Electrochemical Fabrication of Nanostructures and Their Fragments

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Original results used in this overview were obtained in collaboration with Dr Kirill Napolskii and his group
https://www.eng.fnm.msu.ru/en/

Outline

Electrochemical *vs* chemical fabrication techniques: higher complexity, but better controllability

Electrodeposition of low-dimensional fragments/materials for nm-and μm-scale devices

- „underpotential“ deposition: electrochemical ALD

- templated electrodeposition

Template-less localized processes

- local electrodeposition

- local electrochemical etching (dissolution)

Anodization (oxide formation)

Control and monitoring tools

Important advantage: room temperature

Current, charge ↑

REDUCTION: $M^{n+} + n\ e \rightarrow M$

"underpotential" deposition (UPD)

Current, charge ↑

OXIDATION: $M - n\ e \rightarrow M^{n+}$ **or** $M - n\ e + xH_2O \rightarrow$ oxide(s), hydroxide(s)

Potential (free energy)

Equilibrium potential for M^{n+}/M redox couple

Known from EMF measurements

Principle limitation: only conducting supports

Limitation for 'dry' devices: residual solvent

Potential regulates reaction rates (current)

Charge allows to monitor the amount of products

Current-time dependence is specific for morphology evolution
<but its interpretation requires certain models>

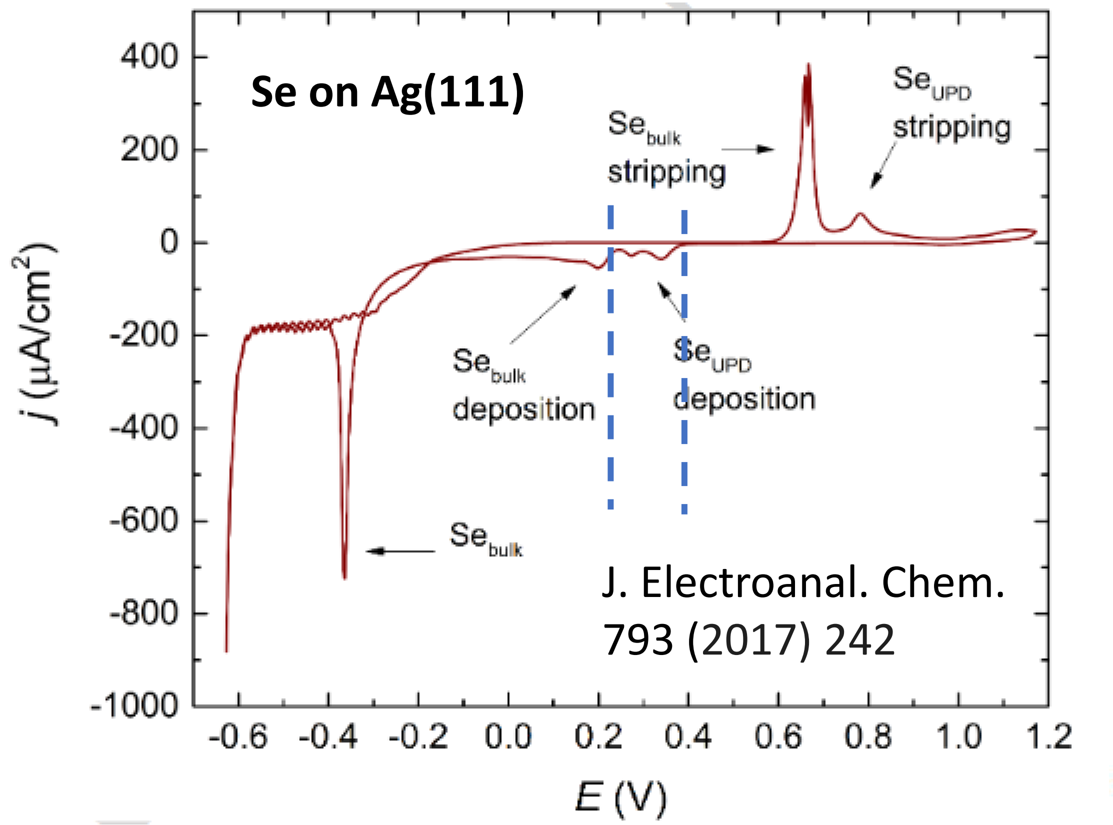
Galvanics (electroplating, galvanoplastics)

Electropolishing, anodizing (color, protective), dimensional processing

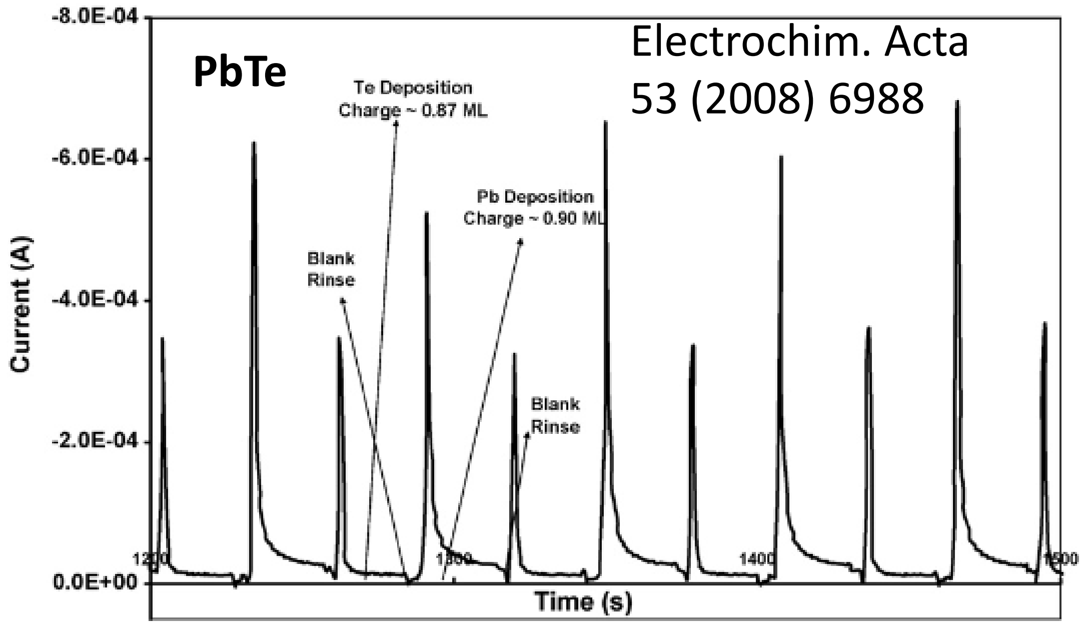
Traditional surface finishing

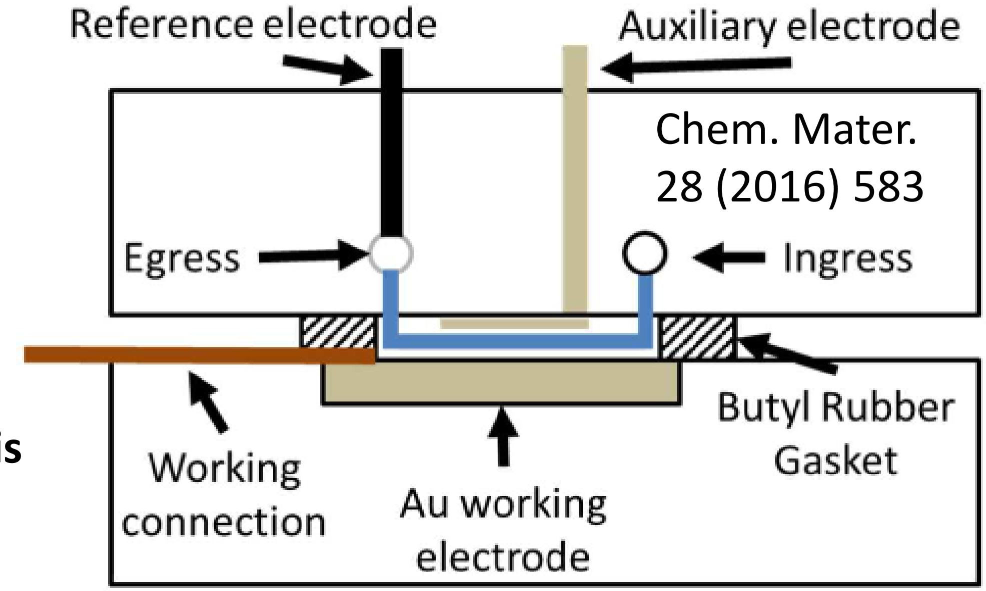
Surface-limited deposition (electrochemical ALD): "underpotential" formation of monolayers

J.L. Stickney, Electrochemical atomic layer epitaxy (EC-ALE): Nanoscale control in the electrodeposition of compound semiconductors, in Adv. Electrochem. Sci. Eng. 2002, v.7.



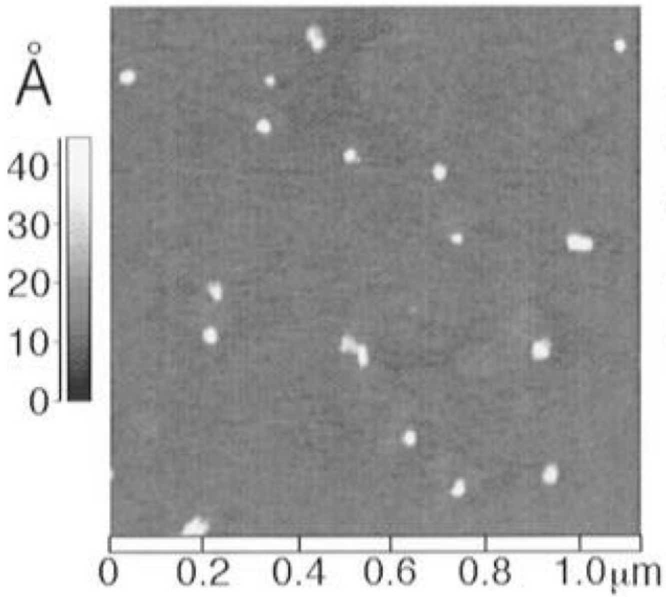
Charge for formation of adatoms monolayer is ~ 200 – 400 $\mu C/cm^2$

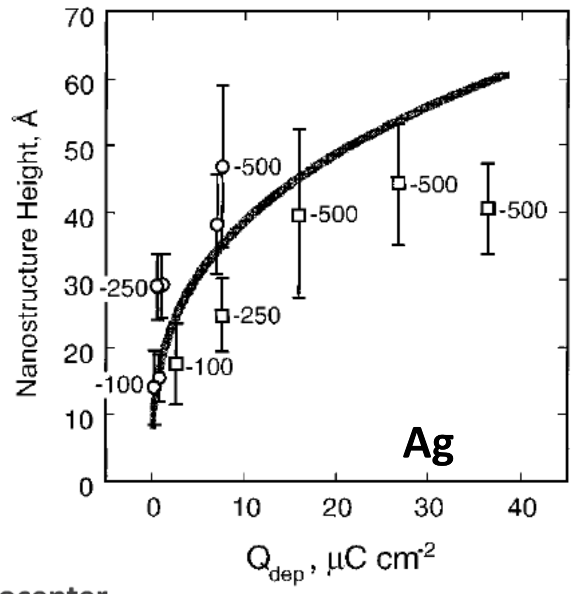


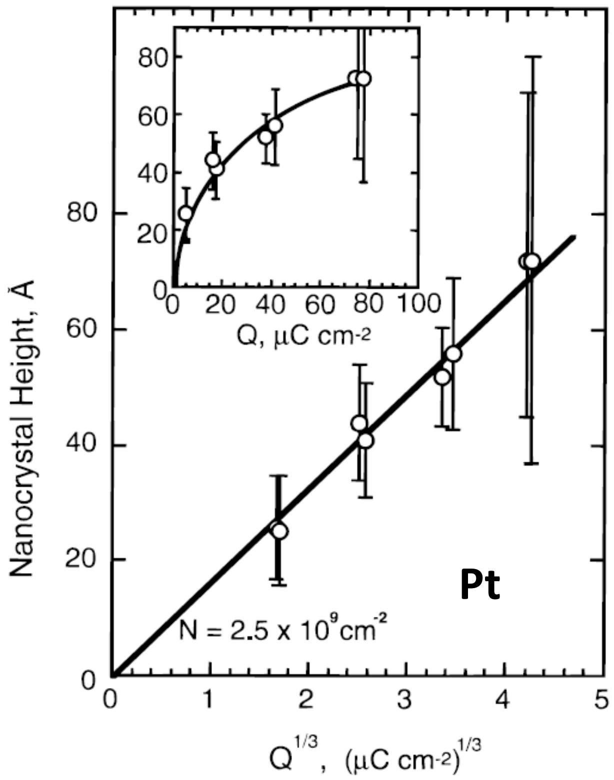


Flow cell for multilayer deposition (solutions of two reagents are introduced alternatively).

Initial electrodeposition steps: single particles and wires (nucleation and growth on HOPG)

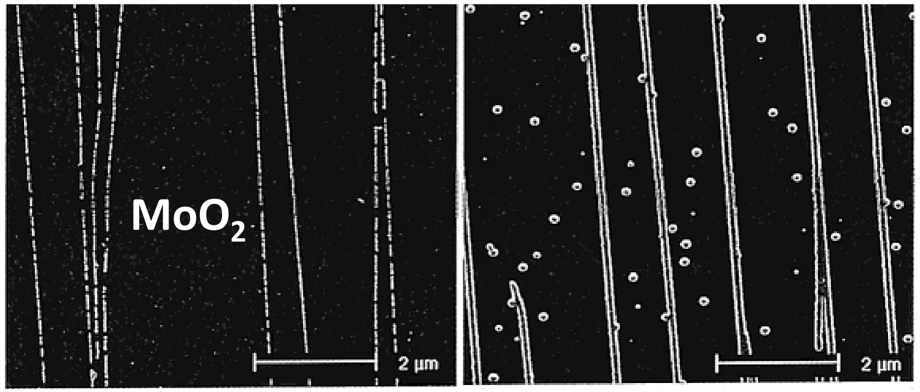


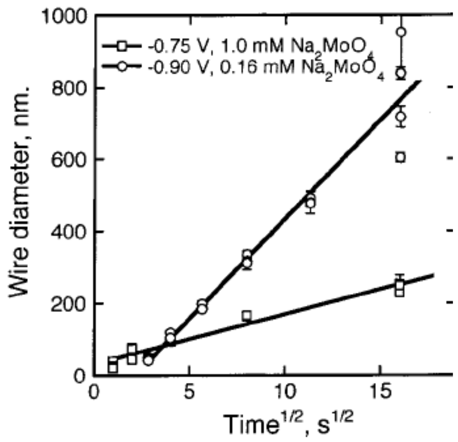


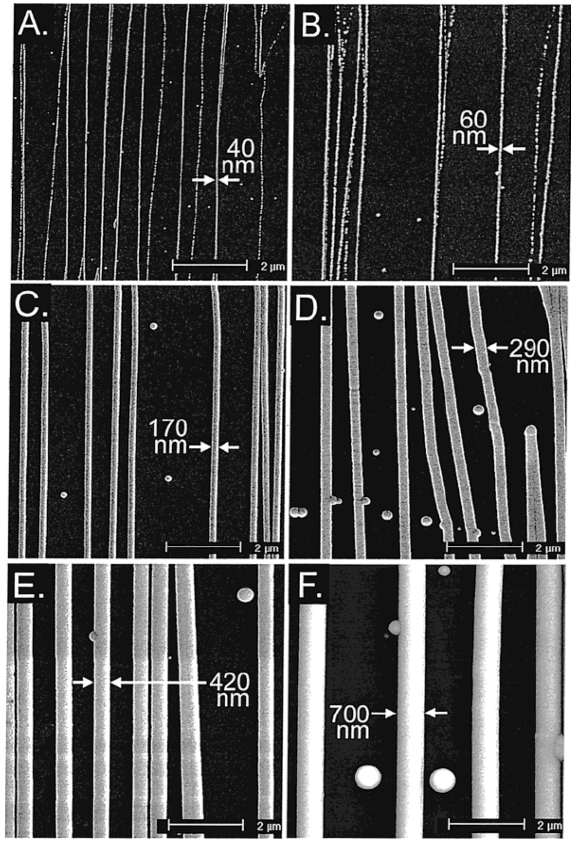


J. Phys. Chem. B
102 (1998) 1160

J. Phys. Chem.
100 (1996) 837







Step decoration,
Chem. Mater.
14 (2002) 3206

R.M. Penner et al.

