Complex Nanostructures by Atomic Layer Deposition

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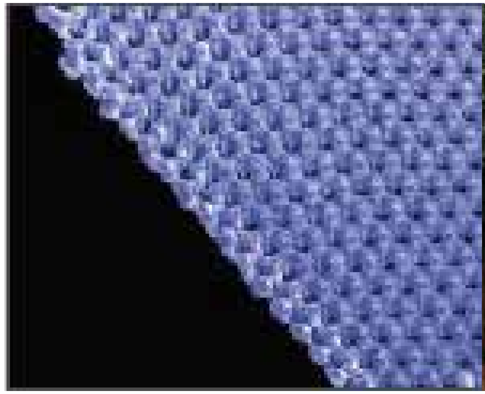

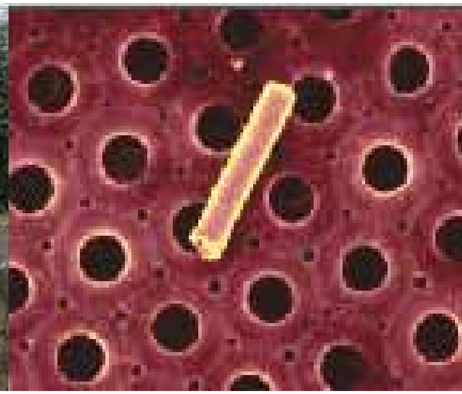


Outline

History and Principle

Ferromagnetic Nanostructures

Low-Temperature Processes and Biomaterials

Novel Synthesis Approach and Nanostructures

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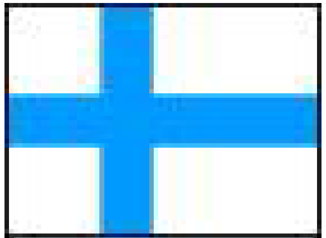
Low-Temperature Processes and Biomaterials

Novel Synthesis Approach and Nanostructures

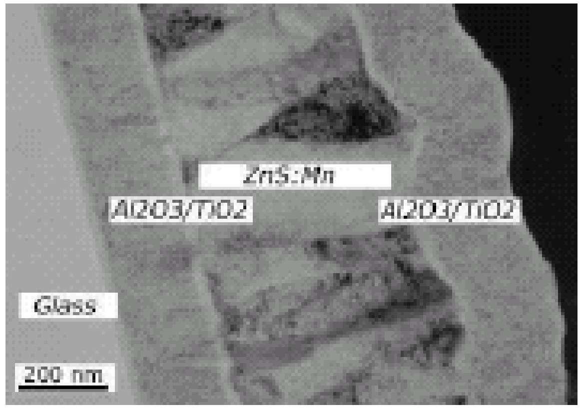
History of Atomic Layer Deposition (ALD)

originally Atomic Layer Epitaxy (ALE)



ALD (ALE) was developed by Dr. T. Suntola for thin film electroluminescent (TFEL) displays

First Finish patent 1974 and first U.S. patent 1977



First commercial use: Flat panel display based on ZnS films (from early 1980s).

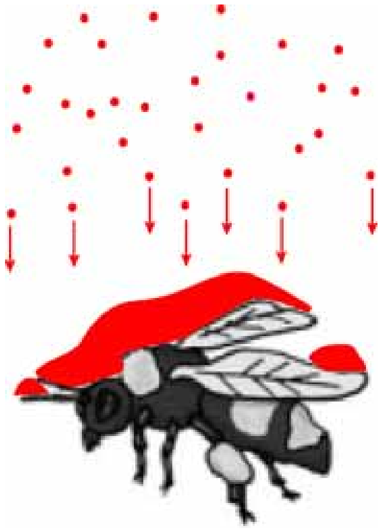
Todays main use:

Deposition of high-*k* (high dielectric constant, e.g. HfO_2) thin films in microelectronic industry and research

Atomic Layer Deposition (ALD)

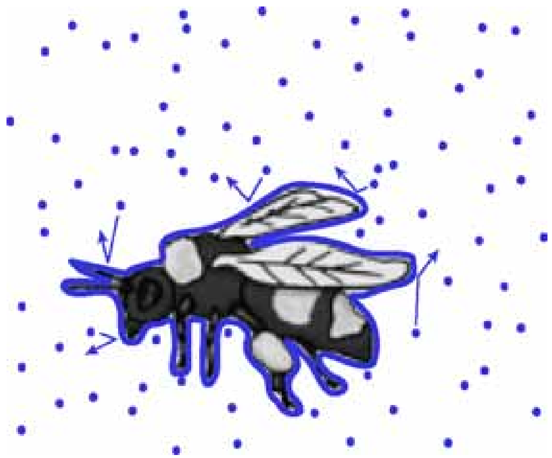
Chemical vapor deposition (CVD):

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

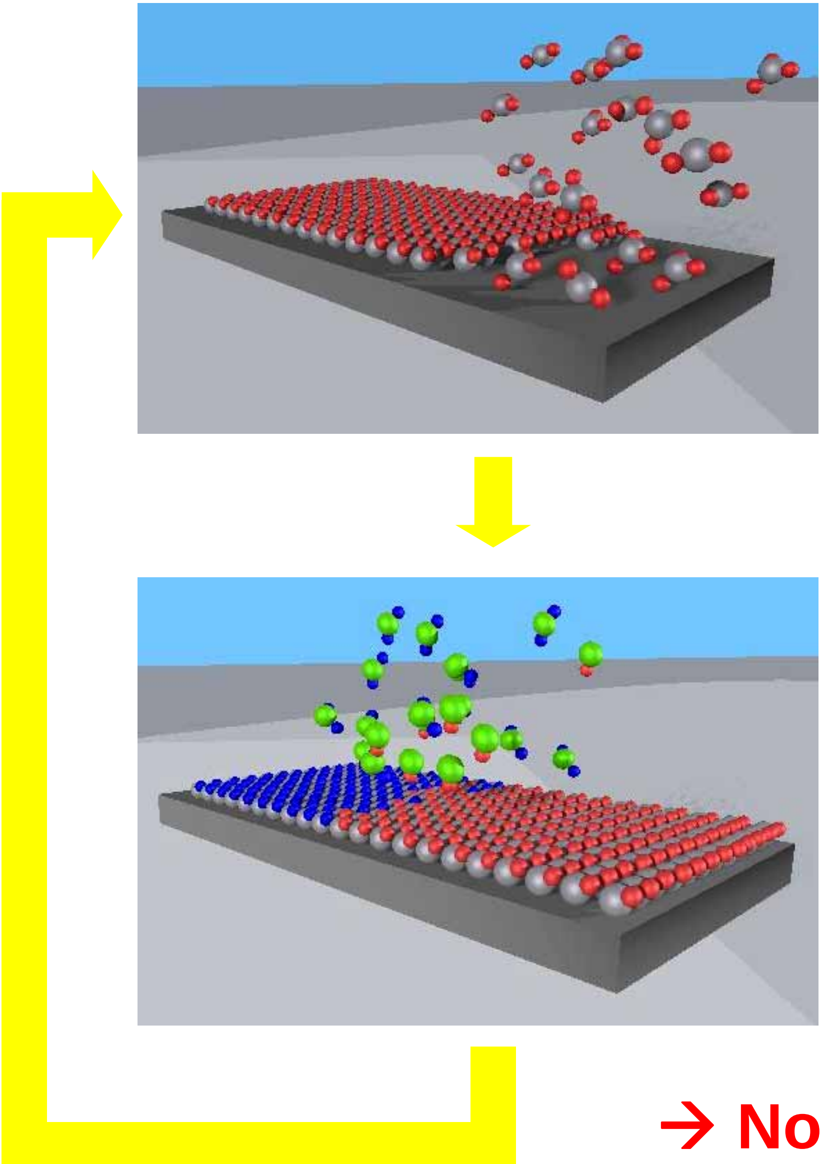


Atomic layer deposition (ALD):

- **self-limited reaction** with excess reactant
- **layer-by-layer** growth



ALD – The Principle



Four stages of one ALD cycle:

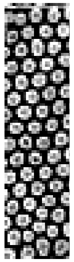
a) Exposure of substrate to precursor 1
→ adsorption

b) Purge with N_2 or Ar
→ removal of excess precursor 1

c) Exposure of substrate with precursor 2
→ reaction

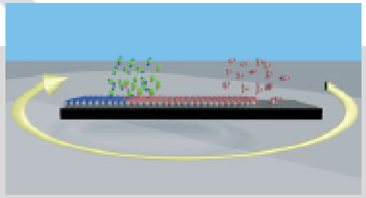
d) Purge with N_2 or Ar
→ removal of excess precursor 2
and reaction products

→ Non-directed deposition method



Synthesis and Surface Engineering of Complex Nanostructures by Atomic Layer Deposition**

By *Mato Knez*,* *Kornelius Nielsch*, and *Lauri Niinistö*
■Correspondence Author?■



Atomic Layer Deposition (ALD) has recently become the method-of-choice for semiconductor industry to conformally process extremely thin insulating layers (high-k oxides) onto large-area silicon substrates. ALD is also a key technology for the surface modification of complex nanostructured materials. After briefly introducing ALD, this review will focus on the various aspects of nanomaterials and their processing by ALD, including nanopores, nanowires and tubes, nanopatterning

0 (2005)

Review – Advanced Materials

Synthesis and Surface Engineering of Complex Nanostructures by Atomic Layer Deposition

Mato Knez, Kornelius Nielsch, Lauri Niinistö (HUT, Finland)
Advanced Materials **19**, 3425-3438 (2007).

Summer 2007

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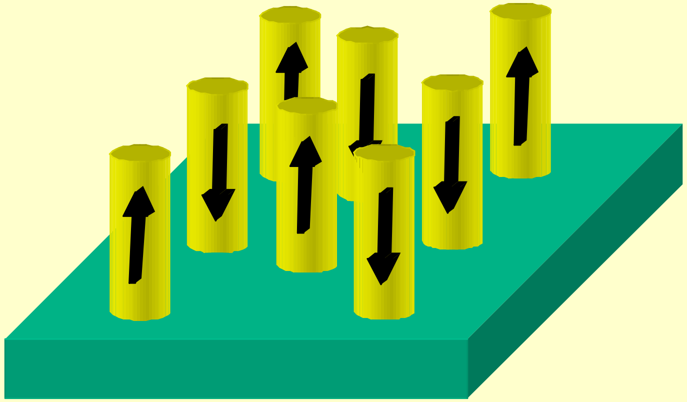
65 nm-Period Nickel Nanowire Array

