Forum *Romanians in Micro- and Nanoelectronics,* *7 November 2018, Romanian Academy, Bucharest, Romania*

Nanoarchitectonics with Silicon Nanowires

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Nanoarchitectonics

- Overview

Nanoarchitectonics with silicon nanowires

- Synthesis
- Applications

Silicon nanowires for Li-ion batteries

- Fabrication of anodes for Li-ion batteries with silicon nanowires
- Lithiathion of silicon nanowires

Nanoarchitectonics

A technology enabling the ordering of nanoscale structural units, which are usually a group of atoms or molecules, in an intended configuration

Nano-synthesis

Synthesis of novel materials not existing in Nature [*e.g.* silicene]

Nano-organization

Development of nanoelectronic circuits [*e.g.* silicene-based circuits]

Richard Feynman [1959] "There's plenty of room at the bottom" – Nanotechnology
Jean-Marie Lehn [1995] "There's even more room at the top" – Supramolecular technology

Nanoarchitectonics with Si nanowires [SiNWs]

VLS [Vapour Liquid Solid]

CVD [Chemical Vapour Deposition]

LCG [Laser-ablation Catalytic Growth]

Low-temperature VLS

FLS [Fluid Liquid Solid]

SLS [Solution Liquid Solid]

OAG [Oxide Assisted Growth]

…

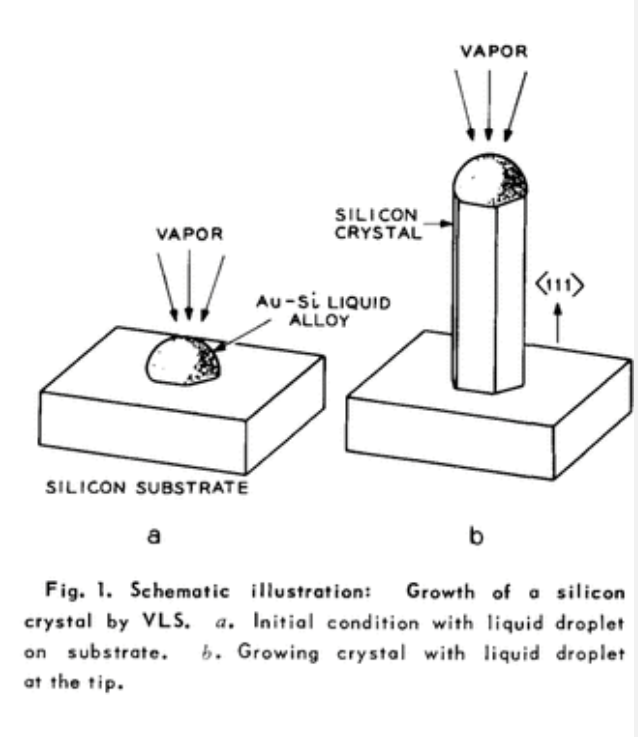
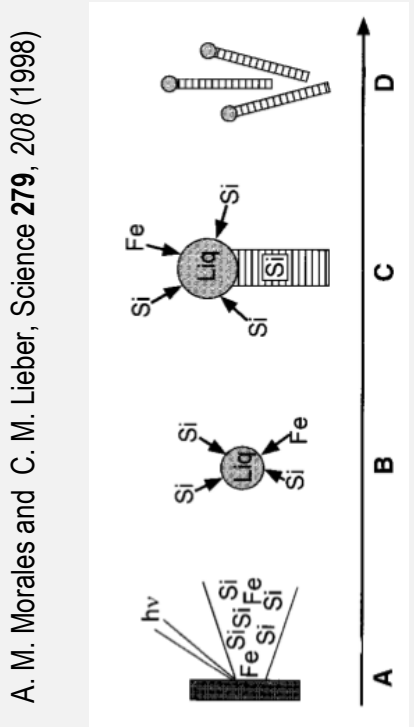
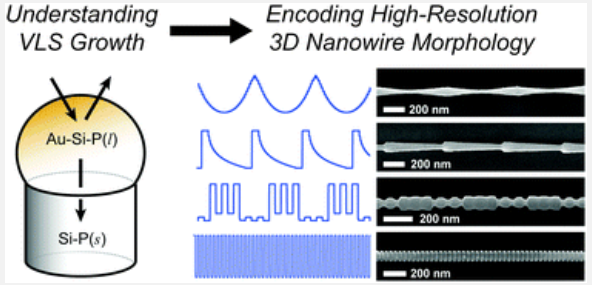


Fig. 1. Schematic illustration: Growth of a silicon crystal by VLS. *a*. Initial condition with liquid droplet on substrate. *b*. Growing crystal with liquid droplet at the tip.

