Fabrication and Characterization of Magnetic Nanowires and Nanotubes

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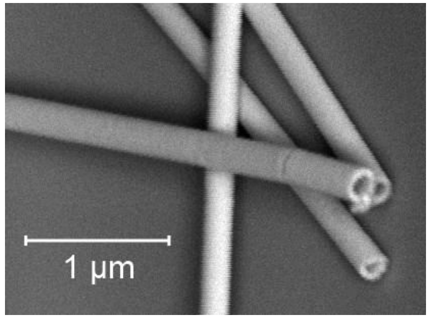
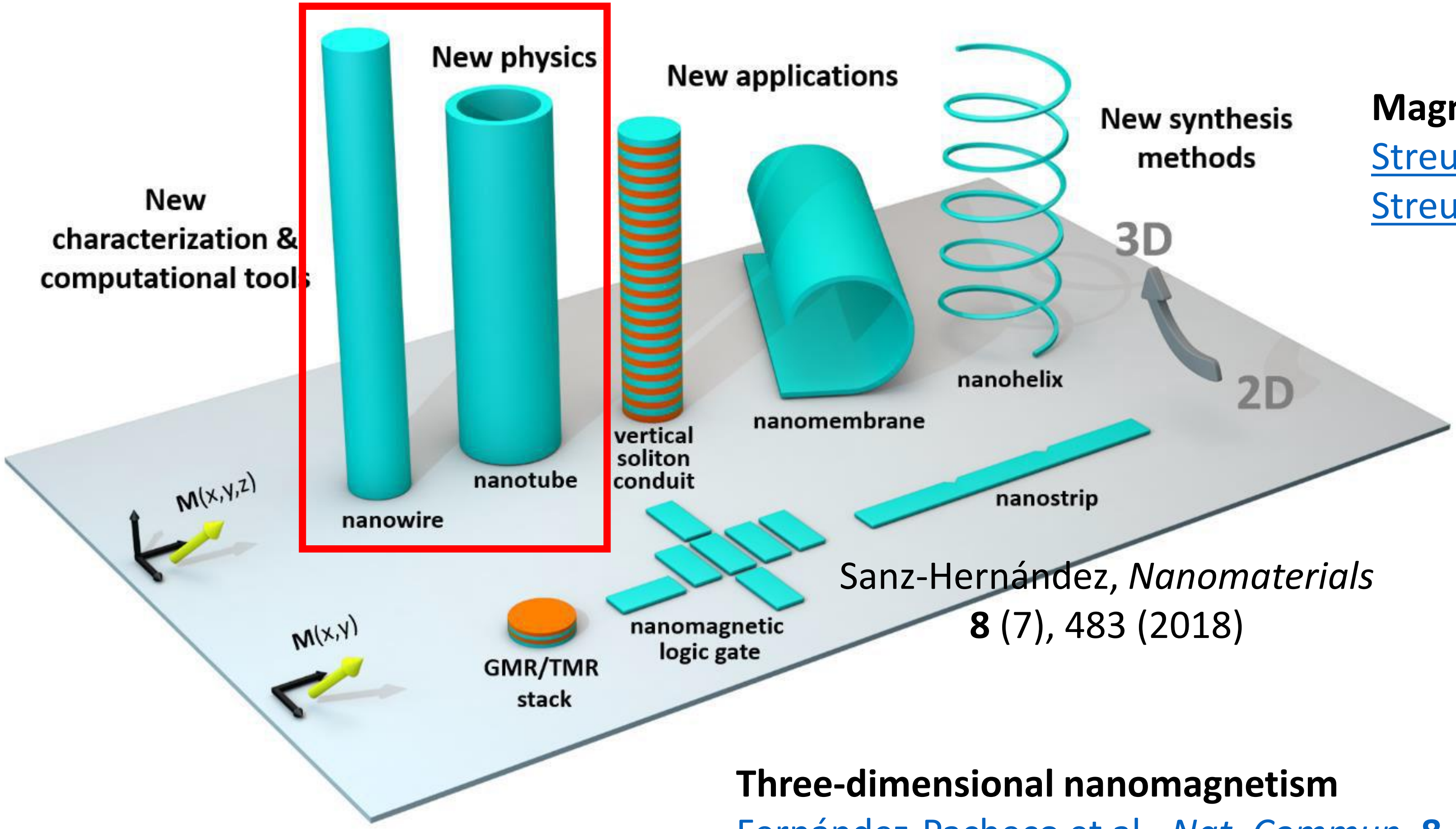


5 June 2025
OPERA COST Action Training School
Applications and Characterization of Epitaxial Materials

3D (curved) magnetic (nano)structures



Sanz-Hernández, *Nanomaterials* **8** (7), 483 (2018)

Magnetism in curved geometries

Streubel, *J. Appl. Phys.* **129**, 210902 (2021)

Streubel, *J. Phys. D: Appl. Phys.* **49**, 363001 (2016)

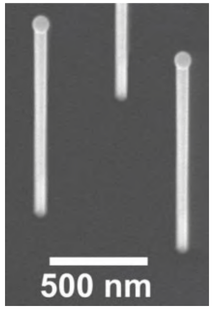
Magnetic anisotropy

- **Crystal structure (-> epitaxy)**
- **Curvature, shape**
- **Deposition in magnetic field**

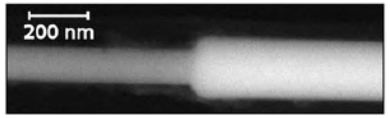
Three-dimensional nanomagnetism

Fernández-Pacheco et al., *Nat. Commun.* **8**, 15756 (2017)

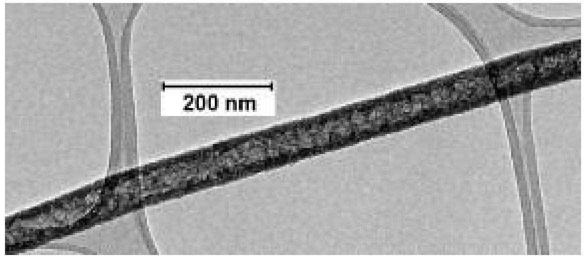
Fabrication of magnetic nanowires (and nanotubes)



- Nanowires from epitaxial thin films
- Molecular beam epitaxy and other vapour depositions



- Engineered structures, templates



- Chemical methods (using templates)
  - Electroplating
  - Electroless plating
  - Atomic layer deposition

- Bonus content
  - Magnetic characterization of single nanowires/nanotubes
  - Additional information on depositions and templates

Scope of the presentation

- Overview (non-comprehensive) of nanowire/nanotube fabrication
- Examples given for magnetic materials (metals), the same methods work also for other materials (fabrication often easier for non-magnets)
- Starting with common epitaxy techniques (and single crystal) and focusing on less conventional ones (and eventually nanocrystals)

More details and further reading:

- Vázquez (Ed.), *Magnetic nano-and microwires: design, synthesis, properties and applications* (1st edition), Woodhead Publishing (2015).
- Vázquez (Ed.), *Magnetic nano-and microwires: design, synthesis, properties and applications* (2nd edition), Woodhead Publishing (2020).
- Staňo & Fruchart, Magnetic nanowires and nanotubes, in *Handbook of magnetic materials* (Vol. 27, pp. 155-267), Elsevier (2018). Also on arXiv.
- Links to other talks of the school (common epitaxy techniques, X-Ray diffraction, ...)

Epitaxy

- crystalline layer formed with well-defined crystal orientation(s) with respect to the substrate (seed layer); ideally single-crystal
- homoepitaxy – overlayer and substrate from the same material
- heteroepitaxy – different materials, with a small lattice mismatch (strain)

Classic: Same crystal structure, similar lattice constant

Domain matching epitaxy

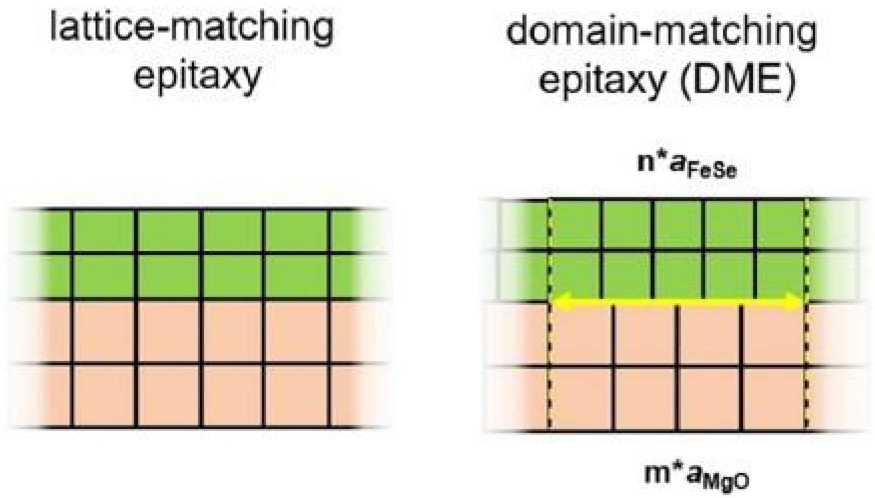
Matching integer multiples of lattice constants

Narayan & Larson, J. Appl. Phys. 93, 278–285 (2003)

Different crystal structure

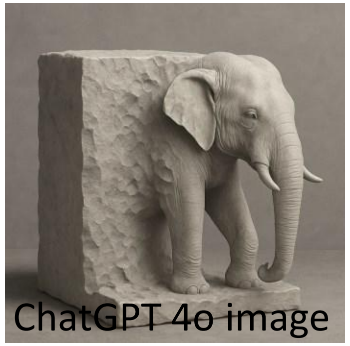
e.g., Nonisostructural complex oxide heteroepitaxy

Wong & Ramanathan, *J. Vac. Sci. Technol. A* **32**, 040801 (2014)



Obata, *ACS Appl. Mater. Interfaces* **13**, 53162–53170 (2021)

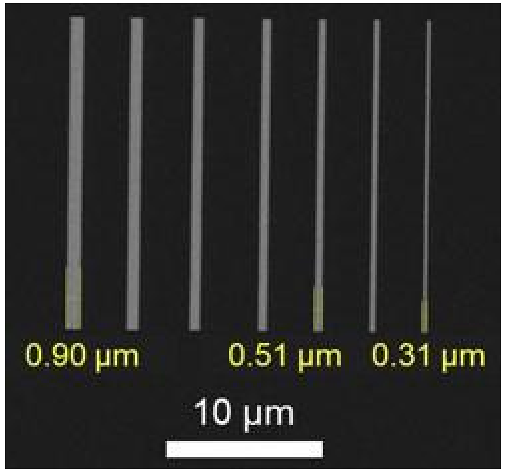
How to make a~~n elephant sculpture~~ nanowire?



Top-down elephant

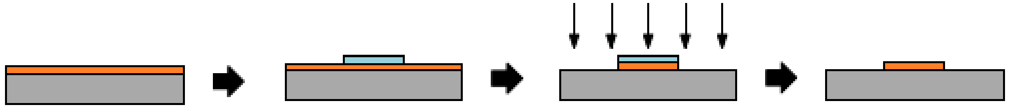
How to make an elephant sculpture?

Start with a block and chip away everything that does not look like an elephant!



Epitaxial FeRh wires with decreasing widths
[Arregi, *J. Phys. D: Appl. Phys.* **51**, 105001 (2018)]

How to make a nanowire?
Start with a block (film) and...



epitaxial thin film | thin film + mask | ion etching | mask removal

pulsed laser deposition, molecular beam epitaxy, magnetron sputtering, ...

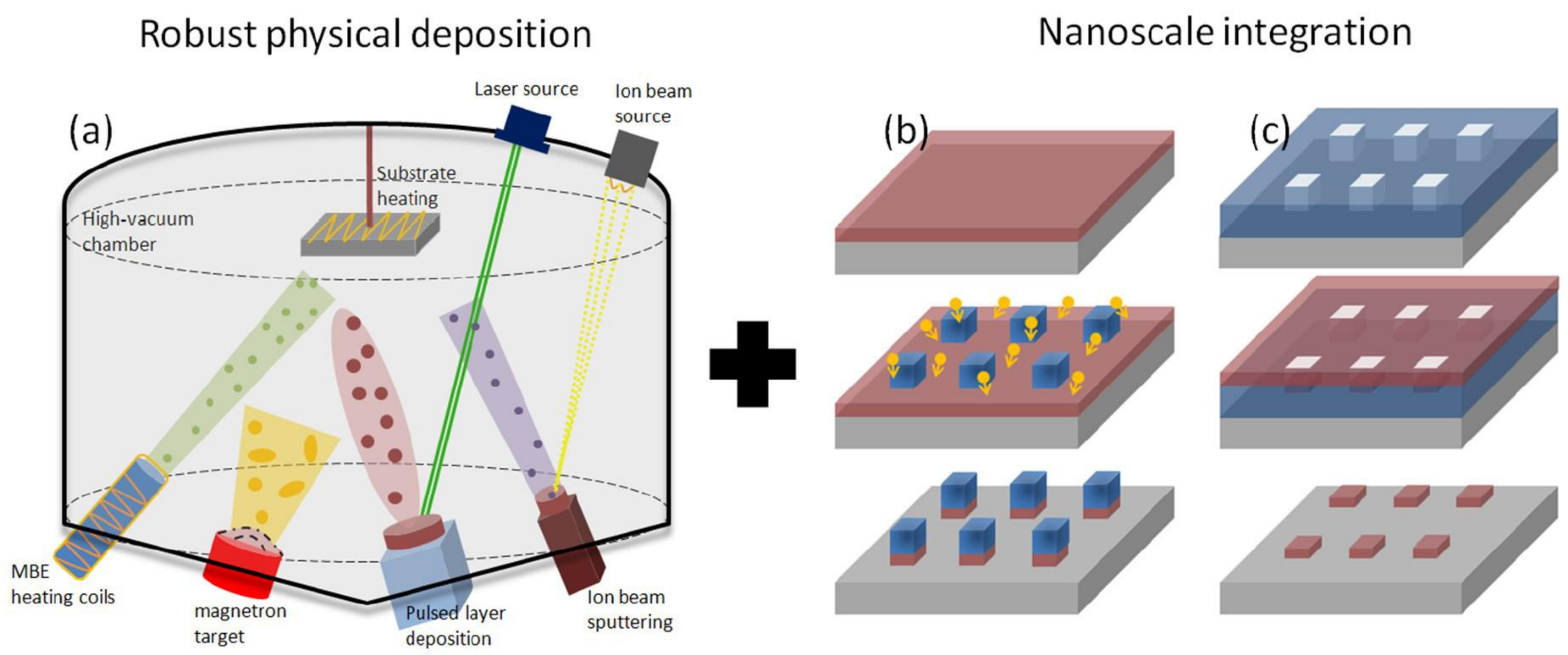
+ patterning by lithography (top-down approach)

+ Control over position and geometry, but rather 2D
+ Reproducible

* Time, resource demanding for large arrays
* Patterning can damage / influence structures

- Not well-suited for vertical, high-aspect-ratio structures
- Challenging for smaller wire diameters & high-density, difficult for nanotubes

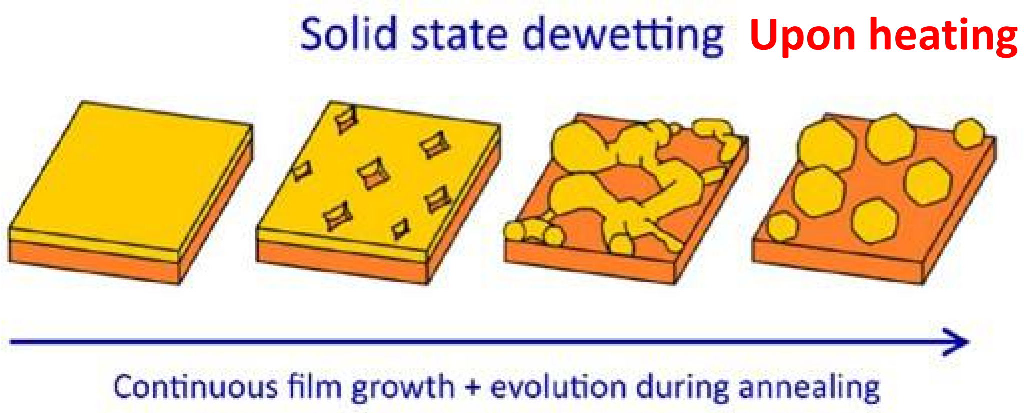
Lithography (patterning) of epitaxial films



Review - Epitaxial patterning of thin-films
[Zhang, *J. Micromech. Microeng.* **24**, 093001 (2014)]()

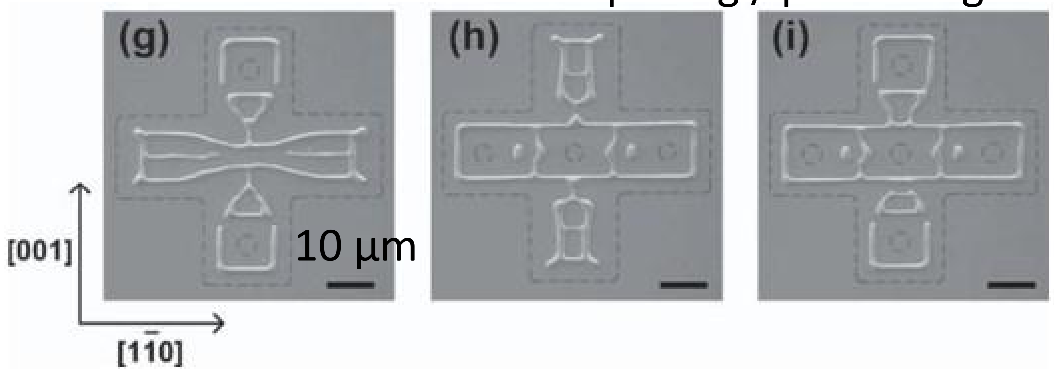
(a) Thin film deposition via physical deposition techniques
(b) Deposition → lithography → ion etching
(c) lithography → deposition → lift-off

