U.S. Department of Energy
Energy Efficiency and Renewable Energy

NSF-DOE Thermoelectrics Partnership:
Novel Nanostructured Interface Solution for Automotive Thermoelectric Modules Application

Stanford University:

Prof. Ken Goodson
Prof. Mehdi Asheghi
Michael T. Barako, Amy Marconnet, WooSung Park, Saniya LeBlanc , Lewis Hom, Yuan Gao

University of South Florida:

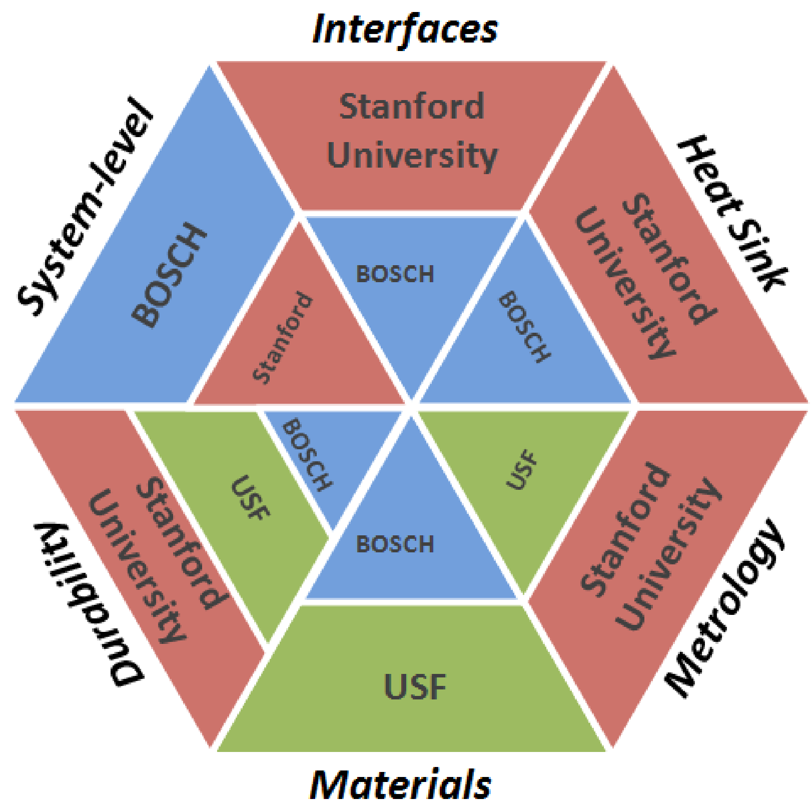
Prof. G. Nolas, Dr. Yongkwan Dong

Novel Materials Laboratory
University of South Florida

Bosch: Dr. Boris Kozinsky

BOSCH

NIST



Leveraged Support: NSF Fellowships, Stanford Graduate Fellowships, Northrop Grumman, ONR, SRC/MARCO

Publications Appearing or Submitted in First Year of DOE-NSF Sponsorship

1. Barako, Gao, Marconnet, Asheghi, Goodson, “Solder-Bonded Nanotube Thermal Interface Materials,” to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

2. Barako, Park, Marconnet, Asheghi, Goodson, “Infrared Imaging and Reliability Study of Thermoelectric Modules under Thermal Cycling,” to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

3. Park, Barako, Marconnet, Asheghi, Goodson, “Effect of Thermal Cycling on Commercial Thermoelectric Modules,” to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

4. Won, Gao, Panzer, Dogbe, Pan, Kenny, Goodson, 2012, "Mechanical Characterization of Aligned Multi-Wall Carbon Nanotube Films," *Carbon*, Vol. 50, pp 347-355.

5. Marconnet, Yamamoto, Panzer, Wardle, Goodson, 2011, "Thermal Conduction in Aligned Carbon Nanotube-Polymer Nanocomposites with High Packing Density," *ACS Nano*, Vol. 5, pp. 4818-4825.

6. Marconnet, Panzer, Goodson, “Thermal Conduction Phenomena in Carbon Nanotubes and Related Nanostructured Materials,” invited and submitted, *Reviews of Modern Physics*.

7. Gao, Kodama, Dogbe, Pan, Goodson, “Nonhomogeneous Mechanical Properties of Vertically Aligned Multi-Walled Carbon Nanotube Films,” submitted to *Carbon*.

8. Marconnet, Motoyama, Barako, Gao, Pozder, Fowler, Ramakrishna, Mortland, Asheghi, and Goodson, “Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films,” to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

9. Gao, Kodama, Won, Dogbe, Pan, and Goodson, “Inhomogeneous Mechanical Properties of Vertically Aligned Multi-walled Carbon Nanotube Films,” to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

10. Garg, Bonini, Kozinsky, Marzari, "Role of Disorder and Anharmonicity in the Thermal Conductivity of Silicon-Germanium Alloys: A First-Principles Study", Physical Review Letters, 106, 045901 (2011).

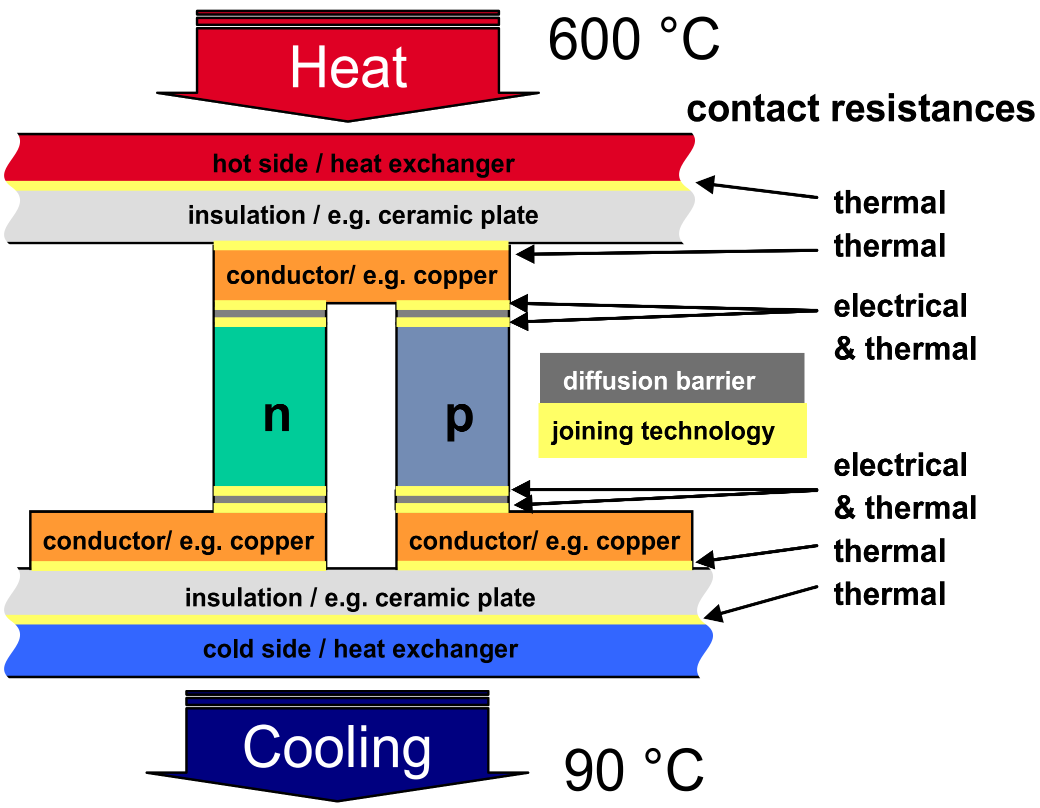
11. Volja, Kozinsky, Li, Wee, Marzari, Fornari, "Electronic, vibrational and transport properties of pnictogen substituted ternary skutterudites", submitted to Physical Review B.

Key Challenges for Thermoelectrics in Combustion Systems

Stable interfaces with targeted electrical, mechanical, thermal properties.

TE materials (p and n-type) that are thermally stable at operating temperatures and cost effective.

Performance testing of TE material–metallization/interface, which allow better prediction of system performance including interfaces

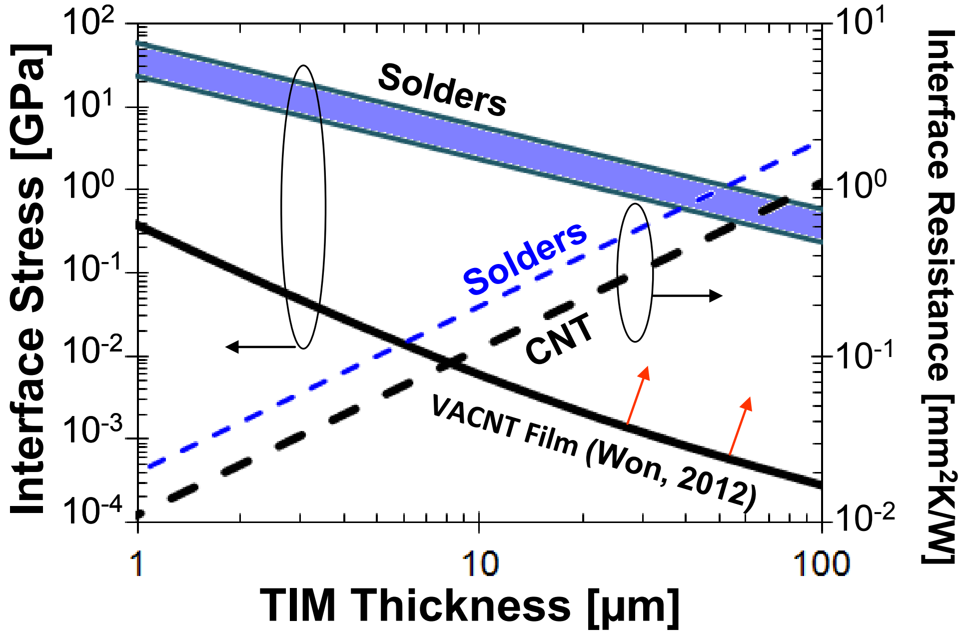


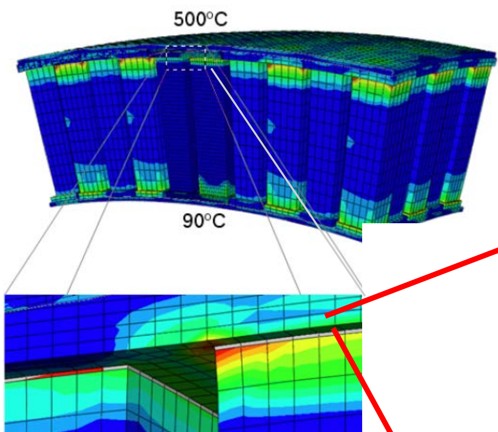
Special Challenges for TEGs

- Thermal interfaces degrade efficiency of waste heat recovery systems (TE)
- Interfaces must accommodate mismatch in thermal expansion coefficient

$$\sigma \approx \frac{GL}{2d} \Delta T \Delta \alpha$$

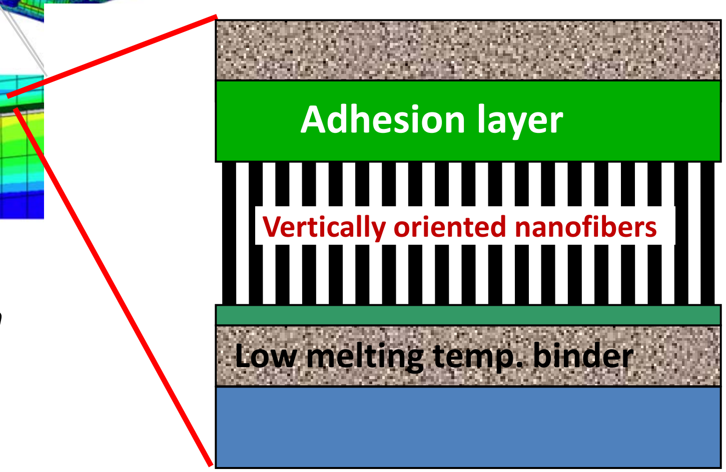
"Nanostructured Interfaces for Thermoelectrics,"
Gao, Panzer, Goodson et al., Proc. ICT 2009, J. Electronic Materials, 2010

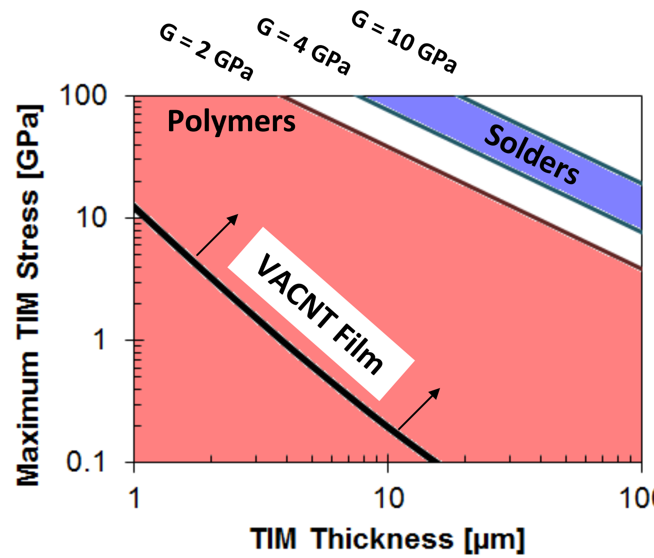




Courtesy of Dr. Kozinsky, Bosch

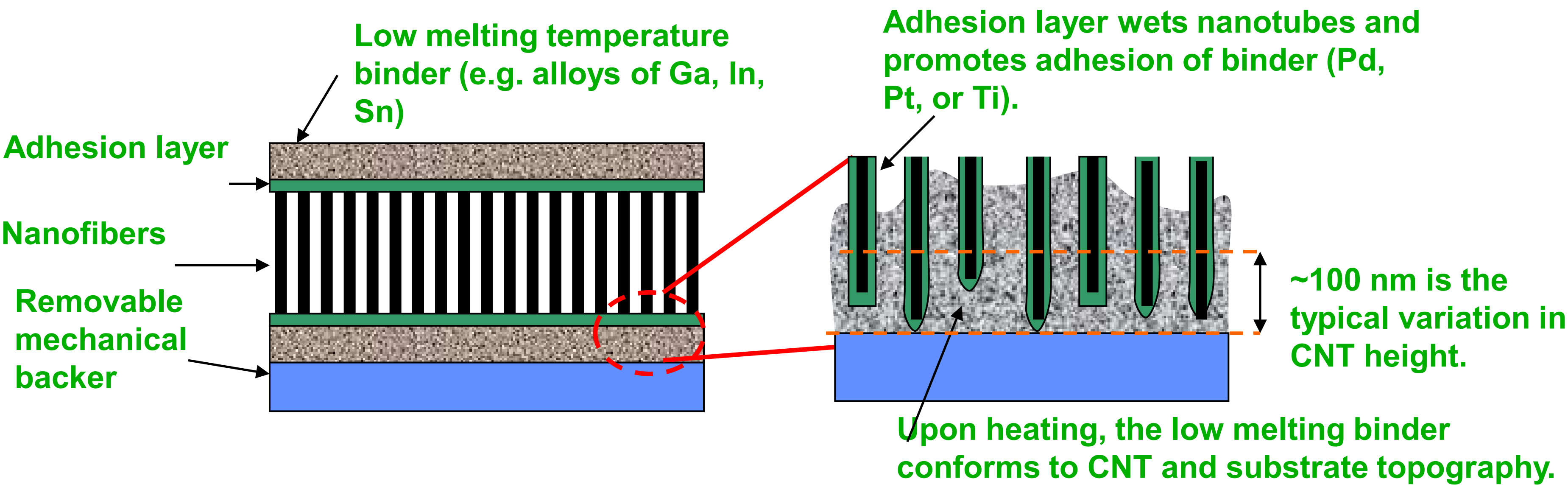
Nanostructured Interface Solutions

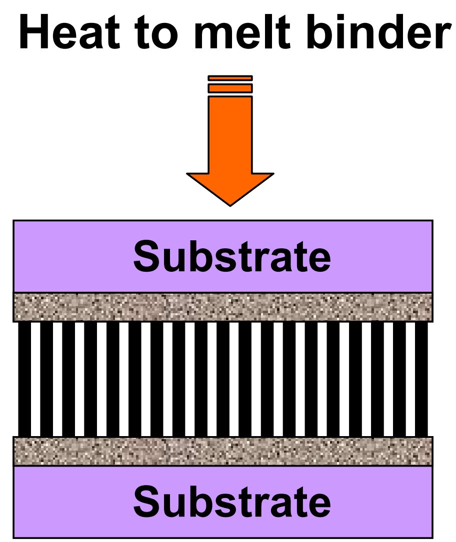




Nanostructured Interface Solutions

Patents issued (SRC sponsorship)