R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, *89* (1964)

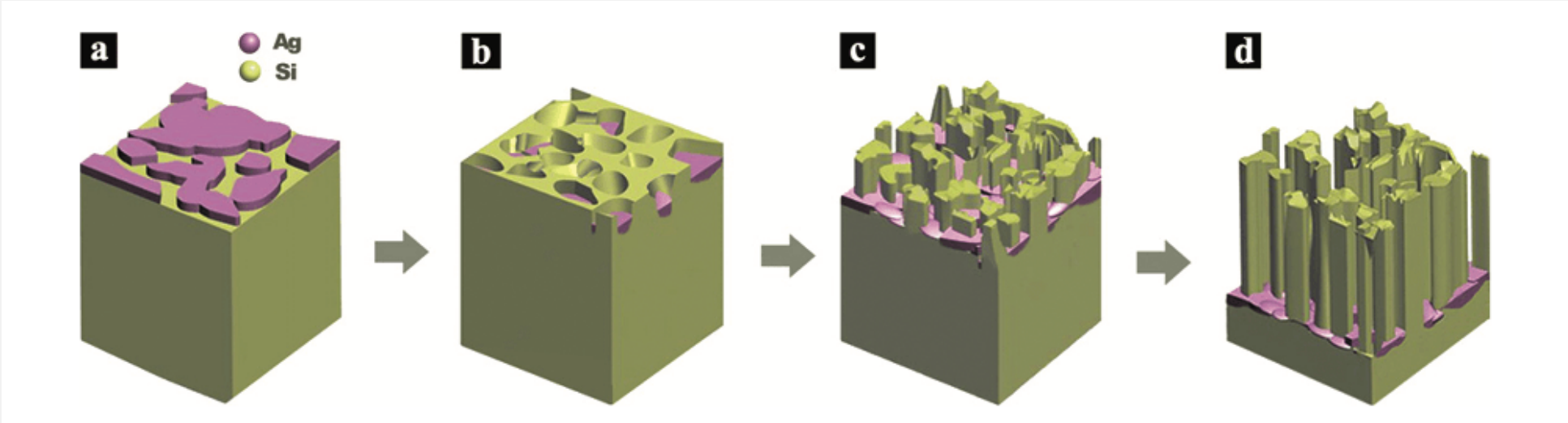




C. W. Pinion *et al.*, J. Mater. Chem. C **4**, 3*890* (2016)

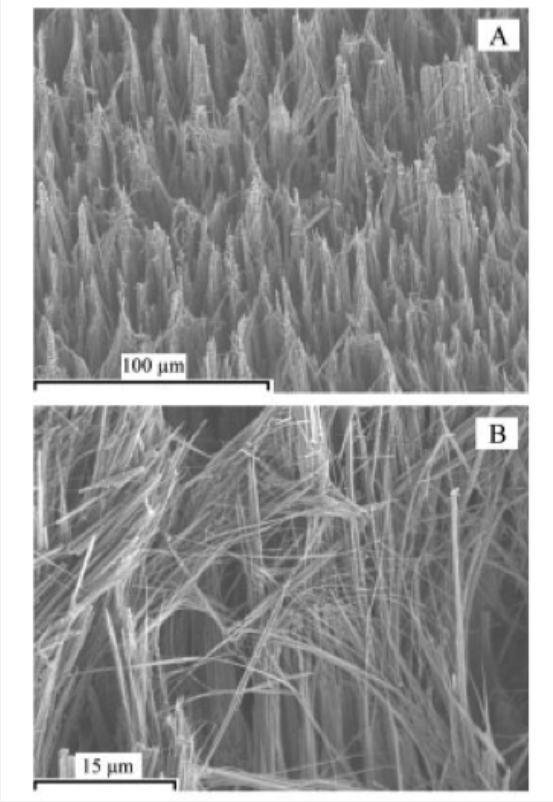
Nanoarchitectonics with Si nanowires [SiNWs]

