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Correlating Microstructural Quality with Thermoelectric Properties to Optimize $Bi_{1-x}Sb_x$ Thin Films

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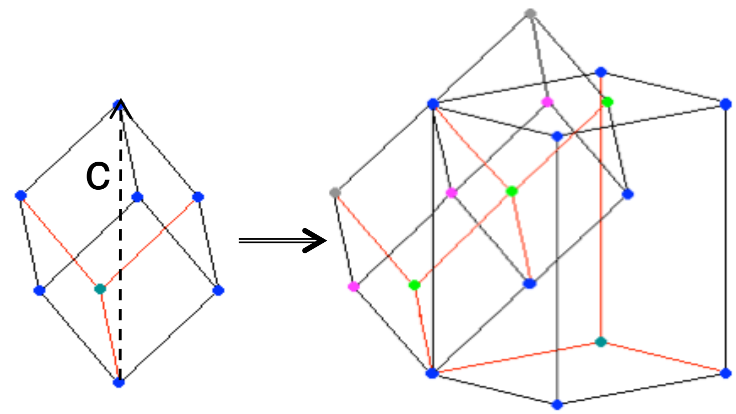
Outline

1. Introduction to $Bi_{1-x}Sb_x$
2. $Bi_{0.8}Sb_{0.2}$ film growth
   - Deposition and post-annealing experiments
   - Role of SiN protective cap
3. Microstructural characterizations (XRD, SEM)
4. Transport properties (resistivity, Seebeck)
5. Structure-property correlations
6. Summary

Introduction to $Bi_{1-x}Sb_x$

- Individually, Bi and Sb are semimetals that form continuous $Bi_{1-x}Sb_x$ solutions.
- Bulk $Bi_{1-x}Sb_x$ is semiconducting for $0.06 < x < 0.22$ with optimal TE properties between 70 – 100K.
- Rhombohedral structure creates an anisotropy in electrical properties that are optimal along the trigonal axis.



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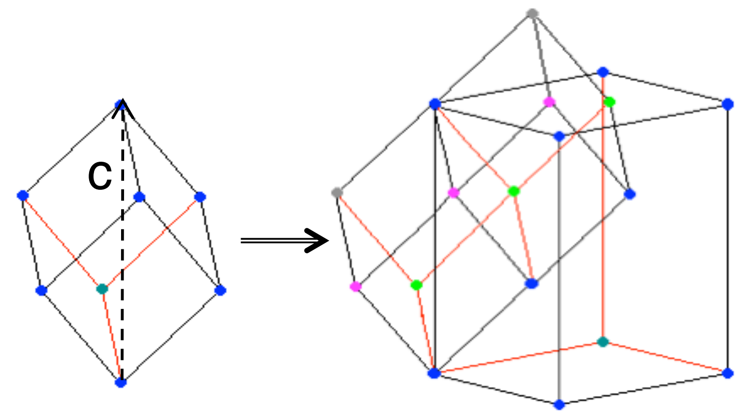
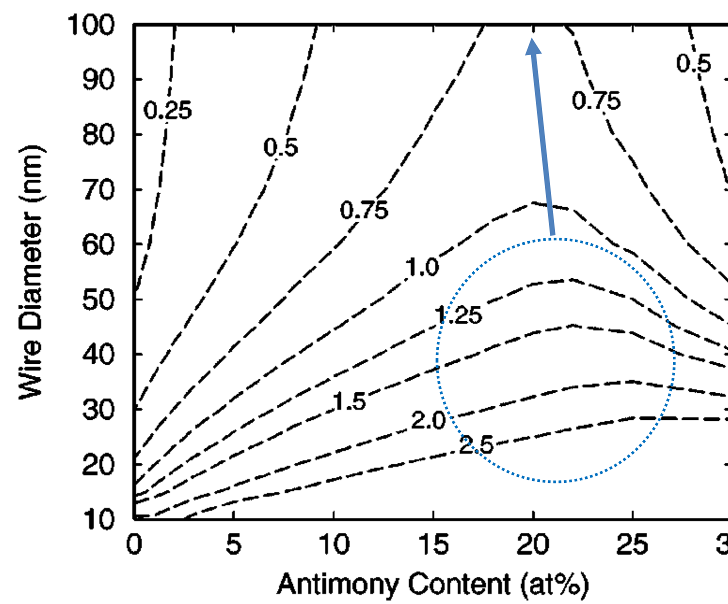
- Rhombohedral structure creates an anisotropy in electrical properties that are optimal along the trigonal axis.
- Single crystal and polycrystalline bulk studies find maximum ZT near x = 0.1.
- Quantum confinement calculations predict higher ZT for $0.20 < x < 0.25$.
- Since we studied 100 nm thick films, we selected x = 0.20 ($Bi_{0.8}Sb_{0.2}$).



ZT (77K) for nano-sized $Bi_{1-x}Sb_x$



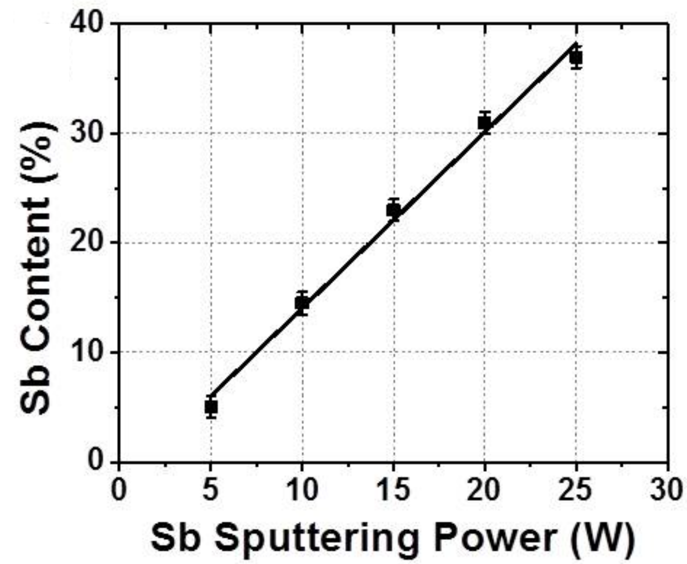
Rabin et al, *Appl. Phys. Lett.* (2001)

$Bi_{1-x}Sb_x$ Film Deposition

Co-deposit Bi and Sb using RF-sputter deposition for compositional control.

