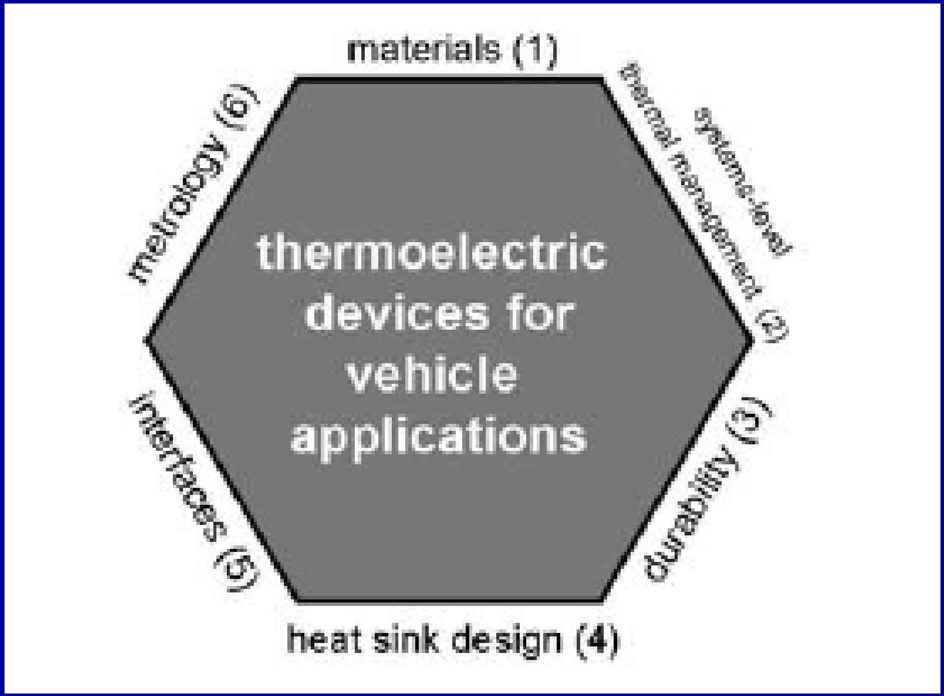
NSF/DOE Thermoelectrics Partnership: Thermoelectrics for Automotive Waste Heat Recovery

Xianfan Xu (ME), Timothy Fisher (ME), Stephen Heister (AAE), Timothy Sands (MSE), Yue Wu (ChemE)

Purdue University
In Partnership with General Motors Global R&D
and Oak Ridge National Laboratory

NSF/DOE Targeted Areas

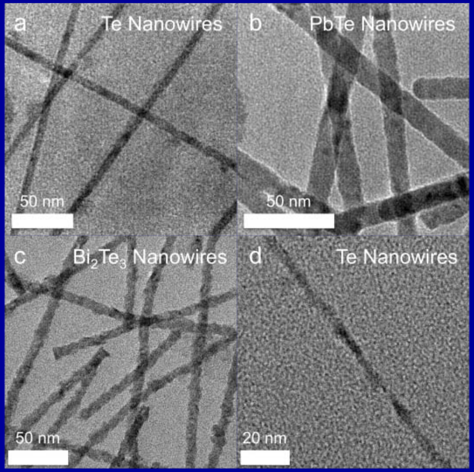


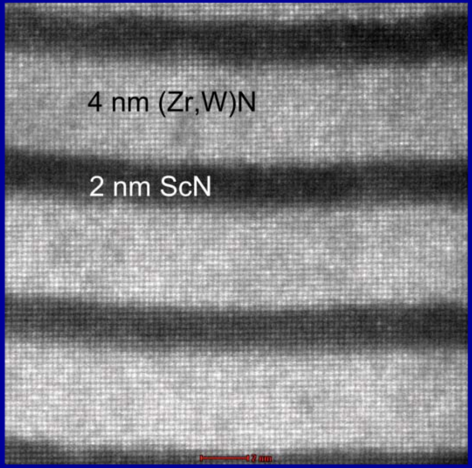
Focused areas of this proposal:

- TE Materials
- Heat sink - high temperature side heat exchanger
- Thermal interface materials
- Metrology

TE Materials

- Skutterudite (GM) ~ 500°C – advanced characterization on thermal conductivity reduction (Xu)
- Nanowires - room-mid temperature PbTe, Bi_2Te_3; and high temperature oxide nanowires (Wu)
- Metal-semiconductor superlattice (Sands)



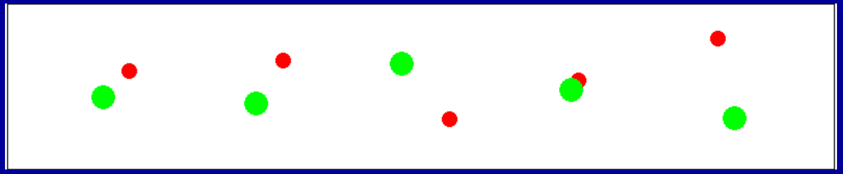


Advanced Characterization of TE Materials

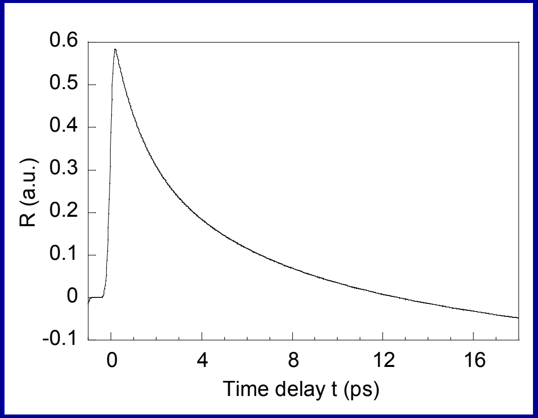
Xianfan Xu

- Commonly used approach to increase *ZT* of TE materials is to the reduce the lattice thermal conductivity
- We conduct femtosecond (10^{-15} s) time-resolved studies of phonon scattering in thermoelectric materials to understand the fundamentals of thermal conductivity reduction

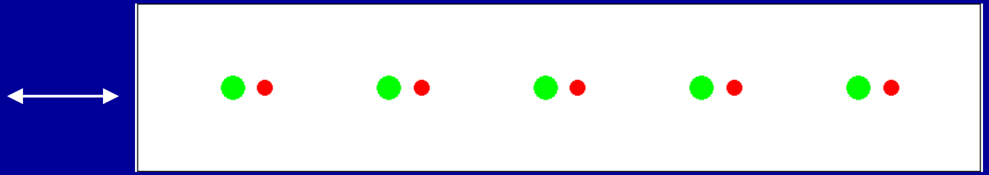
Phonon Detection – Coherent Phonon (coherent vibration of lattice)



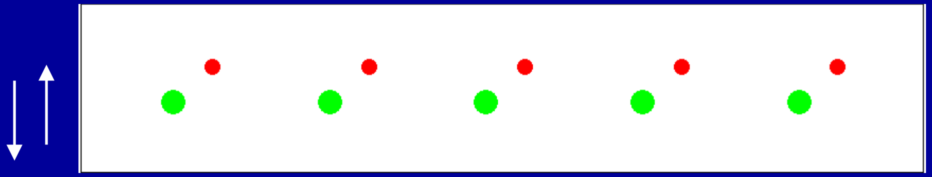
Random thermal vibration



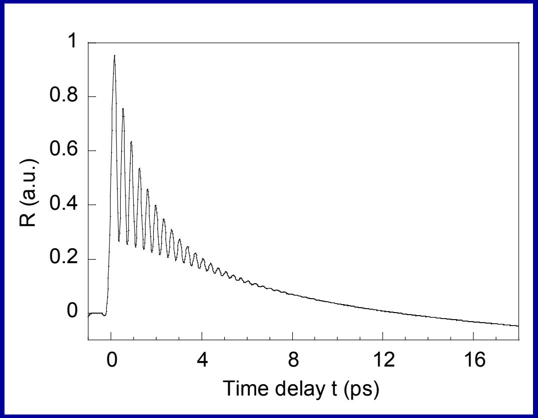
Optical signal when there is no coherent lattice oscillation



