Recent Advances in Liquid-Phase Electron-Beam-Induced Processing (LP-EBIP)

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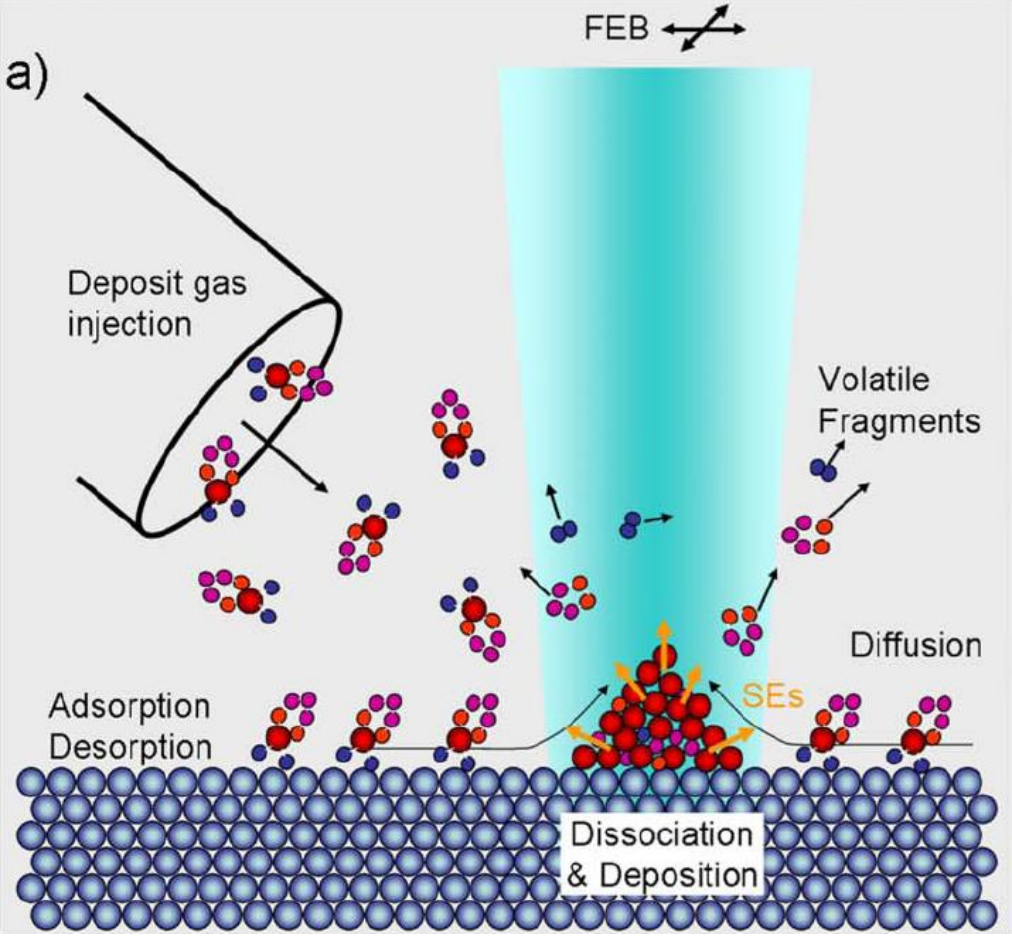
Traditional EBID → Electron-Beam-Induced Deposition using gaseous precursors

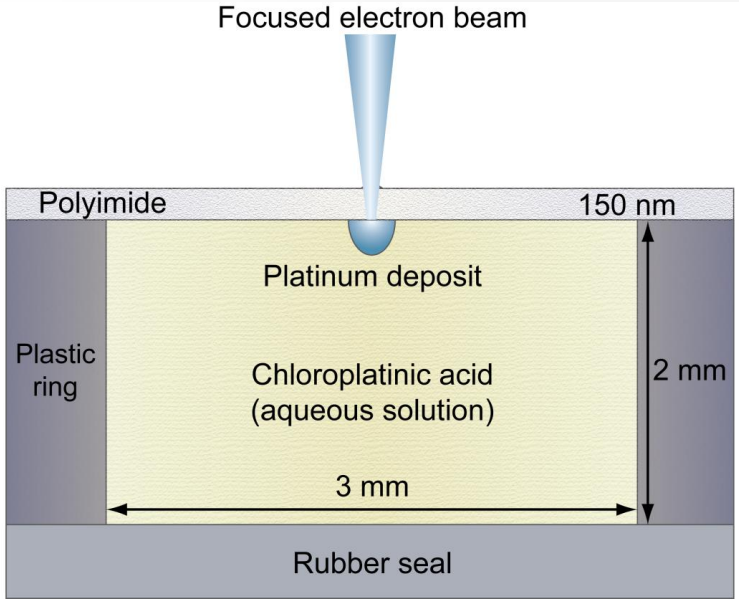
- Benefits:
  - direct patterning → no pre-/post-processing required
  - works on flat and topographical surfaces
  - fast → results ready for inspection immediately

- Drawbacks of gas-phase EBID:
  - charging of non-conducting surfaces
  - costly, hazardous gases
  - low purity of deposits: typically ~20% metal, ~80% carbon and/or other elements

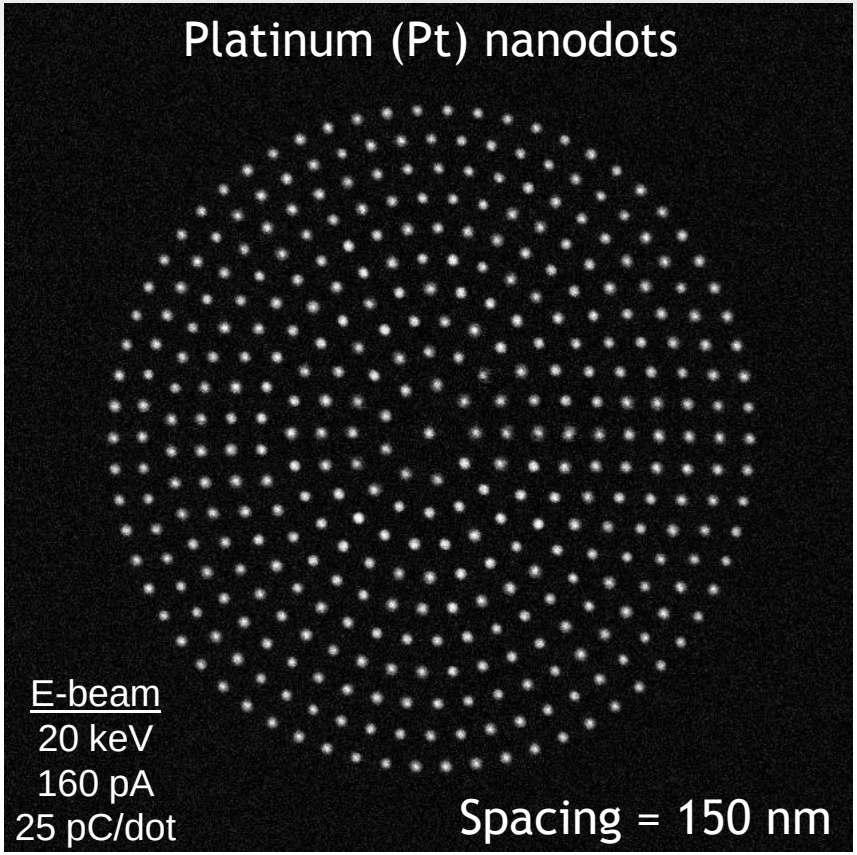


I. Utke *et al.*, *J. Vac. Sci. Technol. B* **26**, 1197 (2008)

LP-EBID → Novel approach using bulk liquid-phase precursors



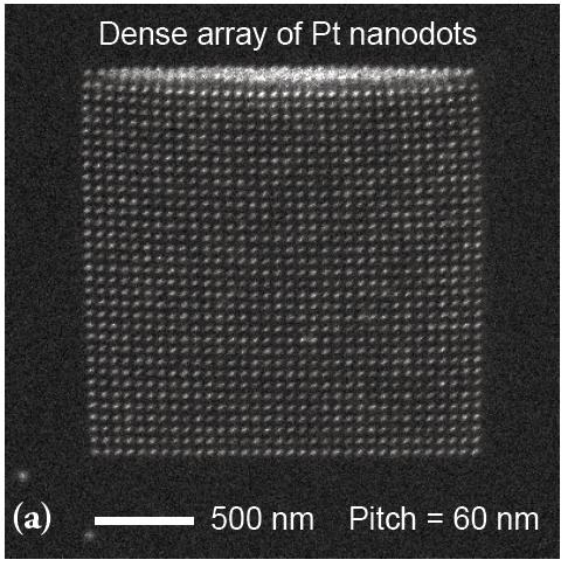
E-beam lithography system: Raith e_LiNE
Processing capsule: QuantomiX WETSEM
Precursor: Aqueous solution of H_2PtCl_6 (20 mM)

