UiO : Centre for Materials Science and Nanotechnology
University of Oslo

Top-down to know thermoelectrics

Part 4

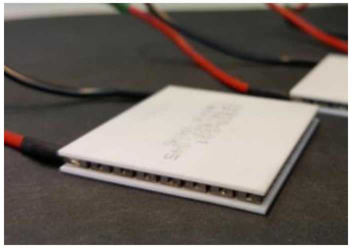
Thermoelectric materials

Top-down to know thermoelectrics (TE)

-- From TE applications to Materials

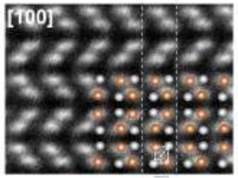
TE industrial applications

TE modules



TE Pairs

TE Materials



Availability and Installation

☐ Zinc Antimonides

Fabrication

☐ Conducting Oxide

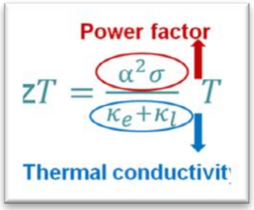
Legs matching

☐ Oxide

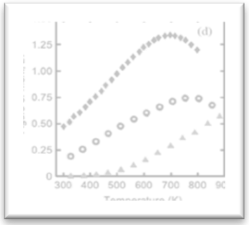
Material properties

☐ Silicide

Outline



- What does matter to TE performance

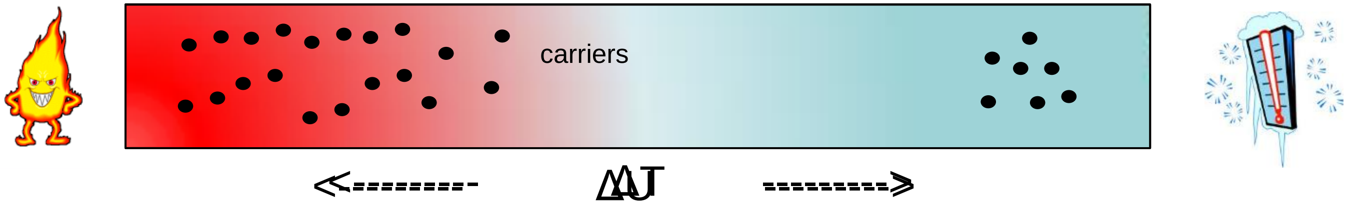


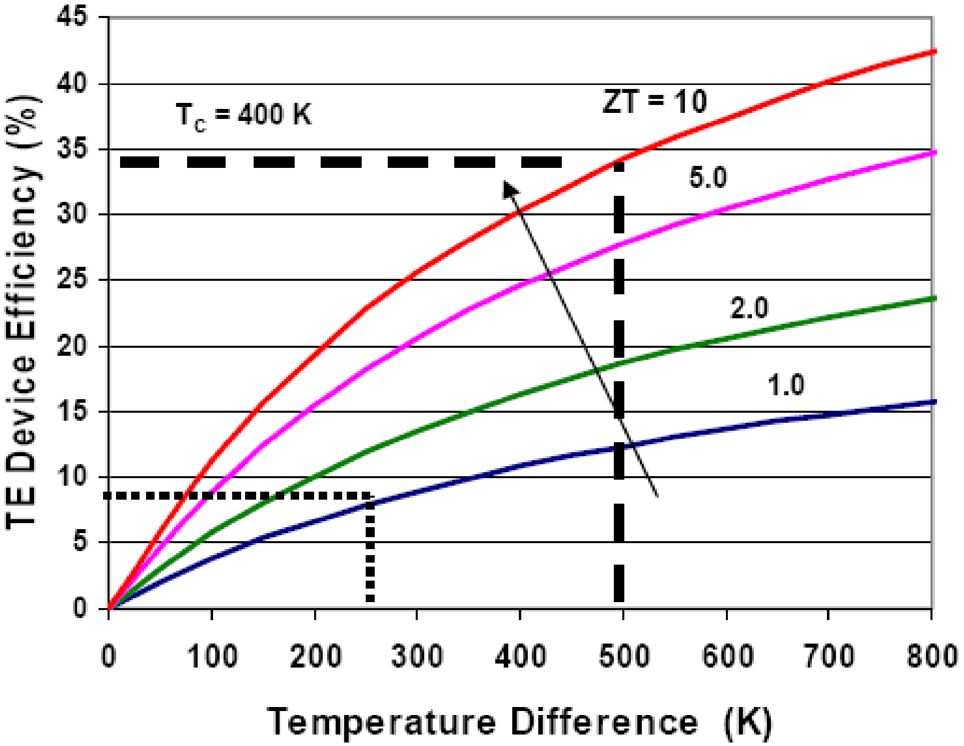
- Material: TE silicide

Raw material
Fab. Process
Bonding
Stability

- Innovation: Lab to Fab

What does matter to TE performance





Power factor

$$zT = \frac{\alpha^2\sigma}{\kappa_e+\kappa_l}T$$

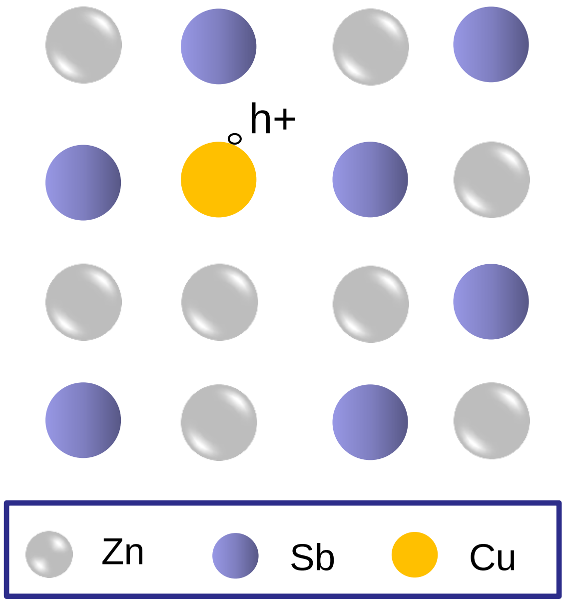
Thermal conductivity

What does matter to TE performance

Improve power factor (PF)

