Materials Science and Engineering
National Tsing Hua University

熱電能源管理實驗室
Thermo-Electric Energy Management (TEEM) Laboratory

Thermoelectrics

廖建能 教授
國立清華大學材料科學工程學系

August 4, 2010

Outline

- Introduction of Thermoelectrics
- Researches on Thermoelectrics
- Example: nanocrystalline Bi-Sb-Te thin film
- Fundamental knowledge/training

Thermoelectric effects

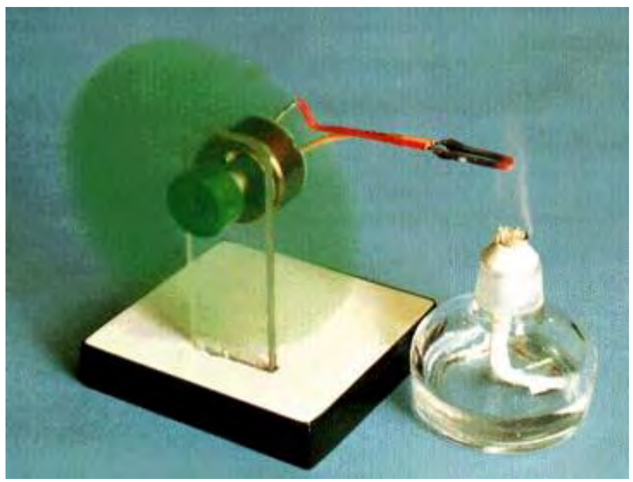
Seebeck effect

Electrical energy ⟷ Thermal energy

Peltier effect

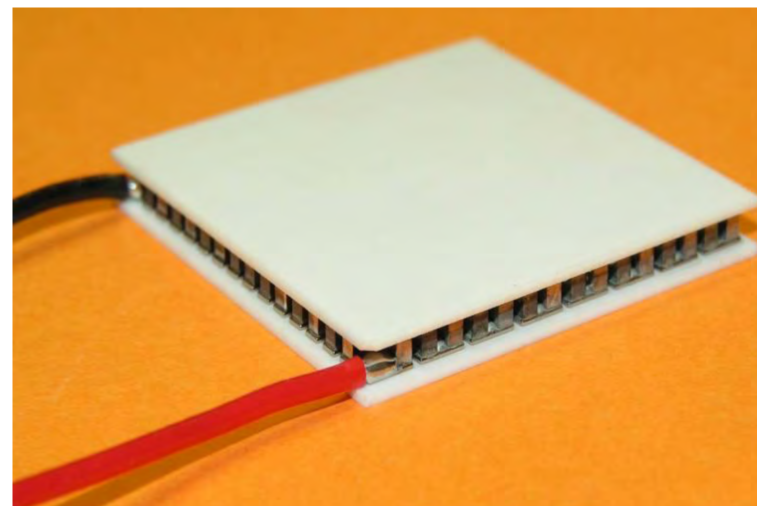
Thermocouple

Seebeck generator



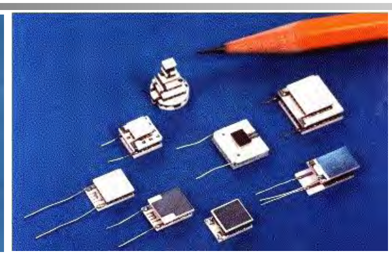
http://www.fgms.net/img/photo/photo6.jpg

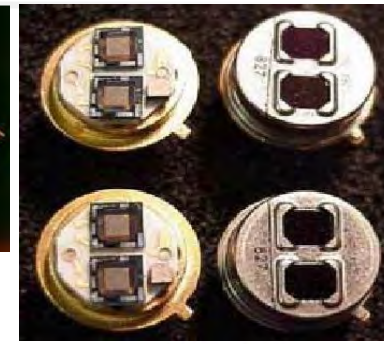
Peltier cooler



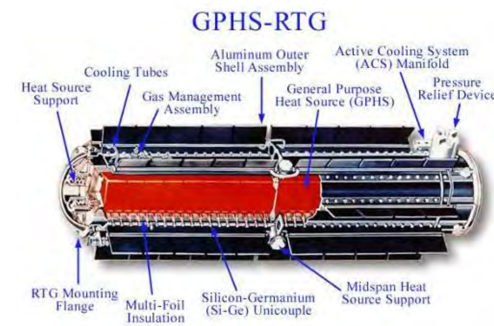
http://www.thermoelectric.com/2005/images/te-1.jpg

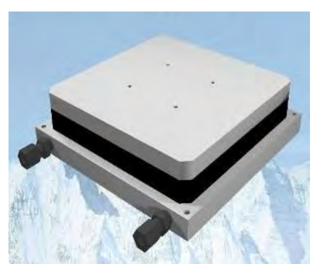
Thermoelectric applications

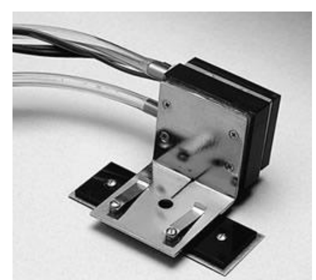


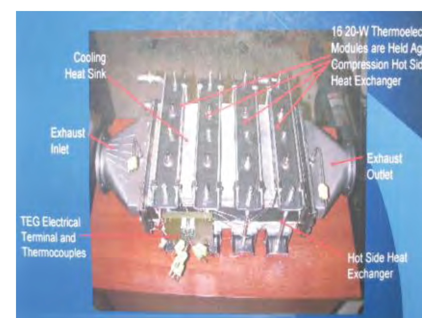


Thermoelectrics









Ideal thermoelectric materials

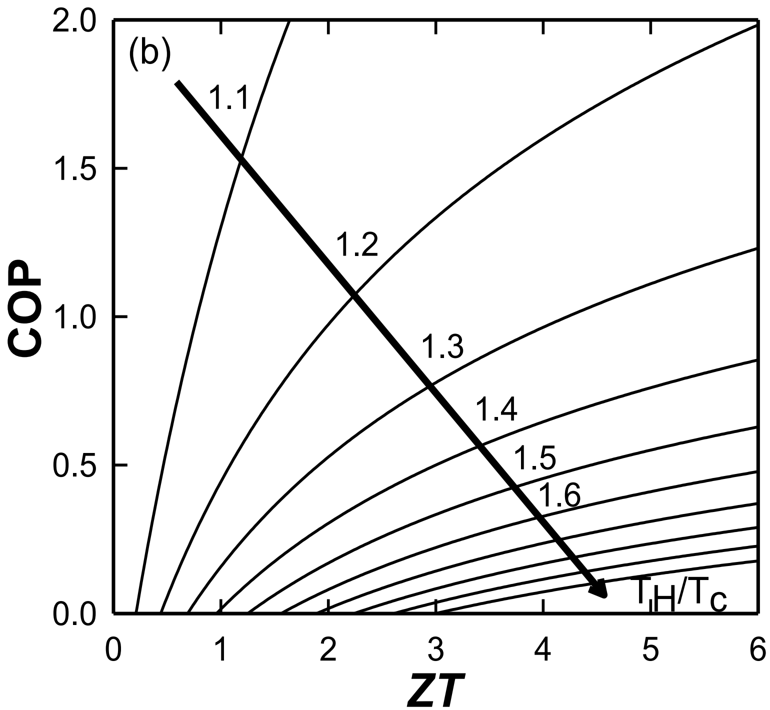
- COP and power generation efficiency ∝ $(1+ZT)^{1/2}$