H. Fang *et al.*, Nanotechnology **17**, *3768* (2006)

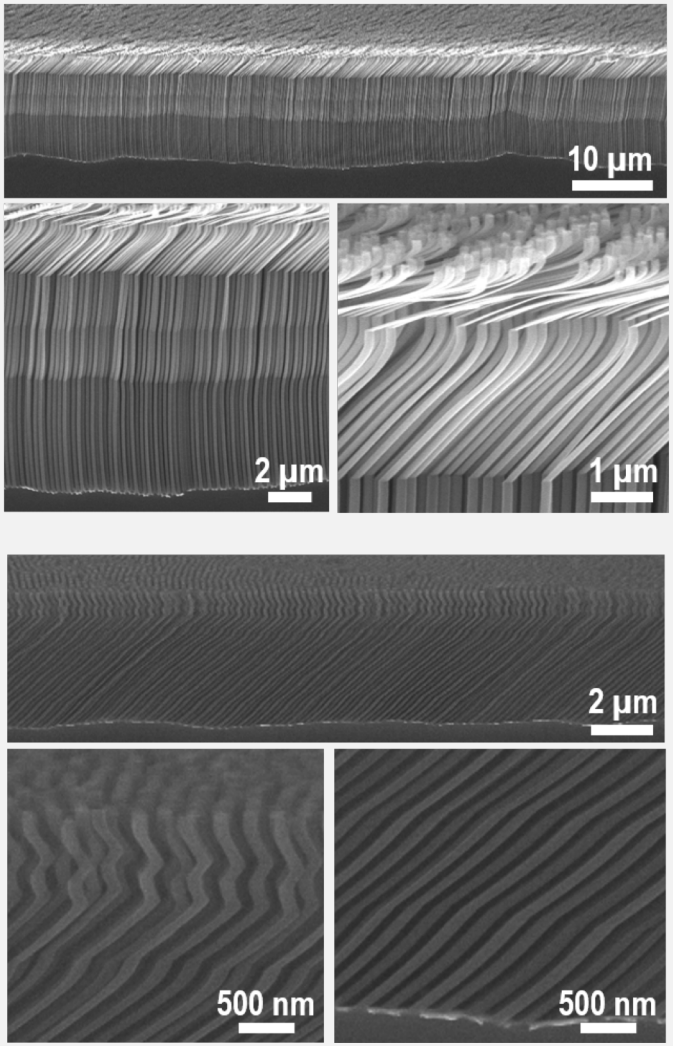


D. McIntosh, J. Phys. Chem. **6**, *15* (1902): Catalytic decomposition of H_2O_2

Nanoarchitectonics with Si nanowires [SiNWs]

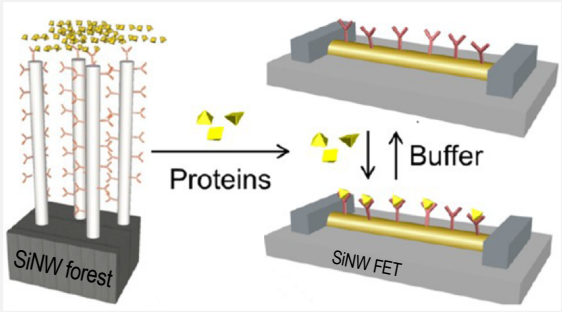


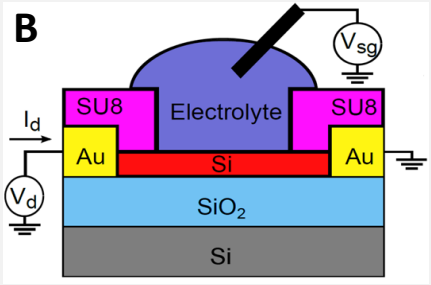
K.-Q. Peng *et al.*, Adv. Mater. **14**, *1164* (2002)

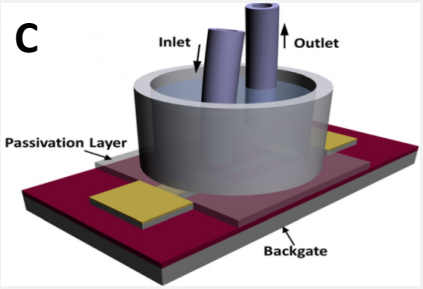


G. Sandu *et al.*, coming soon

Biosensing

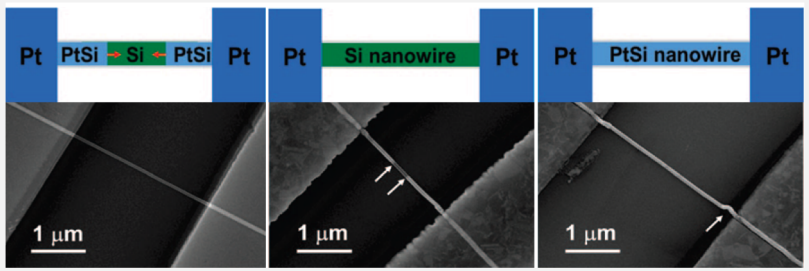




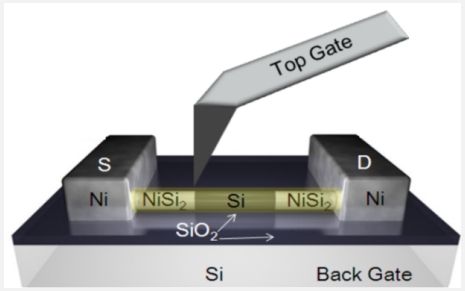


V. Krivitsky *et al.*, Nano Lett. **12**, *4748* (2012) N. K. Rajan *et al.*, APL **98**, *264107* (2011) Q. Guo *et al.*, APL **101**, *093704* (2012)