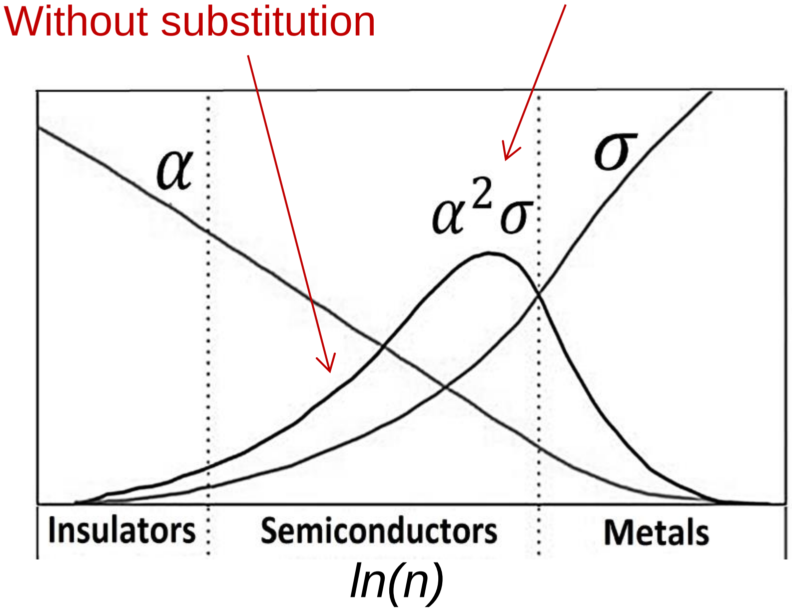
$$zT = \frac{\boxed{\alpha^2\sigma}}{\kappa_e+\kappa_l}\uparrow T$$

