Atomic Layer Deposition (ALD) of Cobalt

Michal Staňo
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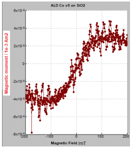
CEITEC Magnetism seminar

June 3, 2020



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Central European Institute of Technology
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STAFF3d-spin project: http://magnetism.ceitec.cz/staff3d-spin/

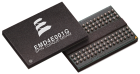
Outline of the presentation

1. Motivation: Magnetic racetrack memory 4.0
2. STAFF3d-spin project: multilayered nanotubes
3. Atomic Layer Deposition
4. Experiments: Co ALD on planar substrates
5. Summary

Motivation: 3D Magnetic racetrack memory 4.0

Available prominent magnetic data storage products (**2D**):

- Hard Disk Drive (HDD, 16 TB @ 3.5” size, sampling 20 TB)
- Magnetoresistive Random-Access Memory (MRAM, 1Gb)



Images: openclipart.org, Everspin.com

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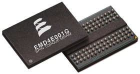

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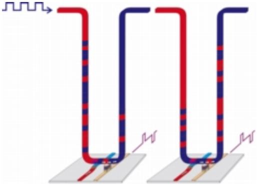

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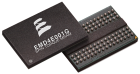

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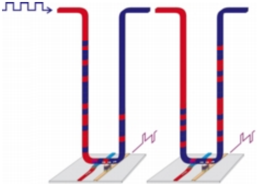

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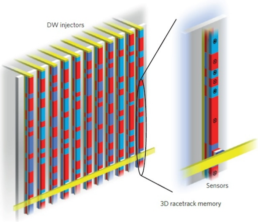

(b) Racetrack memory 4.0

1.0: Parkin et al. *Science* **320**, 190-194 (2008)
4.0: Parkin & Yang, *Nat. Nanotechnol.* **10**(3), 195-198 (2015)
Domain-wall racetrack memory: non-volatile, solid-state memory; 4.0: faster (”SAF”)

STAFF3d-spin project: multilayered nanotubes

Synthesis and investigation of
Synthetic **T**ubular **A**nti**F**erromagnets **F**or **3D Spin**tronics

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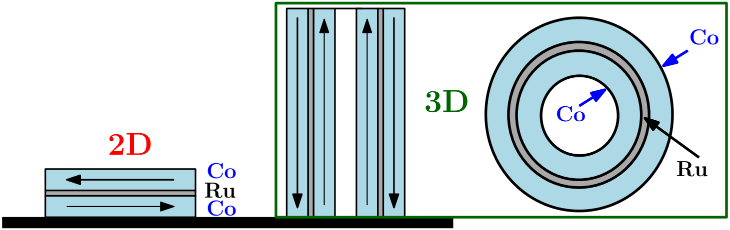

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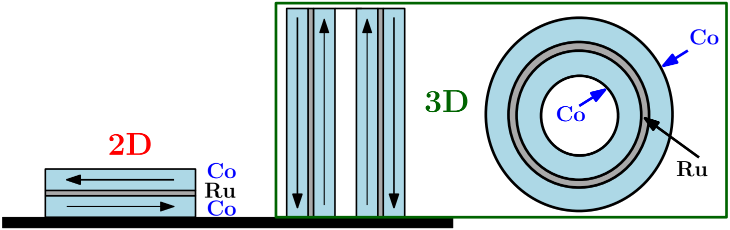
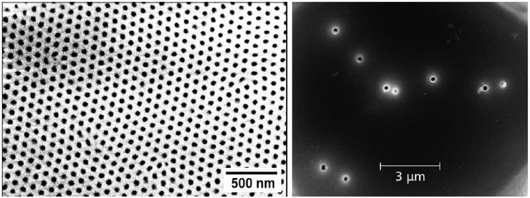


Goals:

- preparation 3D vertical arrays of tubular SAF
- test of interfaces suitability for spintronics (giant magnetoresistance)
- investigation of individual magnetic nanotubes, tubular SAFs

How to prepare nanotube (arrays)?

