Institute for Electron Microscopy and Nanoanalysis
Graz Centre for Electron Microscopy

Focused Electron Beam Induced Deposition:
Basics and Applications

FELMI-ZFE
Electron Microscopy & Nanoanalysis
Work Group S³

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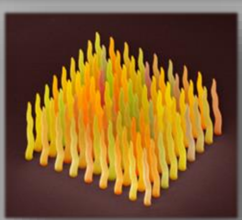
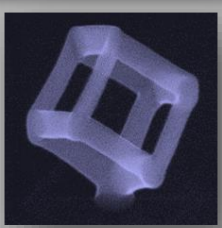
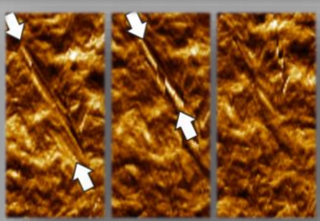
Institute for Electron Microscopy, Graz University of Technology, Graz, Austria.







International Summer School on Nanofabrication and Transmission Electron Microscopy Characterization

July 19th, 2016

Jaca, Spain

TU Graz
ACR

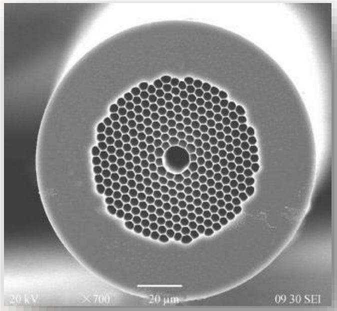
Traditional Nanofabrication and its Limitations

- Classical lithography is not only very powerful but also well established and widely used in fundamental and applied physics
- However, there are situations where they can not be applied!

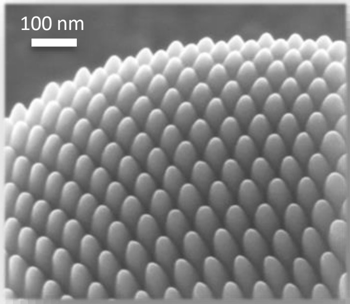
light fiber nano-modification

subtractive (top-down)

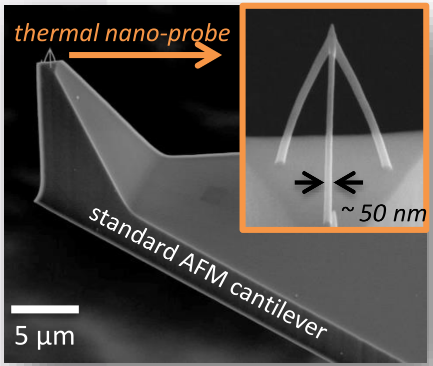
[5]



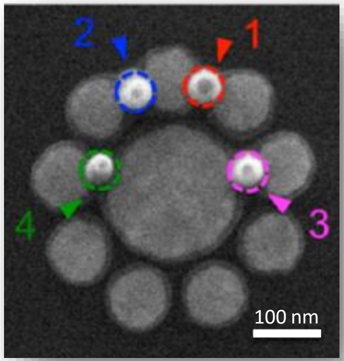
additive (bottom-up)



highly exposed areas



plasmonic transmutation



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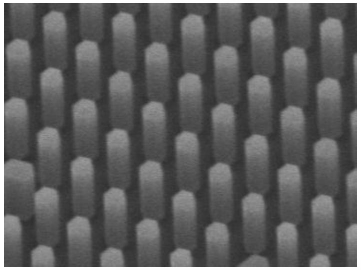

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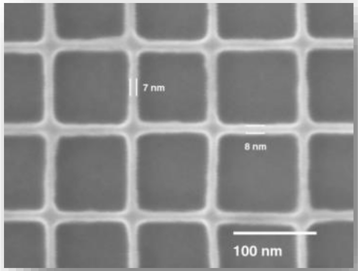

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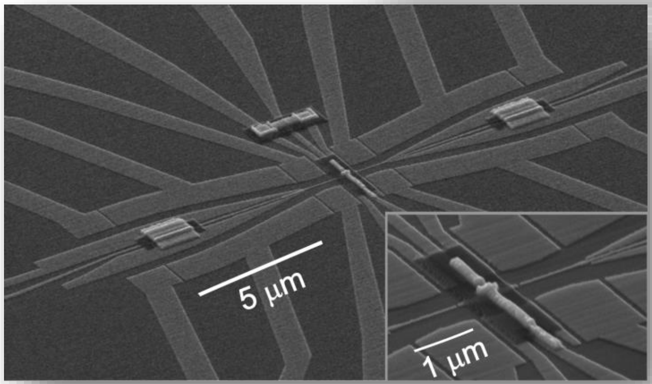

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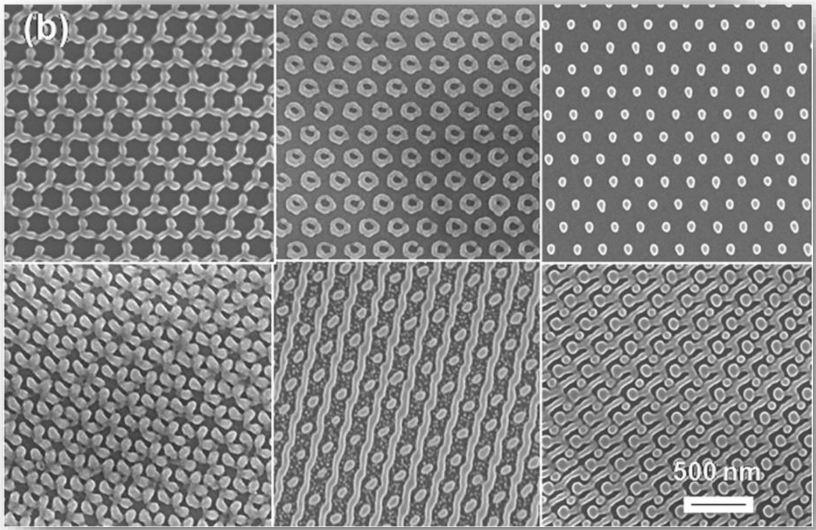

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[2] Kim et-al, *SPIE Newsroom*. DOI: 10.1117/2.1200812.1396
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[5] Jin et-al, *Front. Optoelec*. 2013, 6, 3
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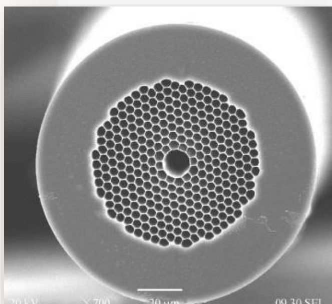

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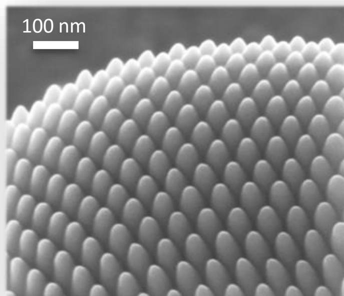

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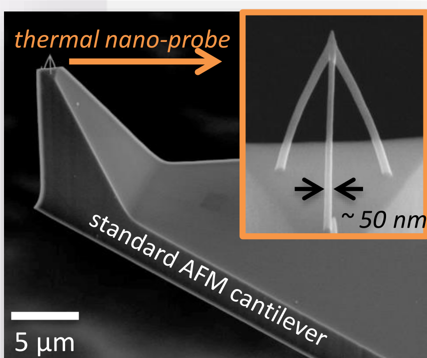

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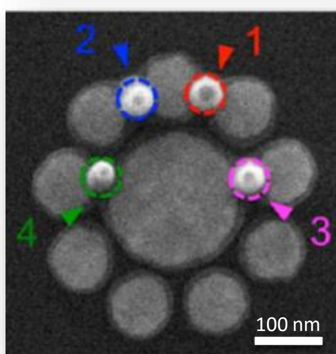

[6]

(nano-) lithography

deposition / removal / modification

lithography removal

IDEAL Situation

- *No **additional layer** prior to fabrication*
- *No **masks** during lithography*
- *No **elevated temperatures** during processing*
- *No **reactive gases** and / or **liquids***
- ***Minimally invasive** process conditions*
- ***3D** capabilities*
- ***Variable materials** capabilities*
- ***Complex shapes** apart from regular structures*
- ***Nanoscale** capabilities*

Mask-less Direct-Write Fabrication
via
Focused Particle Beams

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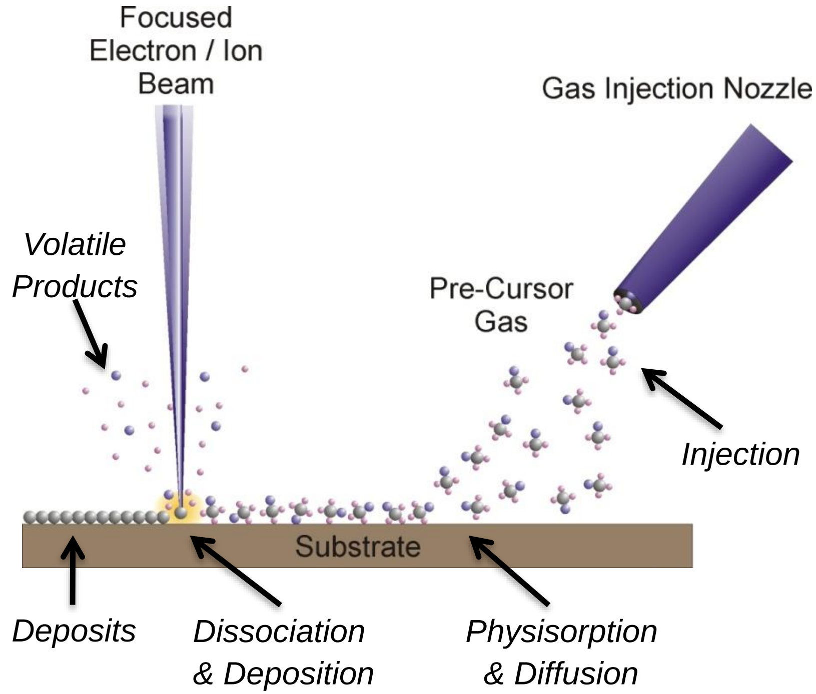
… why Electrons?

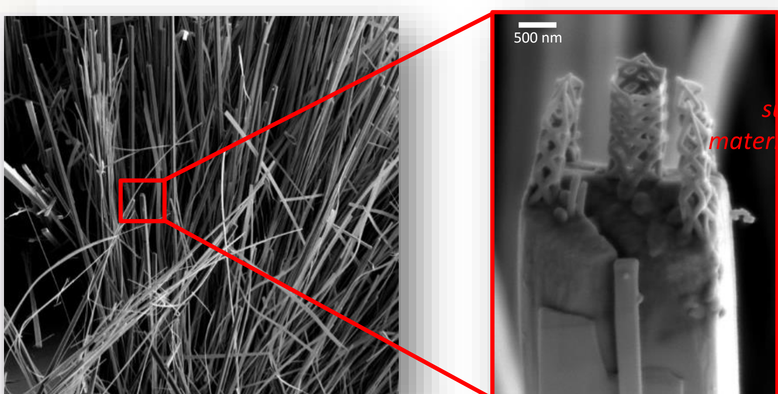
Ion beams can also do bottom-up fabrication …
however, with a few drawbacks:

- Material implantation, heat generation, and more complicated setups due to concurrent sputtering / deposition processes

Electron beams, on the other hand, provide:

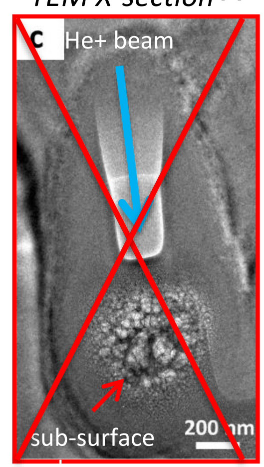
- No unwanted sputtering
- Minimal temperature rise
- No unwanted material implantation in the substrate and the deposit
- Variable functionalities
- Mask-less, direct-write 1D – 3D nano-fabrication on practically any given surface!

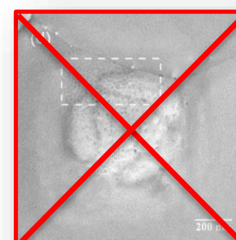




sub-surface
material implantation

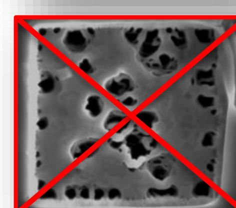
TEM X-section [1]





[1]

surface disruption due
to sub-surface bubbling



[2]

high thermal stress

[1] Fox et-al, *Beilstein J. Nanotechnol.* 2012, 3, 579.
[2] Schmied et-al, *RSC Advances* 2012, 2, 6932.

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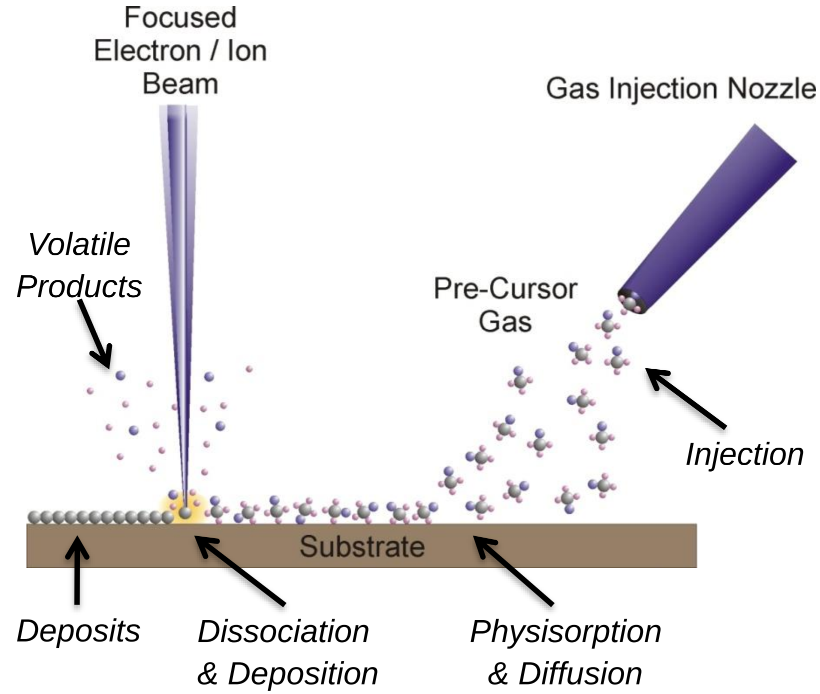

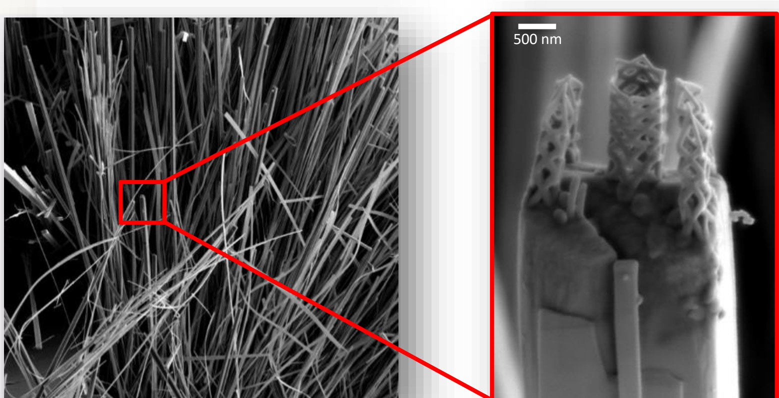

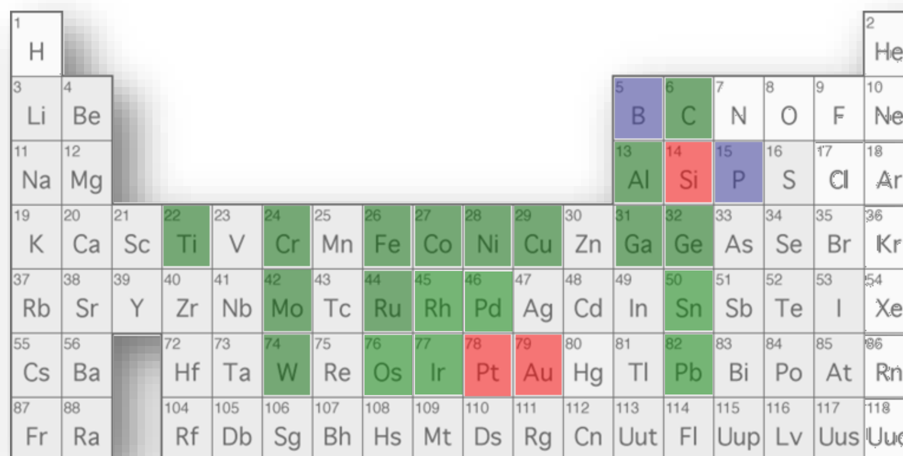

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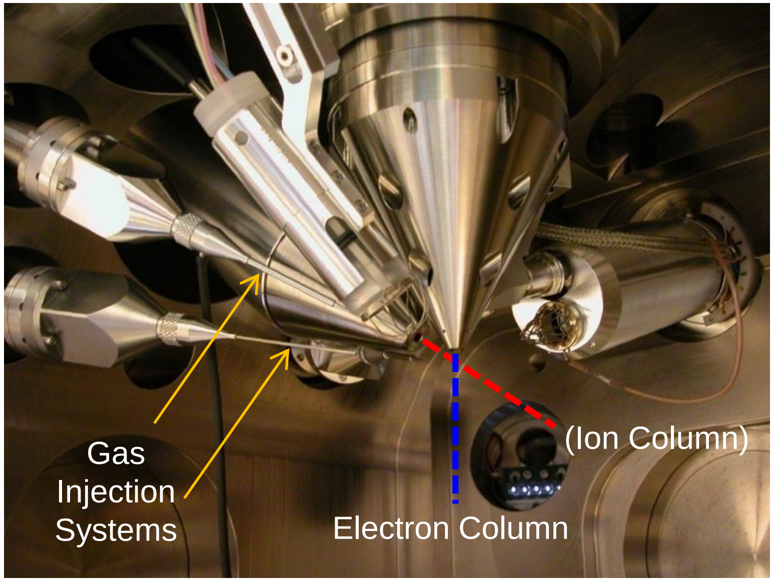
Setup for Focused Electron Beam Induced Deposition

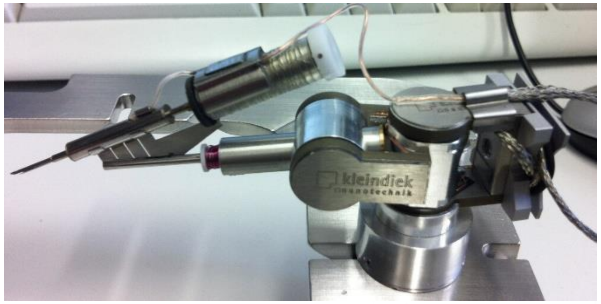
- Mostly, FEBID is performed in electron / ion dual beam microscopes (**DBM**)

- What is needed:
  1. A DBM or a classical SEM
  2. Gas injection system (commercially integrated or expanded, home-built)
  3. Patterning generator (built-in or external hardware; e.g. RAITH)
  4. The precursor of interest
  5. ☺ … some experience … ☺



dual beam system

scanning electron microscope



flexible gas injection system (Kleindiek)

add-on patterning generator

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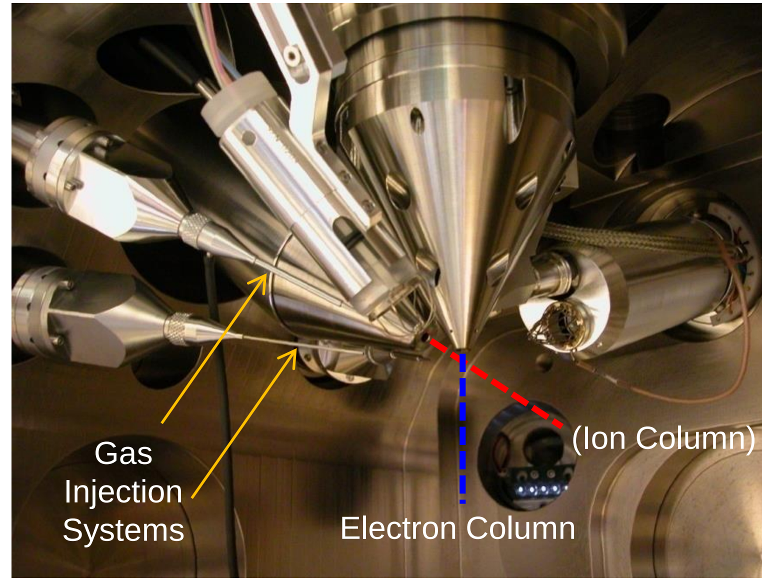

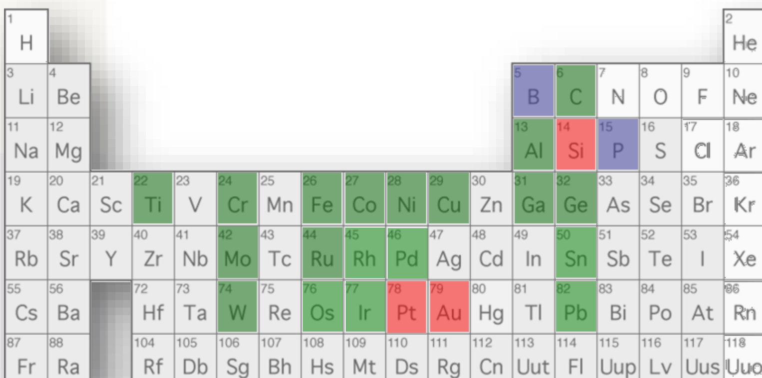

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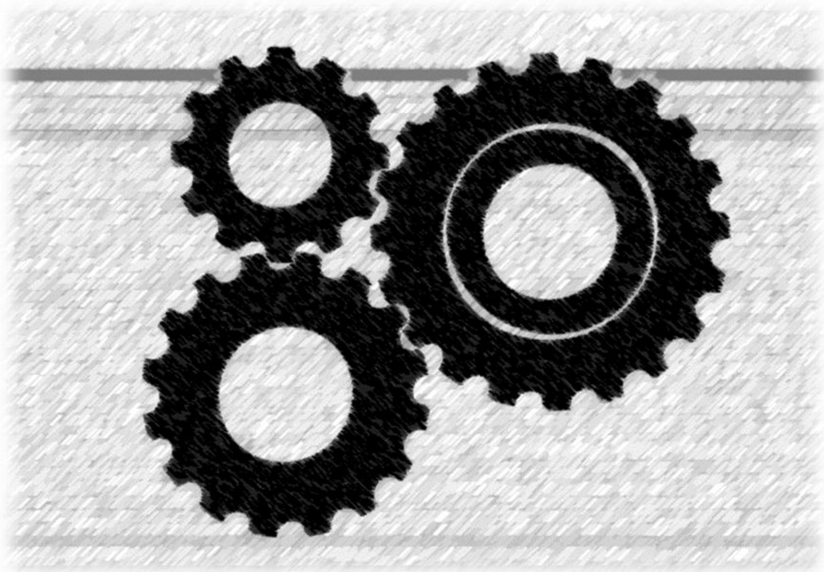
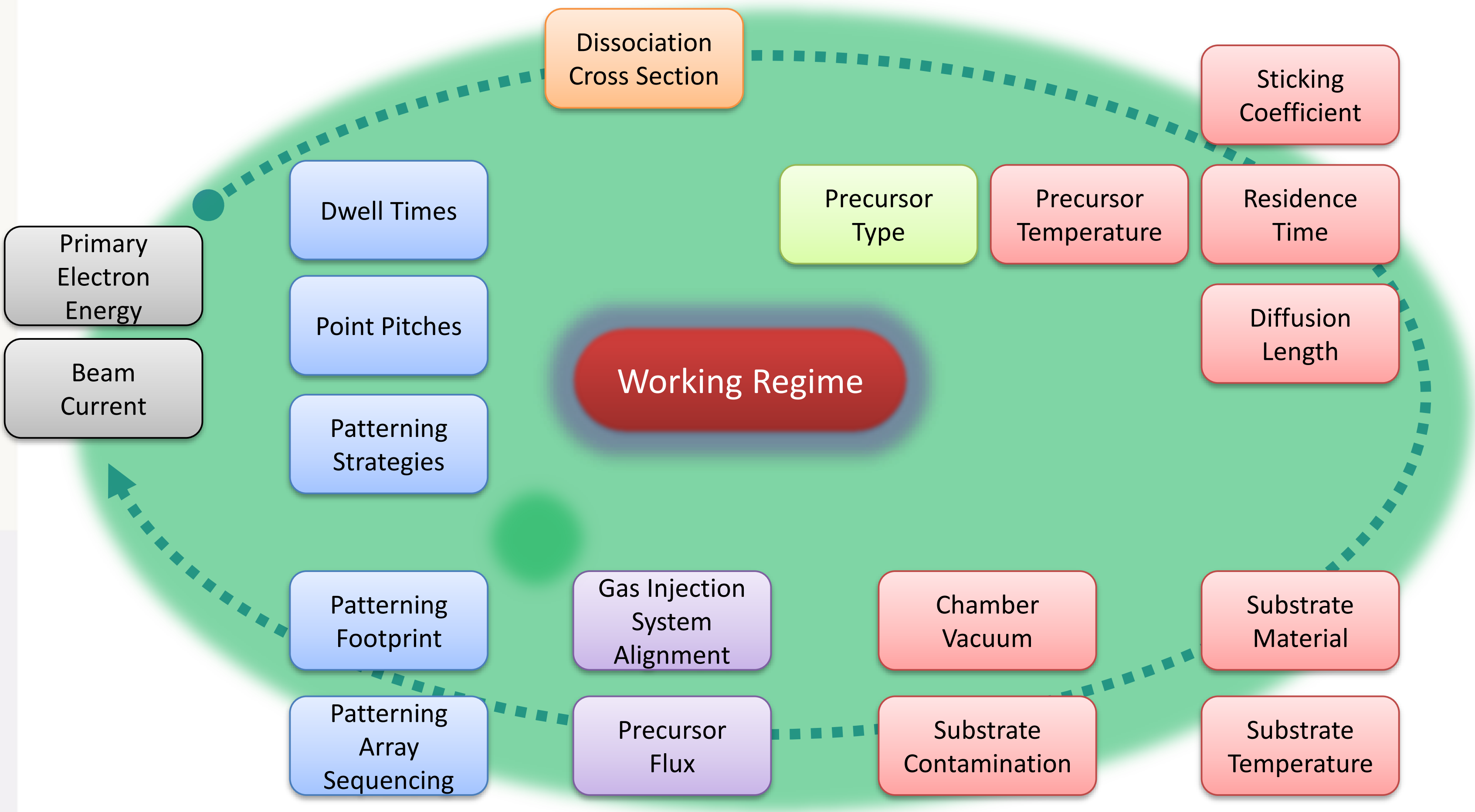
Fundamentals FIRST



