Deposition and growth methods of media films and nanoobjects, lithographic techniques

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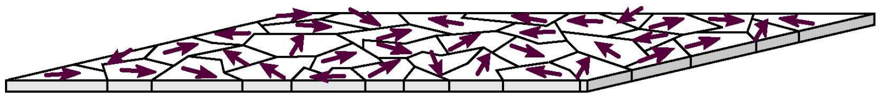
High-density data storage: principle

Current approach



1 bit = many domains

Information storage driven
by domain wall shifts

High density

1 bit = 1 magnetic nanoobject

Single-domain needed
Single easy axis preferred

Hurdle: superparamagnetism

Preparative methods for thin films

- Thermal evaporation
- Sputtering
- Chemical vapor deposition (CVD)
- Pulsed laser deposition (PLD)
- Molecular beam epitaxy (MBE)
- …

For a review of physical vapor deposition techniques:
Reichelt, *Thin Solid Films* **1990**, *191*, 91-126

Deposition rate limited by mass transfer
of “precursor” from the gas phase

⇨ Techniques only applicable to **flat substrates**

High-density data storage: requirements

<u>Requirements</u>

a. Small lateral size
⇨ high density

b. Ferromagnetism along preferred axis
⇨ information storage

c. 2D organization
⇨ information retrieval

d. Controlled geometry and magnetism
⇨ response foreseeable and optimizable

<u>Approaches</u>

A. Pseudo-1D magnetic objects (wires, tubes)
⇨ *a*, *b*

B. Lithography
⇨ *c*

C. Ordered porous templates
⇨ A, *c*, *d*

D. Electrodeposition
⇨ A

E. Atomic layer deposition
⇨ A, *d*

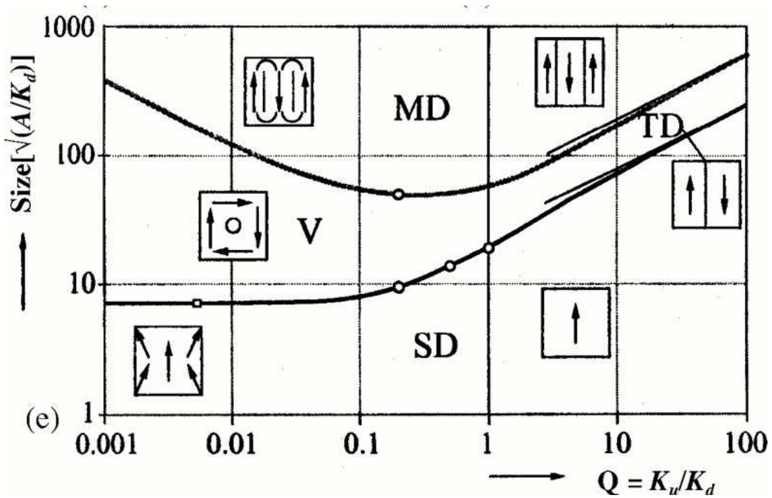
A
1D

Shape anisotropy

- Challenge for small objects: **superparamagnetism** (no ordering because not enough material)
- Solution: set a single **easy magnetization axis** ⇨ $KV >> kT$

  K: magnetic anisotropy; *V*: volume; *k*: Boltzmann's constant; *T*: temperature
- Option 1: use **magnetocrystalline anisotropy**

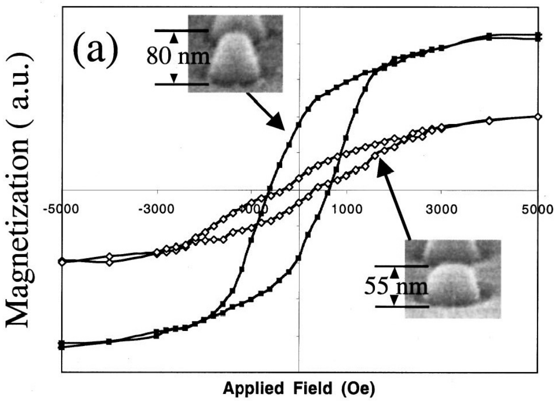
  … difficulties: control of crystallinity and orientation, limitation in terms of materials
- Option 2: pseudo-**1D-objects**



Magnetic phase diagram for a cube with uniaxial anisotropy
Ross, *Annu. Rev. Mater. Res.* **2001**, *31*, 203-235

A
1D

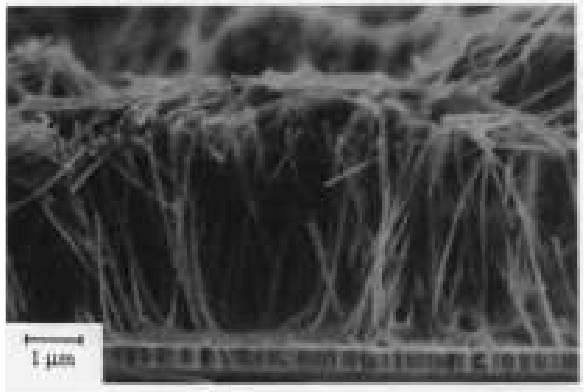
Types of pseudo-1D objects



Rods, pillars

Limited shape anisotropy

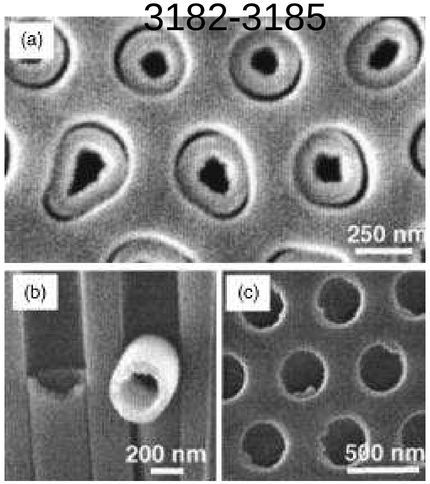
Co pillars: Farhoud, *J. Vac. Sci. Tech. B* **1999**, *17*, 3182-3185



Wires

Most investigated

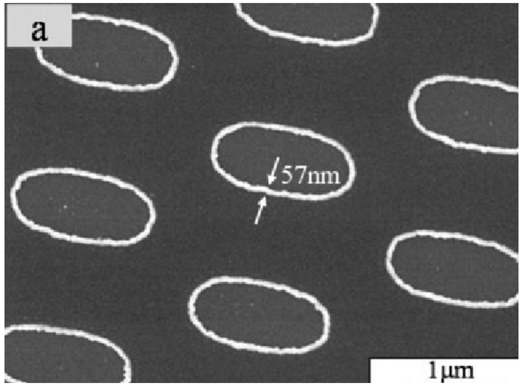
Ni wires: Whitney, *Science* **1993**, *261*, 1316-131



Tubes

Few preparative methods

Co / polymer tubes: Nielsch, *J. Appl. Phys.* **2005**, *98*, 034318



Circles, disks, ellipses

> 1 bit per object ?