Best: use a template with well defined dimensions



(a) porous alumina (b) porous polycarbonate

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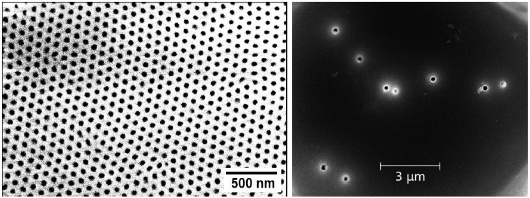

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Nanoporous alumina (AlO_x)

- tunable pore diameter, spacing and length
- well ordered, huge amount of pores (tubes) $10^9 - 10^{10}/cm^2$
- higher temperature stability (cryogenic Temp to $\approx 800^\circ C$)
- book: Losic & Santos, *Nanoporous Alumina*, Springer (2015)

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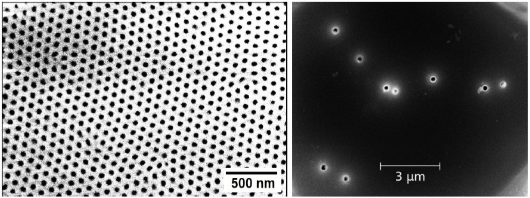

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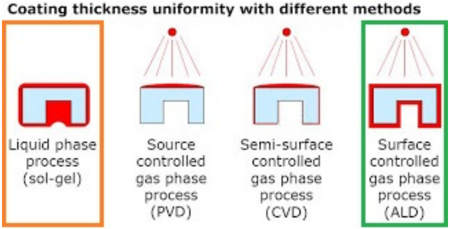
Now how to coat/fill this template?

Atomic Layer Deposition (ALD) – conformal coating



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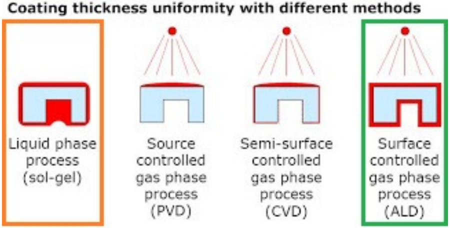

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Atomic Layer Deposition (ALD)

- Special mode of Chemical Vapor Deposition (CVD)
- Chemical reaction only at the surface
- **Conformal coating** of rough surfaces, holes, pillars, . . .
- **Precise control over film thickness** ($\approx$ 0.1 nm per cycle)

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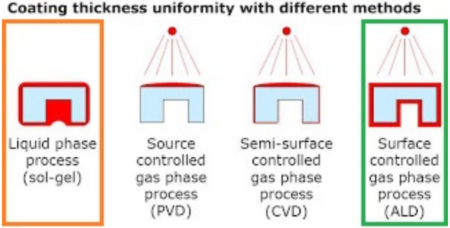

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ALD Review: George, *Chem. Rev.* **110**, 111-131 (2010)
Various info: www.plasma-ald.com

MBE vs CVD vs ALD (vocabulary)

Molecular Beam Epitaxy (MBE): UHV evaporation, semiconductors, reaction of atomic or molecular beams (e.g. Ga, As) with heated monocrystalline substrate; deposition of atomic layers, ”ultrapure”

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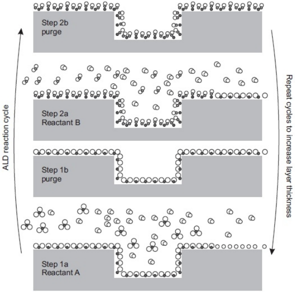
Atomic Layer Deposition (ALD): special CVD reaction limited to surface: precursor 1 + precursor 2 + energy no deposition without the 2nd precursor! *JAP* **113**, 021301 (2013)



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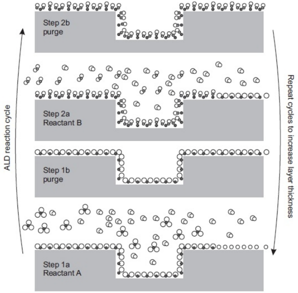

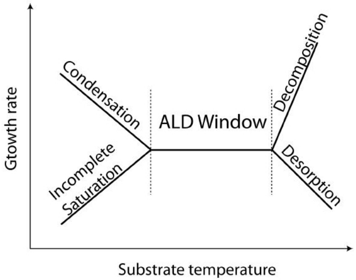

What materials can be deposited by ALD?