Atomic substitution



With proper substitution

Without substitution



- High Seebeck effect
- High electron transport
- Low thermal transport

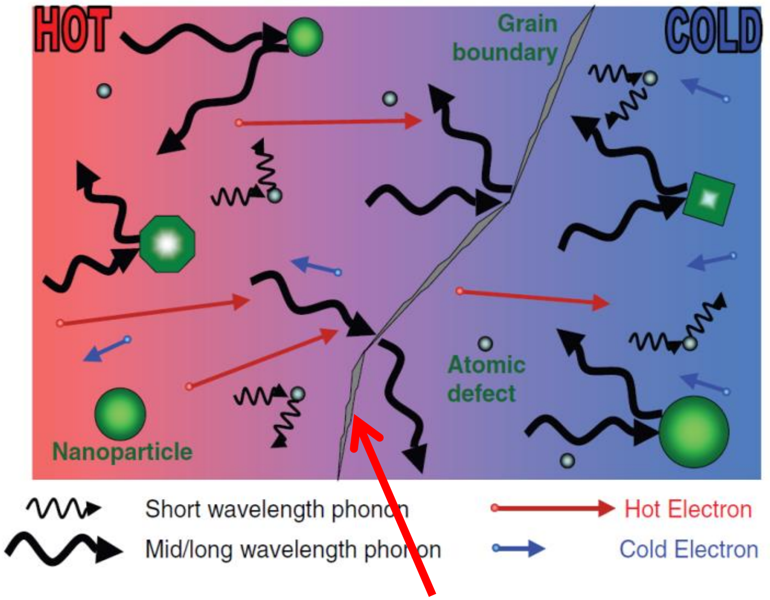
↑PF

What does matter to TE performance

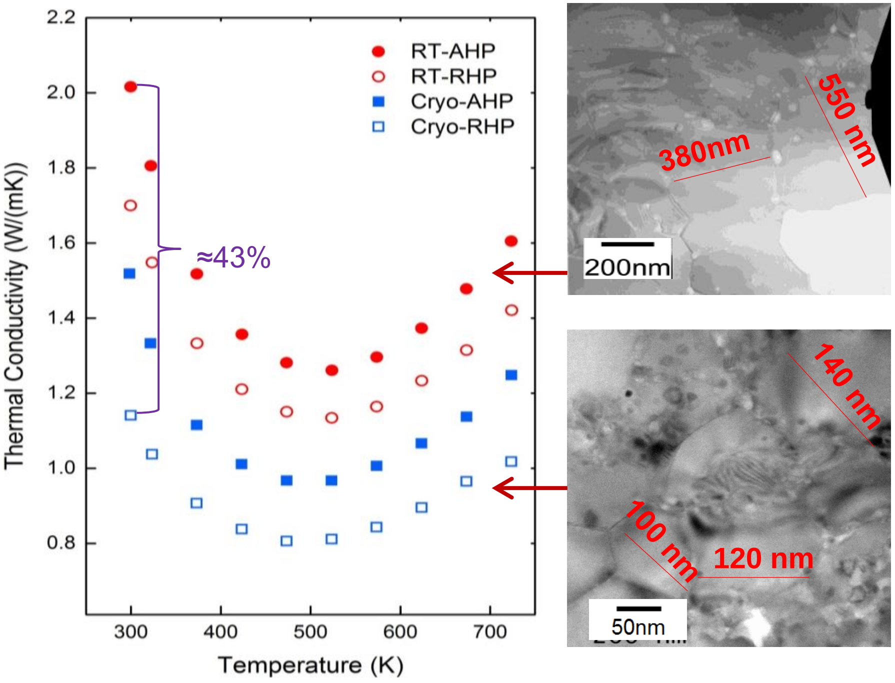
Reduce thermal conductivity

$$zT = \frac{\alpha^2\sigma}{\boxed{\kappa_e+\kappa_l}\downarrow}T$$

Phonon Engineering



Thermal boundary resistance when MFP_{phonon} > spacing of interface

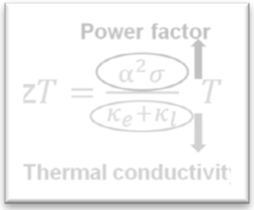


- High Seebeck effect
- High electron transport

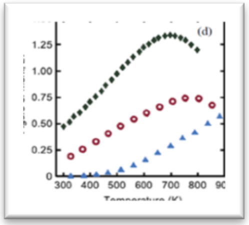
$\}\uparrow$PF

- Low thermal transport

Outline



- What does matter to TE performance



- Material: TE silicide

Raw material
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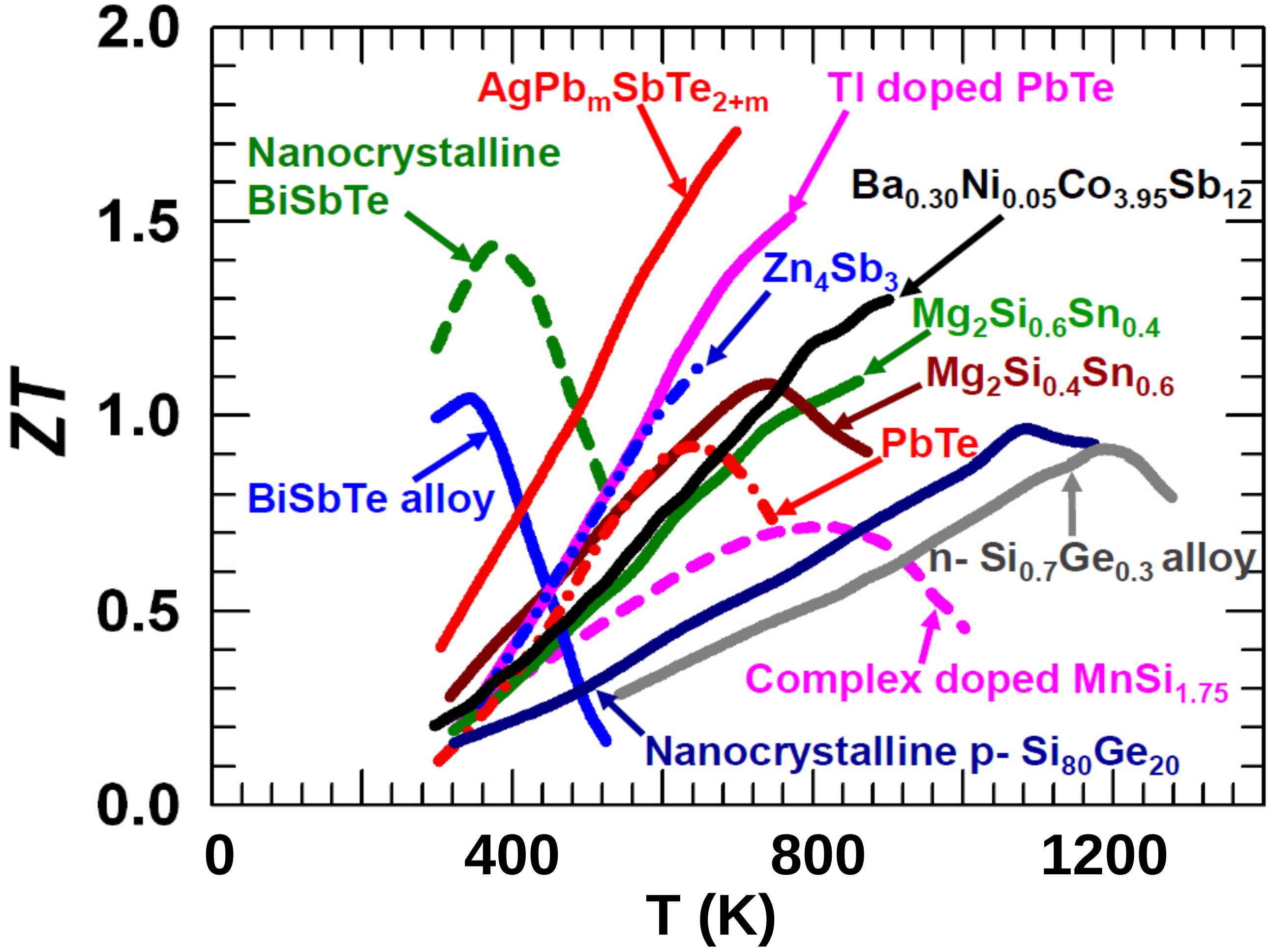
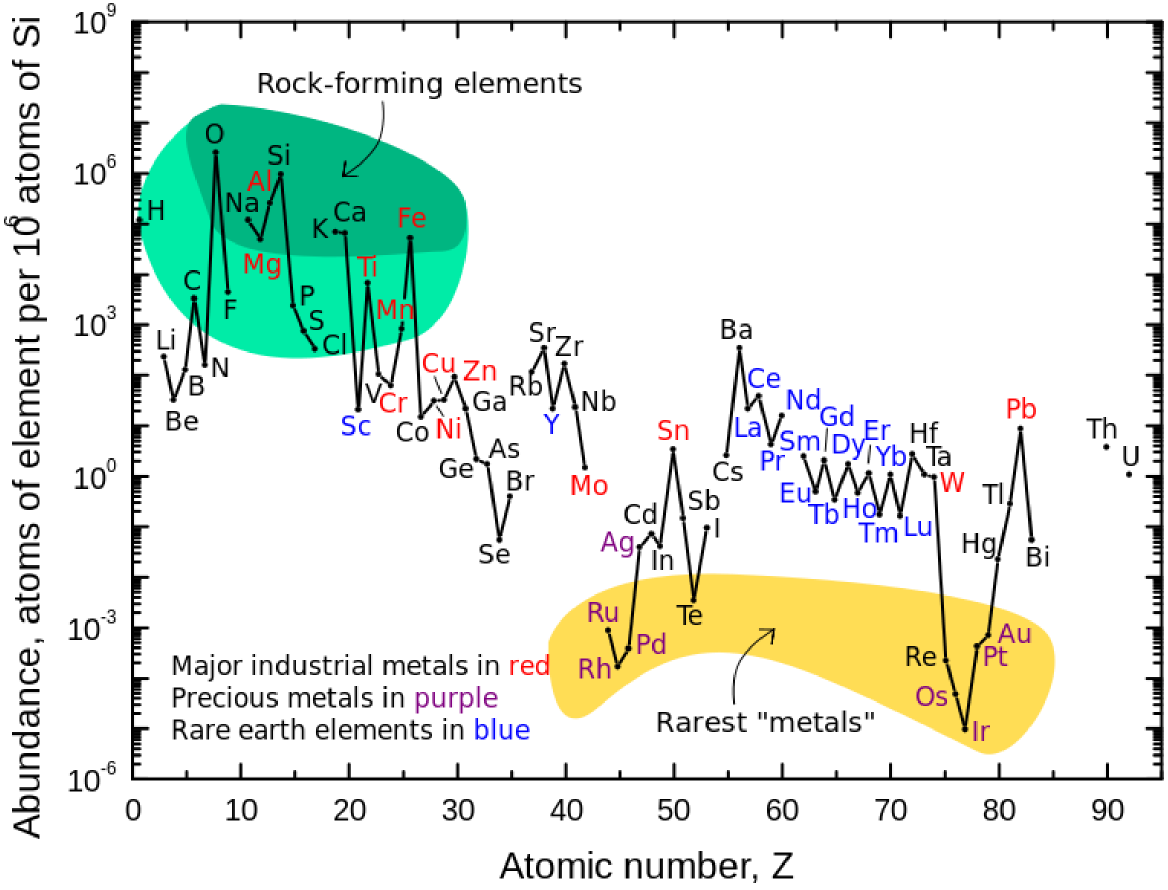
zT of bulk thermoelectric materials