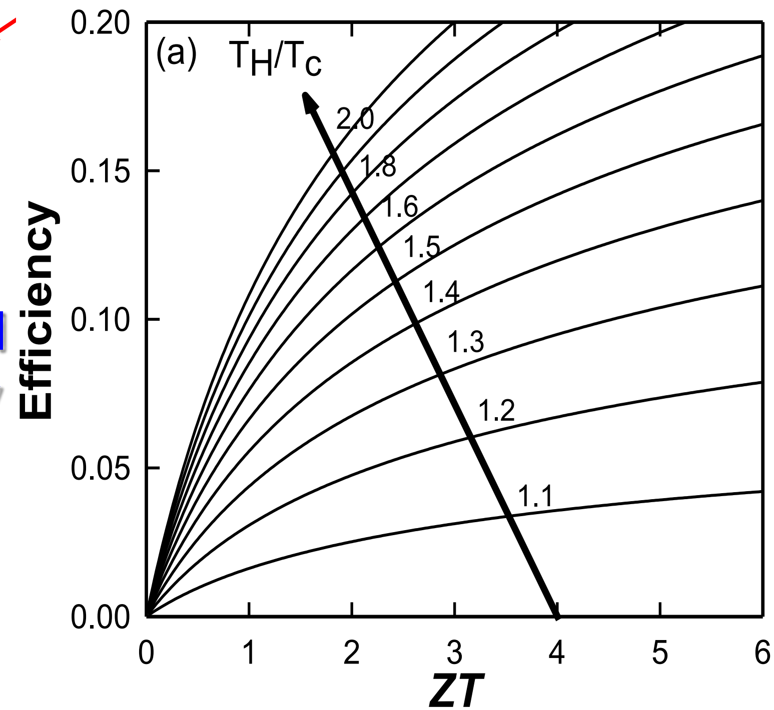
High Seebeck

High electrical conductivity

$$Z = \frac{S^2\sigma}{\lambda}$$

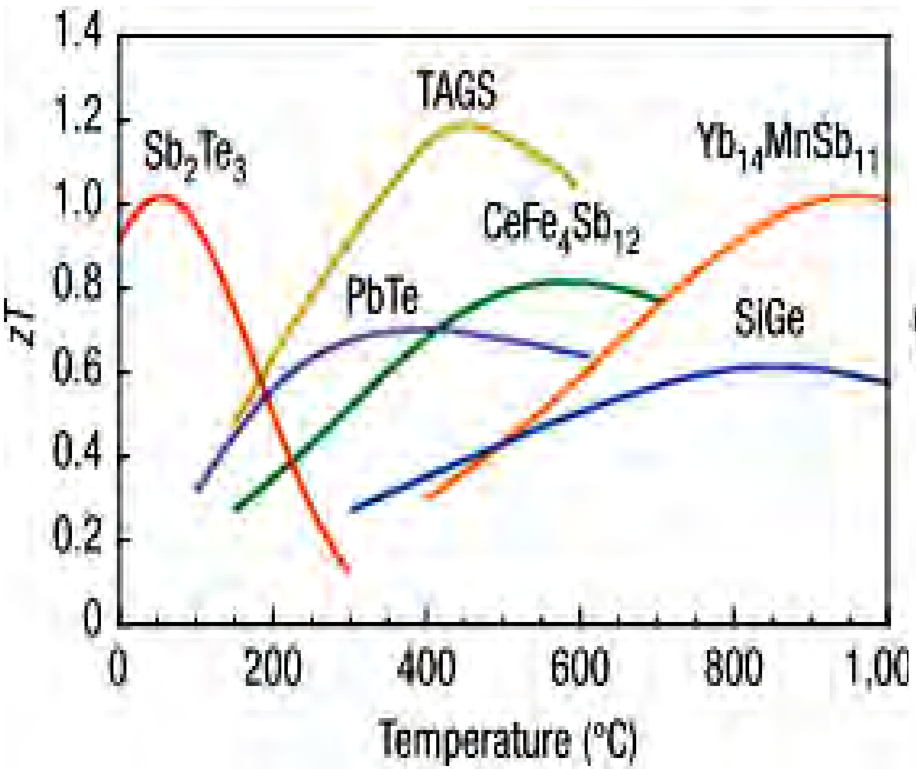
Low thermal conductivity



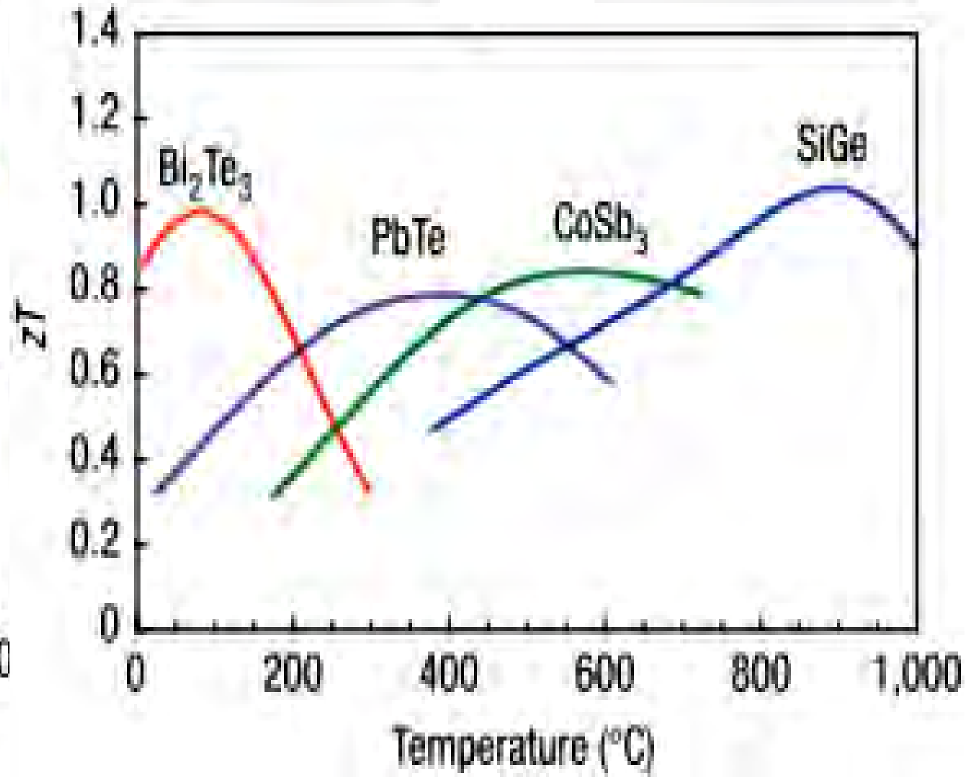


Classical thermoelectric materials

P-type



N-type



Superlattice structure

Bi_2Te_3/Sb_2Te_3 superlattice

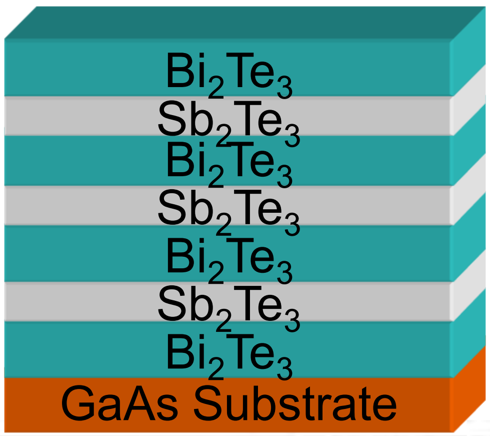
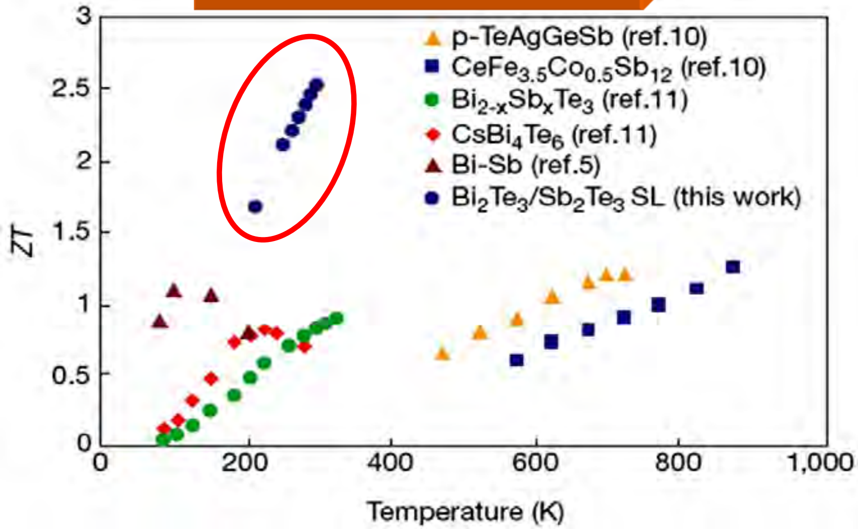


Table 1 Theoretical and experimental lattice thermal conductivities

Material	Thermal conductivity ($W m^{-1} K^{-1}$)
K_{min} of Bi_2Te_3 (*a-b* axis), Slack model[34]	0.55
K_{min} of Bi_2Te_3 (*c* axis), Slack model[34]	0.28
K_{min} of Bi_2Te_3 (*a-b* axis), Cahill model[35]	0.28
K_{min} of Bi_2Te_3 (*c* axis), Cahill model[35]	0.14
K_L of $Bi_{2-x}Sb_xTe_3$ alloy (*a-b* axis)	0.97
K_L of $Bi_{2-x}Sb_xTe_3$ alloy (*c* axis)	0.49
K_L of Bi_2Te_3/Sb_2Te_3 superlattice (*c* axis)	0.22

Lattice thermal conductivity (K_L) of the Bi_2Te_3/Sb_2Te_3 superlattice (period ~50 Å) compared with K_L observed in the respective alloys and the theoretical minimum lattice thermal conductivity (K_{min}) from various models.



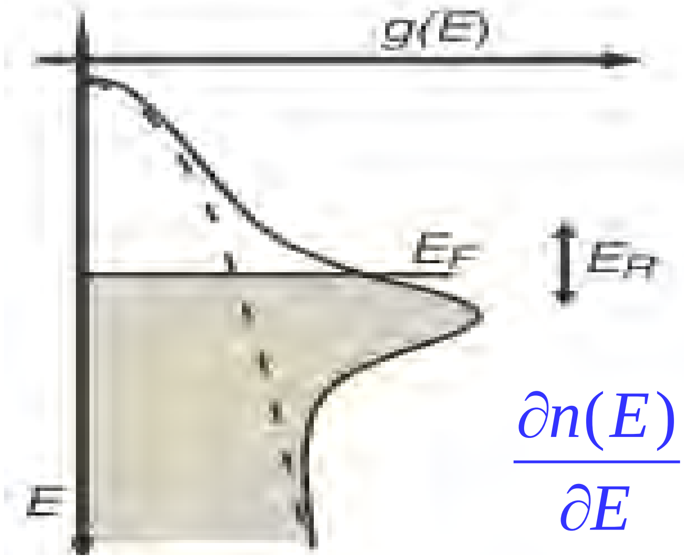
Rama Venkatasubramanian et al. Nature, 413 ,11(2001)

Fine-tuning the phonon & carrier transport

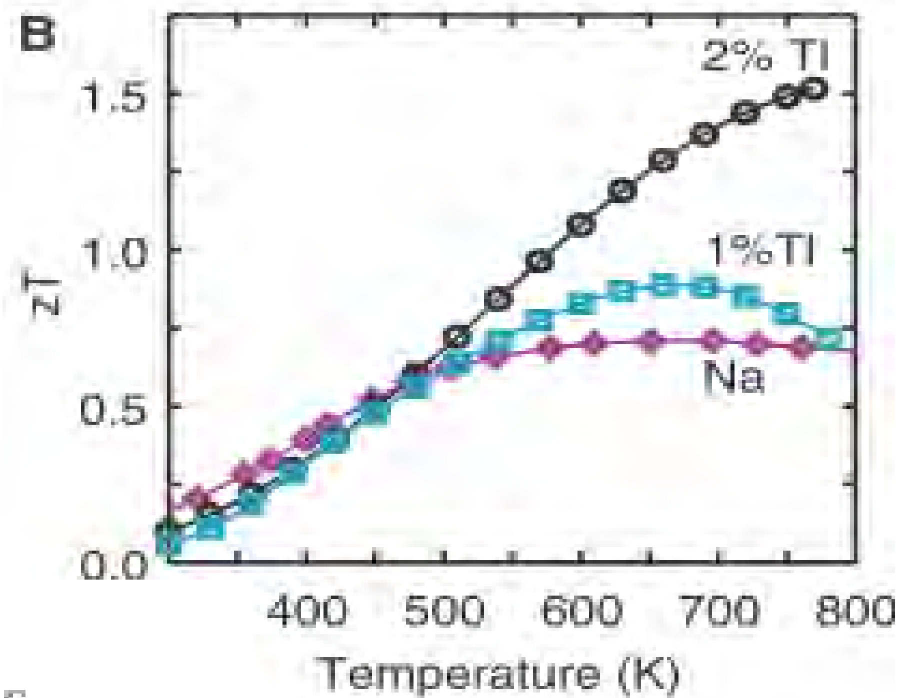
Phonon-blocking/electron-transmitting

ZT=2.4 at 300K

Seebeck enhancement by band structure engineering



$$\frac{\partial n(E)}{\partial E} \uparrow$$



$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F}$$

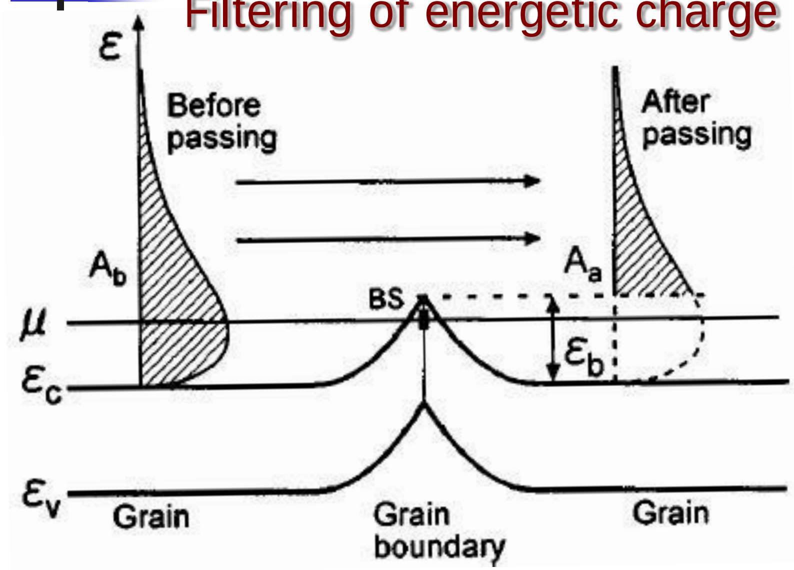
$$= \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{n}\frac{dn(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}$$

→ Enhancement of S

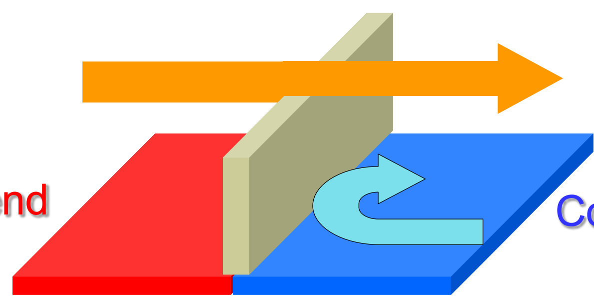
J. P. Heremans et al, *Science*, **321**, 554 (2008)

