STAFF3d-spin: Update on Atomic Layer Deposition for Magnetism & Spintronics

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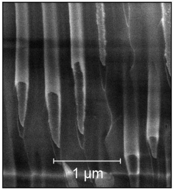

CEITEC Magnetism seminar

June 2, 2021

BRNO UNIVERSITY OF TECHNOLOGY

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

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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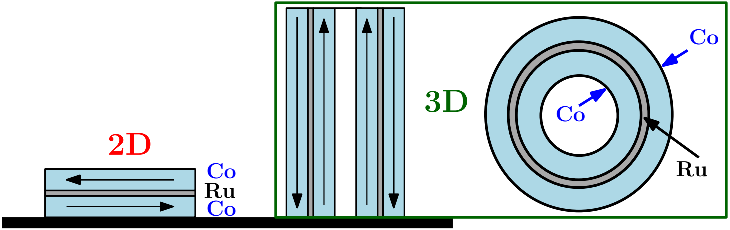

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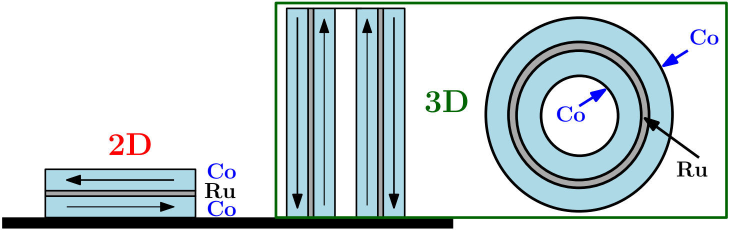

Goals

- Preparation 3D vertical arrays of tubular SAF
- Test of interfaces suitability for spintronics (giant magnetoresistance)
- Investigation of individual magnetic nanotubes, tubular SAFs **experiments and simulations**

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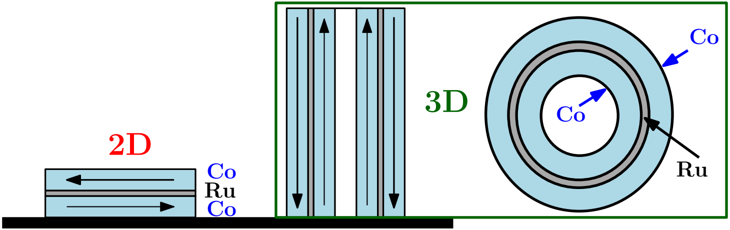

Overview

- Previously: ALD of planar Co (magnetic, not fully optimized)

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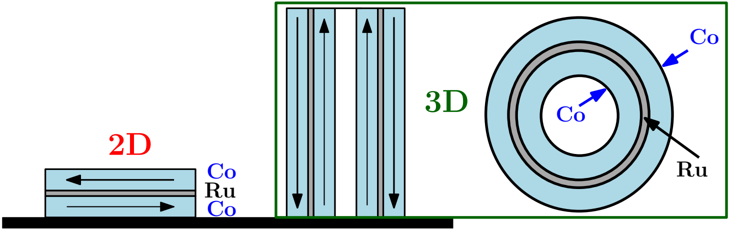


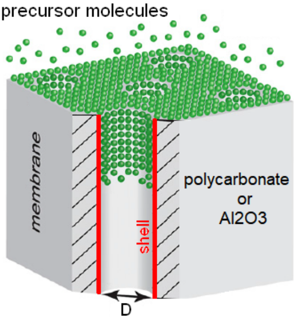
Overview

- Previously: ALD of planar Co (magnetic, not fully optimized)
- Now: ALD of planar Ru; planar Co on Ru
- Now: Nanotubes – optimization on HfOx
- Next: Magnetic nanotubes, Magnetic/Ru/Magnetic layer, imaging, . . .

Outline of the presentation

1. STAFF3d-spin project: multilayered nanotubes
2. Ru(Ox) ALD on planar substrates
3. ALD on high aspect ratio structures – exposure mode
4. HfOx nanotubes by ALD in porous membranes
5. Summary

Atomic Layer Deposition (ALD) – CVD family member



Sequential self-limiting surface chemical reactions

Sample's surface exposed **in cycles** to (for Ru):

1. **precursor** – organometalic ($Ru(EtCp)_2$),
2. Ar purge (removal of excess molecules),
3. **reactant**/2nd precursor (O_2),
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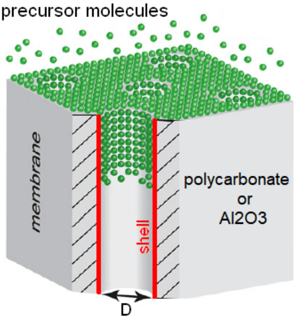