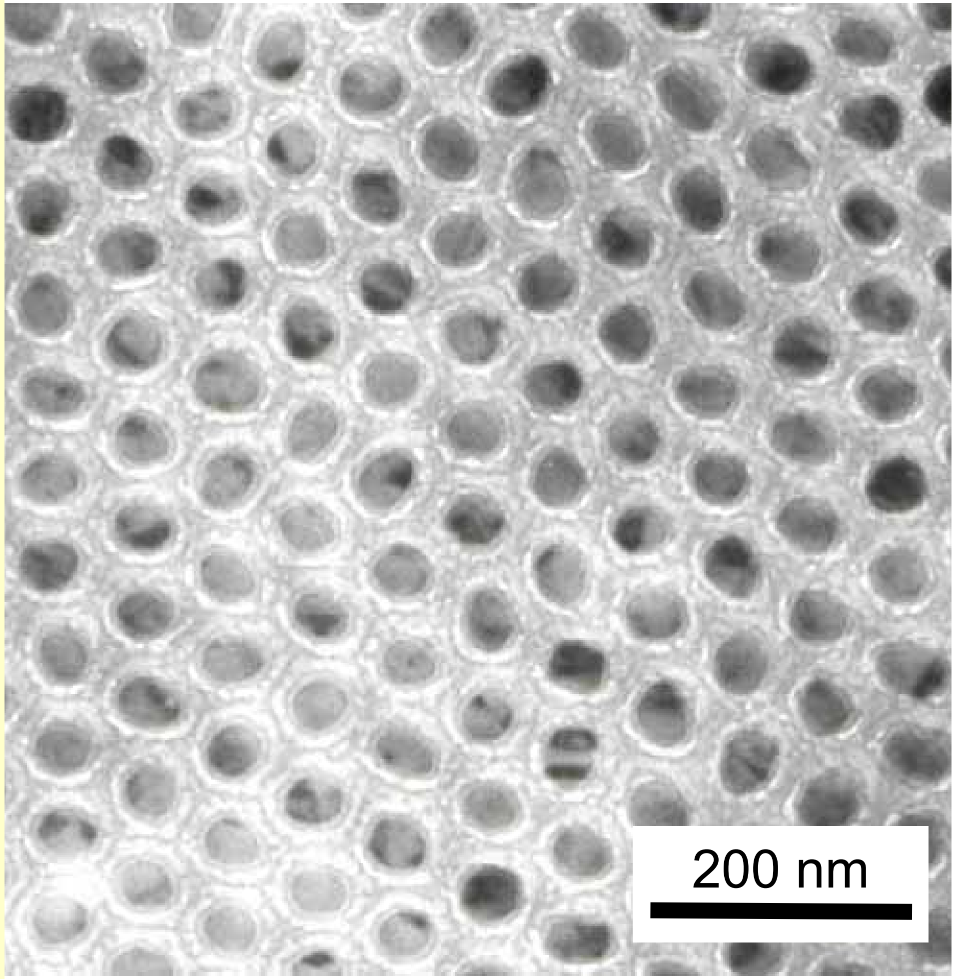
Areal Density: 176 Gbit/in^2

Patterned magnetic medium with perpendicular magnetisation



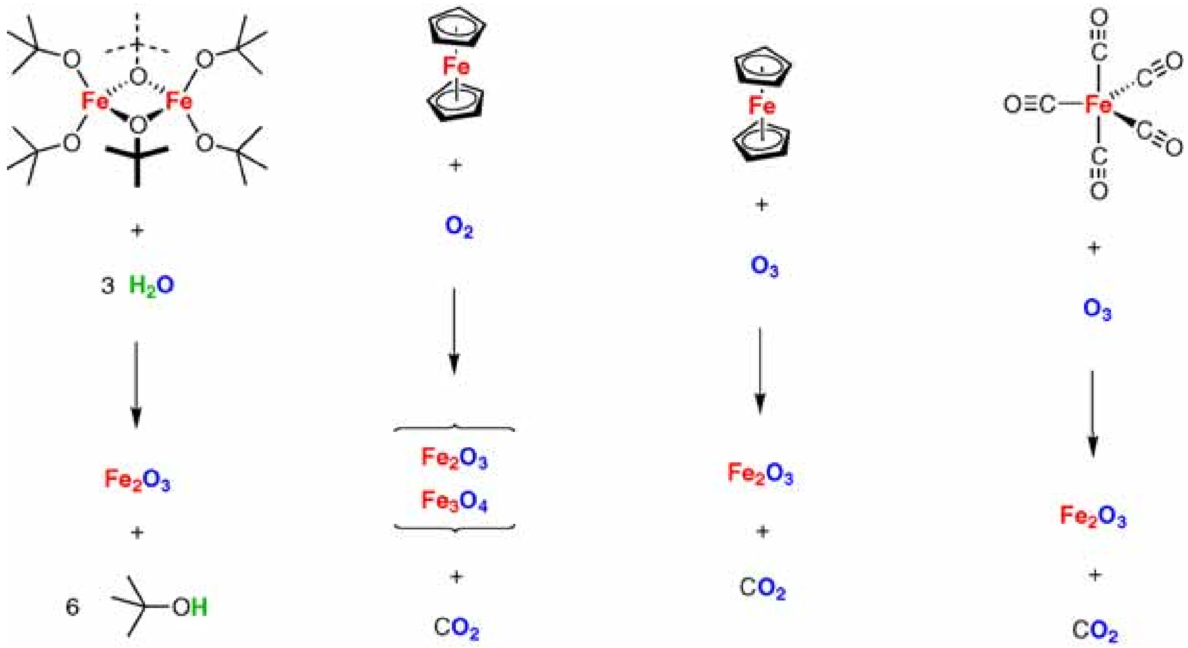
- single domain nanomagnets
- achievable areal density*: **700 Gb/in^2**

*hexagonal array, lattice constant 33 nm



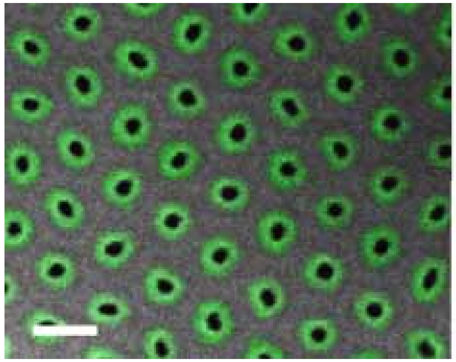
Nanowire diameter: **~ 25 nm**, column length: **~ 800 nm**

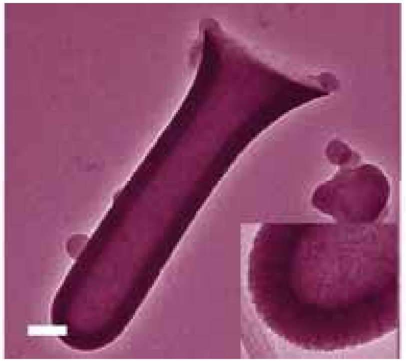
Chemical Approaches to ALD of Iron Oxides

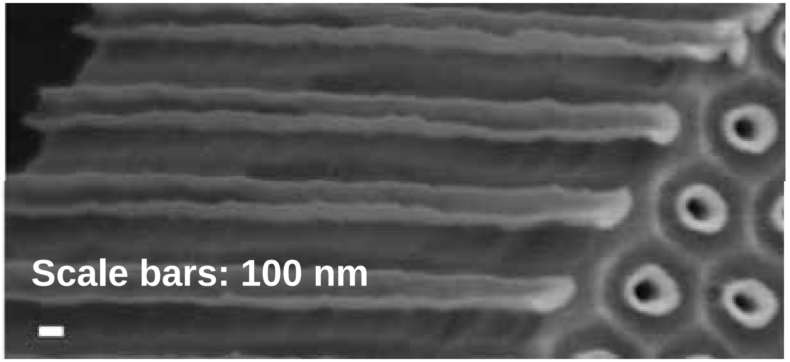


Chemical reaction	well-defined	ill-defined	ill-defined	ill-defined
Product	Fe_2O_3	Fe_2O_3 + Fe_3O_4	Fe_2O_3	?
Temperature…	low-medium	high	medium-high	low
… accessible depth	4 µm	?	50 µm	?
… organic substrates	yes	no	no	yes
Growth rate	0.24 Å/cycle	?	~0.2 Å/cycle	0 Å/cycle
Precursor	air-sensitive	air-stable	air-stable	air-sensitive
	from collaboration	commercial	commercial	commercial

Iron Oxide Nanotubes by ALD in Porous Alumina







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

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

J. Bachmann et al., JACS 129, 9554 (2007).

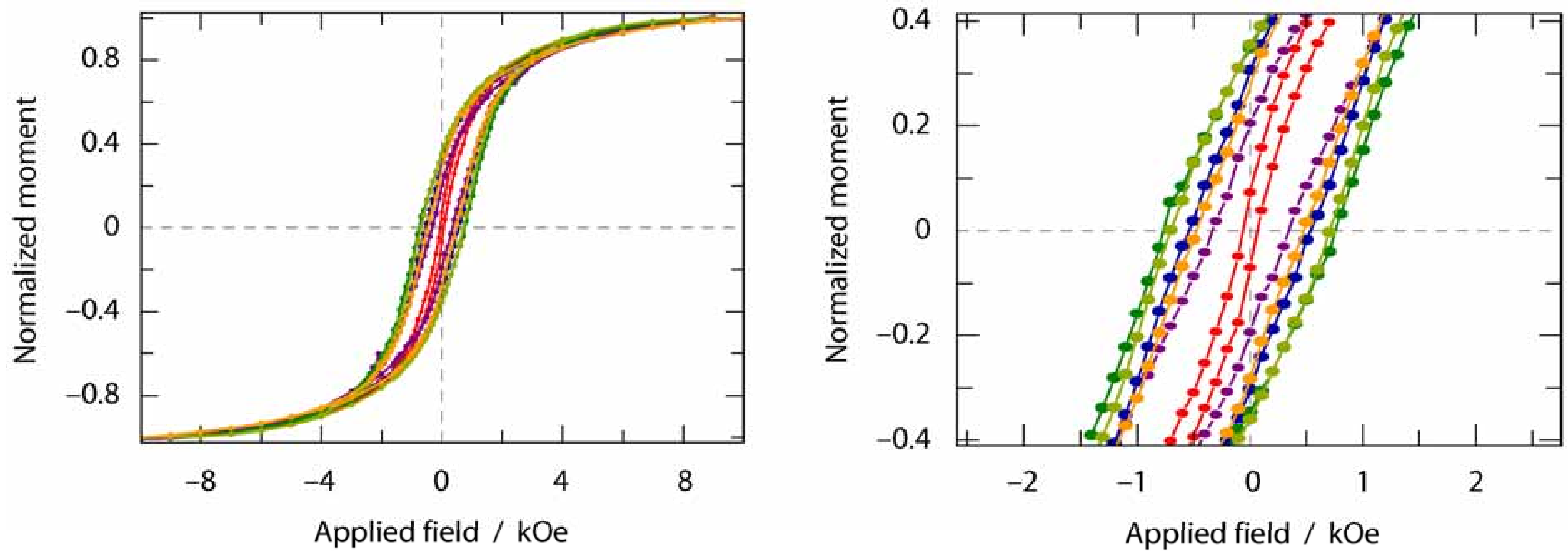
Highlighted in nature nanotechnology

University of Hamburg   BMBF Nanofutur Group   MPI-MSP Halle

Iron Oxide Nanotubes by ALD in Porous Alumina

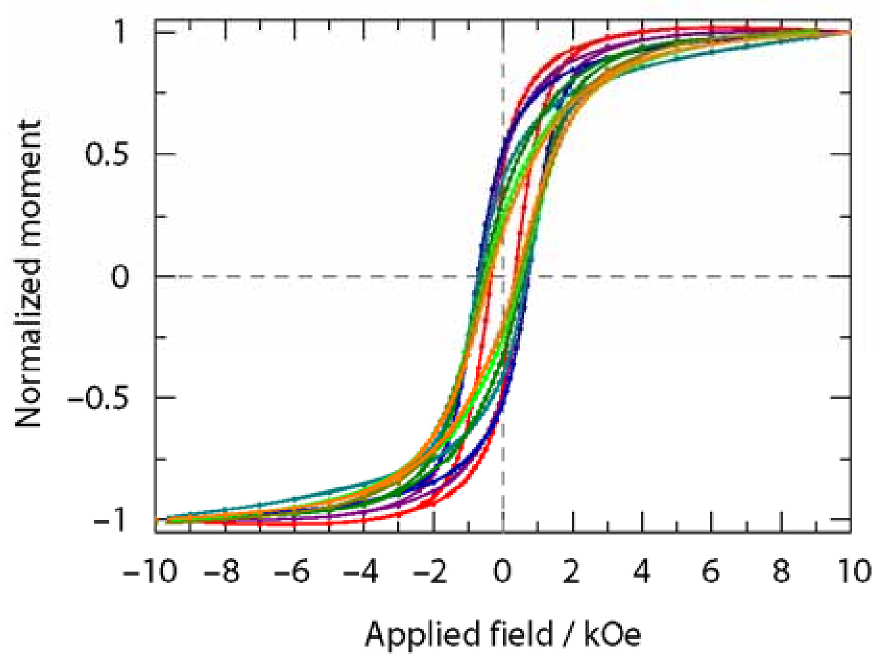
J. Bachmann et al., JACS 129, 9554 (2007).

