RIE for Silicon Nanowire Formation

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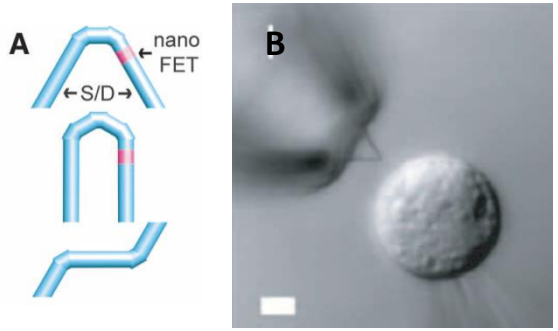
Outline

- **Si-NWs synthesis**
- **Fluorine-plasma treated Si surfaces**
- **Si-NWs surface structures**
- **HRTEM**

  (above results were presented at ICSOS 10 – 10th International Conference on the Structure of Surface)
- **RIE Processing**

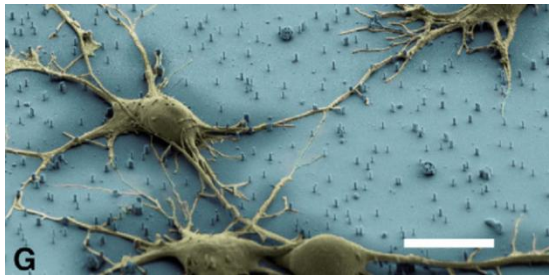
Introduction



A: Multiply kinked nanowires

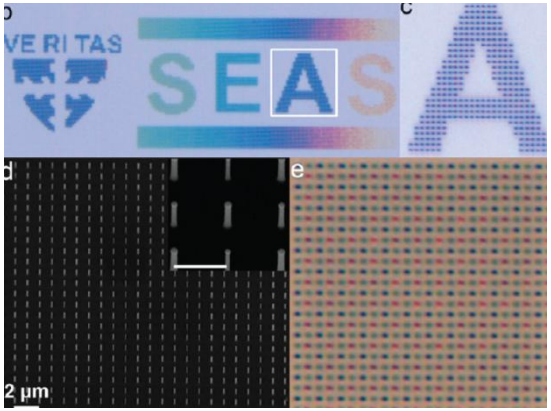
B: A nanoFET probe entrance a cell
The probe can be fabricated as small as 25 nm.

"3-D field effect transistors as bioprobes", B. Tian, etc., Science 329, 830(2010)



"Vertical silicon nanowires as a universal platform for delivering biomolecules into living cells", A. K. Shaleka, etc., Proc. Natl. Acad. Sci. USA 107, 1870(2010)

Si NWs used as a generalized platform for delivering wide range of biological effectors.
G: Rat neurons atop a bed of RIE etched Si NWs

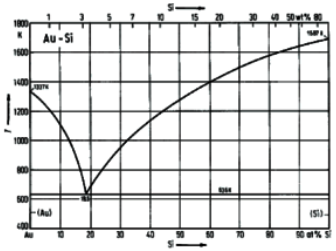


RIE etched Si NW arrays. Under white light, the NW arrays show color variations with the radiuses of the NWs. The NWs' radiuses are 35 – 75 nm and depth is ~ 1.0 µm.

"Multicolored Vertical Silicon Nanowires", K. Seo, etc., Nano Lett. 10, 1529(2010)

Si NWs Formation - VLS

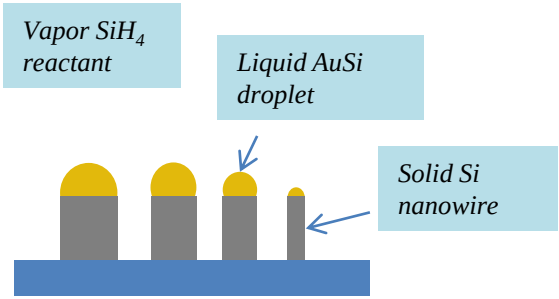
- **Vapor-Liquid-Solid (VLS)**
  - SiO_2 coated substrate
  - 10%SiH_4/He
  - Furnace temperature 455°C



Au-Si eutectic temperature: 362°C

- **Advantages**
  - Axial and radial heterostructures
  - NW diameter can be controlled to 2 nm.

- **Disadvantages**
  - Difficult to pattern
  - Metal contamination



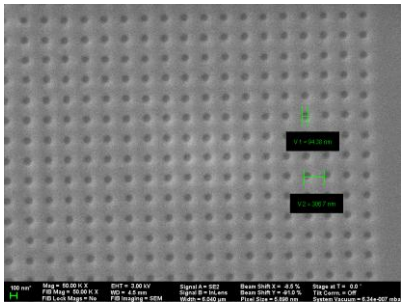
Si NW diameter controlled by sizes of catalysts

Si NWs Formation - RIE

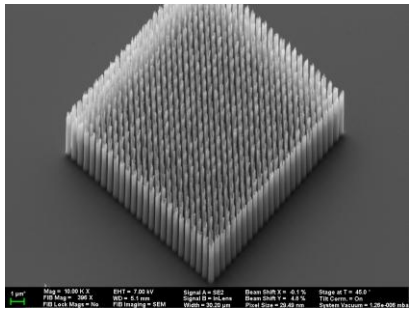
- **Reactive Ion Etch**
  - Top-down process
  - E-beam lithography define etch masks
  - Fluorine based chemistry (C_4F_8 and SF_6)

- **Advantages**
  - Patterned
  - No metal contaminations

- **Disadvantages**
  - Difficult to make NWs with diameter < 20 nm
  - Low aspect ratio NWs



E-beam lithography to define NW diameters and patterns. As small as 20nm in diameter can be obtained.

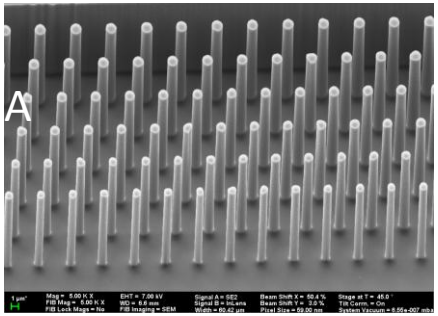


Si NW arrays obtained with reactive ion etch, 300nm in diameter and 5 microns in depth

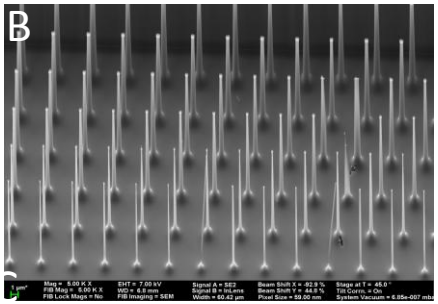
Si NWs Formation – RIE & VHF

- **Reactive ion etch & vapor HF etch**
  - Photolithography define etch mask
  - RIE to form micron or submicron diameter pillars
  - Thermal oxidation
  - Vapor HF remove oxide layer
- **Advantages**
  - Patterned
  - No metal contaminations
  - Atomic-scale smooth surface
  - High aspect ratio
  - Small diameters, comparable to VLS
- **Disadvantages**
  - High temperature process
  - Long process time

