Bi_xSb_{1-x} Nanowire Arrays: A New Generation of Thermoelectric Materials

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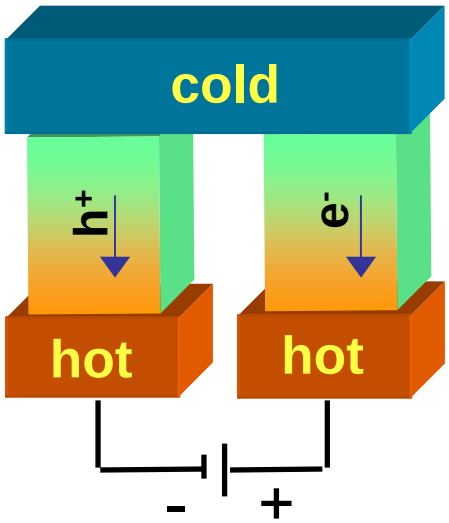


Objective

To enhance the efficiency of thermoelectric devices by replacing the semiconductor legs with $Bi_{1-x}Sb_x$ nanowire arrays.

Approach

Electrochemical growth of nanowires in porous alumina templates.

Major accomplishments

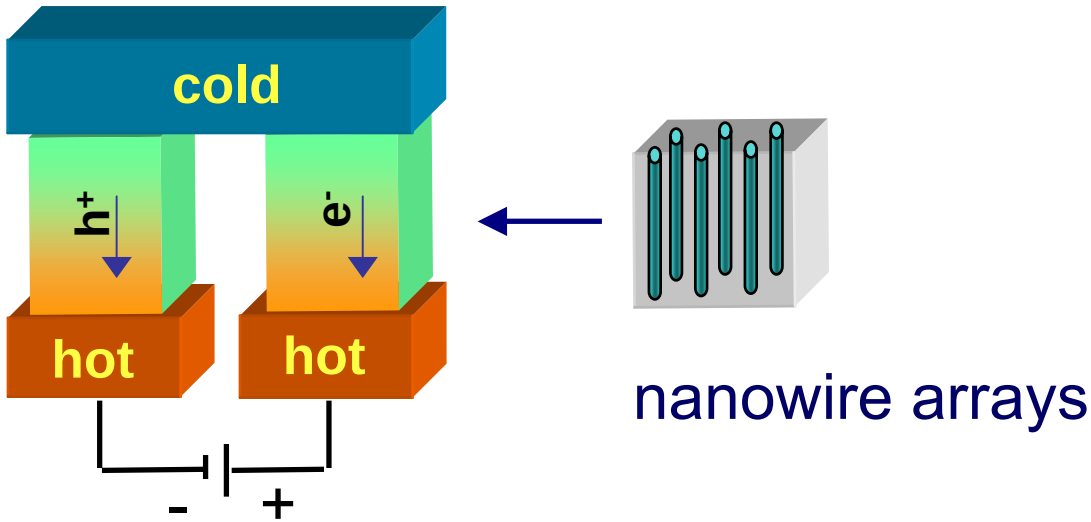
- ✓ Hire wire density
- ✓ Small wire diameters (40 nm)

New

- ✓ Very long wires (130 μm)
- ✓ Control over composition and orientation
- ✓ Equal wire lengths

Research Goals

Replace semiconductor legs with nanowire array

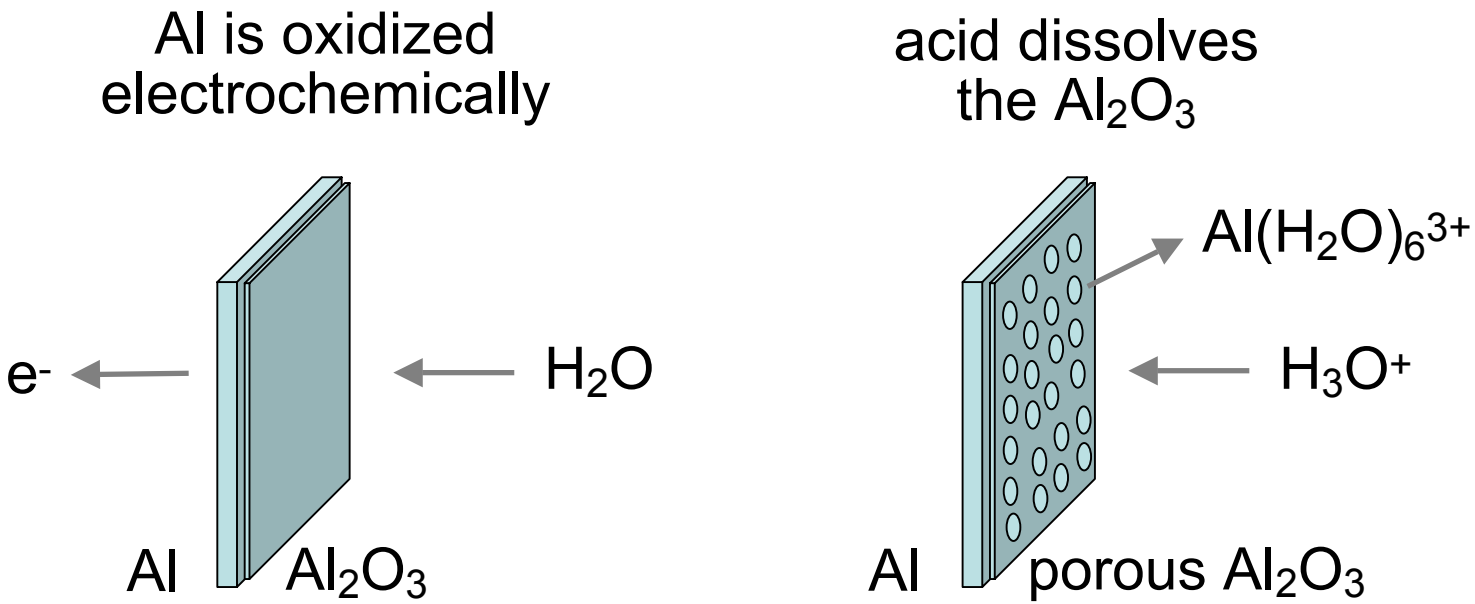


Specifications

- High wire density: >5x10^{10} nanowires/cm^2 over ~0.2 cm^2
- High aspect ratio: 120 µm by 40 nm = 3000:1
- Control over orientation and composition
- Equal wire lengths: Simultaneous growth of 10^{10} wires