Au rings: Ji, *Adv. Mat.* **2006**, *18*, 2593-2596

E-beam lithography, focused ion beam (FIB)

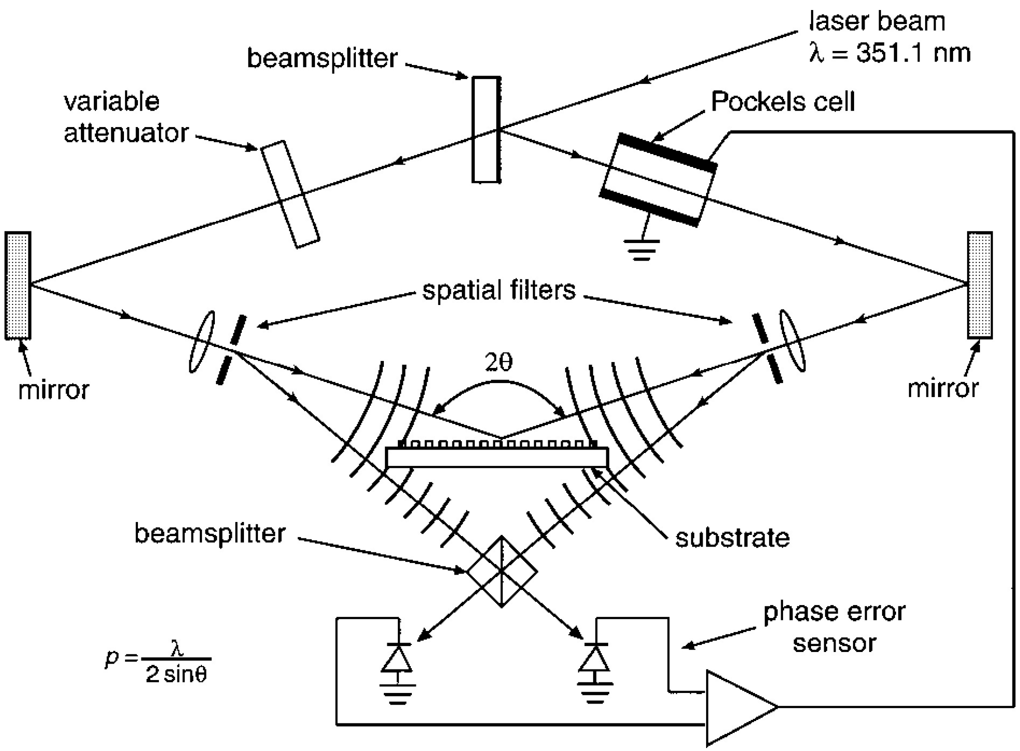
- Principle: exposure of a sensitive layer to a tightly focused beam… its chemical identity changes upon exposure
- Electron beam: electron microscopes provide a convenient source
- FIB: ions are extracted under a high voltage from a liquid Ga droplet wetting a W tip, then mass-selected, collimated and focused

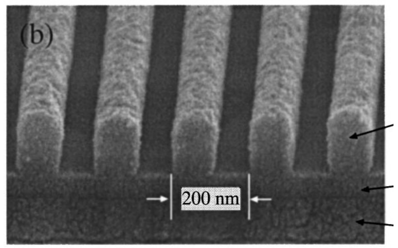
- **Advantage: versatility** — large variety of structures can be designed in a computer and created just by proper control of the beam deflector
- **Disadvantage: not a parallel method** — every object must be prepared individually

Lithographic methods for magnetic nanostructures:
Martin, *J. Magn. Magn Mat.* **2003**, *256*, 449-501

Interference lithography

- Interference btw two beams of monochromatic light creates a **perfectly ordered periodic line pattern** in photoresist:





Farhoud, *J. Vac. Sci. Tech. B* **1999**, *17*, 3182-3185

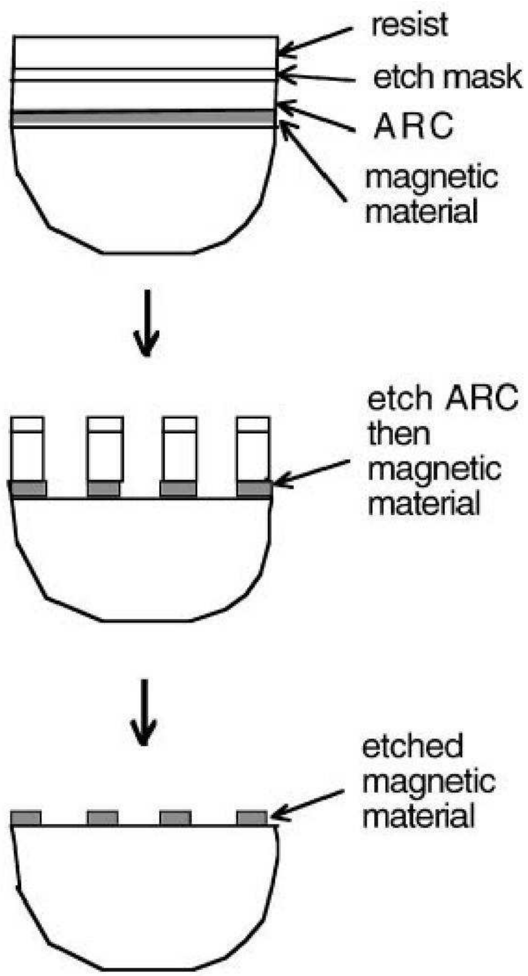
- Double exposure yields circular or elliptical objects
- Advantage: **massively parallel**

Direct pattern transfer: etching

- **Reactive ion etching (RIE):** plasma in a gas creates ions that are both highly reactive and (somewhat) specific

- CHF_3 for SiO_2
  O_2 for organic materials
  Cl_2 for Al_2O_3
  (Ar non-specific: ion milling)

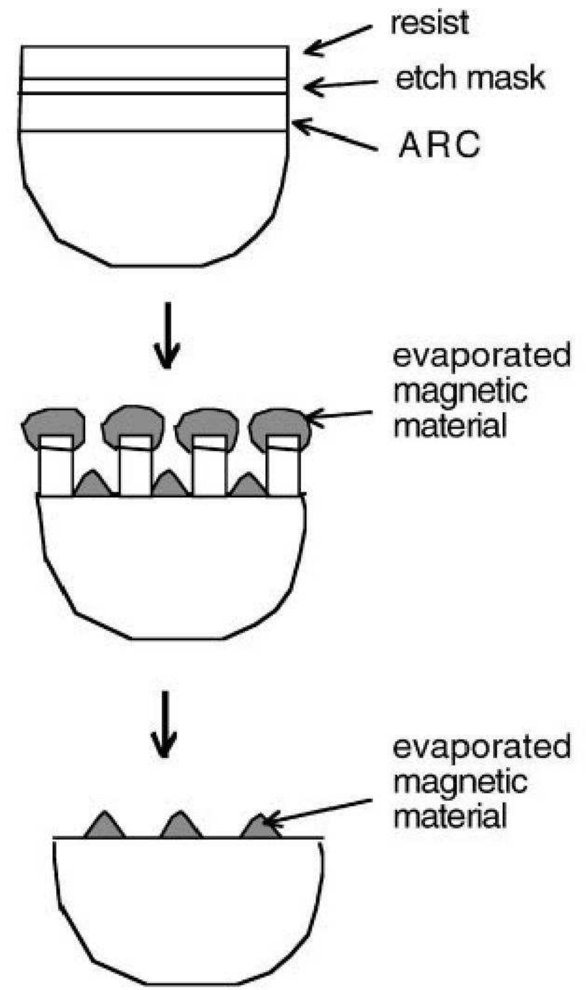
- The plasma is "above"
  ⇨ etching occurs vertically



Ross, *Annu. Rev. Mater. Res.* **2001**, *31*, 203-235

Indirect pattern transfer: mask

- Patterned layer used as a mask for the deposition of magnetic material (sputtering, thermal evaporation, …)
- Patterned layer then **lifted off**
- Alternative: patterned layer is separated, then laid onto a photoresist and used as a **shadow mask**