Nanowires by solid state dewetting of epitaxial films



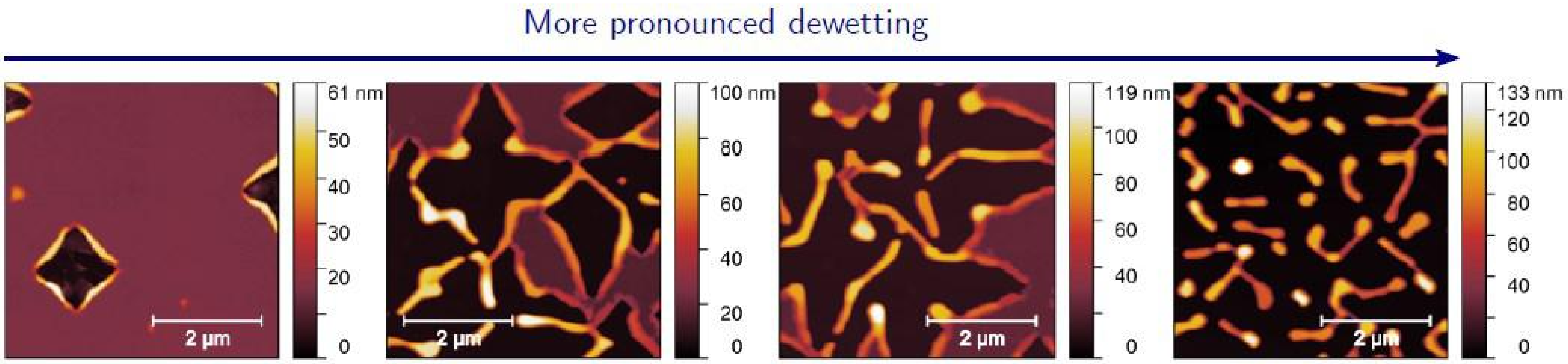
Typically: Metal film on oxide substrate

More control with templating / patterning



Dewetting of pre-patterned Ni (110) films with holes

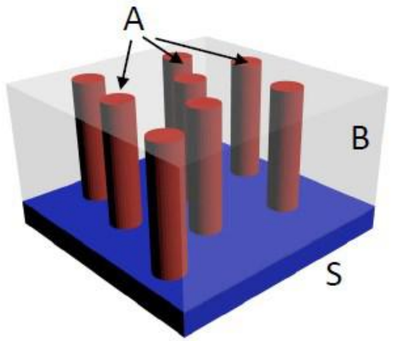
[Ye & Thompson, *Adv. Mater.* **23**(13), 1567-1571 (2011)]



Dewetting of epitaxial FeRh film on MgO (001), atomic force microscopy FeRh wires and islands

[Motyčková, Magnetic Properties of Self-Assembled FeRh Nanomagnets, Brno University of Technology (2020)]

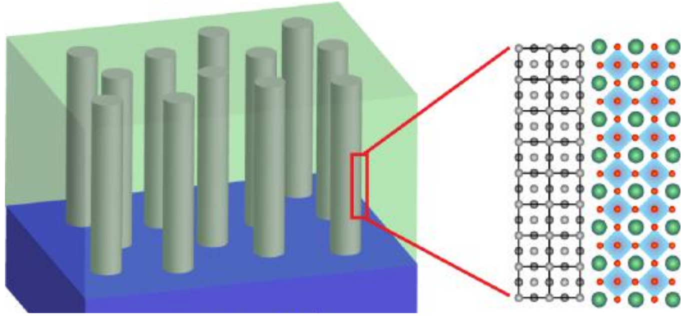
Epitaxial Ni or CoNi NWs in SrTiO3 matrix

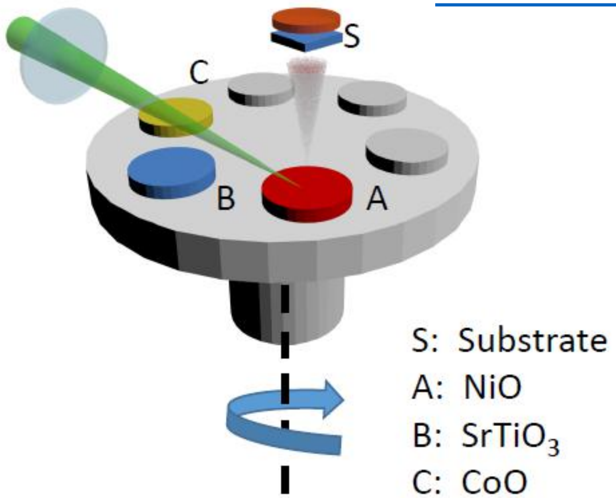


- pulsed laser deposition (PLD)- > see talk by Adam Dubroka
- SrTiO3 (001) substrate

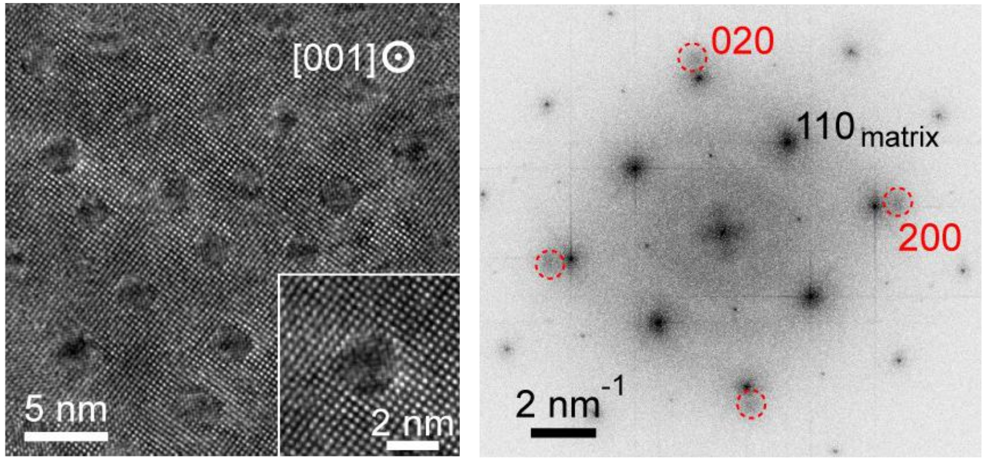
Weng et al., Phys. Rev. Materials 2, 106003 (2018)

Weng, Epitaxial CoxNi1-x nanowires in SrTiO3 matrix: growth, structure and control of magnetic anisotropy, Sorbonne Université (2019)

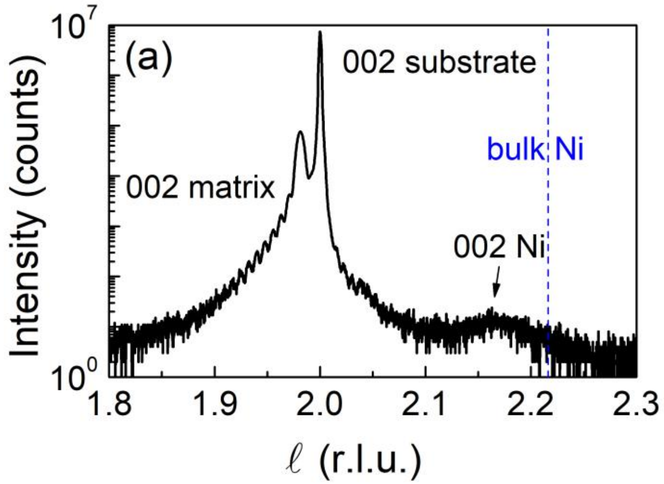




Pulsed Laser Deposition



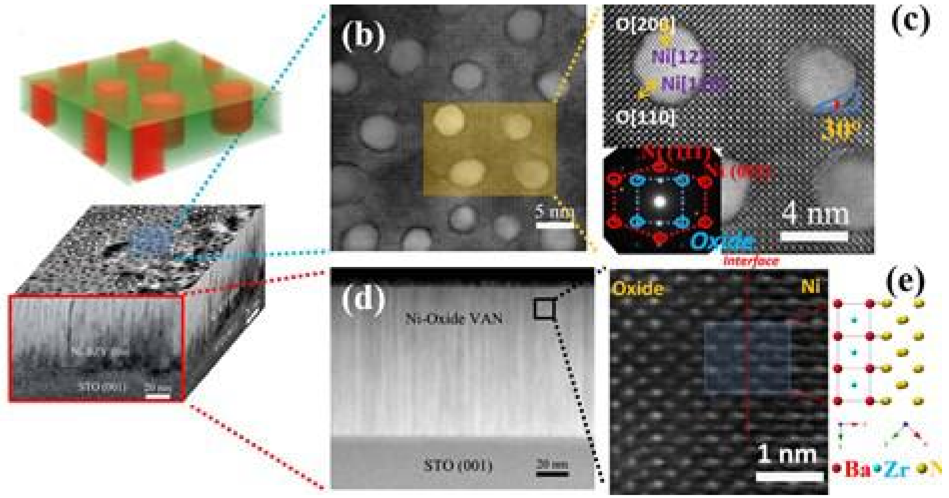
Transmission electron microscopy



X-Ray Diffraction (θ-2θ scan)

See talk by Ondřej Caha

Vertically aligned nanocomposites



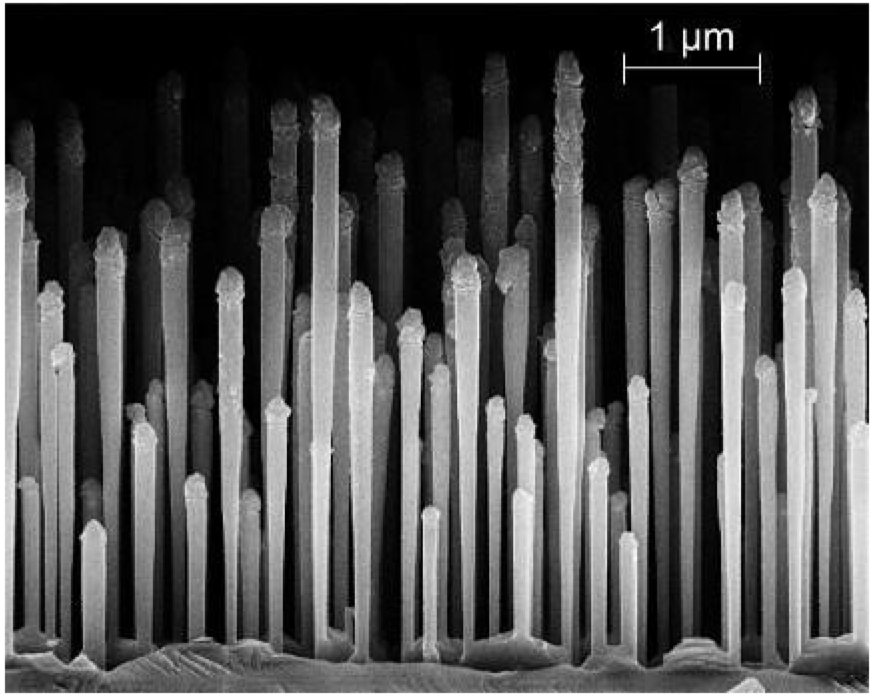
- metal nanopillars embedded in an oxide matrix
  - Co nanowires in CeO2 film on SrTiO3
  - Fe nanowires in BaTiO3 film on SrTiO3

Su et al., *ACS Appl. Mater. Interfaces* **8**, 31, 20283–20291 (2016)

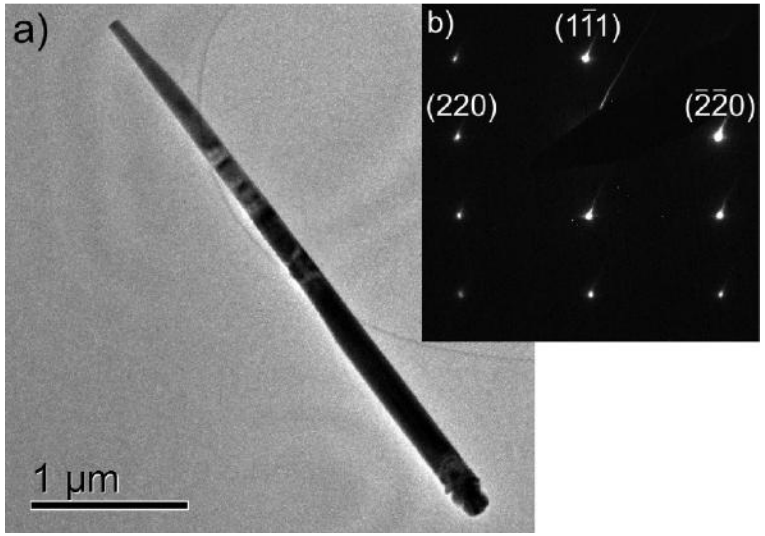
- epitaxial growth of materials with large lattice mismatch
- review: Misra & Wang, *Mater. Horiz.* **8**, 869-884 (2021)
- typical diameter – several nm, length up to 100-200 nm
- formation driven by a combination of strain and surface energy minimization

Molecular Beam Epitaxy

- Molecular Beam Epitaxy – talk by Eduard Hulicius



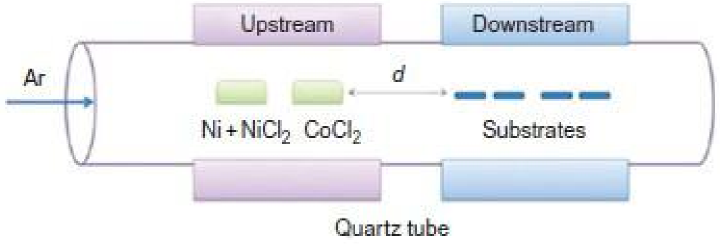
GaMnAs/GaAs core-shell nanowires
Magnetic only below 30K



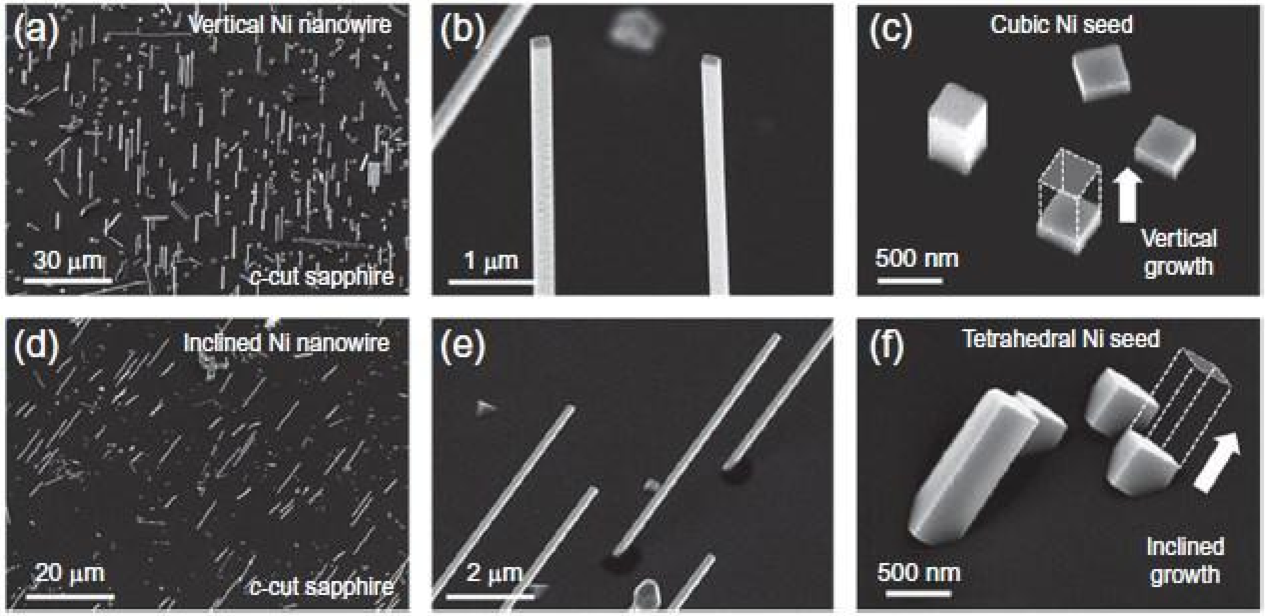
Transmission electron microscopy + diffraction

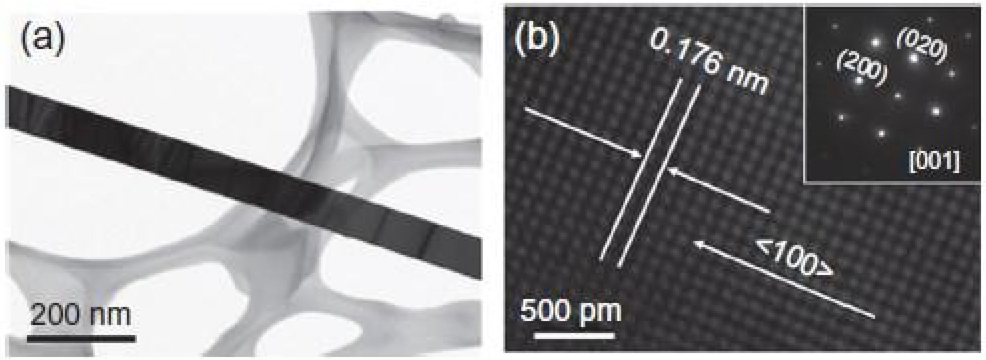
Rudolp, *Nano Lett.* **9**, 11, 3860–3866 (2009)