Anodization of Al

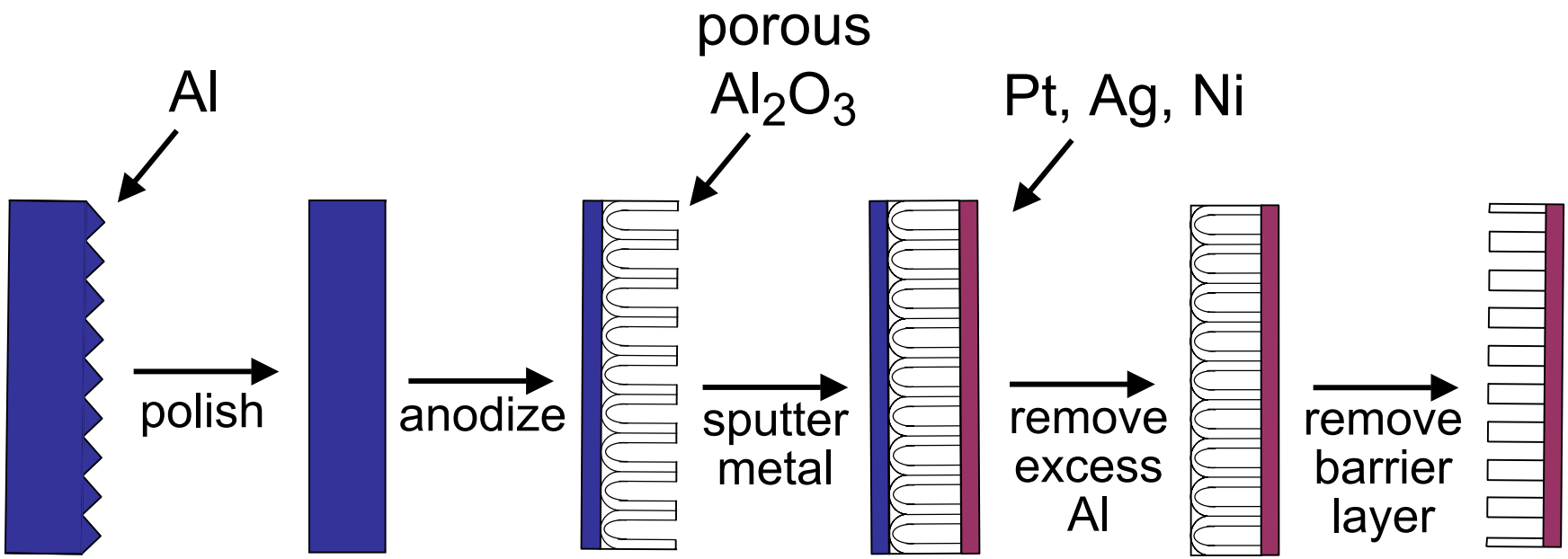
Pores form under continued oxidation and etching



Change overpotential and acid to tune pore diameter from 9 to 300 nm

Keller, F. *J. Electrochem Soc* **1953**, *100*, 411

Template Fabrication



✓ High pore density: > 5×10^{10} pores/cm^2 over ~0.2 cm^2

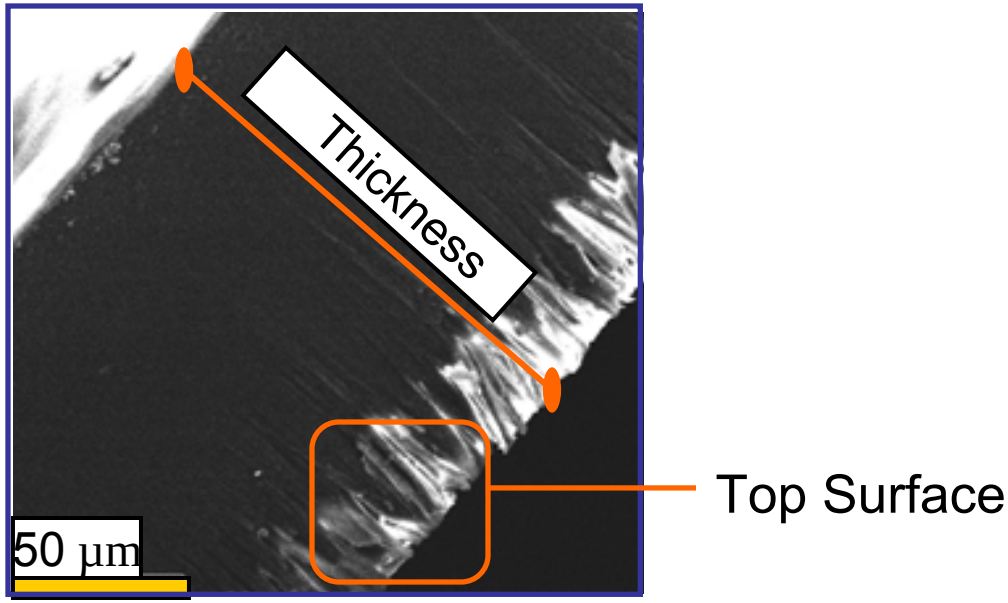
Anodizing Time vs. Thickness

Goal: High aspect ratio wires of ~3000:1

Increase the template thickness by:

- **Increasing anodization time**

6 Day Anodization

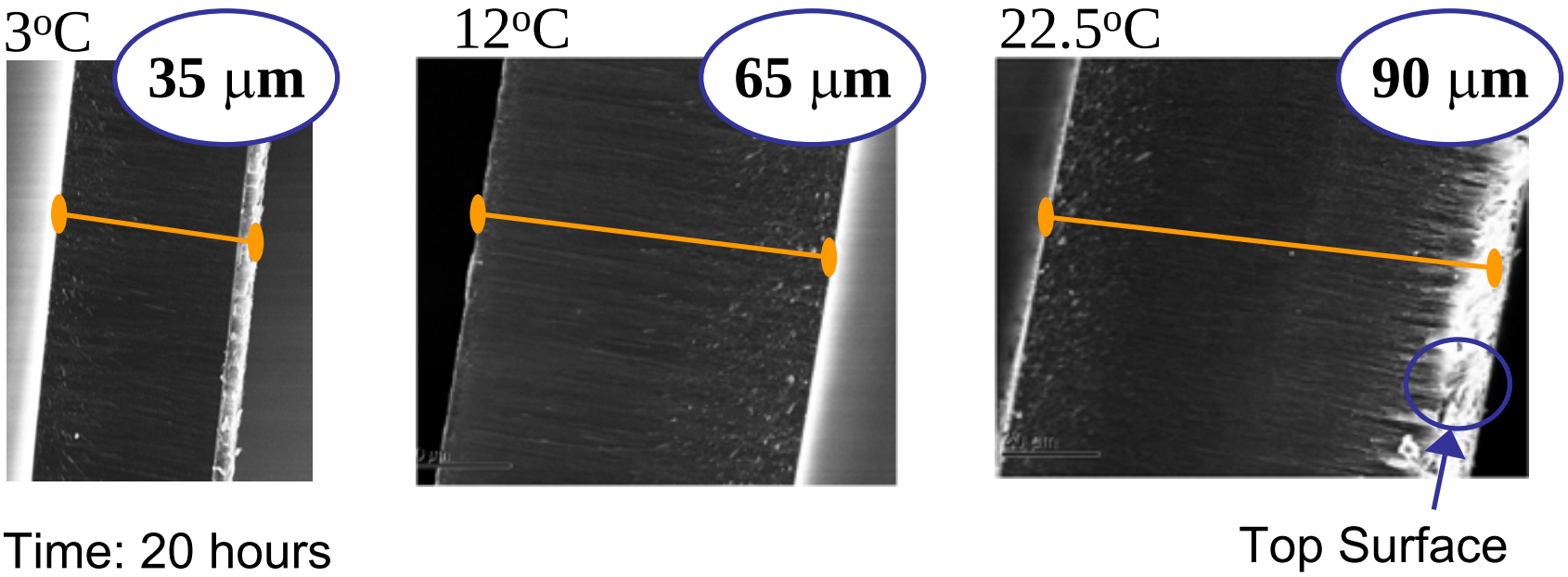


Long anodization times cause template to dissolve.