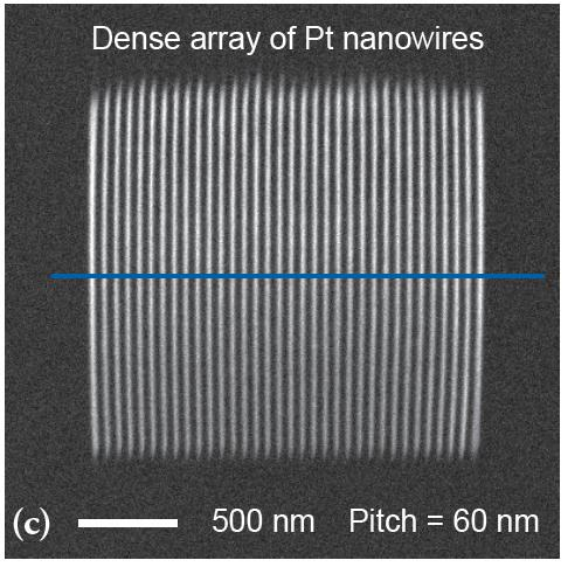


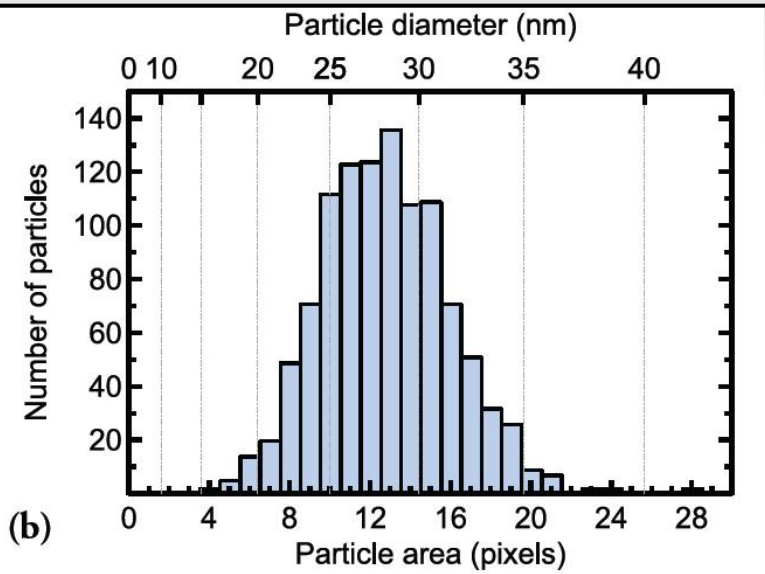
- First demonstration of LP-EBID → Donev & Hastings, *Nano Lett.* (2009)
- High resolution and pattern fidelity → 25-nm lines/dots at 60-nm pitch
- High purity of deposits → 70-95 at.% gold or platinum

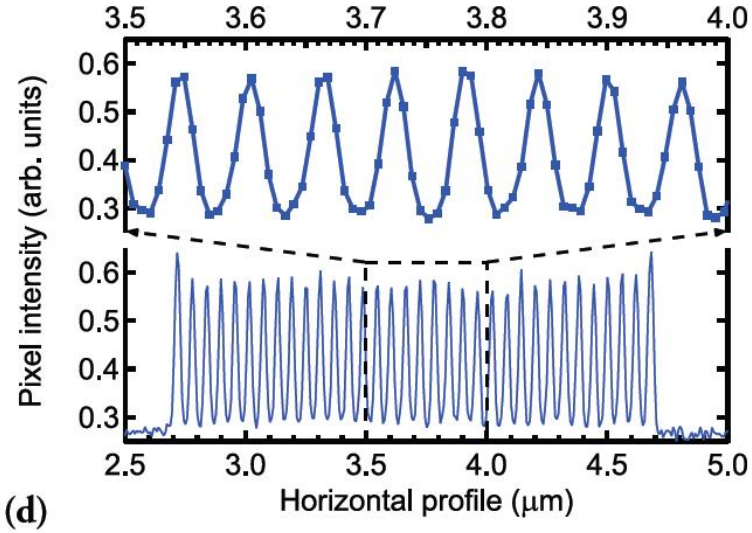
LP-EBID → High-resolution nanopatterning

E-beam
20 keV
160 pA
(a) 8 pC/dot
(c) 240 pC/line



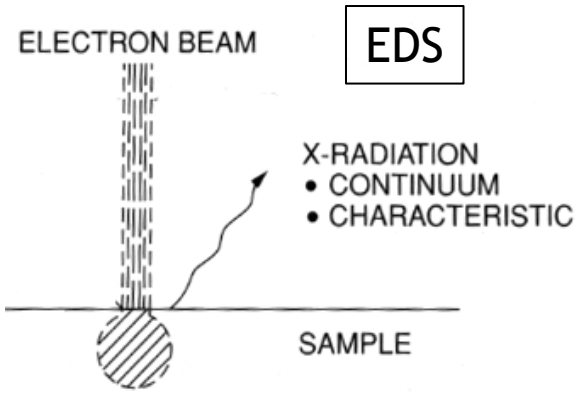




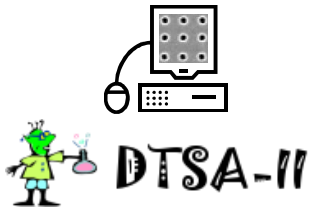


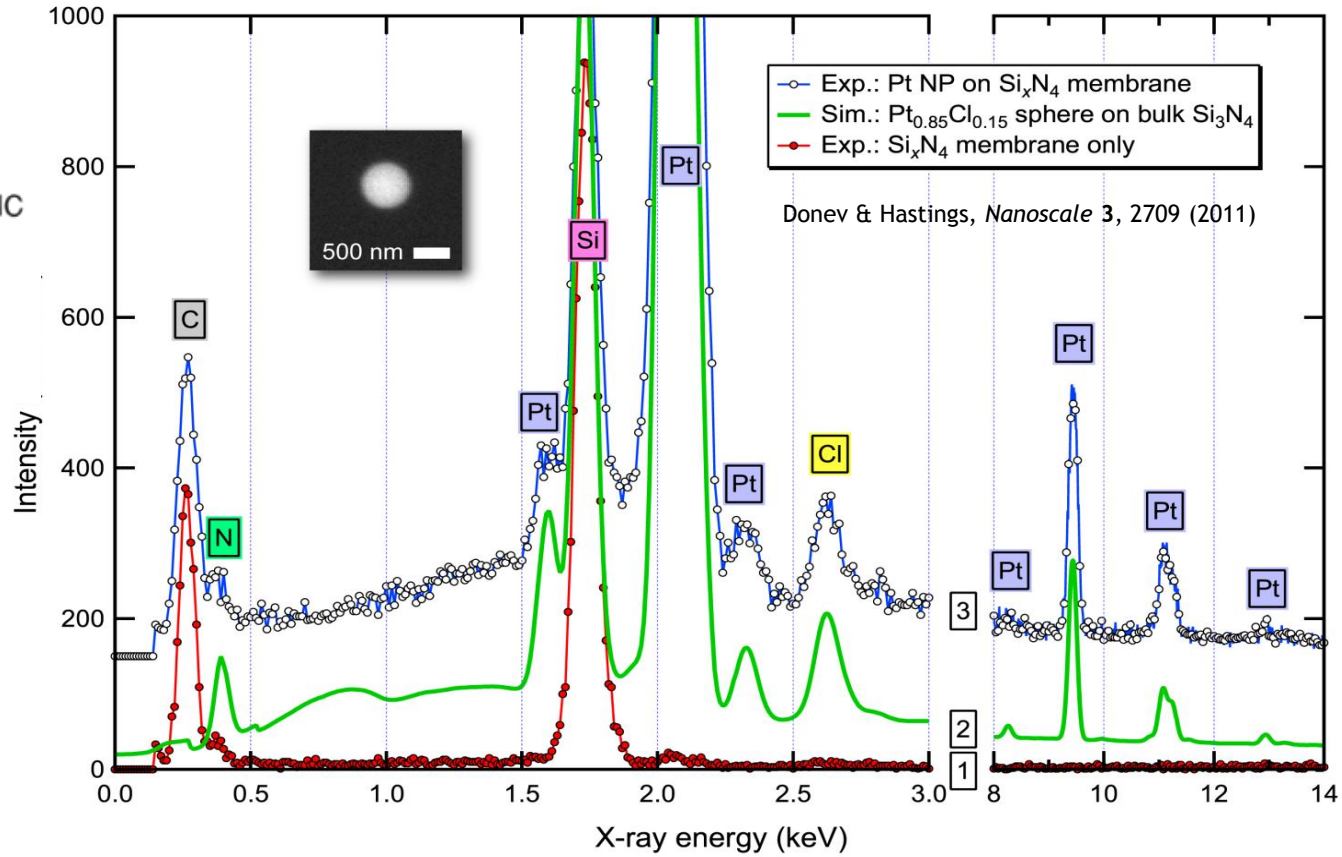
Donev & Hastings, *Nanotechnology* **20**, 505302 (2009)

