- In optical lithography, diffraction phenomena limits the resolution
- Reducing the wavelength of the optical radiation has been one of the ways to improve the resolution

Resolution in projection optical lithography

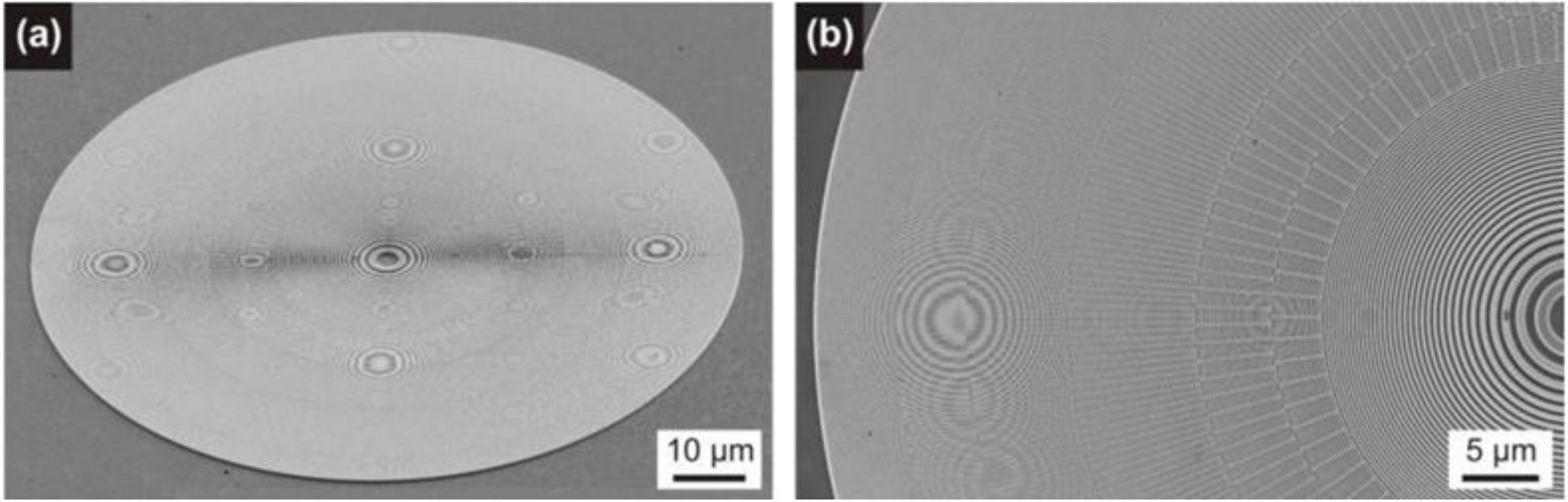
$$R = k_1 \frac{\lambda}{NA}$$

Electrons wavelength: $\lambda_e = \frac{1.226}{\sqrt{V}} (\text{nm})$ <0,1Å!!

Lithographies

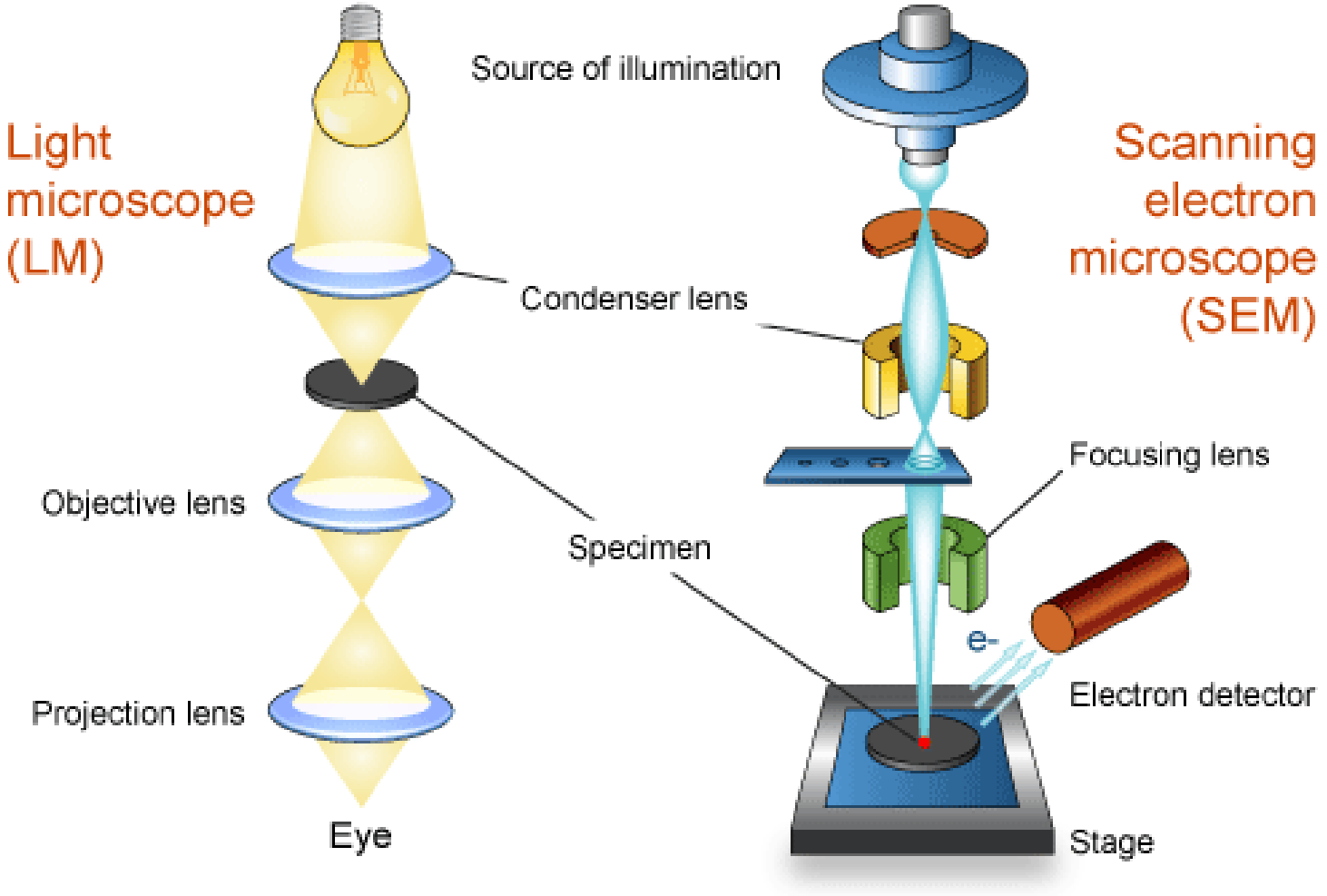


A.1 Electron beam lithography



Joan Vila-Comamala, Sergey Gorelick, Elina Färm, Cameron M. Kewish, Ana Diaz, Ray Barrett, Vitaliy A. Guzenko, Mikko Ritala, Christian David, "Ultra-high resolution zone-doubled diffractive X-ray optics for the multi-keV regime," Opt. Express **19,** 175-184 (2010); https://www.osapublishing.org/oe/abstract.cfm?uri=oe-19-1-175

Optical vs Electron beam lithography

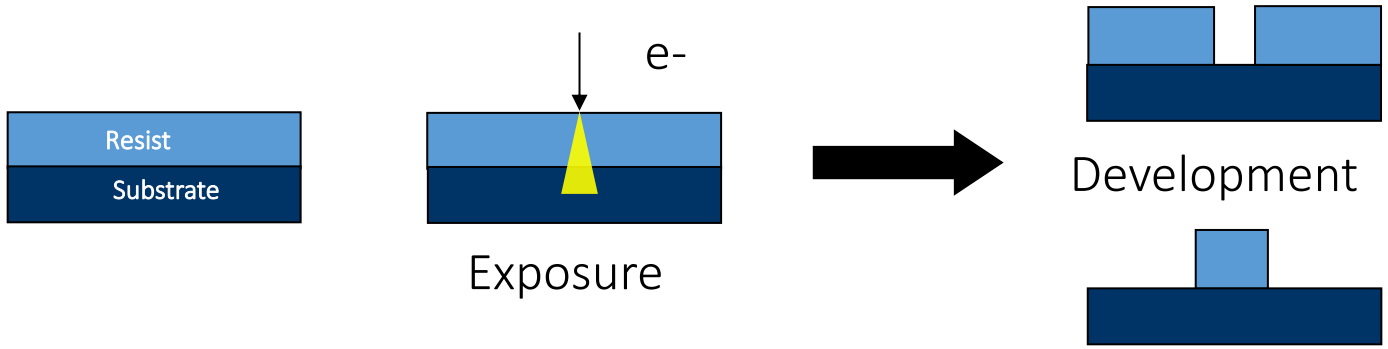


Electron beam lithography is the most commonly used nanolithography method in research

Electron beam lithography (EBL)

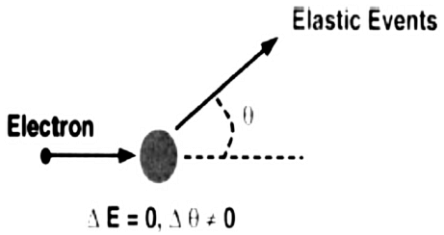
Concept

- Exposure of a focused electron beam on a electron sensitive layer of material (EBL Resist)
- Upon exposure, chemical/physical properties of the resist change
- After development, areas of the resist are selectively eliminated

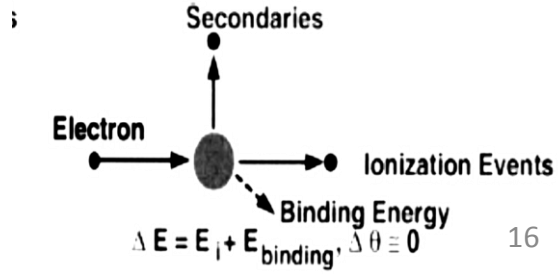


Resolution in electron beam lithography is limited by the scattering of electrons with the atoms of the resist and substrate

Elastic scattering

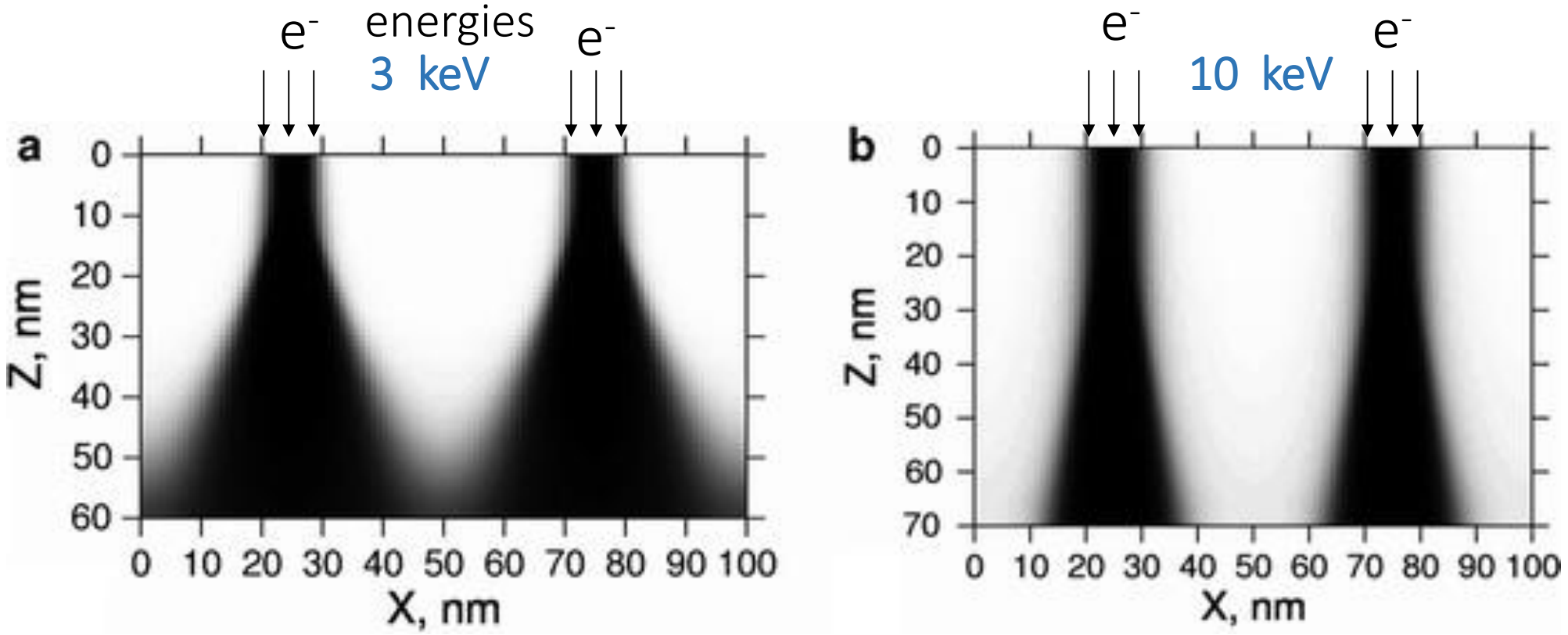


Inelastic scattering



Forward scattering

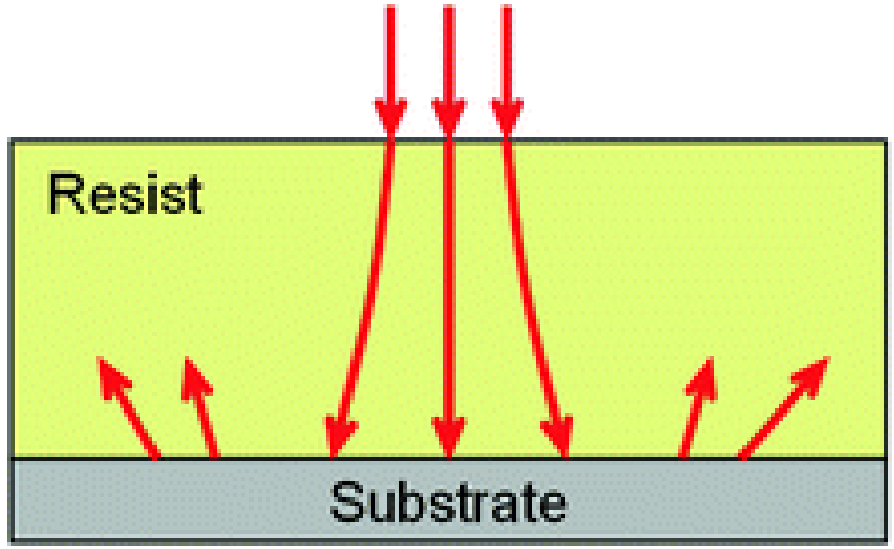
As the electrons enter the resist, they begin a series of low energy elastic collisions, each of which will deflect the electron slightly. This forward scattering broadens the beam by an amount that increases with thickness, and this effect is more pronounced at low incident energies



Mohammad M.A., Muhammad M., Dew S.K., Stepanova M. (2012) Fundamentals of Electron Beam Exposure and Development. In: Stepanova M., Dew S. (eds) Nanofabrication.

Backscattering

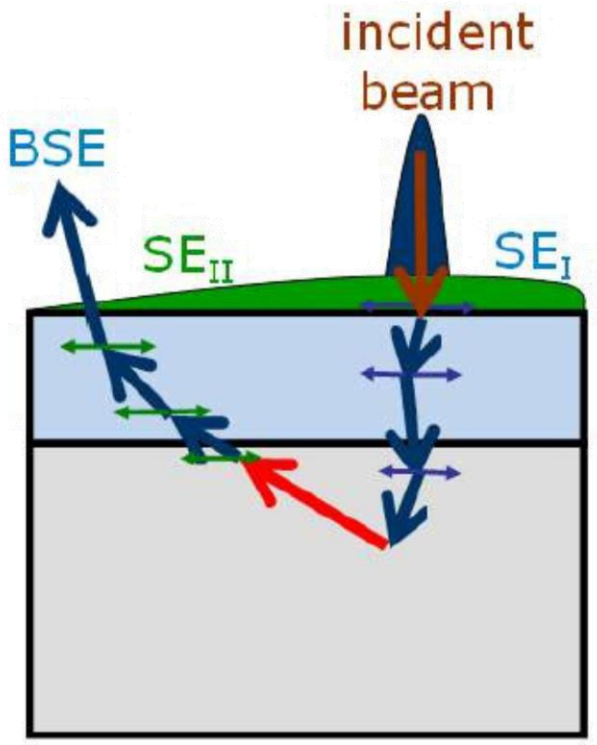
Most of the electrons pass entirely through the resist and penetrate deeply into the substrate. Some fraction of those electrons will eventually undergo enough large angle collisions to re-emerge into the resist at some distance from the point at which they left it. At higher energies, these backscattered electrons may cause exposure microns away from where the beam entered. This leads to the so-called proximity effect



Mohammad M.A., Muhammad M., Dew S.K., Stepanova M. (2012) Fundamentals of Electron Beam Exposure and Development. In: Stepanova M., Dew S. (eds) Nanofabrication.

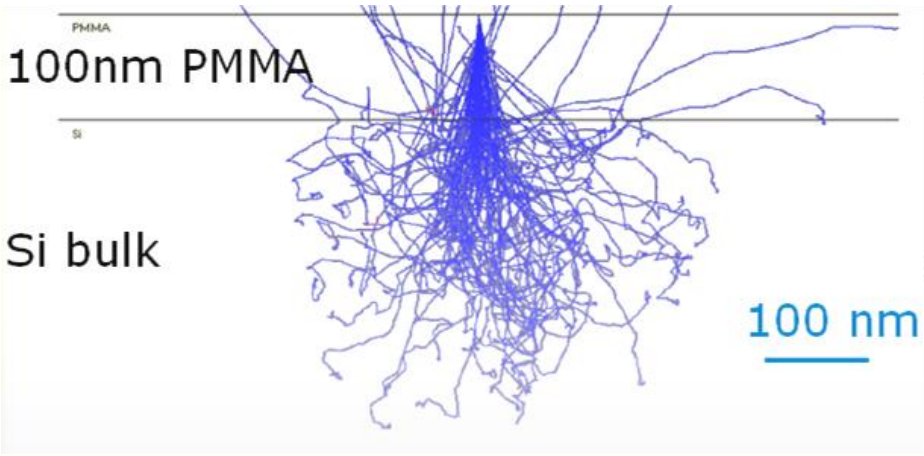
Secondary electrons

Secondary electrons are low energy (10-100 eV) produced by inelastic collisions of the incident electrons. They have short travelling range and fix a limits for the minimum resolution .

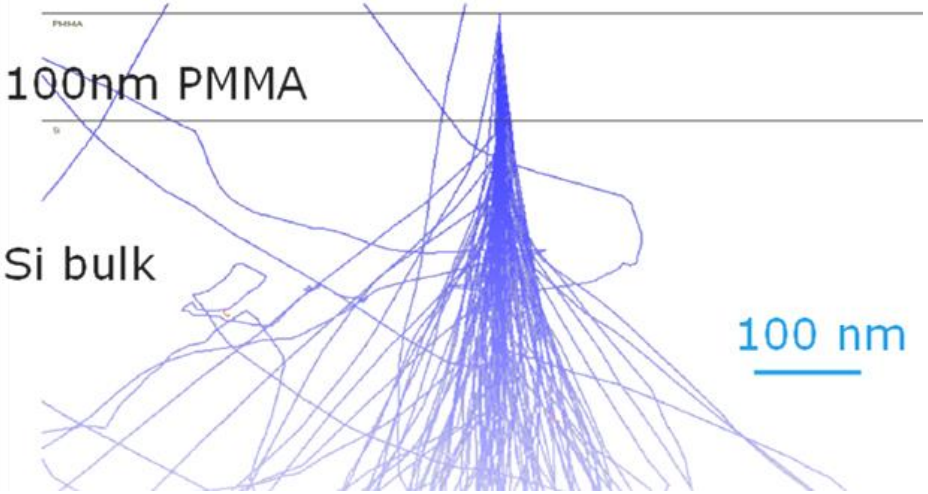


Monte Carlo simulations

Beam Energy: 5keV



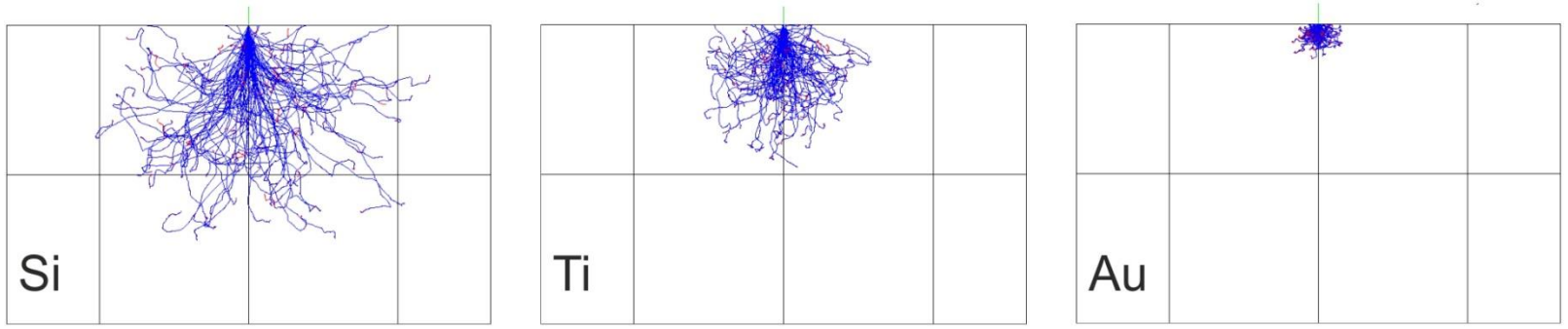
Beam Energy: 20keV



Trajectory of the incident electrons. Each change of direction causes the emission of a secondary electron

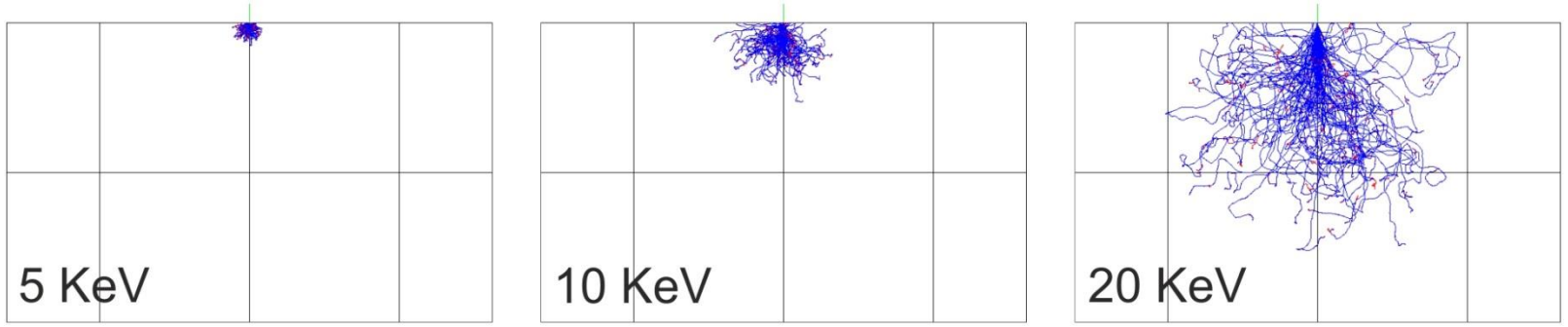
Material /Energy dependence of exposure

Increasing atomic number



E = 10 KeV N trajectories = 100 Beam width = 1 A Grid division = 500 nm

Increasing the energy



Element: Fe N trajectories = 100 Beam width = 1 A Grid division = 500 nm

Beam energy and resist exposure

100 keV

+ Small scattering in resist
+ Small proximity effect

– High beam damage
– Strong sample heating

20 keV

+ Small beam damage
+ Small sample heating
+ Best electron-optical performance (classical columns)

– Scattering in thick resist
– Strong proximity effect

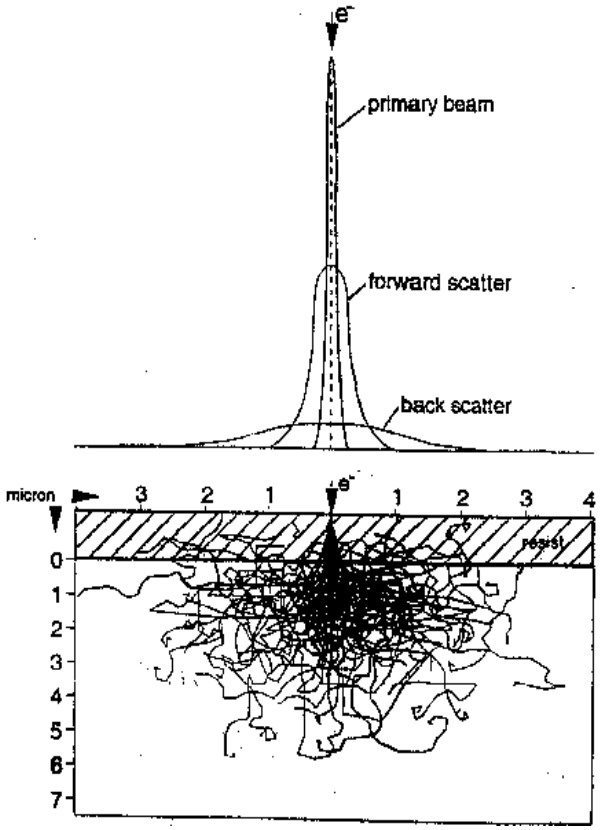
2 keV

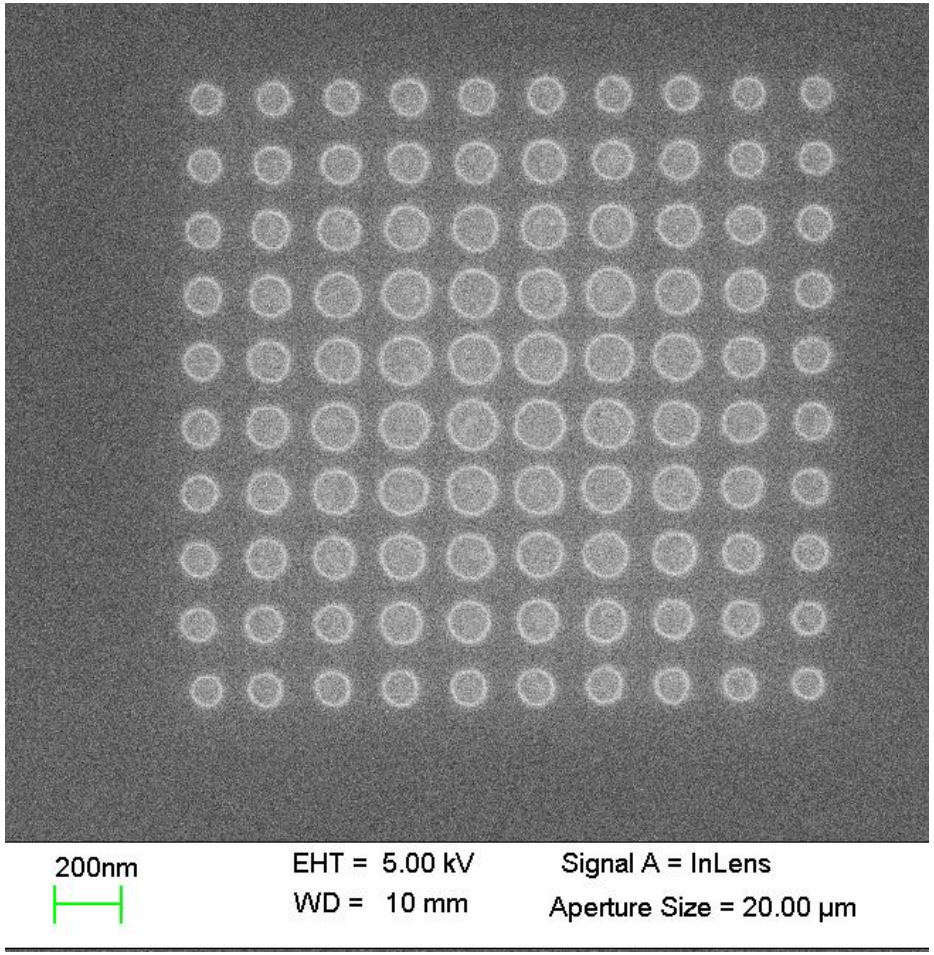
+ No beam damage
+ No proximity effect
+ High throughput (high resist sensitivity)