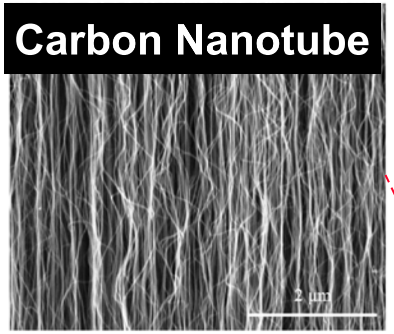


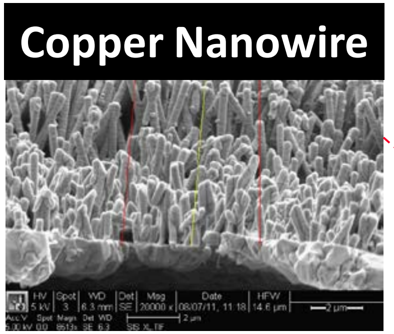


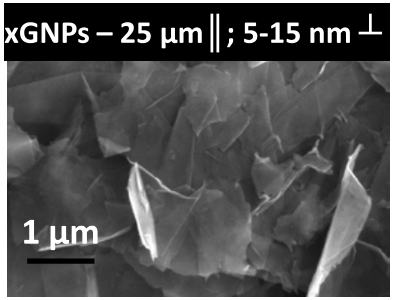
- **Composite interface material combines nanotubes with low melting temperature binders.**
- **Binders improve thermal contact to substrates and allow attachment during packaging/assembly**

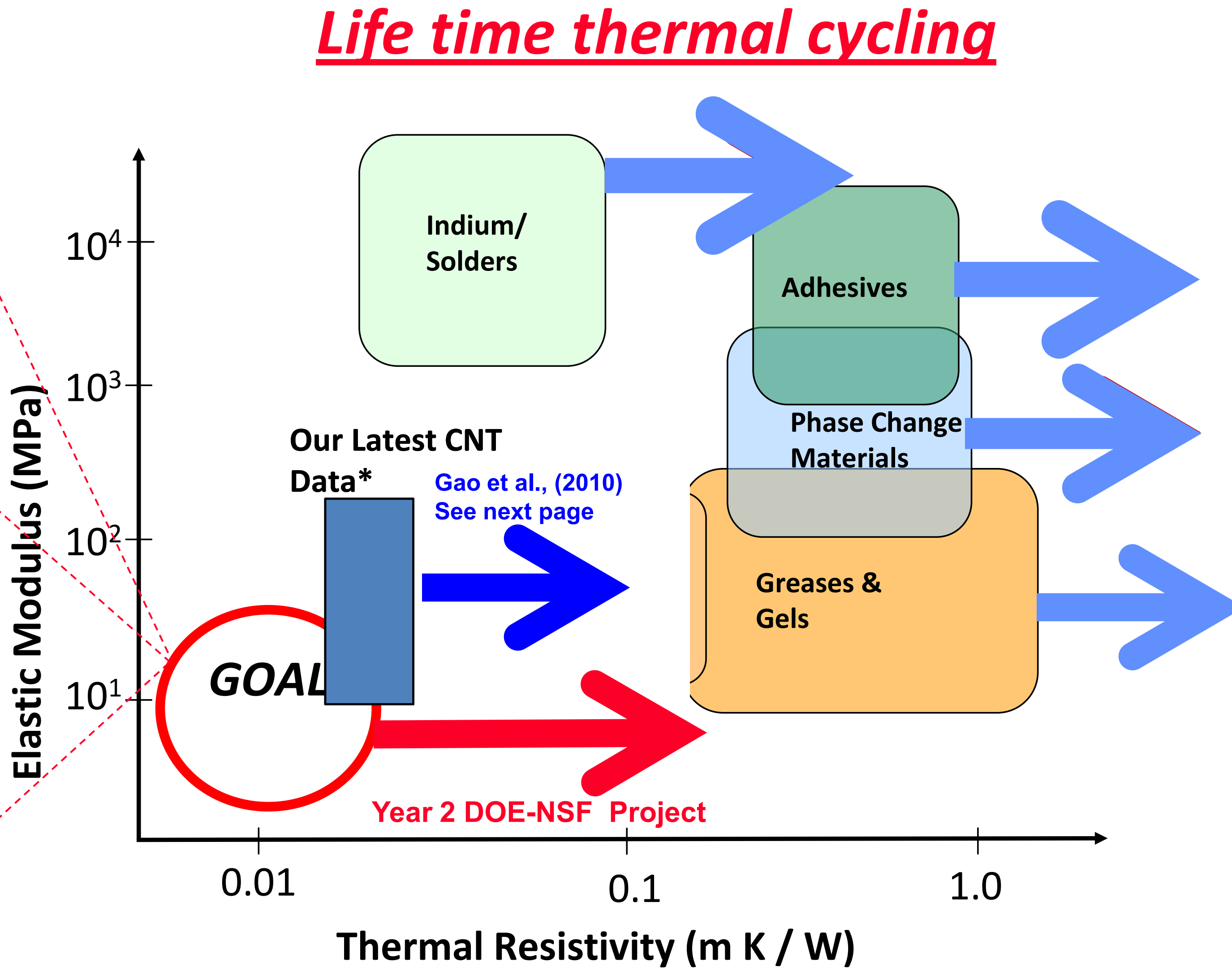
Thermal Interface Materials Requirements

Nanostructured Interfaces







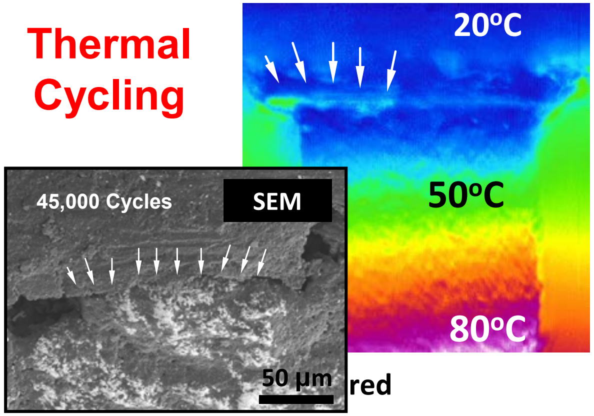


Gao, Shakouri, Goodson et al., "Nanostructured Interfaces for Thermoelectrics," Proc. ICT 2009. J. Electronic Materials (2010).

A Brief Overview of the Research Activities at Stanford

ThermoElectric Module/Pellet

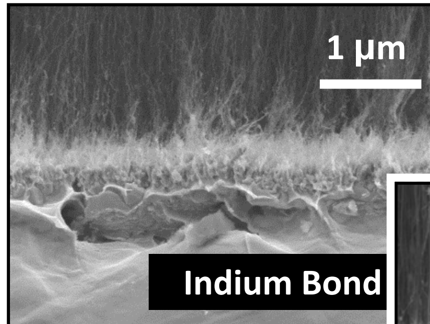
Thermal Cycling



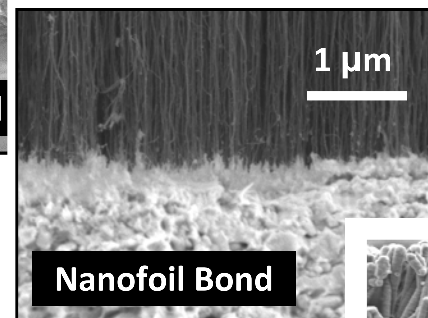
Barako, Park, Marconnet, Asheghi, Goodson, "Infrared Imaging and Reliability Study of Thermoelectric Modules under Thermal Cycling," to appear in Proceedings of ITHERM, San Diego, May, 2012.

Nanostructured Interfaces

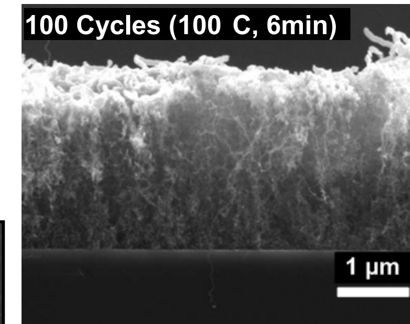
Solder-Bonded Nanotube Thermal Interface Materials



Barako, Gao, Marconnet, Asheghi, Goodson, "Solder-Bonded Nanotube Thermal Interface Materials," to appear in Proceedings of ITHERM, San Diego, May, 2012.



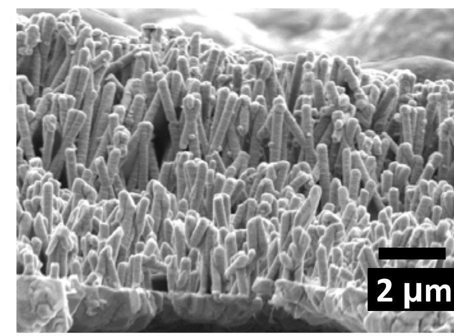
Thermal Cycling



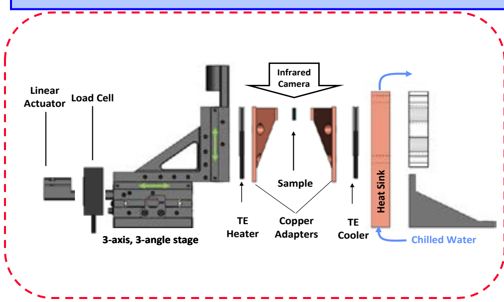
Gao, Panzer, Goodson et al., J. Electronic Materials, 2010

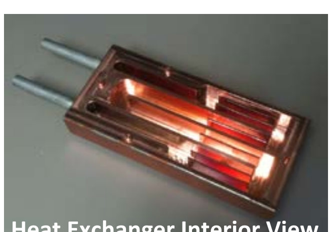
Electrodeposited Metal Nanowire TIMs

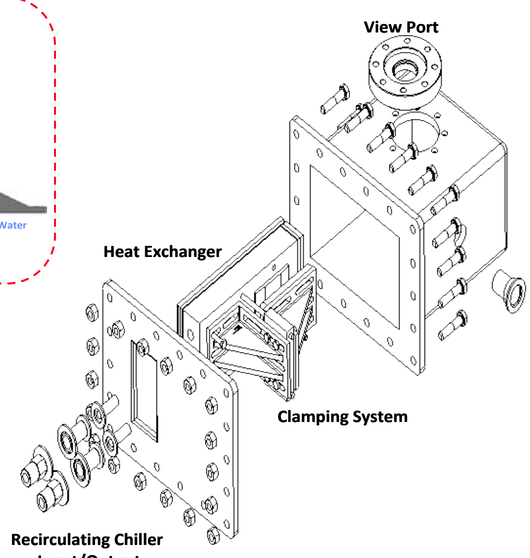
Michael Barako, Unpublished research

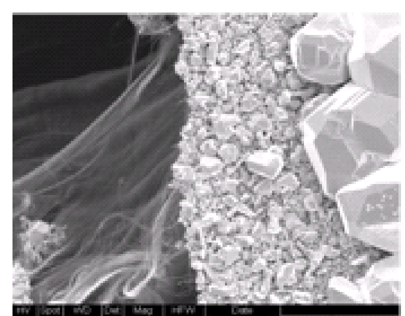


High Temperature IR Imaging & Characterization







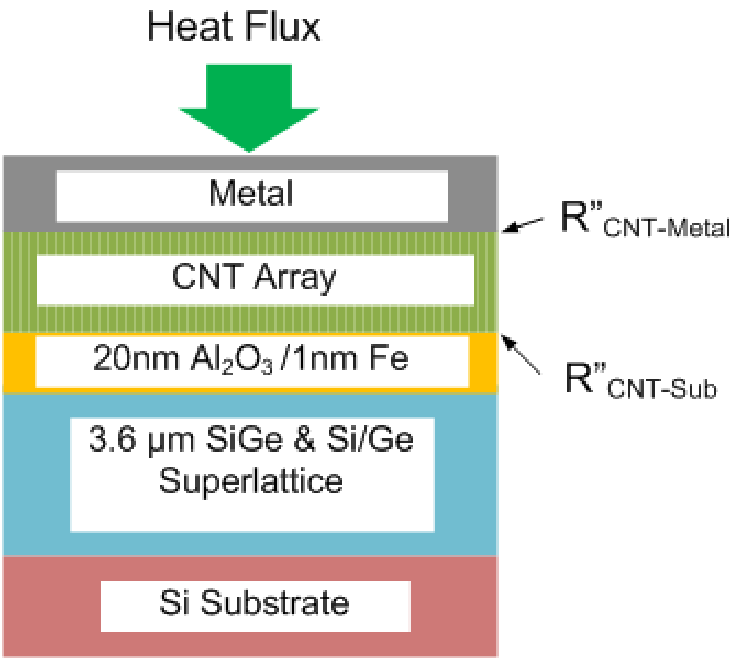


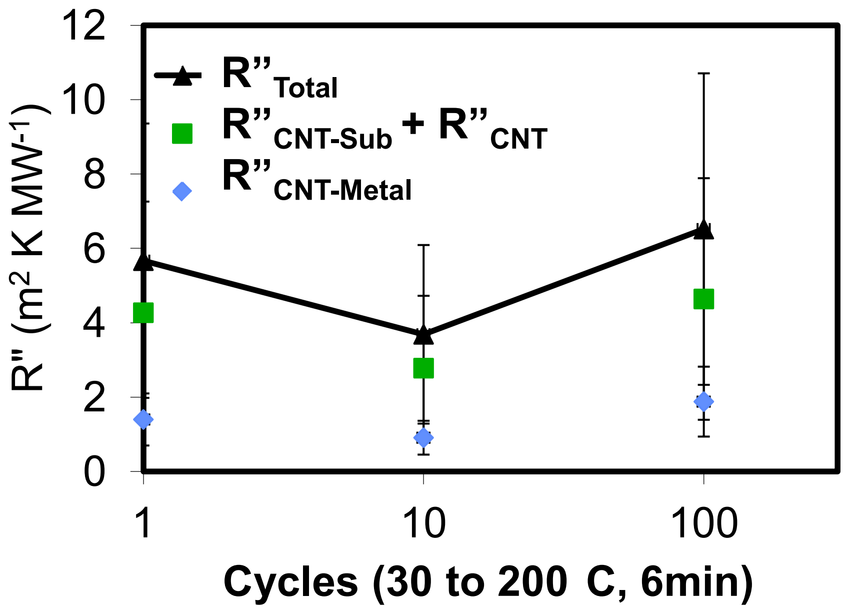
Nanoscale Conformable Coatings for Enhanced Thermal Conduction of CNT Films

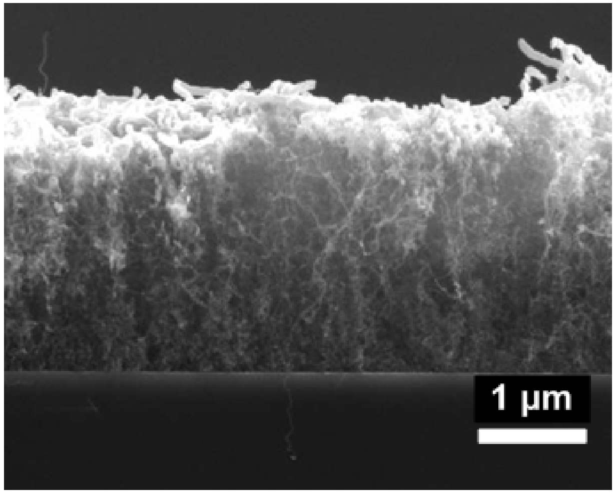
Marconnet, Motoyama, Barako, Gao, Pozder, Fowler, Ramakrishna, Mortland, Asheghi, and Goodson, "Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films," to appear in *Proceedings of ITHERM*, San Diego, May, 2012.

Approach: Interface Characterization on Thermoelectric with Thermal Cycling

Gao, Shakouri, Goodson et al., "Nanostructured Interfaces for Thermoelectrics," Proc. ICT 2009. J. Electronic Materials (2010).