Coherent Phonon - LO

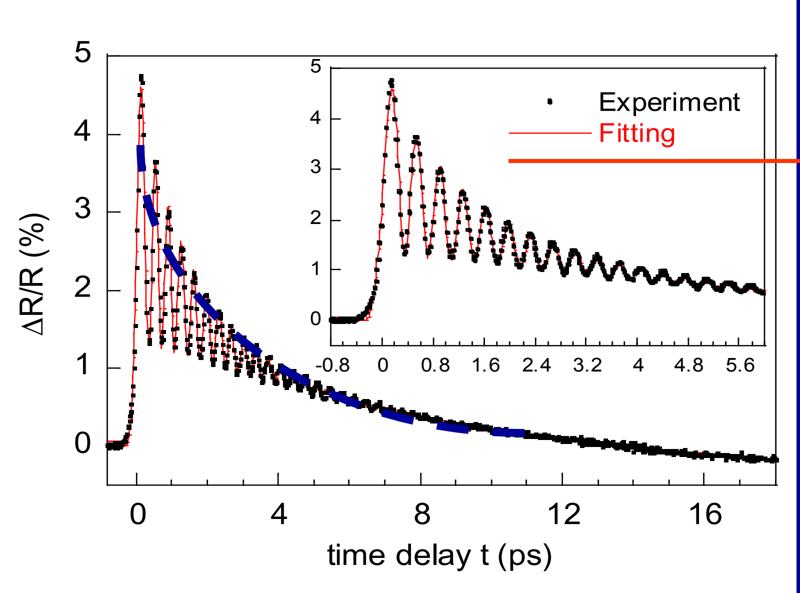


Coherent Phonon - TO



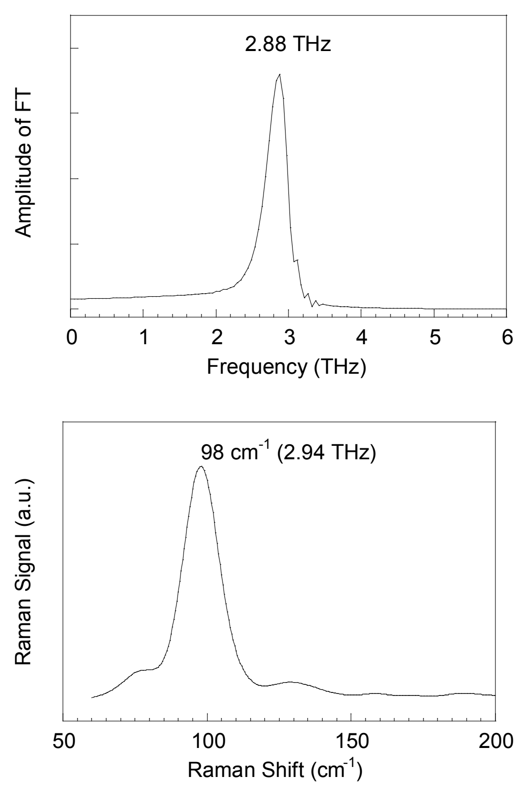
With coherent oscillation

Coherent Phonon Dynamics in Bi



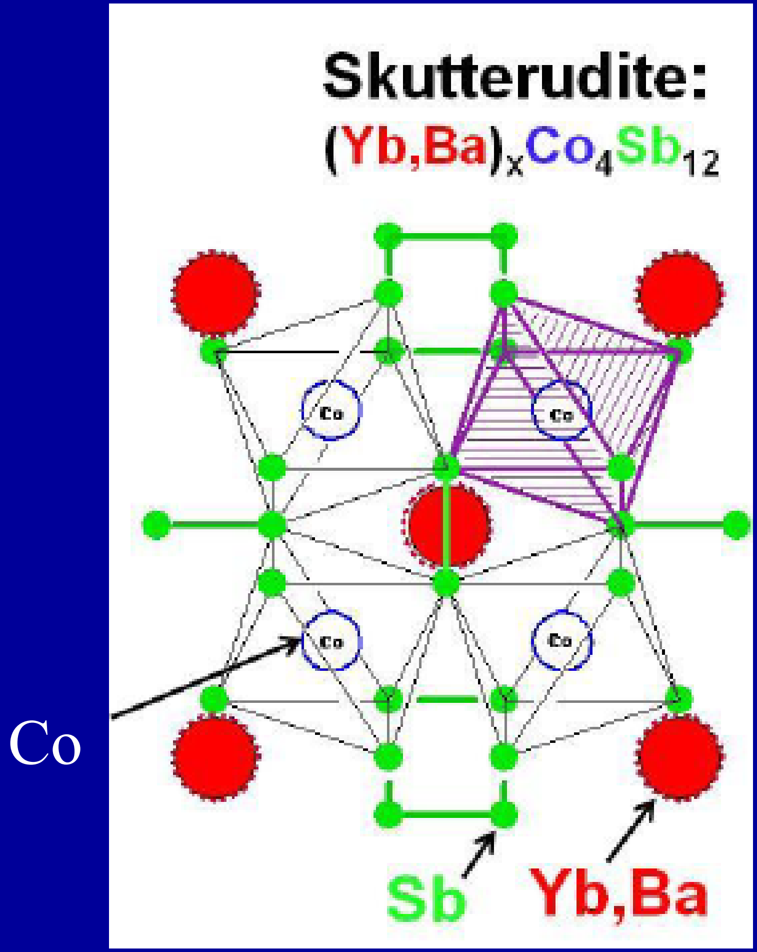
Fourier transform

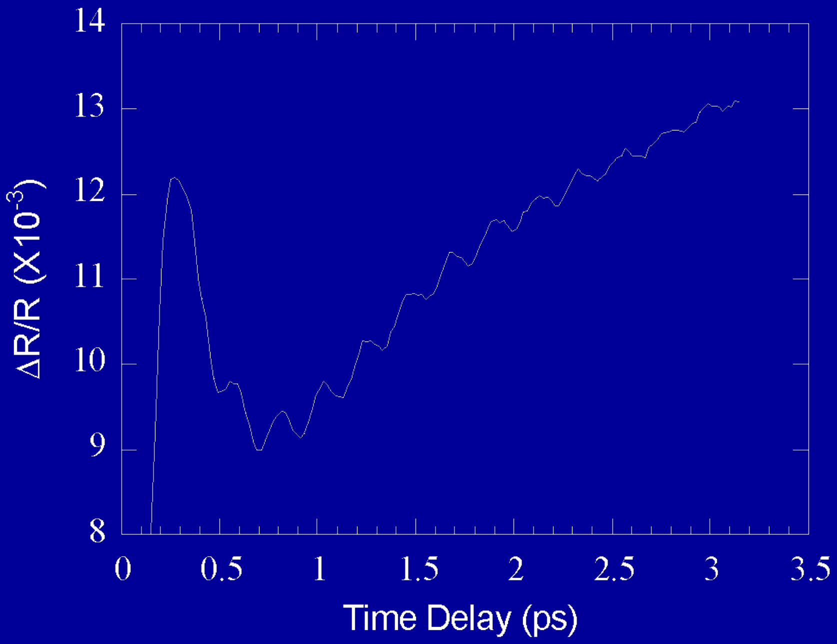
Raman



- Rise of the signal: Photon – electron/exciton (charge) coupling
- Decay of the envelope of the signal: electron/exciton (charge) – phonon coupling - heating
- Phonon oscillation and dephasing: Phonon interactions with charges, other phonon modes, impurities, physical boundaries, etc. – all important for energy transport and conversion processes

Filled Antimony Skutterudites





Oscillation due to filling of guest materials

Lattice Thermal Conductivity Calculation

$$\kappa_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau^{-1}(e^x - 1)}dx$$

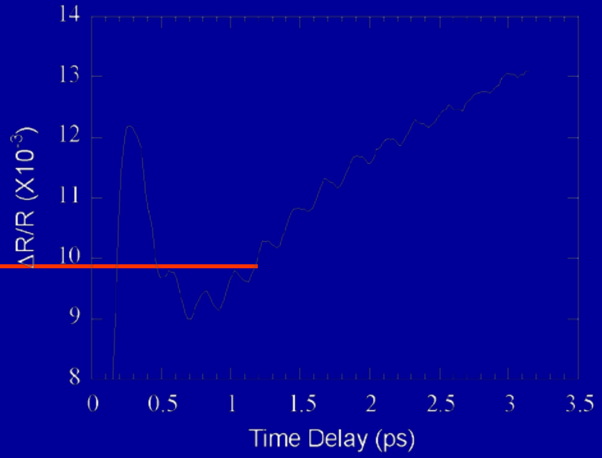
$$\tau^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T e^{-\theta_D/3T} + \boxed{\frac{C\omega^2}{(\omega_0^2 - \omega^2)^2}}$$

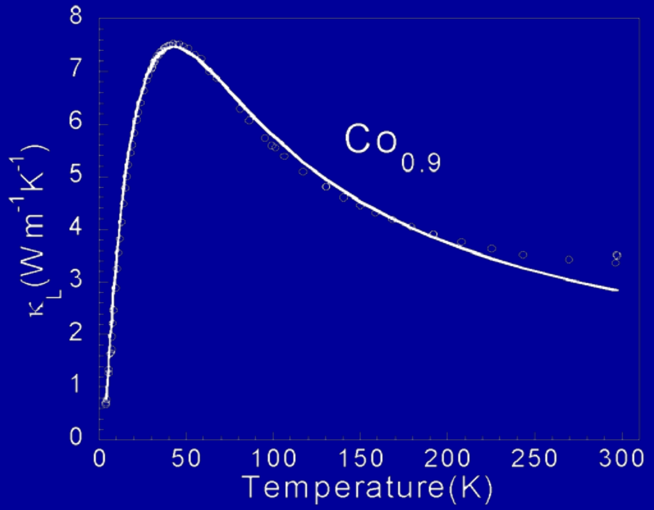
Boundary scattering

Defect scattering

Umklapp scattering

Resonant oscillation due to filling of heavy elements

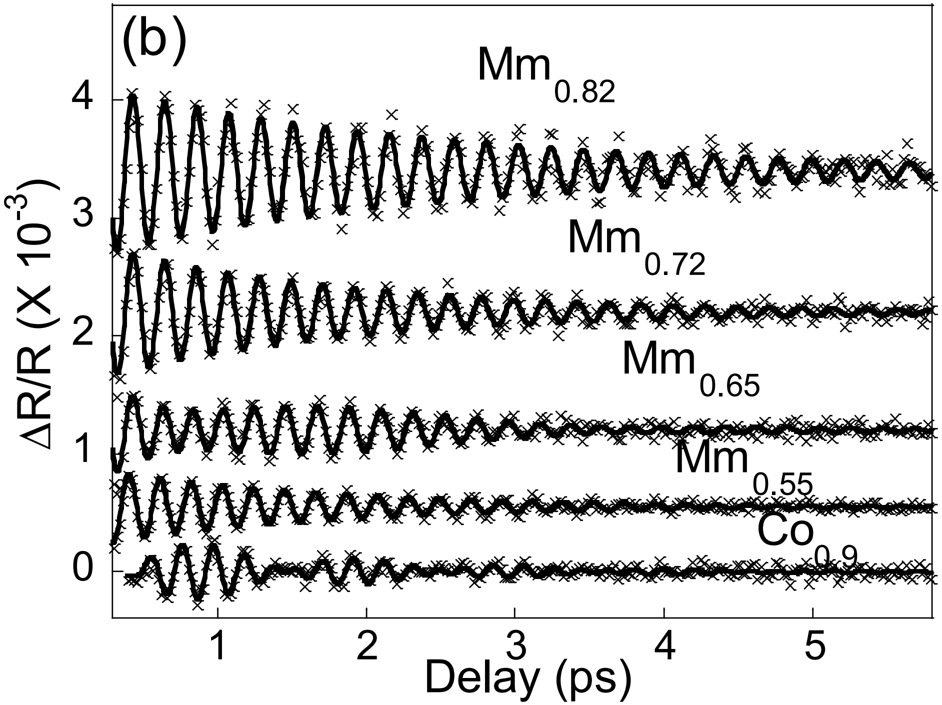


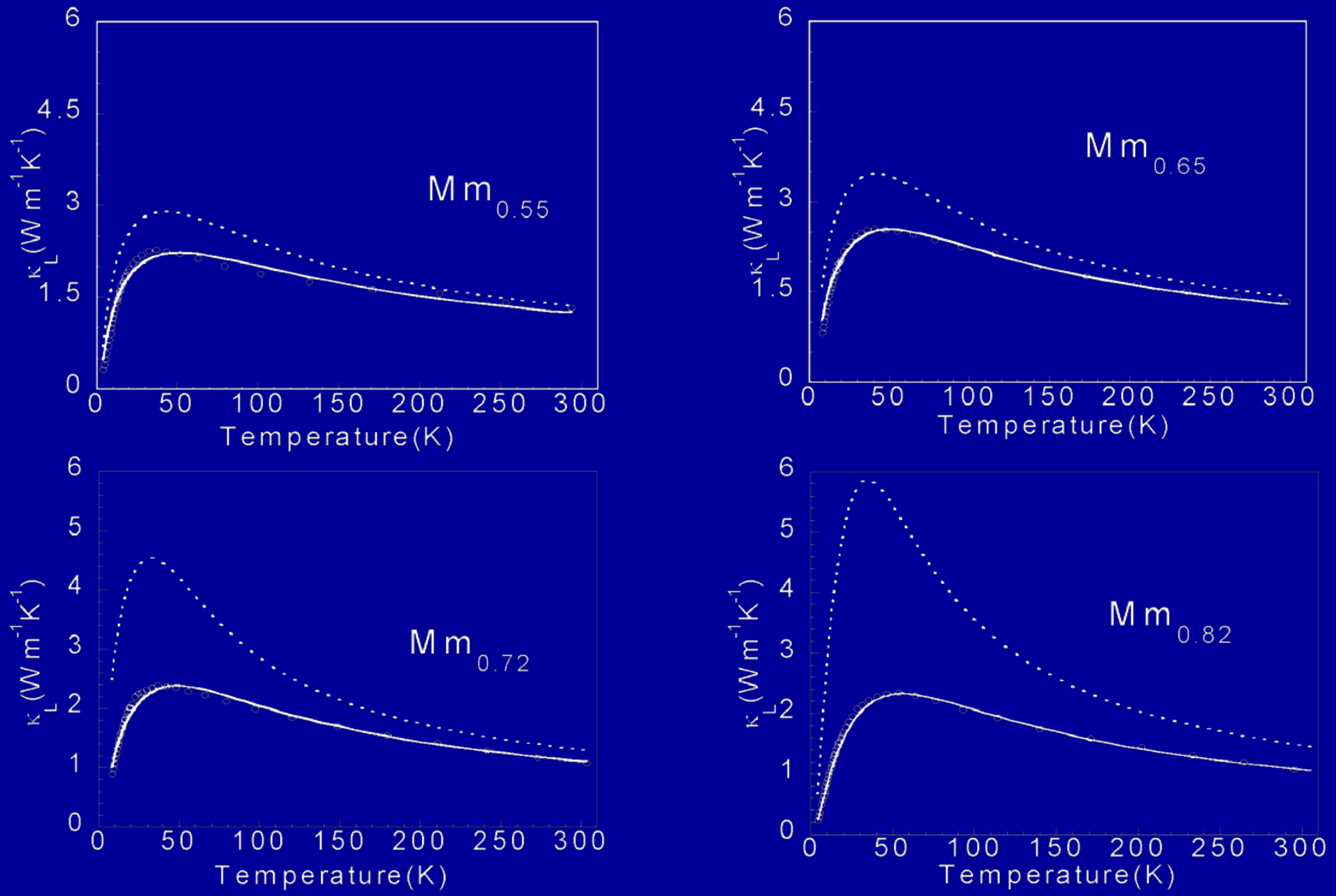


Misch-metal Filled Antimony Skutterudites

Mm: Ce:La:Nd:Pr:Si:Fe:Al:O = 50.75:22.75:16.22:5.72:3.35:0.72:0.50

Nominal representation	Composition
$Co_{0.9}$ (unfilled)	$Co_{0.9}Fe_{0.1}Sb_3$
$Mm_{0.55}$	$Mm_{0.55}Fe_{2.44}Co_{1.56}Sb_{11.96}$
$Mm_{0.65}$	$Mm_{0.65}Fe_{2.92}Co_{1.08}Sb_{11.98}$
$Mm_{0.72}$	$Mm_{0.72}Fe_{3.43}Co_{0.57}Sb_{11.97}$
$Mm_{0.82}$	$Mm_{0.82}Fe_4Sb_{11.96}$