Fabrication Temperature vs. Thickness

Increase the anodization rate by:

- **Increasing temperature** to increase current density
- **Doing a double anodization** to reduce barrier to pore formation



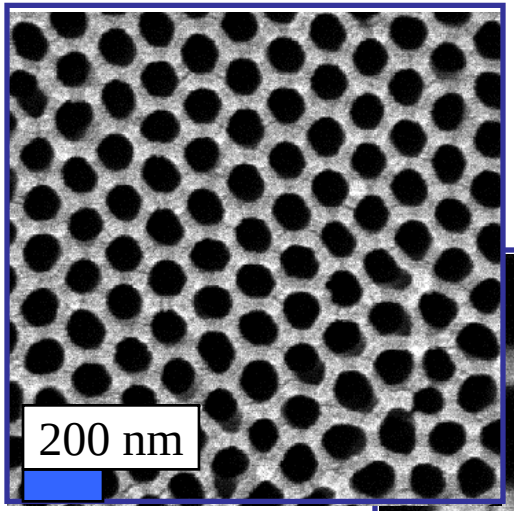
Time: 20 hours

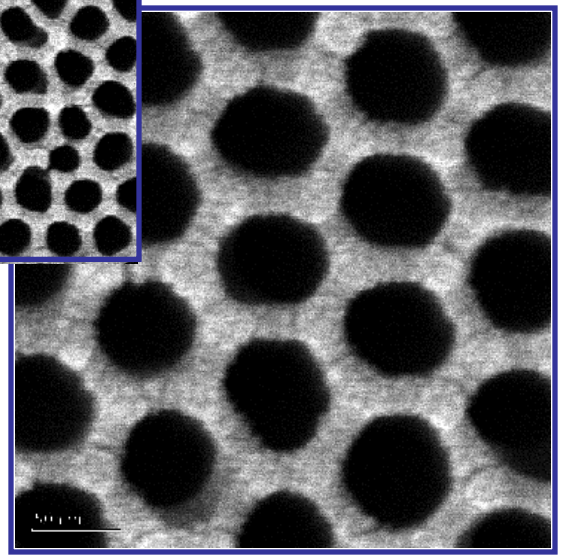
✓ High aspect ratio: 120 μm by 40 nm = 3000:1

Thick Template Results

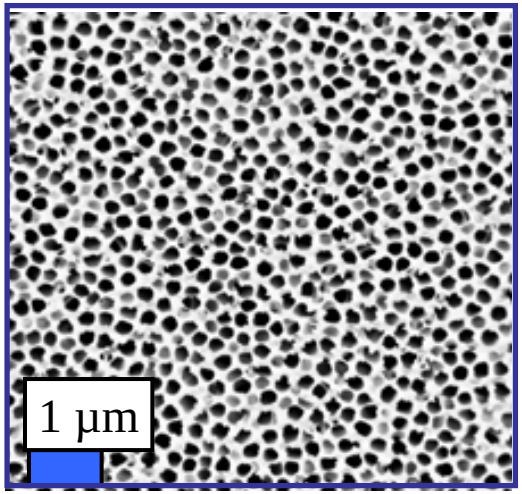
Top Surface Perfectly Intact

Homemade Template

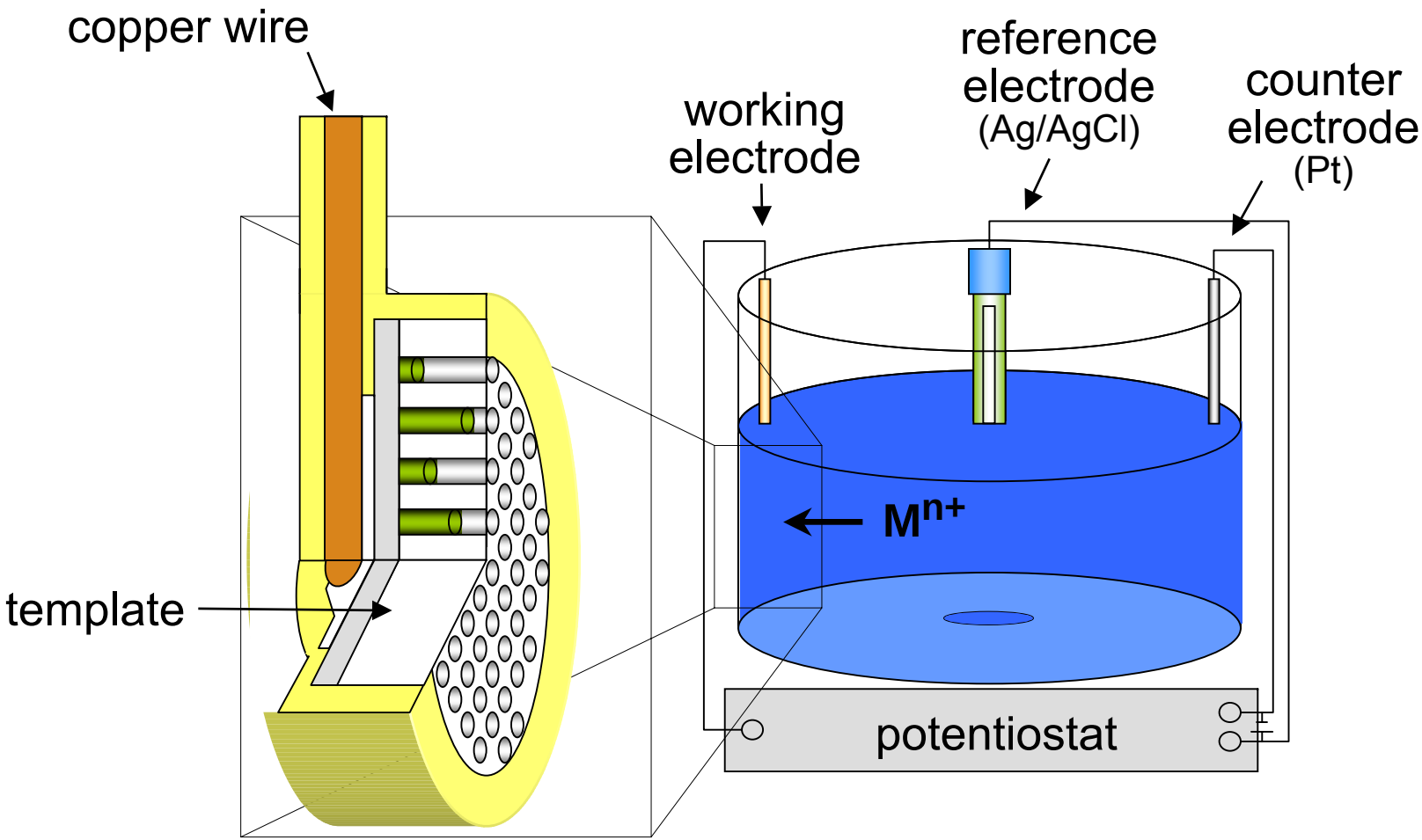




Whatman Filter

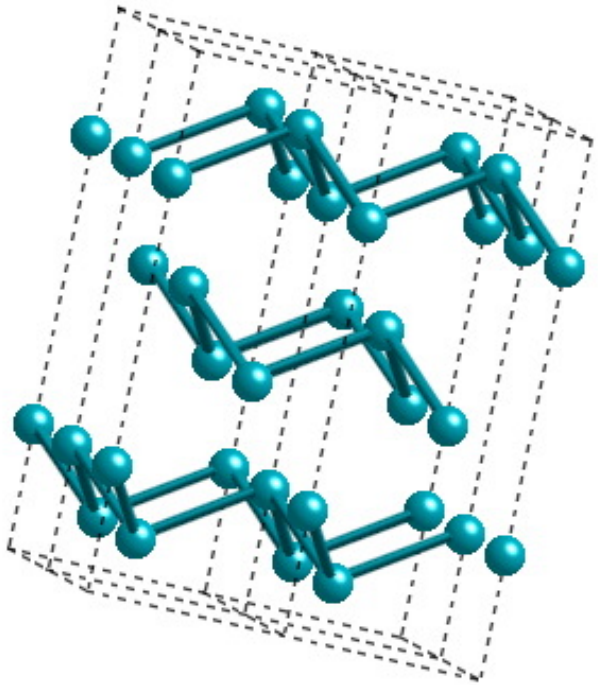


Electrodeposition Setup



Semiconductor wires are electrodeposited in the pores.