Nano Electronics

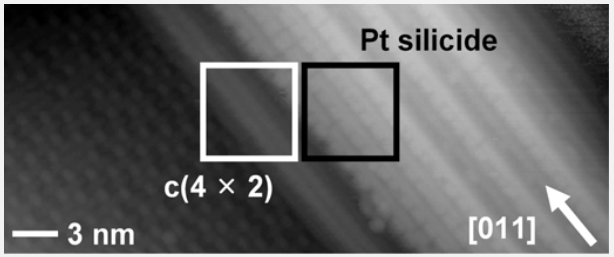


Y. C. Lin *et al.*, Nano Lett. **8**, *913* (2008)

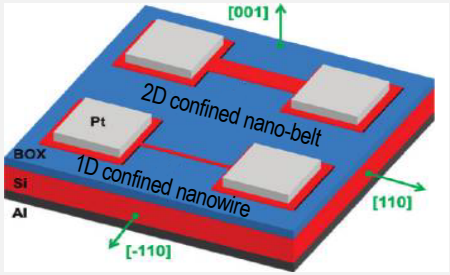


D. Martin *et al.*, PRL **107**, *216807* (2011)

Quantum Technology

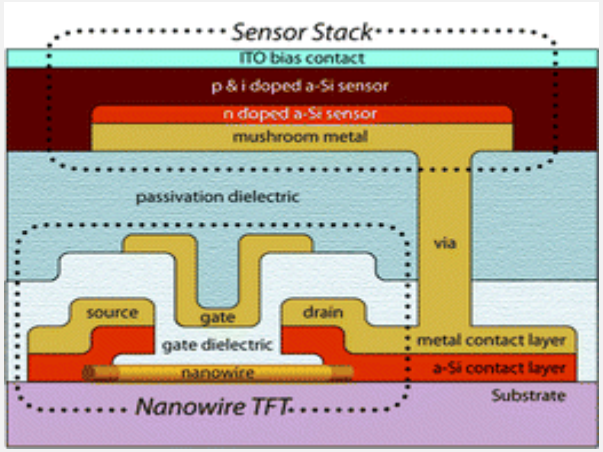


D. K. Lim *et al.*, Nanotechnology **18**, *095706* (2007)



K. Trivedi *et al.*, Nano Lett. **11,** *1412* (2011)

A



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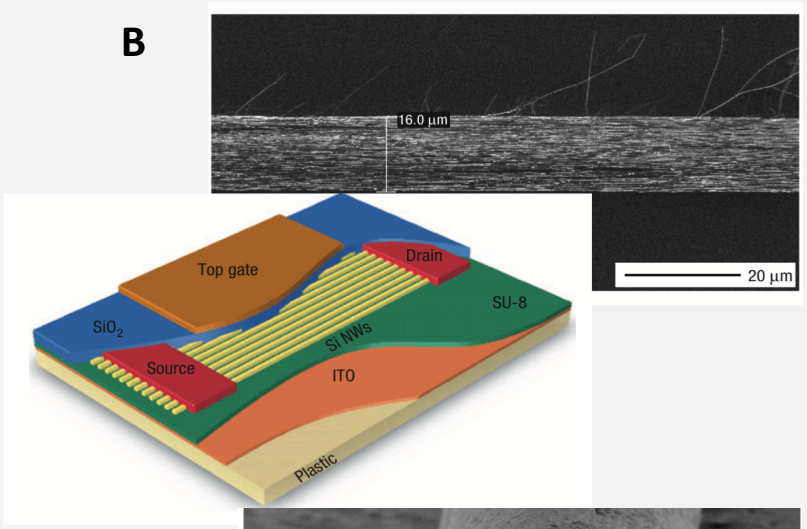

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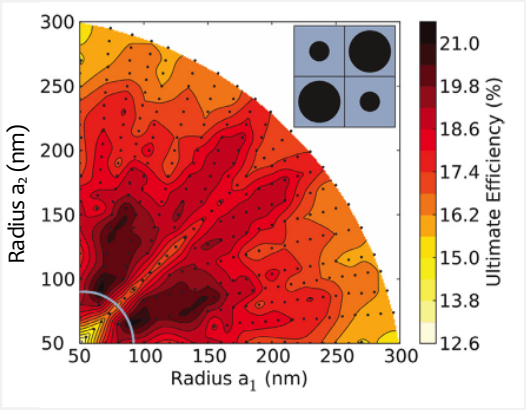
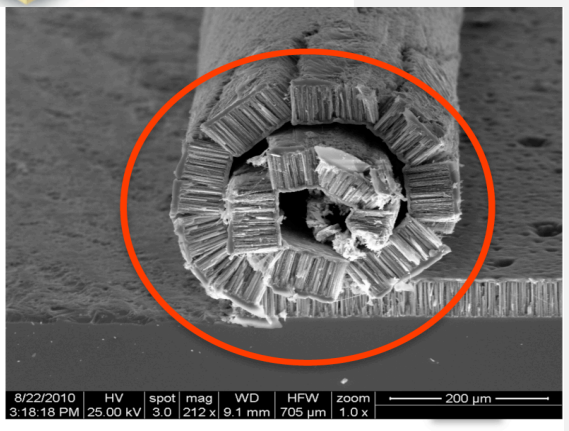


D



[**A**] W. S. Wong *et al.,* Nano Lett. **11**, *2214* (2011)
[**C**] P. Yu *et al.,* Nano Today **11**, *704* (2016)

[**B**] M. C. McAlpine *et al*., Nat. Mater. **6**, *379* (2007)
[**D**] A. Vlad *et al*., PNAS **109**, *15168* (2012)

$_xLi^+ + _xe^- + Si \longrightarrow Li_xSi$ [x ≈ 3.75 at room temperature]