LP-EBID → High purity of deposits



EDS



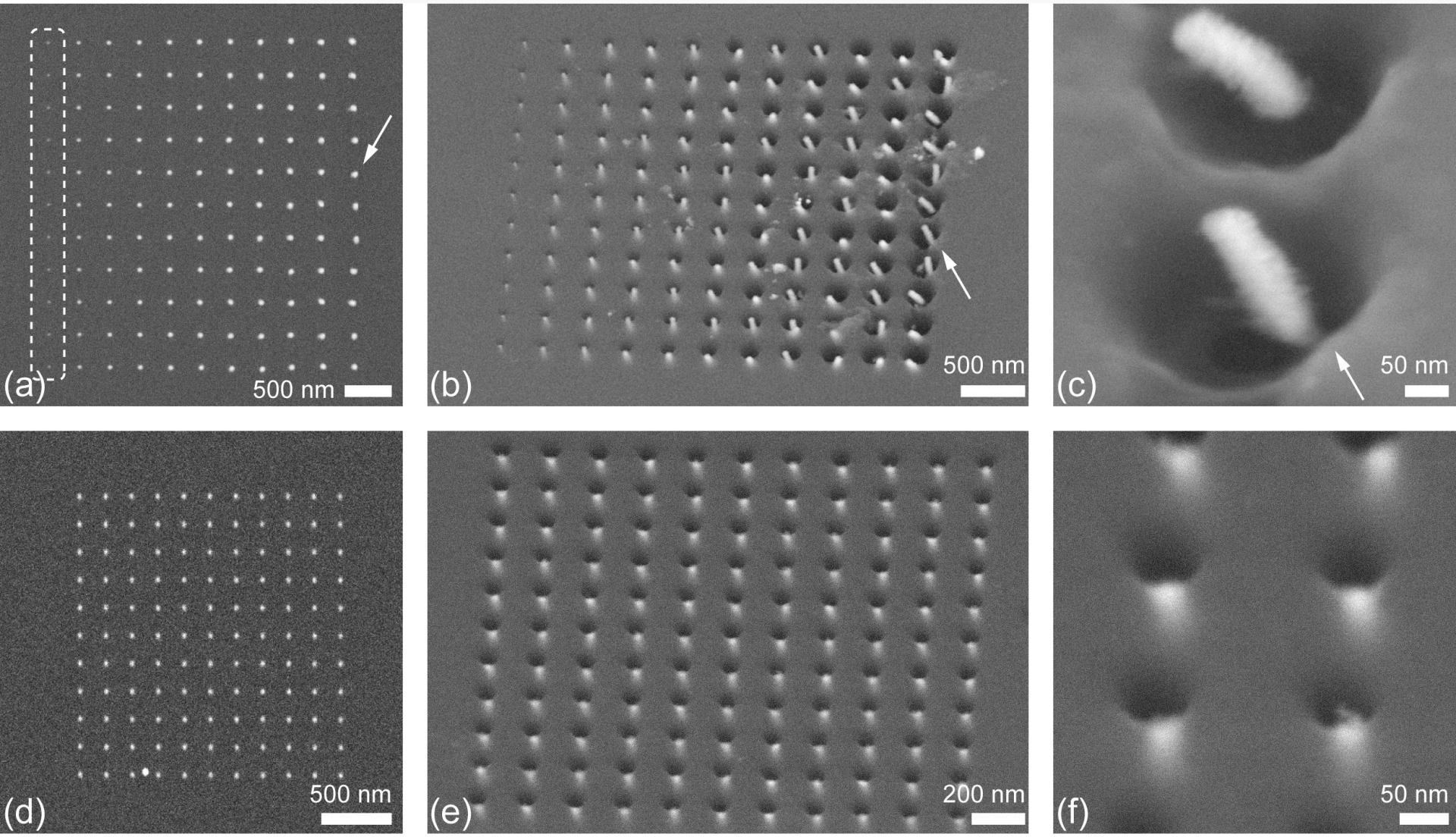


- Composition → energy-dispersive X-ray spectroscopy (EDS) + Monte Carlo simulations (NIST's DTSA-II software) → comparing Pt and Cl peak intensities
- LP-EBID → 85-95 at.% Pt (as deposited)
- Gas-phase EBID → 10-35 at.% Pt (as deposited)

LP-EBID of Pt on polyimide membrane

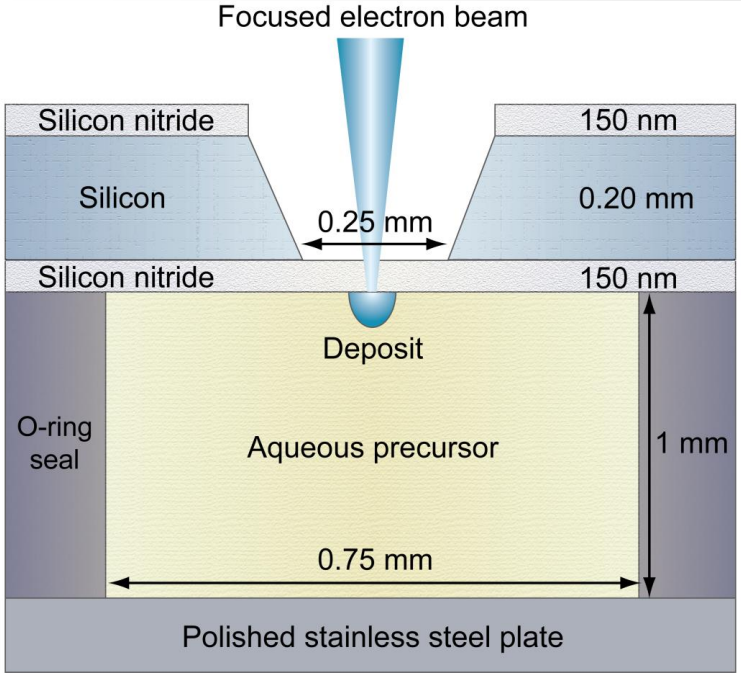
In-situ (liquid in) SEMs

Ex-situ (liquid out), tilted-view SEMs



Donev & Hastings, *Nanoscale* **3**, 2709 (2011)