– High scattering in resist
– Needs very thin resists

Exposure Process: Proximity Effect

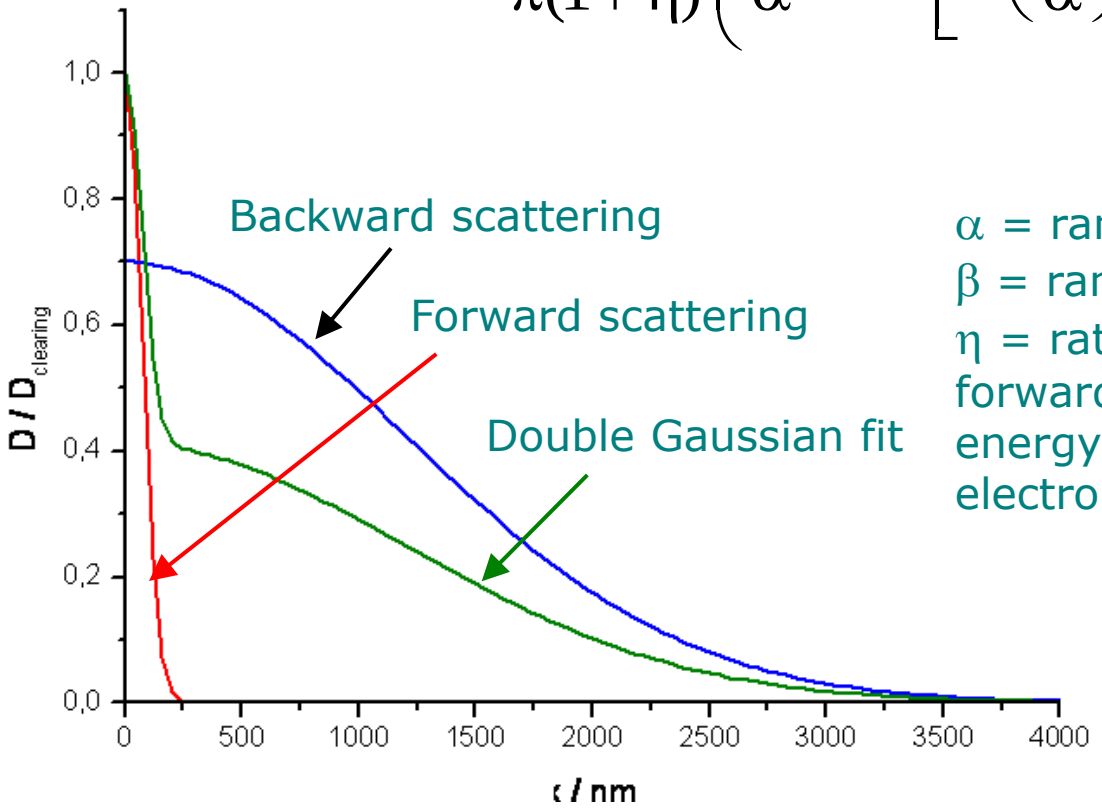
Due to backscattered electrons the resist is also exposed in nearby areas. When exposing a dense pattern this leads to overexposed patters





Proximitty Effect Correction: calculations

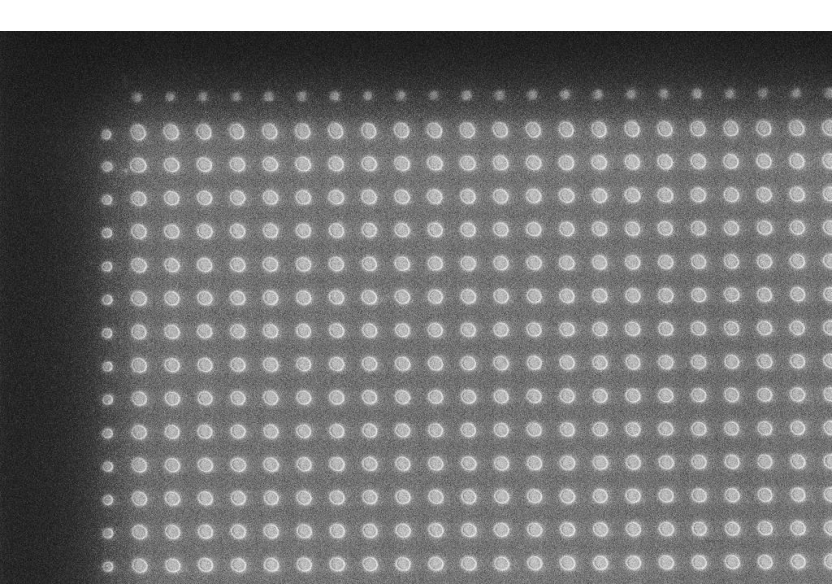
$$f(r) = \frac{1}{\pi(1+\eta)}\left(\frac{1}{\alpha^2}\exp\left[-\left(\frac{r}{\alpha}\right)^2\right] + \frac{\eta}{\beta^2}\exp\left[-\left(\frac{r}{\beta}\right)^2\right]\right)$$

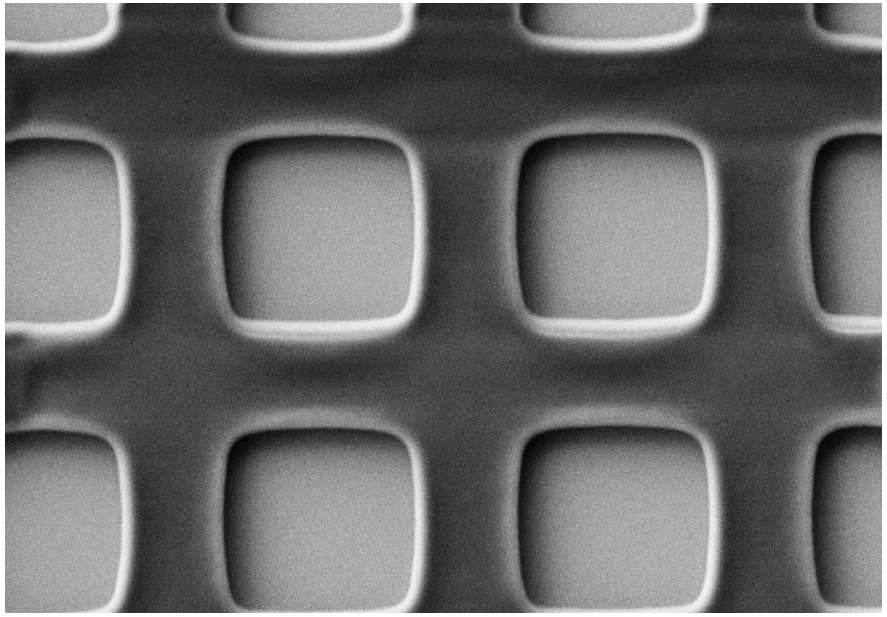


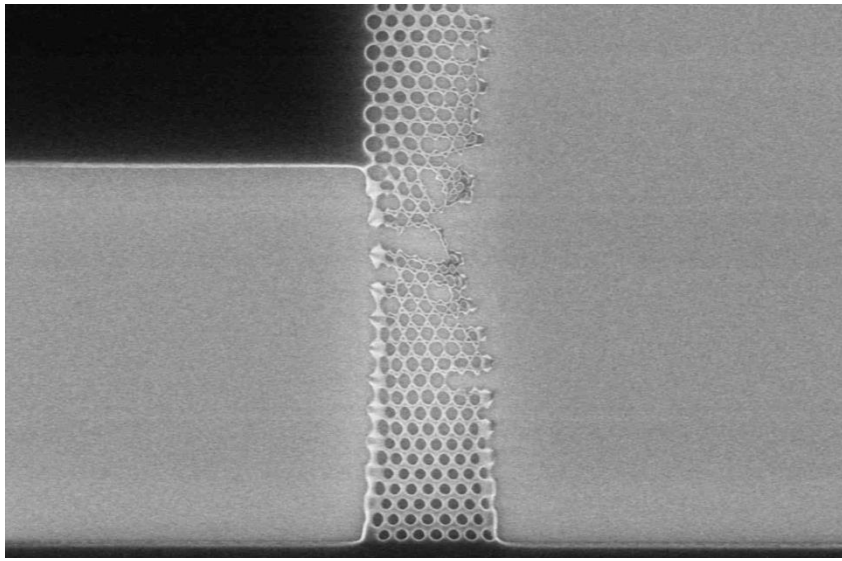
α = range of forward scattering
β = range of backward scttering
η = ratio of energy deposited by forward scatterd electrons to the energy deposited by backscattered electrons

Proximitty Effect Correction: When?

- In the borders of dense or continous patterns
- Mixing small and big features

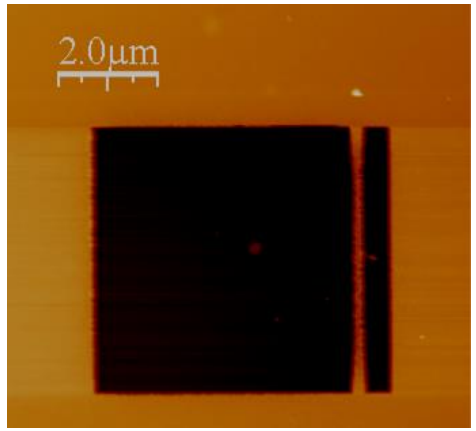


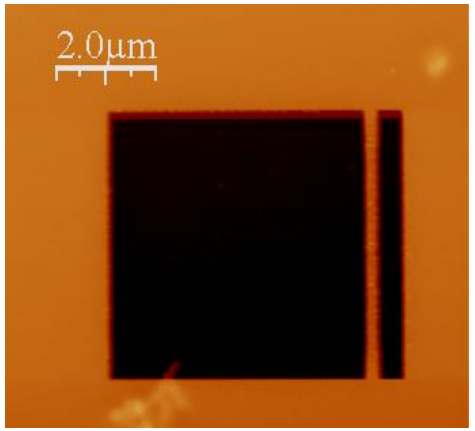




Manual correction possible up to some extend

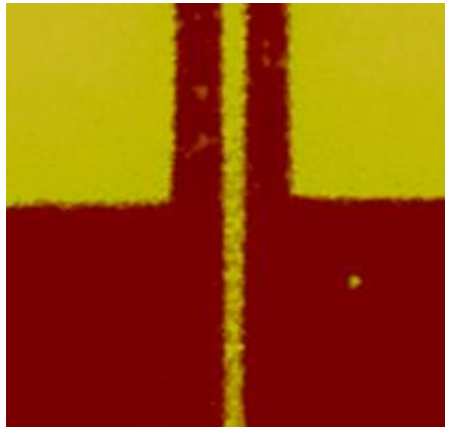
Proximitty Effect Correction: calculations

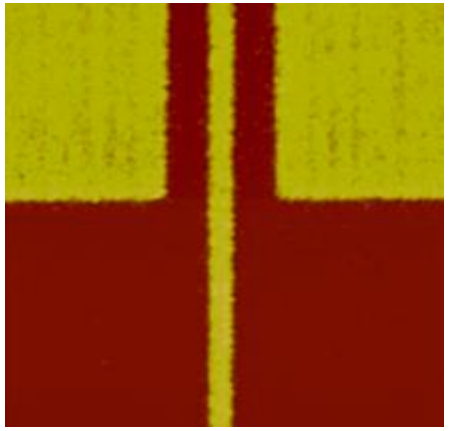




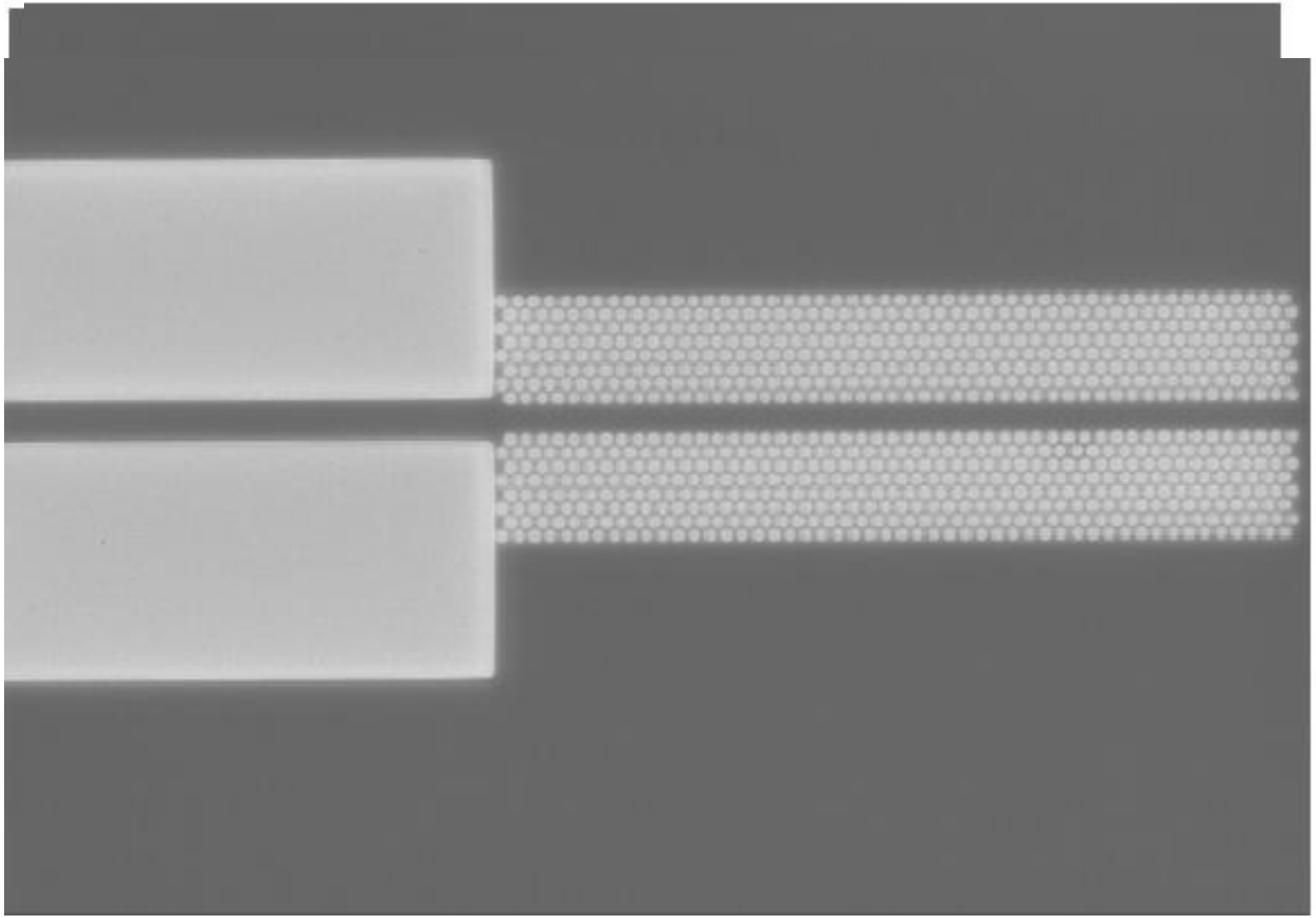
PMMA		α	β	η
10 keV	(µm)	0.4	0.6	0.75

mr–EBL 6000.1		α	β	η
10 keV	(µm)	0.3	0.6	0.75





Proximity effect correction: example



Resolution limits

Beam resolution

Thick resists (forward scattering)

Thin resists (secondary electrons, back scattering)

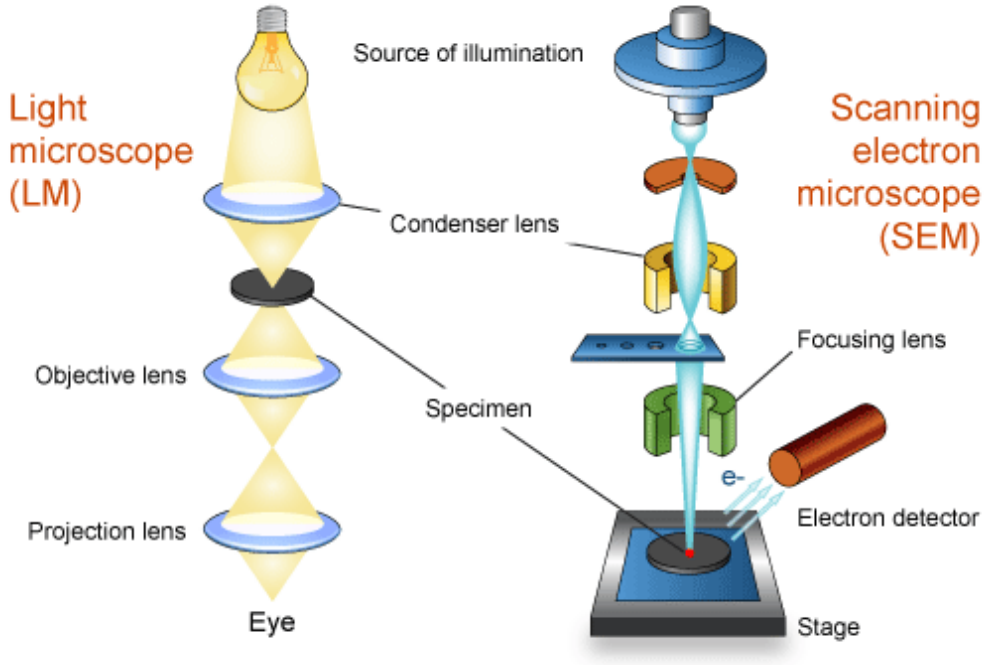
Secondary electron range (~5-10nm)

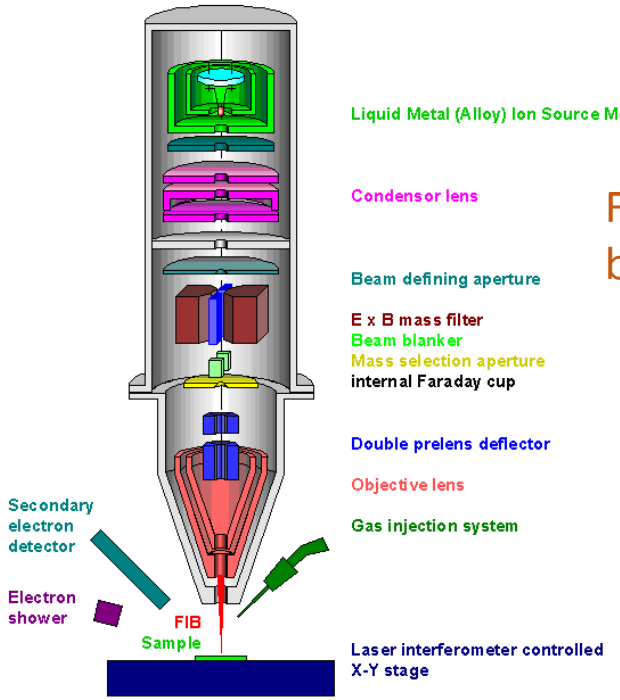
Resist limits

- Polymer size (~5-10nm)
- Chemically amplified resists (acid diffusion ~50nm)

In practice, the achievable resolution in polymeric resists is around 10-20nm

Focused Ion Beam (FIB) fabrcation



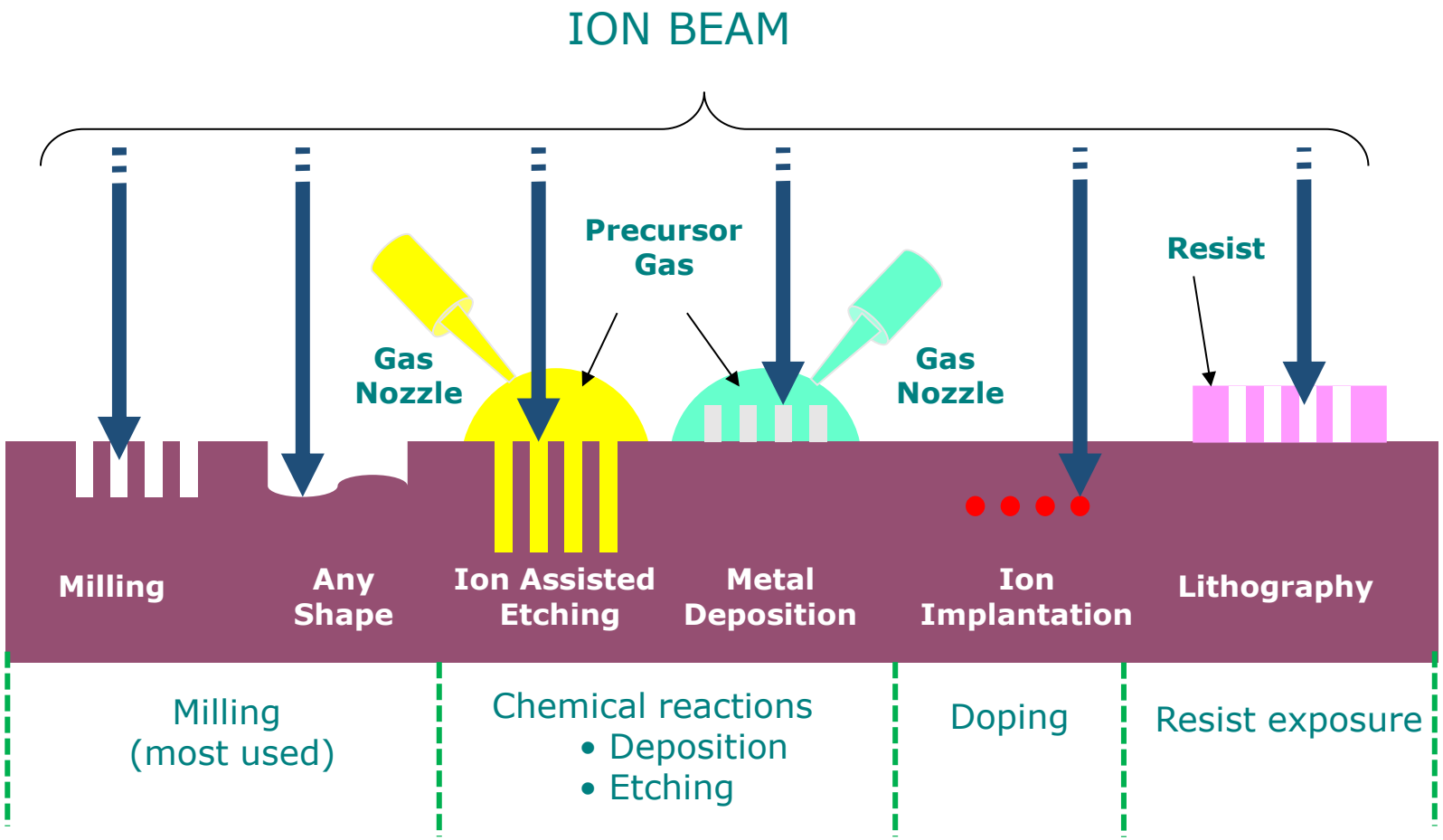


Focused ion beam system

Concept:

- Exposure of a surface by a focused ion beam
- Multiple modes of operation: Resist exposure (lithography), direct writing (milling), induce reactions, doping, …
- Ions have much large mass than electrons

Ion beam interaction processes with surfaces

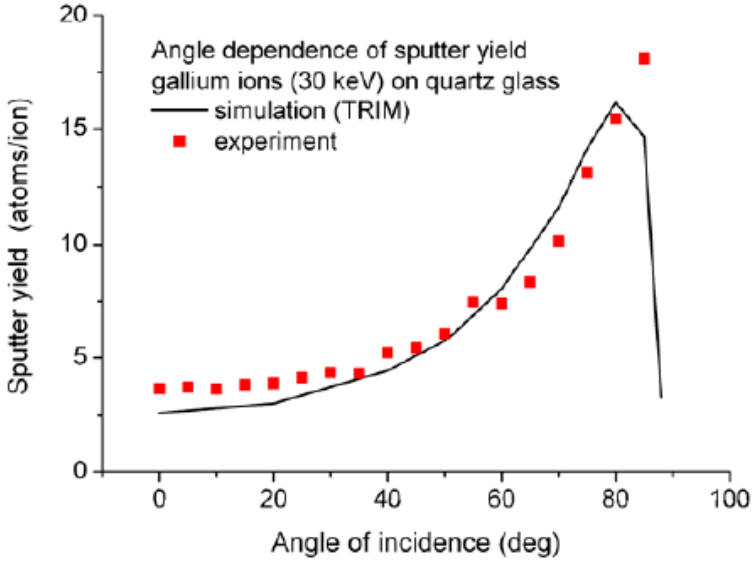


Milling

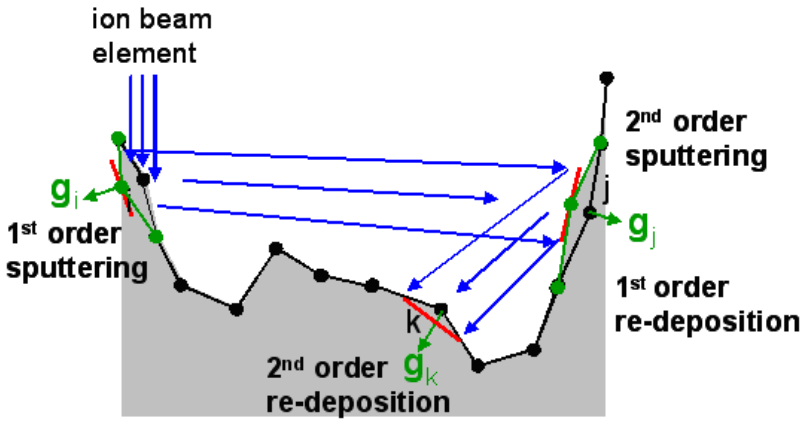
Milling is a process combining physical sputtering, material re-deposition, and amorphization (swelling)

Sputtering: An atom from a material in the solid phase is ejected into the gas phase. It is the major mechanism for material removal

30kV Ga+	Sputtering yield (atoms/ion)	Sputtering Rate (cm^3/nC)
Si	2.1	0.27
Al	2.9	0.3
Au	25	1.5



Re-deposition: the sputtered atoms tend to condense back into the solid phase upon collision with any solid surface nearby and a portion of the ejected atoms may bump into the already sputtered surface and redeposit on it.



Redeposition can be greatly reduced if multiple passes instead of a single pass are used in milling with the same amount of ions With multiple passes, each successive pass removes redeposited material from the previous pass.

Redeposition reduces the milling rate and the aspect ratio of the milled structures

Milling

Milling is a process combining physical sputtering, material re-deposition, and amorphization (swelling)

Amorphization: If the energy or dose level of the incident ions is not high enough for sputtering, amorphization may occur in the bombarded area of a crystalline substrate and may induce the substrate to swell.

In the case of a crystallized Si substrate bombarded by Ga ions, the dose level that causes amorphization is on the order of 10^{15} ions·cm^{-2}, while the effective sputtering dose is more than two orders of magnitude higher

The incident ions in most cases are buried in the target material and may also displace the target atom: Implantation and swelling

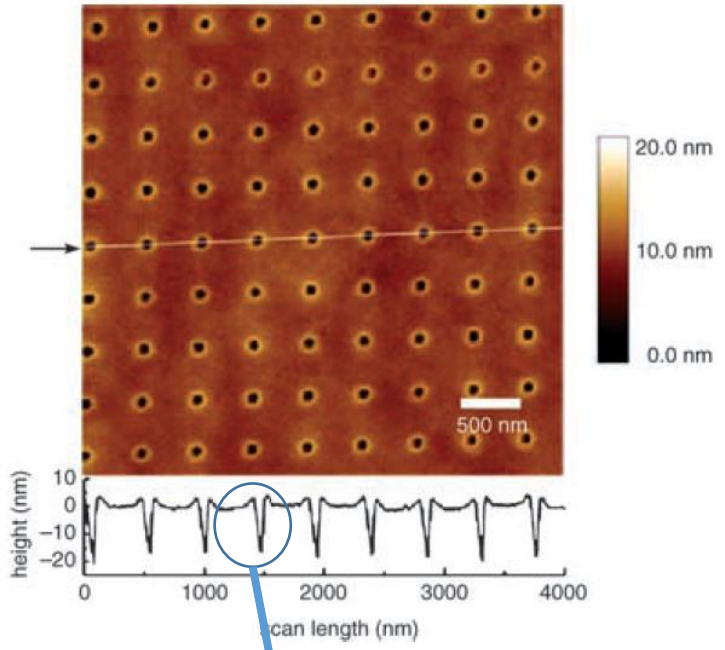
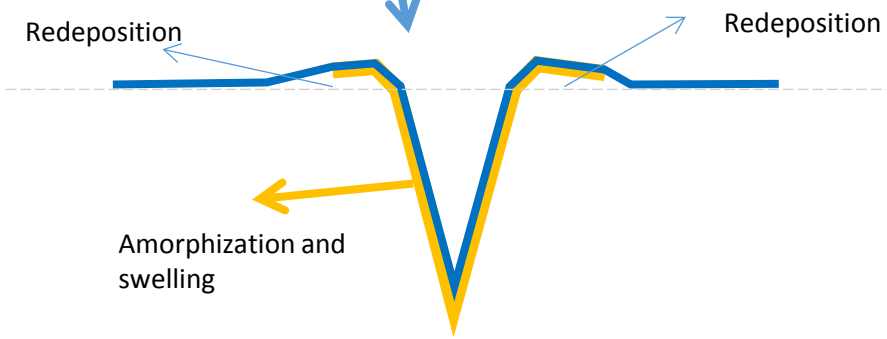


Figure 1. AFM image of hole (dot) array milled by a 30 keV Ga^+ FIB at 1 pA on a Si substrate (after Li et al.[13]).