From Theory to Reality

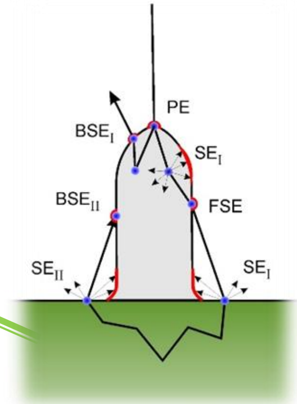
A nano-sized, focused electron beam locally dissociates the precursor into non-volatile (functional) and volatile fragments (which are pumped away)



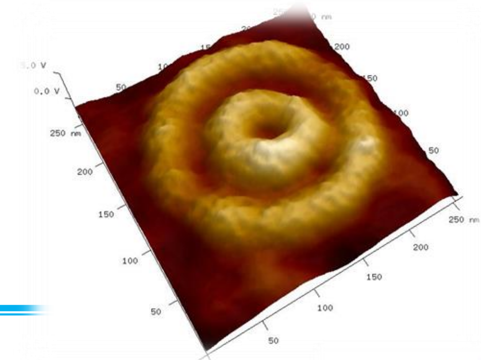
… in reality we have more than 20 variables which mostly depend on each other …

Overview

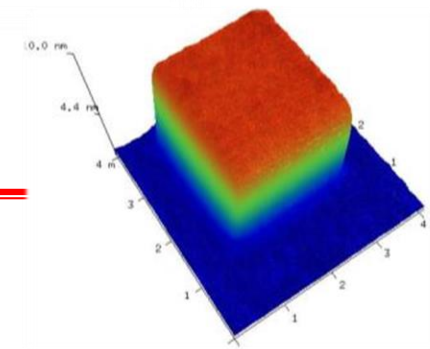
Electrons in Motion

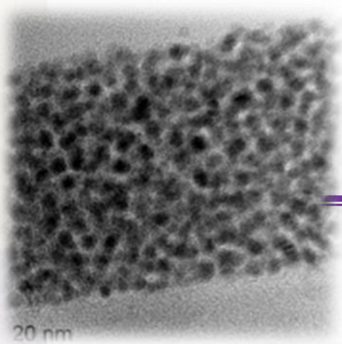


How Small Can we Get

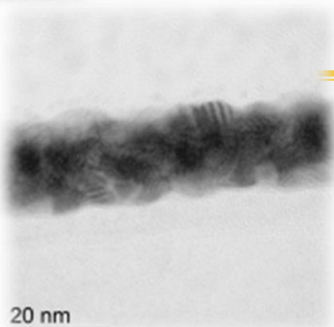


Lets Build a Cube

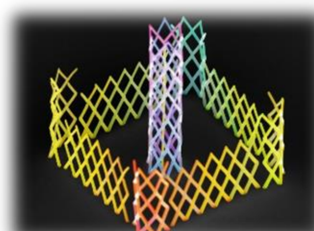




What's Inside



Lets Make It Pure



… and now in 3D …

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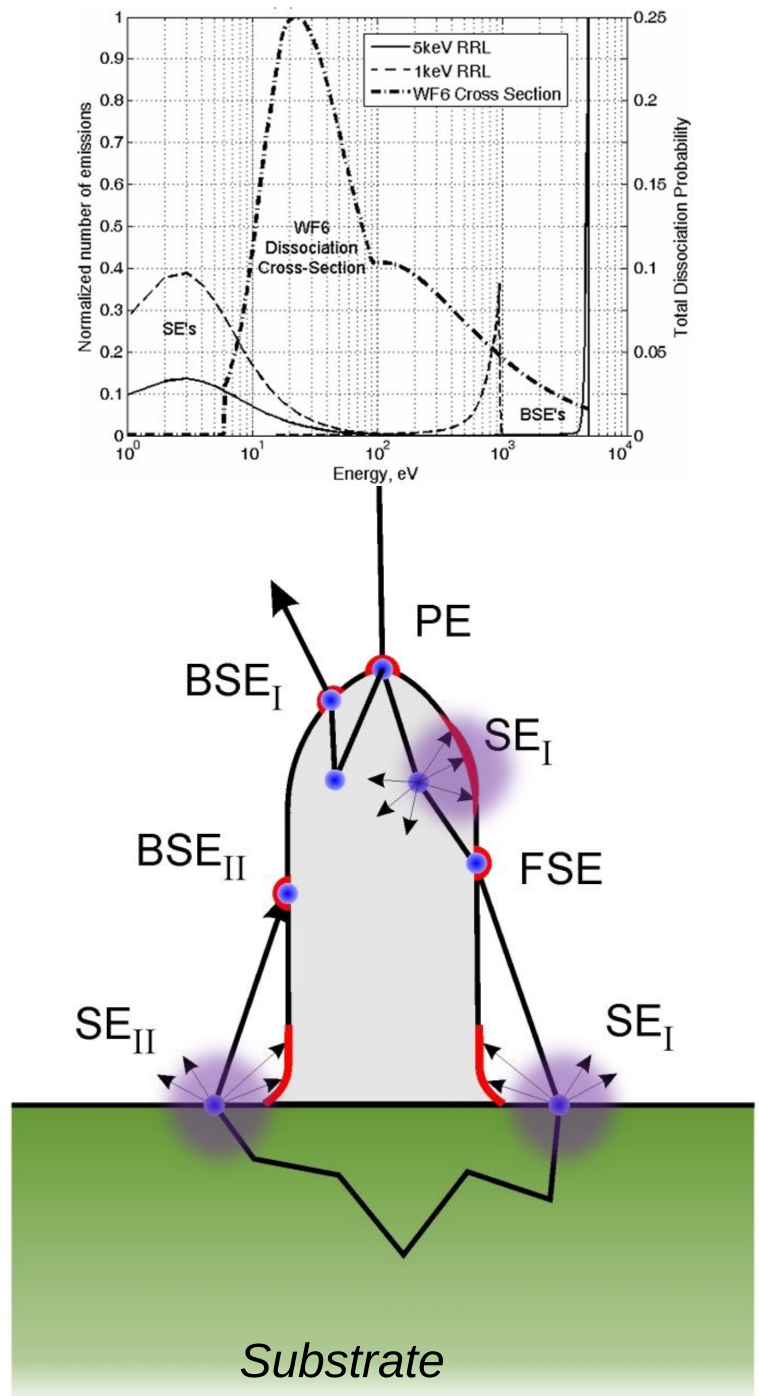
Electron Trajectories

<u>*Electron Trajectories in a Solid:*</u>

- Primary electrons (**PE**)
- Back scattered electrons from the deposit (**BSE$_{I}$**)
- Secondary electrons from the deposit (**SE$_{I}$**)
- Forward scattered electrons (**FSE**)
- Secondary electrons from the substrate surface (**SE$_{I}$**)
- Secondary electrons from the substrate surface (**SE$_{II}$**)
- Back scattered electrons from the substrate (**BSE$_{II}$**)

<u>*Precursor Cross Section:*</u>

- Describes the energy dependent probability for precursor dissociation
- Low energy electrons have HIGHEST probability …
- … hence, **SE** are the major players!
- However, we have to deal with many different SE electrons …
- … which influences the resolution!



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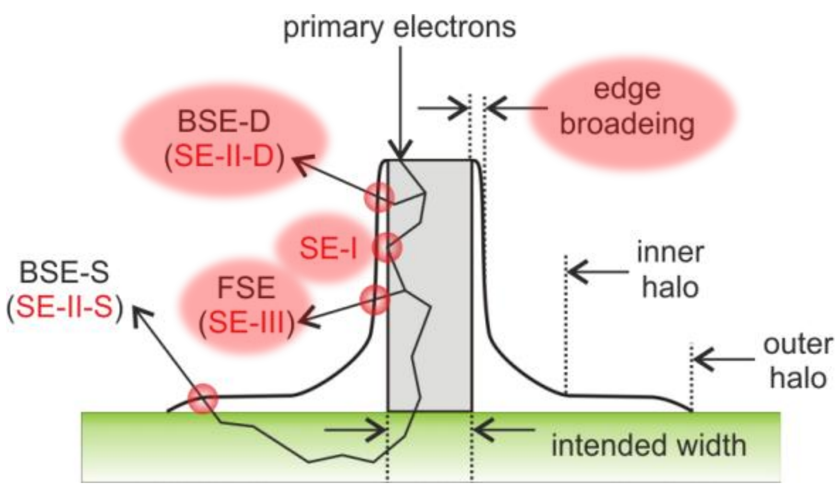
D. Smith et-al, *Nanotechnology* 18, 265308, 2007

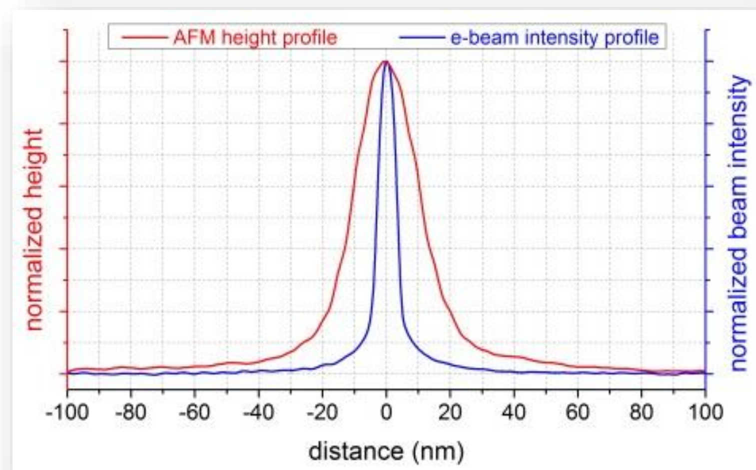
Lateral Resolution

Even optimized single lines reveal a broader appearance compared to the electron beam profile

This is a complex consequence of electron trajectories leading to 4 main broadening effects:

1. Edge broadening: stemming from SE_{I-III} → widely unavoidable and in the range of 2 – 5 nm





Winkler et-al, *ACS Applied Materials and Interfaces* 6, 2987, 2014
Arnold et-al, *ACS Applied Materials and Interfaces* 6, 7380, 2014

Schmied et-al, *Beilstein Journal of Nanotechnology* 6, 462, 2015
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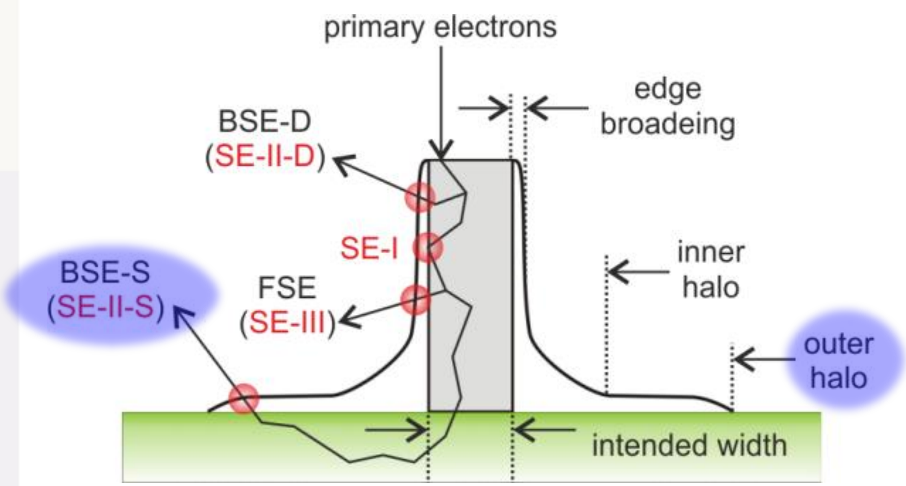
   - Very high or very low primary energies are recommended



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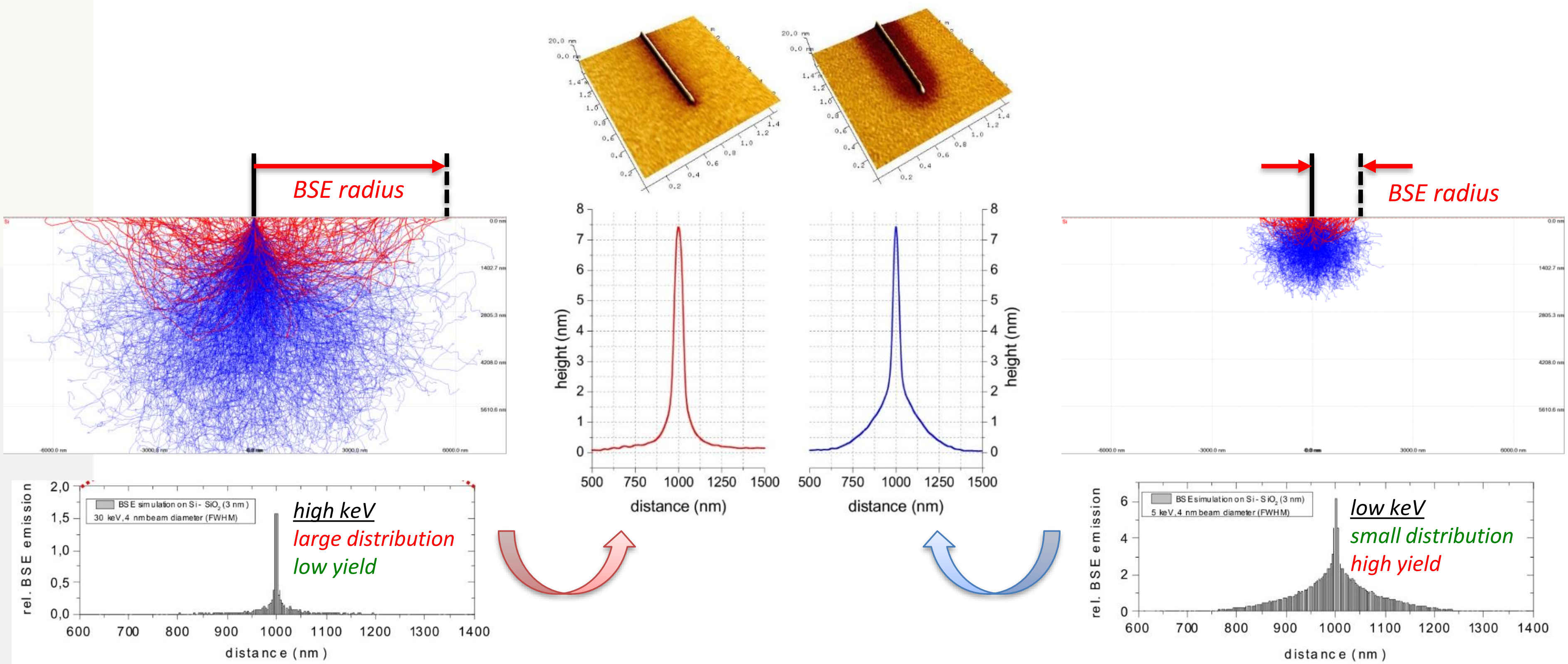

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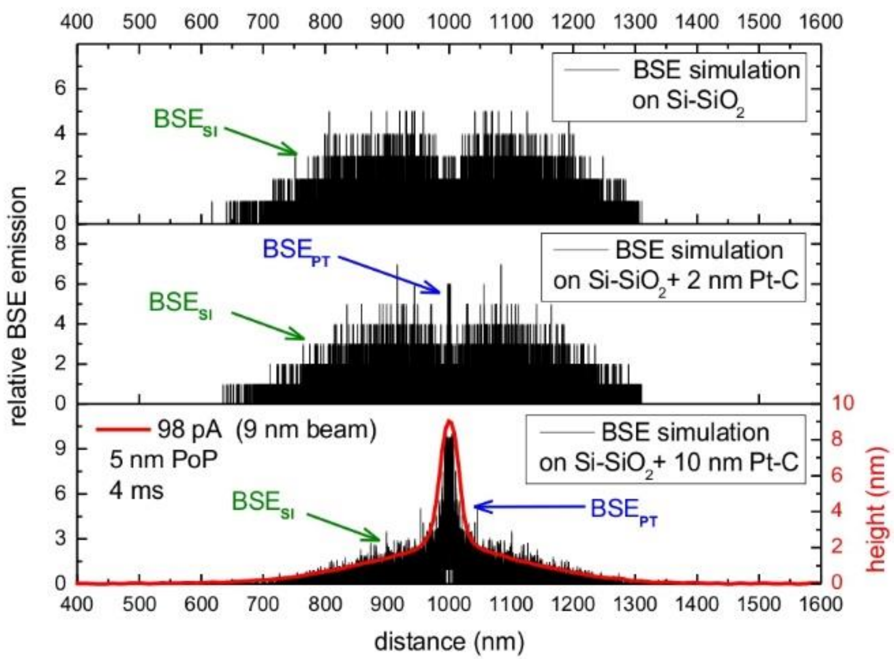
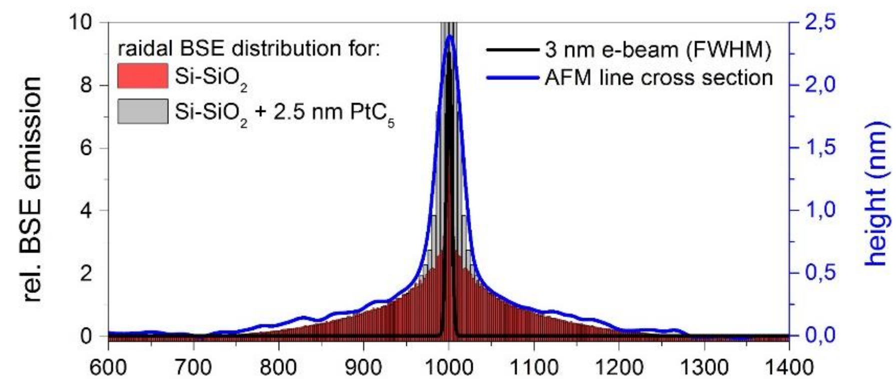
3. Deposit related BSE: these are the real resolution limiting electron species; originate from the growing deposit itself (BSE_D) and entail SE_{II-D} for dissociation (also Z dependent)
   - If available a highly focused e-beam with less than < 1keV would be ideal





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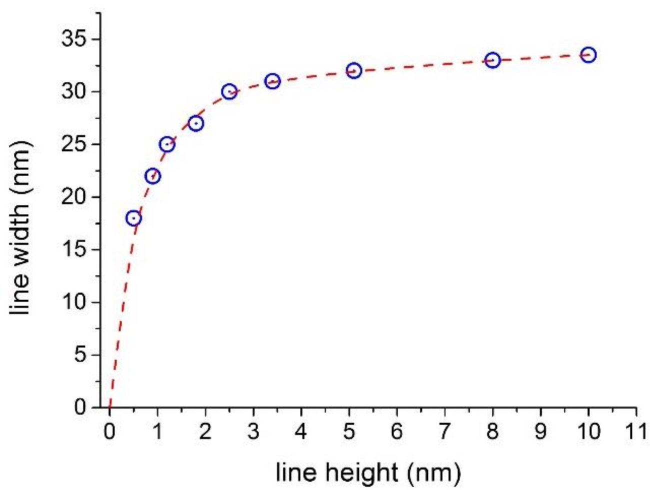

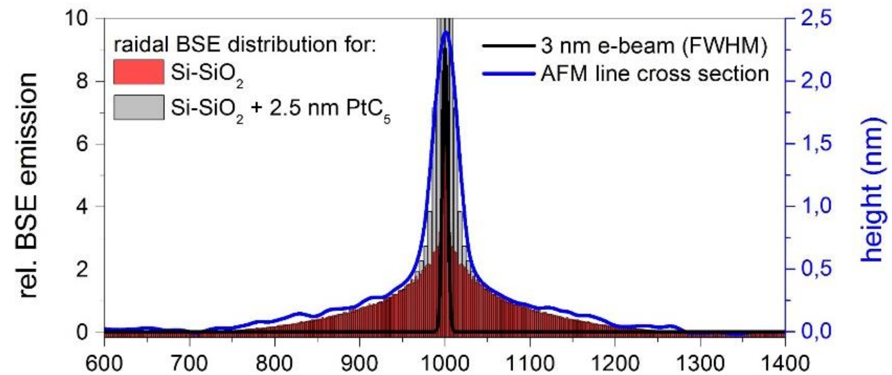

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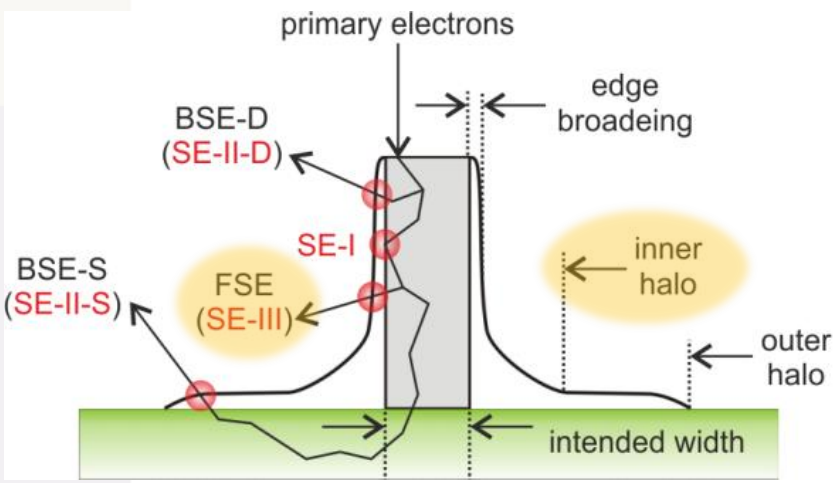
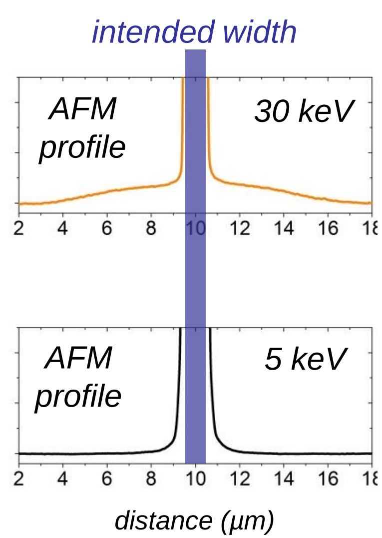
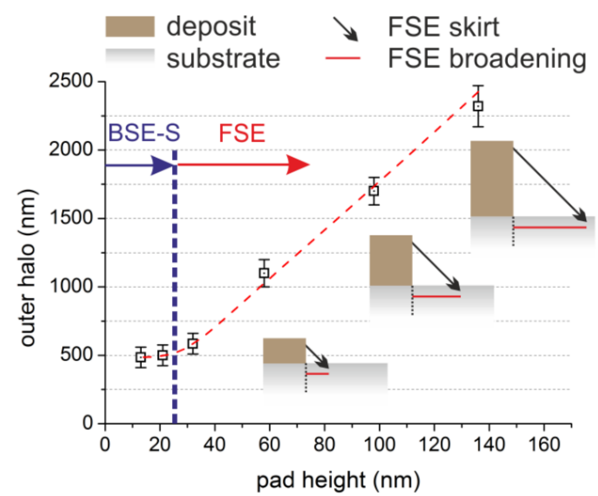
4. Inner halo: mainly caused by FSE / SE_{III} species from the deposit itself
   - Avoidable via very low currents to reduce the FSE contribution







Intermediate Summary

Lateral feature sizes are broader than the electron beam because of:

1. Fundamental SE broadening (unavoidable)
2. Deposit related BSE_D / SE_{II-D} (decaying for lower primary electron energies)
3. Substrate related BSE_S / SE_{II-S} (either very high or very low primary energies are recommended)
4. Deposit related FSE / SE_{III} (decaying for very low currents)

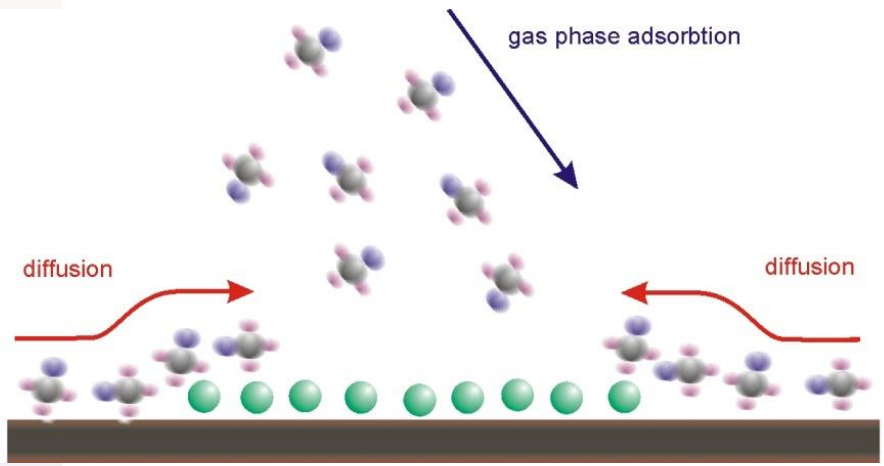
Now we now about the broadening origins and its consequences … lets build a cuboidal deposit!