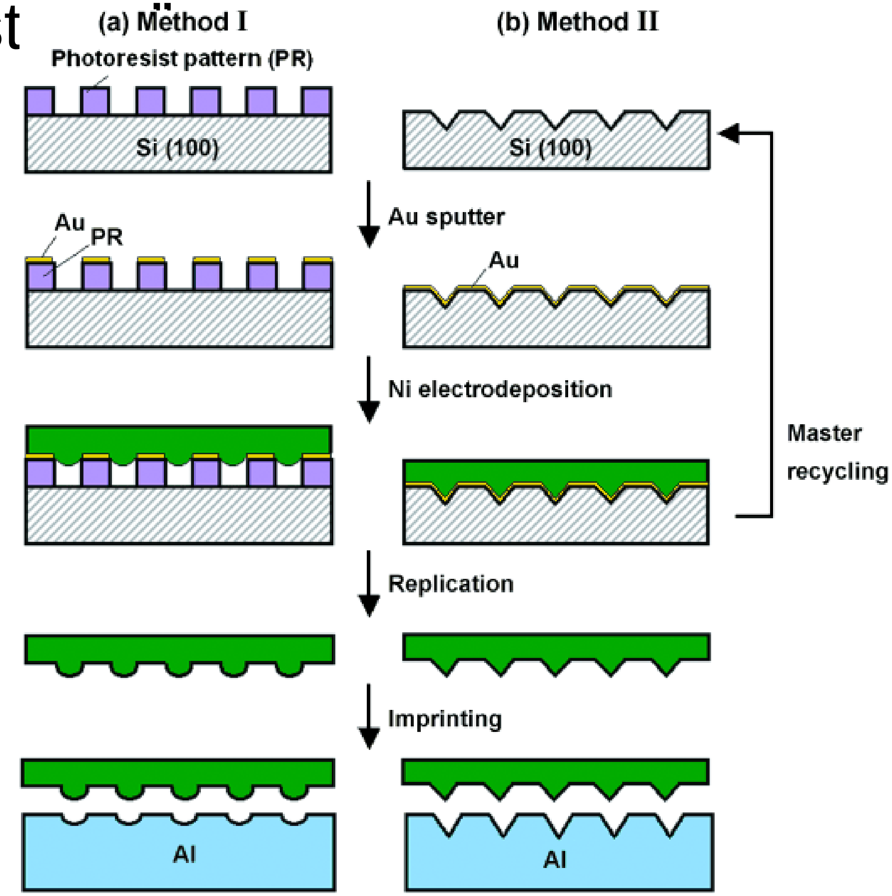


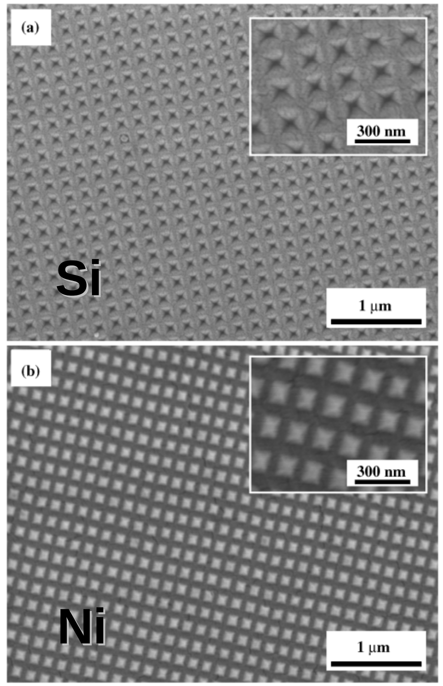
Ross, *Annu. Rev. Mater. Res.* **2001**, *31*, 203-235

B
litho

Indirect pattern transfer: imprint

- **Mechanical indentation** of substrate with patterned "st





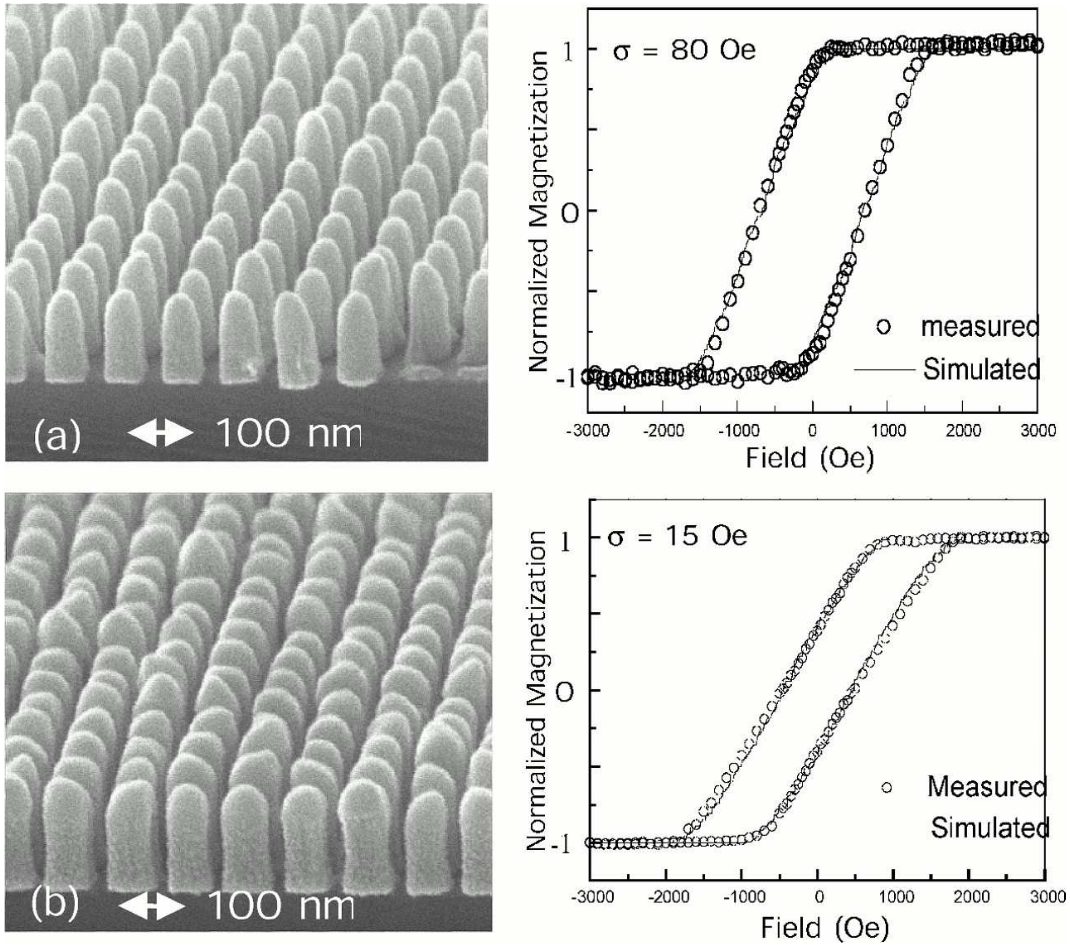
Lee, *Small* **2006**, *2*, 978-982

- **Soft lithography** (using PDMS stamps) more practical

see Xia, *Annu. Rev. Mater. Sci.* **1998**, *28*, 153-184; and *Angew. Chem. Int. Ed.* **1998**, *37*, 551-575