Milling

Milling is a process combining physical sputtering, material re-deposition, and amorphization (swelling)

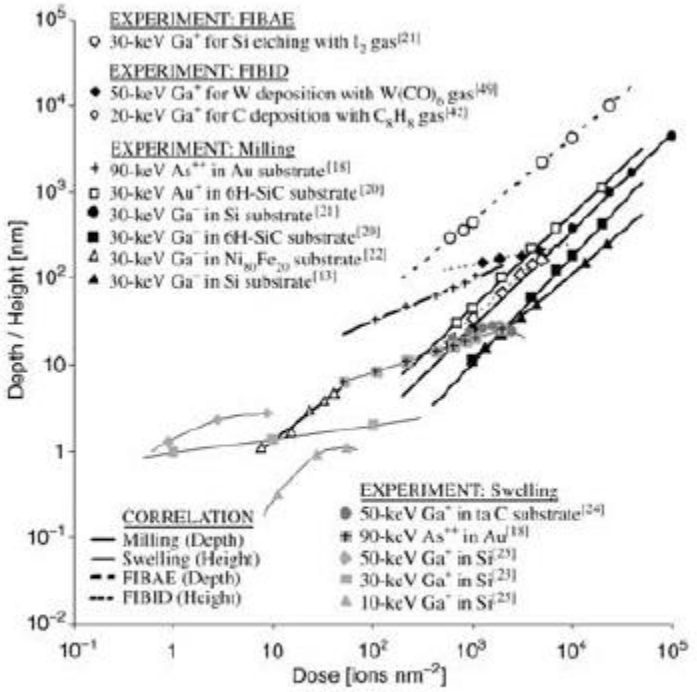


Figure 3. Relationship between feature size (depth by milling and etching or height by swelling and deposition) and ion doses for various ion species and materials.

$$\log(M) = a + b \log(D)$$

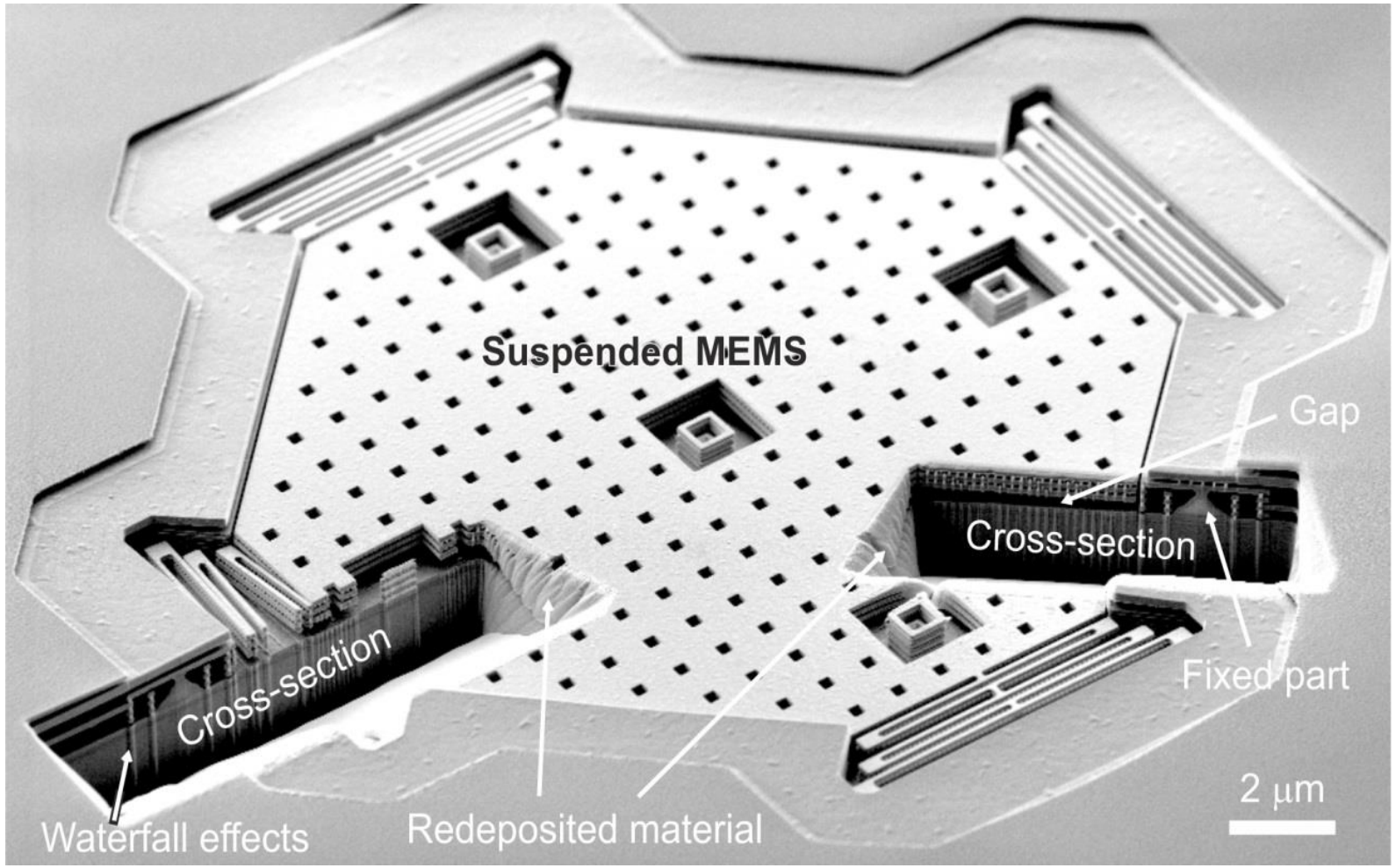
Table 1. Correlation constants for volume yield prediction.

FIB Conditions[a]	a[b]	b[b]
MILLING		
90 keV As^{2+} in Au substrate	0.5297	0.4862
30 keV Au^{+} in 6H-SiC substrate	−1.5855	1.0815
30 keV Ga^{+} in Si substrate	−1.9184	1.1183
30 keV Ga^{+} in 6H-SiC substrate	−2.6769	1.2323
30 keV Ga^{+} in Si substrate	−1.8461	0.9731
30 keV Ga^{+} in $Ni_{80}Fe_{20}$ substrate	−0.7714	0.9001

Relationship between feature size (depth by milling and etching or height by swelling and deposition) and ion doses for various ion species and materials

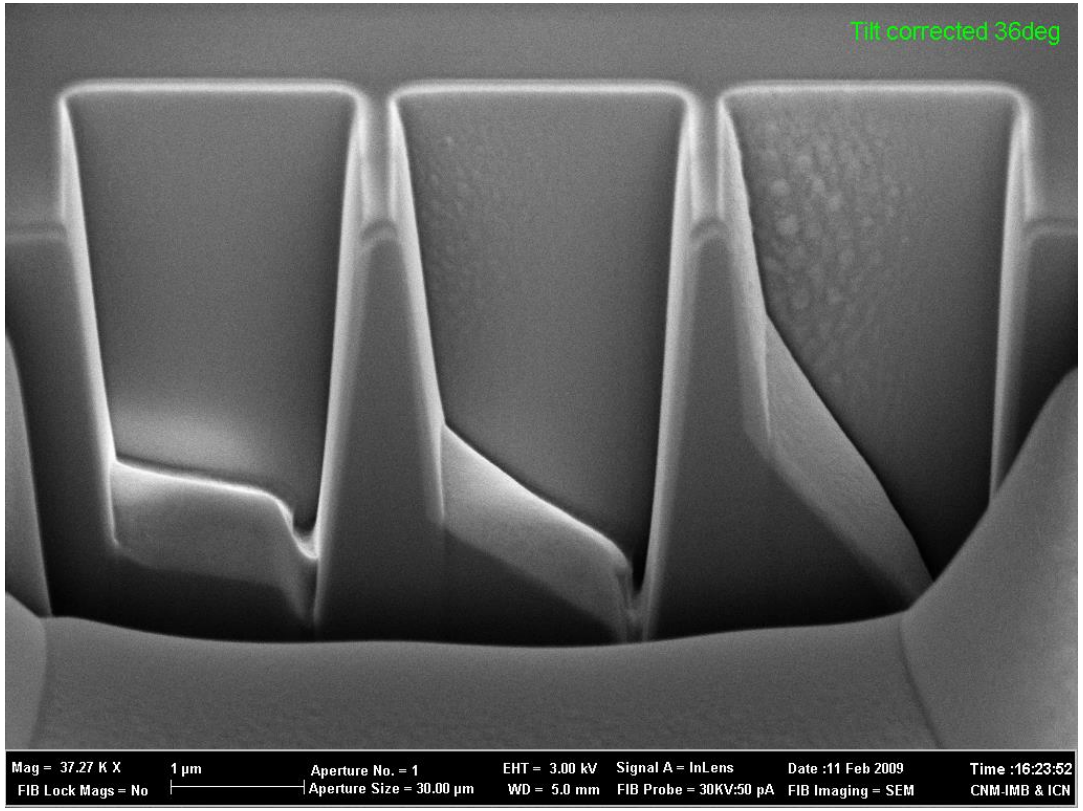
A.A. Tseng Small. 2005

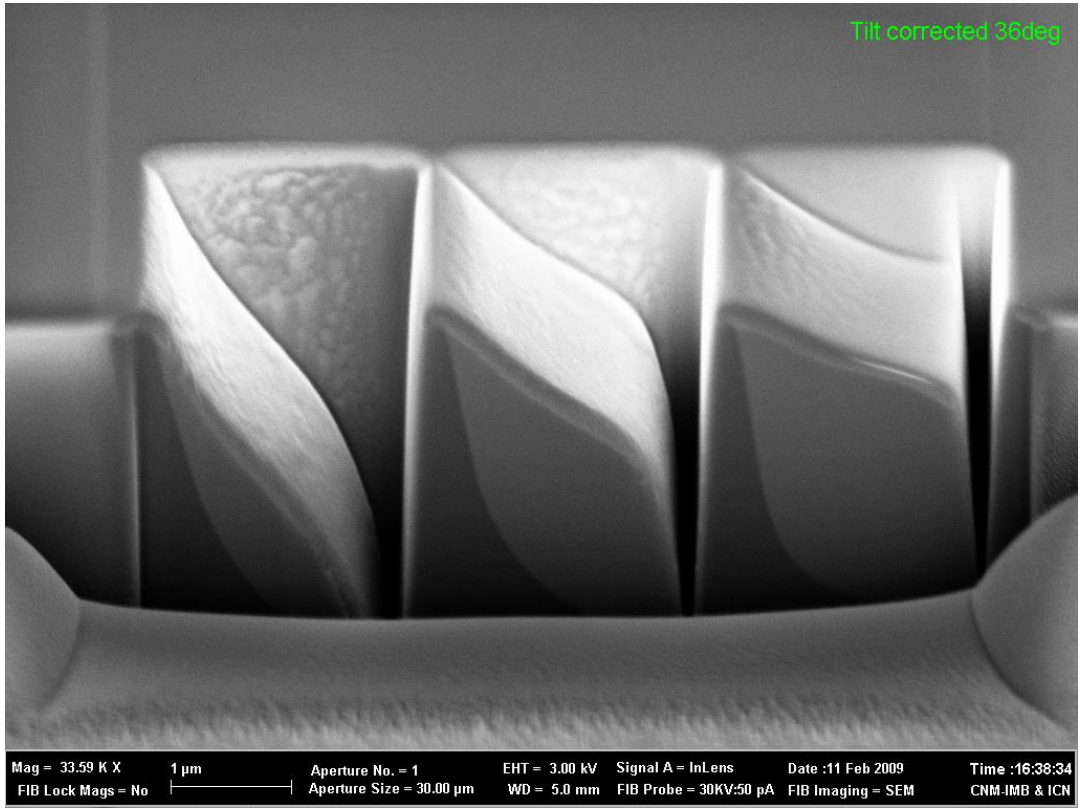
FIB for cross-sectioning using milling



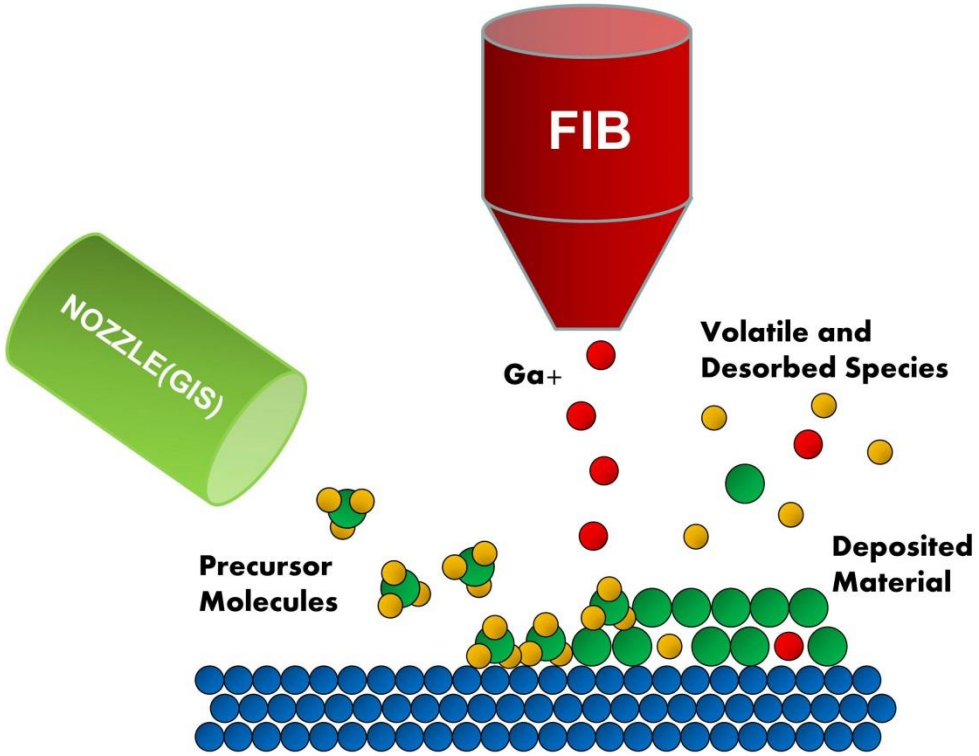
SEM image of two FIB cross-sections done in a suspended MEMS In these cross-sections it is marked a gap that evidences the release of the device, the waterfall effects and the redeposited material that are artefacts introduced during the FIB cross-section processing.

Different Strategies for Milling





FIBID principle

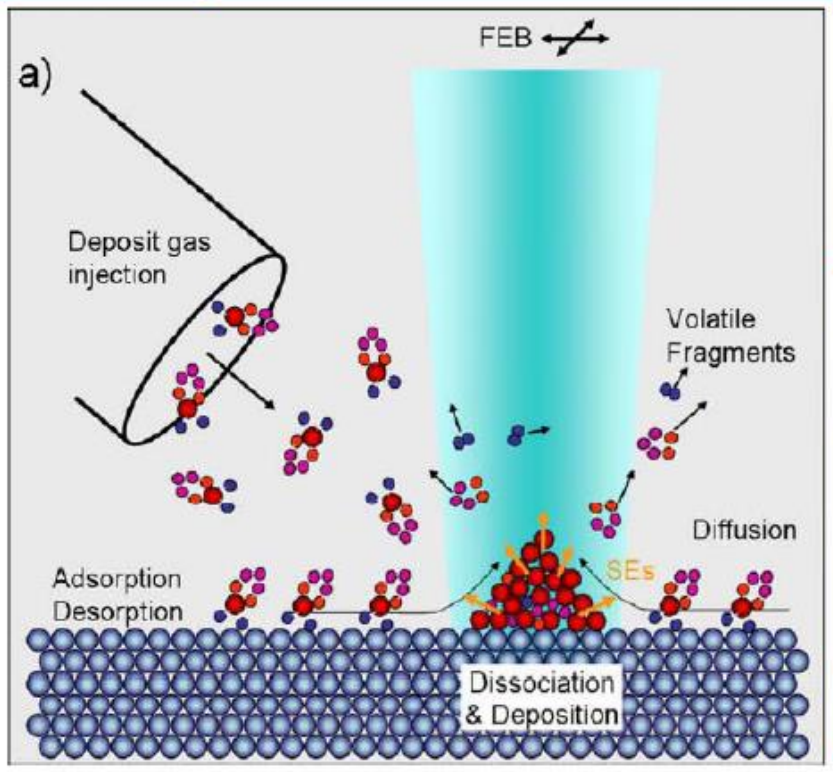


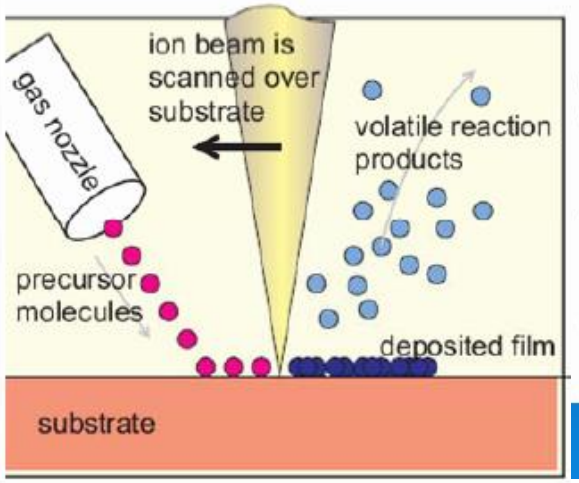
- Precursor Adsorbed on the surface
- Production of SE via FIB, which dissociate the precursor molecule into a volatile product and the deposited material
- Balance between milling and deposition
- Trapping of non desired material
- Low speed (~0,02μm^3/min)

Focused ion beam induced deposition (FIBID)

Decomposition of the gas by the ion beam

- Deposition of the non-volatile components on the





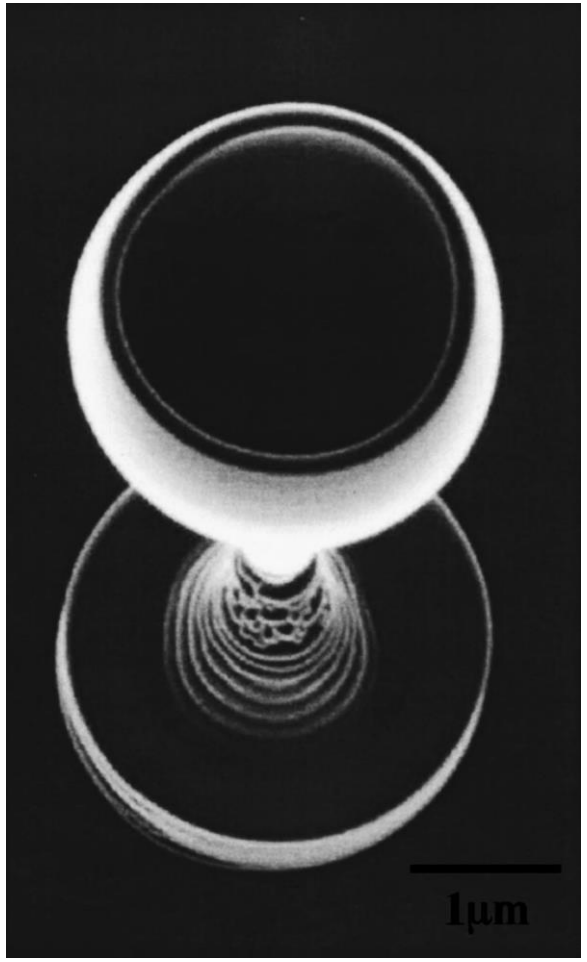
Gas	Ion, Energy	"Yield" (atoms/ion)	Deposit Composition	Resistivity (Ω · cm)
WF_6	Ar^+, 500 eV and 2 keV		W:F:C 93.3:4.4:2.3	15
$W(CO)_6$	Ga^+, 25 keV	2	W:C:Ga:O 75:10:10.5	150–225
$C_7H_7F_6O_2Au$	Ga^+, 40 keV (room temp.)	3–8	Au:C:Ga 50:35:15	500–1500 (bulk Au = 2.44)
	Ga^+, 40 keV at 120°C	3	Au:C:Ga 80:10:10	3–10
$C_9H_{17}Pt$	Ga^+, 35 keV	0.2–30	Pt:C:Ga:O 45:24:28:3 25:55:19:2	70–700 (Bulk Pt = 10.4)
$(CH_3)_3NA1H_3$	Ga^+, 20 keV	4–6	Al:Ga:C:N	900
Cu(hfac)TMVS	Ga^+, 25–35 keV	10–30	Cu:C 60:50 (25°C) 95:5 (100°C)	100 5
$TMOS + O_2$	Si, 60 kV	1 mol/ion	SiO_x	2.5×10^6
$OMCTS + O_2$	Ga, 50 kV		Si:O:Ga 27:56:17	1.2×10^7
TEOS	Ga, 30 kV			10^8
PMCPS	Ga, 30 kV		SiO_x	8×10^{11}

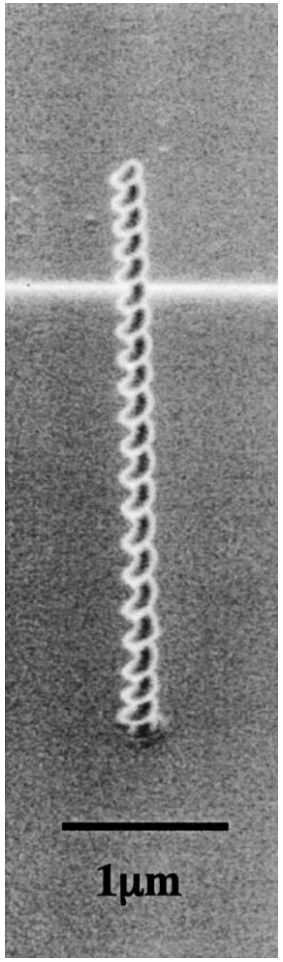
J.Melngailis, U. Maryland

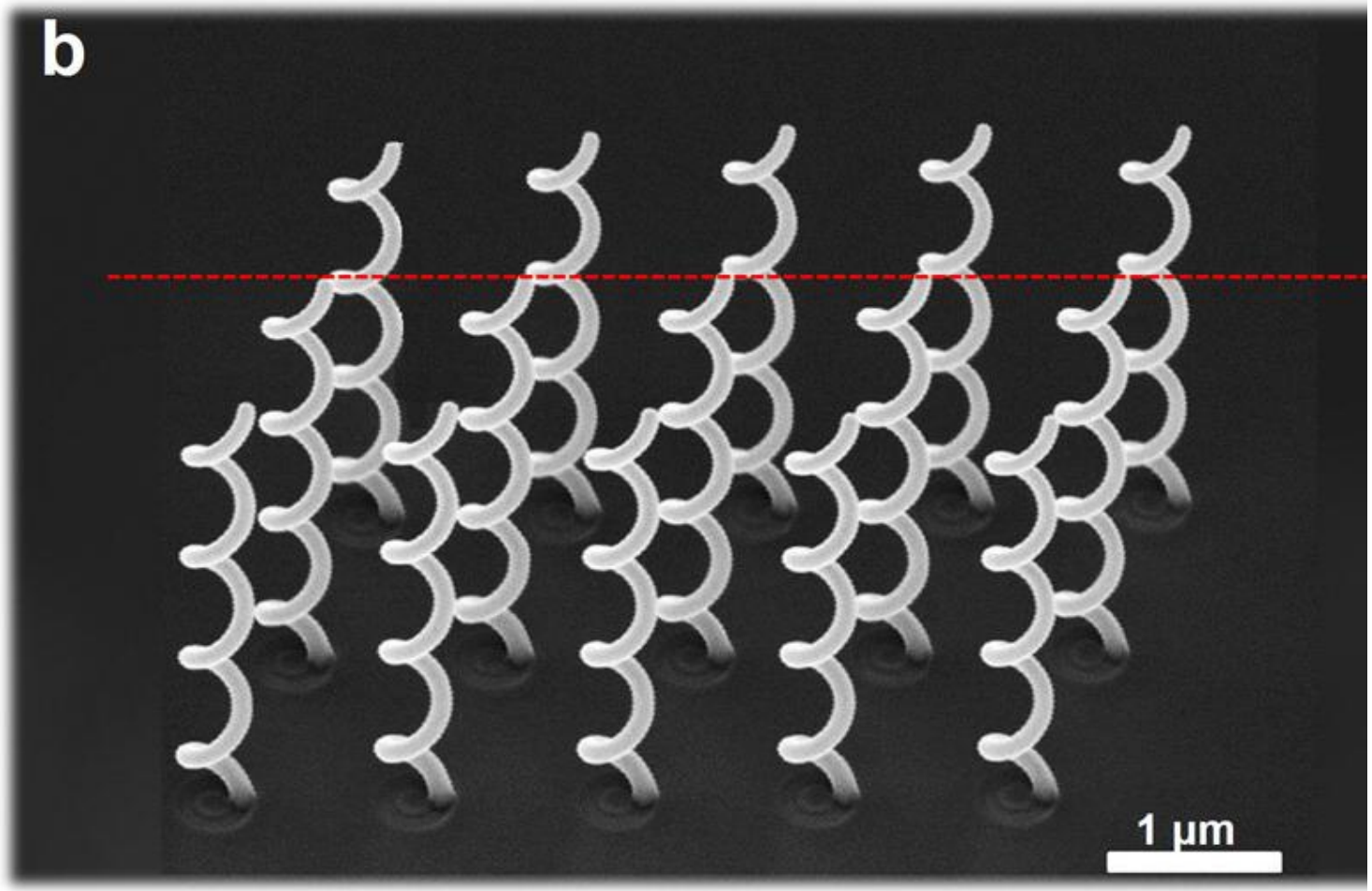
Courtesy of Dr. Albert Romano. UB

Focused ion beam induced deposition (FIBID)

