

Quantum <mark>Design</mark>

Functional Imprinting: Local Modification of Beam Induced Deposits

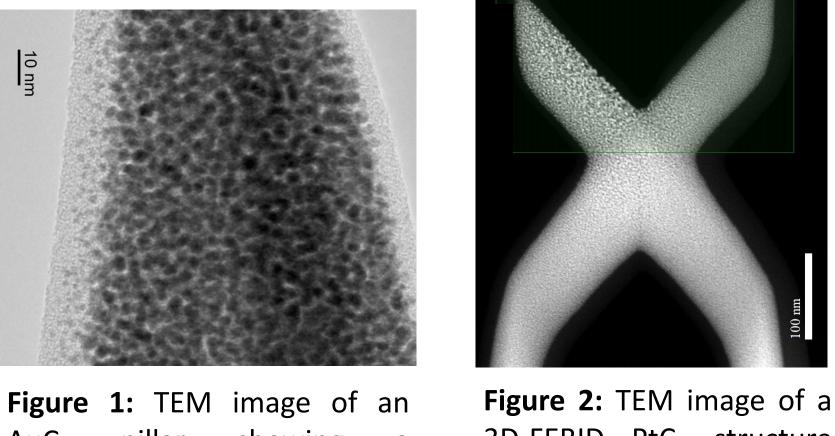
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Introduction

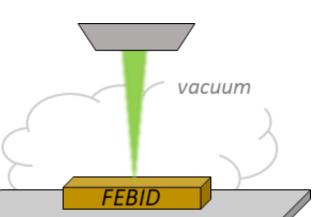
Nanostructures fabricated by Focused Ion/Electron Beam Induced deposition (FIBID/FEBID) can show different functionalities. However, in as-deposited state, typically the materials contain a high the percentage of impurities (mostly carbon, Fig.1), making them unattractive for many applications. However, various *post-processing approaches* allows to tune the material properties^[1].

Here, we focus on post-growth irradiation of the structures with *electrons* under



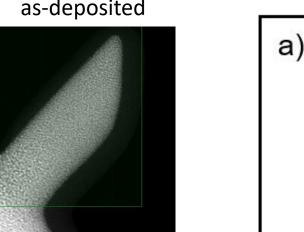
3. Graz Centre for Electron Microscopy, 8010 Graz, Austria

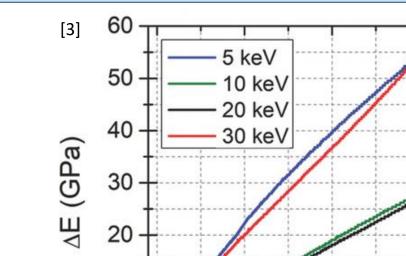
Electron Beam Curing



Electron Beam Curing (EBC) is the irradiation of materials with further electrons. FEBID/FIBID

- Further fragmentation of deposited precursor molecules
- Grain growth (Fig. 2, 3)
- Modification of the carbon matrix (Fig. 4)





- Vacuum condition (Electron Beam Curing)
- Low-vacuum water atmosphere (Purification)

We demonstrate the *local application* of those approaches, denoted as "Functional Imprinting"

pillar showing a AuC_x nanogranular composition

3D-FEBID PtC_x structure with one branch EBC.

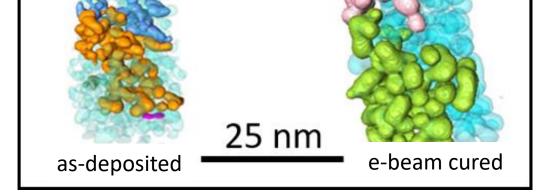
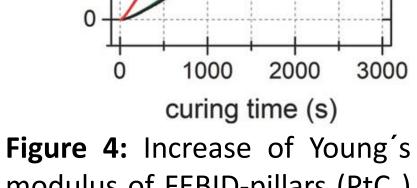


Figure 3: TEM Tomography of a as-

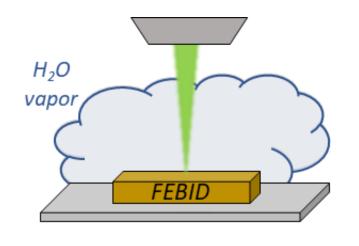
deposited and cured PtC_x pillar

revealing growth of the metal grains.