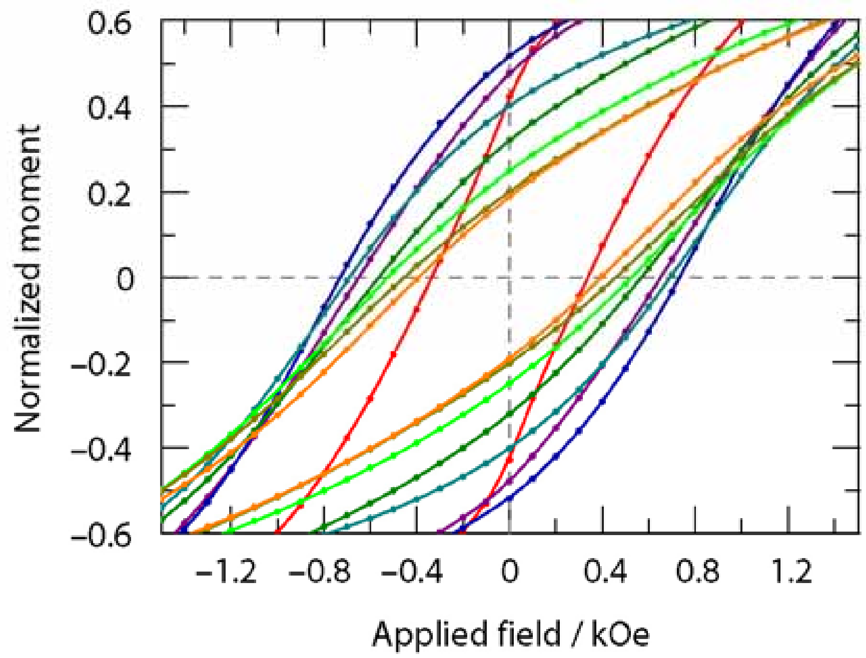
Magnetism of Narrow Fe_3O_4 Tubes

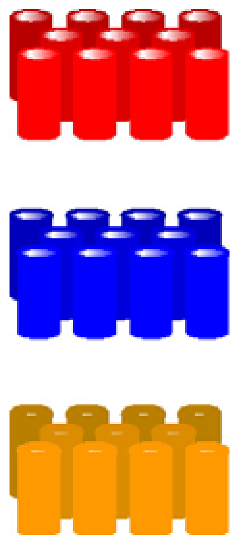


300 K, **H** // *z*
"Oxalic" template:
D_p = 50(±10) nm
D_{int} = 105 (±20) nm

Magnetism of wider Fe_3O_4 tubes

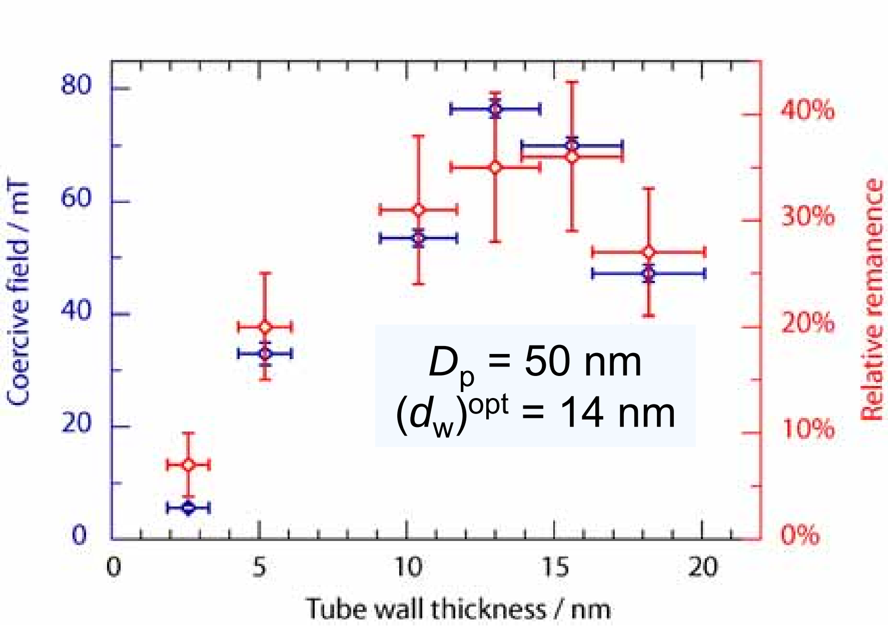


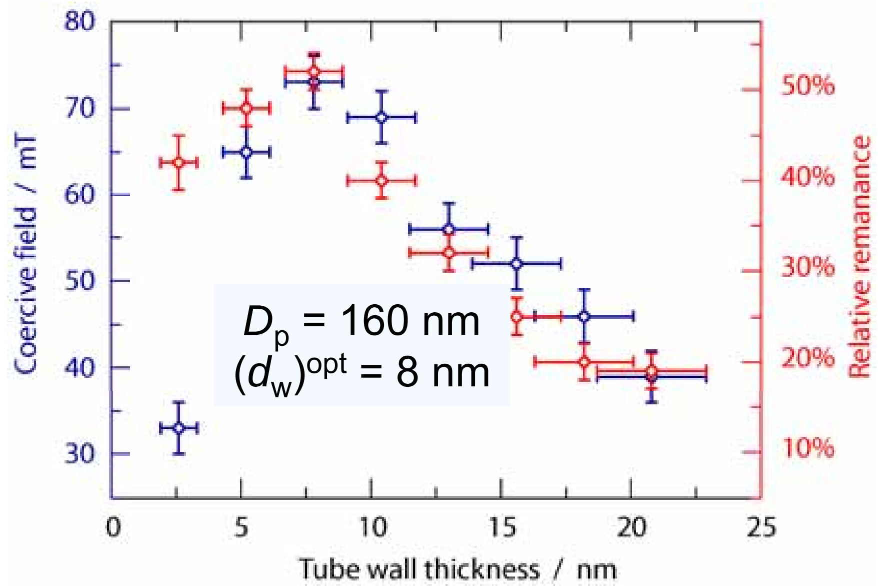




300 K, **H** // *z*
"Phosphoric" template:
D_p = 160(±20) nm
D_{int} = 460 (±50) nm

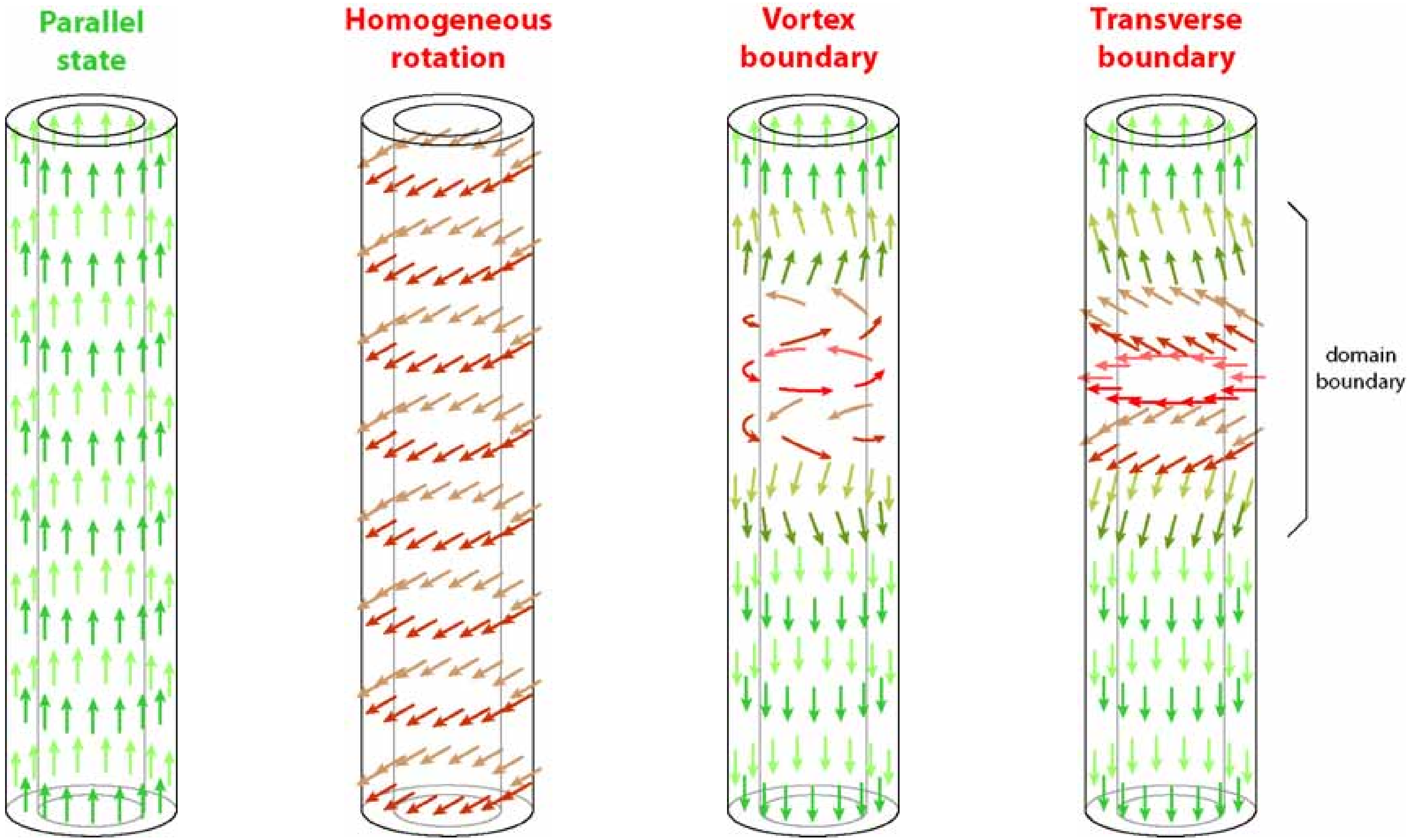
Questions ?





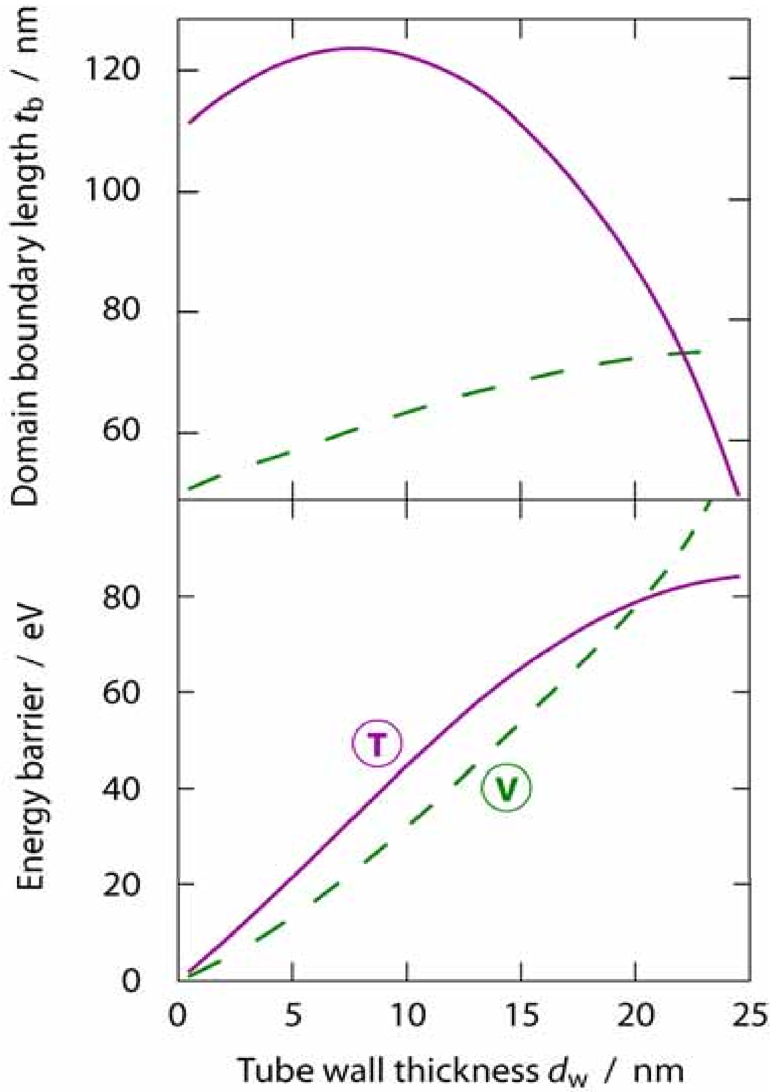
- **Non-monotonic** behavior
- Origin of H_c decay
- Position of optimum

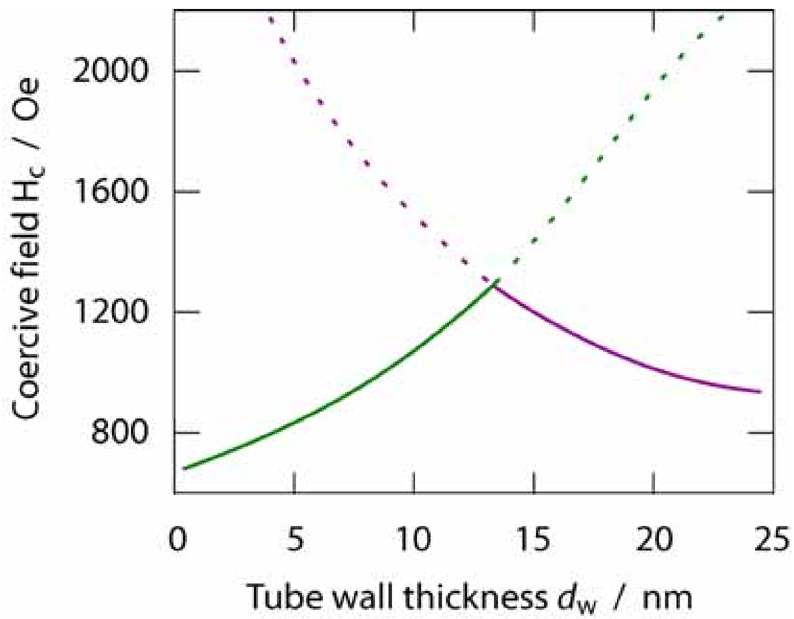
Interpretation: Modes of Magnetization Reversal