Szczech et al. (2011) J. Mater. Chem., 21, 4037–4055

Introduction to TE silicide



https://en.wikipedia.org/wiki/File:Elemental_abundances.svg

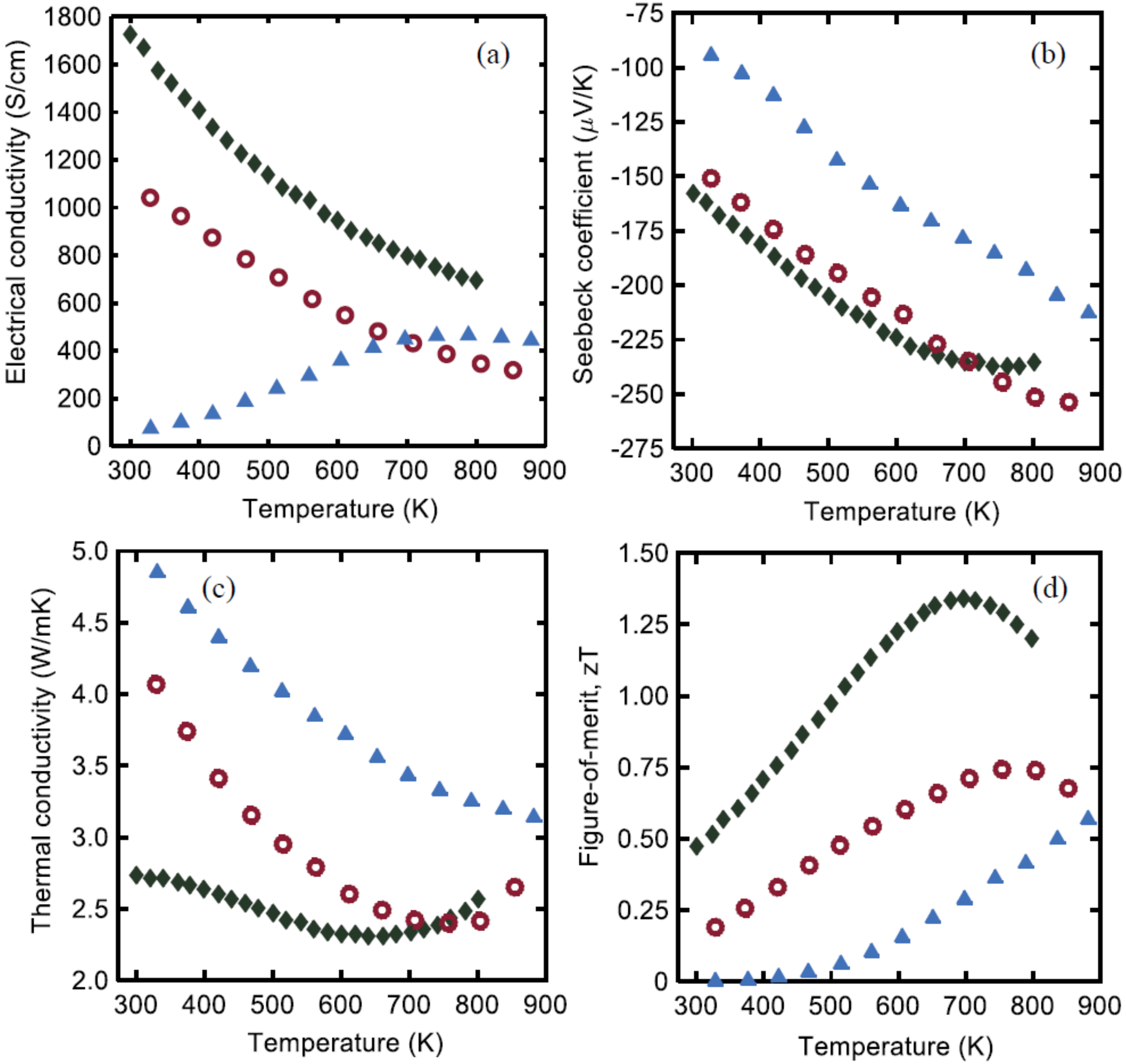
Traditional silicide thermoelectrics:

SiGe
Reported zT 1.3 at 1173K for n type

Other abundant silicide:

Mg - Si
Mn - Si

Mg_2Si



▲ Mg_2Si

Satyala et al., (2014)
Acta Mater. 74, 141

○ $Mg_2Si_{0.95}Ge_{0.05}$

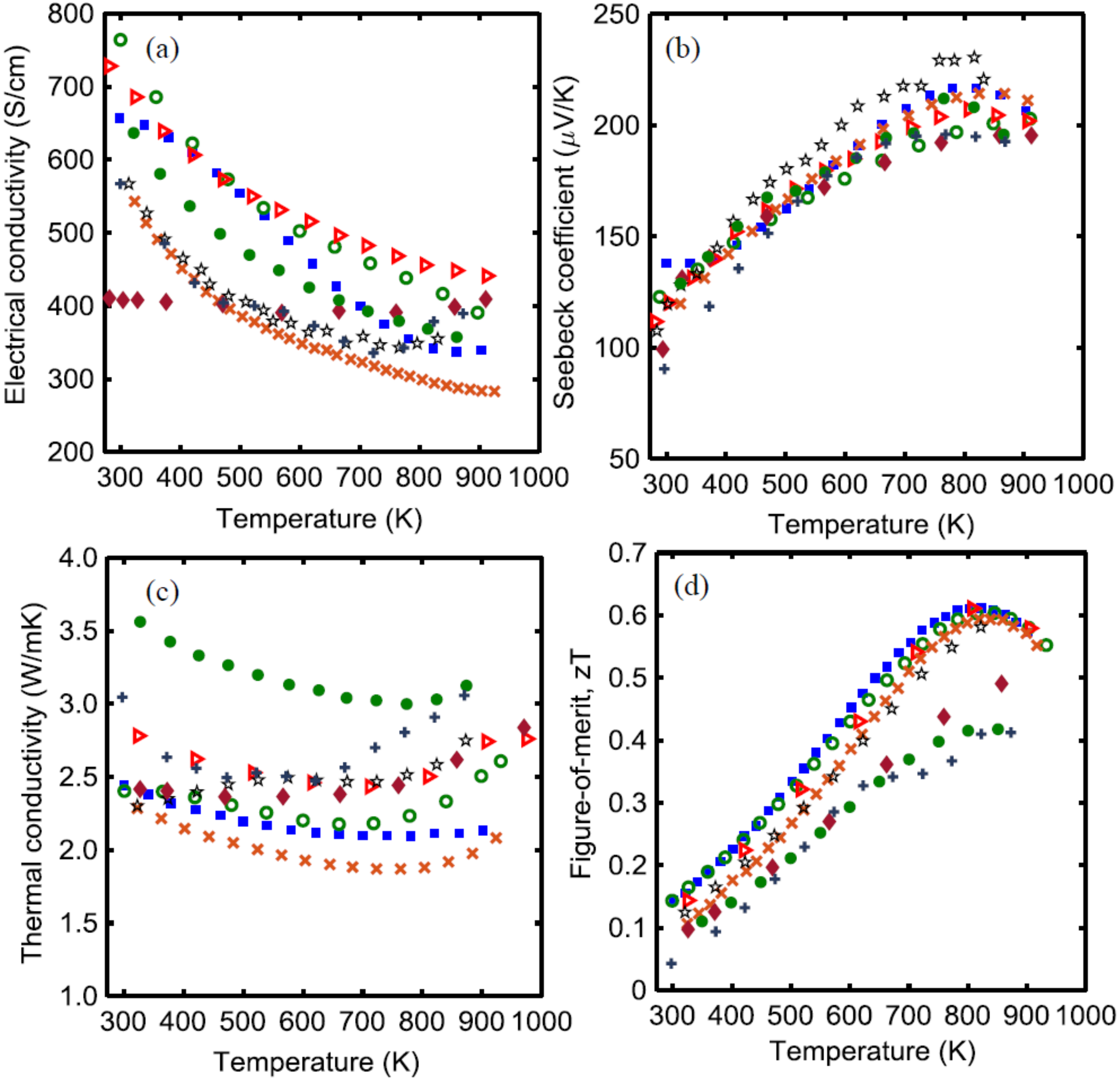
Arai et al., (2015)
Mater. Sci. Eng. B 195, 45