B
litho

Lithographic structures



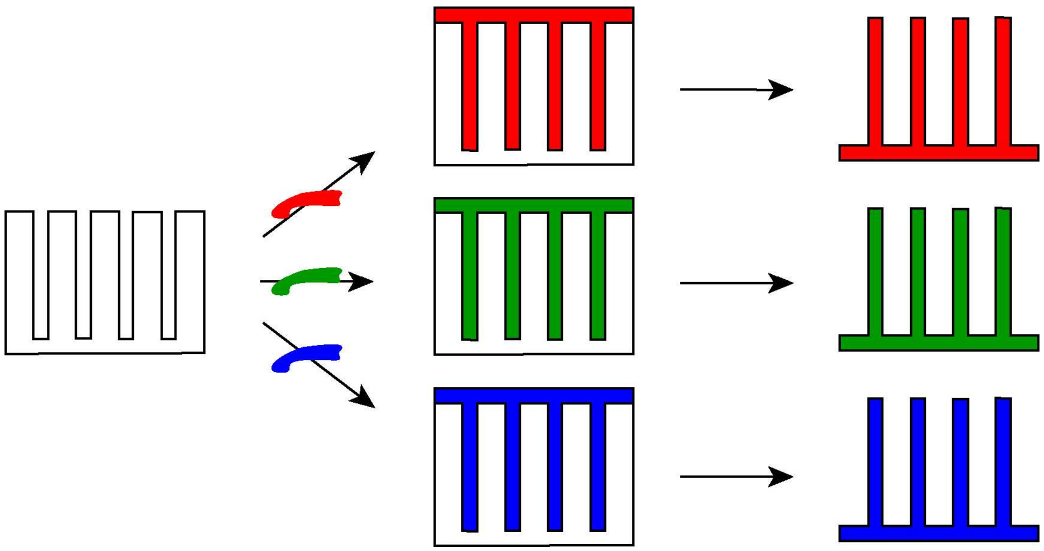
Ni pillars of two different diameters (H // z)
Ross, *Annu. Rev. Mater. Res.* **2001**, *31*, 203-235

Limitation: **aspect ratios accessible in "vertical" geometry**

Porous materials as templates

- An ordered array of vertical pores is the "**negative**" of an array of 1D objects.
- If the pore array is **tunable in geometry**, then the wires / tubes obtained from it are as well.
- The preparation of the porous material may be specific to a certain material system; but if the "filling method" is general, **the quality of the template is transferred** to the 1D objects in general

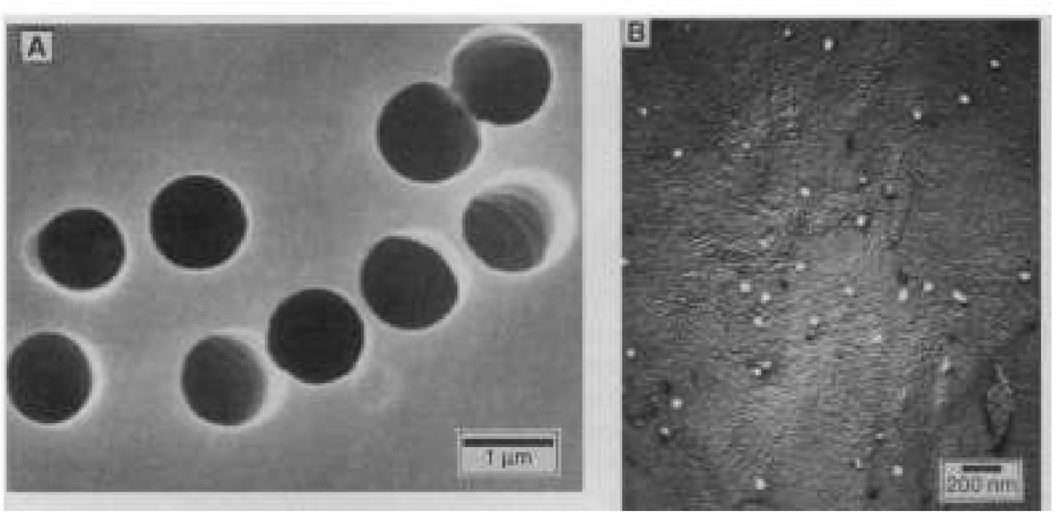
⇨ need to optimize geometric control once and for all !



C
template

Ion track-etch filters

- **Commercially available filters** with pores of controlled diameter: from bombardment with nuclear fission fragments then chemical etch



Martin, *Science* **1994**, *266*, 1961-1966

- Advantages: **variety of pore diameters (<10 nm) available**

  pore diameter homogeneous

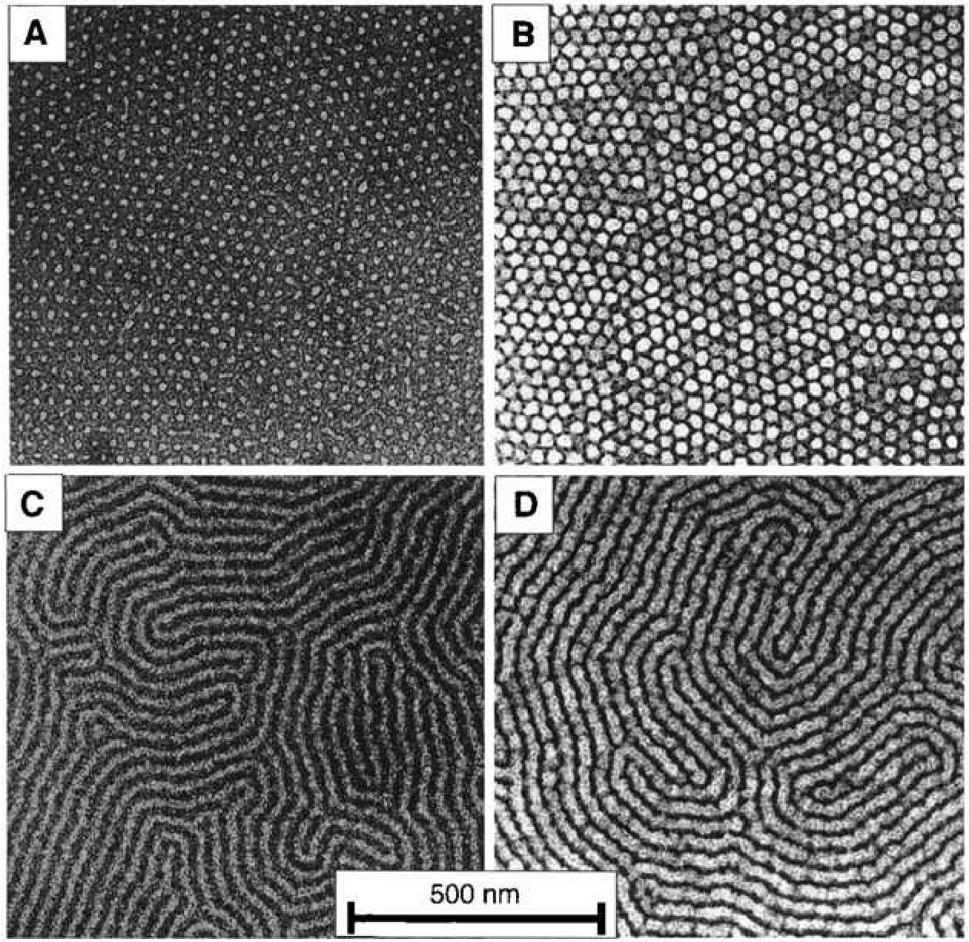
- Disadvantages: **pores randomly scattered**

  pores not parallel

C
template

Phase-separated block copolymers

- **Phase separation** may lead to regular pattern; selective chemical etching then furnishes a porous template or a mask