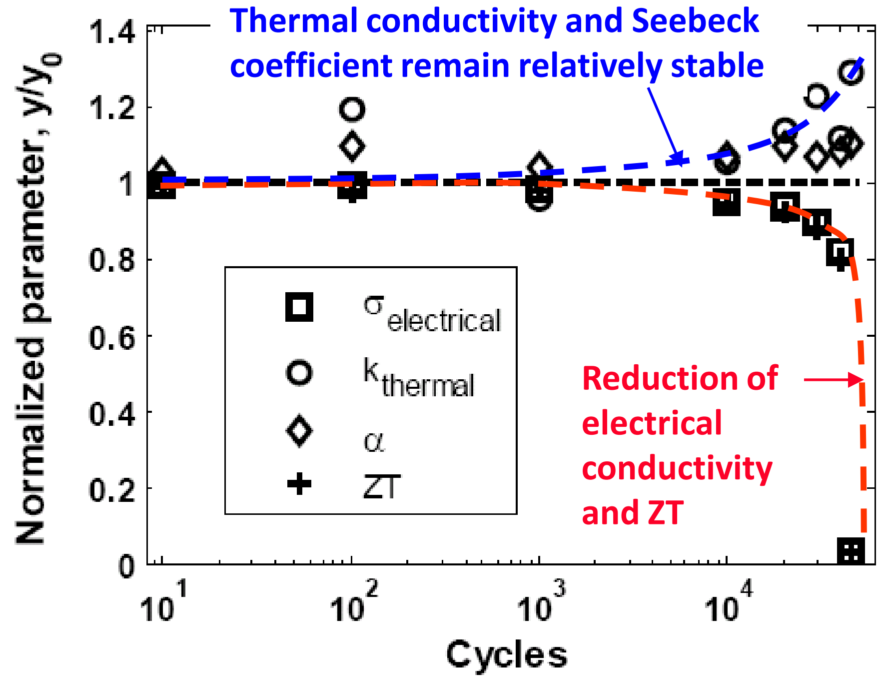


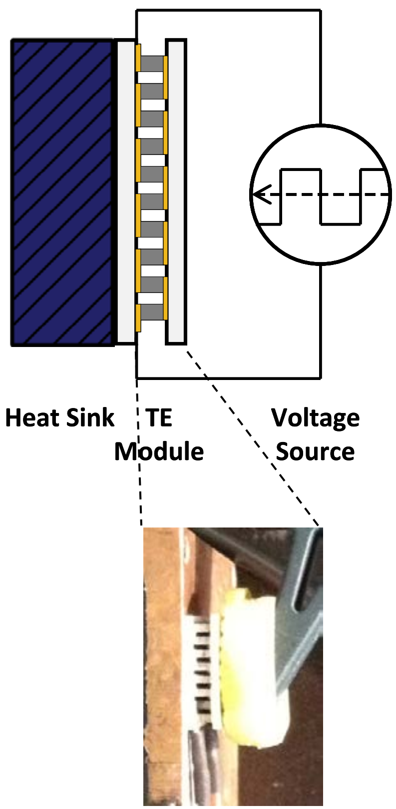
Resistances for 1.5, 2.5, and 40 micron thick CNT films varied between 0.035 and 0.055 cm^2 °C/W, with evidence of decreasing engagement with increasing film thickness.

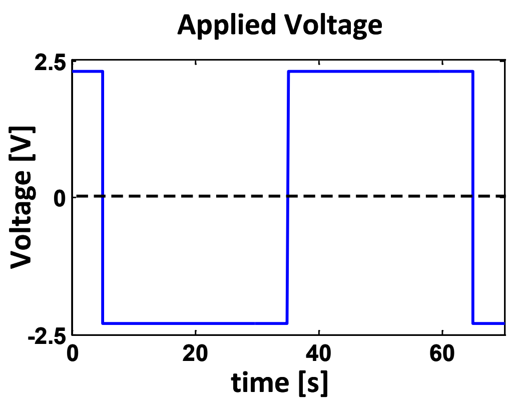
Thermal Cycling of TE Modules

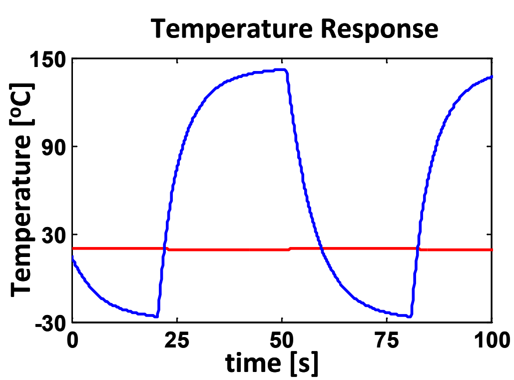
Thermoelectric performance was characterized during thermal cycling. Performance analysis includes:

- **Individual TE properties**
- **Figure of Merit ZT**
- **High resolution imaging of mechanical failure**

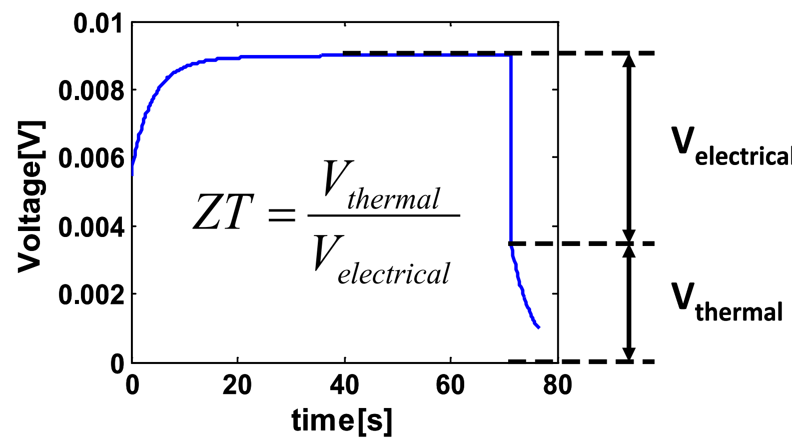








A modified Harman technique was developed to measure the TE figure of merit *ZT* and the electrical resistance *R*.

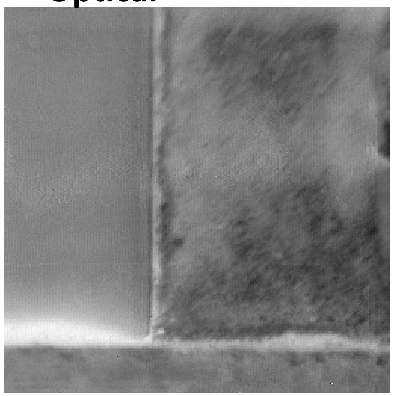


Low DC current is sourced (10 mA) and the thermal and electrical components of voltage are measured.

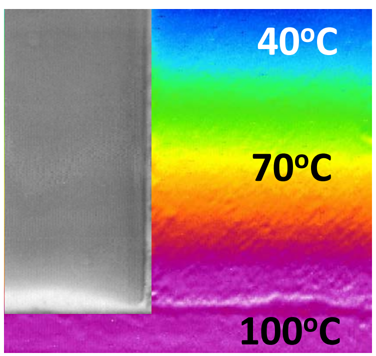
Infrared Failure Analysis of TE Modules

Before Cycling

Optical

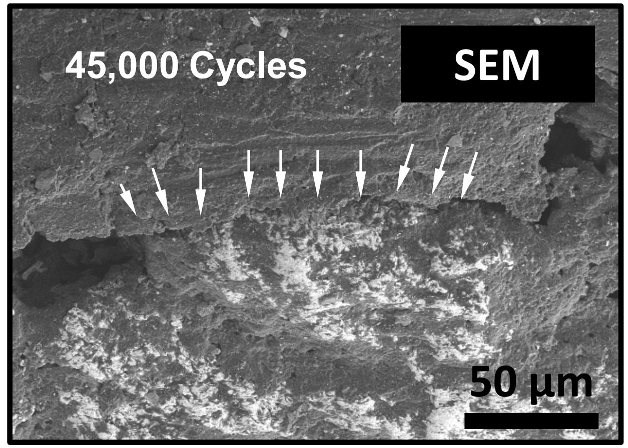


Infrared

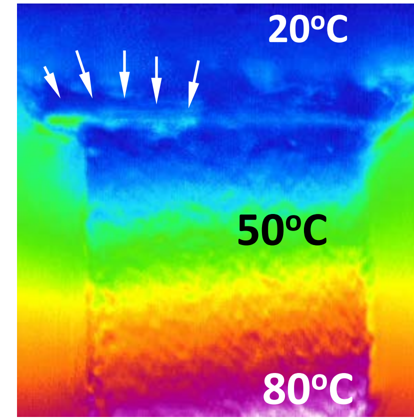


A modified Harman technique was developed to measure the TE figure of merit *ZT* and the electrical resistance *R*.

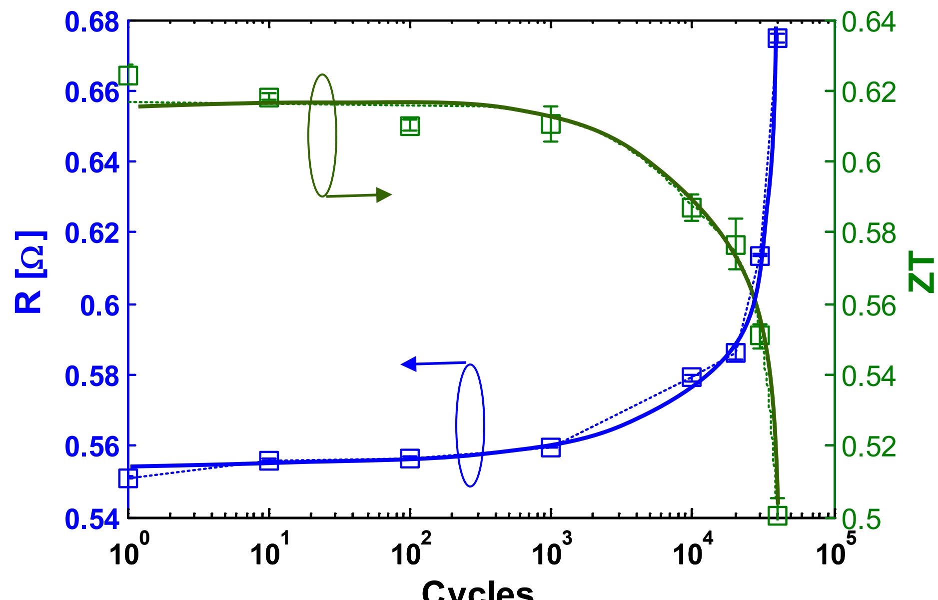
After 45,000 Cycles

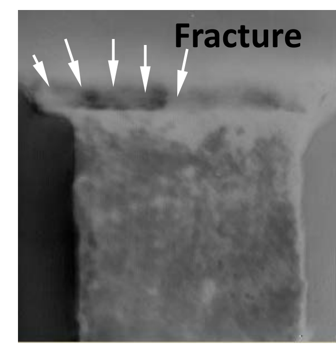


SEM courtesy of Yuan Gao



Infrared



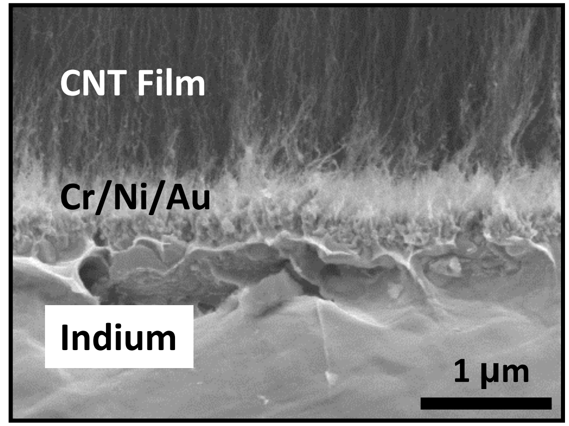


Optical

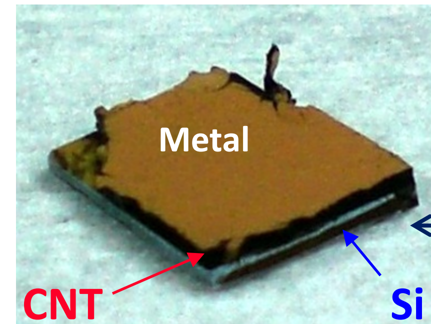
Barako, Gao, Marconnet, Asheghi, Goodson, *"Solder-Bonded Nanotube Thermal Interface Materials," to appear in Proceedings of ITHERM, San Diego, May, 2012.*

Indium Bonding

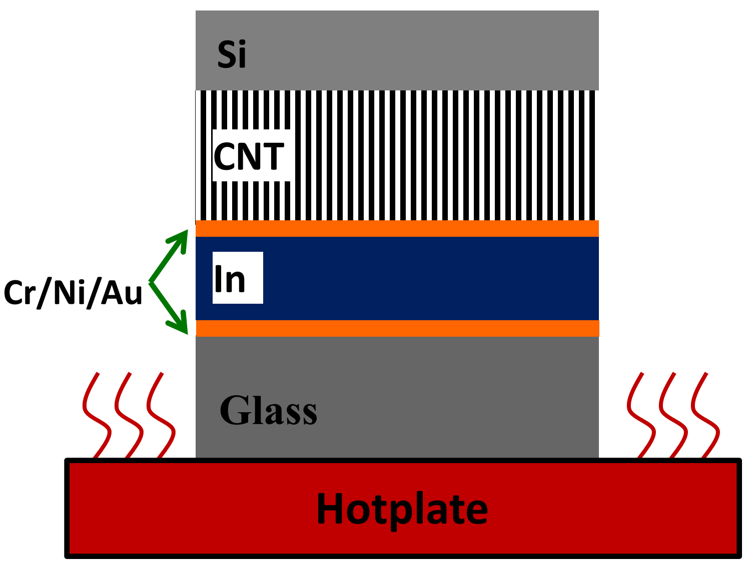
- Indium (In) foil† is obtained (25 µm thick).
- Cleaned and etched using:
    1. Acetone
    2. Isopropyl alcohol
    3. Deionized water
    4. Solder flux 5R



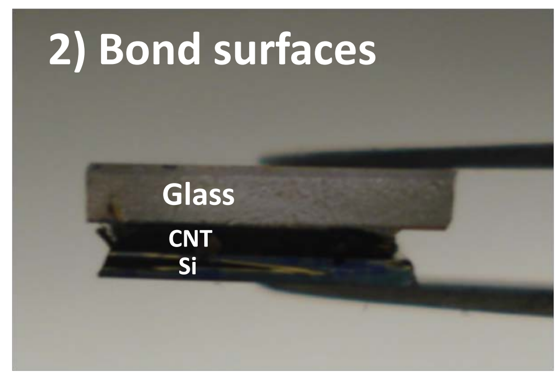
1) Metallize Substrates



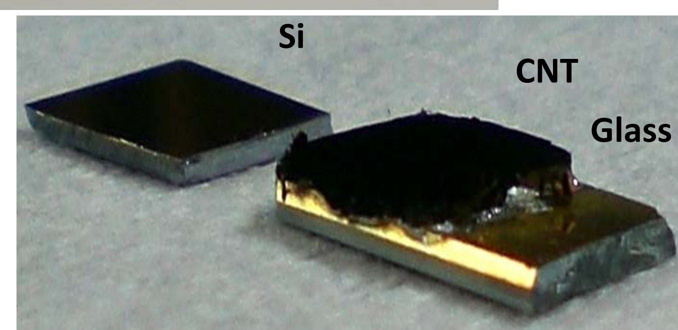
- The foil is compressed between the CNT film and the glass substrate with light pressure
- The stack is placed on a hot plate at 180°C for one minute. This melts and bonds the indium to the adjacent surfaces. (T_{melt} = 156.6°C)



† Indium foil by Indium Corp.


2) Bond surfaces

3) Remove growth Si



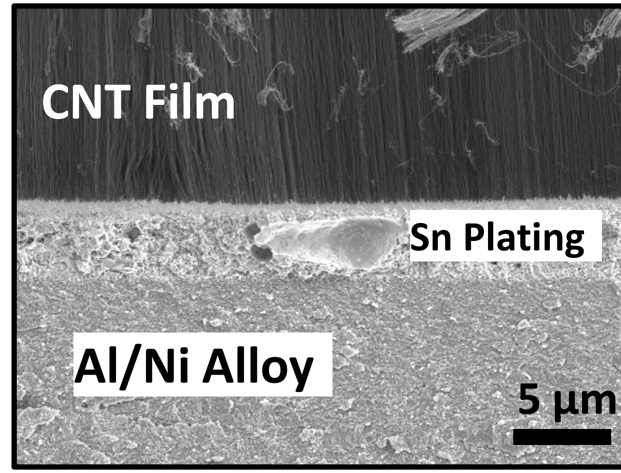
Nanofoil Bonding

Barako, Gao, Marconnet, Asheghi, Goodson, "Solder-Bonded Nanotube Thermal Interface Materials," to appear in Proceedings of ITHERM, San Diego, May, 2012.