Bismuth-Antimony Alloys



$Bi_{1-x}Sb_x$

ZT(12% Sb, 80 K) ≈ 0.9

Goal: ZT~4

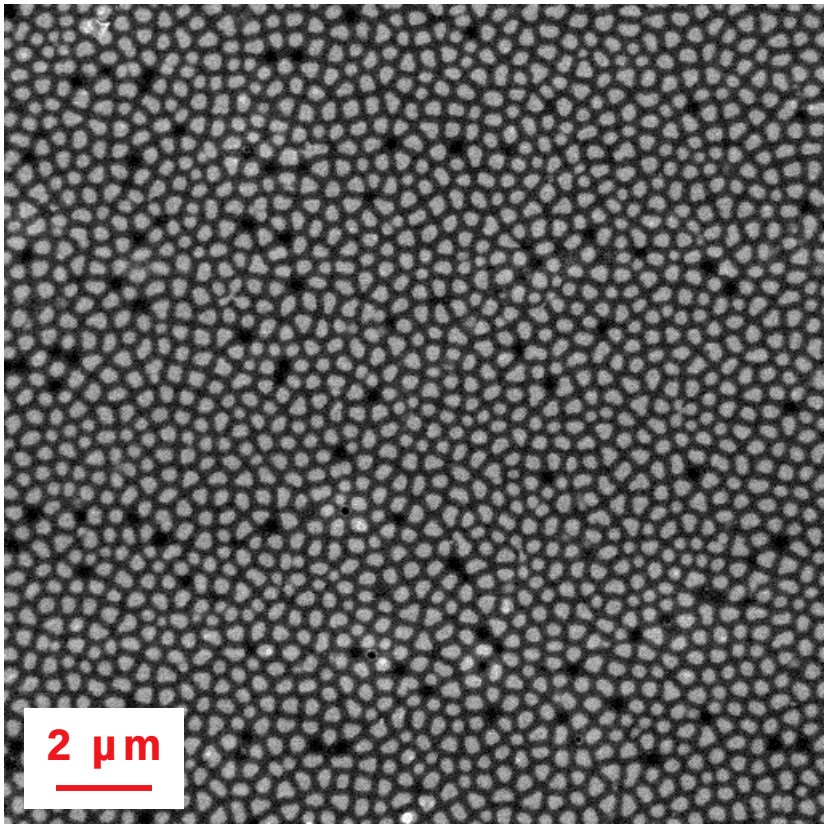
Quantum size effects predicted for 40 nm wire diameters

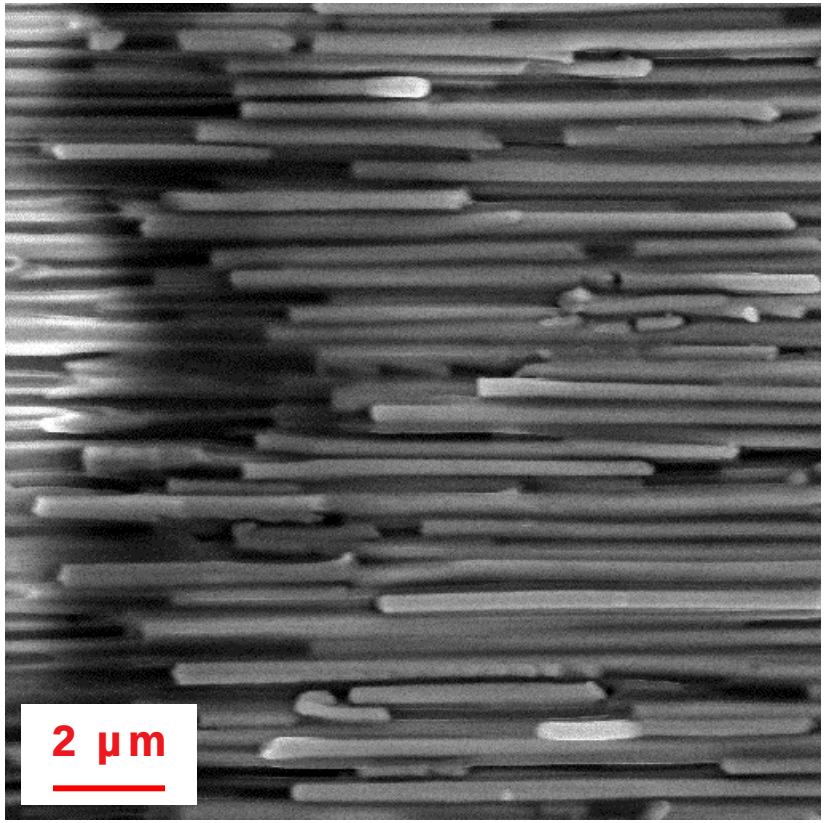
M. Dresselhaus *et. al*

Synthesis: $(1-x)Bi^{3+} + xSb^{3+} + 3e^- \xrightarrow[\text{DMSO}]{} \mathbf{Bi_{1-x}Sb_x(s)}$