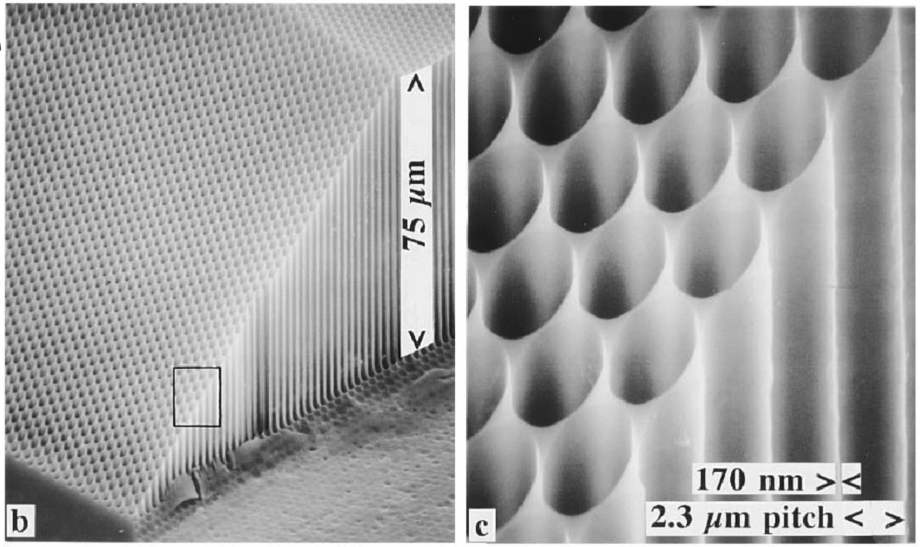
Park, *Science* **1997**, *276*, 1401-1404

A, C: copolymer polystyrene / polybutadiene (PB removed by ozonation);
B, D: etched pattern in Si_3N_4

C
template

Macroporous silicon

- **Electrochemical oxidation** of Si in HF solution under irradiation induces the formation and growth of pores
- Pores are disordered unless lithographically pre-de



Grüning, *Appl. Phys. Lett.* **1996**, *6*, 747-749

Lehmann, *J. Electrochem. Soc.* **1993**, *140*, 2836-2843

- Limitation: **pores rather large (>0.5 μm)**

C
template

Anodic alumina

For references:
Nielsch K, *Nano Lett.* **2002**, *2*, 677-680
Masuda, *Science* **1995**, *266*, 1466-1468.

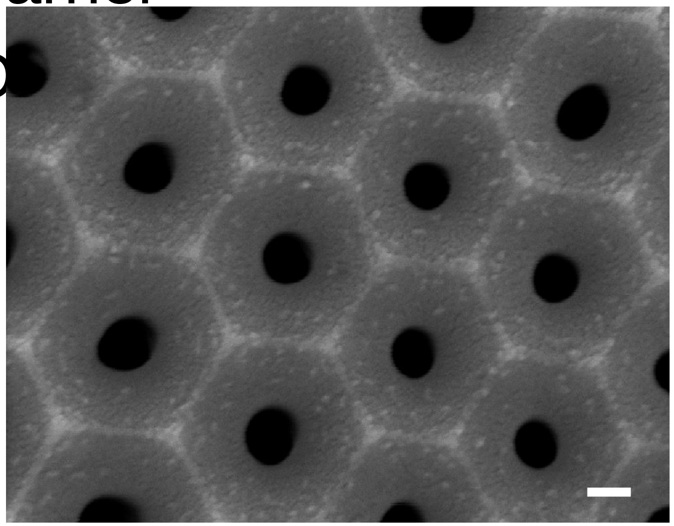
- **Electrochemical oxidation** of Al in acidic solution induces the formation and growth of pores in Al_2O_3.

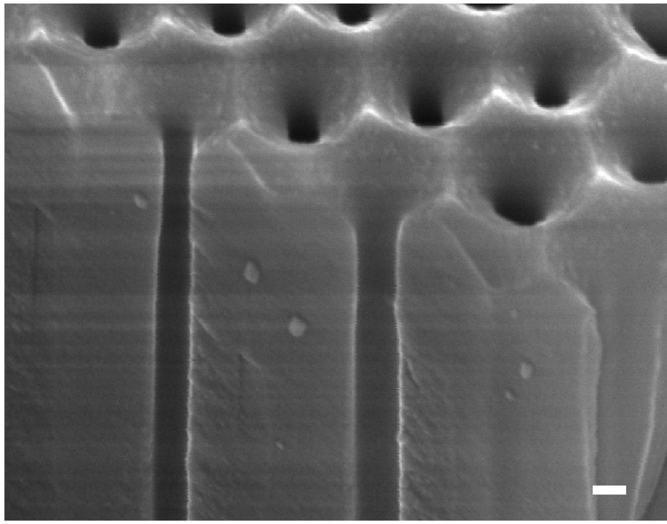
  $Al \rightarrow Al^{3+} + 3\,e^-$ $2\,Al^{3+} + 3\,H_2O \rightarrow Al_2O_3 + 6\,H^+$

  $2\,H^+ + 2\,e^- \rightarrow H_2$ $Al_2O_3 + 6\,H_2X \rightarrow AlX_3^{3-} + 3\,H_2O$

- Ordering depends on balance btw electron transfer processes and diffusion of water through the alumina barrier

- D … yield
  d … n)





Scale bars:
100 nm

Chemistry of electrodeposition

- Electroplating solution: for example
  MX_n / H_yA / H_2O
  M^{n+}: metal ion; X^-: Cl^-, ½ SO_4^{2-}, CN^-, …; H_yA: H_3BO_3, …

- **M^{n+} reduced** at the cathode (working electrode, **W**):
  $M^{n+} + n\,e^- \rightarrow M^0$

- At the anode (auxiliary electrode, **A**): something must be oxidized (electrical circuit is closed, electrons cannot be created or destroyed)…
  $2\,H_2O - 4\,e^- \rightarrow O_2 + 4\,H^+$

- HA and MX_n make the solution **electrically conductive** (charges cannot accumulate)

- To be avoided (or minimized): reduction of protons…
  $2\,H^+ + 2\,e^- \rightarrow H_2$

Thermodynamics of electrodeposition

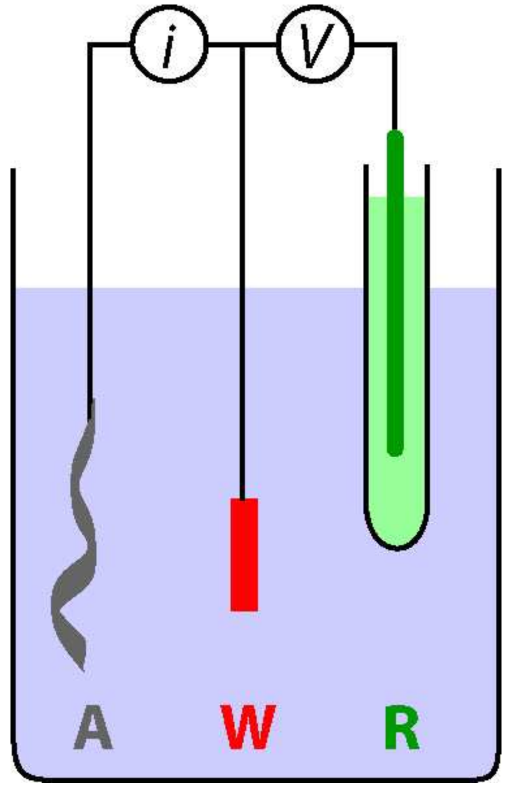
- Some elements are harder to reduce than others…

$Mg^{2+} + H_2 \rightarrow Mg + 2\,H^+$	–2.4 V
$Fe^{2+} + H_2 \rightarrow Fe + 2\,H^+$	–0.4 V
$Pd^{2+} + H_2 \rightarrow Pd + 2\,H^+$	+0.8 V

- List of thermodynamic properties of redox couples:
  table of **standard reduction potentials**
- **Arbitrary reference** of the reduction potentials:
  H^+ / H_2 couple
  (could have been free e^- in vacuum)
- **Practical aspects** influencing potentials necessary for electrodeposition: concentrations, transport phenomena, surface tension effects