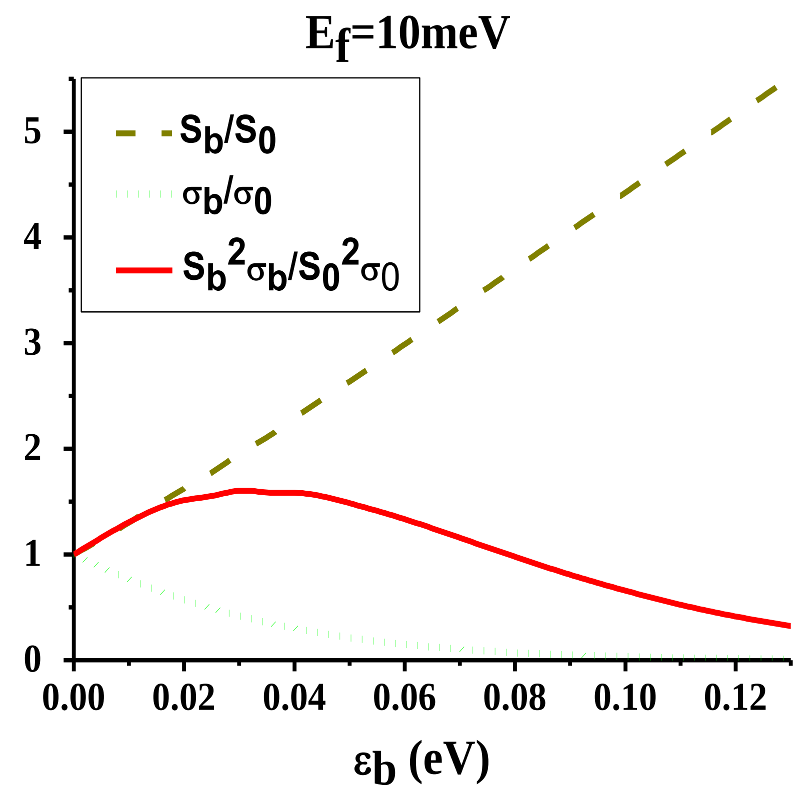
Seebeck enhancement by carrier filtering

Filtering of energetic charge carriers



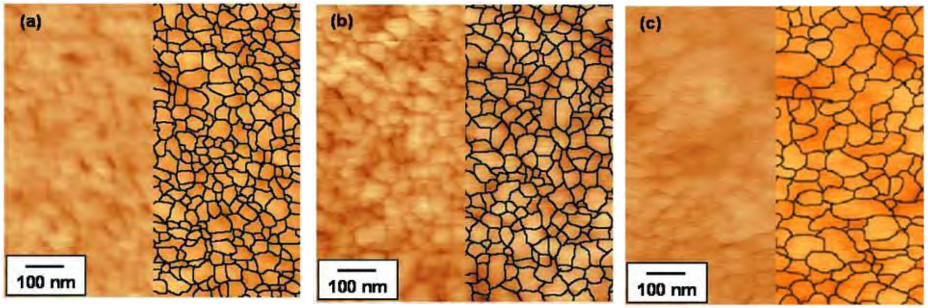
K. Kishimoto, *J. Appl. Phys.* 92, 5331 (2002)





Nanocrystalline Bi-Te based thin films

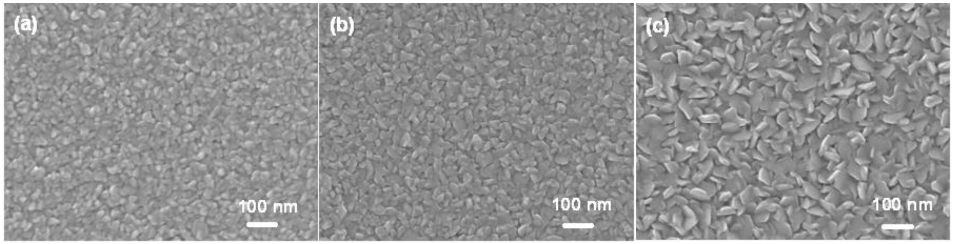
N-type flash-evaportaed Bi-Se-Te films



T_{Anneal} (^{0}C)	Grain size (nm)	κ (W/mK)
as-dep	~10	0.61
150	~27	0.68
250	~60	0.8

Takashiri et al, J. Appl. Phys., 104, 084302 (2008)

P-type sputtered Bi-Sb-Te films

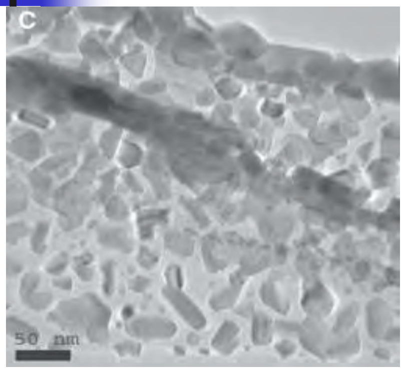


$T_{Deposition}$ (^{0}C)	Grain size (nm)	κ (W/mK)
R.T.	~25	0.46±0.08
50	~45	0.65±0.08
100	~85	0.81±0.06

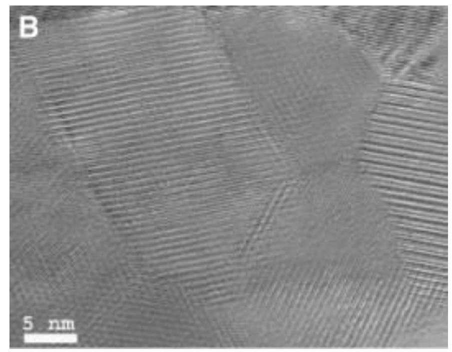
Liao et al, J. Appl. Phys., 104, 104312 (2008)