<u>Control over film composition:</u>

- RBS measurements to ± 1%.
- Bi, Sb co-sputtered on rotating substrate for ~ 2” diameter uniformity.
- Bi sputtering power held constant at 25 W.
- Sb sputtering power varied.
- Sputtering pressure of 10 mTorr chosen for smoothest films.



Rochford et al, *APL Mater.* (2015)

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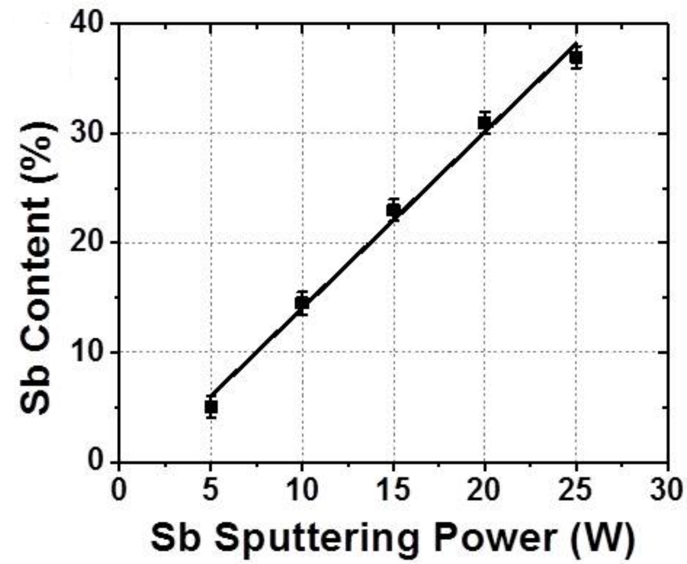
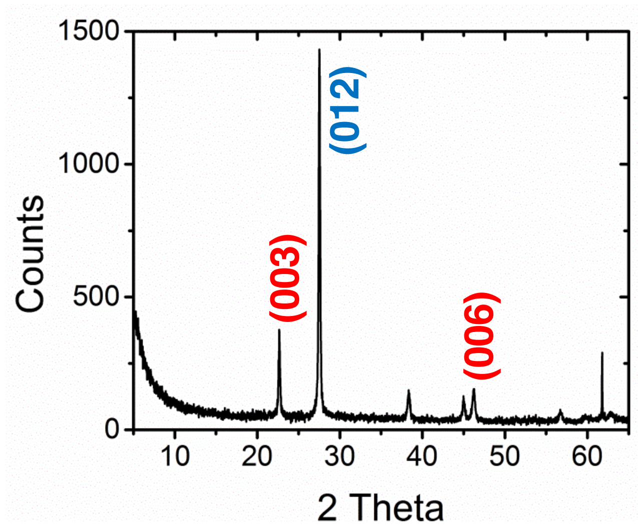


As-deposited BiSb films:

Exhibit weak diffraction peaks with NO preferred orientation, *essentially similar to a powder sample.*

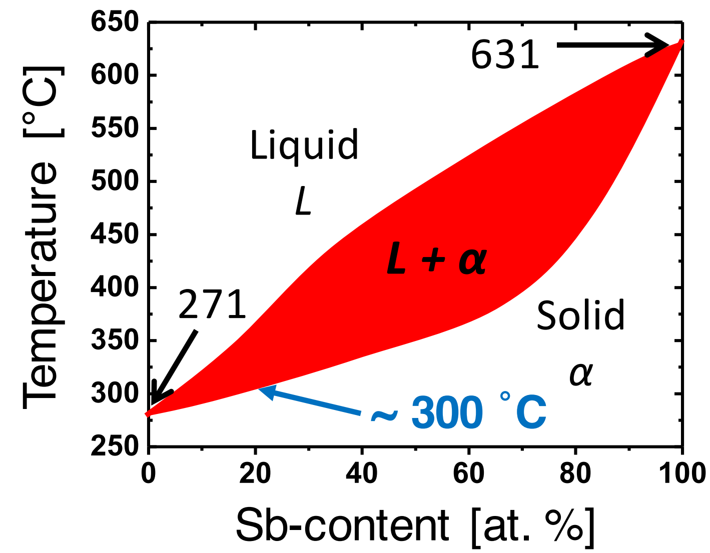


Rochford et al, *APL Mater.* (2015)

$Bi_{0.8}Sb_{0.2}$ *ex situ* Annealing

- All films annealed in 3% H_2 /97% N_2 forming gas to minimize oxidation.
- Rapid cooling is needed to maintain trigonal orientation, suggesting that this is not the lowest free energy surface. [Limmer et al, *Nano Lett.* (2014)]
- For **20% Sb alloys,** it is critical to remain below **300 ˚C** to prevent sample melting.

BiSb Alloy Phase Diagram



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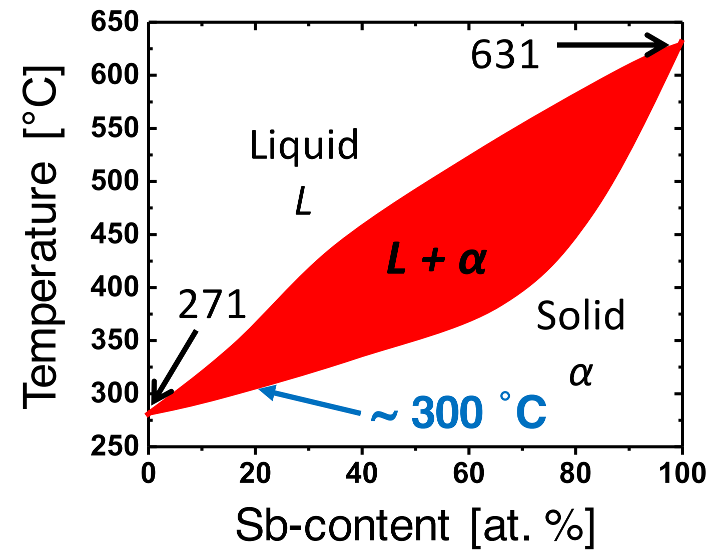
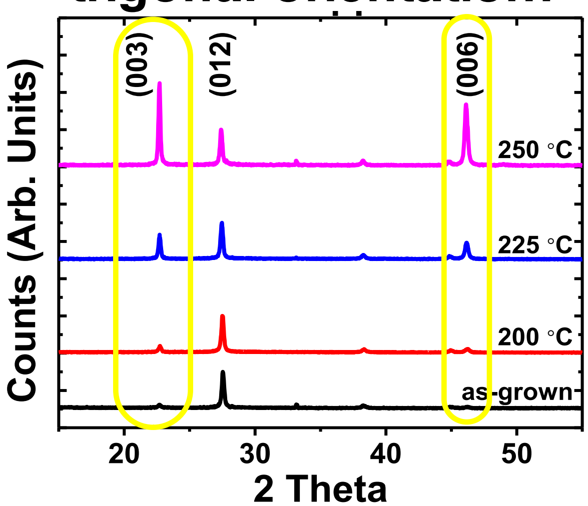


Annealing improves trigonal orientation!



