Nanomagnetism in 3D SPICE workshop Ingelheim, 30/04/2024

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Tutorial on synthesis of 3D magnetic nanostructures







Three-dimensional nanomagnetism



3D nanomagnetism for future green technologies



[AFP et al, Nature Comm. 8, 15756 (2017)]

Some key features of a synthesis technique for 3D nanomagnetism

Geometry

- How complex can the 3D geometries be

Scales:

- Spatial resolution & nanomagnetism lengthscales (10s-100s nm)
- Growth rates: Single element vs collective phenomena
- Multiscale possible (hierarchy)

Materials:

- Magnetic vs polymer/non-magnetic
- Magnetic properties: M_s , A_{ex} , α ...
- Variety of elements & types (ferro, antiferro...)
- Tuneability: composition, crystallinity...

Thin film deposition:

- Degree of conformality
- Minimum/Maximum thickness attainable
- Quality of interfaces

Technology:

- Stage of maturity: emergent vs consolidated : for fundamental studies /real applications
- Compatibility/complementarity with other methods
- On-chip integration possible
- Electrically, optically accessible
- Reproducibility
- Cost

Synthesis techniques for 3D nanomagnetism covered in this tutorial

Nanofabrication

Direct-write	FEBID/FIBID	Two-photon polymerization	FIB
Templates	AIO _x & polycarbonate membranes	Self-assembly	Nanocomposites
PVD-thin film based	Rolled-up	Free-standing	GLAD

In combination with growth techniques

By itself	PVD	CVD	ALD	Electro- deposition	Electroless deposition	Bulk	Nanoparticle
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Focused electron/ion beam induced deposition (FEBID/FIBID)



Materials grown by FEBID/FIBID

Dirty metals

Typically 15-20% (at.) metal, rest carbon & oxygen





[AFP et al, Phys. Rev. B 79, 174204 (2009)]

Ways to create pure (Pt & Au) FEBID materials:



Post-growth methods/ reactive gases during growth

[Winkler et al, ACS Appl. Mater. Interfaces 9, 8233 (2017); Shawrav et al, Sci. Rep. 6, 34003 (2016)]

Superconducting materials

 $W(CO)_6$





(CH₃CH₂)Pb





[Guillamón, Fernández-Pacheco et al, New J. Phys. 10 093005 (2008); Nature Phys. 5, 651 (2009)] [Córdoba et al, Nano Lett. 19, 12, 8597 (2019)]



[Zhakina et al, arxiv.org/2404.12151]

Direct writing of functional superconducting materials

Direct writing of ferromagnetic metals by FEBID



FEBID



[Utke et al, J. Vac. Sci. Technol, 26, 1197 (2008)] [Sanz-Hernández, AFP et al, Beilstein J. Nanotechnol 8, 2151-2161 (2017)] [Skoric et al, Nano Lett. 20, 184 (2020)]

FEBID continuum model – characteristic frequencies

$$rac{\partial heta}{\partial t} =
u_{GAS}(1- heta) -
u_d heta -
u_{el} heta +
u_{d_{\mathit{i}\!f\!f}} heta$$





Monte Carlo simulations

- Gas dynamics
- Electron-matter interactions

FEBID

Recent FEBID computational tools

Gas injector system simulator



[Friedli et al, J. Phys. D: Appl. Phys. 42, 125305 (2009)]

FEBID frequency maps



Monte-Carlo + continuum model simulator



[Fowlkes et al, ACS Nano 10, 6163 (2016)]

FEBID @ the molecular level



3D nano-printing of nanowire-based structures





[Keller, Huth et al., Scientific Reports 8, 6160 (2018)] 11

[Fowlkes et al., ACS Appl. Nano Mater. 1, 1028 (2018)]

f3ast software: 3D printing at the nanoscale by FEBID



Standard 3D printer extruder: Macro/microscale



FEBID: Nanoscale

[Skoric et al, Nano Lett. 20, 184 (2020)]

FEBID 3D Algorithm for STream file generation

First FEBID code:

- Able to print arbitrary 3D geometries
- Rigorously based on theory of FEBID processes
- Simple two-step calibration
 procedure → start to 3D print

3D printing of complex nano-geometries by f3ast software



FEBID

f3ast: 3D nano-printing platform open to the community

f3ast

Tutorial videos: How to install & navigate through the software; how to perform 3D printing experiments, fundamentals of the algorithm... and a few surprises! **Open access since 2022:** https://github.com/Skoricius/f3ast

YouTube channel launched recently!: www.youtube.com/@f3ast-nanofab

3D printing at the nanoscale using f3ast

f3ast installation

f 3ast

FEBID 3D Algorithm for STream file generation

Luka Skoric



FEBID

Direct writing of nanowire-based structures





Unconventional dependences of magnetotransport signals (Hall effect, MR) due to 3D geometry