Landeros, *Appl. Phys. Lett.* **2007**, *90*, 102501

Quantitative Theoretical Modeling

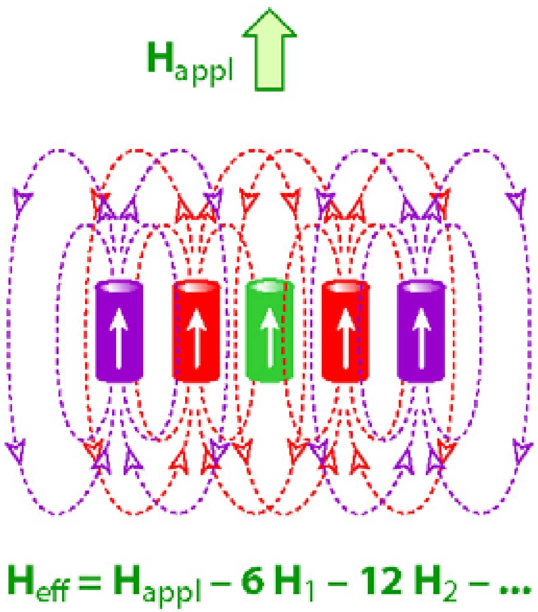


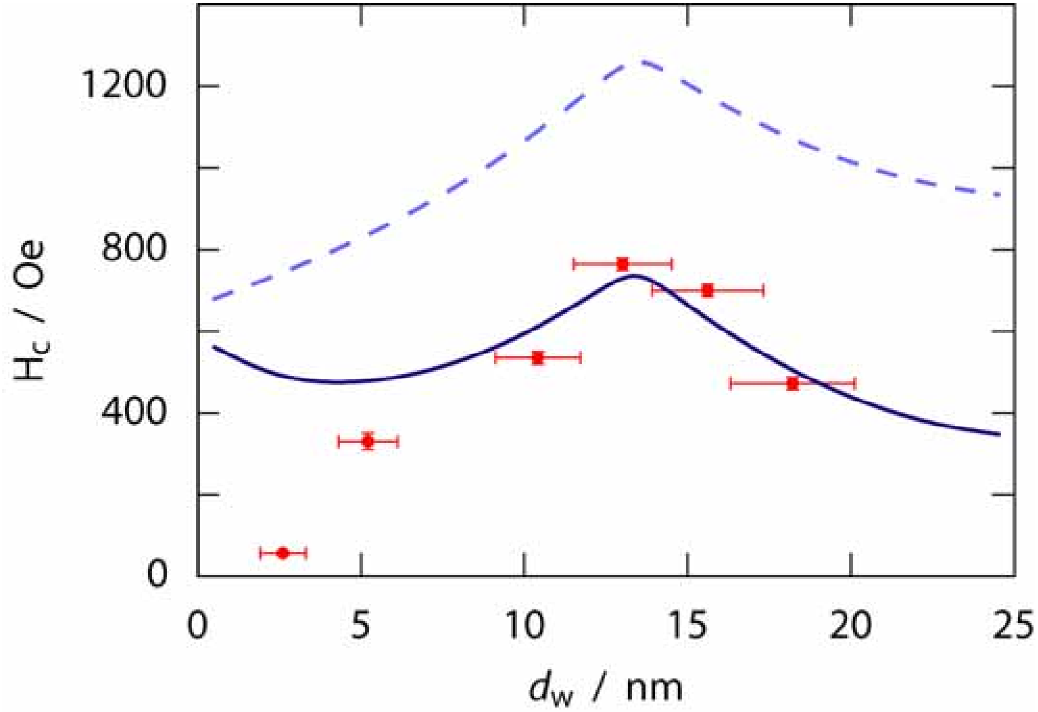


- **Non-monotonic behavior** of $H_c(d_w)$ reproduced !!!
- Originates from **crossover btw two different reversal modes**
- Absolute values of H_c too high

Effect of Stray Fields

- Interaction of each tube with its neighbors (stray field) decreases the magnetic field it effectively experiences
- Consequence: **lower coercivity**