☑ ≈ 3600 mAh/g ≈ 8300 mAh/cm^3
☑ ≈ 0.2 V *vs.* Li/Li$^+$
☑ abundant & low cost

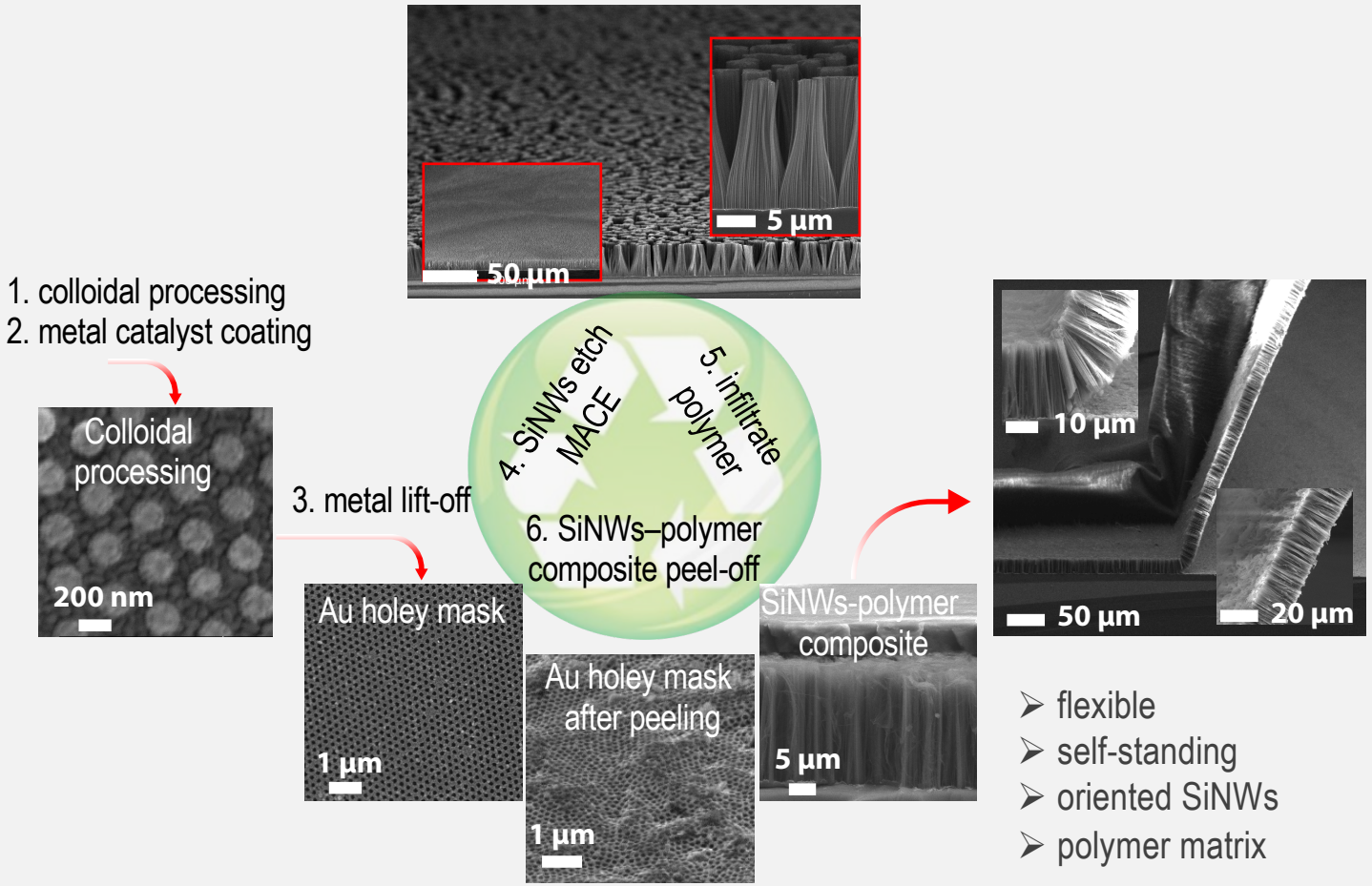
☒ ≈ 300% volume expansion during lithiation & fracture & pulverization
☒ poor solid-electrolyte interphase [SEI] & low electronic conductivity
☒ limited cycling stability under real life battery operation conditions

thesis

Nat. Nanotechnol. **9**, *327* (2014)