◆ $Mg_2Si_{0.3}Sn_{0.7}$

Liu et al., (2012)
Phys. Rev. Lett. 108, 166601

!! But lack of matching p type

MnSi$_x$ (HMS alloy, x = 1.71 – 1.75)



■ nano-phase MnSi
Luo et al. (2011)
Intermetallics 19, 404

○ Ge
She et al., (2915)
J. Mater. Chem. C 3, 12116

▷ Cr
Ponnambalam et al., (2013)
J. Alloys Compd. 580, 598

× Ge
Zhou et al. (2010)
J. Electron. Mater. 39, 2002

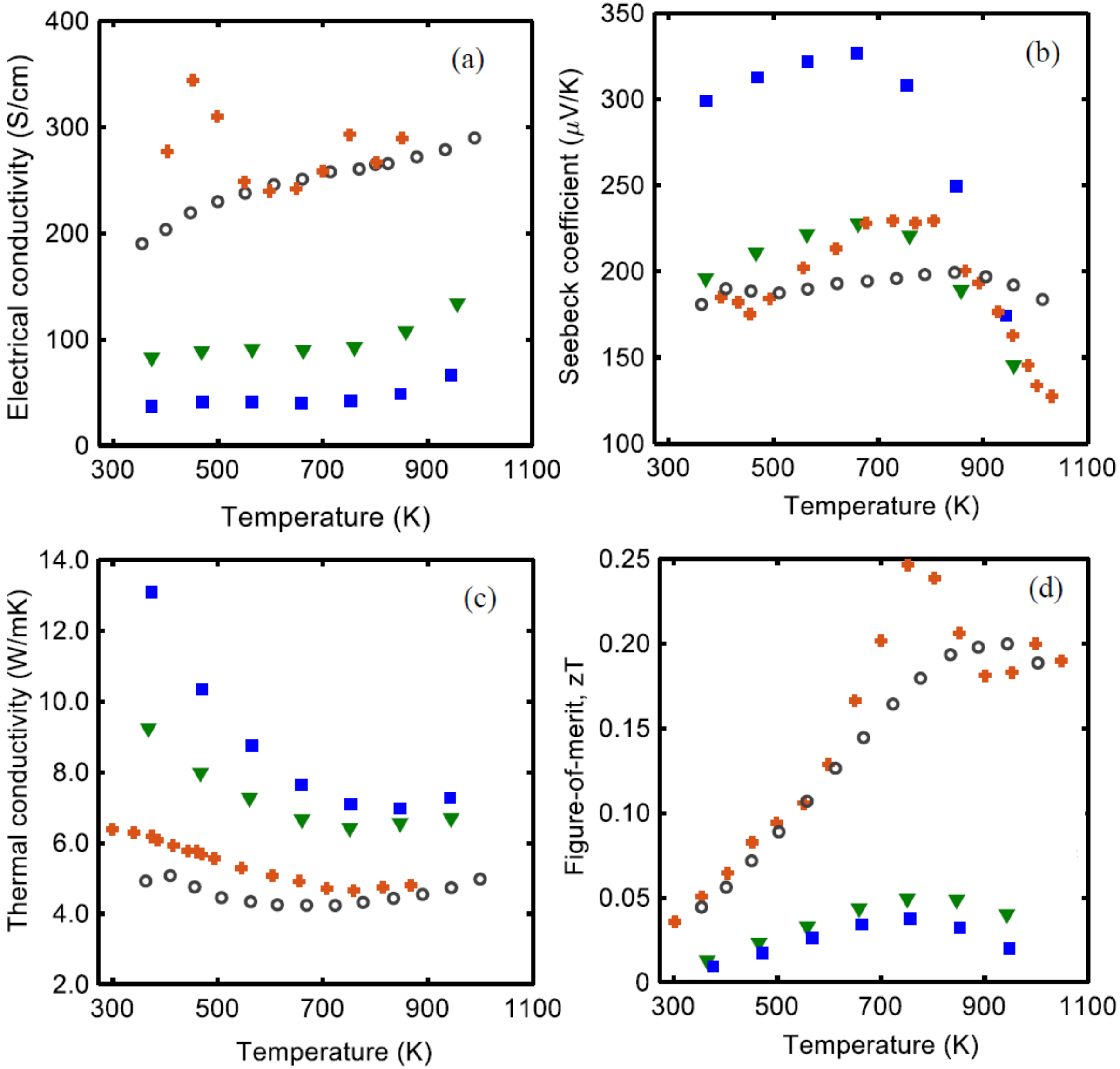
☆ Al+Ge
Chen et al. (2013)
J. Appl. Phys. 114, 173705

◆ Cr+Ru
Ponnambalam et al., (2013)
J. Alloys Compd. 580, 598

● Mo
Nhi Truong et al., (2015)
J. Electron. Mater. 44, 3603

+ Yb
Saleemi et al., (2015)
J. Alloys Compd. 619, 31

$FeSi_2$



✚ $Fe_{0.92}Ru_{0.05}Cr_{0.03}Si_2$

▼ $Fe_{0.95}Cr_{0.045}Si_{1.958}Ge_{0.042}$

Kim et al. (2003),
Intermetallics 11, 399

○ $Fe_{0.93}Co_{0.07}Si_{1.99}Al_{0.01}$
Groβ et al., (1995)
J. Mater. Res. 10, 34

■ $Fe_{0.95}Cr_{0.05}Si_2$

Takizawa et al. (1995)
J. Mater. Sci. 30, 4199

However, nanocomposite of

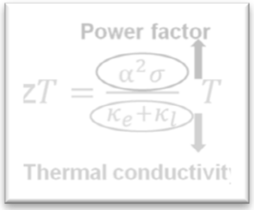
$(FeSi_2)_{0.75}(SiGe)_{0.25}$

zT = 0.55 at 950K

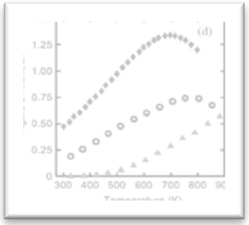
(Mohebali et al. (2015),

Renewable Energy 74, 940)