Grain size ↓ ⇨ κ ↓

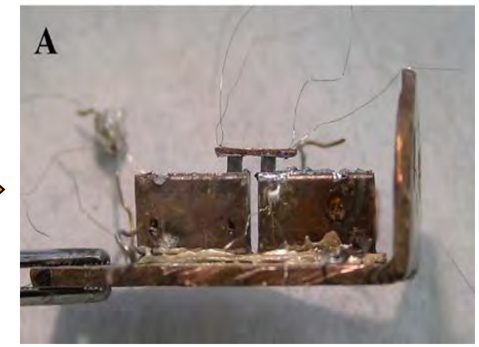
Nanostructured Bi-Sb-Te compounds



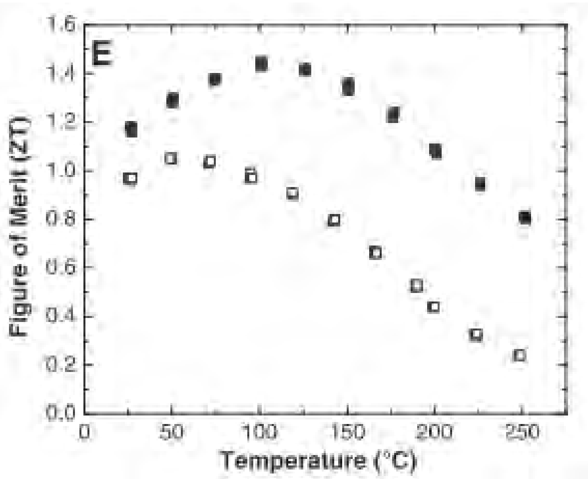
Nano-sized powder

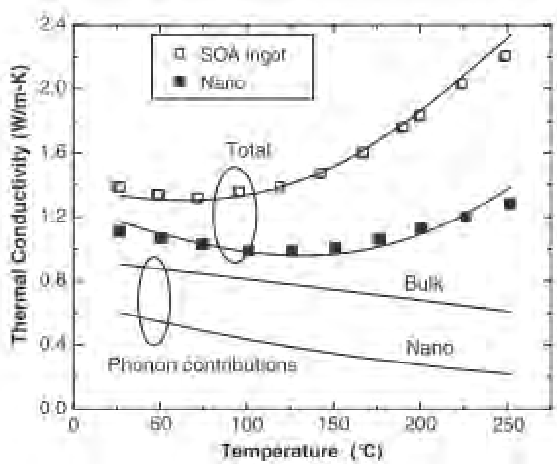


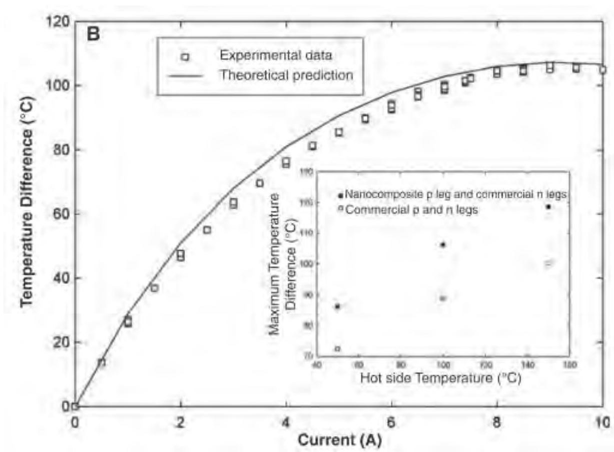
Hot-pressed



assembled

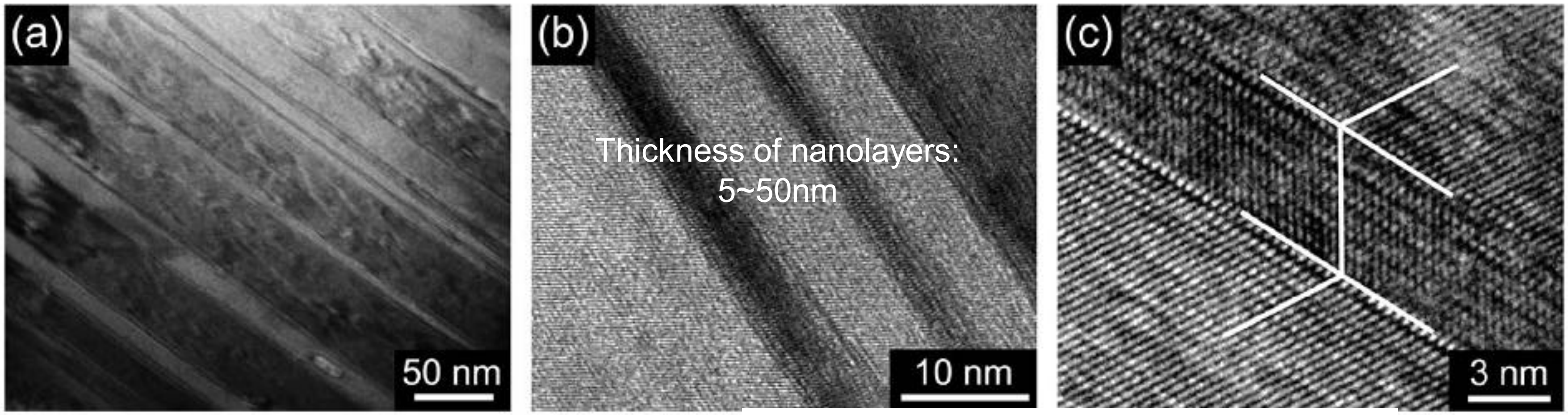


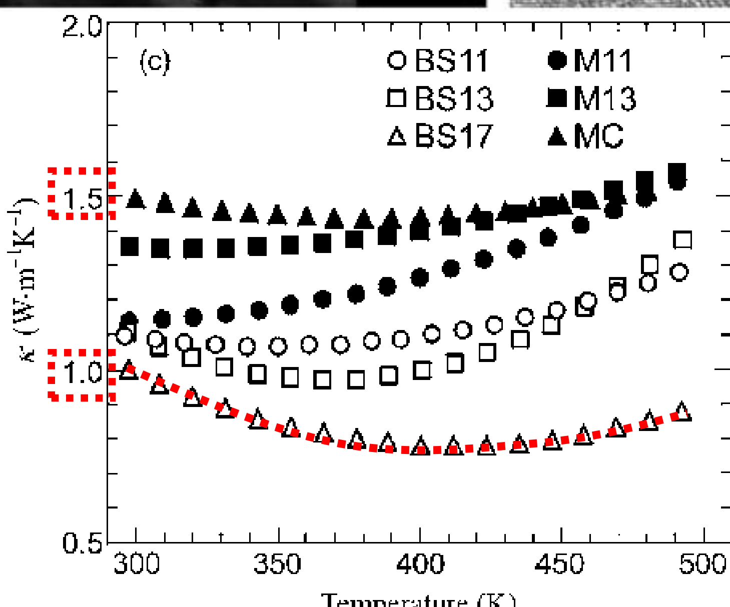


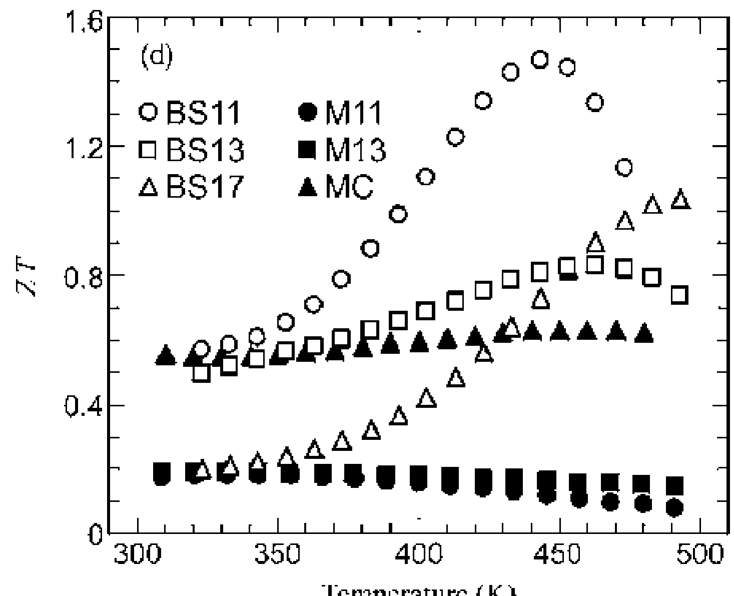


Poudel el al, Science 320, 634 (2008)

Melt-spinning + SPS technique







Appl. Phys. Lett. 92, 143106 (2008)

Spark plasma sintering technique

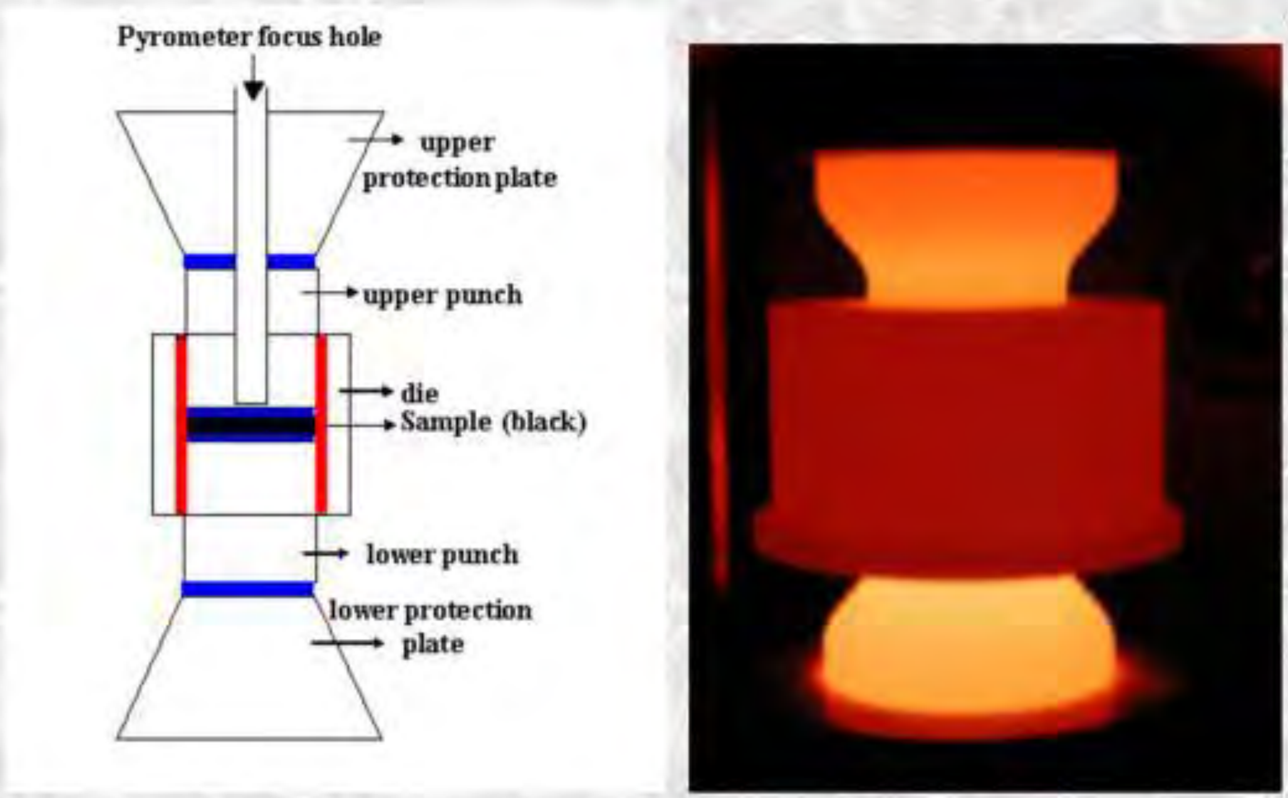


Fig. 1. Overview of the graphite set-up containing a powder sample (black), horizontal graphite papers (blue) and a vertical graphite paper sleeve (red) and a set-up during heating.

Prospectus of material scientists

- Structure/Microstructure
  - Crystal structure
  - Polycrystal vs single crystal (grain size)
  - Crystal defects (antisite, vacancy, interstitial, dislocation)
  - Precipitation
- Processing methods
  - Bulk vs thin film
  - Pre-treatment (purification, milling, doping,…)
  - Processing (deposition, cold/hot pressing, sintering, …)
  - Post treatments (thermal, electrical, …)
- Properties
  - Electrical transport (resistivity, carrier concentration, mobility)
  - Thermal transport (electronic/lattice thermal conductivity)
  - Electro-thermal transport (Seebeck coefficient)
  - Mechanical (strength, brittleness, CTE, …)

Research for what?

- Understanding the structure-processing-property relationship
  - Directions of new material development
  - Model and mechanism?
- Enhanced properties for better performance of existing applications or new applications
  - Experimental and theoretical verification
  - Prototyping applications and feasibility testing
- Confirming known facts is a training procedure not a research goal!

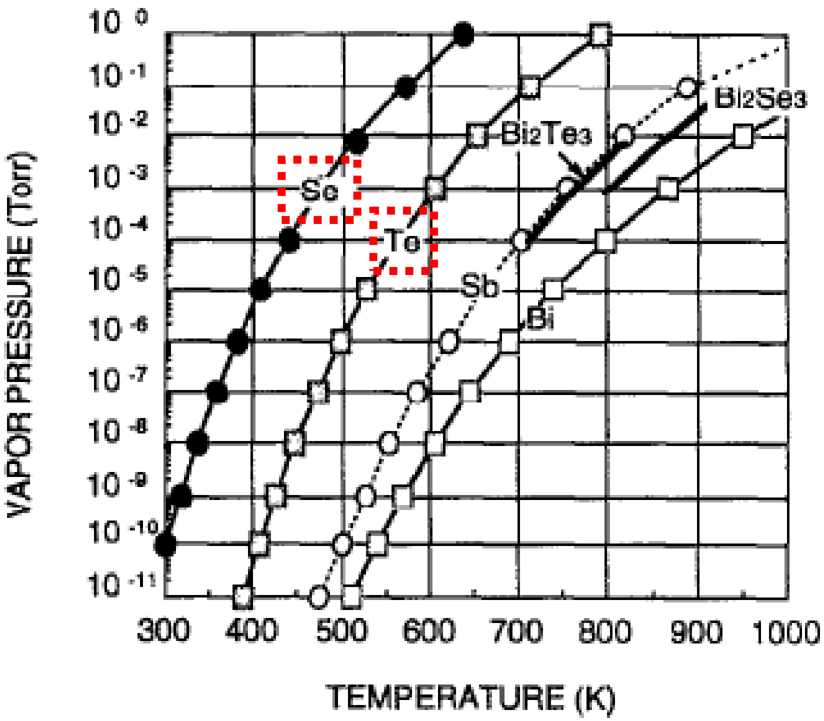
Electronic characteristics of defects in Bi-Sb-Te compounds

- Anti-site defects:
  - Bi_{Te} or Sb_{Te}: single acceptor
  - Te_{Bi} or Te_{Sb}: single donor
- Vacancies:
  - V_{Bi} or V_{Sb}: triple acceptor
  - V_{Te}: double donor
- Non-active interstitials

Electric current assisted annealing

Low deposition temperature → Nanocrystalline TE films

Low λ, **high ρ**



Post-dep annealing

Elimination of crystal defects

Low annealing temperature, short duration

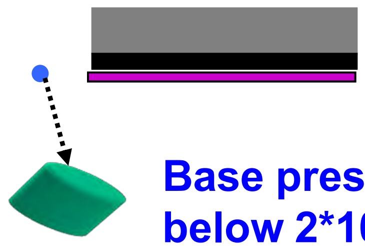
Electric current assisted annealing

Nanocrystalline TE films

Low λ, **low ρ**

Experiment

Si Substrate



Polyimide (2 μ m)

Film (~ 0.5 μ m)