High Wire Density

Goal: Wire density of ~5×10^{10} nanowires/cm^2 over ~1 cm^2



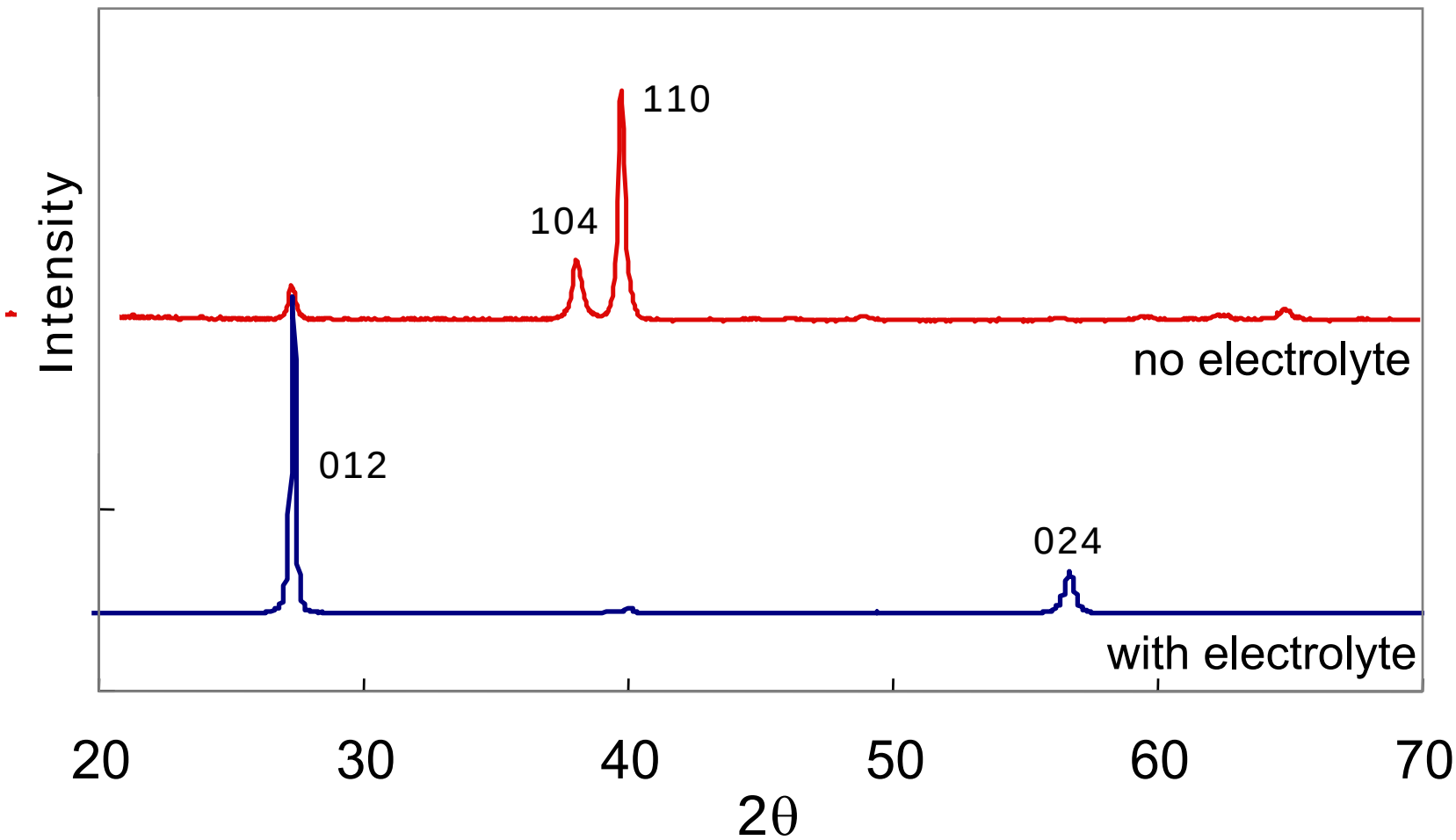


Approximate array composition: $Bi_{0.74}Sb_{0.26}$

Nanowires grown with TBA Cl are smooth and nucleate in >90% of 200 nm pores.

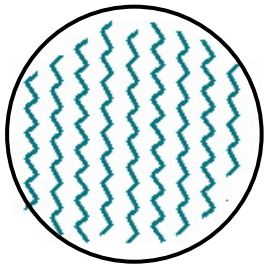
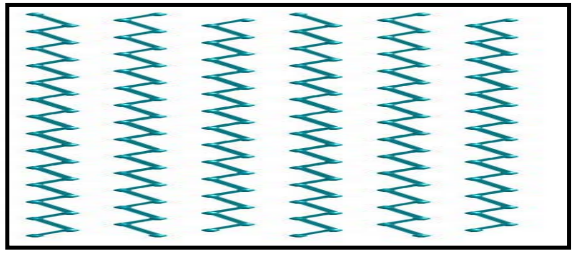
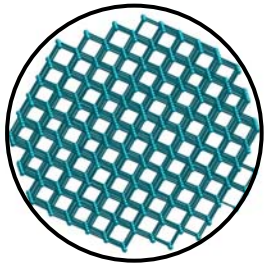
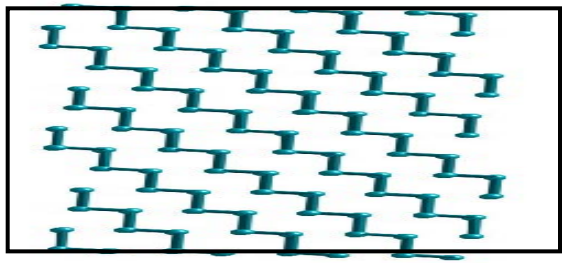
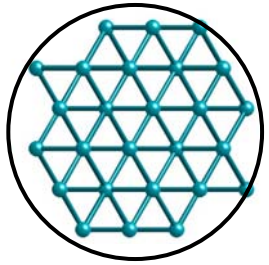
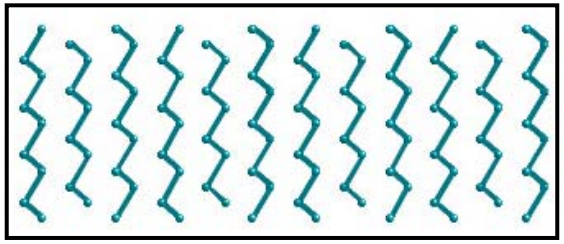
Wire Orientation

Goal: Control the crystallographic orientation of the wires



Wire orientation depends on the presence of electrolyte.

