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Electrochemical Deposition of $Bi_2(Te,Se)_3$ and $Bi_{1-x}Sb_x$ Nanowire Arrays on Silicon

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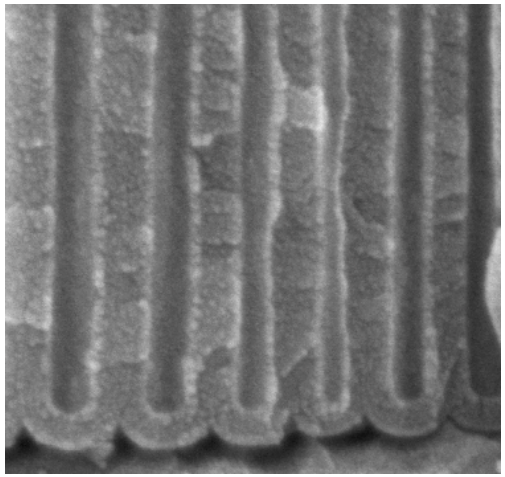
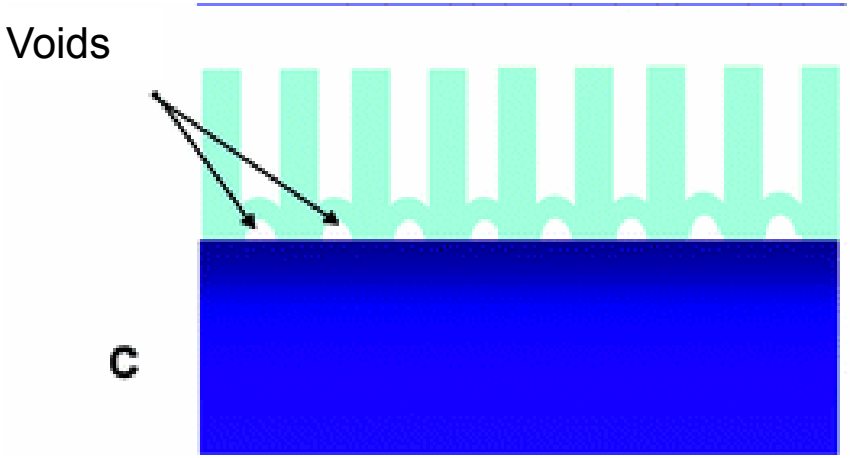
Anodic aluminum oxide (AAO) templates on Si

- Pores in AAO tend to have a “test-tube” shape; open at one end with an oxide cap at the other end
- This barrier oxide interferes with electrodeposition



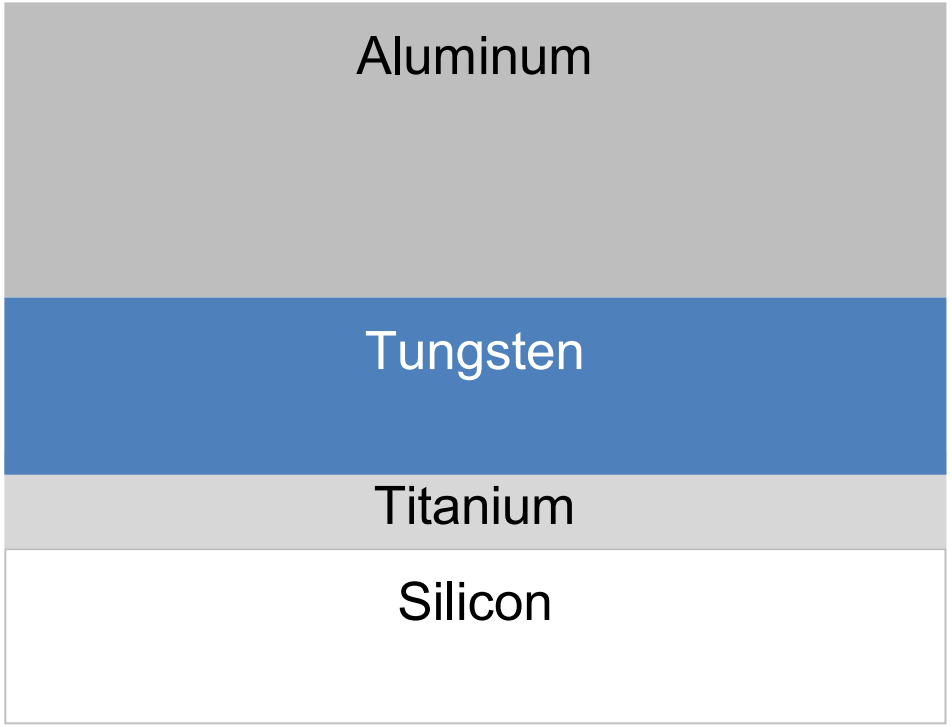


Foong, *ACS Nano* (2008).

- Attempts to form AAO directly on a conductive substrate (Au, Si, ITO…) tend to have voids and delaminate

AAO templates on Si

- Using a valve metal layer (e.g. W, Nb, Ta) under the Al alleviates this problem
  - WO_3 forms solid plugs at pore bottoms
  - WO_3 plugs can be selectively etched, leaving pores open at both ends