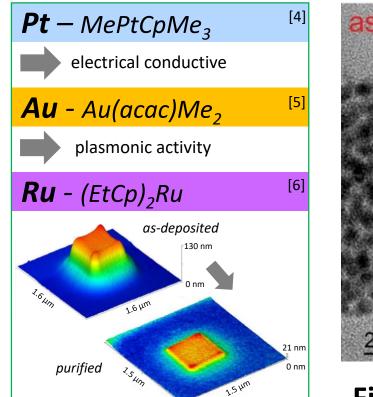


modulus of FEBID-pillars (PtC_x) with curing dose.

Purification in Water Atmosphere



H₂O purification is the irradiation of FEBID/FIBID materials lowin vacuum water vapor with further electrons.



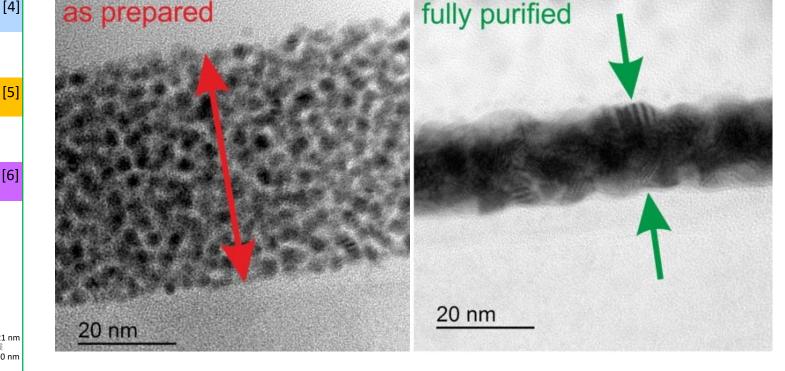


Figure 6: Comparison of PtC_x microstructure in the as-prepared state and after fully purification shows a Figure 5: Precursors for which H₂O purification densification and large, closely packed platinum grains after the treatment.^[4] is successfully shown.

- Carbon is efficiently removed (CH₄, CO)
- The deposit shrinks in height, while the shape is widely maintained
- (Poly)-crystalline, carbon-free material
- Pore/crack free
- Room temperature procedure

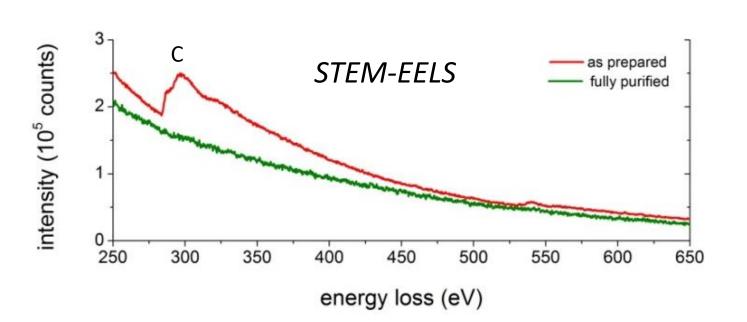
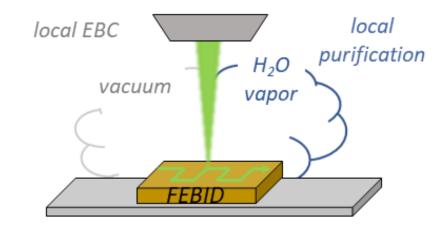


Figure 7: STEM-based Electron Energy Loss

Functional Imprinting



Functional imprinting the İS modification local of FEBID/FIBID materials by either E- Beam curing, or purification in water atmosphere.