Technique of electrodeposition

- Deposition modes:
  DC galvanostatic (no control on thermodynamics)
  DC potentiostatic (thermodynamics set by turning a button)
  pulsed (better kinetic control: reactant delivery to electrode)



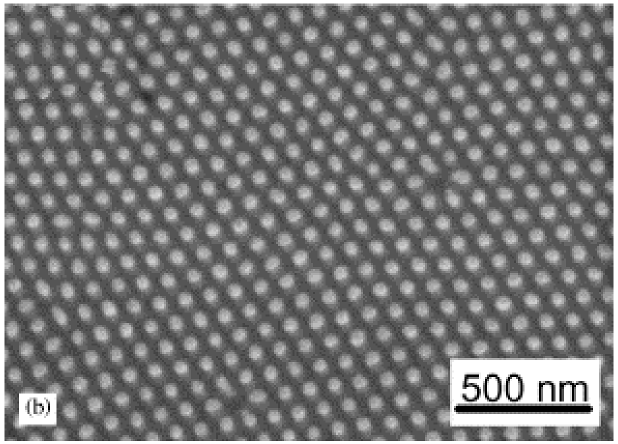
- Proper setup:
  with **reference electrode** (**R**)
  … *V* applied btw **R** and **W**
  … *i* measured btw **A** and **W**
- Two-electrode setup (no **R**)
  often used in practice

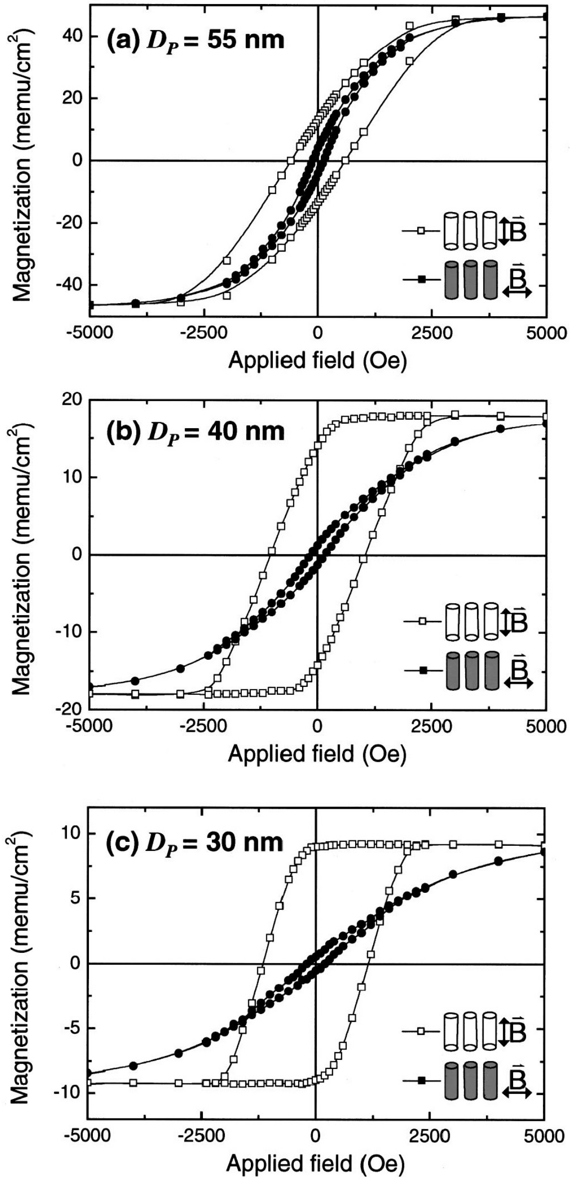
Electrodeposited nickel nanowires

Nielsch, *Appl. Phys. Lett.* **2001**, *79*, 1360-1362

- Porous anodic alumina as template
- Au layer sputtered on one side as electrode
- DC or pulsed electrodeposition
- Pores fill up with Ni from electrode … growth of Ni wires
- Advantages:
  - **wires oriented**
  - **diameter tunable**

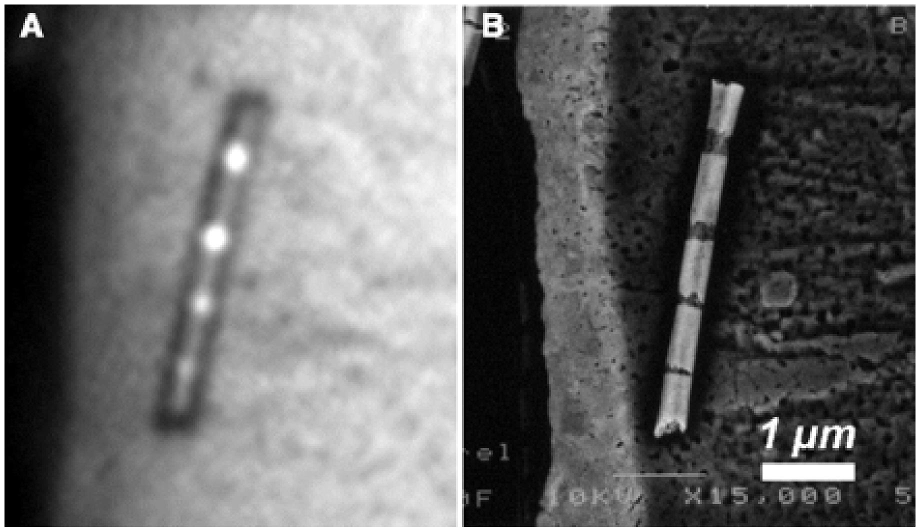
SEM
top view





Segmented wires

- Electrodeposition in porous template with alternation btw several different solutions:
  segments of several different metals
- **Length of segments** defined by total time spent (total charge passed) in each solution



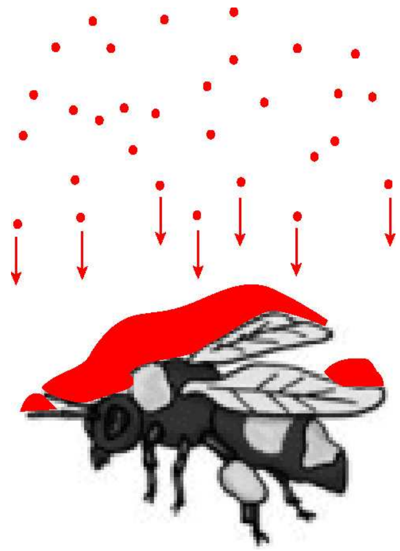
Optical and electron micrographs of a (nonmagnetic) Ag / Au segmented wire

Nicewarner-Peña, *Science* **2001**, *294*, 137-141

Atomic layer deposition: idea

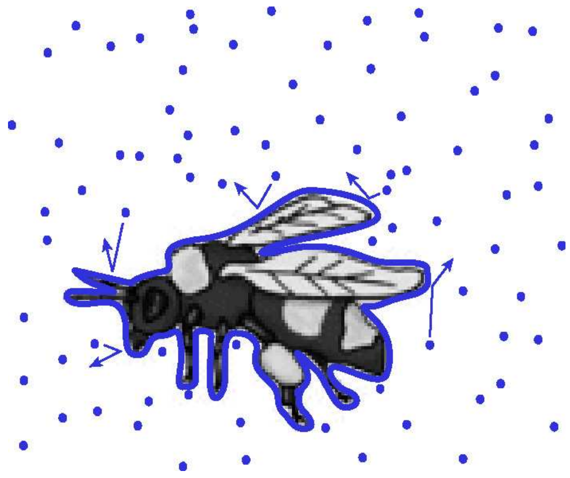
Chemical vapor deposition (CVD):

- **thermal decomposition** on the substrate
- **diffusion** rate-limiting… shadowing