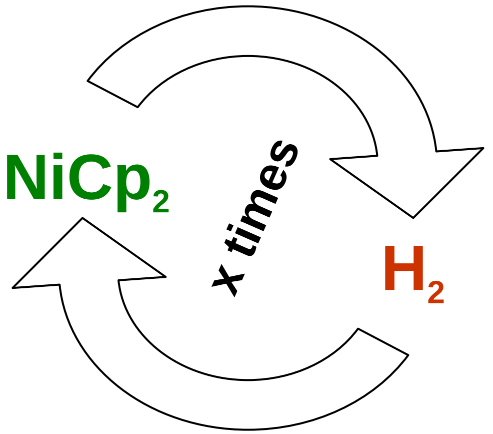


J. Escrig et al, PRB 77, 214421(2008).

ALD Prozesses for Ferromagnetic Materials

1) Direct Reduction

$NiCp_2 + H_2 \rightarrow Ni$

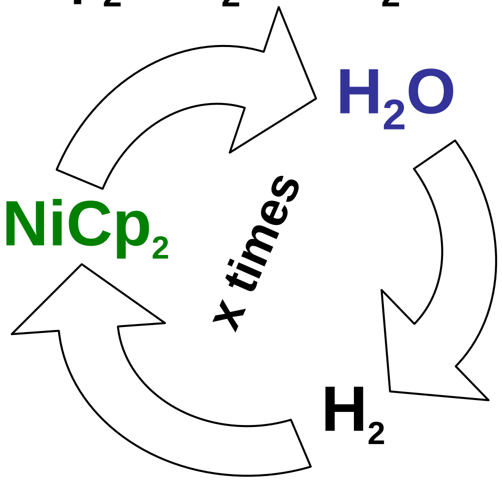


Very Low Deposition Rates:
<20 pm / cycle

Very Granular Metallic Films

2) 3-Step Process

$NiCp_2 + H_2O + H_2 \rightarrow Ni$

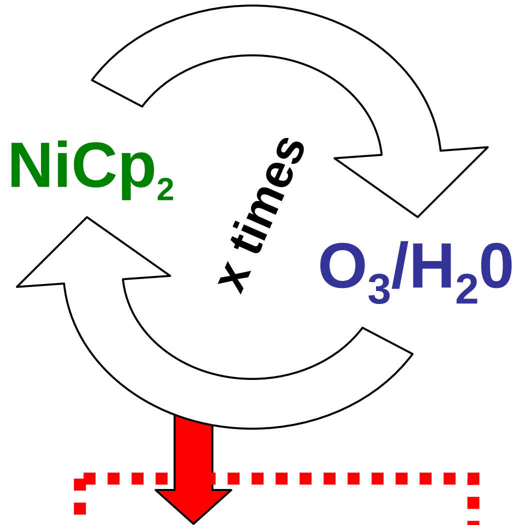


Low Deposition Rates:
20 to 40 pm / cycle

Very Granular Metallic Films

3) After ALD-Reduction

$NiCp_2 + H_2O \rightarrow NiO$



H_2 Reduction
$NiO \rightarrow Ni$

High Deposition Rates:
0.2 to 0.3 Å / cycle
Smooth Metallic Films

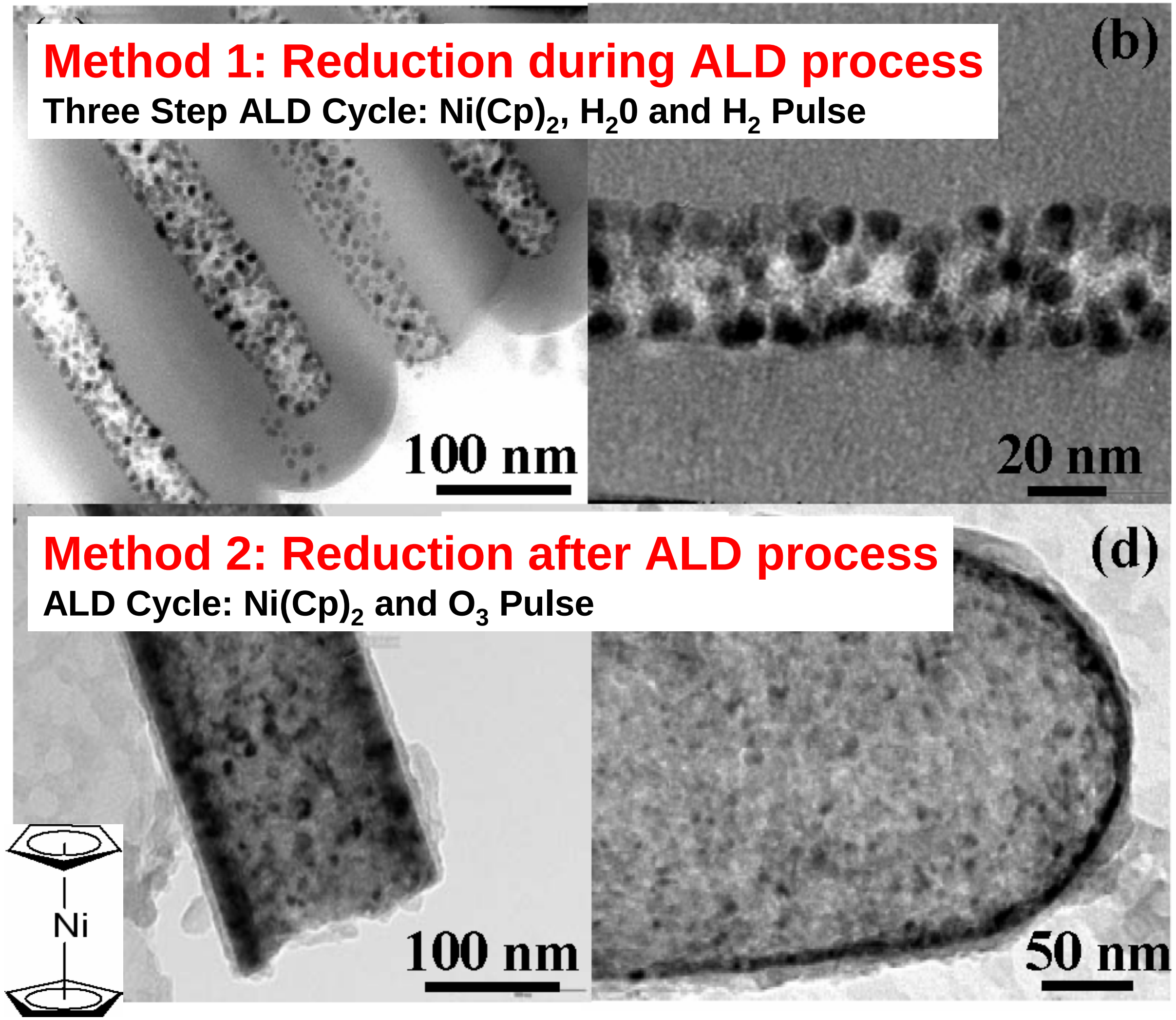
Nickel Nanotubes by ALD

Method 1: Reduction during ALD process

Three Step ALD Cycle: $Ni(Cp)_2$, H_20 and H_2 Pulse

Method 2: Reduction after ALD process

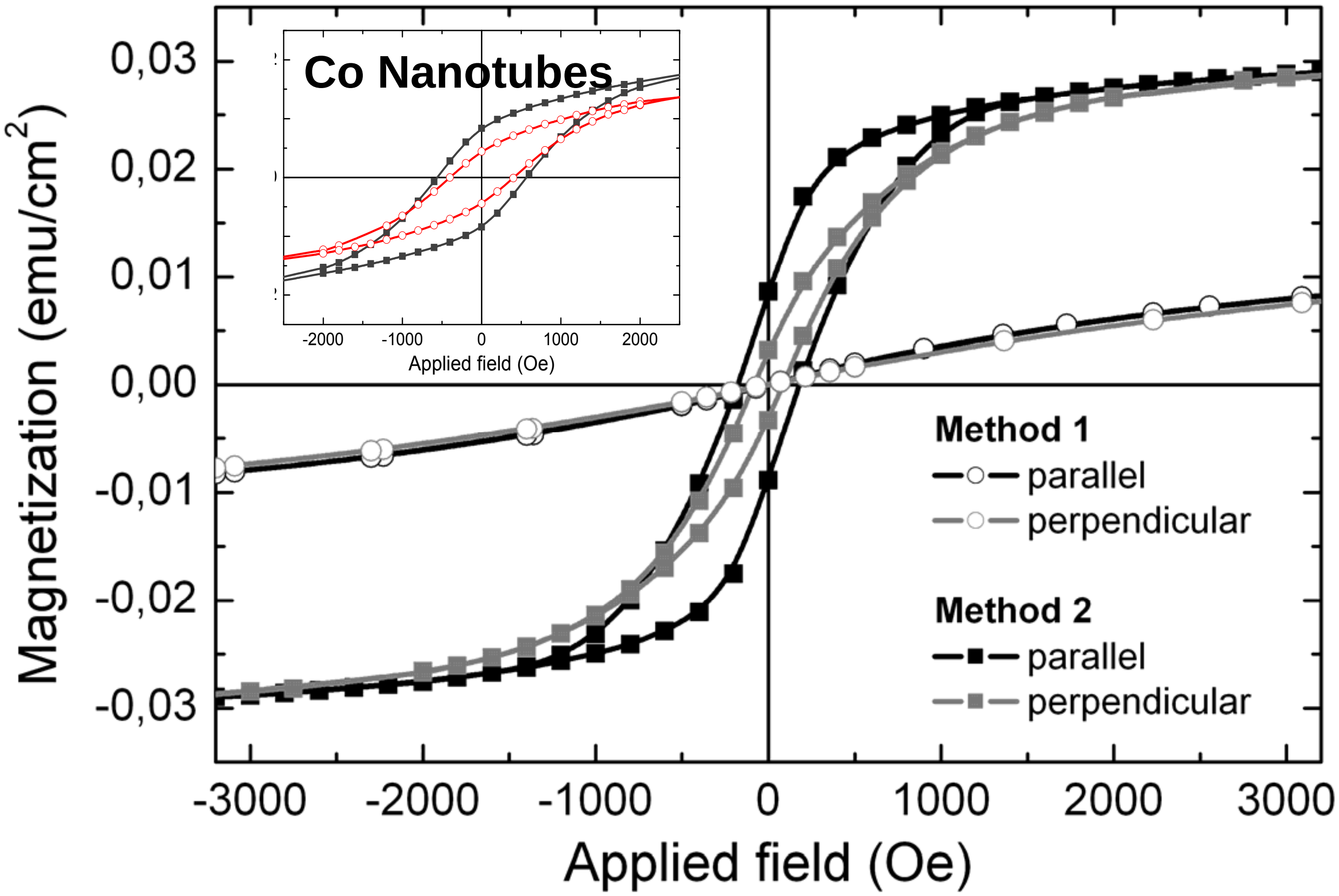
ALD Cycle: $Ni(Cp)_2$ and O_3 Pulse



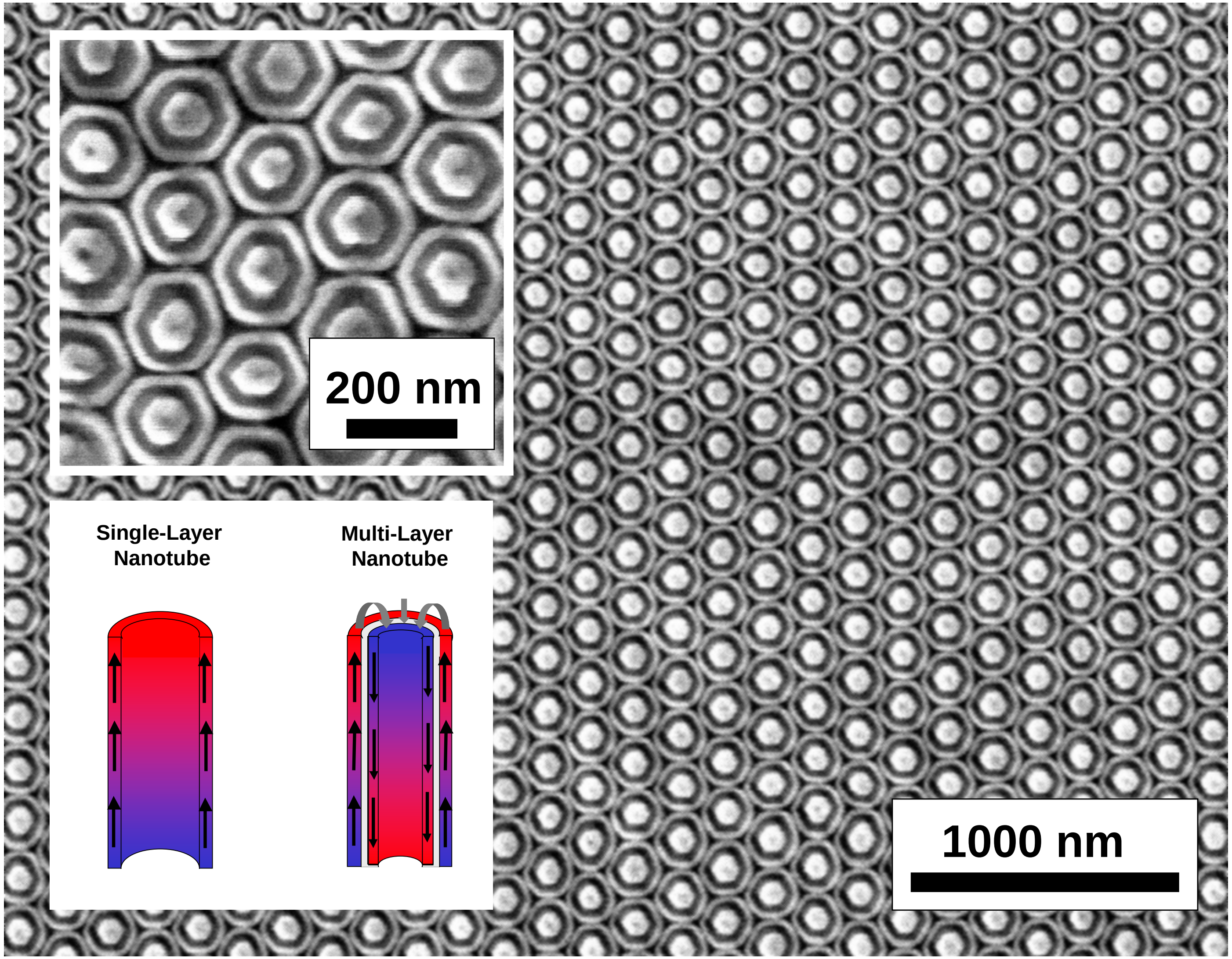
M. Daub et al, J. Appl. Phys. **101**, 09J111 (2007).

Magnetic Properties of Nickel Nanotubes

Tube diameter: 35 nm, wall thickness: 10.. 12 nm



Outlook: Multilayer (Magnetic) Nanotubes



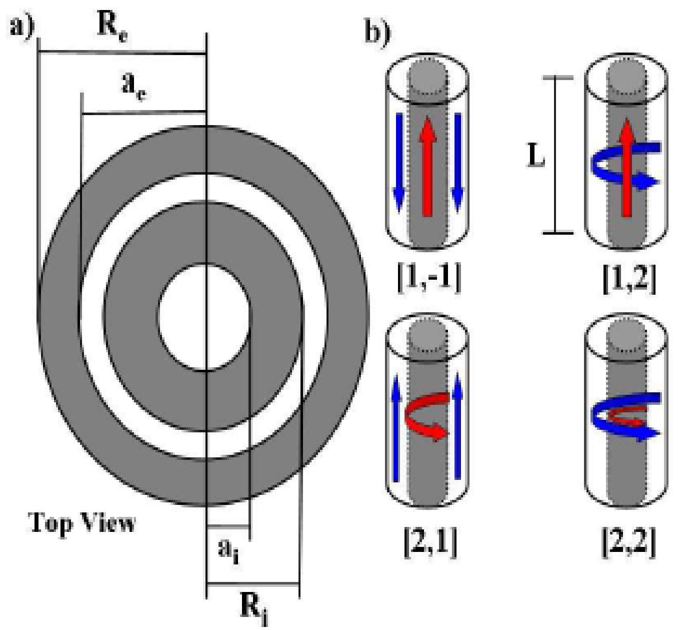
25 nm TiO_2 (light), 30 nm Al_2O_3 (dark) and 35 nm TiO_2

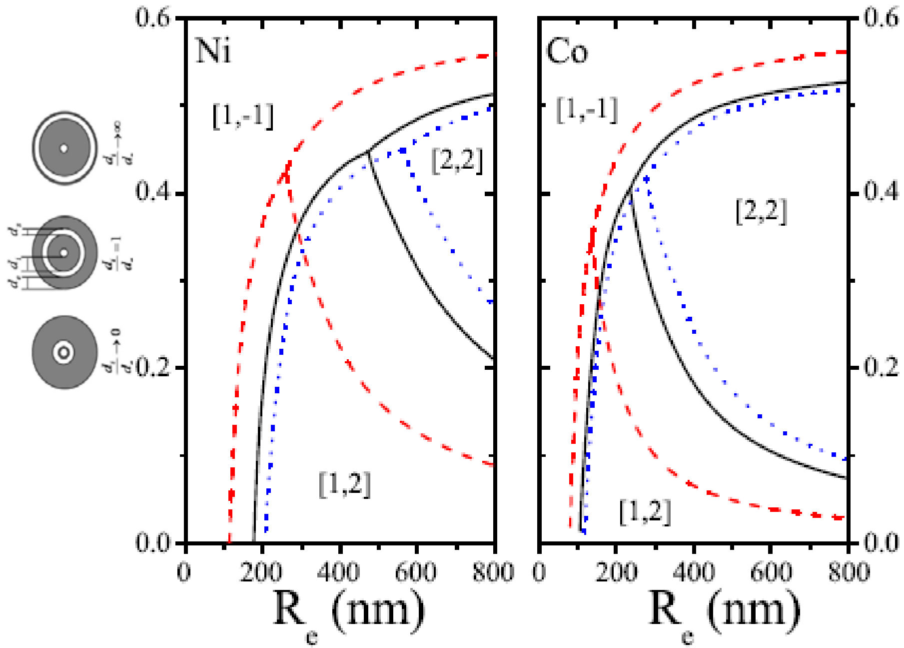
Calculations on Bi-Layer Magnetic Nanotubes

Detailed Investigations on the magnetic behavior of nanotubes:
e.g. potential Transitions:

Parallel (β < 0.2) → Curling (β = 0.3..0.6) → Parallel (β >0.8)

Core-shell Nanotubes and Nanowires





J Escrig, D Altbir, and K Nielsch, *Nanotechnology* **18**,225704 (2007).

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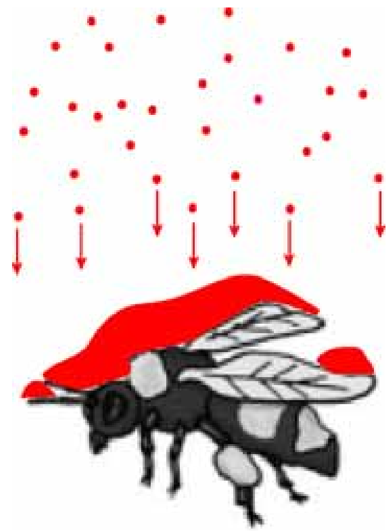
Atomic Layer Deposition (ALD)

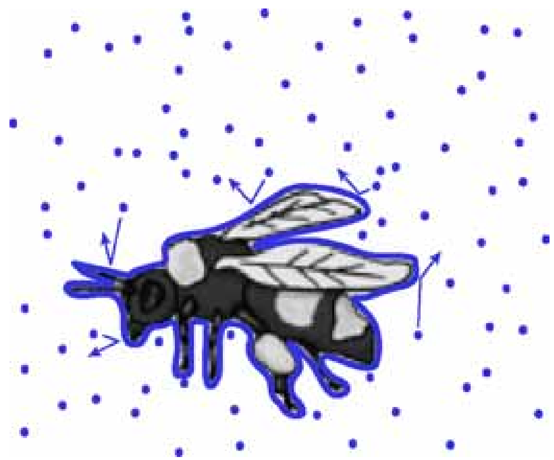
Chemical vapor deposition (CVD):