Epitaxial growth of magnetic nanowires by chemical vapor transport



Ni(001) on c-Al_2O_3 (0001); inefficient control over geometry (diameter >100 nm); also NiCo





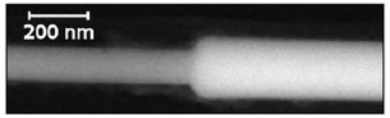
Transmission electron microscopy + diffraction

Lee, Chapter 6 of *Magnetic nano-and microwires: design, synthesis, properties and applications (1st edition)*, Woodhead Publishing (2015)

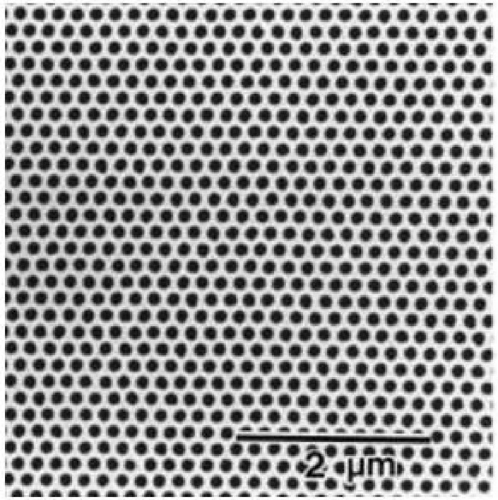
Fabrication of magnetic nanowires (and nanotubes)

- Nanowires from epitaxial thin films
- Molecular beam epitaxy and other vapour depositions

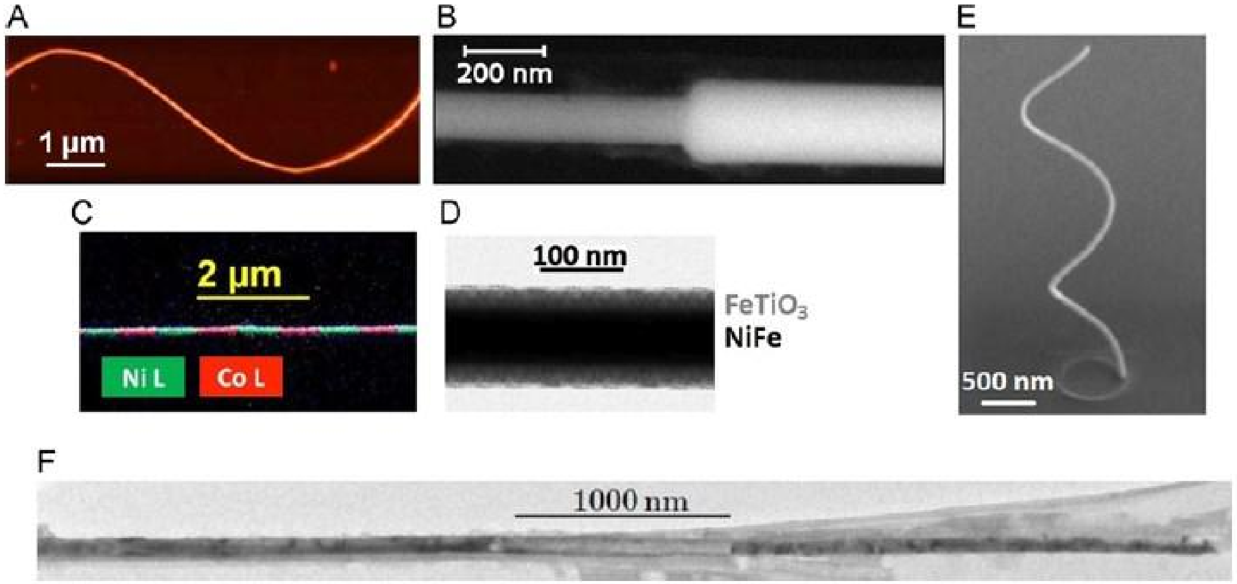
- **Engineered structures, templates**



- Chemical methods (using templates)
  - Electroplating
  - Electroless plating
  - Atomic layer deposition



Simple and engineered structures



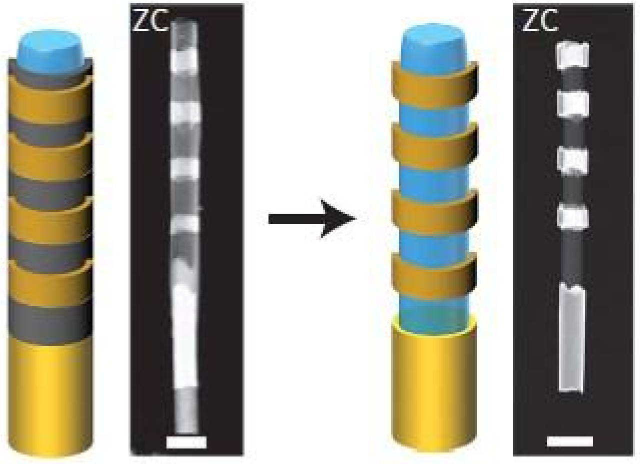
Nanowires (similar for tubes)

- simple (+bent and 3D helix)
- segmented
- modulated diameter
- core-shell (multilayers)
- graded (composition in axial or radial direction)

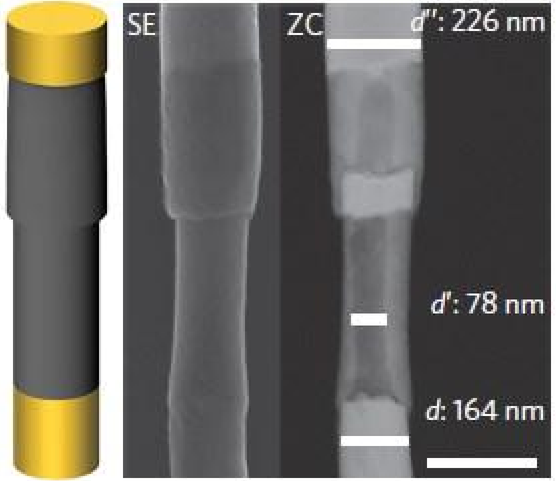
Wire-tube elements

Possible to combine all: **Coaxial lithography**

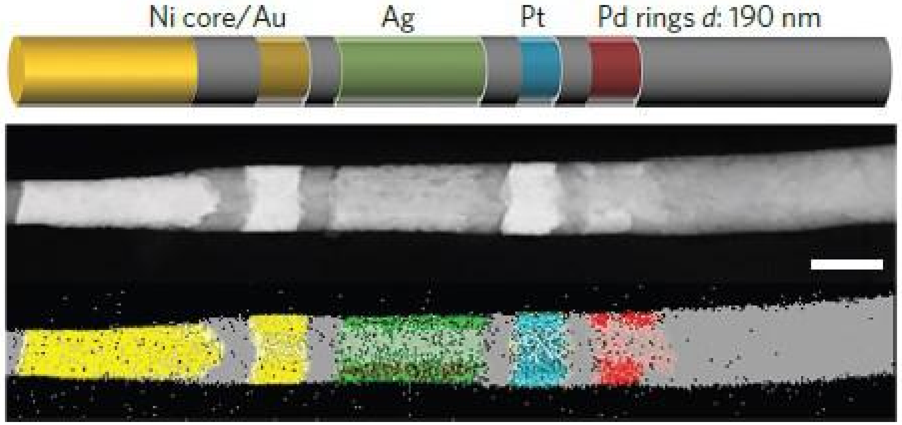
Coaxial ‚lithography‘ (from liquid solution)



Scalebars 500 nm



Scale bar 250 nm



Scale bar 200 nm

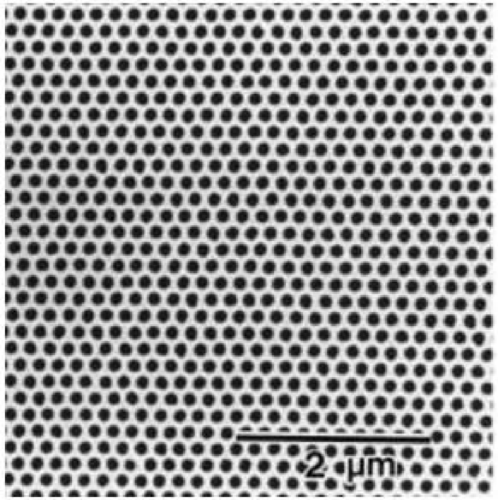
Yellow: Au, Grey: Ni, blue: polymer (polypyrrole or polyaniline)
Combination of chemical methods, selective etching, polymer shrinking, ...
No epitaxy (so far)

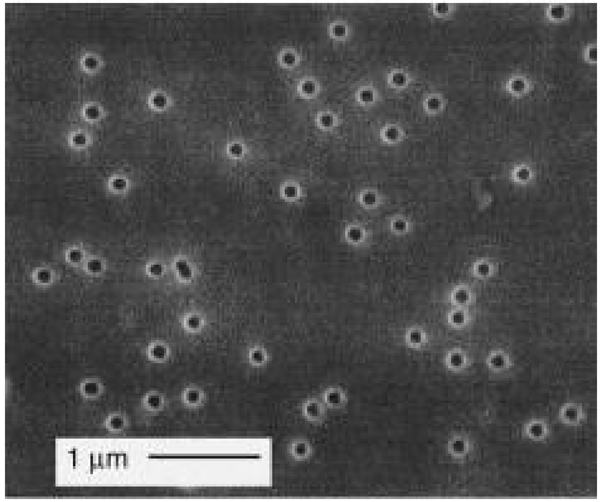
Ozel et al., *Nat. Nanotechnol.* ***10***(4), 319-324 (2015)

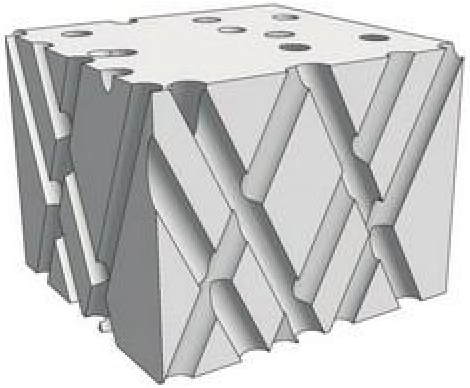
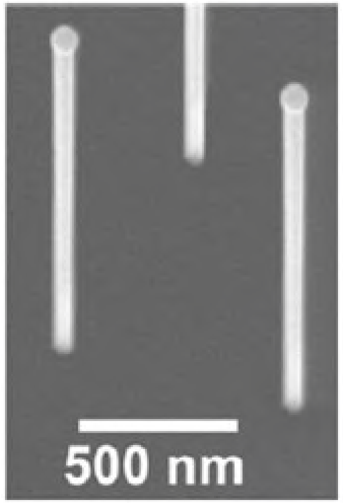
Elephant from clay pieces

Templates, scaffolds

- Aim: Direct and control the growth, obtain desired geometry
- Large scale production, arrays - easier manipulation and measurements
- Option: Dissolve template to release single nanostructures





- Nanoporous templates – nanoporous anodic alumina, ion-track-etched polycarbonate, complex pores in resist via 2photon lithography
- For nanotubes: Arrays of nanowires (often epitaxial semiconductors)

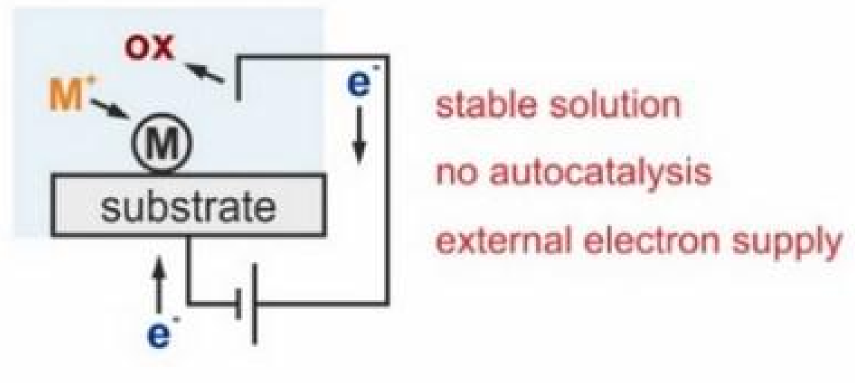
Fabrication of magnetic nanowires (and nanotubes)

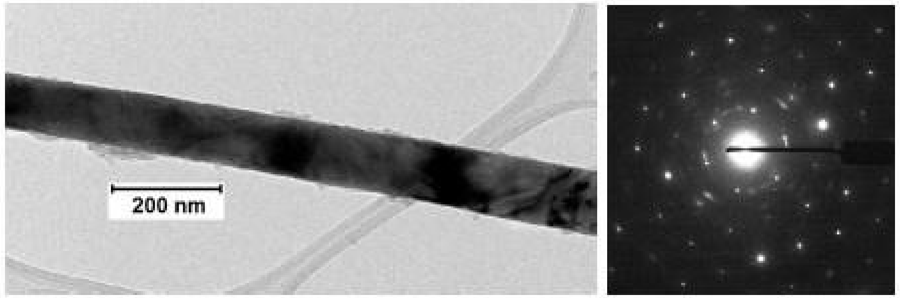
- Nanowires from epitaxial thin films
- Molecular beam epitaxy and other vapour depositions

- Engineered structures, templates

- **Liquid solution-based depositions (using templates)**
  - Electroplating
  - Electroless plating

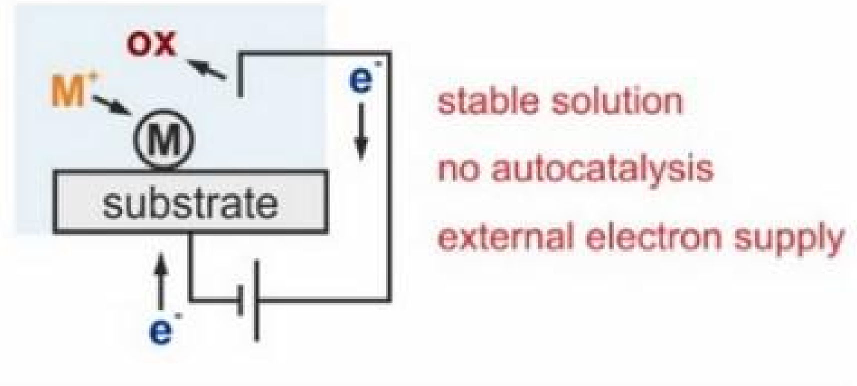
- Atomic layer deposition (using templates)

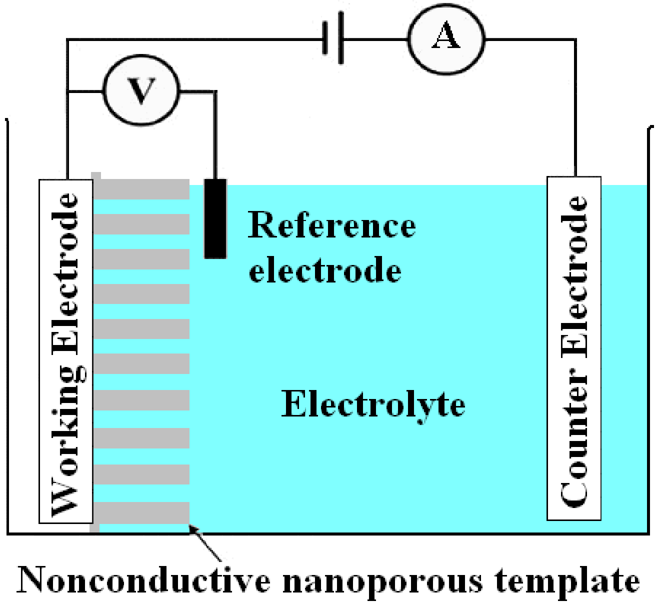




Electroplating (Electrodeposition)

- Reduction of metal cations at cathode (negative electrode); $Ni^{2+} + 2e^{-} \rightarrow Ni$
- Electrolyte = ionic conductor (e.g., $NiSO_4$ dissolved in water + additives)
- Materials - electrically conductive metals, semiconductors, conductive polymers
- For nanowires/tubes: spatially restricted nucleation and growth – nanoporous Al_2O_3 template