Base pressure below 2*10^{-6} torr

P-type: Bi-Sb-Te target

N-type: Bi-Se-Te target

Step1: Thin films deposition by sputtering

Modified quartz holder

ULVAC MILA-3000

MATSUSADA AU-2P150

Annealing time: 5 min

Annealing temp.: 230~330 ^{0}C

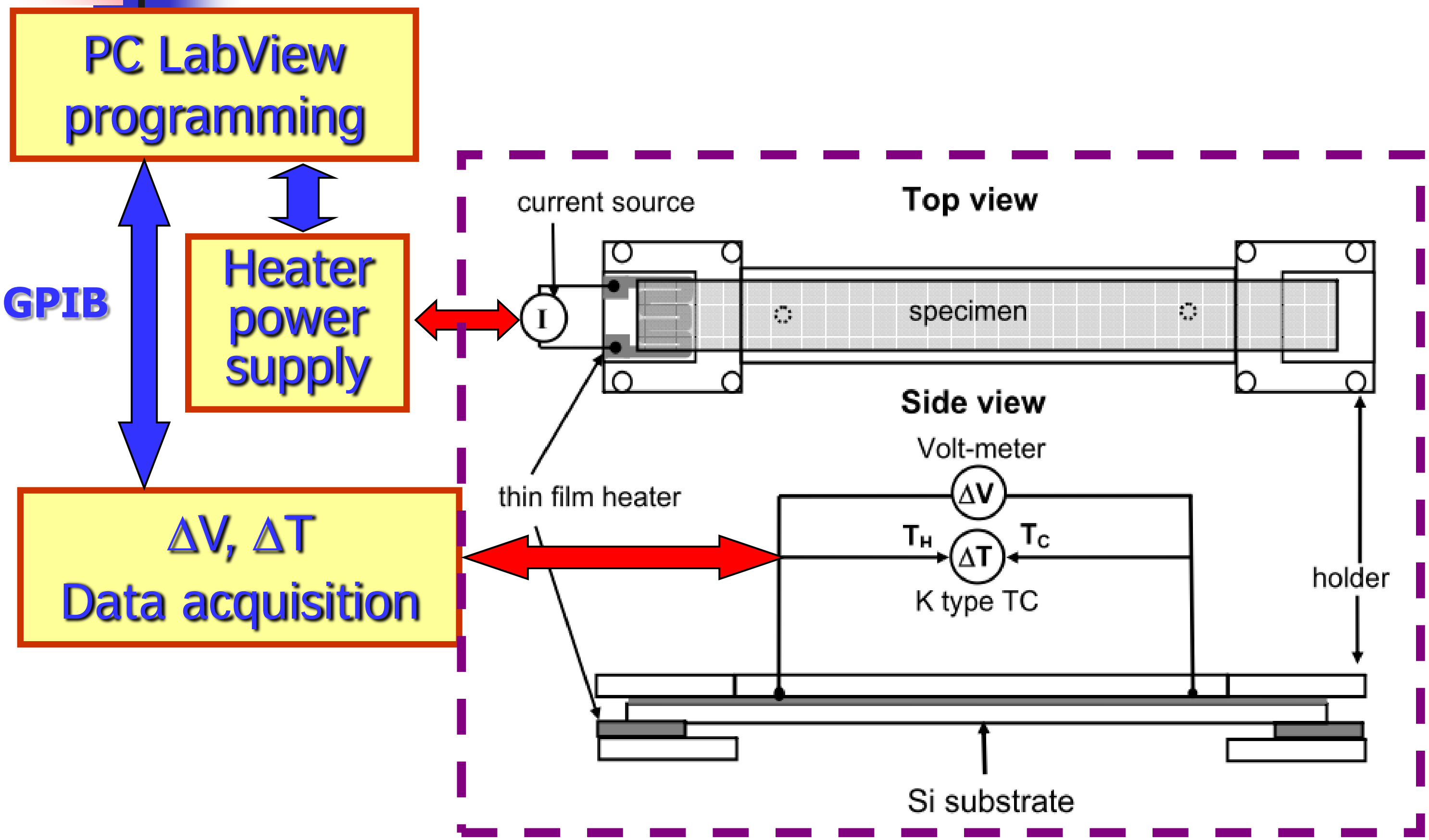
Electric current density ~10^3 Amp/cm^2

Step 2: Heat treatment by ULVAC MILA-3000 equipped with a high voltage power supply

S, ρ, n and μ measurement

SEM, AES,TEM…analysis

Seebeck coefficient measurement



R.T.- 200 °C sample stage and chamber under development

Resistivity, carrier concentration and mobility measurement

HMS-3000 Hall Measurement System

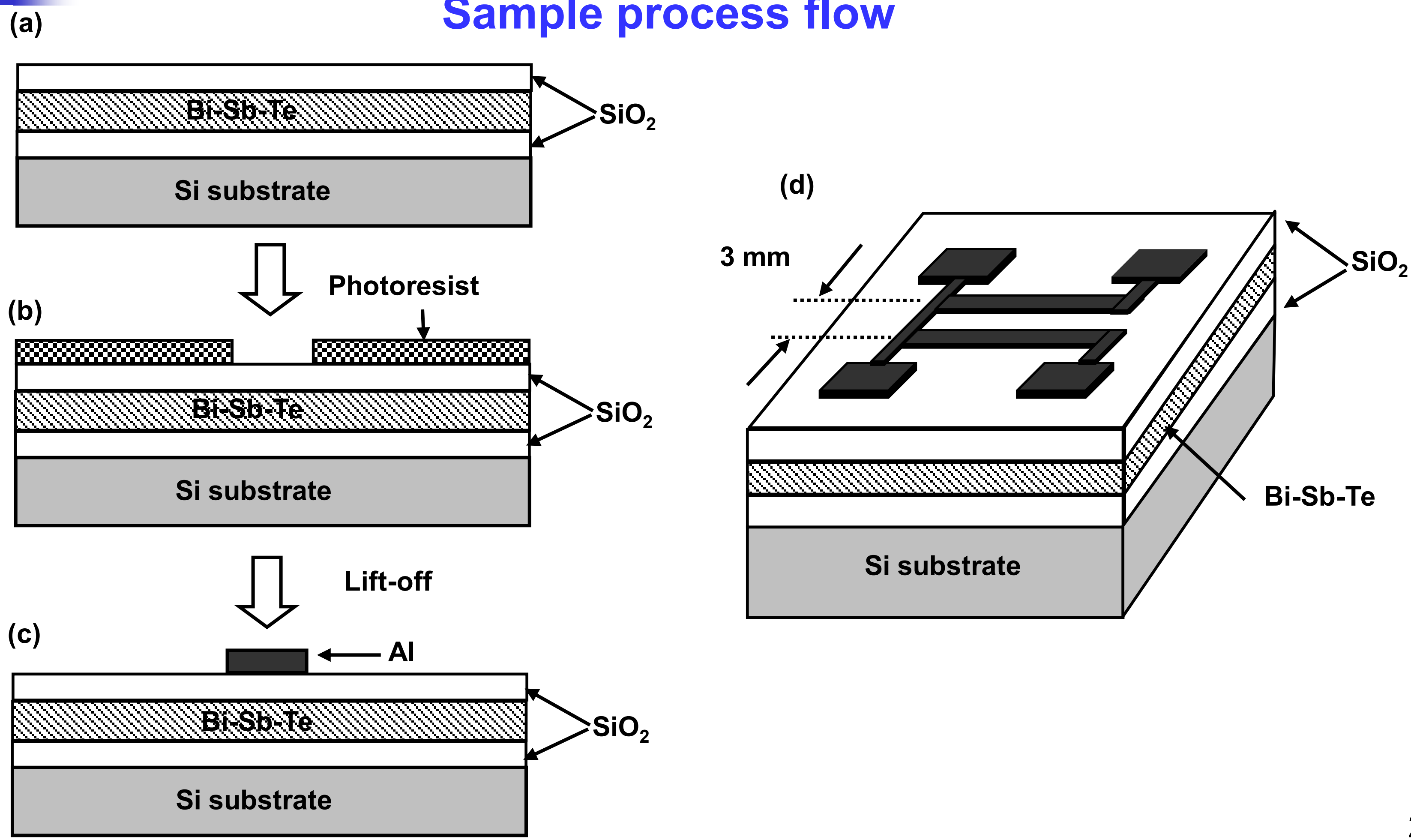
HMS-5000 Variable Temperature Hall Effect Measurement System (80K -350K)