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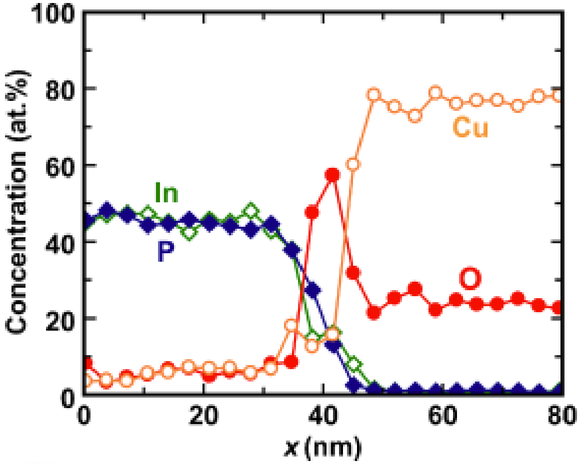
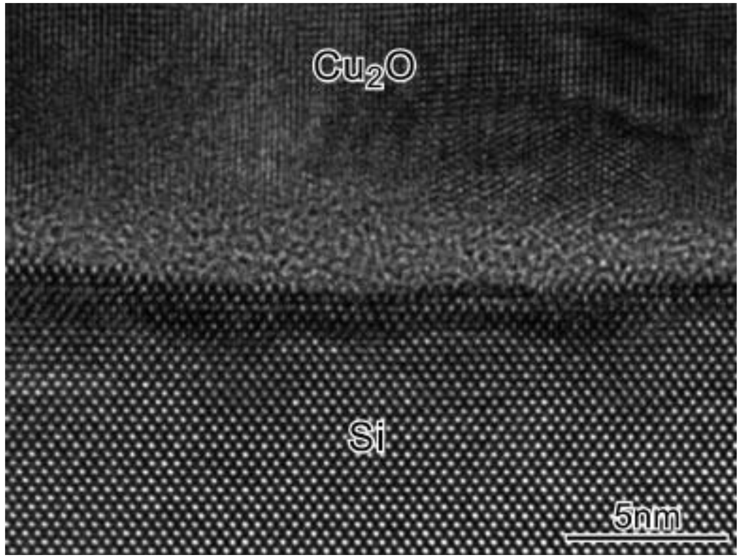
Oxides, sulfides, and selenides can be also electrodeposited <conducting polymers as well>

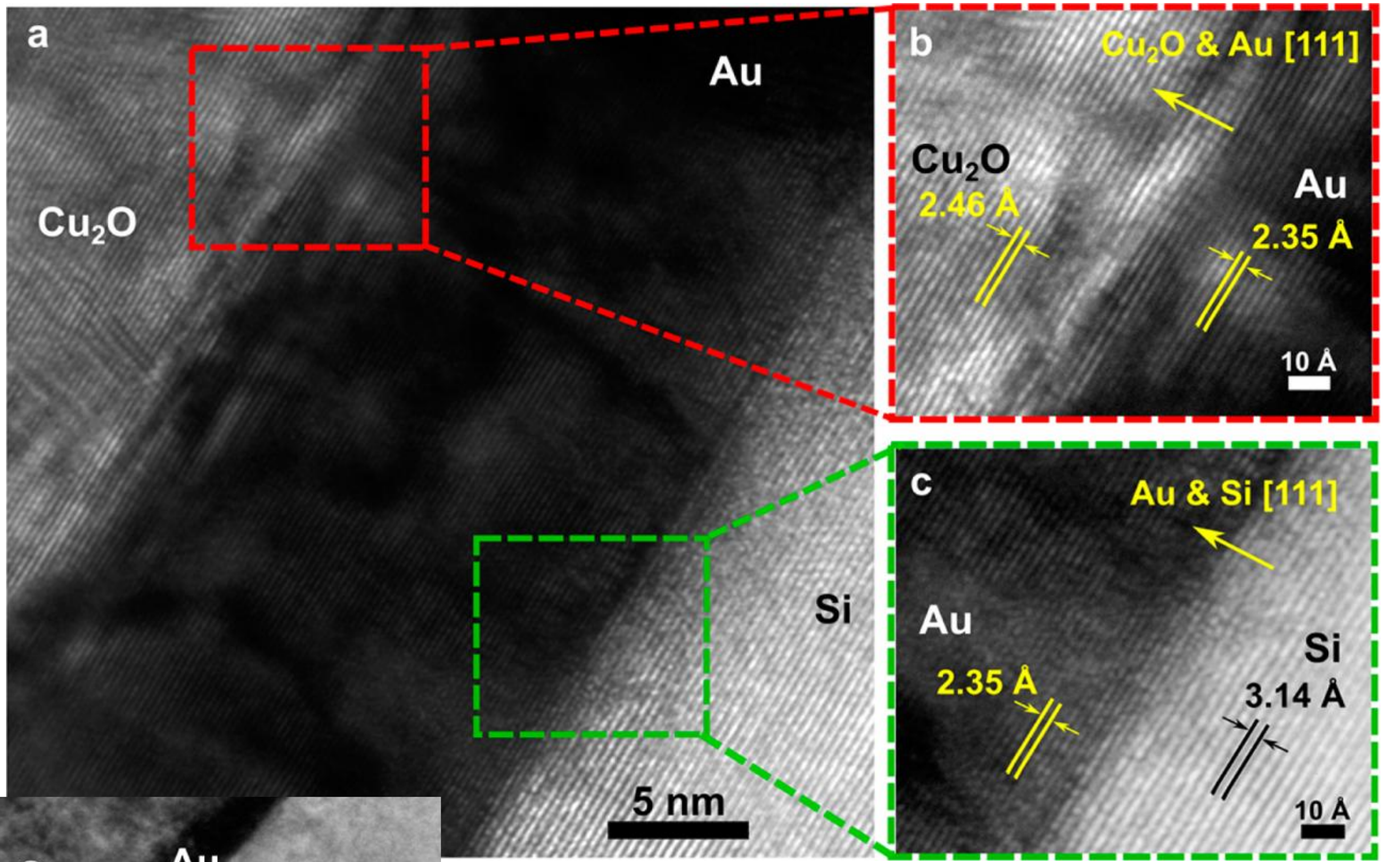
J. A. Switzer et al.

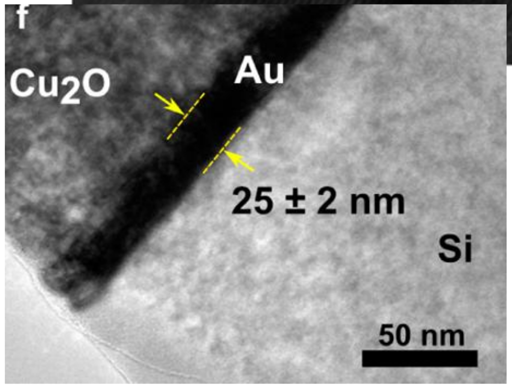
Problems with semiconductor supports



J. Am. Ceram. Soc.
88 (2005) 253





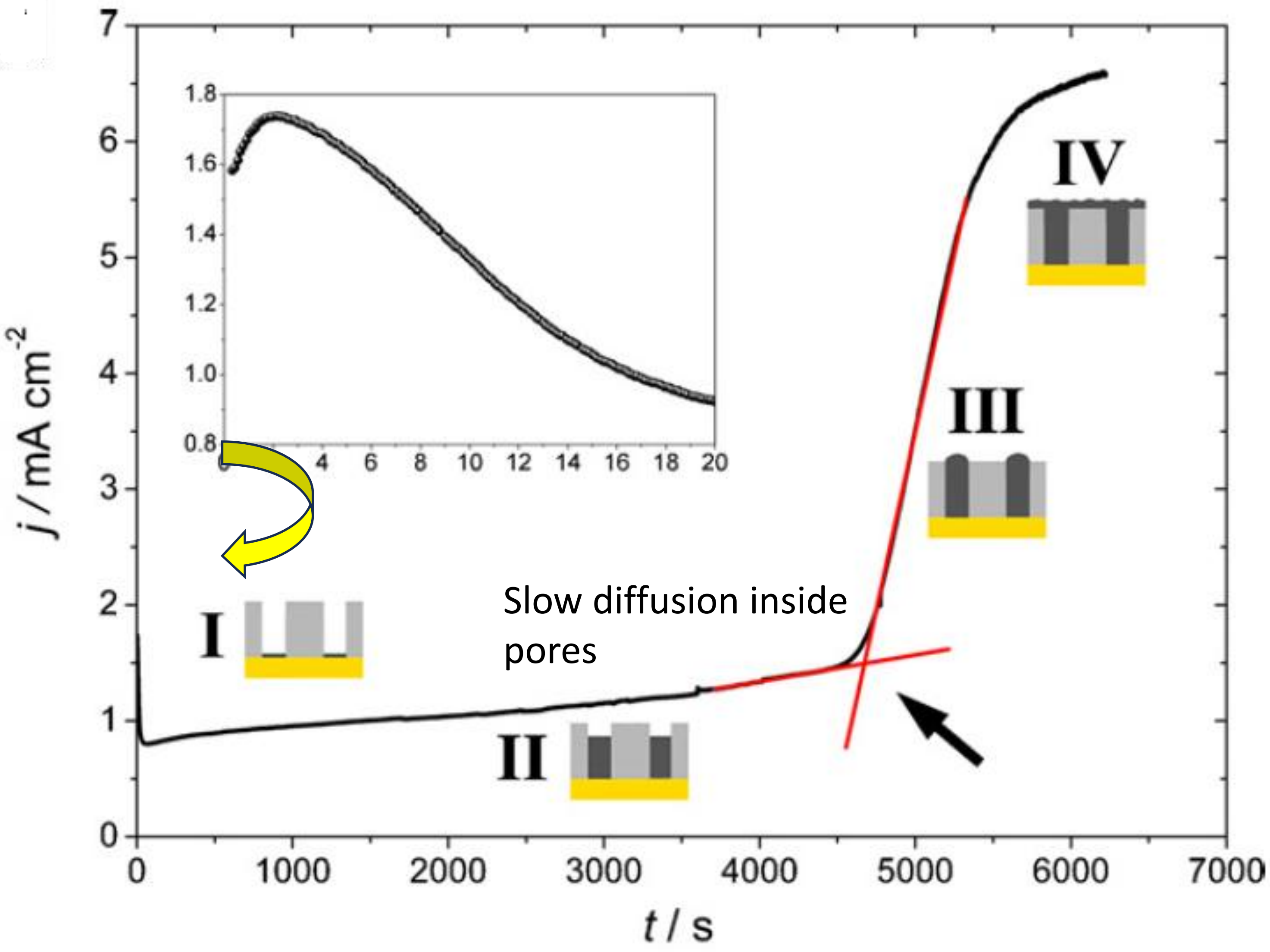


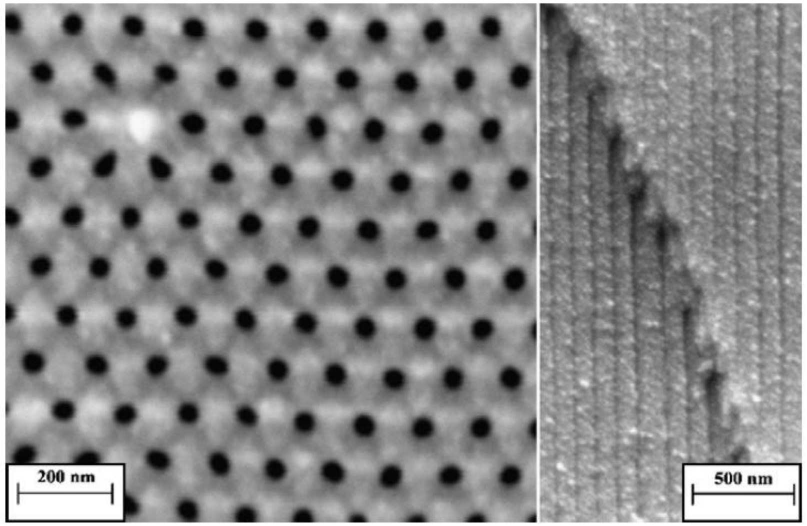
Much better with metal interlayer

ACS Appl. Mater. Interfaces
8 (2016) 15828

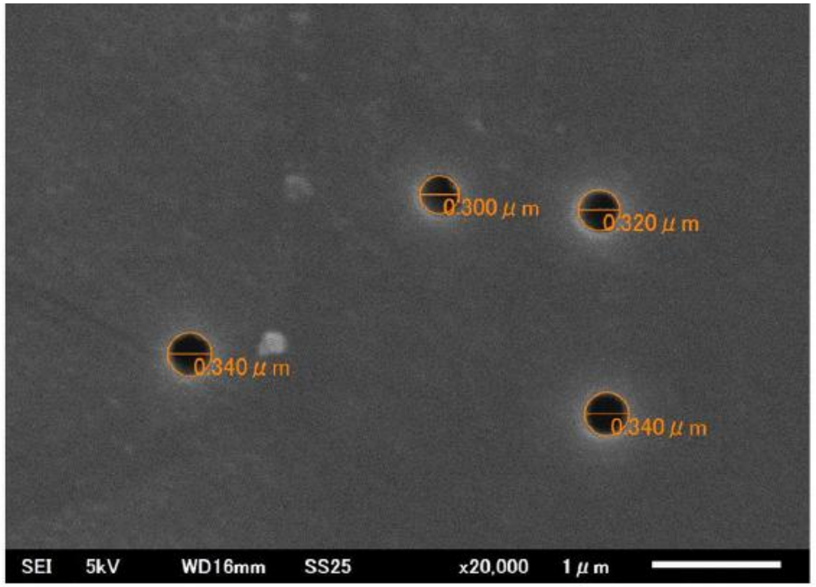
Templated deposition: spatial limitations of growth, wires

M^{n+}(in solution bulk) $\rightarrow$ M^{n+} (near the surface) + n e $\rightarrow$ M



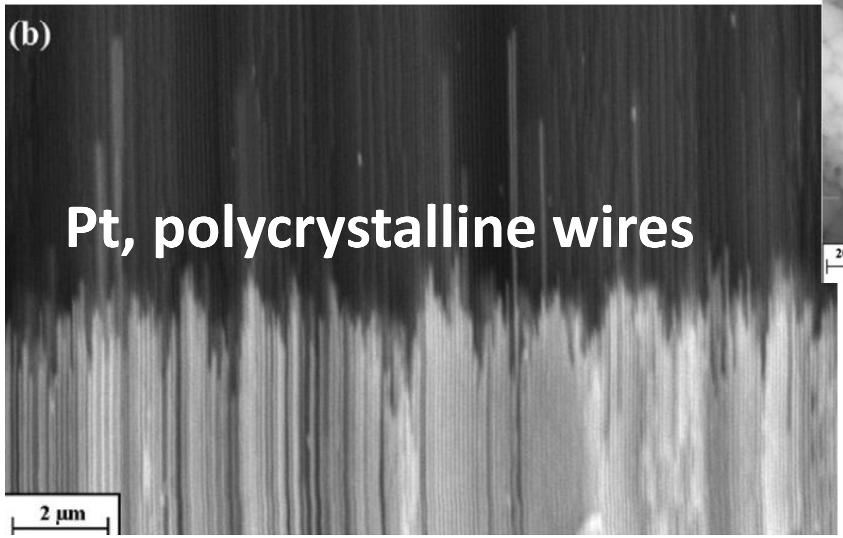


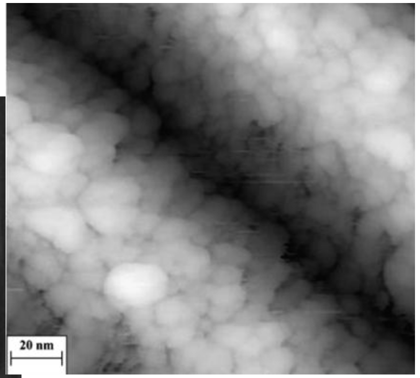
Anodic aluminum oxide (AAO), Electrochim. Acta 52 (2007) 7910