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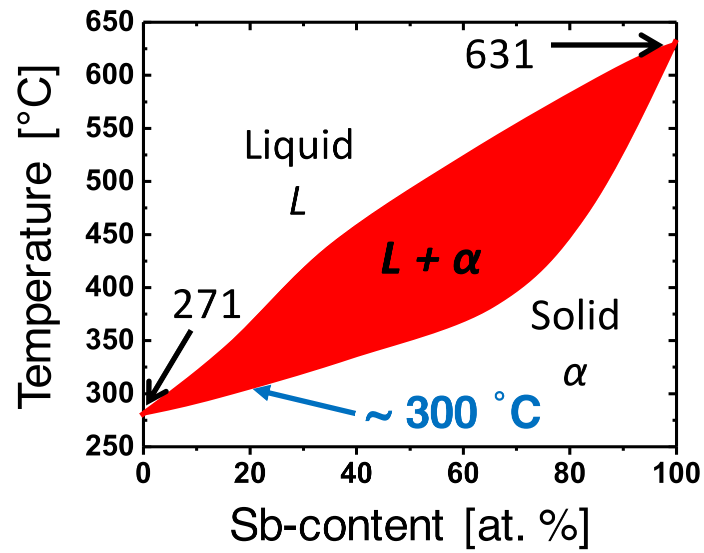

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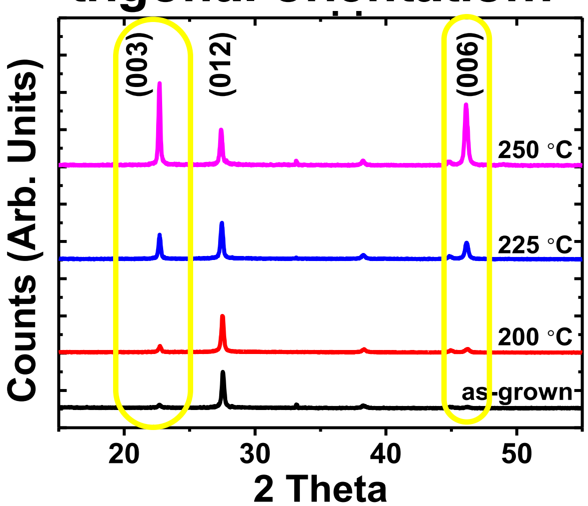
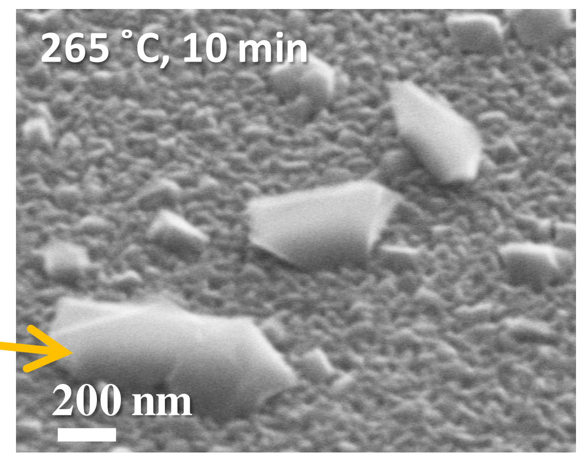


- However, surface roughens with large grain formation.
- Selected area diffraction in TEM indexes large surface grains as Sb_2O_3.
- Where does O come from?



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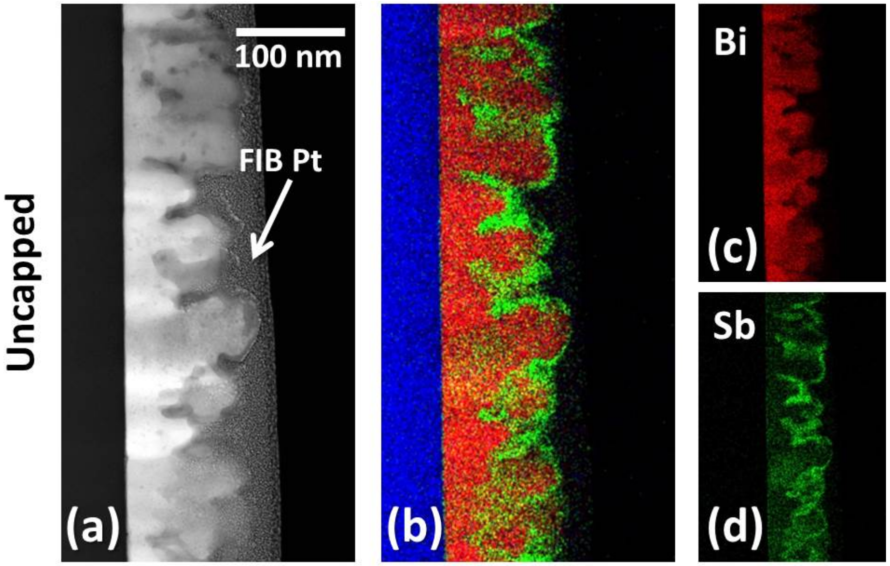
Role of Surface Oxide and SiN Protective Capping Layers



- Since films annealed in forming gas, oxide layer must form immediately on as-deposited film upon exposure to air.
- Further analysis with cross-sectional TEM and EDS finds that without capping, between 50 – 95 % of the Sb segregates to the surface.
- Hence, such films WILL NOT have the assumed composition from deposition. ***They will be Bi-rich.***

