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The impact of annealing on the properties of p-type $Bi_{0.4}Sb_{1.6}Te_3$ films

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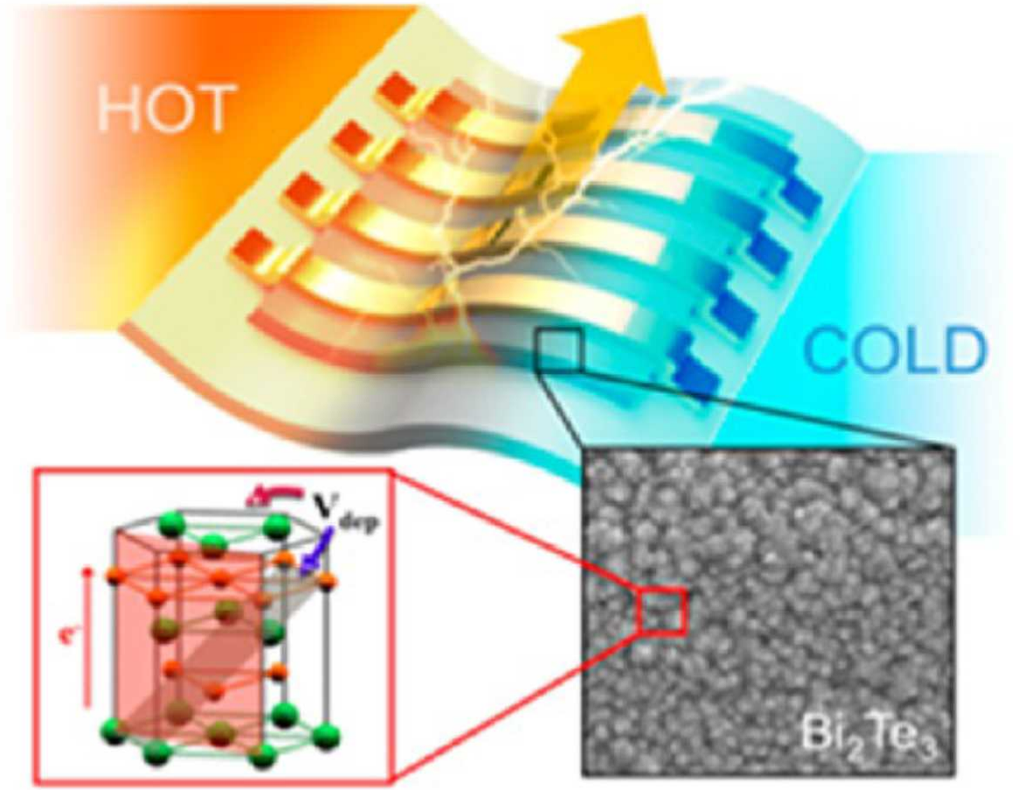
Outline

- Motivation for $Bi_{0.4}Sb_{1.6}Te_3$ thin films
- Alloyed film deposition
- *Ex situ* annealing
- Surface morphology
- Crystallographic properties
- TEM microstructure
- Transport properties
- Summary

Motivation

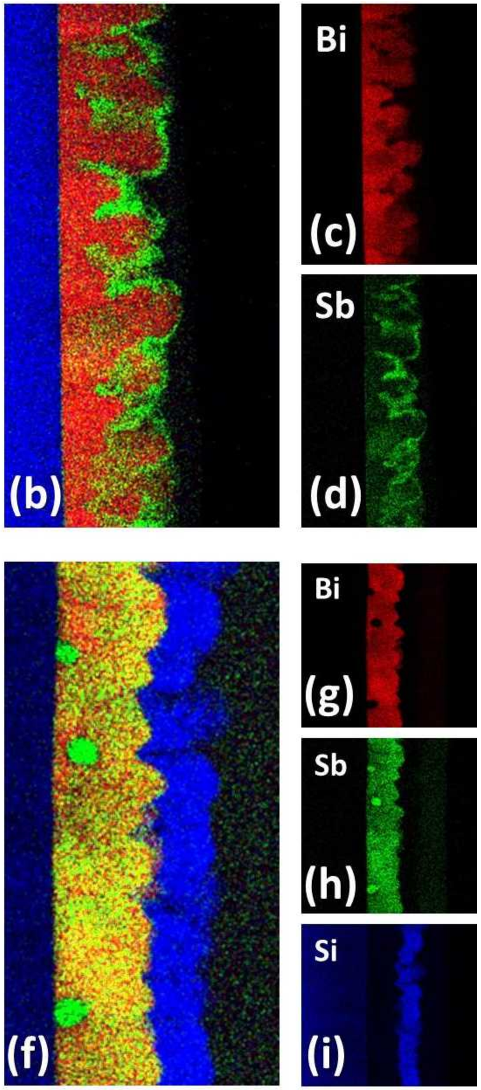
- Integrate TEs into devices
- Need high quality thin films
- Simple processes for improved TE performance
- Ternary alloys difficult to make yet best properties
- Find balance between electron and phonon transport



Na *et al,* ACS Appl. Mater. Interfaces (2016)