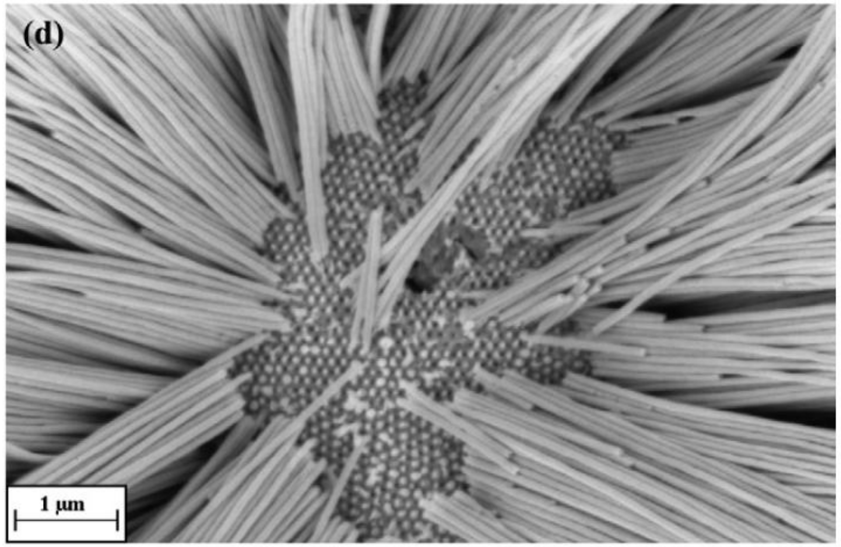


Nucl. Instr. Meth. Physics Res. B 394 (2017) 121

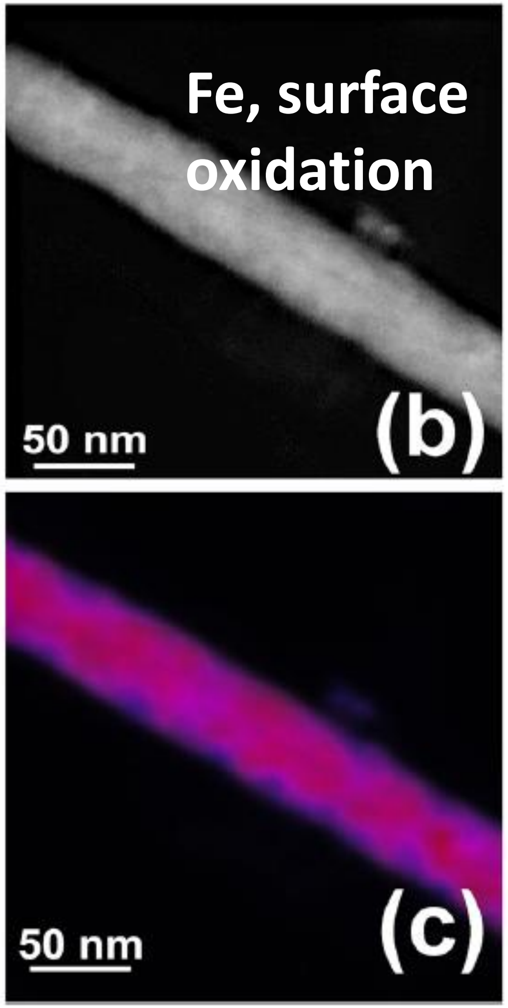
Wires: examples of problems



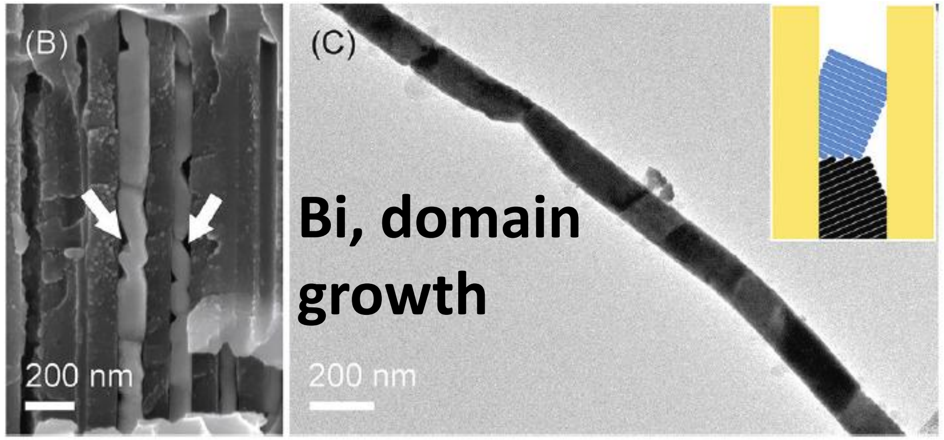


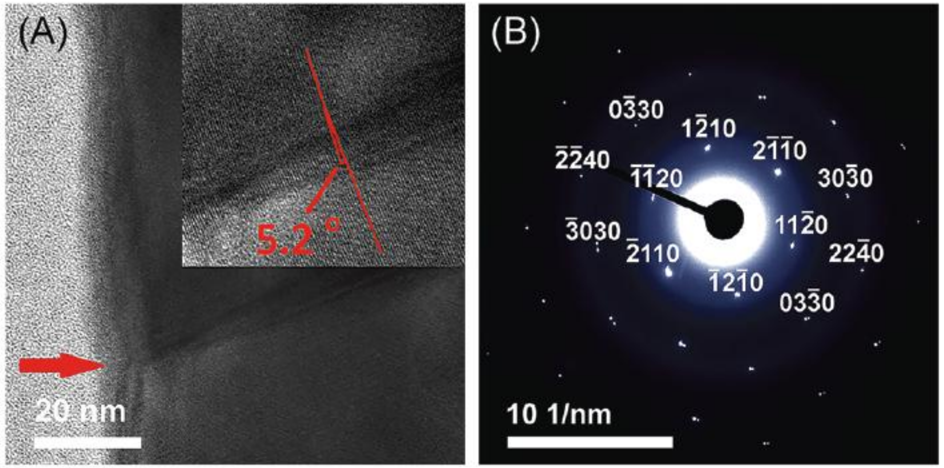


Electrochim. Acta 52 (2007) 7910



J. Sol-Gel Sci. Technol.
81 (2017) 327

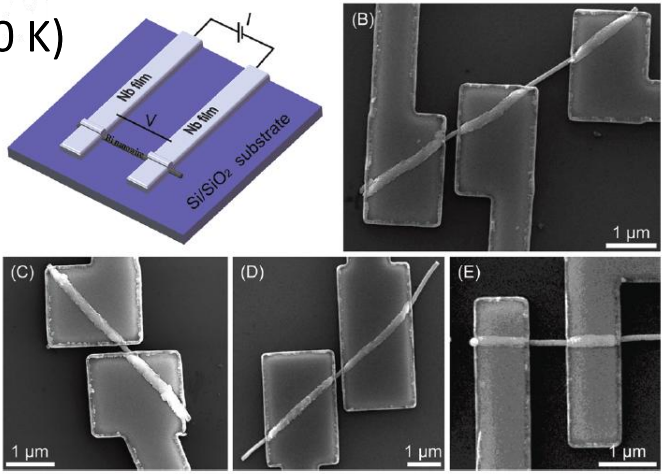




13-22 µOhm*m (10 K)

PCCP
22 (2020) 14953

<low temperature
data in PRB
90 (2014) 245427>



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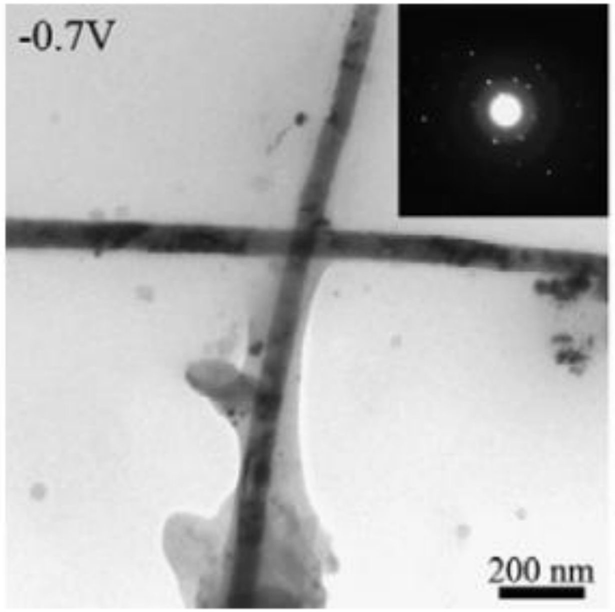
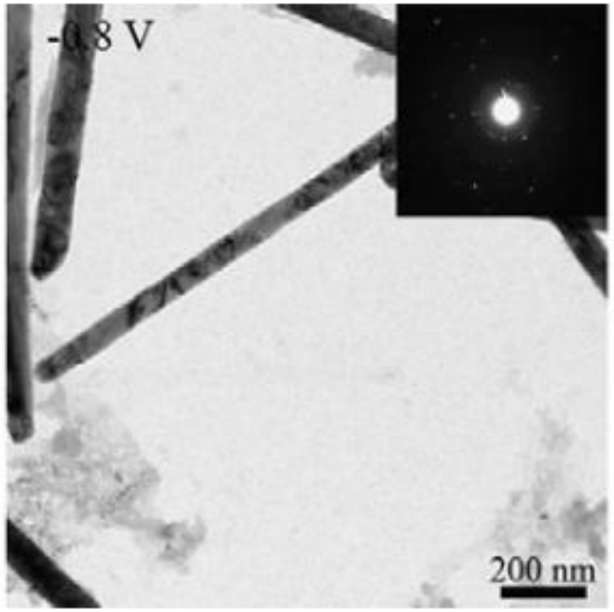
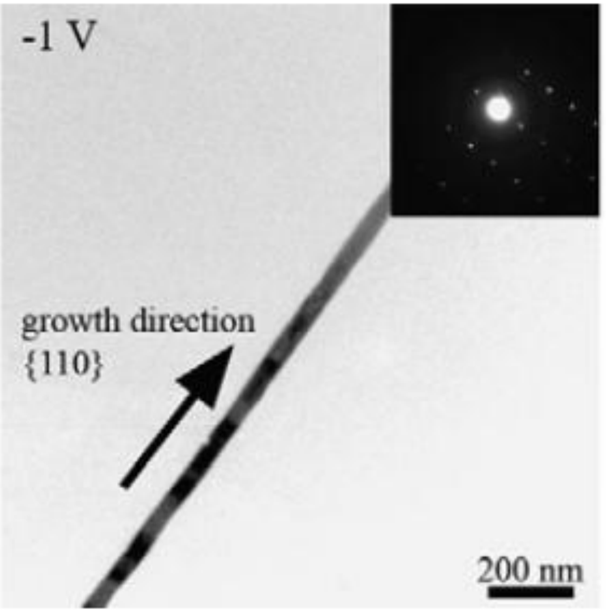
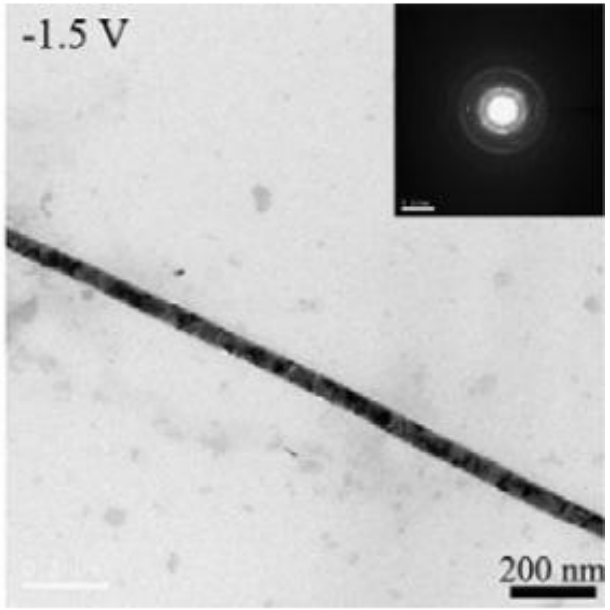
Center of Excellence in Nanoscience and Nanotechnology

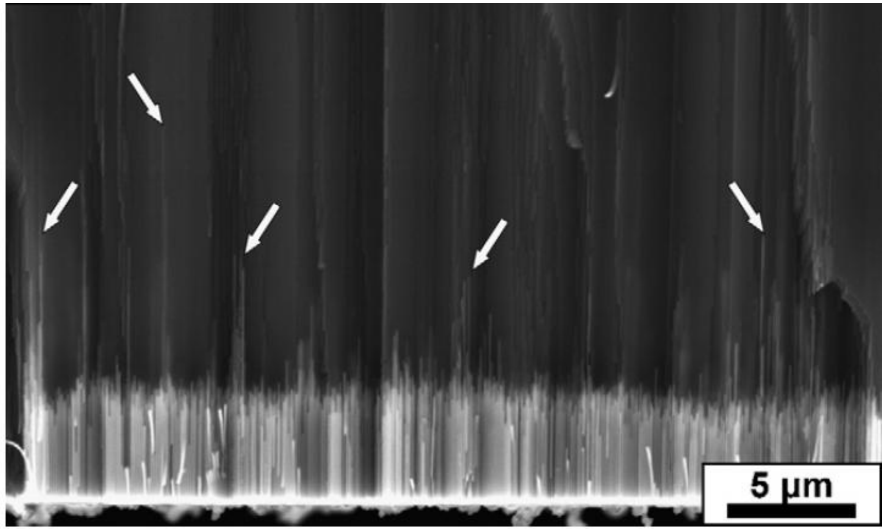
Wires: more lucky example (Ni), deposition potential effect on microstructure



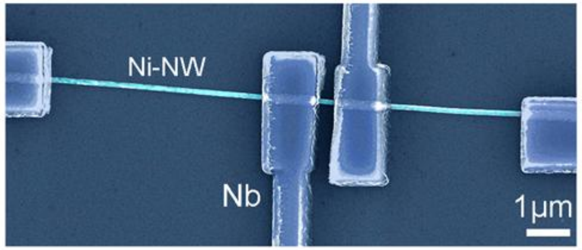




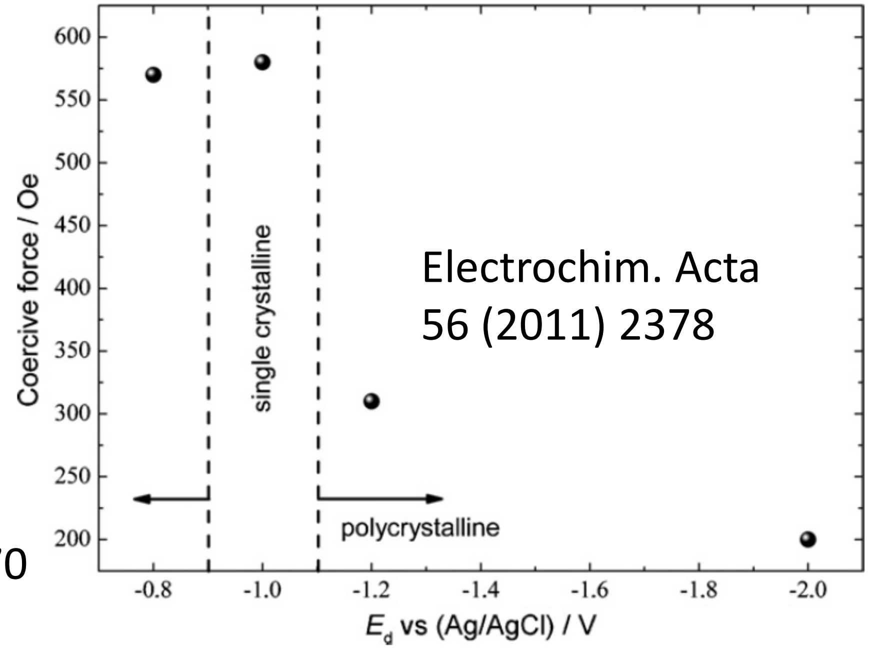




Growth front becomes less homogeneous at more negative potentials (higher growth rates)

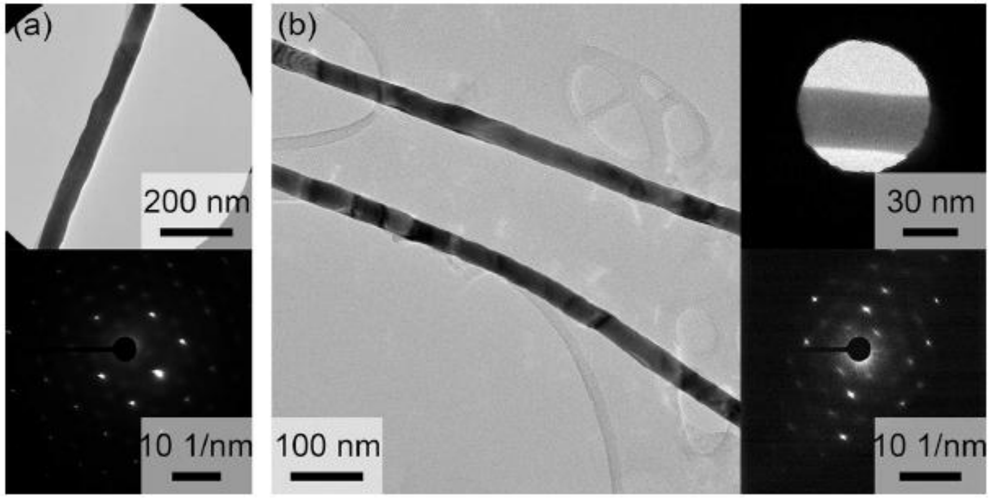


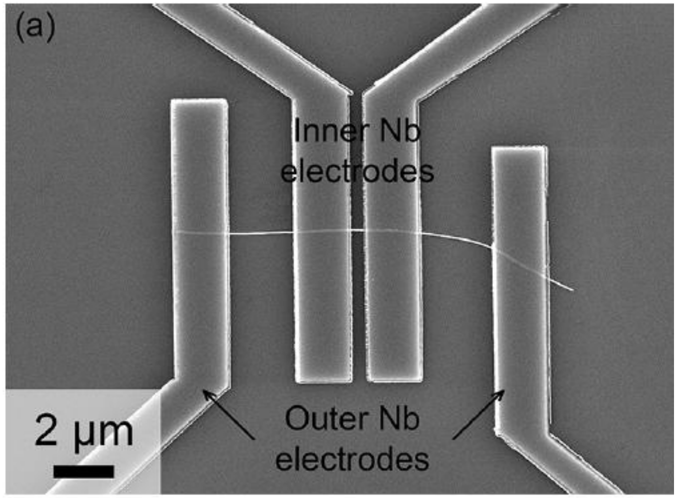
SFS junction: Sci. Rep. 9 (2019) 14470



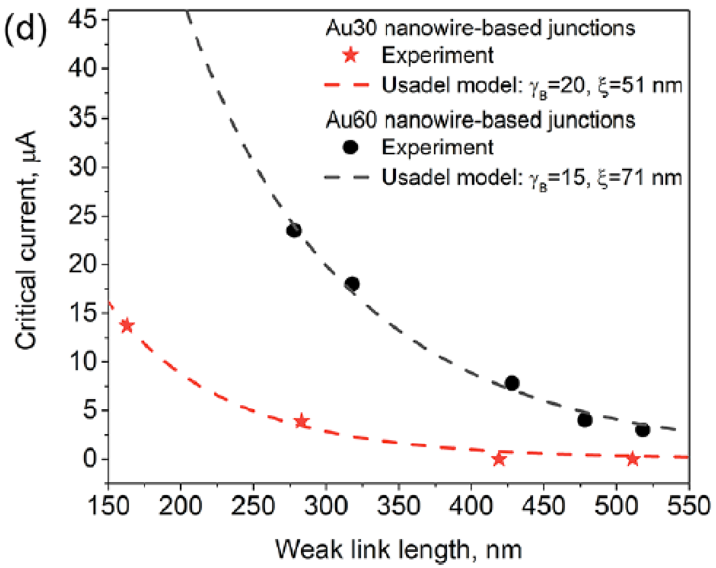
Electrochim. Acta 56 (2011) 2378

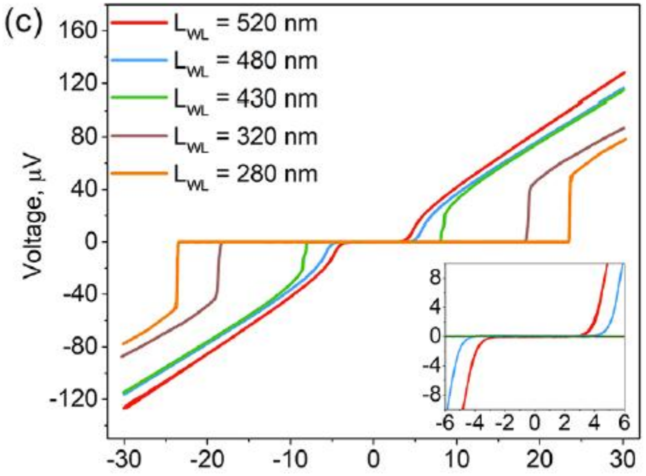
Wires: one more example (Au), the most promising?