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- surface chemistry-dependent (→ functionalization)
- slow, coating could be very granular
+ thickness control @ atomic scale
+ conformal coating (uneven surfaces)
* variety of materials: mainly oxides, but also metals (Co, Ru, Cu)

A nice ALD review: George, *Chem. Rev.* **110**, 111-131 (2010)
List of materials: Miikkulainen et al., *JAP* **113**, 021301 (2013)

Atomic layer deposition of ruthenium (Ru)

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- Ru with ALD booster: Kozodaev et al., *J. Chem. Phys.* **151**, 204701 (2019)
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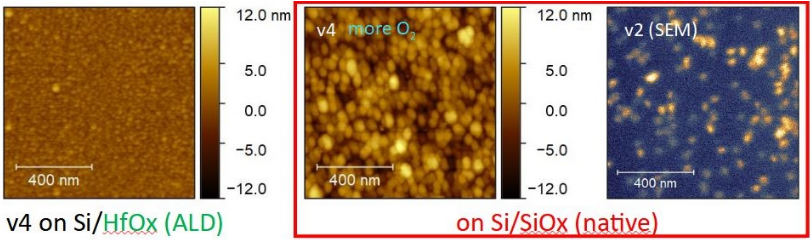
More O_2: partial oxidation of Ru, but better surface coverage (smooth, more compact layers); also **temperature-dependent** (here 300°C+)



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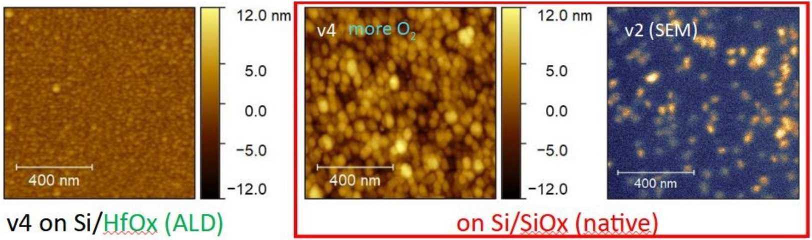

H_2 reduction of RuO_x in ALD cycle, or after the deposition (tested)

Ru/Co combination (H_2 used for Co deposition)

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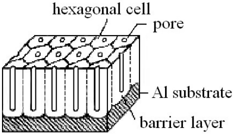

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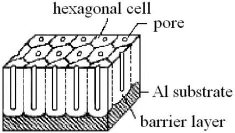

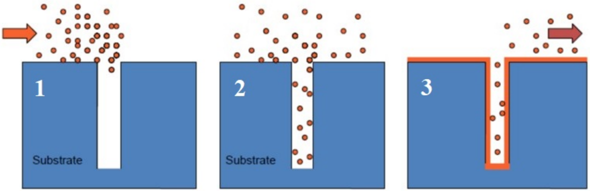

Isolate chamber to static vacuum;

Introduce a dose of precursor

Allow time X for precursor to diffuse into trenches, pores

Purge for time > X to remove excess precursor. Repeat for second precursor.

Enjoy uniform coatings.

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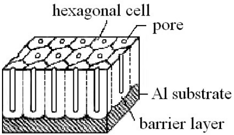

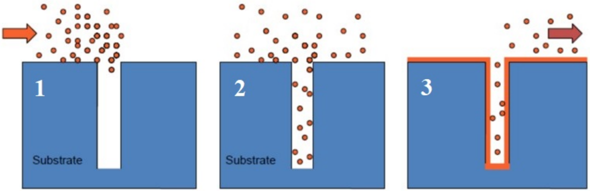

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- Common solution: stopvalve (pumping stopped for a while)
- Molecules have to diffuse inside: time · temperature helps
- Thermal ALD only (not for plasma-assistance)

Deposition of HfOx nanotubes in porous alumina

Why HfO_x?