Si NWs array formed with the top-down approach

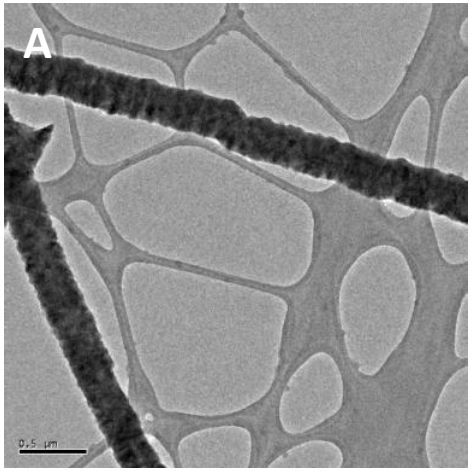


A: 1.0-1.5 μm in diameter and 10 μm depth Si micropillars were etched with ICP RIE

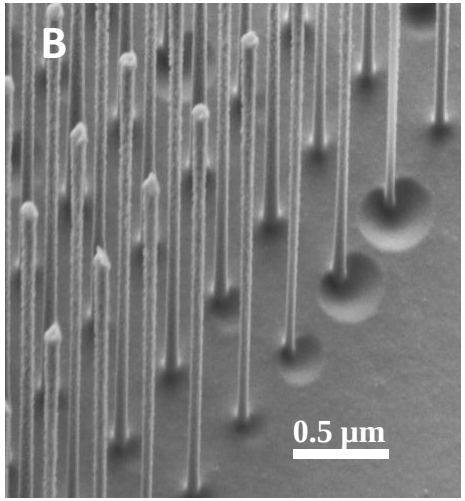


B: Wet oxidation was performed and then the oxide was removed with vapor HF to form nanowires.

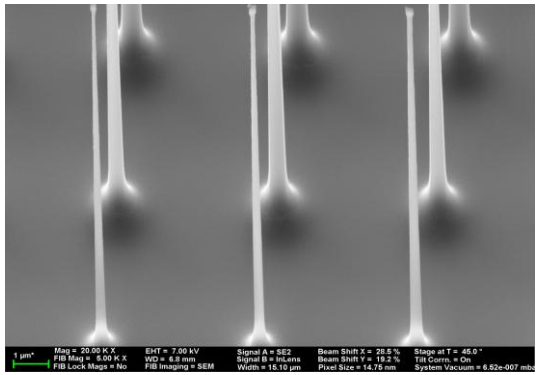
Si NWs Surface Morphology



TEM image of Si NWs formed with VLS method. Scallop morphology and non-homogeneous radical dimension along the growth axis are the characteristics

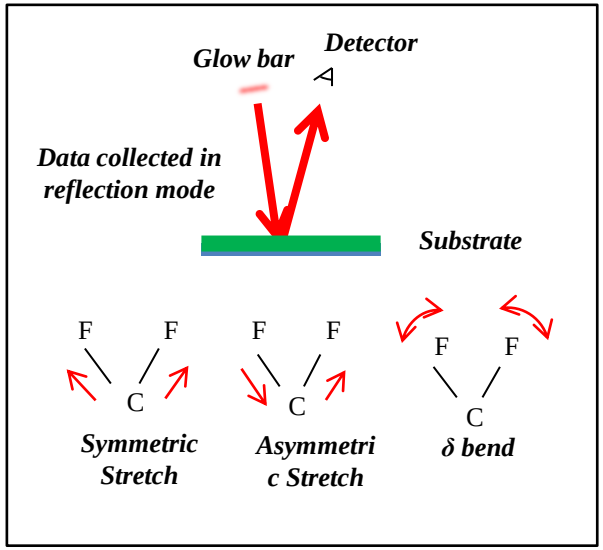


FESEM image of Si NW by RIE
The rough surface was possibly the fluoropolymer layer formed during etch.



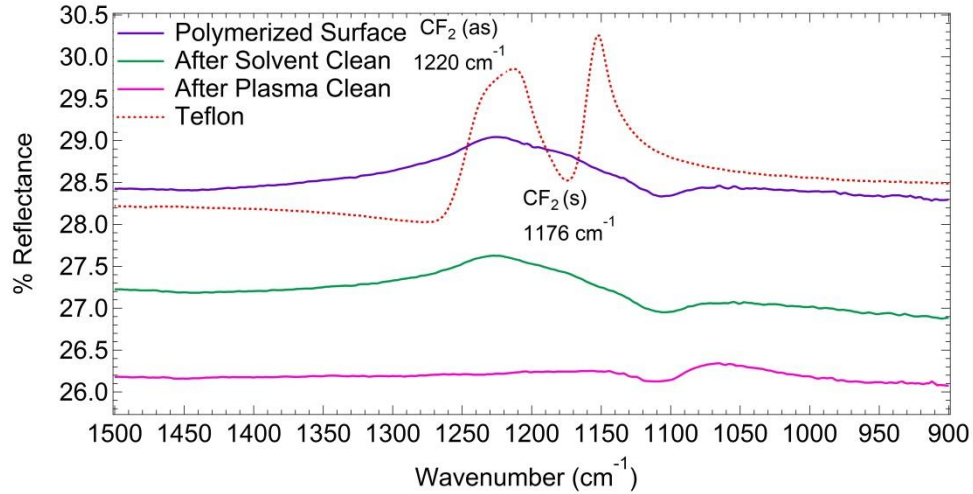
FESEM image of Si NWs formed with RIE and VHF
Si NWs with diameter 20-100 nm in diameter and length 10 um were obtained, an aspect ration of 500:1 was reached.
NWs formed in this way have monolayer surface smoothness.

FTIR of Plasma Treated Si Surfaces



Nicolet ECO 1000s FTIR, N_2 purge, spectra collected in reflection mode, 128 scans, 4 cm^{-1} resolution

Reflected signal convolution of IR absorption and changes in reflectivity due to changes in refractive index



Peak assignments of FTIR spectra

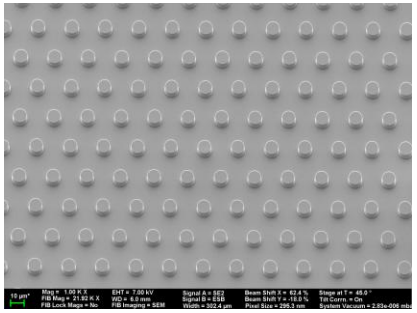
Wavenumber (cm-1)	Functional group	Peak assignment
1120	CF_2	asymmetric stretch
1176	CF_2	symmetric stretch
1103	Si-O	

C_4F_8 gas is commonly used in Si RIE processes as an agent to polymerize etched surface and obtain anisotropic etch. This polymer layer has to be removed after etching. It was found that O_2 plasma is effective to remove this polymer. This work found that the type of reactors used also play important roles to effectively remove it.