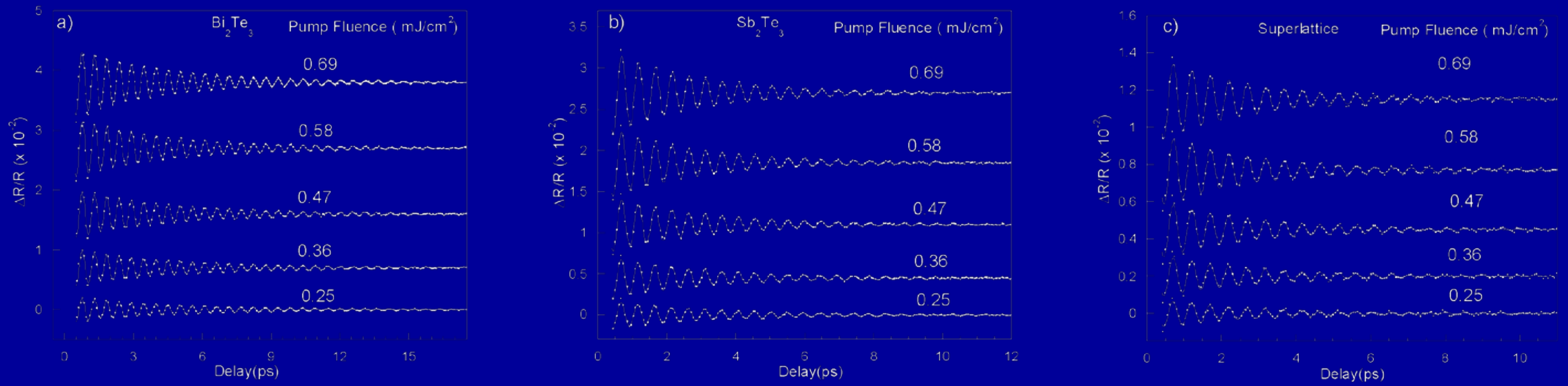


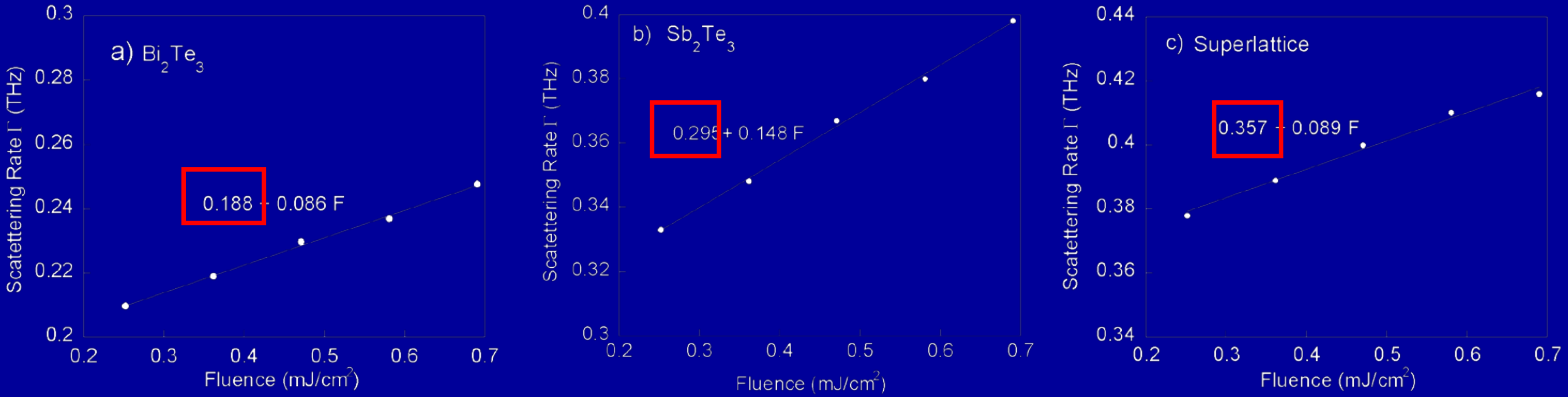


- Computation of κ based on resonant oscillation model and ultrafast measurement results agree well with k value measured from ~ 0 to 300 K.
- Role of filled material: resonant vibration vs. defect generation

(Phys. Rev. Lett, 2009)

Phonon Scattering in Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3/Sb_2Te_3 Superlattice



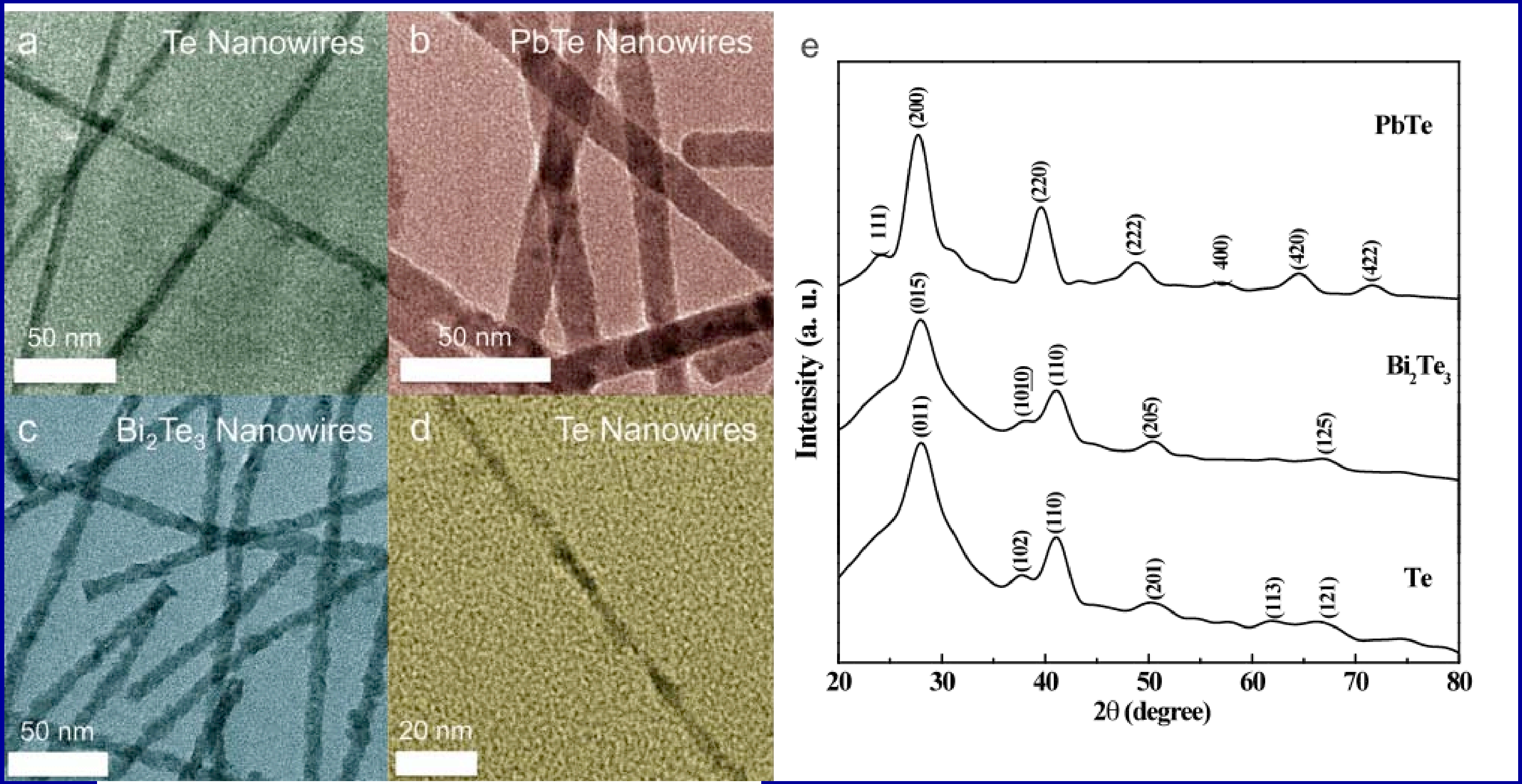


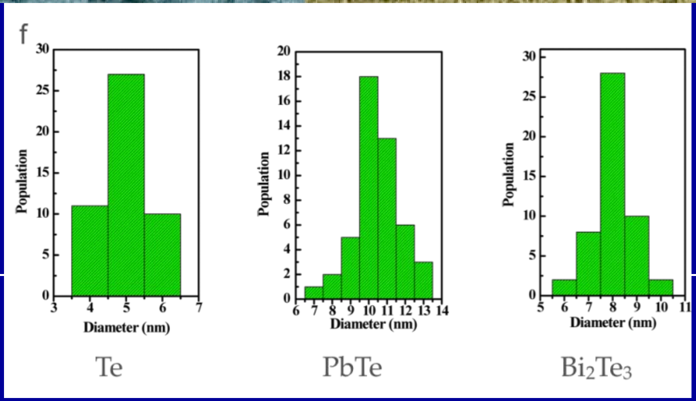
(in collaboration with RTI)

Nanowire TE Materials

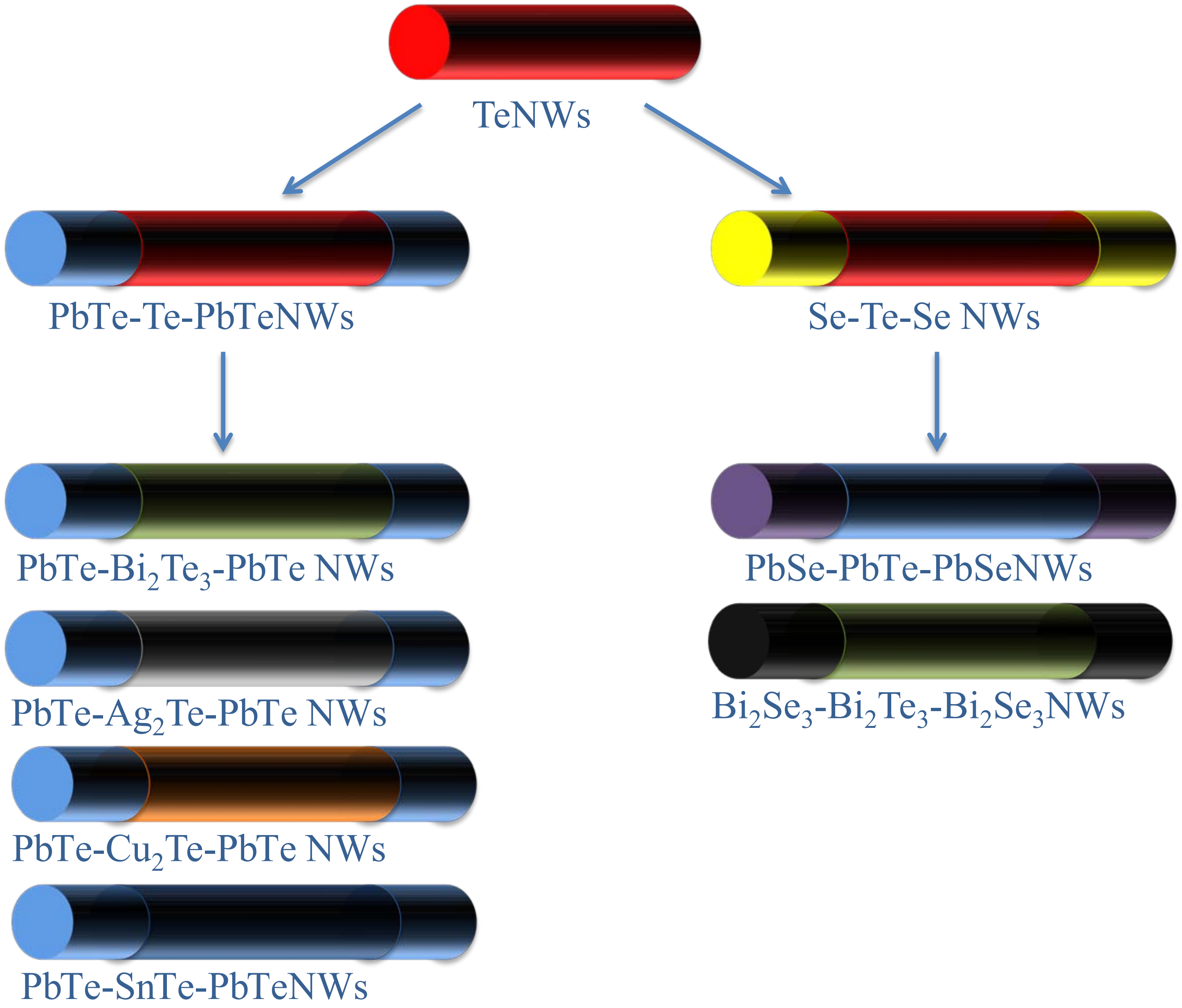
Yue Wu, School of Chemical Engineering

Synthesis of Molecular-scale Chalcogenide Nanowires





Scalable and high yield (93%)



TeNWs

PbTe-Te-PbTeNWs

Se-Te-Se NWs

PbTe-Bi_2Te_3-PbTe NWs

PbTe-Ag_2Te-PbTe NWs

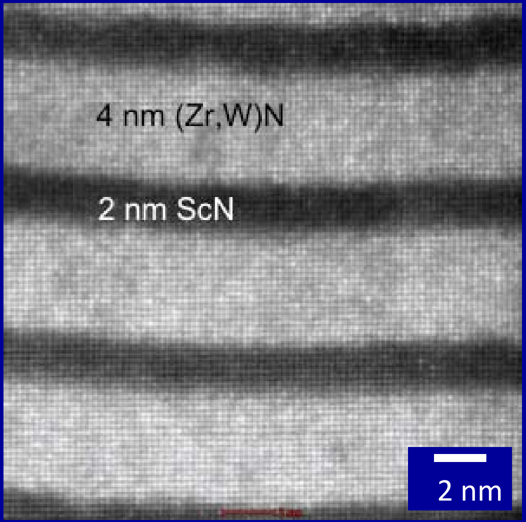
PbTe-Cu_2Te-PbTe NWs

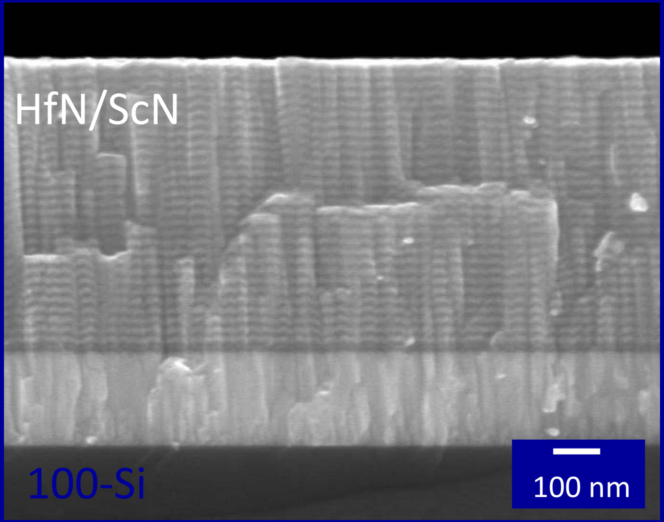
PbTe-SnTe-PbTeNWs

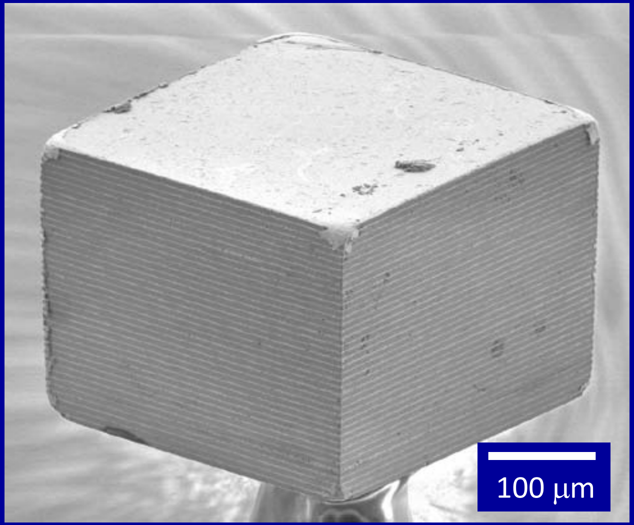
PbSe-PbTe-PbSeNWs

Bi_2Se_3-Bi_2Te_3-Bi_2Se_3NWs

Bulk-like Thermionic Energy Conversion Device Fabricated from Laminated Nanostructured Metal/Semiconductor Superlattices