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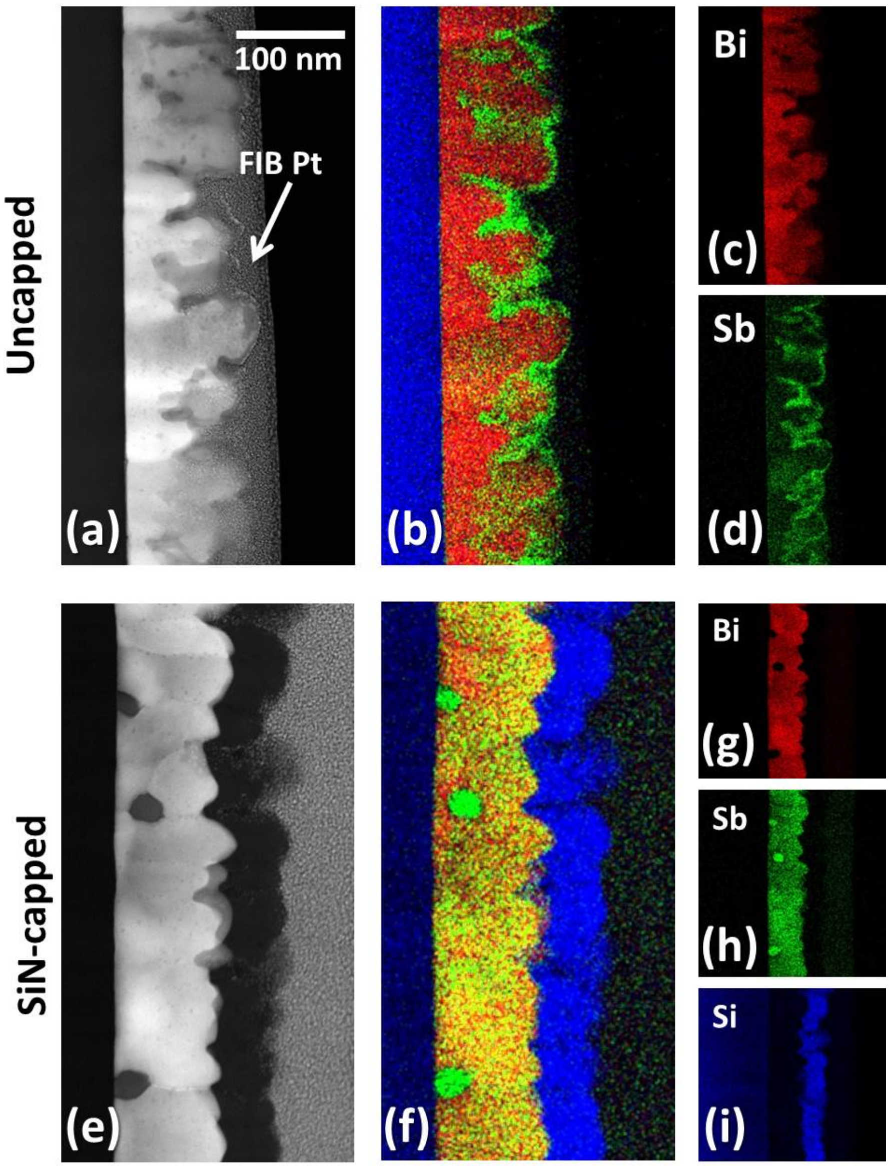

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- Hence, such films WILL NOT have the assumed composition from deposition. ***They will be Bi-rich.***
- **50 nm thick SiN conformal cap layer** prevents oxide formation and results in a smoother films with uniform Bi-Sb composition throughout the film, even after annealing.
- **Should result in films with desired TE properties for a given composition.**

$Bi_{0.8}Sb_{0.2}$ Film Morphology vs. Annealing

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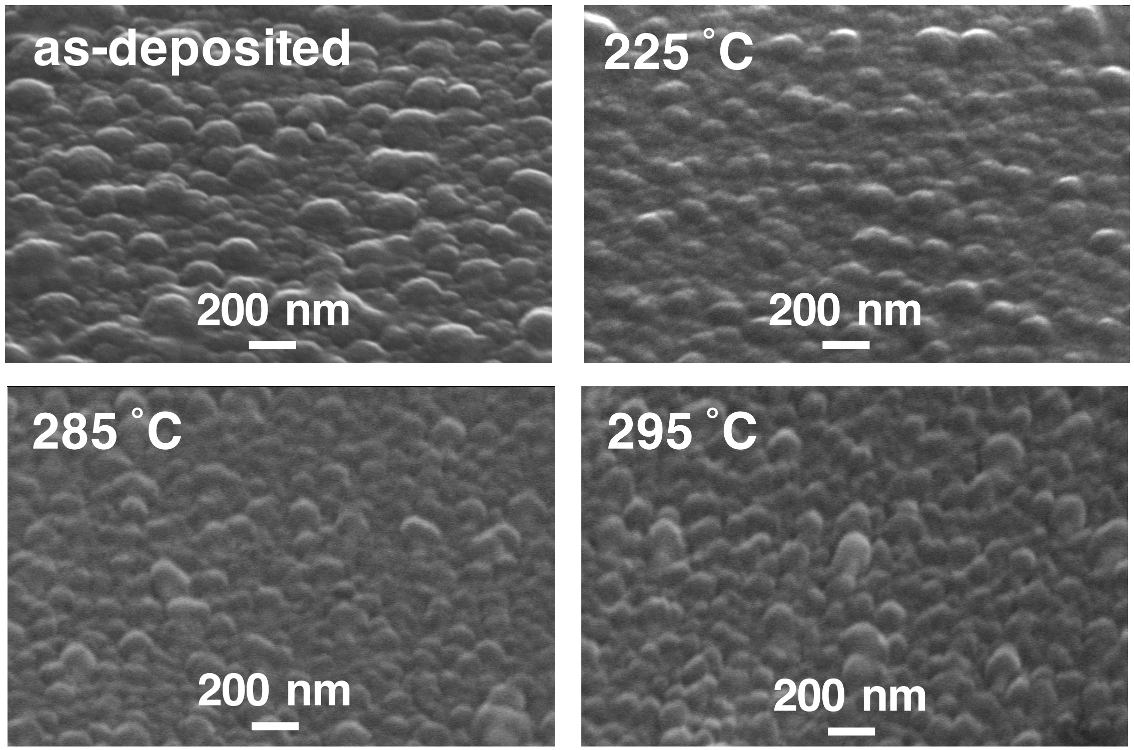
How does annealing SiN-capped films affect morphology?