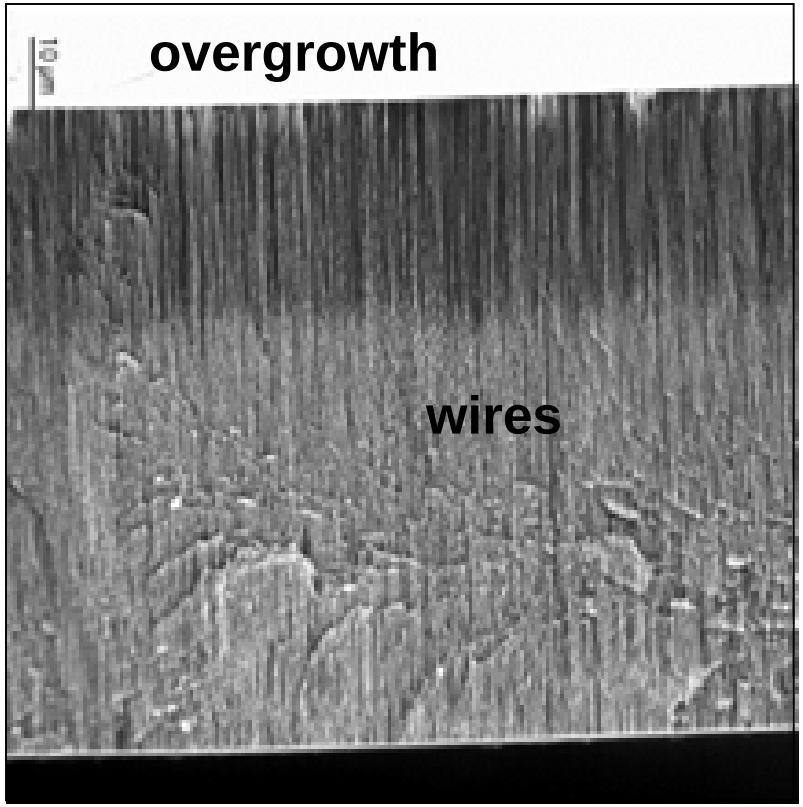
Wire Growth Orientation

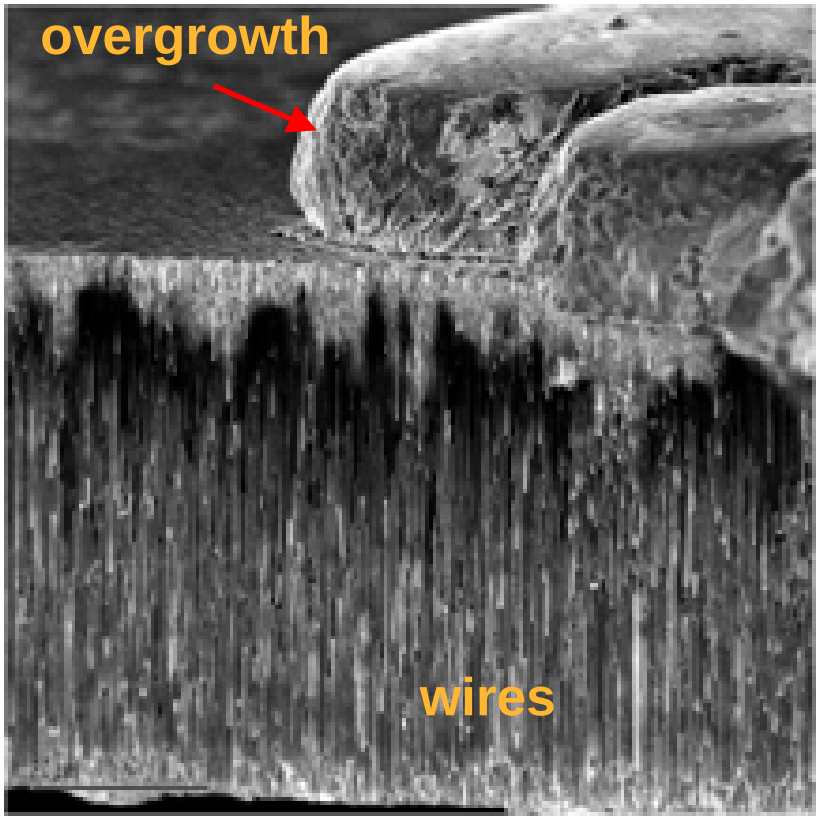
Wire Axis	Plan View	Cross Section
<110> DMSO		
<012> DMSO with TBA Cl		
<001> bulk		

Quantum confinement depends on orientation.

Equal Wire Lengths

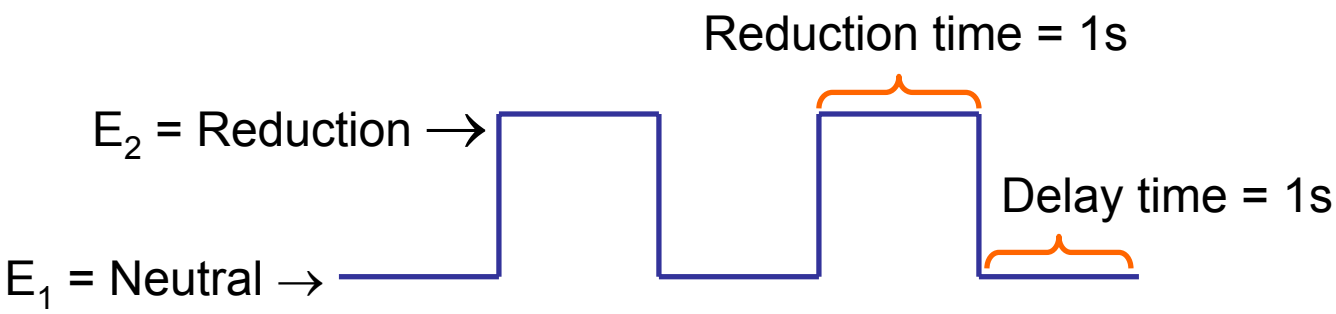
Goal: Simultaneous growth of 10^{10} wires to top of template

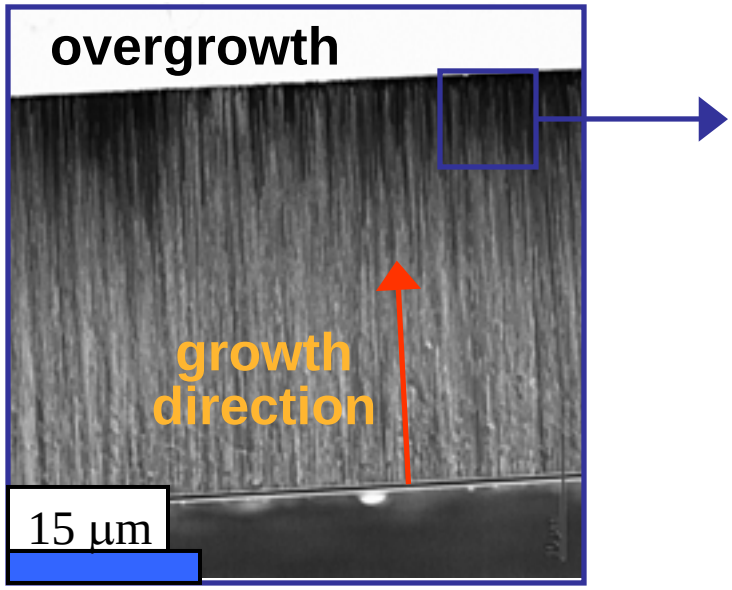


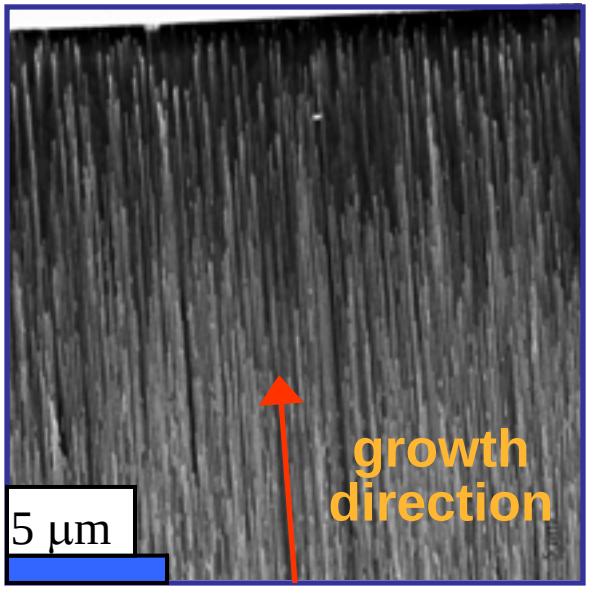


Wire growth is uniform except for a few runaway wires.

