Fabrication and nanomanipulation of nanowires for basic science and applications

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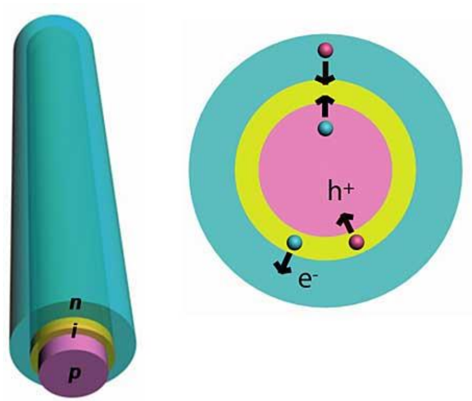
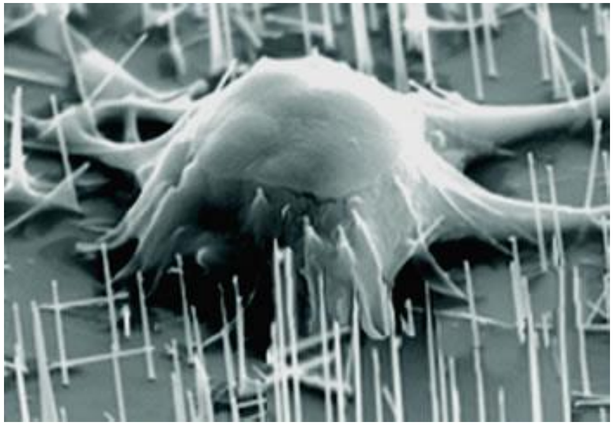
Nano Innovation 2016 Rome, 20-23 September
Conference & Exhibition

Motivation

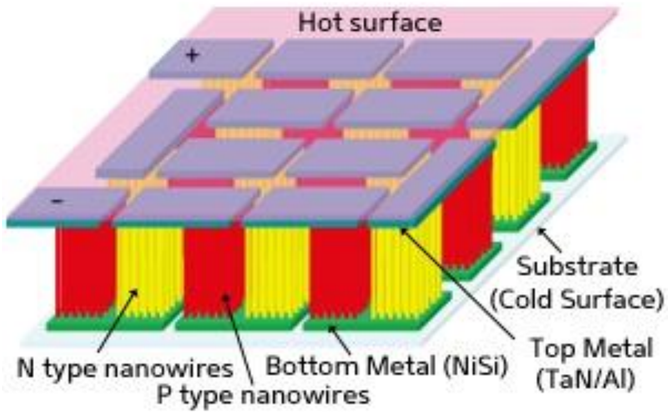
Energy Harvesting



Bio-sensing



Thermoelectric Devices



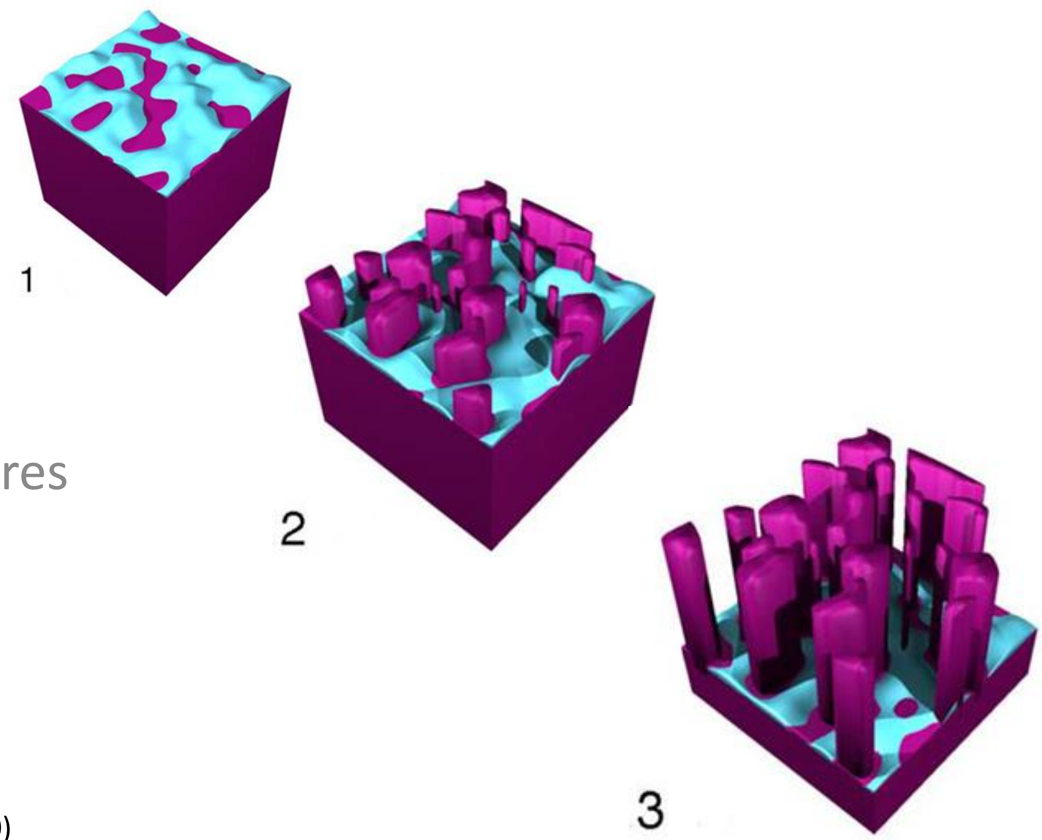
Energy Storage

Introduction

Metal Assisted Chemical Etching on Silicon

MACE was first observed by Li and Bohn*

- Low-cost process
- Precise tuning of
  - Length
  - Crystalline orientation
- High crystalline quality
- High aspect ration of structures
- Porosity depends on
  - Etching solution
  - Doping level