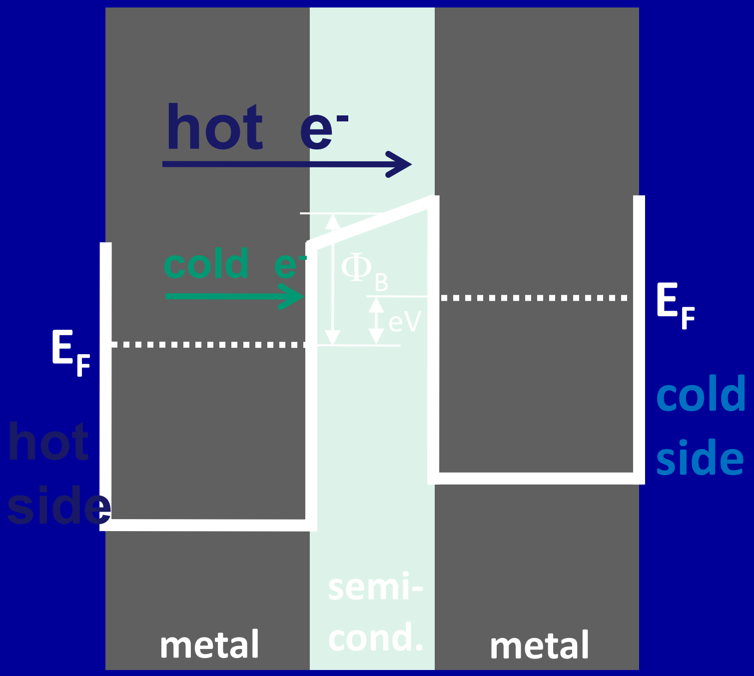
Co-PI: Tim Sands

Research Associate: Jeremy Schroeder

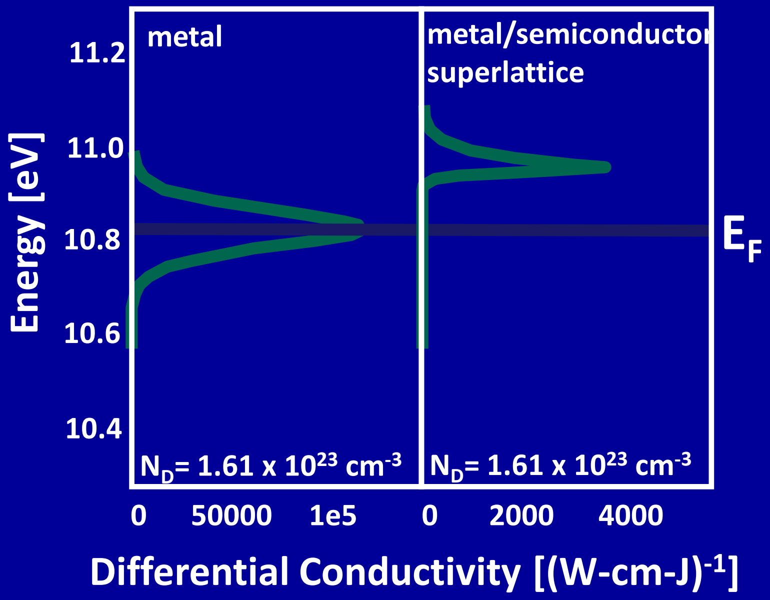
Graduate Student: Bivas Saha

Benefit of M-S superlattice

Thermionic transport



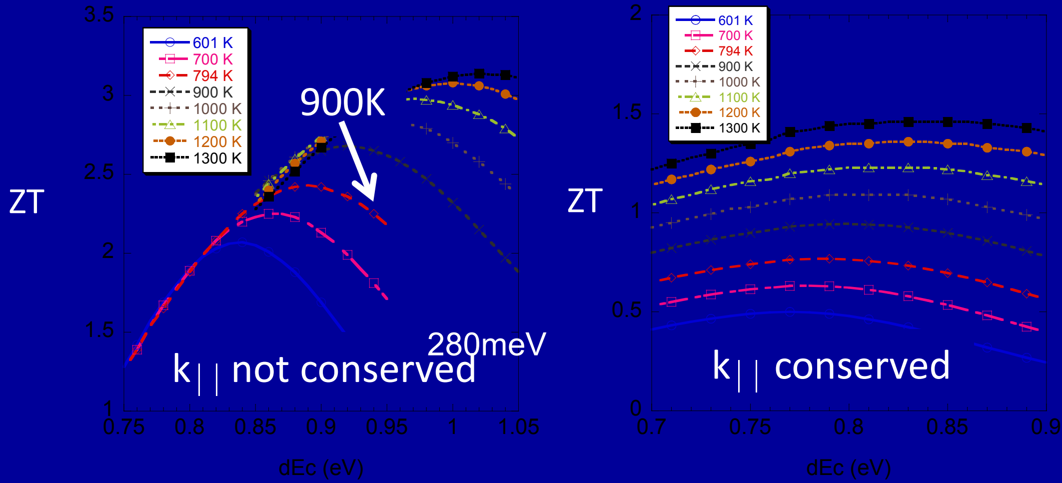
conduction band minima profile



D. Vashaee and A. Shakouri, Phys. Rev. Lett. 92, 106103 (2004)

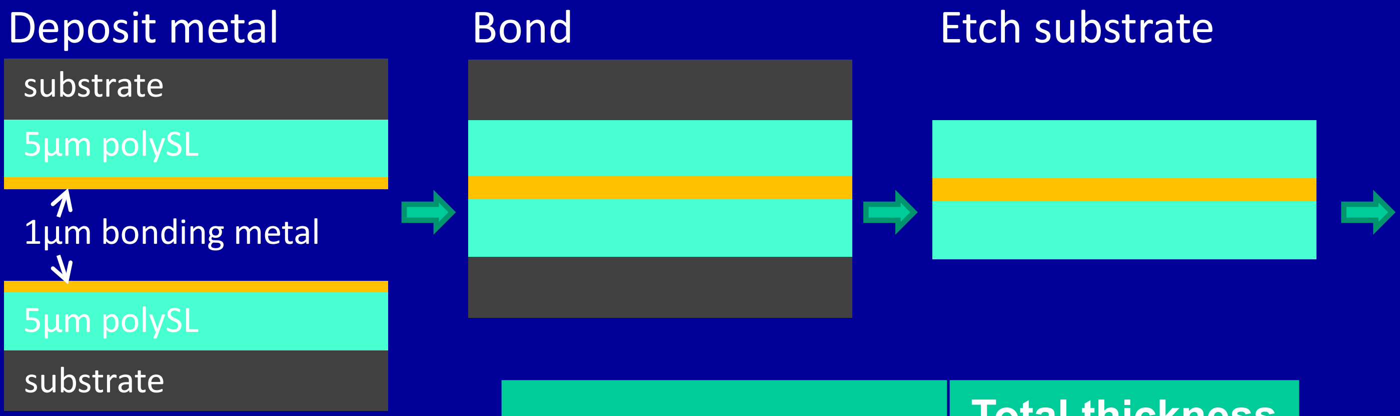
ZT predictions

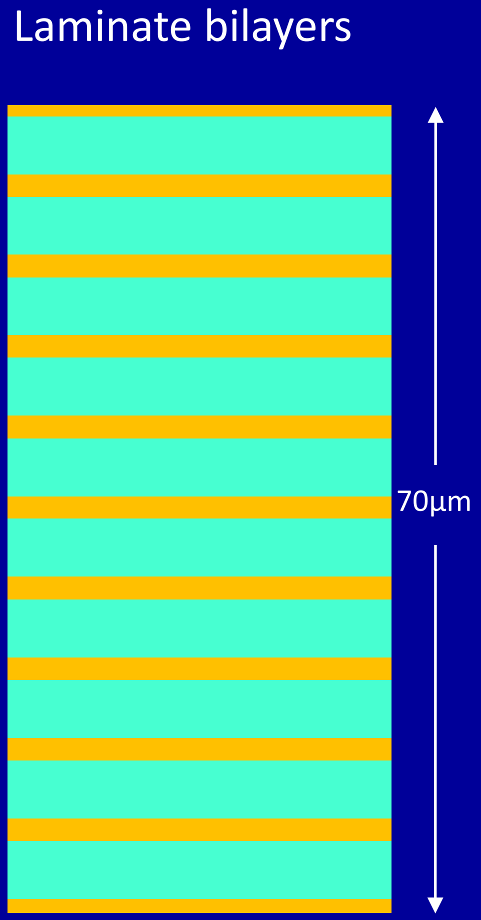
- Experimental data:
  - κ = 1.8 W/m-K
  - Φ_B = 280 meV
  - S = -820μV/K



Zebarjadi et al., J Elect. Mat., (2009)

Laminates





	Total thickness
TE layers	50µm
Au bonding layers	20µm

Thermal properties

κ_{TE} = 3 W/m-K

κ_{Au} = 300 W/m-K

$R_{c,thermal} \approx 7 \times 10^{-8}$ K-m^2/W

Electrical properties

$\rho_c = 1 \times 10^{-8}\ \Omega\text{-cm}^2$

ρ_{TE} = 1 mΩ -cm

ρ_{Au} = 25 µΩ -cm

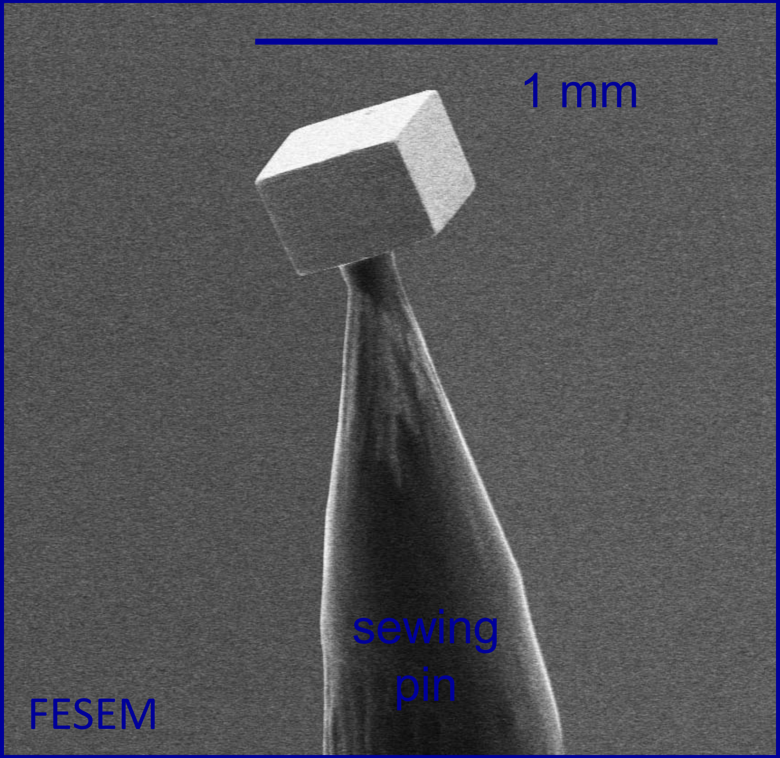
TE layers {
93% of total thermal impedance
96% of total electrical impedance