Pulse Deposition Results for Bi_2Te_3



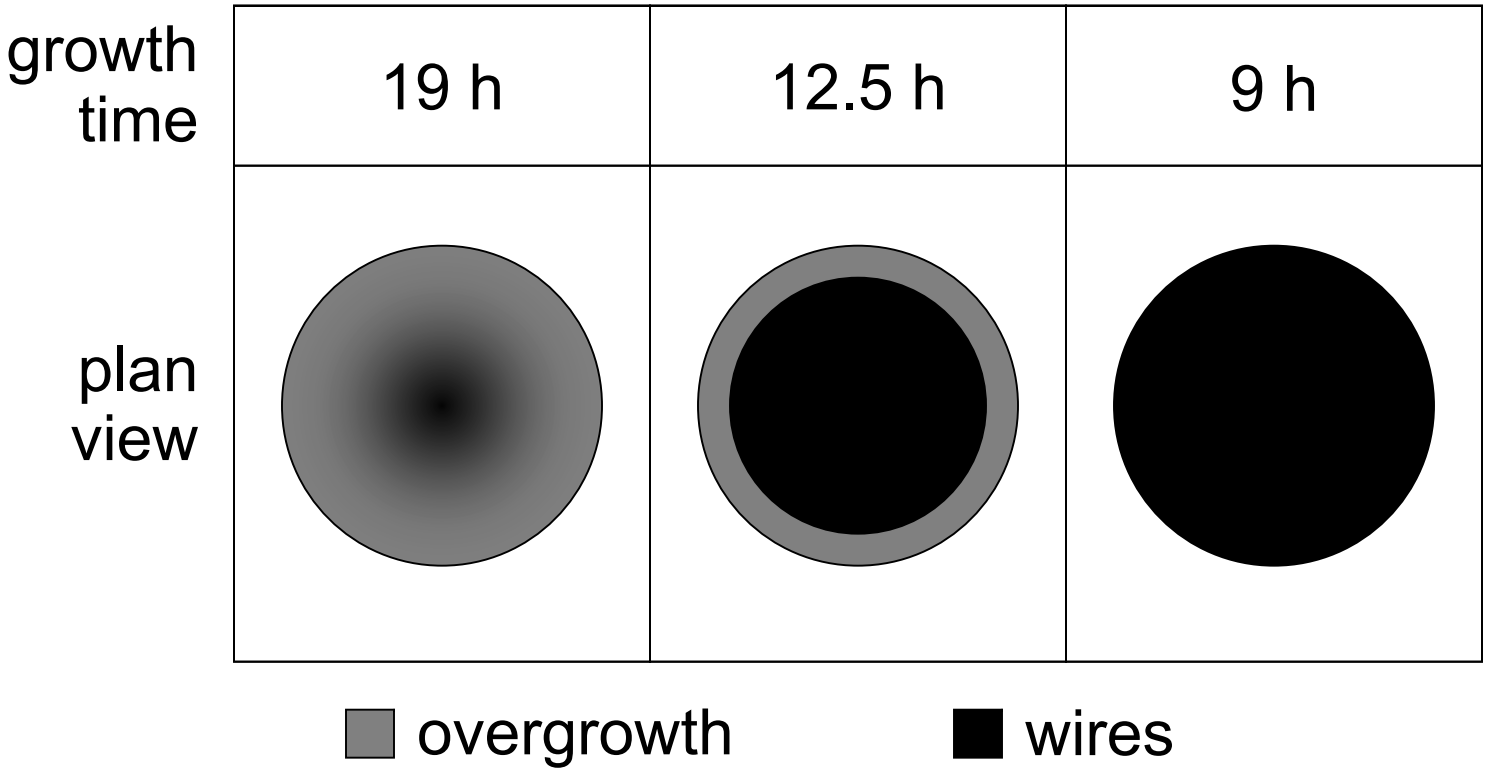




Many more wires reach the top before overgrowth.

100 nm Whatman Filters

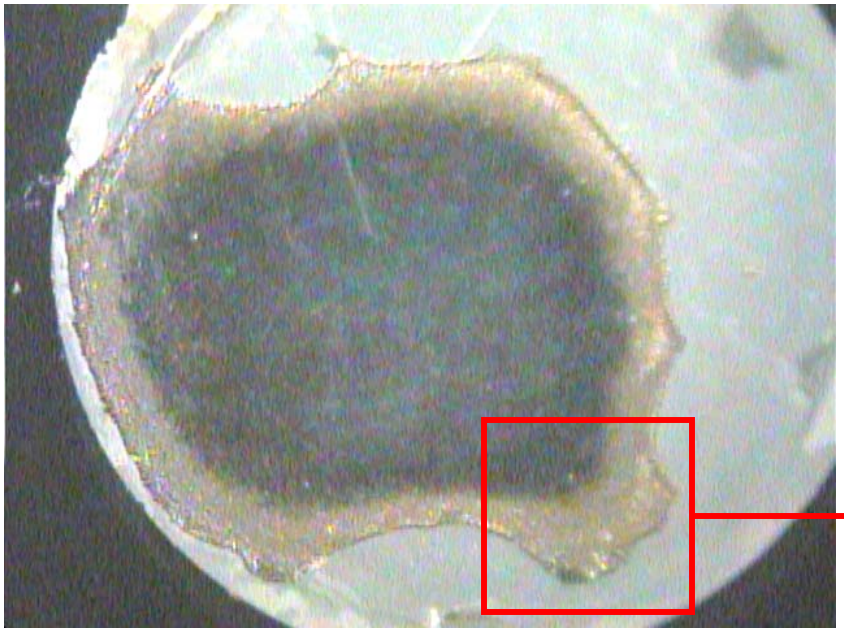
Macroscopic views of templates with BiSb wires

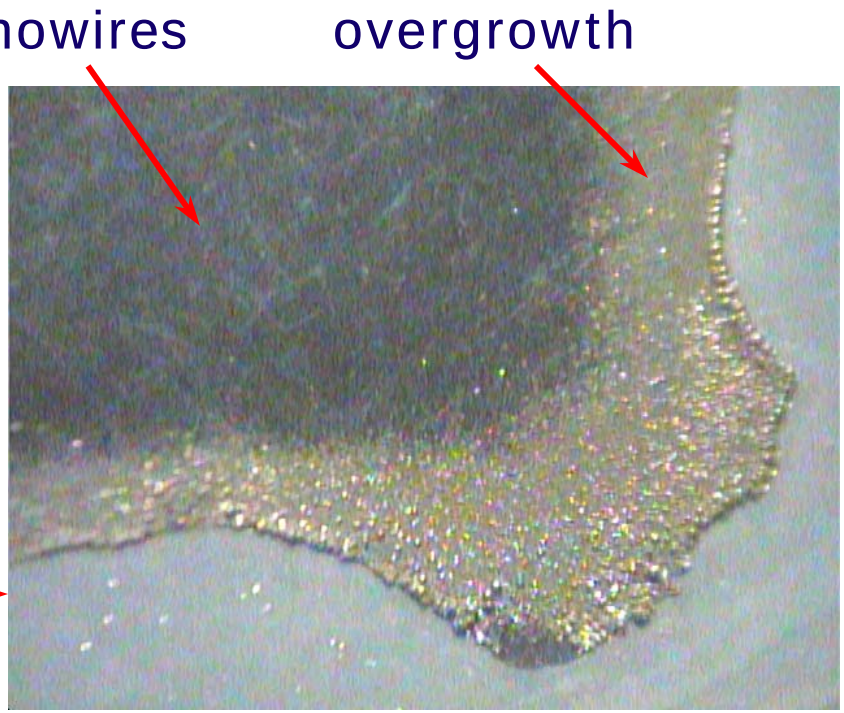


Overgrowth begins at outside edge and spreads toward center

Optical Microscope Images

12.5 h sample

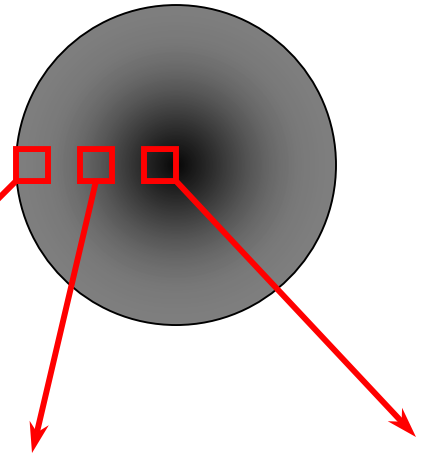




- Overgrowth visible to eye after 12.5h
- Some overgrowth visible in optical microscope after 9h