Motivation

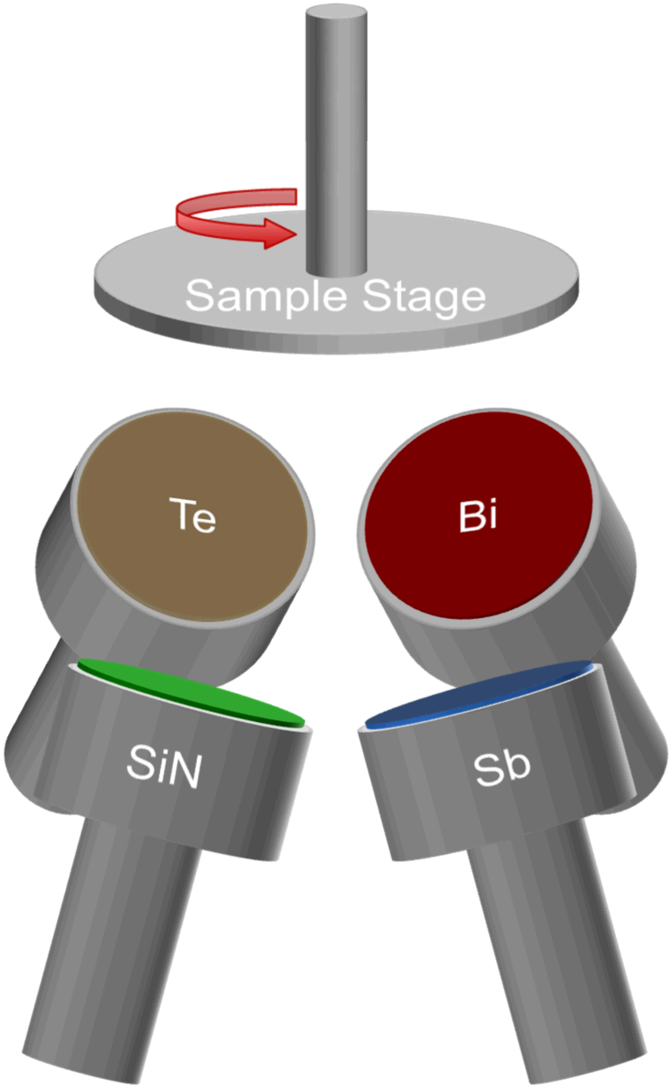
- *Ex situ* annealing can improve crystallinity and film orientation
- Previously shown that SiN cap
  - Prevents surface oxidation
  - Sb segregation during annealing
- Use SiN cap to map the bounds of *ex situ* annealed $Bi_{0.4}Sb_{1.6}Te_3$
- Tune into Michael Siegal's talk B62 at 10:15 AM for more details



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

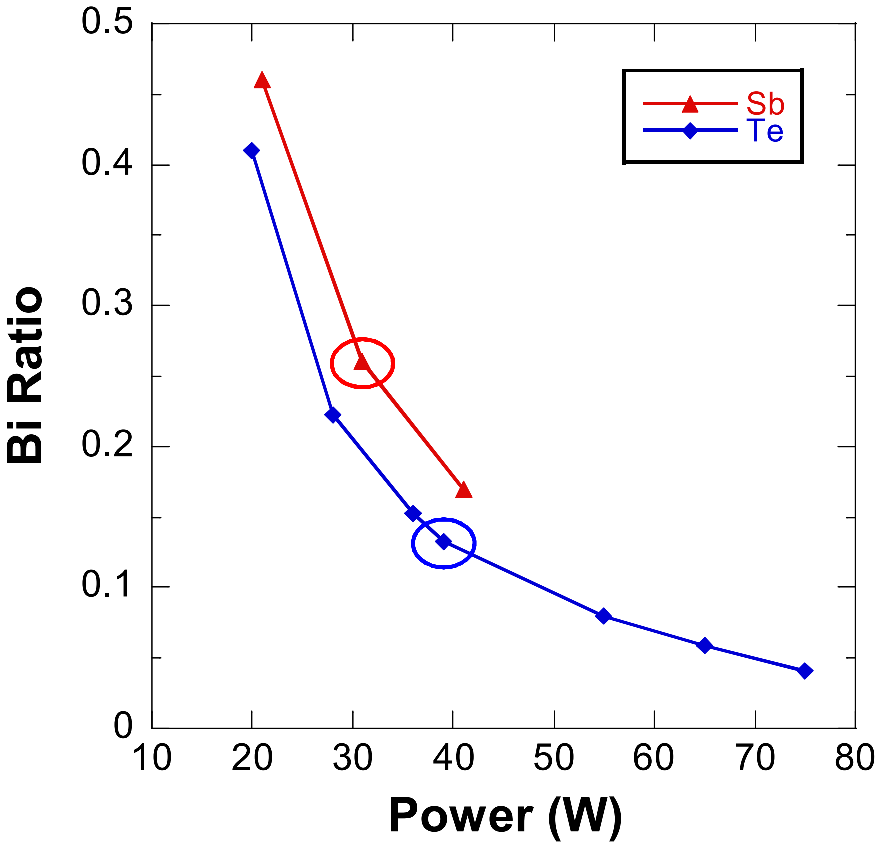
Alloyed Film Deposition

- Confocal deposition
- Bi-Te-Sb co-deposited
- Capped immediately with SiN to prevent oxidation
- Sample stage rotates, >2" diameter uniformity
- Grow 0.1, 0.5, 1, and 2 µm thick films



Alloyed Film Deposition

- RBS used to determine composition
- Te and Sb RBS peaks overlap
- Measure BiTe and BiSb separately
- Fix Bi power and adjust Te and Sb to achieve $Bi_{0.4}Sb_{1.6}Te_3$

