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Uniform Synthesis of Compositionally and Highly Crystalline $Bi_{1-x}Sb_x$ Nanowire Arrays

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Session: Novel Thermoelectric Material IV
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Overview of the talk

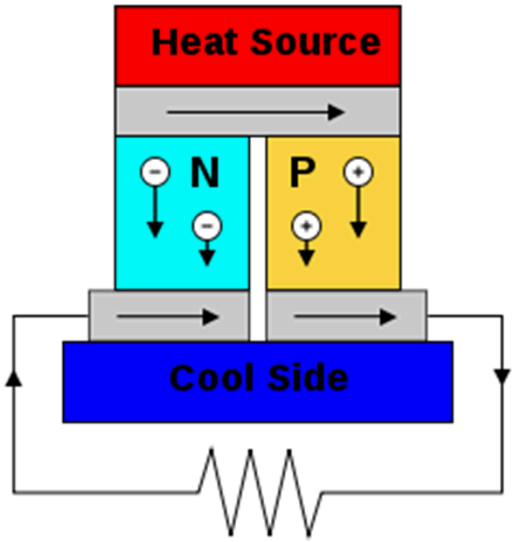
- Thermo-electric Theory: *why the dependency on size and crystallinity?*
- Electrochemistry of the system: *SbI_3 vs. $SbCl_3$.*
- Macro-uniformity issues: *why the concern?*
- Nano-uniformity worries: *n-type, p-type, zT's.*
- Nano-wire characterization: *SEM, XRD, TEM.*

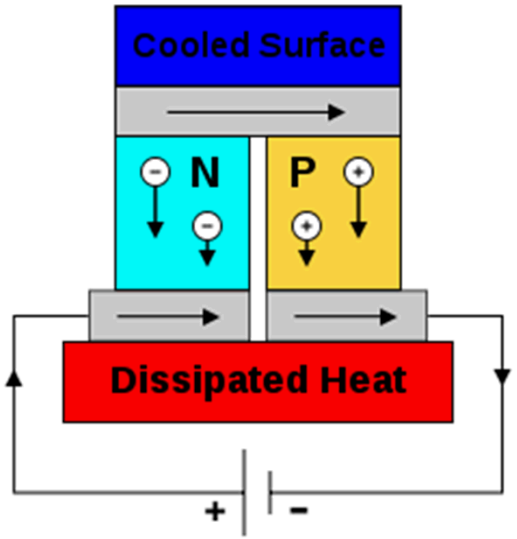
Thermoelectric theory: *Thermoelectric Effect*

the direct conversion of temperature differences into electric voltage and vice-versa

This effect can be used to:

1. **Generate electricity (Seebeck effect – 1821):** dissimilar metals, or semiconductors, connected at two locations (junctions) develop a μ-voltage if the junctions are held at different temperatures. *The Seebeck effect is the basis for thermocouple thermometers.*
2. **Generate a temperature gradient (Peltier effect – 1834):** applying a voltage to a thermocouple generates a temperature difference between the junctions. *The result is a small heat pump, or TEC (thermoelectric cooler).*





Thermoelectric (TE) Performance

Need High TE Figure of Merit

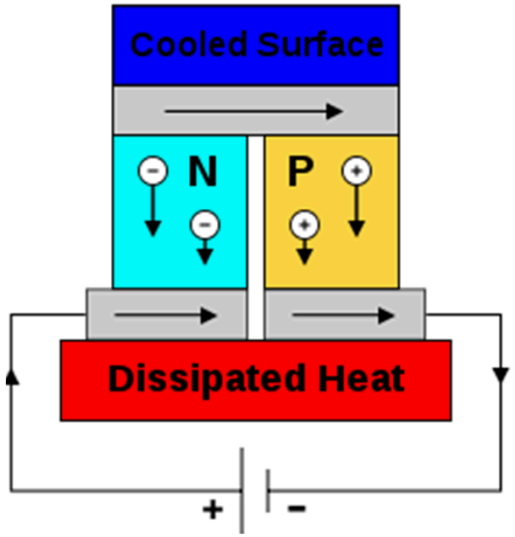
$$zT = \frac{S^2\sigma}{\kappa} T$$

***NEED*:**

high electrical conductivity

low thermal conductivity

high thermopower (Seebeck coefficient)



Seebeck coefficient (thermopower)

Measure of the magnitude of an induced TE voltage in response to a temperature difference across that material (μV/K)

Causes charge carriers (electrons or holes) to diffuse from the hot to the cold side, similar to a gas expansion due to heat.

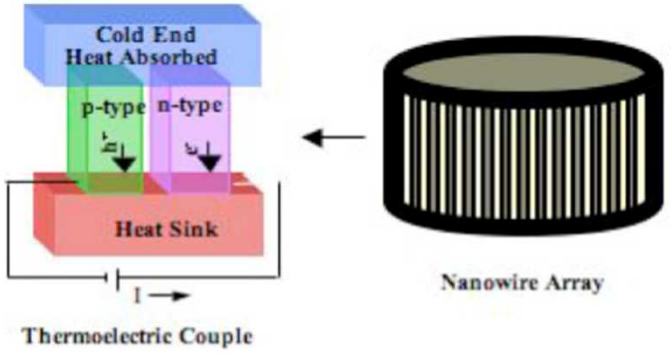
This separation of charges creates an electric field.

Metals have very low S since electrons and holes will cancel each other out.

Semiconductors can be doped with excess electrons or holes, and can have large negative or positive values of S.