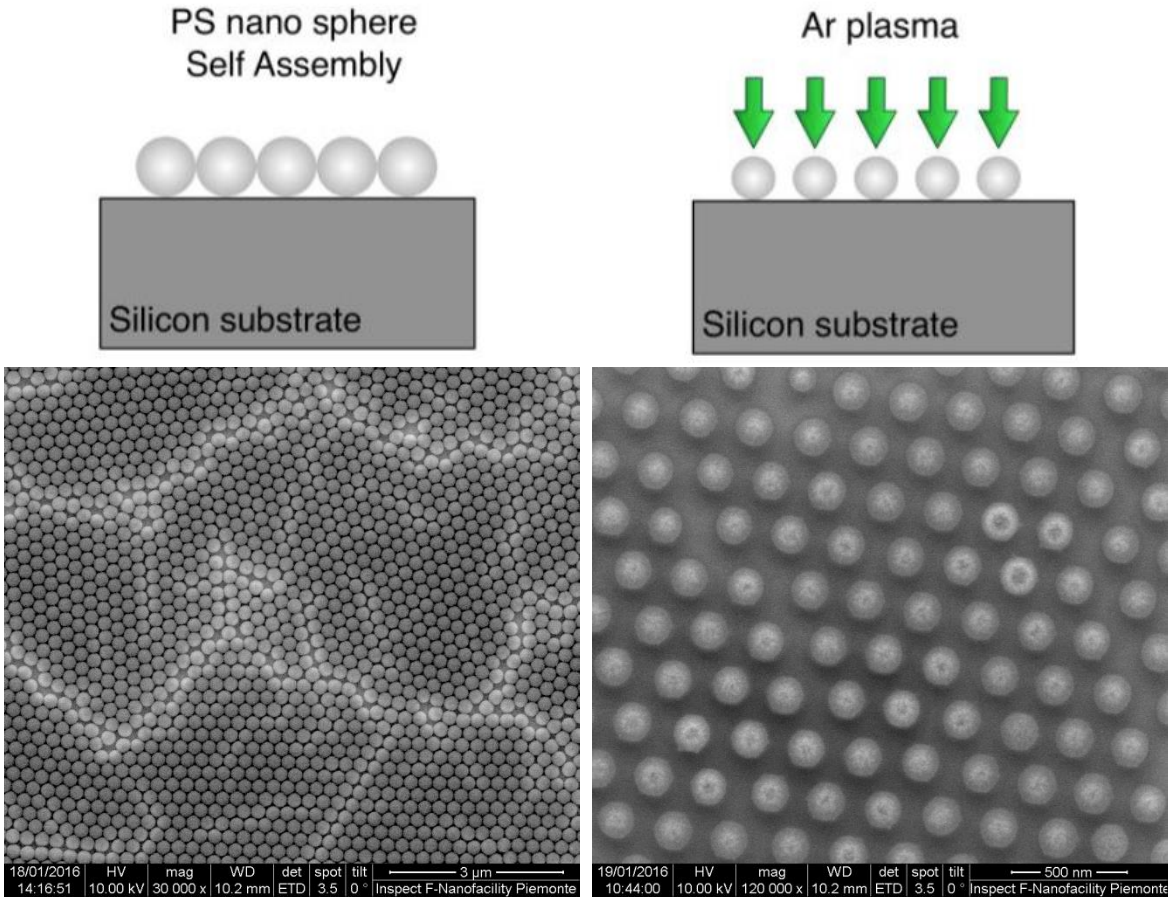


*X. Li and P. W. Bohn, Appl. Phys. Lett. **77**, 2572 (2000)

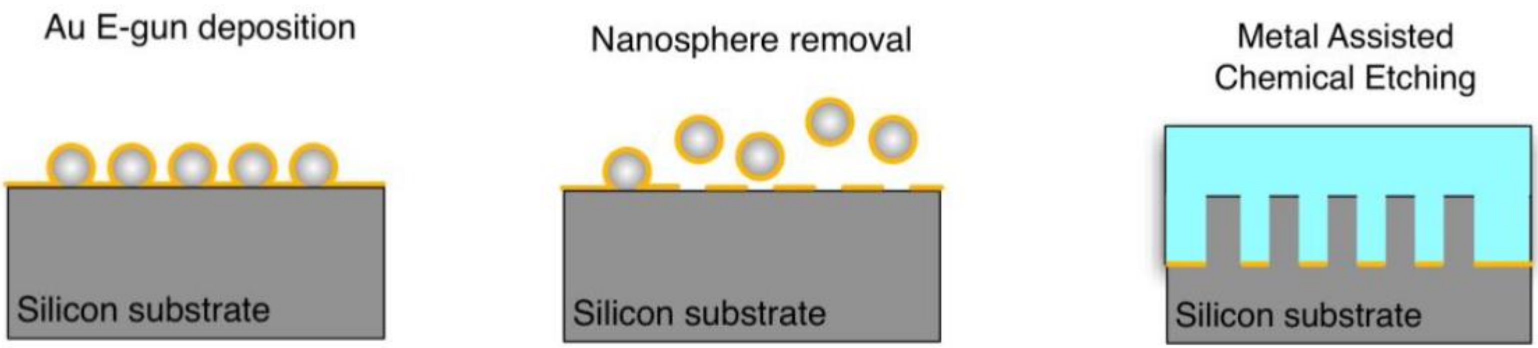
Fabrication

NanoSpheres Lithography

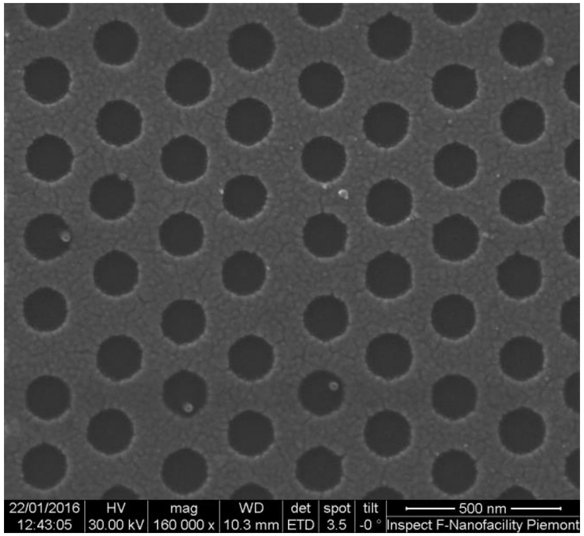
- Functionalisation: piranha solution
- hcp monolayer of polystyrene nano spheres: original diameter 260 nm
- Plasma etching (Ar 75 W): final diameter 130 nm

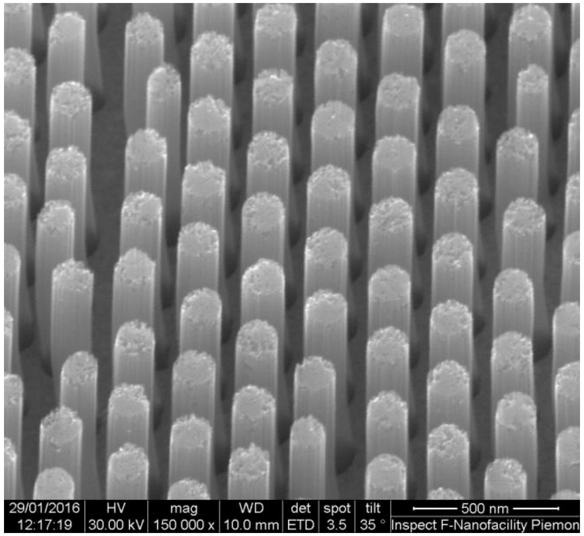


Anti-dot Mask and MACE



- E-beam evaporation: 20 nm of Au
- Lift-off
- Anti-dot mask
- MACE: $HF:H_2O_2:H_2O=3:1:1$