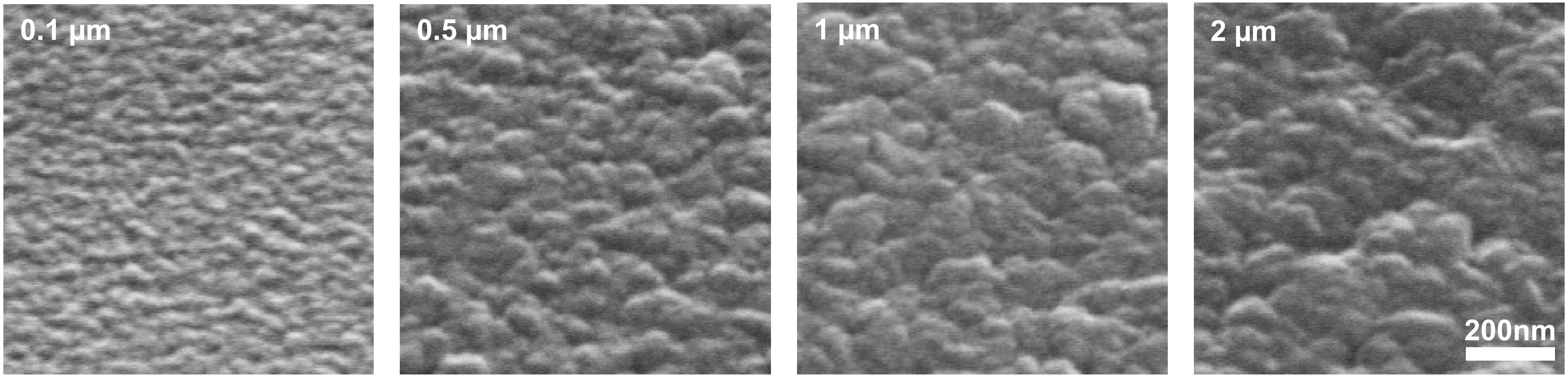


Ex situ Annealing

- SiN cap has 2 fold purpose
  - Prevent native oxide from forming in air
  - Prevent volatile species from escaping during anneal
- Films were annealed in a tube furnace with flowing 3% H_2/97% N_2 forming gas
- Annealed films for 30 mins starting at 200 ˚C up to 550 ˚C at 50 degree intervals
- Samples were furnace cooled to RT