Pt Nanohelices



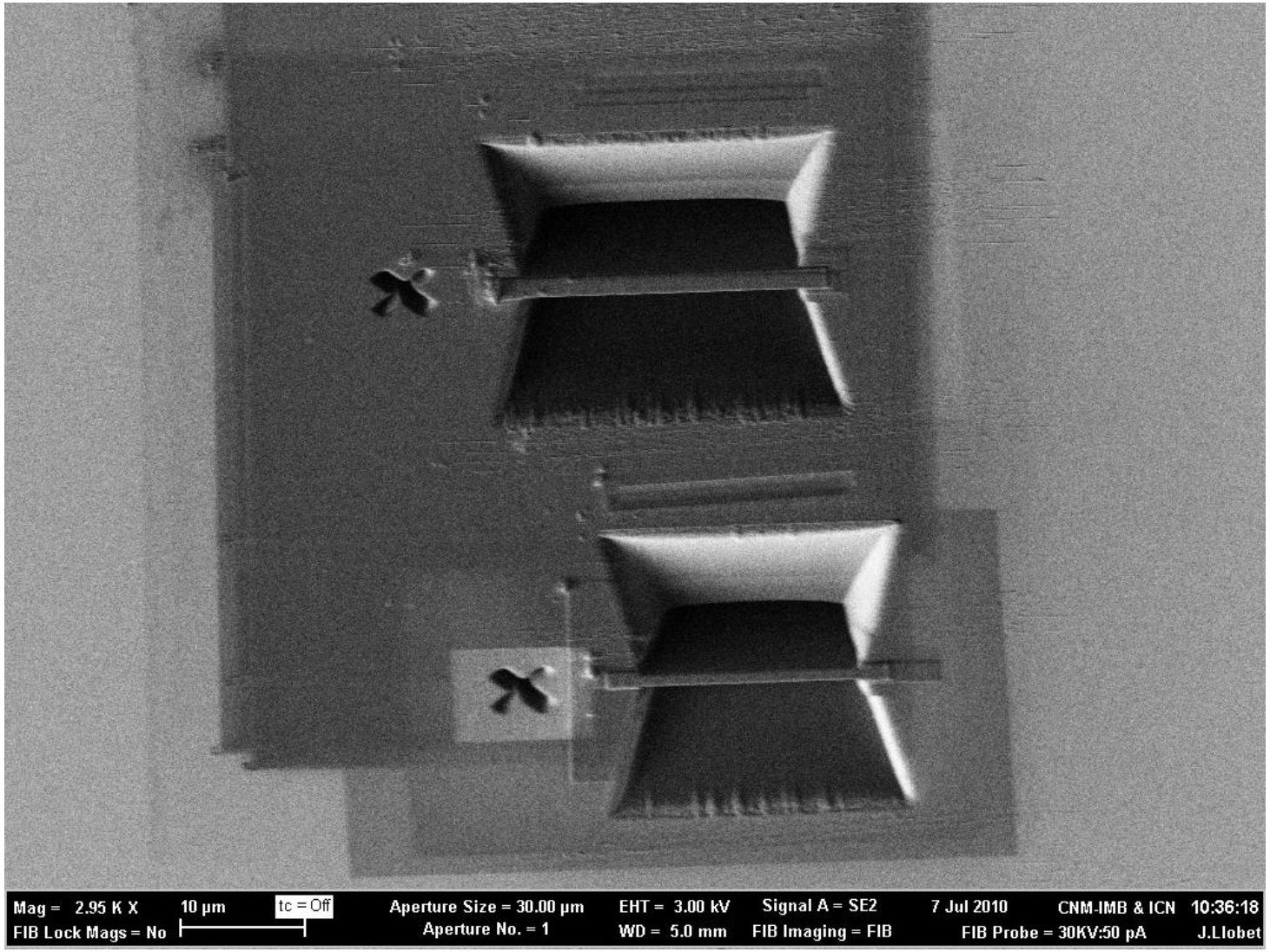




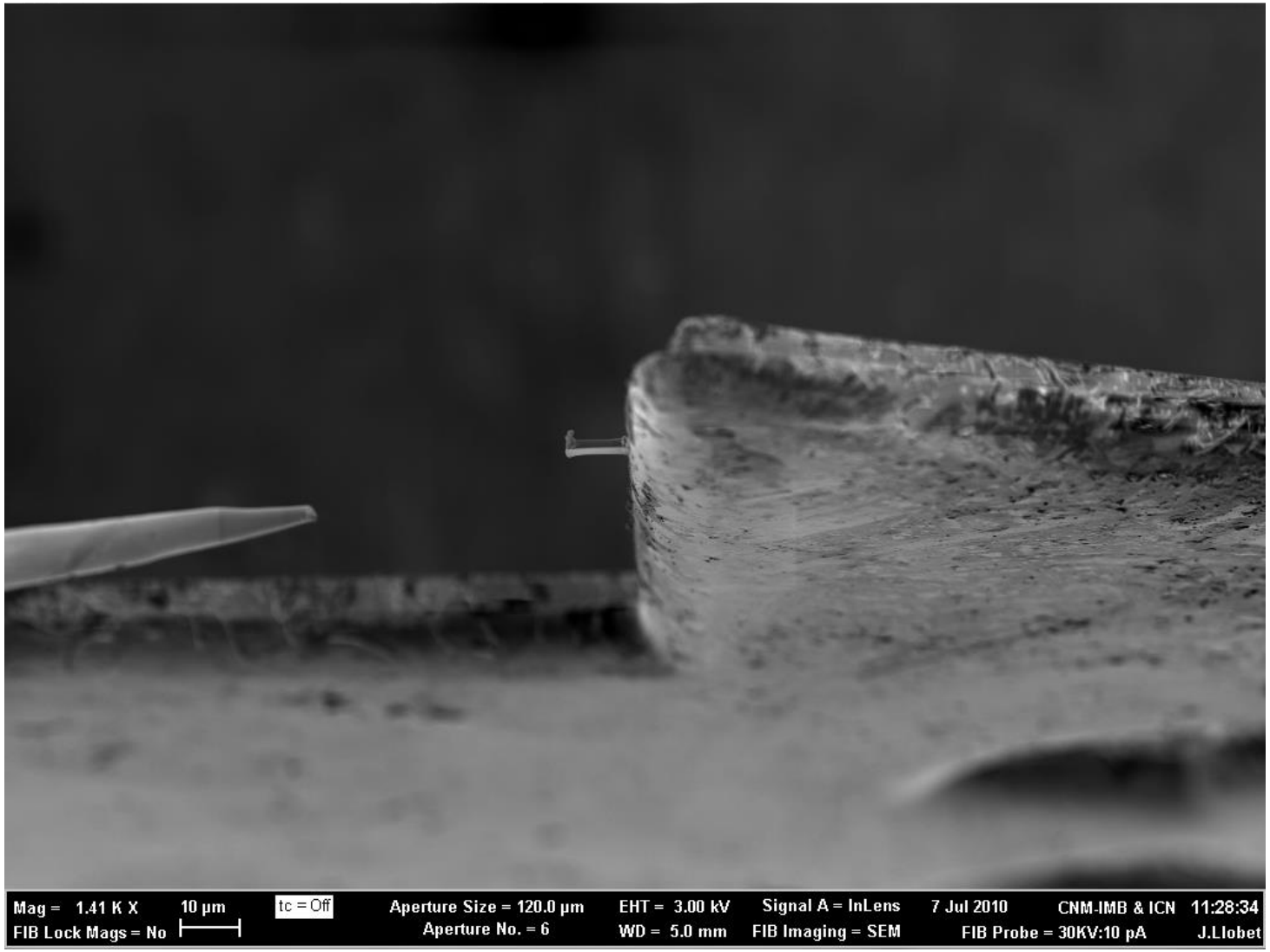
A.A. Tseng Small. 2005

Esposito et al. ACS Photonics. 2015

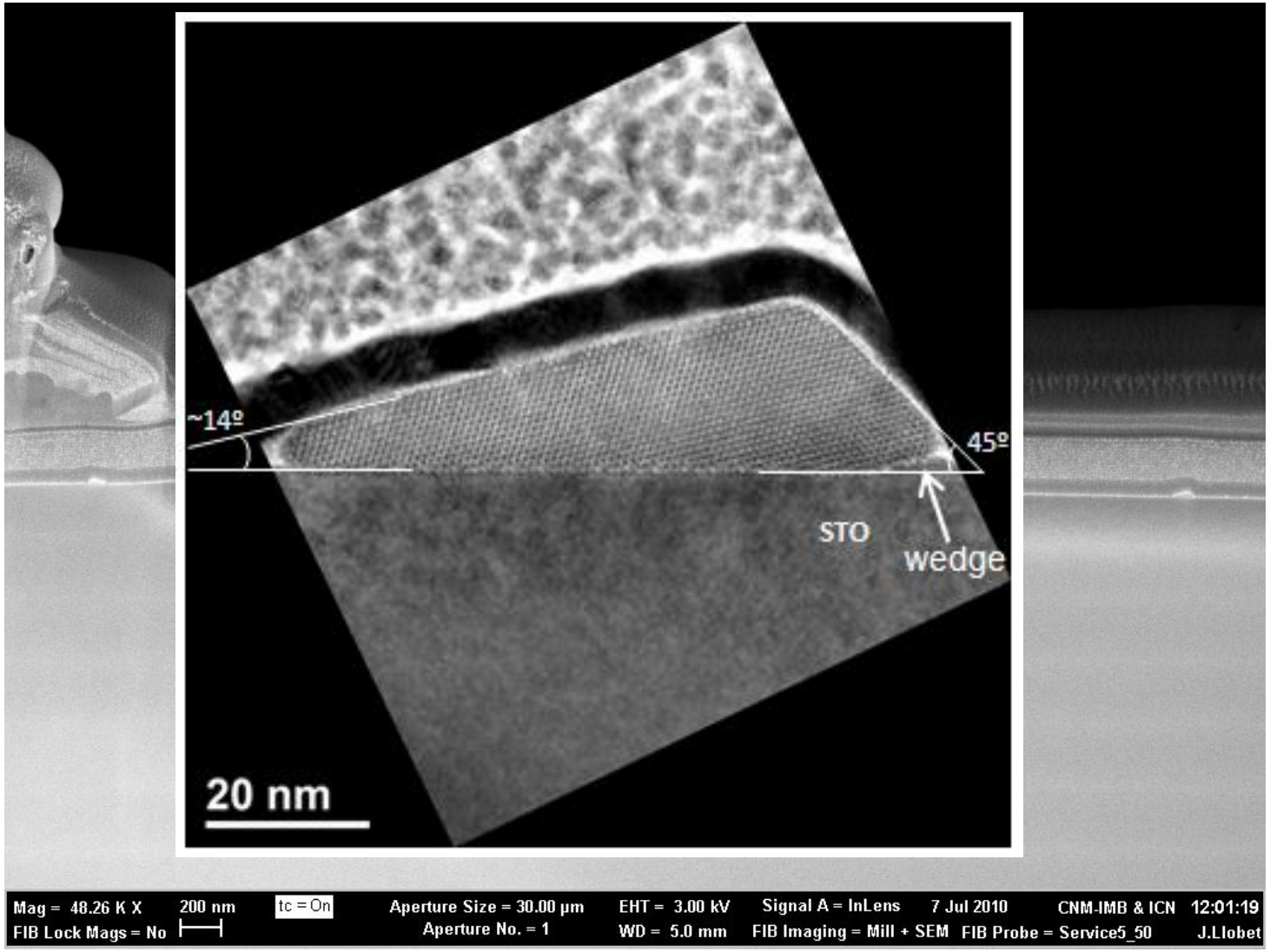
TEM lamella preparation



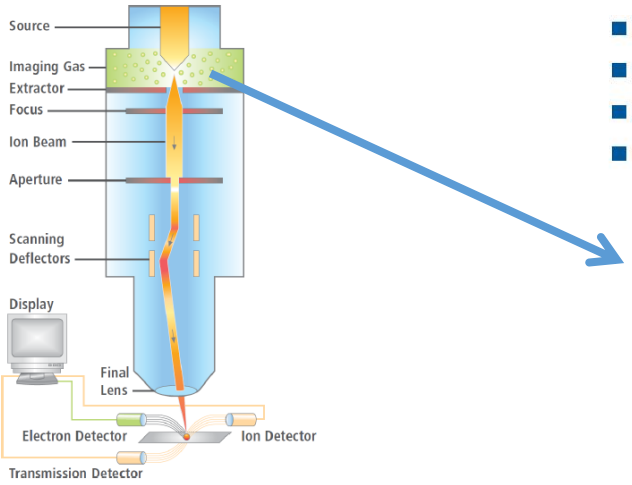
TEM lamella preparation



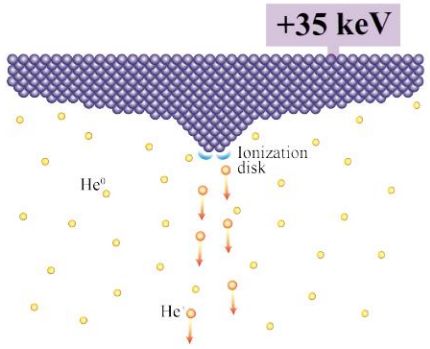
TEM lamella preparation



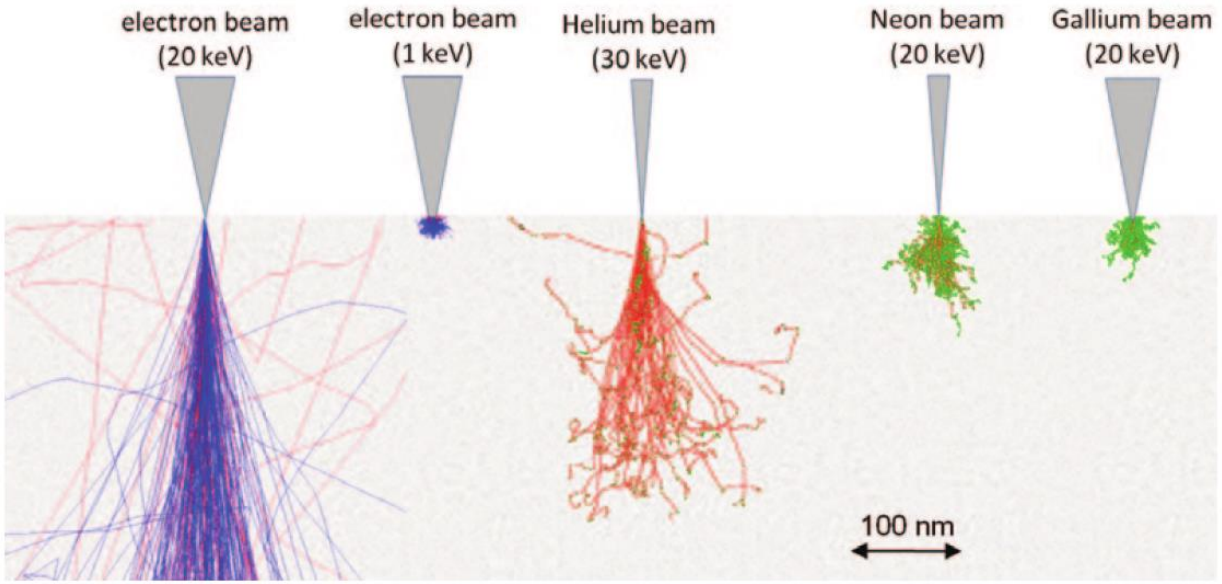
Hellium and Neon Focused ion beam



- Tungsten trimer on apex
- Field ionization
- Helium (Neon) gas
- Single atom selected for beam formation



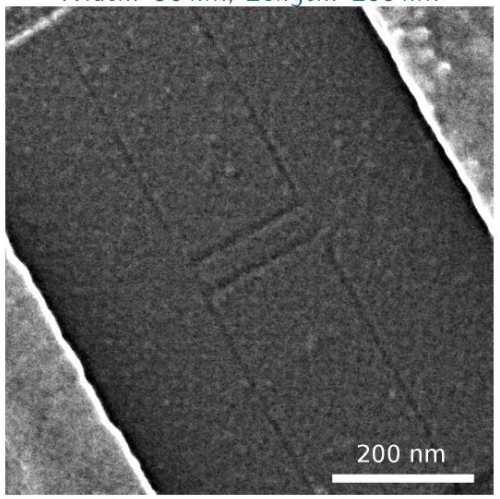
Helium Ion Microscopy, G. Hlawacek & A. Gölzhäuser, Springer 2016



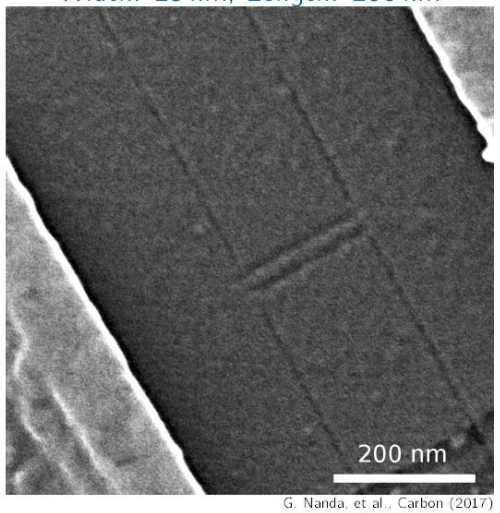
SRIM: Ga, Ne, He; CASINO: e⁻

Nanoribbons in h-BN/Gr/h-BN stacks

Width: 50 nm; Length: 200 nm

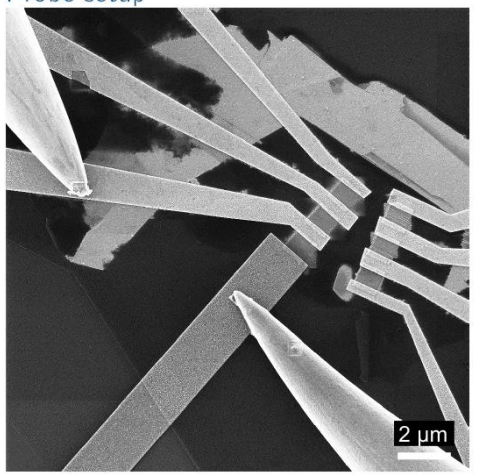


Width: 25 nm; Length: 200 nm

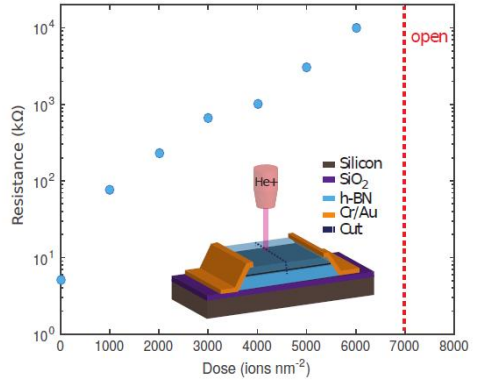


G. Nanda, et al., Carbon (2017)

Probe setup



Resistance vs. fluence



G. Nanda, et al. Carbon, 2017

FIB TOP-DOWN PROTOTYPING OF NANOSTRUCTURES

Modes of Operation

Direct Writing

Lithography — *Resist exposure*

Irradiation — *Material structure or property modification*

Subtractive

Milling — *3D or quasi 3D nanostructuring*

Sputtering — *Thin films High resolution*

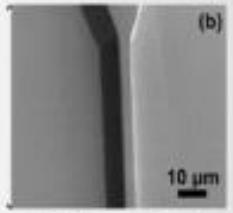
Additive

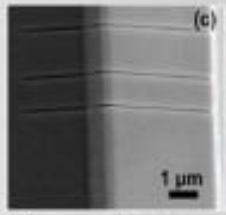
Implantation — *Material doping Amorphization*

FIBID — *Functional layer Etching masking*

Fabrication & Integration

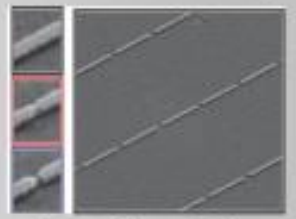
Mix and Match



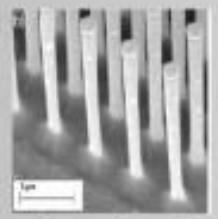


Milling + Optical lithography
[Kildishev; Lebedev 2021]

Hybrid Processing

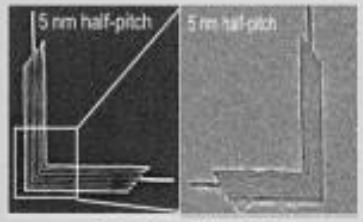


Sputtering + EBL
[Hentschel 2020]

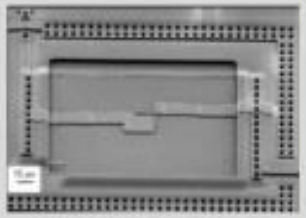


Implantation + RIE
[Chekurov 2009]

Heterogenous Tech.



FIB Mould + NIL
[Li 2012]



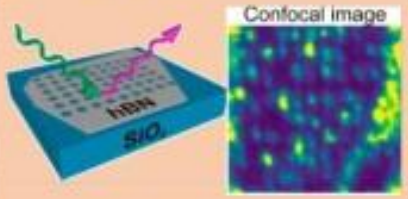
FIB NEMS + CMOS
[Rius 2011]

Fields of Application

Plasmonics

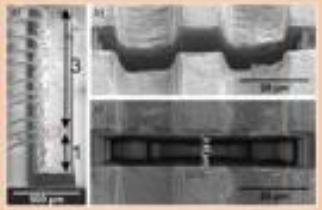
3D Janus structures
[Chen 2019]

Quantum



Quantum emitter
[Ziegler 2019]

Photonics

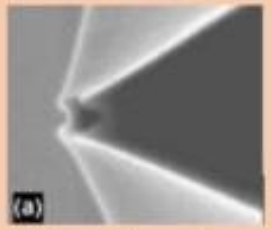


Coupled-cavity lasers
[Pierscinski 2018]

NEMS

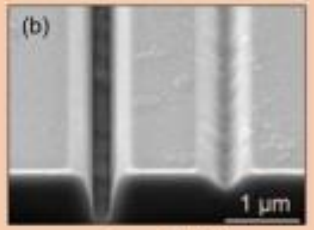
Mechanical resonators
[Llobet 2018]

AFM tool



Nanodispensing
[Meister 2004]

Lab-on-a-chip



Nanofluidics
[Esmek 2019]

Lothar Bischop et al. In preparation

Take home messages

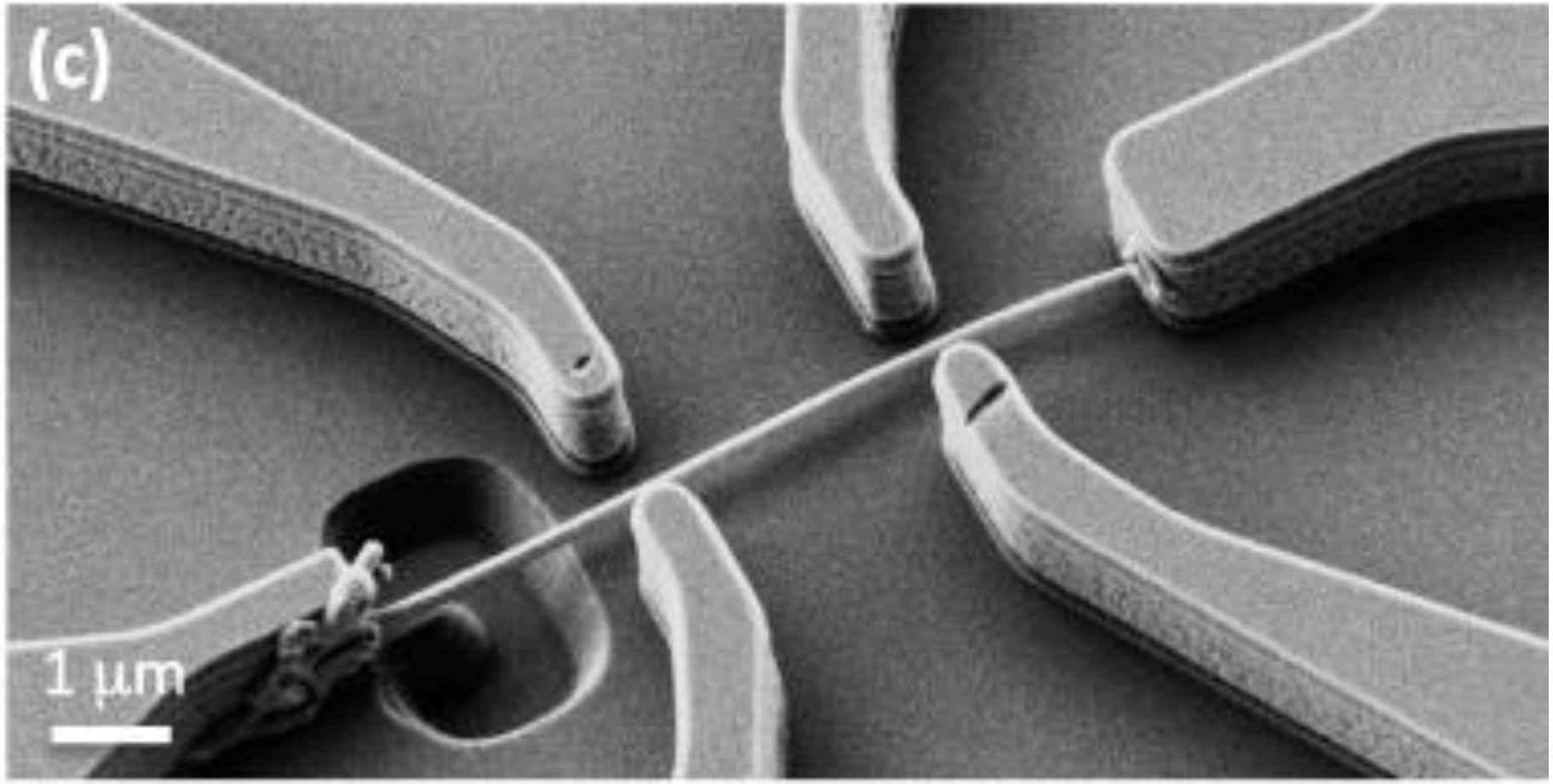
Electron beam lithography

- Exposure of a focused electron beam on a electron sensitive layer of material (EBL Resist)
- Main method used for nanolithograpy in research laboratories
- Resolution in electron beam lithography is limited by the scattering of electrons with the atoms of the resist and substrate. Usually, back scattering dominates
- Proximity effects are important
- Resolution: difficult to go below 10 nm

Focused Ion beam patterning

- Exposure of a focused ion beam to a surface can induce milling, re- deposition and amorphization
-
- Much lower penetration depth than for electrons: no proximity effect.
- Cross-sectioning, 3D fabrication and TEM lamella fabrication are unique features of FIB
- Ion beam assisted etching and deposition allows to improve the etching rate or deposit material
- Helium and Neon Focused Ion Beam provide improve performance in terms of resolution and damage free

Botom-up fabrication



Fernandez-Regulez et al (2013)

Limits of optical lithography

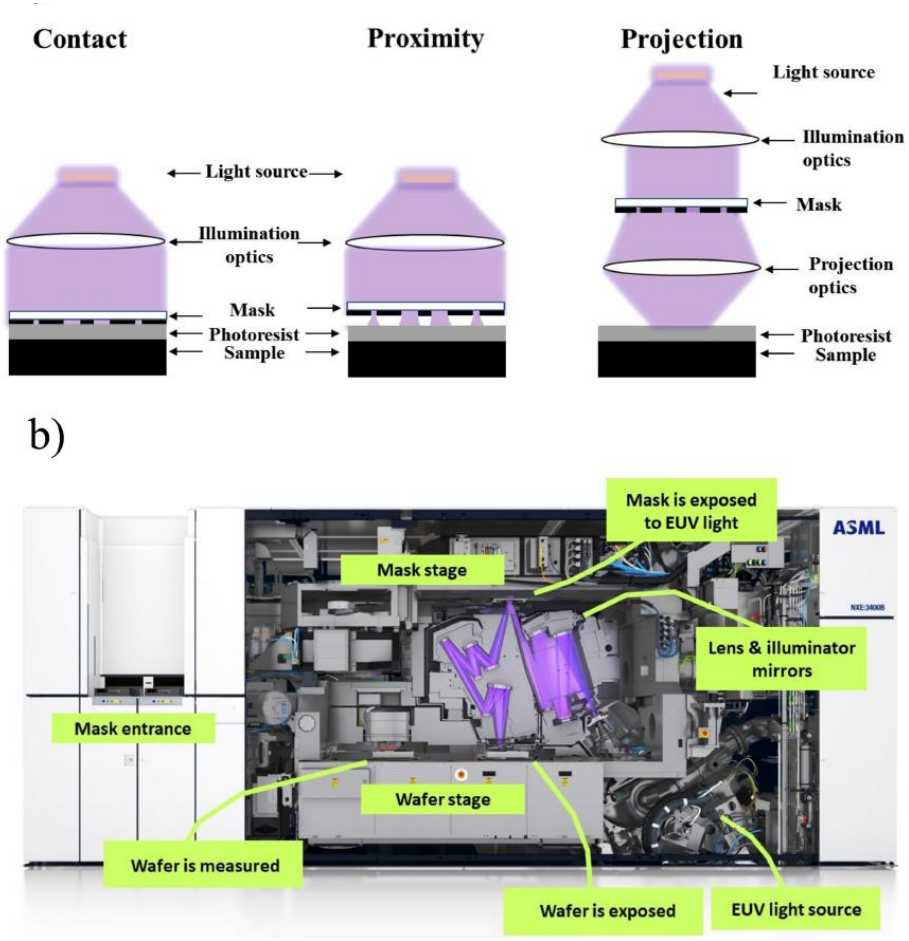


Figure 2.3. (a) Optical lithography modes using an optical mask: contact, proximity and projection. (b) Photograph of an extreme-UV optical lithography system. The main elements are labelled.

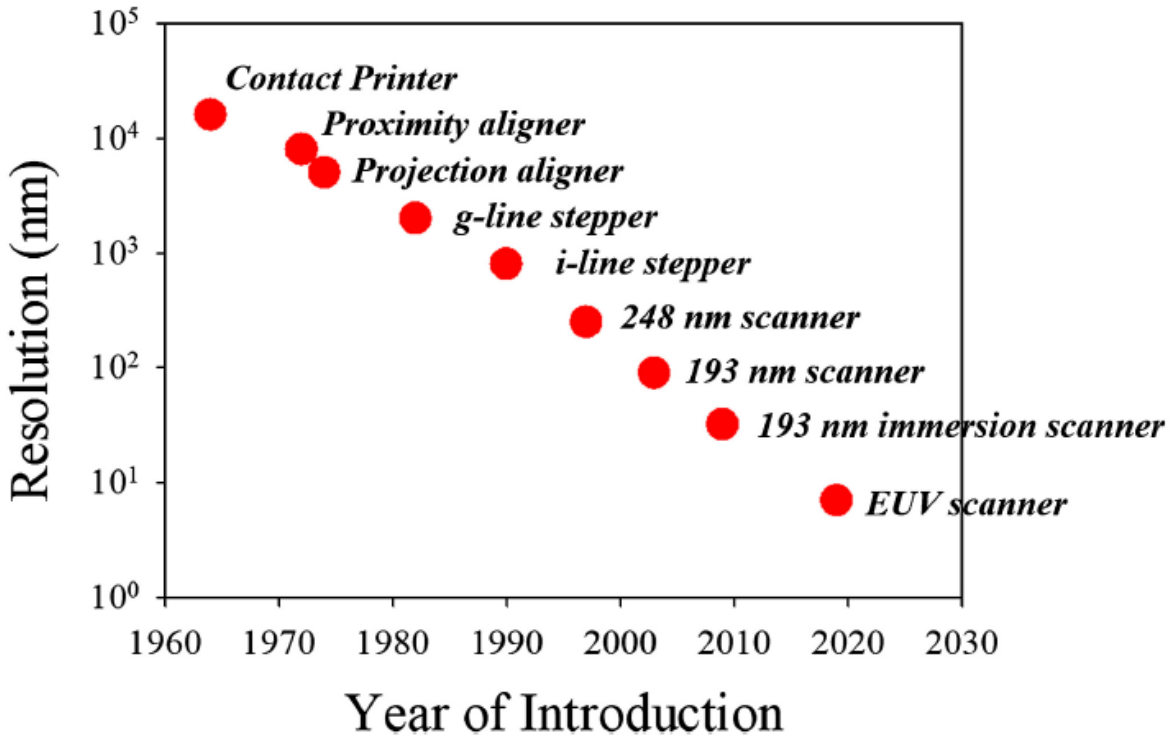
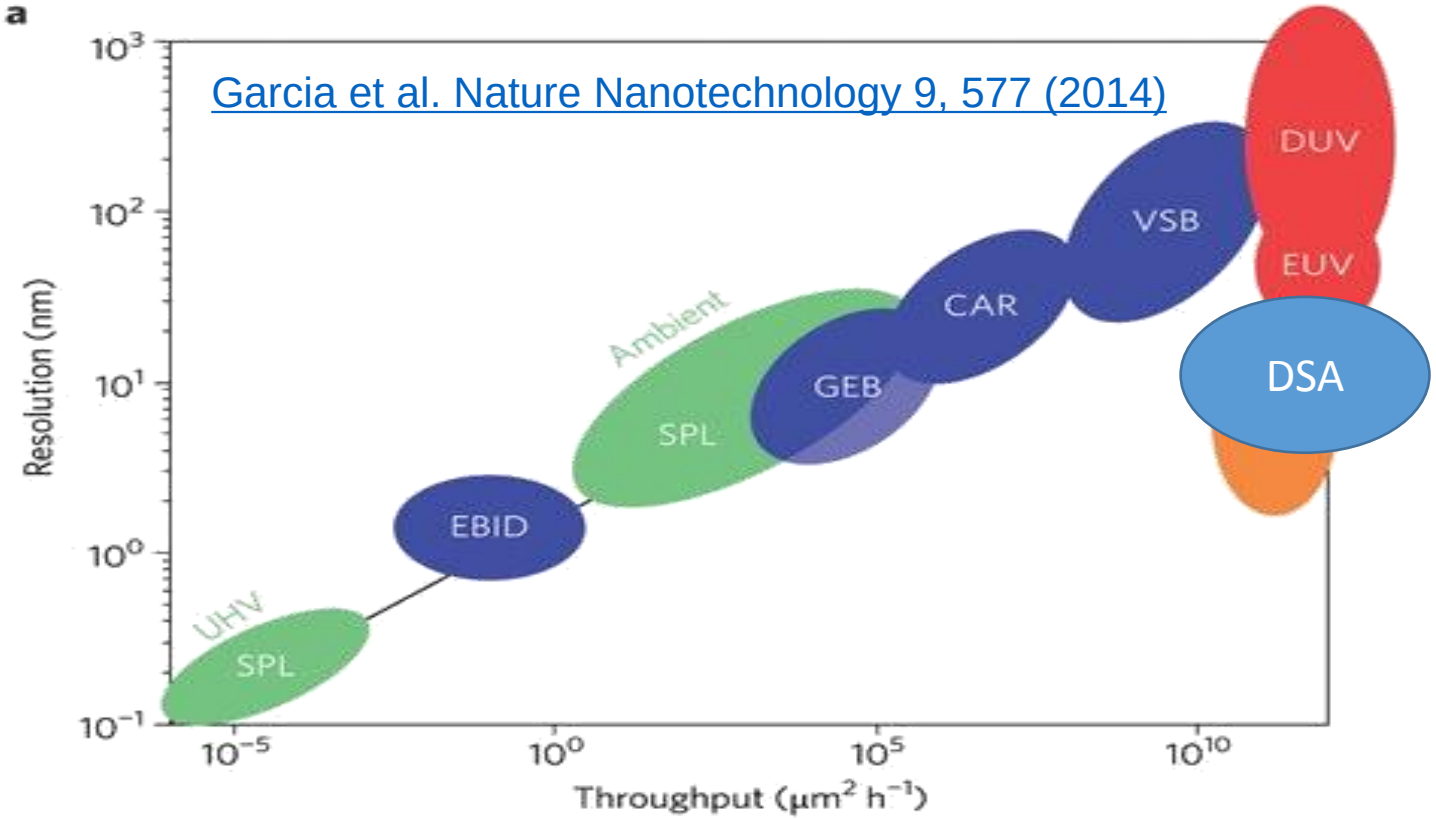


Figure 2.4. Evolution of the optical resolution during the years. Data extracted from [2].