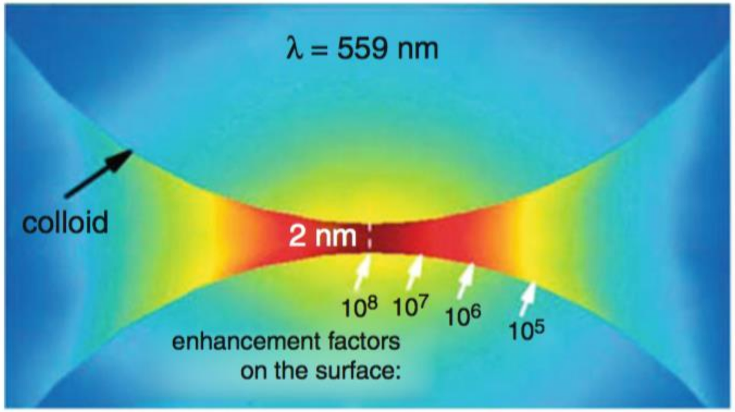




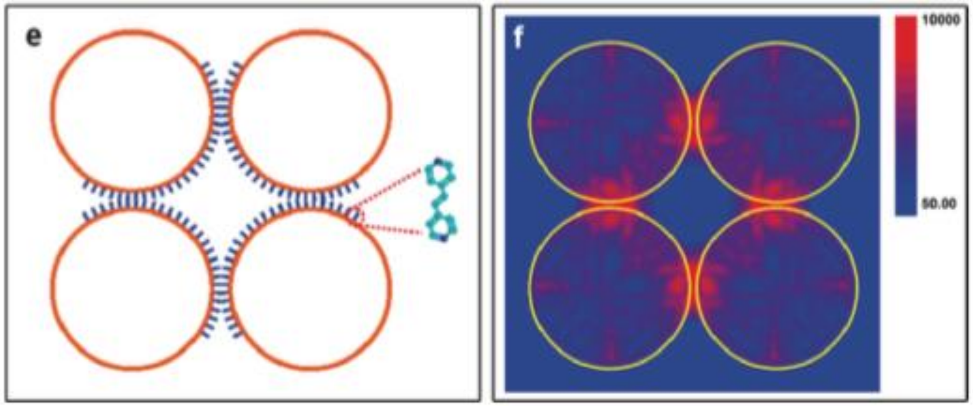
Surface Enhanced Raman Scattering (SERS) phenomenon

- Amplification of Raman signal
- Mainly based on the em field enhancement occurring preferentially in gaps or sharp features at the surface of noble metals.
- Particularly large em field is found in hot spots, in between metal nanostructure separated by a few nanometers

Goal: engineering hot spots



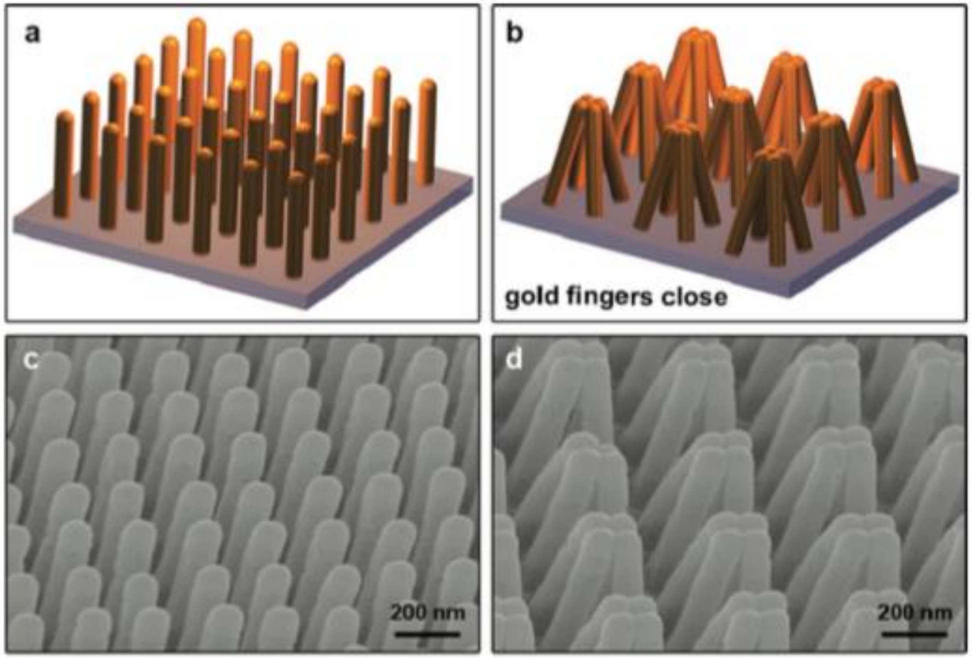
Etchegoin, PG, Le Ru EC. Phys Chem Chem Phys (2008) 10(40):6079-6089



Hu, M et al. JACS (2010) 132(37):12820-12822

SERS substrate

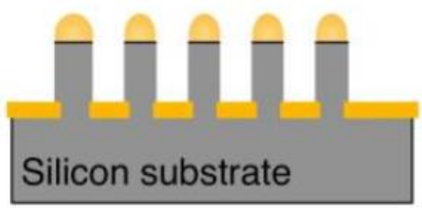
- Substrate fabrication is a critical issue for controlling hot spots.
- Reproducibility and uniformity VS enhancement.
- New strategy: flexible coated nano pillars, self-closing ability.
- Various techniques: optical lithography, EBL, FIB, NIL



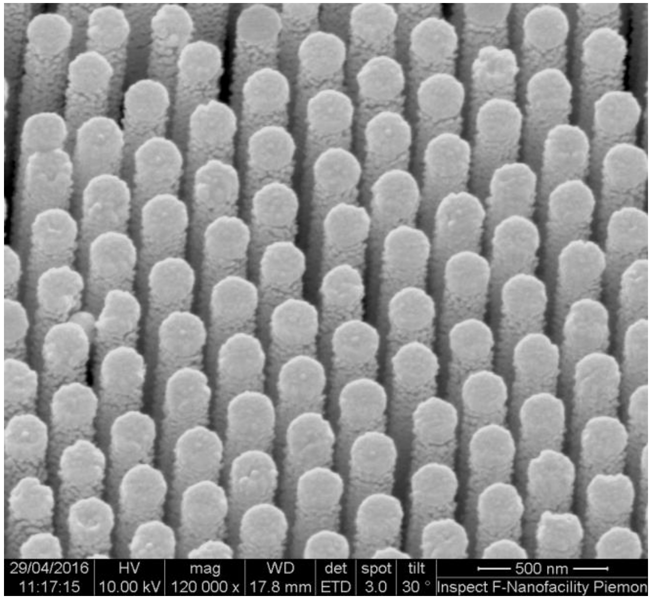
Hu, M et al. JACS (2010) 132(37):12820-12822

SERS substrate with our SiNWs

80 nm Au E-gun deposition



- Matrix of standing gold-capped SiNWs
- Tuning etching parameters (time, concentration) allows to control the length of SiNWs
- Aspect ratio: crucial parameter for flexibility



EMPIR project MetVBadBugs 15HLT01

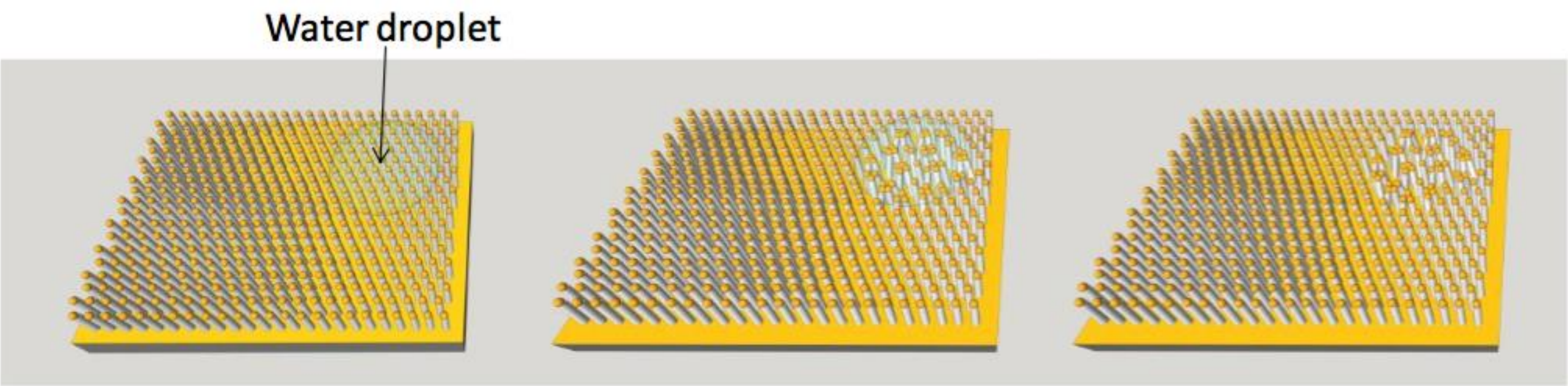
Applications

SERS substrate with our SiNWs

Capillary force during evaporation of water: leaning of flexible silicon nanowires