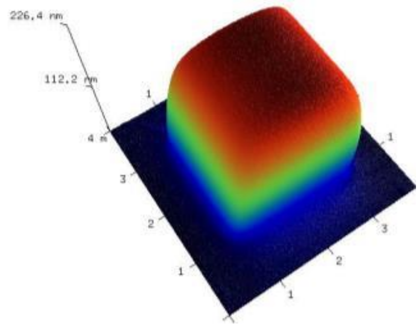
Patterning

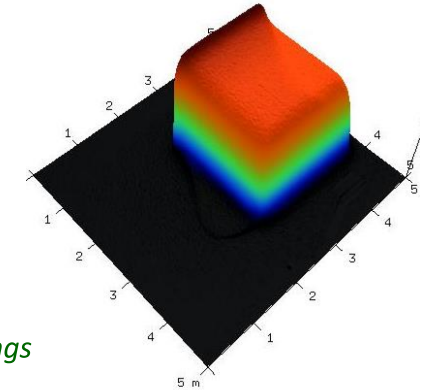
Actually, we would like a cuboidal structure …

… however, we often end up with different and disrupted morphologies!

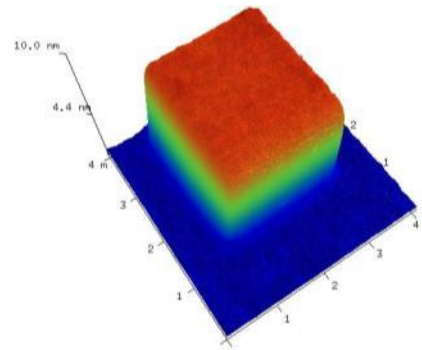
- The reason for these deviations is the precursor working regime
- It describes the local balance between available precursor molecules and dissociating electron species …
- … and that depends on the replenishment!

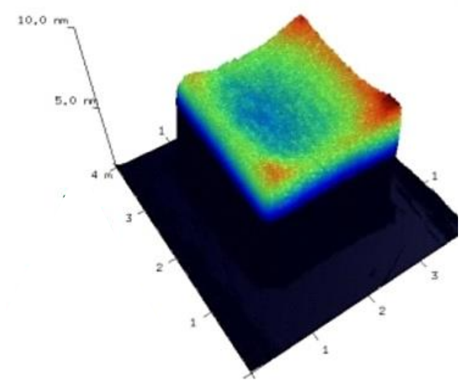


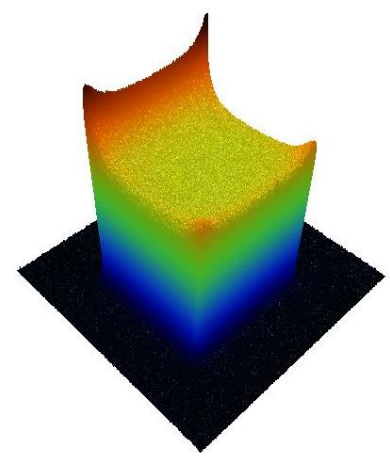




ideal settings





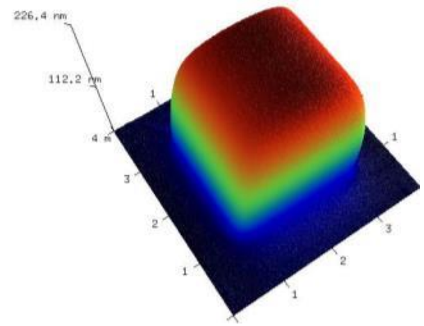


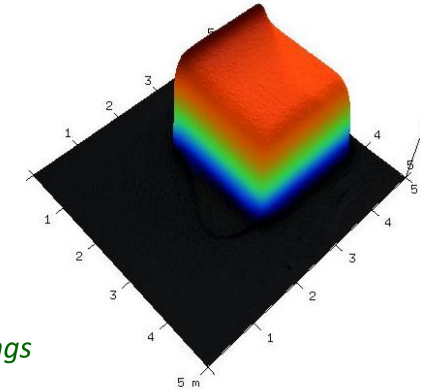
Patterning

Actually, we would like a cuboidal structure …

… however, we often end up with different and disrupted morphologies!

- The reason for these deviations is the precursor working regime
- It describes the local balance between available precursor molecules and dissociating electron species …
- … and that depends on the replenishment!





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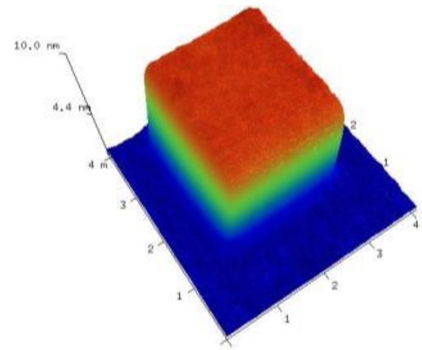
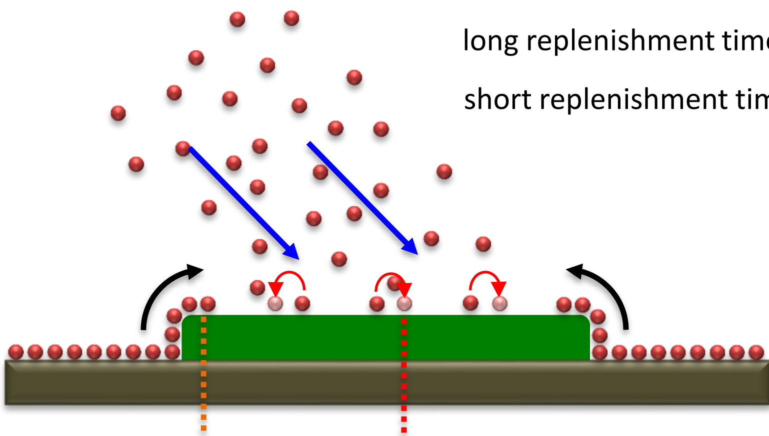
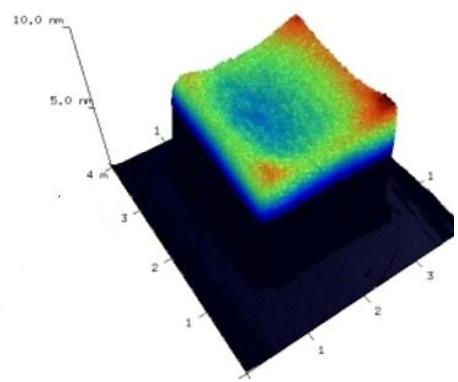


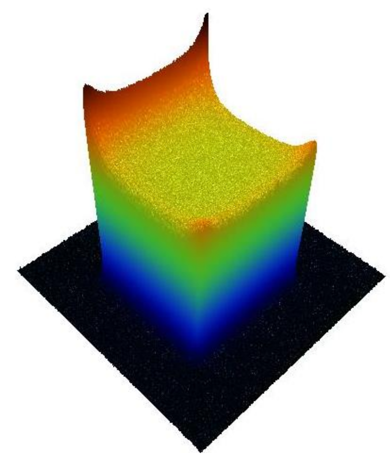


long replenishment time

short replenishment time

$\Rightarrow$ $VGR_E > VGR_M$

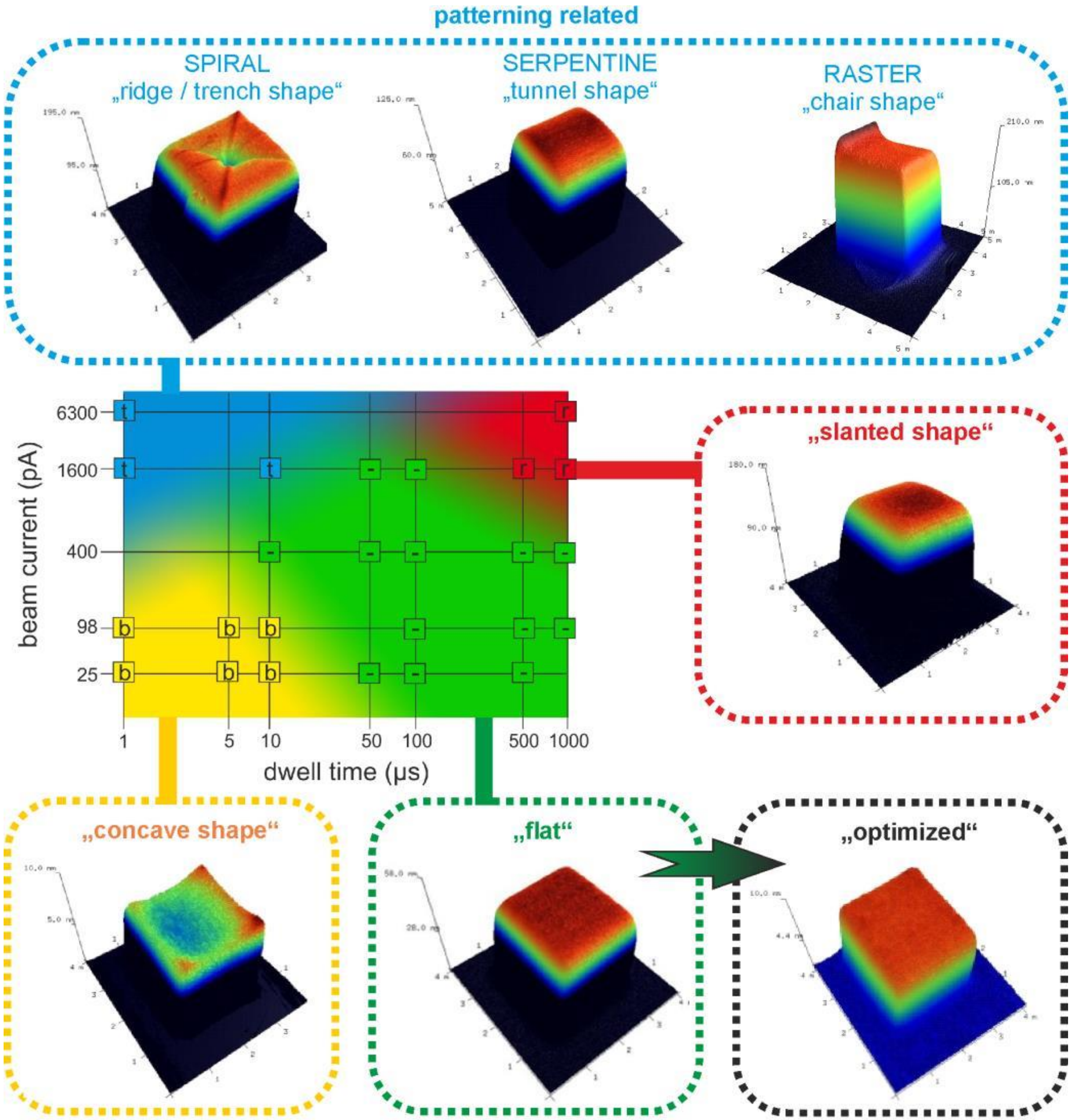




how to handle that?

Morphology Optimization

- Although complex in detail, there is a systematic transition between different morphologies
- A parameter map can help to identify the issues and adapt the process parameters accordingly
- As evident, there are four different types: ideal, concave, patterning related and slanted (only for extreme conditions barely used)
- Please note, each system, substrate conditions and precursor type can shift and scale this regions … but the interdependencies are similar!



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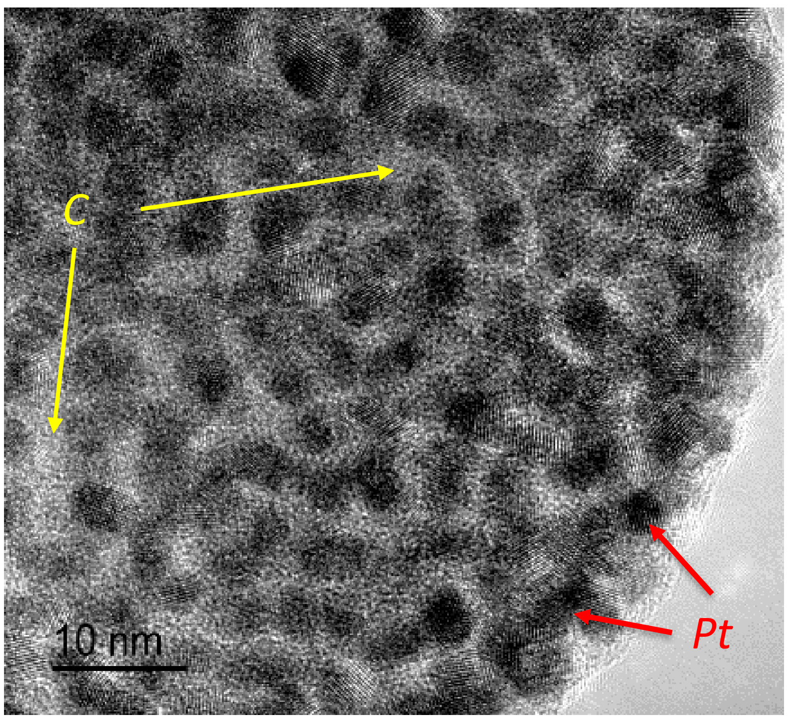
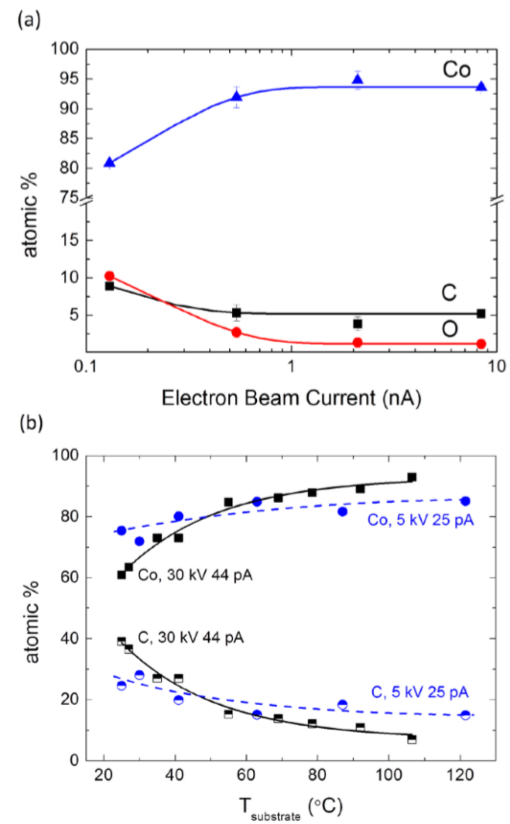
After this shape discussion the question remains "what's inside?"

Chemistry and Internal Structure

- In many cases FEBID materials reveal metal-matrix composition consisting of 2-6 nm large metal grains which are spatially homogenously embedded in an (hydro-)carbon matrix (up to 90 at.%)
- That mainly stems from incompletely dissociated pre-cursor molecules or from e-beam assisted polymerized carbon fragments
- Depending on the precursor there are examples where the former and the latter can be compensated by adapted process parameters or by different sample conditions, respectively



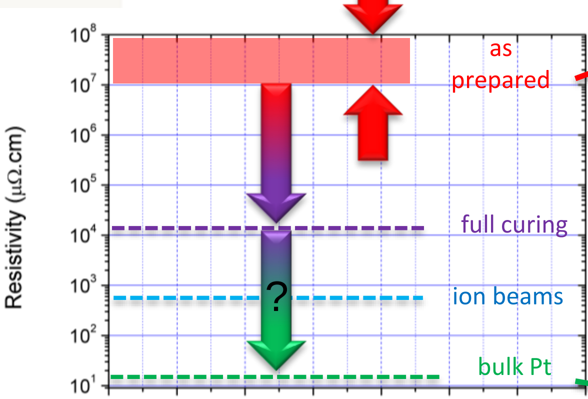


J. M. de Teresa et-al, *J. Phys. D: Appl. Phys.* 49, 243003, 2016
A. Fernández-Pacheco et-al, *J. Phys. D: Appl. Phys.* 42, 055005, 2009
R. Córdoba et-al, *Microelectron. Eng.* 87, 1550–3, 2010
TEM tomography done by G. Haberfehlner & G. Kothleitner (TU Graz)

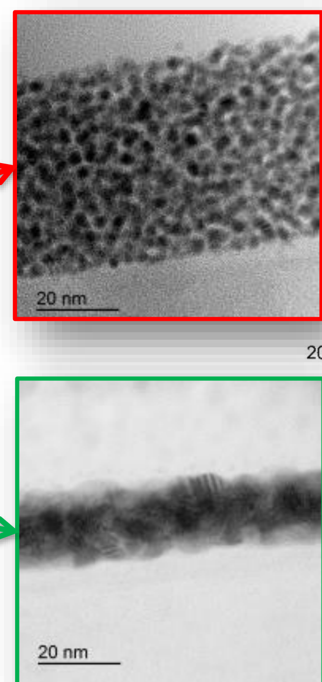
FEBID Materials: Tunability

- As example, Pt based FEBID materials reveal electric resistivities, 6 – 7 orders of magnitude higher compared to pure metals, thus reducing or even masking the intended functionality
- However, there are two stages of tunability: ***1)*** **tuning** & ***2)*** **purification**
- The former bases on a post-growth e-beam exposure which finalizes the dissociation leading to increasing grain sizes at constant grain-to-grain distance → this improves the tunnelling probability and allows precise tuning of electric conductivity by more than 3 orders of magnitude from insulating to metallic behaviour (works also well for Au based precursor)

max. tunability via process parameters

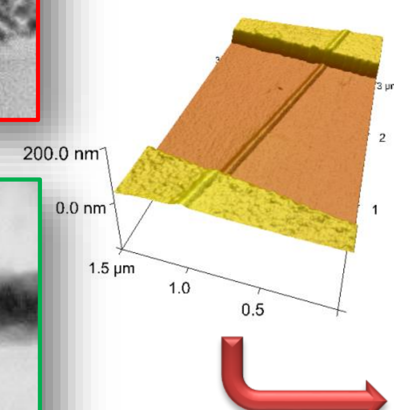


Is full purification possible?