3D bridge circuits

[Meng, AFP et al, ACS Nano 15, 6765 (2021)]

Artificial spin lattice elements



Tetrapods characterized by Hall magnetometry

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[Keller et al, Sci Rep. 8, 6160 (2018)]



Higher order vorticity 3D spin textures at the vertices [Volkov et al, Nature Comm. 15, 2193 (2024)]

Direct writing of helical nanomagnets



Domain wall devices via PVD + FEBID



Step 1: 3D nano-printing of non-magnetic scaffold



[Sanz-Hernández, AFP et al, ACS Nano 1, 11066 (2017)]



Step 2: Deposition of ferromagnetic thin films



[Skoric, AFP et al, ACS Nano 16, 8860 (2022)]



Multistep (if electrical connection needed): Combined with EBL & FIB



[Meng, AFP et al, Micromachines 12, 859 (2021)]





3D magnetic "nanoelevator" of domain walls Automotion due to large thickness gradients imprinted by 3D geometry

PVD (non-conformal) + 3D geometries: shadowing, textures, BUT high-quality materials, functional interfaces...

Thermal CVD on electrically-connected FEBID circuits



Site-Selective Chemical Vapor Deposition around FEBID structures Conformal deposition only at the circuits addressed electrically

[Porrati et al, ACS Nano 17, 4704-4715 (2023)]

FEBID

Largest scales targeted by FEBID



40 x 40 array of Pt helices

[Esposito, Marco, et al. "Nanoscale 3D chiral plasmonic helices with circular dichroism at visible frequencies." ACS Photonics 2.1 (2014): 105-114.]

FEBID is great for single-3D nanostructure studies:

- Unmatched resolution
- Direct-write of ferromagnetic materials

but... main drawbacks

- Limited number of precursors
- No epitaxial
- Residual carbon if not optimised
- Poor interfaces
- Difficult on-chip integration
- High cost
- Slow

FEBID

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Two-photon lithography

* thanks to Sam Ladak



 $\frac{dW}{dt} = \frac{8\rho^2 W}{c^2 n^2} I^2 \operatorname{Im} \overset{\circ}{\mathbb{B}} C^{(3)} \overset{\circ}{\mathbb{B}}$

Third-order non-linear optical process:

- low probability.
- tightly focused pulsed laser required (fs or ps)

Quadratic dependence: feature sizes below the diffraction limit (hundreds of nm)



Combination of galvo-mirrors and piezo-stage for fast/highest resolution process

Exposure only within focal volume of laser

Two photon lithography + thin film deposition methods

2 photon



Wires, solid geometries

Williams et al. Nano Research 11, 845 (2018) Sahoo et al. Nanoscale 10, 9981 (2018) Gliga et al. Materials Today 26, 100-101 (2019)

Donnelly et al. PRL 114, 115501 (2015) May et al. Communications Physics 2, 13 (2019) May et al. Nature Communications 12, 3217 (2021)

Nanotubes, closed-shell geometries

Gliga et al. Materials Today 26, 100-101 (2019) Gui et al. Advanced Materials 35, 2303292 (2023) 22

Examples of recent works – Ladak's group

* thanks to Sam Ladak

2 photon

1.72µm

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[Sahoo et al. Nanoscale 10, 9981 (2018)]



15





2 µm

20

[May et al. Nature Communications 12, 3217 (2021)]

23

ALD of ferromagnetic metals (Ni and NiFe)

Plasma-enhanced ALD for conformal deposition of FM metals



ALD: Conformal, atomic-level (self-limiting process) control of thickness, great for oxides. Here, FM metals: Nickelocene as precursor Water as the oxidant agent Hydrogen for in-cycle plasma-enhanced reduction

[Giordano et al, ACS Appl. Mater. Interfaces 12, 36 (2020)]

3D artificial magnonic lattice



Observation of distinct Surface spin-wave modes in woodpile structure: large dipolar & exchange coupling in 3D

[Guo et al Advanced Materials 35.39 (2023): 2303292]

Electroless deposition of permalloy



Similar process than electrodeposition, but without applying Catalytic process with sample immersed in liquid, promoted

Successful coverage of a variety of 3D geometries

[Pip et al, Small 16, 2004099 (2020)]

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Electrodeposition of templates: fundamentals



Electrodeposition process

Back electrode (cathode) Potential between cathode and reference electrode in electrochemical cell Current monitoring to control growth regimes

Templates for nanowire deposition: very large areas possible



Etched ion-track polymeric nanoporous membranes (random, 10-100nm diameter)



Self-organized alumina templates (selforganized, hundreds to tens of nm)

Electrodeposited systems: great flexibility



ED on templates

Domain walls in cylindrical nanowires: spin singularities

[Da Col, Phys. Rev. B 89, 180405 (2014) Schöbitz et al, Phys. Rev. Lett. **123**, 217201 (2019)]