Close to everything:

- oxides [AlO_x], nitrides
- metals, including Fe, Co, Ni, Pt, W, Ta, Ru, Rh, . . .
- alloys, ternary and more complex compounds

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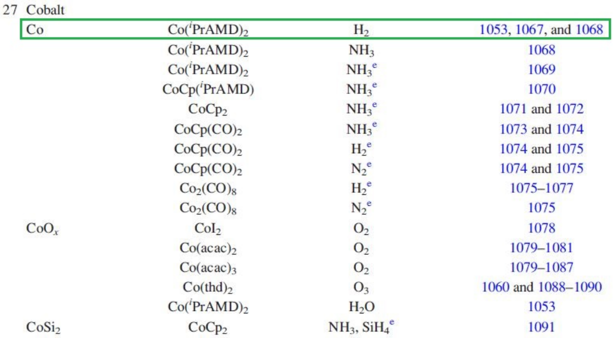
List of materials: Miikkulainen et al., *JAP* **113**, 021301 (2013)



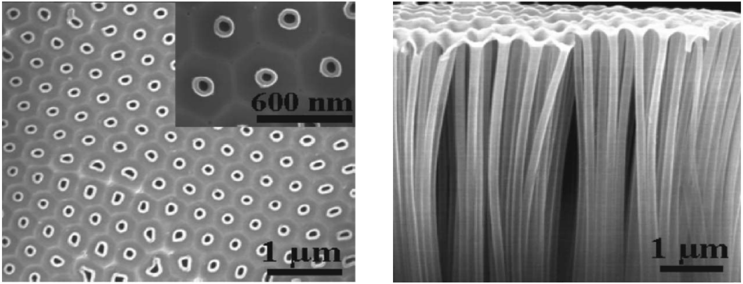
27 Cobalt

Co	$Co(^iPrAMD)_2$	H_2	1053, 1067, and 1068
	$Co(^iPrAMD)_2$	NH_3	1068
	$Co(^iPrAMD)_2$	NH_3^e	1069
	$CoCp(^iPrAMD)$	NH_3^e	1070
	$CoCp_2$	NH_3^e	1071 and 1072
	$CoCp(CO)_2$	NH_3^e	1073 and 1074
	$CoCp(CO)_2$	H_2^e	1074 and 1075
	$CoCp(CO)_2$	N_2^e	1074 and 1075
	$Co_2(CO)_8$	H_2^e	1075–1077
	$Co_2(CO)_8$	N_2^e	1075
CoO_x	CoI_2	O_2	1078
	$Co(acac)_2$	O_2	1079–1081
	$Co(acac)_3$	O_2	1079–1087
	$Co(thd)_2$	O_3	1060 and 1088–1090
	$Co(^iPrAMD)_2$	H_2O	1053
$CoSi_2$	$CoCp_2$	NH_3, SiH_4^e	1091

Magnetic nanotubes deposited using ALD so far

Deposition of (non-ferromagnetic) oxide, reduction to metal later
→ usually lower quality (also magnetism-wise)

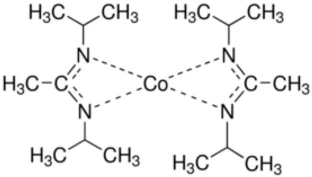
Example: Ni, Co Nanotubes – *JAP* **111**, 09J111 (2007)
Template: pore diameter 35 nm and 160 nm, length 2-50µm
Precursor: nickelocene (NiCp2)+H_2O vapour – gives oxide
Reduction better after ALD – Ar+5 % H_2 (lower grain size)



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

Co Precursor

Co (iPr-Me-AMD)$_2$: bis(N,N'-diisopropylacetamidinato) Cobalt (II)



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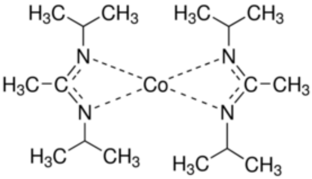

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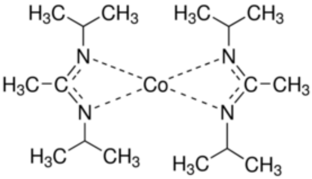