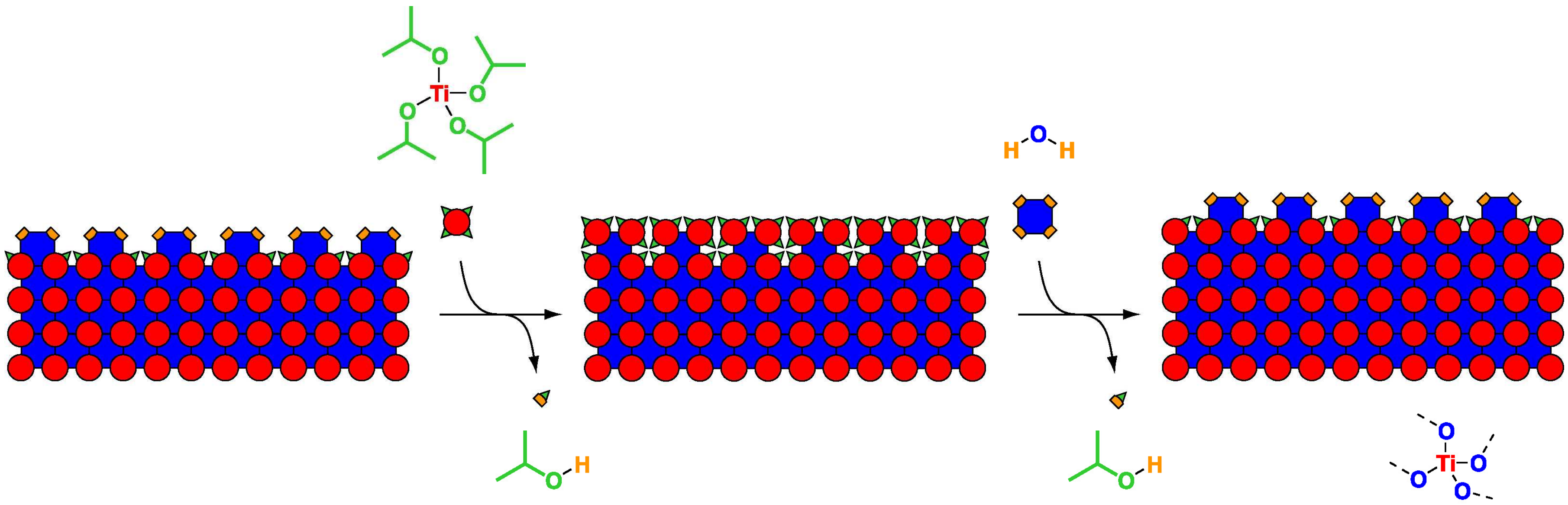


Atomic layer deposition (ALD):

- **limiting chemical reaction** with excess reactant
- **layer-by-layer** growth with **arbitrary substrate geometry**



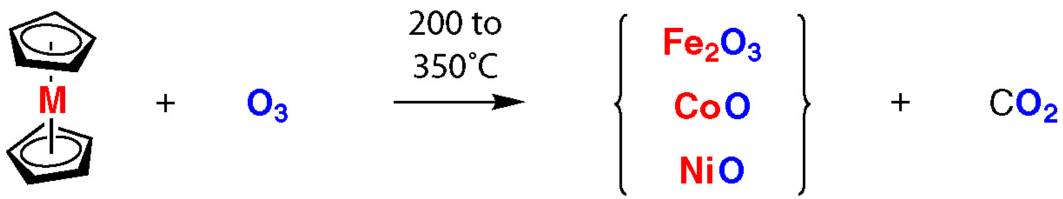
Atomic layer deposition: method

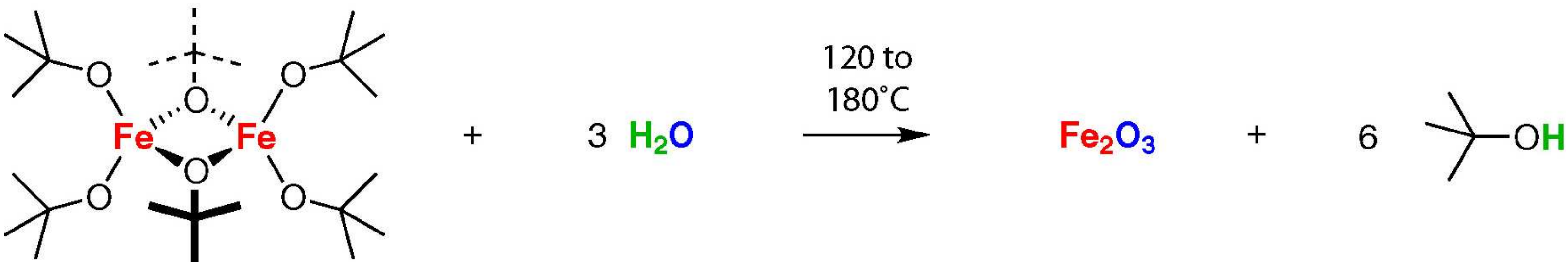


- Two alternatively pulsed precursors
  - no reaction in the gas phase
- Precursors **thermally stable but reactive** towards each other
  - specific chemical reaction, no decomposition
- Each precursor pulse = one chemisorbed monolayer
  - no matter excess of precursor… **conformal coating**
- **Thickness proportional to number of ALD cycles**

Magnetic materials by ALD

- ALD reactions:





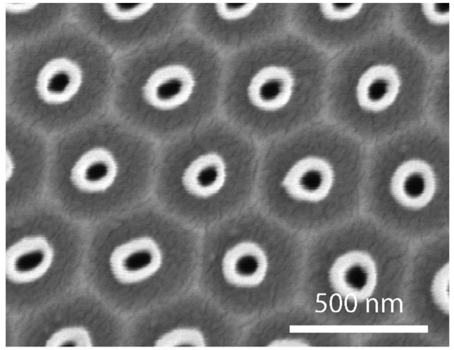
- Reduction of Fe_2O_3, CoO and NiO to **Fe_3O_4, Co and Ni** by H_2.

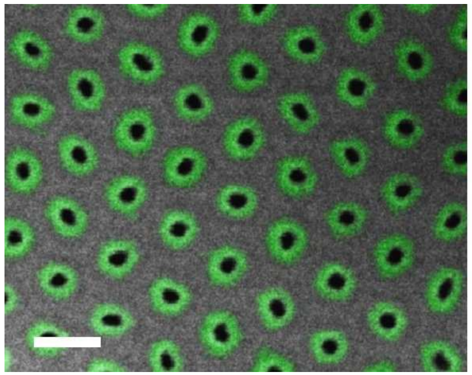
- More granular material obtained at higher temperature and if reduction causes a large volume change

E
ALD

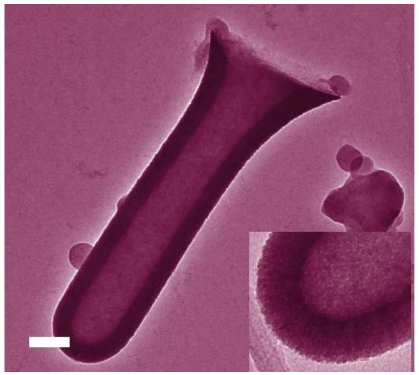
Iron oxide nanotubes by ALD

Bachmann, *J. Am. Chem. Soc.* **2007**, *129*, 9554-9555

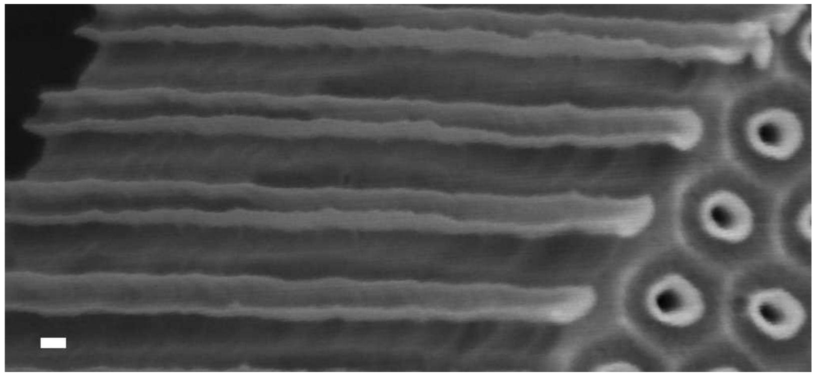




11 nm **Fe_2O_3** in Al_2O_3
$Fe_2(O^tBu)_6 + H_2O$ @ 140℃
D_p = 50 nm, D_{int} = 105