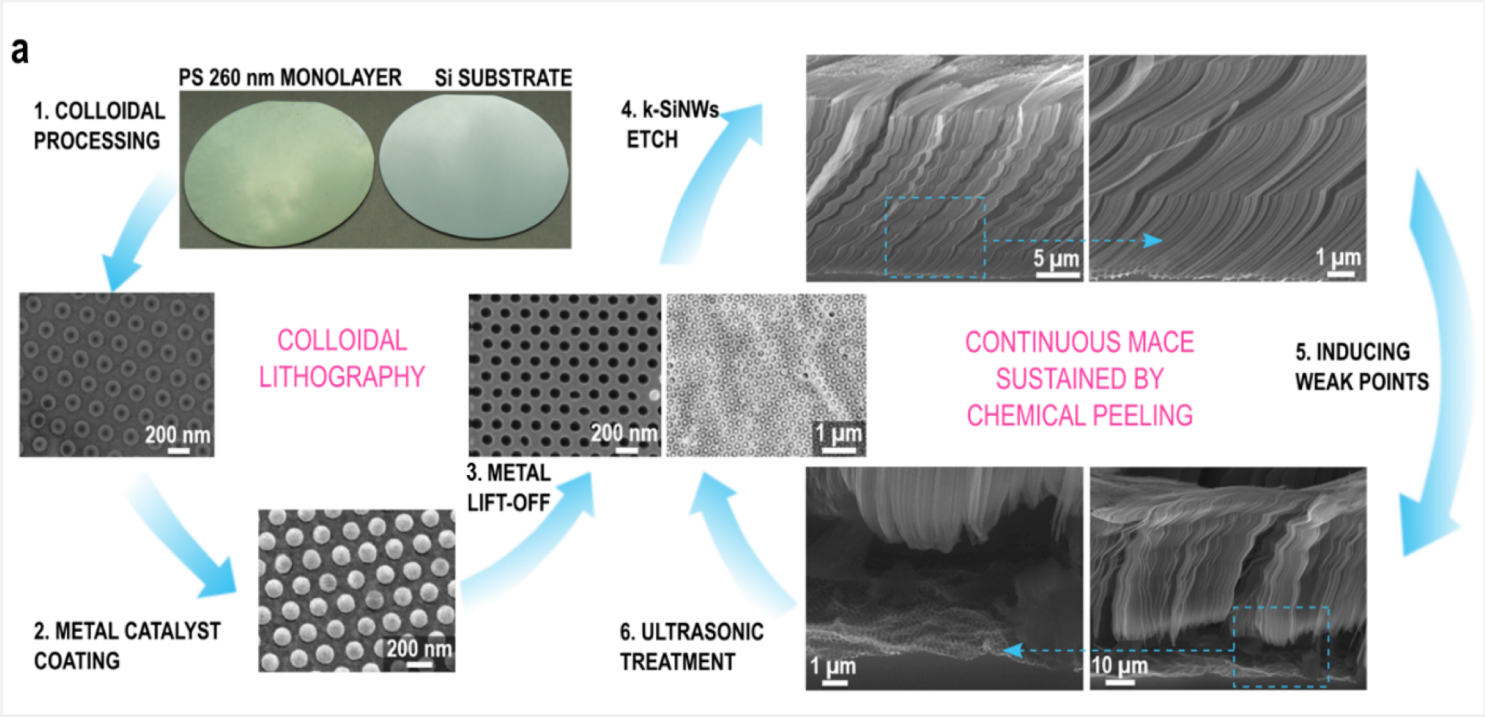
Driving change in the battery industry

High-capacity silicon anodes could improve the performance of lithium-ion batteries for electric vehicles, but their cyclability has been limited. **Christian Martin** analyses recent progress in nanoscale engineering that addresses this shortcoming.

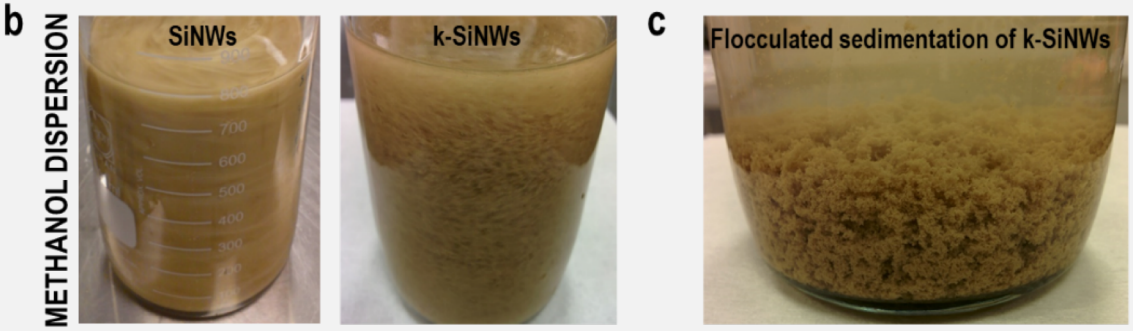


PNAS **109**, *15168* (2012): Metal-assisted chemical etching [MACE] high-throughput SiNWs processing

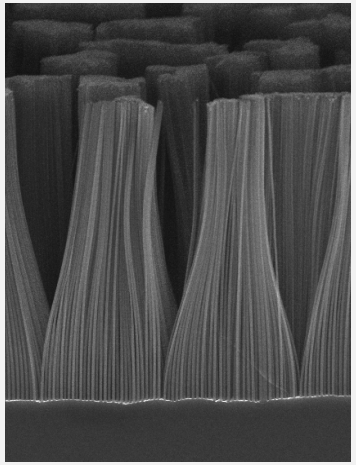
Kinked silicon nanowires [k-SiNWs]