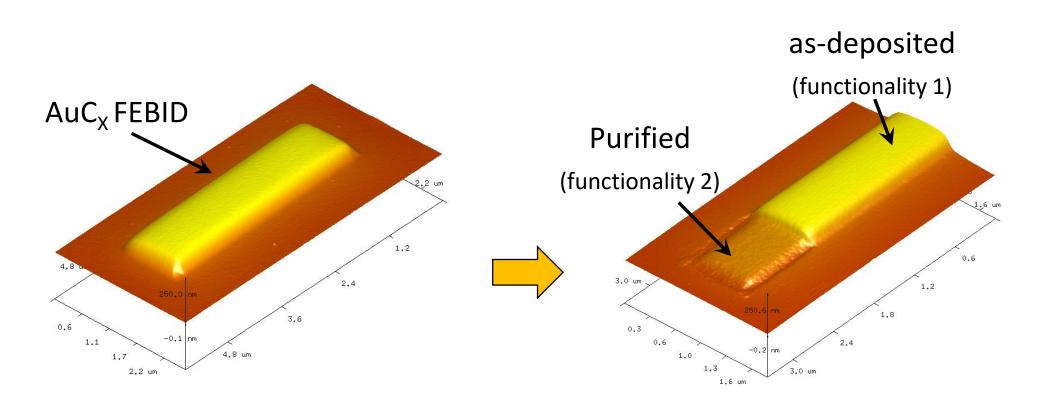
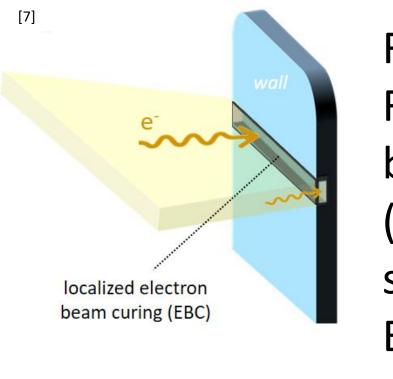


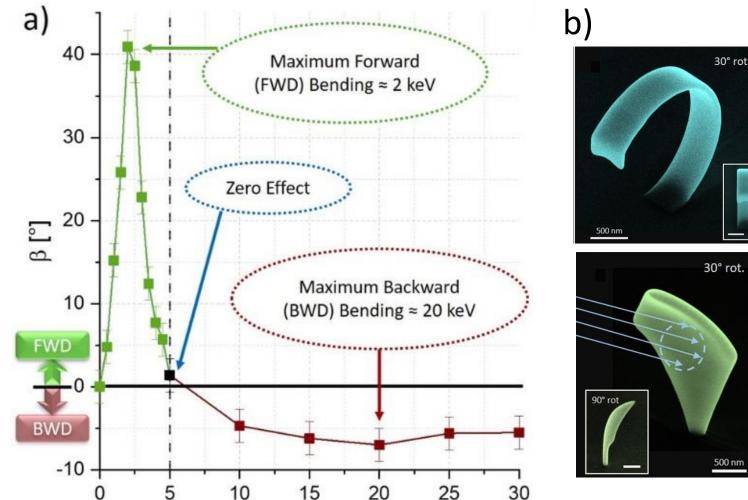
Figure 8: AFM image showing that the as-deposited material is used as scaffold to imprint areas of different functionality (pure gold areas).

Spectroscopy confirms the removal of carbon.^[4]

Functional Imprinting – **Electron Beam Curing**



Freestanding PtC_x FEBID walls have deposited been (5 keV/40 pA) and subjected to local E-Beam Curing.



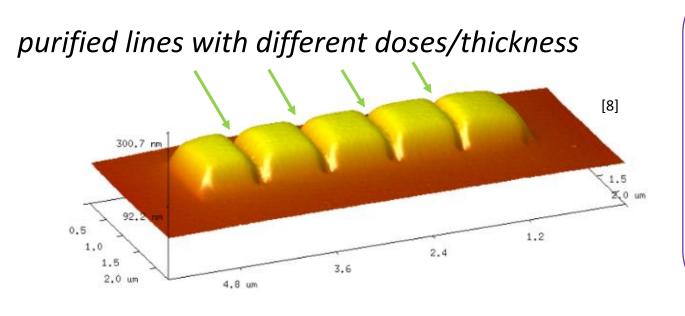


Figure 10: AFM image of an AuC_x rectangle that has been deposited and purified at the indicated locations using different thickesses and electron doses. The significant volume loss is clearly visible.^[8]

To answer questions about

(1) crystallinity and grain sizes

(2) *chemistry* and carbon contents

(3) possible *resolution* of the imprint

a TEM lamella was prepared from the cross-setion.