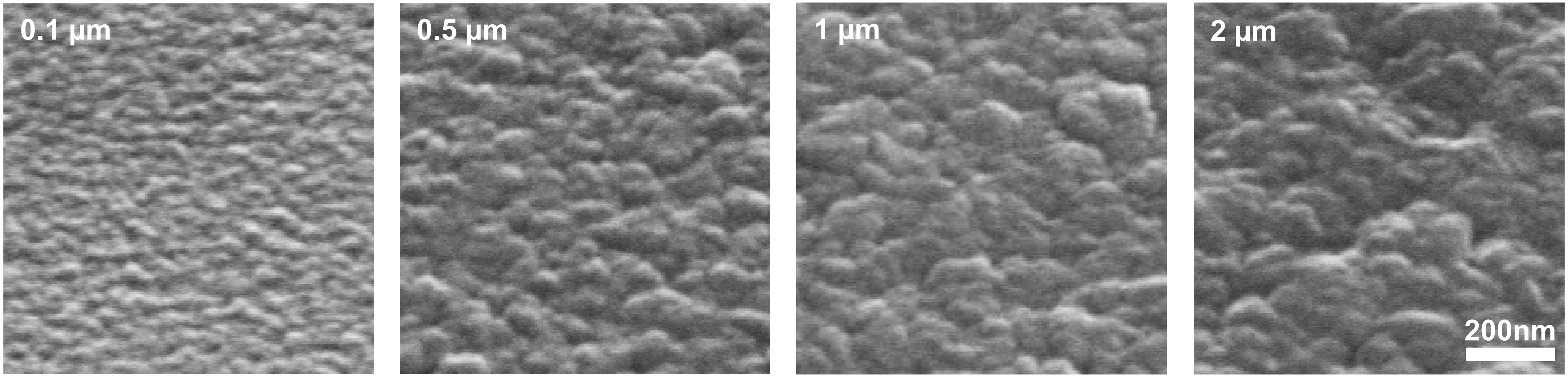
Surface Morphology

As-deposited

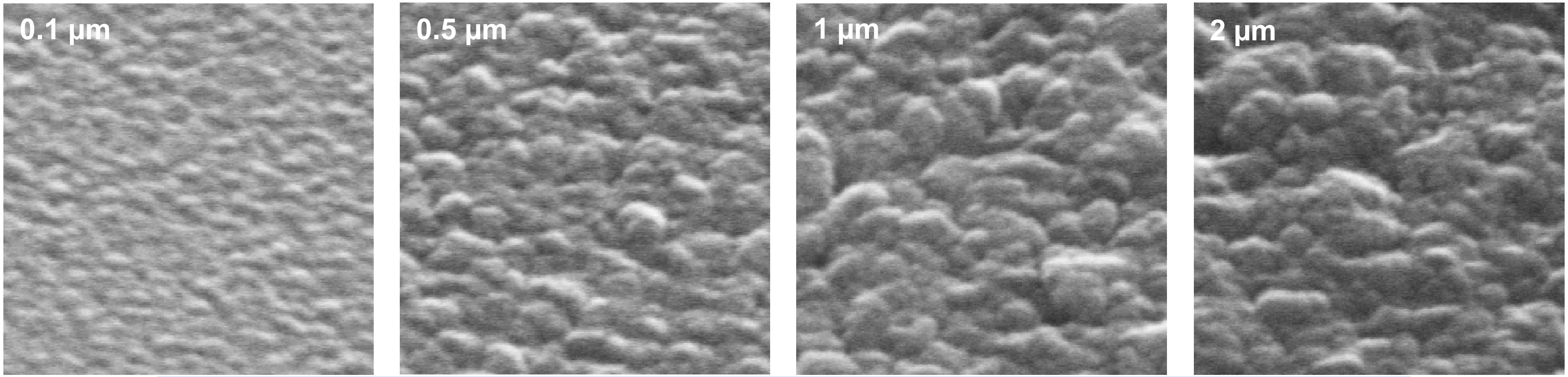


Surface Morphology

As-deposited

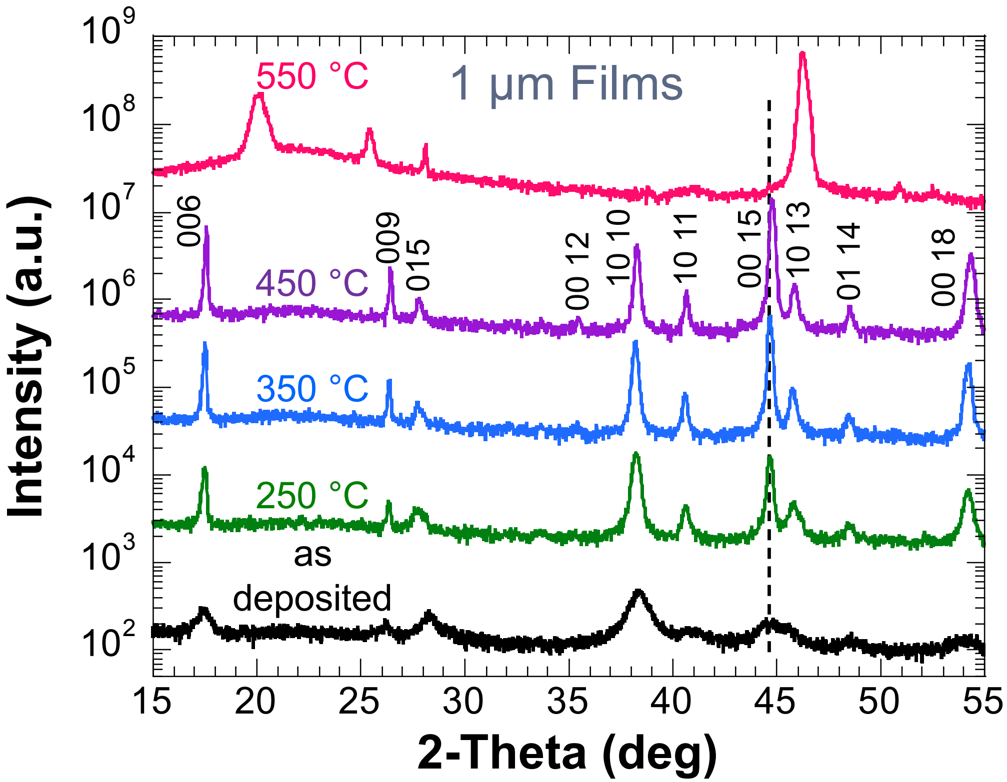


300 °C

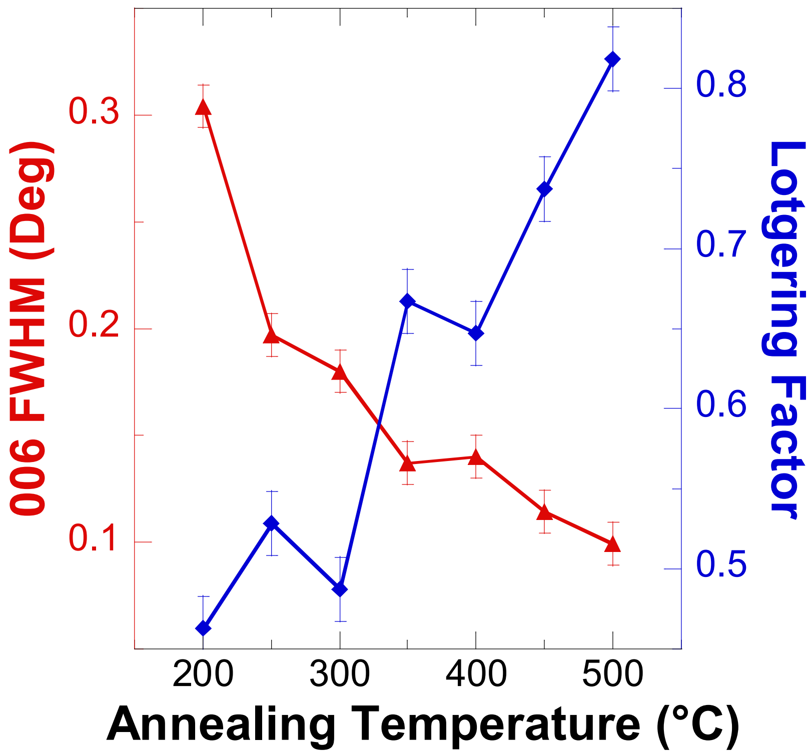


No <u>major</u> change in morphology after annealing due to stiff SiN cap