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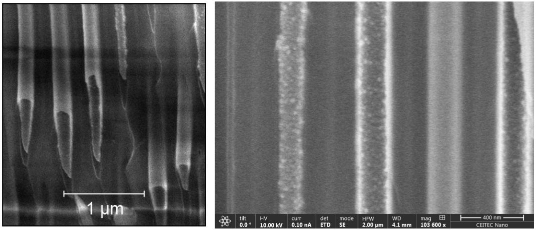
200°C, $\approx$ 70 s exposure for pore aspect ratio 175 ($\phi = 200\,\text{nm}$, $L = 35\,\mu\text{m}$)



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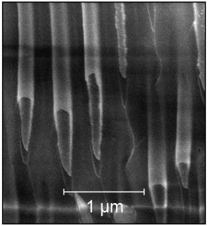

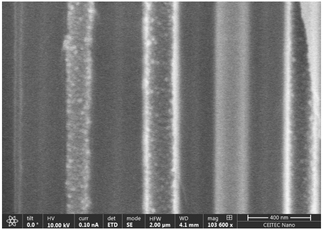

How about other materials (Ru, Co)? Required exposure depends on:

- pore geometry (aspect ratio; dominating): OK, it will be the same
- temperature: OK, it will be even higher
- materials: Ru, Co more difficult (technical issues rather than chemistry)

Summary

Atomic layer deposition (ALD) experiments

- Ru planar layers: poor on Si, nice on HfOx buffer layer
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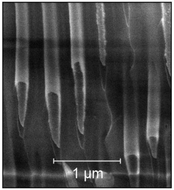
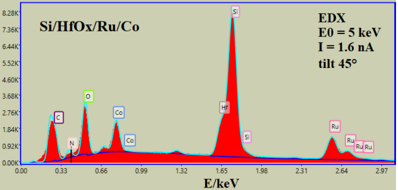


HfO_x nanotubes



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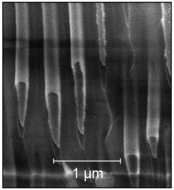

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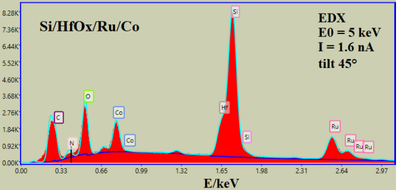

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Plan

- Electroless plating of nanotubes (CoB or CoNiB)
- Investigation of isolated magnetic nanotubes
- Combining electroless magnetic layer + Ru spacer by ALD
- ? Co nanotubes, Co/Ru/Co by ALD

Acknowledgements

Thank you for your attention!

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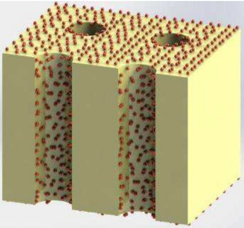
(slides of presentations, updates, . . .)

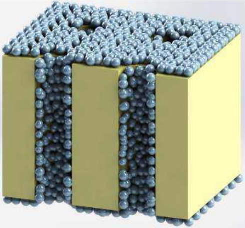
Electroless deposition of nanotubes

Conformal coating of modified walls of porous template

- Silanization of pore walls (Al_2O_3 only) – APTES
- Sensitization of pore walls – $SnCl_2$
- Activation – $PdCl_2$ (Pd seeds)
- Deposition – immersion in a plating bath
- Removal top/bottom layer, template dissolution



Template with seed particles



Initial growth

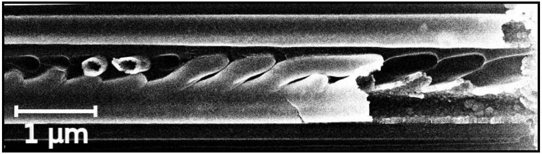
Images from *ECS Trans.* **64** (31), 39-48 (2015).

Plating bath:

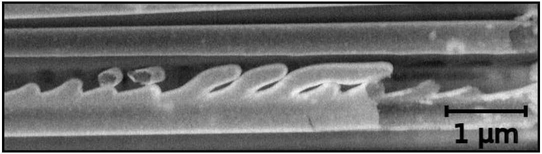
- metal salt ($CoSO_4$)
- reducing agent (DMAB)
- stabilizing agent (sodium citrate)

CoNiB electroless plating in Al_2O_3 porous template

Commercial template with pore branching close to the end;
cross-section, template and deposit (partially) broken



Secondary electrons



Back-scattered electrons (less charging, more material contrast)

Electroless plating '*replicates*' the pore shape, including defects.

Towards nanotubes: deposition routes

How about nanotubes when the porous template is from Al_2O_3?!

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  Giordano et al., *ACS Appl. Mater. Interfaces* 12, 40443-40452 (2020)

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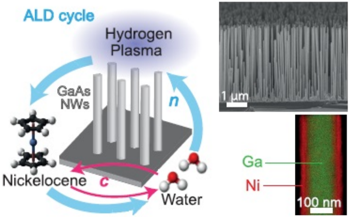

- physical vapour deposition on vertical nanowires – Dr. Kolíbal
- electroless plating, also seed metallic layer for ALD in nanopores (acquired chemicals for CoB, CoNiB)