Figures extracted from: Francesc Perez-Murano, José Ignacio Martín y José María de Teresa. Optical Lithgroaphy, Chapter 2. Nanofabrication. IOP books

Patterning resolution vs Throughput



SEQUENTIAL LITHOGRAPHY

Scanning probe lithography

Electron beam lithography

PARALLEL LITHOGRAPHY

Optical lithography

Directed self assembly

Nanofabrication: Bottom-up vs top-down

Photo by mia nonna, CC BY-SA 4.0

Photo by Didier Descouens , CC BY-SA 4.0

Top-down Nanofabrication

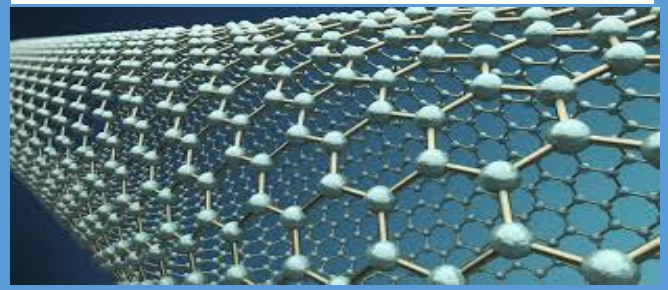
- Resolution limited by resolution
- Surface defects, roughness and crystallographic damage
- Device no assembly step is needed
- Low defectivity

Bottom-up Nanofabrication

- High resolution, limited by the size of the building blocks
- High throughput at low cost
- Device fabrication difficult (position, orientation…)
- Less flexibility
- More defectivity

Examples of bottom-up fabrication

Carbon nanotubes transistors

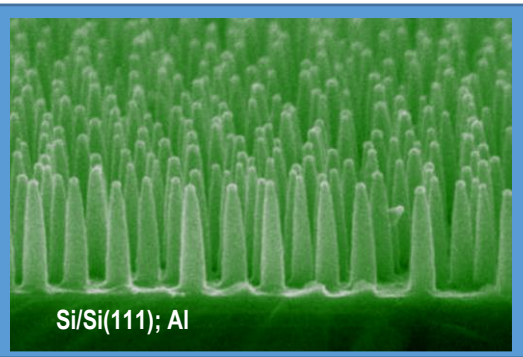


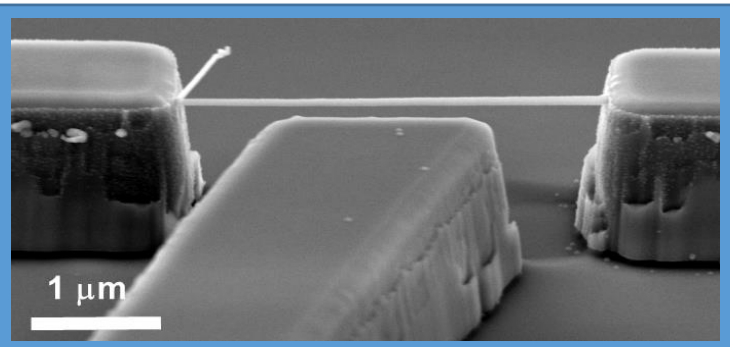
Logic Circuits with Carbon Nanotube Transistors

Bachtold et al. Science. 2001

Silicon nanowire resonators

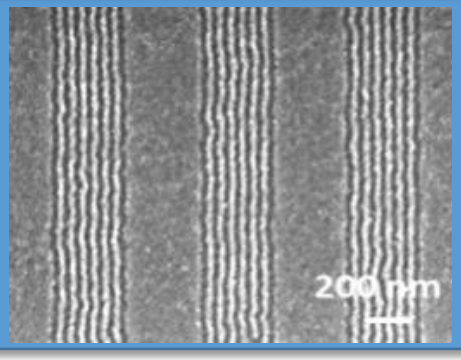
Sansa et al. Nature comm 2014.





Block copolymer self-assembly

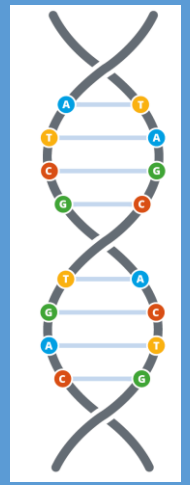
Oria et al. Microelectronic Engineering 2006

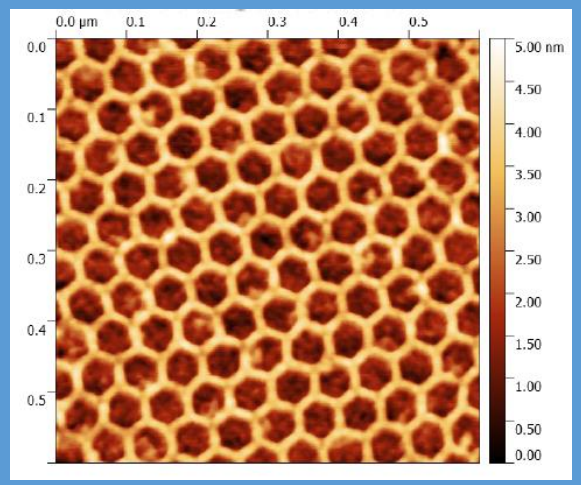


Assembly of DNA

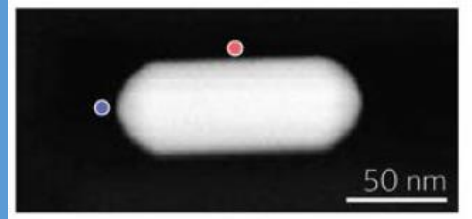
DNA Origami

P. Wang et al. J.Am.Chem.Soc. 2016.

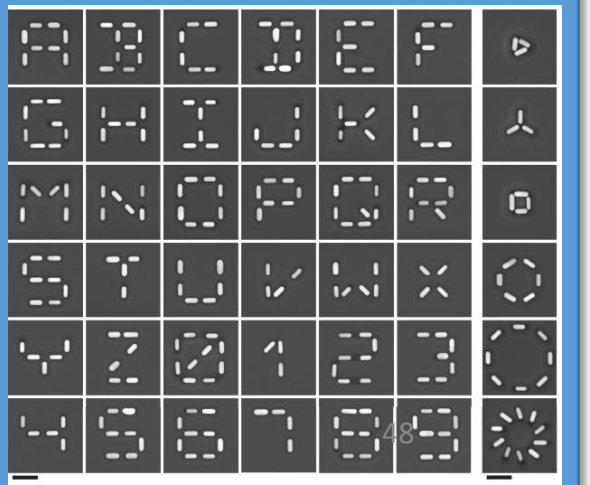




Assembly of nanocrystals



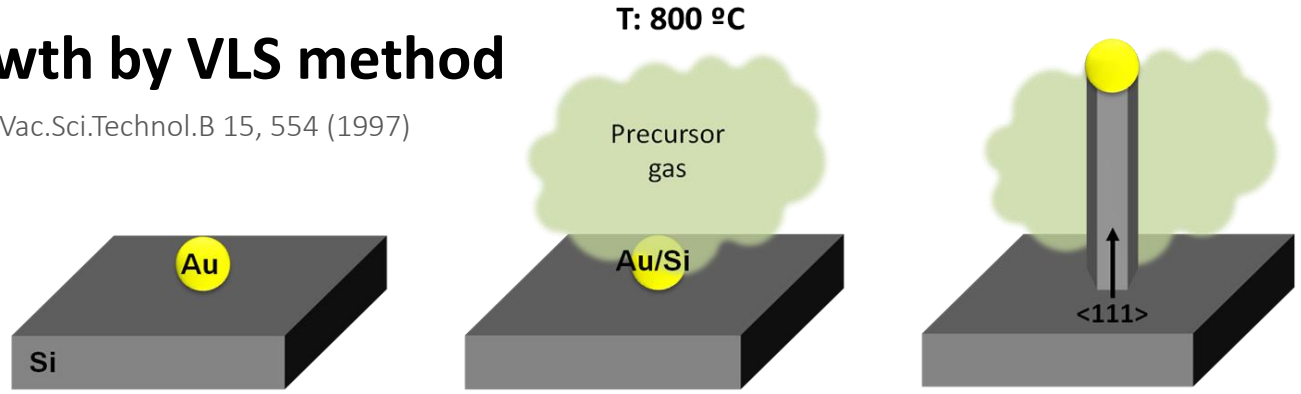
Flauraud et al. Nat.Nanotech. 2016

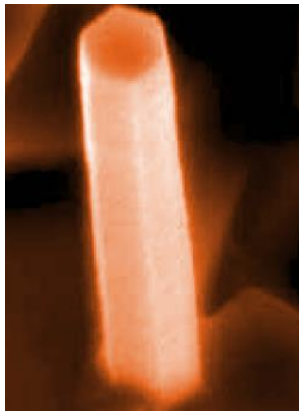


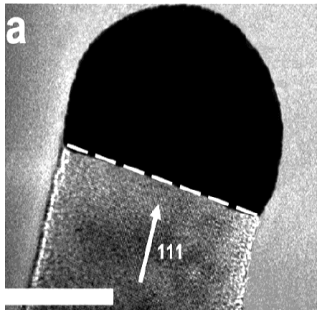
Top-down and bottom-up fabrication synergy

Si NW growth by VLS method

J. Westwater et al. J.Vac.Sci.Technol.B 15, 554 (1997)



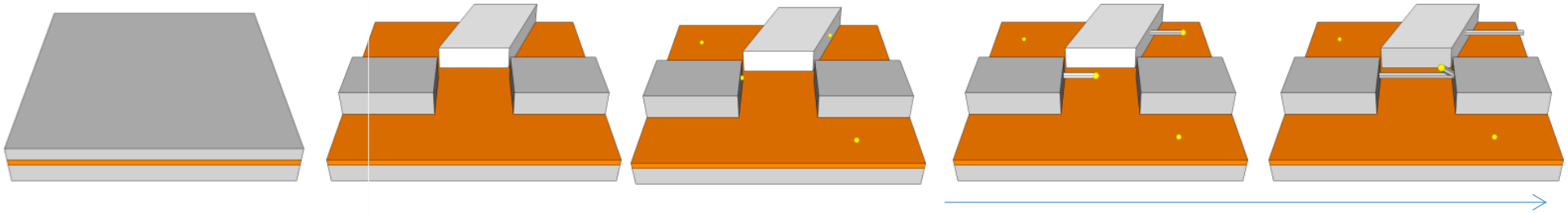




The nanowire grows from a catalyst particle deposited on a crystalline Si substrate:

- Diameter of the nanowires is defined by the diameter of the catalyst particle
- Nanowire grows along the <111> direction of the substrate. Shape: hexagonal prism. Epitaxial contact to the substrate

Suspended SiNW mechanical resonator

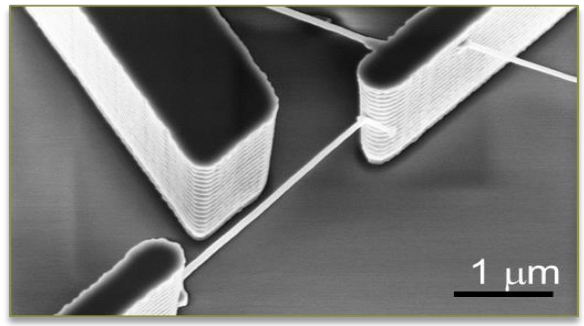


SOI substrate

Optical lithography
Reactive ion etching

Au nanocrystal deposition

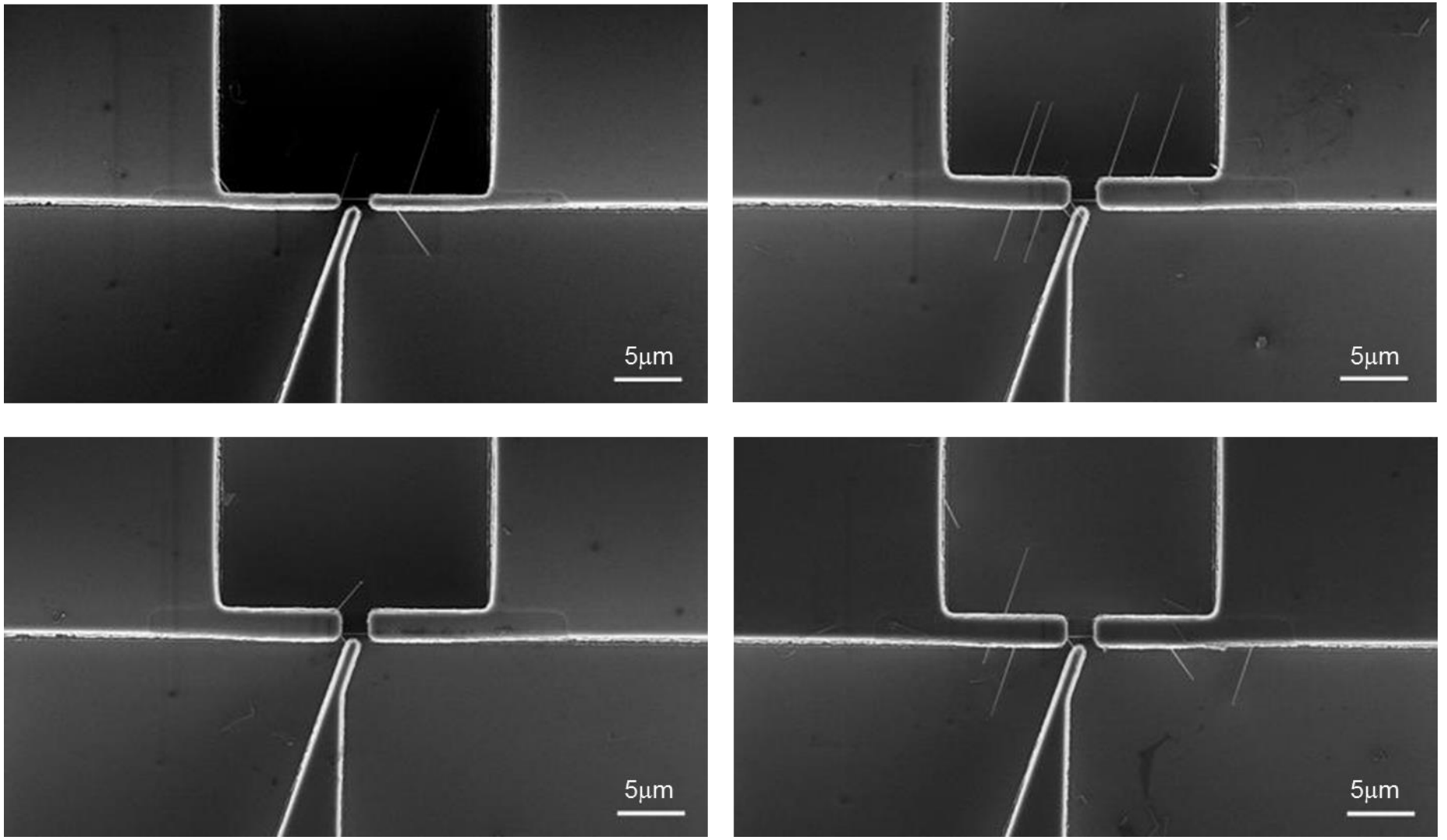
Si NW growth



Sansa et al. Appl.Phys.Lett. (2012) Sansa et al. Nature comm (2014)

Top-down and bottom-up fabrication synergy

Random Au nanocrystal deposition



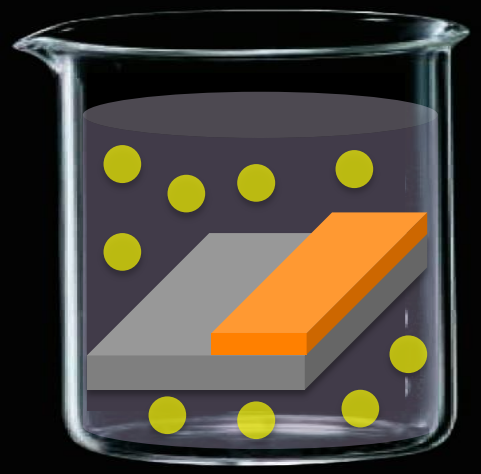
Top-down and bottom-up fabrication synergy

Deterministic Au nanocrystal deposition

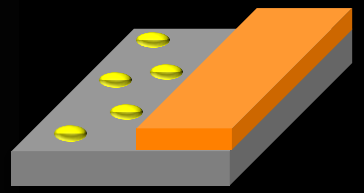
Plating solution 0.2M HF/KF + 0.01M $KAuCl_4$

+

0.33M AOT (surfactant) in n-heptane



Au NPs deposition only at Si surface

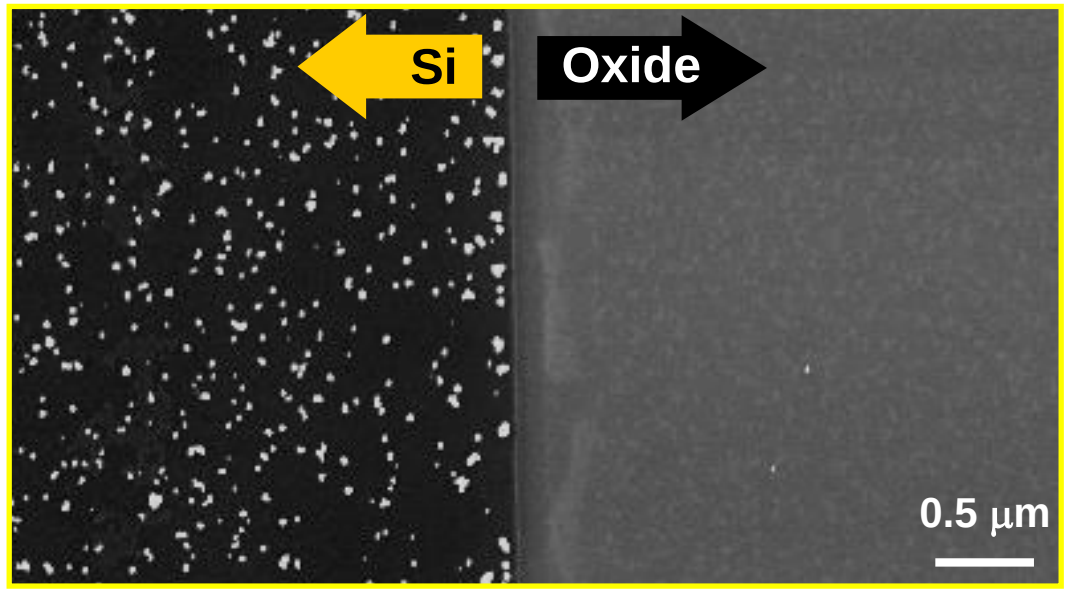


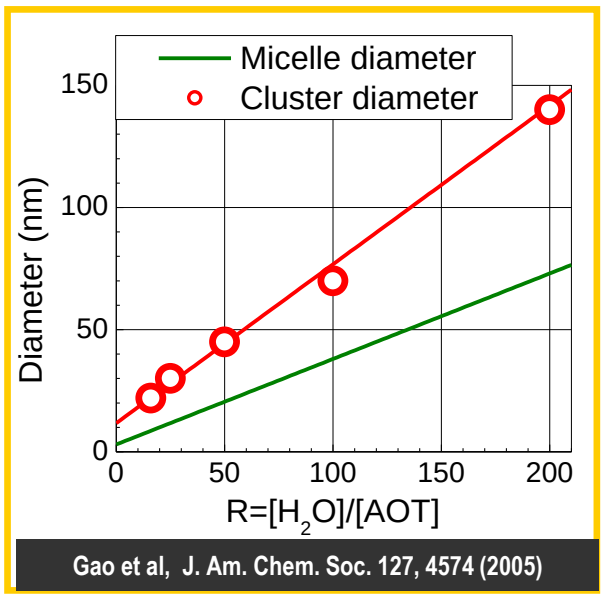
$Si + 6F^- \rightarrow SiF_6^{-2} + 4e^-$

$Au^{+3} + 3e^- \rightarrow Au$

$R=[H_20]/[AOT]$

$R_{micelle}(nm)= 0.175\ R+1.5$

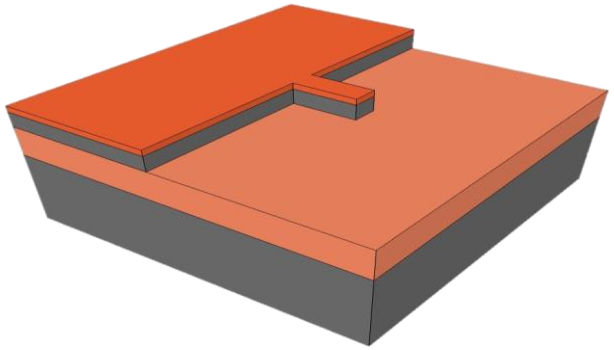




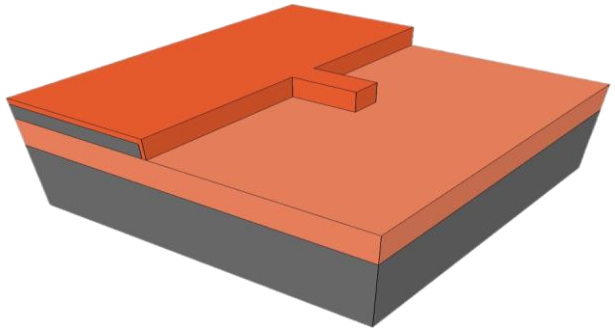
Gao et al, J. Am. Chem. Soc. 127, 4574 (2005)

Top-down and bottom-up fabrication synergy

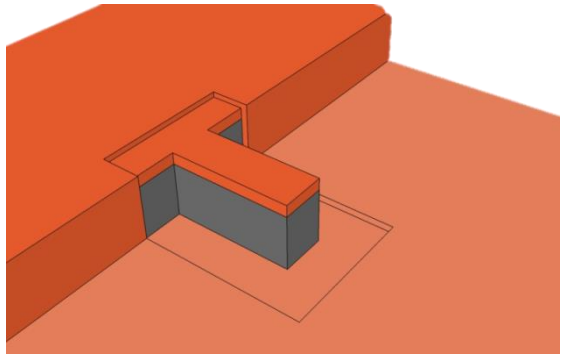
Deterministic Au nanocrystal deposition



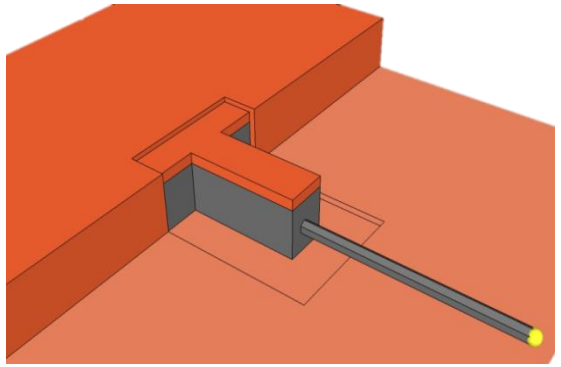
Device top down patterning



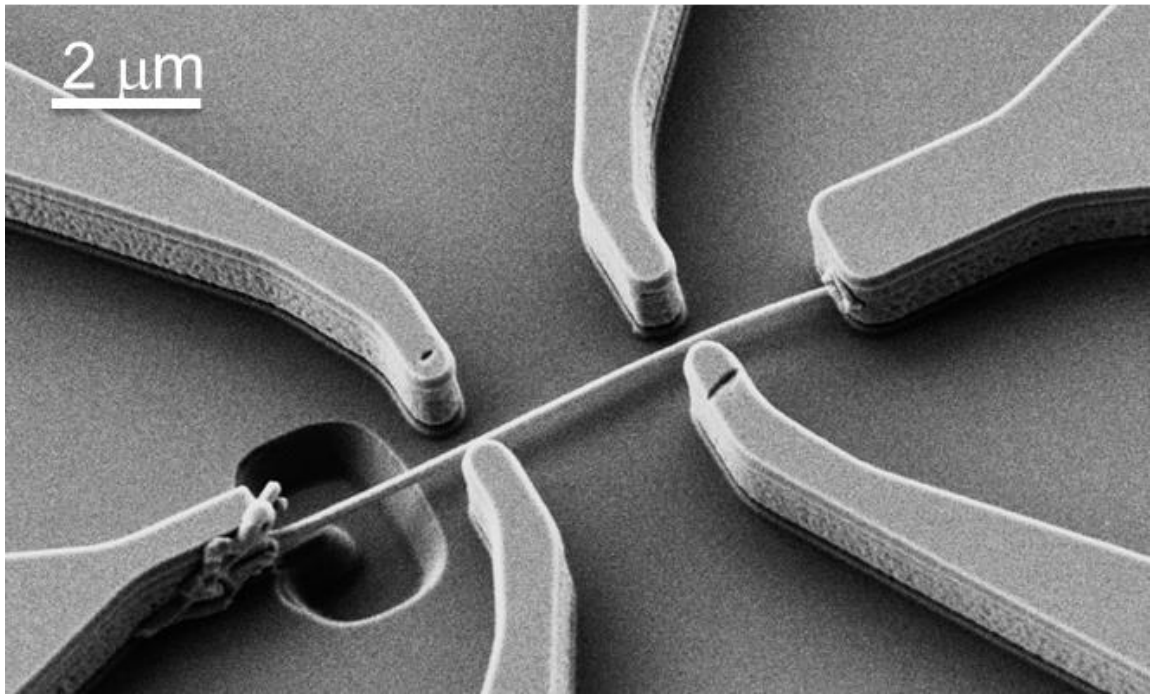
Thermal oxidation



Wet etching of thermal oxide on areas for nanowire growth

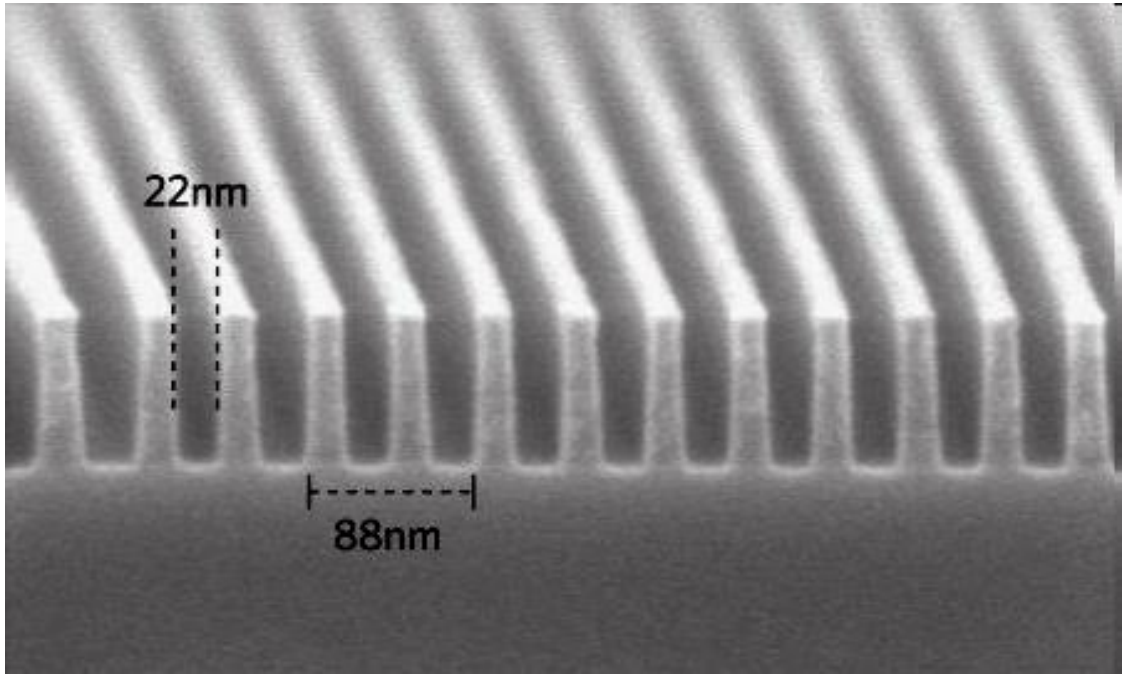


Colloidal nanoparticle deposition and nanowire growth

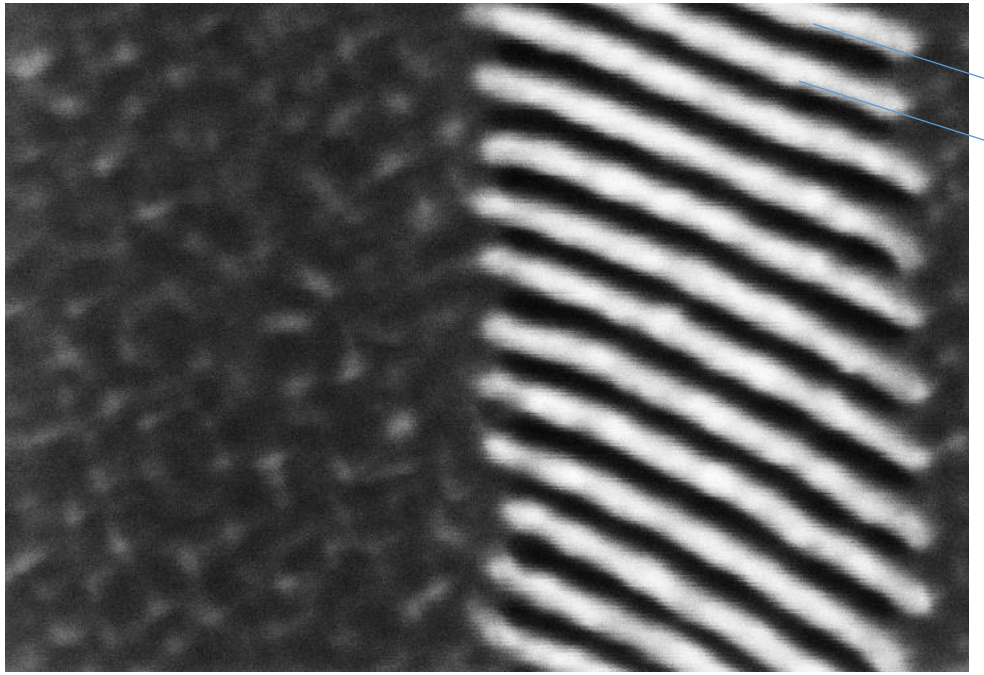


M. Fernández-Regúlez. Nanotechnology (2013)

Directed self-assembly of block copolymers



By optical lithography



By directed sef-assembly of block copolymers

State of the art optical lithography

EUV optical lithography (λ=13.5 nm)