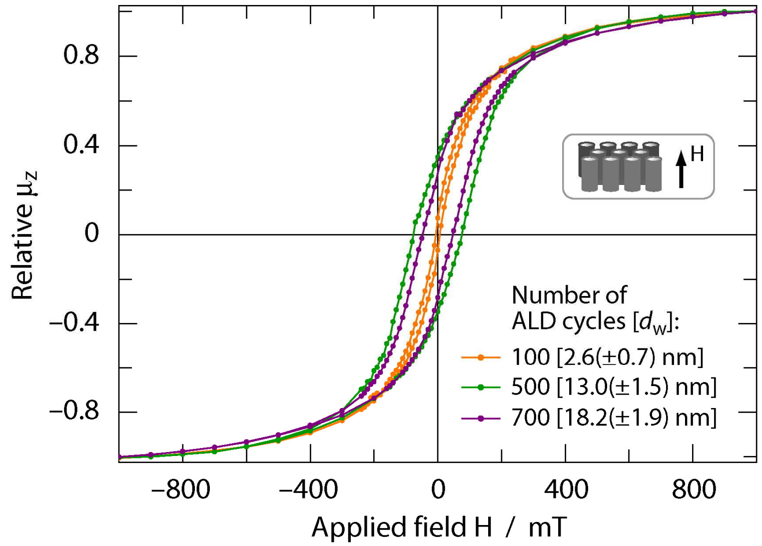
42 nm **Fe_3O_4**, isolated tube
$Fe_2(O^tBu)_6 + H_2O$ @ 140℃
D_p = 160 nm, D_{int} = 460 nm

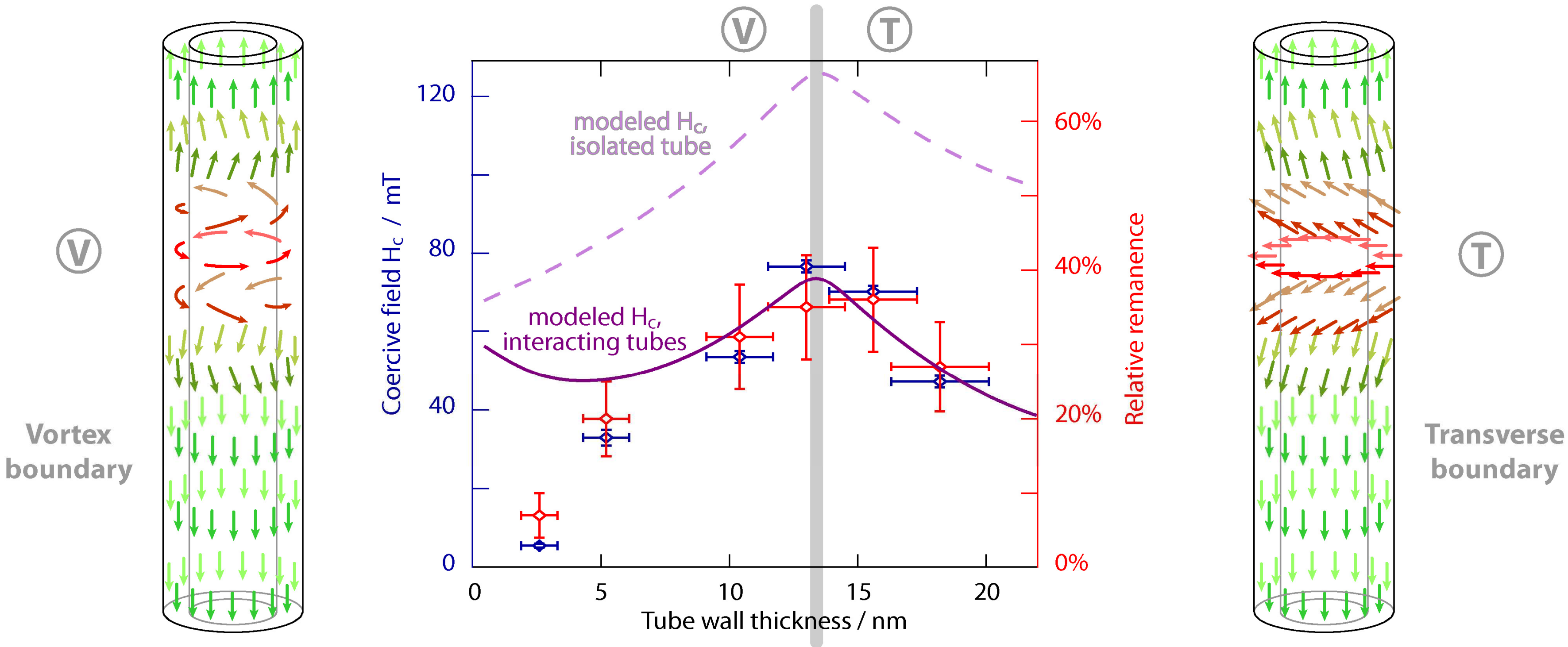


ZrO_2 / Fe_2O_3 / ZrO_2 in Al_2O_3
$Fe_2(O^tBu)_6 + H_2O$ @ 140℃
D_p = 160 nm, D_{int} = 460 nm

Scale bars: 100 nm

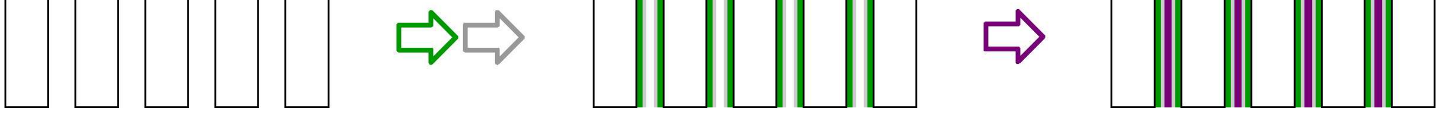
E_{ALD} Two distinct magnetization reversal modes



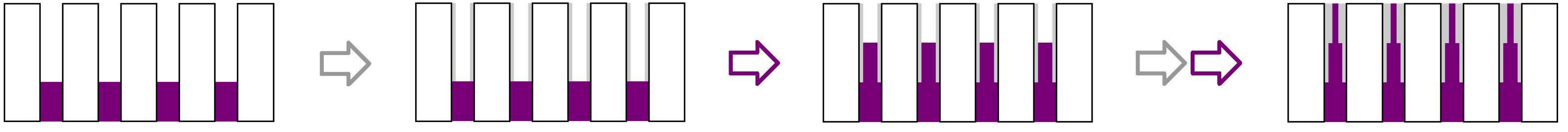


Heterostructures by combining techniques

- Core / shell wires:



- Wires modulated in diameter:



Conclusions

Clean, controlled preparation methods

for

reproducible, adjustable physical properties

With

versatile, accurate preparation methods,

your imagination is the limit !