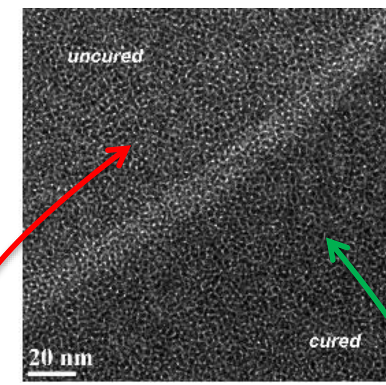
5 keV, 98 pA, single wire

~ 50 x 8 x 2000 nm

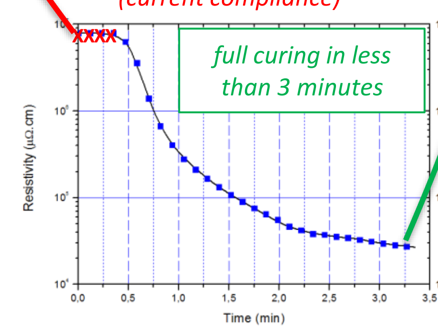


post-growth e-bam curing

~ 1.7 → 2.2 nm Pt grain Ø



NOT conductive after deposition (current compliance)



Plank et-al, *J. Vacu. Sci. Tech. B* 2011, 29, 051801
Plank et-al, *Nanotechnology* 2013, 24, 1753052013
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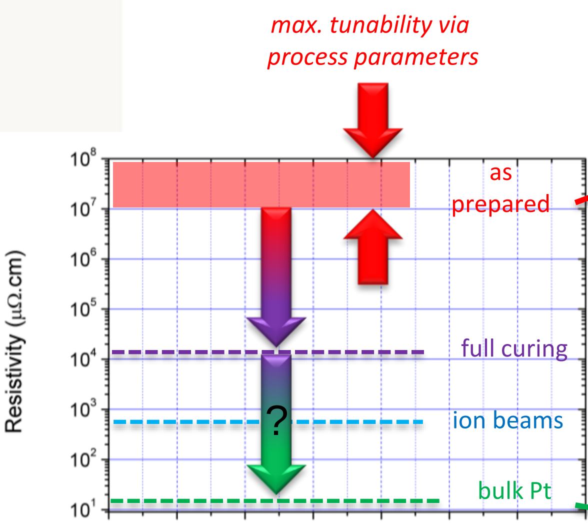

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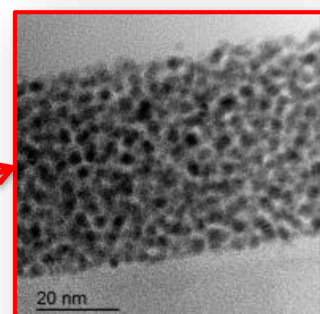

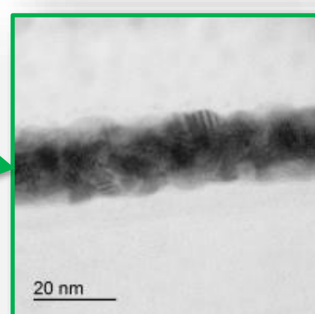

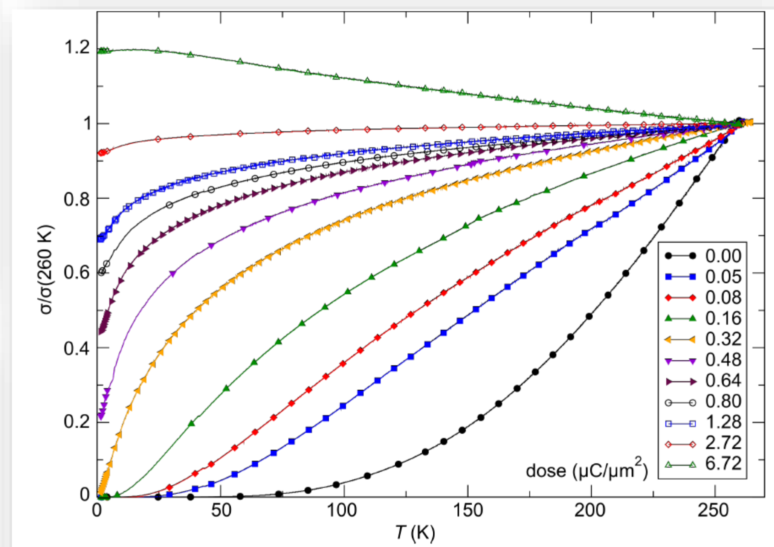

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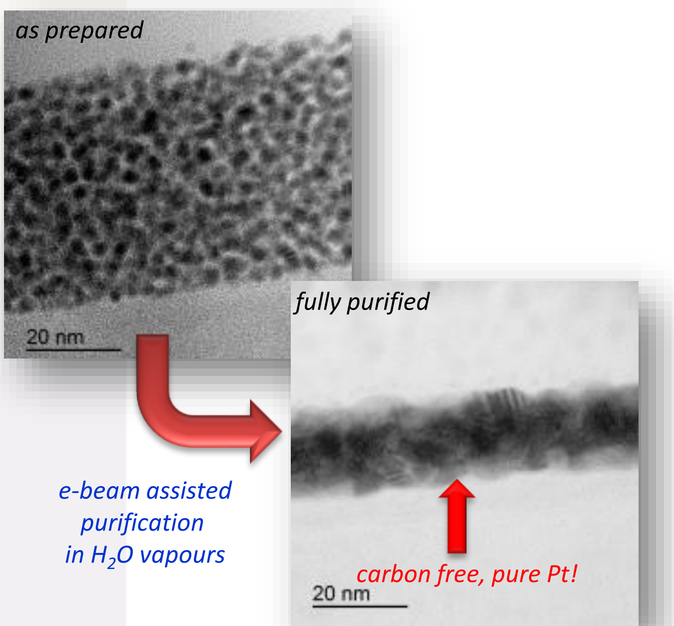
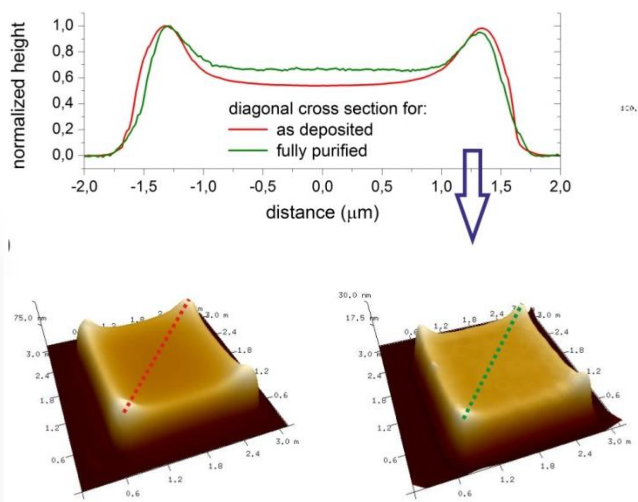
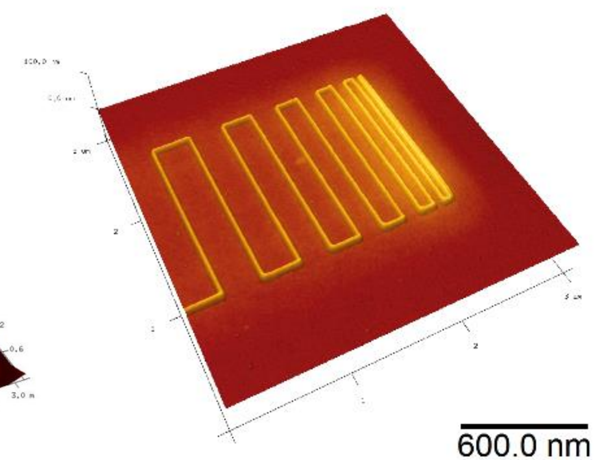




line widths < 30 nm



☺ on-demand plasmonics ☺

Plank et-al, *ACS Applied Materials & Interfaces* 2014, 6 1018
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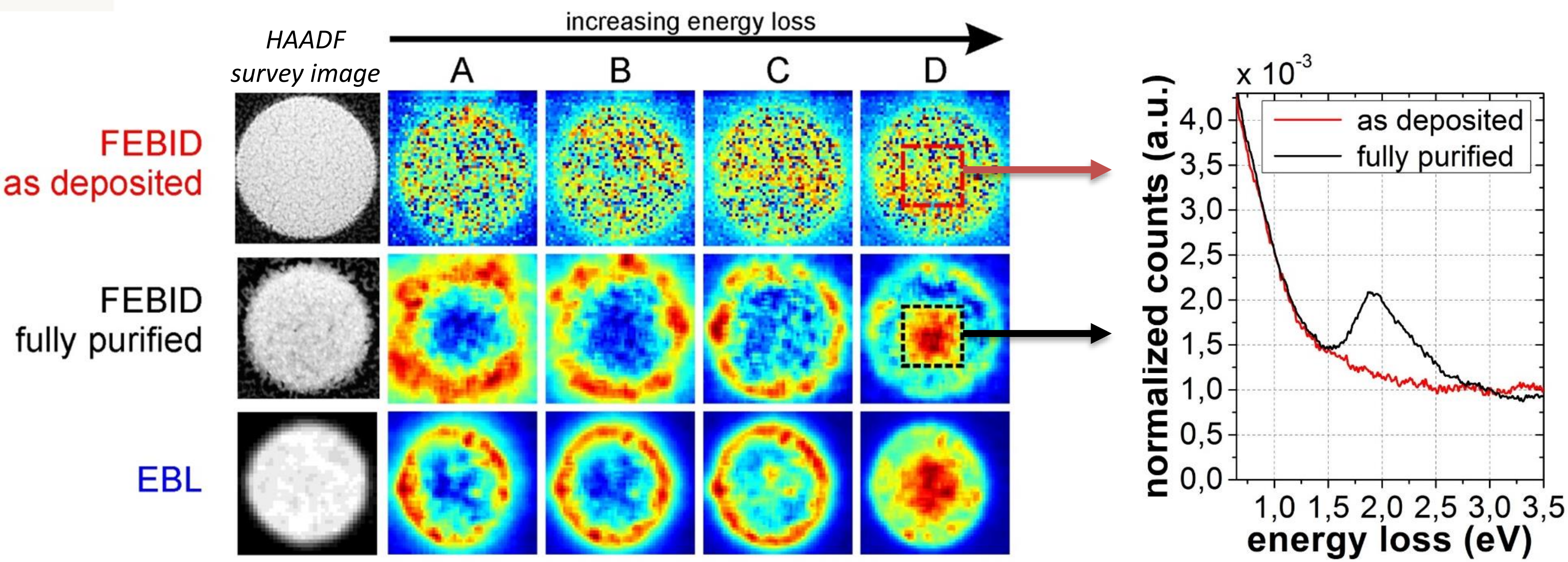

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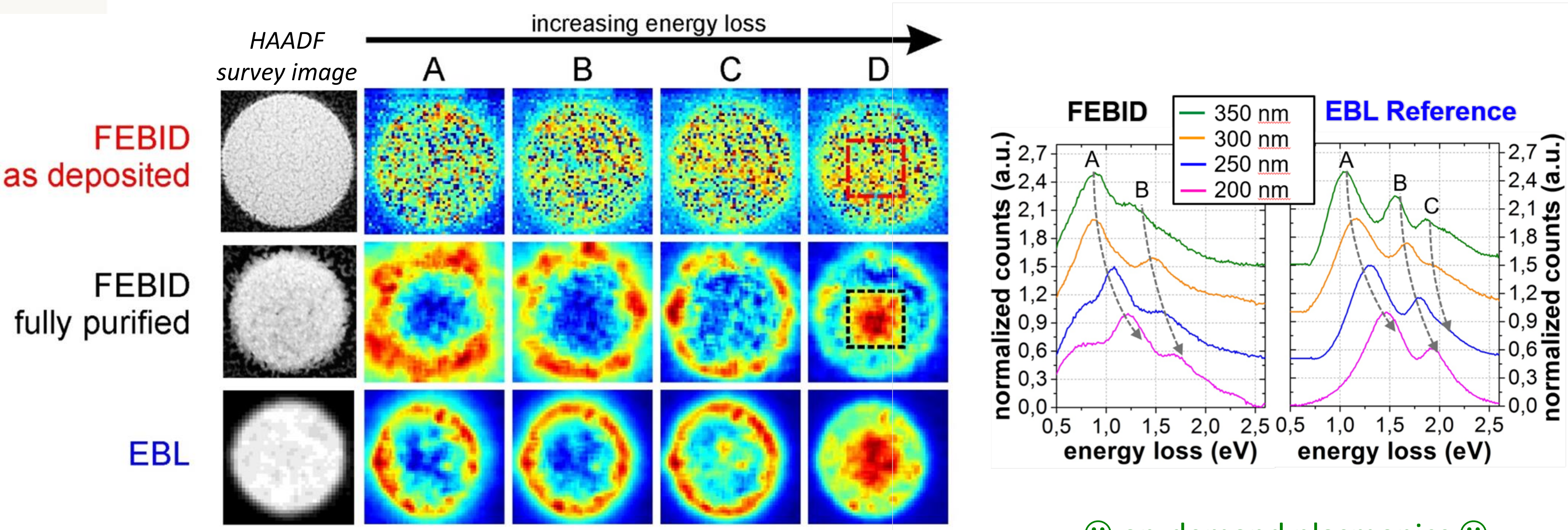

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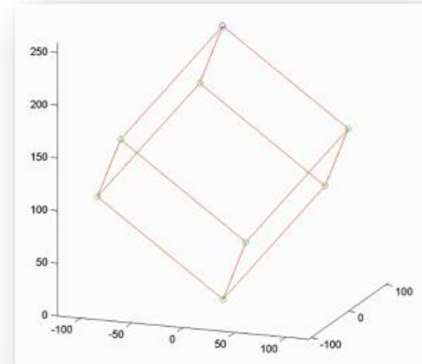
2. However, the functionality can precisely be tuned from insulating to conductive
3. Recent development also allow full transfer into pure metals (problematic with O sensitive mat.)

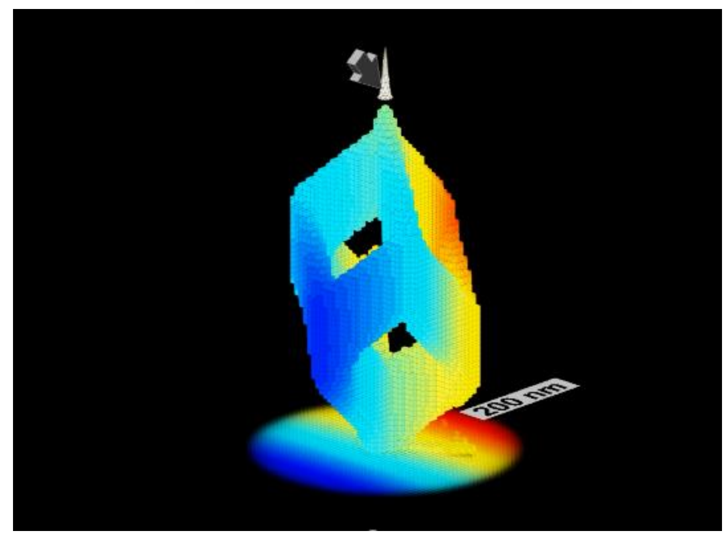
OK … so we have a direct-write bottom-up technology, applicable on virtually any given surface … not bad but is there another unique selling point?

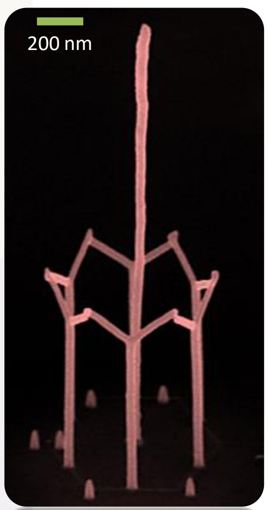
True 3D Nanoprinting

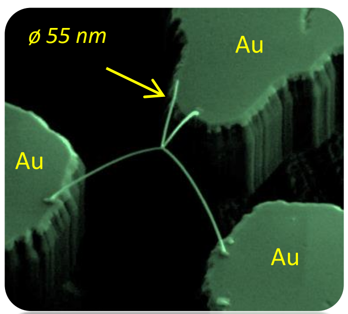
- In principle, this technology allows the fabrication of free-standing 3D structures … however, often via time-consuming trial-and-error approaches
- Recently, we have managed to turn around the situation and can now use CAD models as input for simulations which then can directly be fabricated

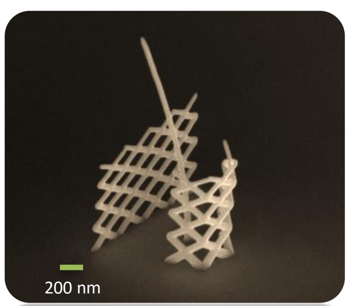
CAD based modeling











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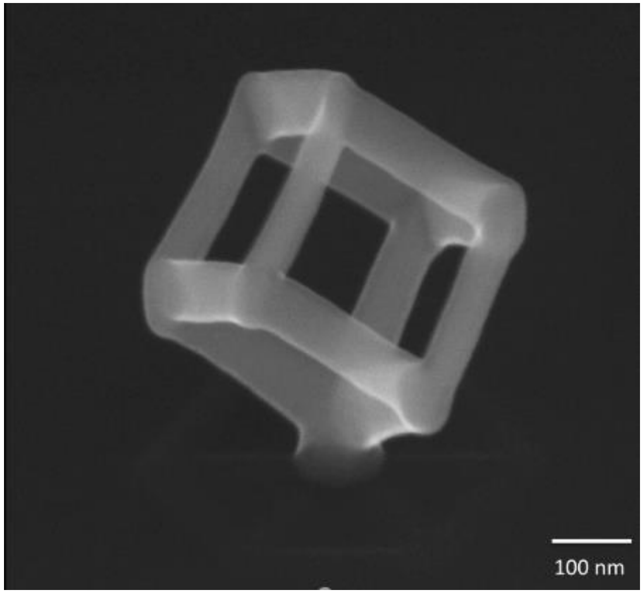

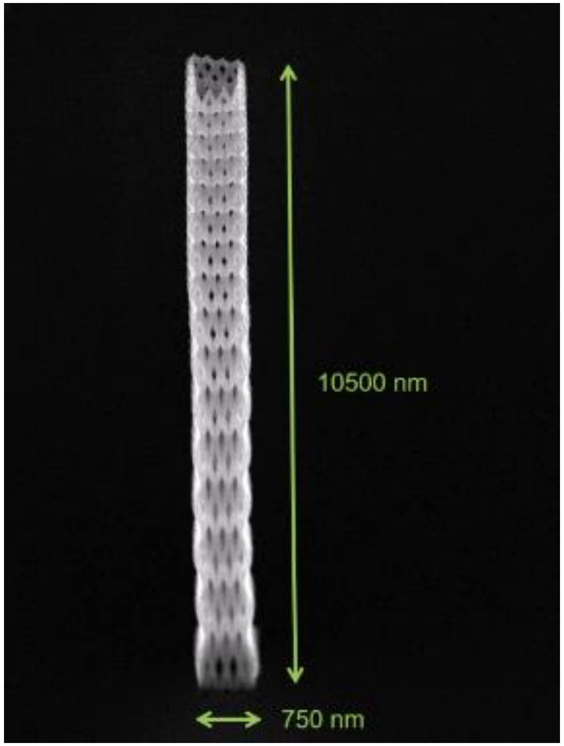

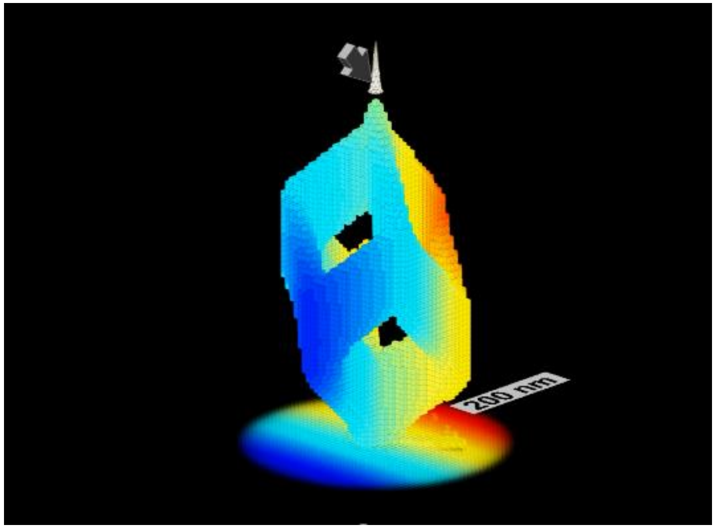

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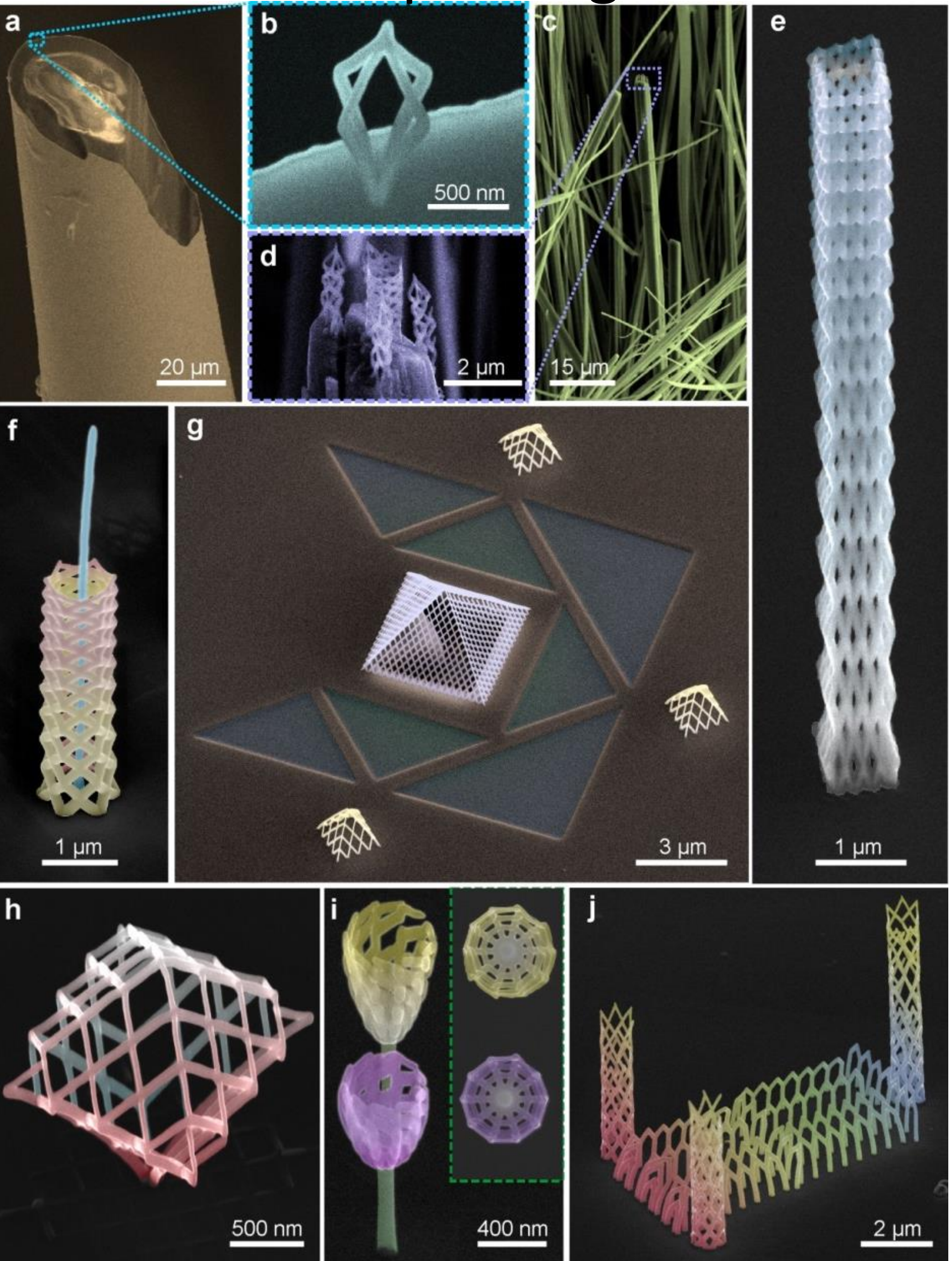

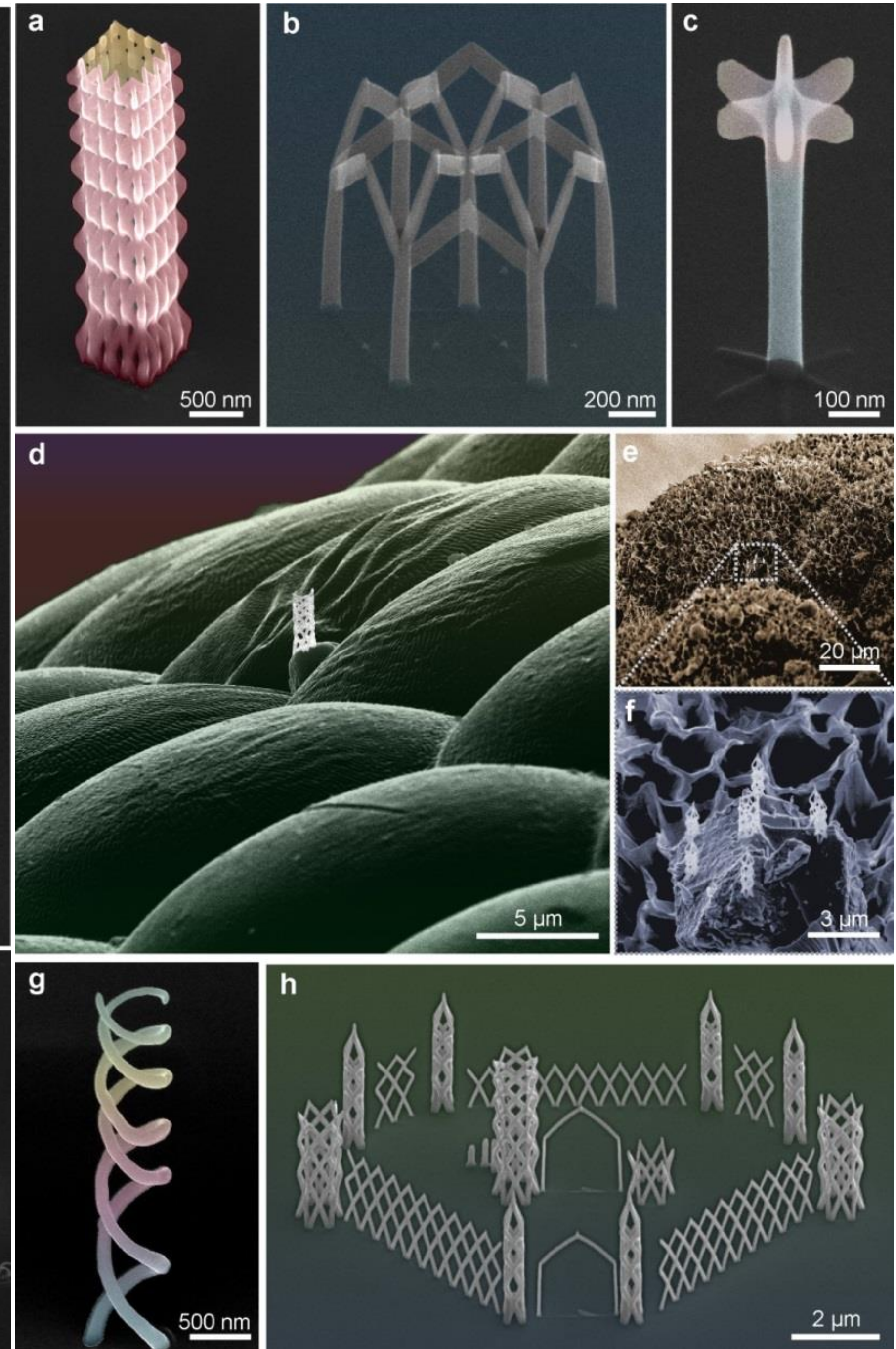

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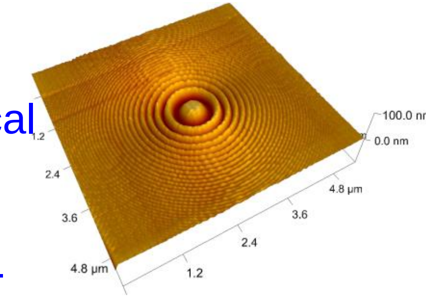
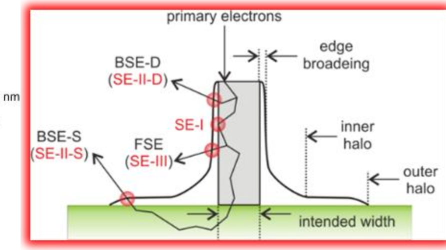
FEBID has evolved from a flexible direct-write process into a true 3D nano-printing technology

1. In combination with simulations, the fabrication of complex, free-standing 3D architectures becomes possible with branch diameters of less than 30 nm …
2. … and that on virtually ANY given surface!