Aspect ratio 1:10 flexible

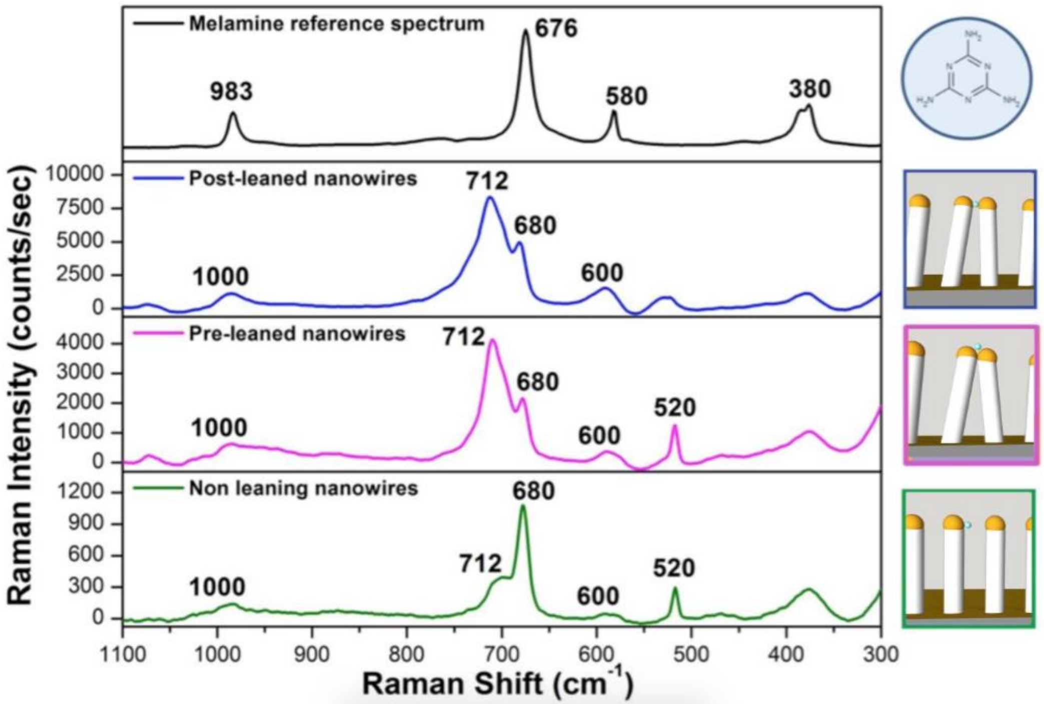
Aspect ratio 1:5 stiff



EMPIR project MetVBadBugs

15HLT01

SERS substrate with our SiNWs



EMPIR project MetVBadBugs

15HLT01

Applications

Use of Si nanowires in lithium-ion batteries

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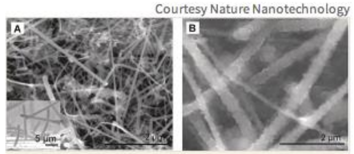
Stanford Report, December 18, 2007

Nanowire battery can hold 10 times the charge of existing lithium-ion battery

BY DAN STOBER

Courtesy Nature Nanotechnology



Photos taken by a scanning electron microscope of silicon nanowires before (left) and after (right) absorbing lithium. Both photos were taken at the same magnification. The work is described in "High-performance lithium battery anodes using silicon nanowires," published online Dec. 16 in *Nature Nanotechnology*.

Stanford researchers have found a way to use silicon nanowires to reinvent the rechargeable lithium-ion batteries that power laptops, iPods, video cameras, cell phones, and countless other devices.

The new technology, developed through research led by Yi Cui, assistant professor of materials science and engineering, produces 10 times the amount of electricity of existing lithium-ion, known as Li-ion, batteries. A laptop that now runs on battery for two hours could operate for 20 hours, a boon to ocean-hopping business travelers.

"It's not a small improvement," Cui said. "It's a revolutionary development."

nature nanotechnology

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Letter

Nature Nanotechnology **3**, 31 - 35 (2008)
Published online: 16 December 2007 | doi:10.1038/nnano.2007.411

Subject term: Electronic properties and devices

High-performance lithium battery anodes using silicon nanowires

Candace K. Chan[1], Hailin Peng[2], Gao Liu[3], Kevin McIlwrath[4], Xiao Feng Zhang[4], Robert A. Huggins[2] & Yi Cui[2]

There is great interest in developing rechargeable lithium batteries with higher energy capacity and longer cycle life for applications in portable electronic devices, electric vehicles and implantable medical devices[1]. Silicon is an attractive anode material for lithium batteries because it has a low discharge potential and the highest known theoretical charge capacity (4,200 mAh g^{-1}; ref. 2). Although this is more than ten times higher than existing graphite anodes and much larger than

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Applications

Ordered microwires as anode in lithium-ion batteries

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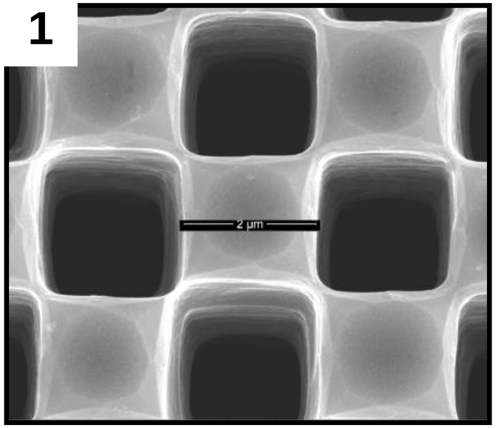

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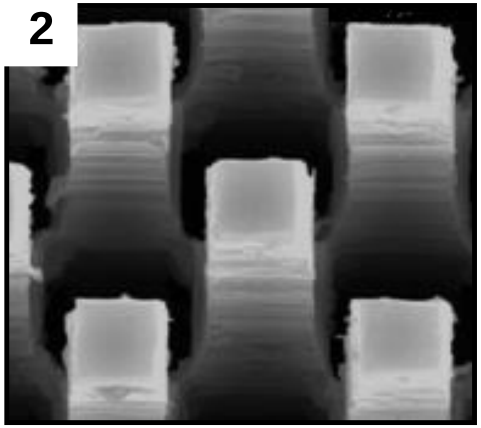
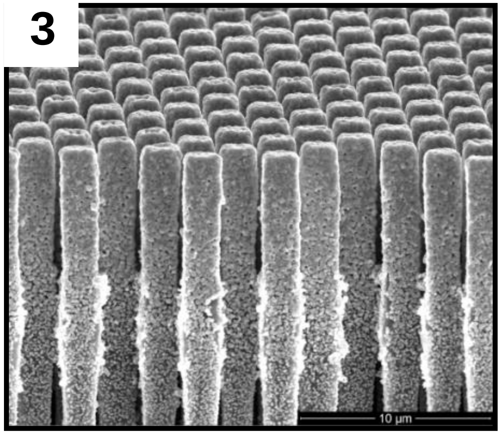