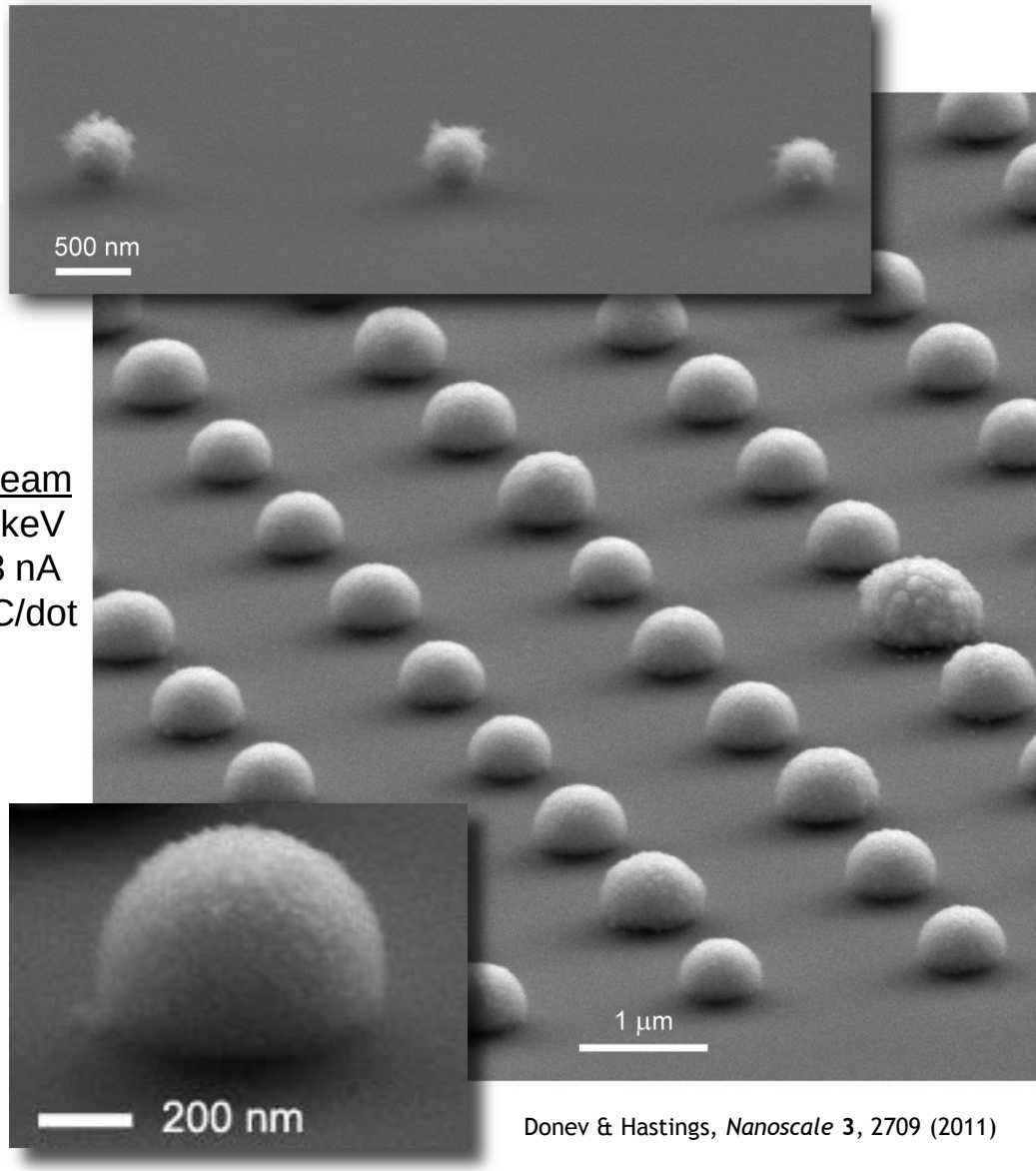
LP-EBID of Pt on silicon nitride membrane



E-beam lithography system: Raith e_LiNE
Processing capsule: homemade (type 1)
Precursor: H_2PtCl_6(aq)

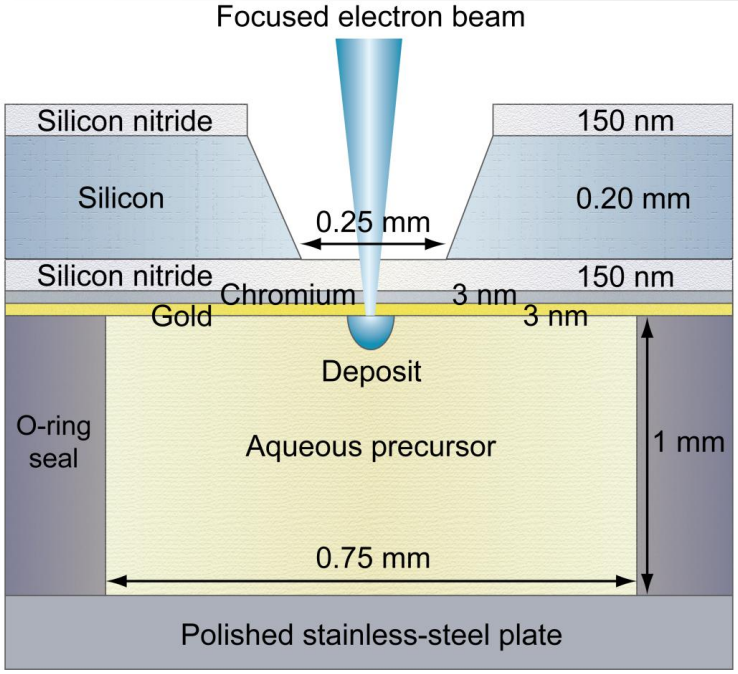
- Bare (uncoated) Si_3N_4 membrane
- Threshold dose 300 times larger than on polyimide membrane
- Morphology → (hemi)spherical *vs* rod-shaped on polyimide membrane

<u>E-beam</u>
20 keV
1.3 nA
5 nC/dot



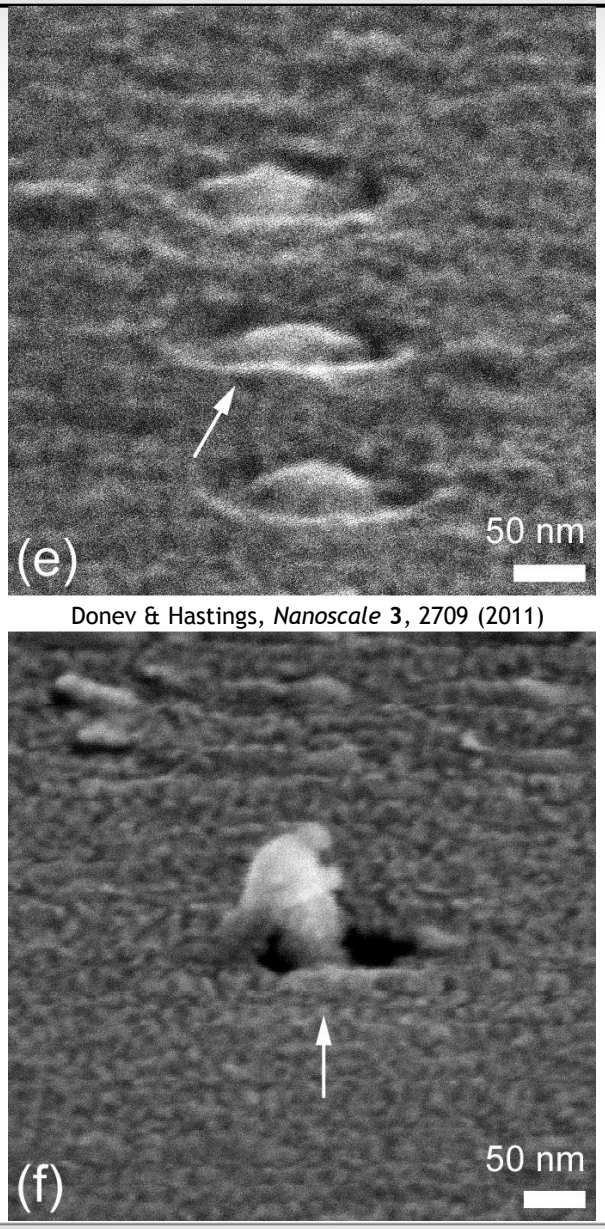
Donev & Hastings, *Nanoscale* **3**, 2709 (2011)