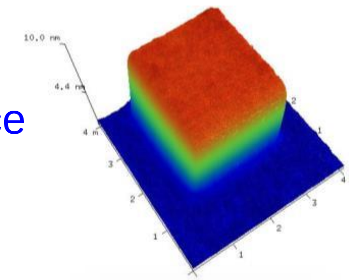
FEBID Processing: PROs & CONs

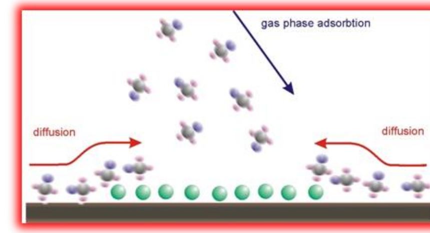
FEBID uses as nano-sized electron beam for local decomposition of surface adsorbed precursor molecules allowing the fabrication of complex nanostructures with conductive, insulating, semi-conducting, magnetically (…) properties





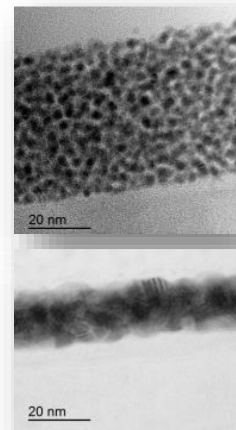
+ It can be applied on virtually ANY given surface → charging / e-beam sensitive surfaces are challenging

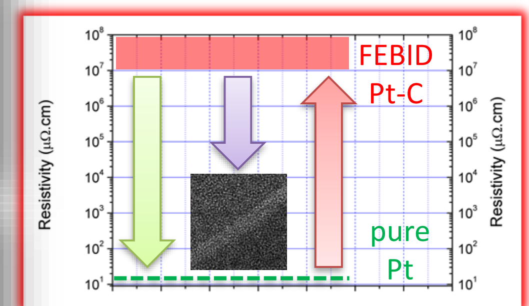




+ Feature sizes can be on the real nanoscale → limited by electron trajectory related effects

+ High shape fidelities can be achieved → requires careful process setup due to local depletion effects

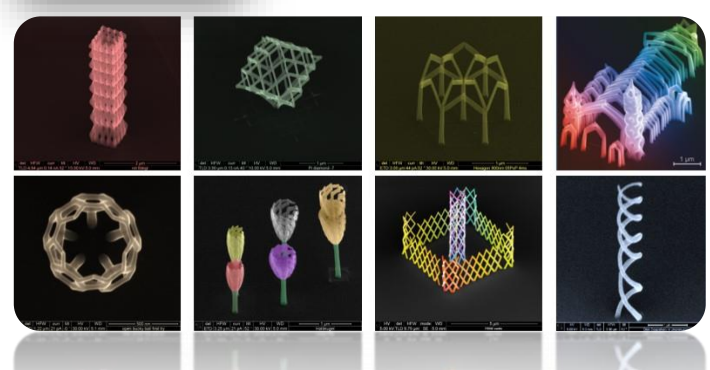




+ Provides unique metal-matrix nano-composition → can reduce / mask the main functionality

+ Allows structural / chemical / functional / mechanical tunability → from tuning to full purification → currently via post-processing

+ Enables true **3D nano-printing** → requires simulations



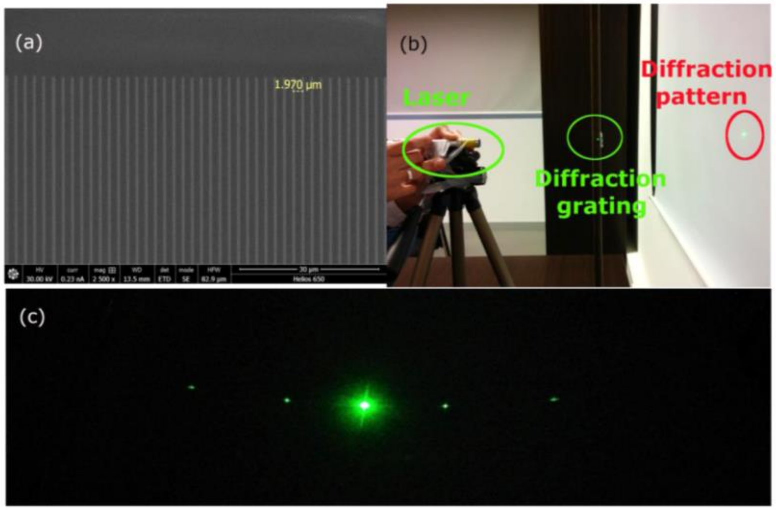
FELMI-ZFE

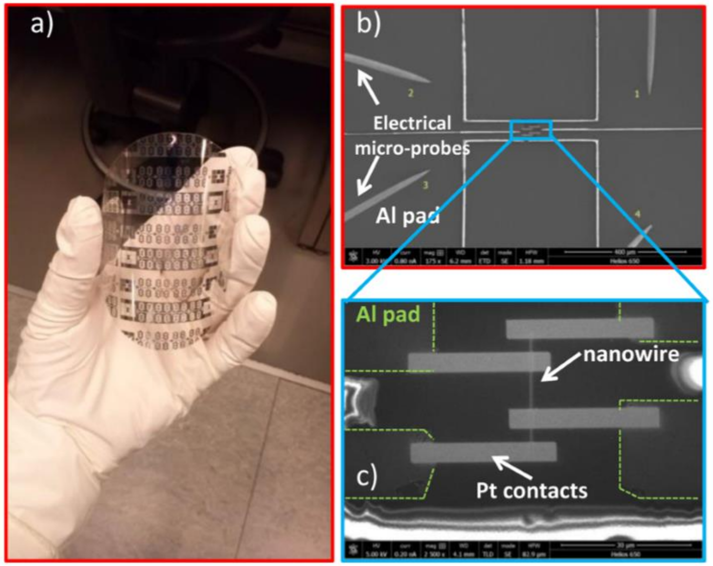
From Fundamentals Towards Applications

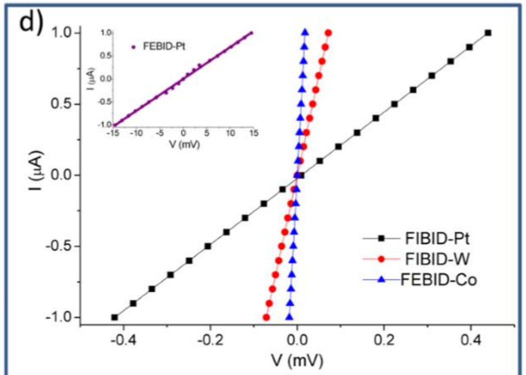
FEBID on (Charging) Polymeric Surfaces

Courtesy of Patricia Peinado, Soraya Sangiao, and José María de Teresa; successfully developed at the Universidad de Zaragoza (Spain)

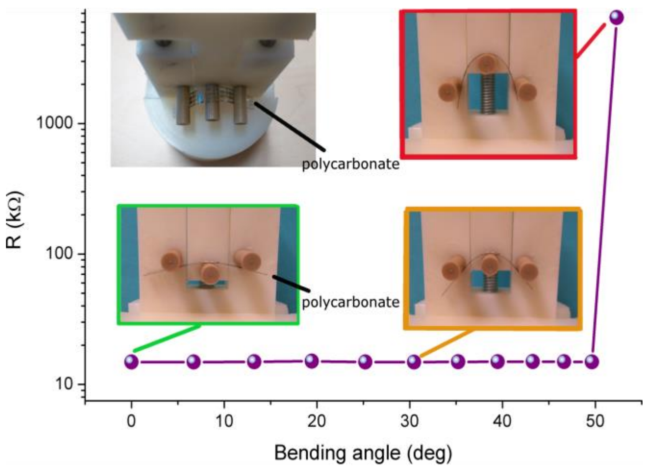
- FEBID can also be performed on basically insulating polymer substrates (with a few tricks)
- The biggest advantage in this respect is the combination with flexible substrates as the functionality is maintained over a huge range!
- By that e.g. FEBID based (nano)optical applications on flexible and transparent surfaces becomes possible which has been widely ignored in the past







Material	ρ (µΩ cm)
FEBID-Co	30.5
FIBID-W	80.4
FIBID-Pt	438.9
FEBID-Pt	3.18 x 10⁴

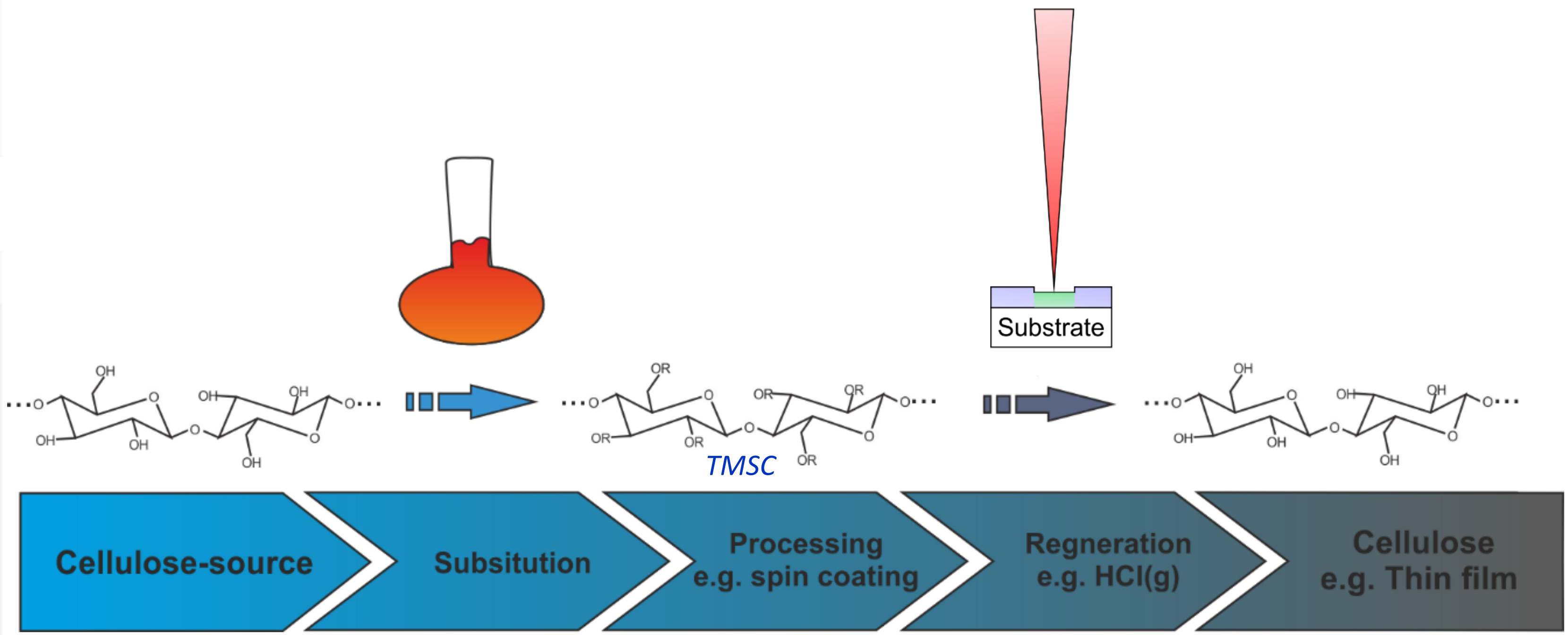


Peinado et-al, ACS Nano, 9 (6), 2016

Combination with Cellulosic Material

- Recently, the fabrication of pure cellulose nanostructures via direct-write Focused Electron Beam Induced Conversion (**FEBIC**) was successfully demonstrated

- This allows for the first time to **create biomaterials structures in the sub-100 nm regime ☺**



Ganner et-al, *Nature Scientific Reports,* re-submitted, 2016

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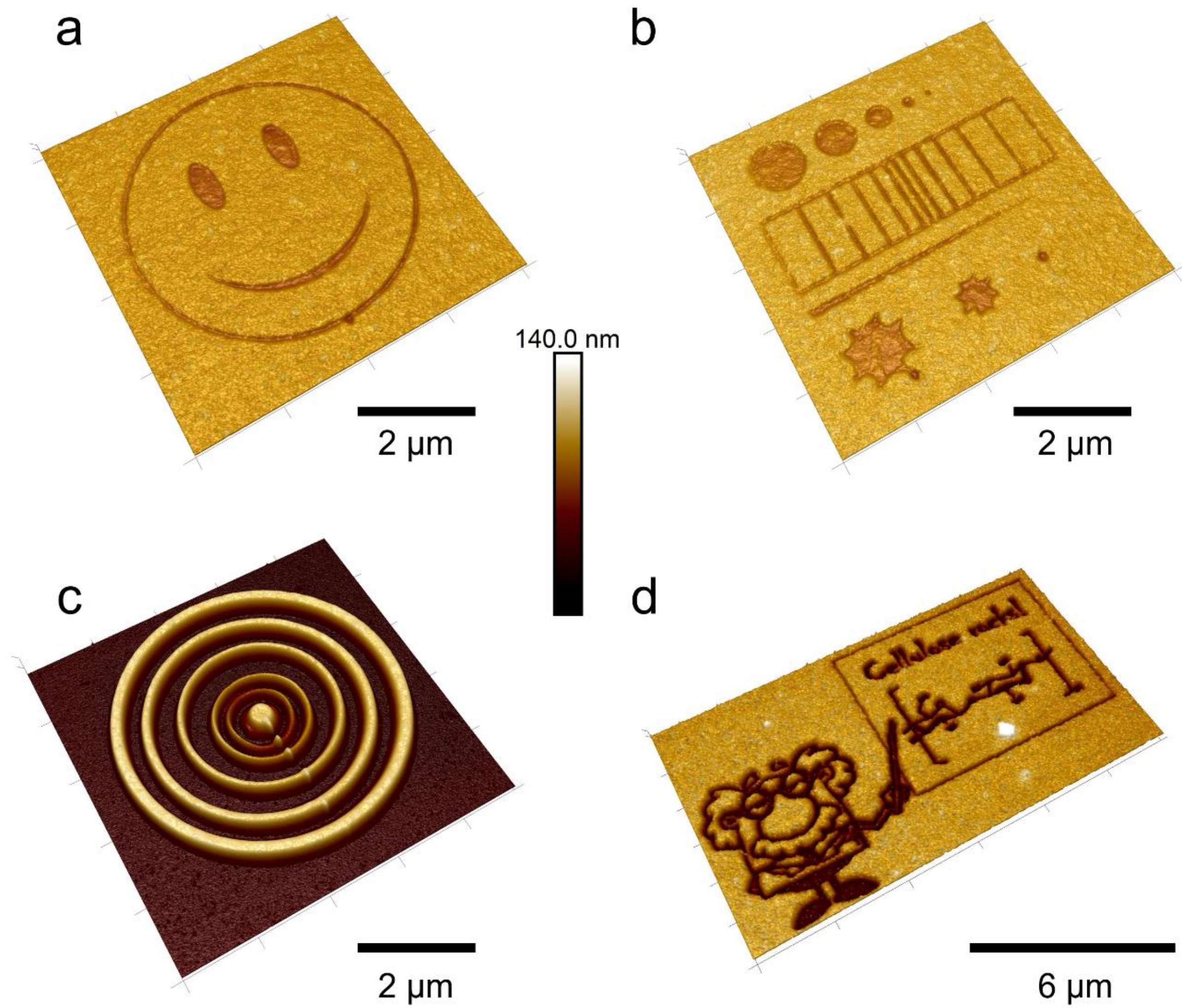
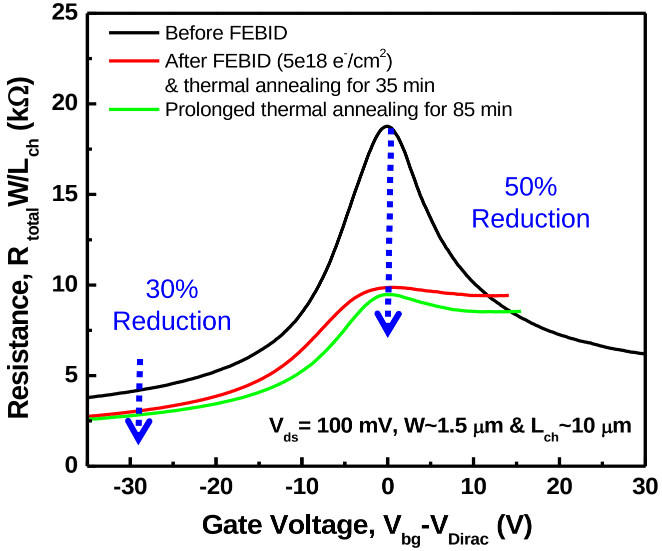


Ganner et-al, *Nature Scientific Reports,* re-submitted, 2016

FEBID Nanowelding: Reducing Graphene Contact Resistances

Unique Advantages of the FEBID nanowelding:

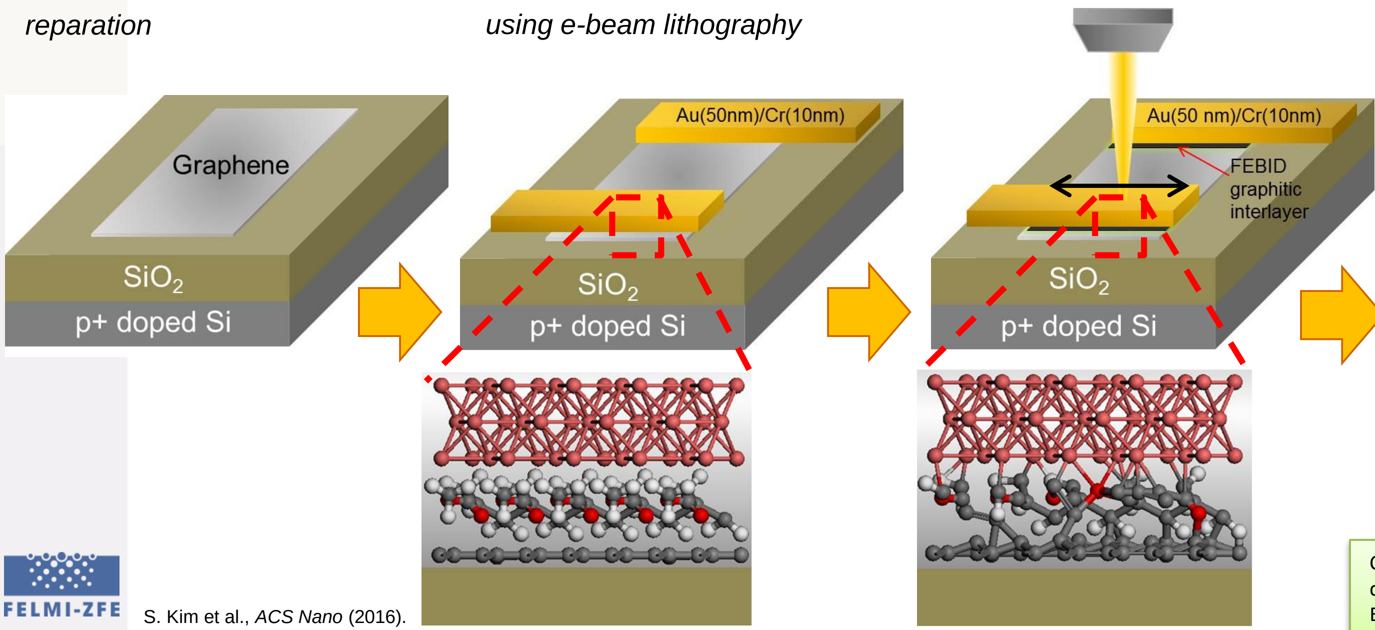
- Up to 50% reduction of contact resistance: due to enhanced electrochemical coupling
- Fast processing time for enhanced scalability: only a few seconds per 1 μm² contact area
- High insertion potential into conventional CMOS deice fabrication workflows for 2D materials
- Turning the negative impact of PMMA residues into an advantage!



Step 1. *Graphene transfer and p reparation*

Step 2. *Nanodevice fabrication using e-beam lithography*

Step 3. *Nanowelding of the interfaces using focused electron beam*



Step 4. Postdeposition thermal annealing in air at 350 °C to achieve:
→ *Removal of parasitic carbon contamination from the channel*
→ *Complete graphitization of FEBID interlayer "glue"*

S. Kim et al., *ACS Nano* (2016).

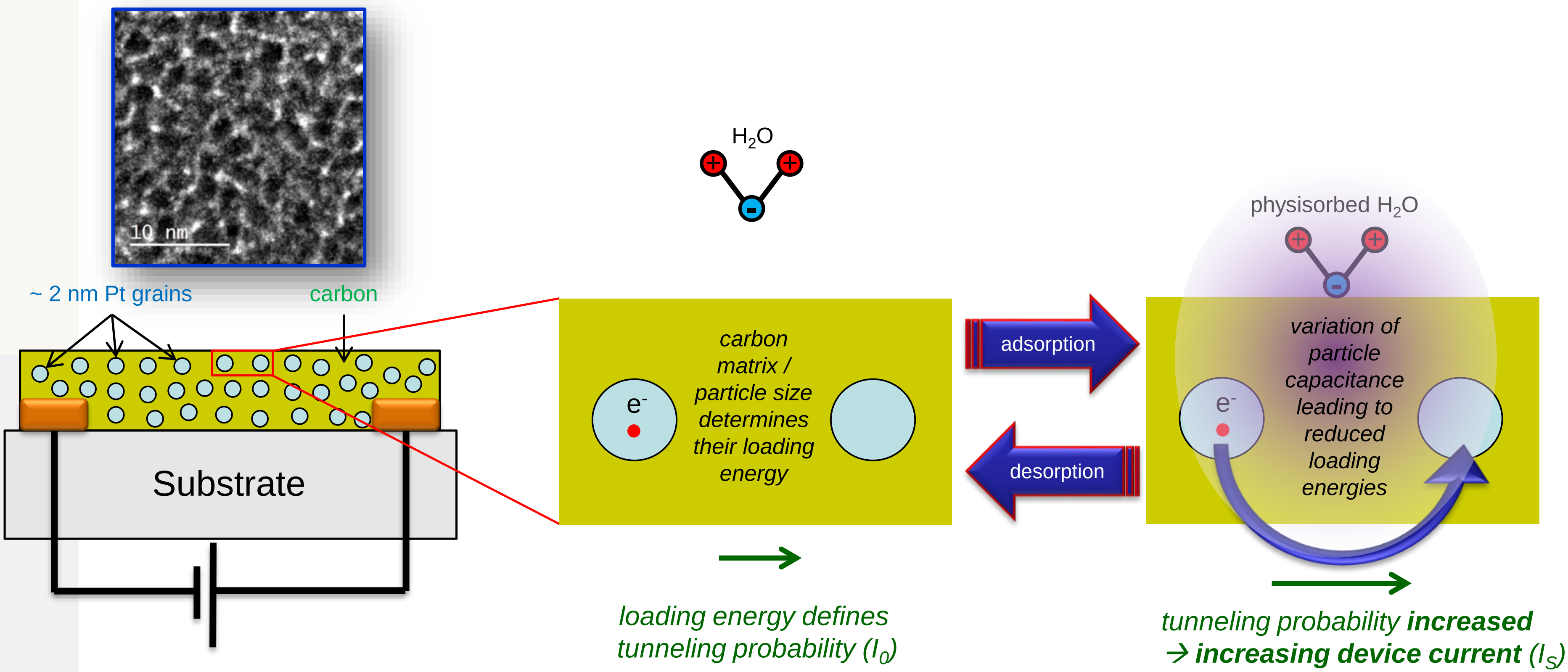
Courtesy of Songkil Kim and Andrei G. Fedorov; successfully developed at the Woodruff School of Mechanical Engineering / Georgia Institute of Technology (USA)

FELMI-ZFE

Metal-Matrix Nanocomposits: Quasi-2D Gas Sensors

- The application of nano-granular materials for sensor applications has also been demonstrated
- Adsorbed polar molecules vary the charging energy due to variation of the particle capacitance which influences the tunneling probability and by that the macroscopic device current
- *Such sensors react fast, reversible, selective, and quantitative without any reformation cycles*

fabrication time ~ 60 sec.