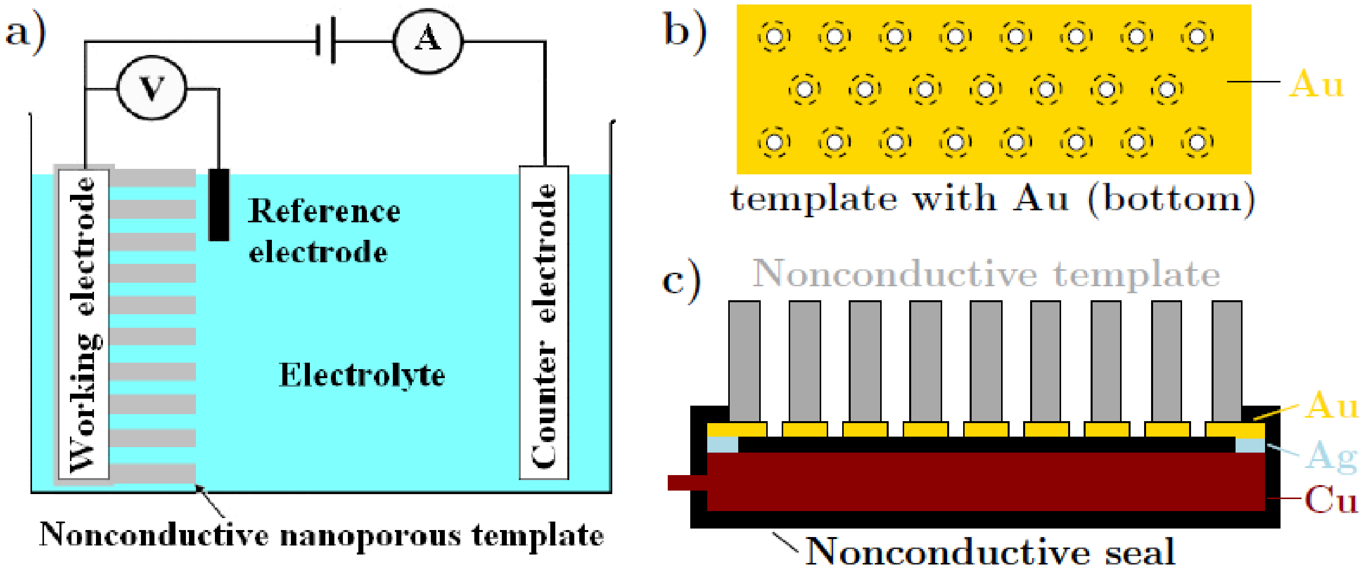


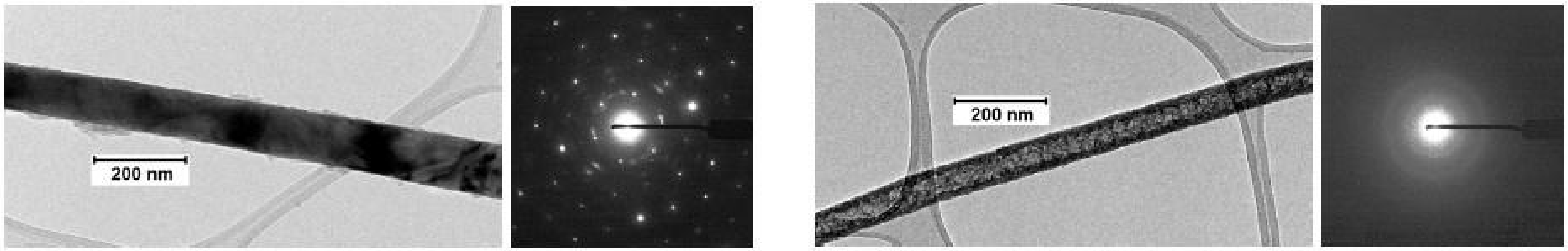
Book: *Modern electroplating* (5th ed.), John Wiley & Sons (2010)

Epitaxial growth (films, islands) – reviews (mostly non-magnetic):
Switzer & Banik, *Acc. Chem. Res.* **56**(13), 1710-1719 (2023)
Guo, *Nano Trends* **4**, 100024 (2023) – some works only textured deposits or preferred crystal orientation

Electroplating - How to get nanotubes instead of solid nanowires

- porous working electrode
- low pH (acidic solution)
- more negative potential
- lower concentration of metal ions



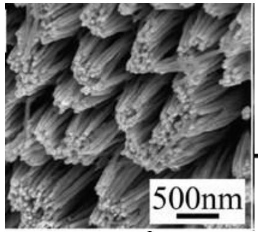


(a) Nanowire (diameter ≈ 100 nm)

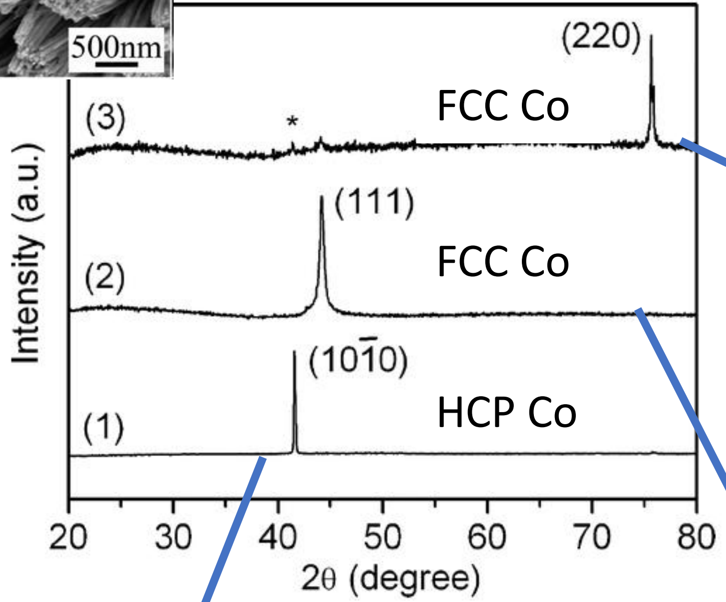
(b) Nanotube (diameter ≈ 70 nm, tube wall 10-18 nm)

Electroplated NiCo nanostructures: (a) nanowire, (b) nanotube. Transmission electron microscopy + selected area electron diffraction (Laurent Cagnon, Institut Néel).

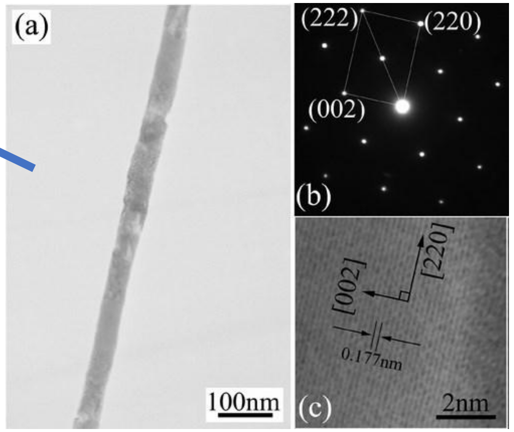
Electroplating - Crystal Control (Co example)

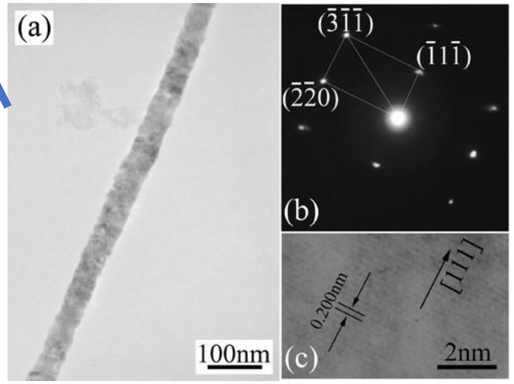


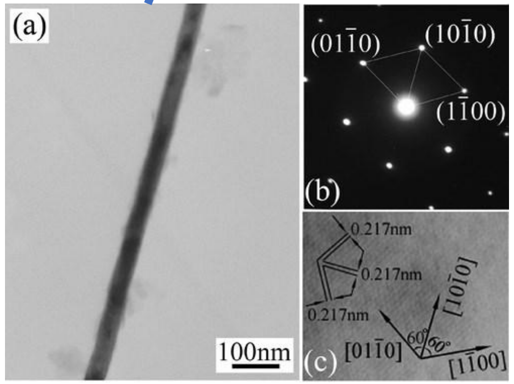
X-Ray Diffraction on arrays
-> talk by Ondřej Caha



Co Nanowires,
40 nm diameter





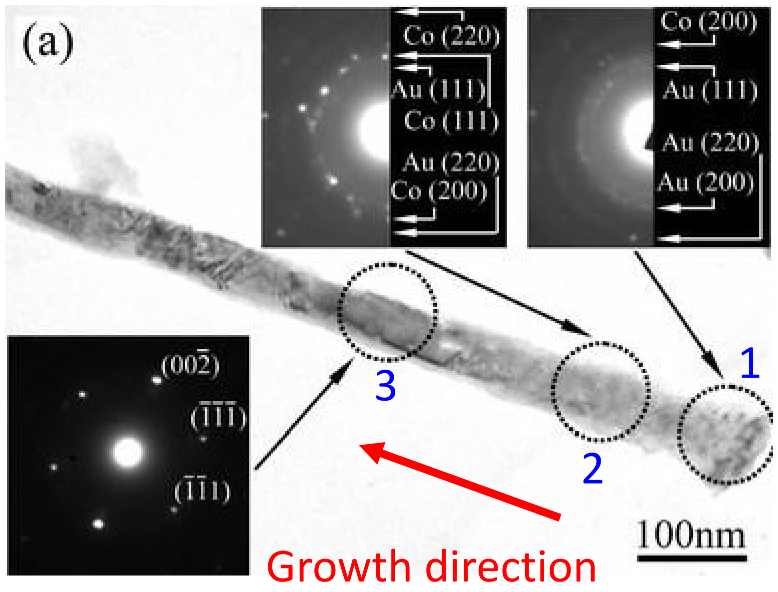


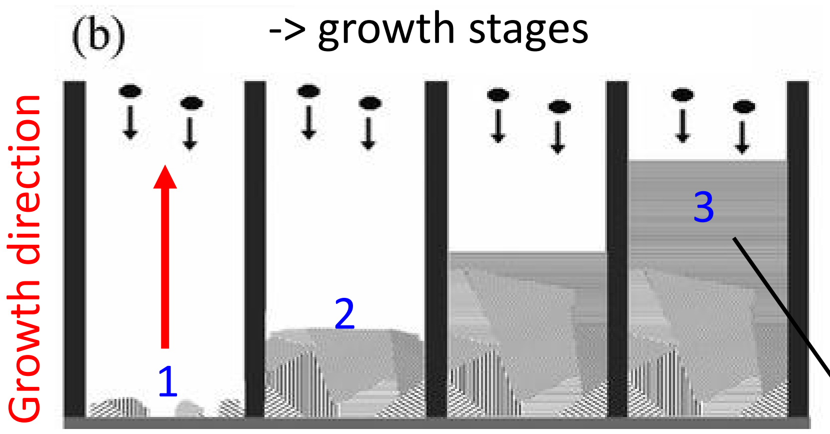
Same template, different deposition conditions

(voltage pulses and acidity)

Orientation-Controlled Synthesis and Ferromagnetism of Single Crystalline Co Nanowire Arrays, Huang, *J. Phys. Chem. C* **112**, 1468-1472 (2008)

Electroplating - Crystal Control (Co example)





Deposition typically on polycrystalline Au electrode

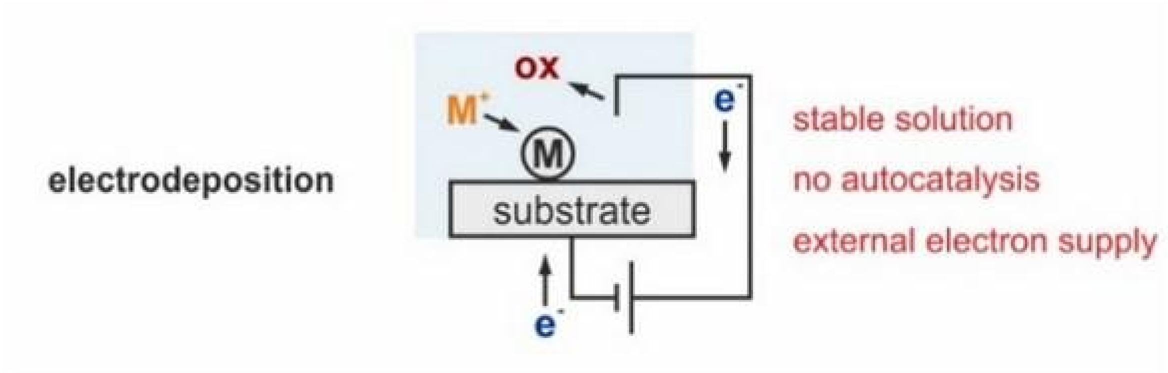
Prefered Co crystal orientation set by deposition parameters (voltage, acidity, ...). Then homoepitaxy.

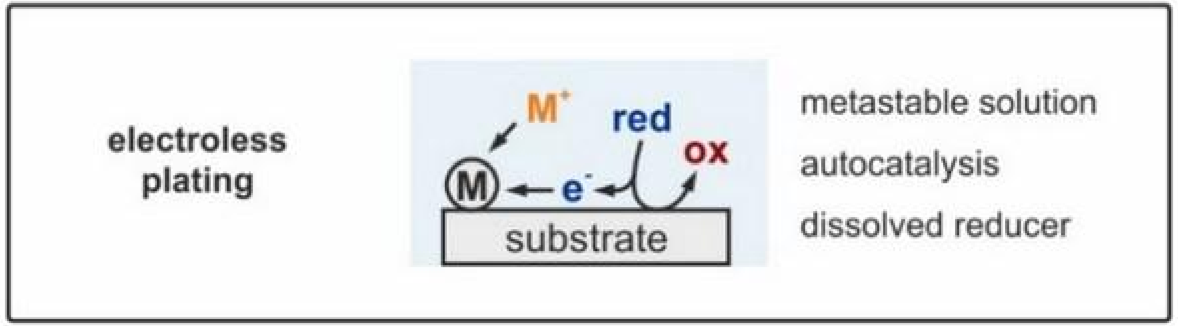
Co starts as polycrystal (following Au electrode)

Orientation-Controlled Synthesis and Ferromagnetism of Single Crystalline Co Nanowire Arrays, Huang, *J. Phys. Chem. C* **112**, 1468-1472 (2008)

Electroless plating

Similar to electroplating – reduction of metal ions from solution



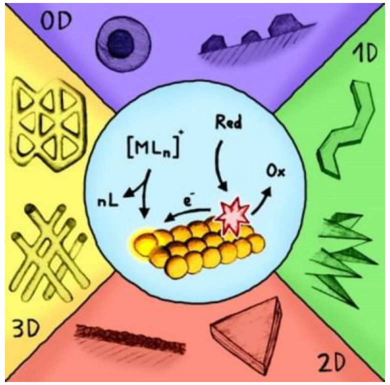


Difference: electrons for reduction from added reducing agent

(auto)catalysis – reduction only on catalyst seeds or already grown material

Review: Electroless Plating of Metal Nanomaterials

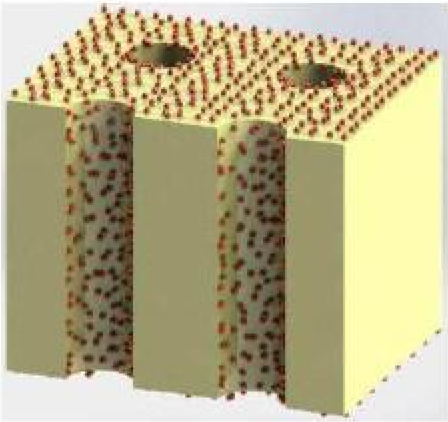
[Muench, *ChemElectroChem* **8**(16), 2993-3012 (2021)]



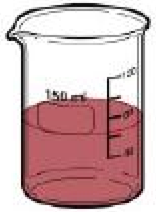
Electroless plating of nanotubes

Conformal coating of modified walls of porous template

- Surface sensitization ($SnCl_2$), activation with Pd seeds ($PdCl_2$)
- Selective deposition (metal reduction) on Pd seeds (plating bath)
- Removal of top/bottom layer, template dissolution

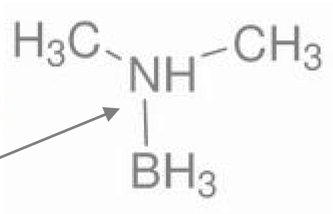


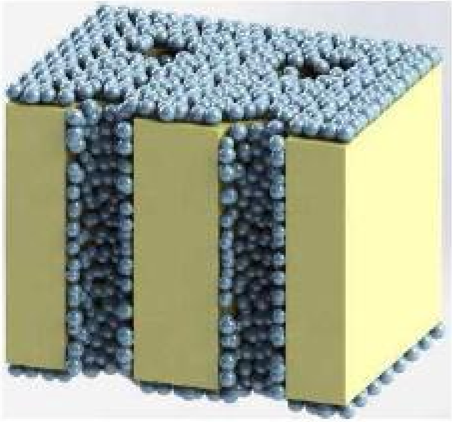
Template with Pd seeds



Plating bath

metal salts ($CoSO_4$, $NiSO_4$)
reducing agent (DMAB)
stabilizing agent (sodium citrate)