Images of the steps for the production of Si microwire array anodes

1. Electrochemical etching of pores
2. Chemical over-etching of the pore walls to get microwires

3. Deposition of a Cu seed layer
4. Electrochemical deposition of Cu

3


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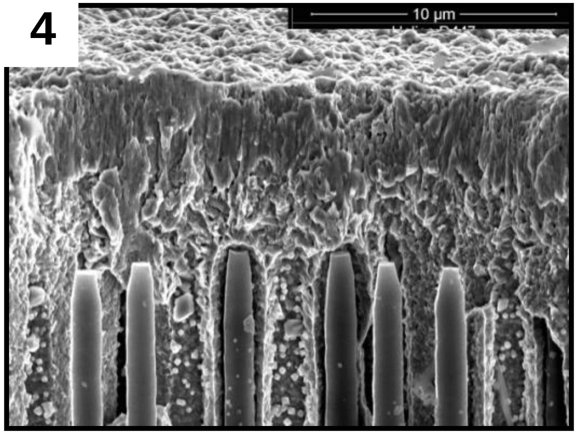
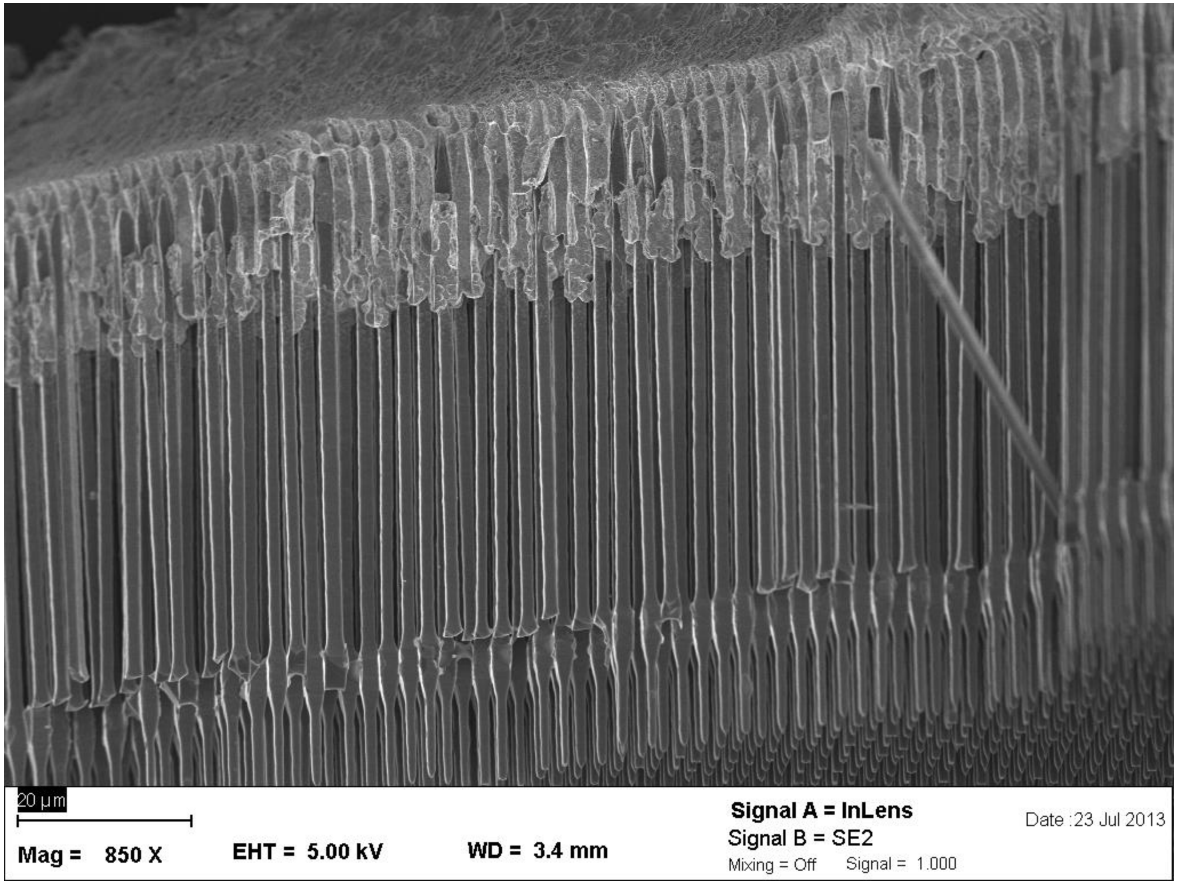


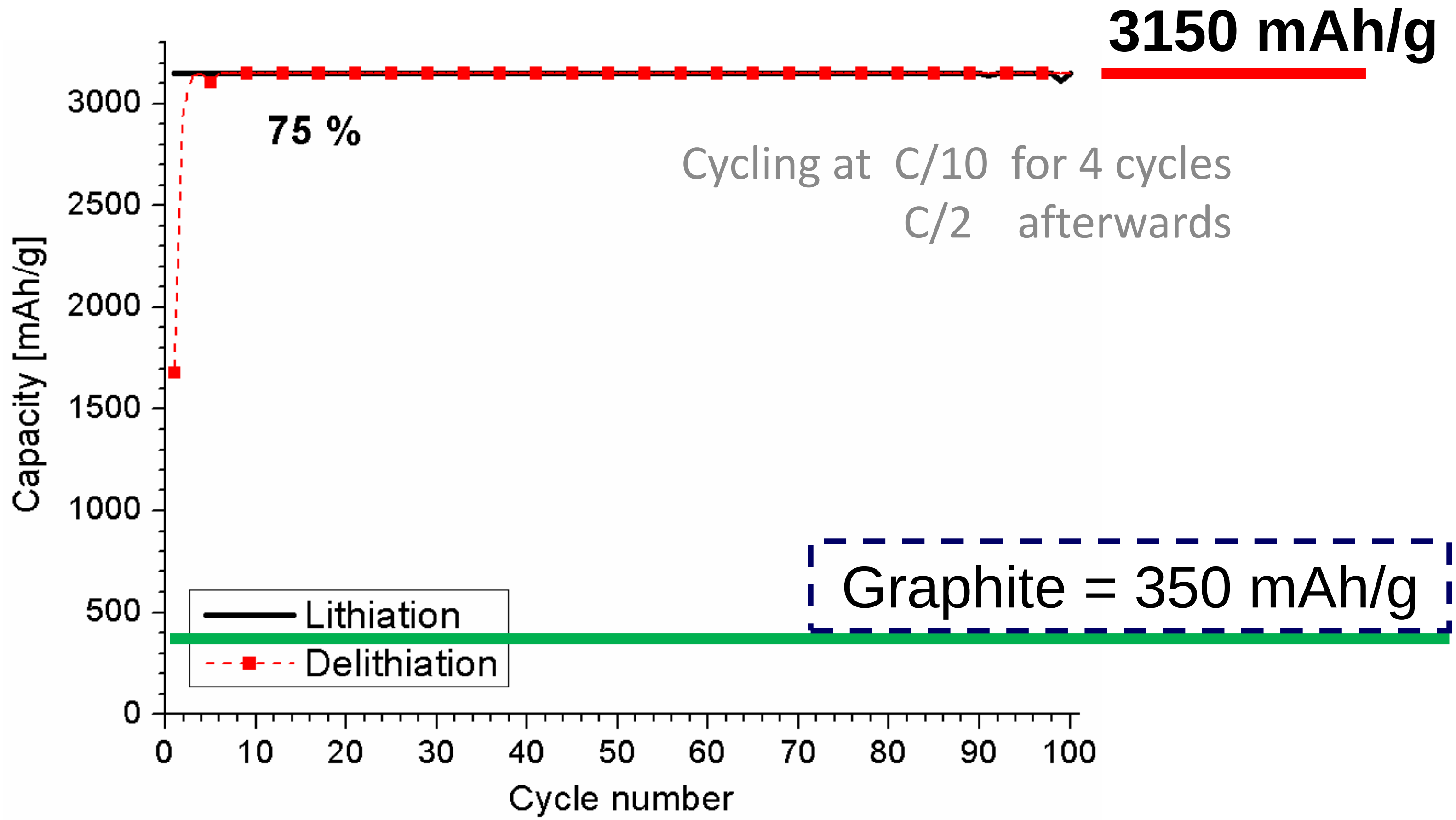
E. Quiroga-González et al., *J. Electrochem. Soc*. 158 (2011) E119-E123.