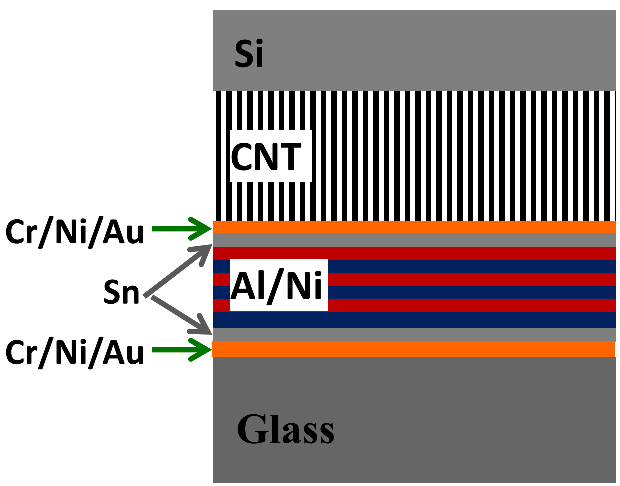
- Nanofoil‡ (NF) is a 40µm Al/Ni superlattice which ignites and exothermically alloys to adjacent surfaces

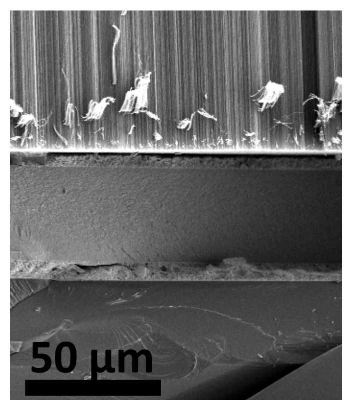
- NF is placed between two gold surfaces. Pressure is applied and the NF is ignited, bonding the two surfaces

- Sn-plated NF bonds Au surfaces (forming Sn-Au bonds). The resulting intermetallic is stable up to 1000°C

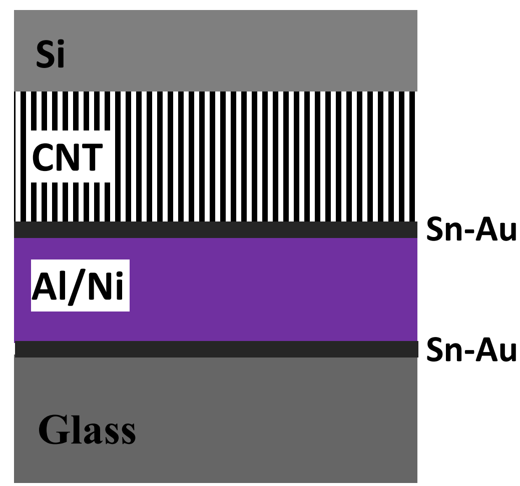


a) NF is placed between CNT and adjacent surface





b) NF alloys to form Sn-Au bonds to adjacent surfaces



‡ Nanofoil® by Indium Corp.

Infrared Microscopy

Comparative infrared (IR) microscopy is used to determine:

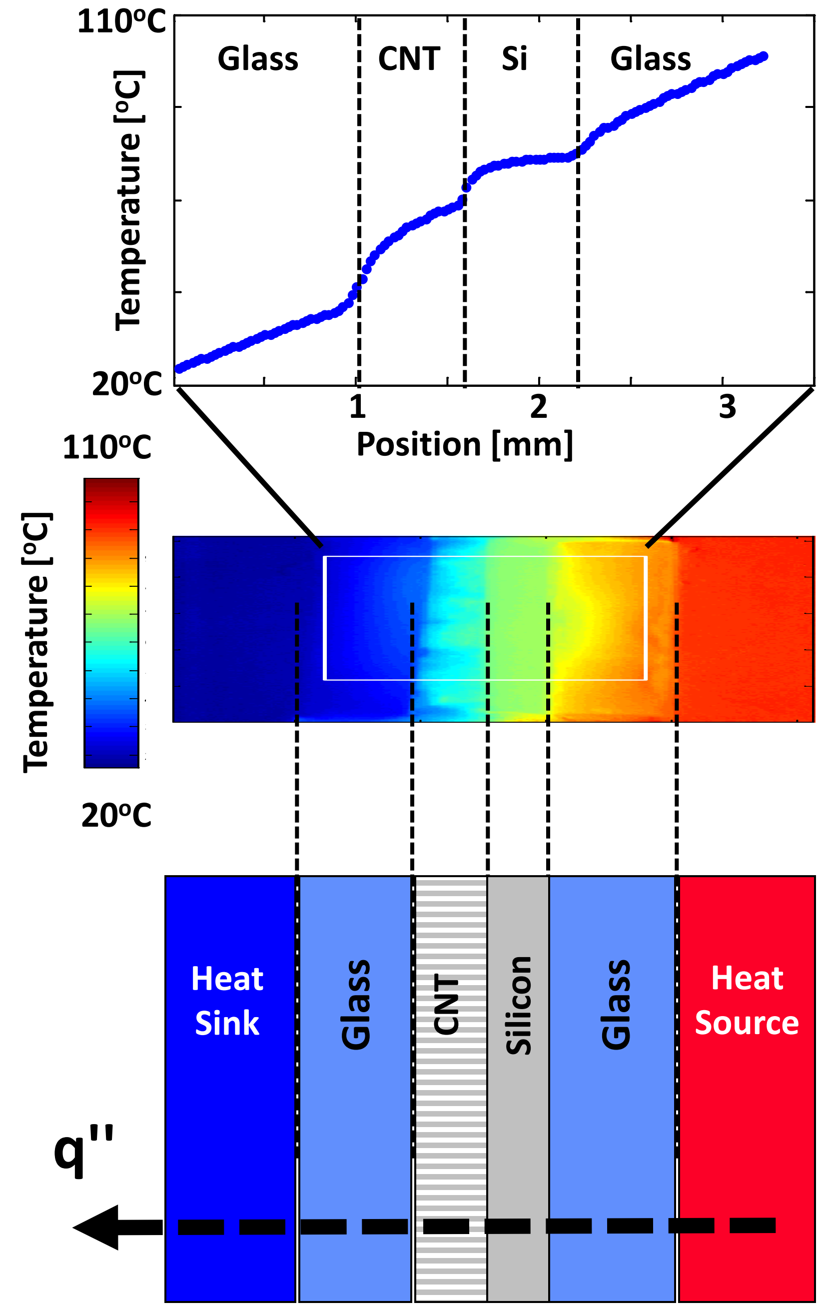
- **thermal conductivity of the CNT film**
- **boundary resistance of the bonded interface**

Measurement Procedure &Data analysis:

1. The sample is placed between two pieces of glass. This entire stack is placed between a heat source and a heat sink.
2. Heat conducts through the sample and a steady state, 1-D temperature field is established according to Fourier's Law.
3. The cross-sectional temperature map is recorded using the IR microscope
4. From the IR temperature map, each cross-section is averaged to generate a 1-D temperature profile through the stack
5. The conduction heat flux is calculated using the temperature gradient in the glass reference layers and Fourier's Law:

$$q'' = k\frac{dT}{dx}$$

6. The amount of heat lost to convection and radiation is equal to the difference in heat flux values from the two reference layers. This was always found to be less than 10% of the total heat transfer.



IR Thermal Characterization

Thermal Conductivity

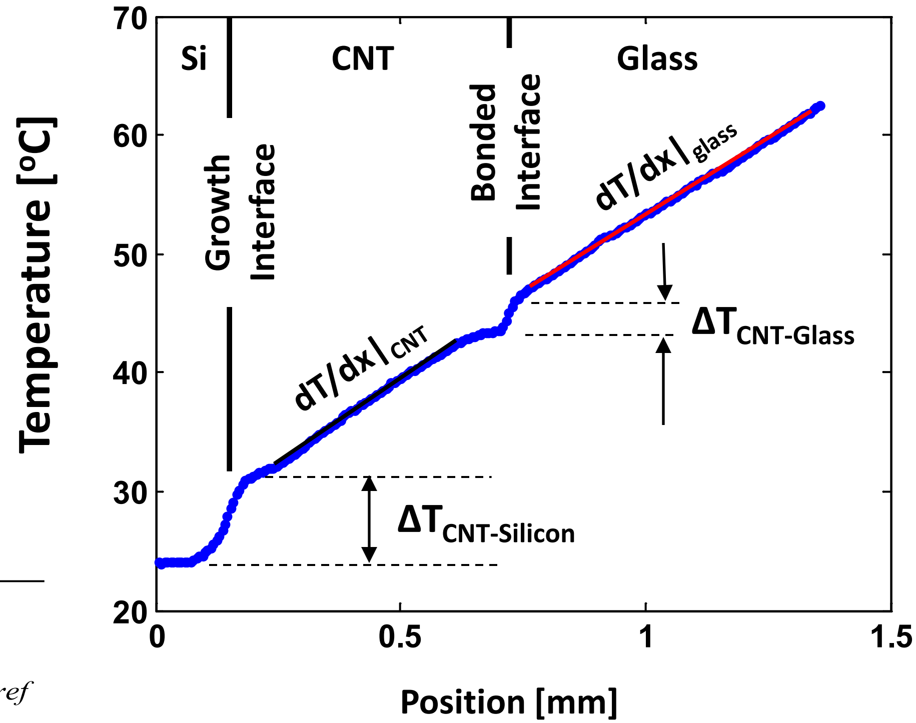
Using conservation of energy, Fourier's Law, and neglecting convection/radiation, we get:

$$\frac{k_{sample}}{k_{ref}} = \frac{\left.\frac{dT}{dx}\right|_{ref}}{\left.\frac{dT}{dx}\right|_{sample}}$$

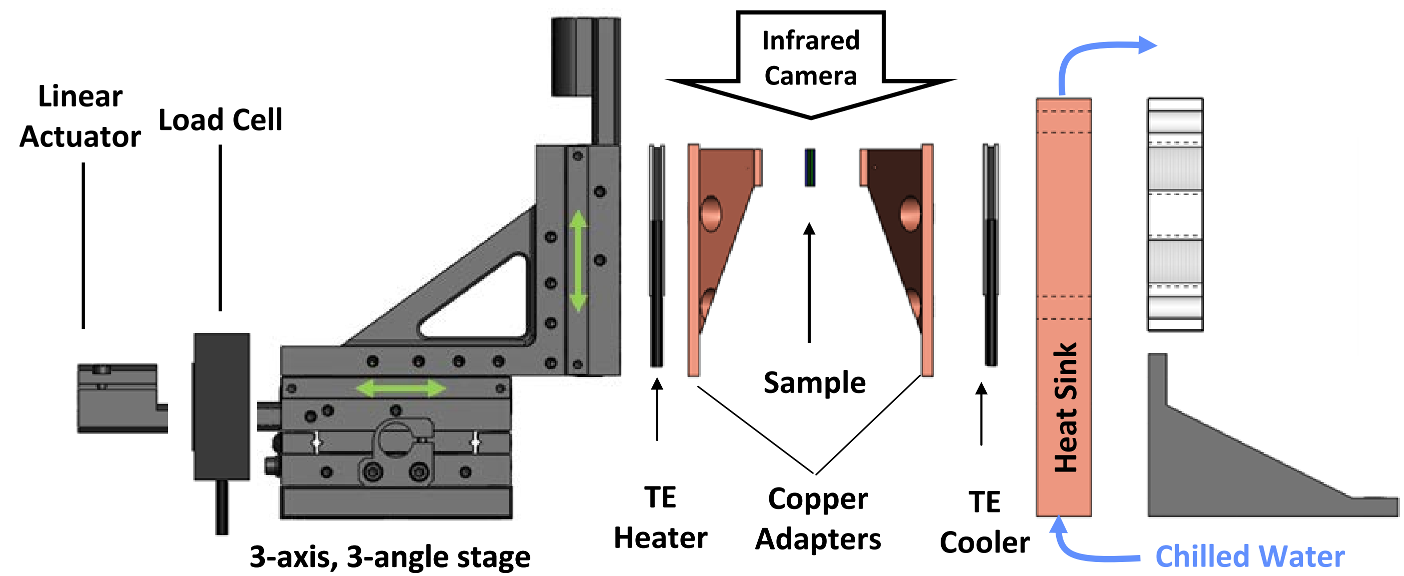
Thermal Boundary Resistance

Using the temperature drop at the interface and Fourier's Law

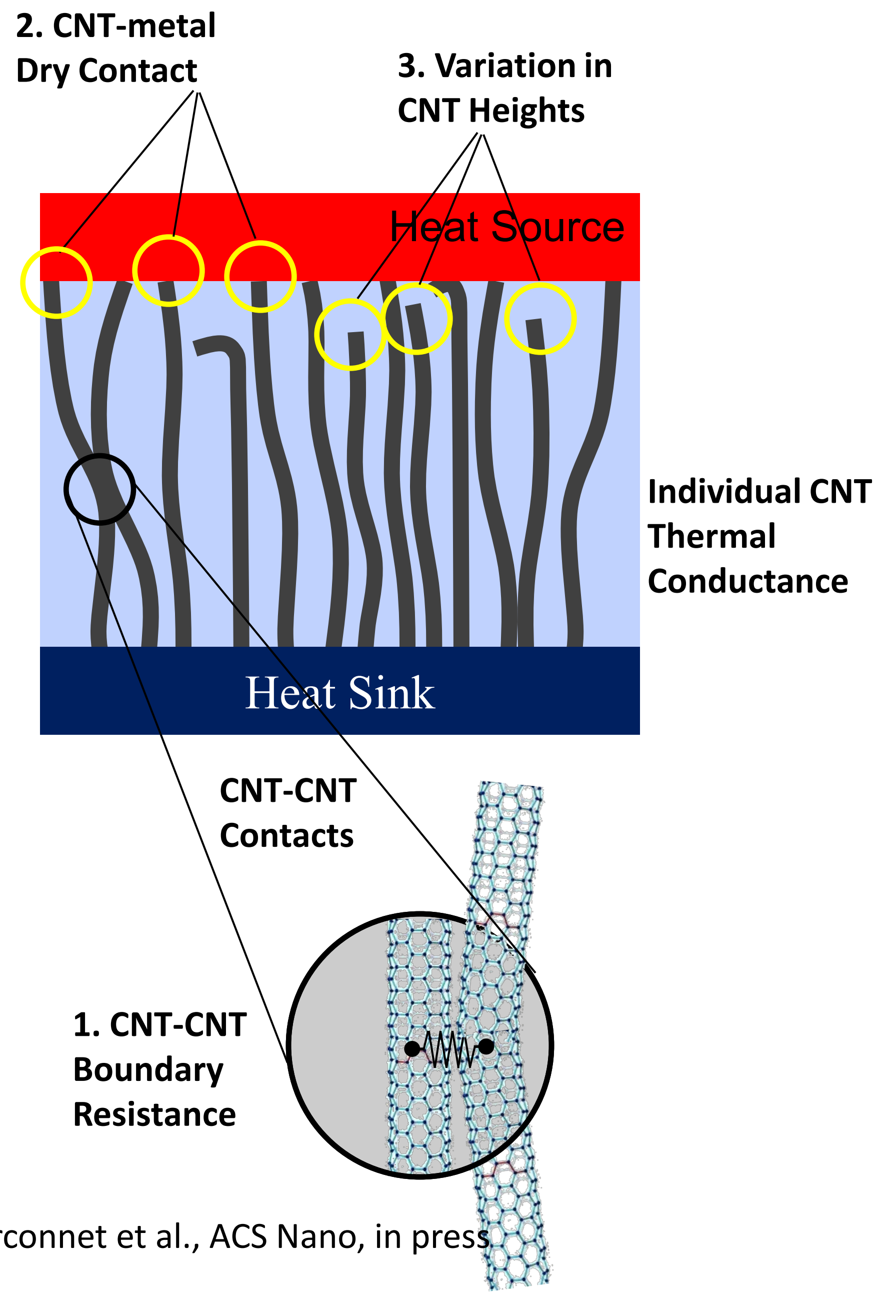
$$R''_{CNT-ref} = \frac{\Delta T_{int}}{q''} = \frac{\Delta T_{int}}{k_{ref}\left.\frac{dT}{dx}\right|_{ref}}$$