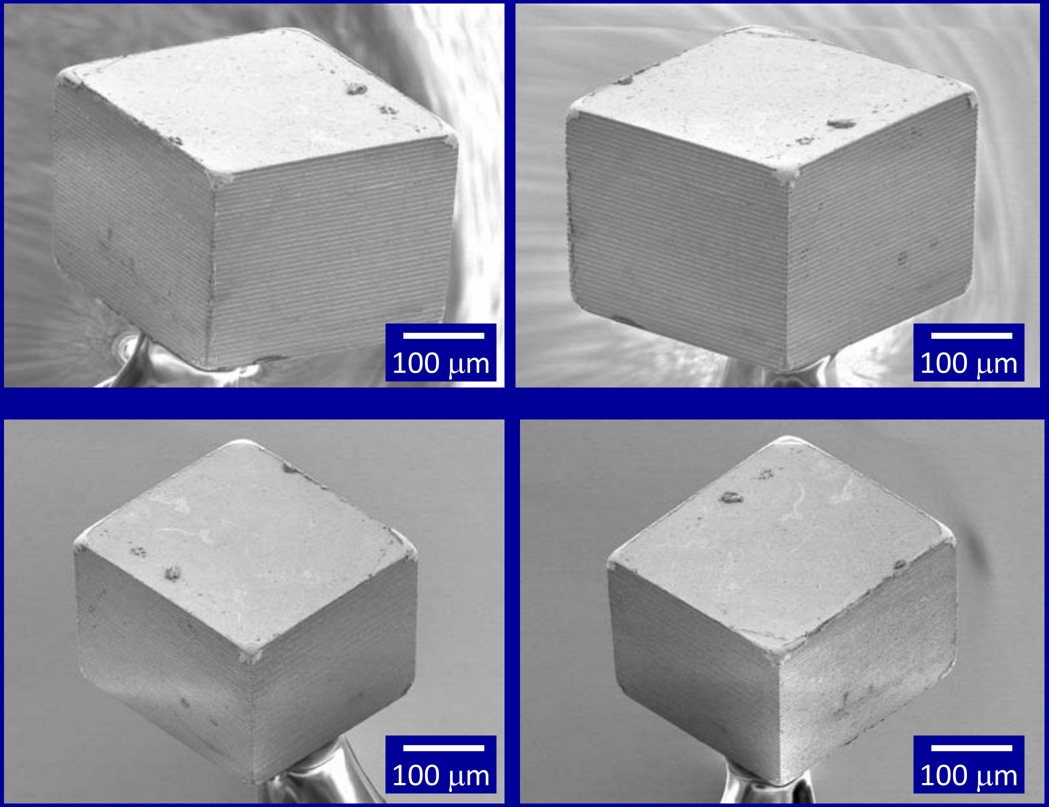
Purdue University

Process requires low metal-nitride/metal-bond contact resistance

Bulk-like laminate

- 40 thermoelectric layers (5 µm each)
- 80 gold layers (1 µm each)
- ~300 µm x 300 µm x 280 µm
- diced and polished (3 µm diamond lapping disc)





SEM of four sides of polished cube

Heat Exchangers for Automotive Exhaust Applications

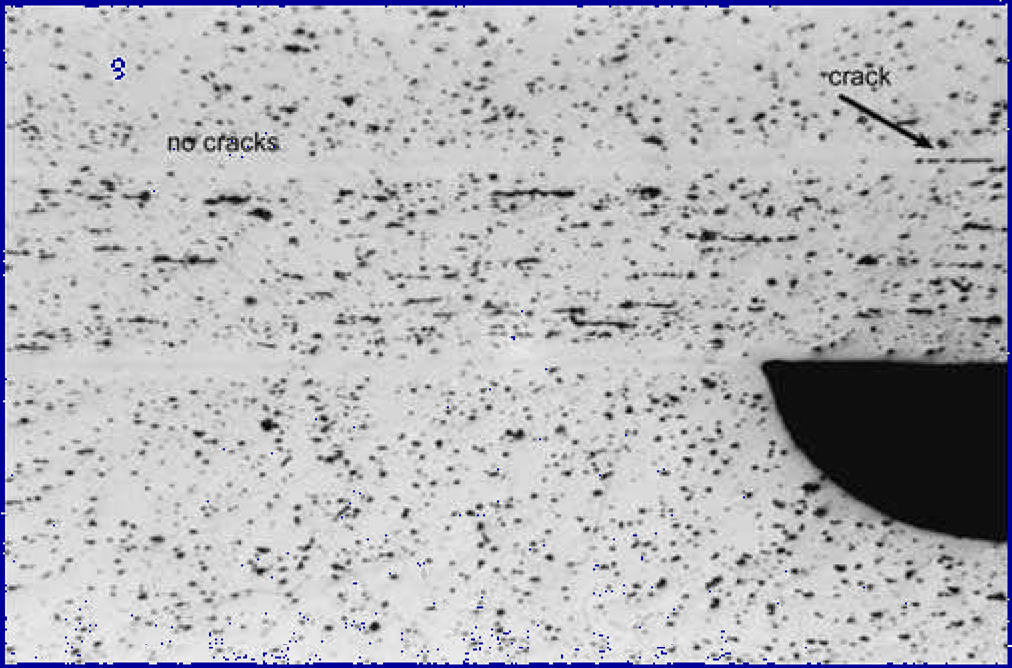
Professor Steve Heister

School of Aeronautics & Astronautics

Background

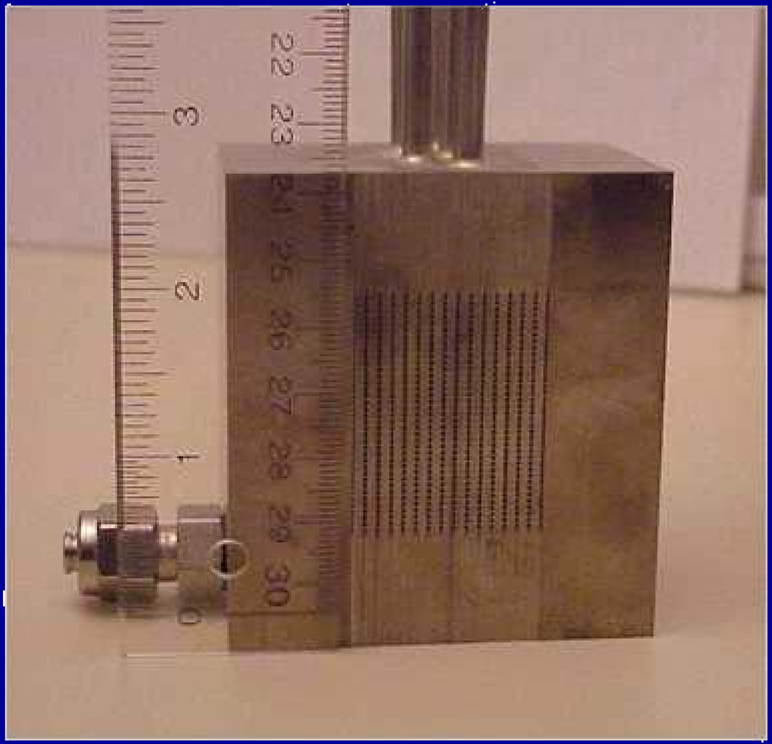
- Rolls-Royce established a University Technology Center (UTC) at Purdue in 2003 to study High Mach Propulsion for aerospace applications
- A key technology to enable high Mach flight is a **heat exchanger** that cools some compressor exhaust gases for use in turbine blade cooling
  - Air temps 1000-1200F (550-650 C) pressures to 40 bar
  - Fuel temps to 1000F (550 C) at pressures to 90 bar
- UTC has graduated roughly 10 students working in technologies to enable a fuel/air heat exchanger for operation in difficult environments
  - fuel coking/thermal stability
  - tube/shell HEX design
  - plate/fin HEX design
  - heat transfer augmentation

Foil Laminate Construction



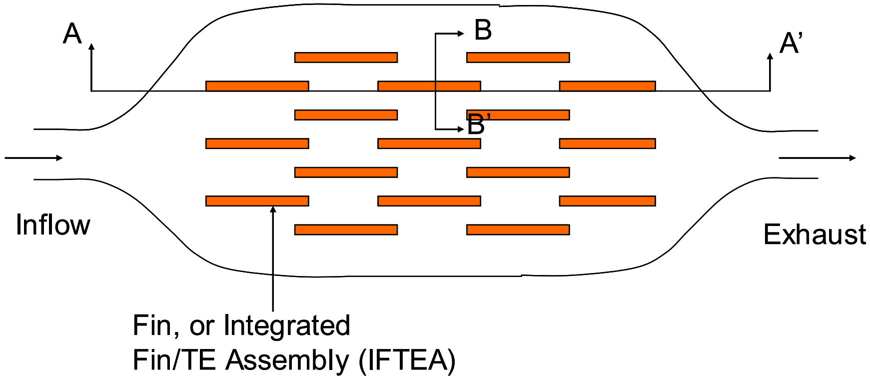
Chemical etching produces microscale flow passages on individual foils.

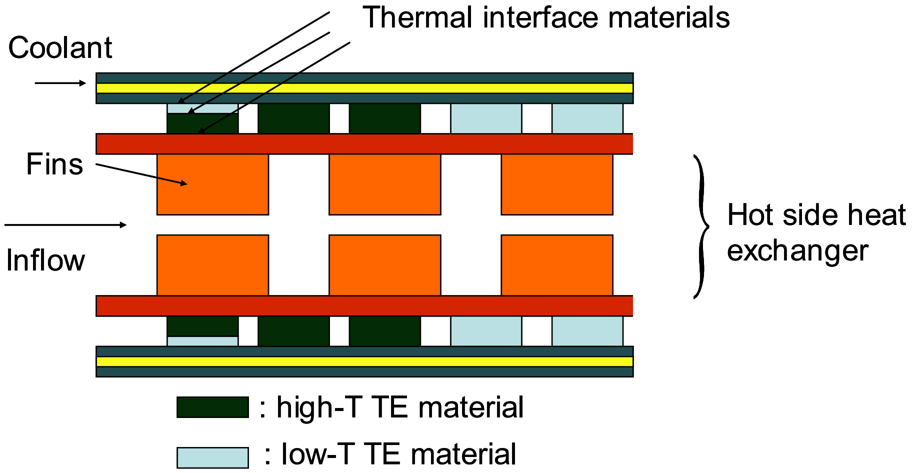
The foils are then stacked, aligned, and diffusion bonded under heat and pressure.

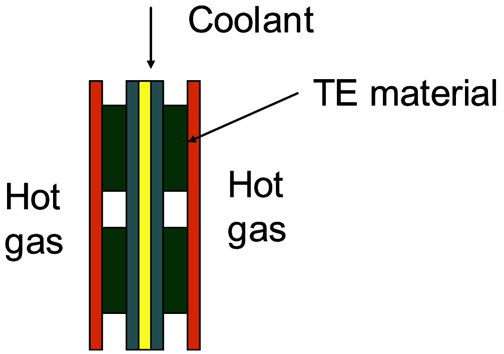


From “*Compact Superalloy Heat Exchangers for Cooled Cooling Air Applications*”, G. Campbell, J Fryer, Saddleback Aerspace, Turbine Symposium Presentation ca. 2002

Heat Exchanger for Waste Heat Recovery







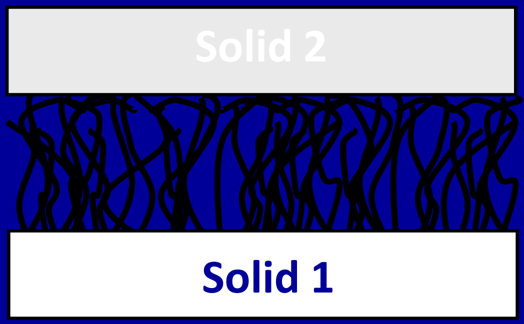
And many other possible topologies (cylindrical etc.)

CNT Array Thermal Interfaces Materials

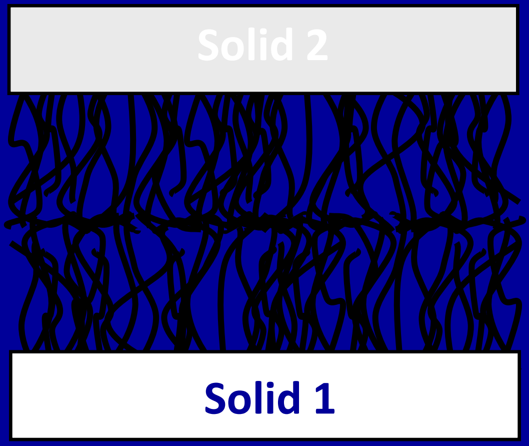
Timothy S. Fisher, Mechanical Engineering

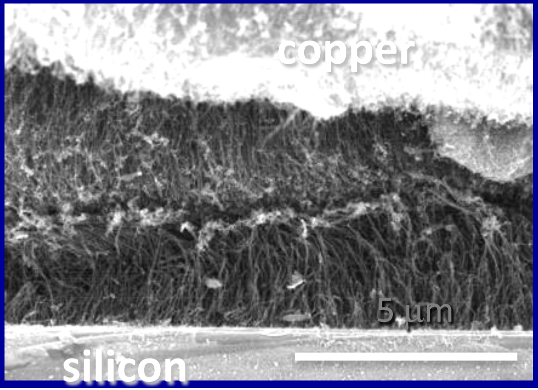
CNT Array Thermal and Electrical Interfaces