Crystallographic Properties

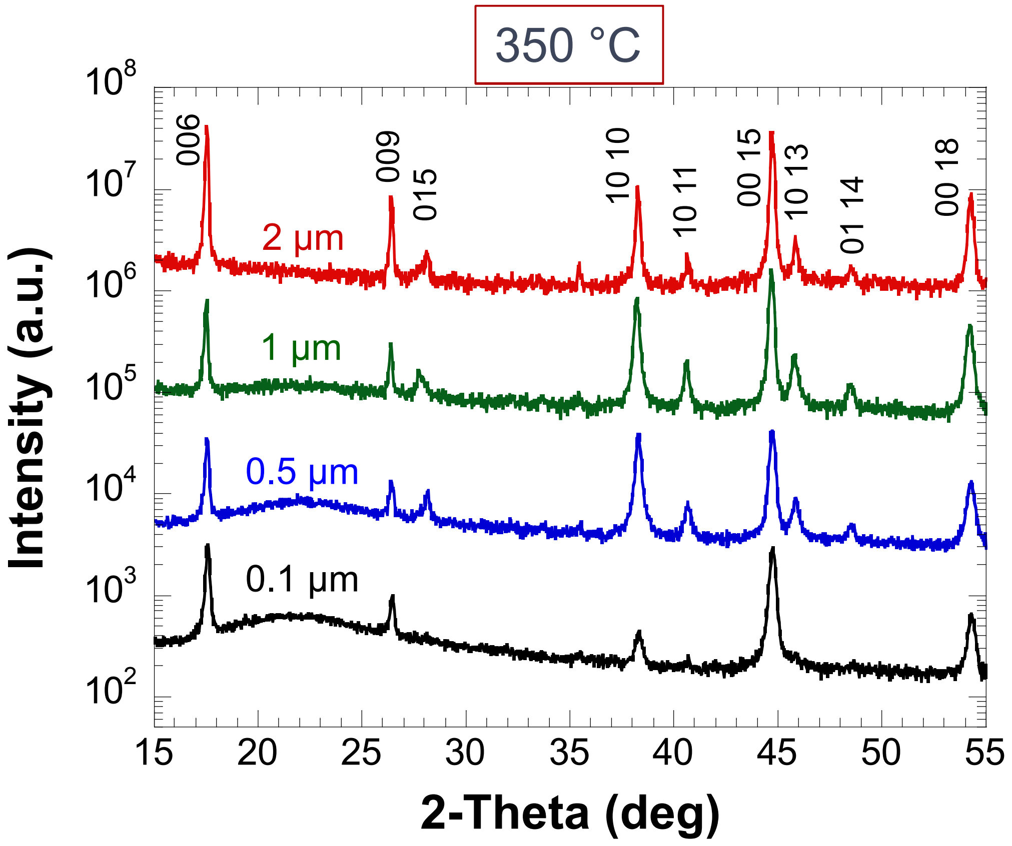


Starting at 450 °C peaks begin to shift

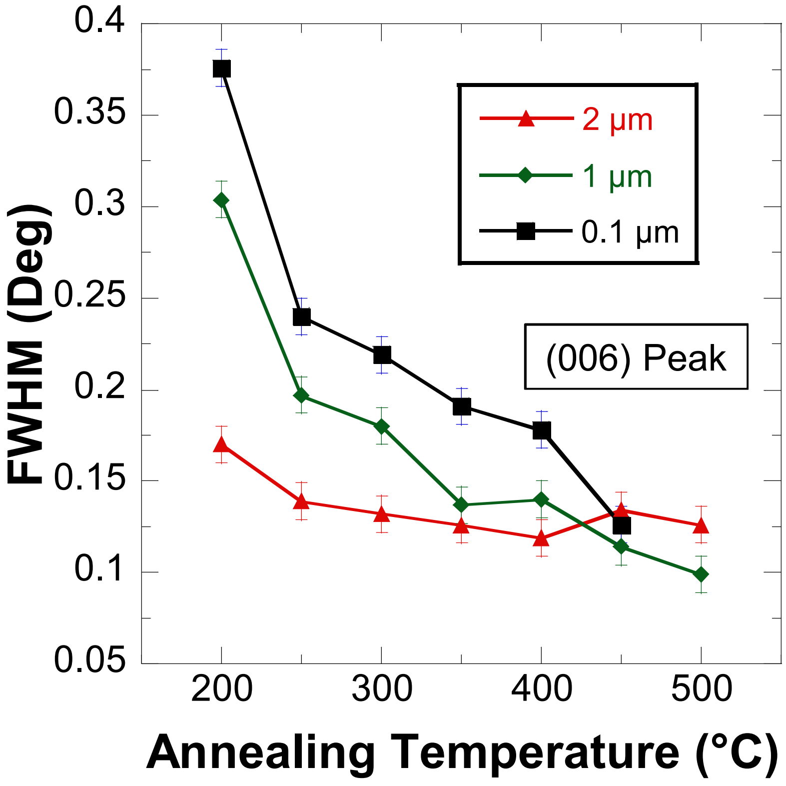


Films quickly become (00l) oriented with sizeable grain growth

Crystallographic Properties



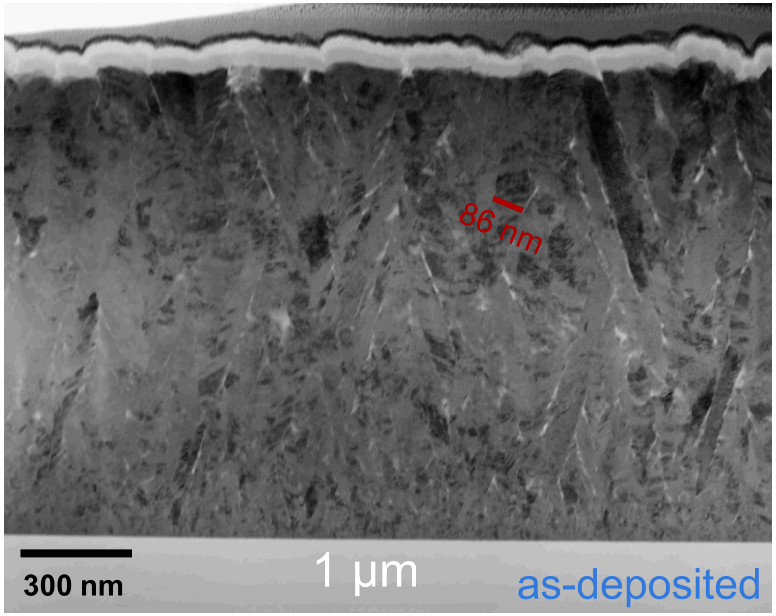