Compressive Measurement Apparatus

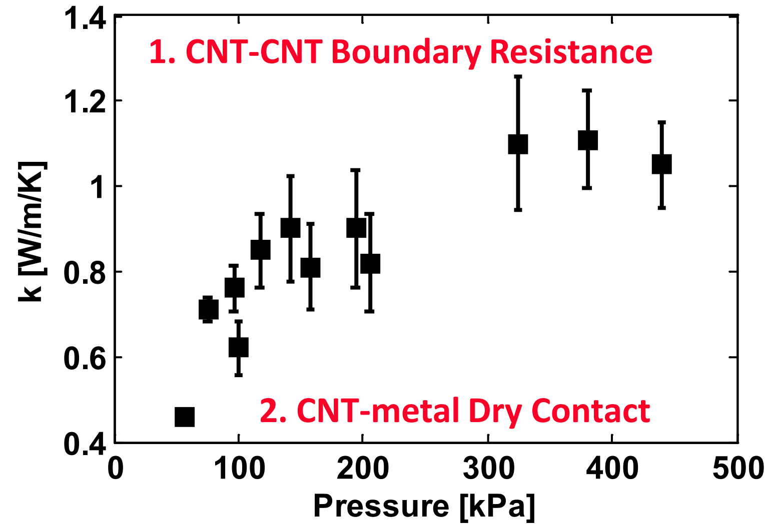


Thermal Properties Before Bonding

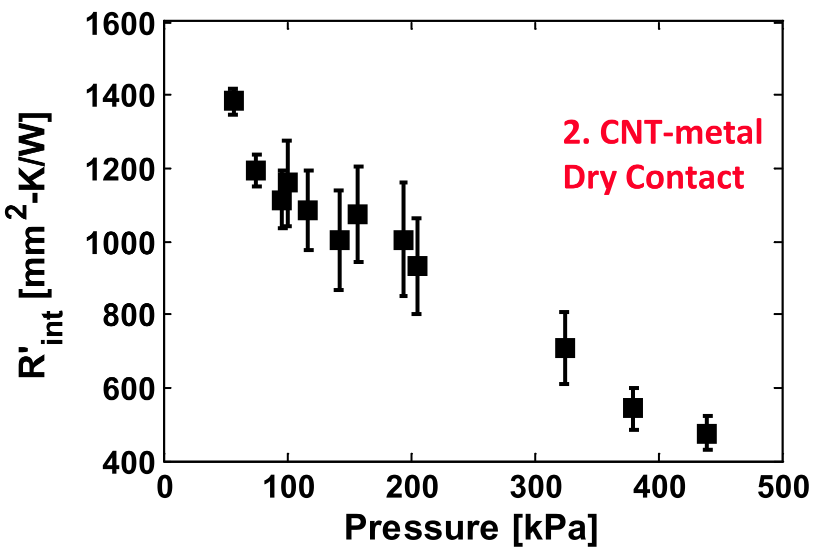


Marconnet et al., ACS Nano, in press

Intrinsic Thermal Conductivity, k_{CNT}



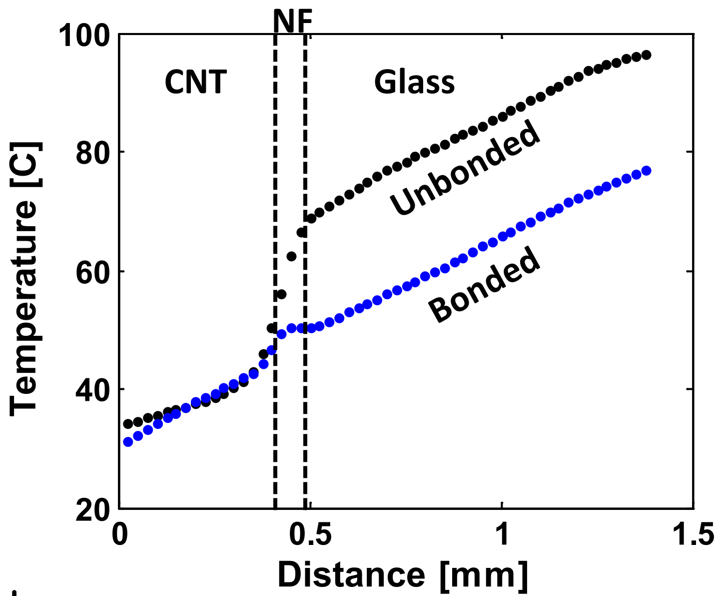
Thermal Boundary Resistance, R''_{int}



Bonded CNT Thermal Properties

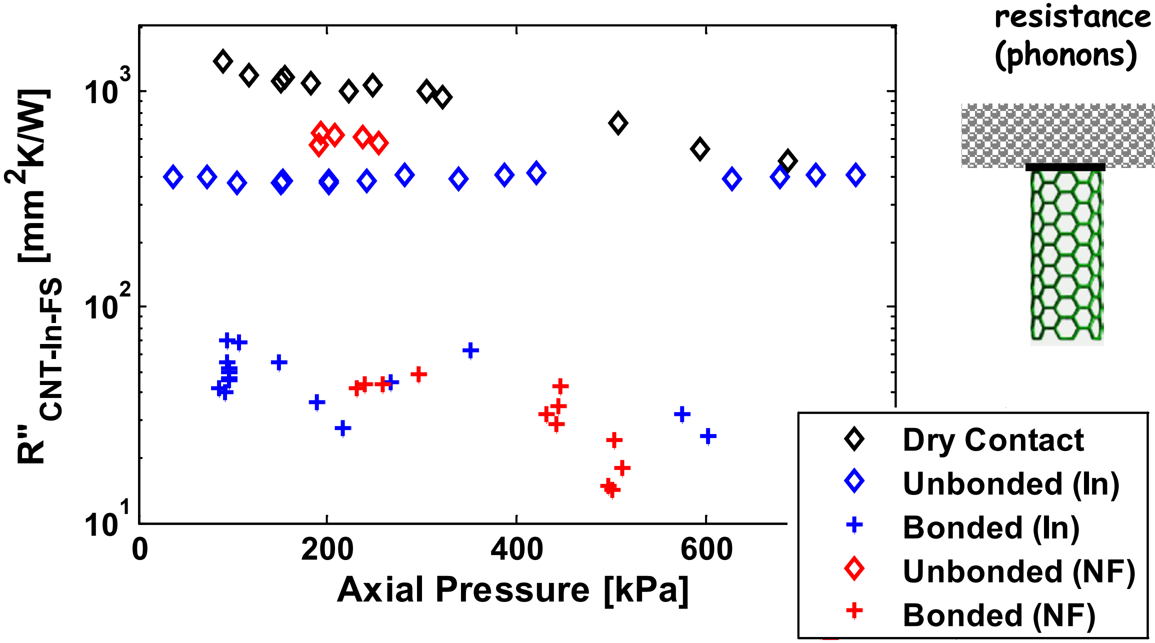
Thermal Properties after Bonding:

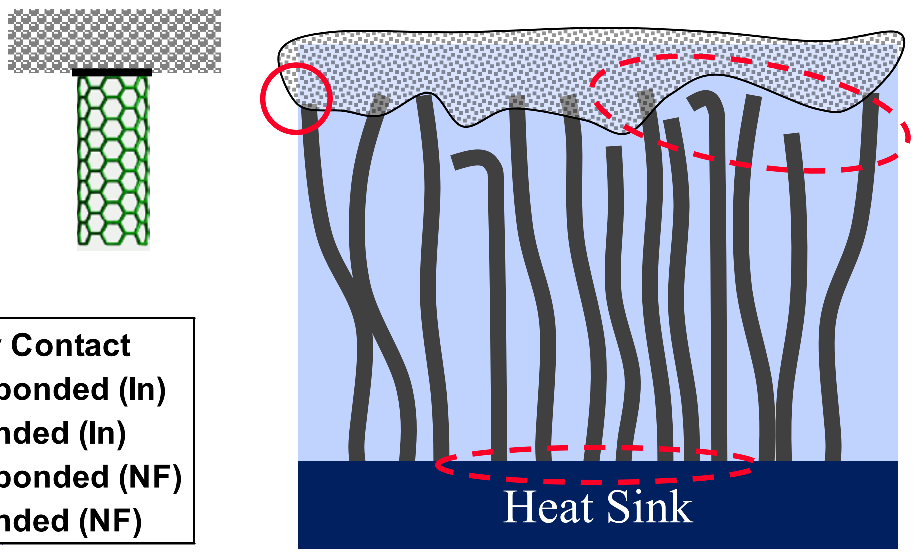
For constant q'', the interfacial temperature drop is reduced by an order of magnitude through solder bonding



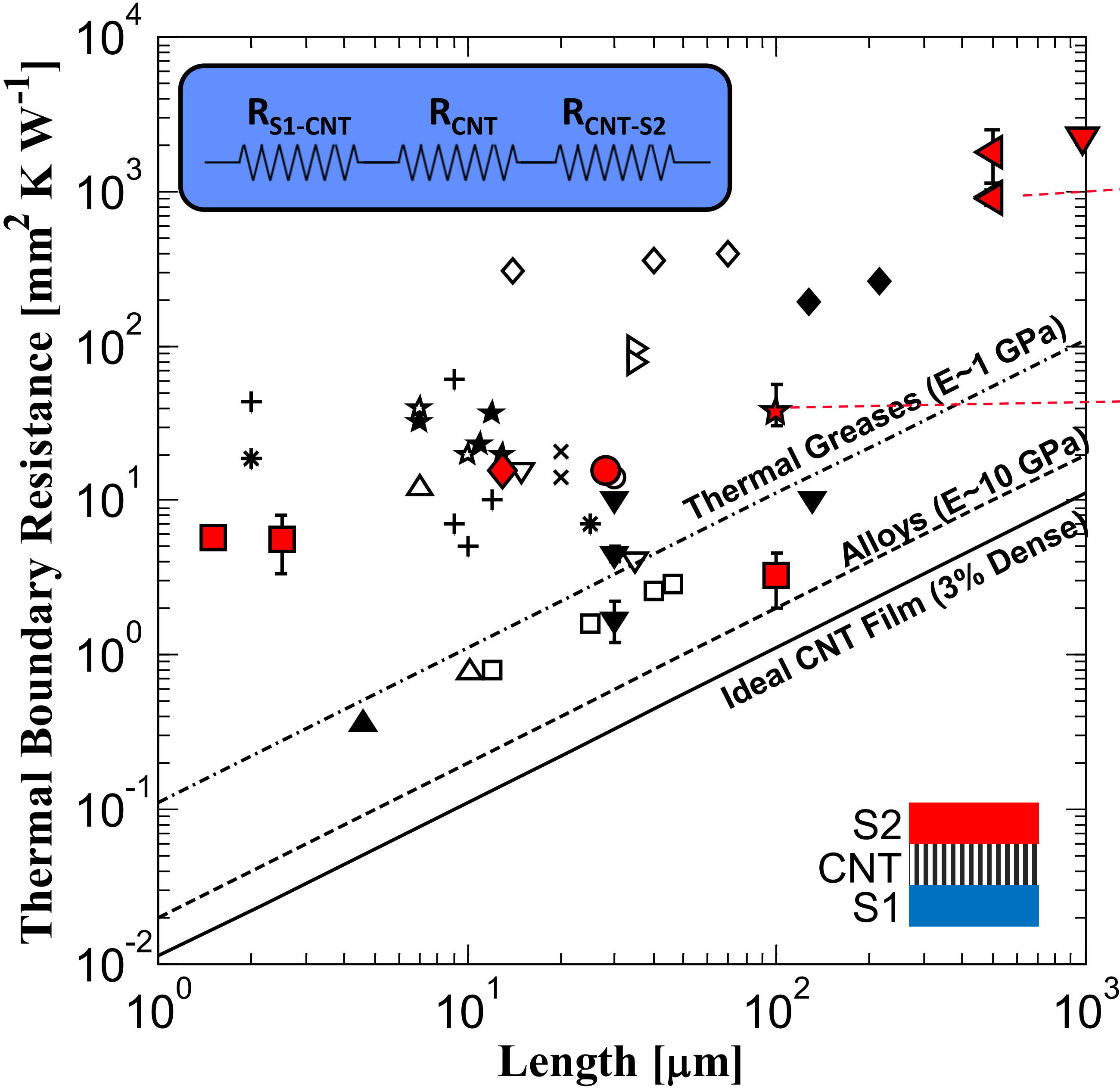
Indium wets to CNTs and engages more CNTs in conduction, increasing the bulk thermal conductivity of the film

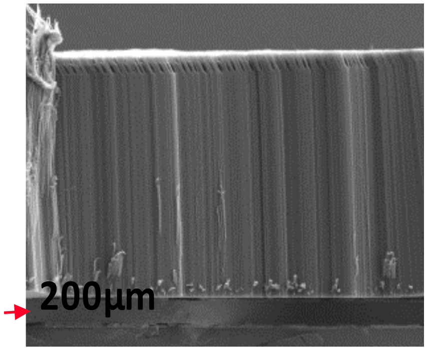
Thermal Boundary Resistance, R''_{int}

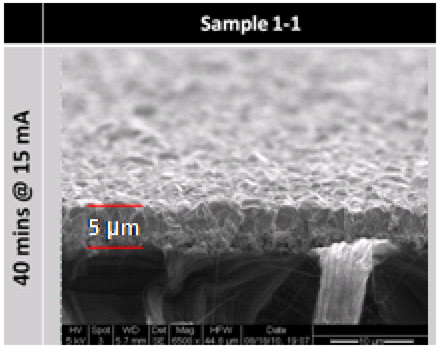




Total Thermal Resistance (S1-CNT-S2)

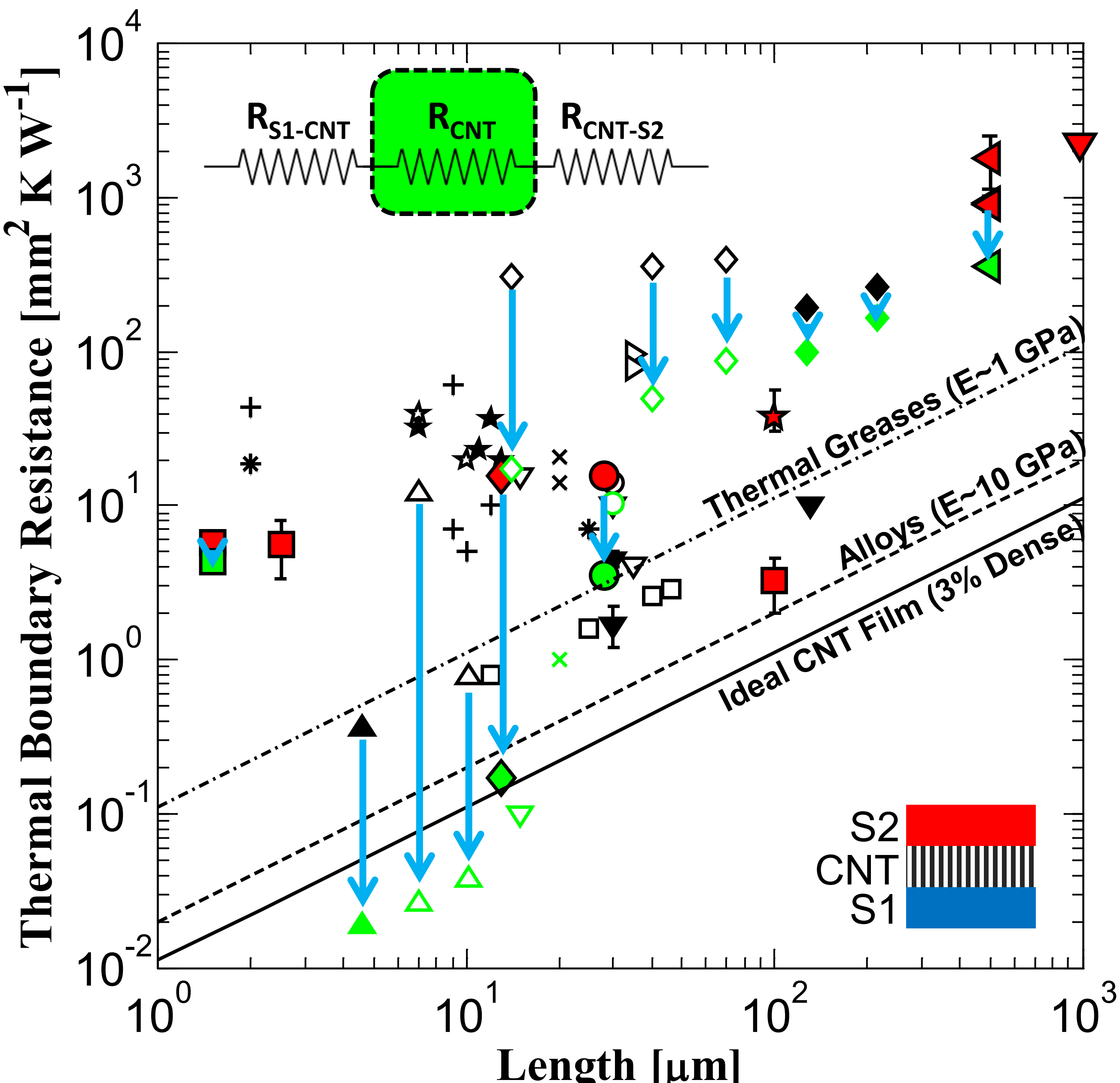






□ Yang *et al.* (2002,2004)
▲ Tong *et al.* (2007)
△ Tong *et al.* (2006)
◇ Pal *et al.* (2008)
◆ Son *et al.* (2008)
○ Xu *et al.* (2006)
+ Zhang *et al.* (2008)
★ Xu *et al.* (2006a)
☆ Xu *et al.* (2006b)
✱ Cola *et al.* (2008)
× Hodson *et al.* (2011)
▽ Cola *et al.* (2007)
▷ Aradhya *et al.* (2008)
▼ Cross *et al.* (2010)
● Panzer *et al.* (2008)
◆ Hu *et al.* (2006)
■ Gao *et al.* (2010)
◀ Barako *et al.* (2012)
▼ Marconnet *et al.* (2011)
★ Marconnet *et al.* (2012)