Thermoelectric Nanowires

represents the ideal geometry for a thermoelectric material



for nanowires

$$zT = \frac{S^2\sigma}{\kappa} T$$

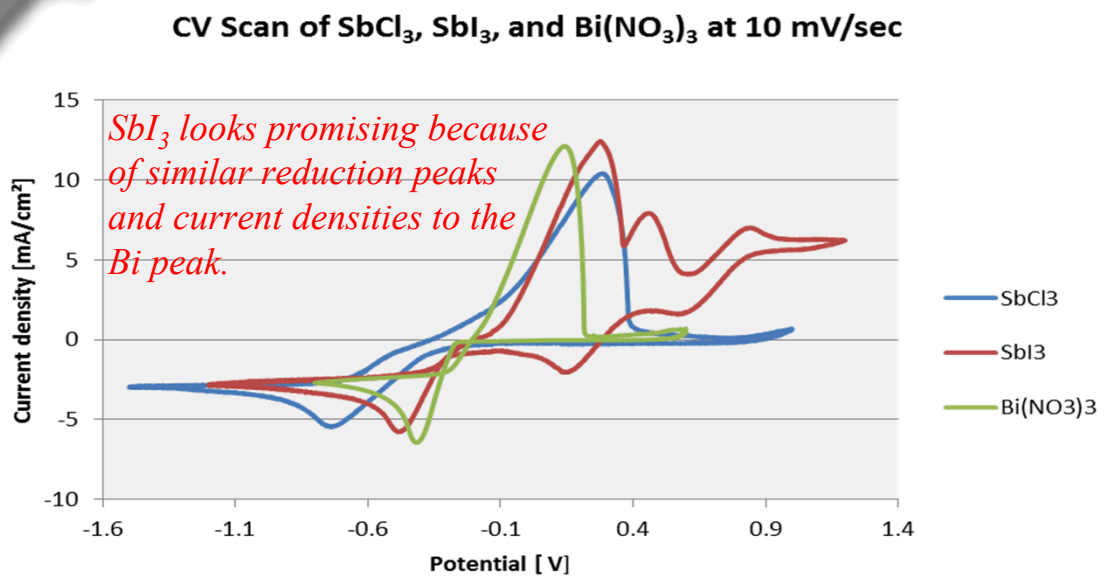
even if single (or highly-crystalline):

- wall diameters enable phonon scattering low thermal conductivity
- optimal electrical conductivity and Seebeck coefficient
- has the potential to greatly surpass TE performance from pressed and sintered nanomaterials

One transitional path from theory to nano-wire arrays is electroforming

- *Certain key items need addressed*:
  - A template to control size and direction of nano-wires during growth.
  - Finding chemistries with high enough solubility's to support electroforming species.
  - Determining the "right" electrolyte for the job
    - Wide electrochemical window
    - Supports high (enough) concentrations of the reducing species and any conducting salts.
    - Chemical compatibility with substrate and any pre- or post-processing operations

Electrochemistry of the systems: *SbI_3 vs. $SbCl_3$*



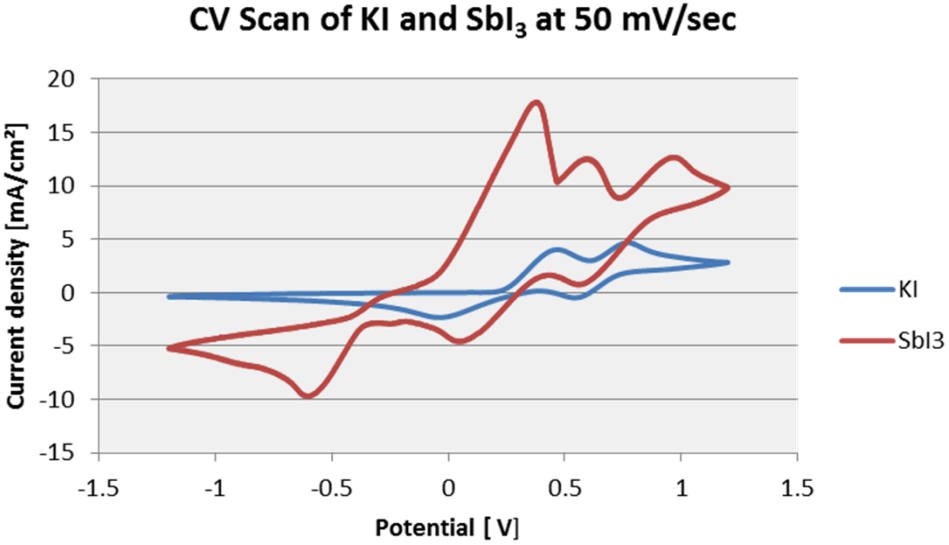
Bath 1: $Bi(NO_3)_3$ and SbI_3 Chemistry

$Bi(NO_3)_3$: 3.635g (0.05M)
SbI_3: 3.766g (0.05M)
$KClO_4$: 2.079g (0.10M)
DMSO to achieve a total volume of 150 ml
Conductance: 0.352 υ/m