J. Oh, *Adv. Mater.* (2008)

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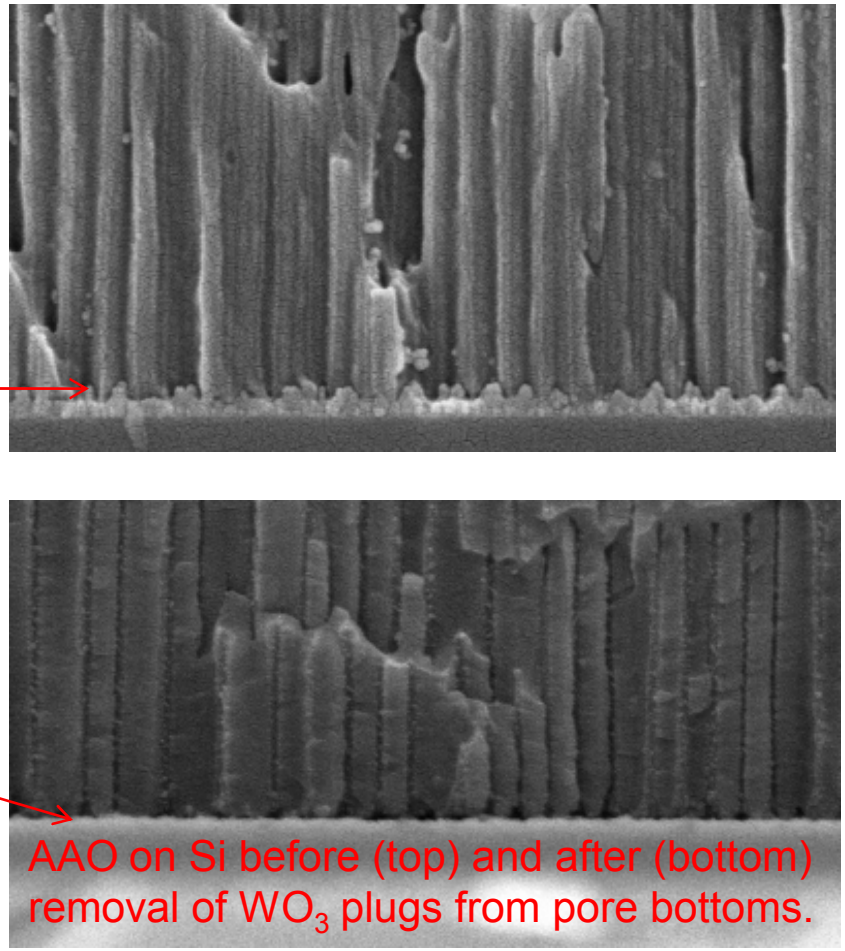


AAO on Si before (top) and after (bottom) removal of WO_3 plugs from pore bottoms.

J. Oh, *Adv. Mater.* (2008)

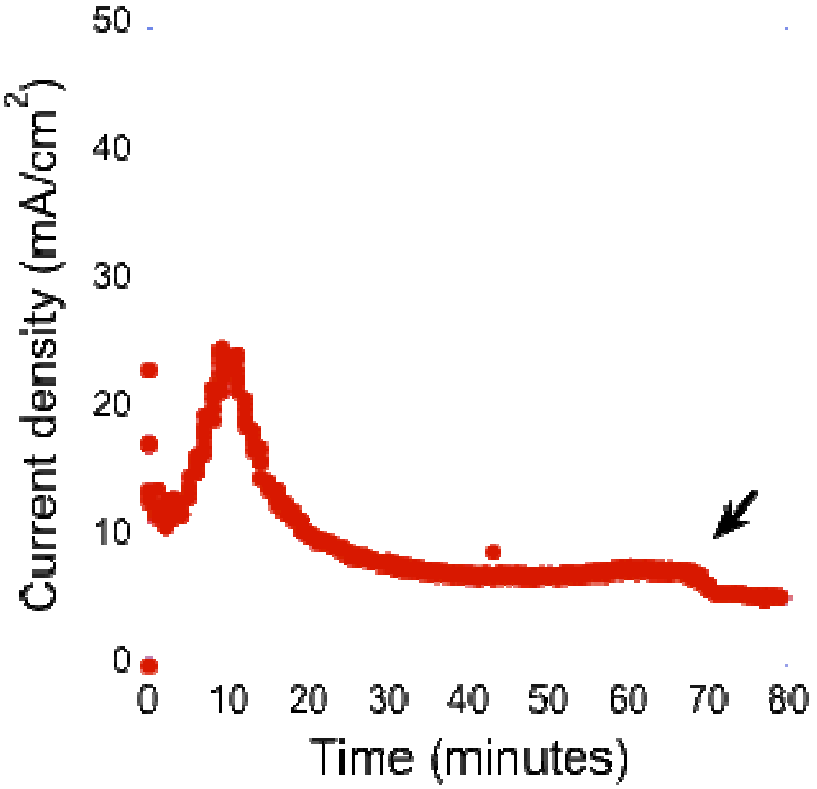
Forming AAO templates on Si

Target AAO dimensions:

75 nm pores

lengths up to ~15 μm

- Anodize (~45 nm pores)
  - 3 wt% oxalic acid, 1 °C, 40 V
  - ~20% dip in current signals that Al is converted to AAO
- Selective etch
  - pH 7 phosphate buffer
- Widening pores to ~75 nm
  - 20 min 30 °C 5 wt% H_3PO_4