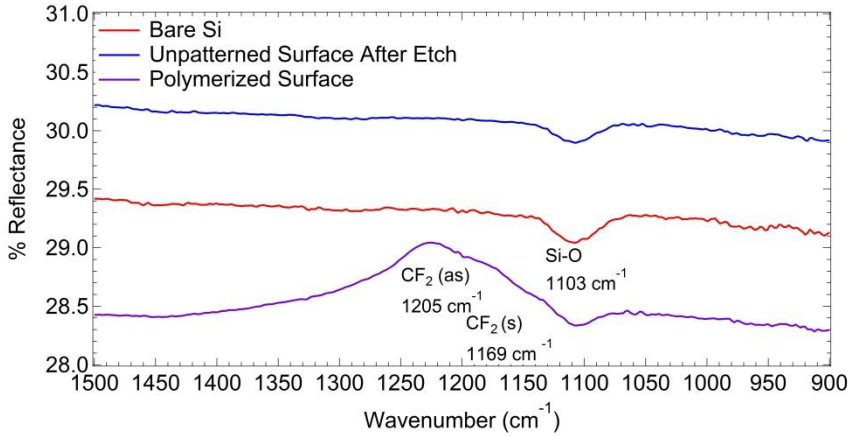
Si Surfaces after Plasma Etching

Etching Process

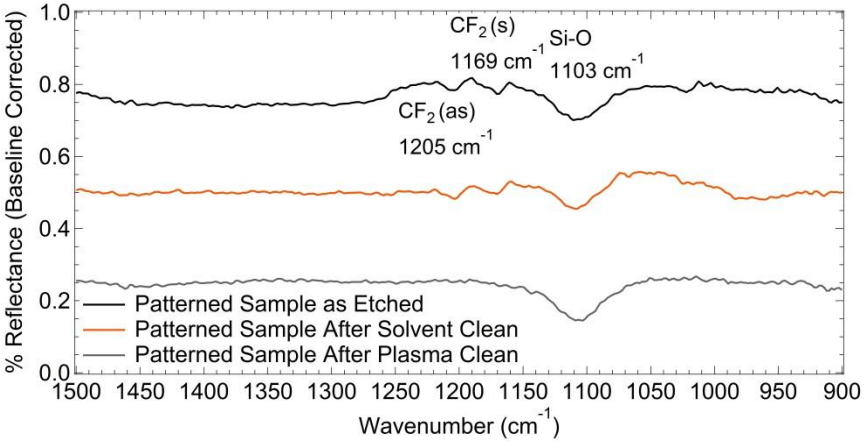
- STS ICP etcher
- C_4F_8 and SF_6 gases mixture
- Ions and radicals
- Chemical reactions and ion bombardments
- By-products desorption and polymer formation



Si micropillars with 10 um in diameter and 4 um in depth. They were etched under the same conditions

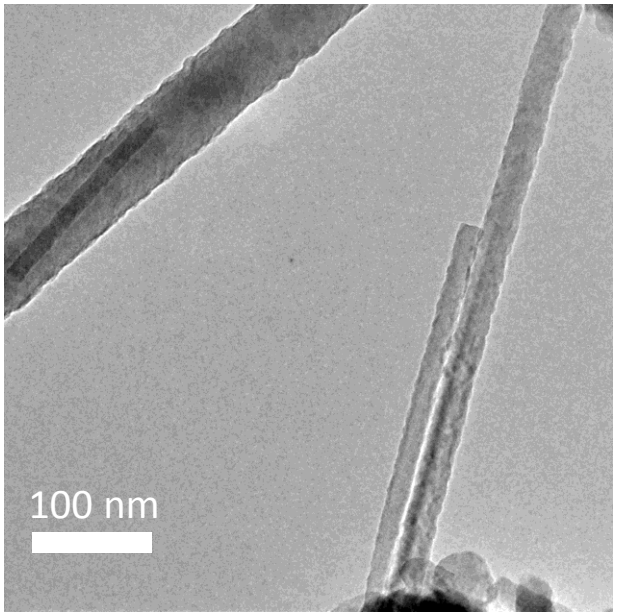


FTIR spectra of the unpatterned Si samples etched with C_4F_8 and SF_6 plasma under the conditions for anisotropic etch. Fluoropolymers were not detected on this sample.

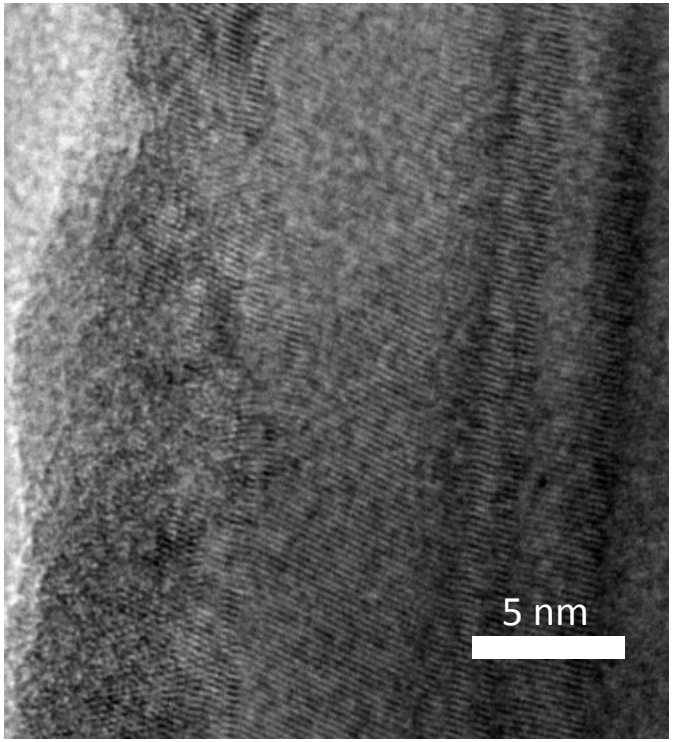


FTIR spectra of the patterned Si samples. Fluoropolymers presented. By comparing with the results from the unpatterned samples, it can be revealed that these polymers only deposited on the sidewalls but not on the bottom surfaces. After O_2 plasma cleaning, the polymers were removed.
Data was collected with the samples slightly tilted. Distortion in the baseline due to diffraction from the patterned surface was subtracted out.