350 °C

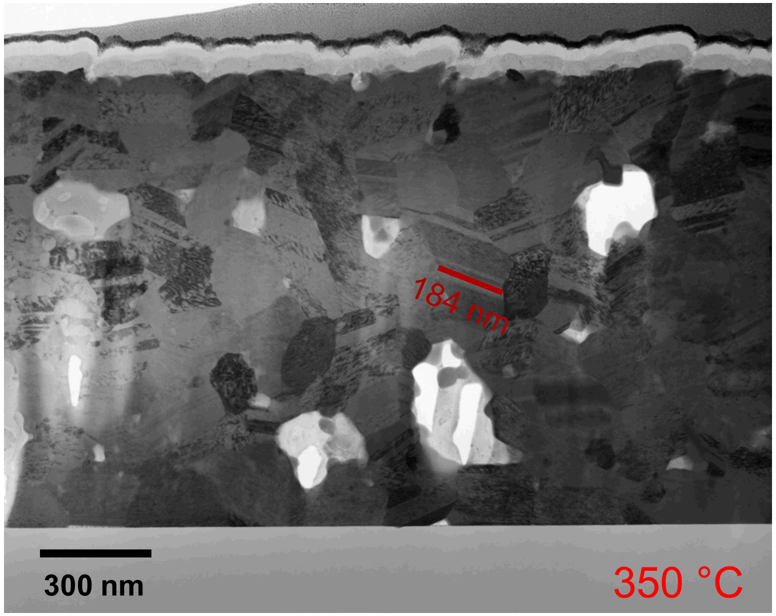


All thicknesses show (00l) preferred orientation

As expected thicker films show larger grains

TEM Microstructure

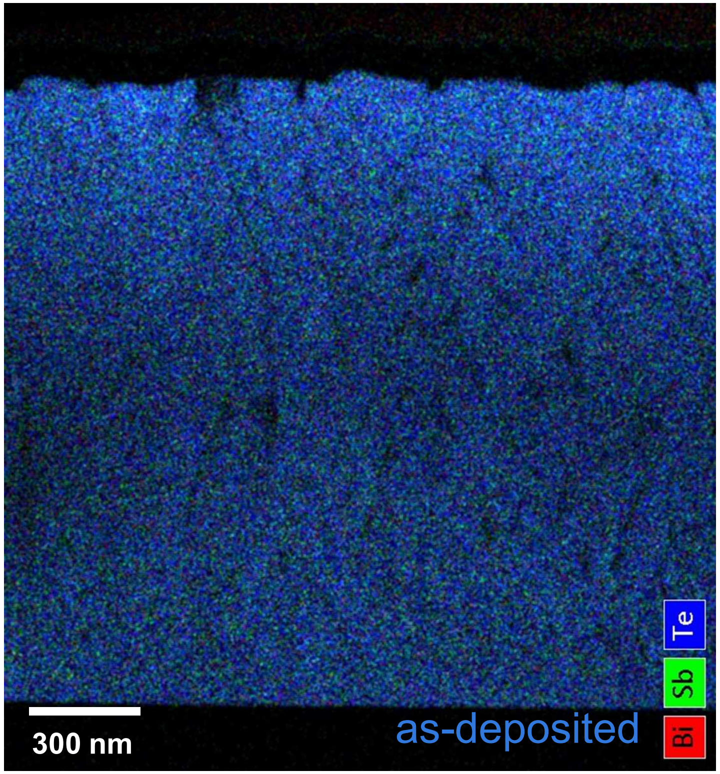




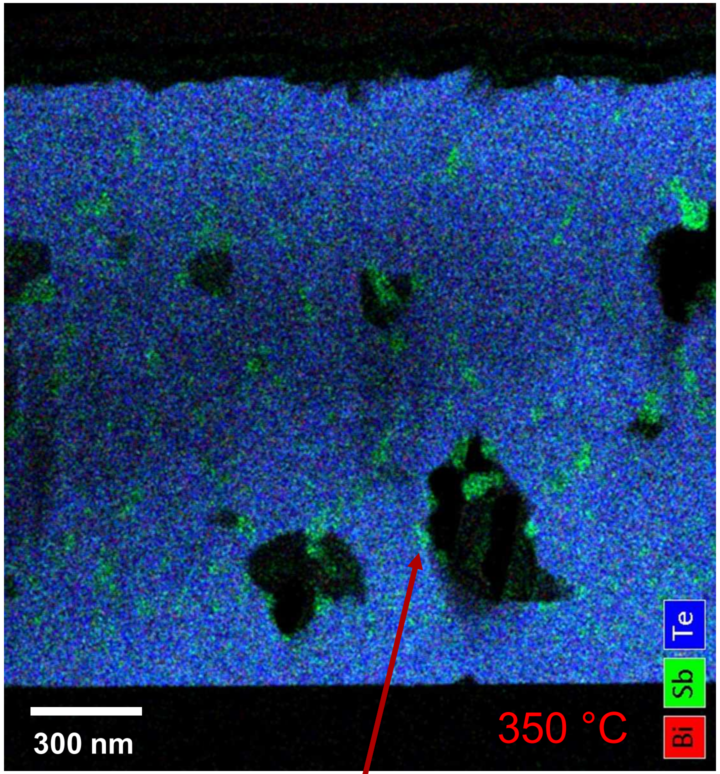
Clearly observe significant grain growth