Outline



- What does matter to TE performance

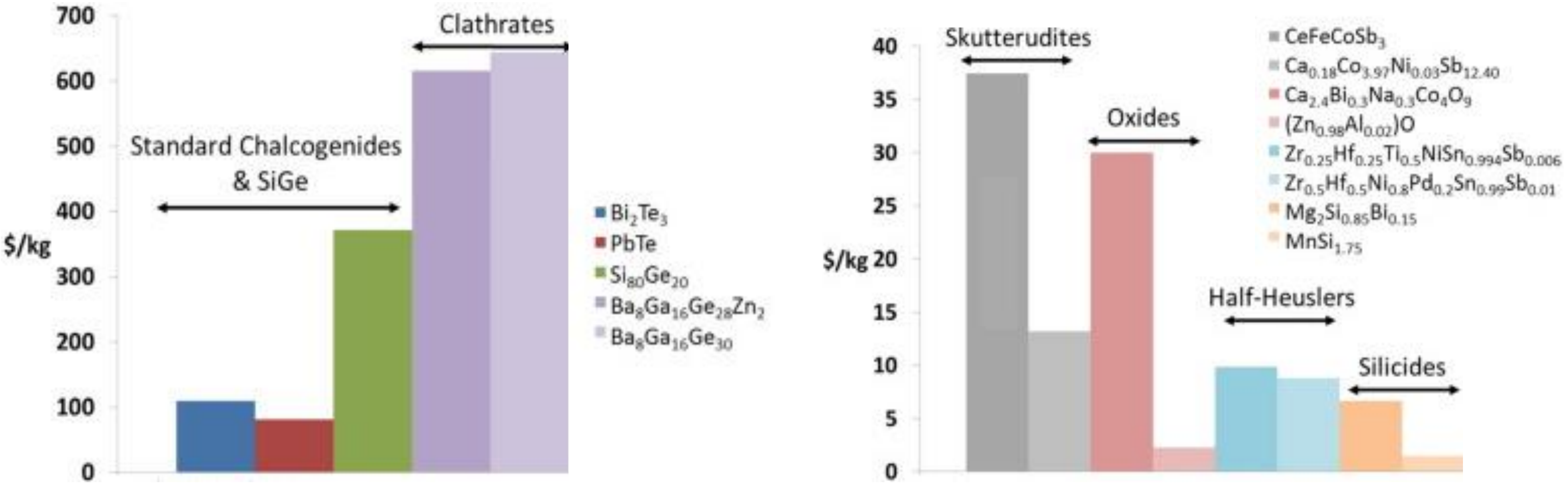


- Material: TE silicide

Raw material
Fab.Process
Bonding
Stability

- Innovation: Lab to Fab

Raw material Fab. process Bonding Stability



Saniya LeBlanc (2014)
Sustainable Materials and Technologies, Volumes 1–2, 2014, 26–35

For each material system, more work on :

- optimizing electrical properties (low solid solubility)
- nanostructuring (grain growth at high temperature)

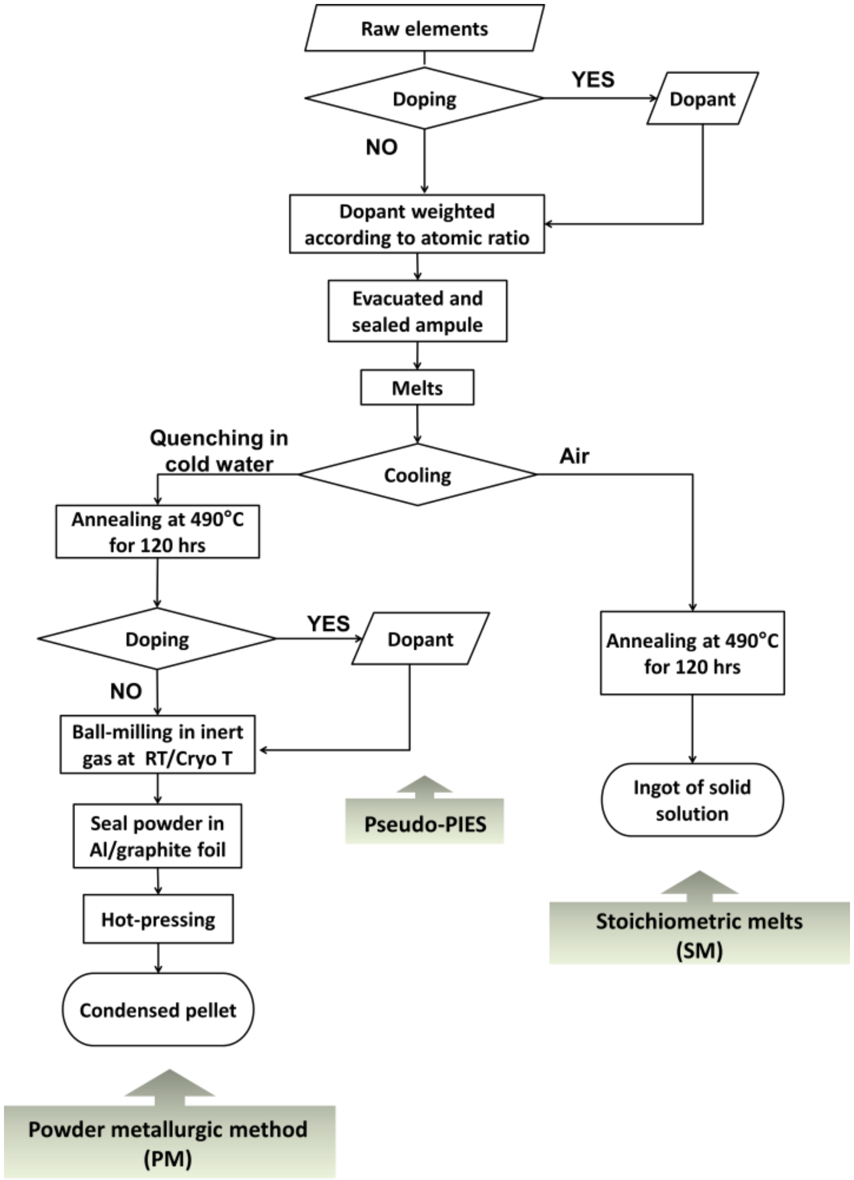
still need to be done.

Nanocomposite approach:

Fabricated by bulk process instead of atomic layer deposition, cheaper, quicker.