- dark green crystals
- low vapour pressure 50 mtorr ($\approx$ 7 Pa) @ 40°C (reactor $\approx$ 150 mtorr, 20 Pa)
- low deposition rate in ALD $<<$ 0.4 Å/cycle (@ 350°C, close to decomposition)
- +NH$_3$: better purity; +H$_2$: smaller grains, maybe better magnetic properties

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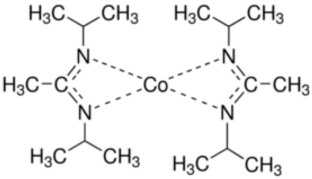

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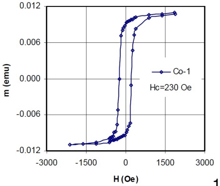
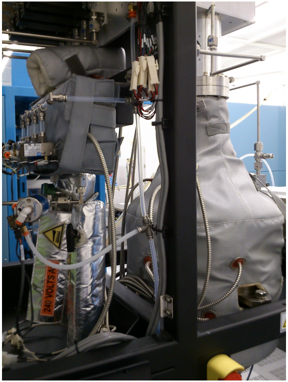
Lim et al., Nat. Mater. **2**(11), 749-754 (2003) → magnetometry
Lee et al., *J. Electrochem. Soc.* **157**(1), D10-D15 (2010)



Atomic Layer Deposition @ CEITEC Nano



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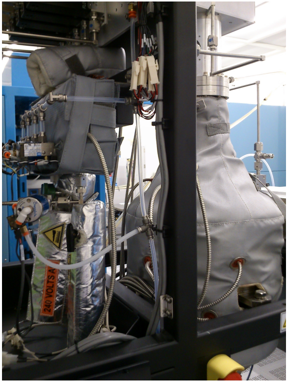
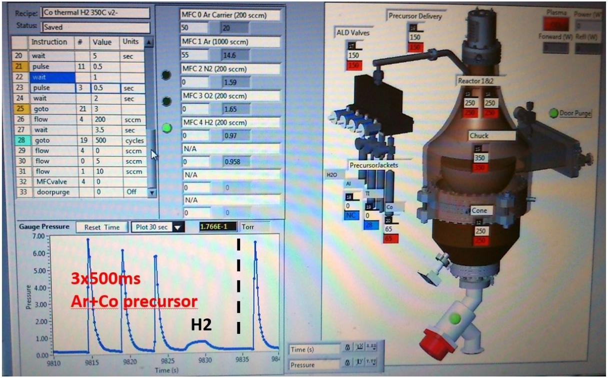




Recipe: Co thermal H2 350C v2-
Status: Saved

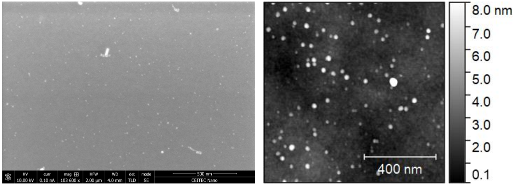
	Instruction	#	Value	Units
20	wait		5	sec
21	pulse	11	0.5	
22	wait		1	
23	pulse	3	0.5	sec
24	wait		2	sec
25	goto	21	3	
26	flow	4	200	sccm
27	wait		3.5	sec
28	goto	19	500	cycles
29	flow	4	0	sccm
30	flow	0	5	sccm
31	flow	1	10	sccm
32	MFCvalve	4	0	
33	doorpurge		0	Off

MFC 0 Ar Carrier (200 sccm): 50 | 20
MFC 1 Ar (1000 sccm): 55 | 14.6
MFC 2 N2 (200 sccm): 0 | 1.59
MFC 3 O2 (200 sccm): 0 | 1.65
MFC 4 H2 (200 sccm): 0 | 0.97
N/A: 0 | 0.958
N/A: 0 | 0
N/A: 0 | 0

Gauge Pressure: 1.766E-1 Torr

More information on the instrument:
http://nano.ceitec.cz/atomic-layer-deposition-system-ultratech-cambridgenanotech-fiji-200-ald/

Co ALD test v5 on SiO_2 @ 350 °C



(a) Electron microscopy (b) Topography (AFM)