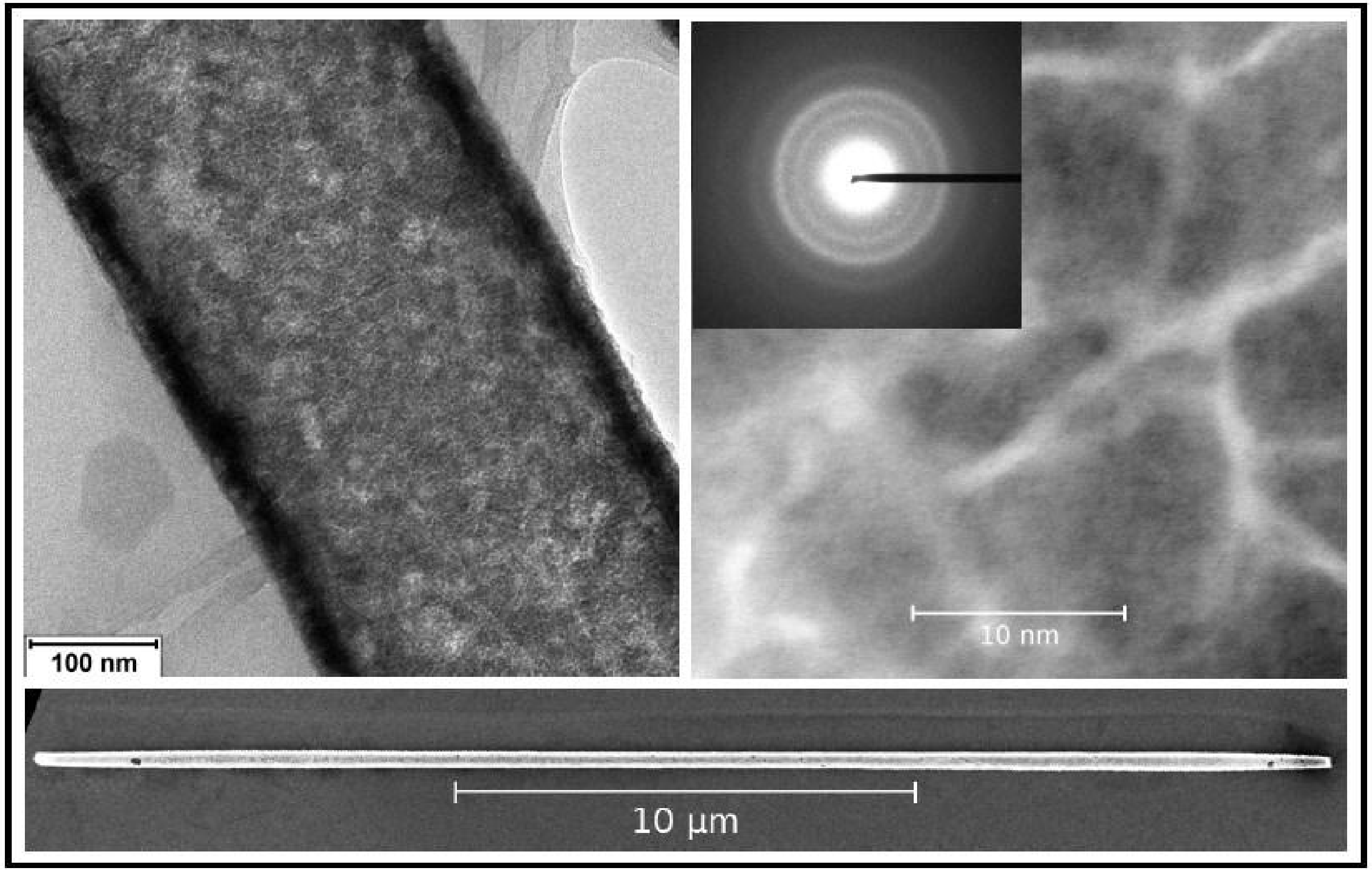


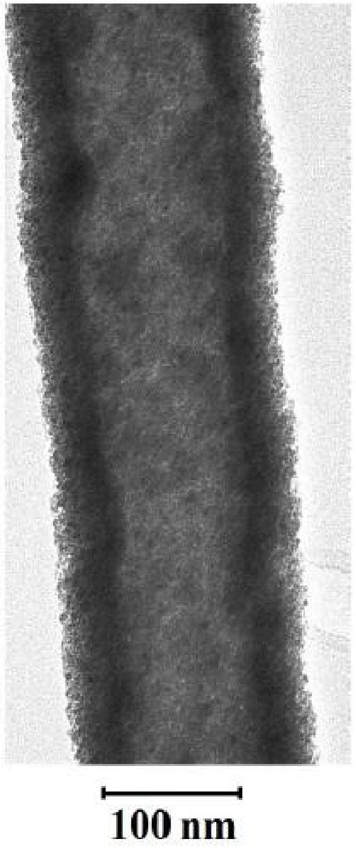
Initial tube growth

Images of templates: Richardson et al., *ECS Trans.* **64** (31), 39-48 (2015)

Deposition of **metals, alloys, oxides**; no need for conductive substrate

Electroless plating - CoNiB nanotubes (example)





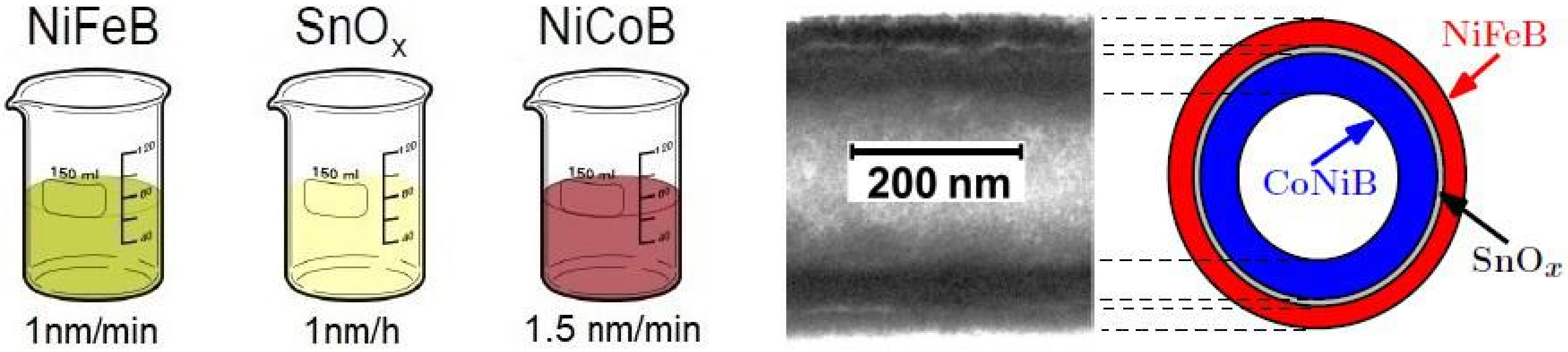
$(Co_{80}Ni_{20})B$ nanocrystalline tubes: *RSC Adv.* **6**, 70033-70039 (2016)
Diameter 300-400 nm, length 30 µm, wall thickness ≈ 30 nm

Staňo et al., *SciPost Phys.* **5**, 038 (2018)

Electroless plating - Multilayered nanotubes

Electroless plating of $NiFeB/SnO_X/CoNiB$ multilayered tubes

SnO_X - non-magnetic spacer; selected for ease of deposition

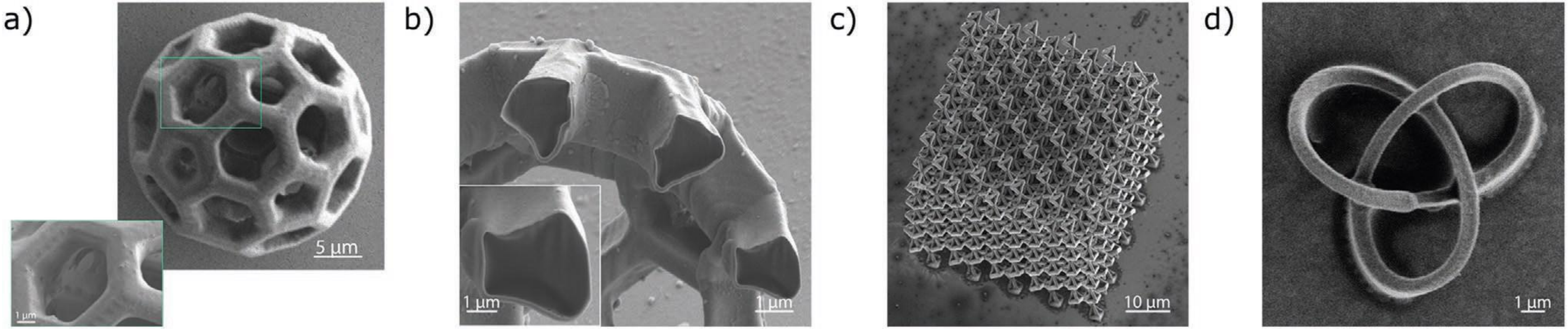


Different deposition solutions with layer deposition rates

[Staňo, *Magnetic microscopy of domains and domain walls in ferromagnetic nanotubes*, Université Grenoble Alpes (2017)]

Electroless plating – Coating of complex 3D scaffolds

Conformal = covers uneven surfaces, holes, ... nearly everything ☺
3D scaffolds created by two-photon lithography

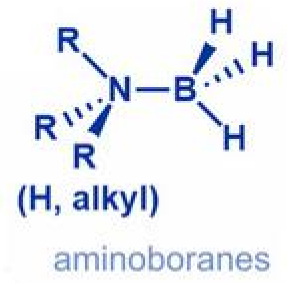


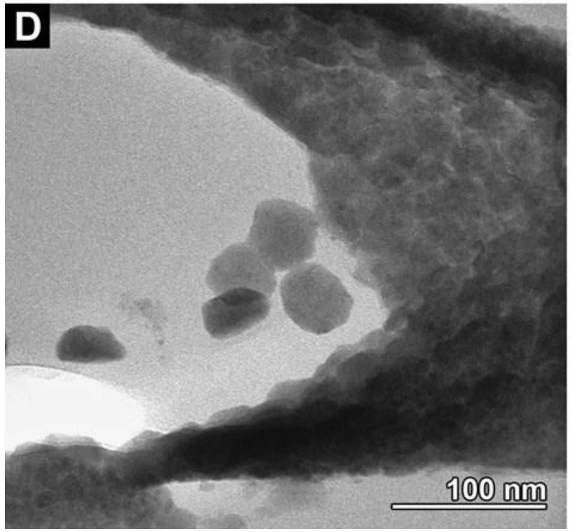
3D polymer structures with magnetic NiFe(B) coating by electroless plating

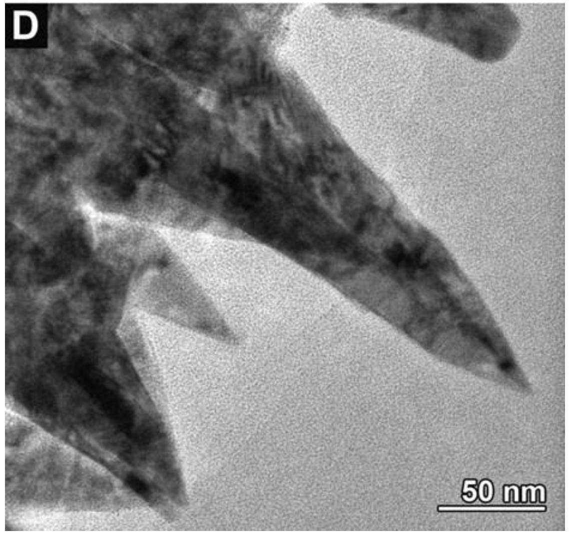
Pip, *Small* **16**, 2004099 (2020)

Crystallinity control via reducing agent

- Reducing agents (chemicals) often contain: Boron, Phosphorus
  These can be incorporated in the deposit
- Larger amount of boron/phosphorus -> amorphous
  Small amount -> (poly)crystalline
- Different agent (no B or P, like hydrazine): crystals, but spiky surface



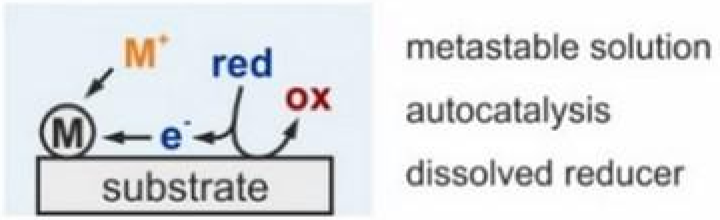


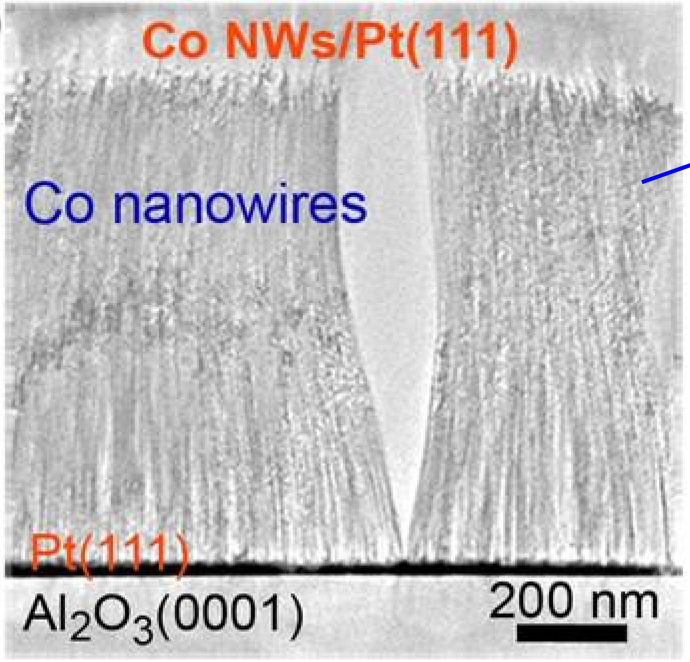


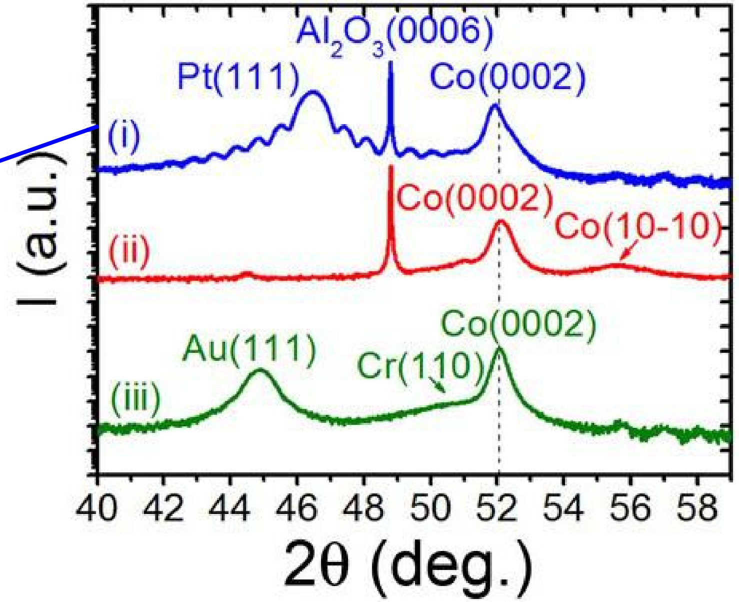
Ni deposits, Muench, J. Power Sources **222**, 243-252 (2013)

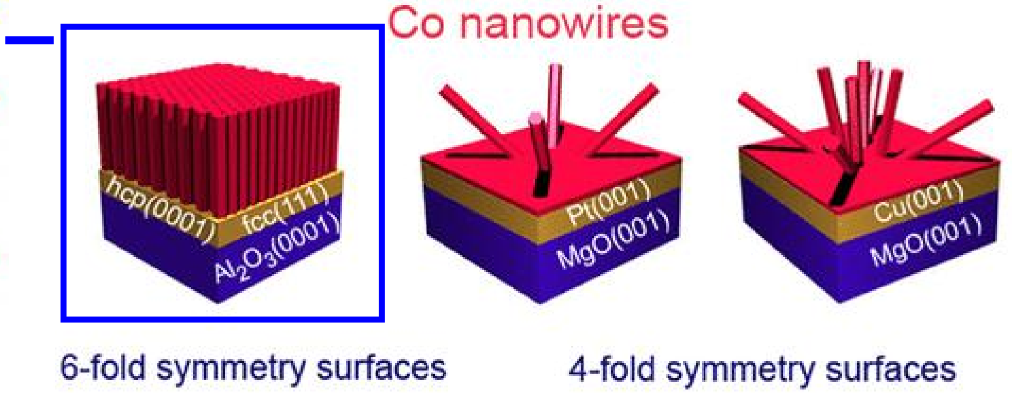
Epitaxial Growth from liquid solution (no template)

- Deposition from non-aquous Co solution (reduction of metal complex on seed films)
- Epitaxy on Pt(111), Co(0001), Au(111), ... -> dense arrays of Co nanowires
- „Solution Epitaxial Growth“, no mention of electroless plating; yet similar (heterogenous catalyzed reduction with dissolved reducing agent;
  extra: ligands blocking lateral growth – so not conformal coating)









X-Ray diffraction (talk by Ondřej Caha)

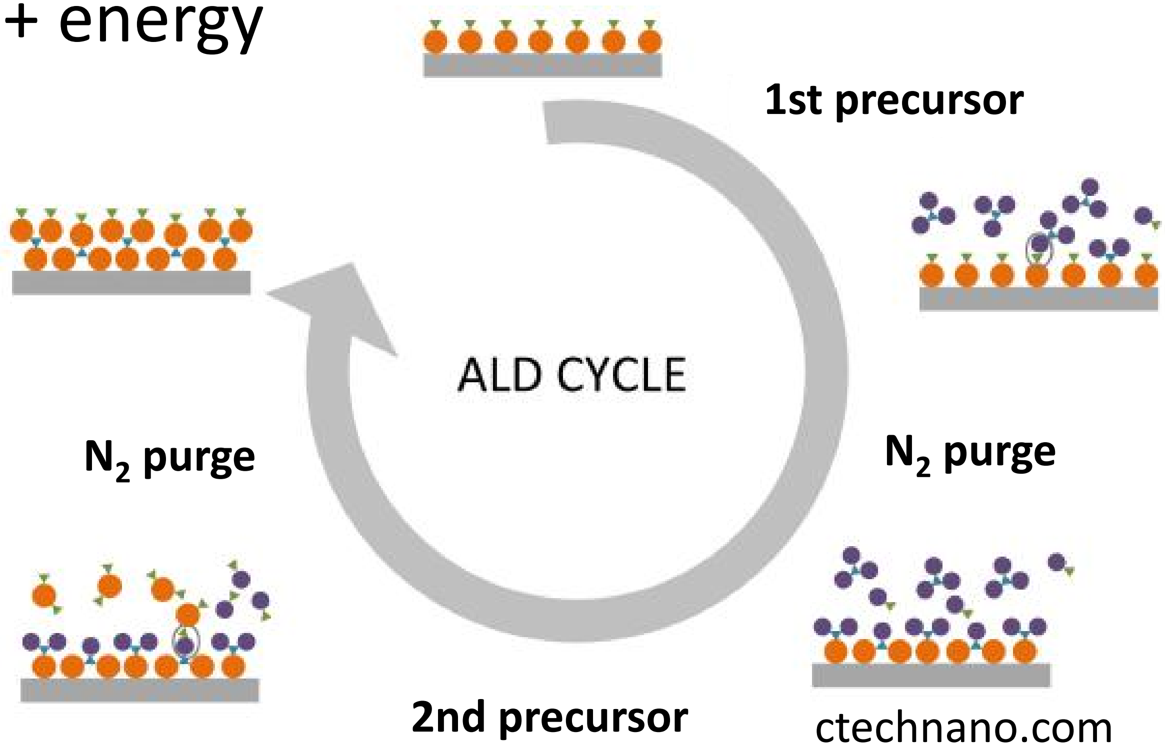
Liakakos, *ACS Nano* **9**, 10, 9665–9677 (2015)