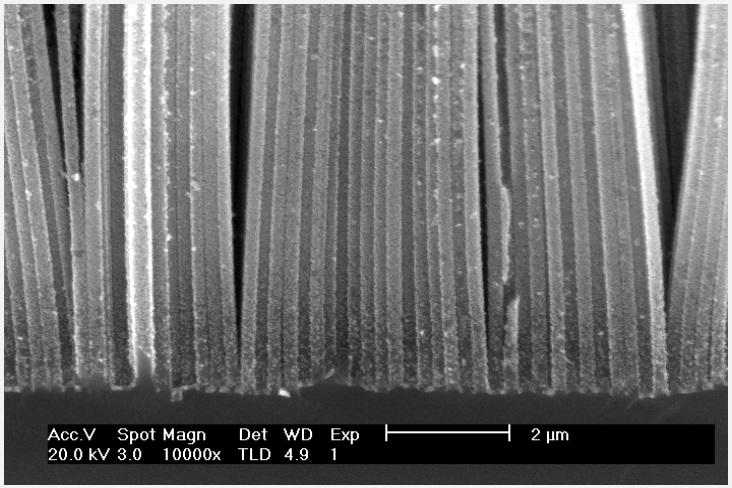
SiNWs *vs* k-SiNWs

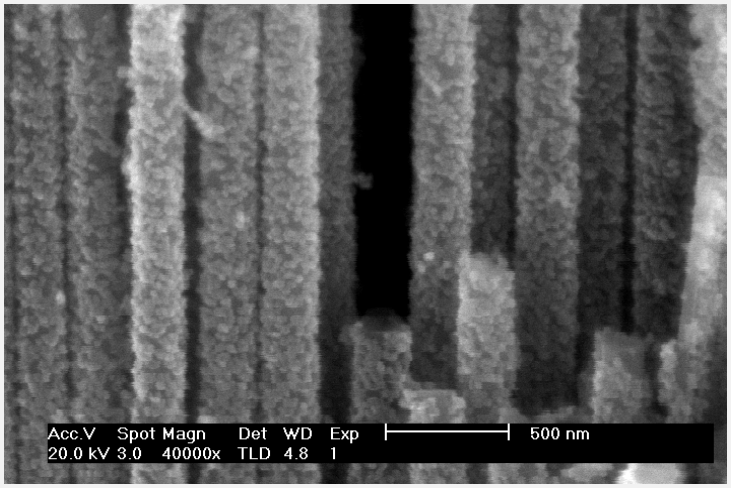


Sci. Rep. **8,** *9794* (2018)

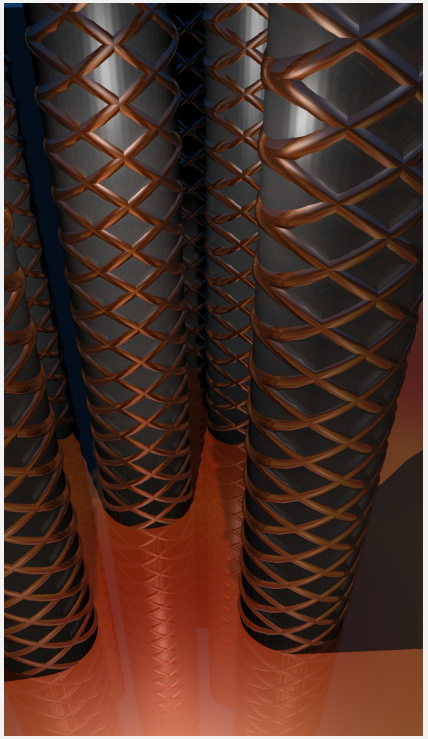


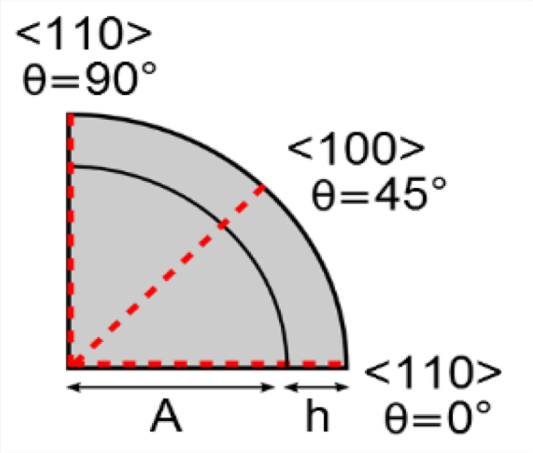
Sputtering, electron-beam physical vapor deposition, *etc* are too directional