Kolb et-al, *Nanotechnology* 2013, 24, 305501
Huth et-al, *Applied Physics A* 2014, 117, 1689

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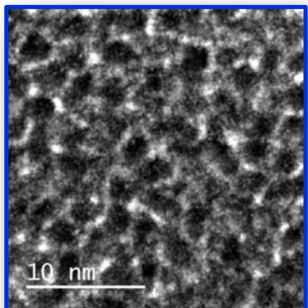
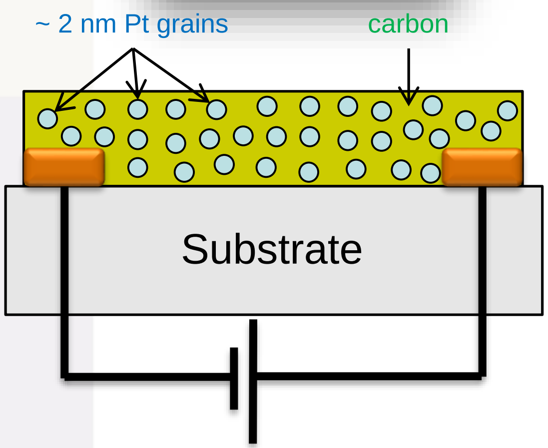
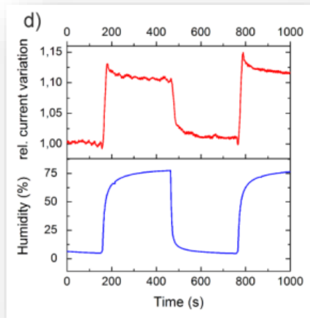
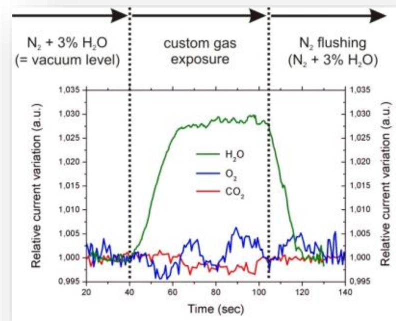




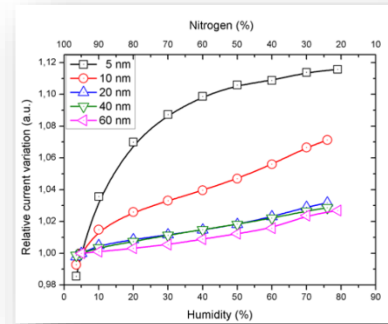
fast & reversible

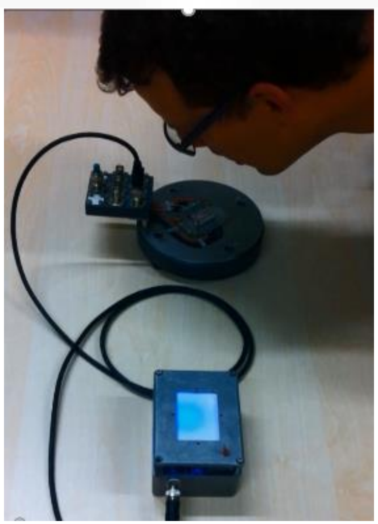


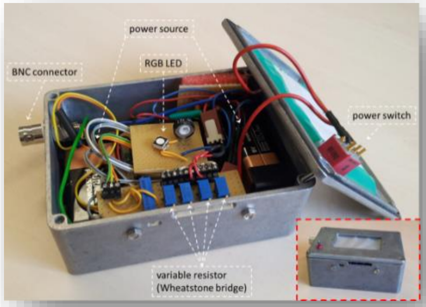
selective



quantitative



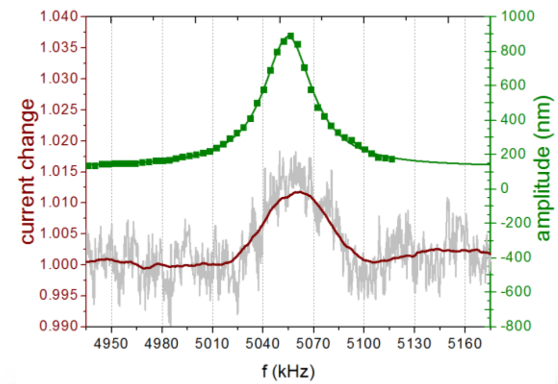


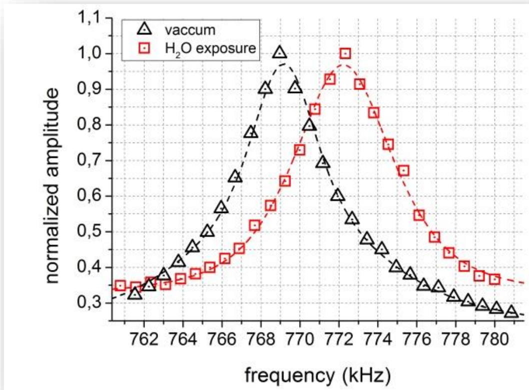


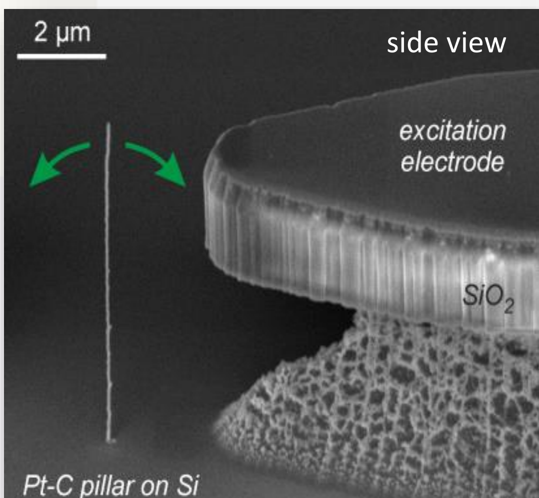
Kolb et-al, *Nanotechnology* 2013, 24, 305501
Huth et-al, *Applied Physics A* 2014, 117, 1689

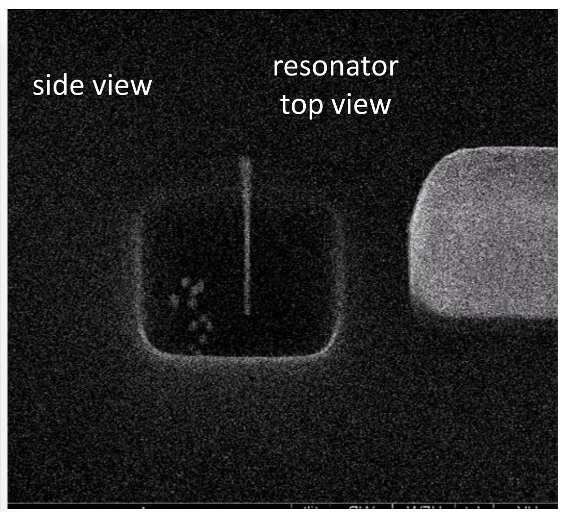
Metal-Matrix Nanocomposits: Quasi-1D Gas / Mass Sensors

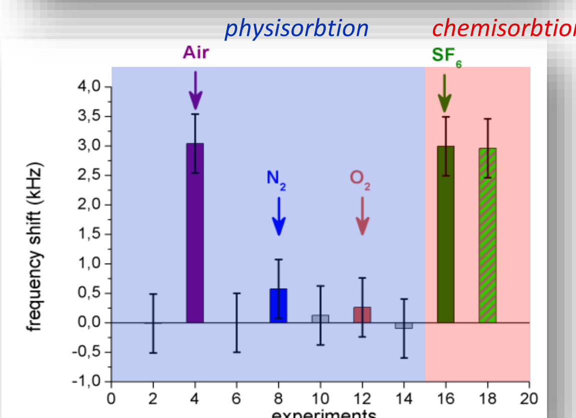
- Quasi-1D Pt-C nano-pillars can be excited via electric AC-fields according to their mechanical resonance frequency
- The small dimensions, the soft mechanical character and the electric conductivity allow highly sensitive
  - gas sensing (reversible)
  - mass sensing (irreversible)
- External electric read-out possible!
- Also, these materials allow mechanical post-fabrication tuning











Arnold et-al, *in submission,* 2016
Winkler et-al, *in preparation* 2016

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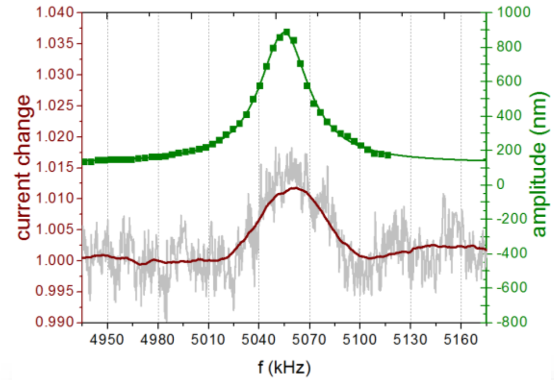

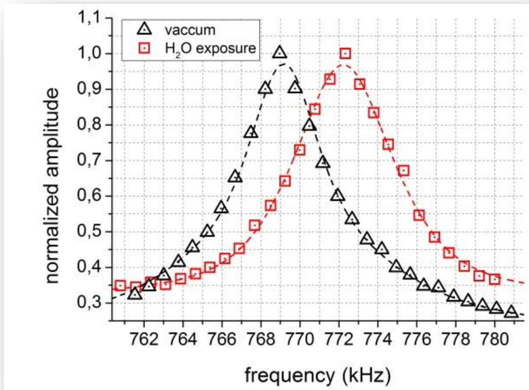

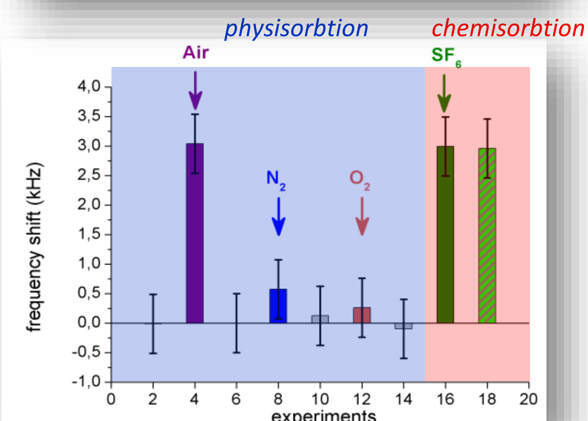

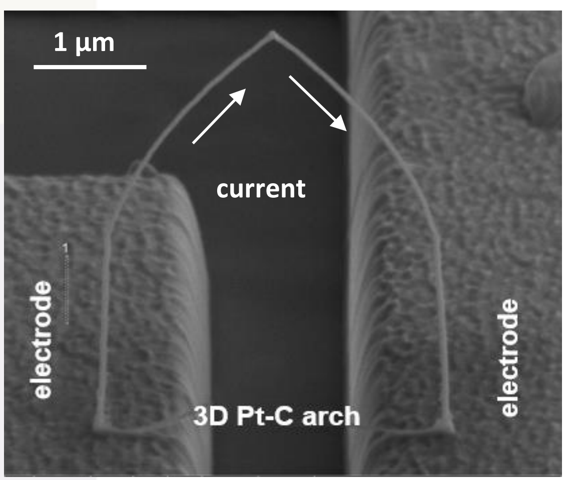

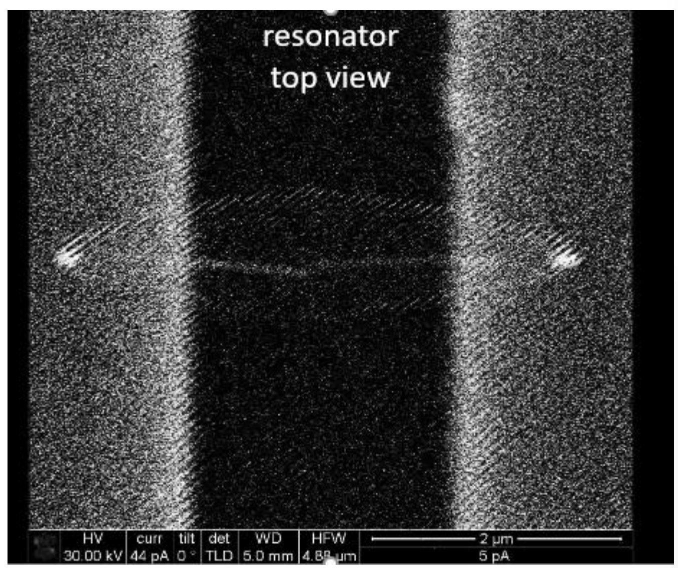

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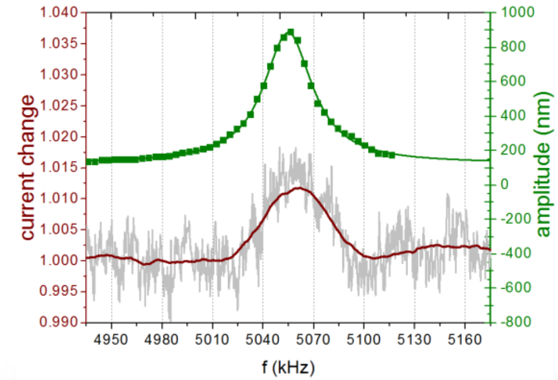

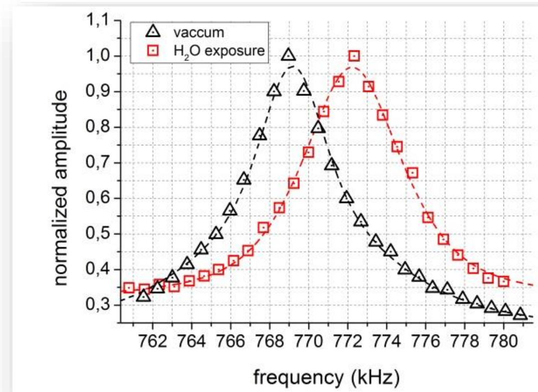

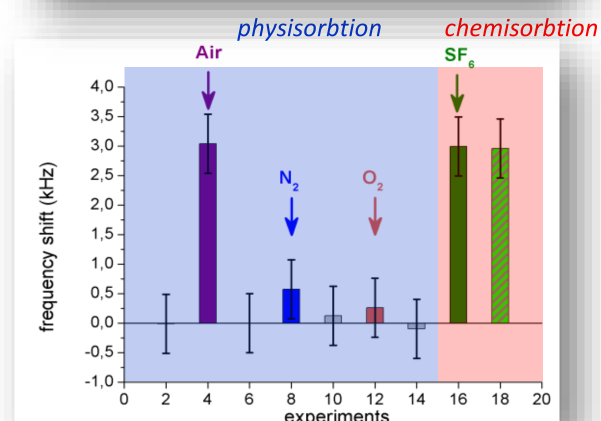

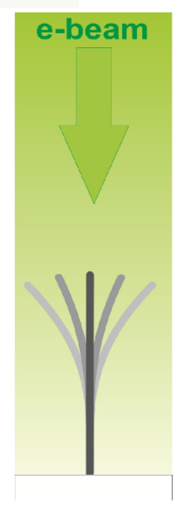

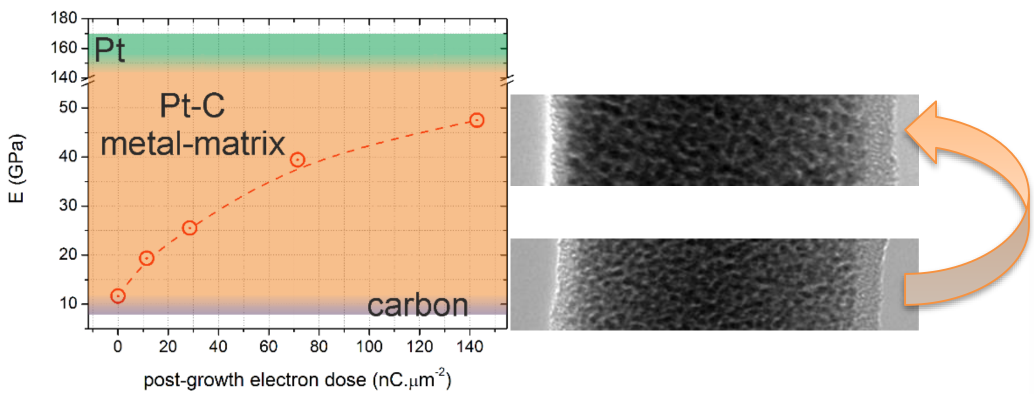

Arnold et-al, *in submission,* 2016
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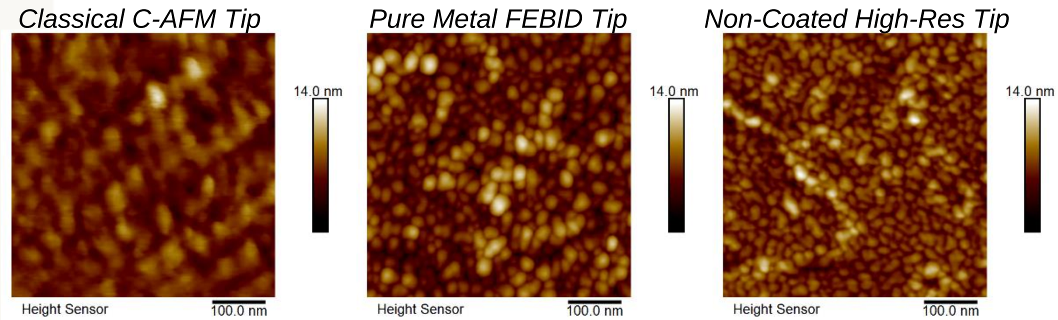
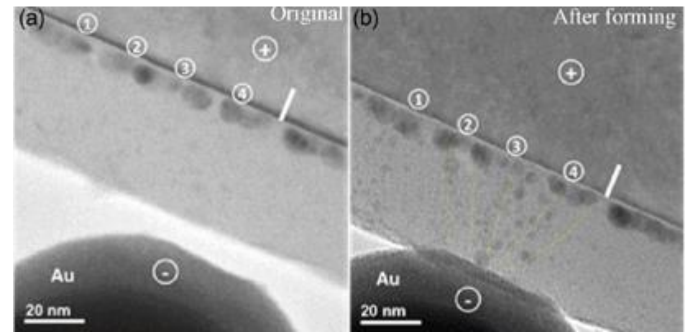
AFM Tip Modification

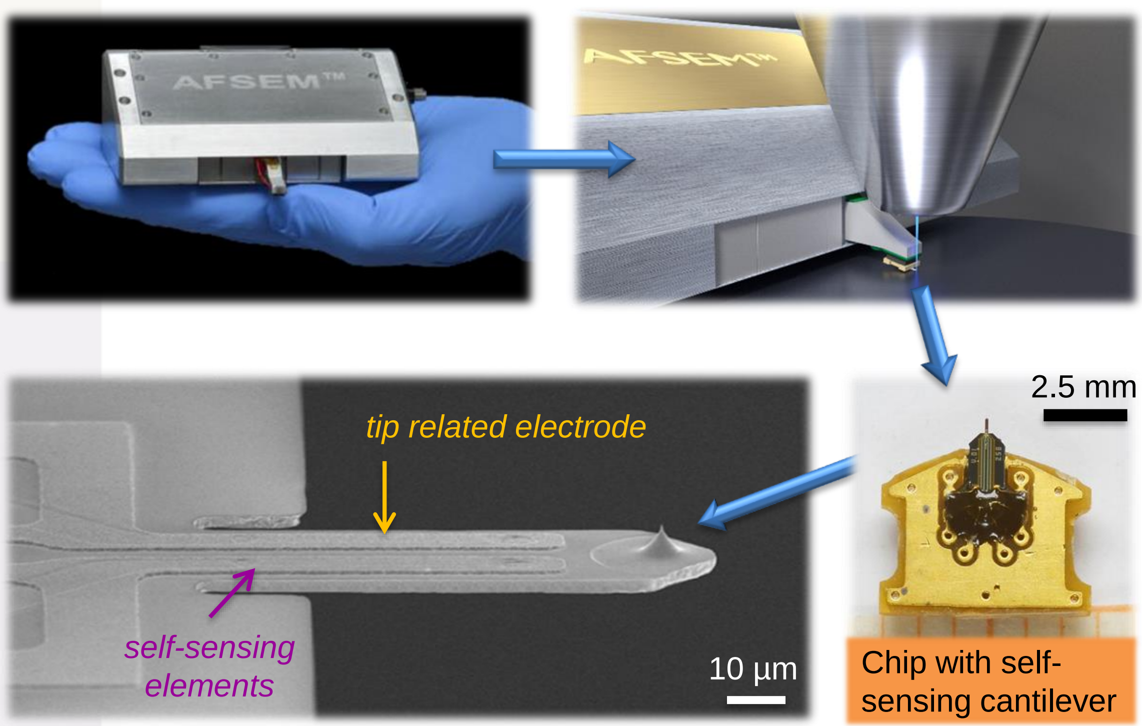
- We work together with the company GETec Microscopy (Vienna, Austria) on the cantilever development for a fast, non-optical, *in-situ* AFM for <u>seamless integration</u> in **SEMs / FIBs**

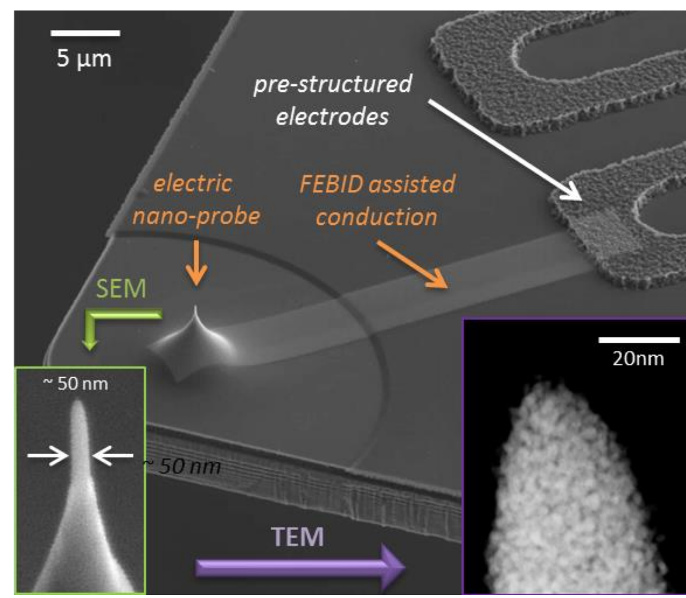
- FEBID Application 1: fully metallic high-resolution tips for C-AFM & point-probing



