Surface Characteristics of Silicon Nanowires

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Outline

• Si-NW formation processes
• FTIR of plasma treated Si surfaces
• HRTEM of Si NWs
Introduction


Si NWs used as a generalized platform for delivering wide range of biological effectors.

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

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


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 and depth is ~ 1.0 µm.

G: Rat neurons atop a bed of RIE etched Si NWs
Si NWs Formation - VLS

• **Vapor-Liquid-Solid (VLS)**
  – SiO$_2$ coated substrate
  – 10%SiH$_4$/He
  – Furnace temperature 455°C

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

• **Disadvantages**
  – Difficult to pattern
  – Metal contamination

**Au-Si eutectic temperature**: 362°C

**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 (C₄F₈ and SF₆)

• **Advantages**
  – Patterned
  – No metal contaminations

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

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

*E-beam lithography to define NW diameters and patterns. As small as 20nm in diameter can be obtained.*
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 um in diameter and
10 um 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 µm 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\textsubscript{2} purge, spectra collected in reflection mode, 128 scans, 4 cm\textsuperscript{-1} resolution

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

Peak assignments of FTIR spectra

<table>
<thead>
<tr>
<th>Wavenumber (cm\textsuperscript{-1})</th>
<th>Functional group</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1120</td>
<td>CF\textsubscript{2}</td>
<td>asymmetric stretch</td>
</tr>
<tr>
<td>1176</td>
<td>CF\textsubscript{2}</td>
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<tr>
<td>1103</td>
<td>Si-O</td>
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</table>

C\textsubscript{4}F\textsubscript{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\textsubscript{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
- C₄F₈ and SF₆ gases mixture
- Ions and radicals
- Chemical reactions and ion bombardments
- By-products desorption and polymer formation

FTIR spectra of the patterned Si samples etched with C₄F₈ and SF₆ plasma under the conditions for anisotropic etch. Fluoropolymers were not detected on this sample.

FTIR spectra of the unpatterned Si samples etched with C₄F₈ and SF₆ plasma under the conditions for anisotropic etch. Fluoropolymers were not detected on this sample. 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 O₂ 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.

10 nm
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 Tip acquired o 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 tip and tip attached to ring are loaded in TEM for imaging

Liftout tips are nanomachined

Step 1: Shank area cleared to tip (a few microns) at 0°
Step 2: 30° rotation for first sharpening mill rotation
Step 3: 120° rotation for second sharpening mill
Si NWs Obtained with RIE & RIE+VHF

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

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.
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Thank you for your attention!