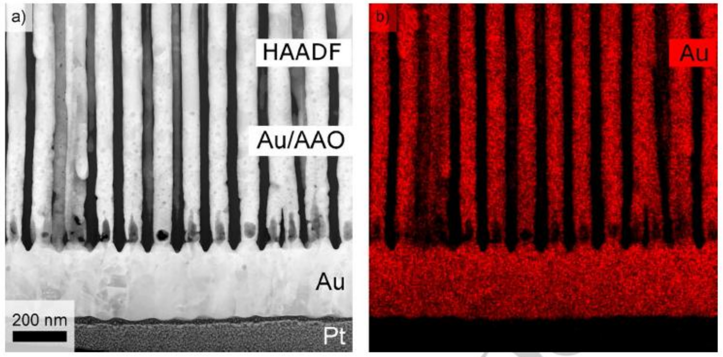


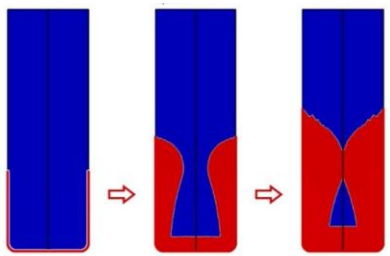
Problems with initial part of wires were discovered when short wires were studied for magneto-optics <Opt. Lett. 43 (2018) 3917>





ACS Appl. Nano Mater. 5 (2022) 17059

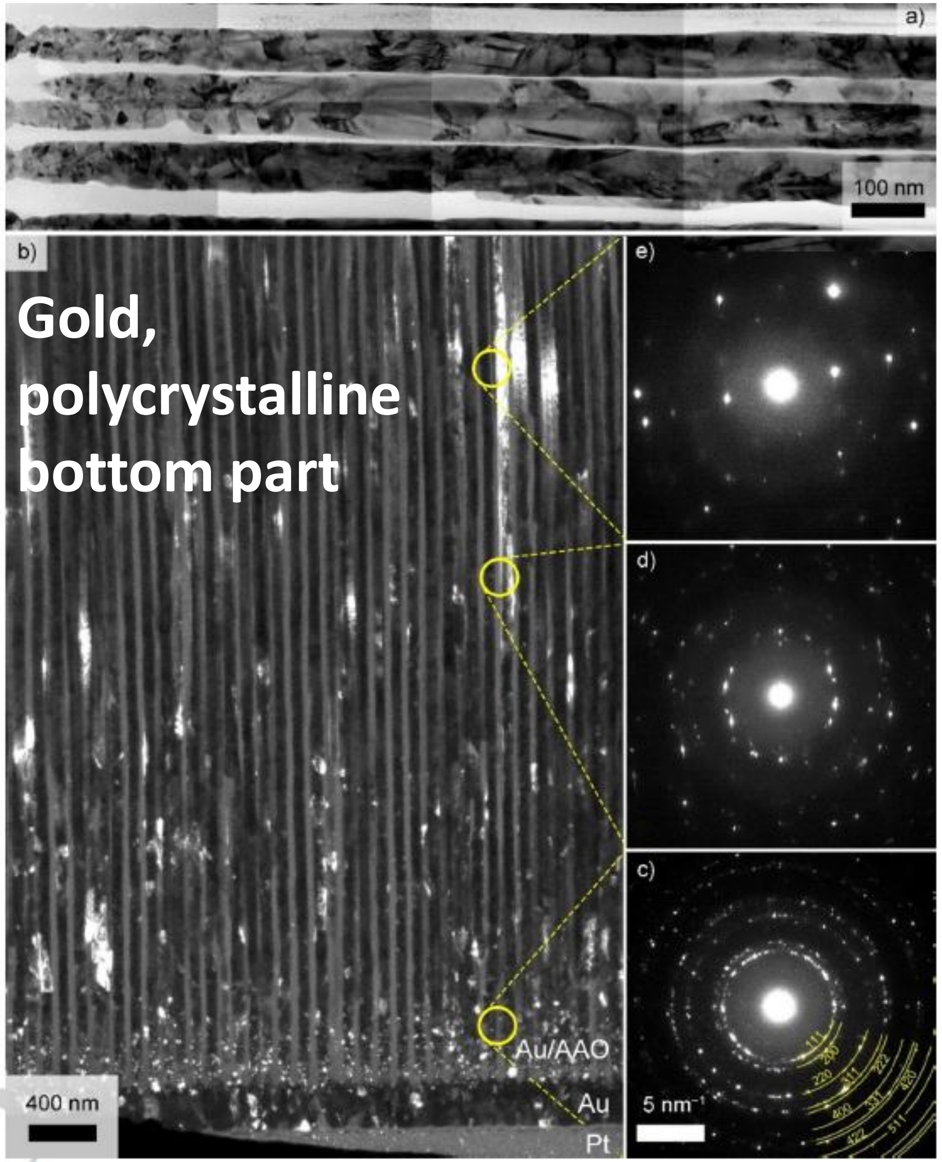




Growth starts from tubes

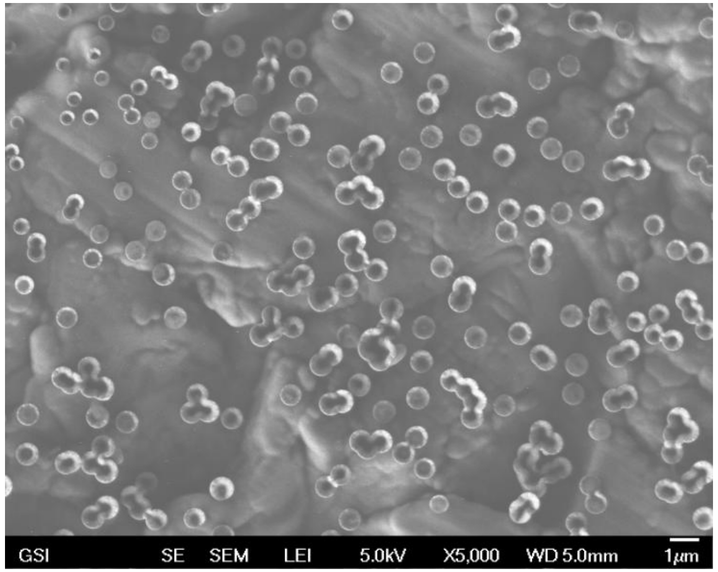
J. Solid State Electrochem. 2024

Wires: complications in the course of growth, at least two reasons:



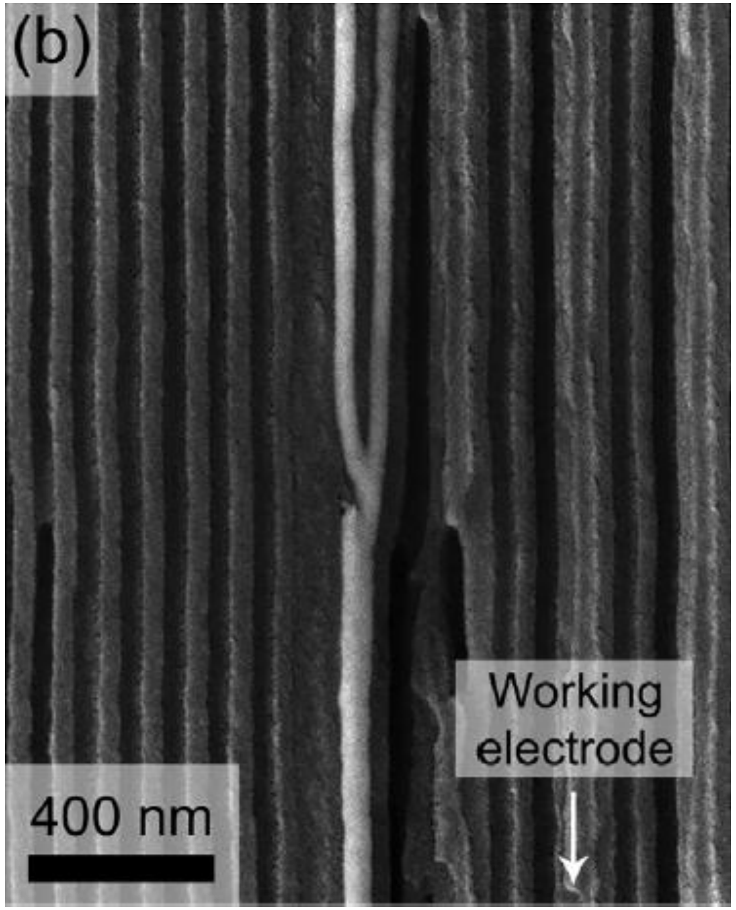
J. Solid State Electrochem. 2024

Geometry of conducting gold sublayer



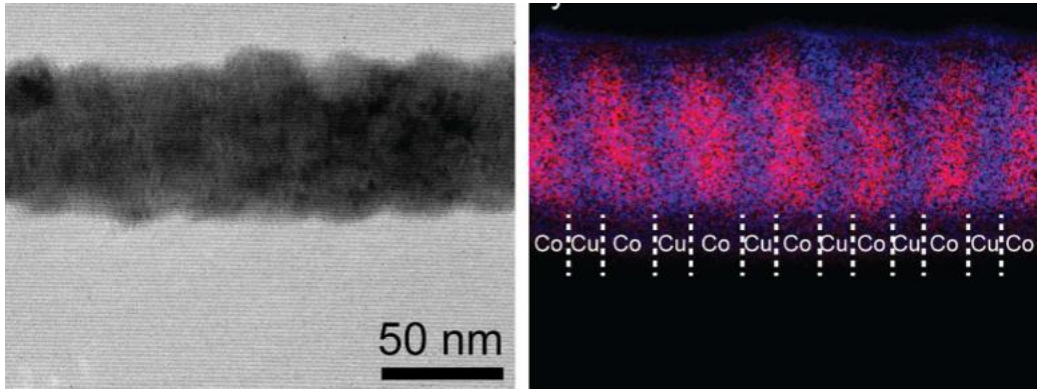
Back side of template with sputtered gold, which penetrates into the pores.

Imperfections of AAO

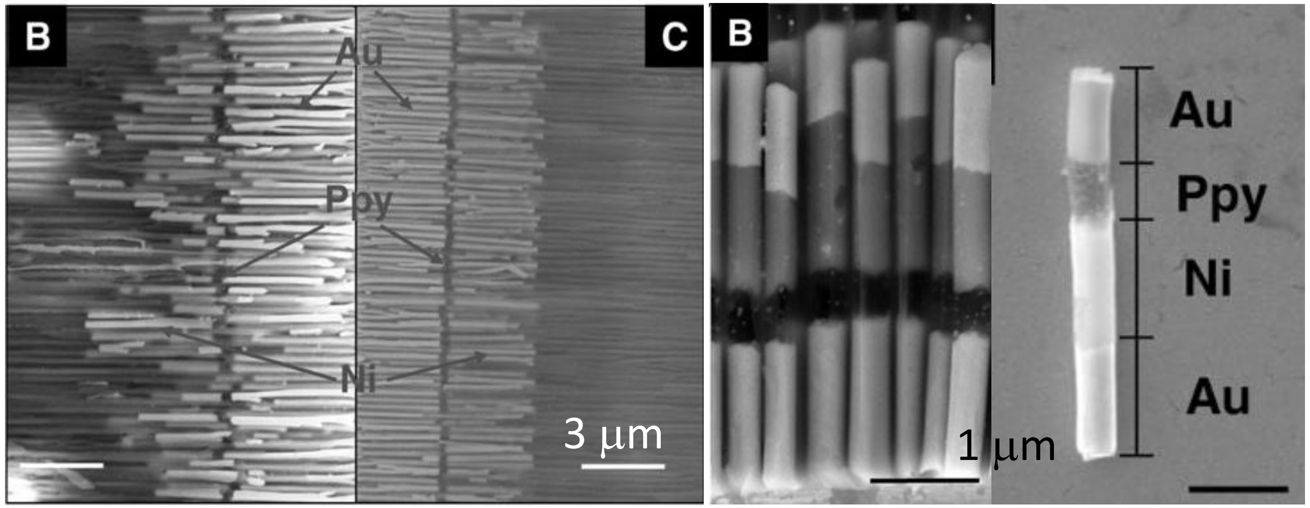


Electrochim. Acta 226 (2017) 60

Wires: prospects of heterojunctions



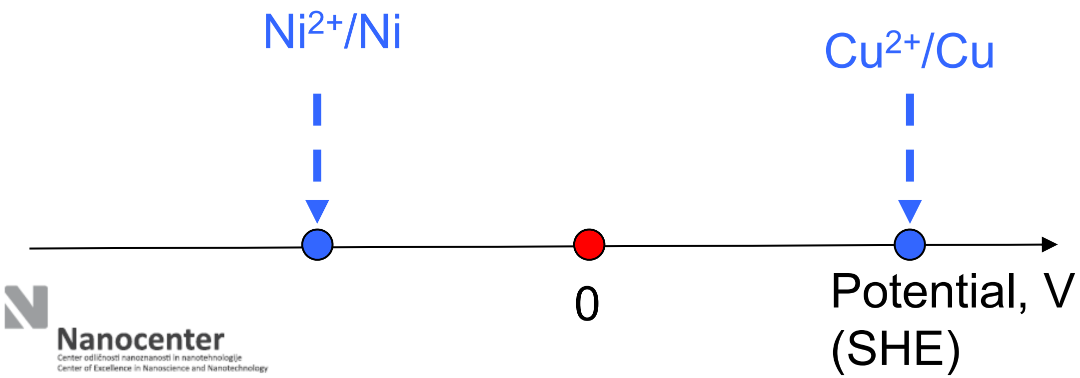
Cobalt/copper, Nano Lett. 16 (2016) 1230

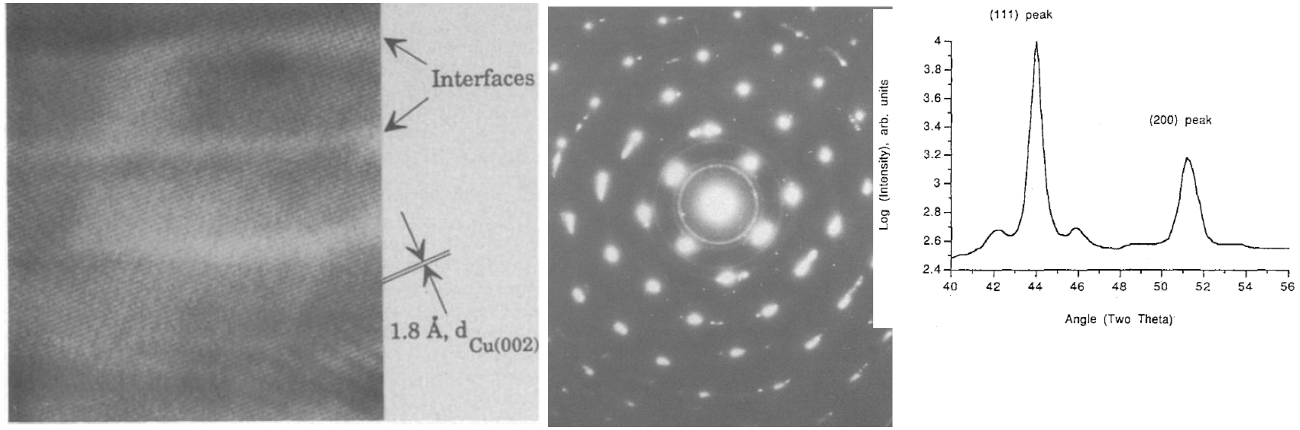


Gold/polypyrrol/nickel/gold, Electroanalysis 21 (2009) 61

Old experience of electrochemical deposition of bimetallic superlattices: single or dual bath

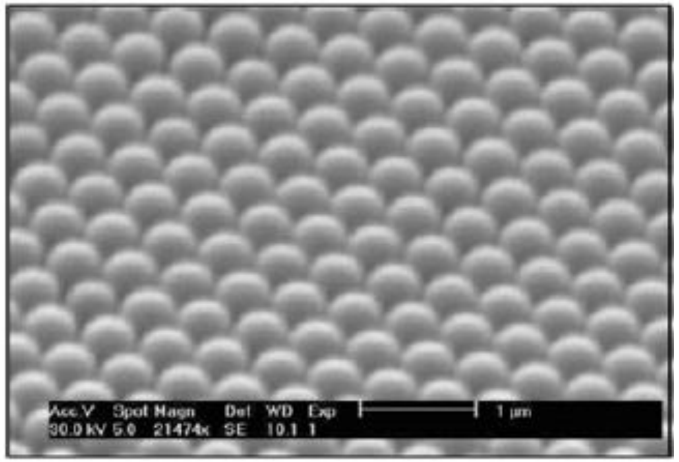
“Single bath” requires numerous changes of solution.
“Dual bath” assumes Cu:Ni ratio in solution ~ 1:100, for slower Cu deposition.