Surfaces of VLS-Si NWs -as grown

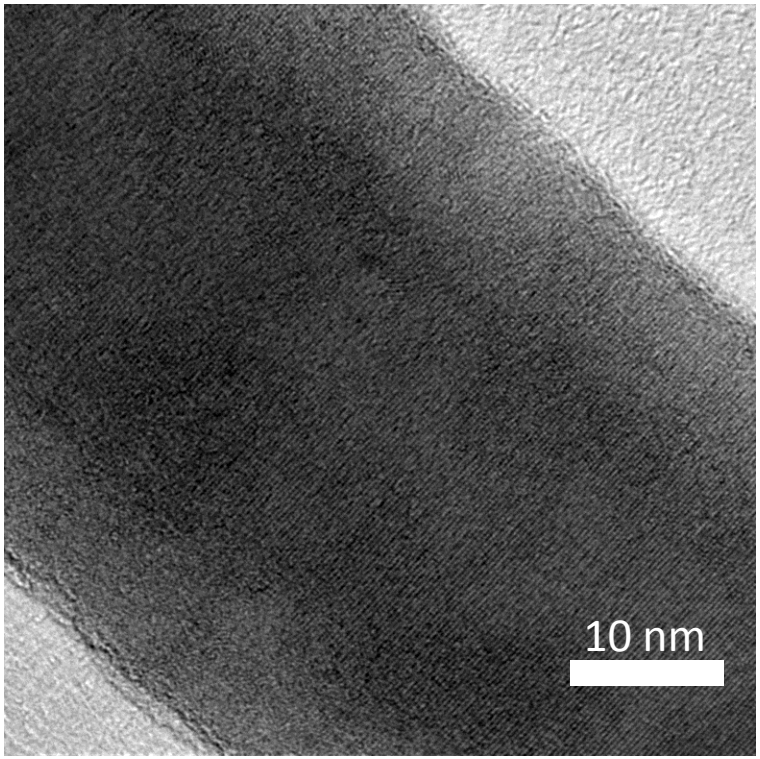


Imaging nanowires using a thermal field emission JEOL 2010F
Growing surface



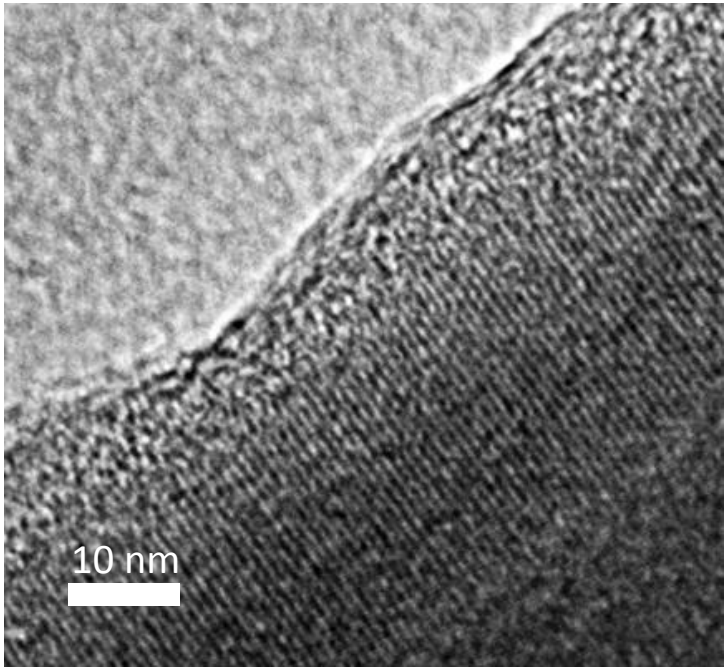
HRTEM of as-grown Si NW. A amorphous layer with a thickness 2 -4 nm was shown up. Its thickness varied along the growing axis. It was reported that this surface layer is silicon oxide.

Surfaces of VLS-Si NWs – 10s Etch

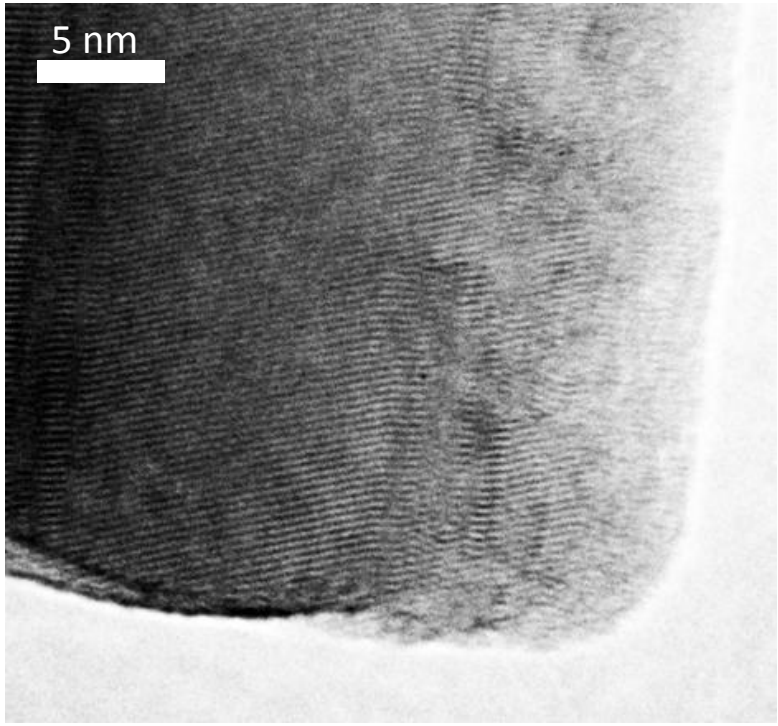


Si NW sample was etched in BOE 7:1 to remove the oxide layer then the TEM sample was prepared and loaded into TEM chamber with in one hour.
The HRTEM showed the oxide layer was not removed completely.

Surfaces of VLS-Si NWs – after 60s Etch



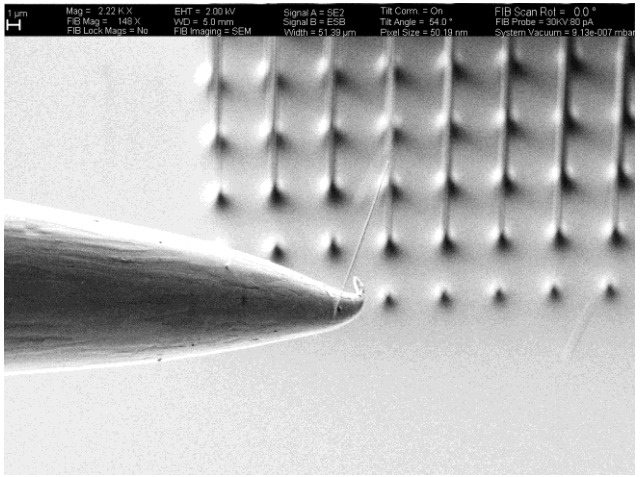
HRTEM of a Si NW after 60s BOE etch. The amorphous layer still existed, which indicates that the amorphous layer is not pure silicon oxide.



HRTEM image at broken edge of a Si NW. The native oxide was not observed at the broken edge.

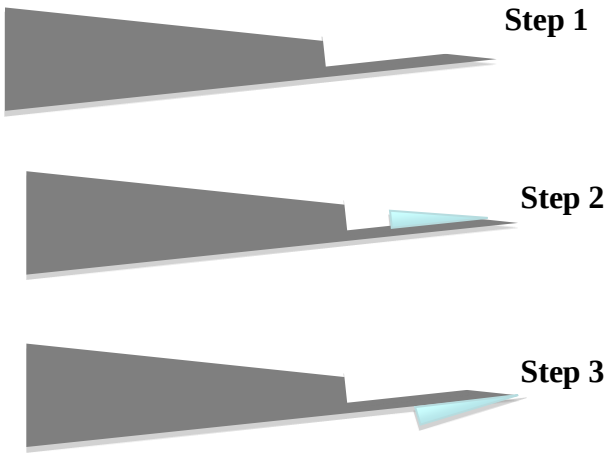
Preparing Si NWs for TEM Imaging

Harvesting Si NWs



- Tip acquired on nanomanipulator in FIB
- Tip sharpened using rotation in FIB
- Nanowires harvested by natural forces between wire and tungsten tip
- Tip attached to copper ring by cold pressing in Omniprobe's short cut system
- Sample on the tip and the tip attached to ring are loaded in TEM for imaging