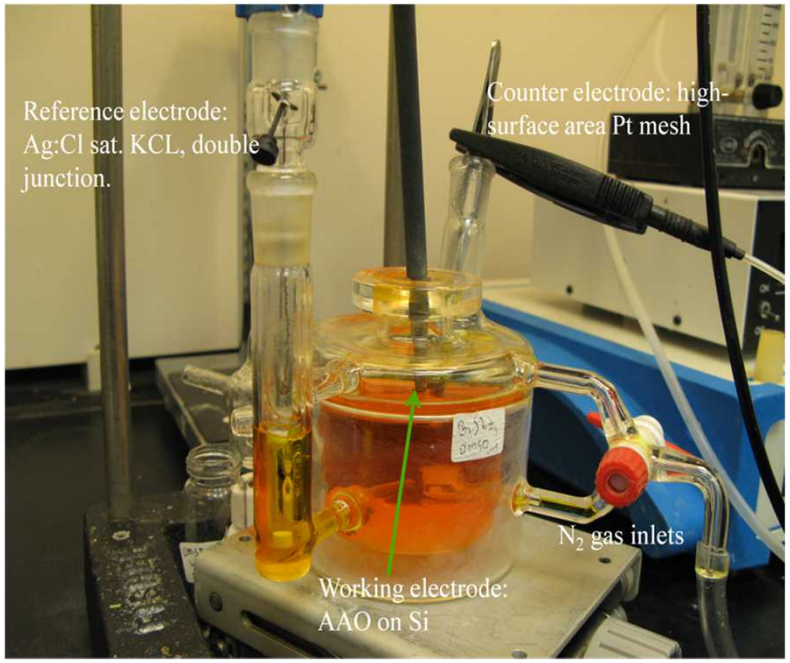
Bath 2: $Bi(NO_3)_3$ and $SbCl_3$ Chemistry:

$Bi(NO_3)_3$: 3.639g (0.05M)
$SbCl_3$: 1.711g (0.05M)
$KClO_4$: 2.078g (0.10M)
DMSO to achieve a total volume of 150 ml
Conductance: 0.439 υ/m

Comparing the CV's of KI to SbI_3 we see the contribution of extra oxidation peaks from the iodine in DMSO.



Electrochemistry of the system: *cell and supporting equipment*

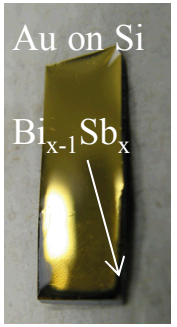


To minimize the incorporation of oxides of Bi or Sb into the alloy, the nanowire arrays were electroformed under nitrogen purged solution and cell. Anodic reactions were minimized by using a larger ***conforming*** counter electrode.

Typical Baths: 30-50 mM $Bi(NO_3)_3$, and 30-50 mM SbI_3 or $SbCl_3$ with 0.1 M KClO4 in DMSO, Nitrogen purge/agitation (bright orange solution is SbI_3 based)

Macro-uniformity issues: *why the concerns?*

- Chemistry behaves in the Primary Distribution mode
  - Ohmic overpotentials dominate ($\eta_\Omega \gg \eta_a + \eta_c$)
  - Strong potential field effects due to geometry
  - Current distribution depends only on the geometry
  - Highly non-uniform deposition
  - Singularities (current spikes) at sharp corners



Primary disruption behavior from the basic solution with deposition only along edges

- Prefer to operate in a Secondary Distribution mode without compromising the purity of the nanowires
  - Ohmic and Activation overpotentials dominate ($\eta_\Omega + \eta_a \gg \eta_c$)
  - Improved conductivity by adding supporting electrolyte
  - Decrease edge effects with shape and location of anode
  - Pulse strike the substrate to provide uniform nucleation at to the bottom of the pores

Uniformity of deposit greatly improved across the coupon without additives

Macro-uniformity issues: *Macro uniform current flux is crucial at the substrate.*

Predicted performance of nanowires are highly depended on a **uniform** composition of the alloy along the lengths of the wire; equally important but overlooked, is the **macro-uniformity** across the array.

Varying alloy compositions tend to favor the element with the fastest kinetics

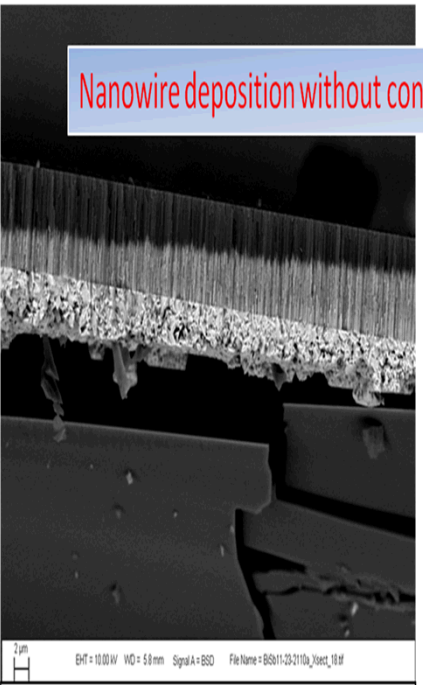


Figure 1a: Macro Non-uniformity: cross section of AAO on Si with an uneven Bi-Sb nanowire growth-front , longer wires toward the outer edge of the template (see figure 1b).