One-sided interface

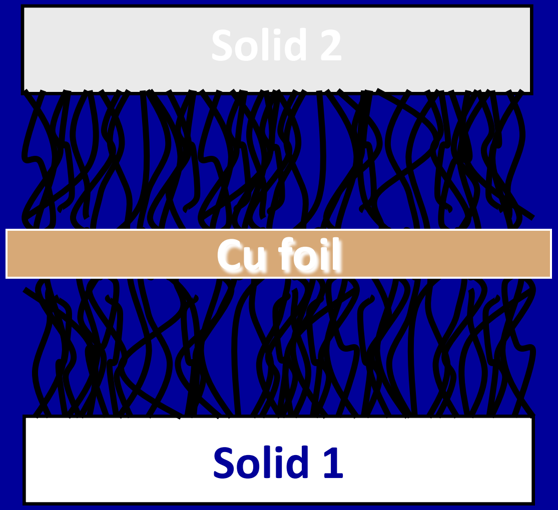


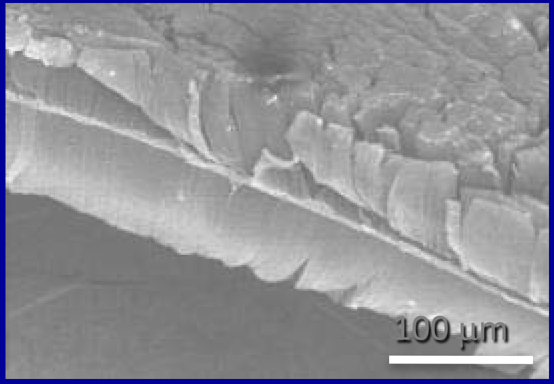
Two-sided interface





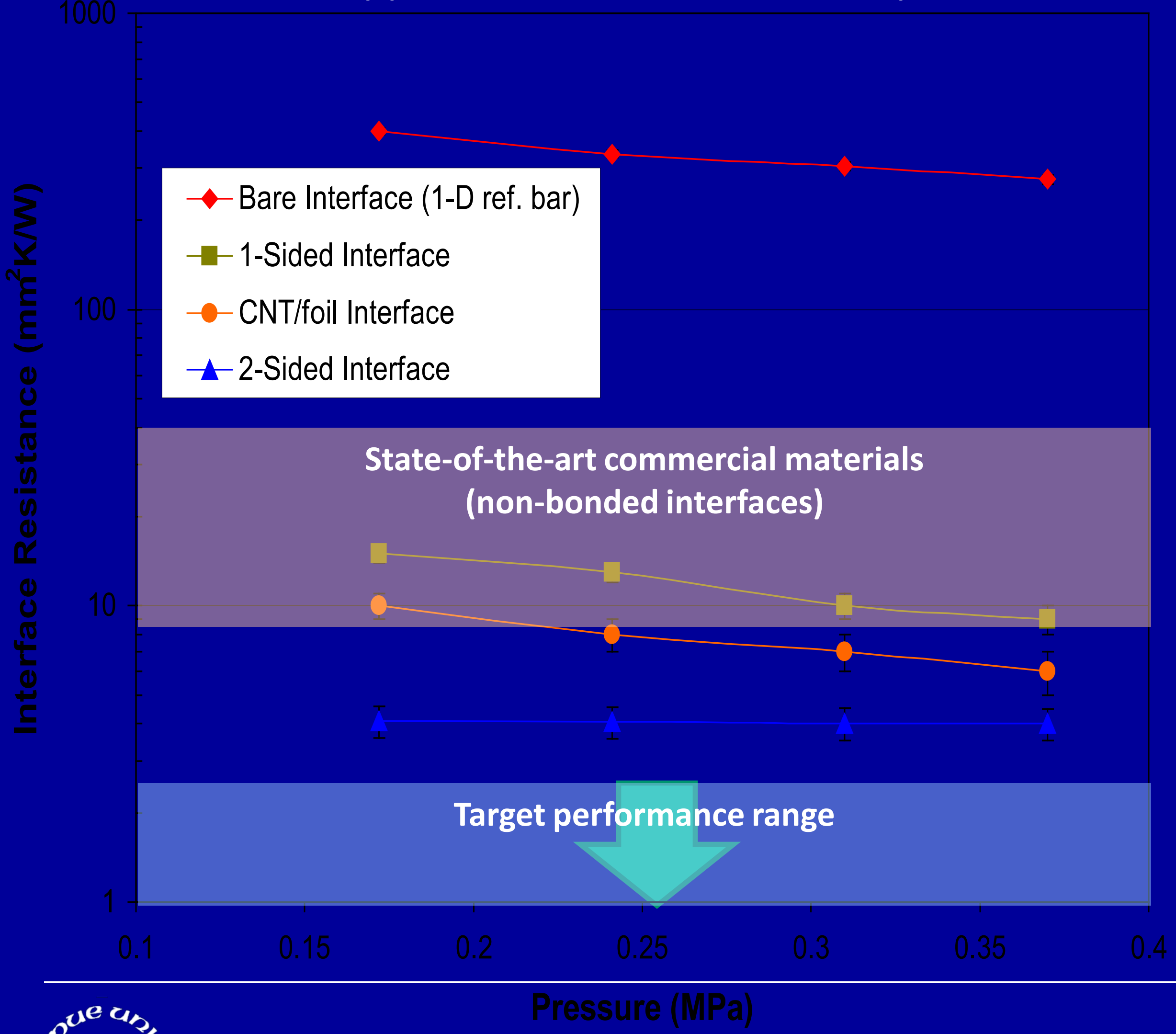
CNT/foil interface





Thermal Interface Results: Summary

silicon/copper substrates at room temperature



References:

B.A. Cola, J. Xu, T.S. Fisher,*Int J Heat Mass Transfer*, 52, 3490-3503 (2009).

B.A. Cola, J. Xu, C. Cheng, H. Hu, X. Xu, and T.S. Fisher, *J. Appl. Phys.* 101, 054313 (2007).

B.A. Cola, X. Xu, and T.S. Fisher, *Appl. Phys. Lett.* 90, 093513 (2007).

J. Xu and T.S. Fisher, *Int. J. Heat Mass Trans.* 49, 1658 (2006).

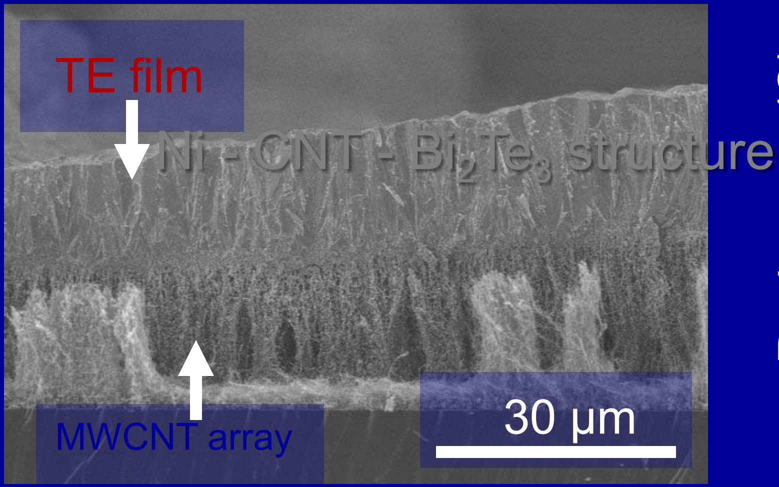
J. Xu, T.S. Fisher, *IEEE Trans. CPT*, 29, 261 (2006).

CNT Interfaces to Thermoelectrics

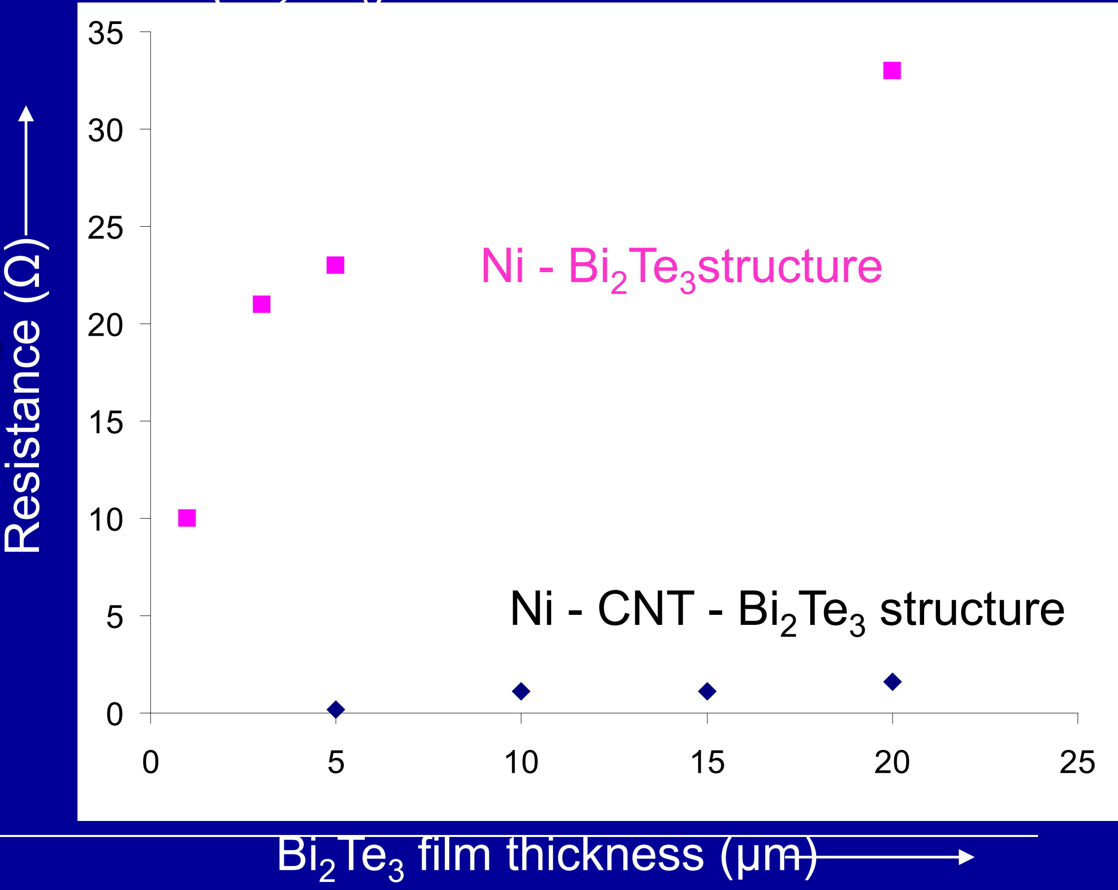
With Sands group

Motivation

- Parasitic electrical contact resistance can strongly degrade the efficiency of thermoelectric devices
- Direct electrodeposited thermoelectric (Bi_2Te_3) on CNTs shows reduced interface resistance

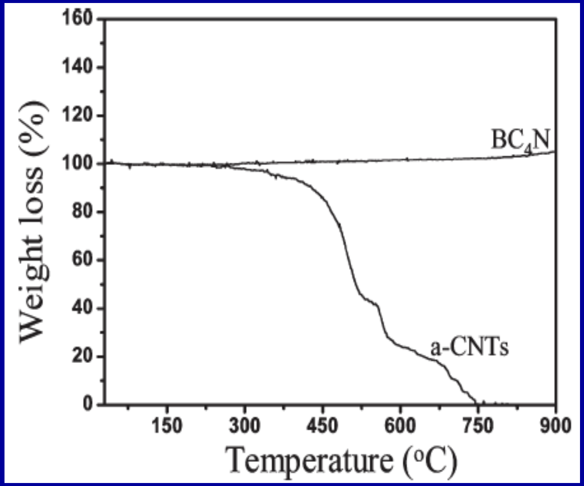


Mishra et al., Adv Mat **21** 4280, 2009

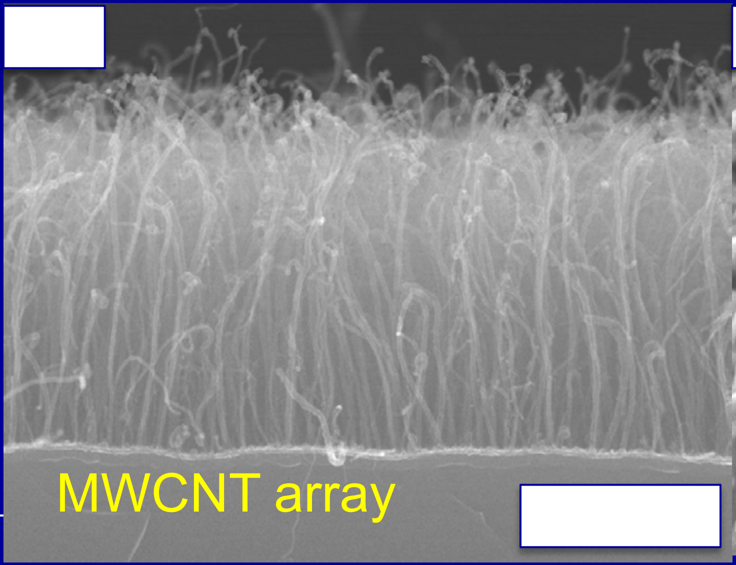


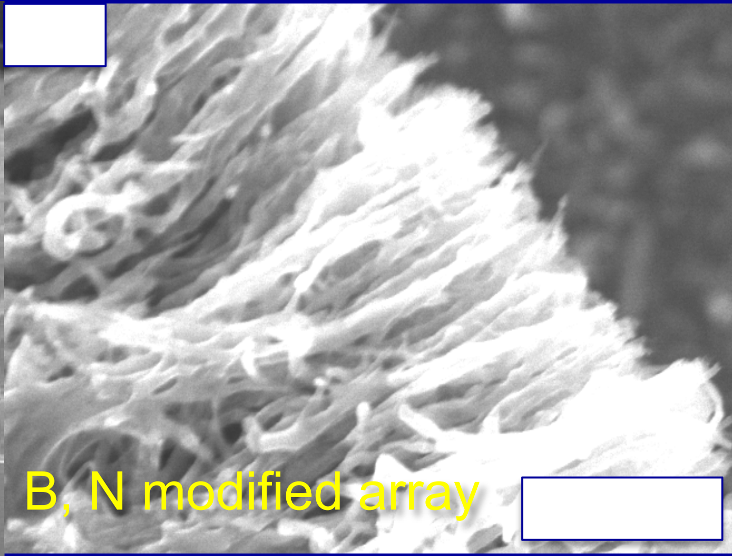
Improving Thermal Stability

Raidongia et al. (J. Mater. Chem. 2008, 18, 83-90) demonstrated large improvements in thermal stability of nanotubes by conversion to BC_4N