Smaller pores coalesce at higher annealing temperatures

TEM Microstructure

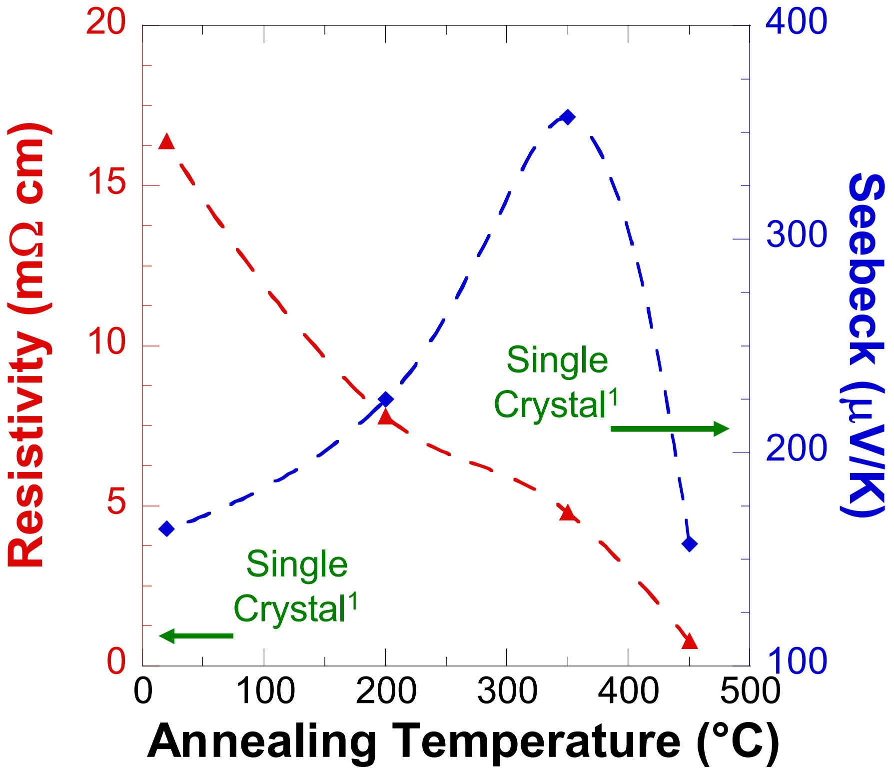


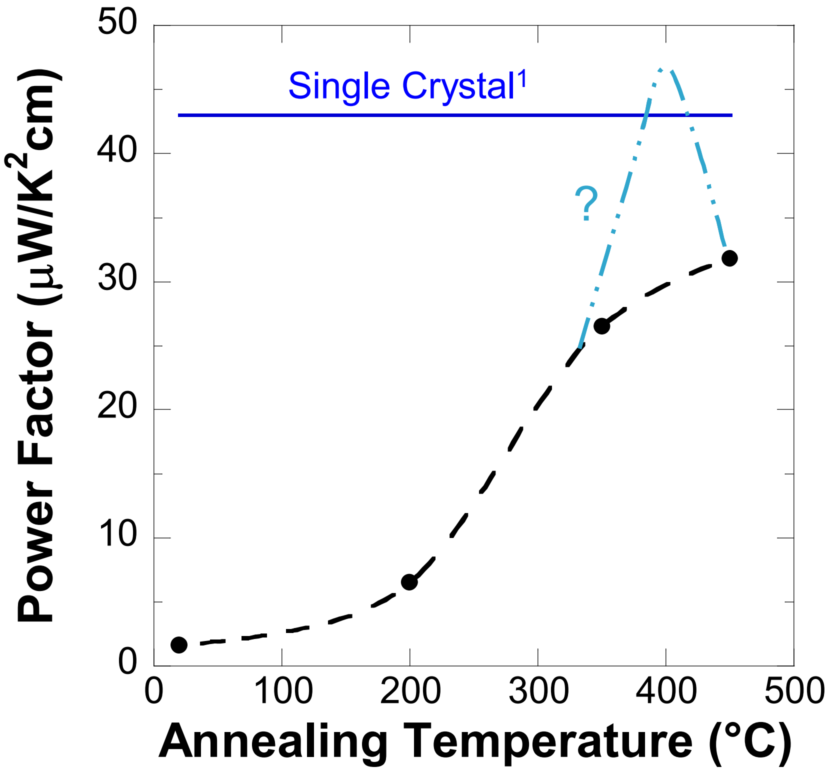
As-deposited films are highly uniform



Some evidence of Sb clusters

Transport Properties





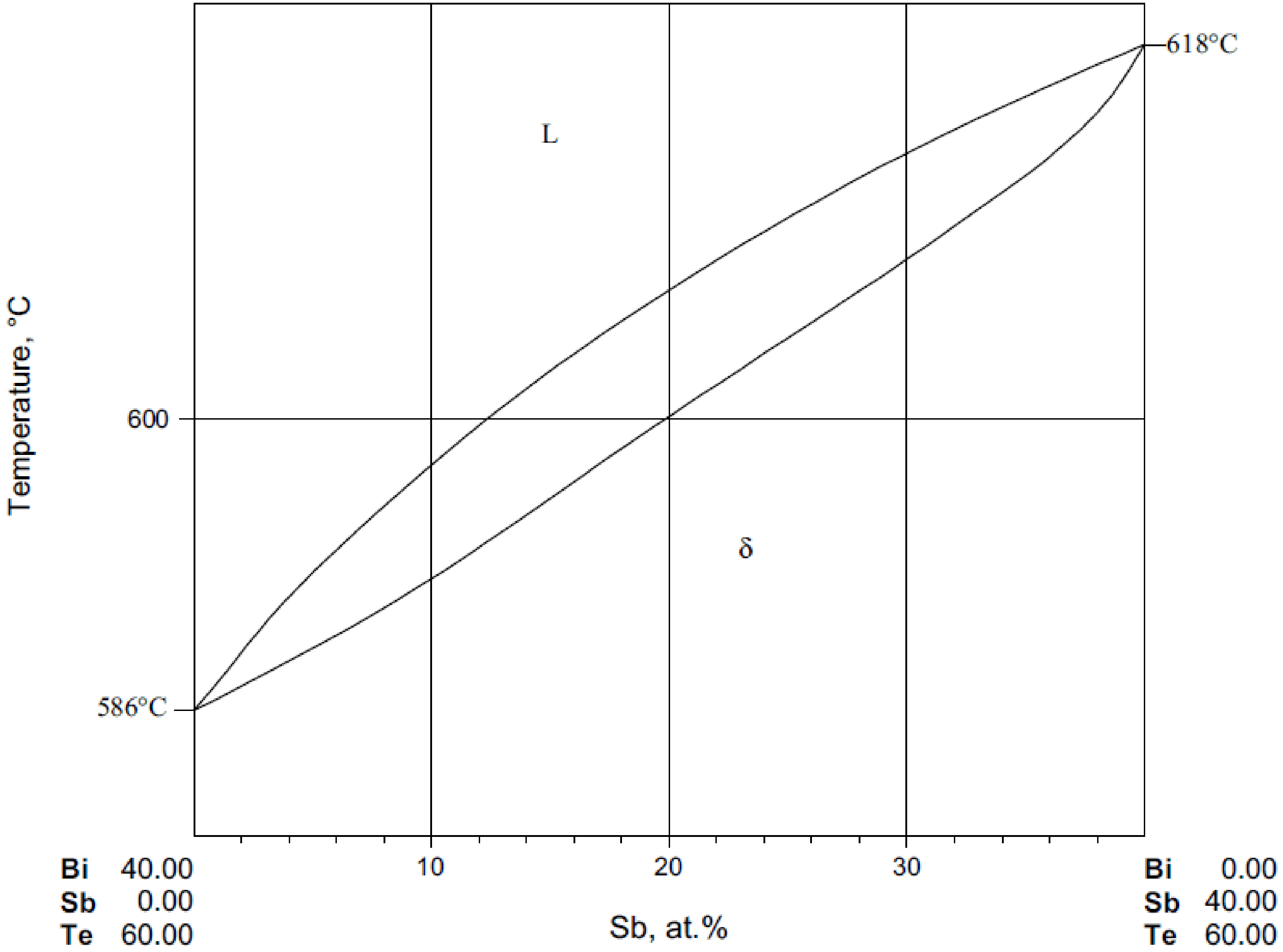
Maximum PF between 350 and 450 °C ??