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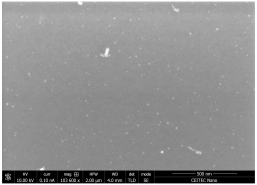

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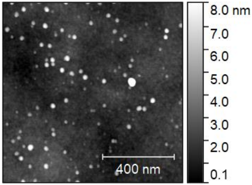

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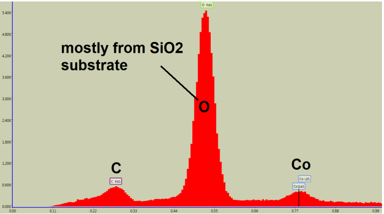

(c) Chemical analysis (EDX 1.6 kV)

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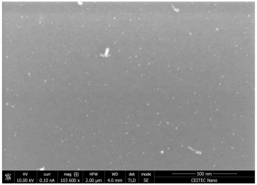

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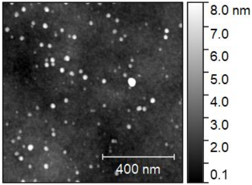

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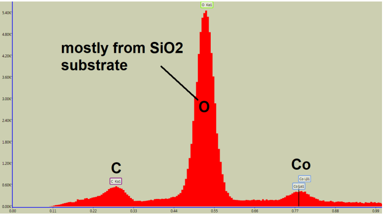

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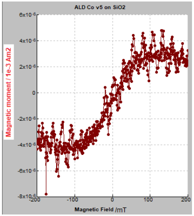

(d) Magnetometry

Magnetometry (VSM): close to the limit, sample centering issue → redo
To do: Auger mapping (Co particles or film+particles?), XPS?, . . .

Our ALD depositions @ CEITEC Nano

First: coating planar substrate; Later: porous AlO_x templates

Proper substrate needed

Si: very low coverage, mostly on dirty surfaces, defects

SiO_2 (thermal, 80 nm): some Co there

Fe 30 nm on Si: some Co there

Al_2O_3 (0001): no or extremely weak Co signal

Current issues:

- low precursor dose (low vapour pressure), low thickness
- Is the film continuous or just particles?
- Will it grow on SiO_2 prepared by ALD?

Also: Will it grow on Ru? It should, but…

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- ALD of Cobalt explored in the literature, but mostly only for microelectronics, not spintronics
- magnetic nanotubes prepared by ALD before, but as oxides and reduced afterwards (lower quality?)

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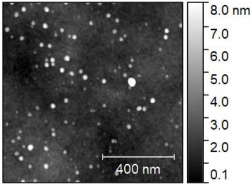
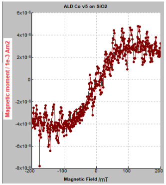
Our work – direct metallic+ferromagnetic Co by ALD

Preliminary observations / results [Co(iPrMeAMD)$_2$]

- deposition quite substrate dependent
- very low deposition rate and thickness (particles?)
- first cobalt deposits obtained, v5 seems magnetic
- more optimization needed to have thicker continuous films





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Marek Eliáš ALD – technical assistance
Marek Vaňatka, Kristýna Davídková SiO_2, Si substrates

Thank you for your attention!

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YOUTH AND SPORTS

STAFF3d-spin project: http://magnetism.ceitec.cz/staff3d-spin/
(slides of presentations, updates, . . .)

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, . . .)

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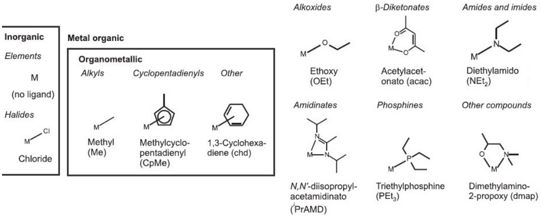

(a) precursors – mostly metallo-organics

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, . . .)