rough morphology and large grain size variation

best morphology and most uniform grain sizes



annealing smooths morphology and homogenizes grain sizes

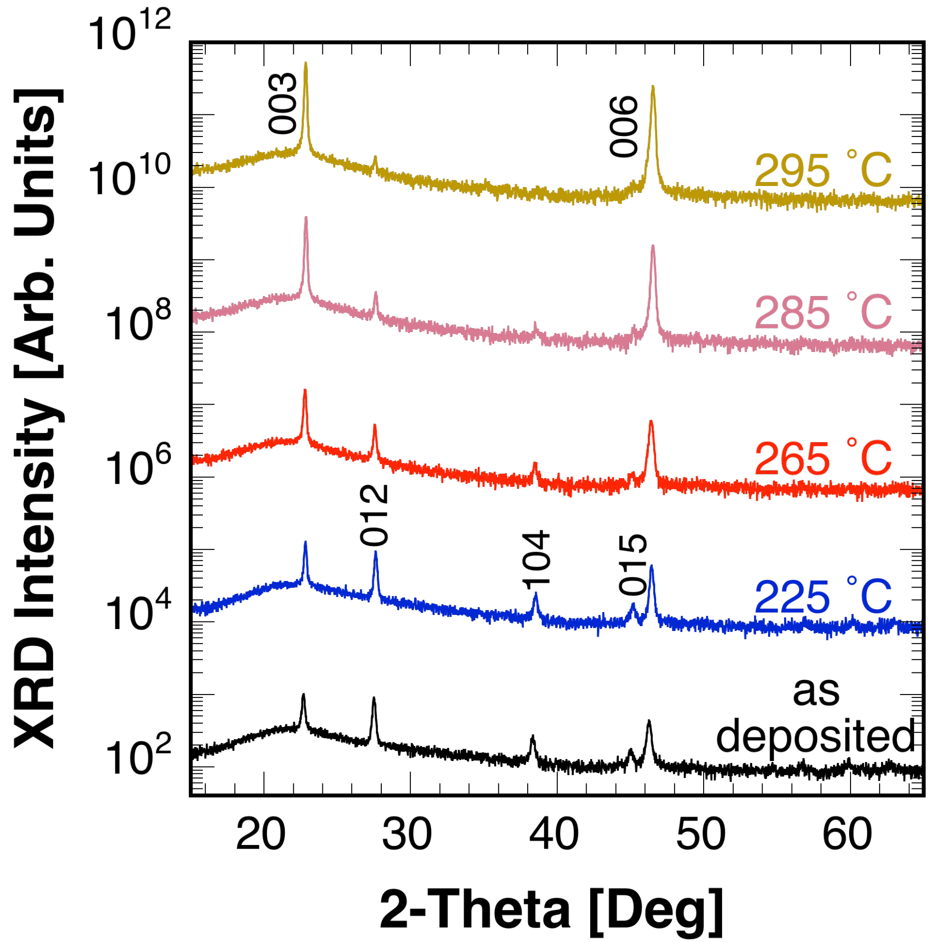
very close to melting point, distinct grain boundaries.

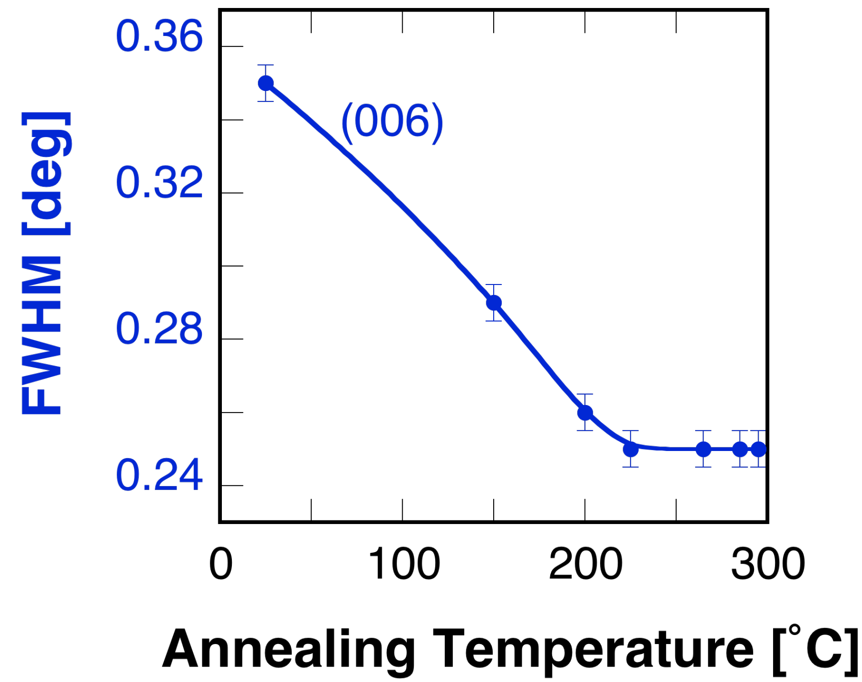
Annealing leads to smoother morphologies and more homogeneous grain sizes, however, grain boundaries become more distinct close to the melting point.

Siegal et al, *APL* (2017)

Annealing to Further Improve $Bi_{0.8}Sb_{0.2}$

crystalline quality and trigonal orientation steadily improves with annealing





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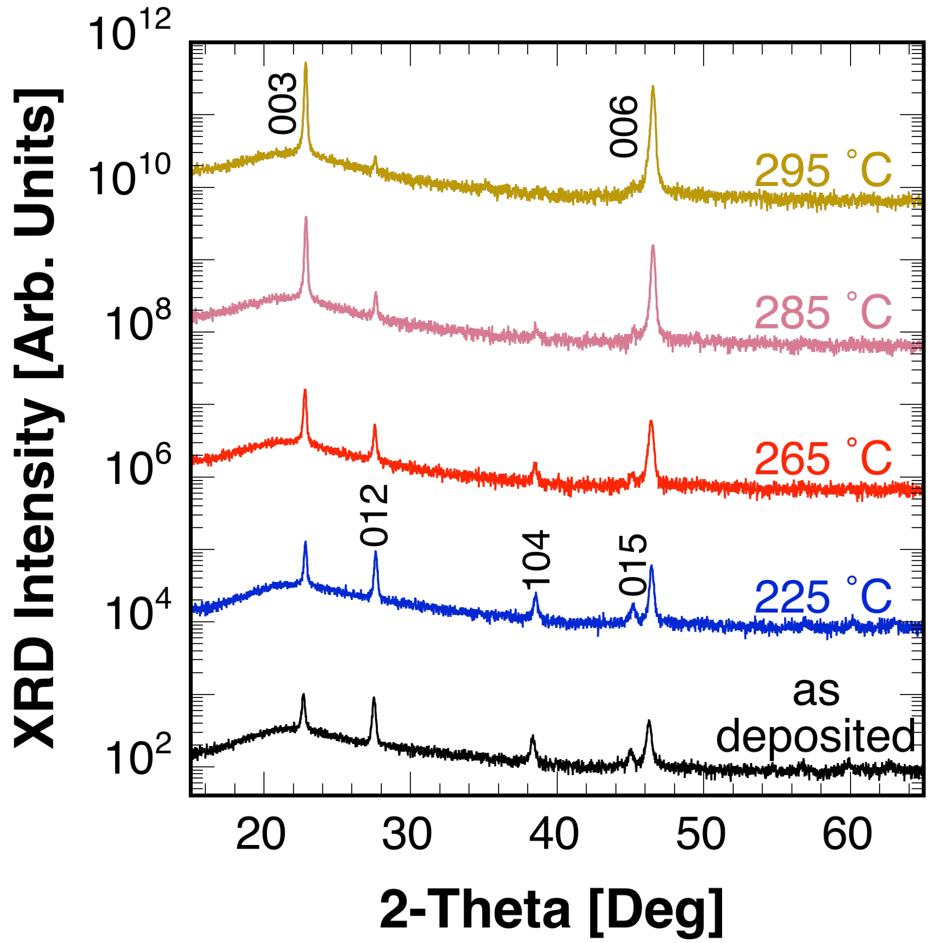