Lift-out tips are nanomachined



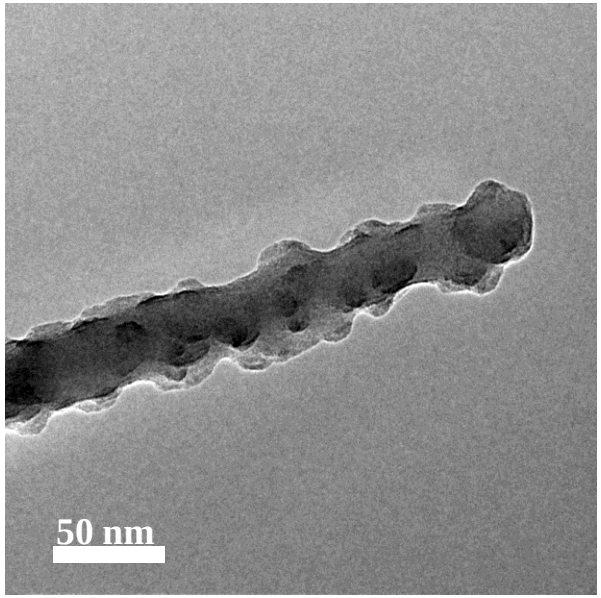
Step 1: Shank area cleared to tip (a few microns) at 0^0

Step 2: 30^0 rotation for first sharpening mill rotation

Step 3: 120^0 rotation for second sharpening mill

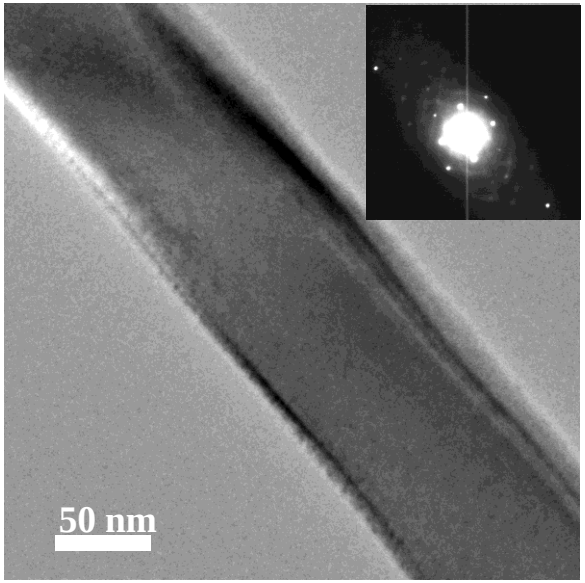
Si NWs Obtained with RIE & RIE+VHF

RIE



TEM image of Si NW etched with RIE The rough surface was believed to be fluoropolymer according to previous FTIR results.

RIE & VHF

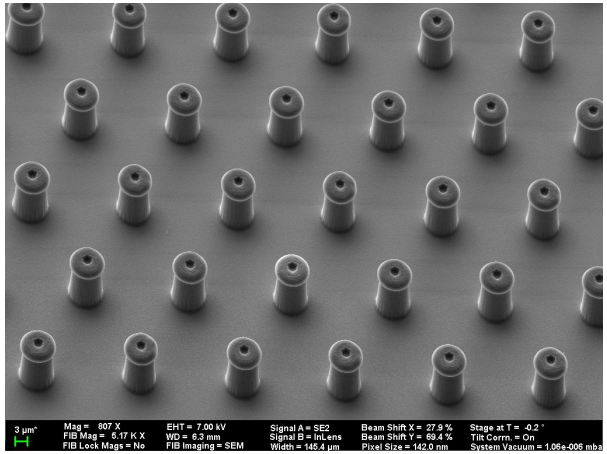


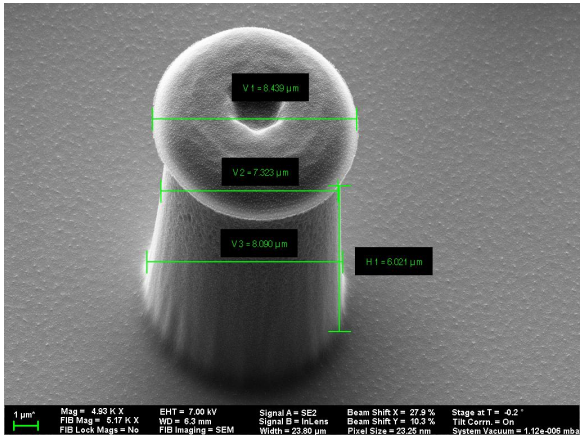
TEM image of Si NW obtained with RIE & VHF. Metal coating was observed on the wire, which is believed to be platinum from TEM sample preparation. However, the atomic scale smoothness is still can be seen.

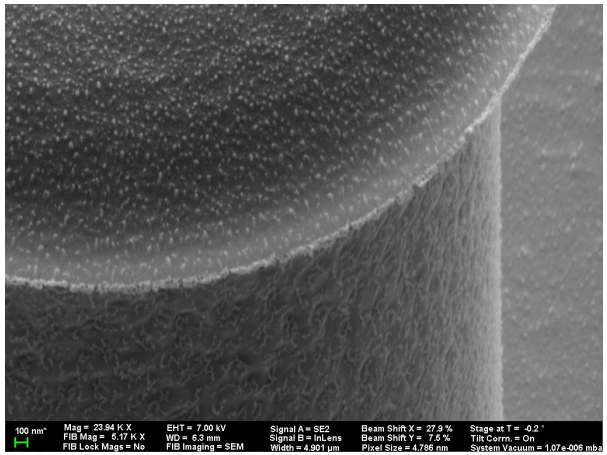
Summary

- Si NWs were fabricated in three different ways, VLS, RIE, RIE & VHF. The surface morphologies of these NWs are different for different formation methods.
- Fluoropolymer was only detected on vertical side walls of RIE etched micropillars.
- HRTEM and BOE etch results indicated the amorphous layer of VLS Si NWs could not be removed after 60s etch time, which could indicate that the amorphous is not pour silicon oxide.
- Si NWs made with RIE showed a layer of fluoropolymer.
- Si NWs formed with RIE & VHF have atomic scale smooth surfaces.