Si anode



E. Quiroga-González et al., *J. Electrochem. Soc*. 158 (2011) E119-E123.

Performance

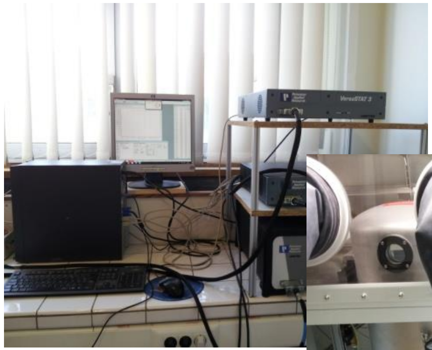


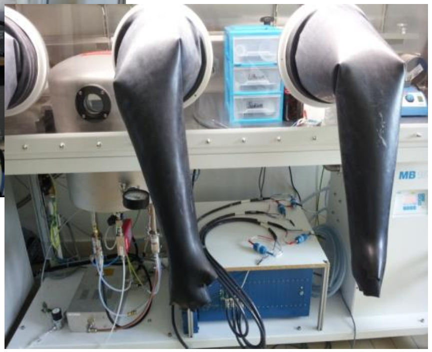
E. Quiroga-González et al., *Electrochim. Acta* 101 (2013) 93.

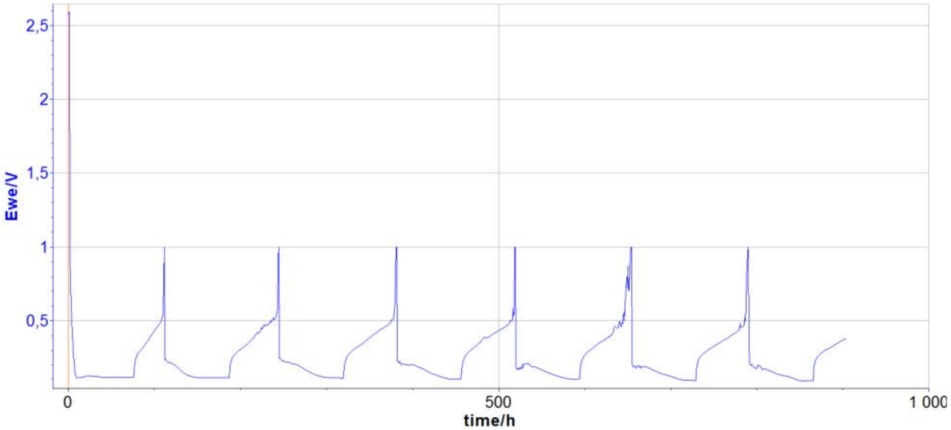
Our SiNWs as Anode in Lithion-ion Battery

	C 11	F 11	G 11	Sample 6
Dimensions of Si wafer (length x width), mm	5 x 7	5 x 7	6 x 6	7 x 6
Length of SiNWs (µm)	4-5	6	0-15	0-20
Approximate mass (mg)	0.20	0.24	0.35	0.55
Open circuit voltage (V)	2.762	2.576	2.976	2.543
Applied current (µA)	19.1	22.9	33.4	52.5

Facilities for battery tests







Charge and discharge curves performed at a rate of C/10 (one Li (de)inserted in 10 hours per Si atom) between 0.005 V and 1.0 V vs Li/Li+ in an organic liquid electrolyte

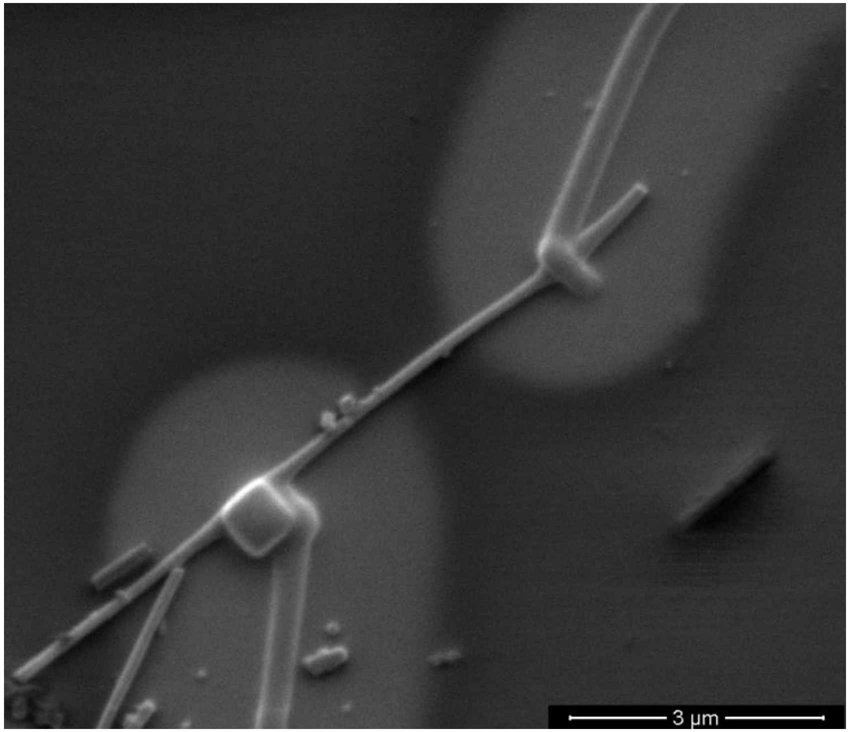
Electrical characterization

- SiNWs obtained via MACE are porous
- Quantum confinement effect can be observed (e.g. Coulomb Blockade*)
- Besides porosity affects electrical properties influencing depletion region, band structure and charge traps
- Realization of proper electrical contacts is tricky