Magnetic field
0.55Tesla

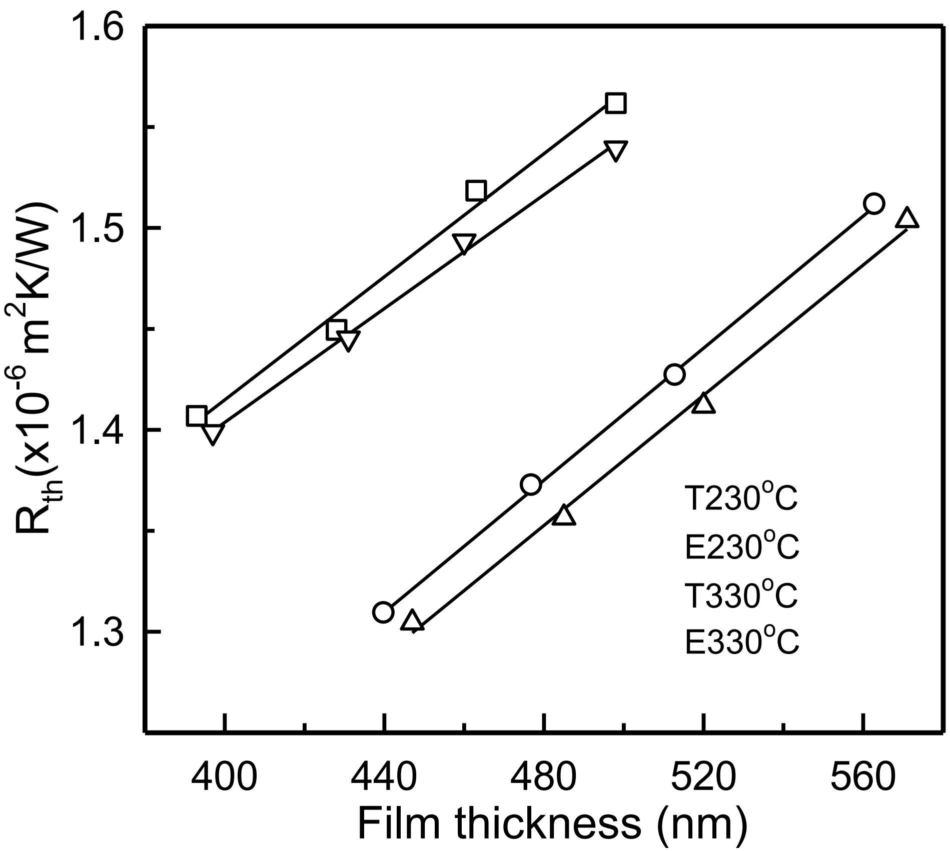
Sample holder

3ωThermal conductivity measurement

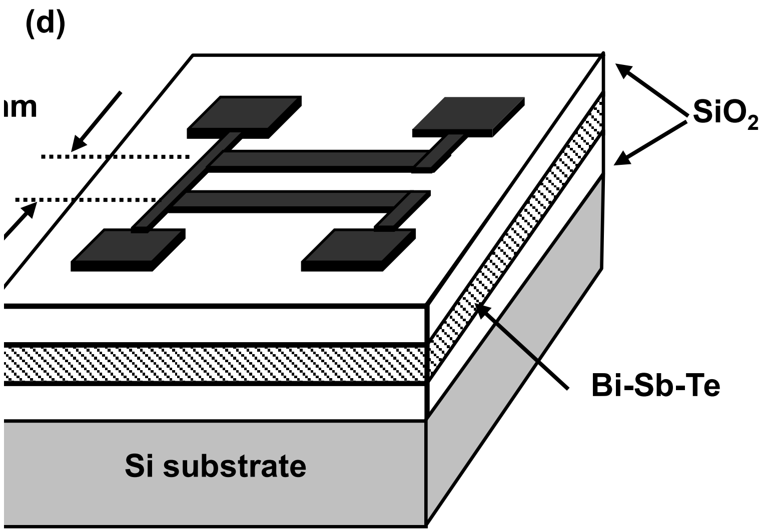
Sample process flow



Total thermal resistance versus film thickness

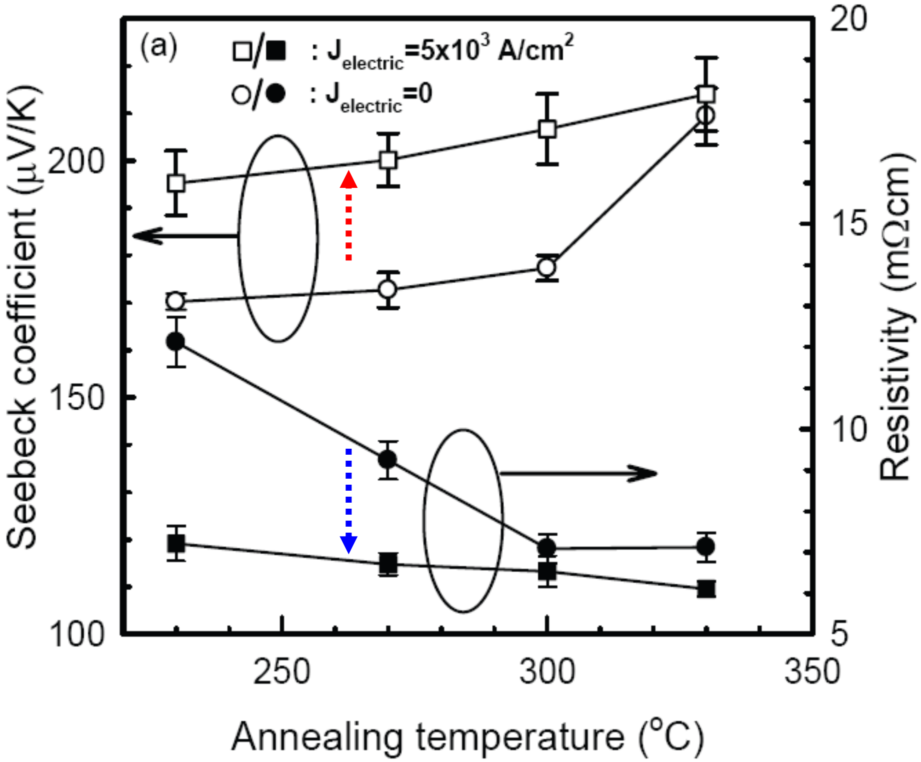


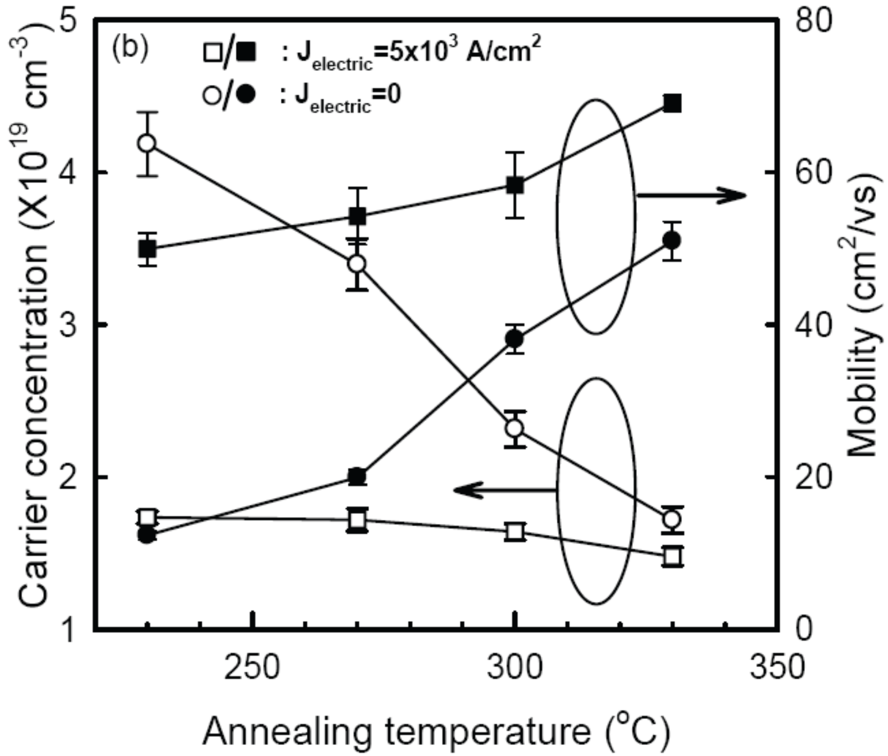
$$R_{th} = \frac{t_f}{\lambda_f} + \frac{t_d}{\lambda_d} + R_B$$



o et al, J. Appl. Phys., 104, 104312 (2008)

Electrical transport properties of p-type films (Bi:Sb:Te = 11:29:60)





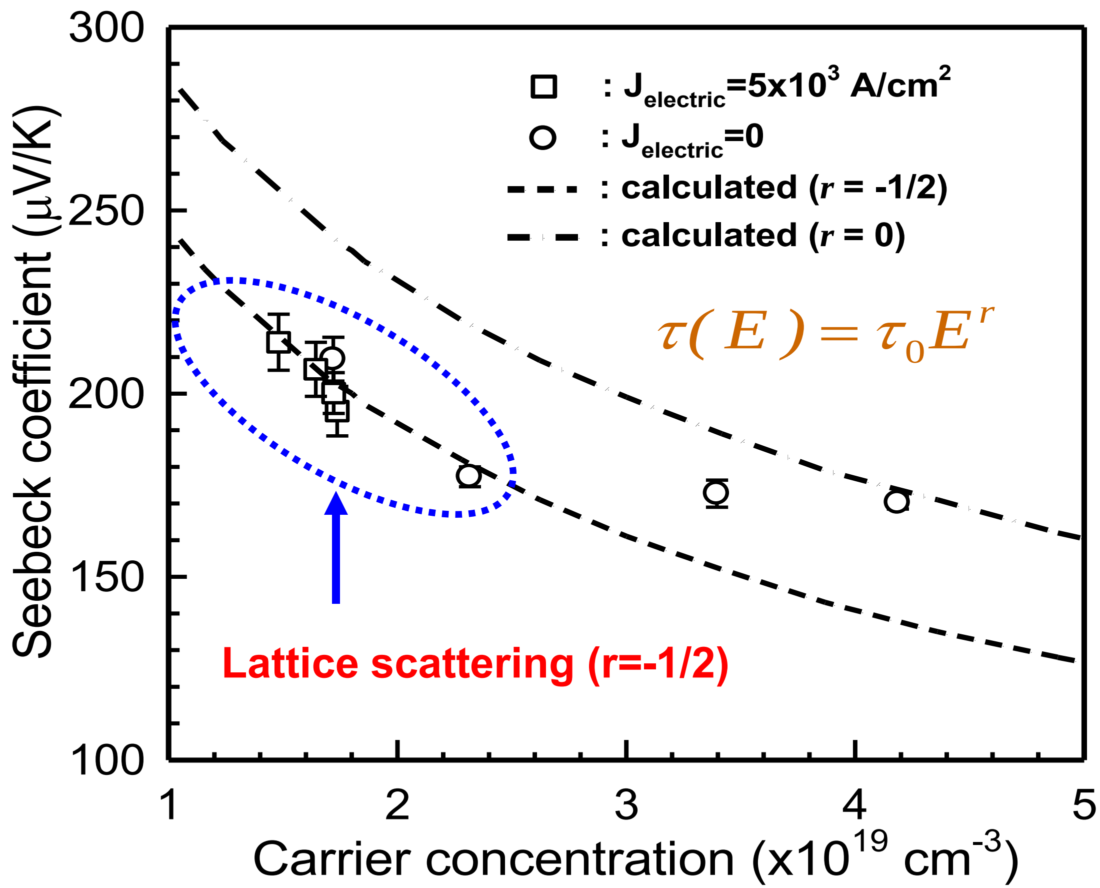
Electric current stressing

⋯▸ Lower resistivity

⋯▸ Higher Seebeck coefficient

Seebeck coefficient vs. carrier conc.

(Bi Sb Te films)

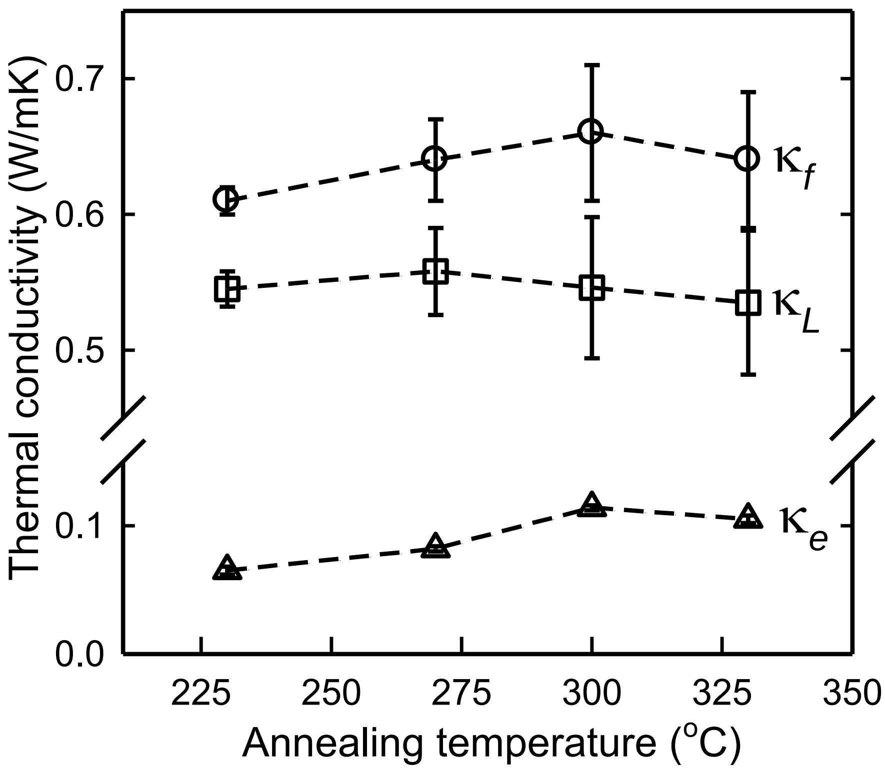


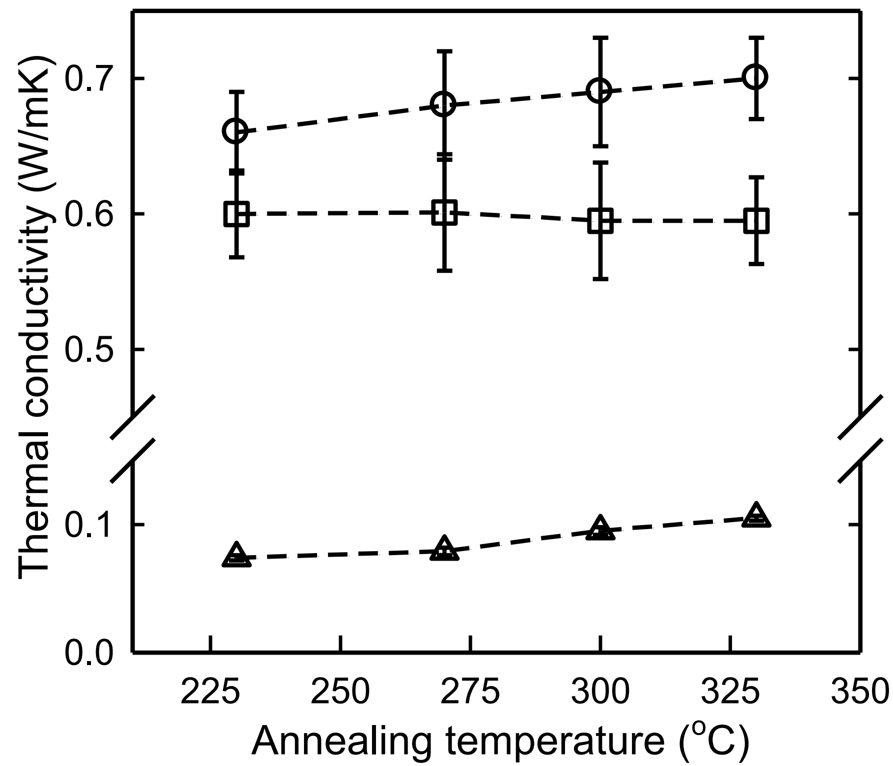
High ⟵⟶ **Low**

Annealing temperature

Liao et al, Appl. Phys. Lett., **93**, 042103 (2008)

Thermal conductivity vs. annealing temperature (Bi-Sb-Te films)