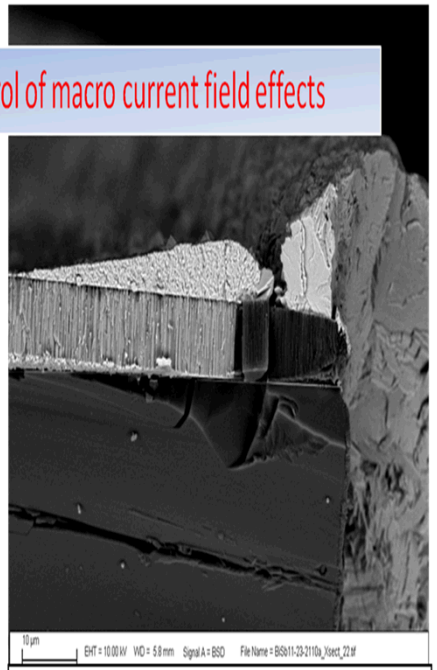
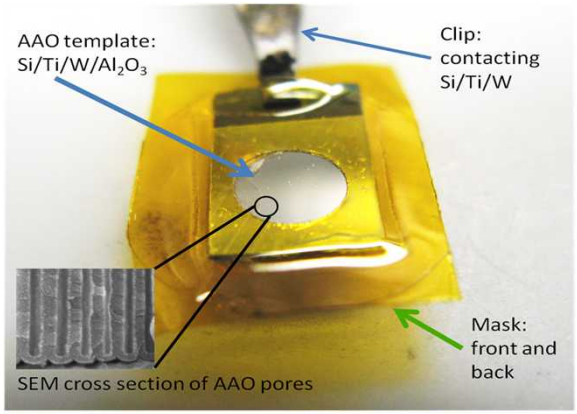
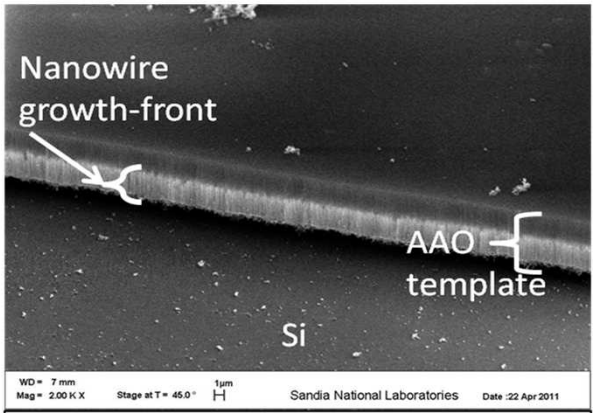


Figure 1b: Cross section of AAO on Si with massive "run-away" deposition of Bi-Sb on top of Bi-Sb nanowires along the edges. No nanowires were found around the center of the template.

Masking the substrate shields high current density corners, but more importantly, the circular pattern and 90° angle of the masking "wall" along the circular perimeter forces the current to a finite value.

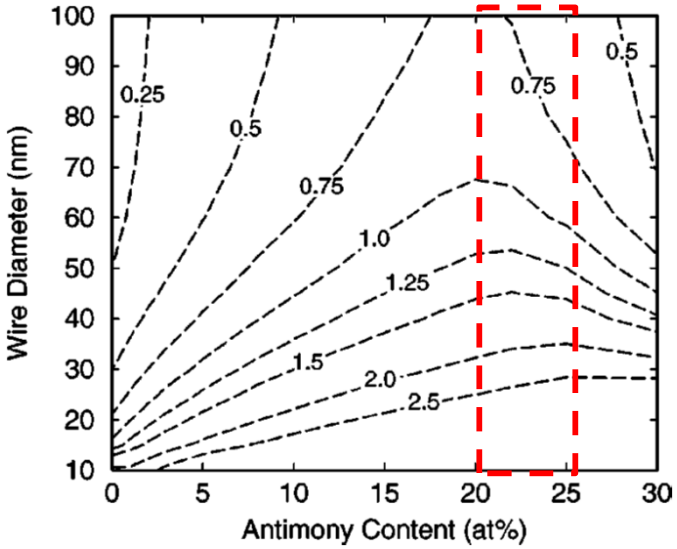


AAO template masked exposing a 4mm diameter circular area to minimize **high current density** corners and edge effects.

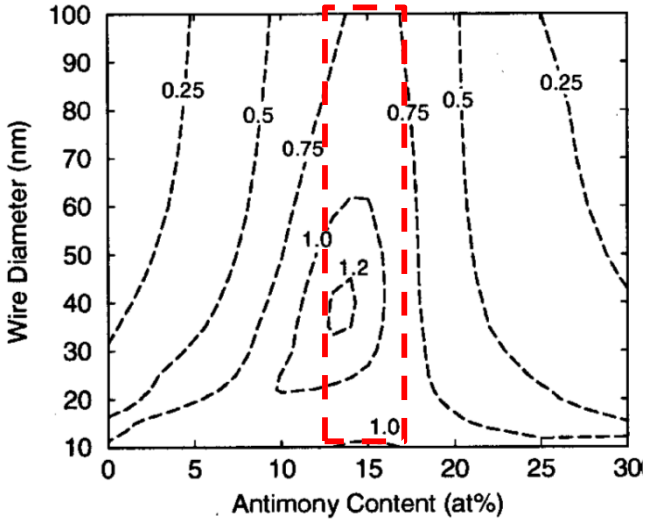


Macro-uniformity after applying measures to control current field flux: fractured cross section of AAO template on Si with even Bi-Sb nanowire growth-front. SEM of NW's (bright layer) taken from the center of the AAO template.

Nano-uniformity worries: *target n-type, p-type, zT's*



Optimal ZT values for n-type $Bi_{1-x}Sb_x$ nanowires vs. wire diameter and antimony concentration.



Optimal ZT values for p-type $Bi_{1-x}Sb_x$ nanowires vs. wire diameter and antimony concentration.

Rabin, Lin, and Dresselhaus Appl. Phys. Lett., Vol. 79, No. 1, 2 July 2001

Worries: how to maintain compositional uniformity of two simultaneity deposited electro-active species, with different kinetics, along the length of billions of nanowires in blind pores ?