Etch Profile vs. C_4F_8/SF_6 Flow Ratio



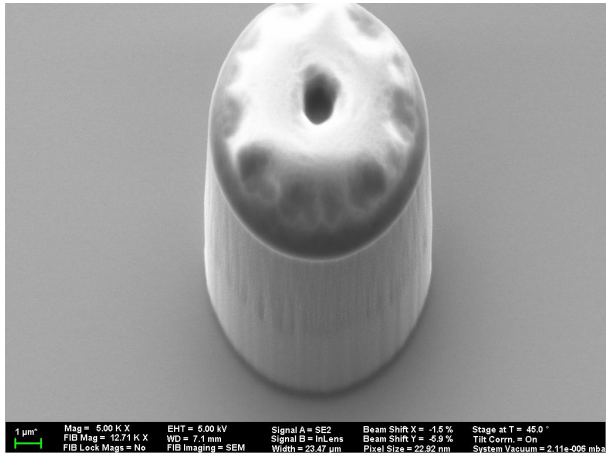


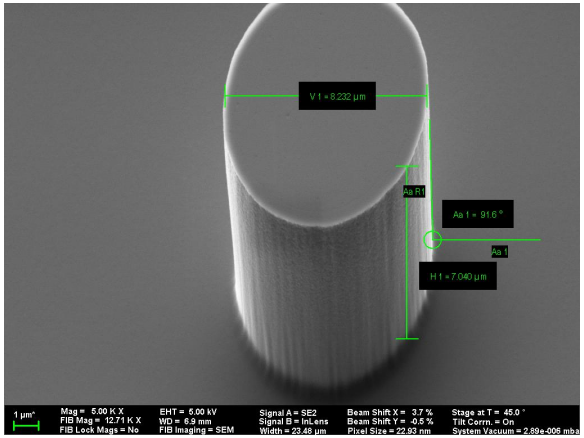


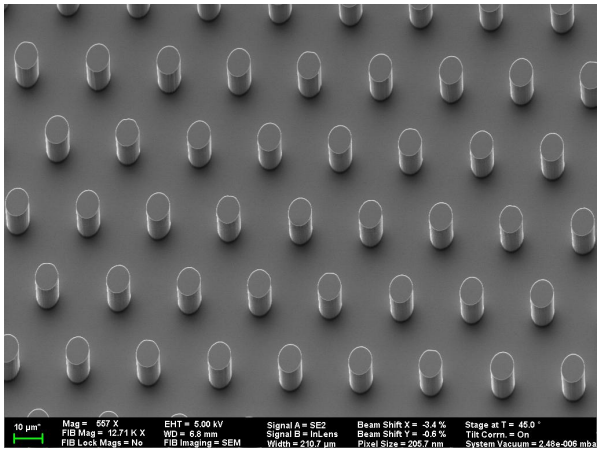
Processe conditions:

- Pillar diameter: 8 µm
- Mask: 1.25 µm PR
- STS ICP RIE etch
  C4F8/SF6 = 1.6:1
- Depth: 6.0 µm

Etch Profile vs. C_4F_8/SF_6 Flow Ratio





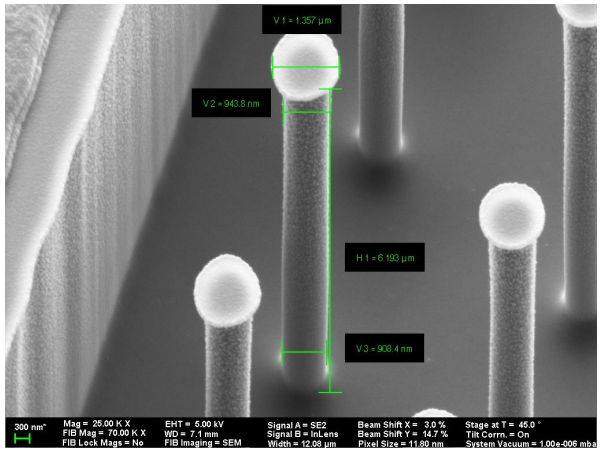


Processes: Nov. 3, 2009 run#1

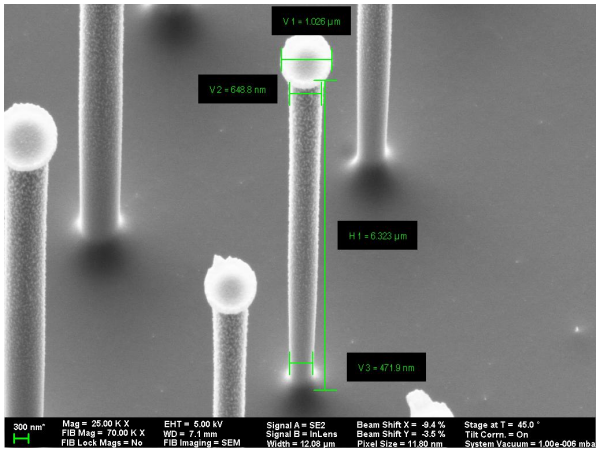
- Pillar diameter: 8 µm
- Mask: 1.25 µm PR
- STS ICP RIE etch

  C4F8/SF6 = 2:1
- Selectivity: 12:1
- Depth: 7.0 µm

Etch Profile vs. Pillar Diameter



A pillar from row a, metal mask diameter 1.35 µm, pillar diameter 0.943 µm at top and 0.908 µm at bottom, etch depth 6.2 µm

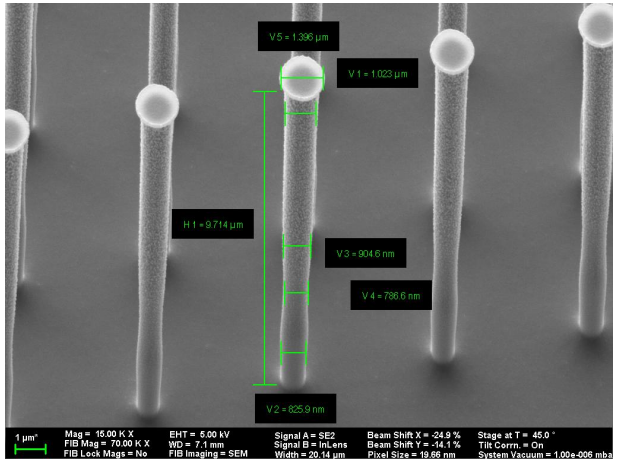


A pillar from row d, metal mask diameter 1.02 µm, pillar diameters 0.65 µm at top, 0.47 µm at bottom, depth 6.2 µm

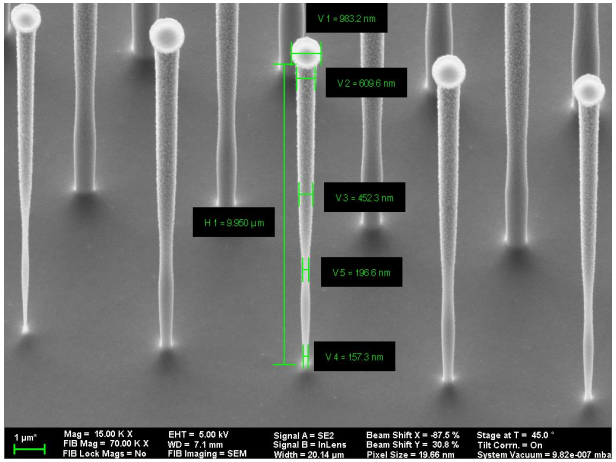
Processes: Dev. 9, 2009

- Pillar diameter: 1.0-1.5 µm
- Mask: 0.1 µm Al
- STS ICP RIE etch
  C4F8/SF6 = 2:1
- Selectivity: >150:1
- Depth: ~ 6.0 µm

Etch Profile vs. Etch Depth



A pillar from row a, metal mask diameter 1.38 µm, pillar diameter 1.02 µm at top and 0.825 µm at bottom, etch depth 9.8 µm



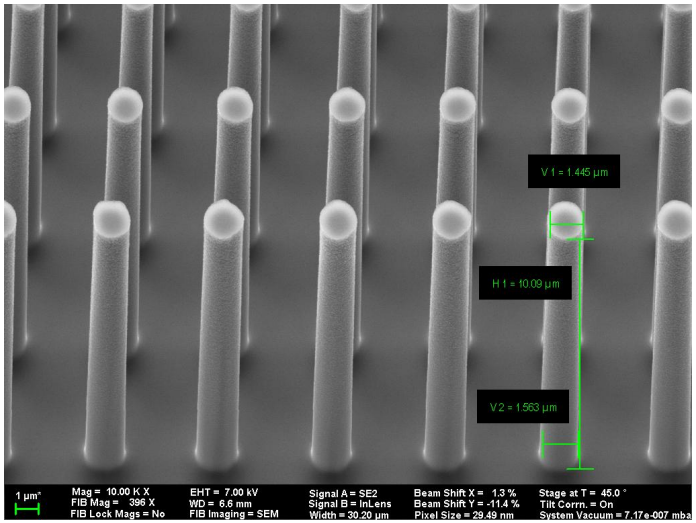
A pillar from row d, metal mask diameter 1.06 µm, pillar diameter 0.766 µm at top and 0.393 µm at bottom, etch depth 9.8 µm