Atomic layer deposition (ALD)

Started as Atomic layer epitaxy
J. Appl. Phys. **60**, R65–R82 (1986); Short history

- Special mode of Chemical Vapour Deposition (CVD)
- Sequential self-limiting surface chemical reactions
  precursor 1 + precursor 2 (reactant) + energy

pros and cons
- surface chemistry-dependent
- slow, coating could be very granular
+ thickness control @ atomic scale
+ conformal coating (uneven surfaces, pores)



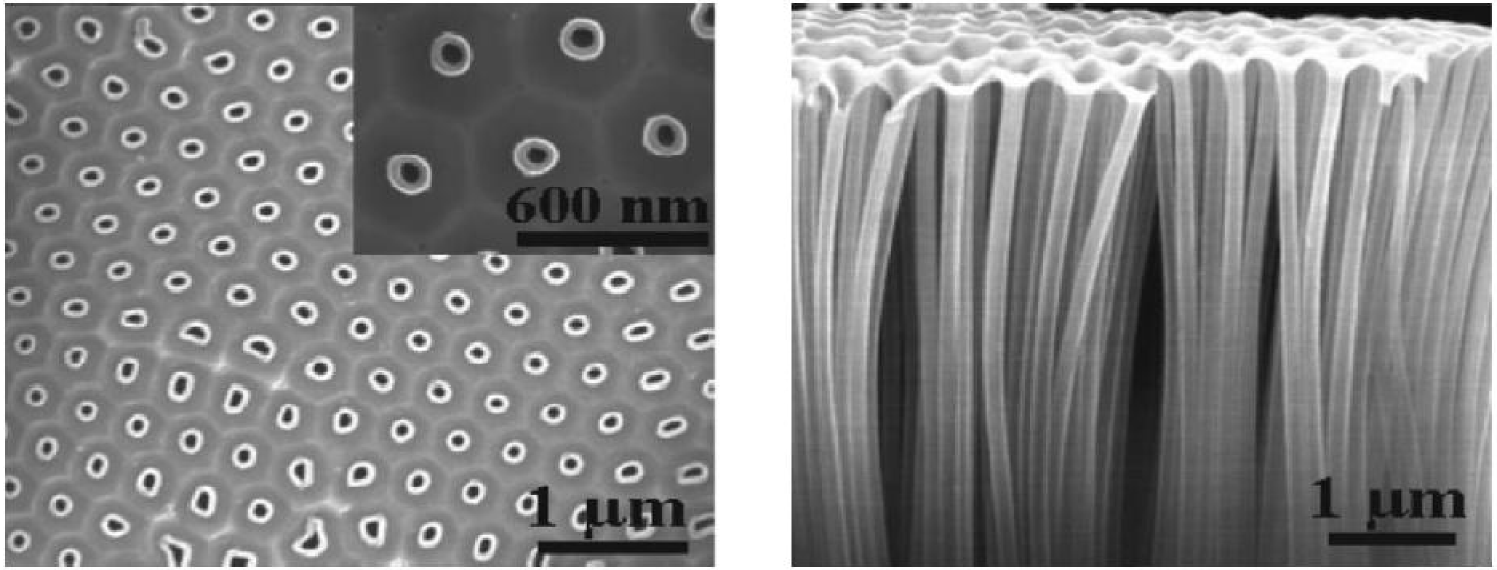
ctechnano.com

ALD Review: George, *Chem. Rev.* **110**, 1, 111–131 (2010)
List of materials (oxides, nitrides, metals, …): Miikkulainen, *J. Appl. Phys.* **113**, 021301 (2013)
Recipes and various info: https://www.plasma-ald.com/

ALD example – Nanotubes in porous template

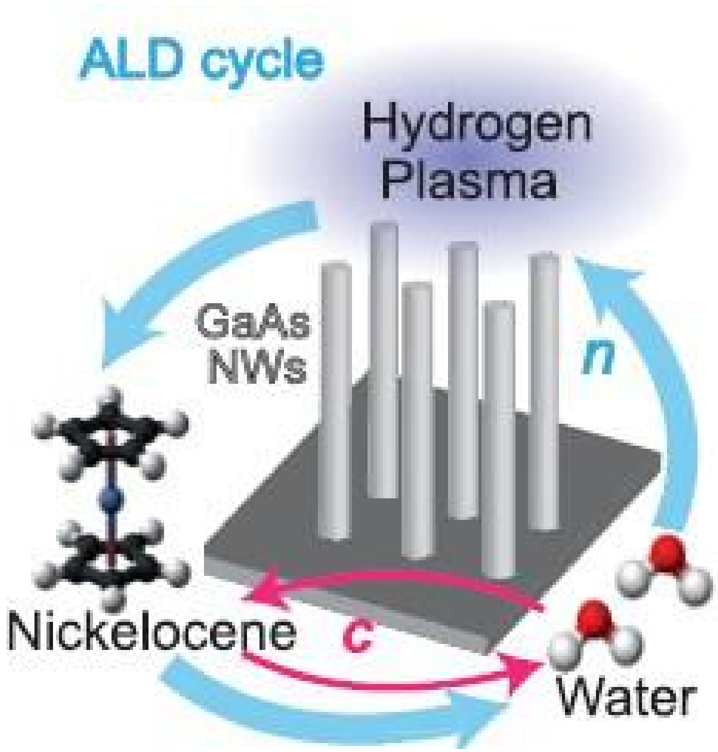
Deposition of (non-ferromagnetic) oxide, reduction to metal later

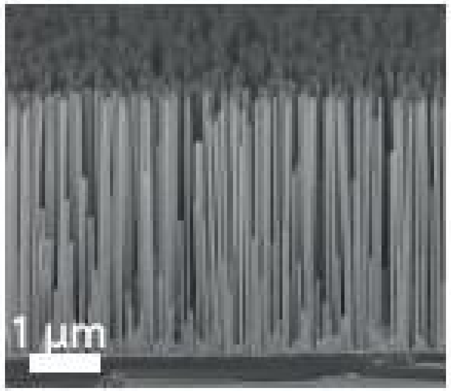
Example: Ni, Co Nanotubes – *JAP* **111**, 09J111 (2007)
Template: pore diameter 35 nm and 160 nm, length 2-50µm
Precursor: nickelocene (NiCp2)+H_2O vapour – gives oxide
Reduction better after ALD – Ar+5 % H_2 (lower grain size)

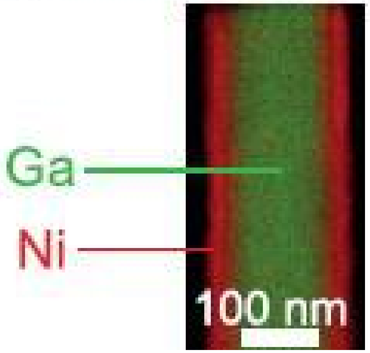


SEM images: TiO_2/Ni/TiO_2 tubes. Left: in template (top-view), Right: liberated.

ALD example – Nanotubes on single-crystalline GaAs nanowires

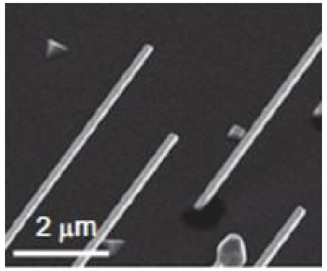




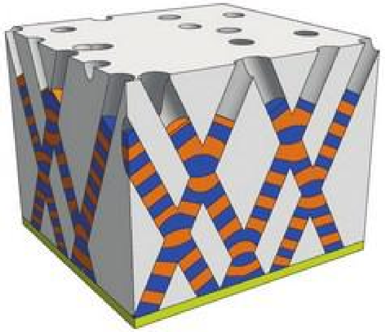


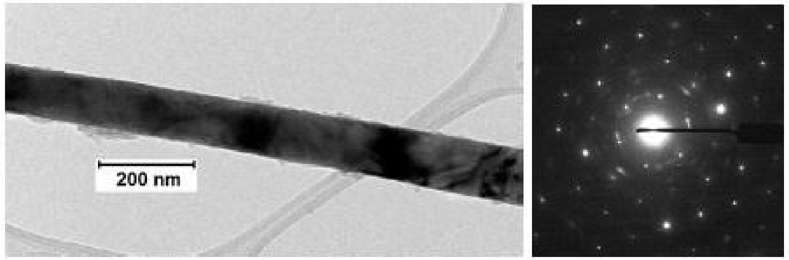
Giordano, ACS Appl. Mater. Interfaces 12, 40443–40452 (2020)

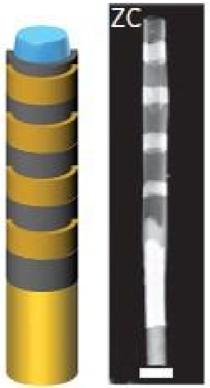
Summary – Nanowire & nanotube depositions



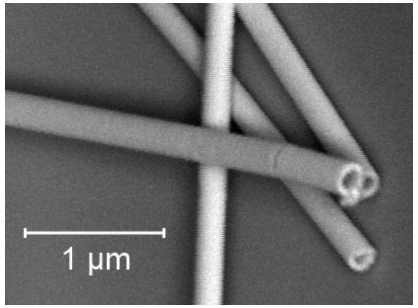
- **Common epitaxy techniques (vapour depositions):**
  vacuum & temperature; high crystal quality, limited geometry control
- **Electrodeposition in templates** (liquid solution / water based)
  complex structures and geometry, crystal control possible







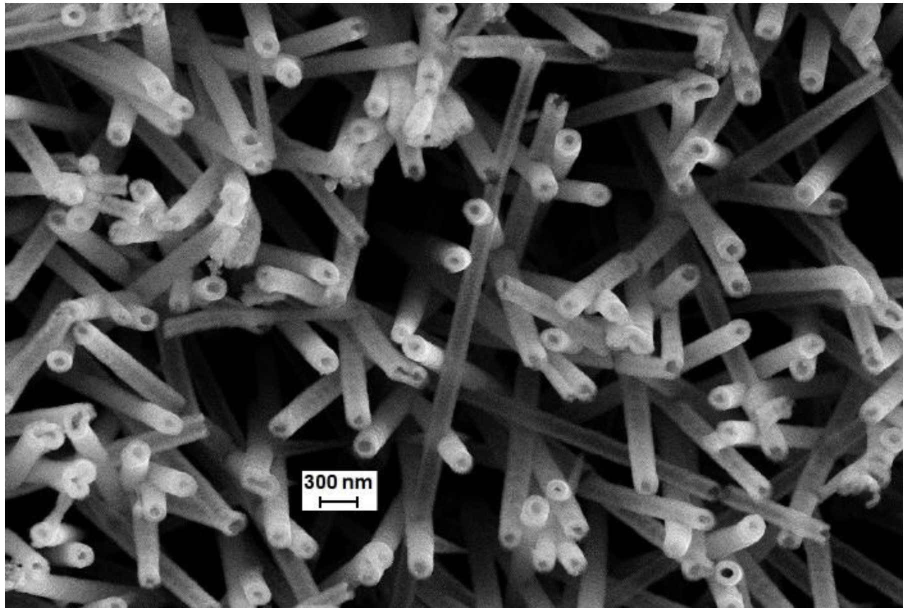
- Nanotubes: **electroless plating, atomic layer deposition**
  conformal coating of complex scaffolds; often nanocrystalline



Acknowledgement

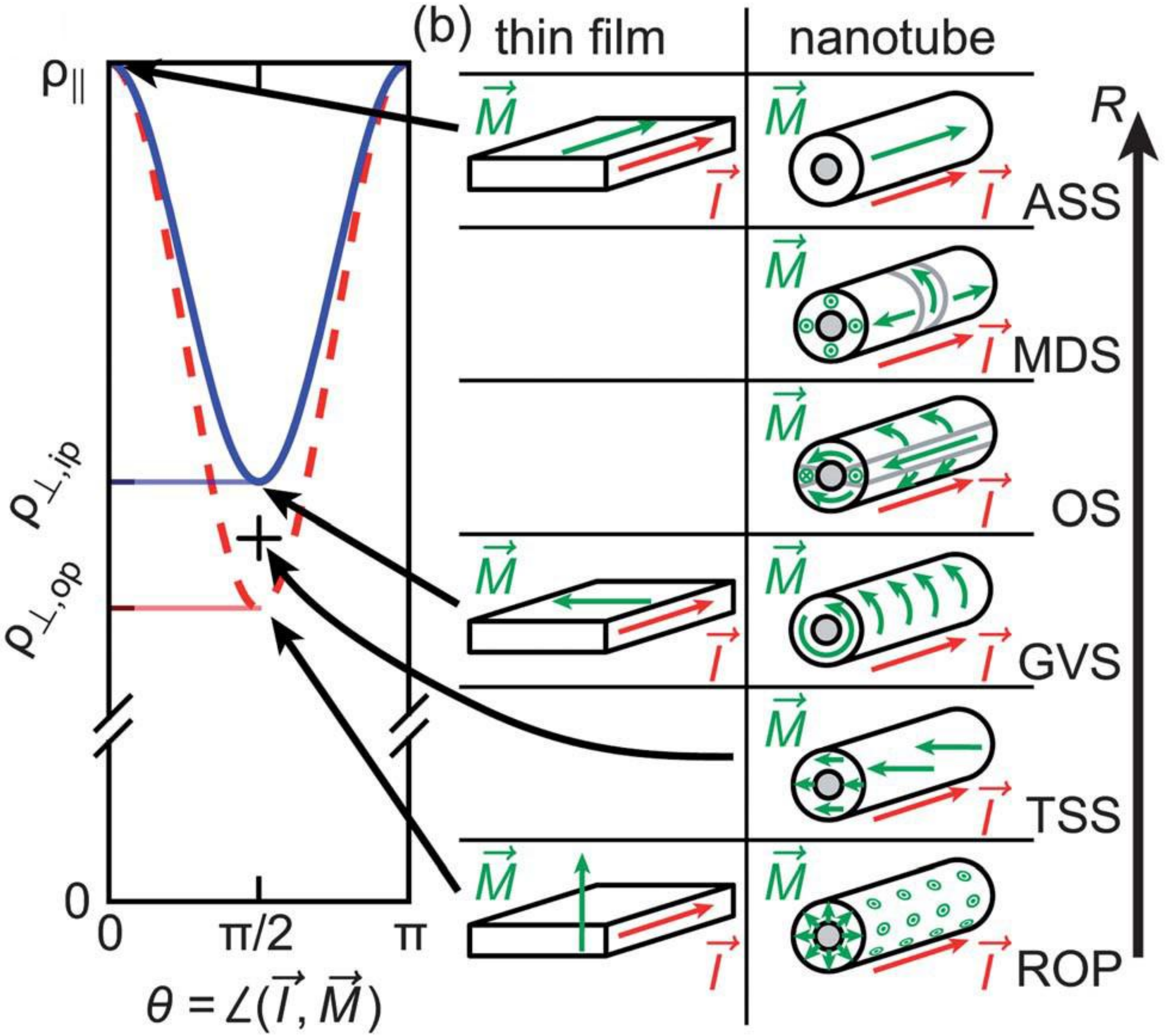
Jon Ander Arregi, Ondřej Wojewoda, Vojtěch Uhlíř

Questions & Discussion



Additional slides

Anisotropic Magnetoresistance (AMR)

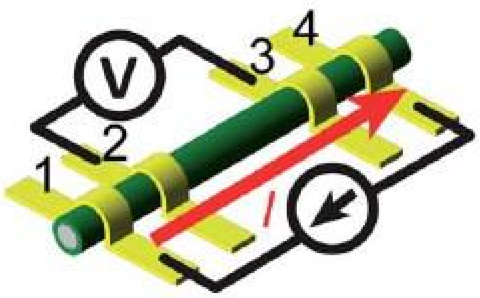


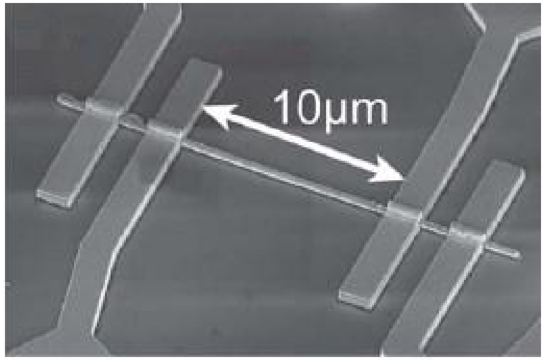
Resistance depends on angle between magnetization and applied current

max R: **M**, **I** parallel

min R: **M**, **I** perpendicular

M can be set by external magnetic field





Rüffer, *Nanoscale* **4**, 4989 (2012)

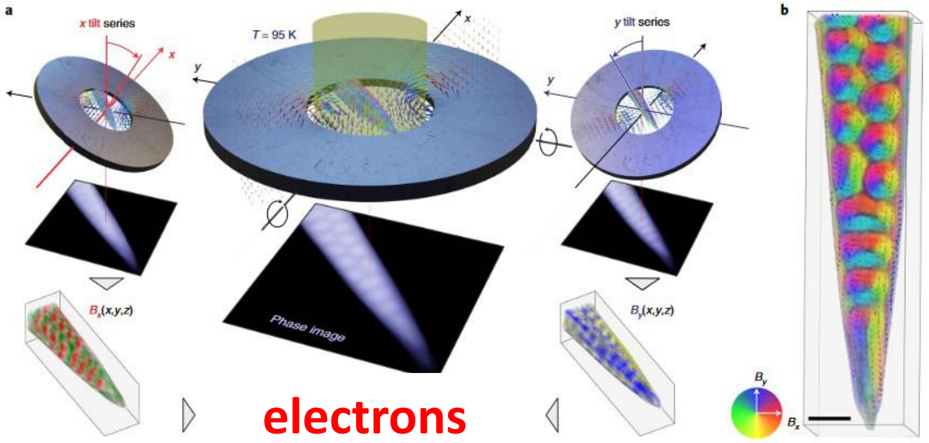
Longitudinal resistance, 4 probes

How to resolve magnetization in 3D?