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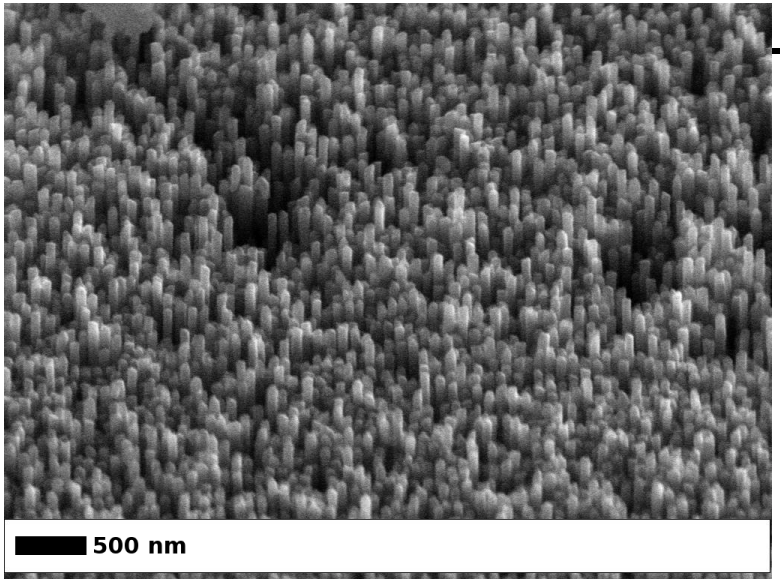
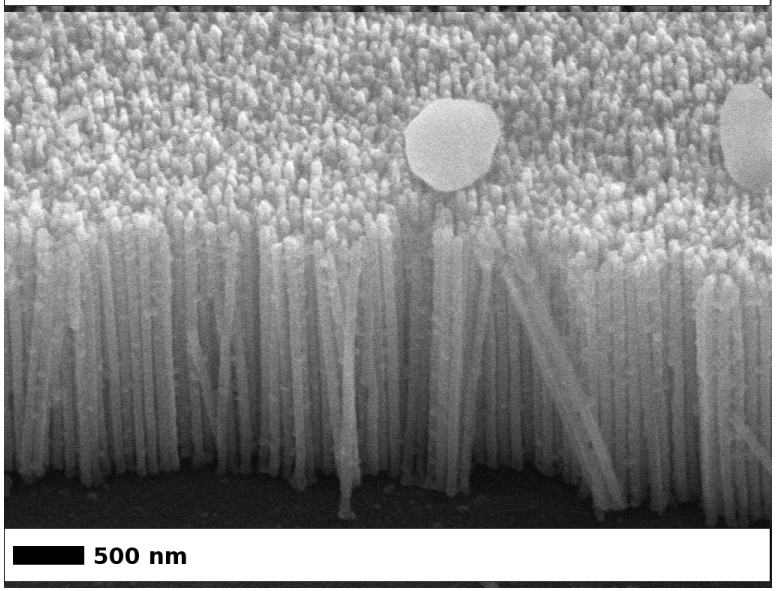
Electrodeposition of $Bi_2(Te,Se)_3$ nanowire arrays





- Non-aqueous bath
  - 80 mM $Bi(NO_3)_3$, 40-80 mM $TeCl_4$ and 0.8-1.2 mM SeO_2 with 0.1 M $KClO_4$ in DMSO
- Pulsed electrochemical deposition
  - 1 s off, 20-500 ms on
  - On currents: 0.2-10 mA/cm^2

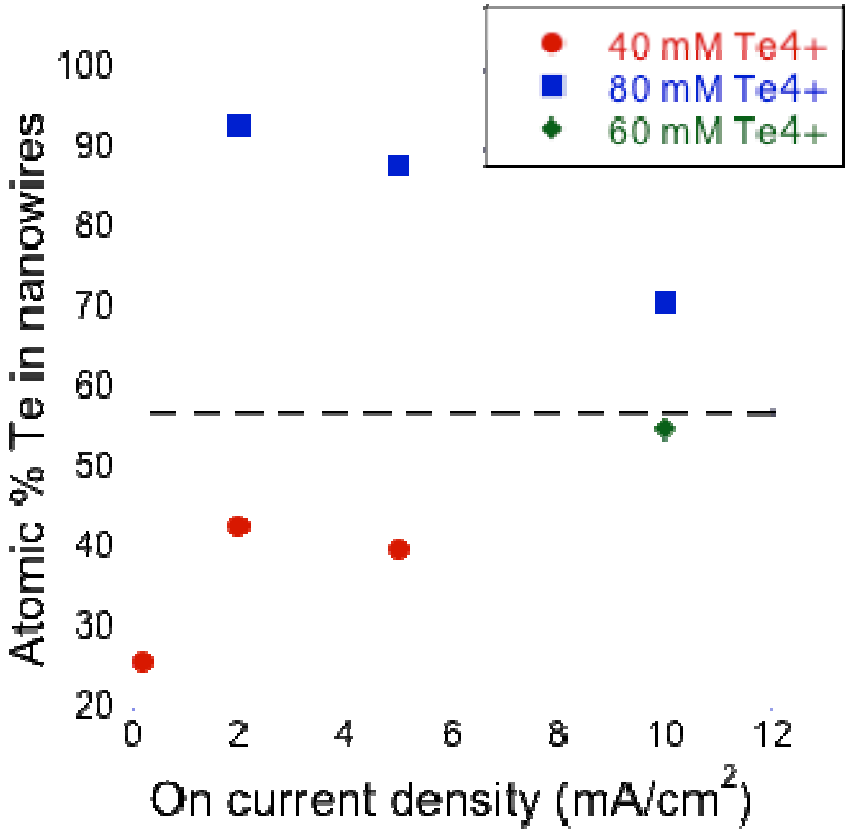
Electrodeposition of $Bi_2(Te,Se)_3$ nanowire arrays

Target composition (to start) :