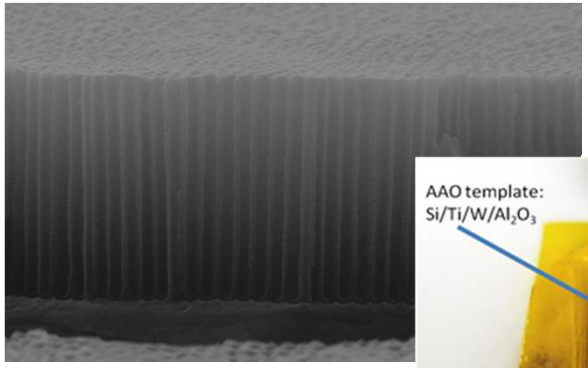
Controlling Geometry: Nanopore Templates

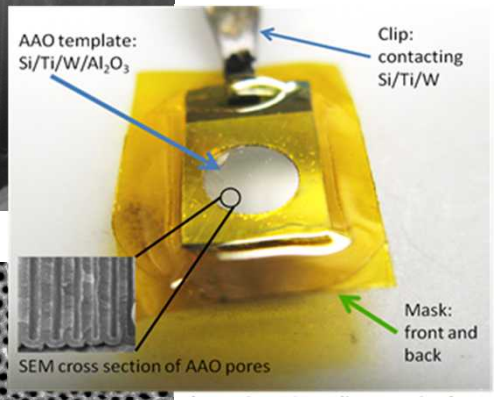
Anodized Aluminum Oxide (AAO) Nanopore Templates on Si(100)

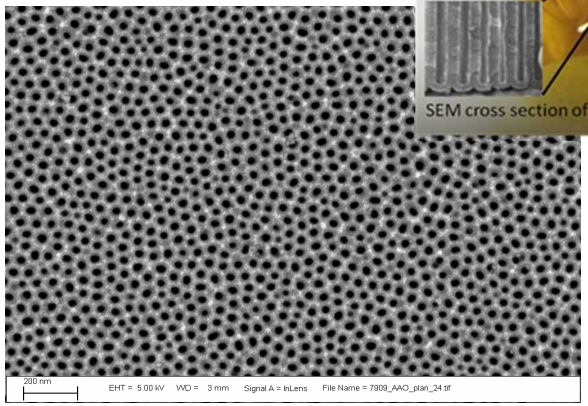
Sputter low-stress, mirror-smooth Nd-doped Al films to define NW lengths onto Si wafers.

Anodize and pore etched to form arrays with controlled pore diameters ranging from 10 – 75 nm.

1 to 10's µm Nd-doped Al	**forms nanopore template following anodization**
50 nm W *(Ti and W)*	**sacrificial layer that prevents Al-oxide at pore bottoms**
Si(100)	**viable, ultra-smooth substrate surface**

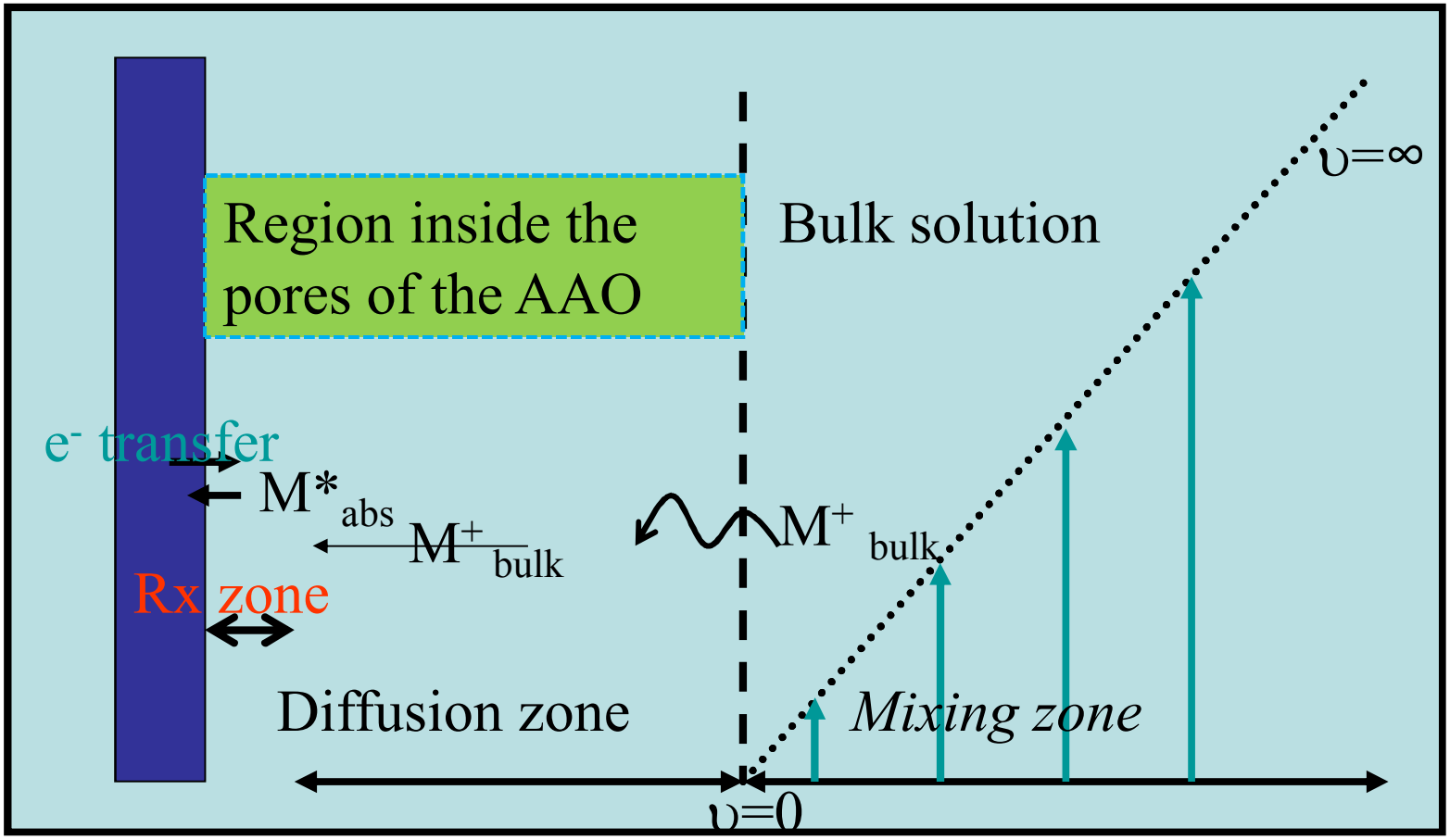






Minimizing the resistance of Mass transport limitations in the AAO:

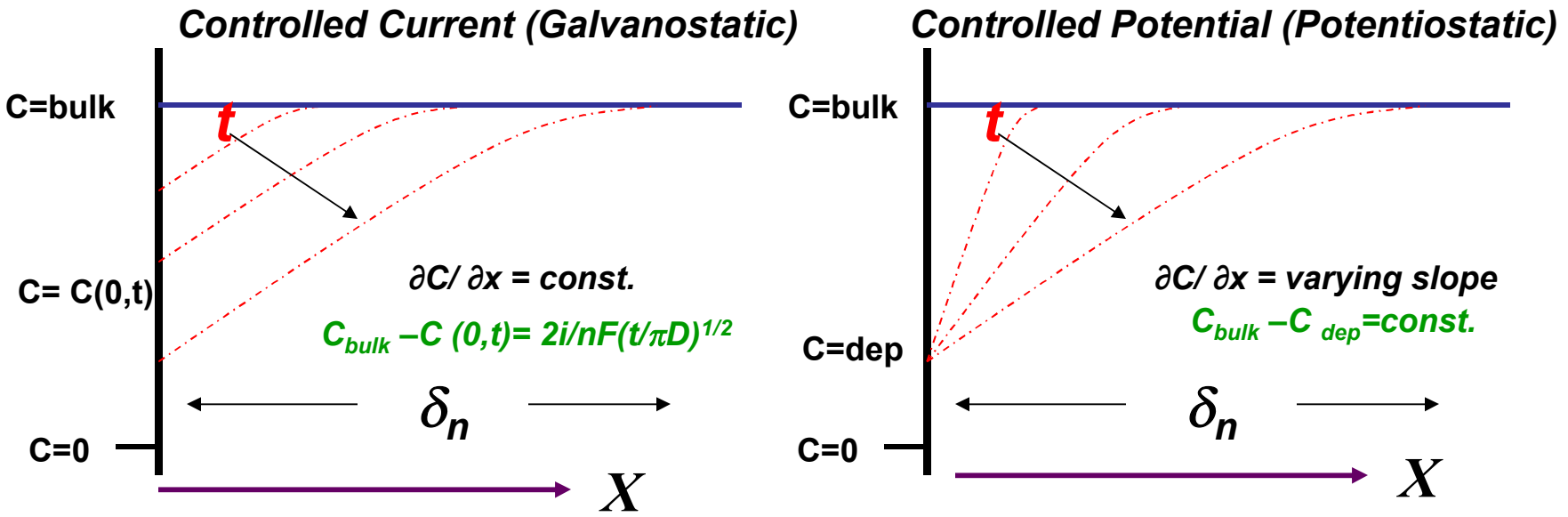
Migratory Zones of Ionic species in the *Interphase* when $\eta_c \gg \eta_a + \eta_\Omega$



*The flux from mass transport limits are driven by the diffusion across the concentration gradient…minimizing **changes** in both the concentration gradient and bulk concentration controls changes in $(flux)_{mt}$ within the pores as nanowires grow.*

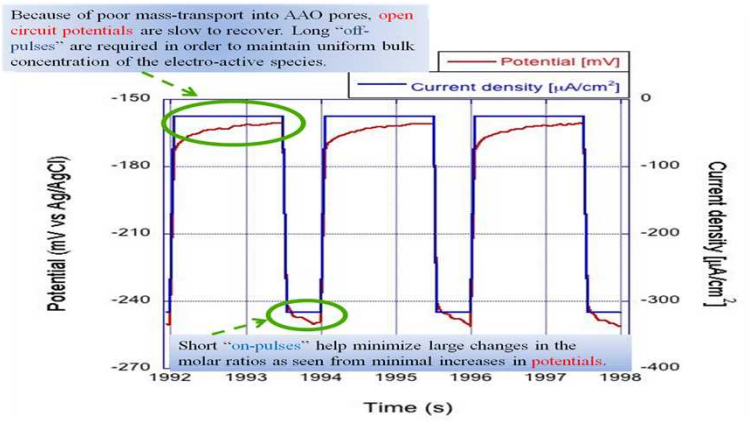
Control the Current, or Control the Potential: What is best for electroforming nanowires in high-aspect blind templates?