Crystallinity • Highly crystalline in purified areas

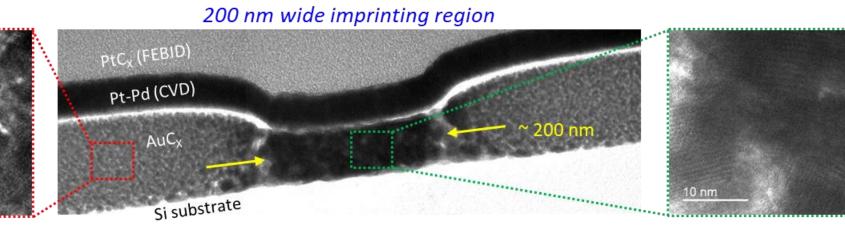
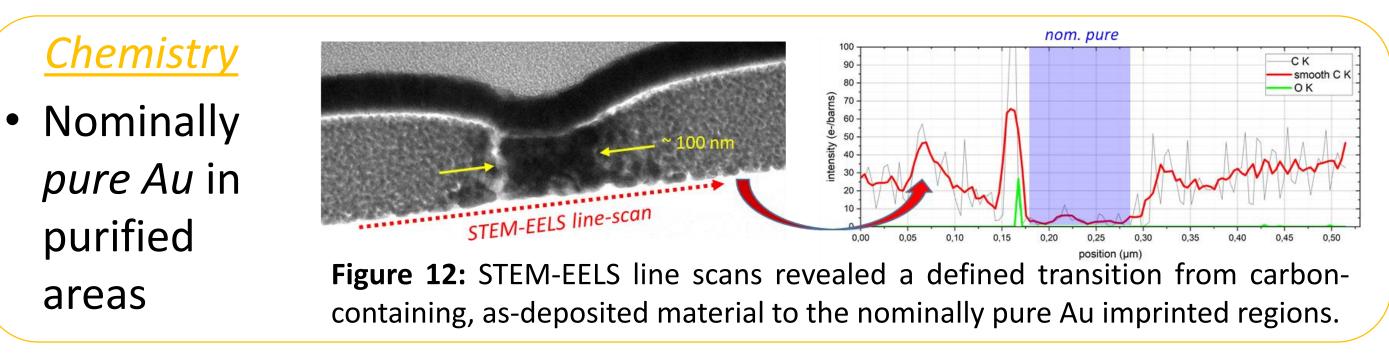


Figure 11: HR-TEM grain characterization revealed highly crystalline material at the 200 nm wide imprinted (purified) region.



Resolution

- Trapezoidal shape • Line width of 35 nm (FWHM)

single line with beam diameter ~ 25 nm (FWHM) @ 1 nA

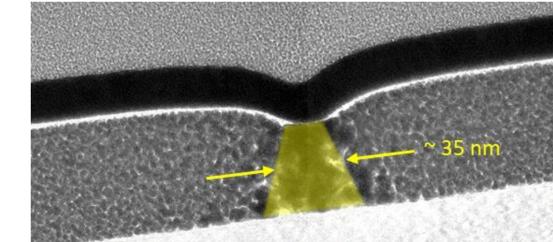


Figure 13: TEM image of single-line purification. The shape of the purified areas corresponds to the beam interaction volume.

Functional Imprinting – Local Purification

E₀ [keV]

Figure 9: (a) Electron beam curing leads to a bending of the wall at the area of exposure. While for low energies the wall is bending towards the incoming beam, for electron beam energies larger than 5 keV, a backward bending is observed. (b) Examples of controlled bending of closed FEBID structures, which can not be fabricated directly by FEBID/FIBID.^[7]

References

[1] Barth et al., *J. Mater. Chem. C* 8 (2020) [2] Trummer et al., ACS Appl. Nano Mater. 2 (2019) [3] Arnold et al., Adv. Funct. Mater. 28 (2018) [4] Geier et al., J. Phys. Chem. C 118 (2014) [5] Winkler et al., ACS AMI 9 (2017) [6] Rohdenburg et al., ACS Appl. Nano Mater. 3 (2020) [7] Weitzer et al., Nanomaterials 12 (2022) [8] Loibner et al., in preparation (2023)

Conclusion

Functional Imprinting is the localized modification by electron beam irradiation of deposits fabricated via Focused Electron/Ion Beam Induced Deposition. For changing the local functionality a focused electron beam was used either under vacuum conditions (Electron Beam Curing) or under low-vacuum water atmosphere (Purification). Both approaches were presented and then locally applied on FEBID deposits. The local Electron Beam Curing leads to an energy-dependent bending effect of freestanding walls. Local Purification revealed crystalline and nominally pure Au areas with a line width below 40 nm.



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