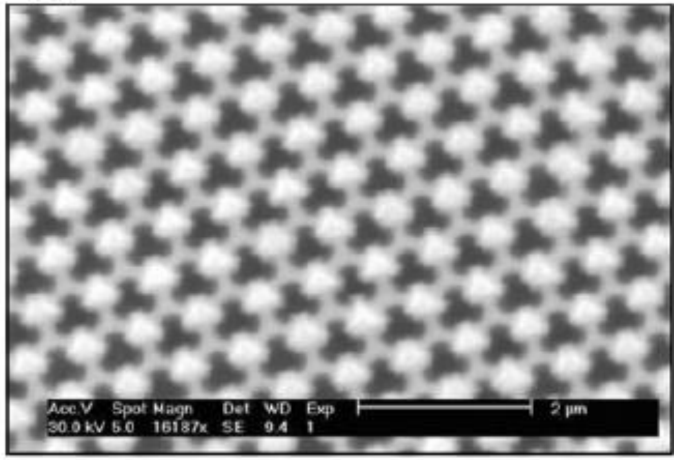


J. Electrochem. Soc. 135 (1988) 1218; 141 (1994) 230

Templated deposition: polystyrene spheres, inverse opals are formed

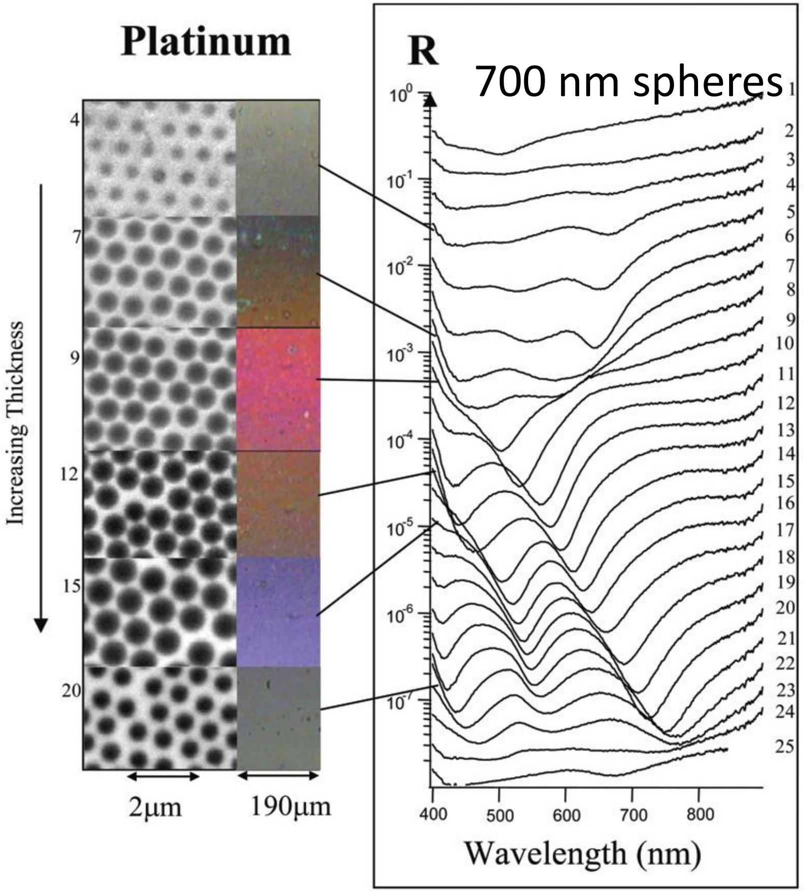


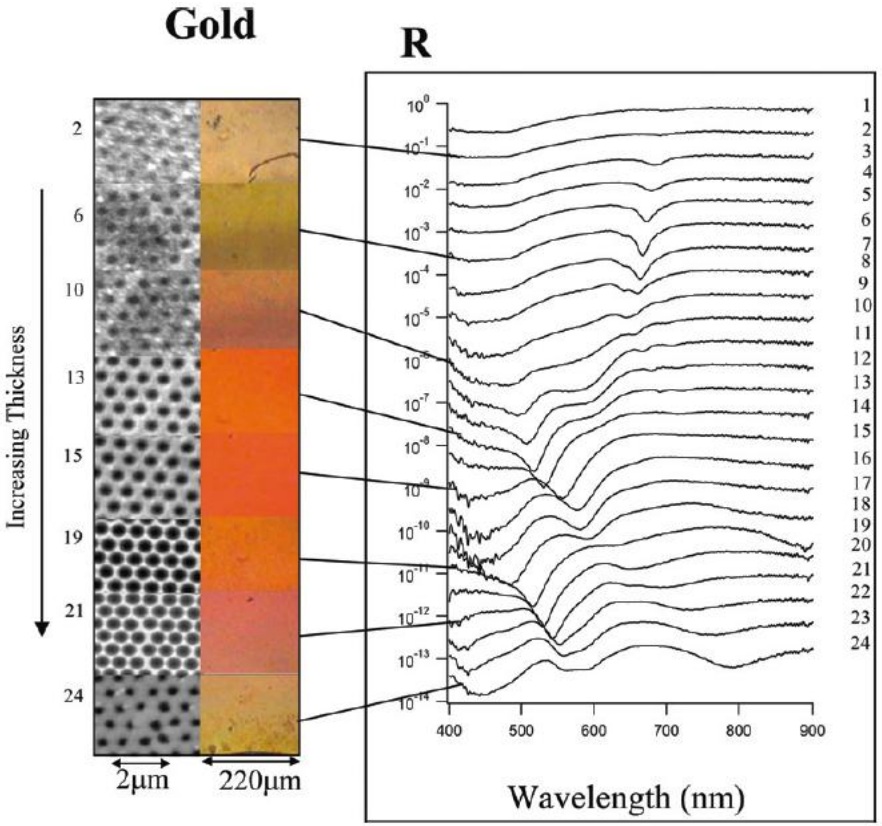
Polystyrene self-assembly



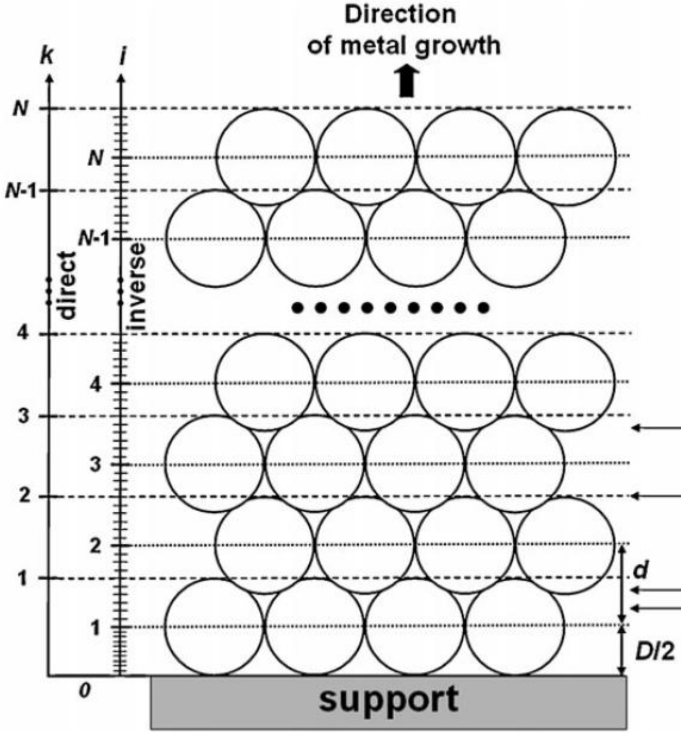
Metal after deposition and dissolution of polystyrene

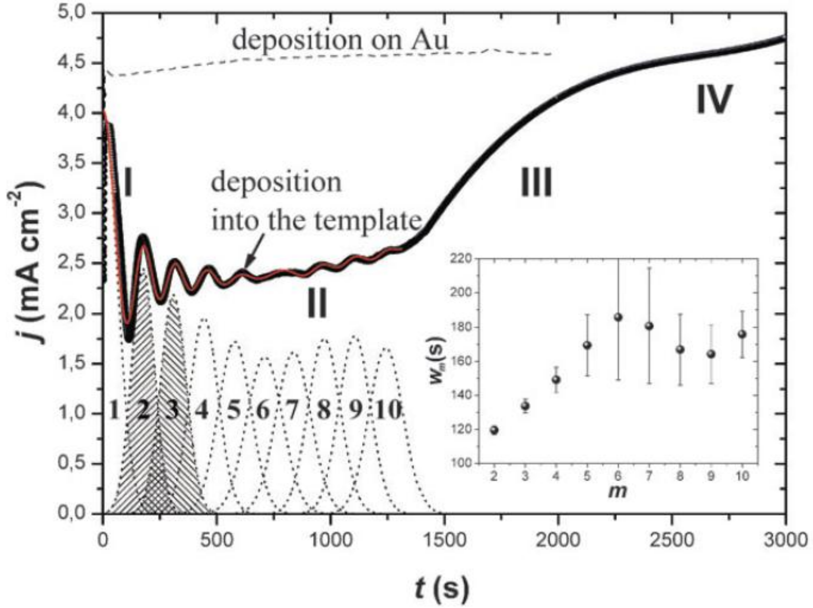
P.N. Bartlett et al., Optical properties of nanostructured metal films, Faraday Discuss. 125 (2004) 117

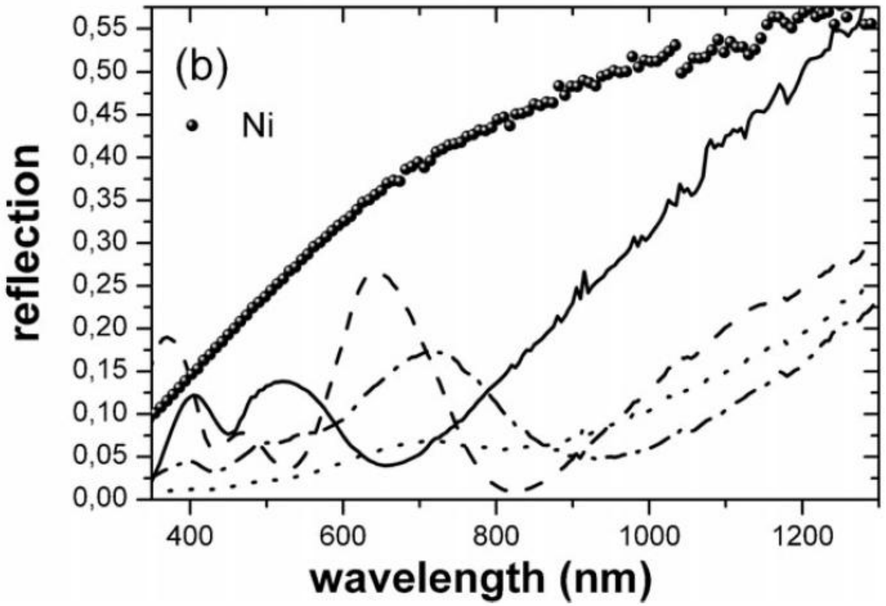


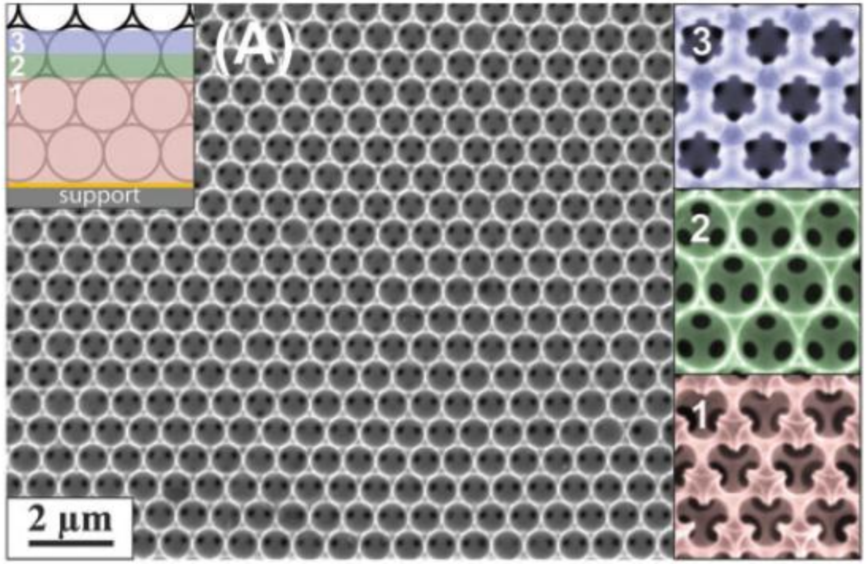


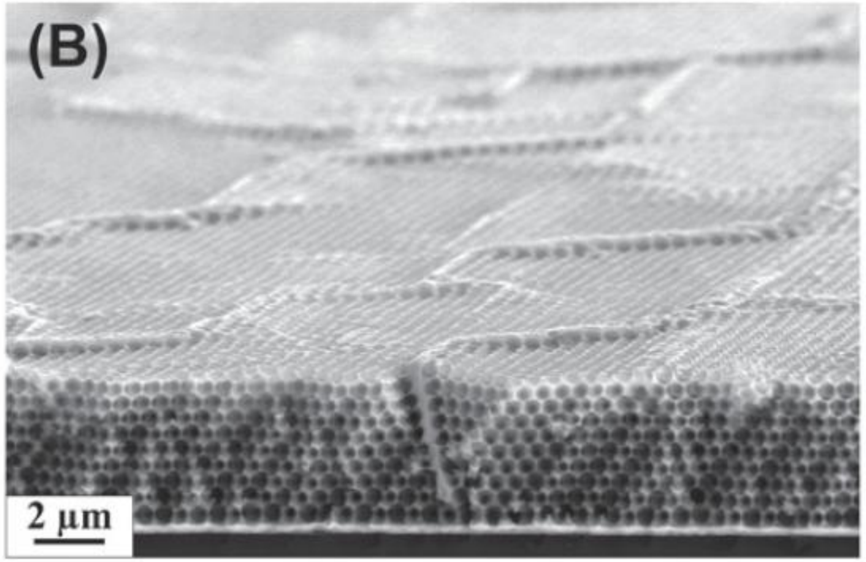
Templated deposition of inverse opals: monitoring









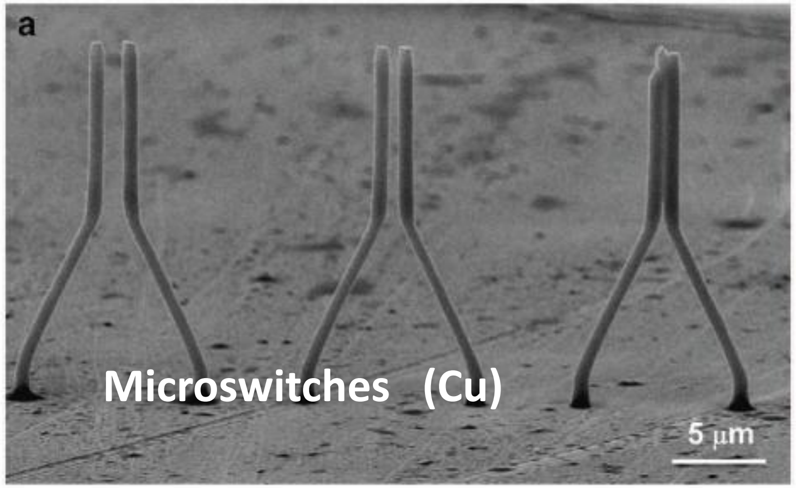


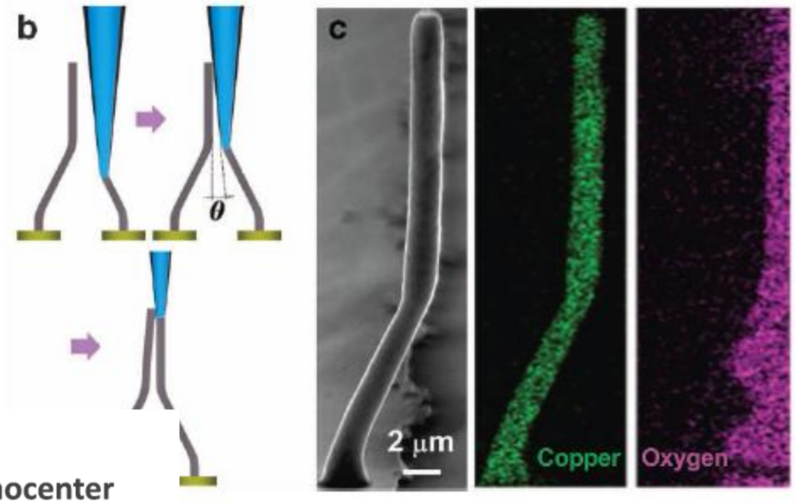
Phys. Chem. Chem. Phys. 12 (2010) 15414

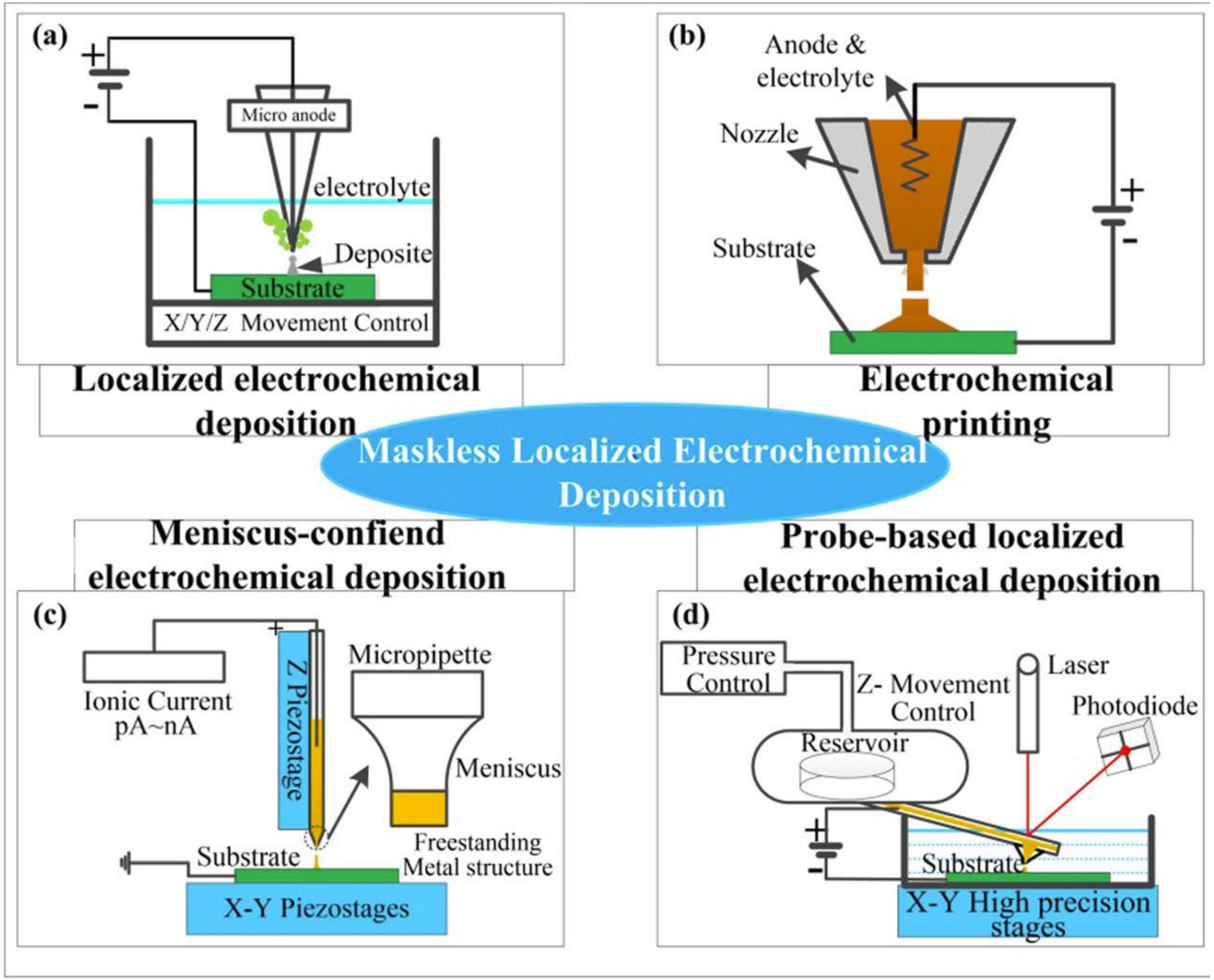
Maskless localized electrodeposition: microelectrodes (in probe microscopes as well) or micropipettes