Ratio ranging from 55 to 400

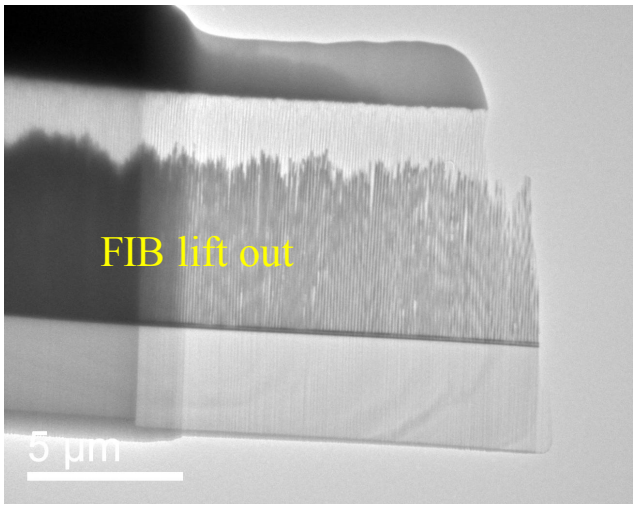


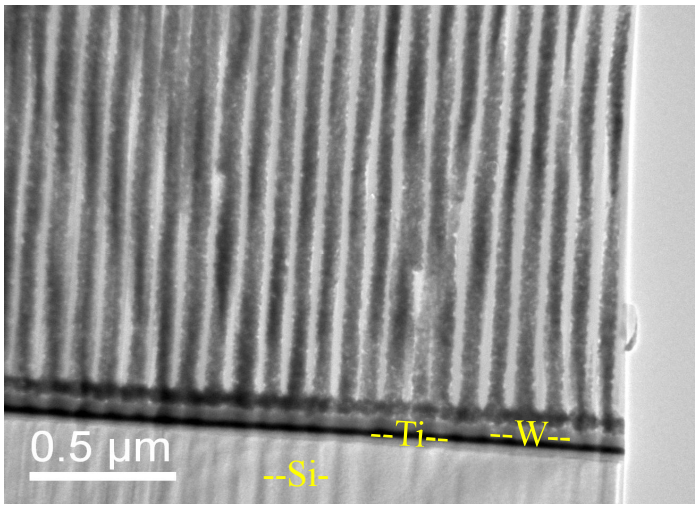
Distance X into the Nernst diffusion zone (interphase) from the substrate surface

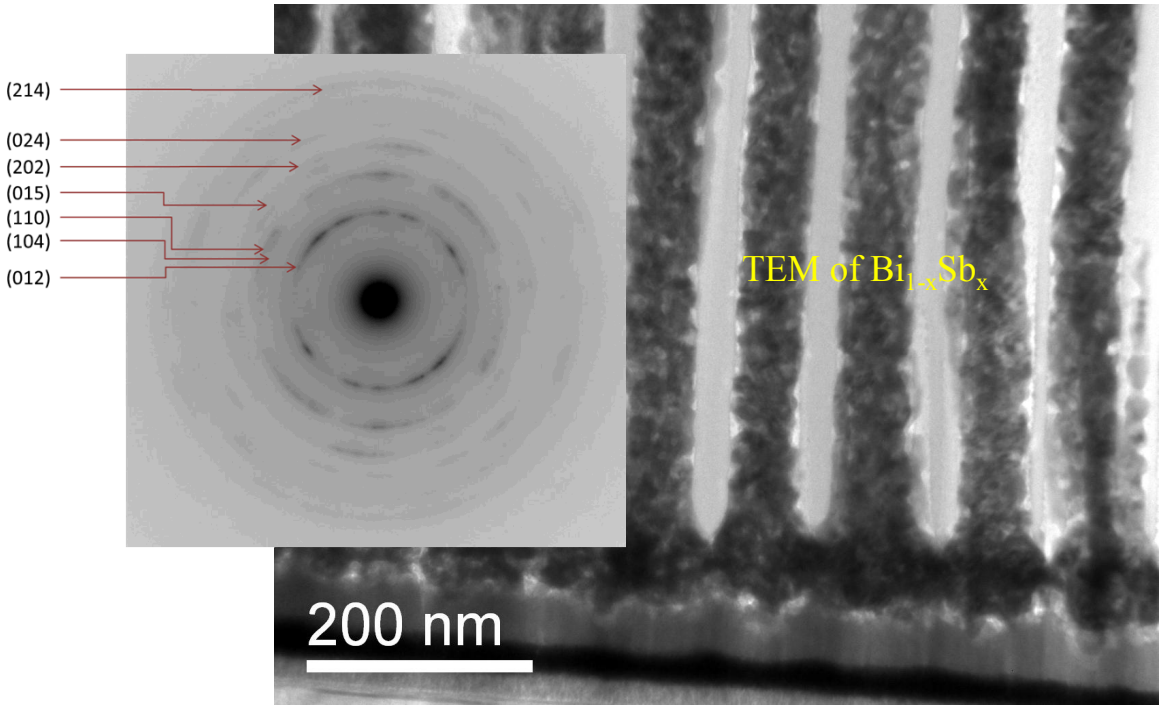
"Conceivably" best to work within a transient behavior of the galvanostatic mode to limit changes in ∂C/ ∂x and C_{bulk} .



Nano-wire characterization : *Iodine based Sb*







These nanowires are:

- 5 micron long with d ~ 60 nm
- *polycrystalline* with the Bi crystal structure
- grains up to 20 nm (≈5-8 across diameter)
- 2-8 at. % Sb in Bi throughout nanowire length

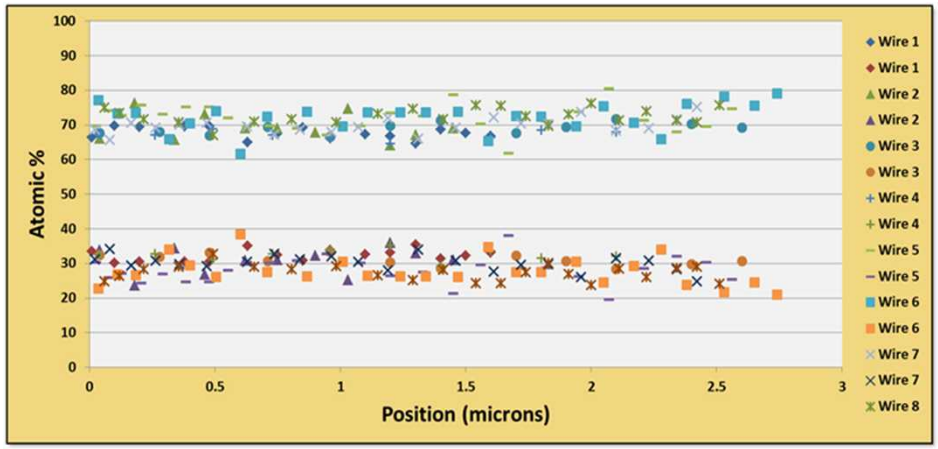
Other notes:

- *Composition varies* from grain to grain
- No clear "strike zone" as in earlier nanowires
- More typical of *Progressive Nucleation**

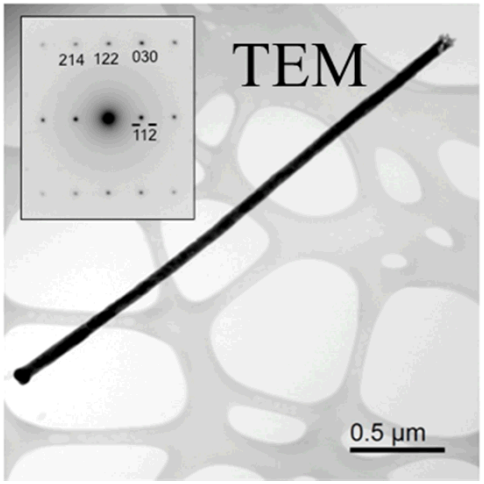
* J. Pillars and W. Yelton, Poster #200, A1 - General Student Poster Session

TEM on BiSb: *$SbCl_3$-based bath*

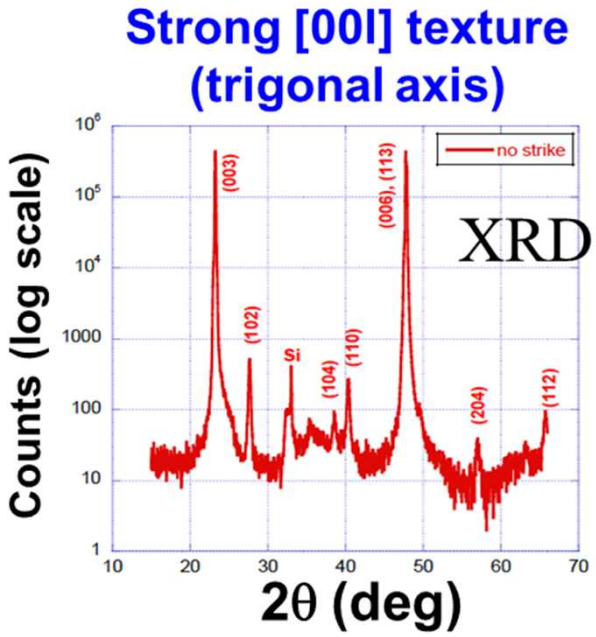
The as-grown wires exhibit good compositional uniformity, demonstrating the effectiveness of pulsed electroforming in growing BiSb wires arrays.



EDS measurements from several different BiSb wires. Data was collected in STEM mode on a JEOL 2010F TEM. Compositions were determined using a k-factor derived from the prepared bulk BiSb standard.



The grain size of the deposited wires is large, with grains typically observed extending at least 0.5 to 1.5 microns along the wire length. More typical of Instantaneous Nucleation.



Notable different in crystallinity of the NW's between SbI_3 and $SbCl_3$ base baths

- ***We don't have any hard answers, but we believe there are reasonable hypotheses***
  - Is there a difference in ion adsorbtion: Anions are specifically adsorbed from DMSO solutions in the order:

    I- > Br- > Cl- > NO3- > ClO4- > PF6-

    T. R. Koch and W. C. Purdy, Talanta, 19, 989 (1972).
  - Is iodide reacting with DMSO?

    $(CH_3)_2SO + 3I^- + 2H^+ \rightarrow (CH_3)_2S + I_3^- + H_2O$

    J. H. Krueger, Inorg. Chem., 5, 132 (1966).
  - Is the solvent decomposition relevant?
  - Is the tri-iodide ion being reduced back to I- at the same time as deposition?

Was DMSO right for the Job?

- The reduction of Bi and Sb in DMSO is well within a stable electrochemical water "window"
  - But the solubility of Sb is poor in water requiring highly acidic solutions *(This can be improved by complexing)*
- Water is a better conductor, were as DMSO is poorly conductive
  - adding conductive salts greatly improves the conductivity without probable side reactions
- ***Main reason: we have found Sb is very reactive with other solvents/electrolytes***
  - post-processing with other DMSO based solutions are possible

Conclusion

- Control of composition and crystallinity will be critical for achieving the enhanced thermoelectric performance in BiSb-nanowire arrays.
- Results show that chemistry, masking, cell configuration and pulsed electroforming are effective at achieving uniform alloy composition along the wire length and at overcoming the mass transport limitations that could hinder compositional control in high aspect ratio AAO templates.
- Our measurements find that the present wires are somewhat richer in Sb (~30 at %) than the targeted composition (~20 at % Sb), predicted by theory to be optimal for zT enhancement.
- Excellent crystalline quality in the as-grown wires, with large grains extending to at least 0.5-1.5 microns along the wire length.
- Small misorientations observed in the wires likely represent the presence of low angle grain boundaries and dislocations, structural defects that will need to further controlled. Further refinement of the compositional uniformity and crystallinity should be achievable through subsequent annealing of the as-grown wires.

Acknowledgment

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