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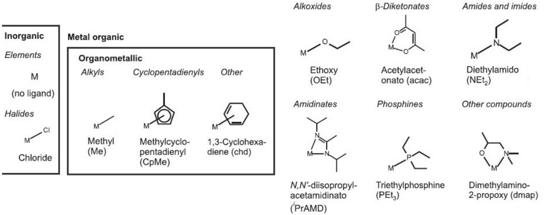

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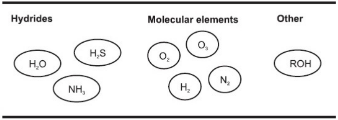

Miikkulainen et al., *JAP* **113**, 021301 (2013)

(b) reactants

ALD depositions of metallic cobalt

Explored for microelectronics (seed, conductive layer, interconnects), but almost no magnetic investigation

Review on ALD and (MO-)CVD of cobalt thin films: Kaloyeros et al., *ECS J. Solid State Sci. Technol.* **8**(2), P119-P152 (2019)

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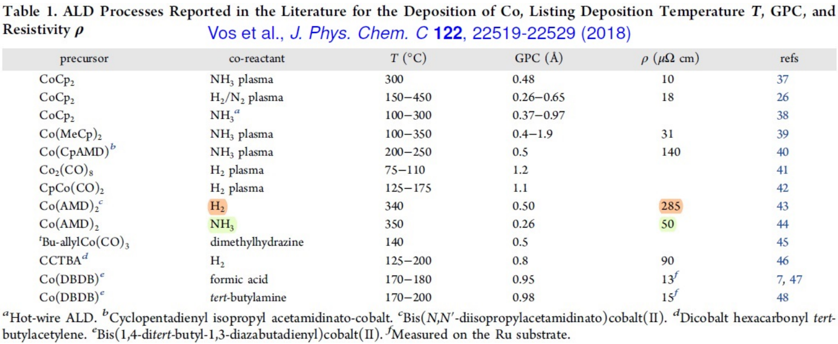


Table 1. ALD Processes Reported in the Literature for the Deposition of Co, Listing Deposition Temperature *T*, GPC, and Resistivity *ρ*

Vos et al., *J. Phys. Chem. C* **122**, 22519-22529 (2018)

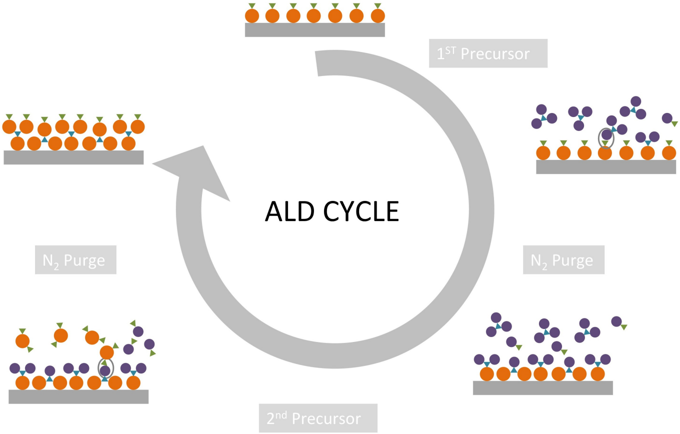
precursor	co-reactant	*T* (°C)	GPC (Å)	ρ ($\mu\Omega$ cm)	refs
$CoCp_2$	NH_3 plasma	300	0.48	10	37
$CoCp_2$	H_2/N_2 plasma	150−450	0.26−0.65	18	26
$CoCp_2$	NH_3[a]	100−300	0.37−0.97		38
$Co(MeCp)_2$	NH_3 plasma	100−350	0.4−1.9	31	39
Co(CpAMD)[b]	NH_3 plasma	200−250	0.5	140	40
$Co_2(CO)_8$	H_2 plasma	75−110	1.2		41
$CpCo(CO)_2$	H_2 plasma	125−175	1.1		42
$Co(AMD)_2$[c]	H_2	340	0.50	285	43
$Co(AMD)_2$	NH_3	350	0.26	50	44
^{t}Bu-allylCo$(CO)_3$	dimethylhydrazine	140	0.5		45
CCTBA[d]	H_2	125−200	0.8	90	46
Co(DBDB)[e]	formic acid	170−180	0.95	13[f]	7, 47
Co(DBDB)[e]	*tert*-butylamine	170−200	0.98	15[f]	48

[a] Hot-wire ALD. [b] Cyclopentadienyl isopropyl acetamidinato-cobalt. [c] Bis(*N*,*N*′-diisopropylacetamidinato)cobalt(II). [d] Dicobalt hexacarbonyl *tert*-butylacetylene. [e] Bis(1,4-di*tert*-butyl-1,3-diazabutadienyl)cobalt(II). [f] Measured on the Ru substrate.