[1] Champness *et al.*, Can. J. Phys. 1965

Summary

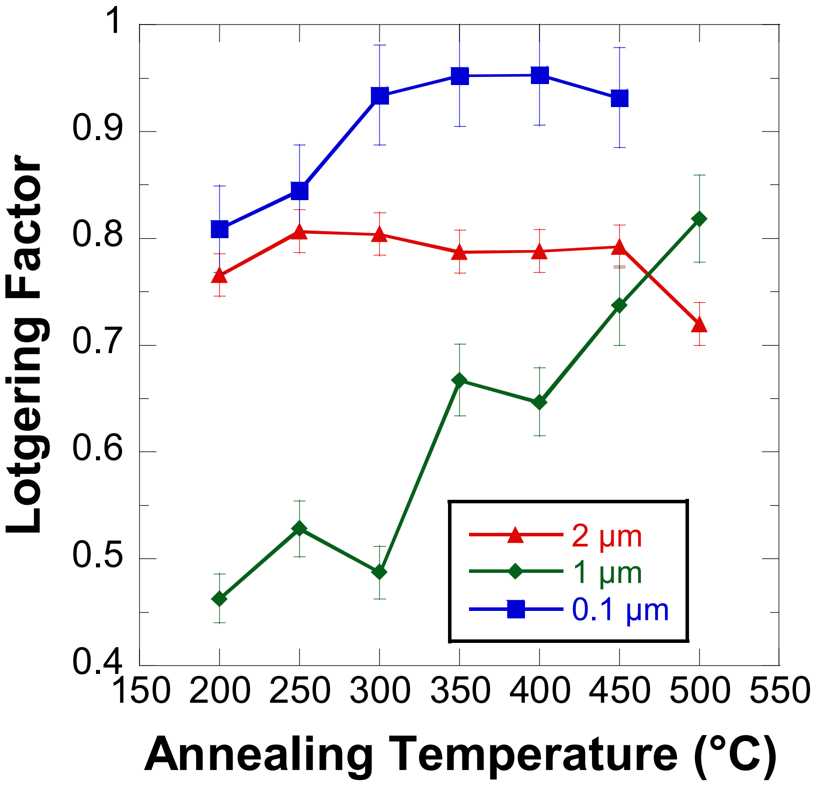
- Homogeneous $Bi_{0.4}Sb_{1.6}Te_3$ films up to 2 μm thick were sputter deposited
- Samples of varying thickness were annealed up 550 ˚C
- Films completely deteriorated above 500 ˚C
- As-deposited films have very small columnar grains
- Annealed films have significant grain growth and improved crystallinity
- Observe some evidence of Sb segregation and pore coalescence in annealed films
- Films annealed at 450 ˚C have a PF of 31.8 $\mu W/K^2 cm$
- Still room to improve!

Phase Diagram

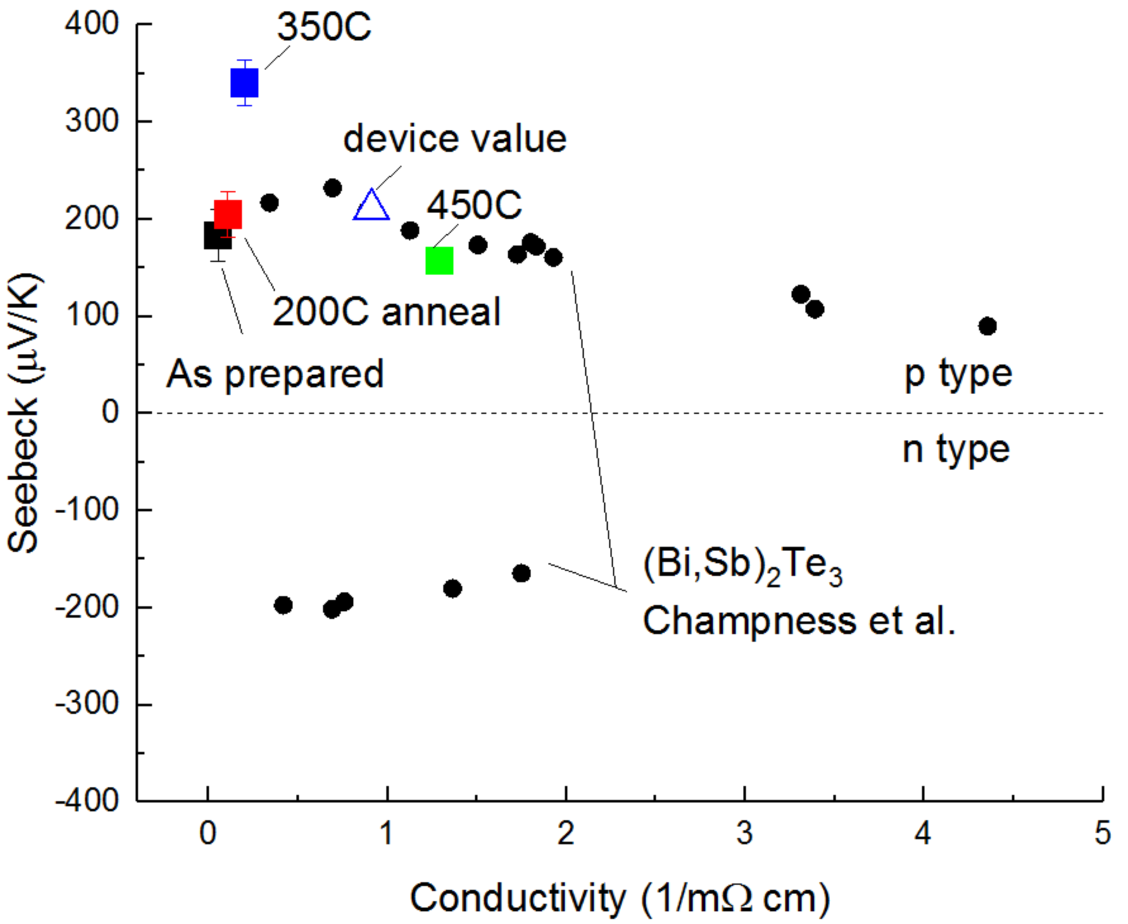


Vasyl Tomashik, Pierre Perrot, Springer Materials (2006)

LF for different film thicknesses



Jonker Plot


350C
device value
450C
200C anneal
As prepared
p type
n type
$(Bi,Sb)_2Te_3$
Champness et al.
Seebeck (µV/K)
400
300
200
100
0
-100
-200
-300
-400
0
1
2
3
4
5
Conductivity (1/mΩ cm)