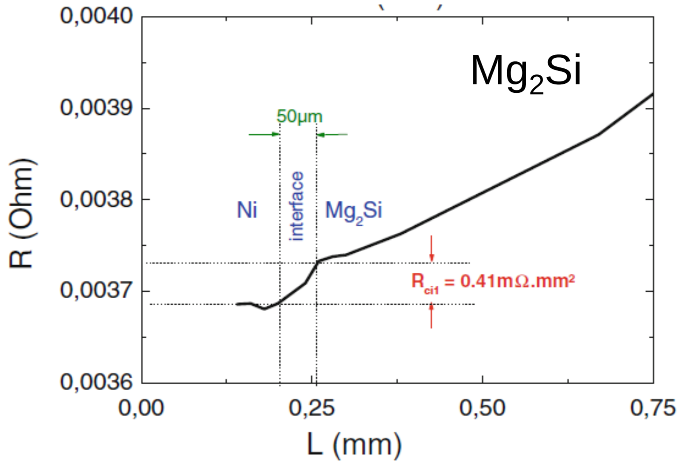
Challenges at each step

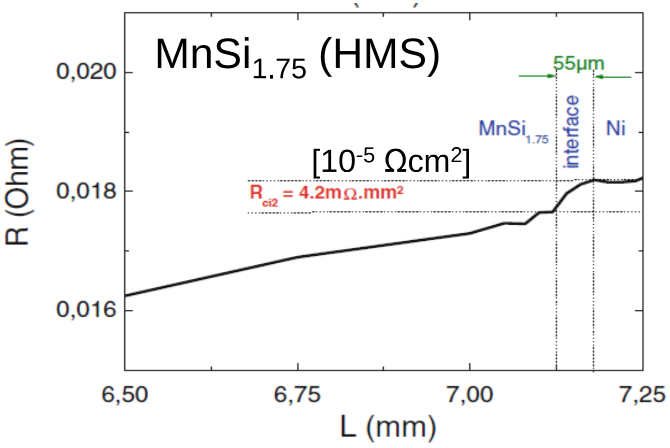
Step	problem	solution
Melt	Sublimation	Atmosphere furnace
Pulverization	Contamination	Milling condition
Consolidation	Phase transition	Accurate temperature and pressure control
All steps	oxidation	Getter / coating



1. Contact resistance:

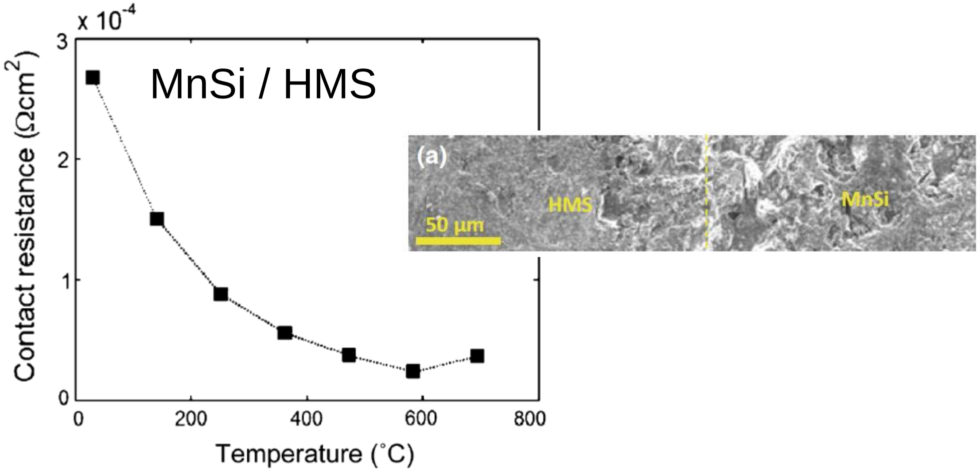
Metal electrodes

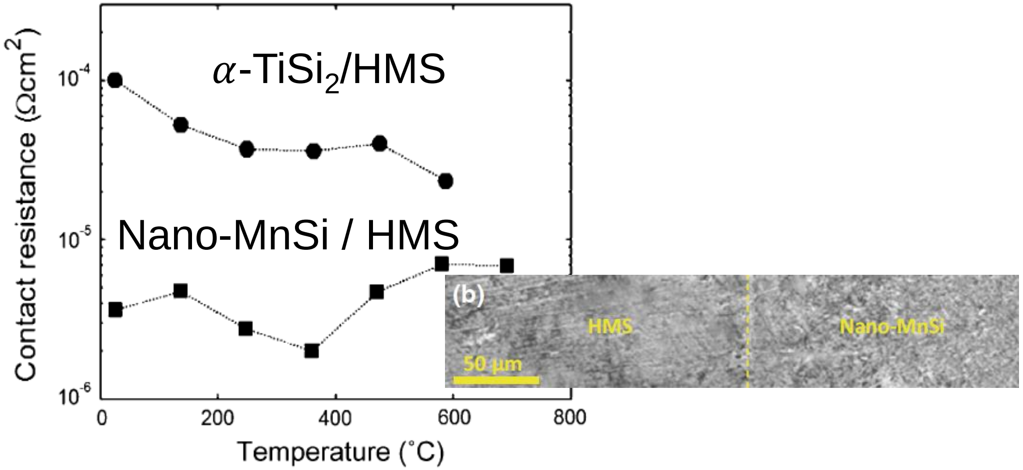




THIMONT et al. (2014) J. Elec.Mat, Vol. 43, No. 6

Composition electrodes





Shi et al. [2012) J. Elec.Mat, Vol. 41, No. 9

2. Thermal matching avoid cracks and mechanical failure

Coefficient of variation (CV)

Coefficient of thermal expansion (CTE)

SiGe

CV = 4.72% (1273K), CTE = 6.0 $\times 10^{-6}$/K (1273K)

TiSi2 and CoSi2 at lower temperature but not high temperature

Mo and W CTE (4 - 5) $\times 10^{-6}$/K

Mg_2Si

Ni contact

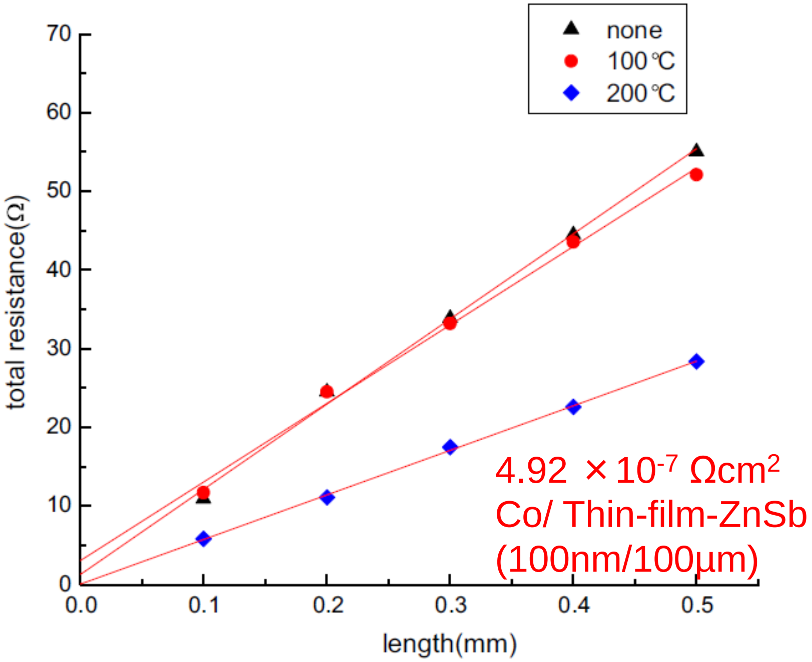
HMS

MnSi and α-$TiSi_2$/HMS

Contact **reliability** at operation temperture for a **long term** need to be studied.