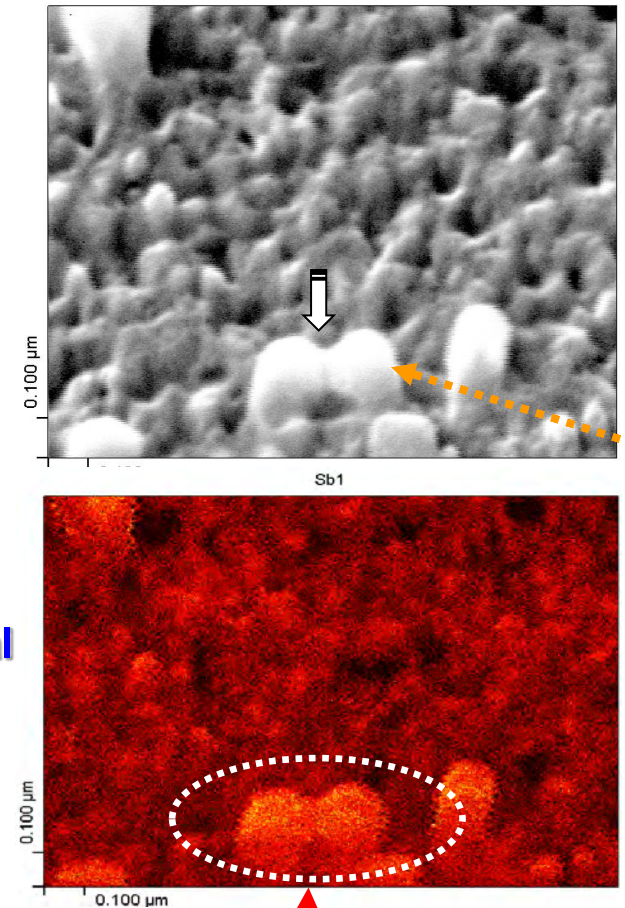




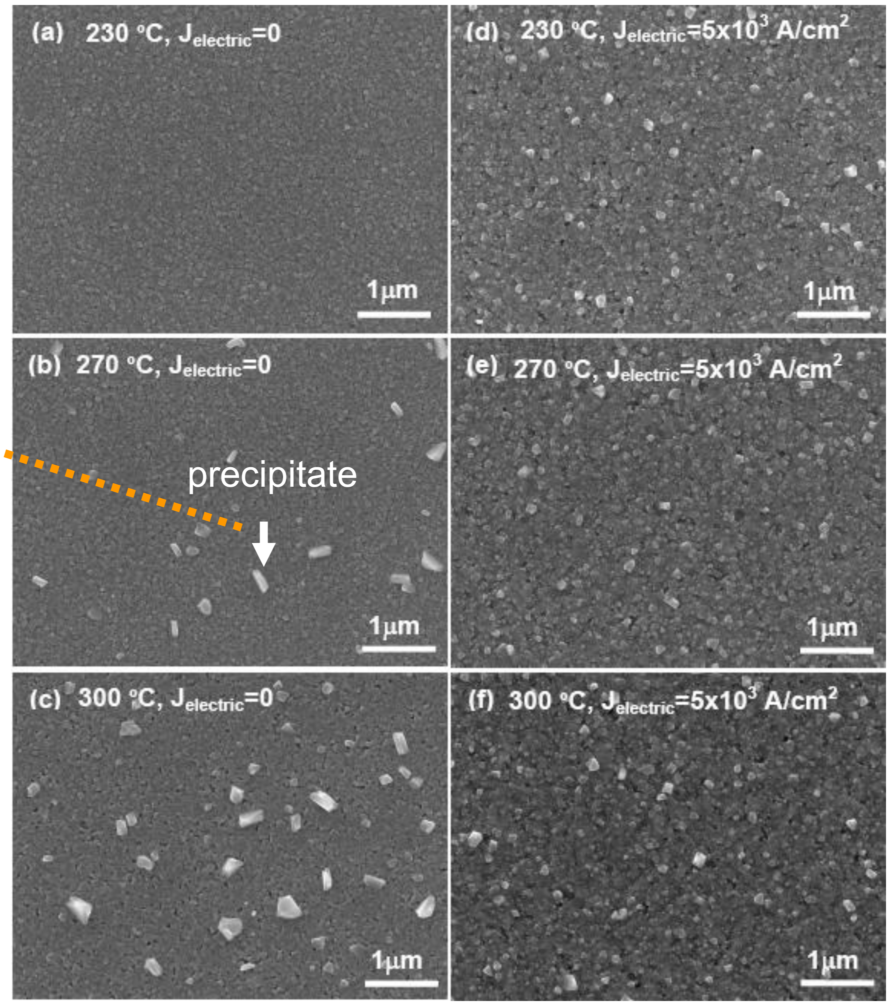
Morphology and elemental analysis of the Bi-Sb-Te films

AES analysis

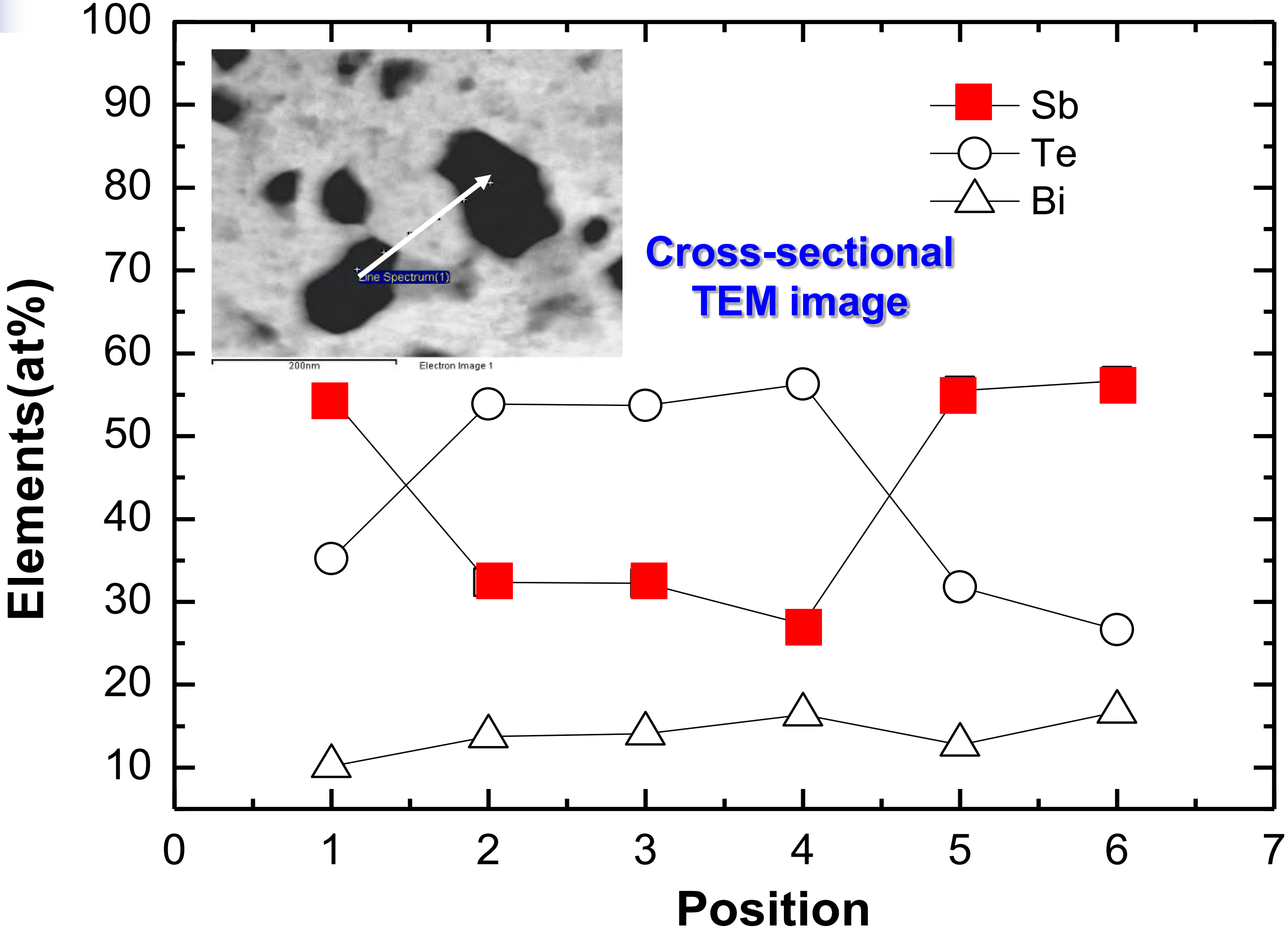
Sb elemental mapping



Sb-rich phase

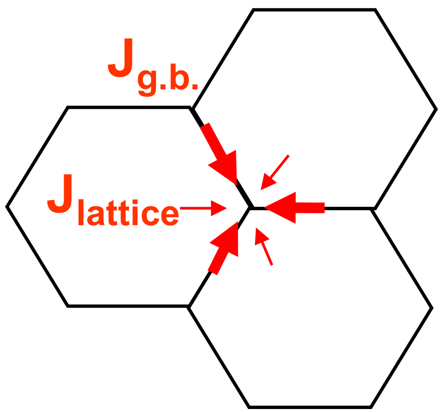


Compositional analysis of electrically stressed Bi-Sb-Te thin film by TEM



Electromigration-induced Sb precipitation

Thermal annealing



Electromigartion

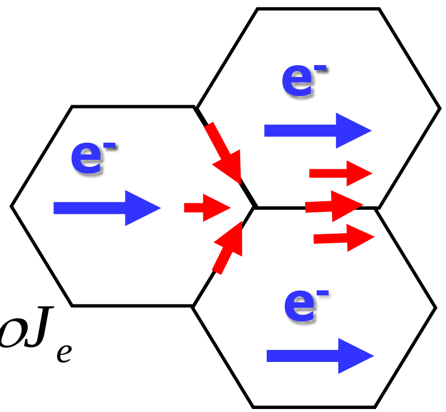
$$J = -D\frac{\partial C}{\partial x} + C\frac{D}{kT}F_{em}$$

EM driving force:

$$F_{em} = Z^{*}e\varepsilon = (Z_{el}^{*} + Z_{wd}^{*})e\rho J_{e}$$

Electrostatic force Electron wind force

Under current stressing

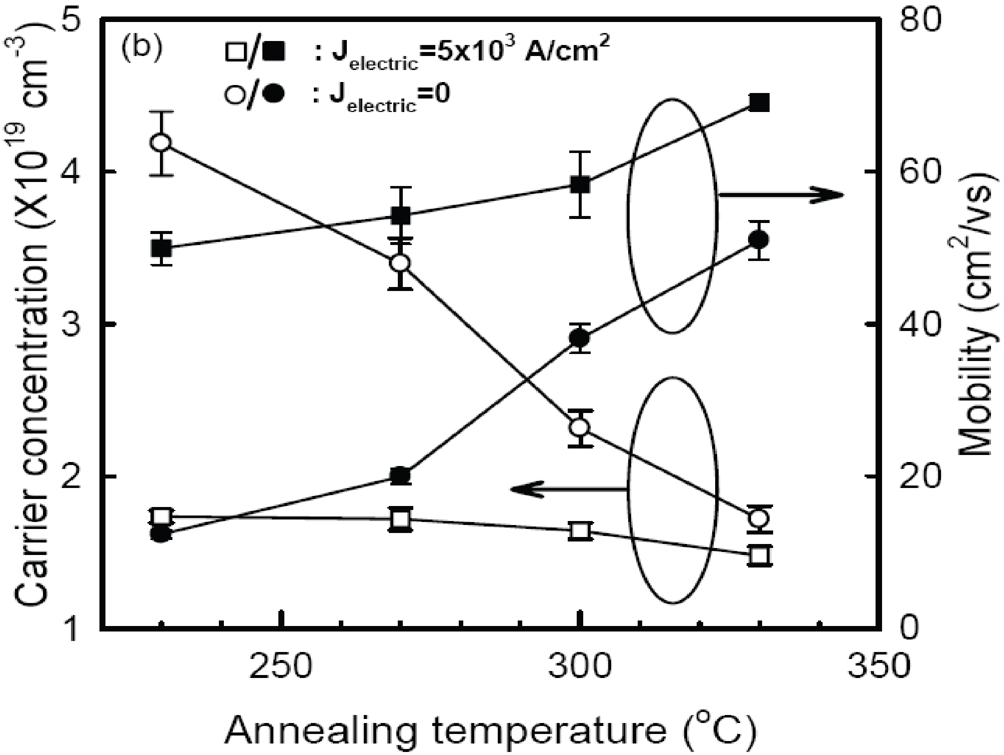


Sb atoms have a very high effective charge for EM (~140)