~$Bi_2(Te_{0.95}Se_{0.05})_3$

40% Bi, 57% Te and 3% Se

•Plating parameters and bath composition must all be tuned to reach goal



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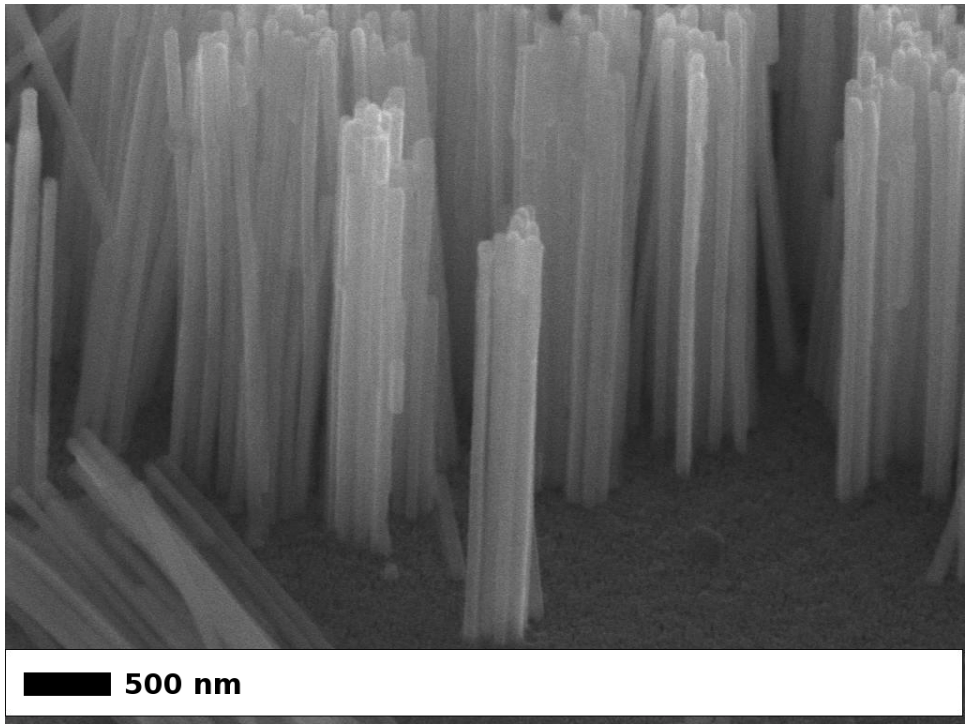
$Bi_2(Te,Se)_3$ nanowire arrays

Present iteration:

- 80 mM $Bi(NO_3)_3$, 60 mM $TeCl_4$ and 1.1 mM SeO_2
- 1 s off, 500 ms on at 10 mA/cm^2

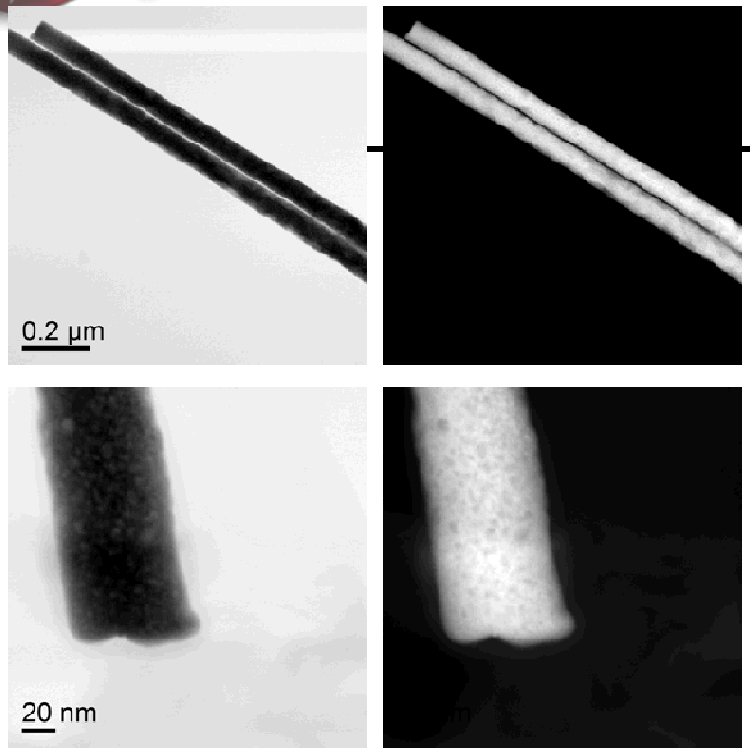
~75 nm diam, up to ~ 10 μm long

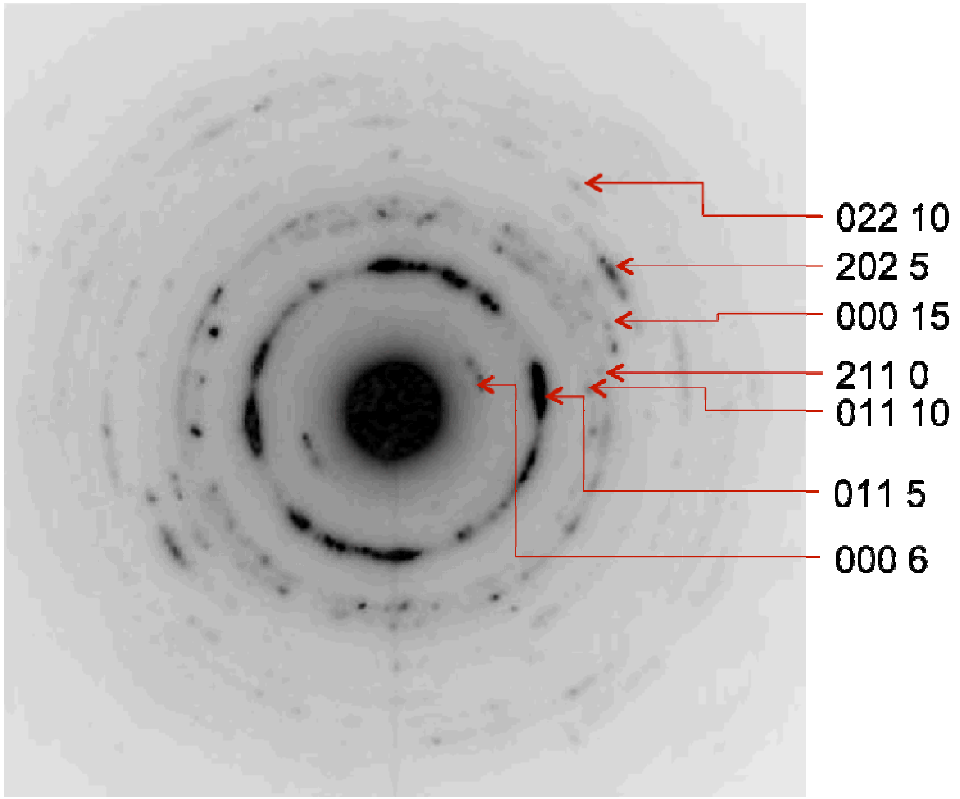


- Overall average composition (SEM EDS):
  - 41.2 ± 1.1 at. % Bi
  - 55.3 ± 1.0 at. % Te
  - 3.4 ± 0.04 at. % Se