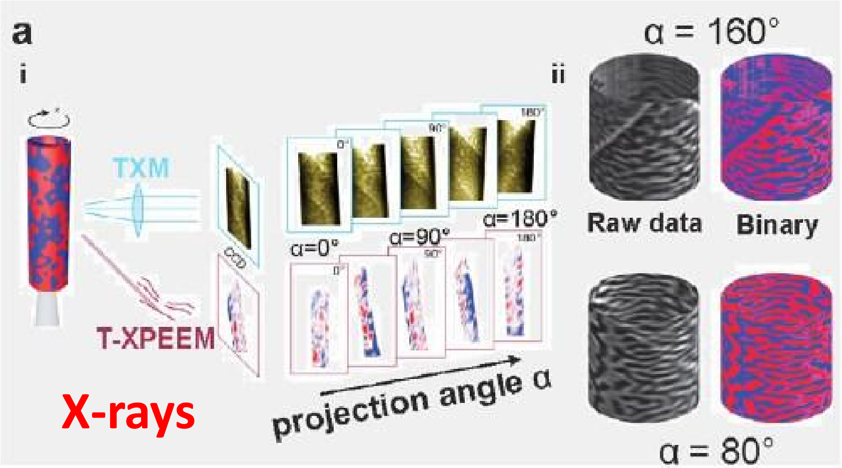
Typical approach - **Tomography using electrons or polarized photons** (X-Rays):

Electrons - Transmission electron microscopy, e.g., electron holography

Polarized photons – synchrotron X-rays, utilizing X-ray magnetic (circular) dichroism: transmission X-ray microscopy, ptychography, holography (lense-less)



Wolf, *Nat. Nanotechnol.* **17**(3), 250-255 (2022)



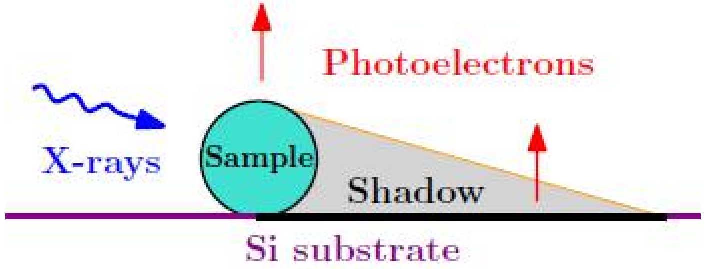
Streubel, *Nat. Commun.* **6**, 7612 (2015)

<u>Review (3D with X-rays)</u>: Donnelly, *J. Phys.: Condens. Matter* **32**, 213001 (2020)

Alternative: The dark side - shadow

Shadow X-Ray PhotoEmission Electron Microscopy

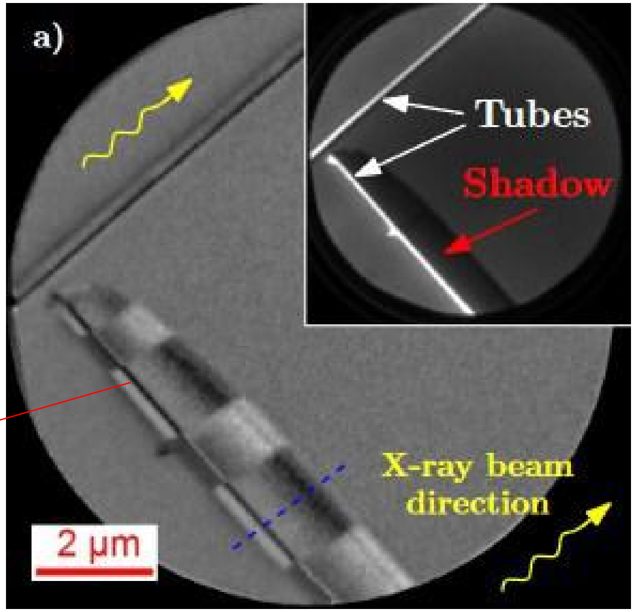
- **X-PEEM**, shadow = transmission info
- **Both surface and volume** info, no tomography
  projection of magnetization to beam direction
- Technique: [Jamet et al., *PRB* **92**, 144428 (2015)]



Co-C nanowire

[Wartelle, *Nanotechnology* **29**, 045704 (2018)]

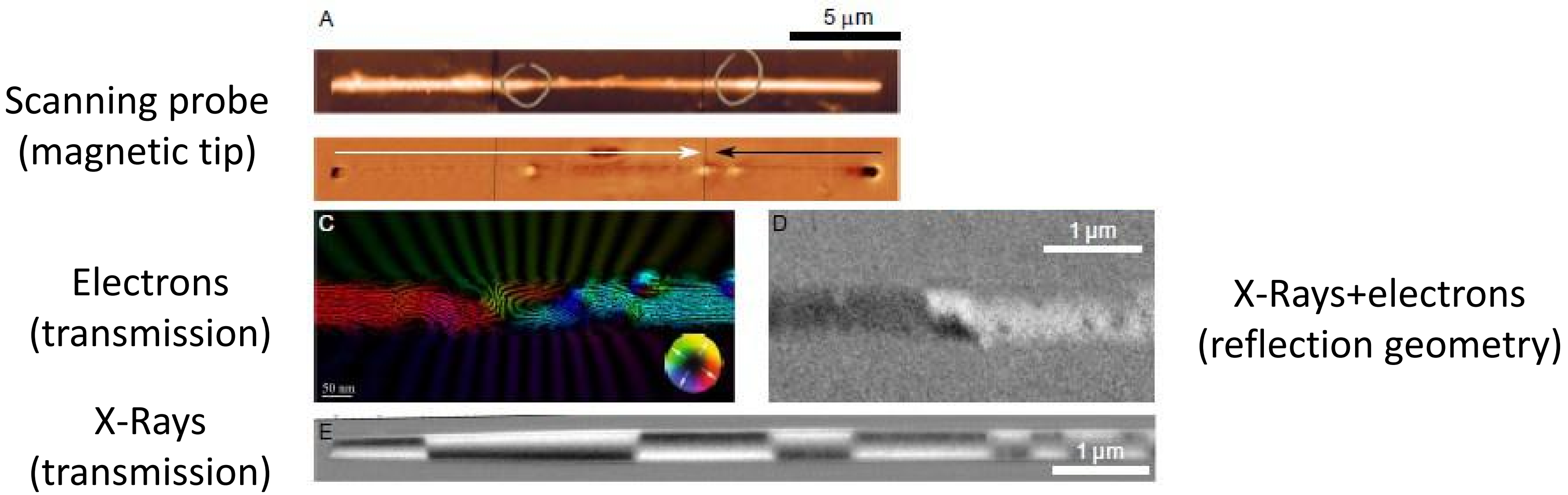
Different magnetic domains



CoNiB nanotubes

Staňo, *SciPost Phys.* **5**, 038 (2018)

Additional magnetic imaging techniques

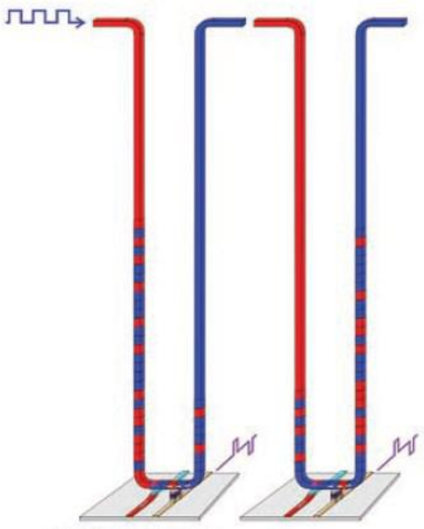


A) CoNi wire: Atomic force microscopy (top) and Magnetic force microscopy (MFM)
C) CoNi wire: Electron holography – reconstructed magnetic induction near domain wall
D) CoNi wire: Shadow XMCD-PEEM with circularly polarized X-Rays near domain wall
E) CoNiB tube: Scanning transmission X-Ray microscopy with circularly polarized X-Rays, many domains

Staňo & Fruchart, Magnetic nanowires and nanotubes, in *Handbook of magnetic materials* (Vol. 27, pp. 155-267), Elsevier (2018). Also on arXiv.

Magnetic nanowires - Applications

- Biomed: magnetic resonance imaging, magnetic hyperthermia, catalysis
- Sensors: magnetoresistance sensors; giant magnetoimpedance
- RF signal processing: microwave absorption, filters, phase shifters, ...

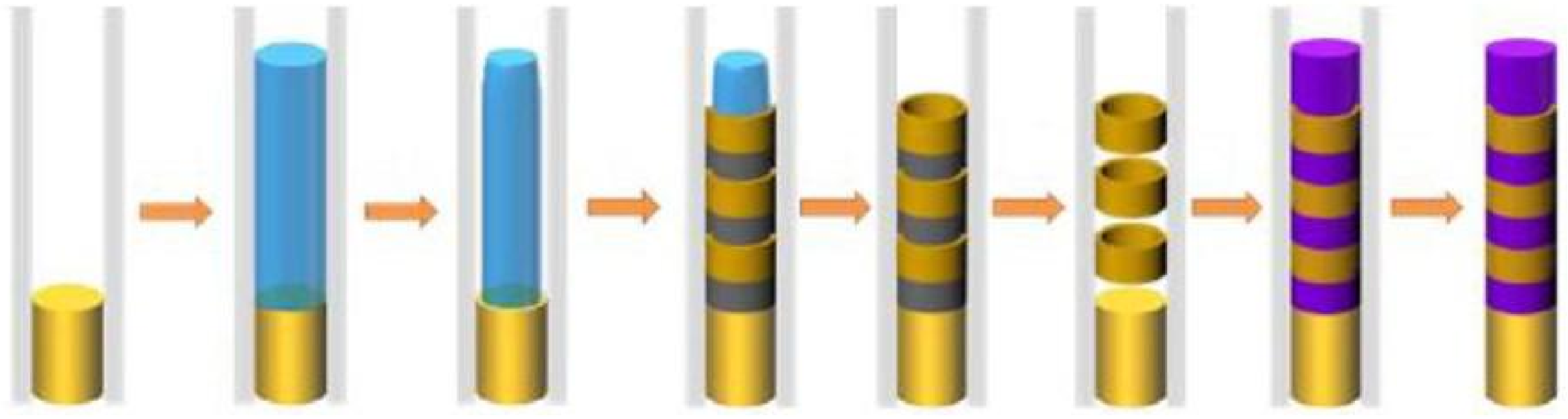


Magnetic racetrack memory (**concept**)
Parkin, Science 320(5873), 190-194 (2008)

Commercial products available in case of microwires

Staňo & Fruchart, Magnetic nanowires and nanotubes, in *Handbook of magnetic materials* (Vol. 27, pp. 155-267), Elsevier (2018). Also on arXiv.

Coaxial lithography – sequence example



Yellow: target material (Au)
Blue: sacrificial organic core (polyaniline)
Purple: any conductive material
Grey: sacrificial material (Ni)

ED = ElectroDeposition

Ozel et al., *Nat. Nanotechnol.* ***10***(4), 319-324 (2015)

Au ED

polymer ED

polymer shrinking ↑ vacuum drying

Ni/Au ED

polymer dissolution ↑ acetone

Ni etching ↑ $FeCl_3$

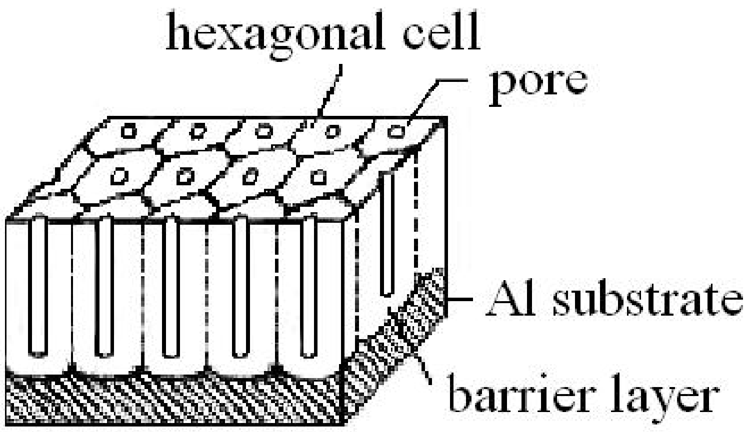
MnO2 ED

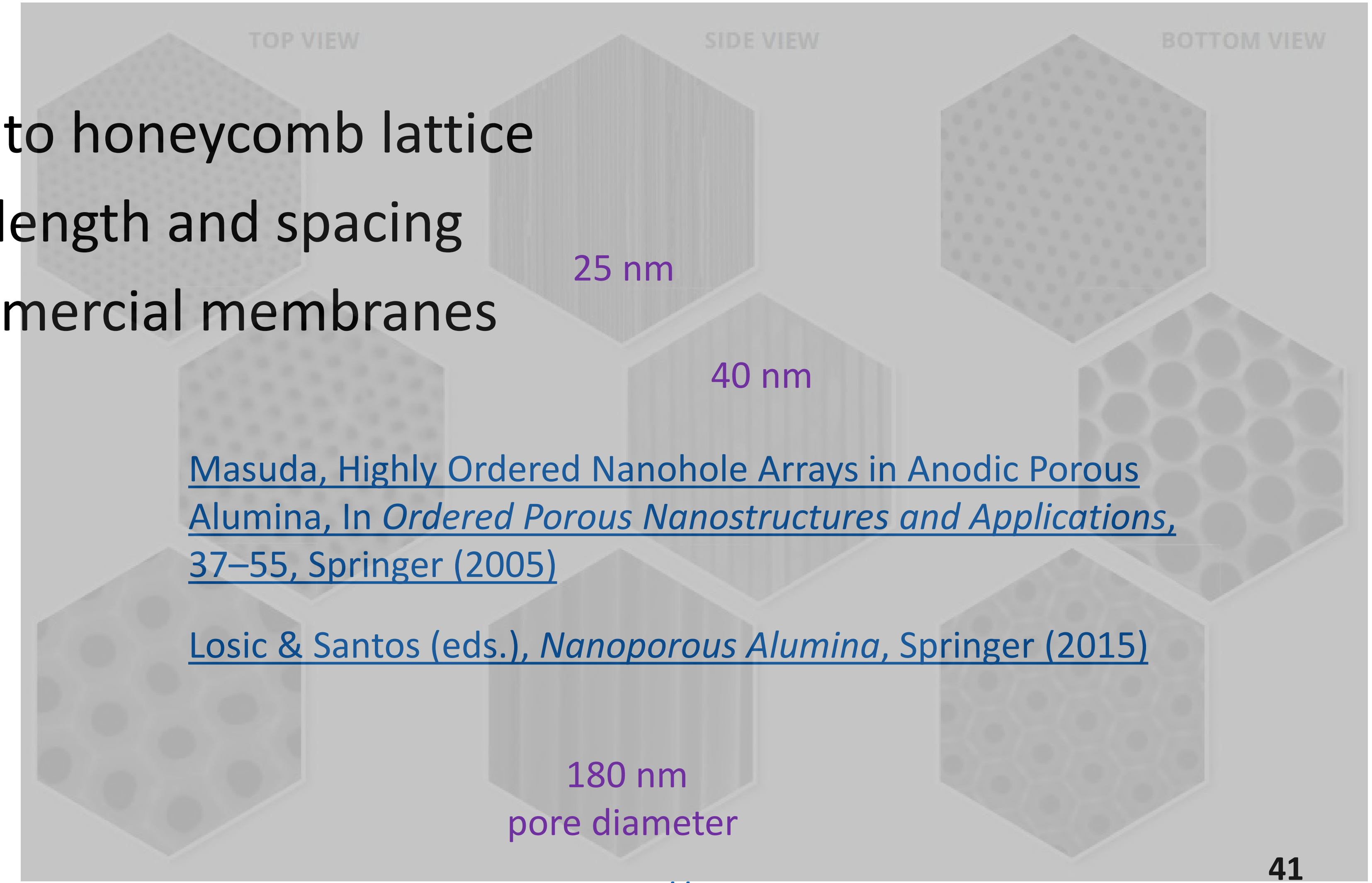
template dissolution NaOH

Electrodeposition: Au, Ag, Pd, Ni, Pt, polypyrrole, polyaniline, polythiophene, CdSe, CdS, MnO2, ...