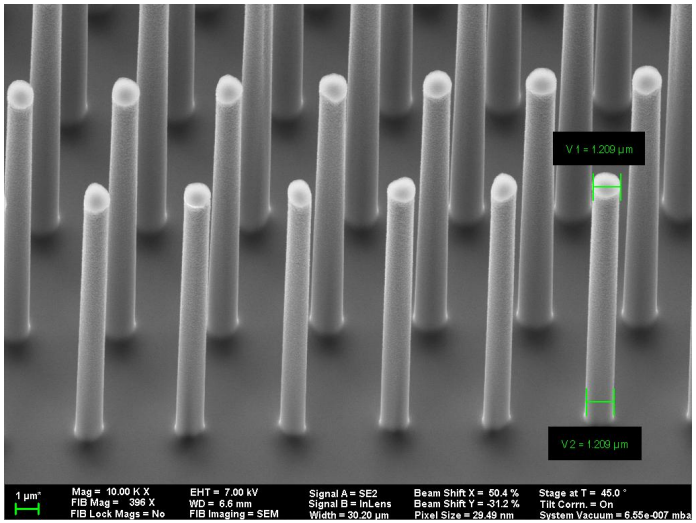
Processes: Dev. 9, 2009

- Pillar diameter: 1.0-1.5 µm
- Mask: 0.1 um Al
- STS ICP RIE etch

  C4F8/SF6 = 2:1
- Selectivity: >150:1
- Depth: ~ 10 um

Higher C4F8/SF6 Ratio for Smaller Pillar



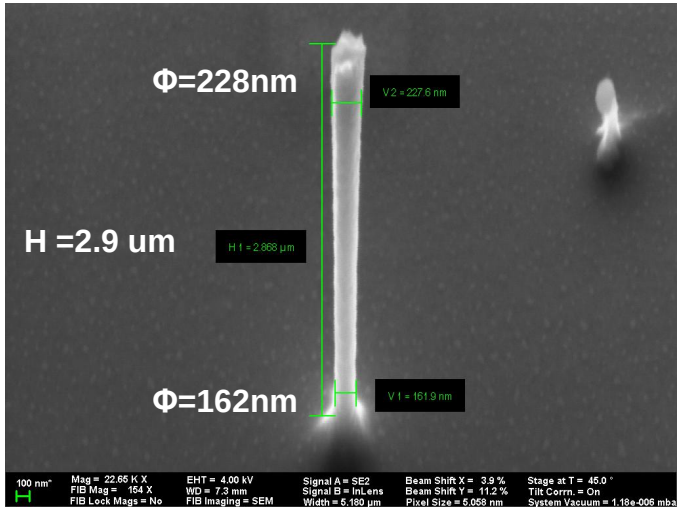


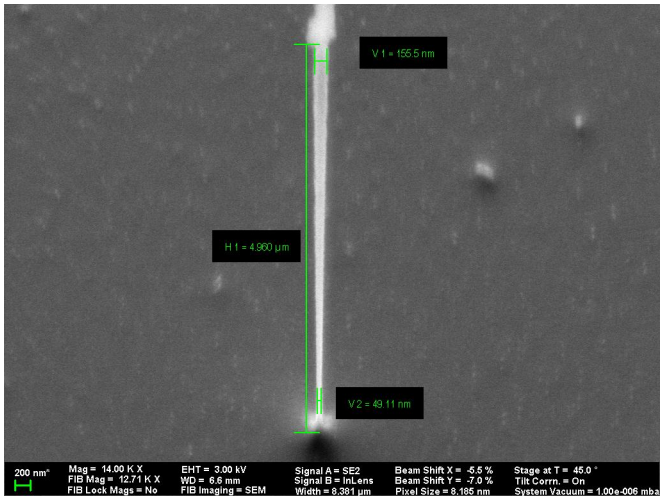
Processes: Dev. 9, 2009

- Pillar diameter: 1.0-1.5 µm
- Mask: 0.1 um Al
- STS ICP RIE etch

  C4F8/SF6 = 2.3:1
- Selectivity: >150:1
- Depth: ~ 10 um

Nano-scale Pillars

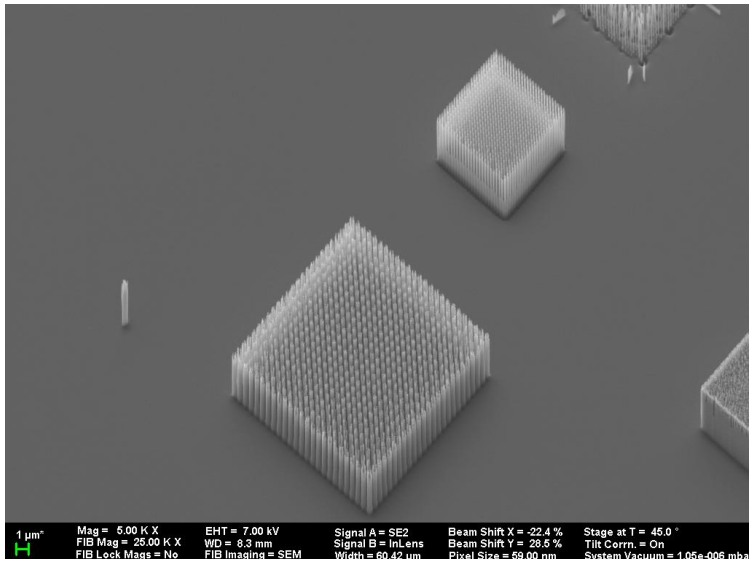




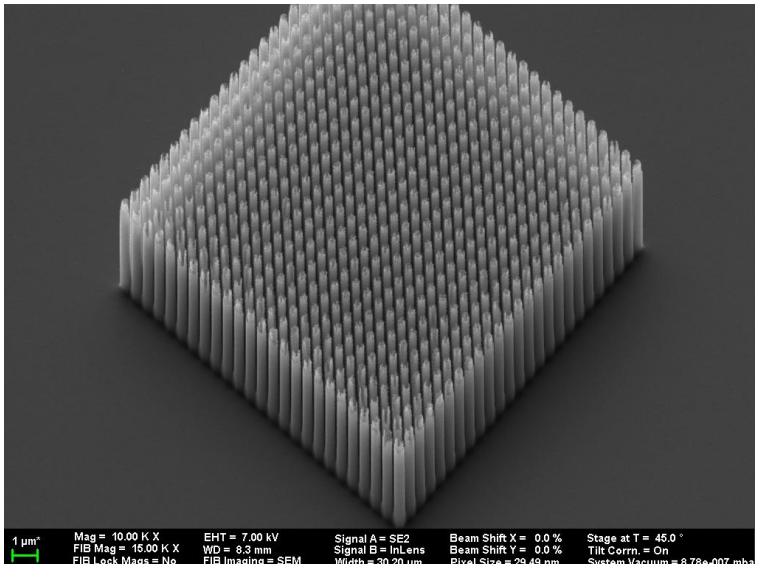
Process conditions:
- Mask: 1.25 um PR
- STS ICP RIE etch
  - C4F8/SF6 = 1.89:1
- SEM measure depth: 2.9 µm