Experimental observation of Blochpoint domain walls

Strong influence of Oersted field to stabilize them & favour high-speed motion



ED on templates

Formation of highly-interconnected 3D nanowire networks

* thanks to Kai Liu



Polycarbonate membranes etched at multiple angles (normal incidence + additional irradiation at 45-degree colatitude angle

Continum propagation of domain walls identified by FORC (memristive behaviour)



Quasi-ordered Interconnected metallic nanowire networks constructed via multiple angle ion-tracking and electrodeposition

Growth of nanowires by electrodeposition without a template

* thanks to Kai Liu

[Chen et al., Sci. Adv. 8, eabk0180 (2022)]



Freezing of the electrolyte solution Ultra-thin electrolyte in between substrate and frozen film: thickness modulated by voltage across lateral electrodes

Applied to pre-patterned substrates: 3D racetracks!

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Self-assembled nanoparticles + PVD



Self-powered colloidal Janus motors

[Baraban et al, ACS Nano 6, 3383–3389 (2012)]



Vortex in a symmetric nanodisk

Source of curvature-DMI

[Volkov et al, Nature Com. 14, 1491 (2023)]

Self-assembly

Block co-polymer self-assembly



BCP morphologies based upon respective volume fraction change between two/three constituent polymer blocks

[Cummins et al. Nano Today 35 100936 (2020)]



[Ross et al, Adv. Mater. 26, 4386 (2014)]

Self-assembly

Single and double gyroid nanostructures



https://www.nanotec.or.th/en/photonic-gyroids-mimic-butterfly-wings/



Electrodeposited material inside the extremely small 3D gyroid templates

[Llandro et al, Nano Lett. 20, 3642–3650 (2020)]



Observation of complex magnetic remanent states in single and double gyroid structures: route towards high interconnectivity, frustration & curvature effects

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Rolled-up technology



Photoresist acting as sacrificial layer Roll-up depends on strain

Tunable diameter (typically a few micron) of rolled-up tubes Control of number of windings in "Swiss-roll architecture" Wide class of materials, including multilayered heterostructures

[Bermúdez-Ureña et al., J. Phys. D: Appl. Phys. **42**, 055001 (2009)] [Mei et al., Adv. Mater. **20**, 4085 (2008)]



Total thickness (nm)

* thanks to Denys Makarov

Strain-engineered architectures ("Origami")



Courtesy: Robert Streubel

[Smith et al., Phys. Rev. Lett. **107**, 097204 (2011); Smith et al., Soft Matter **7**, 11309 (2011)] ₃₈

Straightforward on-chip integration: 3D field nanomagnetic sensors



X and Y Sensors https://rutronik-tec.com/infineon-3d-magnetic-sensor-tlv493da1b6-for-consumer-and-industrial-markets/

Standard approach for 3D magnetic field micro-sensors:

3 linear Hall sensors: additional daughter board for z-axis→ complex and costly How to do it micro/nano?





[Ha et al, Adv. Mater. 33, 2005521 (2021)]

Rolled-up technology : GMR sensors on different planes Vector angular encoders in all directions



[Becker et al, Sci. Adv. 5 : eaay7459 (2019)]

Towards flexible magnetic electronics e-skin susceptible to strain & magnetic fields

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Free-standing metallic layers on pre-patterned substrates for 3D racetracks





Proof-of-concept method for the fabrication of 3D vertical racetracks

SOT- based CIDWM highly unaffected, particularly for SAFs



Freestanding-2D vs Freestanding-3D

[Gu et al, Nature Nanotechnology 17, 1065–1071 (2022)]

Free-standing micro robot with multiple motion degrees of freedom



Helical micro-swimmers with SU8 lithography





- Bio-compatible
- Remotely driven by rotating fields coupled to chiral geometry
- Excellent swimming performance
- New optimised geometries for multiple swimming strokes

[Tottori et al, Adv. Mater. 24 811-816 (2012)

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Glancing Angle Deposition (GLAD)



Nanostructure morphology controlled by

- Incoming particle flux at a high angle (α ~ 80 90°)
- Substrate rotation (speed, direction)

Possible geometries



[K. Robbie, et al. Review of Scientific Instruments 75(4), 1089–1097 (2004)]

Magneto-chiral dichroic effects in GLAD helices





Chiral artificial nanomaterial: helical monodomain antiparallel state

[Eslami et al, ACS Photonics 1, 1231–1236 (2014); Phatak et al, Nano Letters 14,759-764 (2014)] Magnetochiral dichroic effect observed in the visible Effect normally present in molecules: simultaneous spatial & time reversal symmetry breaking

Conclusions & thank you

Synthesis of 3D nanomagnets:

- Flourishing field leading to new scientific discoveries
- Application to real technologies is currently limited
- Each technique has prons & cons
- Combination leads to advanced functionalities



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