3. Special interest for ZnSb

Thin film



4.92 ×10^{-7} Ωcm^2
Co/ Thin-film-ZnSb
(100nm/100µm)

Yin et al. (2017) J. Elec.Mat, Vol. 46, No. 5

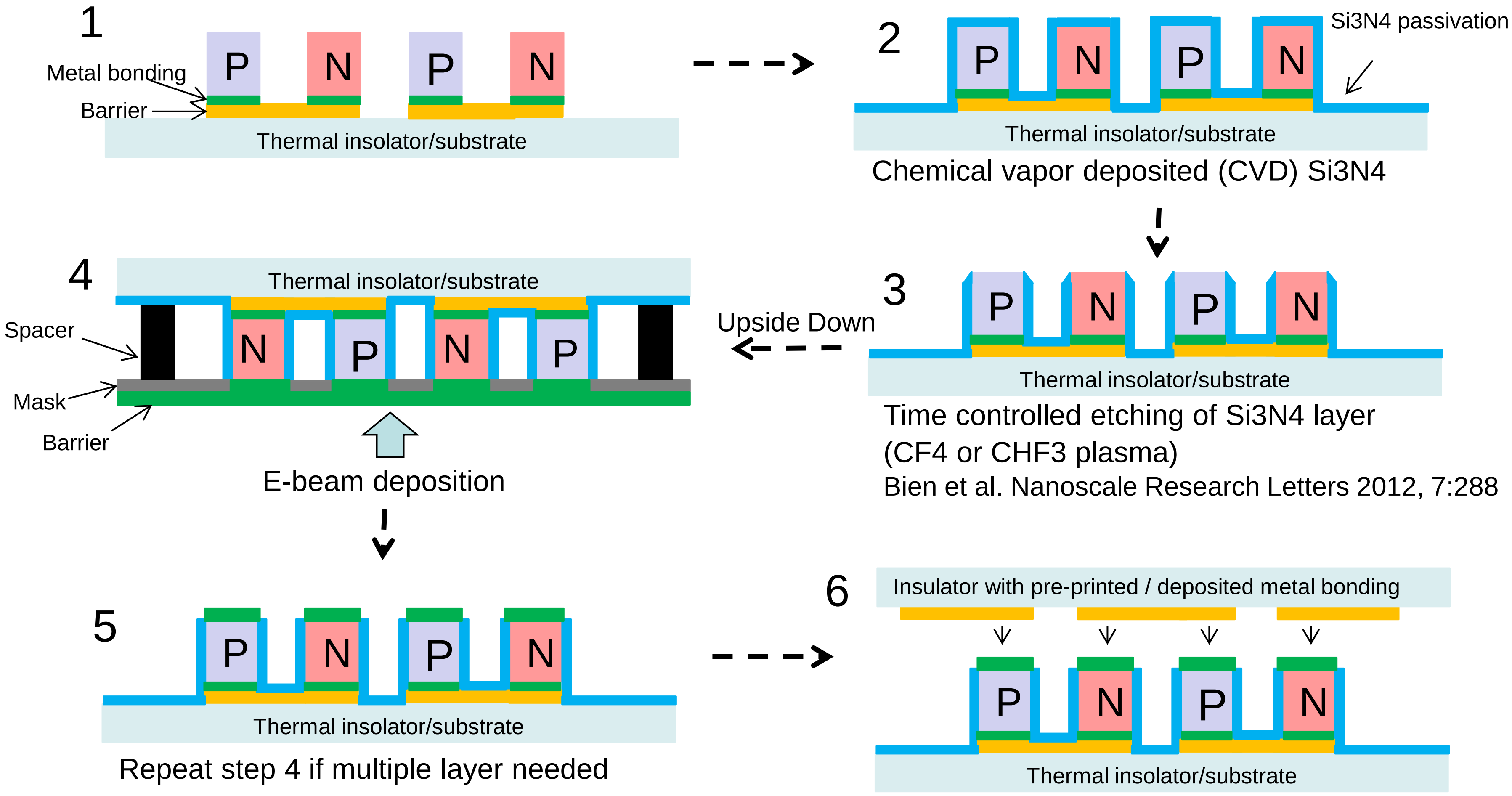
Bulk

CTE at room temperature
3.4 ~ 4.15 ×10^{-5}/K
Hermet et al. RSC Adv., 5, 87118 (2015)
Fischer et al. PHY. REV. B **91**, 224309 (2015)

Cu: 5.1 × 10^{-5}/K
Au: 4.2 × 10^{-5}/K

Perhaps any composition electrode?

Prevent sublimation and oxidation at high temperature;
Coating technique, widely used in CMOS industry.



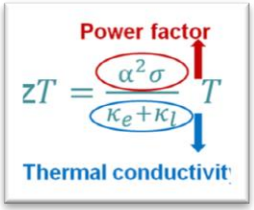
Chemical vapor deposited (CVD) Si3N4

Time controlled etching of Si3N4 layer
(CF4 or CHF3 plasma)
Bien et al. Nanoscale Research Letters 2012, 7:288

E-beam deposition

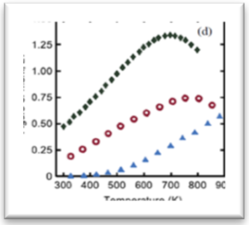
Repeat step 4 if multiple layer needed

Sum up



- What does matter to TE performance

Correlation between TE transport coefficient α, σ and κ



- Material: TE silicide

High TE performance of Mg_2Si and HMS

Raw material
Fab.Process
Bonding
Stability

- Innovation: Lab to Fab

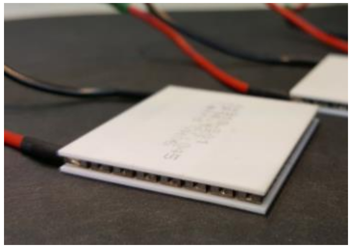
Bonding (contact) and coating

Top-down to know thermoelectrics (TE)

-- From TE applications to Materials

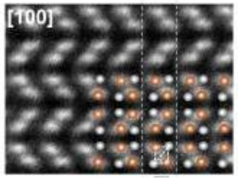
TE industrial applications

TE modules



TE Pairs

TE Materials



Availability and Installation

Fabrication

Legs matching

Material properties

- ☐ Zinc Antimonides
- ☐ Conducting Oxide
- ☐ Oxide
- ☐ Silicide