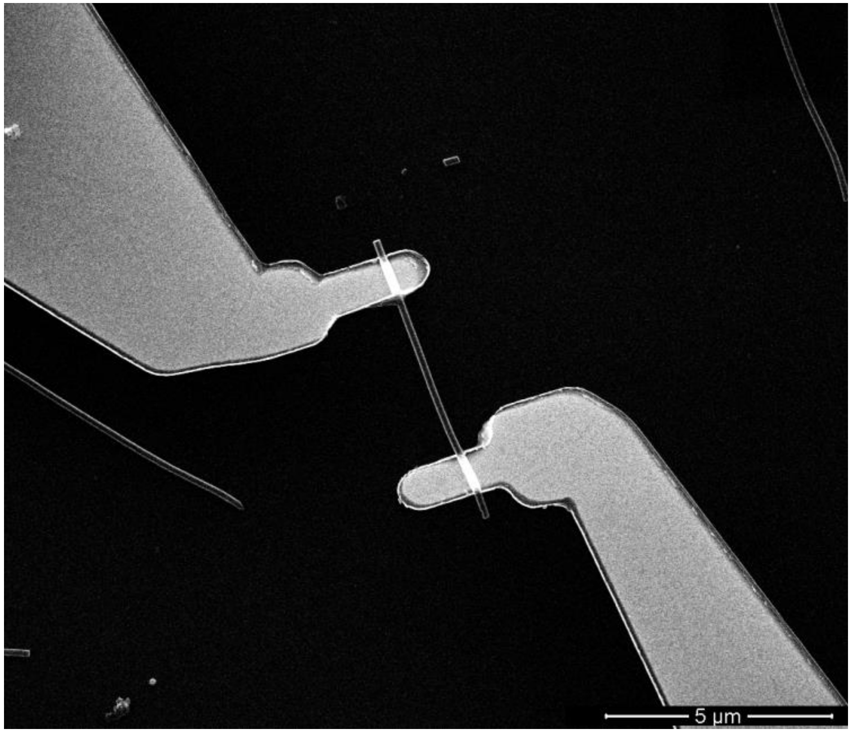
*Hamilton et al, Nature 393, 443 (1998)
Borini S, Boarino L, Amato G, Appl.Phys. Lett. 89 (13) 132111 (2006)

Electrical characterization: ways of wiring

- Wiring with Gas Injector System and Focused Ion Beam



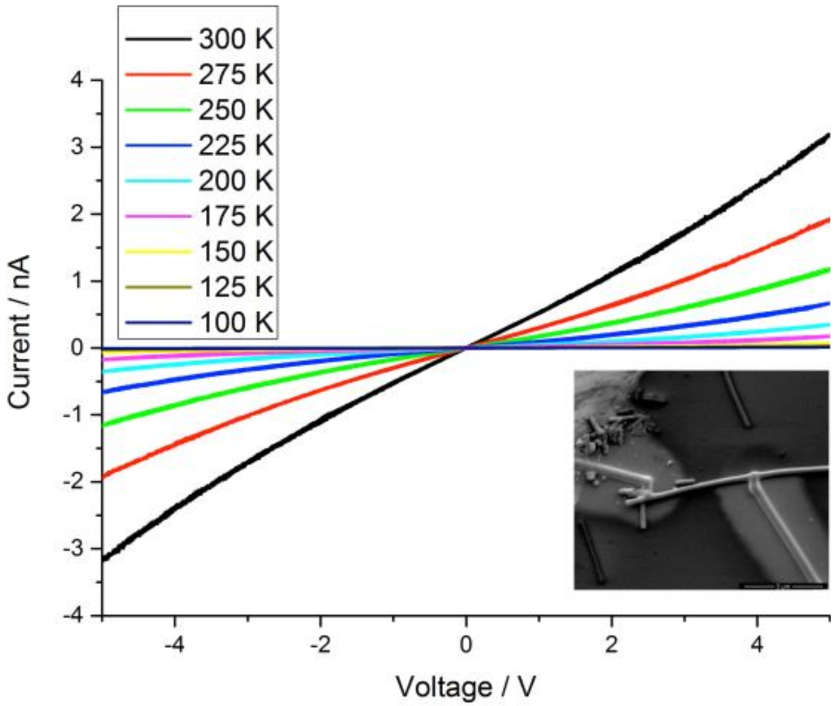
- Wiring with Electron Beam Lithography and conventional metal sputtering