- Optimal range
  - 40% Bi
  - 57-58.5% Te
  - 1.5-3% Se

$Bi_2(Te,Se)_3$ nanowires

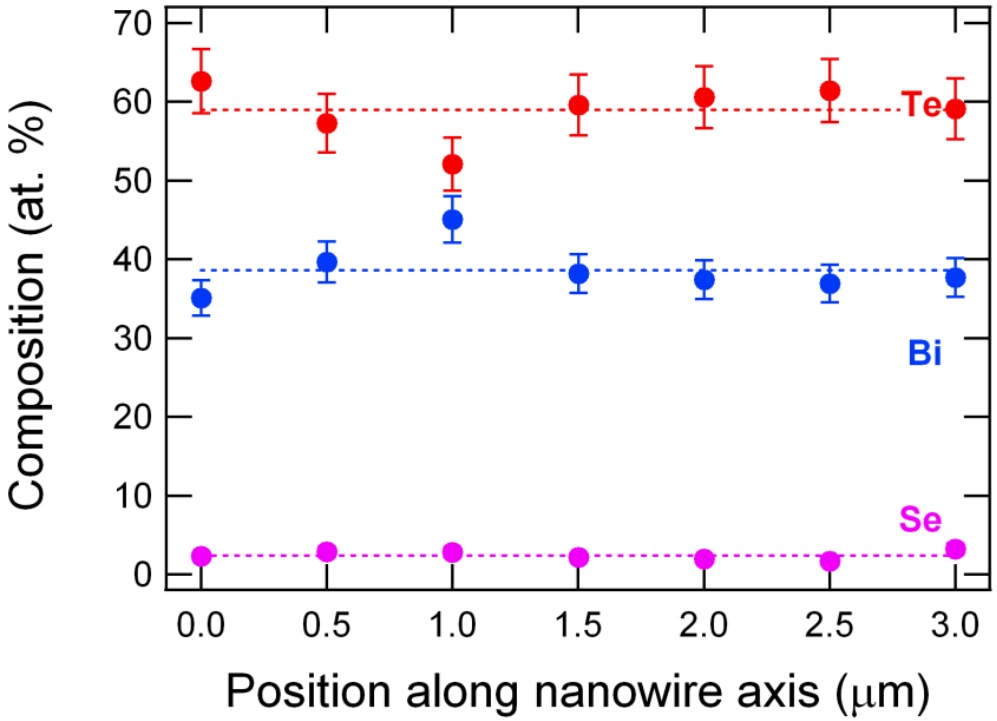


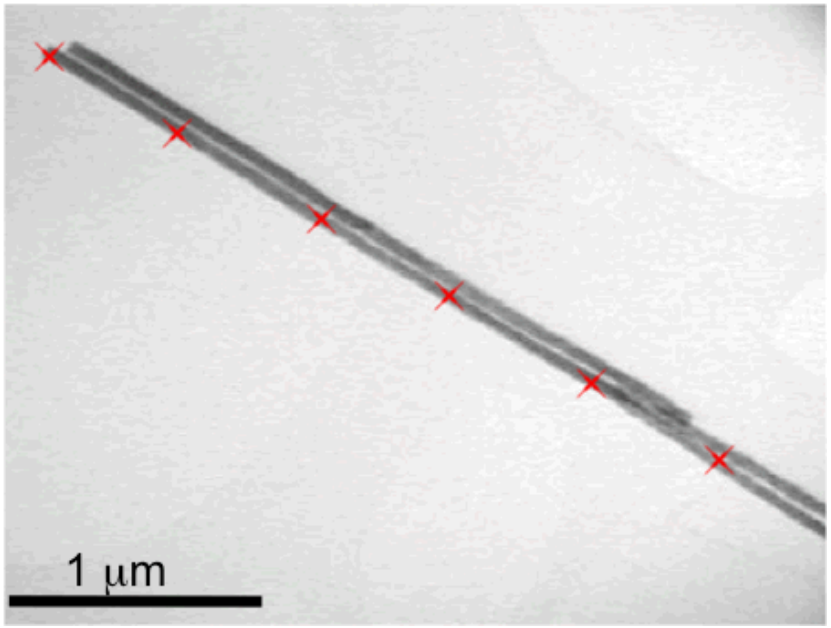


- Composition averaged over several nanowires (TEM EDS):
  - 38.6 ± 2.8 at. % Bi
  - 58.9 ± 4.3 at. % Te
  - 2.5 ± 0.5 at. % Se