LP-EBID of Pt on modified silicon nitride membrane



E-beam lithography system: Raith e_LiNE
Processing capsule: homemade (type 2)
Precursor: H_2PtCl_6(aq)

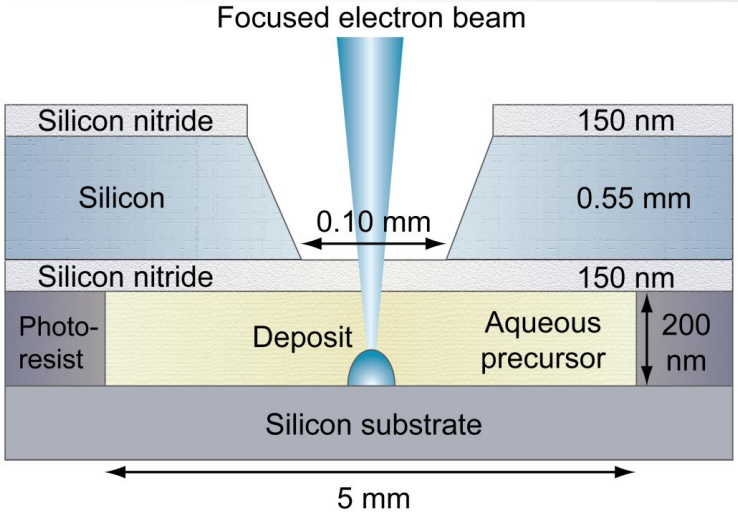
- Si_3N_4 membrane coated with Cr and Au
- Threshold dose 5 times larger than on bare Si_3N_4
- Morphology → from "bumps" to "pillars"



Donev & Hastings, *Nanoscale* **3**, 2709 (2011)

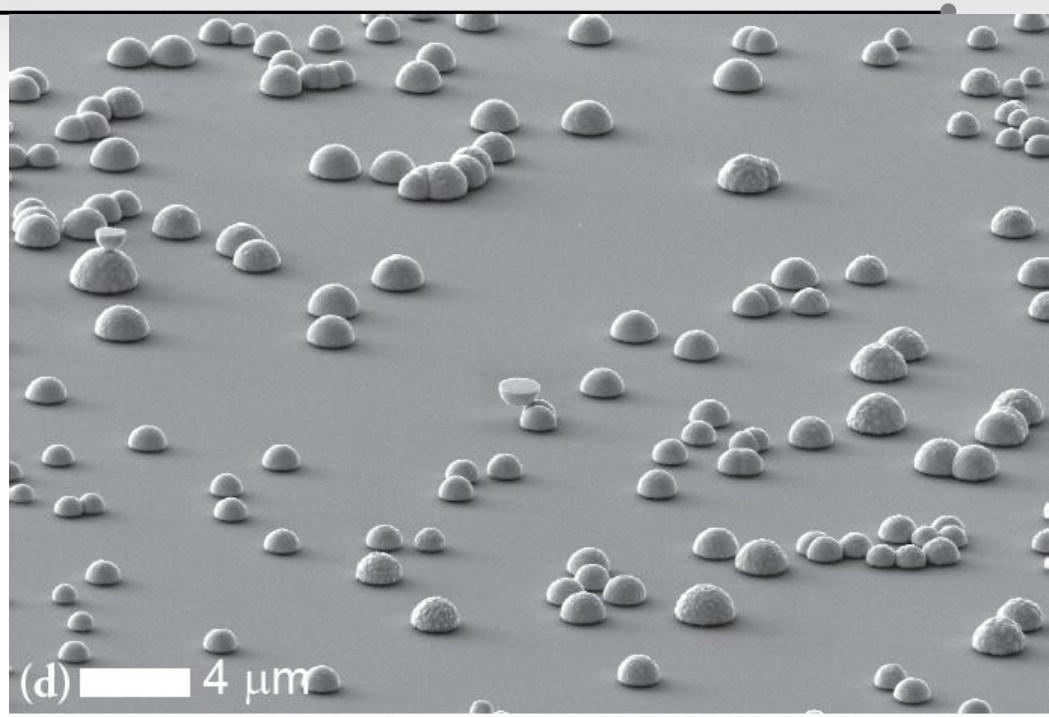
E-beam
20 keV
1.3 nA
(e) 20 nC/dot
(f) 50 nC/dot

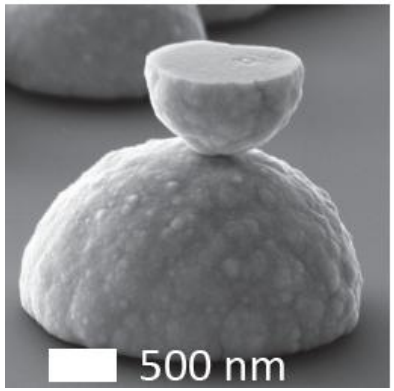
LP-EBID of Pt on separate substrate

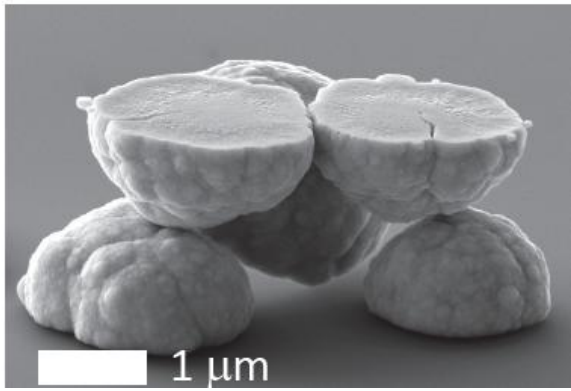


E-beam lithography system: Raith e_LiNE
Processing capsule: homemade (type 3)
Precursor: H_2PtCl_6(aq)

- Silicon (Si) substrate below Si_3N_4 membrane
- Threshold dose and morphology similar to those for bare Si_3N_4
- Patterns not deterministic… yet