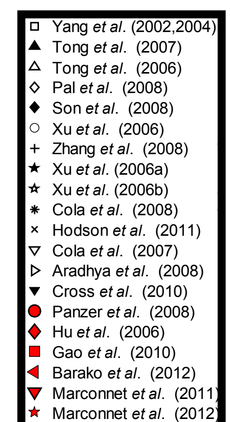
The Intrinsic Thermal Resistance of The CNT Films



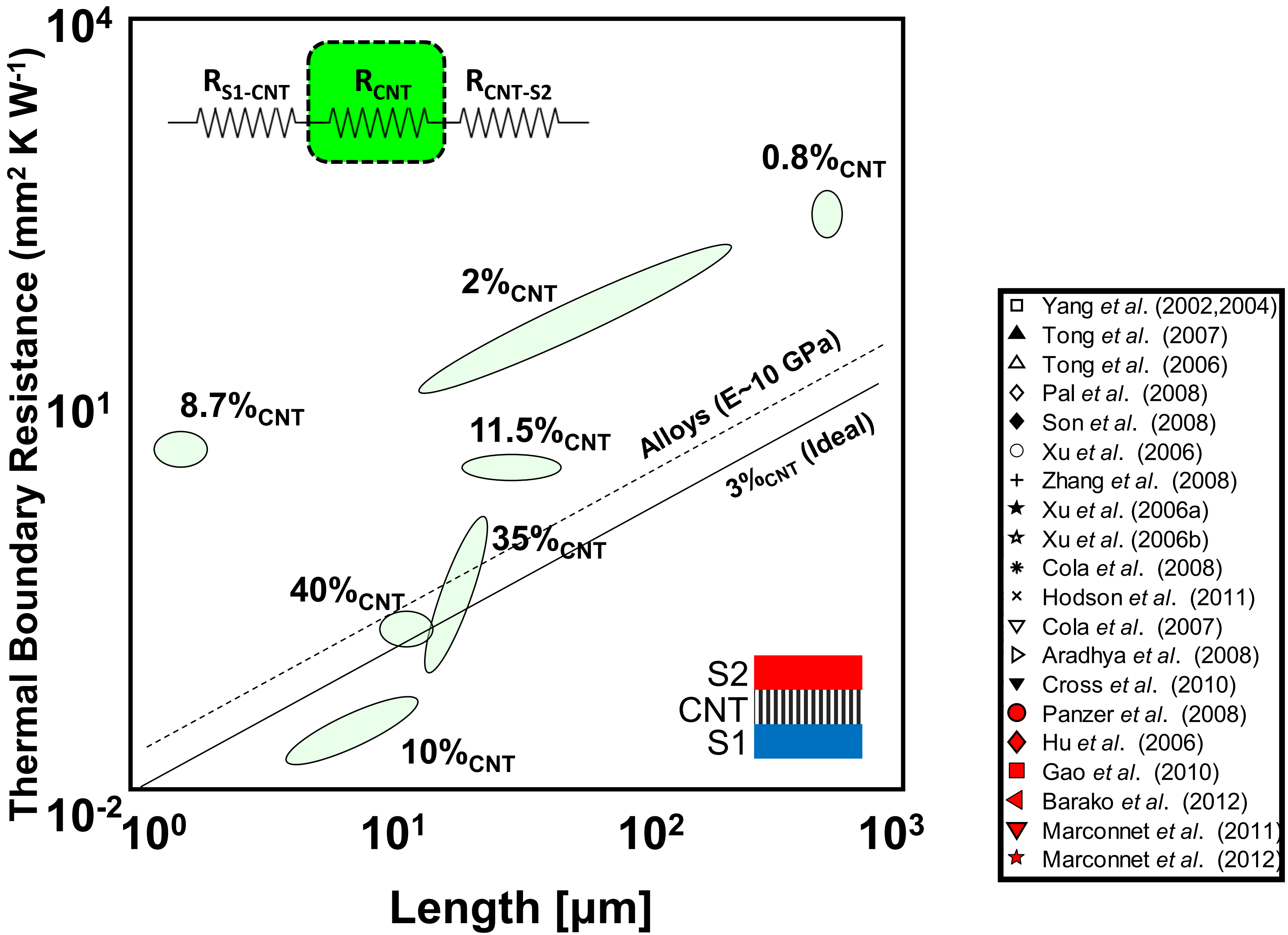
If the CNT-Substrate/ metalization interface resistance could be reduced, the intrinsic thermal resistance of the CNT films would outperform solders

The blue arrow shows the magnitude of R_S1-CNT and R_CNT-S2).

The green data points indicate the magnitude of the intrinsic R_CNT.



Impact of CNT Volume Fraction on Intrinsic Thermal Conductivity



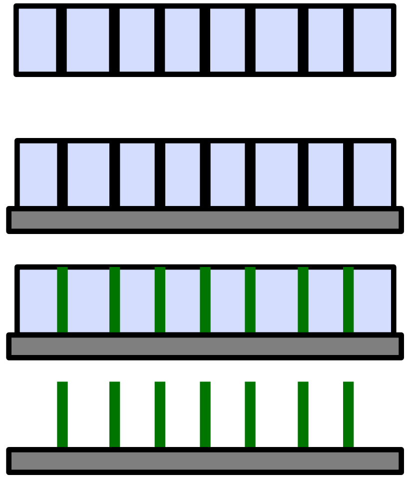
Electrodeposited Metal Nanowire TIMs

a) Polycarbonate membrane is etched to create cylindrical pores

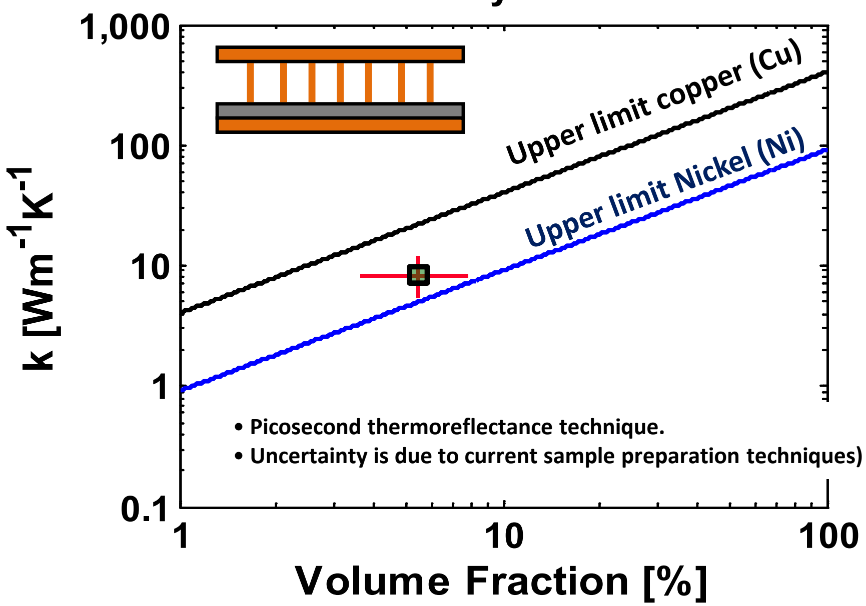
b) Catalyst Pt/Pd is deposited on one side of the membrane

c) Metal is eletrodeposited into the pores

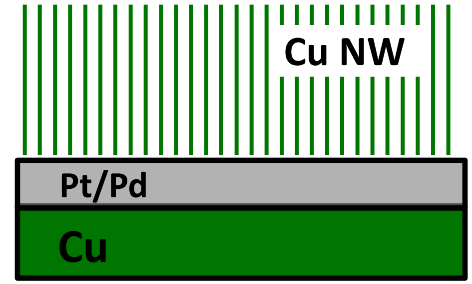
d) Membrane is etched away, leaving freestanding nanowires

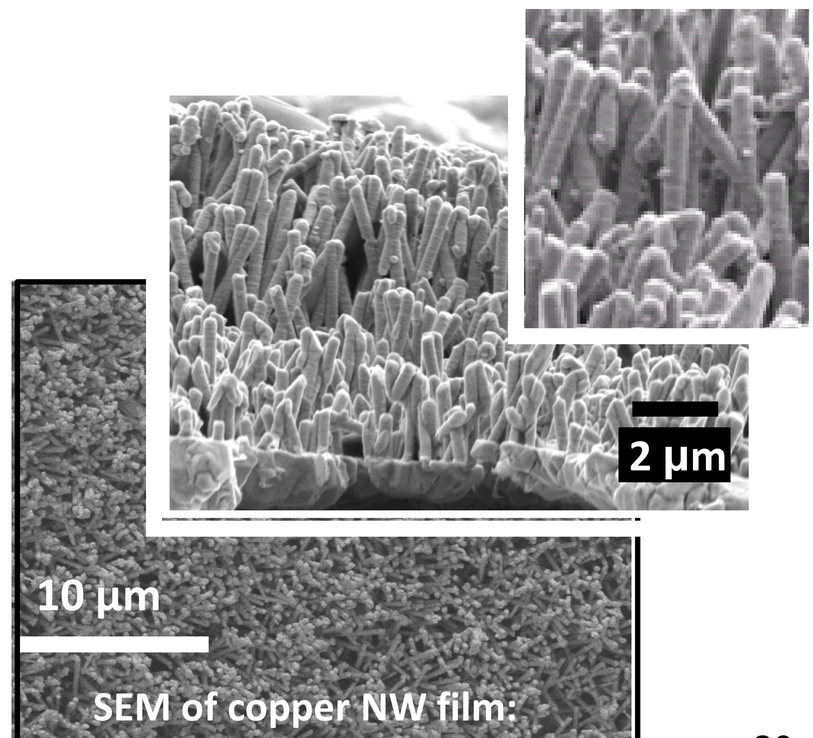


Thermal Conductivity vs. Volume Fraction

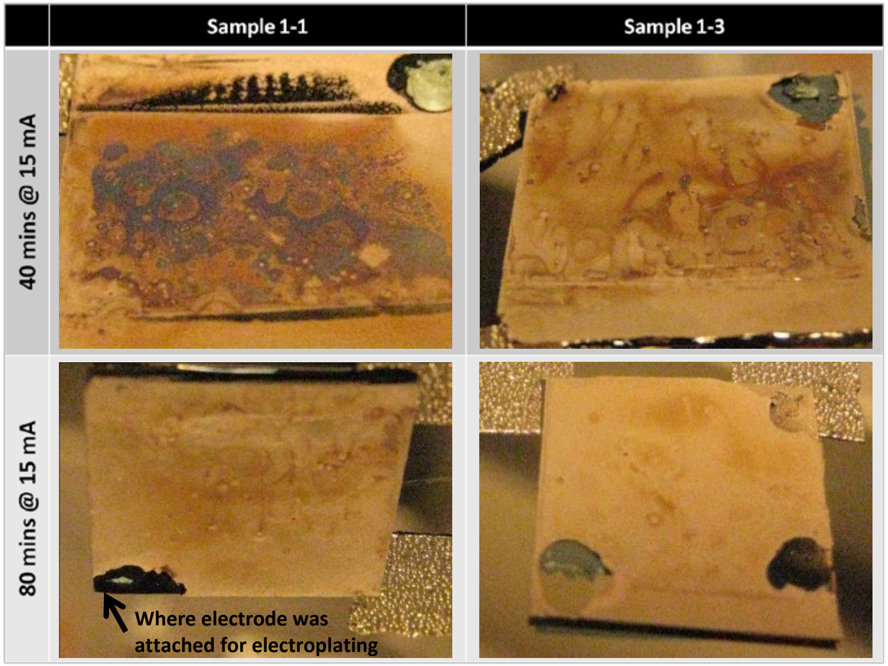


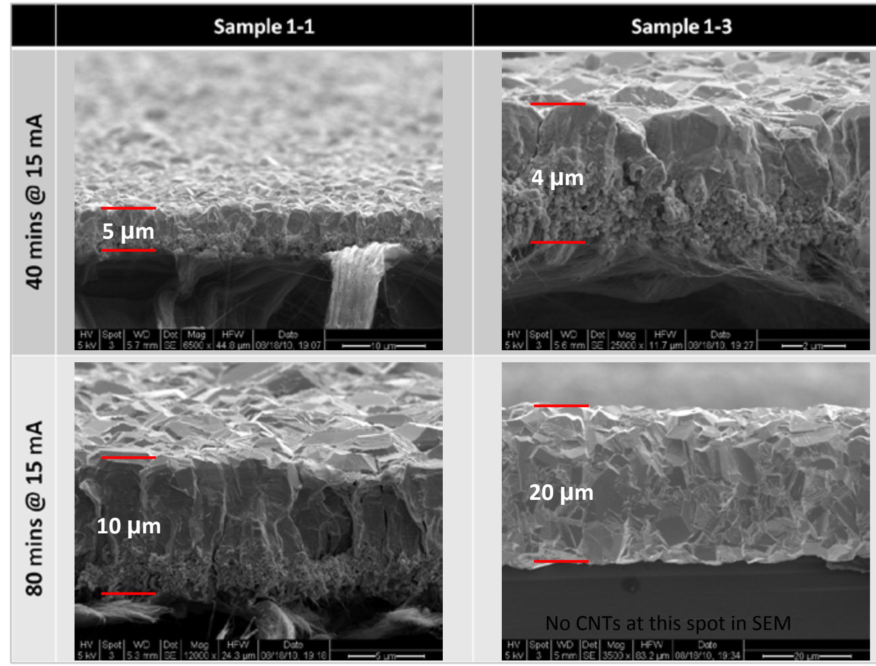
Nominal geometry:
•Cylindrical NWs
•10 µm film thickness
•200 nm diameter