TWINSCAN NXE:3400C (ASML)

EUV volume production at the 7 and 5 nm nodes

170 wafers per hour

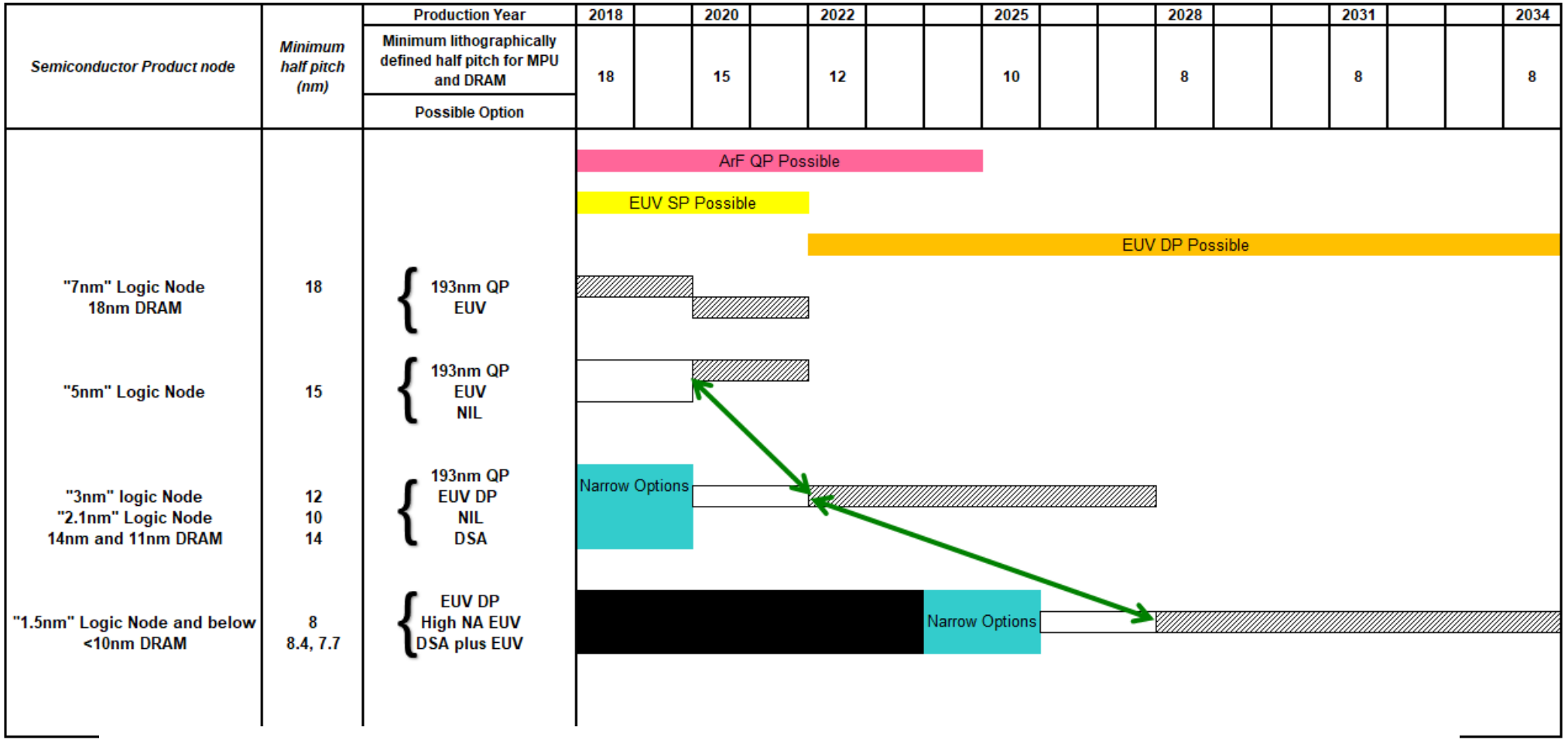
Dose: 20mJ/cm2,
Wafer size: 300 mm
Die size: 26 x 33 mm

NA: 0.33
Resolution 13 nm
Overlay accuracy: 1.4 nm

IEEE IRDS ROADMAP 2021

https://irds.ieee.org/

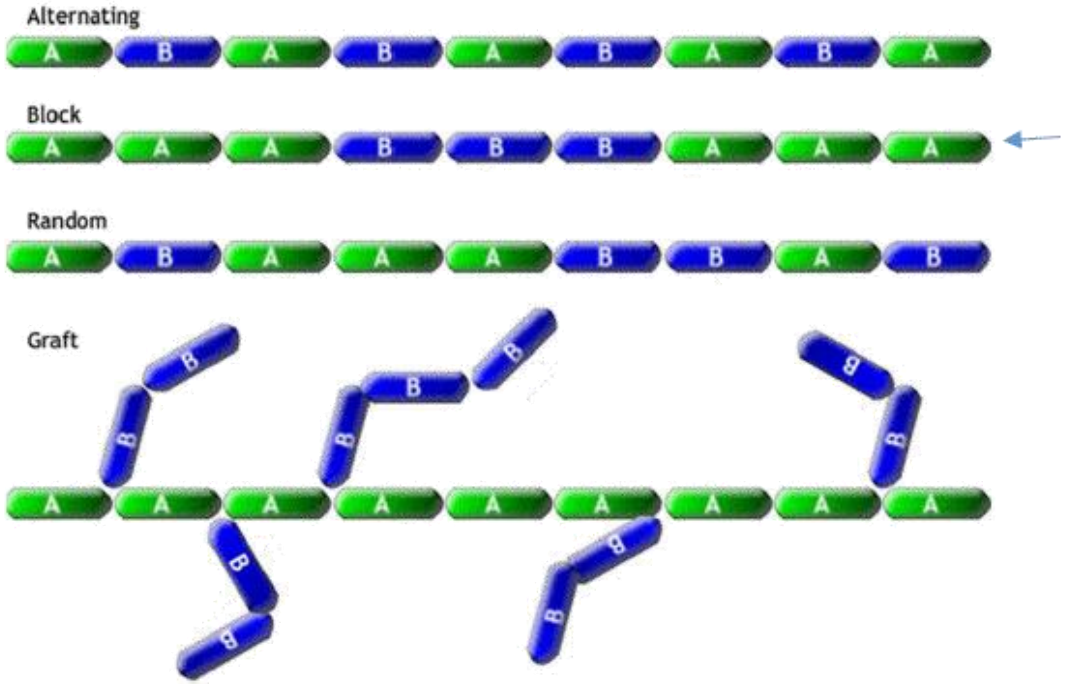
The IRDS™ is a set of predictions that intent to provide a clear outline to simplify academic, manufacturing, supply, and research coordination regarding the development of electronic devices and systems.

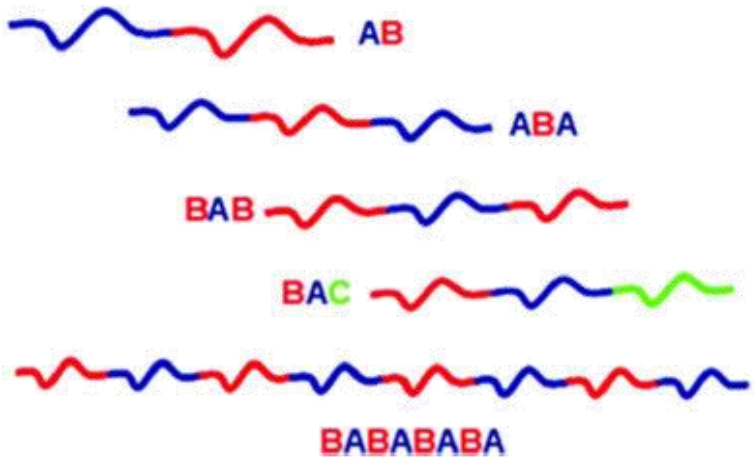


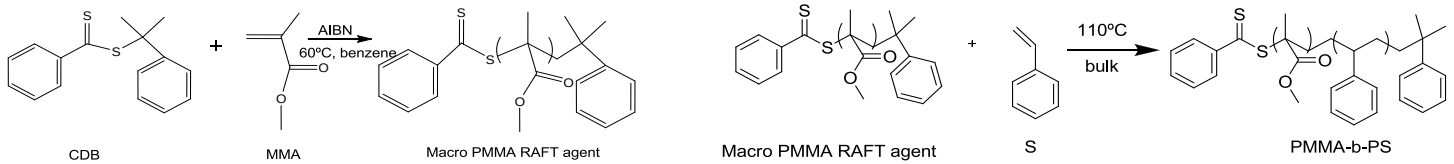
LINE AND SPACE POTENTIAL SOLUTIONS

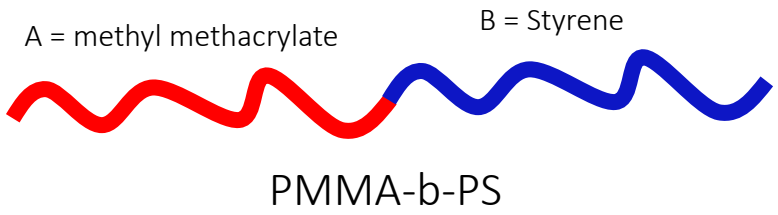
BLOCK CO-POLYMER

When two or more different monomers unite together to polymerize, their result is called a co-polymer and the synthetizing process is called co-polymerization. A block copolymer can be thought of as two or more distinct homopolymers linked end to end through covalent bonds. The number of distinct homopolymer homogeneous sections determines the molecular architecture of block copolymer; diblock, triblock, and higher multiblock copolymers are possible





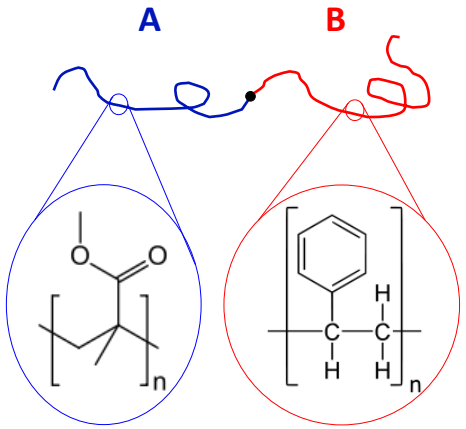




Ho-Cheol Kim et al. **Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics. Chem. Rev. 2010, 110, 146-177**

BLOCK CO-POLYMER SELF-ASSEMBLY

- ***What are block copolymers?***

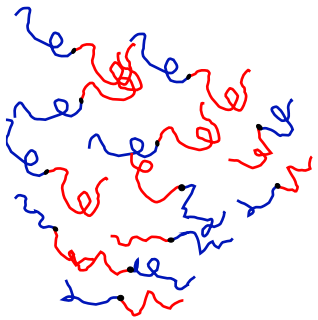


***f*:** Volume fraction of one block in a BCP

χ: Flory-Huggins interaction parameter

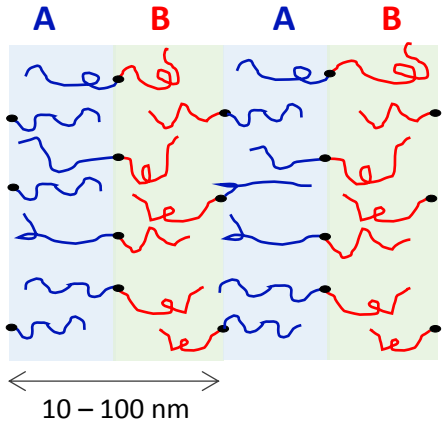
N: Polymerization index

Disordered state

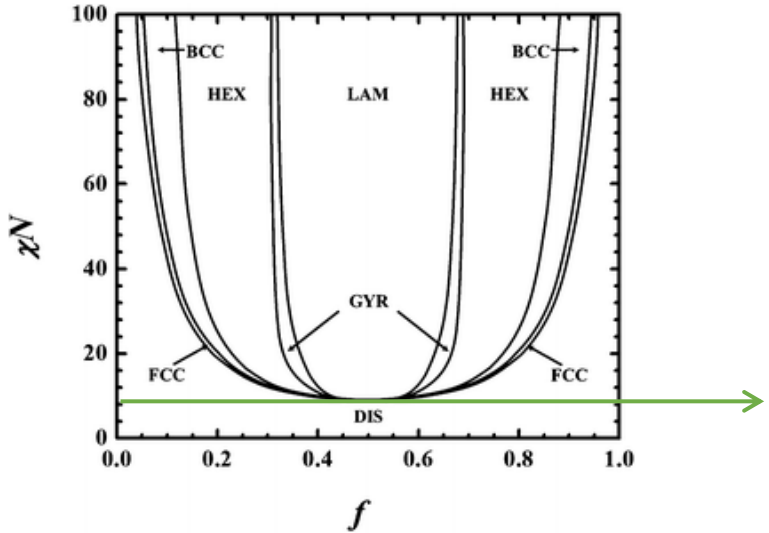


χN

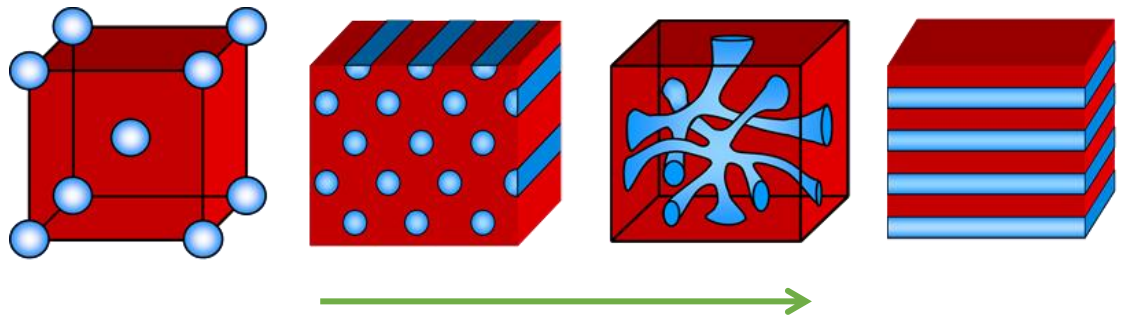
Ordered state



- ***Phase diagram of A-B diblock copolymer***



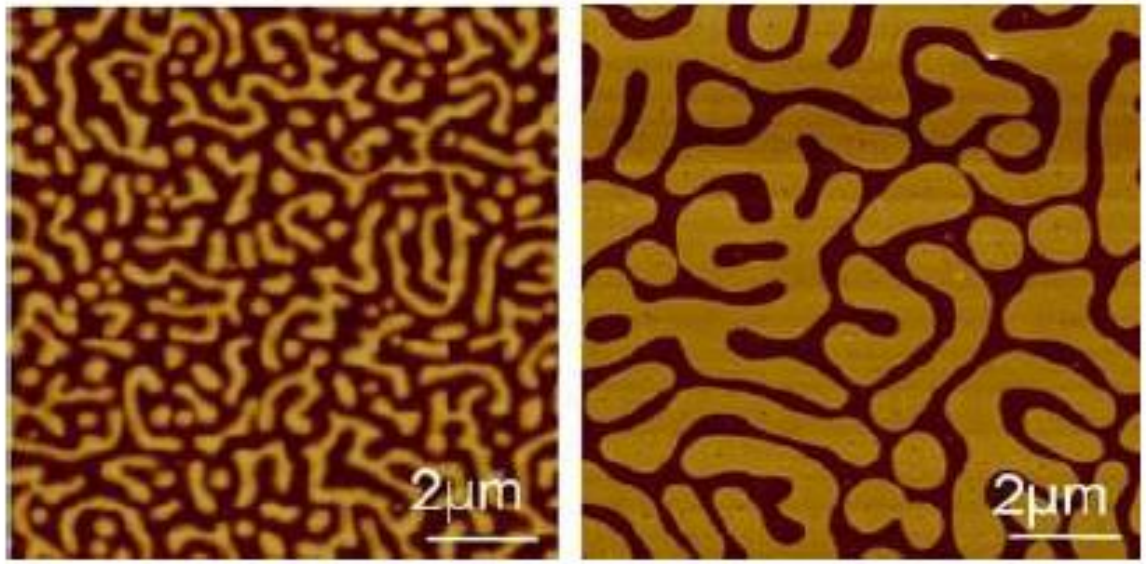
$\chi N = 10.5$



Bates, F.S. and Fredrickson, G.H. "Block Copolymers – Designer Soft Materials", Physics Today, 52, 2 (1992)

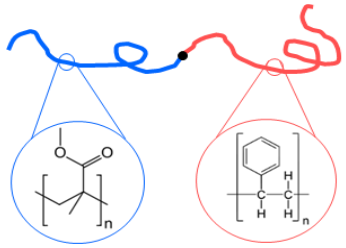
PHASE SEPARATION

- **Macrophase-separation of homopolymer blends**
  - Immiscible polymer demix
  - Occurs on the micron-scale
  - The resulting phase separated polymeric domains are generally larger than the length of polymer chain and have not peculiar morphology

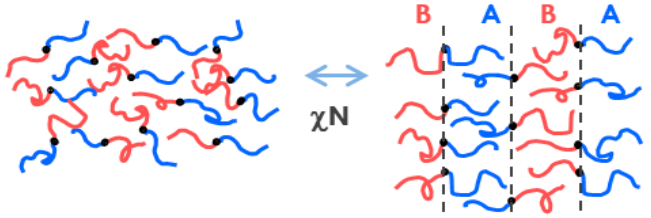


R. Pugin et al. J. Photopolymer Science and tech. 2009

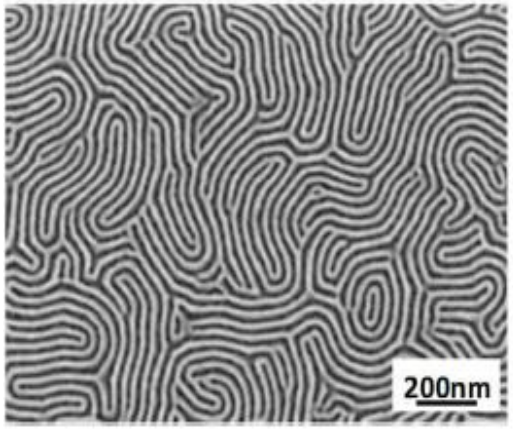
- **Microphase-separation of block copolymers**
  - Immiscible blocks demix
  - Occurs on the nanoscale, since the two blocks are covalently bound

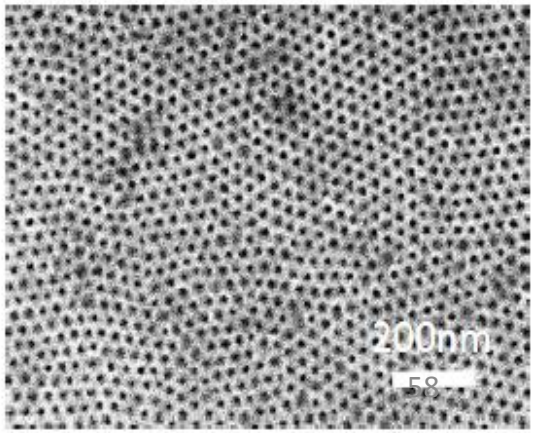


Disorder-order transition



f: Volume fraction of one block in a BCP
N: Polymerization index
χ: Flory-Huggins interaction parameter





Phase separation in block copolymers

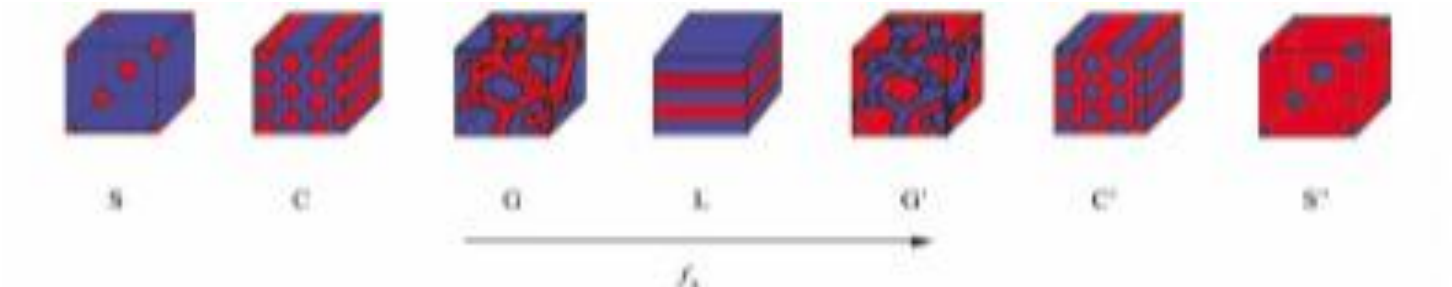
Bates, F.S. and Fredrickson, G..H., *Physics Today*, 52, 2 (1992)

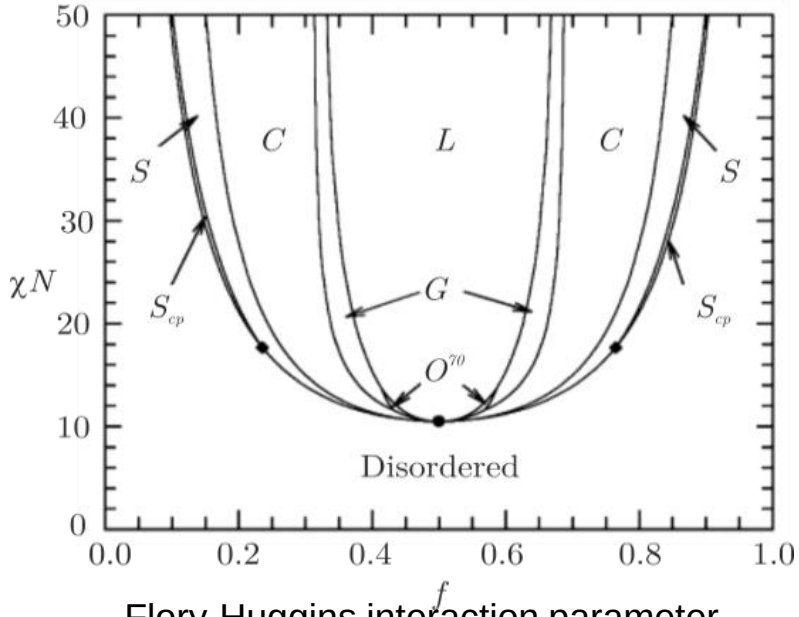
- The propensity for block copolymers to phase separate into periodic microdomains is determined by the strength of the repulsive interaction

- It is characterized by the product χN:
  - χ is the Flory-Higgins interaction parameter
  - N is the number of monomers in the diblock copolymer

- Microphase separation can occur when χN exceeds the critical value for the order-disorder transition.

- At equilibrium, this microphase separation is established by the energy balance between the stretching energy for the polymer chains and the energy of interactions at the interface between A and B microdomains.





Flory-Huggins interaction parameter

$$\chi_{AB} = (^{Z}/_{k_B T})[\varepsilon_{AB} - 0.5 * (\varepsilon_{AA} - \varepsilon_{BB})]$$

ε_{ij} is the interaction energy between two monomers *i* and *j*

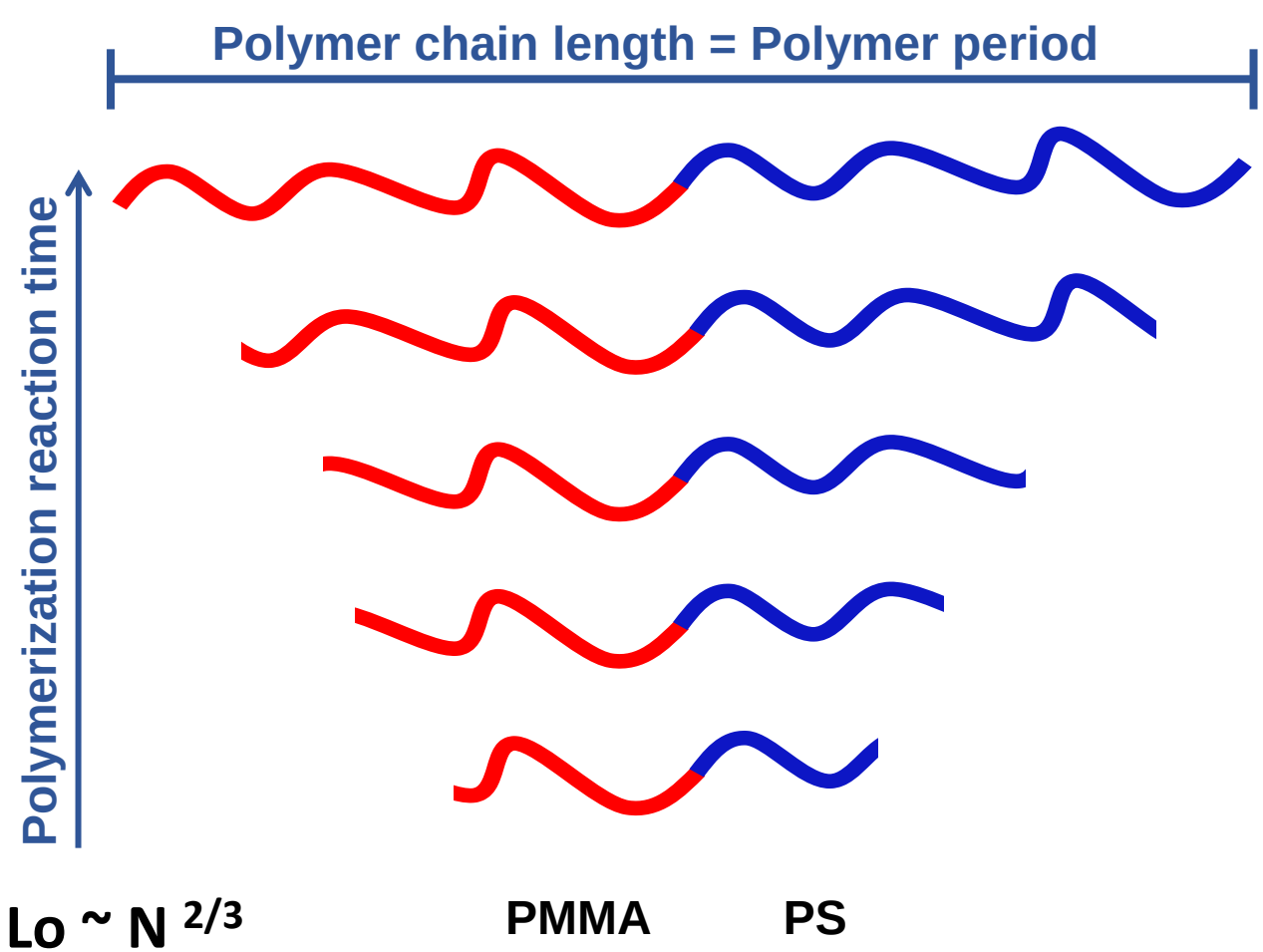
Z is the number of nearest neighbours of a unit

Lamellar period

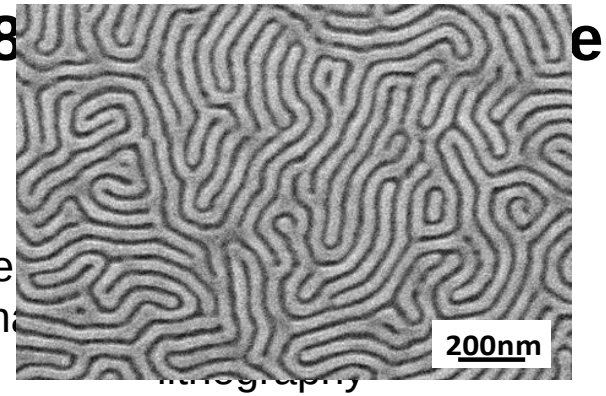
$$L_0 = 1.03\, b\, \chi_{AB}^{1/6}\, N^{2/3}$$