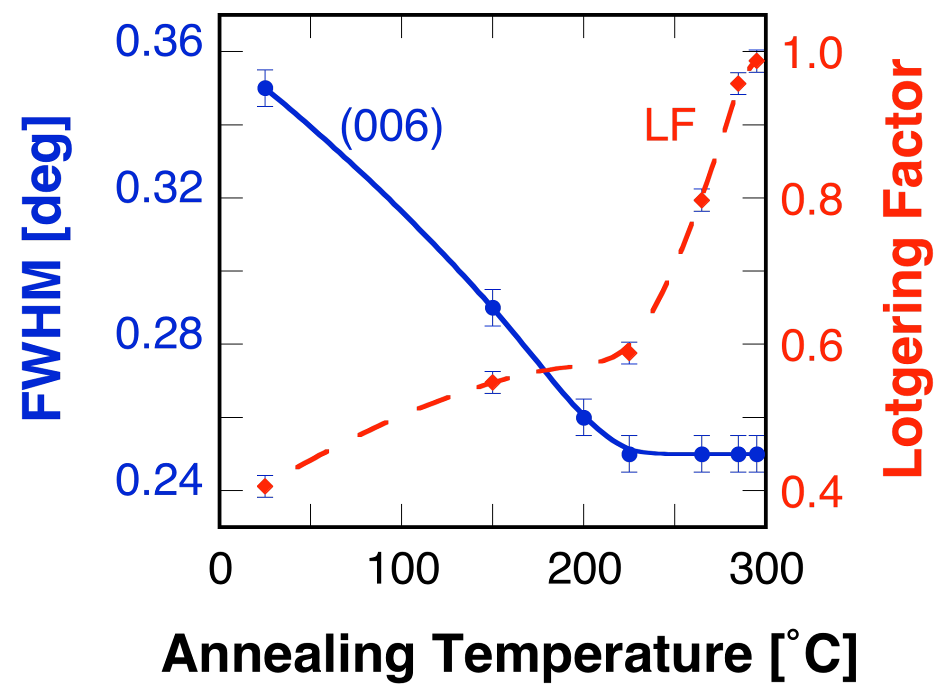

Siegal et al, *APL* (2017)

Electrical Transport Characterization

- Since we utilize an insulating SiN cap, electrical contacts must be patterned **BEFORE** BiSb film deposition. Many metals fail because native oxides introduce an unacceptable contact resistance (e.g. Al, Ni, Ti).
- Many Bi-metal alloys (e.g. Au, Ag, Pd) have a eutectic point which causes melting well below our desired temperatures approaching 300 ˚C for optimal crystalline quality and trigonal orientation.

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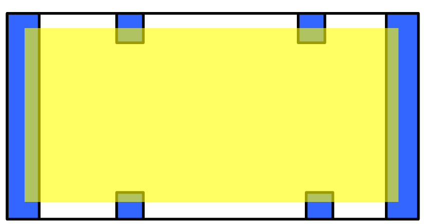
- Many Bi-metal alloys (e.g. Au, Ag, Pd) have a eutectic point which causes melting well below our desired temperatures approaching 300 ˚C for optimal crystalline quality and trigonal orientation.
- Instead, we use 2 wt% Nd-doped Al. There is no eutectic point in the Bi-Al or Bi-Nd phase diagrams, and the Nd prevents surface oxidation yielding low resistance Ohmic contacts.

Van der Pauw measurement



Seebeck measurement

Note: all transport measurements will be made in the direction perpendicular to the trigonal orientation. This is NOT optimal, but still useful to correlate properties with microstructure.

Siegal et al, *APL* (2017)

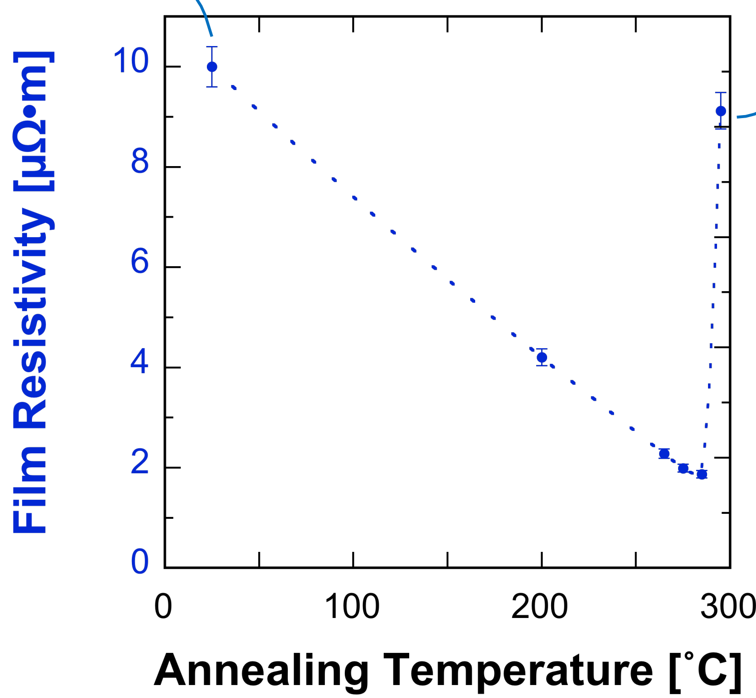
Thermoelectric Transport Properties

Resistivity vs. Annealing Temperature

all measurements at T = 300K

(perpendicular to the trigonal axis)

As-deposited films have the worst overall microstructure.