H. M. Gilder and D. Lazarus, Phys. Rev. 145, 507 (1966)

- **EM-induced Sb precipitation preferentially nucleate at G.B. at high T**

Sb precipitation on electrical properties of the Bi-Sb-Te films

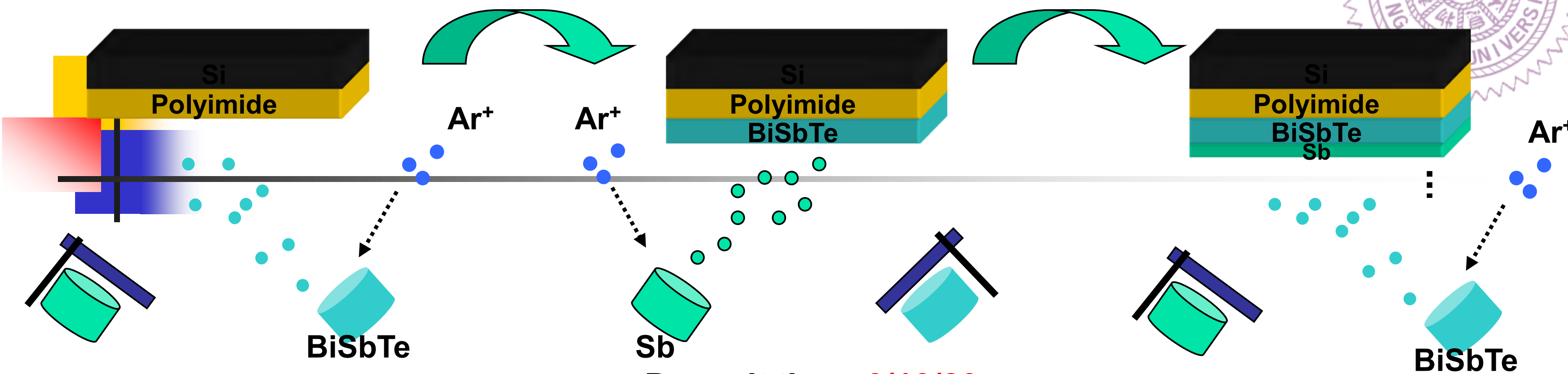


- **EM-induced Sb precipitation preferentially nucleate at G.B.**

Lower anti-site defects (Sb_{Te}) → Carrier concentration decrease

Lattice defects elimination → Carrier mobility increase

Film thickness: 415~465 nm

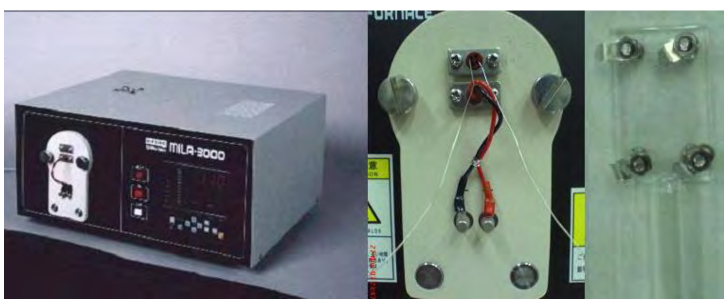


Deposit time: 6 minutes

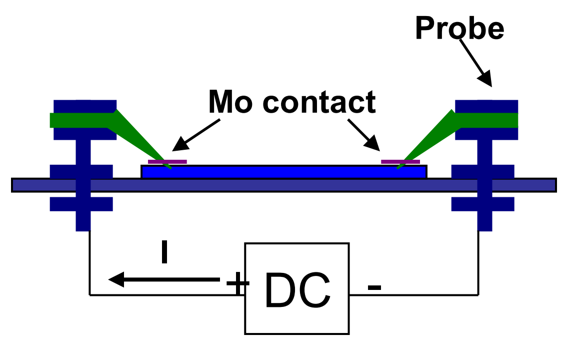
Deposit time: 0/10/20 s
Ultra-thin Sb layer

Layer #: BiSbTe*10 , Sb*9

Current-assisted thermal annealing



ULVAC MILA-3000



Annealing temp. & time: 230~330℃ 5 minutes

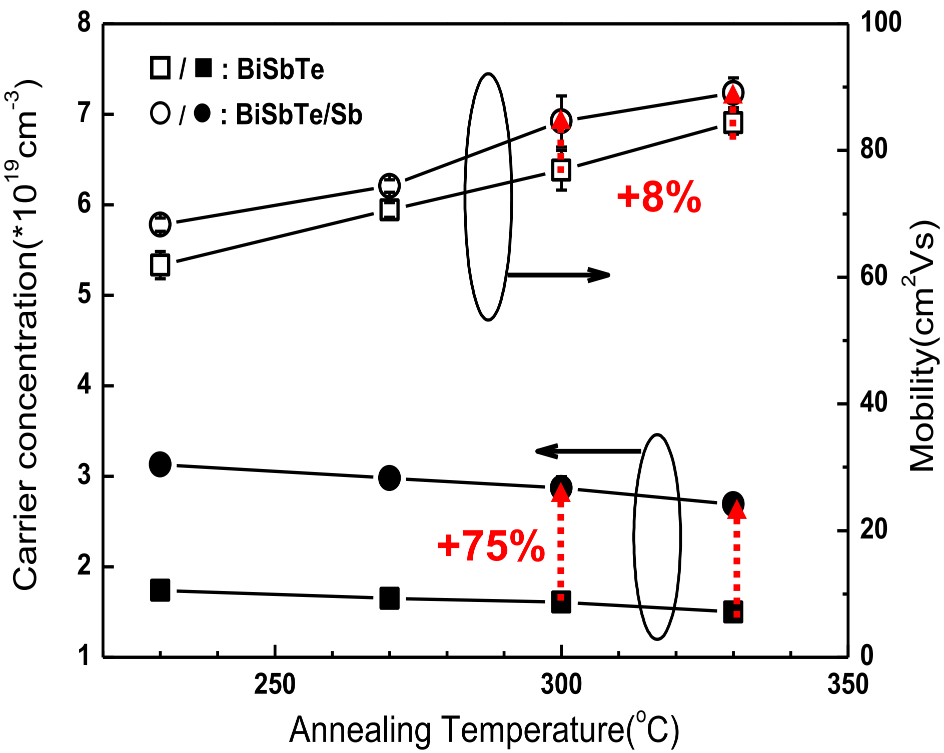
MATSUSADA AU-2P150

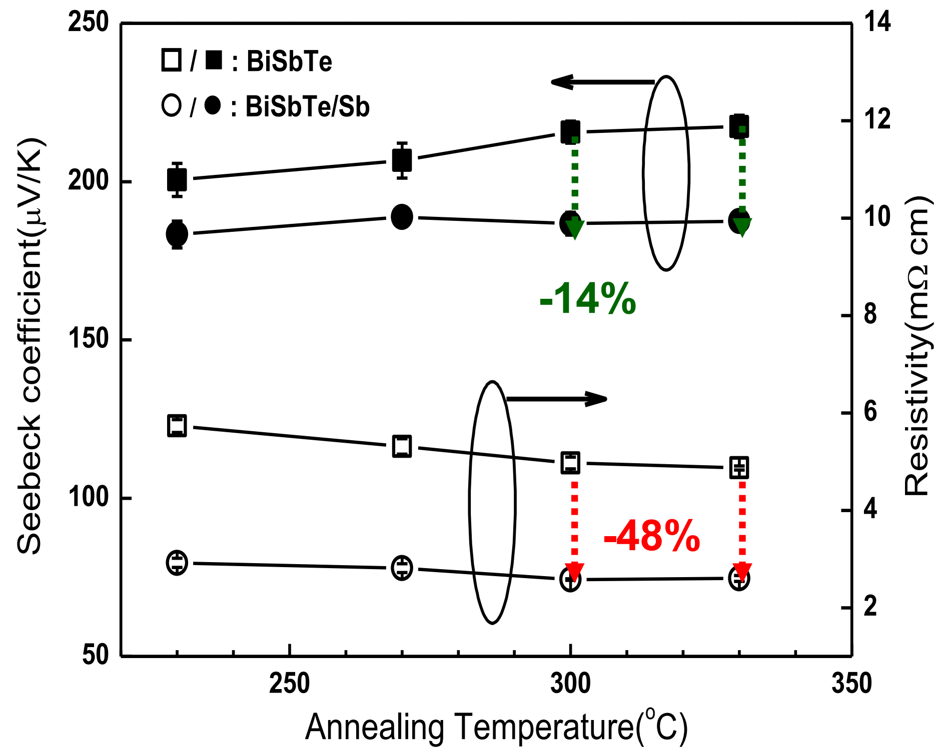
Applied current density: ~$5*10^3$ A/cm^2

Analysis
SEM / EDS
EPMA / TEM

Measurement
Seebeck / Hall

Electrical transport properties of Bi-Sb-Te/Sb films





Overall composition

- **Bi:Sb:Te = 10.1 : 28.8 : 61.1 for BiSbTe film**
- **Bi:Sb:Te = 9.6 : 33.2 : 57.2 for BiSbTe/Sb10s film**

Bi-Sb-Te/Sb film electrically stressed at 330 °C for 5 min

	BiSbTe	BiSbTe/Sb10s	BiSbTe/Sb20s
S (μV/K)	217 ± 4	188 ± 2	175 ± 2
ρ(mΩcm)	4.9 ± 0.1	2.6 ± 0.1	2.5 ± 0.1
μ(cm^2Vs)	84 ± 2	89 ± 2	75 ± 2
p ($*10^{19}cm^{-3}$)	1.5 ± 0.1	2.7 ± 0.1	3.4 ± 0.1
S^2/ρ(mW/K^2m)	0.96 ± 0.05	1.36 ± 0.08	1.23 ± 0.08

Microstructure & electrical transport properties of BiSbTe/Sb20s film:

- More Sb precipitates in the film
- Carrier concentration ↑ , but mobility ↓
- Worse thermoelectric properties than BiSbTe/Sb10s film

Fundamental knowledge/training

- Fundamental knowledge:
  - Solid-state physics: Energy bands in crystals, Electrons in crystals, Semiconductor physics, Classical electron theory, Boltzmann transport theory, Phonons, Electrical/thermal transport properties,…
- Equipment training:
  - Power supply/multimeter operation, 4-point probe electrical measurement, Van der Pauw measurement, Hall effect measurement, Seebeck coefficient measurement, 3ω thermal conductivity measurement, Laser flash thermal conductivity measurement, Hall effect measurement, Sputter, …
- Lab skills:
  - SEM, XRD, Origin, LabView, Image processing, …
  - **Design what you need!!!**

Potential research topics

- Effect of Sb-rich precipitates on transport properties
- Electrical contact resistivity of Metal/Bi-Te
- Thermal contact resistance of Metal/Bi-Te and Dielectric/Bi-Te
- Long-range electromigration in Bi-Te based compound
- Grain size effect on transport properties