- Optimal range
  - 40% Bi
  - 57-58.5% Te
  - 1.5-3% Se

$Bi_2(Te,Se)_3$ nanowire composition is largely uniform along nanowire axis





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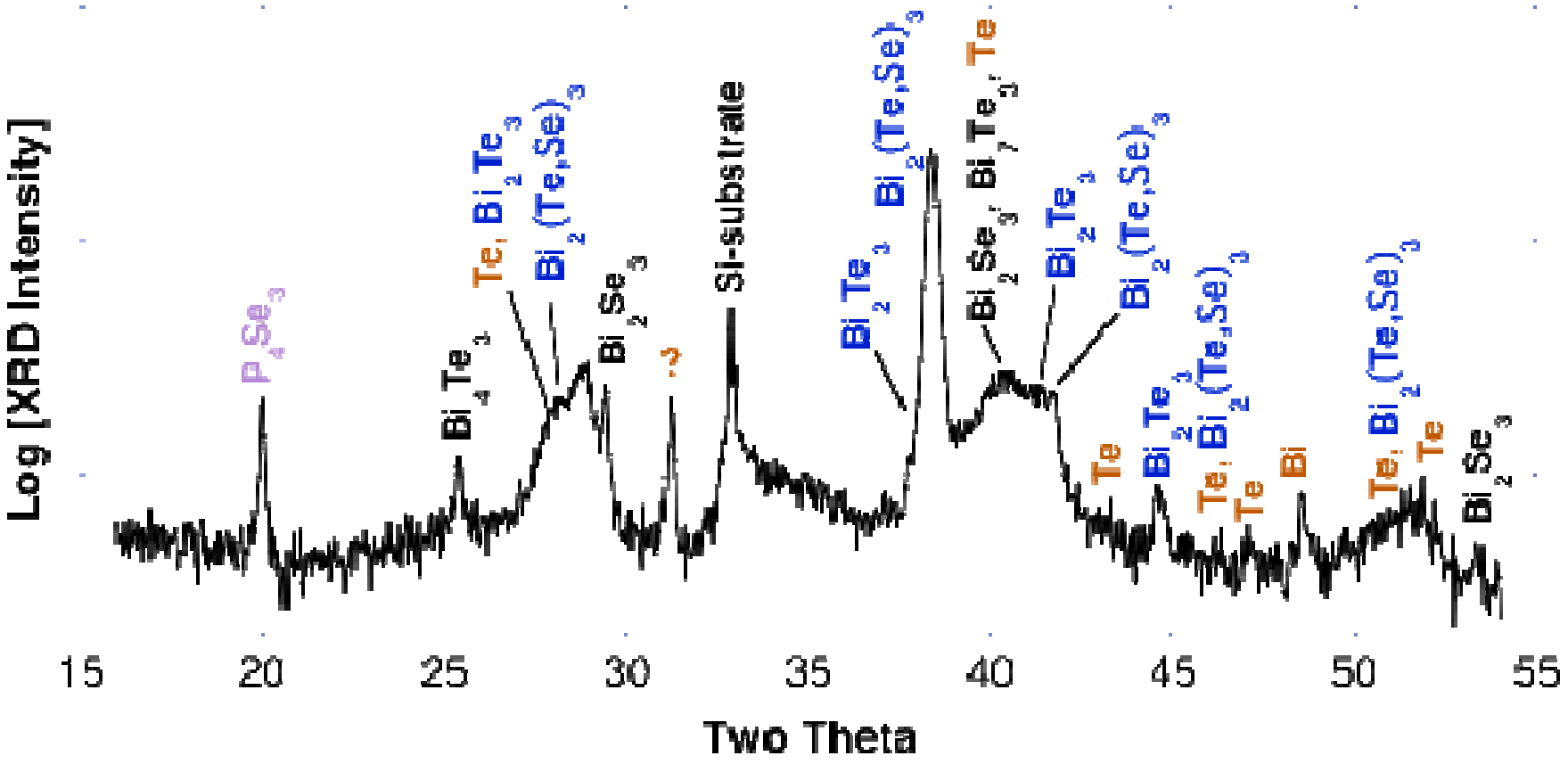
$Bi_2(Te,Se)_3$ nanowire arrays

Composition	Reference
Optimal range $Bi_2Te_{2.925}Se_{0.075}$ – $Bi_2Te_{2.85}Se_{0.15}$	Xio, *Electrochim. Acta* (2008)
$Bi_{1.93}Te_{2.95}Se_{0.13}$	This work
$Bi_{2.1}Te_{2.4}Se_{0.5}$	Martín-González, *Nano Lett.* (2003)
$Bi_2Te_{2.3}Se_{0.7}$	Li, *Cryst. Growth Des.* (2008)
$Bi_2Te_{2.7}Se_{0.3}$	Li,. *Superlattices Microstruct. (2010)*