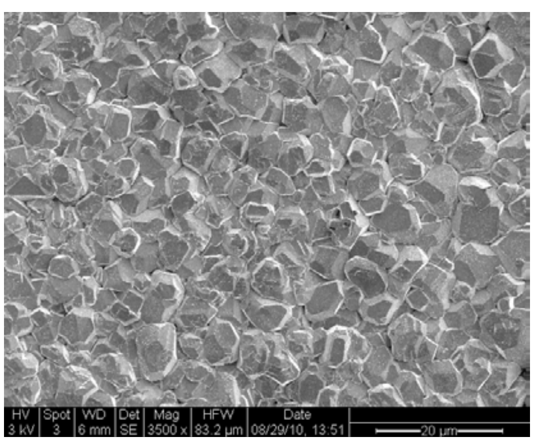


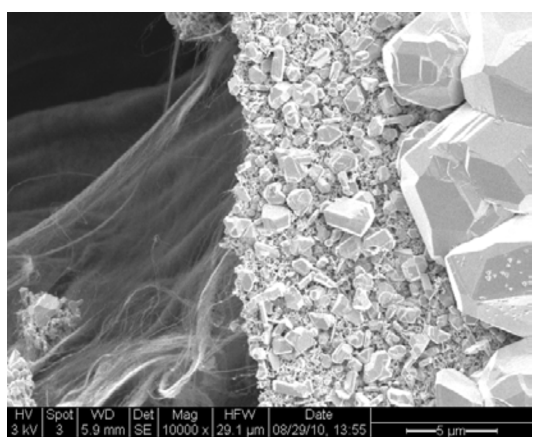


Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films





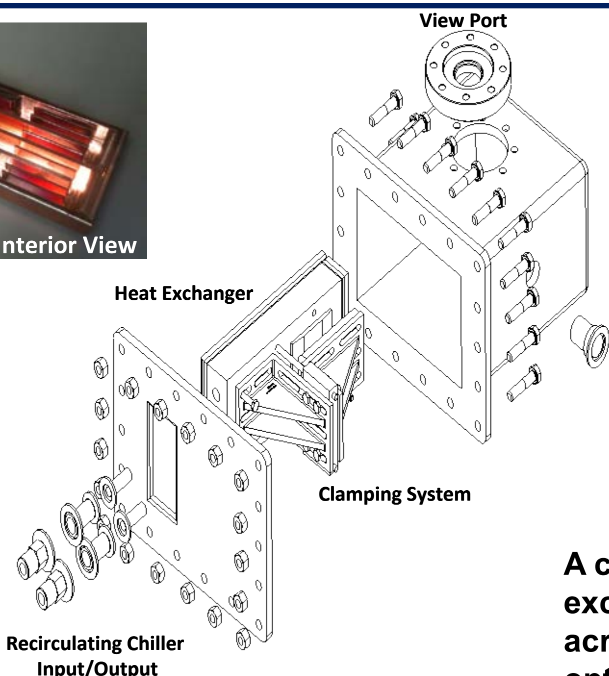


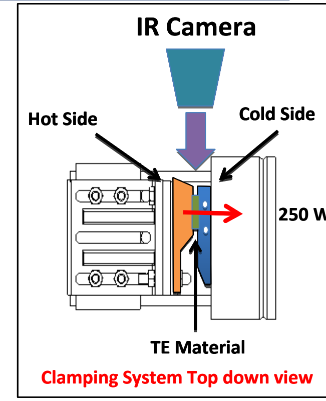


Uniform coating & Grain Size most of the area except where the electrode is attached

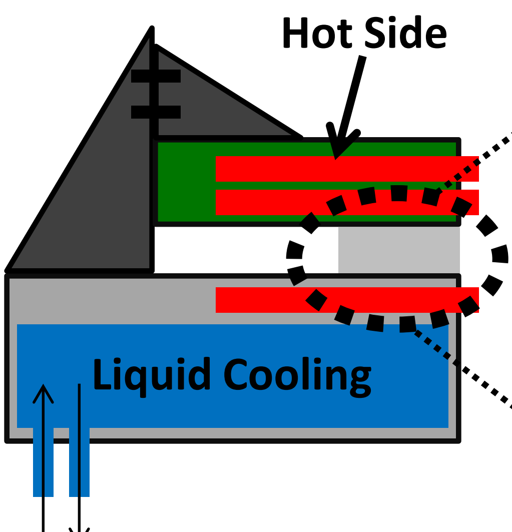
Marconnet, Motoyama, Barako, Gao, Pozder, Fowler, Ramakrishna, Mortland, Asheghi, and Goodson, "Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films," to appear in Proceedings of ITHERM, San Diego, May, 2012.

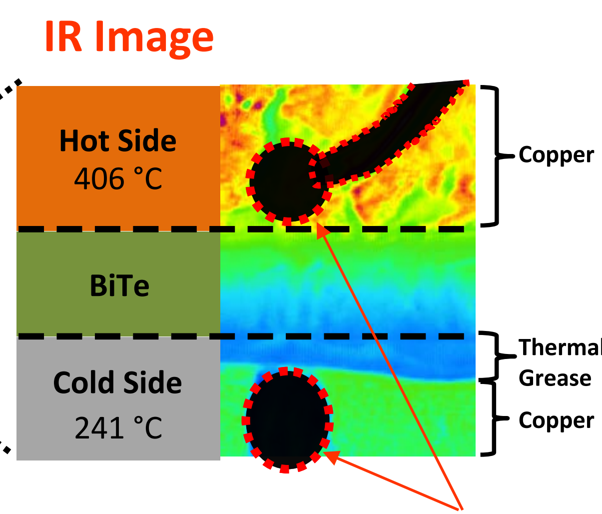
High Temperature Infrared Imaging

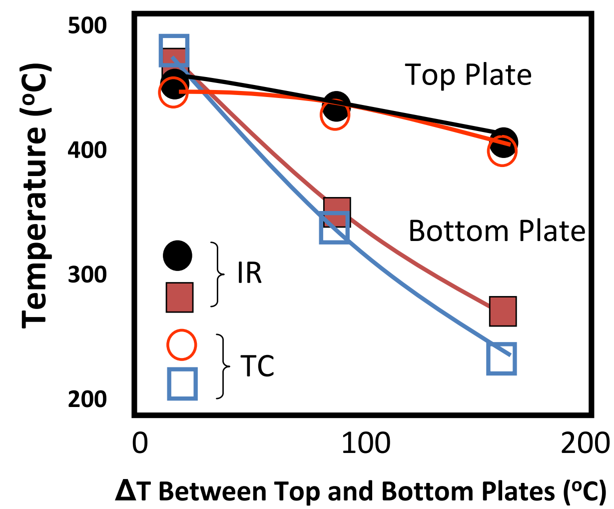




A custom-fabricated vacuum enclosure with integrated heat exchanger will be built to achieve >500 C temperature gradient across a TE sample and facilitate simultaneous electrical and optical measurements.

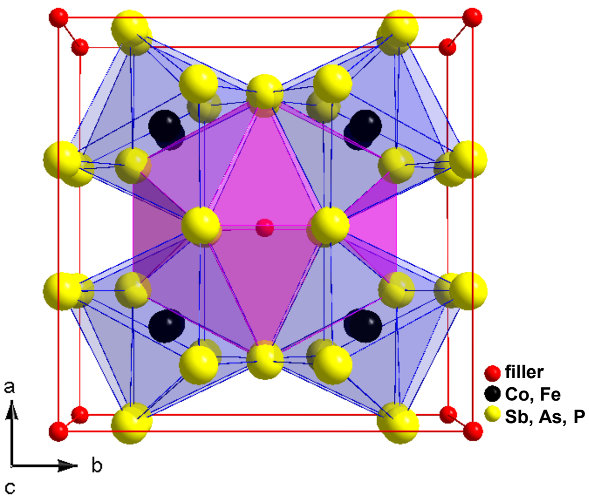






Bulk TE Materials for Automotive Applications

Prof. G. Nolas, Dr. Yongkwan Dong



Glen Slack initiated PGEC concept with skutterudites:

- ✓ Fillers should be loosely bonded to the cage-forming atoms.
- ✓ Fillers should have large atomic displacements.
- ✓ Fillers act as independent oscillators (“rattlers”).
- ✓ Interaction of rattlers with the normal modes should lower lattice thermal conductivity.
- ✓ Phonon-scattering centers (“rattlers”) should not greatly affect electronic properties.

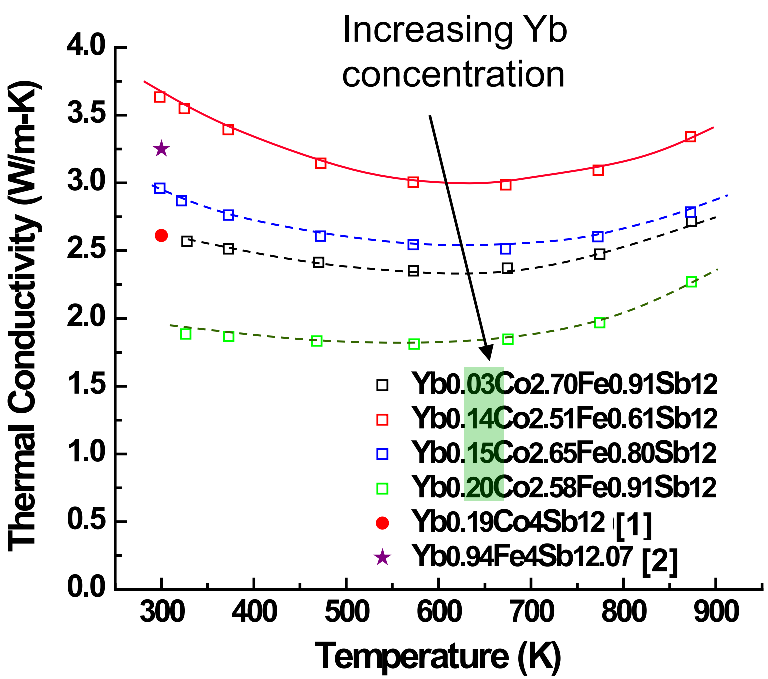
- Ytterbium (Yb) partially-filled skutterudites
  - Partial filling optimizes lattice thermal conductivity reduction[1]
  - Yb intermediate valence in $CoSb_3$ maximizes filler concentration while minimizing added carriers[2]
- P-type Ba partially filled skutterudites (high temp measurements at NIST & Clemson U.)
- Amorphous intermetallic alloys[3] (in collaboration with General Motors)
- Bi_2Te_3-alloys for High Resolution Infra-Red Thermometry (in collaboration with Marlow Ind.)
- Survey of other material systems with potential for enhanced thermoelectric properties

1. G.S. Nolas, et al, Phys. Rev. B 58, 164 (1998)
2. G.S. Nolas, et al, Appl. Phys. Lett. 77, 1855 (2000)
3. G.S. Nolas and H.J. Goldsmid, Phys. Stat. Sol. 194, 271 (2002)

Novel Materials Laboratory
University of South Florida

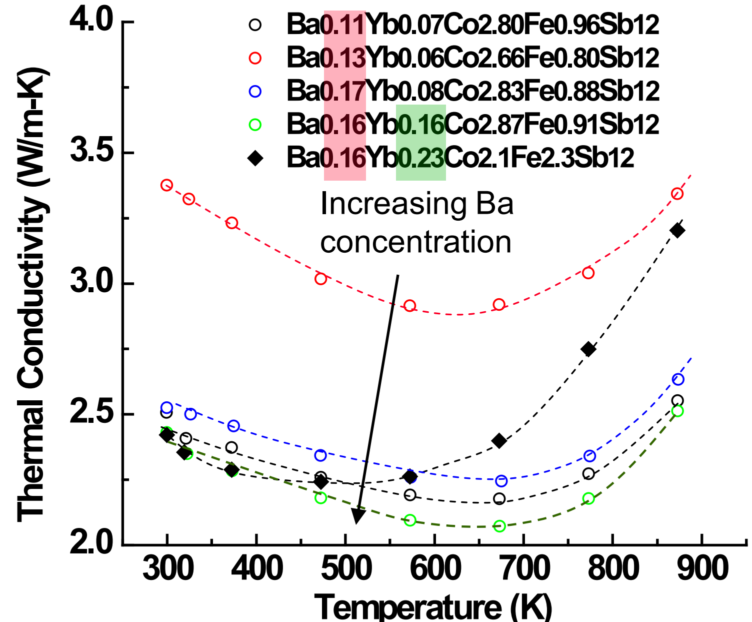
Thermal Conductivity of Yb-filled Skutterudites

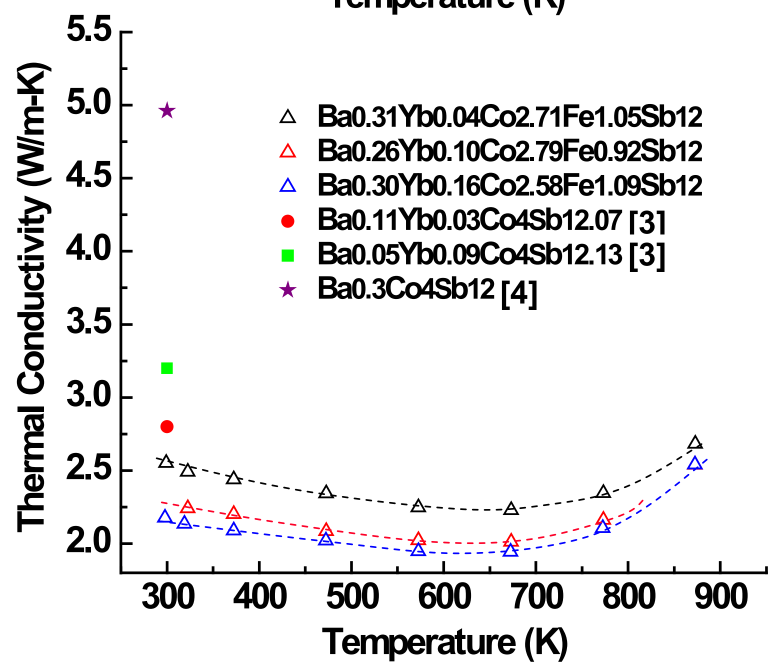
Partial filling optimizes lattice thermal conductivity reduction



1. G. S. Nolas, et al, Appl. Phys. Lett. 77, 1855 (2000)
2. P. F. Qiu, et al, J. Appl. Phys. 109, 063713 (2011)
3. X. Shi, et al, Appl. Phys. Lett. 92, 182101 (2008)
4. L. D. Chen, et al, J. Appl. Phys. 90, 1864 (2001)

p-type Ba + Yb filled Skutterudites





Dr. Boris Kozinsky

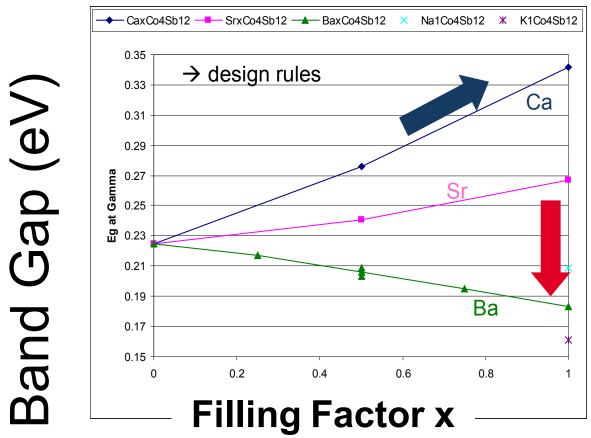
Effects of Fillers on electronic Properties of Skutterudites

•The effect of filling distorts the structure **locally**.

•Soft Sb rings accommodate the distortion.

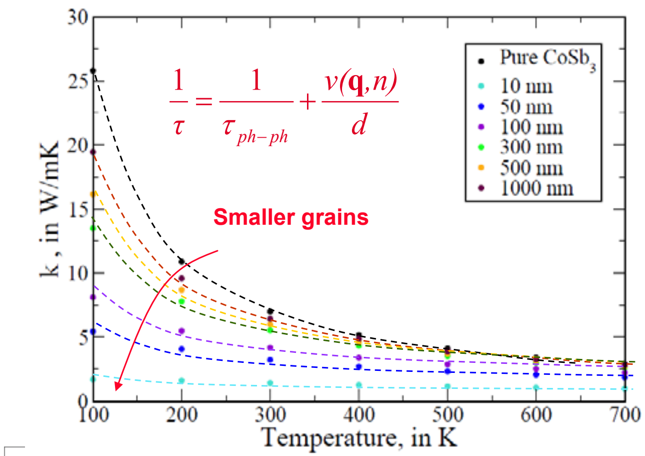
•Electrons from filler open **band gap**, while volume expansion closes the gap.

•Effect of **force constants** more important than filler mass.