Despite having the most narrow XRD peaks and best trigonal orientation, SEM identifies distinct grain boundaries for films annealed just below the melting point.

Siegal et al, *APL* (2017)

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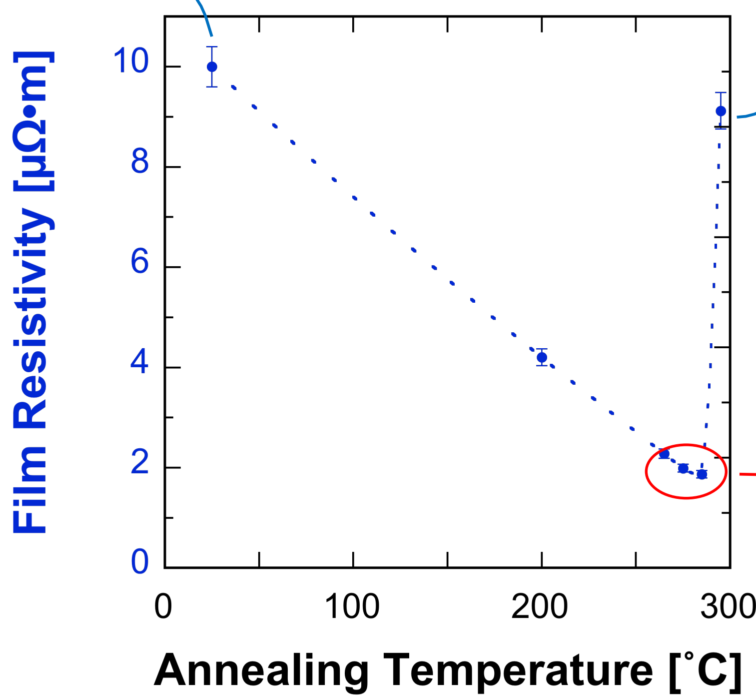

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Focus on films with best overall microstructure.

Siegal et al, *APL* (2017)

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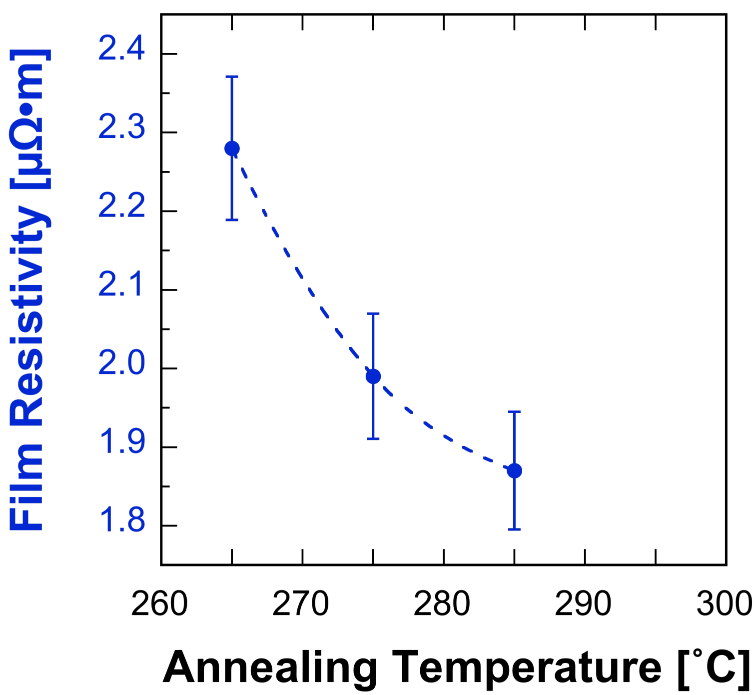


Best ρ = 1.9 *μ*Ω•m (± 4%)

For reference:

single crystal (18.2% Sb)
= 1.6 *μ*Ω•m [Yim et al, *SSE* (1972) and Lenoir et al, *JPCS* (1996)]

polycrystalline bulk disks (20% Sb)
= 4.5 *μ*Ω•m [Malik et al, *JAP* (2012)]

epitaxial MBE films (18.3% Sb, 1 *μ*m thick)
= 2.0 *μ*Ω•m [Cho et al. *PRB* (1999)]

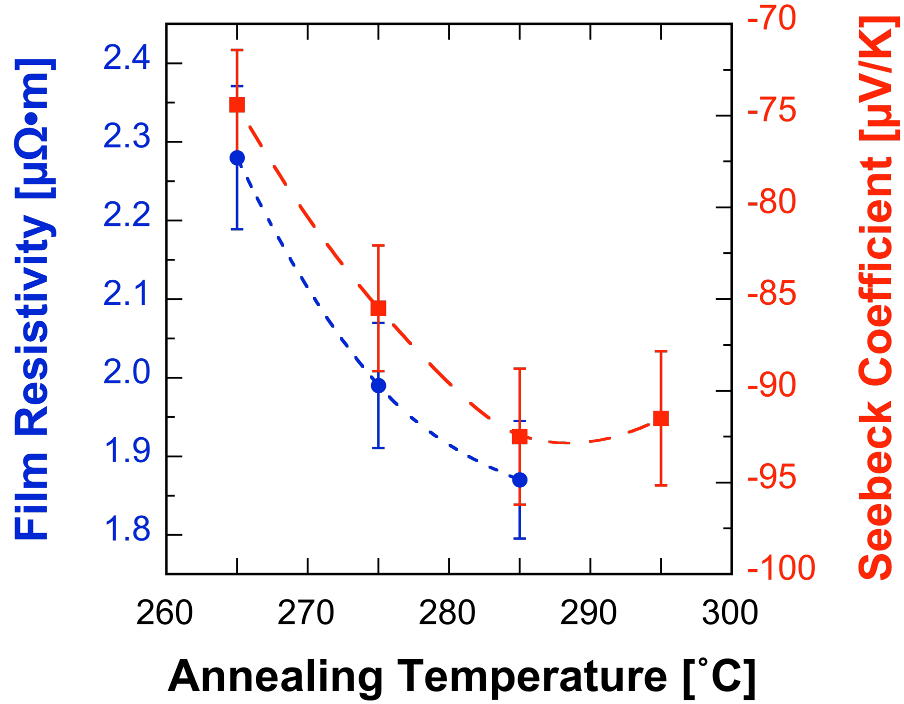
Siegal et al, *APL* (2017)