Our recent work:


MWCNT array

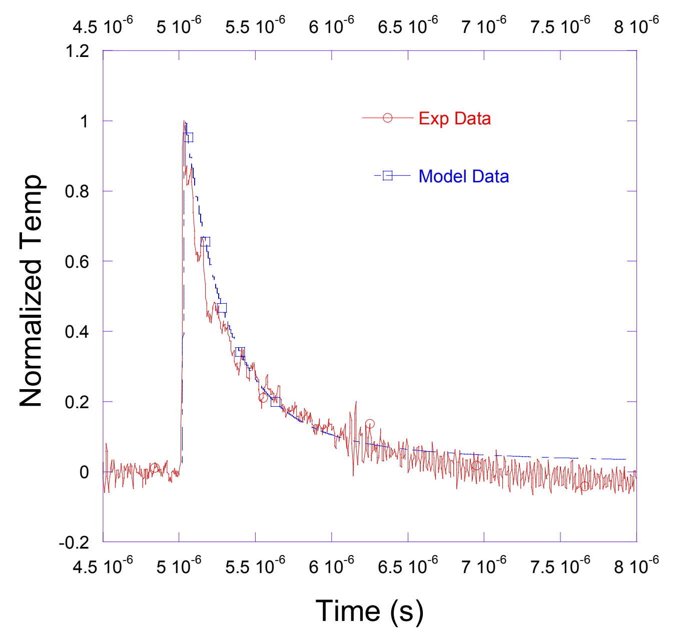

B, N modified array

Thermal Property Characterization: Laser Thermal Reflectance Measurement

- To determine contact resistance and thermal conductivity
- Temperature up to 700°C
- Use either a femtosecond laser pulse or nanosecond laser pulse for different range of contact resistance

  - femtosecond laser for measuring $R_{ct} < 10^{-6}$ m^2W/K

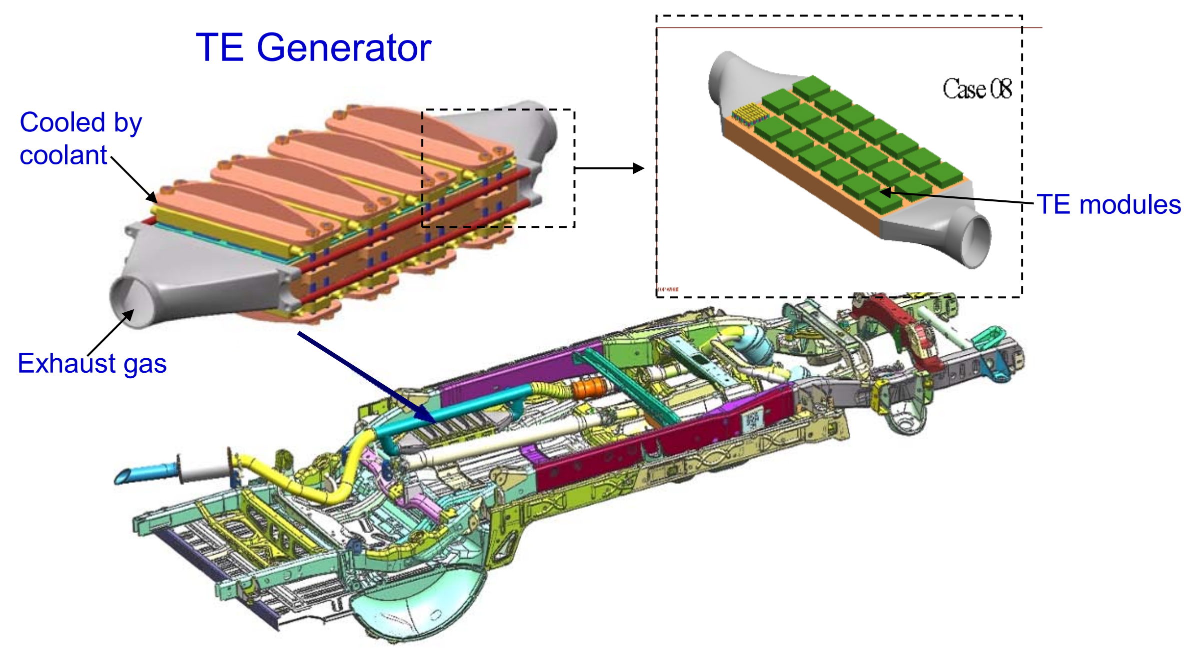
  - nanosecond laser for measuring $R_{ct} > 10^{-7}$ m^2W/K



$R_{ct}=2 \times 10^{-6}$ m^2W/K

TEG System-level Design and Testing

- System level thermal/TEG design (TE modules, thermal interface materials, heat sinks, constraints, etc.)
- Durability
- Cost
- Test strategy, i.e., components vs. sub-systems vs. TEG

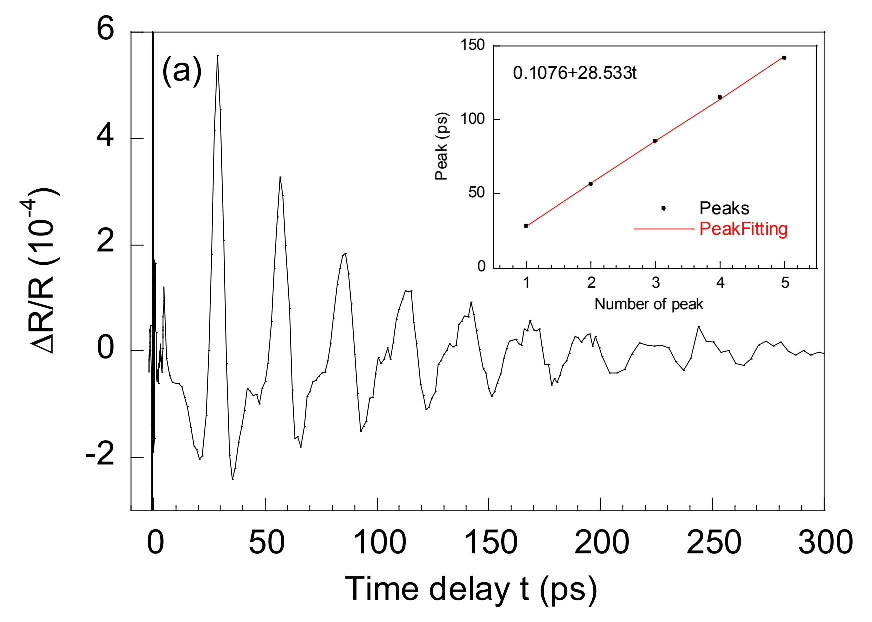


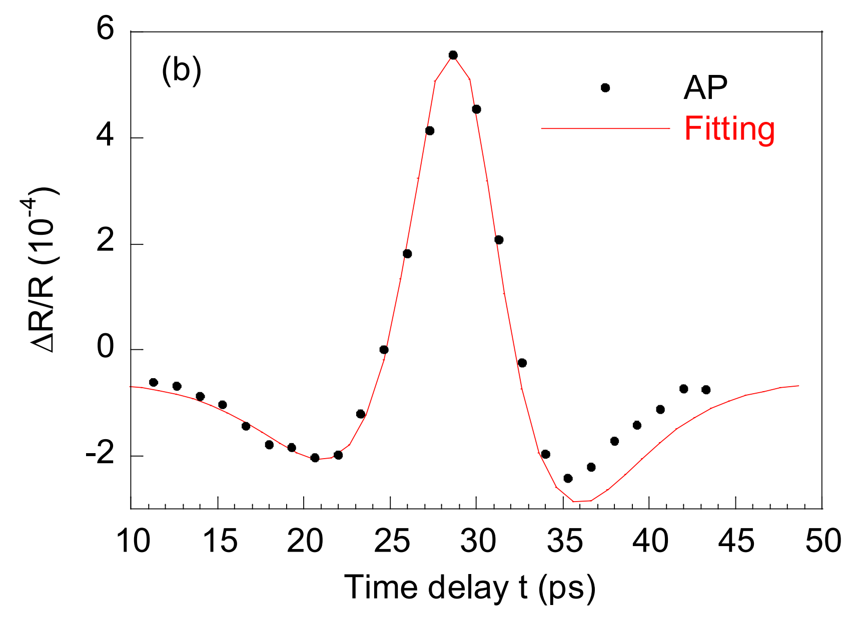
(Image courtesy: GM)

- Project started from Jan. 1st, 2011
- Purdue/GM project kick-off meeting on Dec. 13, 2010, at Purdue

We thank the support from:
NSF, PM: Dr. Ted Bergman
DOE, PM: Dr. John Fairbanks, Dr. Tom Avedisian

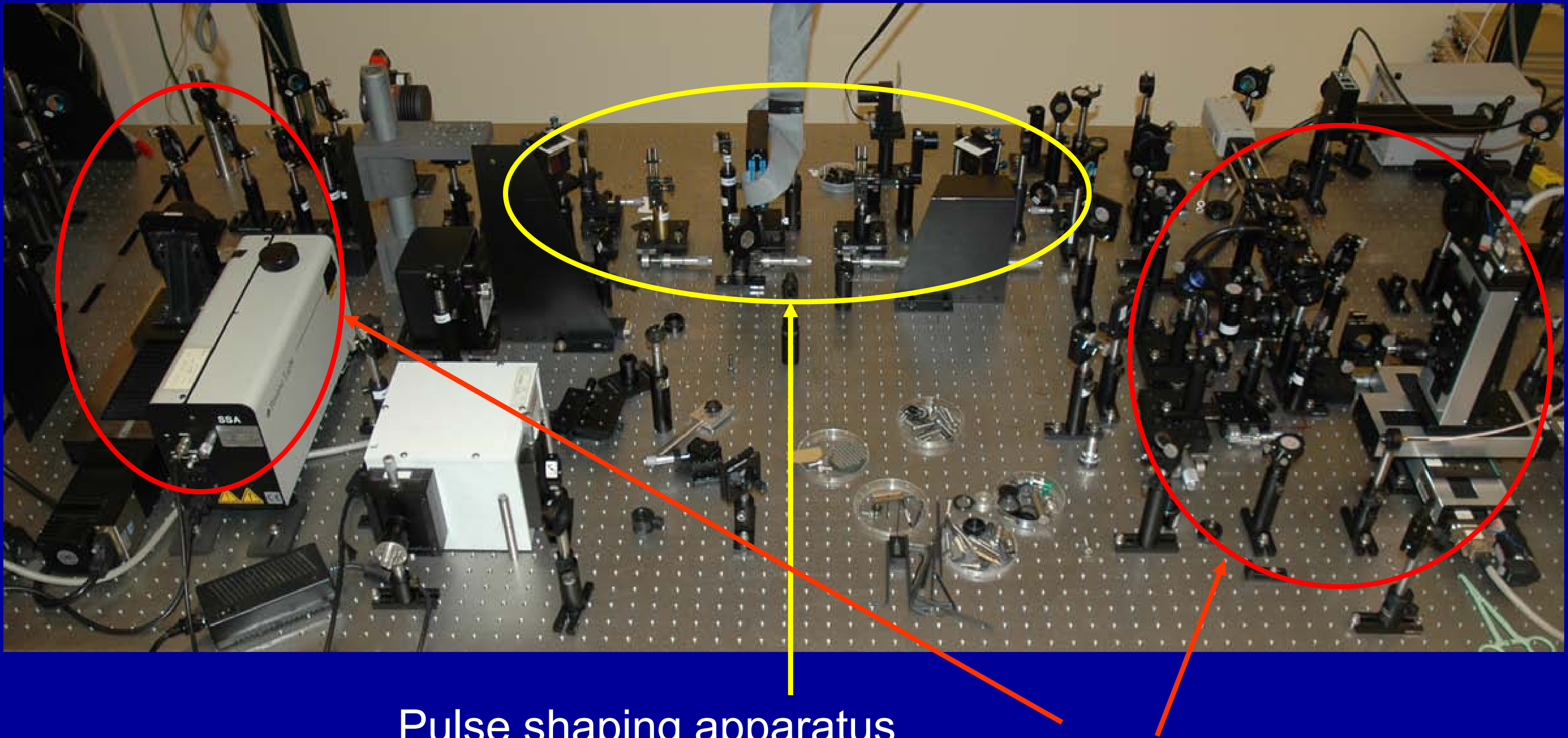
Coherent Acoustic Phonon





- Wave propagation equation: $$\frac{\partial^2 \eta}{\partial t^2} = v^2 \frac{\partial^2 \eta}{\partial z^2} + \frac{1}{\rho}\frac{\partial^2 S}{\partial z^2}$$
- Driving source: $$S = -3\,B\,\beta\,\Delta T$$
- Temperature increase: $$\Delta T_{(z,t)} = \Delta T_0 \int_{-\infty}^{\infty} \frac{1}{\sqrt{4\pi\alpha t}} e^{-(z-z')^2/4\alpha t} e^{-|z'|/\xi} dz'$$