Process conditions:
- Mask: 1.25 um PR
- STS ICP RIE etch
  - C4F8/SF6 = 2.1:1
- SEM measure depth: 2.9 µm

Si NWs Array

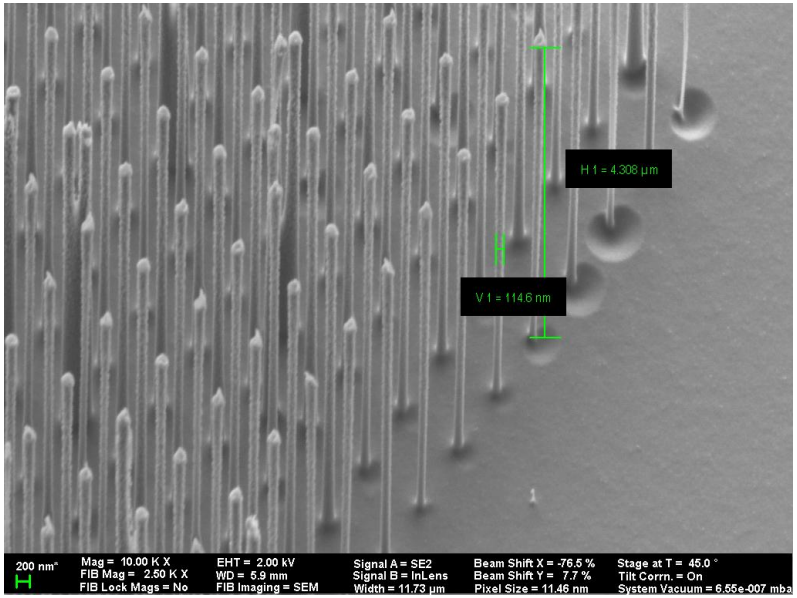


300nm, 200nm, and 100nm Si NWs array



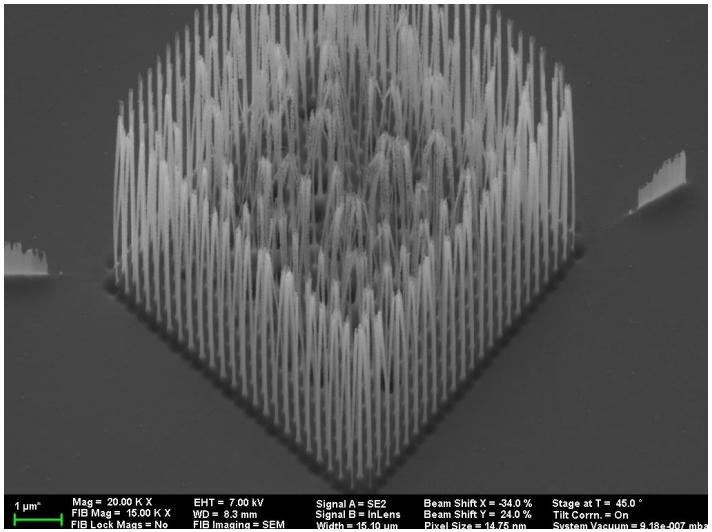
300nm Si NWs

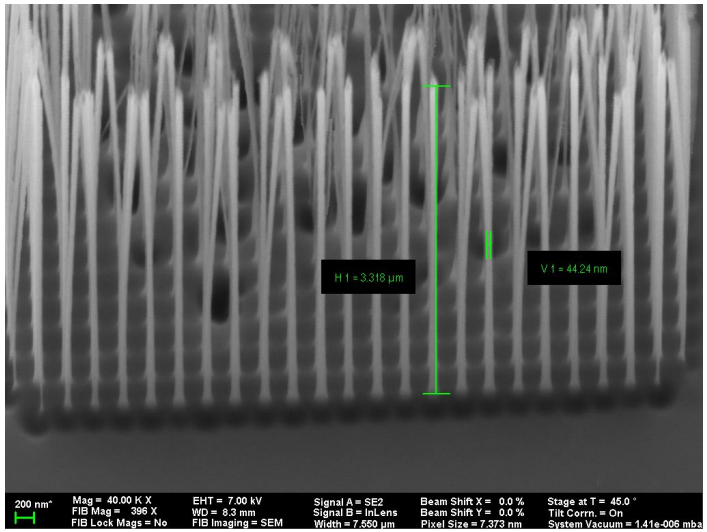
Si NWs Array



100 nm in diameter, 4 µm in depth, 1.0 µm in space

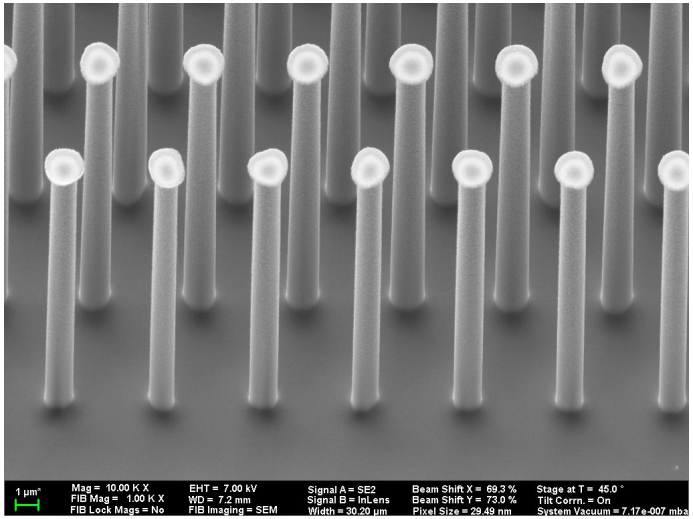
Stiction



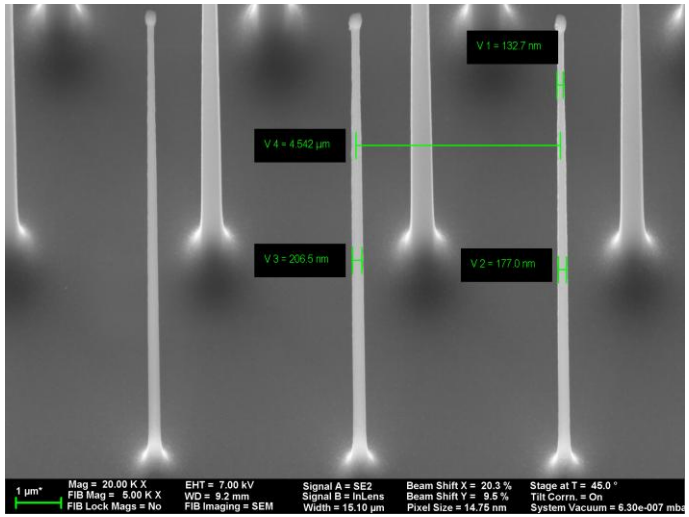


44 nm in diameter, 3.3 µm in depth, 300 nm in space Si NWs

Si NWs Formation by RIE & VHF



After etching, 1um in diameter, 10um in depth



100nm in diameter, 10 µm in depth