Closer to target composition than many reported $Bi_2(Te,Se)_3$ nanowires

$Bi_2(Te,Se)_3$ nanowire arrays



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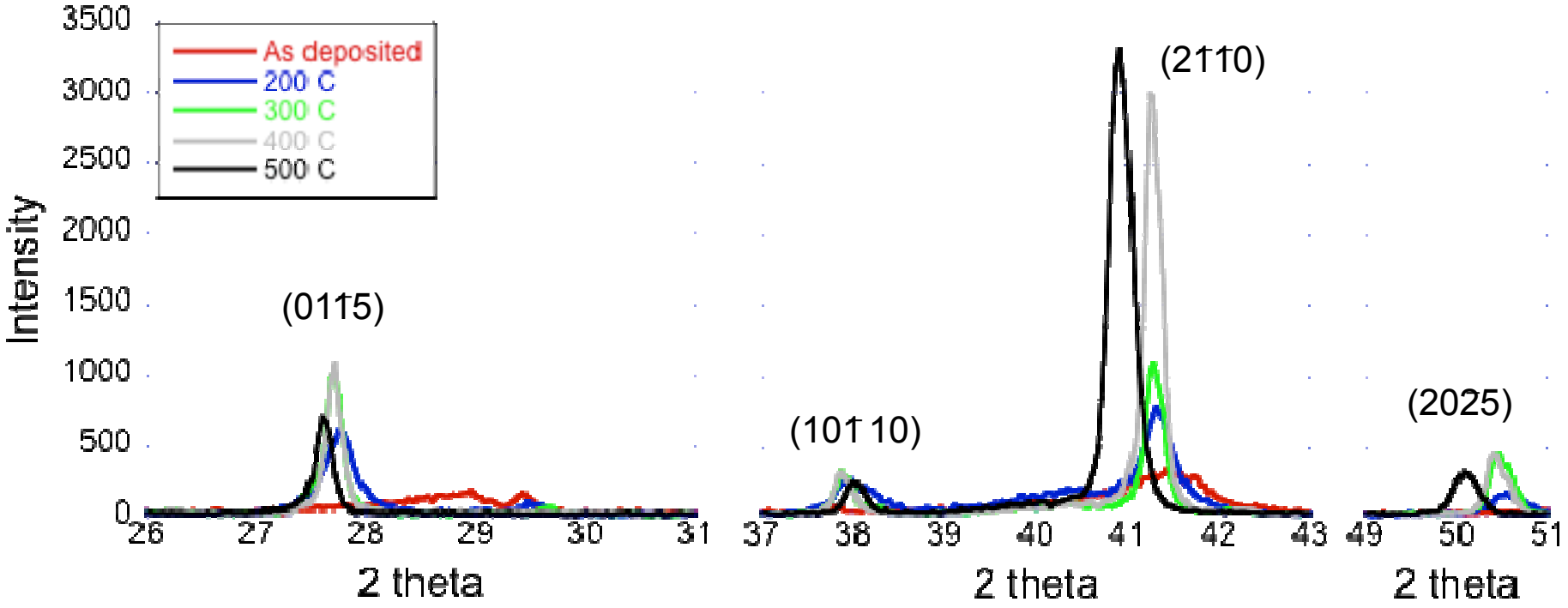
Annealing $Bi_2(Te,Se)_3$ nanowire arrays (Mike Siegal W2.2)



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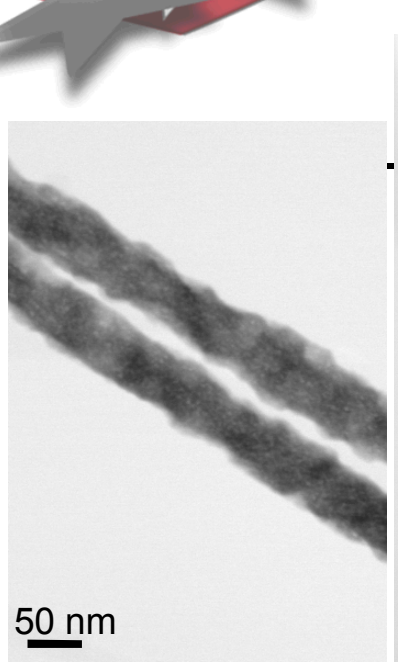
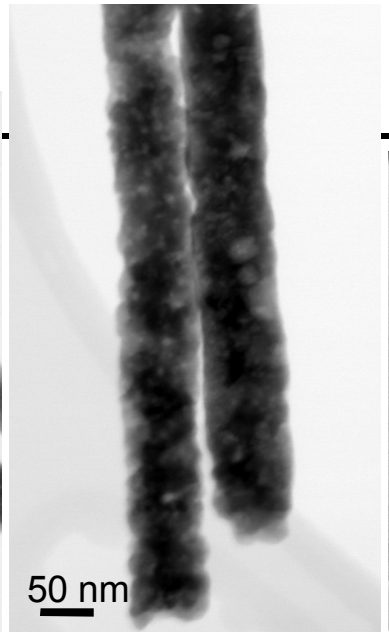
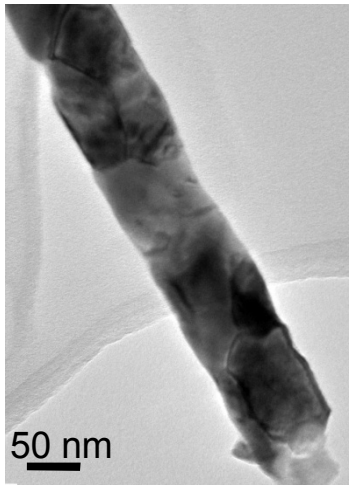
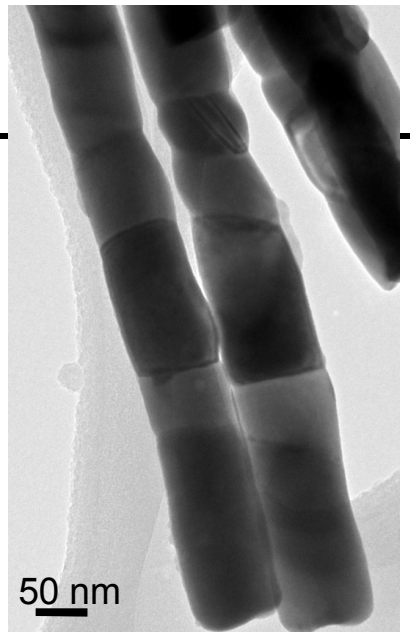