Review: Int. J. Adv. Manuf. Technol. 110 (2020) 1731–1757

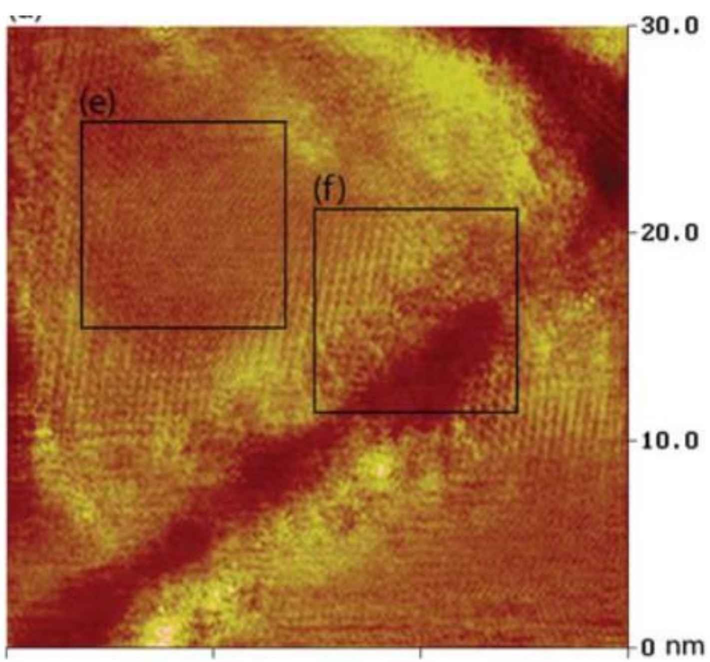
Microsyst. Nanoeng. 2 (2016) 16010

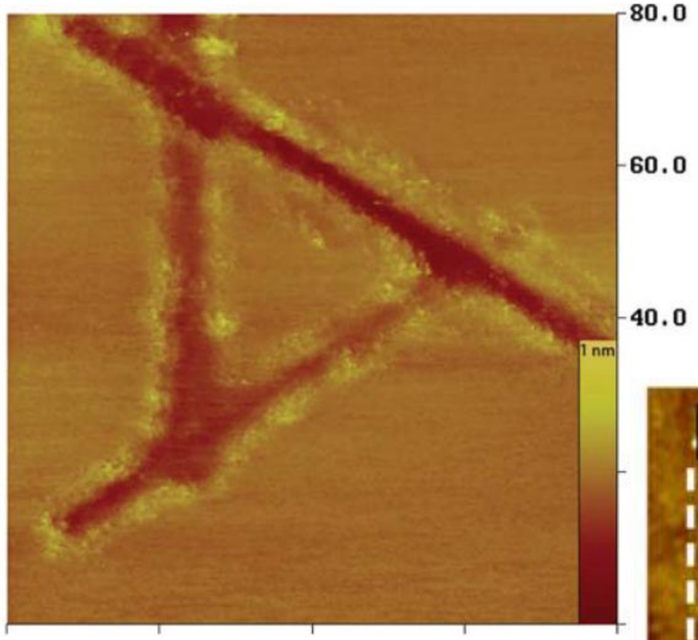


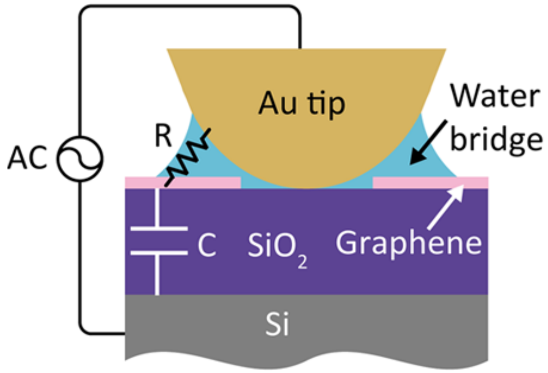




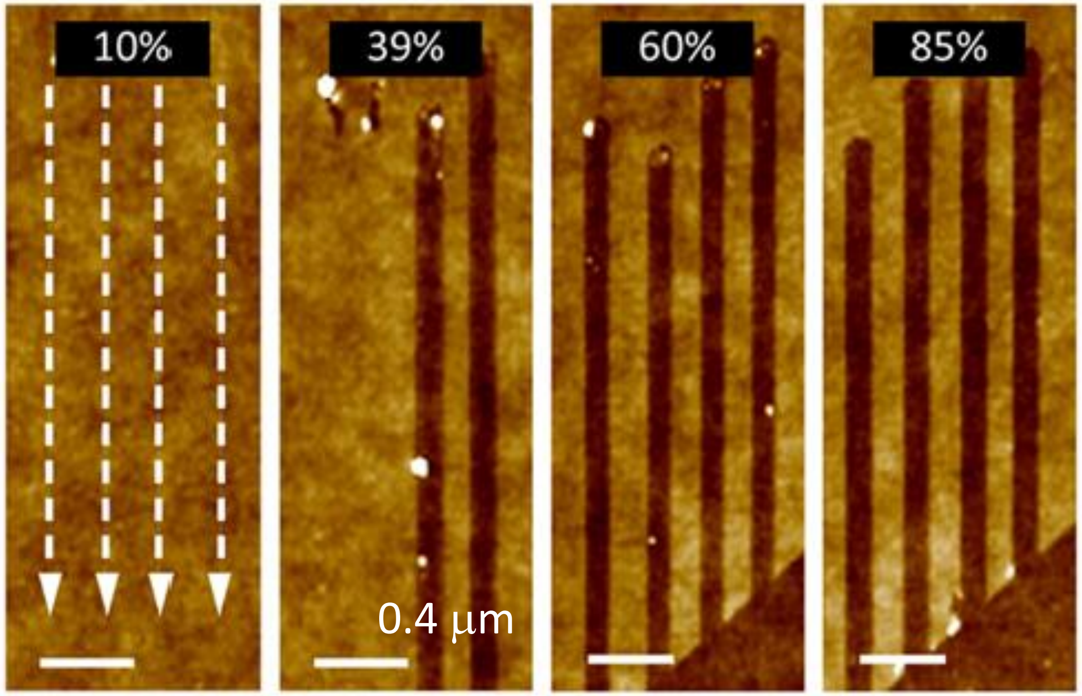
Cutting graphene with STM tip in condensed water layer

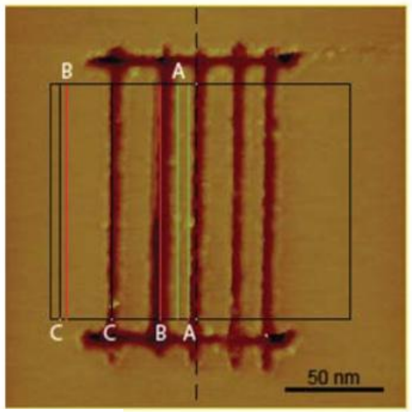


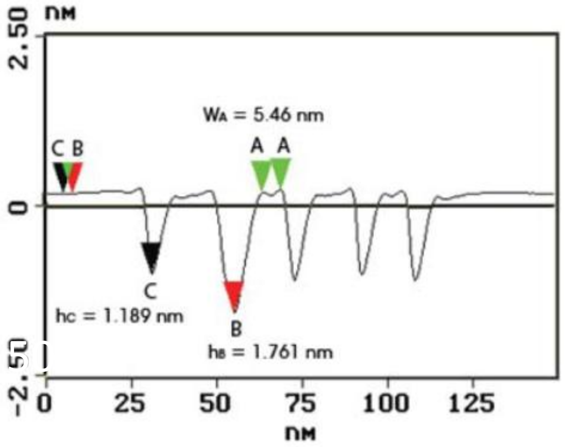




Humidity 10….85%:





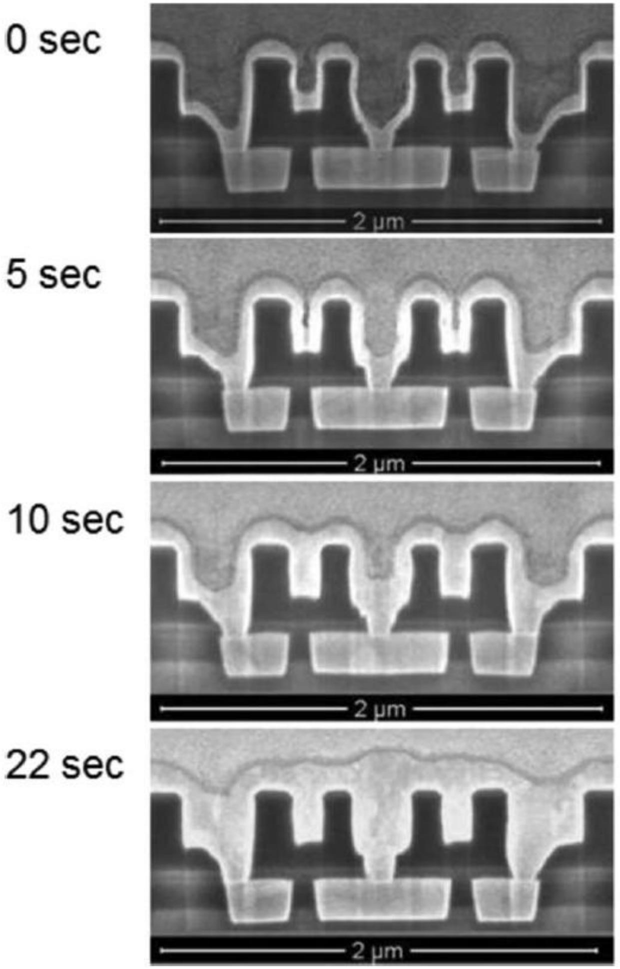


Nanopages 7 (2012) 1

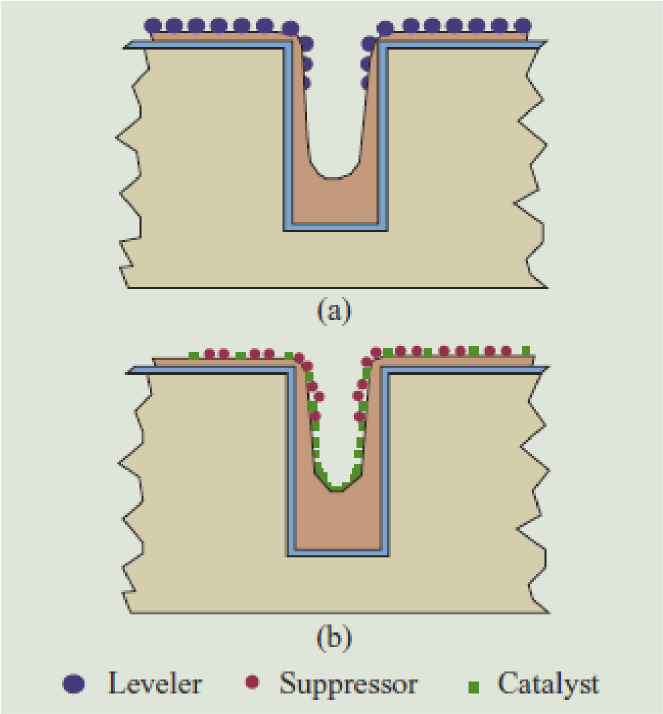
Nano Lett. 18 (2018) 8011

Maskless localized electrodeposition: additives

Damascene technology, IBM 1998



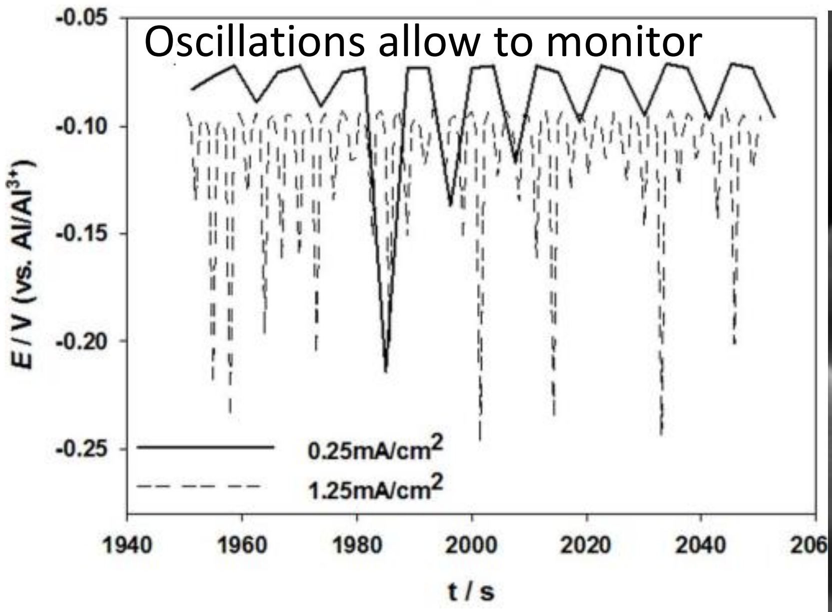
J. Electrochem. Soc. 163 (2016) D213

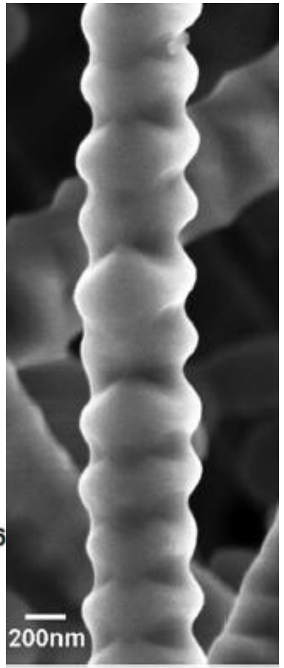


IBM J. Res. Devel. 49 (2005) 3

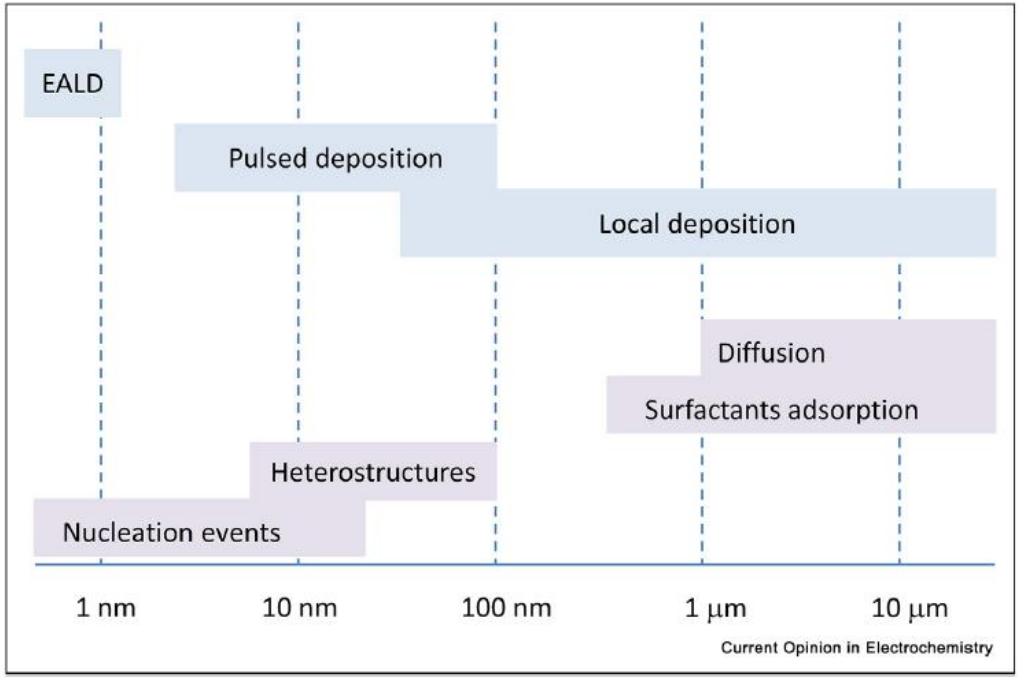
The secret is to combine adsorbing additives which inhibit and enhance deposition, with different diffusion behaviors.