AFSEM™ powered by *GETec Microscopy*







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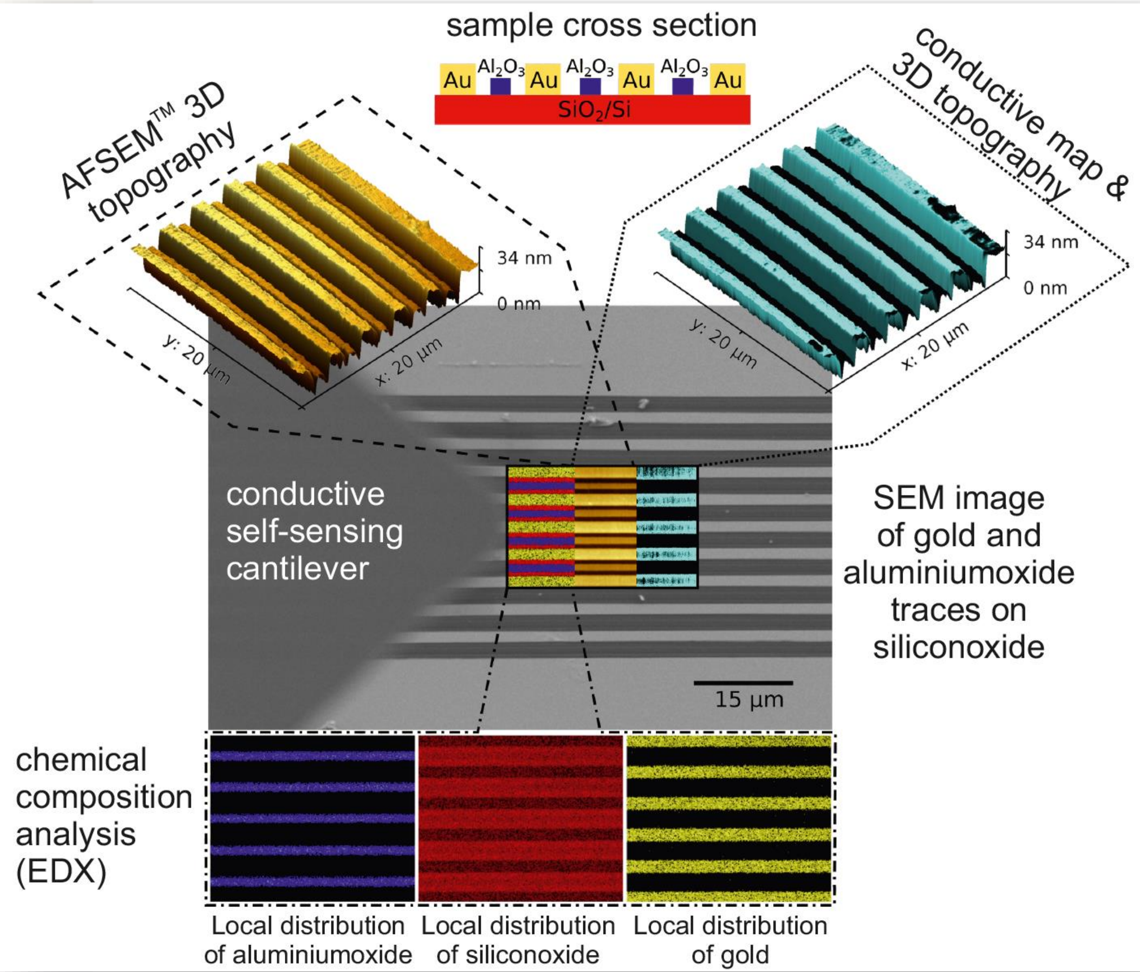

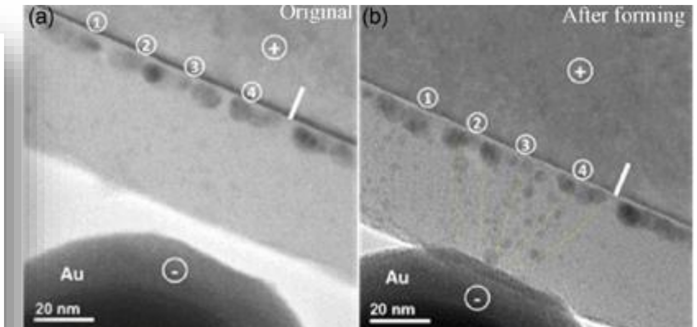

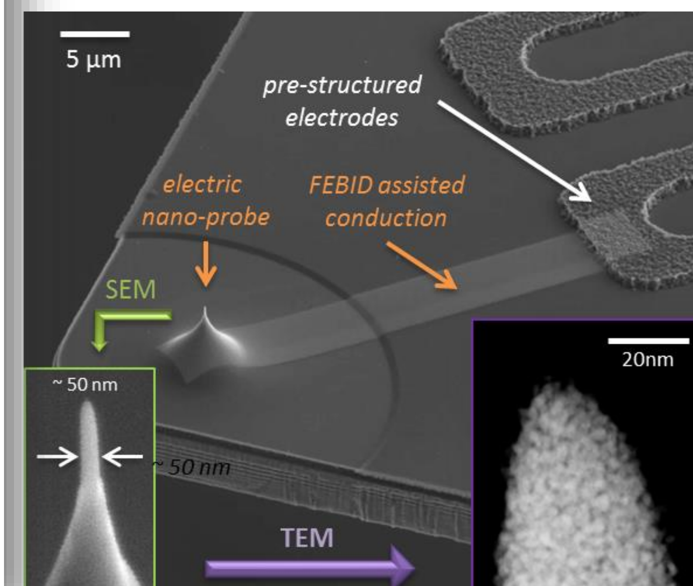

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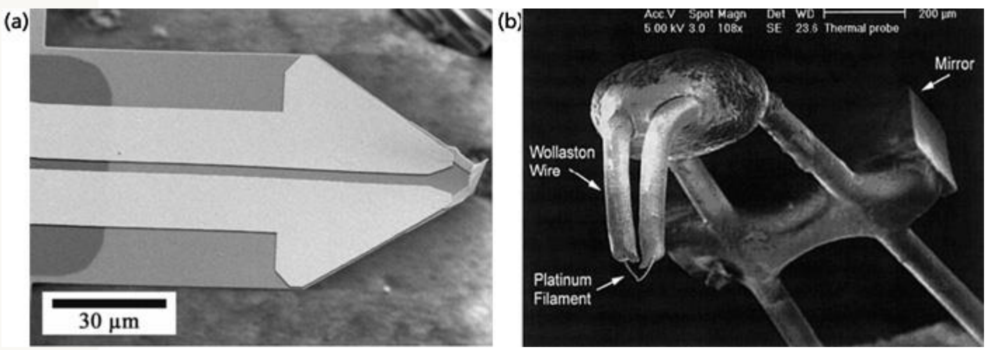
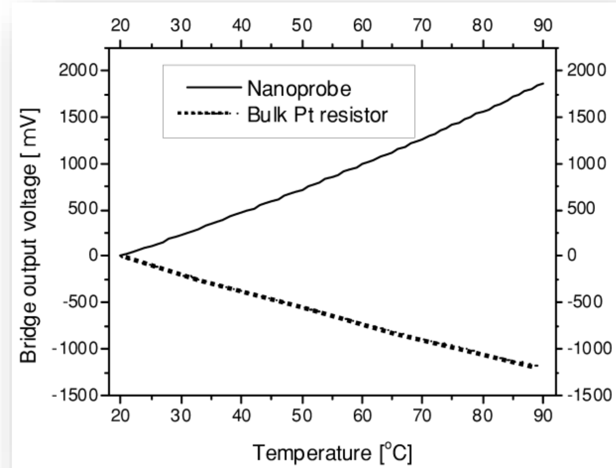
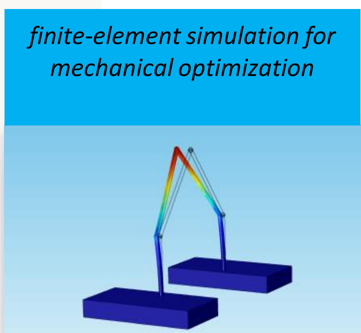
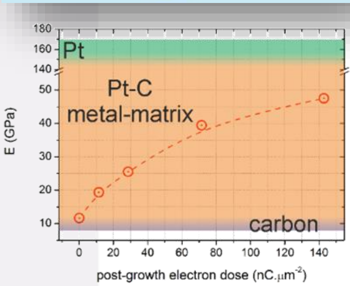
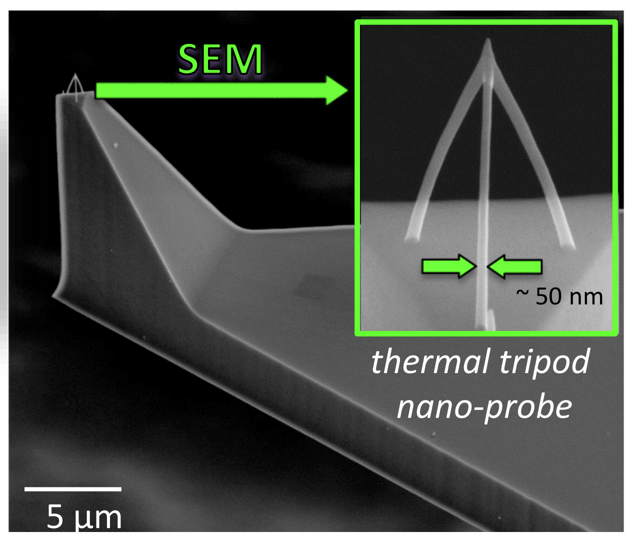
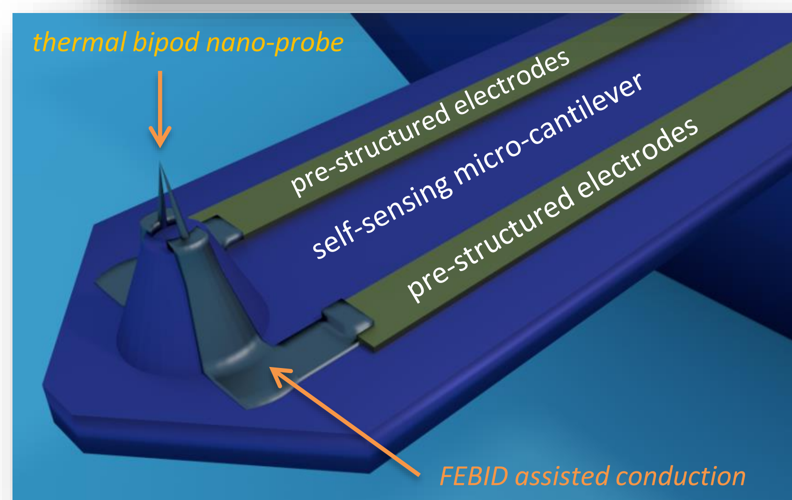










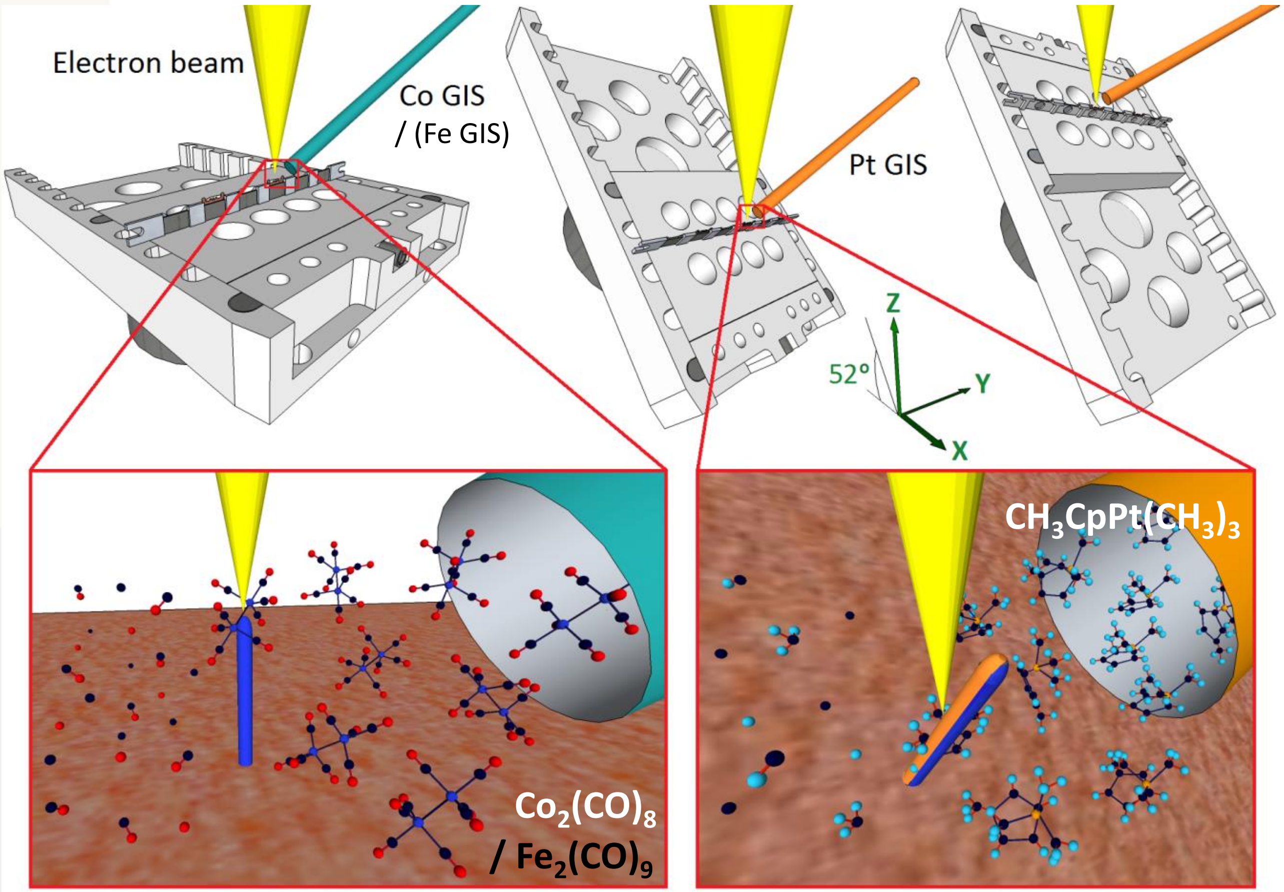


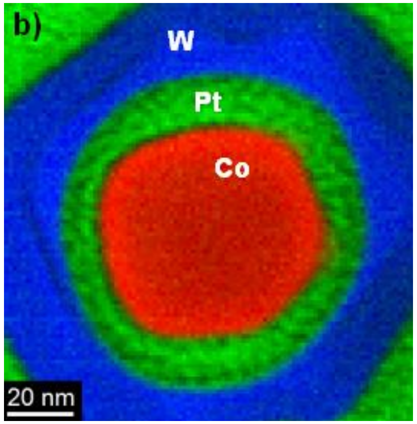
I.W. Rangelow et al, *Microelectronic Engineering*, 57, 2001

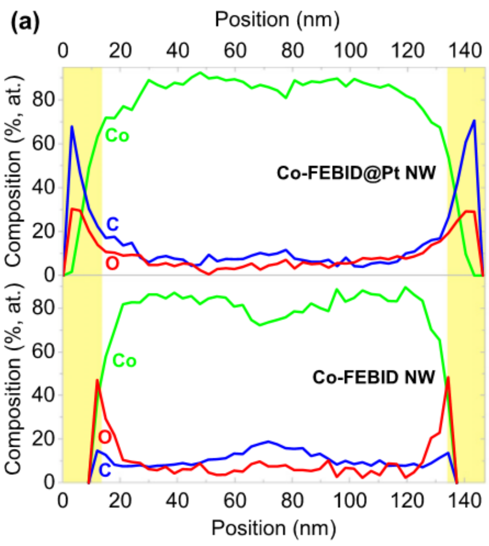
3D Core-Shell Magnetic Co Nanowires

Courtesy of Javier Pablo-Navarro, César Magén and José María de Teresa; successfully developed at the Universidad de Zaragoza (Spain)

- Very recently, the fabrication of quasi-1D Pt / Co core-shell nano-pillars was successfully shown
- Thus, the Co core can be protected from oxidation which is of essential importance on that scale





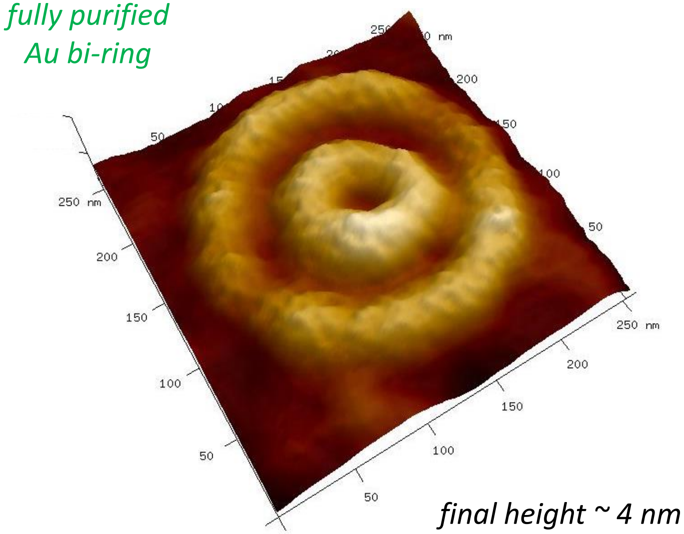


J. Pablo-Navarro et-al, Nanotechnology 27, 285302 (2016)

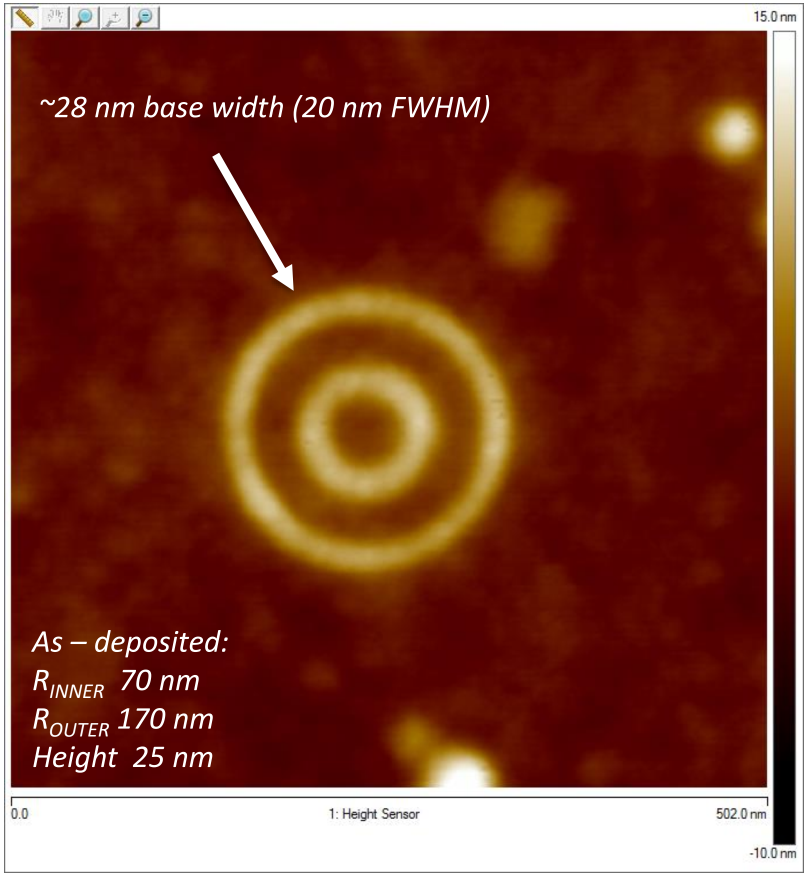
Quasi-Planar Plasmonics

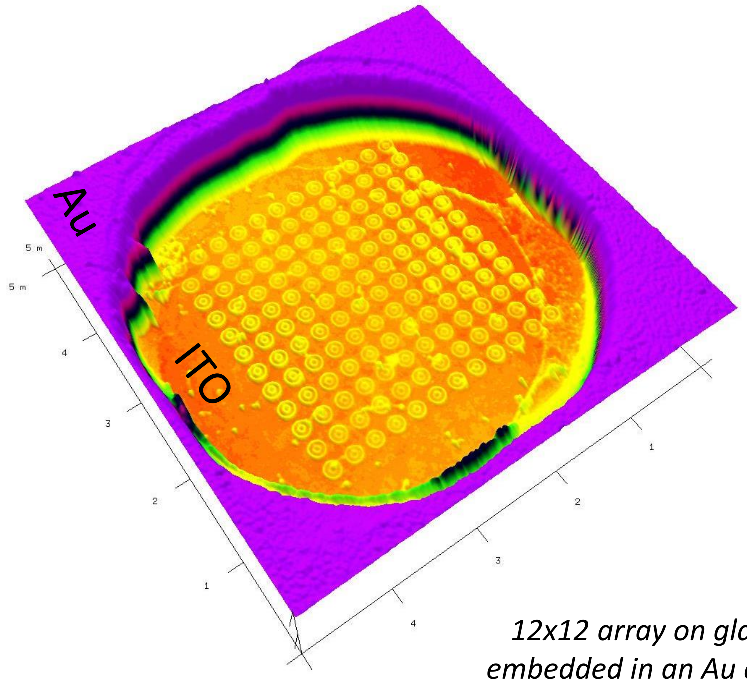
- FEBID high-resolution fabrication & purification of Au structures enables fast and flexible on-demand plasmonic applications (THz communication, spectroscopy, …) (collaboration with **Michael Huth**)
- Although possible, FEBID approaches its resolution and shape-fidelity limitation which requires careful optimization …

fully purified Au bi-ring



final height ~ 4 nm





12x12 array on glass-ITO embedded in an Au aperture

M. Thomson / U. Radeschnig et-al, *in preparation,* 2016

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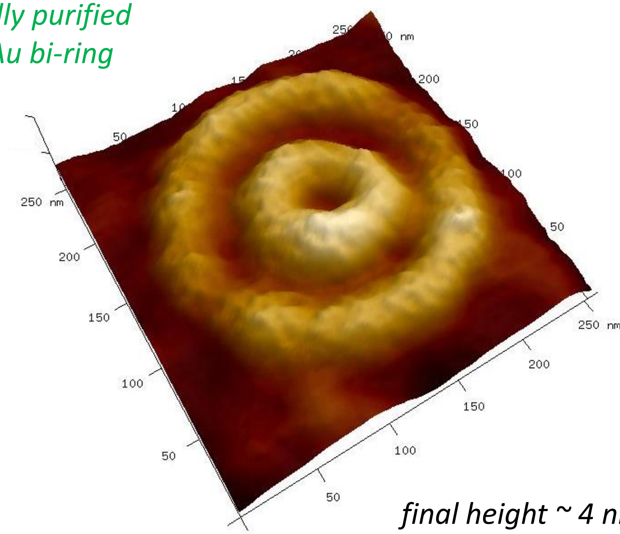

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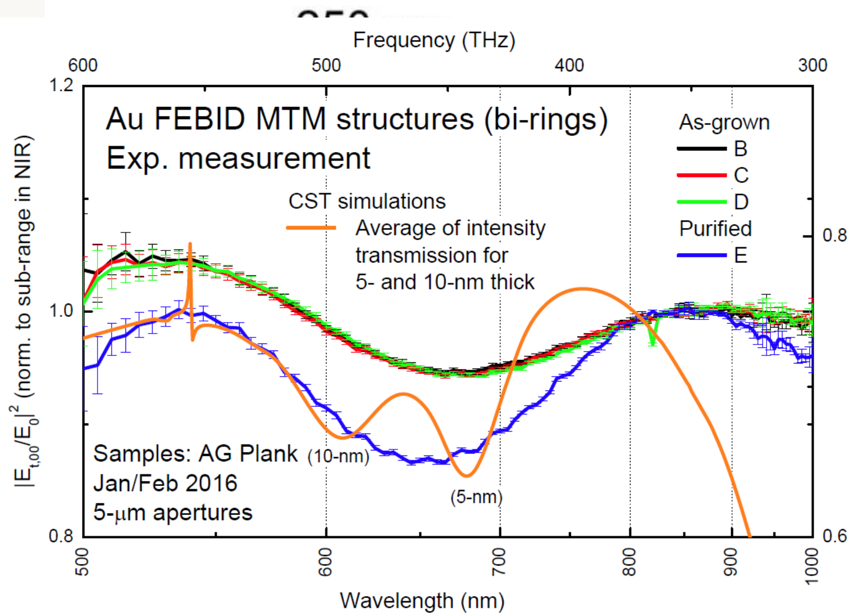