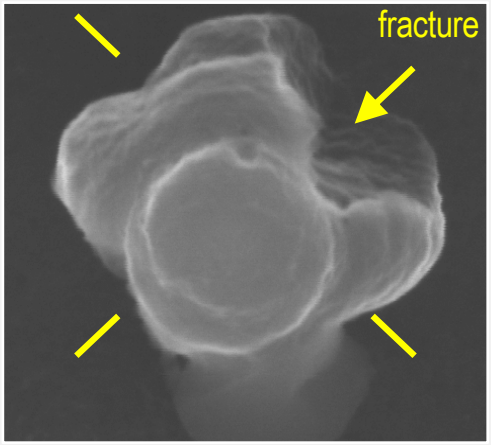




Electroless plating







Ø = 2A = 480 nm
h = 0 nm
h/A = 0

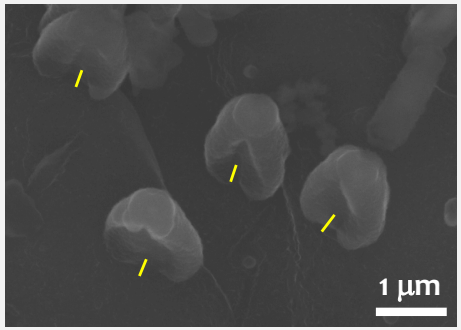
Swelling: ***Anisotropic***

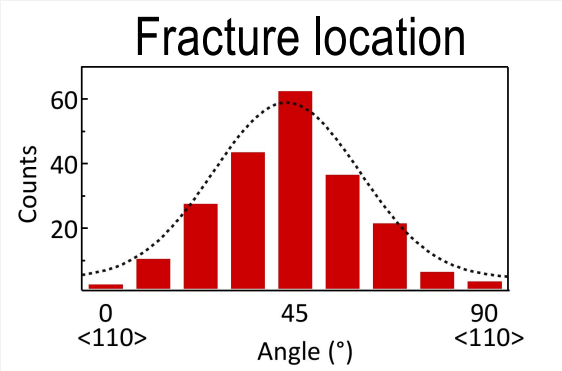
Fracture: **Along {100}**

$Si_{2A}@Ni_h$

A – Si core radius

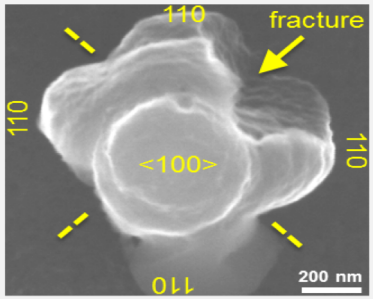
h – Ni shell thickness





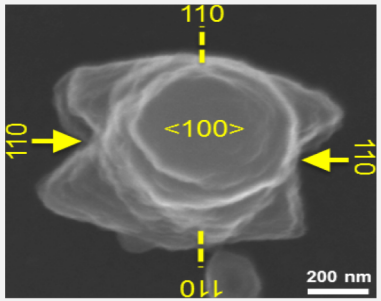
consistent with previous reports: Nano Lett. **11**, *3312* (2011); Adv. Mater. **23**, *1563* (2011); Nano Lett. **11**, *3034* (2011); PNAS **109**, *4080* (2012)

$Si_{480}@Ni_0$



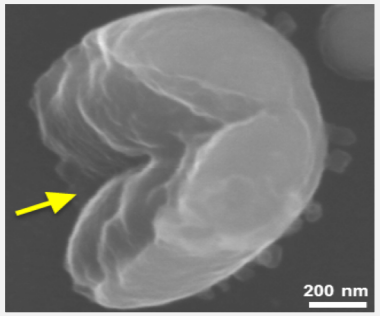
h/A = 0
Swelling: **Anisotropic**
Cracks: **{100}**

$Si_{480}@Ni_{40}$



h/A = 1/3 to h/A = 1/6
Swelling: **Anisotropic**
Cracks: **{110}**

$Si_{480}@Ni_{120}$



h/A = 1/2
Swelling: **Isotropic**
Cracks: **Random**

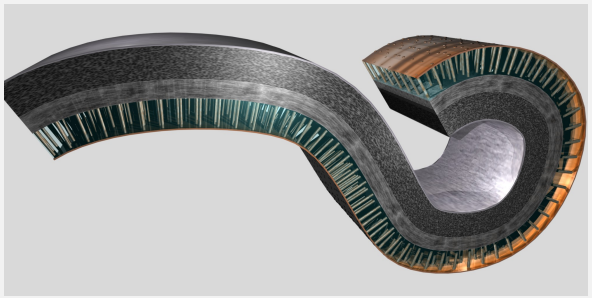
- **Lithium transport**
  - Li_xSi ~10^{-12} – 10^{-14} cm^2/s
  - Ni ~10^{-9} – 10^{-11} cm^2/s

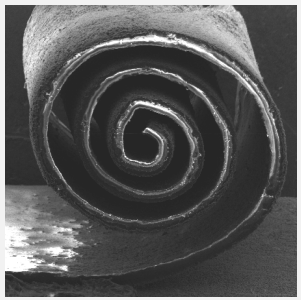
Not a diffusion limited process!

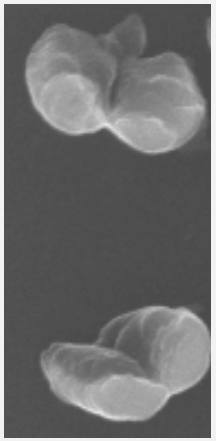
- **Buffering effect of the Ni coating**
  - $V_{<110>}$ / $V_{<100>}$

- Si Nanowires for Li-ion Battery Anodes:
  flexible design, high areal mass loading, aqueous binder formulation
- Enhanced Performances of Si@Cu and Si@Ni Nanowires:
  better metal-polymer interface
- Ni Shell Mediated Swelling in Si@Ni Nanowires:
  transition from anisotropic to isotropic fracture
- **The isotropic single fracture regime is desirable as it resembles the thin-film configuration on a metallic Ni substrate**

PNAS **109**, *15168* (2012)
ACS Nano **8**, *9427* (2014)
ACS Appl. Mater. Interfaces **9**, *34865* (2017)
Sci. Rep. **8,** *9794* (2018)







Thank you for your attention!

Many thanks

S. Blanco Alvarez, D. Caina, F. Chaltin, C.A. Duțu,
P.O. Mouthuy, G. Sandu, D.A. Serban, A. Vlad, R. Ye
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