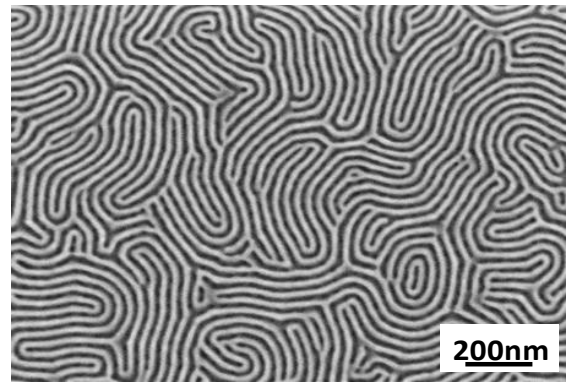
BLOCK CO-POLYMER SELF-ASEMBLY: HALF PITCH SIZE SETTING

The pitch we obtain depends on the molecular weight and the CD uniformity depends on the polidispersity index

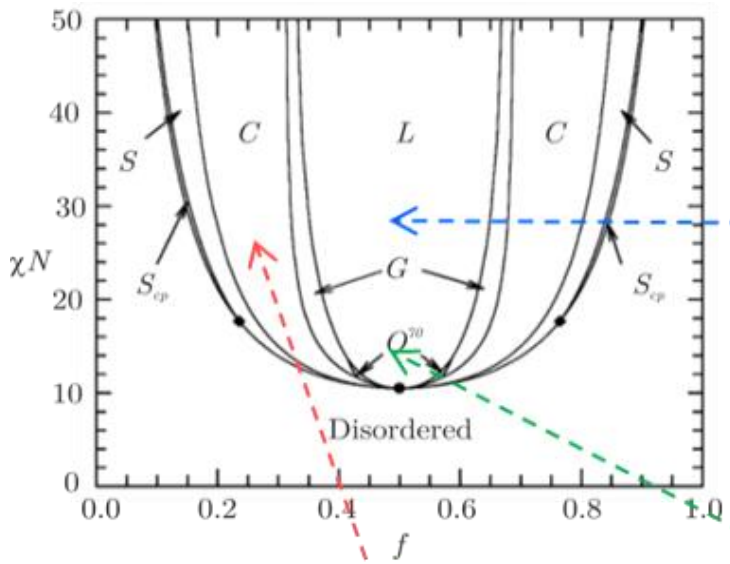


Mn = 45 kg/mol & 1.12 PDI

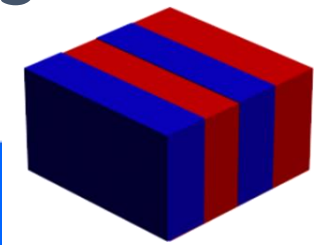




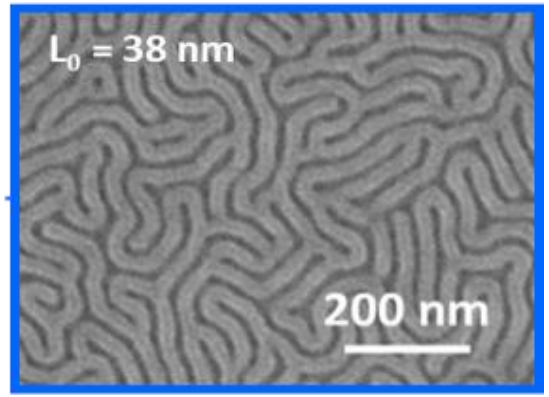
Morphologies of diblock copolymers



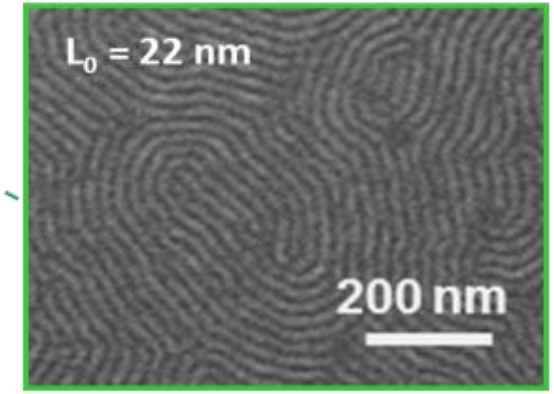
50:50



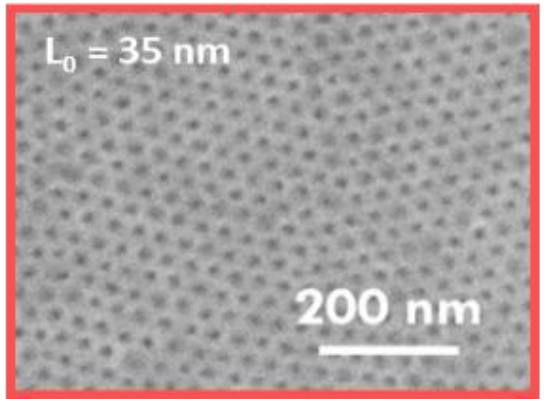
L_0 = 38 nm



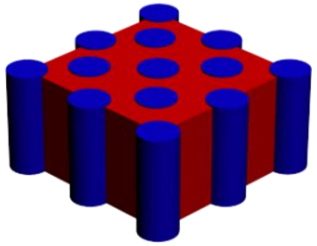
L_0 = 22 nm



L_0 = 35 nm



70:30



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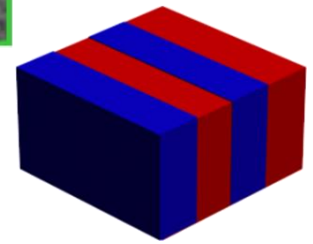
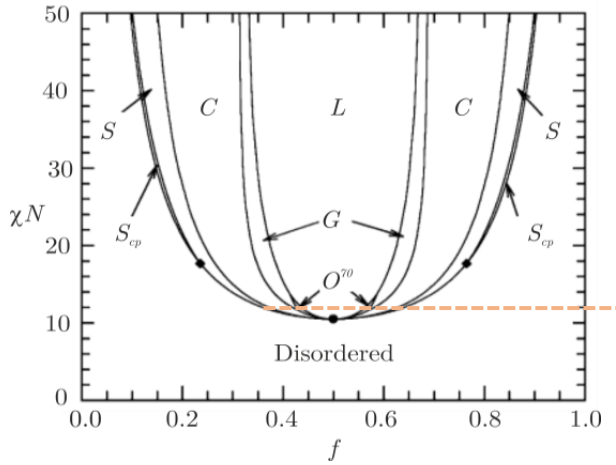


Bates, F.S. and Fredrickson, G.H. “Block copolymer thermodynamics: Theory and experiment”, *Annu. Rev. Phys. Chem.*, 41 (1990)

High-χ block co-polymers

Development of **new DSA processes** and materials to scale to **5 nm** with potential to fulfill the future requirements of microelectronics industry



PS-*b*-PMMA

χ ≈ 0.04

Resolution limit to 11 nm

χN ≈ 10.5

High- χ materials requirements

- High χ
- Good etching selectivity
- Mechanical stability
- Orientation control and alignment availability with low defectivity

Organic BCPs		Inorganic BCPs	
BCP system	χ value	**BCP system**	χ value
PS-b-PMMA	0.041	**PS-b-PFS**	0.08
PS-b-PEO	0.077	**PS-b-PDMS**	0.26
PS-b-P2VP	0.178	**PTMSS-b-PLA**	0.46
PS-b-PLA	0.233	**PS-b-MH**	0.58
PS-b-PI	0.110	**PLA-b-PDMS-b-PLA**	1.4

Organic high- χ materials

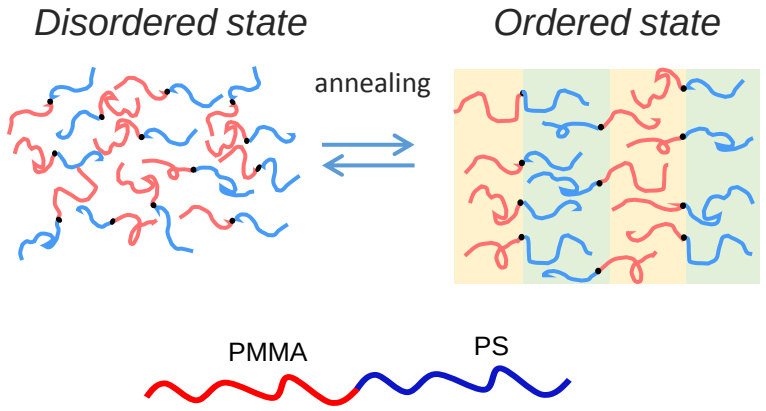
- Low etching contrast between blocks
- Not very high- χ values

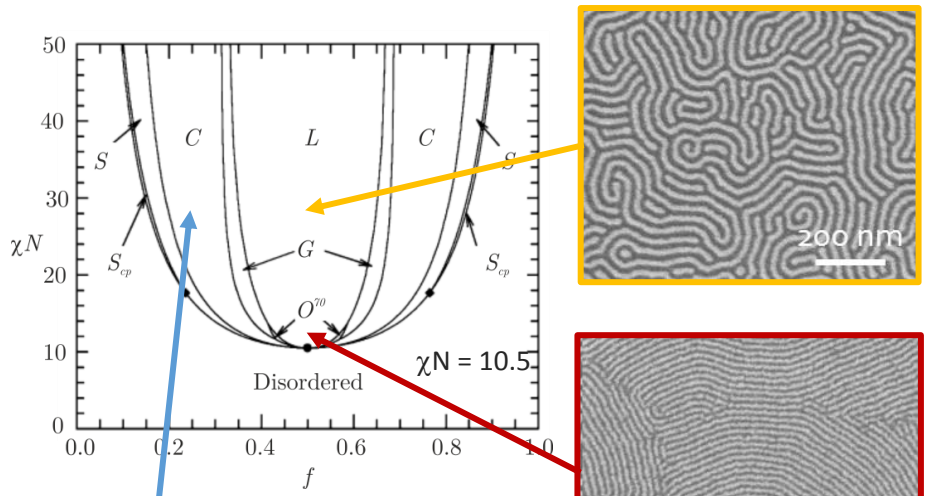
Inorganic high- χ materials

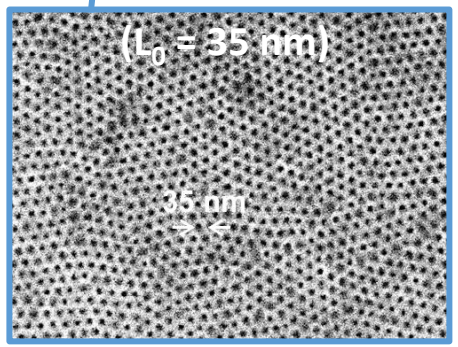
- High etching contrast between blocks
- High- χ values

Each block copolymer requires the proper neutralization layer

PHASE SEPARATION AND SURFACE/INTERFASE ENERGY



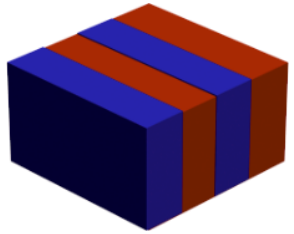


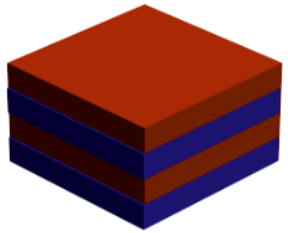


Neutral surface

Non-neutral surface

50:50





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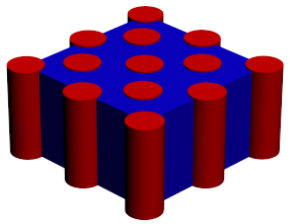

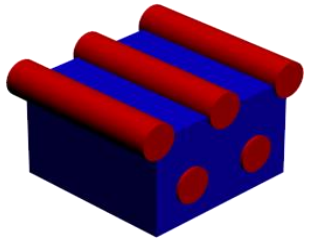

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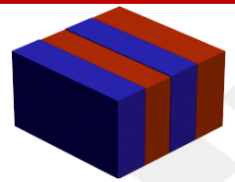

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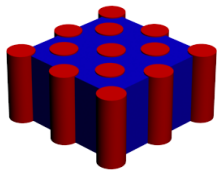
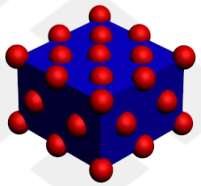
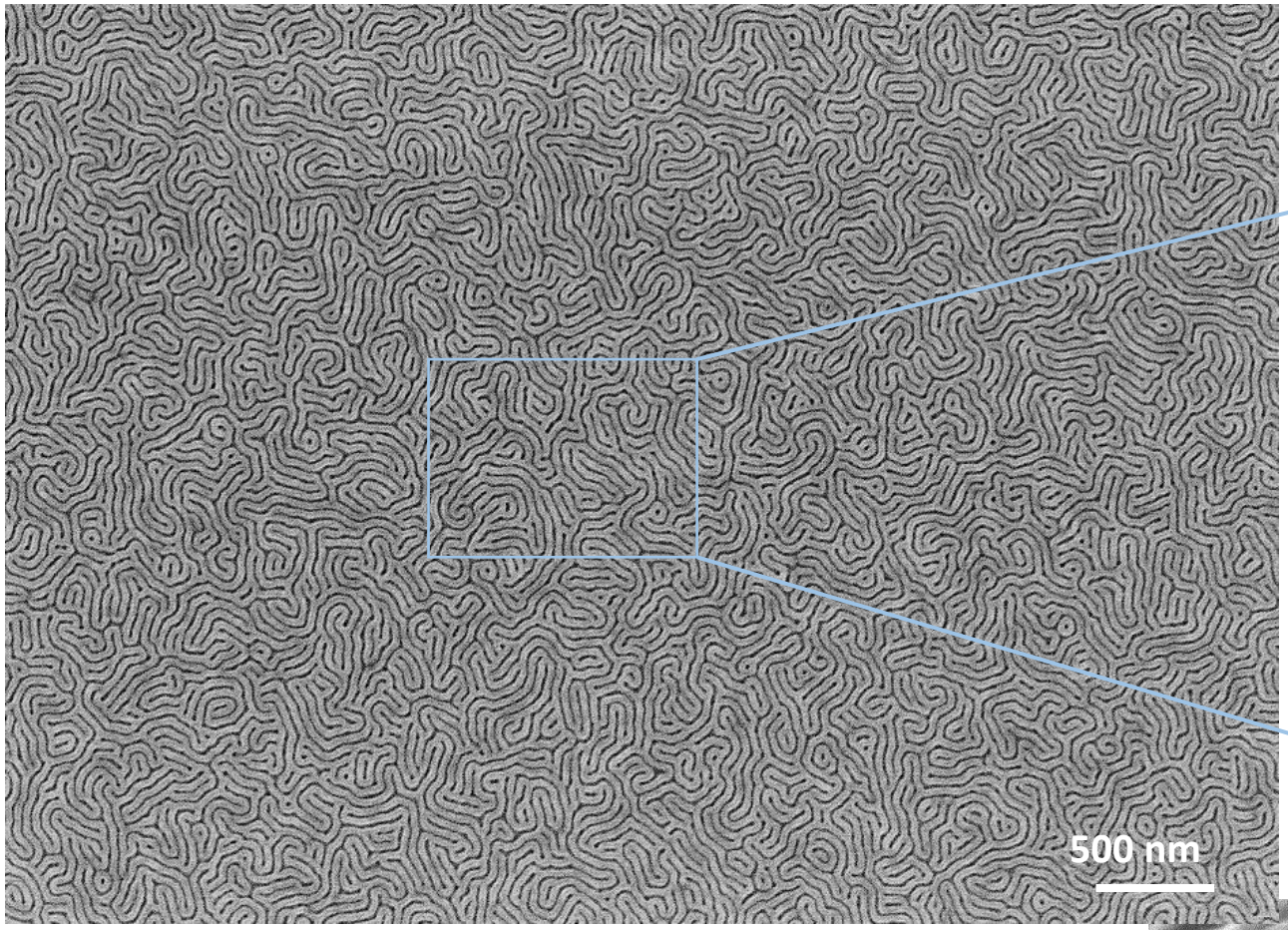
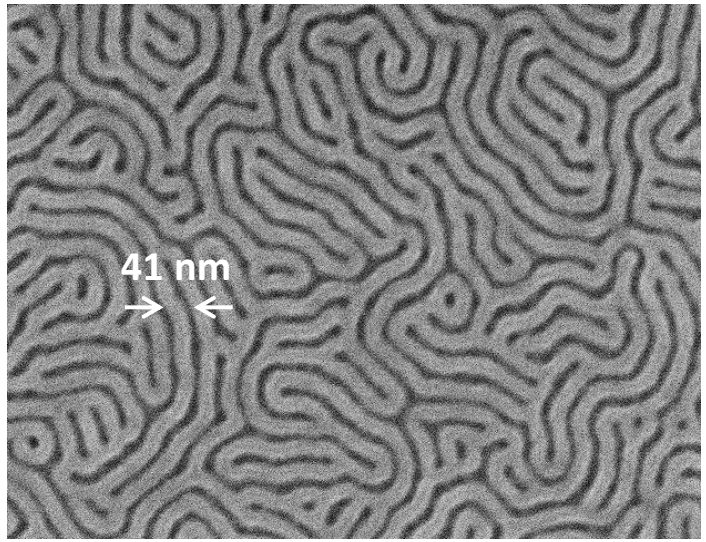


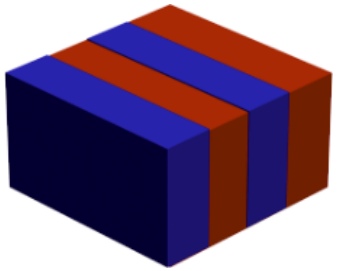
20:80

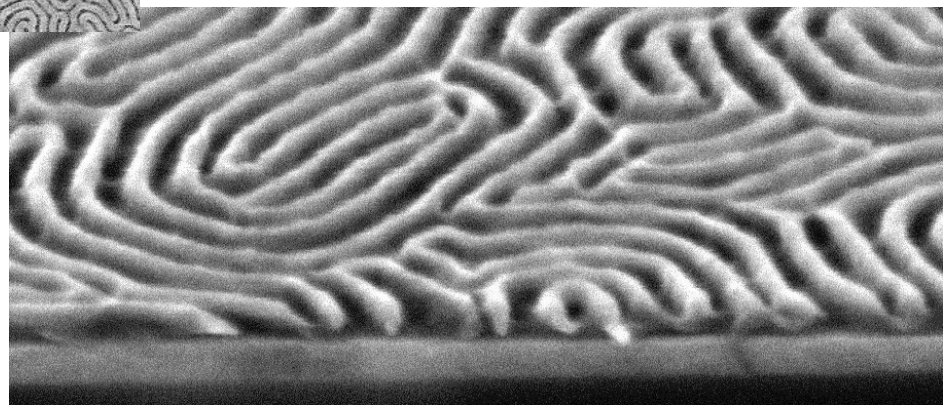


Examples of phase segregation
Lamellar forming block copolymers

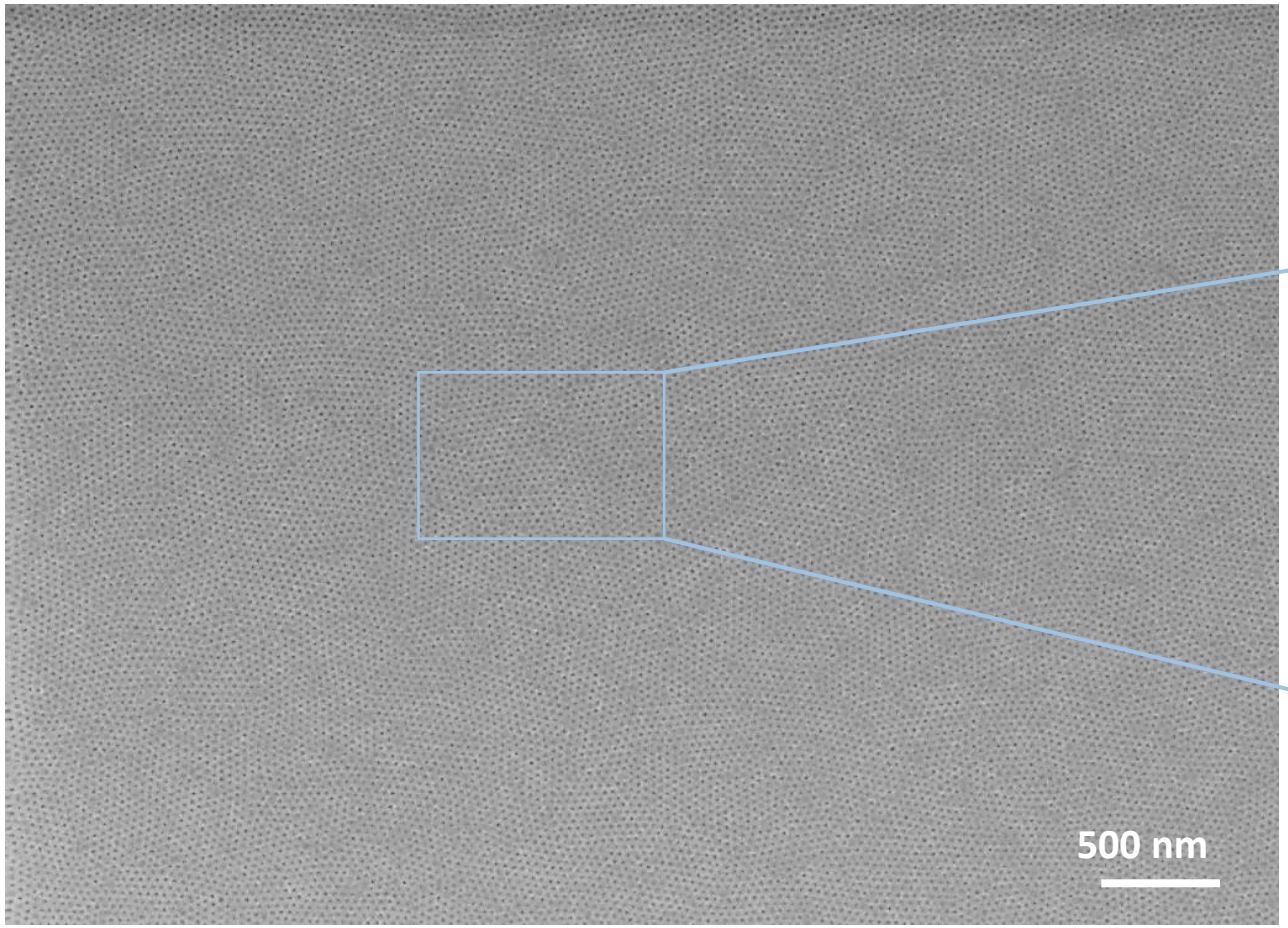


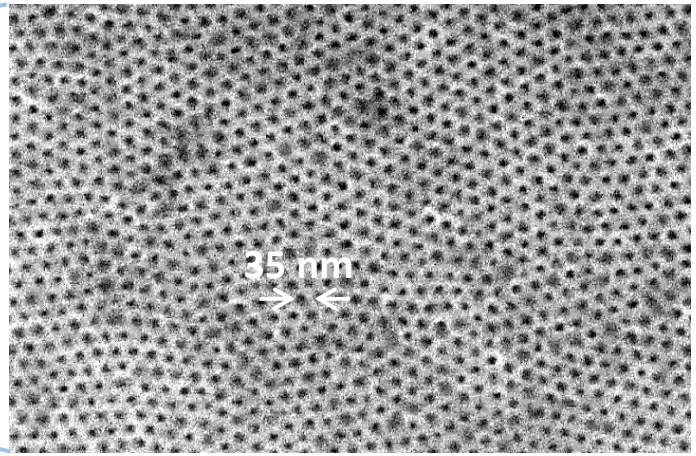


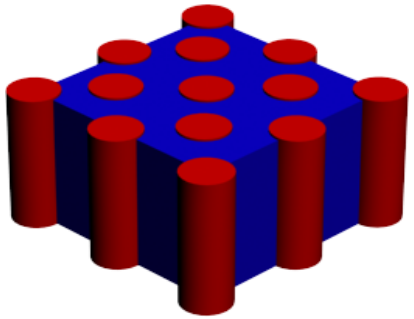




Cylindrical forming of block copolymers



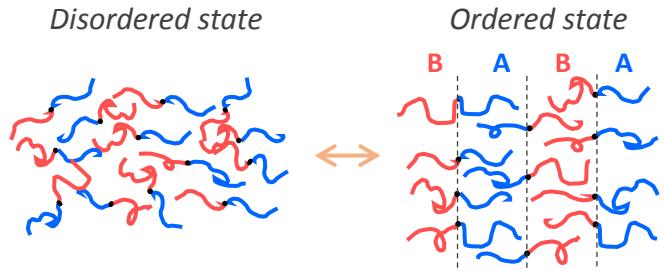




Thin film preparation of block co-polymers

In order to promote and **enhance** the **ordering** of BCP microdomains it is necessary to **induce some mobility** on polymer chains to facilitate the microphase separation process.

- *Thermal annealing*
- *Solvent annealing*



Thermal annealing

Heating **above T_g** and **below degradation** T

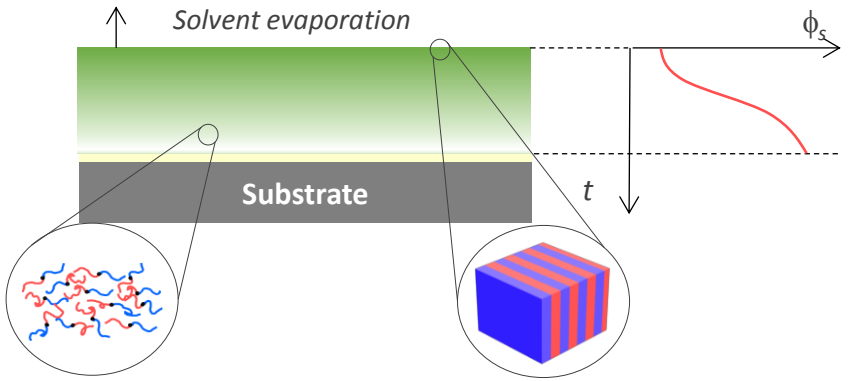
$$D = D_0 e^{-0.28\cdot(\chi N - 3.5)}$$

$$\chi_{AB} = \frac{Z}{k_B T}\left[\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right] \qquad T \uparrow \chi \downarrow$$

✓ Equipment already implemented in the industry
✓ No waste stream
✘ Systems which undergo degradation at high temperatures

Solvent annealing

Exposure to a solvent **below T_g** to form a swollen and mobile polymer film



Thin film preparation of block co-polymers

1. Preparation of a surface with the proper interface energy (usually, deposition of a monolayer of molecules)
2. Dissolution of the block co-polymer in a solvent
3. Spinning of the solution
4. Annealing (Thermal annealing or solvent annealing)

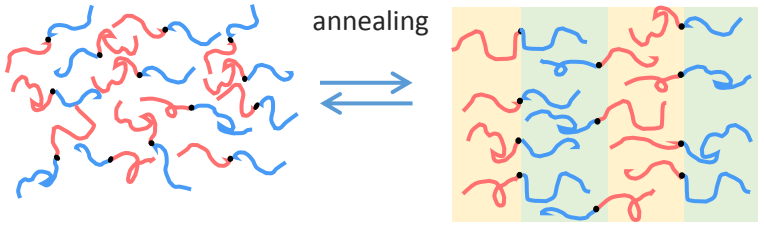
Annealing increases the mobility of the copolymer molecules, so the film rapidly reaches its final structure

In thermal annealing the sample is held at a temperature above the glass transition temperatures but below decomposition temperatures of the blocks for a time sufficient to allow approach to the equilibrium morphology.

In solvent vapor annealing the sample is held in a controlled atmosphere containing selected solvent vapors. Absorption of the vapor imparts greater mobility within the film.