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

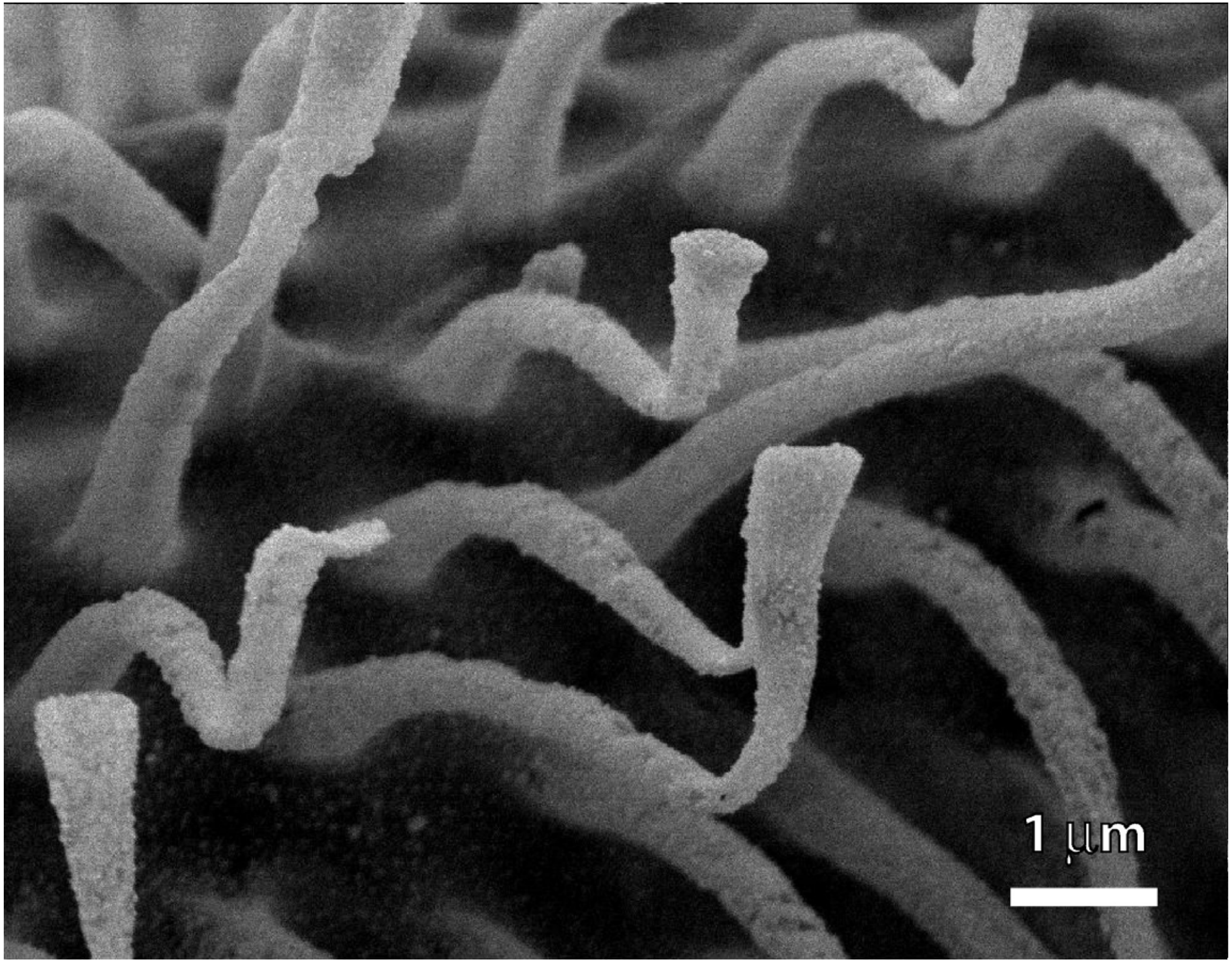


Atomic layer deposition (ALD):

- **self-limited reaction** with excess reactant
- **layer-by-layer** growth



ALD on a Complex Substrate



ALD on a Complex Substrate

Summary of low Temperature Processes

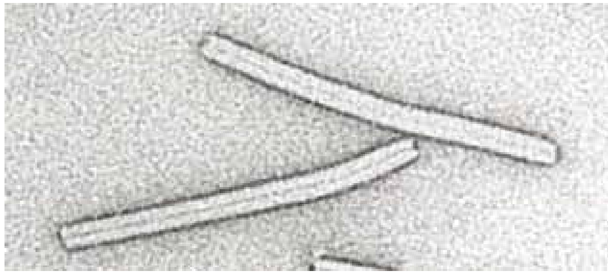
Material	Temperature	Precursor 1	Precrusor 2	Reference
SiO_2	30°C [a]	$SiCl_4$	H_2O	[68]
	27°C [b]	$SiCl_4$	H_2O	[59]
	RT	$Si(NCO)_4$	H_2O	[58]
CdS	RT	$Cd(Me)_2$	H_2S	[60]
Al_2O_3	33°C, 58°C	TMA	H_2O	[61]
	77°C			[62]
	80°C			[63]
	45°C			[64]
	35°C			[65]
	100°C			[66]
TiO_2	35°C	$Ti(OiPr)_4$	H_2O	[65]
	100°C	$TiCl_4$	H_2O	[69]
B_2O_3	20°C	BBr_3	H_2O	[70]
V_2O_5	90°C	$VO(OiPr)_3$	O_2	[71]
HfO_2	100°C	$Hf[N(Me)_2]_4$	H_2O	[46]
	90°C			[72]
ZrO_2	100°C	$Zr[N(Me)_2]_4$	H_2O	[46]
ZnO	85°C	$ZnEt_2$	H_2O	[73]
Pd	80°C	$Pd(Hfac)_2$	H_2	[74]
	80°C	$Pd(Hfac)_2$	H_2-Plasma	[75]

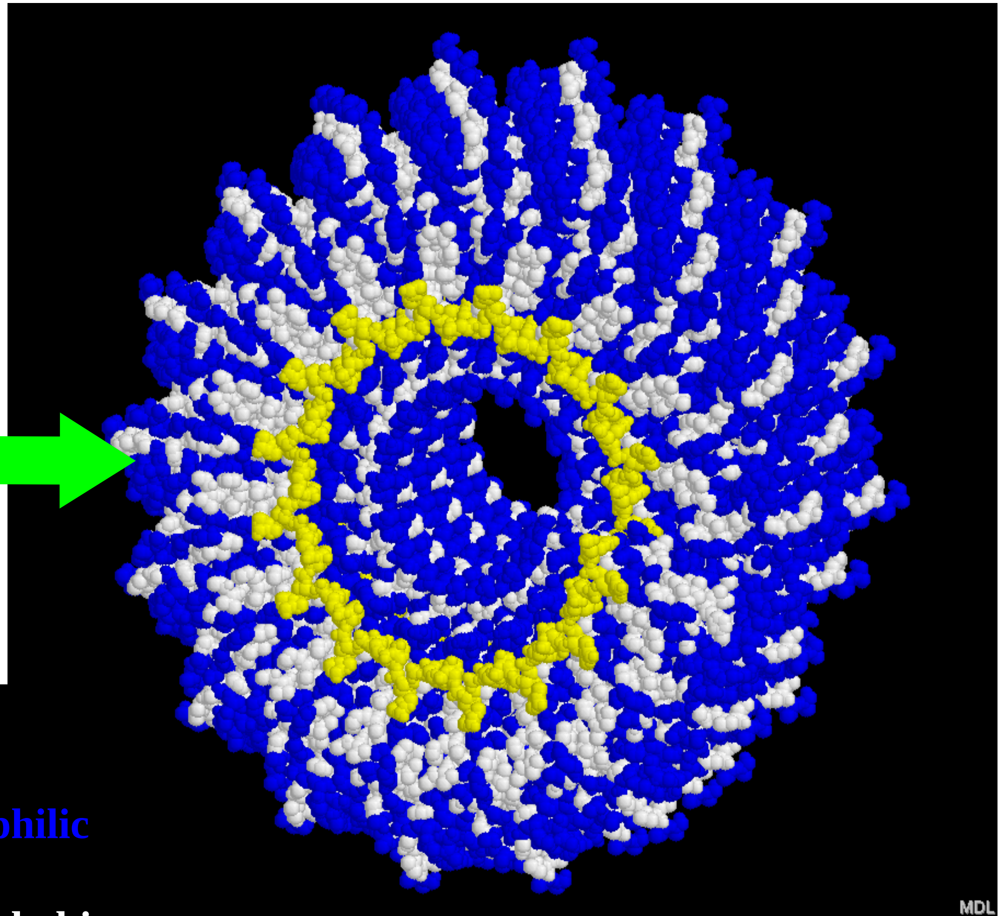
[a] Catalyzed with NH_3. [b] Catalyzed with pyridine.

M. Knez, K. Nielsch and L. Niinistö, Advanced Materials **19**, 3425-3438 (2007).

Tobacco Mosaic Virus (TMV)

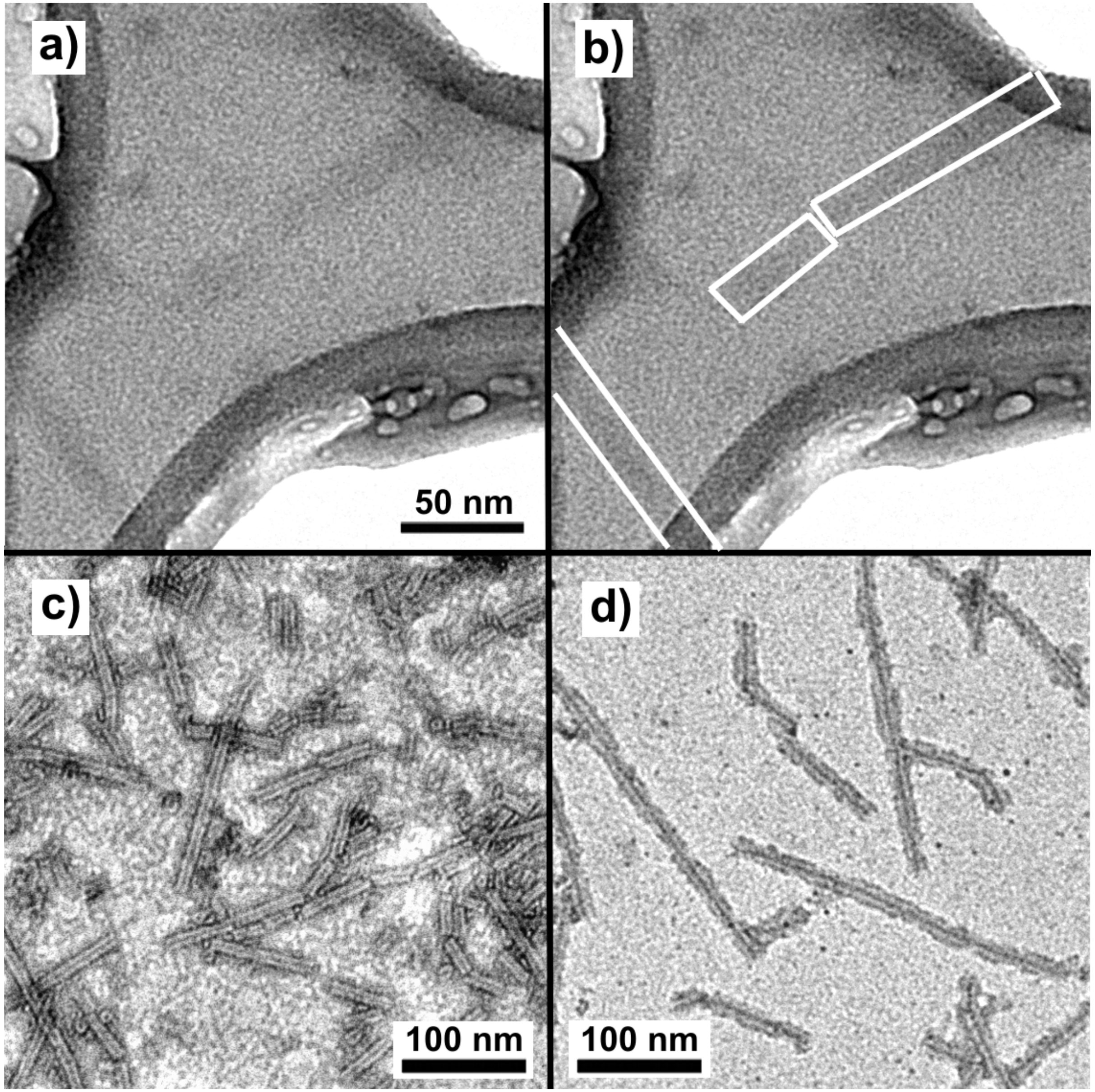
Length: 300 nm
outer Ø : 18 nm
inner Ø : 4 nm