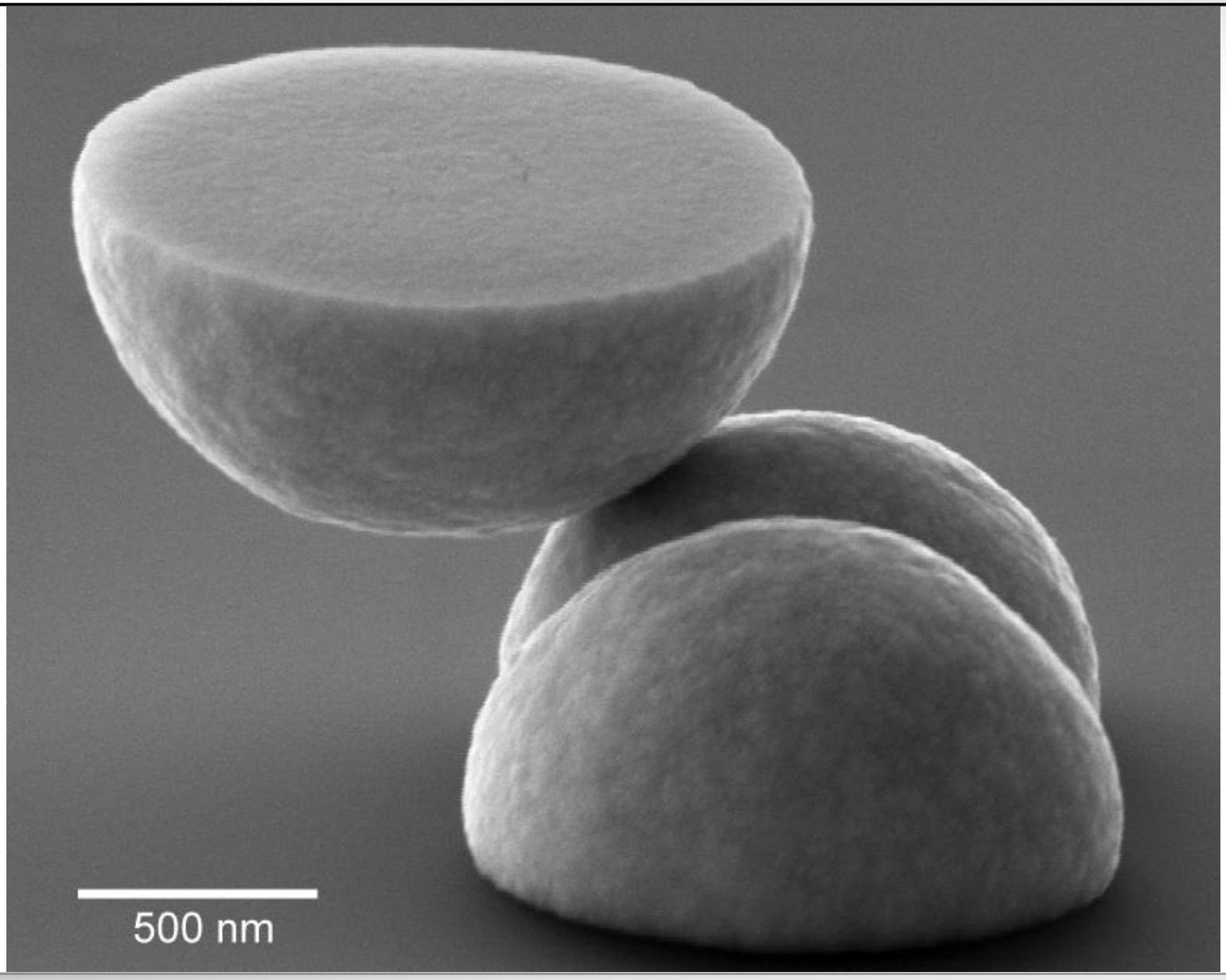






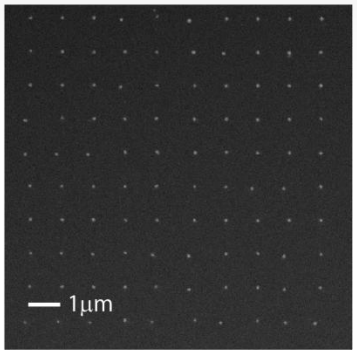
E-beam: 20 keV, 1.7 nA, ~10 nC/dot

LP-EBID of Pt on Si substrate

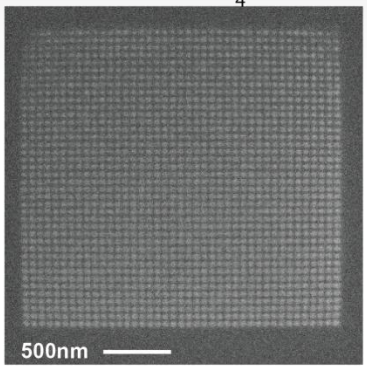


LP-EBID → Materials deposited so far

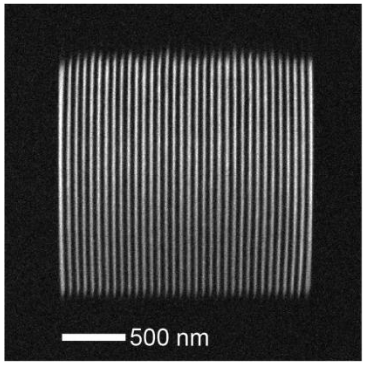
Ag from $AgNO_3$



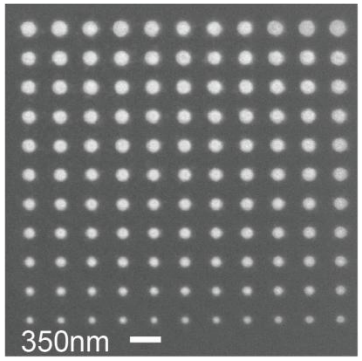
Ni from $NiSO_4$

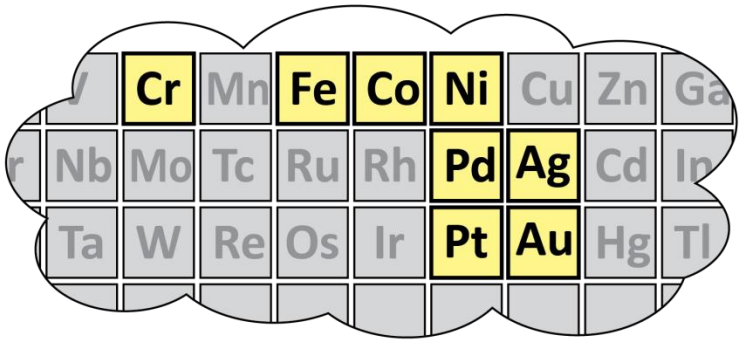


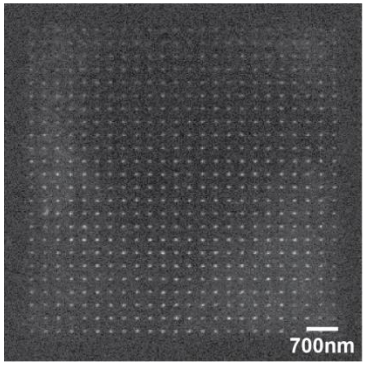
Pt from H_2PtCl_6



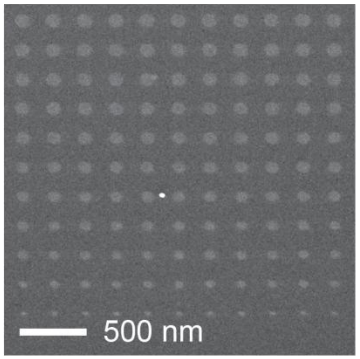
AuPt from $HAuCl_4$ and H_2PtCl_6



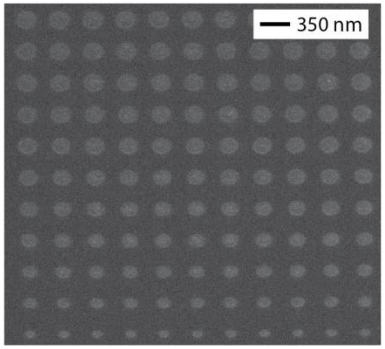




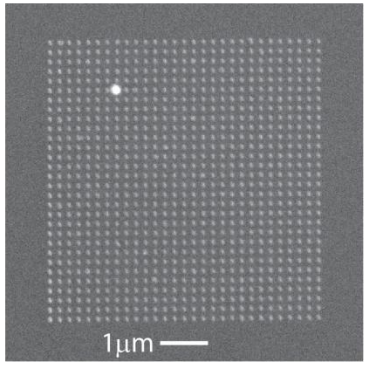
Au from $[AuCl4]^-$ or $[Au(SO_3)]^{3-}$