Oscillations allow to monitor





ECS Electrochem. Lett. 4 (2015) D21



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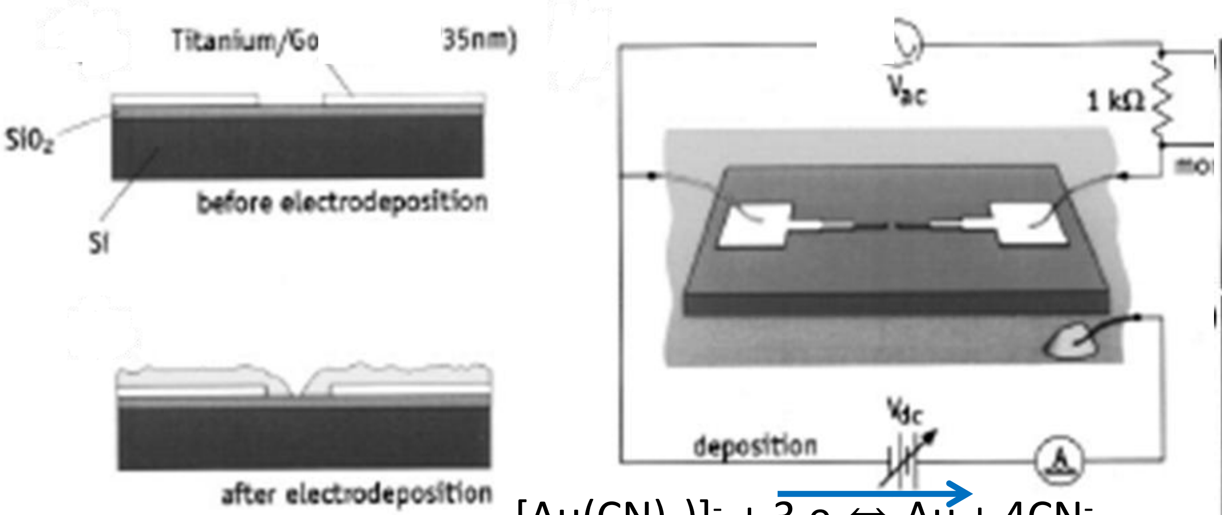
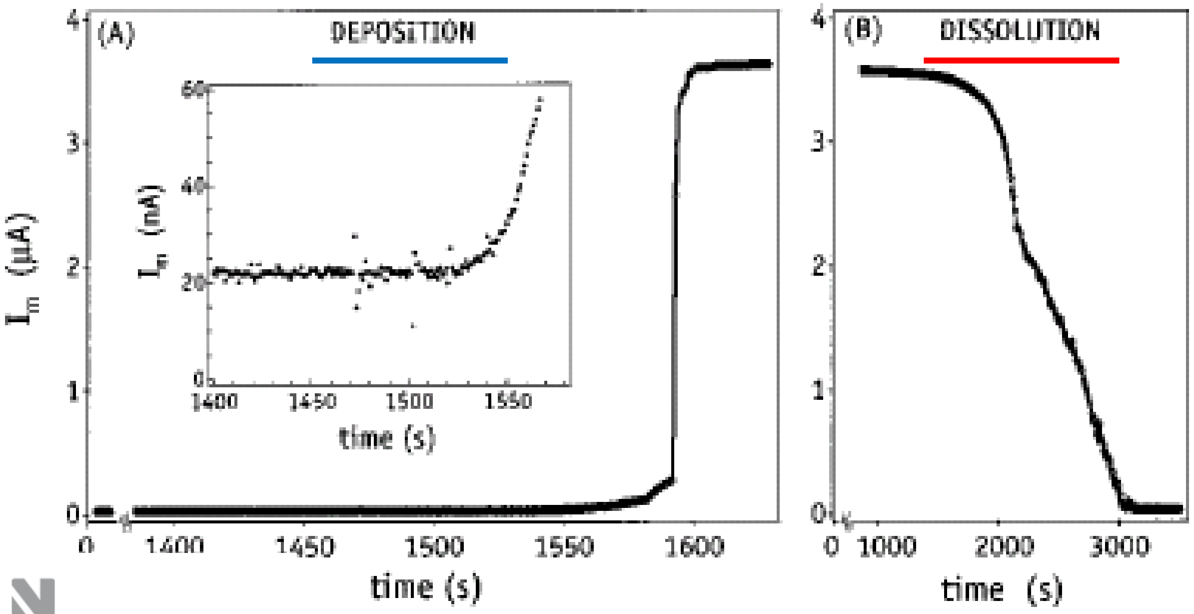
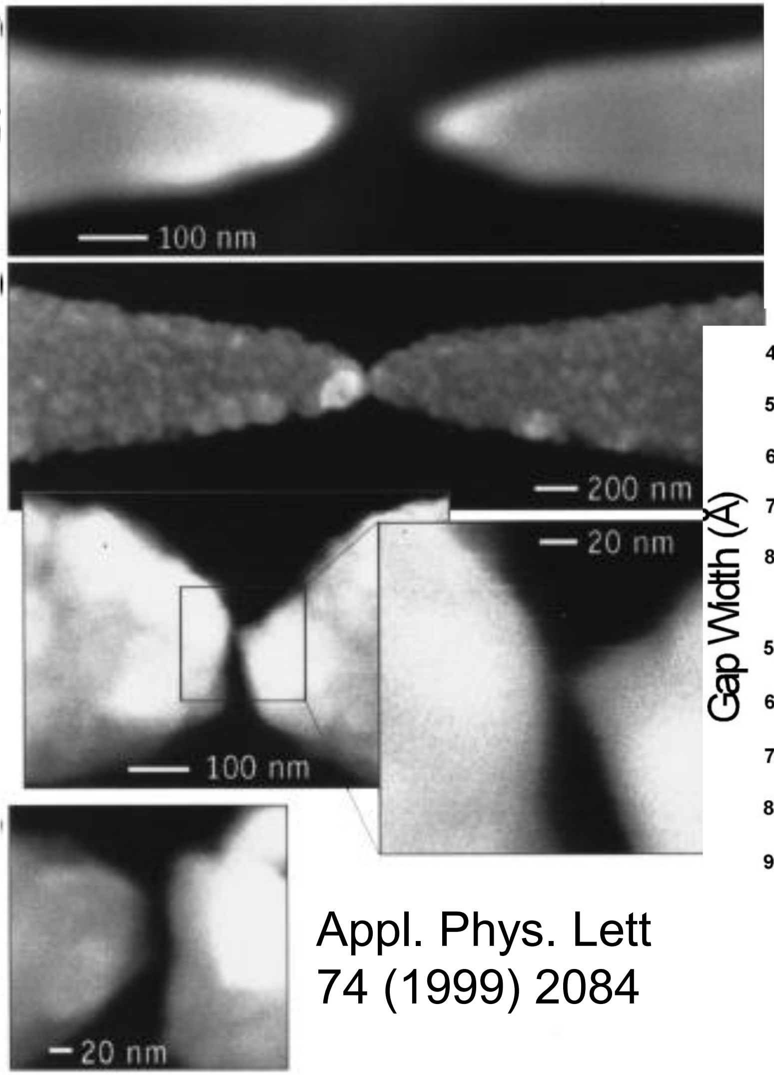
Gaps formed by electrodeposition and dissolution due to specific distribution of current lines

Resistance monitoring OR tunneling current feedback

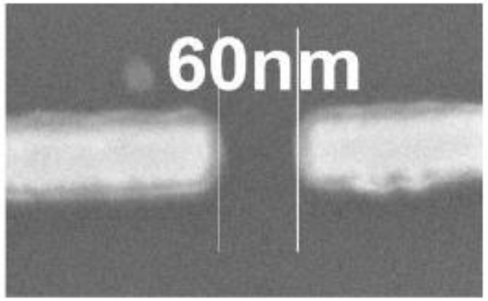


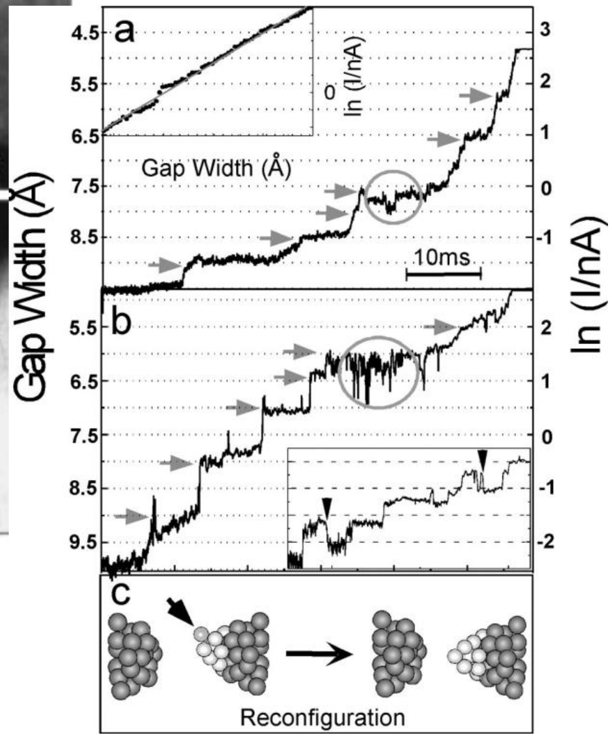
$[Au(CN)_4)]^- + 3\ e \Leftrightarrow Au + 4CN^-$





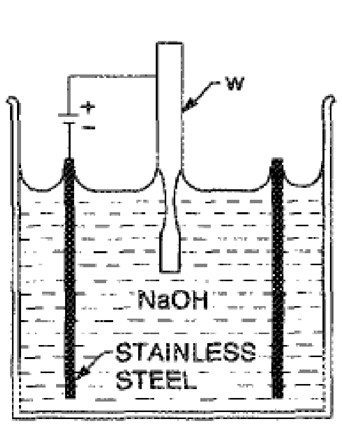
Appl. Phys. Lett 74 (1999) 2084

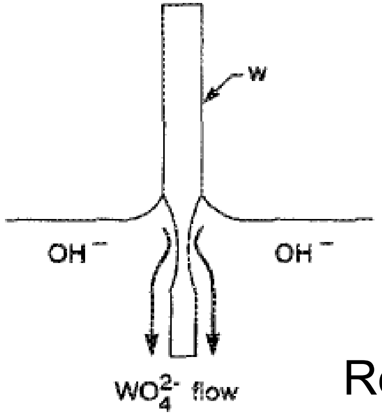


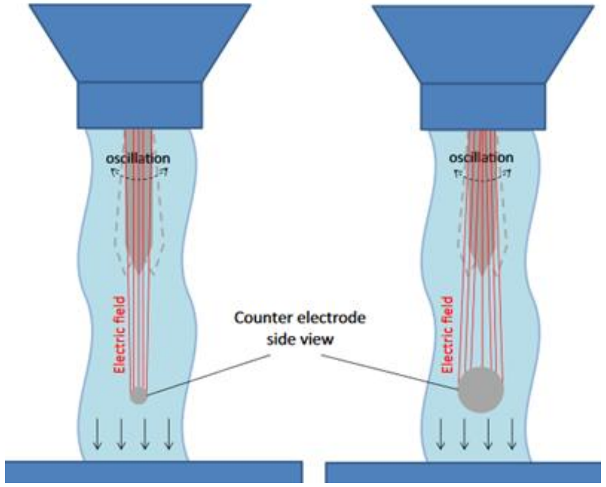


Appl. Phys. Lett 72 (1998) 894

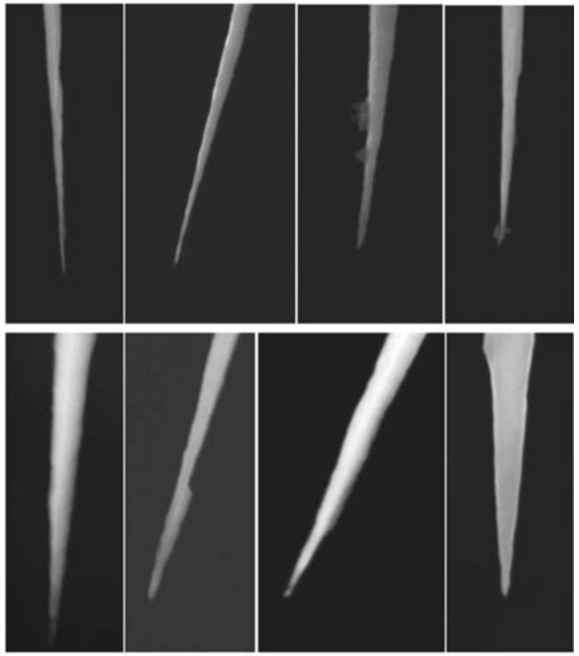
Anodic etching of tips (probes)
due to specific distribution of current lines and diffusion flows



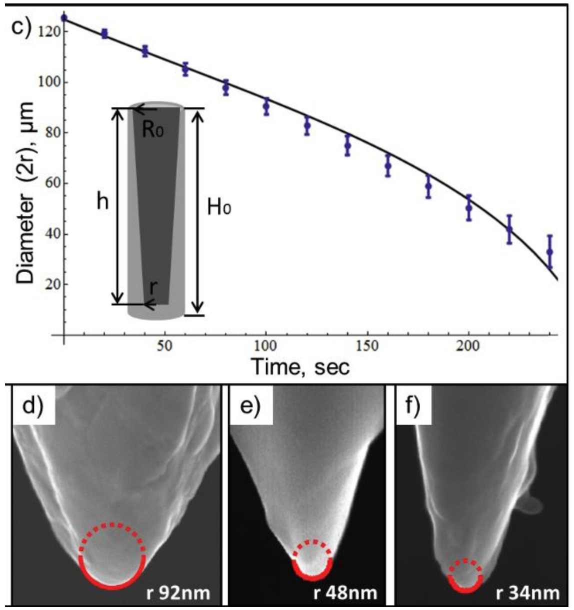


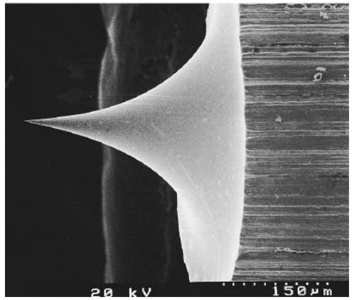


Rev. Sci. Instrum.85 (2014) 095109

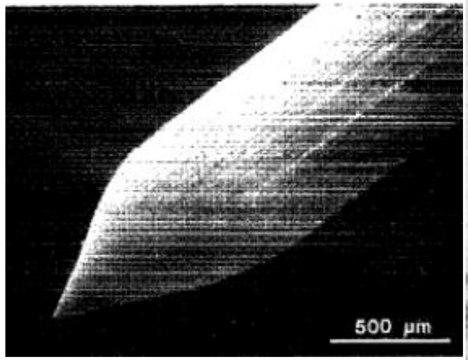


Tungsten: NaOH, KOH; Pt-Ir: alkali with cyanide additives

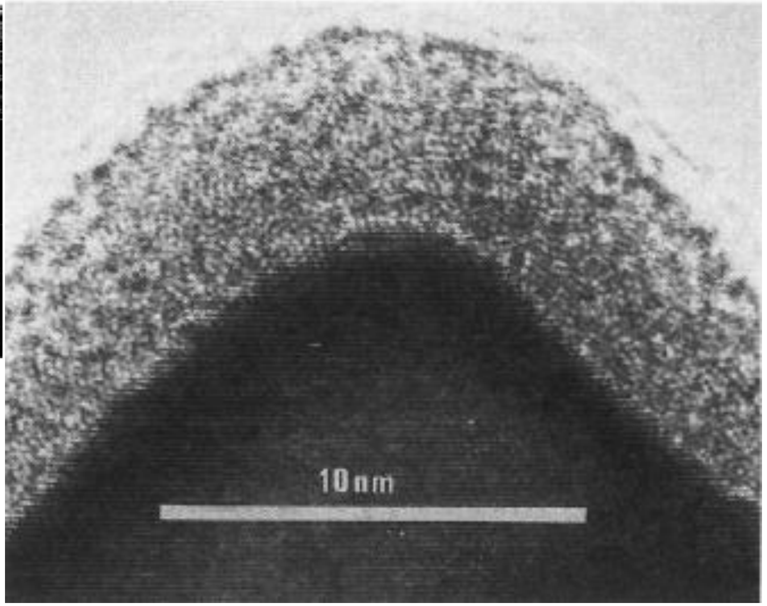




J.Vac.Sci.Technol.
B 14(1996)1



Rev.Sci.Instrum.
64 (1993) 159



Nanotechnology
24(2013) 355702

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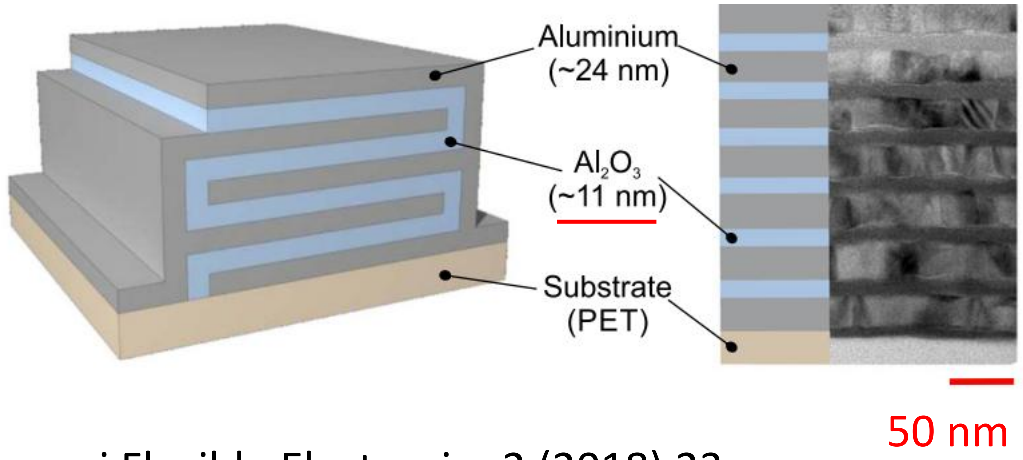
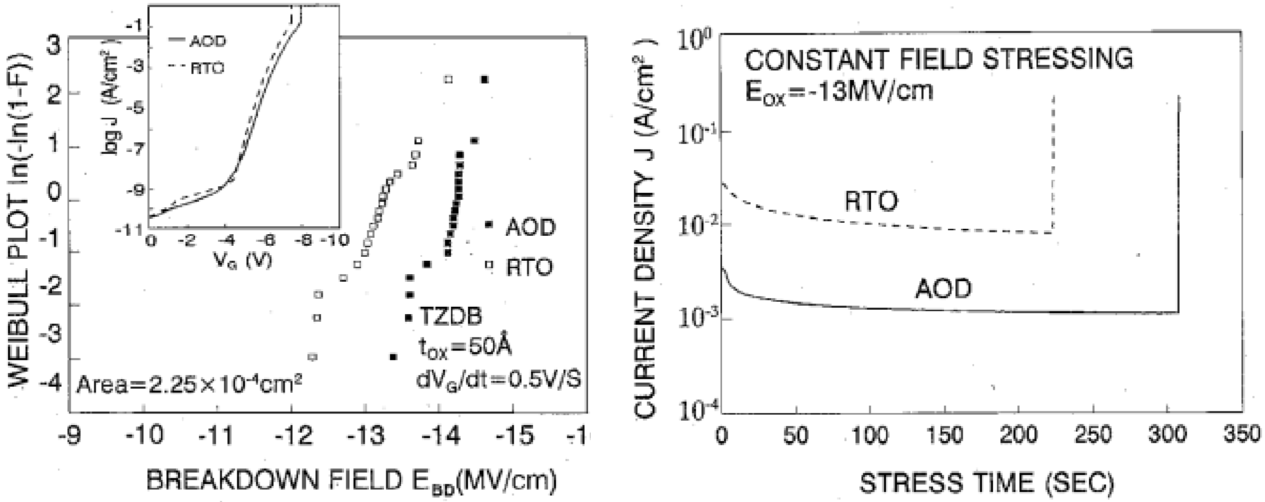
Anodization (oxidation with formation of insoluble products)



npj Flexible Electronics 2 (2018) 23

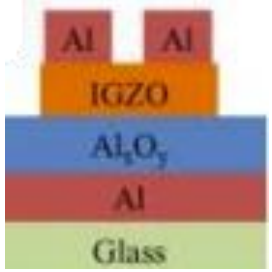
Comparison of anodization + rapid thermal densification (ADO) and rapid thermal oxidation (RTO):