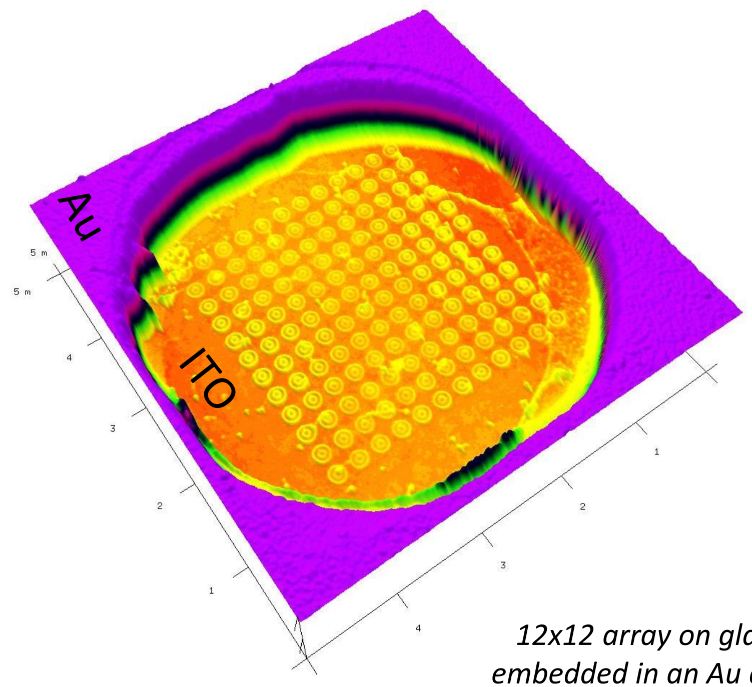

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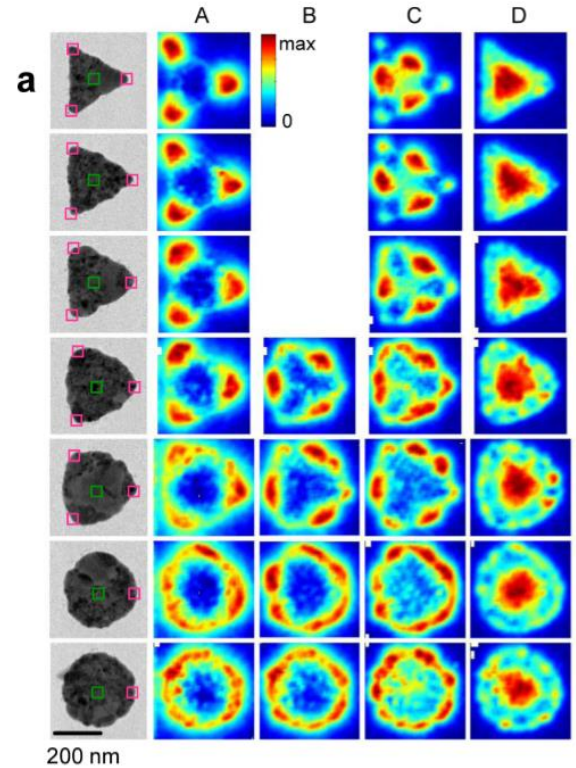
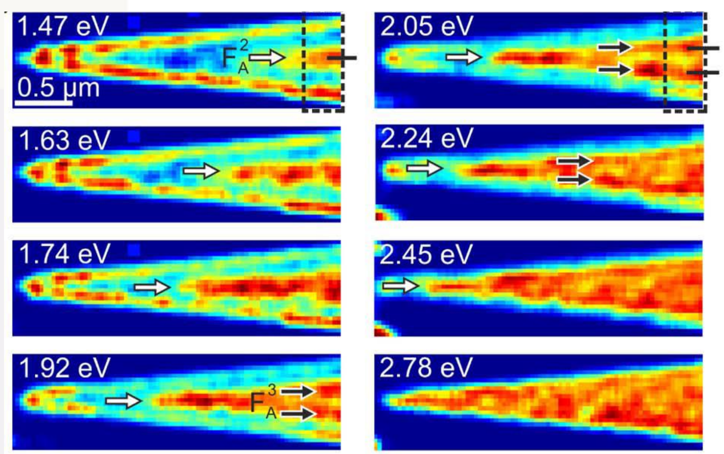
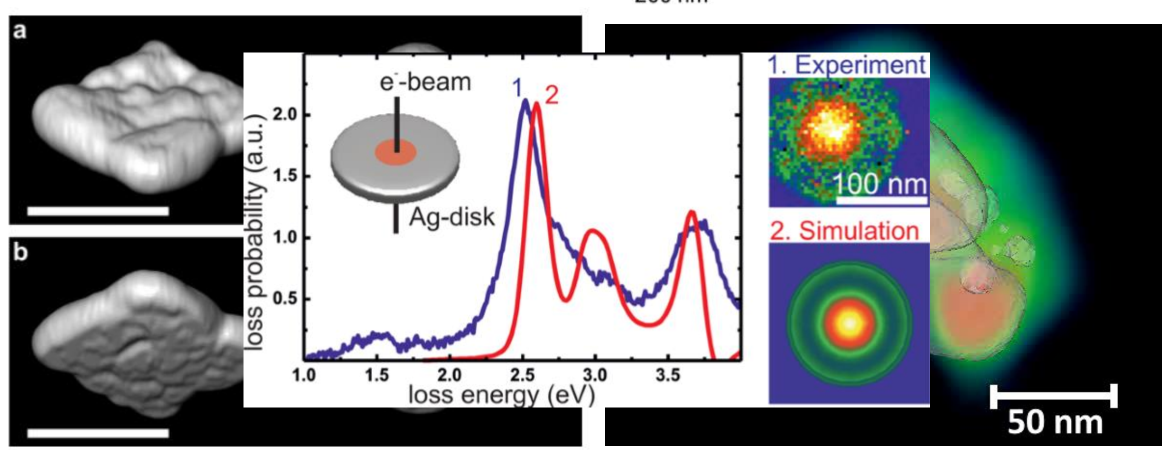
M. Thomson / U. Radeschnig et-al, *in preparation,* 2016

Motivation

- (Scanning) transmission electron microscopy ((S)TEM) based electron energy loss spectroscopy (EELS) has been proven to be a very powerful tool for studying plasmonic behaviour down to the lower nanoscale
- Several new effects have been identified in (depth-convoluted) 2D but also in 3D
- A common element of many investigations, however, is the quasi-2D / planar character of the plasmonic elements
- Although highly interesting for both theoretical and application orientated aspects, fabrication of complex & free-standing 3D nano-architectures remain a real challenge







Schmidt et-al, *Optics Letters* **(2015)**, 40 (23), 5670.
Haberfehlner et-al, *Nano Letters* **(2015)**, 15 (11),7726.

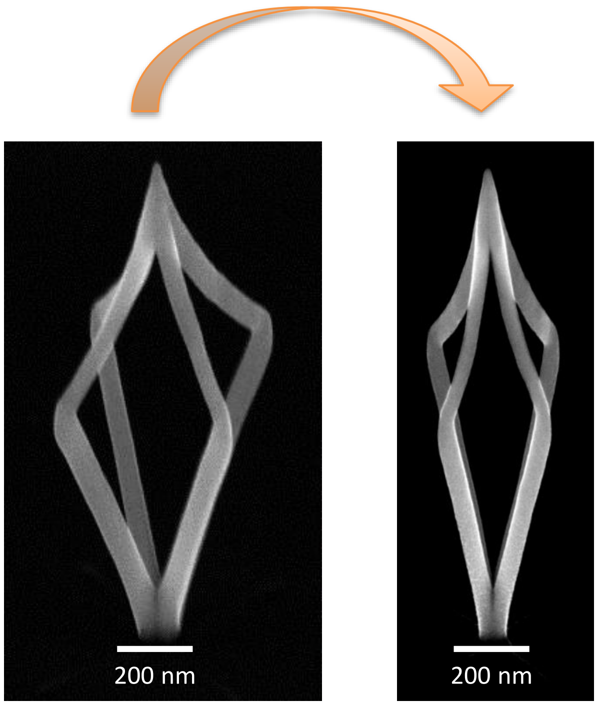
Schmidt et-al, *Nano Letters* **(2014)**, 14, 4810
Schmidt et-al, *Nature Communications* **(2014)**, 5, 3604

Garcia de Abajo et-al, *Rev. Mod. Phys.* **(2010)**, 82, 209
Kociak et-al, *Chem. Soc. Rev. (***2014***)*, 43, 3865

3D Nano-Plasmonics: Beyond Current Limitations!

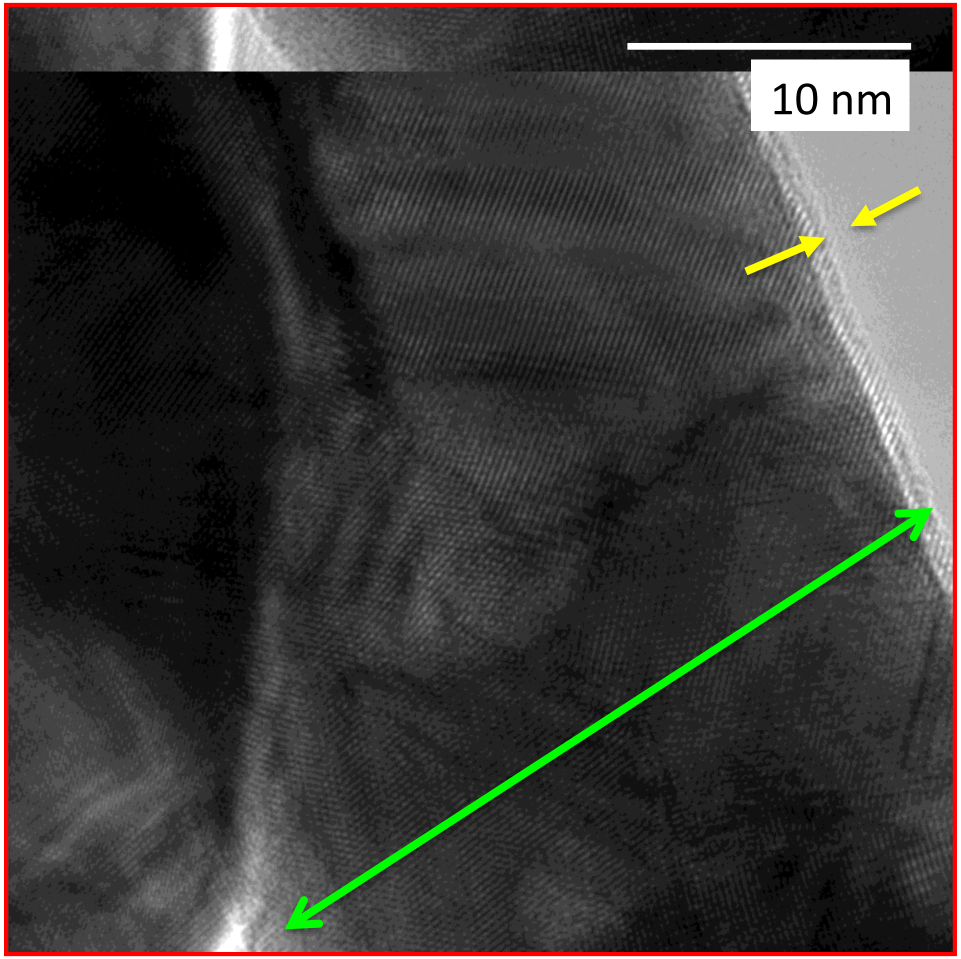
- The combination of FEBIDs 3D capabilities with (Au) purification opens up entire new capabilities
- Although more complicated during purification, ideal conditions lead to free-standing, compact, and structurally dense Au structures with minimal surface contamination and branch diameters below 25 nm → 3D PLASMONICS!

e-beam assisted H_2O purification



3D Nanoprinting

mechanical instabilities slightly change the shape



Winkler et-al, *in preparation* **2016**

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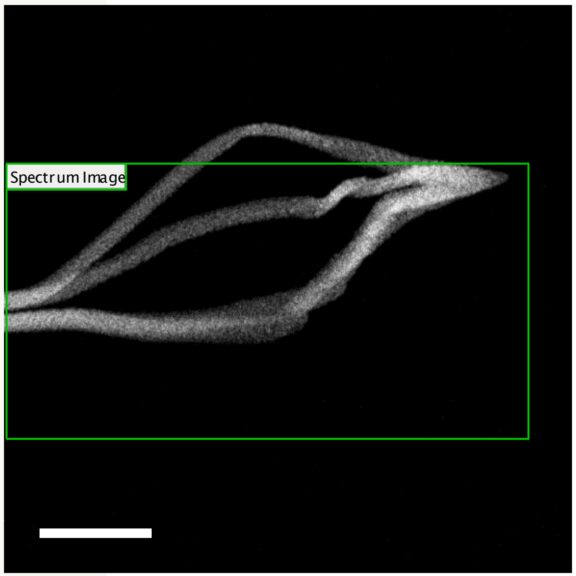
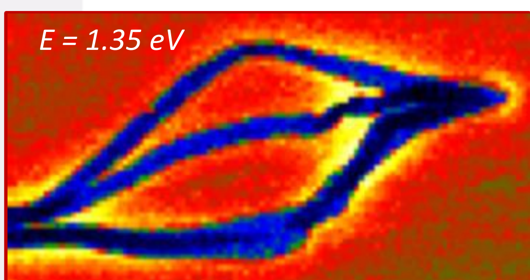
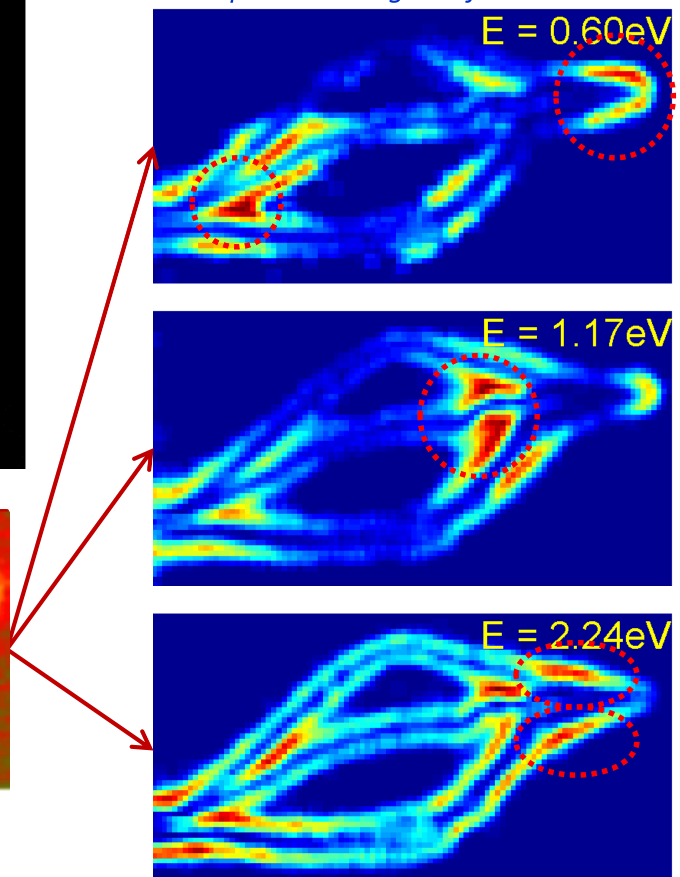
- The combination of FEBIDs 3D capabilities with (Au) purification opens up entire new capabilities
- Although more complicated during purification, ideal conditions lead to free-standing, compact, and structurally dense Au structures with minimal surface contamination and branch diameters below 25 nm → 3D PLASMONICS!



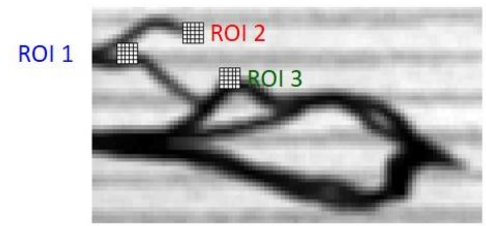


TEM image (HAADF) of purified FEBID structure

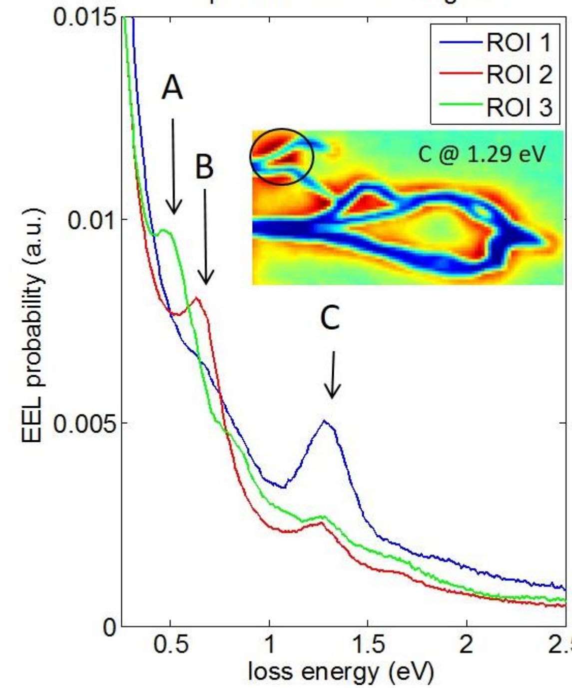
EEL maps @ 3 different energies showing plasmonic signal of SP modes



spectrum image

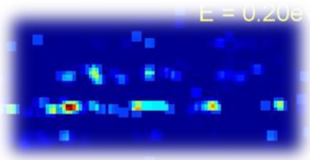


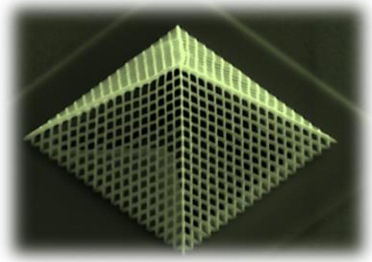
Spectra of selected region



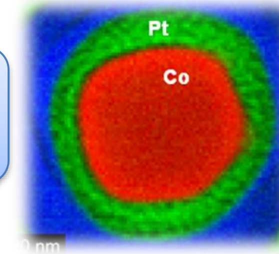
Winkler et-al, *in preparation* **2016**

1D – 3D Plasmonics



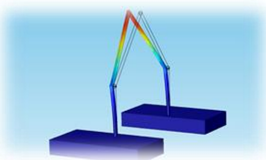


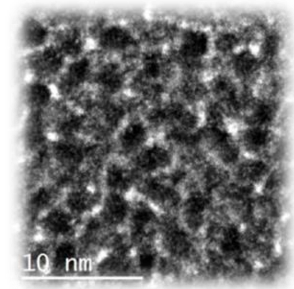
Multi-Layer Materials



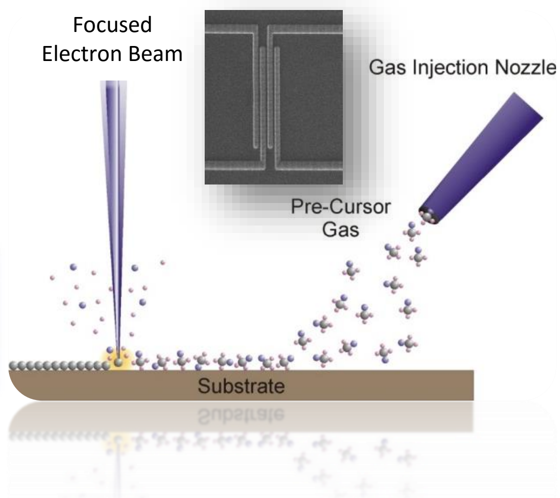
3D Nanoprinter

Nano Mechanics

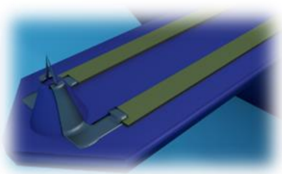




Gas / Mass Sensors

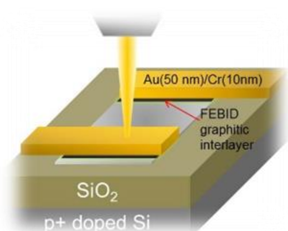


High-Resolution Nanoprobes



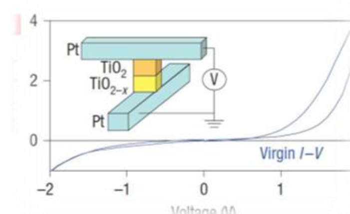
Flexible Electronics

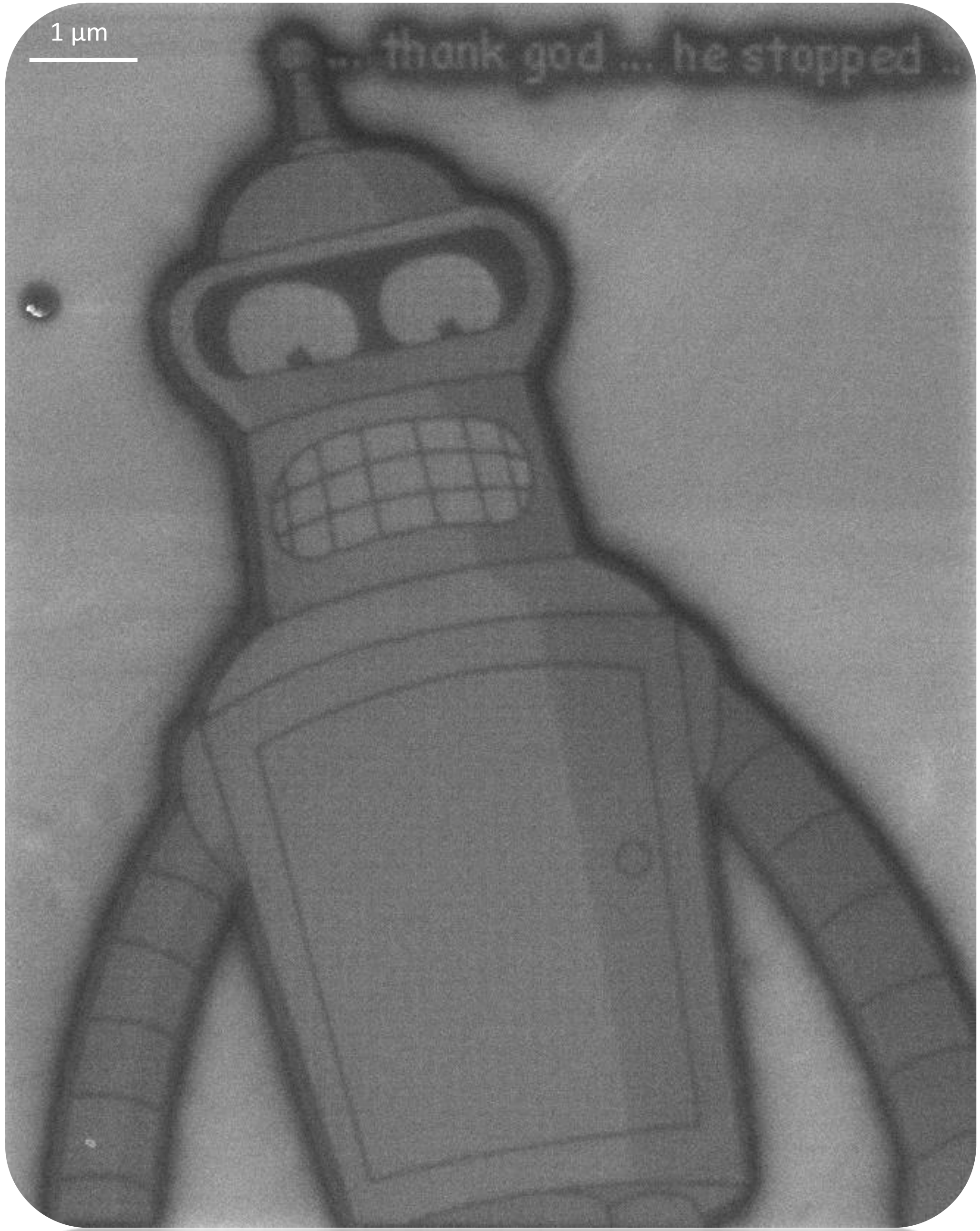
2D Material Modification



YOUR Ideas

Electronic Memristors




1 µm
... thank god ... he stopped ...

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Thank you for your attention!

done by DI Martin Stermitz following a little joke during coffee ☺