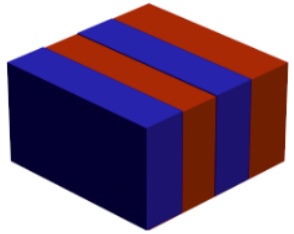
Thin film preparation of block co-polymers

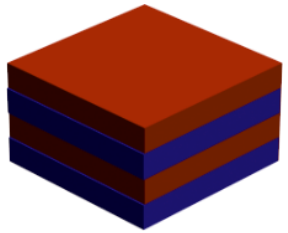
Disordered state *Ordered state*



Neutral surface **Non-neutral surface**

50:50





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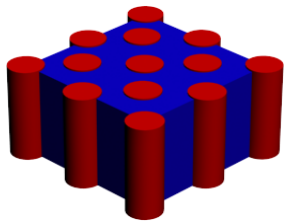
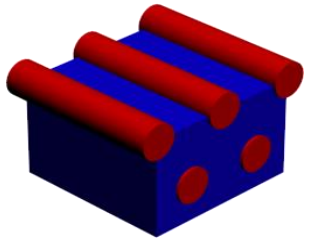
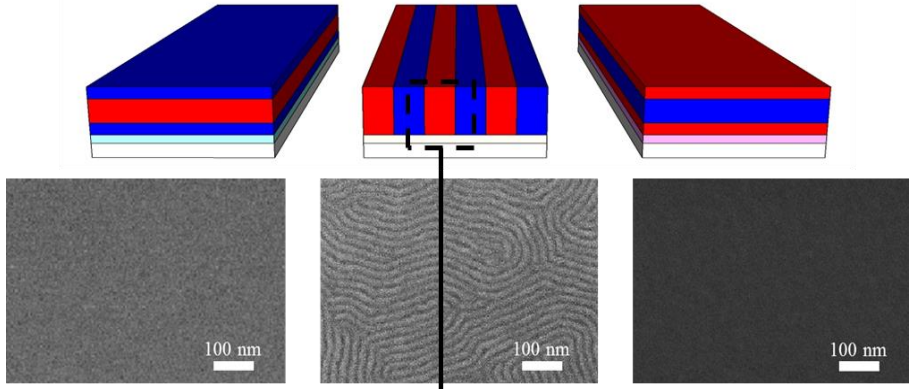
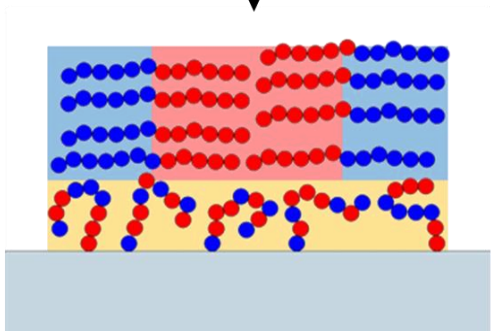


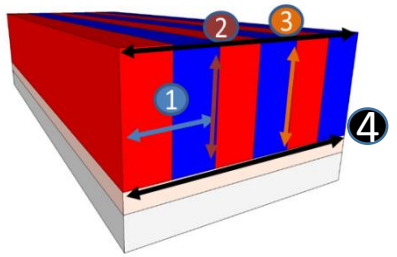


The **surface affinity** is controlled by a **Brush layer**





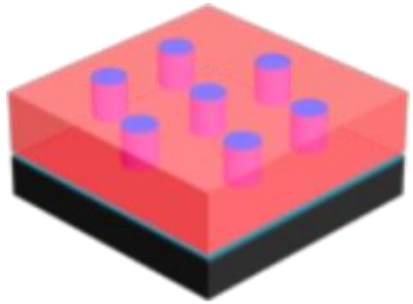
$$E_{tot} = \sum E = E_{stretch} + E_{curvature} + E_{interblock} + E_{surface}$$

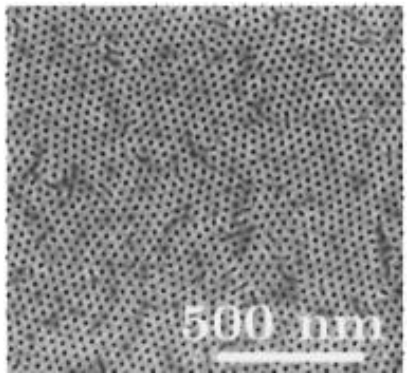


Block copolymer – surface interaction: *Role of surface affinity*

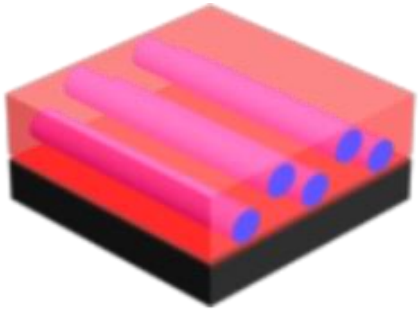
Interaction energies $E = \boxed{(E_{A/B} + E_{conf})} + \boxed{(E_{A/Subs} + E_{B/subs} + E_{A/air} + E_{B/air})}$

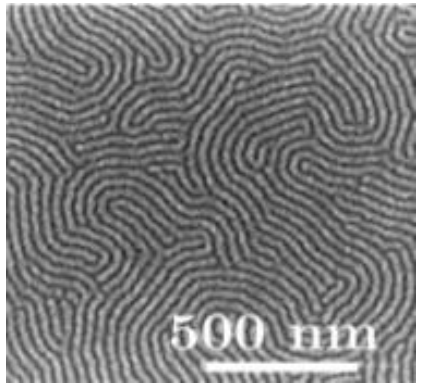
Neutral surface



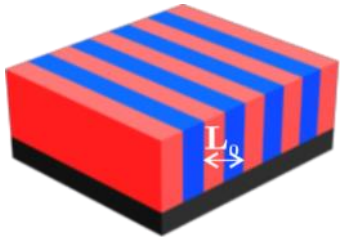


Affine surface





Neutral surface



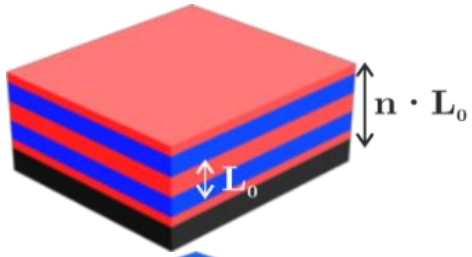
$\gamma_{A\text{-air}} \approx \gamma_{B\text{-air}}$

$\gamma_{A\text{-subs}} \approx \gamma_{B\text{-subs}}$

AFFINE SURFACE

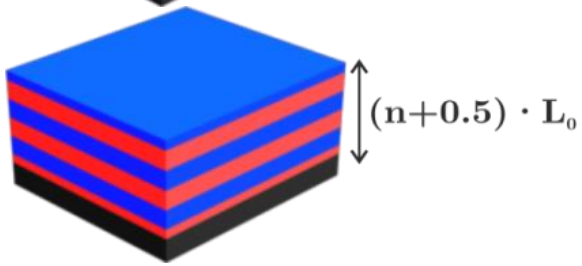
$\gamma_{A\text{-air}} < \gamma_{B\text{-air}}$

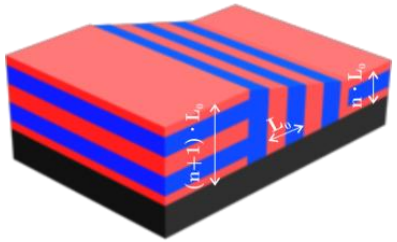
$\gamma_{A\text{-subs}} < \gamma_{B\text{-subs}}$

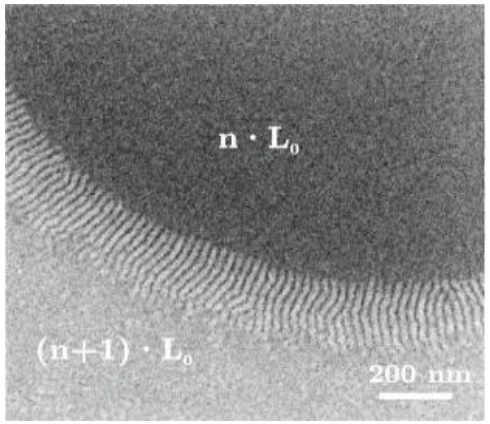


$\gamma_{A\text{-air}} > \gamma_{B\text{-air}}$

$\gamma_{A\text{-subs}} < \gamma_{B\text{-subs}}$





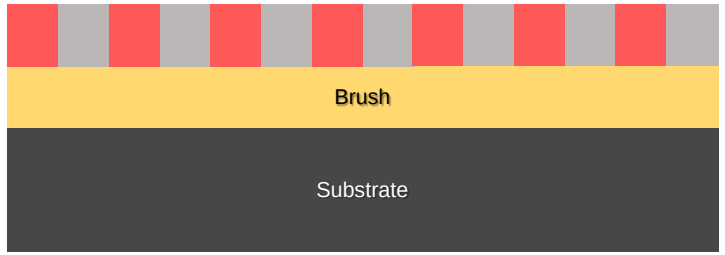


When the BCP **does not** fulfill the film thickness **commensurability** condition, the BCP tend to create some **holes** or **terraces**

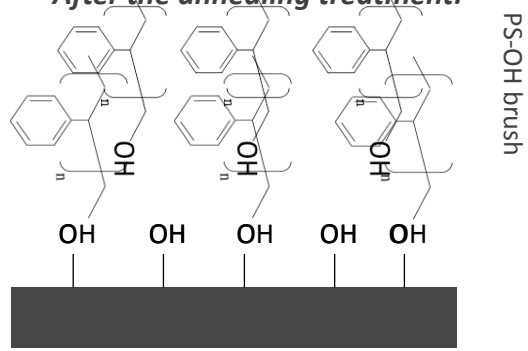
Surface neutralization

For technological applications there is the need to control the BCP morphology, and thus **avoid wetting morphologies** at the polymer-brush interface.

Use of **brush polymer** to create a neutral layer which balances the surface free energy between the BCP domains

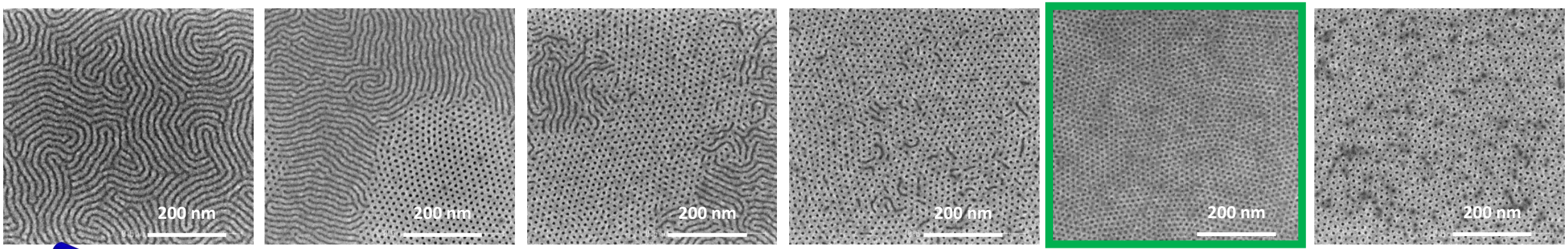


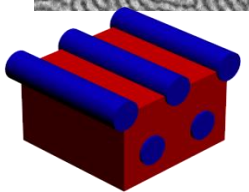
After the annealing treatment:



Mansky, P., "Controlling polymer-surface interactions with random copolymer brushes", Science, 275, 1458-1460 (1997)

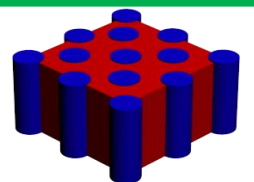
% PMMA (PS-r-PMMA)



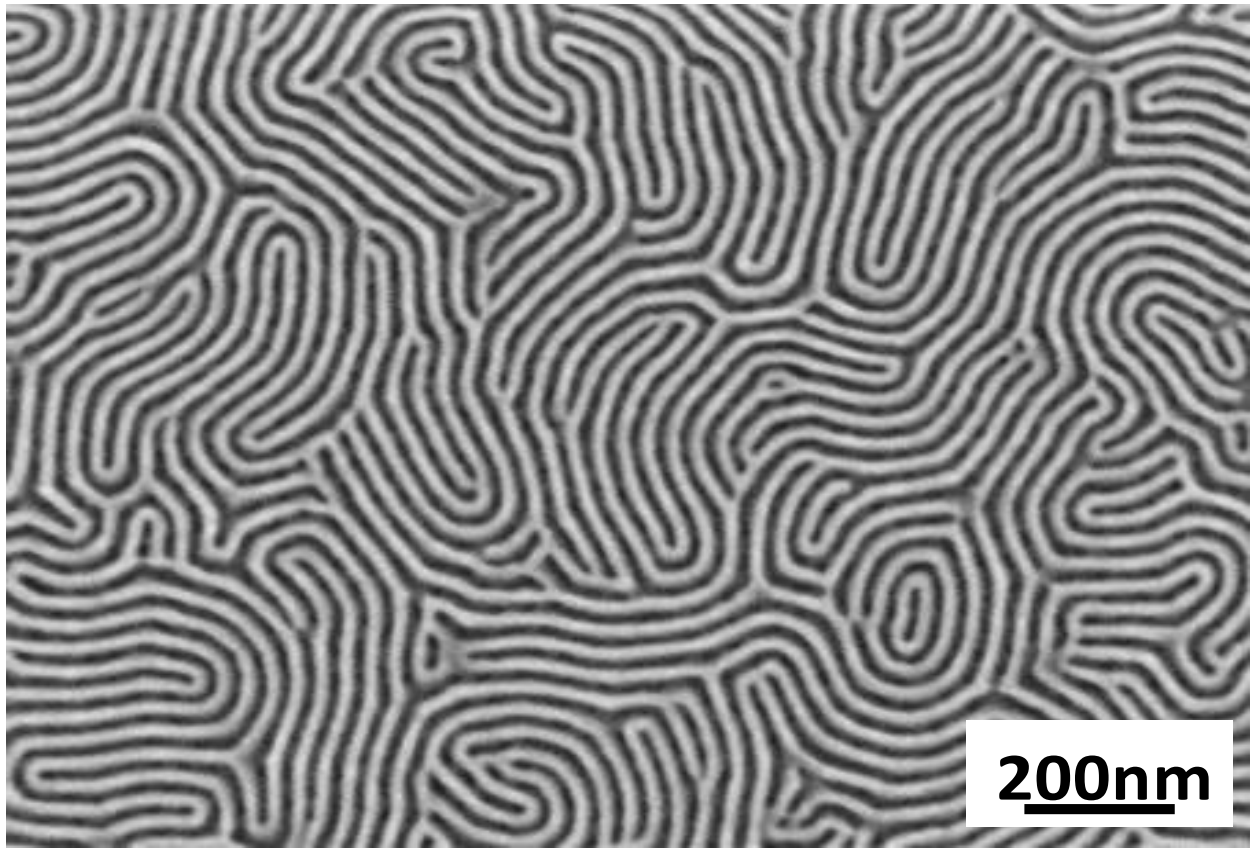


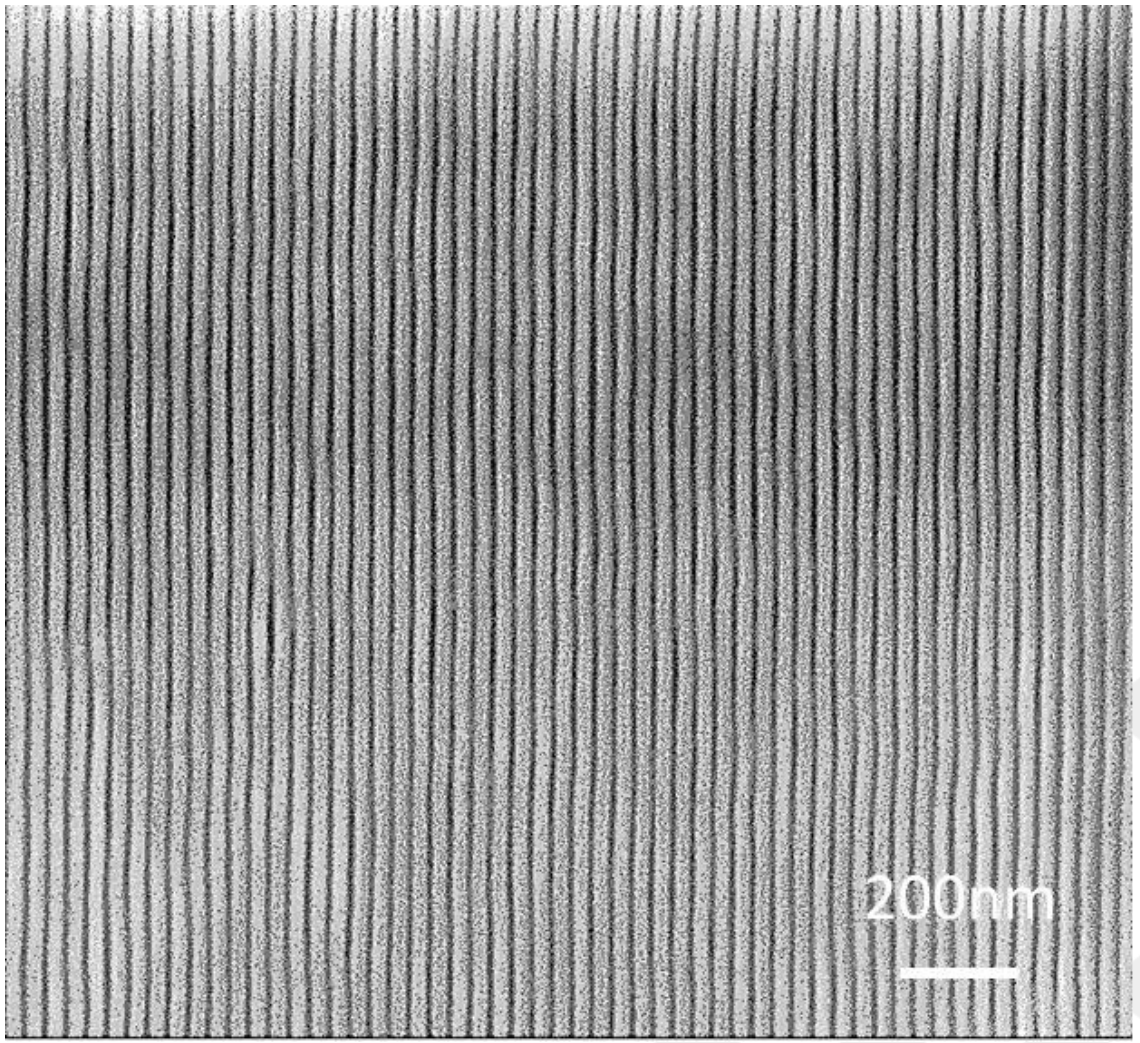
Cylindrical PS-b-PMMA

SEM images taken after PMMA removal



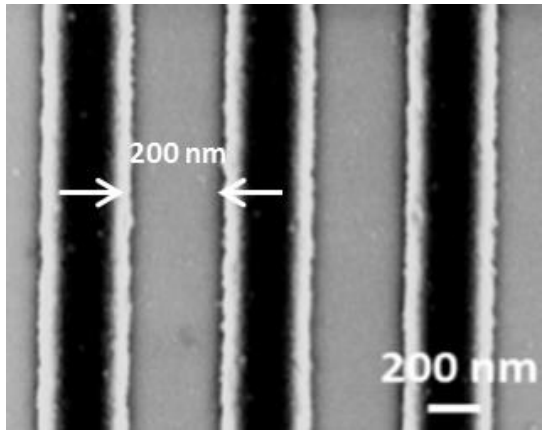
Directed Self-Assembly (DSA): Short-range order to long-range order





Directed self-assembly (DSA) methods

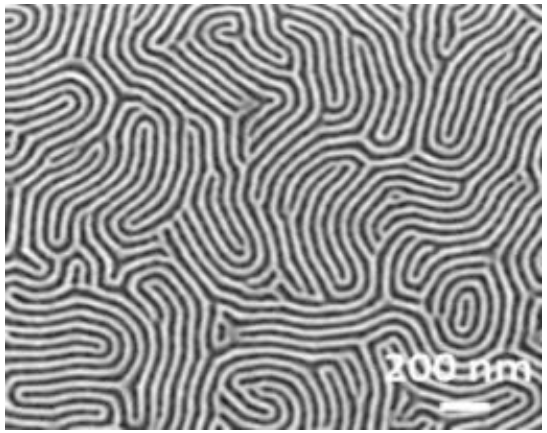
Conventional Lithographic methods



Guiding patterns

+

Block copolymer self-assembly



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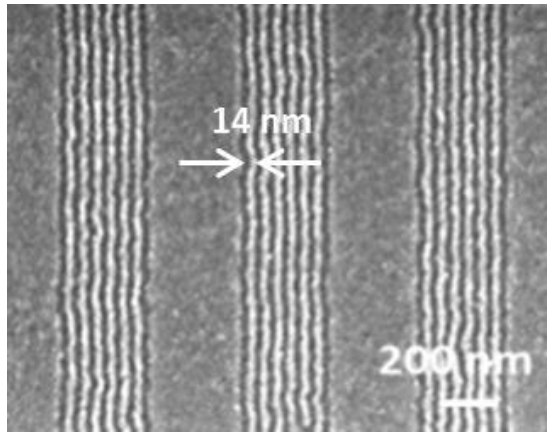
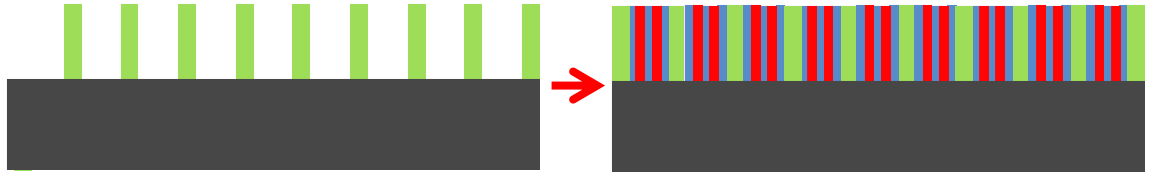


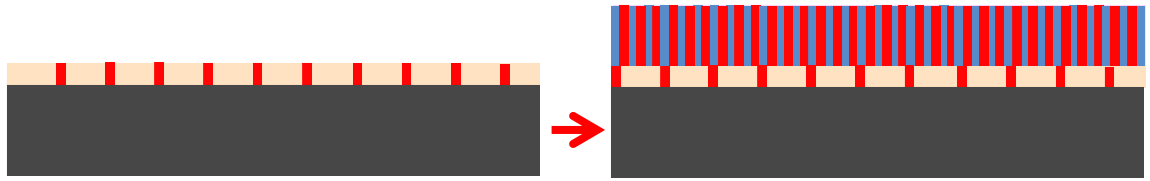
Directed *Self-Assembly of Block Copolymers* ***(DSA)***

Methodologies to DSA

Graphoepitaxy



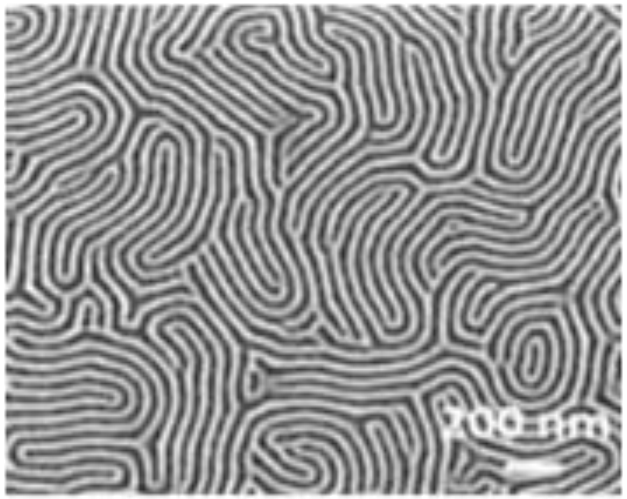
Chemoepitaxy



The density multiplication and pattern rectification are the main advantages of DSA, since they allow achieving dense patterns with tight size and placement tolerances, low defect densities and reduced e-beam writing times.

Directed self-assembly (DSA) methods

Density multiplication factor: n



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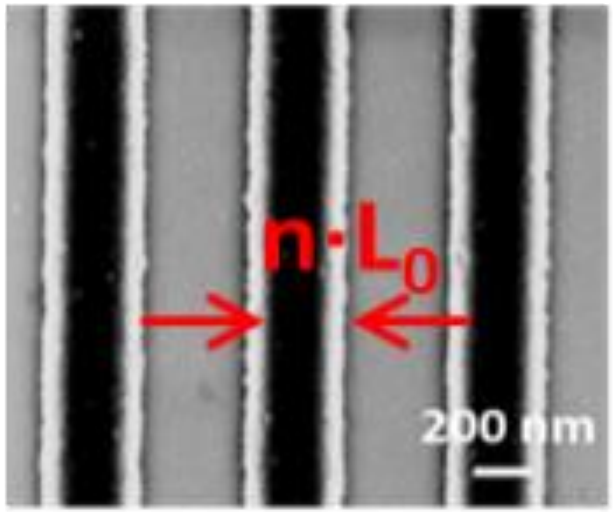

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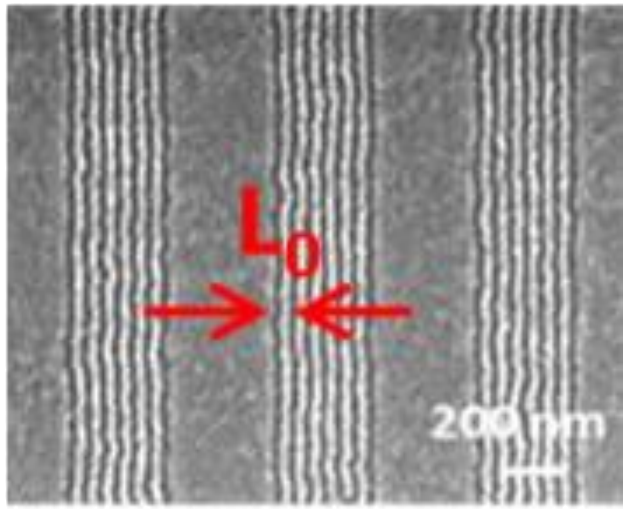
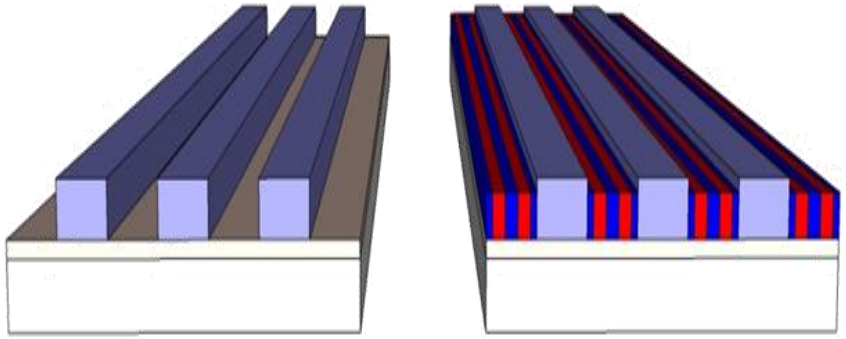
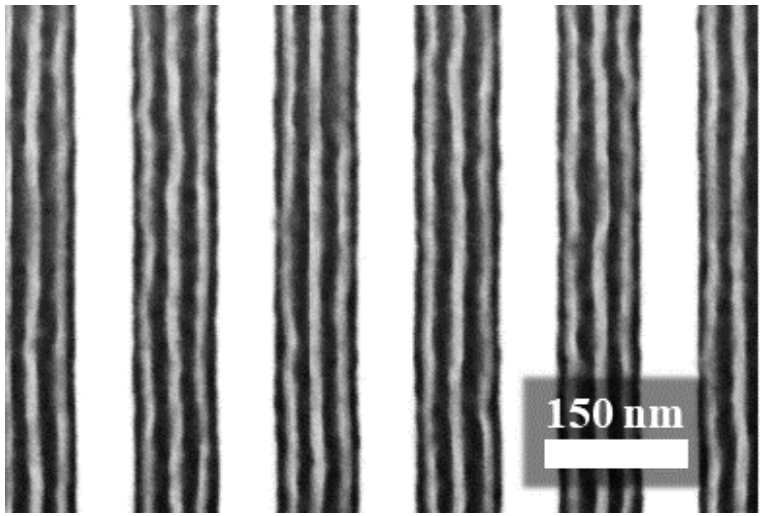


Intrinsic property of BCP to self-assemble

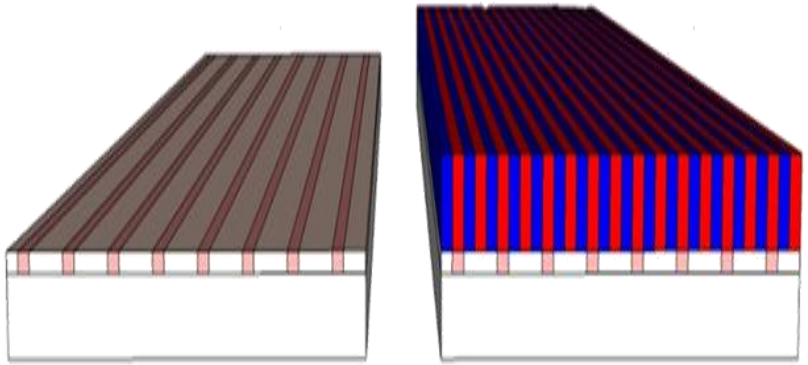
Directed self-assembly: guiding patterns

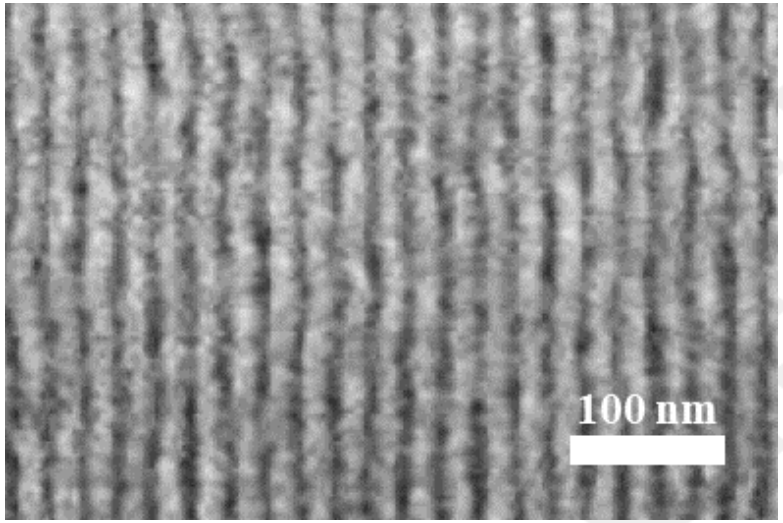
Graphoepitaxy





Chemoepitaxy





Take home message

- Bottom-up fabrication takes advantage of the small size of nano-objects to build-up devices.
- Combination with top-down fabrication allows deterministic fabrication
- Block copolymers are made of two or more distinct homopolymers linked end to end through covalent bonds. Upon annealing, they suffer a micro-phase separation, creating nanoscale patterns.
- Thin films of self-assembled block copolymers can be used as lithographic masks. The resolution is dictated by the size of the block copolymer molecules.
- By means of guiding patterns, the orientation and position of the self-assembled patterns can be controlled: graphoepitaxy and chemoepitaxy

STRUCTURE

Introductory lectures

A. Electron and ion beam lithography

- Recap on principles and limitations
- Relevant examples of ion-beam patterning

B. Directed self-assembly (DSA)

- Bottom-up vs top down fabrication
- DSA for high volume manufacturing
- Principles of DSA of block co-polymers

Advanced lessons

- Ion beam patterning for the fabrication of Nanoelectronic and nanomechanical devices

Advanced DSA aspects: Creation of guiding paterns and applications