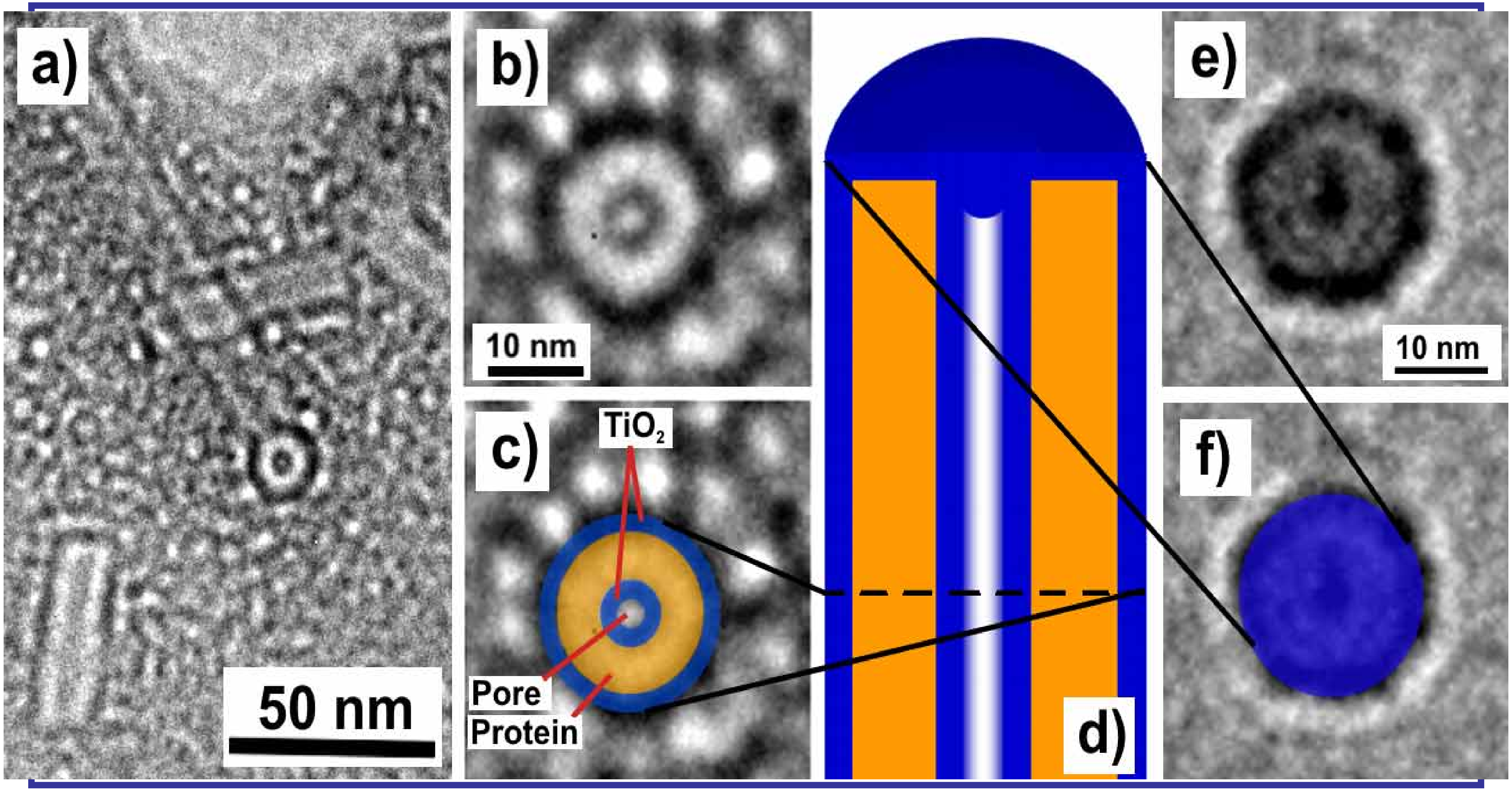


T < 80°C
2.8 < pH < 8.5
pI = 3.5

TiO_2 - deposition on TMV



ALD on Biomaterials



M. Knez et al., Nano Lett. 6, 1172 (2006).

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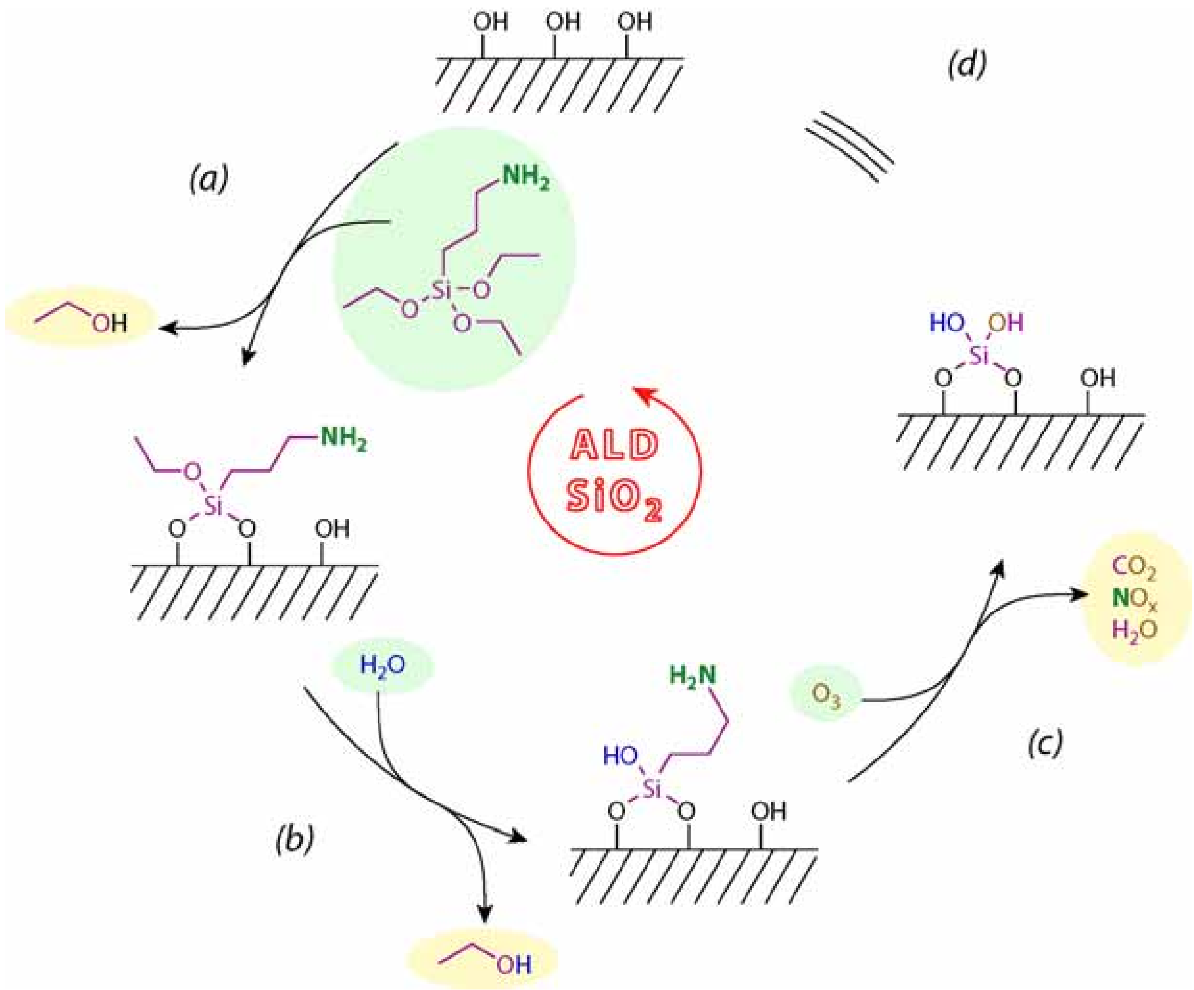
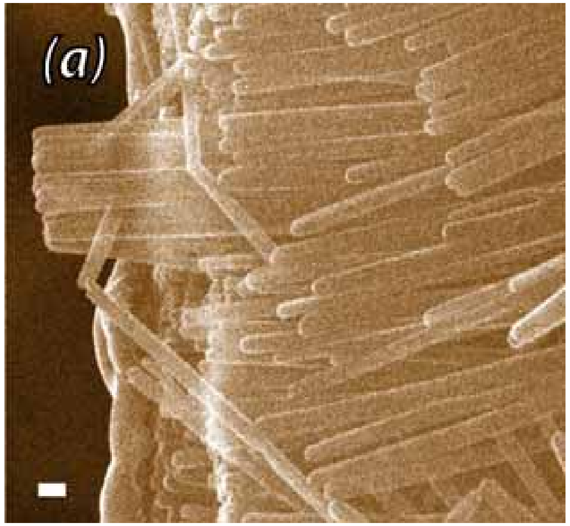
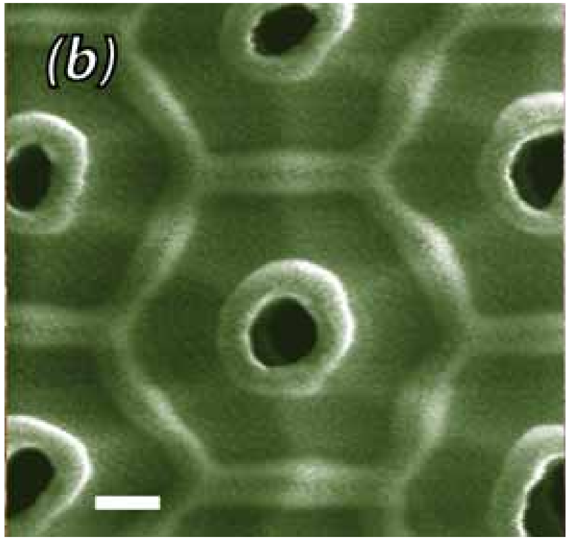
Development of ALD Processes: SiO_2