Co from $CoCl_2$

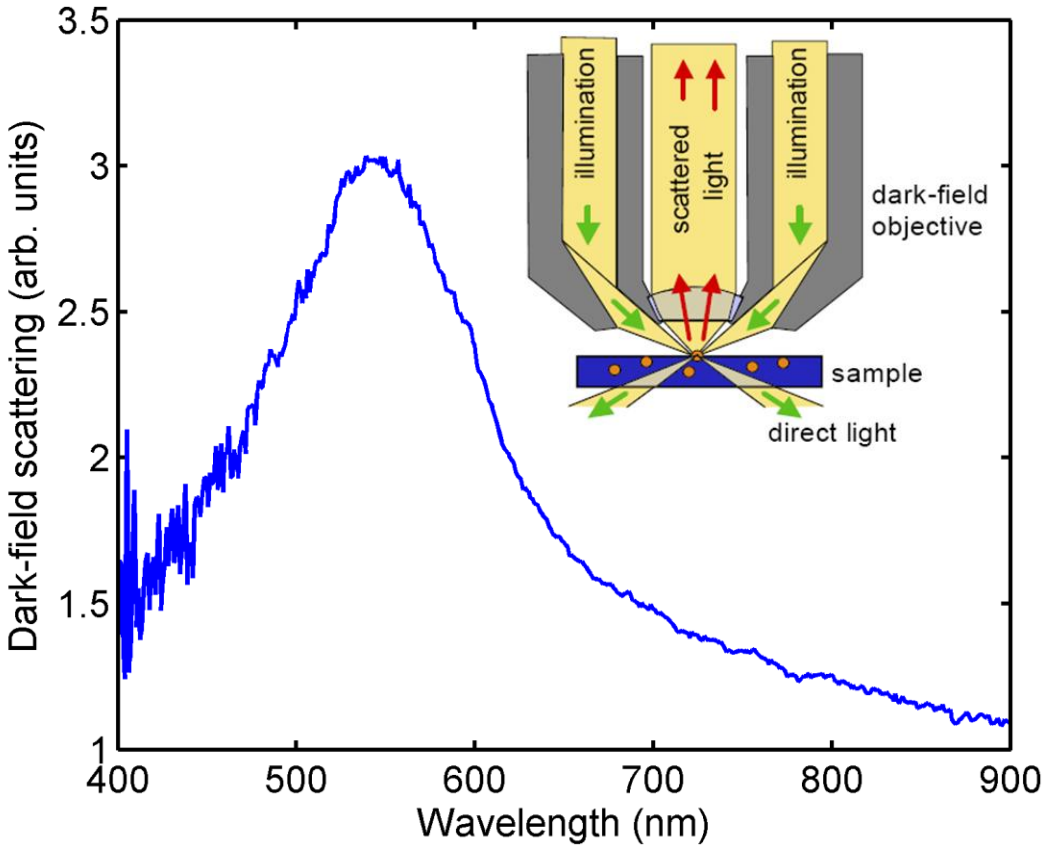


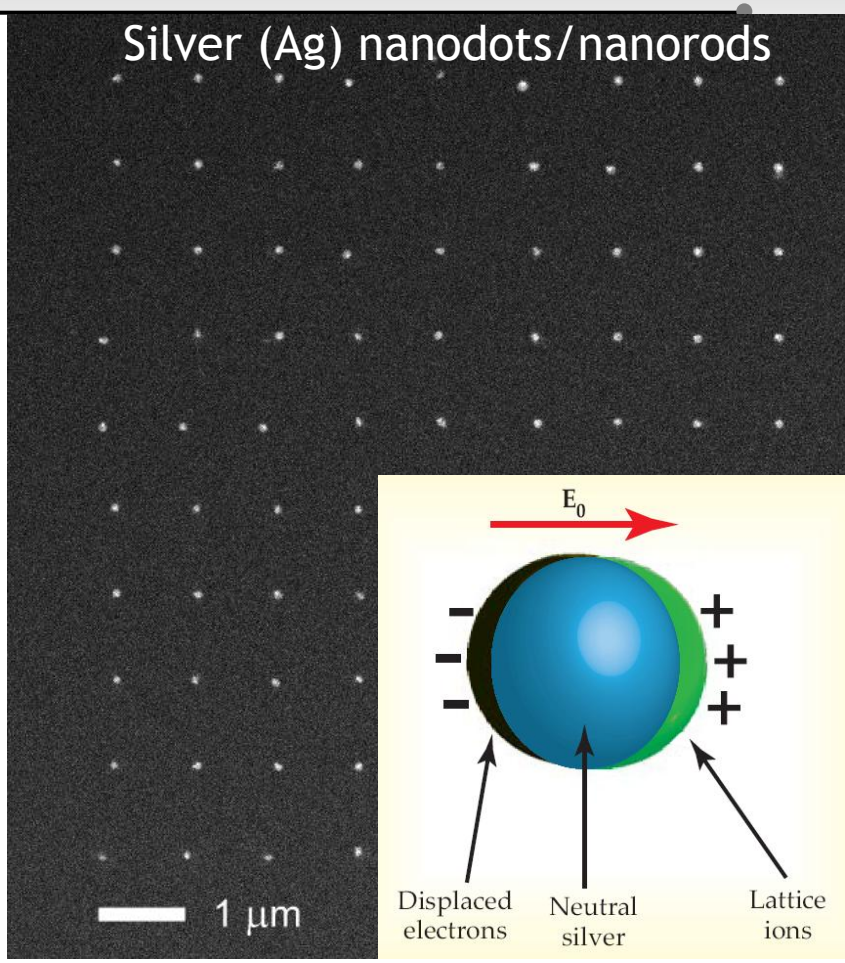
Pd from $NaPdCl_4$



Cr from $Cr_2(SO_3)_2$ and $CrCl_3$

LP-EBID of plasmonic nanostructures

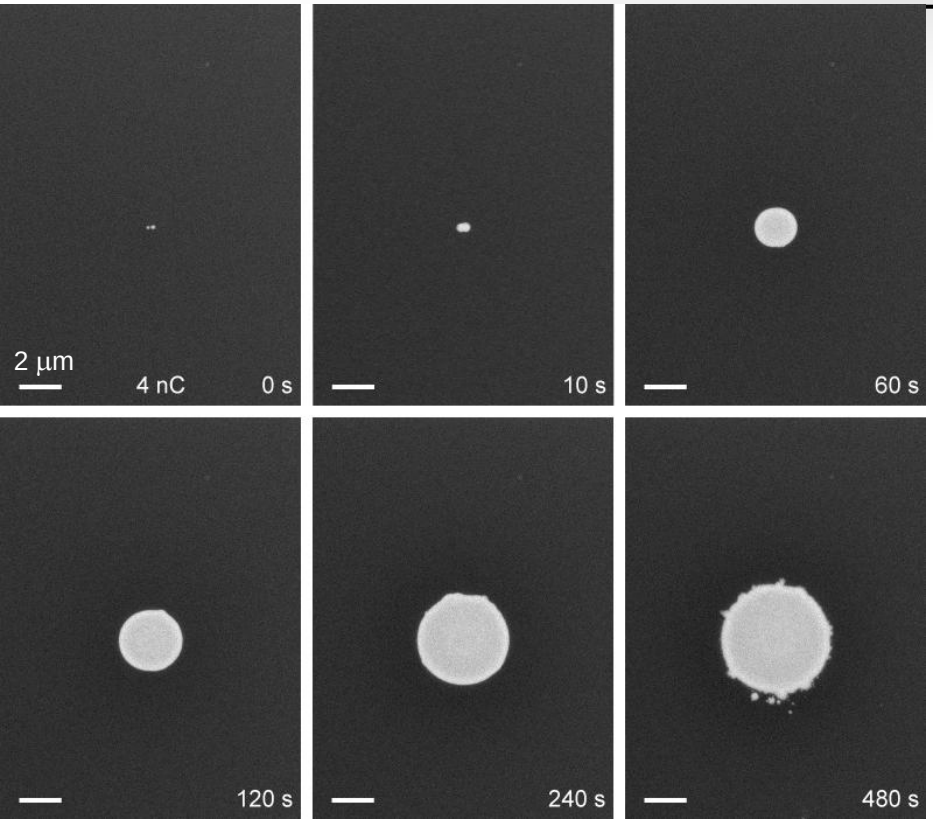


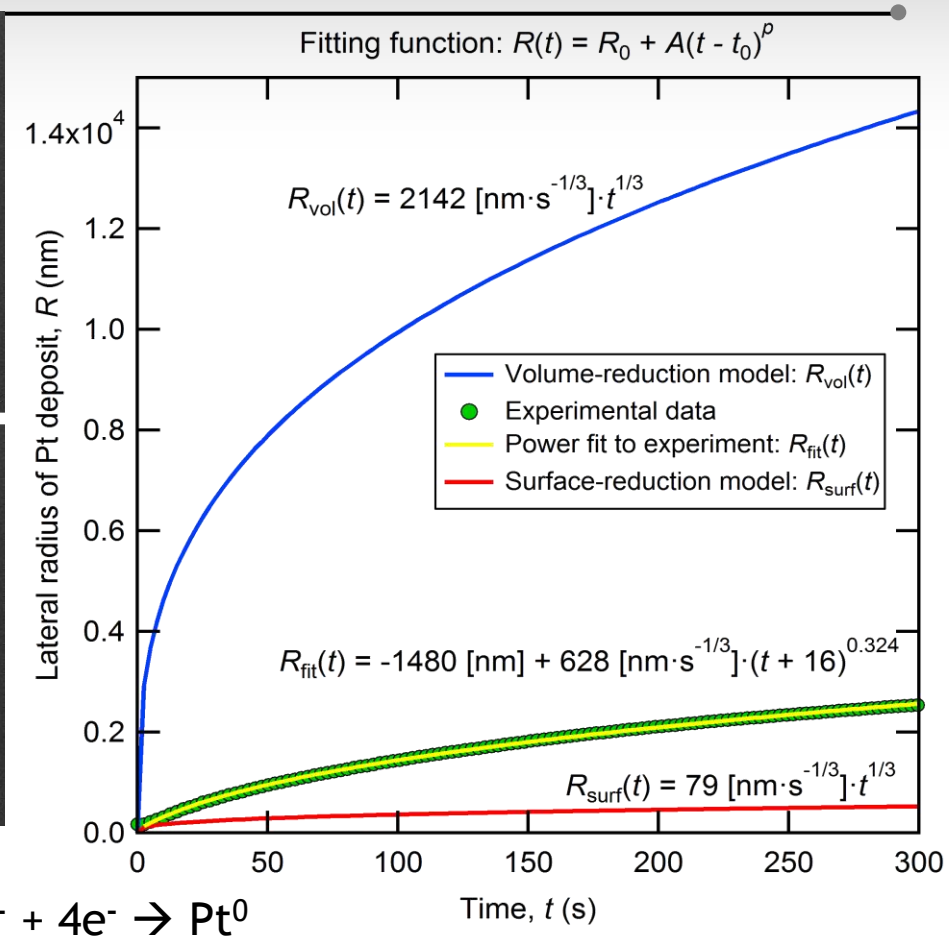


- Optical response → surface-plasmon resonance (SPR) → evidence of high-quality, functional deposits
- Potential applications in SPR biosensing and surface-enhanced Raman spectroscopy (SERS)

E-beam
20 keV
160 pA
150 pC/dot

LP-EBID of Pt on S_3N_4 membrane → Growth dynamics

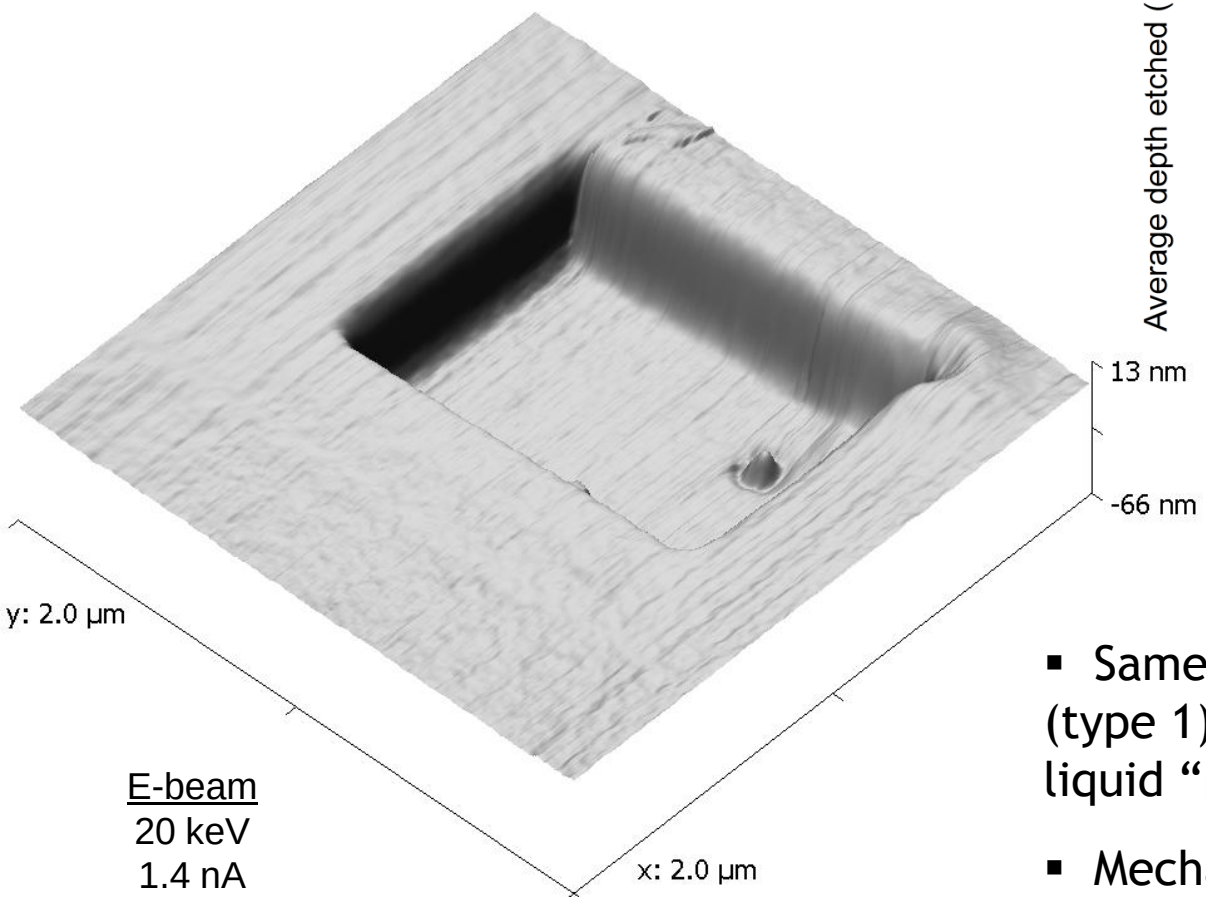




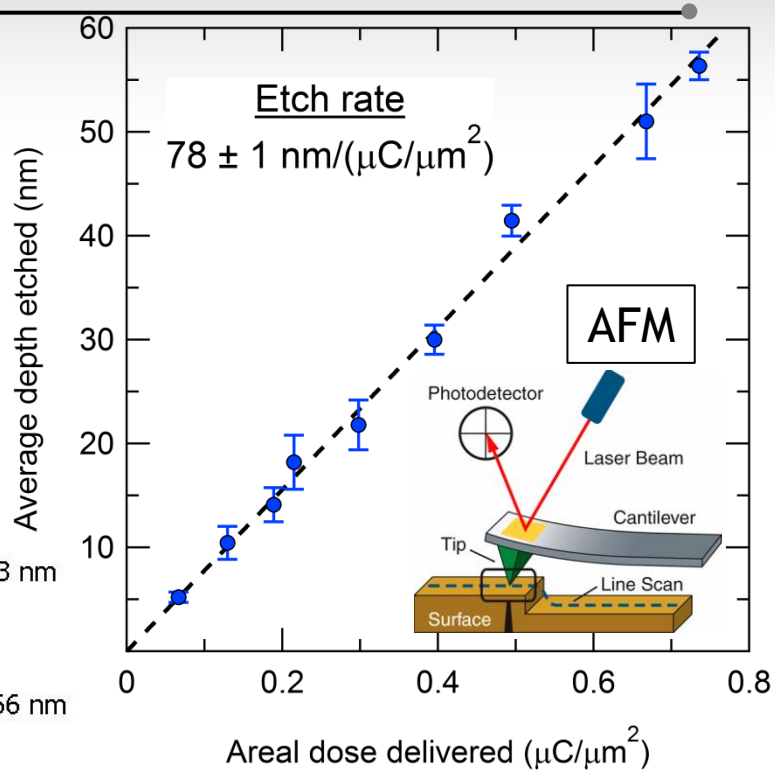
- Simplified reduction mechanism: $[PtCl_6]^{2-} + 4e^- \rightarrow Pt^0$
- "Zero-order" models → reduction assumed to occur only in solution volume ($R_{vol}(t)$) or on depost's surface ($R_{surf}(t)$); diffusion, dissociation efficiency, competitive reactions, multiple reduction steps, etc. → all neglected… for now

E-beam
20 keV
1.3 nA
4 nC/seed-dot
2.5 sec/scan

LP-EBIE → Etching of silicon nitride



E-beam
20 keV
1.4 nA
2.5 sec/scan
240 scans



- Same bare-Si_3N_4 cell configuration (type 1) but with 1 wt% KOH(aq) as liquid "precursor"/etchant
- Mechanism(s) not clear yet → KOH necessary or H_2O radicals do (most of) the etching?

Acknowledgements

LP-EBIP, SEM, AFM

EDS

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