IEE Electron Device Lett. 17 (1996) 575

Device	A	B	C
Anodization voltage (V)	1.54	2.30	3.08
Approximate Al_xO_y thickness (nm)	2	3	4
C/A (nF/cm²)	1100	1000	875
Current on/off ratio	7.2×10^5	1.6×10^6	2.1×10^6
SS (mV/dec)	75	68	70
D_{it} (cm⁻² eV⁻¹)	1.7×10^{12}	8.5×10^{11}	9.2×10^{11}
RMS roughness (nm)	1.58	1.54	1.53
V_{TH} (V)	0.52	0.48	0.51
μ (cm²/Vs)	~ 4.3	~ 5.4	~ 3.5

IEE Electron Device Lett. 39 (2018) 375



- Anodic oxides can contain water (more for Al and Si, than for Ta, Nb, etc.).
- Anodic oxides formation cannot be done at constant potential because of essential Ohmic contribution.
- However it can be done at room temperature.

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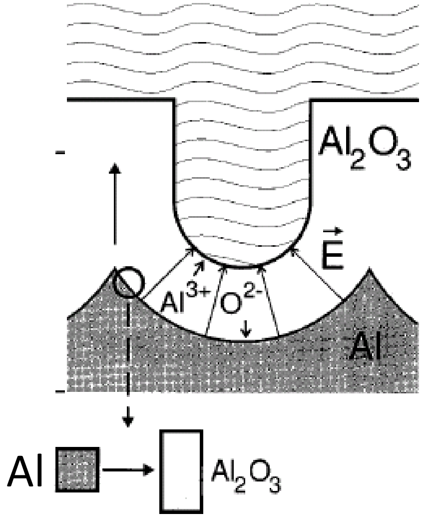
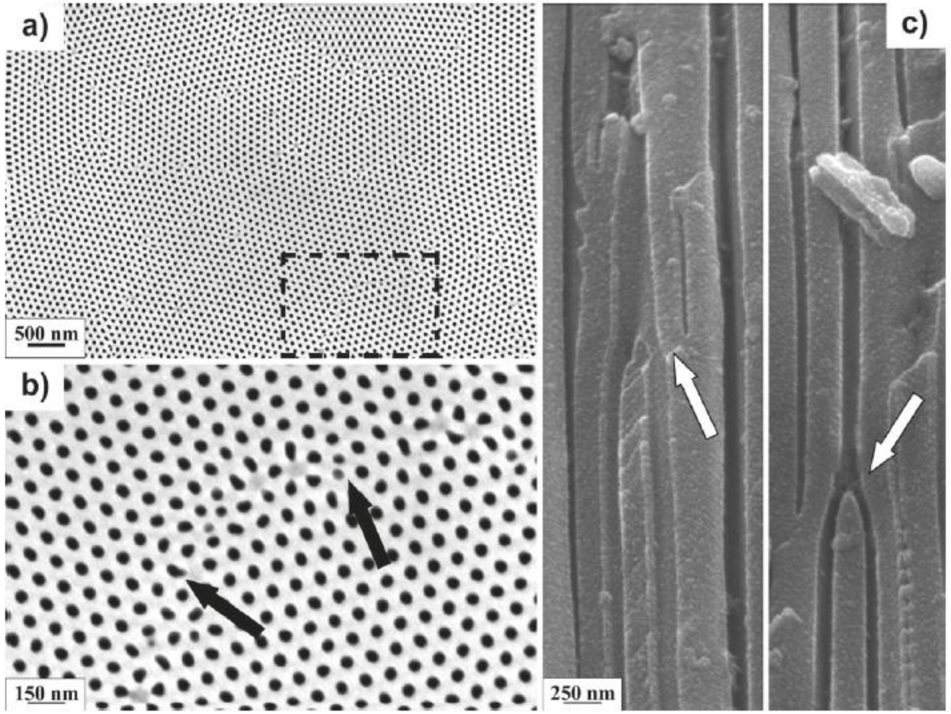
Anodization, ordered arrays of pores in aluminum oxide

Al oxide (AAO) is already commercialized,

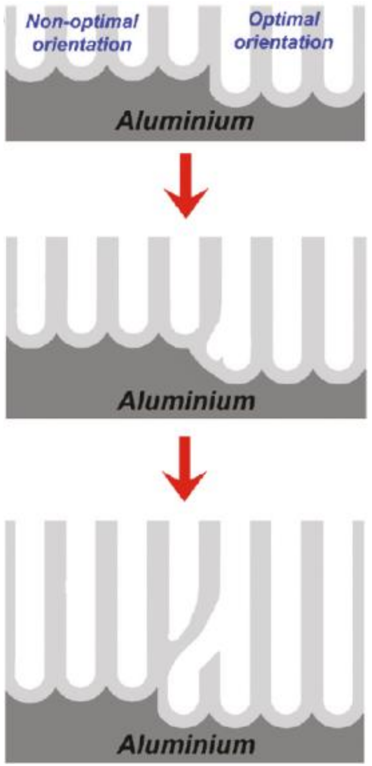
but for templating we still need home-made.

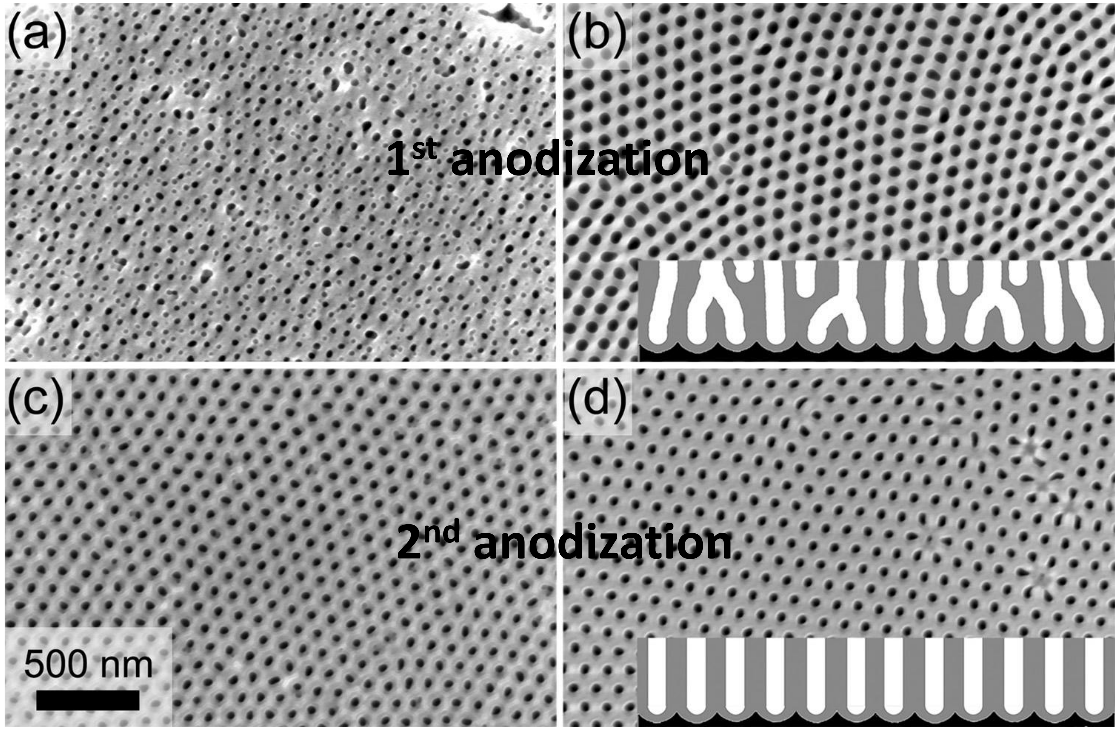
SPI Supplies	Pore Geometries for Isotropic AAO Membranes					
Parameter						Tolerance
Pore Diameter (nm)	10	20	40	100	200	±(10%+2nm)
Pore Period (nm)	26	44	107	250	470	±(15%+5nm)
Pore Density (cm-2)	$1.6\cdot10^{11}$	$5.8\cdot10^{10}$	$1.0\cdot10^{10}$	$2\cdot10^{9}$	$5\cdot10^{8}$	±20%
Porosity (%)	12	12	12	15	15	±3





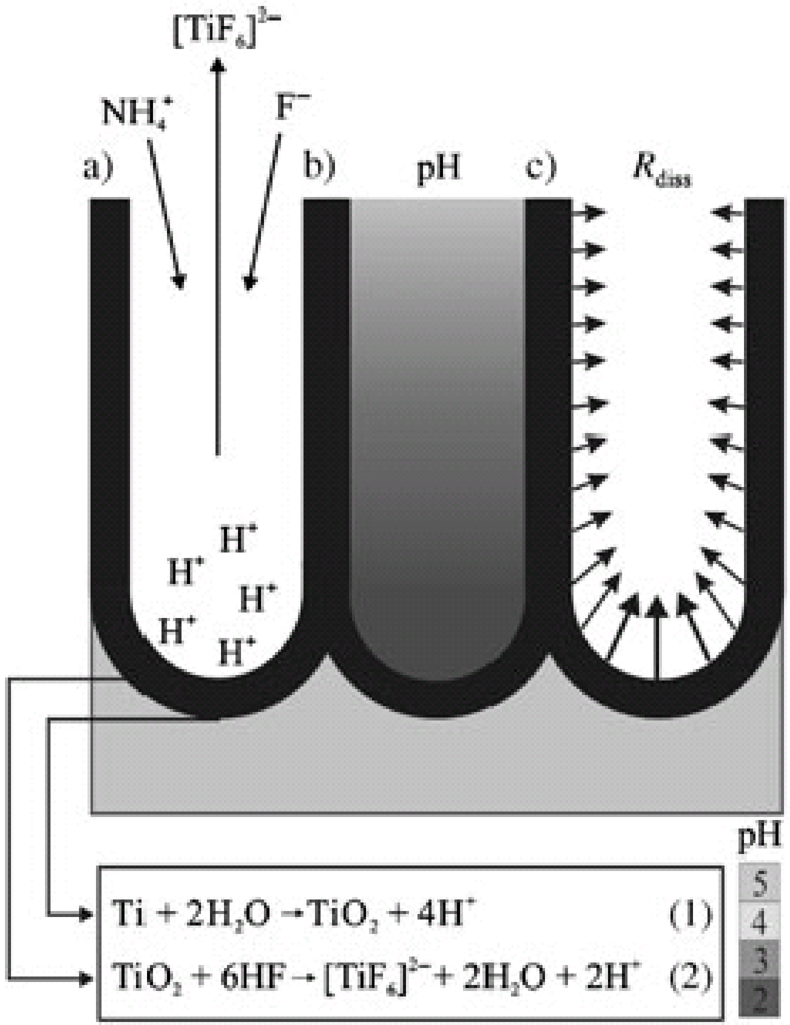
J. Phys. Chem. C 115 (2011) 23726

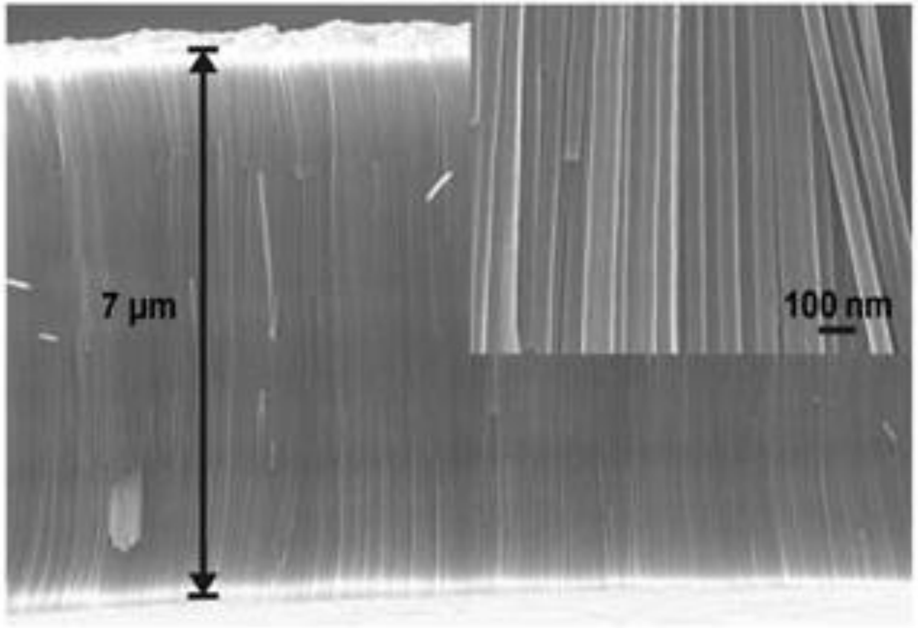


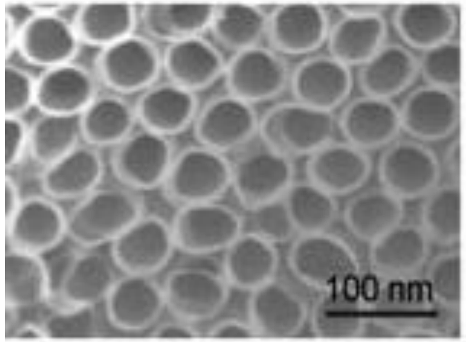


Electrochim. Acta 226 (2017) 60

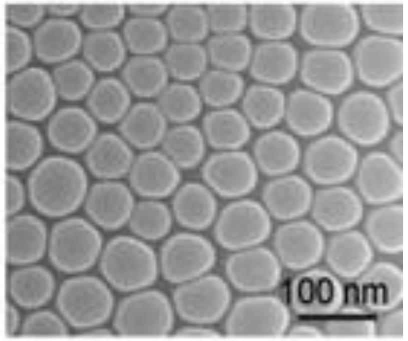
Anodization, less ordered pores in titanum oxide





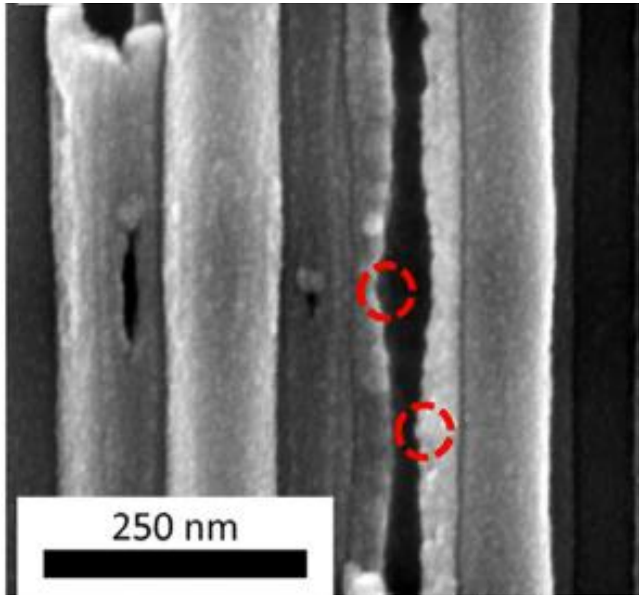


d)



External surface

Bottom



1D photonic crystals:
periodically varied pore diameter

Scripta Mater. 178 (2020) 13

Angew. Chem. Int. Ed. 44 (2005) 7463

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To conclude:

- useful **nm-size** fragments can be fabricated by electrochemical room-temperature techniques;

- some of them can be assembled to obtain useful devices;

- many useful things can be done in **μm-size** scale;

- controllability can be further increased, by involving the knowledge of electrochemical kinetics.