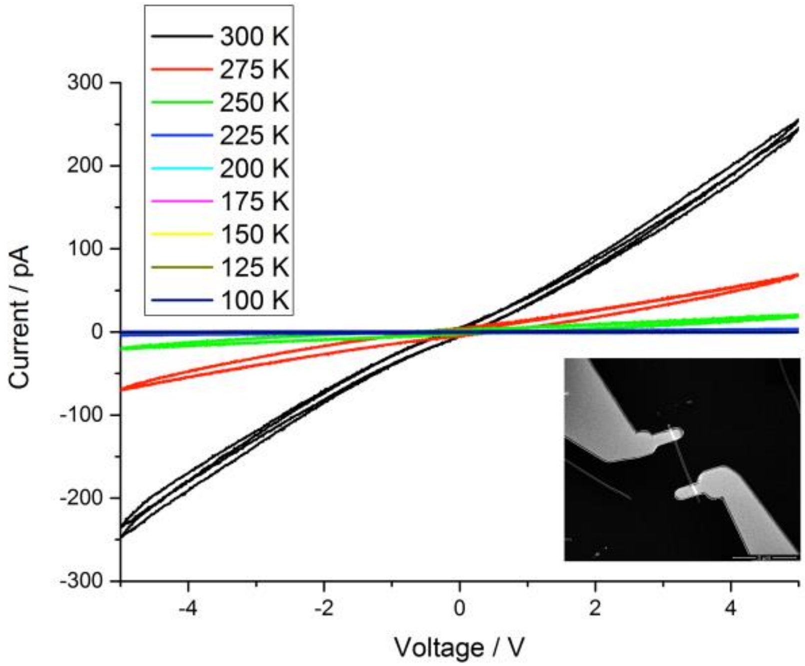
Single SiNWs

I-V curves

- FIB/GIS method

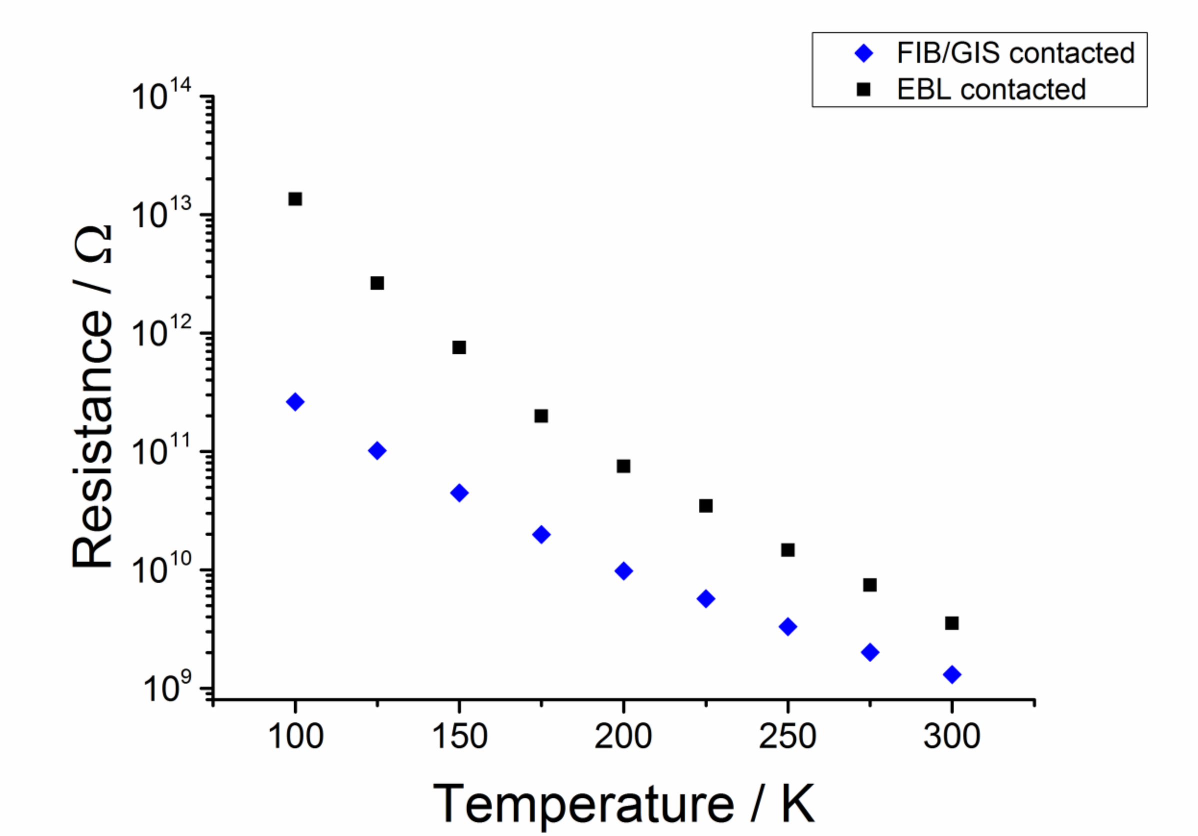


- EBL method

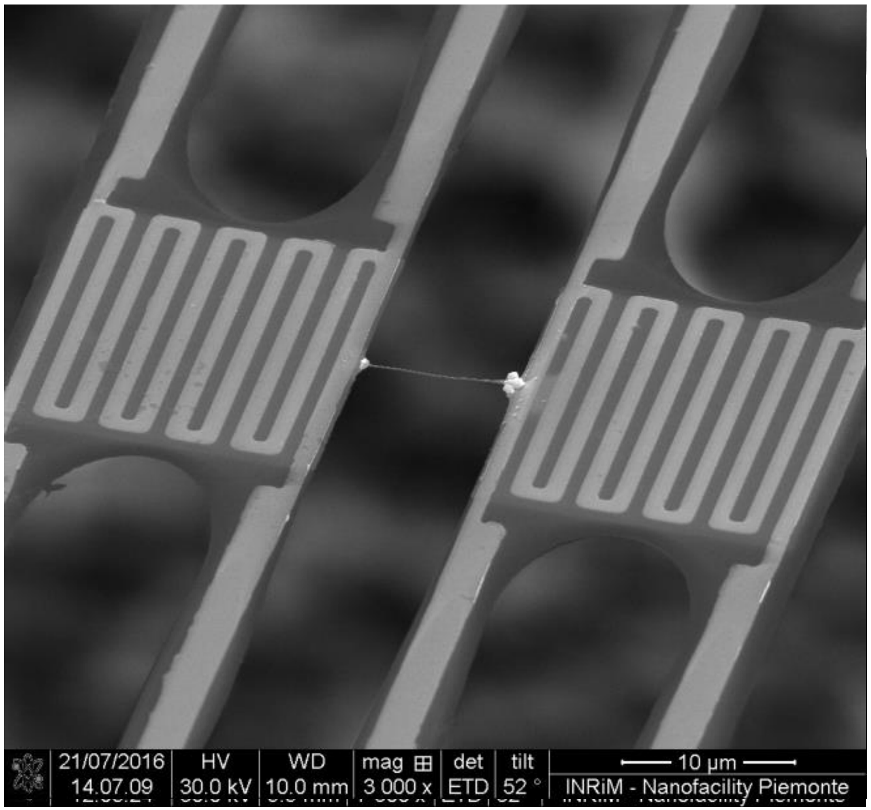


I-V curves

- Higher increment of resistance at low T for EBL contacted nanowire
- A reason could be the presence of a barrier at interface



Nanomanipolation



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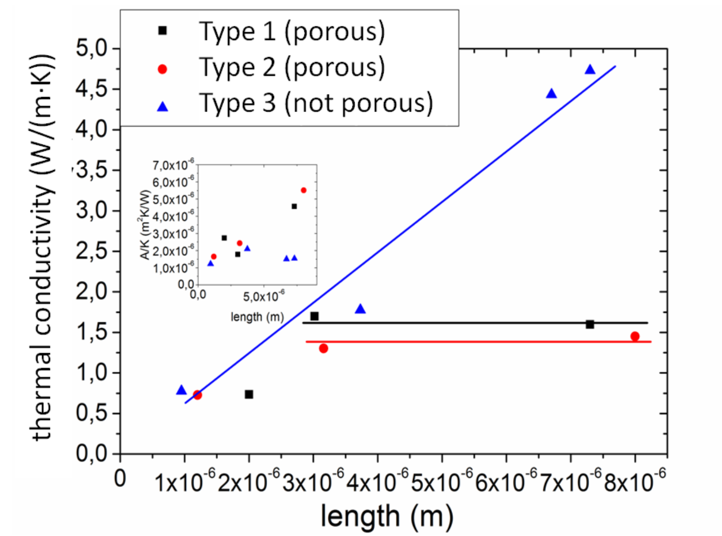
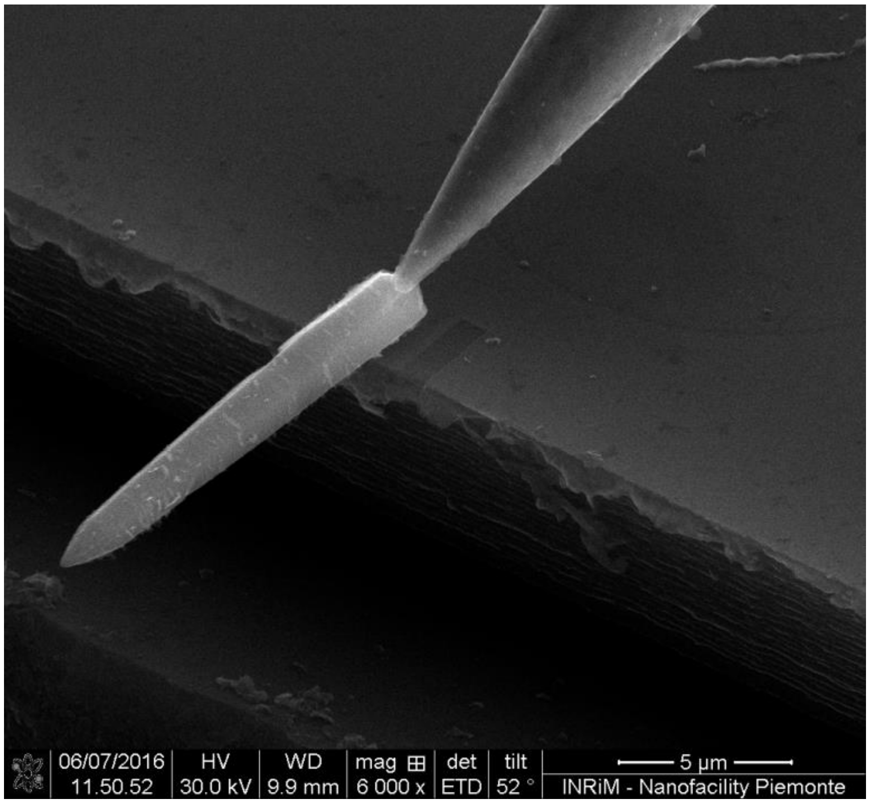


Single NWs and NTs

Nanomanipolation



Acknowledgement

Thank you for your attention