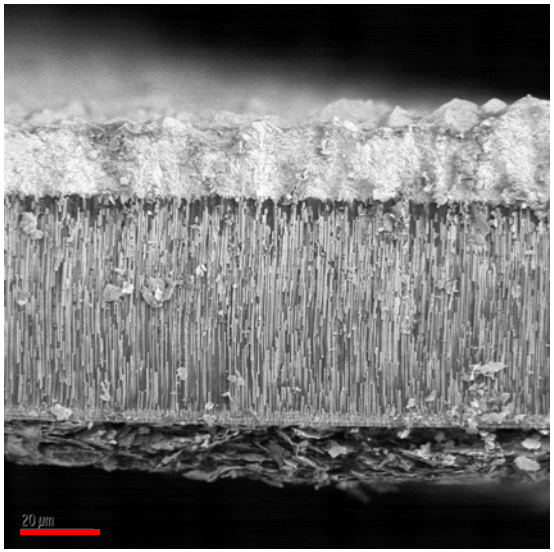
Microscopic View

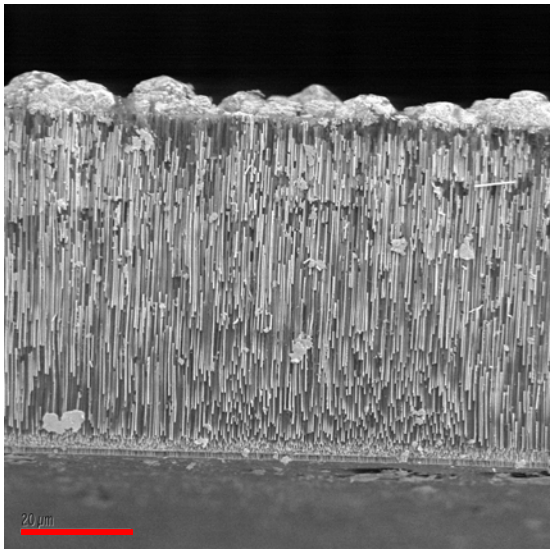
19 h sample
(plan view)

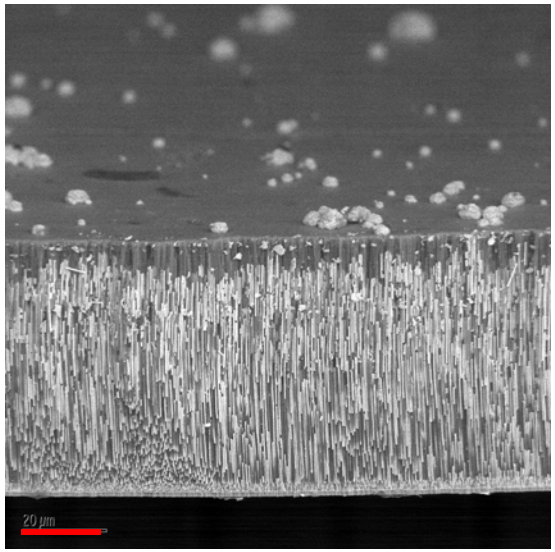


All scale bars
= 20 µm

Backscattered SEM x-sections



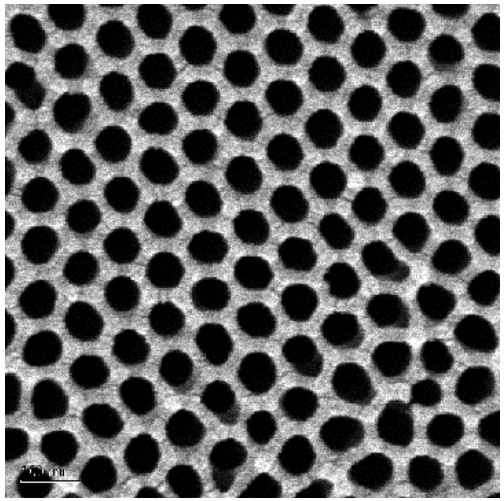


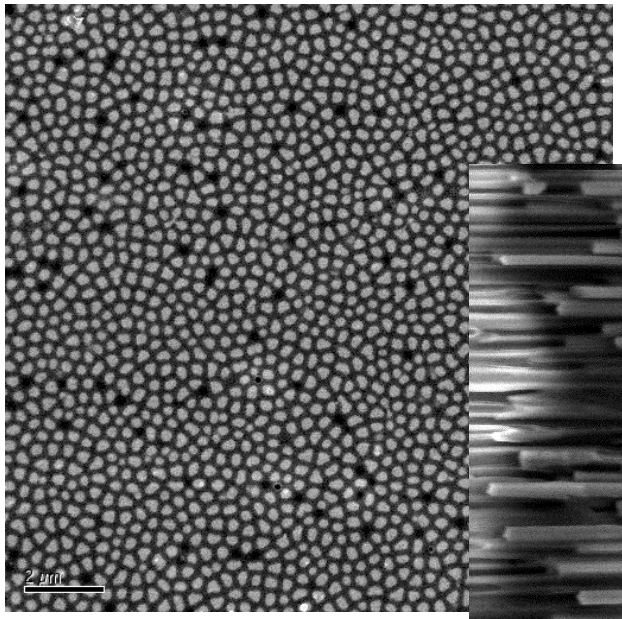


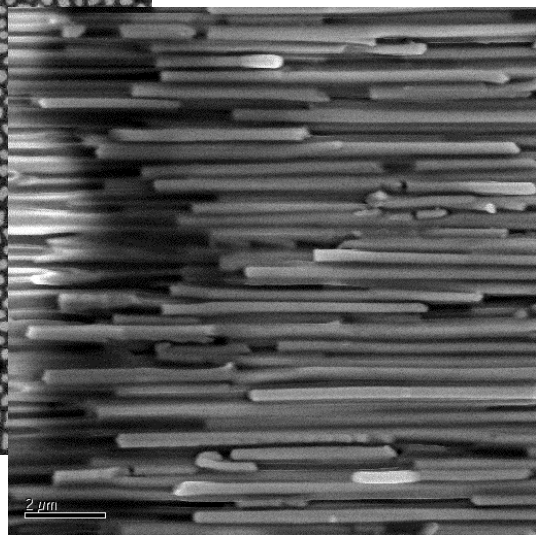
✓ Uniform wire length with wires very near the top.

Accomplishments

- High wire density
- High aspect ratio
- Control over composition and orientation
- Uniform wire lengths with wires near the top of the template







Current Work

Make contacts with 10^{10} wires

- ➢ Electrodeposition
- ➢ Electroless deposition
- ➢ Metal injection

X Etch back followed by deposition

Measure thermoelectric efficiencies

with Marlow Industries