Nanoporous anodic alumina (Al_2O_3) templates

- Preparation: Electrochemical oxidation of aluminium in acidic solutions (electrolytes)
- Self-ordering of pores into honeycomb lattice
- Tunable pore diameter, length and spacing
- Both lab-made and commercial membranes





Masuda, Highly Ordered Nanohole Arrays in Anodic Porous Alumina, In *Ordered Porous Nanostructures and Applications*, 37–55, Springer (2005)

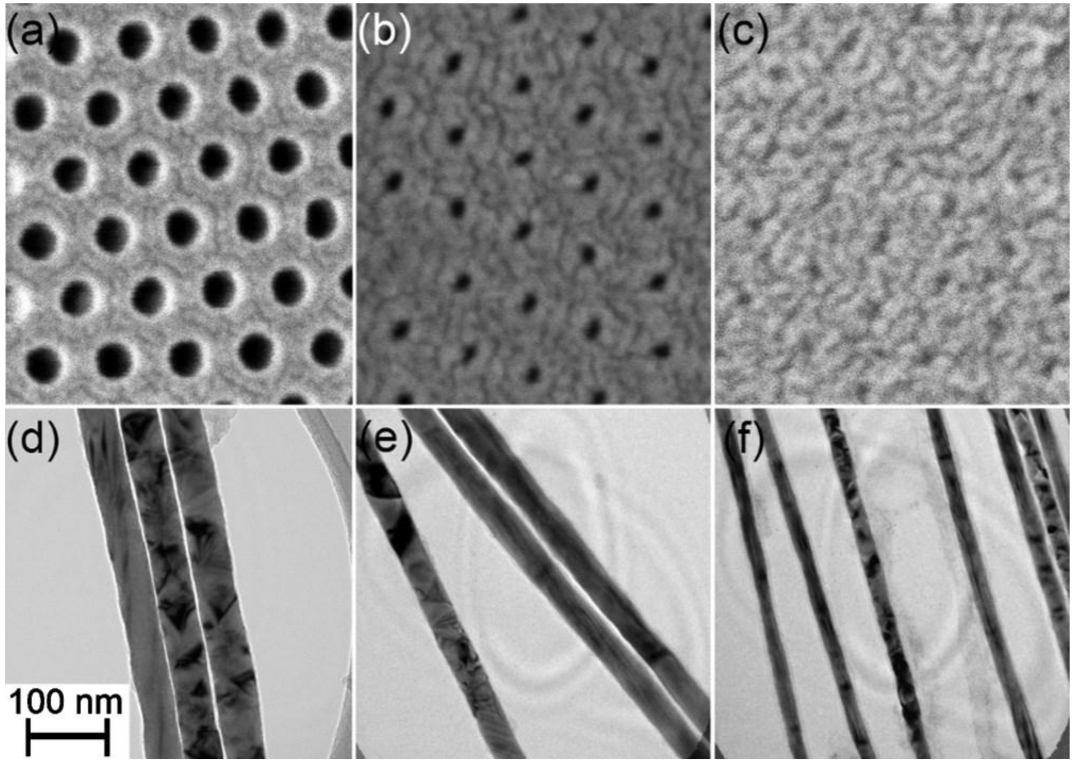
Losic & Santos (eds.), *Nanoporous Alumina*, Springer (2015)

Background images: https://www.smartmembranes.de

Nanoporous alumina – pore tuning

- Fine adjustment of pore diameter by chemical etching (wider pores) or atomic layer deposition (ALD) of Al_2O_3 (narrower pores)

no ALD ALD 100 cycles ALD 150 cycles



Nanoporous templates with pore diameter reduction by atomic alyer deposition (pore walls covered with extra Al_2O_3)

Ni nanowires prepared in the modified templates (transmission electron microscopy after dissolving the template)

Da Col et al., *Appl. Phys. Lett.* **98**, 112501 (2011)

Elephants (Fabrication methods)

Top-down elephant from stone block

- Removing material

Bottom-up elephant from clay pieces

+ Adding material

Practical realization – combination (adding+removing material)

Bottom-up elephant + scaffold for trunk

Bottom-up elephant (done)

https://www.youtube.com/@claycrafts

Electrodeposition: Standard reduction potentials

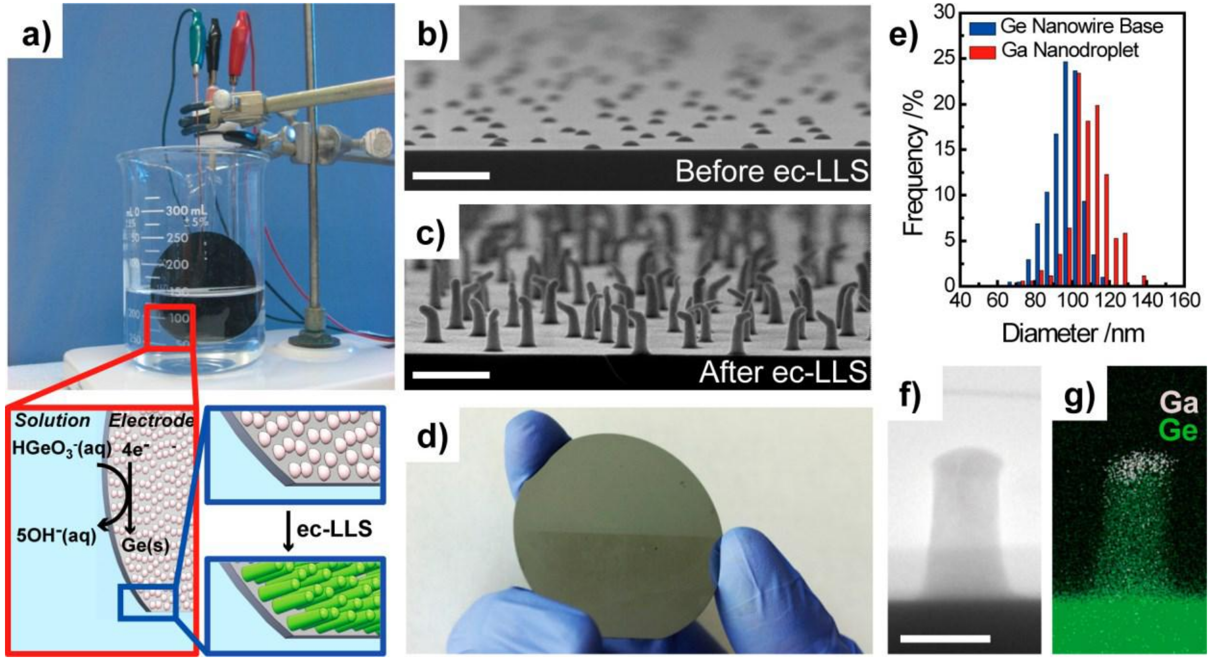
Reaction	Standard potential E^0
$H_2O + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-$	–0.828 V
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	–0.277 V
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	–0.257 V
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0 V (reference – standard hydrogen electrode - SHE)
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.342 V
$Cu^+ + e^- \rightleftharpoons Cu(s)$	+0.520 V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.800 V

(s) – solid, (g) - gas

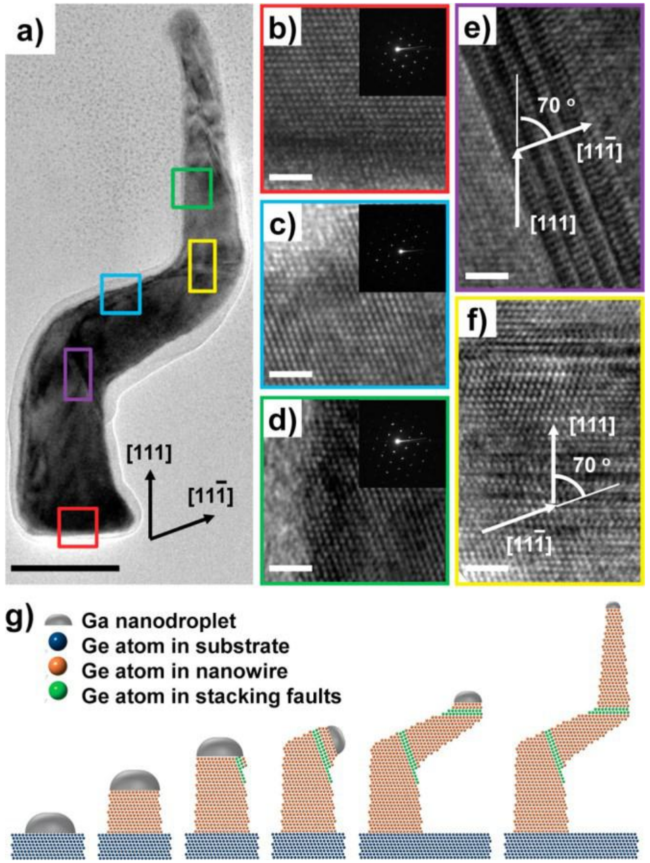
More positive potential – easier to reduce
Deposition possible for $E \leq E^0$ (thermodynamics)
Rate control via concentration (kinetics)

Example – electrolyte with both Co^{2+} and Cu^{2+}
@ +0.1 V vs SHE: only Cu deposited
@ -0.4 V vs SHE: both Co and Cu deposited; low Cu^{2+} concentration is used to have negligible Cu deposition

Epitaxial electrodeposition of Ge nanowires
(curiosity)



Fahrenkrug, *Nano Lett.* **14**, 2, 847–852 (2014)



Electroless plating – What can be achieved?

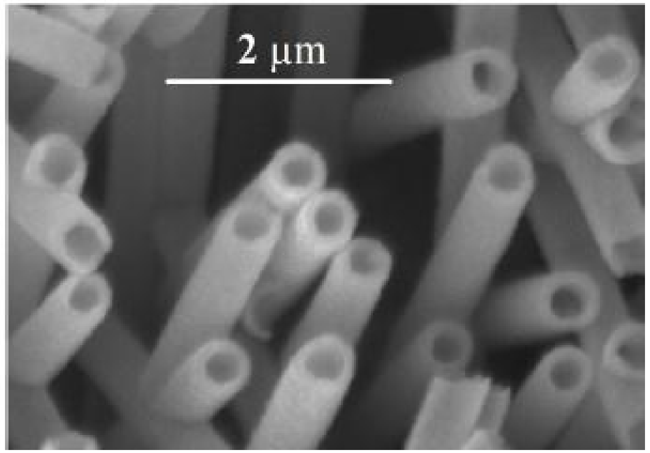
Examples from the literature:

U Limerick, Prof. Rhen:

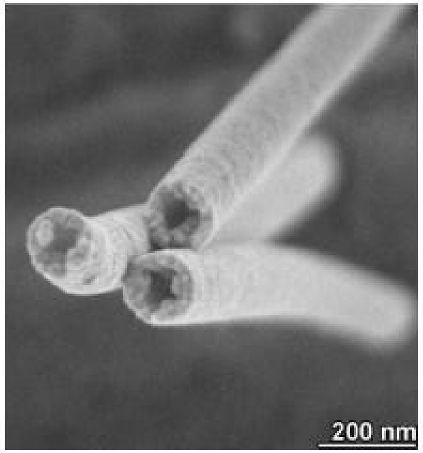
- NiFeB, CoB, NiCuB, CoNiFeB [*Phys. Procedia* **75**, 1158-1166 (2015)]

TU Darmstadt, Prof. Ensinger:

- Pd, Rh, Pt, Au, Ag, Cu, Ni [*ChemPlusChem* **80**, 1448-1456 (2015)]
- CoB, CoNiB, NiFeB [*SciPost Phys.* **5**, 038 (2018)]



NiFeB [U Limerick]



Au [TU Darmstadt]

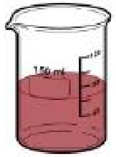
'tube' from Arrakis [Dune 2021]

Electroless plating – How it works

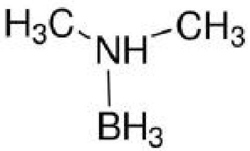
Autocatalytic deposition: catalyzed reduction of metallic ions
$M^{n+} + ne^- \rightarrow M^0$ (s) ; e.g. $Co^{2+} + 2e^- \rightarrow Co^0$

Ingredients:

- source of metal to be deposited ($CoSO_4$+H_2O), additives

- source of electrons (DMAB, Na hypophosphite)



- catalyst (e.g., Pd, later Co itself $\rightarrow$ autocatalysis)

- energy (thermal energy)

Additional element in the deposit: B, P, N (from the reducing agent)

Electroless plating: ±, industrial applications

+ conformal uniform coating (uneven surfaces, complex shapes)
+ low cost (simple 'beaker chemistry')
+ low processing temperature (room temperature or $< 100\,^\circ$C)
* variety of materials, variety of substrates (inc. non-conductive)
* growth rate spanning 1-100 nm/min (up to 10^1 microns/h)
- less precise thickness control (compared to ALD)
- challenge: getting continuous < 10 nm metallic layers
- plating solution – limited lifetime, complex composition

Book: Zhang, Amorphous and Nano Alloys Electroless Depositions, Elsevier (2015)
Review: Electroless plating for semiconductor and polymer micro-systems, *Microelectron. Eng.* **132**, 35-45 (2015)

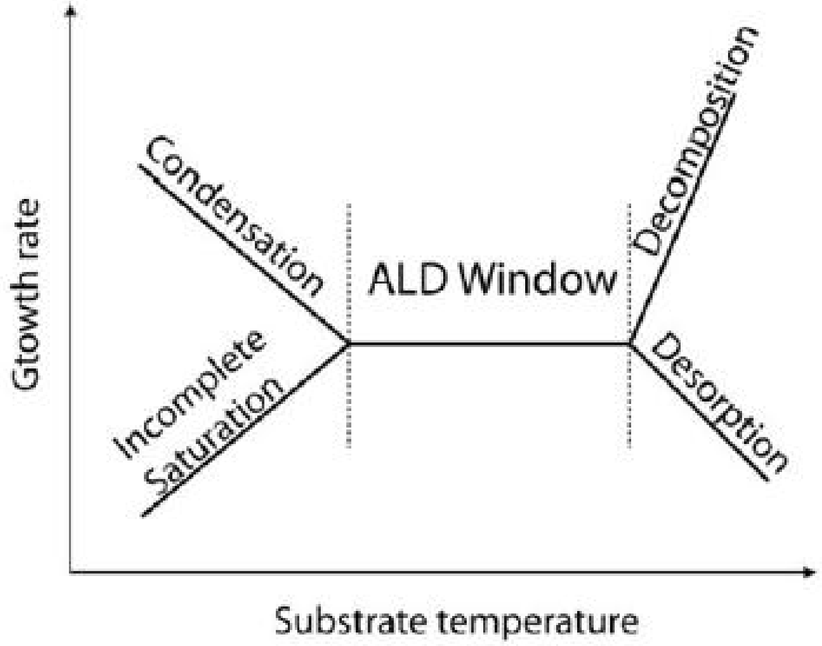
http://www.silchrome.co.uk/

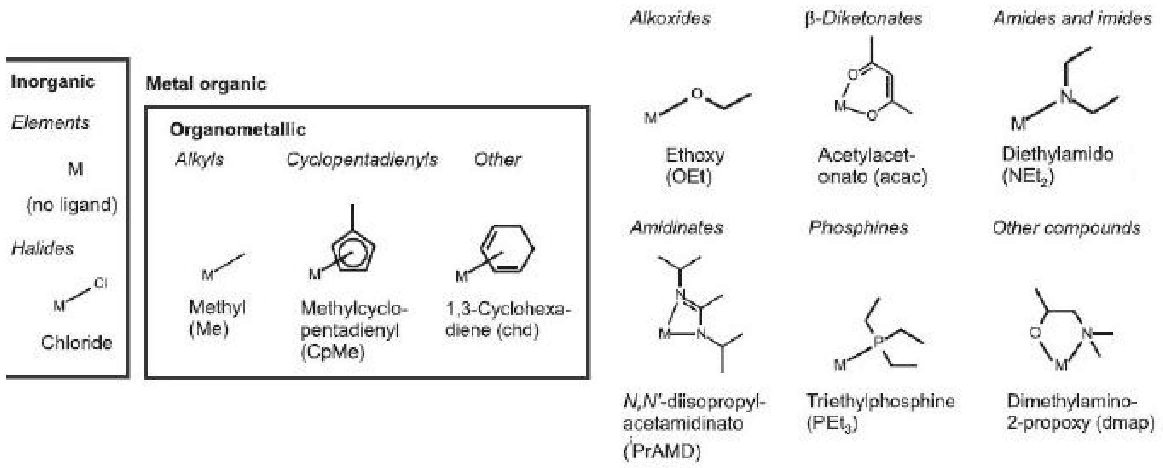
- **Industry**: automotive, oil & chemistry, electronics, aerospace, . . .
- **corrosion and wear protection**, conductive paths (seed layers), shielding
- electroless **Ni-P**, Cu, composites

ALD cooking: Recipe and ingredients

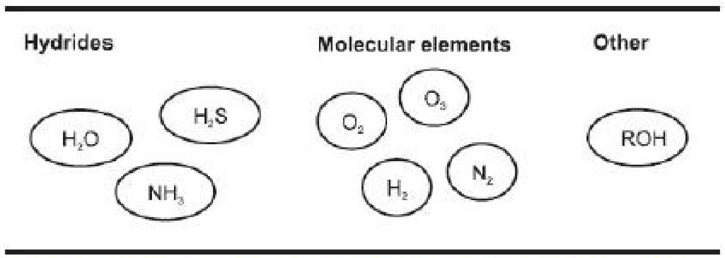
ALD deposition – what is needed

- **vessel**: reactor (rough vacuum, temperature control, gas inlets)
- **ingredients**: precursors and reactants
- **energy**: temperature and/or plasma
- **recipe** (process parameters: how much, how long, . . .)





(a) precursors – mostly metallo-organics



Miikkulainen et al., *JAP* **113**, 021301 (2013)

(b) reactants