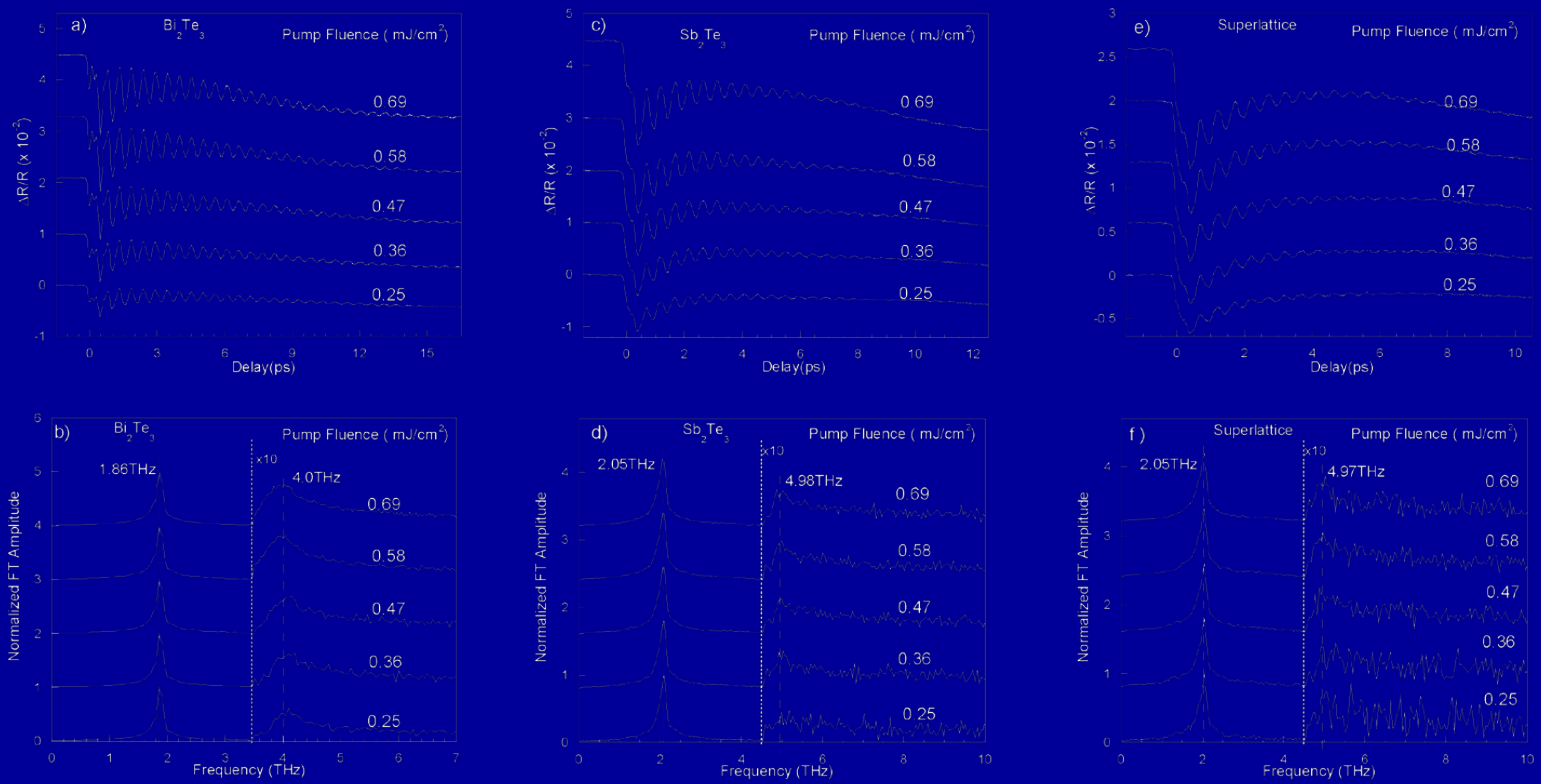
Experimental Setup for Pump-and-probe Measurements



Pulse shaping apparatus

Pump-and-probe set-up

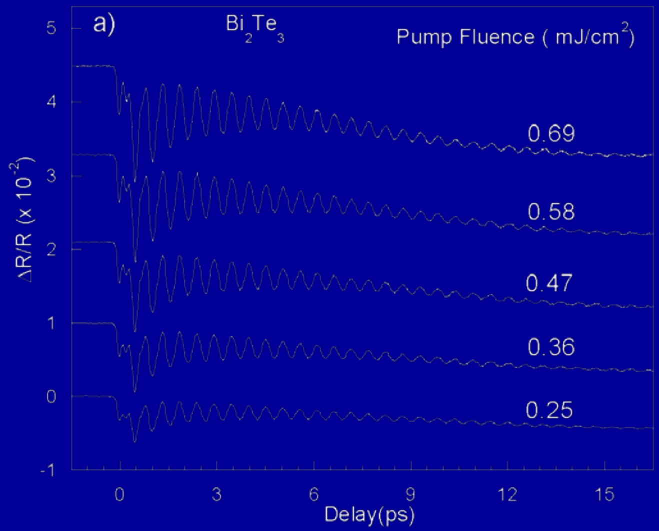
Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3/Sb_2Te_3 Superlattice

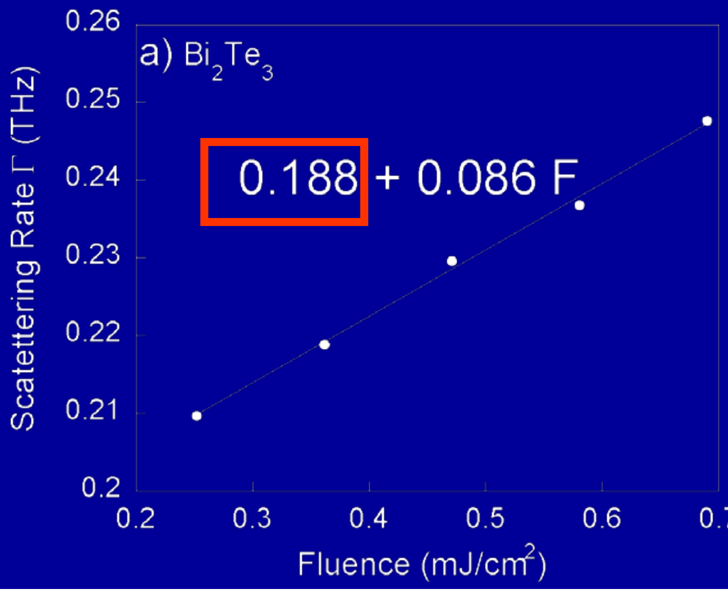


Bi_2Te_3 Sb_2Te_3 Superlattice

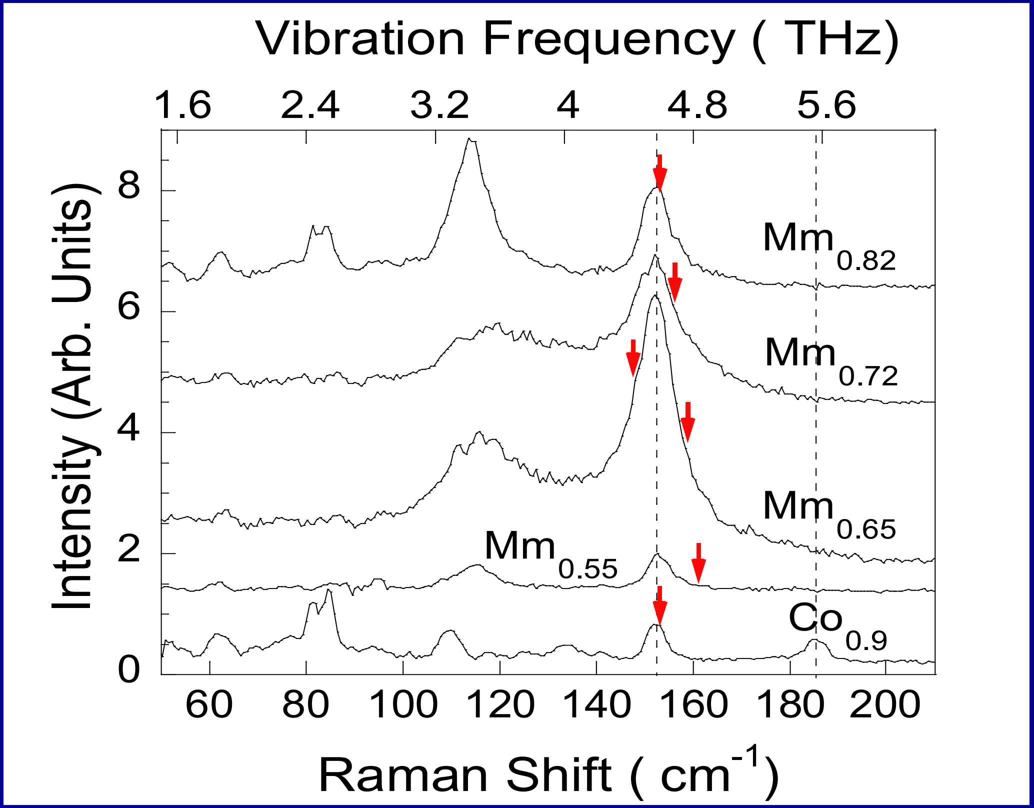
Phonon Scattering in Bi_2Te_3/Sb_2Te_3 Superlattice

- Scattering of phonon is due to phonon-charge, phonon-phonon, and phonon-boundary/interface interactions.
- Scattering rate of coherent phonon increases linearly with pump fluence.
- Phonon scattering in bulk Bi_2Te_3, bulk Sb_2Te_3 and Bi_2Te_3/Sb_2Te_3 superlattice is measured and compared.





Ultrafast Measurement vs. Raman



Red arrows: frequencies from ultrafast measurements

- Raman measurement detects the Sb_4 ring frequency: 4.6 THz
- Ultrafast measured frequencies are different from the Raman frequency, but approach that of Sb_4 ring at high filling ratio, indicating strong interactions between the guest atoms and the lattice (Sb_4 ring).

Figure of merit:

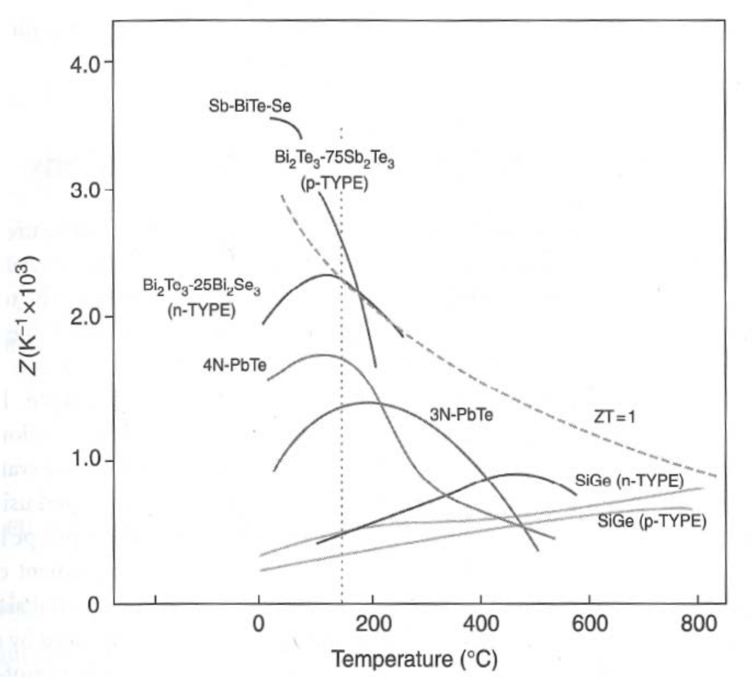
$$ZT = \frac{S^2 T}{\rho \kappa_{total}} = \frac{S^2 T}{\rho(\kappa_L + \kappa_e)}$$

A good thermoelectric material means low electric resistivity ρ and low thermal conductivity κ (phonon glass electron crystal – PGEC)

ZT ~ 1 in typical bulk thermal electric materials.

- Carnot efficiency: $\eta = \frac{T_{cold}}{T_{hot} - T_{cold}}$

- $ZT = 1$ corresponds to $\eta = 10\%$
- $ZT = 4$ corresponds to $\eta = 30\%$
- Home refrigerator: $\eta \sim 30\%$
- Bi_2Te_3/Sb_2Te_3 Superlattice: $ZT = 2.4$



Rowe, Thermoelectrics Handbook: Macro to Nano, CRC Press (2006).

- A systematic study of the effect of phonon scattering in TE materials, and the resulting thermal conductivity reduction.

- Effect of filling ratio of misch metal in different family of skutterudites.

- A theoretical understanding on the effect of the rattling behavior of the filled elements.