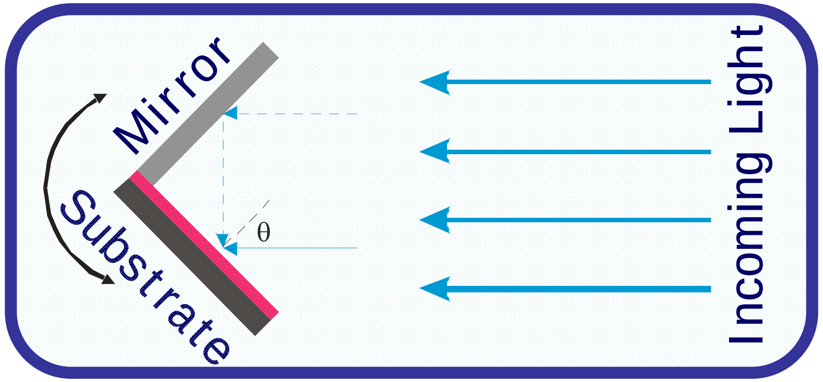


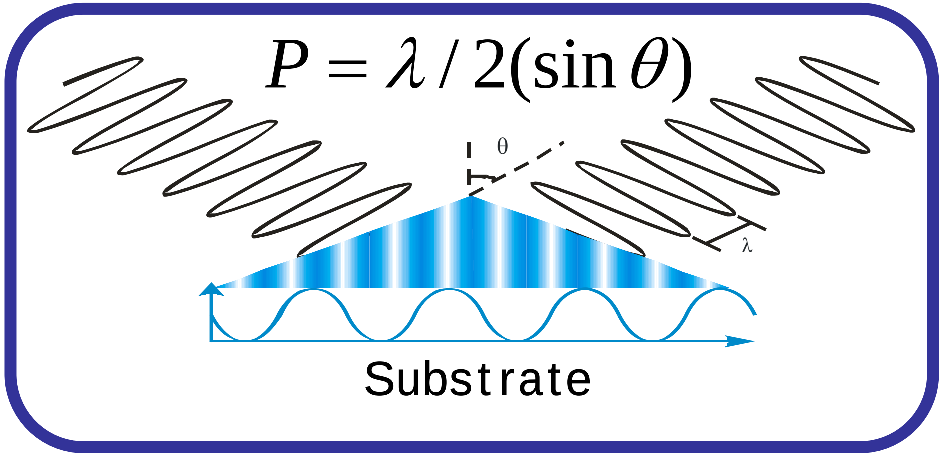


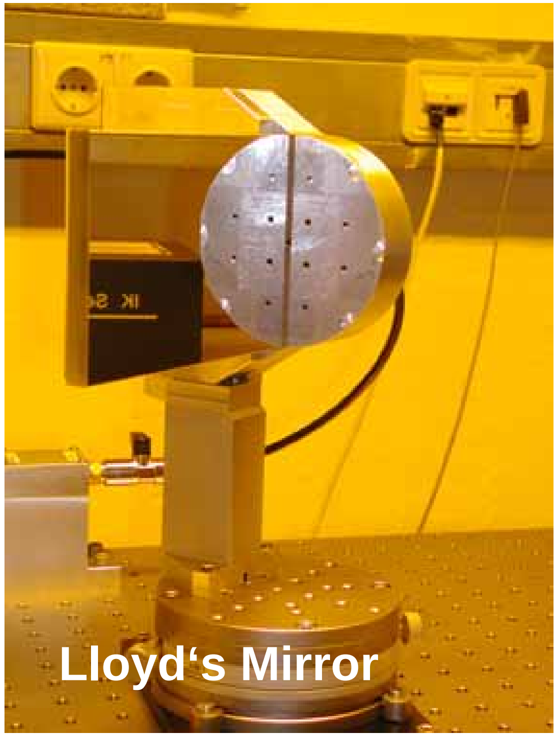


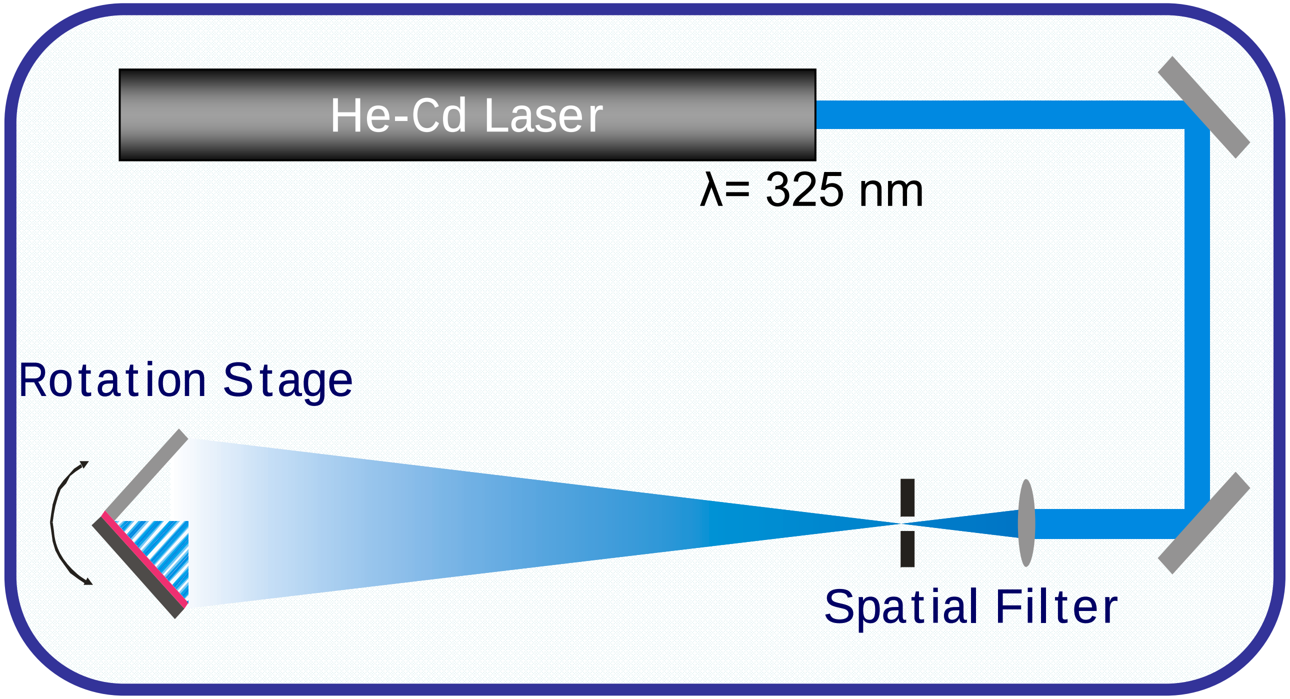
J. Bachmann et al. Angew. Chemie(2008).

Laser Interference Lithography (LIL)



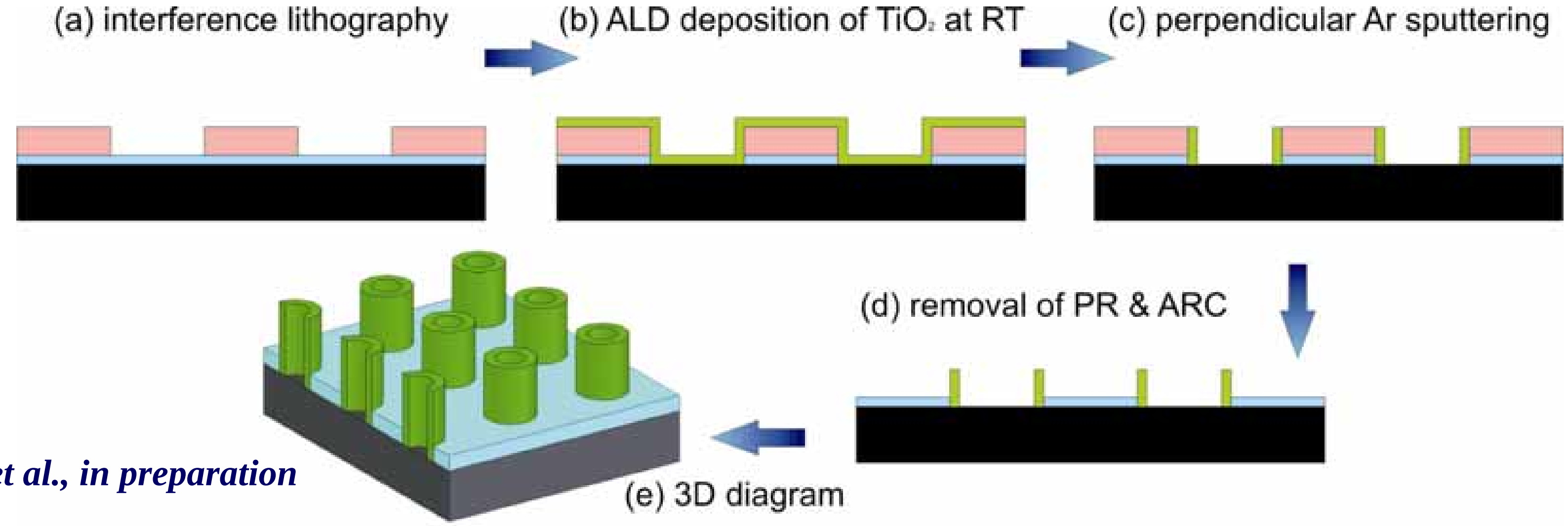




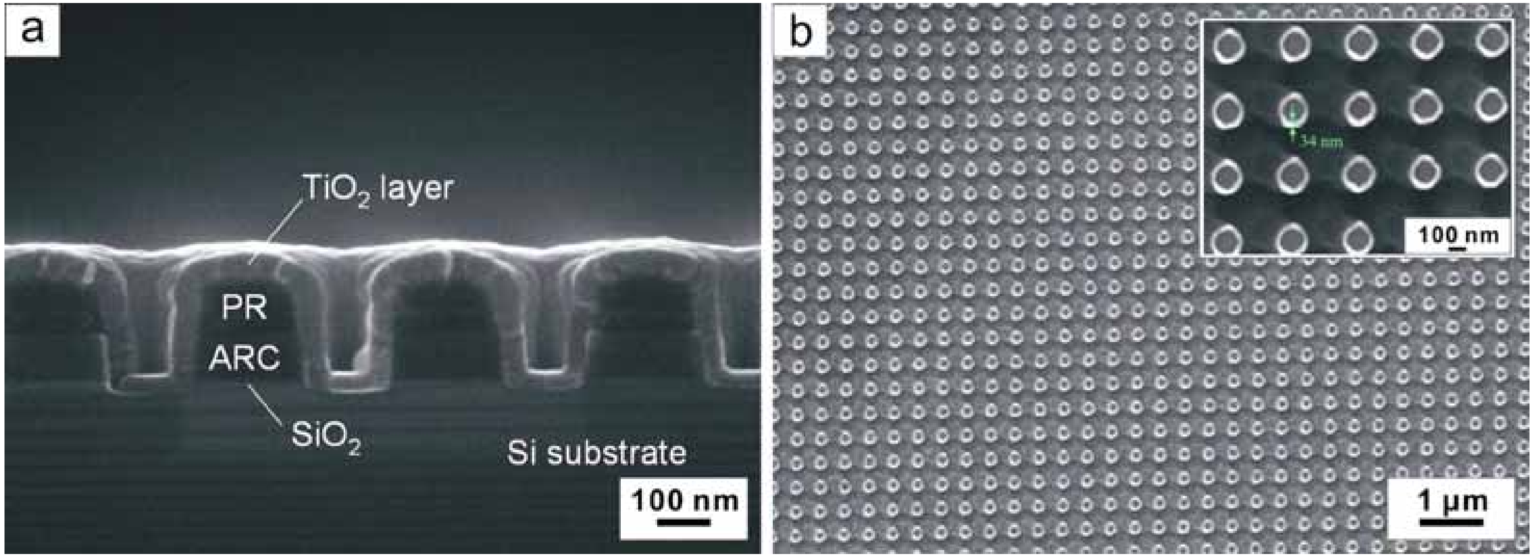


Limits: 175 nm (HeCd Laser), 140 nm (NdYAG Laser)

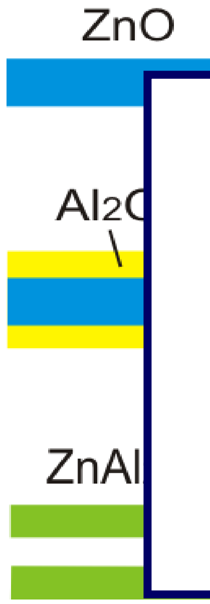
Nanoring Arrays by IL Lithography and ALD



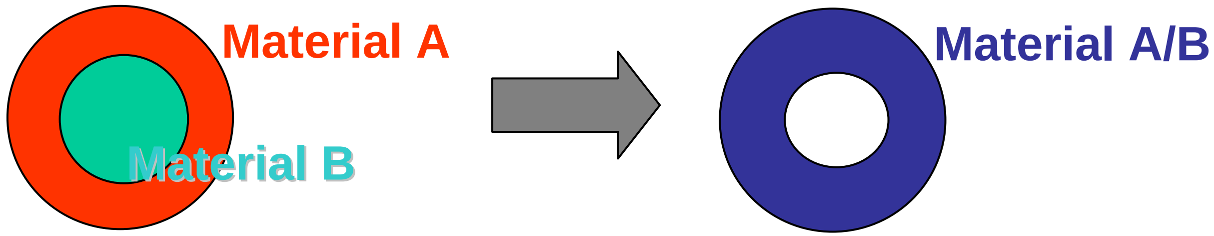
R. Ji et al., in preparation

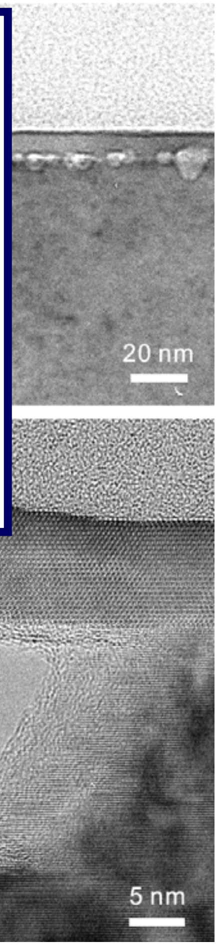


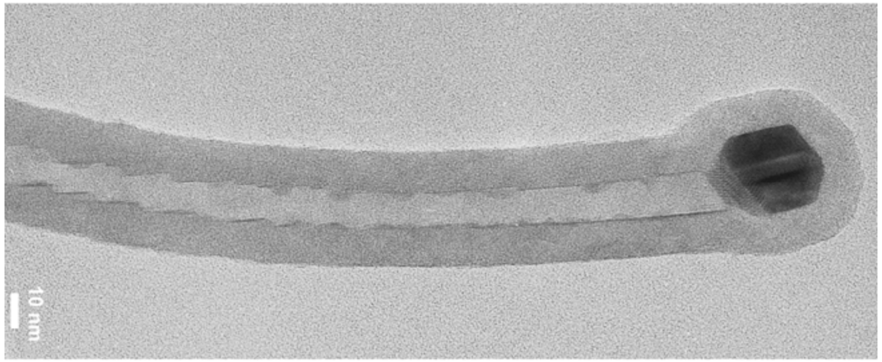
ALD and Solid State Reactions



Kirkendall Effect:







H.J. Fan, M. Knez et al., Nature Materials. 5, 627 (2006).

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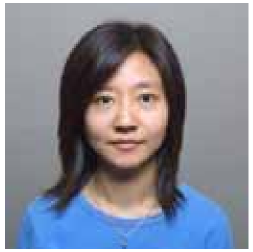

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