Lim et al., Nat. Mater. **2**(11), 749-754 (2003) – magnetometry on films

Lee et al., *J. Electrochem. Soc.* **157**(1), D10-D15 (2010)

ALD cycle – How it works



ctechnano.com

See also https://www.plasma-ald.com/

ALD in spintronics / magnetism

- [microelectronics]: insulating, protective layers (AlO_x), conductive seed layers (Cu, Co, Ru)
- spin-Hall-active Pt thin films (order of magnitude worse than sputtered Pt, but detectable & room for improvement)
  APL **112**, 242403 (2018)
- **oxide barrier in magnetic tunnel junctions**
- **magnetic nanotubes**

Oxide barrier in magnetic tunnel junctions

Magnetic Tunnel Junction (MTJ): magnet/insulator/magnet

Tunneling MagnetoResistance (TMR=$\frac{R_{\uparrow\downarrow}(H)-R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}}$) 100s % @ RT

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AlO_x	24 % TMR @ 40 K, 1.6 nm, *APL* **102**, 202401 (2013) ≈ 1.2 Å & still good barrier height: *AIP Adv.* **9**, 025018 (2019)
HfO_2	10 % TMR @ RT, 2 nm, *APL* **105**, 132405 (2014)
MgO	$Fe_{3-\delta}O_4$/MgO/Co – all CVD (barrier ALD): 6 % TMR @ RT *J. Phys. D: Appl. Phys.* **47**, 102002 (2014)

Also relevant for Josephson junctions (superconductor/insulator/superconductor)

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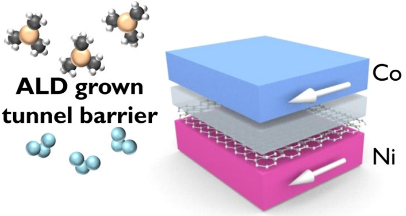
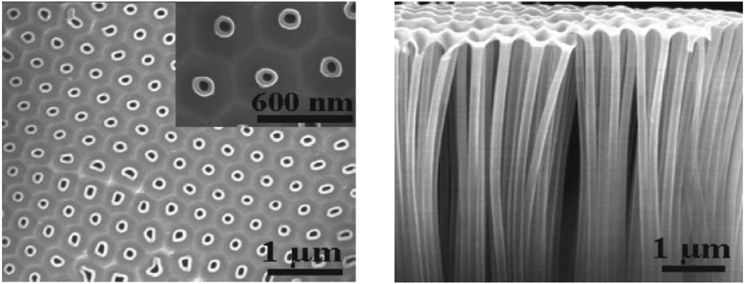


2D materials (graphene, black P)
+ ≤ 1 nm ALD barrier in MTJs
ACS Nano **8**(8), 7890-7895 (2014)

Magnetic nanotubes deposited using ALD

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.

Summary: ALD in spintronics/magnetism

+ conformal coating, high-aspect ratio structures (even 1000:1)
+ precise control over thickness, easy for core-shell
- slow, not suitable for thicker coatings ($\geq$ 100 nm)
- typically highly granular
- challenge: high purity, good magnetic properties

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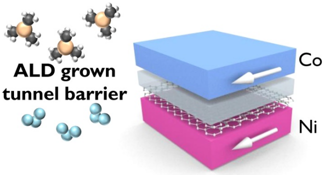

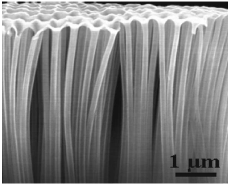

- still **mostly oxides** (cover layers, barriers in MTJs)
- first tests with **Pt for spintronics** (spin Hall effect)
- deposition of **magnetic nanotubes**, but mostly oxides or reduces from oxides (lower quality)
- only few magnetic measurements on ALD magnets (VSM)