Thermoelectric Transport Properties

Resistivity and Seebeck vs. Annealing Temperature

all measurements at T = 300K

(perpendicular to the trigonal axis)



Best S = -92.5 μV/K (± 4%)

For reference:

single crystal (18.2% Sb)
= -76 μV/K [Yim et al, *SSE* (1972)]

epitaxial MBE 1 μm films (18.3% Sb)
= -55 μV/K [Cho et al. *PRB* (1999)]

100 nm evaporated films annealed to 150 ˚C (20% Sb)
= -97 μV/K, but have ρ = 20 μΩ•m,
severely compromising performance
[Malik et al, *IEEE ICT* (2003)]

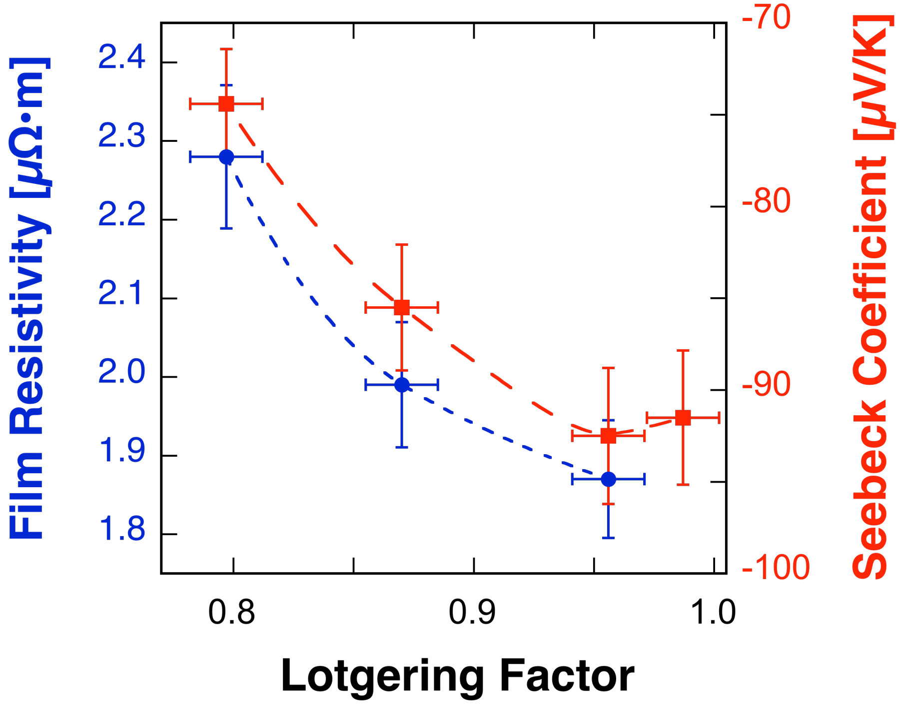
Siegal et al, *APL* (2017)

Correlating Transport with Microstructure

Resistivity and Seebeck vs. Lotgering Factor

all measurements at T = 300K

(perpendicular to the trigonal axis)



Both resistivity and Seebeck coefficient improve with trigonal orientation until annealing temperature gets too close to the alloy melting point.

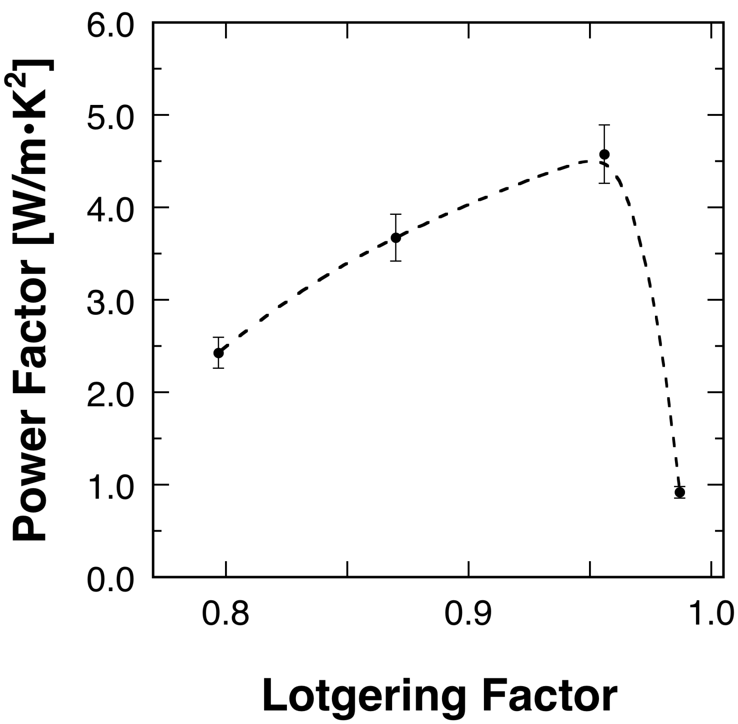
Siegal et al, *APL* (2017)

Correlating Transport with Microstructure

Power Factor = (Seebeck)^2/(Resistivity)

all measurements at T = 300K

(perpendicular to the trigonal axis)



Best PF = 4.6 mW/m·K^2 (± 7%). This value is 28, 64, and 207% higher than the best reported single crystal, polycrystalline bulk alloy, and MBE film, respectively.

For reference:

single crystal (18.2% Sb)
= 3.6 mW/m·K^2 [Yim et al, *SSE* (1972)]

polycrystalline bulk disks (20% Sb)
= 2.8 mW/m·K^2 [Malik et al, *JAP* (2012)]

epitaxial MBE films (18.3% Sb, 1 μm thick)
= 1.5 mW/m·K^2 [Cho et al. *PRB* (1999)]

Siegal et al, *APL* (2017)

$Bi_{0.8}Sb_{0.2}$ Film Summary

- Surface oxide presence depletes Sb from films during annealing, resulting in Bi-rich film compositions.
  - SiN cap layer prevents Sb-oxide formation.
  - enables correlation of microstructure and transport properties.
- If electrical contacts are deposited prior to thermal annealing, then
  - helpful if they neither oxidize nor react with $Bi_{1-x}Sb_x$, such as Nd-doped Al.
- Microstructural quality improves with annealing temperature.
  - crystalline quality (XRD-FWHM)
  - trigonal orientation (LF)
  - morphology (SEM), until near the alloy melting point.
- Film resistivity and thermopower both systematically improve with <u>overall</u> microstructural quality.
  - results in TE power factors better than those previously reported for thin films, polycrystalline bulk alloys, and even single crystals.