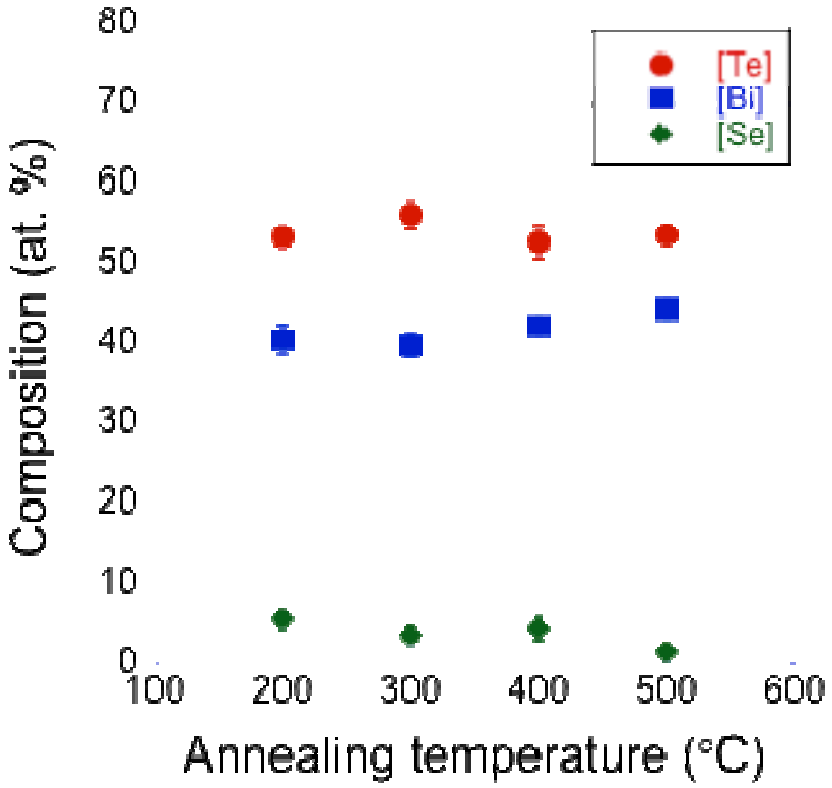


As Deposited	200°C	300°C	400°C	500°C
Grains < 10 nm most ~ 5 nm	Grains < 40 nm most ~ 20 nm	Grains up to 250 nm x full width Ave: 56 nm x 98 nm	Grains up to 320 nm x full width Ave: 74 nm x 145 nm	Grains up to 350 nm x full width

TEM images of $Bi_2(Te_{1-x}Se_x)_3$ nanowires annealed for 30 minutes in 3 % H_2/Ar

Annealing $Bi_2(Te,Se)_3$ nanowire arrays

Temp (°C)	Phases (from XRD)
As deposited	Bi_2Te_3 type Bismuth-rich phases (Bi_4Te_3, Bi_7Te_3 types) Elemental Bi and Te
90	Bi_2Te_3 type
200	Bi_2Te_3 type
300	Bi_2Te_3 type
400	Bi_2Te_3 type
500	Bi_2Te_3 type, Bi_4Te_5 type



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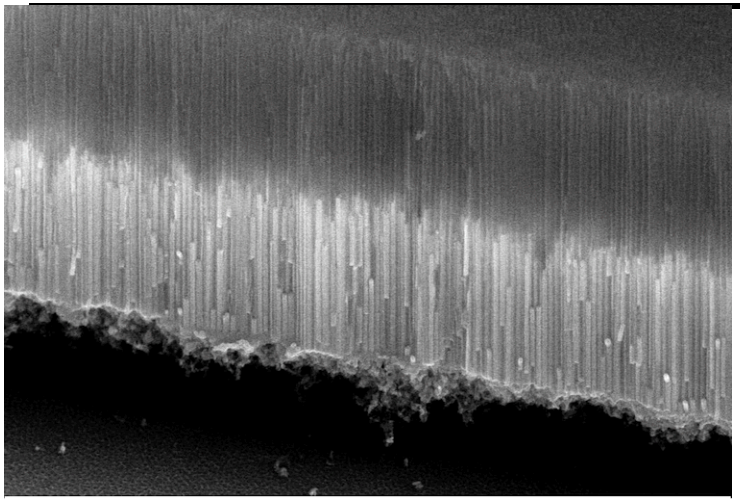
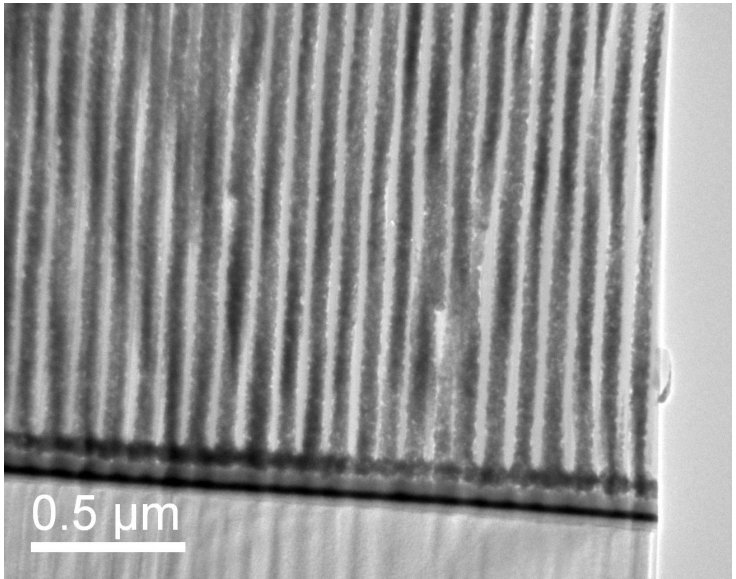
Electrodeposition of $Bi_{1-x}Sb_x$ nanowire arrays (Graham Yelton, Poster 17)





- Bath: 30-50 mM $Bi(NO_3)_3$, and 30-50 mM SbI_3 with 0.1 M $KClO_4$ in DMSO

- Galvanostatic Pulse Strike (10 cycles):
  - T off=1.0 s, I off = -0.2 mA/cm^2
  - T on = 0.2 s, I on = -30-40 mA/cm^2
- Galvanostatic Pulse plating:
  - T off=1.5 s, I off = -0.2 mA/cm^2
  - T on = 0.5 s, I on = -1-3 mA/cm^2

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