Nanostructure Design for Thermal Transport

- New method developed for ab-initio thermal conductivity prediction. Grain boundary scattering term included in thermal conductivity
- Effect of scattering noticeable at 300K for 500nm grains
- Grain boundary scattering much less effective at high T for skutterudites



Computational Composition Engineering

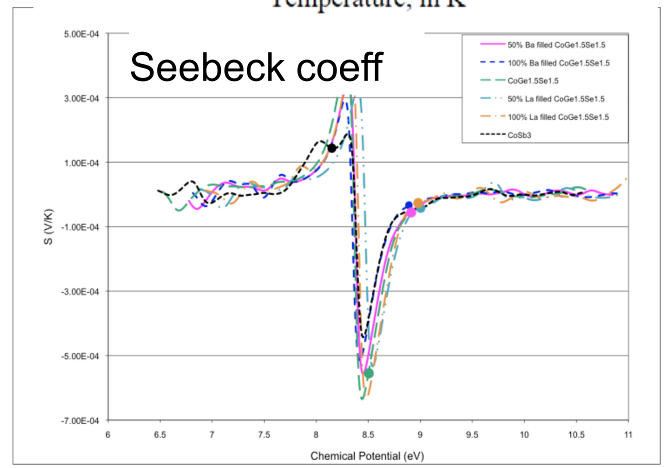
Ternary-substituted skutterudites may hold more potential for n-type

- XCo_4B_{12} B = Sb → (Ge,Sn)/ (S,Se,Te)
- Higher Seebeck coeffs than $CoSb_3$

Filling of ternary skutterudites weakly affects the Seebeck maxima

- Changes the carrier concentration significantly

→



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Concluding Remarks and Future Work

- *It appears that the CNT-based nanostructured thermal interface material (TIM) can meet (and possibly exceed) both the thermal and mechanical property requirements for TEGs application.*

- *Extensive life time thermal cycling and high temperature stability studies of the nanostructures interface materials are required and will be the focus our effort in the 2^{nd} year of the DOE-NSF project.*

The authors gratefully acknowledge financial support from the NSF/DOE Partnership on Thermoelectric Devices for Vehicle Applications (Grant No. 1048796), the National Science Foundation Graduate Research Fellowship program, the Stanford Graduate Fellowship program.

Extra Material

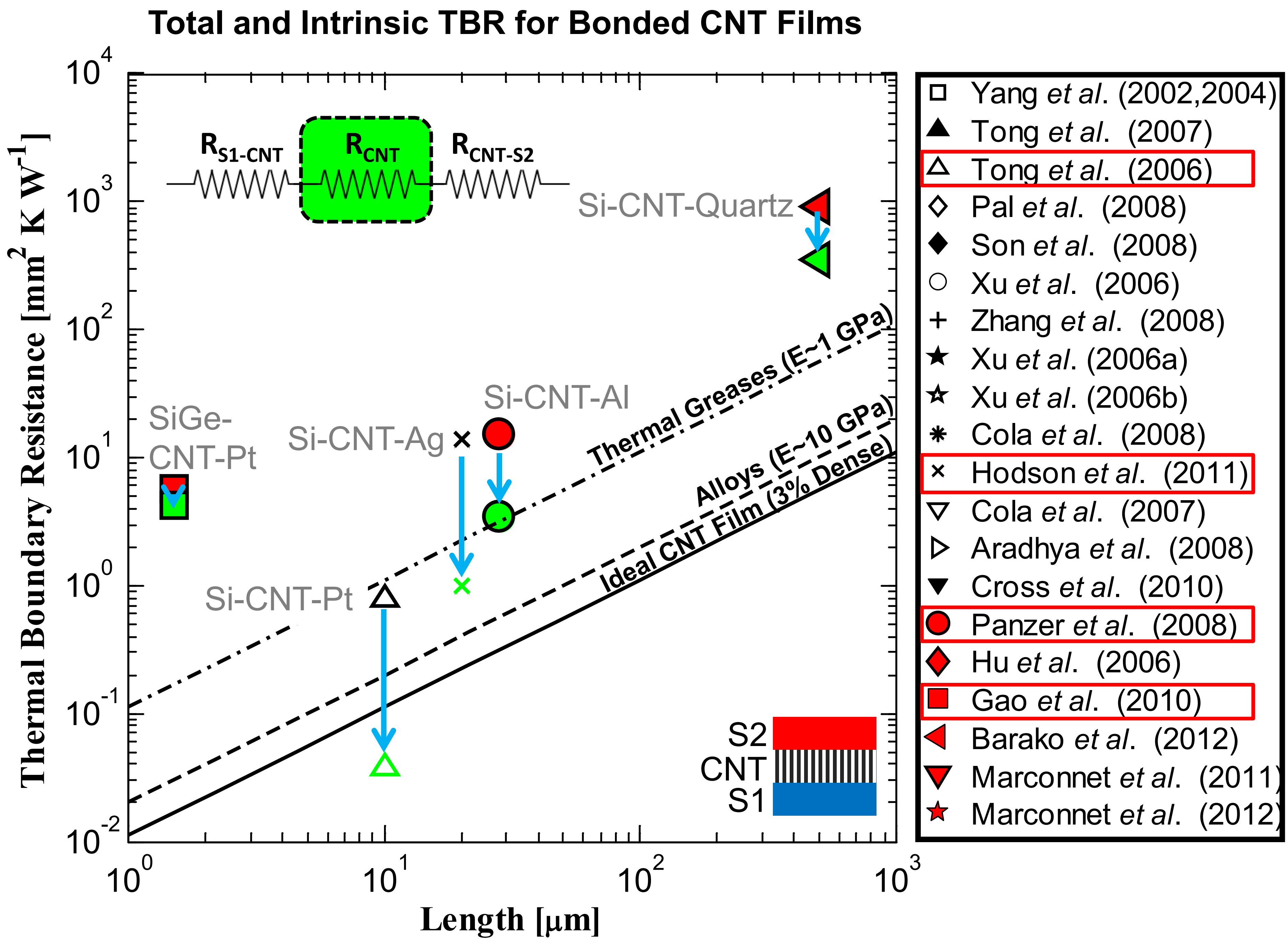
Project Goals and Deliverables

Major Goals

• Development of CNT-nanostructured interface materials with enhanced thermal/mechanical/electrical properties for high-T TE applications.
• Development of high-temperature thermoelectric materials (e.g., filled Skutterudites) with enhanced transport properties.
• Ab-initio atomic-level modeling of high-temperature thermoelectric materials and interfaces in conjunction with experimental design and optimization, see above.
• Development of novel experiments and characterization tools for in-situ performance and reliability testing of TE module (pellet pairs and CNT-interfaces) and constituent components.
• System design optimization by combining all thermal, fluidics, stress, electrical and thermoelectric components for realistic gas flow conditions.

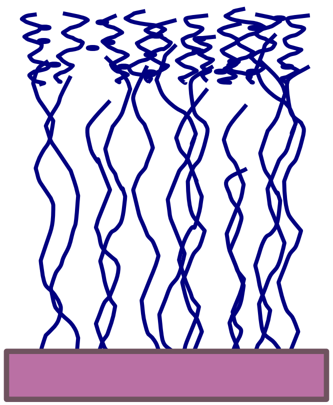
•***Deliverables***

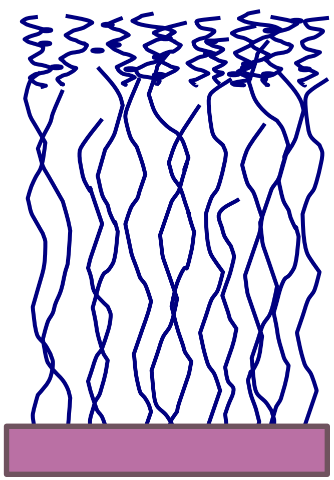
•Development of materials and techniques for integration of CNT TIMs into thermoelectric devices.
•Thermal (thermal conductivity and thermal interface resistance), mechanical (Young's Modulus) and electrical characterization of stand-alone CNTs films
•In-situ IR imaging for reliability testing of TE module.
•In-situ TE module performance and reliability evaluations under realistic thermal cycling senarios.
•Thermoelectric material (high-T) engineering and design: optimization of partial void filling, including optimized iron-substituted compositions for p-type conduction; small grain and nano-scale inclusions from refractory materials within bulk polycrystalline skutterudites. Investigation of the structural, morphological, chemical and low-temperature transport with filling fraction, doping, grain-size, and inclusion concentration.
•Ab-initio modeling of interfaces (thermodynamic stability (e.g., phase diagrams) and mechanical characteristics (e.g., Thermal expansion coefficients and elastic moduli of materials
•Ab-initio modeling of transport properties of TE materials
•System design optimization by combining all thermal, fluidics, stress, electrical and thermoelectric components for realistic gas flow conditions.



Total and Intrinsic TBR for Bonded CNT Films
Thermal Boundary Resistance [mm² K W⁻¹]
Length [μm]
R S1-CNT
R CNT
R CNT-S2
Si-CNT-Quartz
SiGe-
CNT-Pt
Si-CNT-Ag
Si-CNT-Al
Si-CNT-Pt
Thermal Greases (E~1 GPa)
Alloys (E~10 GPa)
Ideal CNT Film (3% Dense)
S2
CNT
S1
Yang et al. (2002,2004)
Tong et al. (2007)
Tong et al. (2006)
Pal et al. (2008)
Son et al. (2008)
Xu et al. (2006)
Zhang et al. (2008)
Xu et al. (2006a)
Xu et al. (2006b)
Cola et al. (2008)
Hodson et al. (2011)
Cola et al. (2007)
Aradhya et al. (2008)
Cross et al. (2010)
Panzer et al. (2008)
Hu et al. (2006)
Gao et al. (2010)
Barako et al. (2012)
Marconnet et al. (2011)
Marconnet et al. (2012)

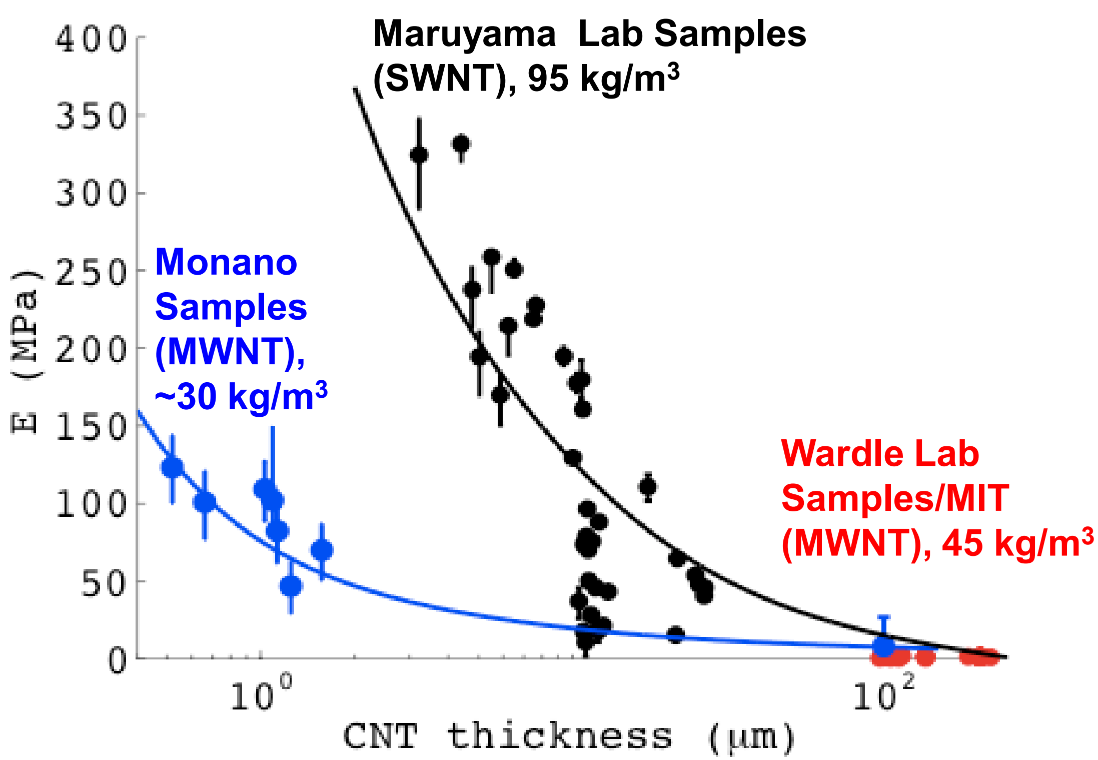
Modulus Variation with CNT Thickness



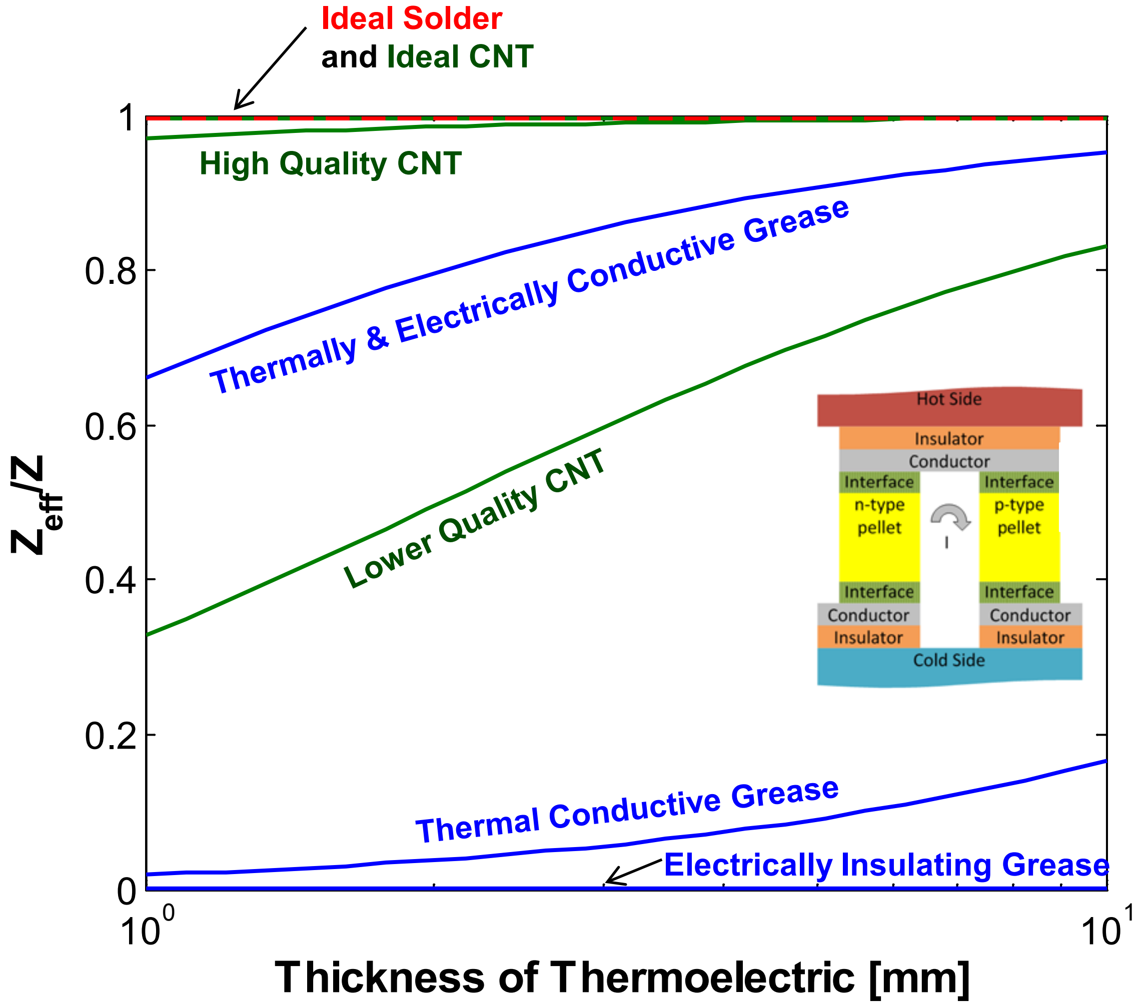


Crust Model for Monano Samples

	Thickness (μm)	Modulus (MPa)	Density (kg/m^3)
CNT_{Top}	0.4	140	>29
CNT_{Middle}	0-150	7	29
Si	8.7	155e3	2330



Effect of Interface Resistances on Thermoelectric Device Properties



Interface Material	R''_{th} [W/m²/K]	R''_e [Ω m²]
Solders And Ideal CNT	$\sim10^{-7}$	$\sim10^{-12}$
High Quality CNT	$\sim10^{-6}$	$\sim10^{-10}$
Lower Quality CNT	$\sim10^{-5}$	$\sim10^{-8}$
Thermally & Electrically Conductive Grease	$\sim3\times10^{-6}$	$\sim3\times10^{-9}$
Thermal Conductive Grease	$\sim8\times10^{-6}$	$\sim3\times10^{-7}$
Electrically Insulating Grease	$\sim8\times10^{-6}$	$>10^{-5}$