NSF-DOE Thermoelectrics Partnership:

Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

Prof. Ken Goodson
Department of Mechanical Engineering
Stanford University

Prof. George Nolas
Department of Physics
University of South Florida

Dr. Boris Kozinsky
Energy Modeling, Control, & Computation
R. Bosch LLC

ACE067

Overview

Timeline

- Start – January 2011
- End – December 2013
- ~10% complete

Budget

- $1.22 Million (DOE+NSF)
- FY11 Funding = $395K
- Leveraging:
  - ONR (FY09-11)
  - Fellowships (3 NSF, Sandia, Stanford DARE)

Barriers (2.3.2)

- Thermoelectric Device/System Packaging
- Component/System Durability
- Scaleup

Partners

- K.E. Goodson, Stanford (lead)
- George Nolas, USF
- Boris Kozinsky, Bosch

Relevance: Addressing Key Challenges for Thermoelectrics in Combustion Systems

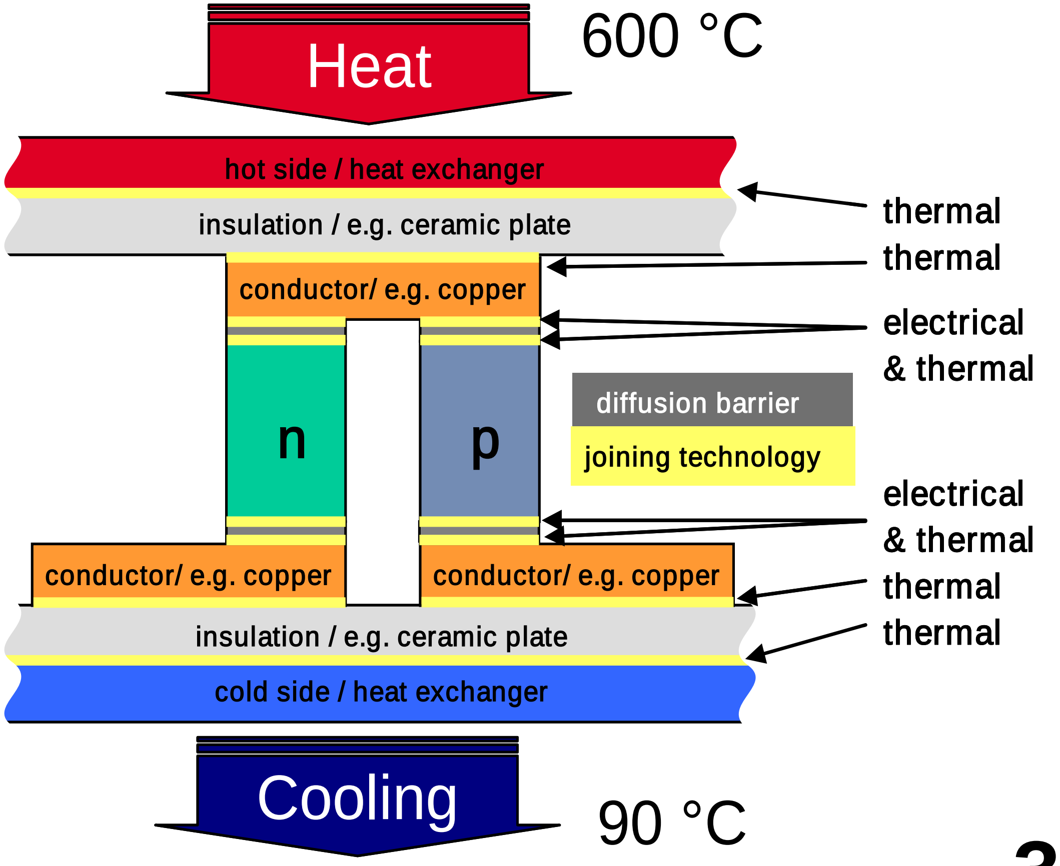
Improvements in the intrinsic ZT of TE materials are proving to be very difficult to translate into efficient, reliable power recovery systems.

Major needs include…

…Low resistance interfaces that are stable under thermal cycling.

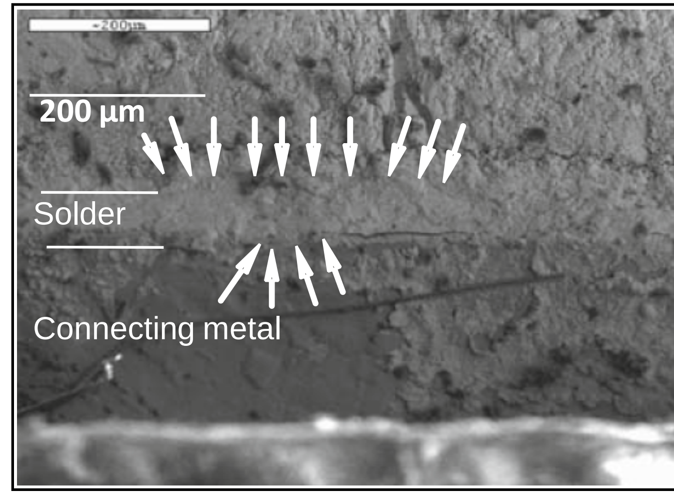
…High-temperature TE materials that are stable and promise low-cost scaleup.

…Characterization methods that include interfaces and correlate better with system performance.

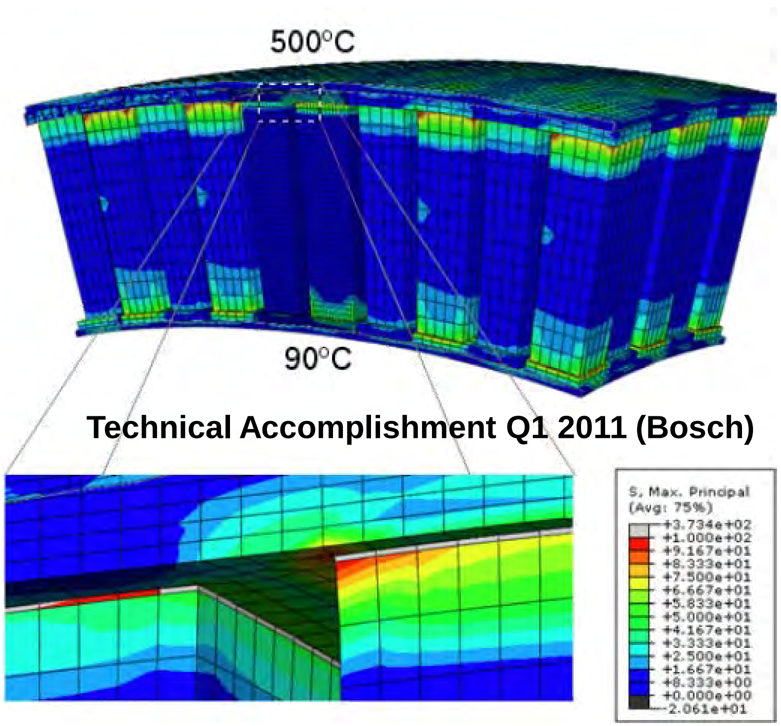


Relevance: Thermoelectric Interface Challenge

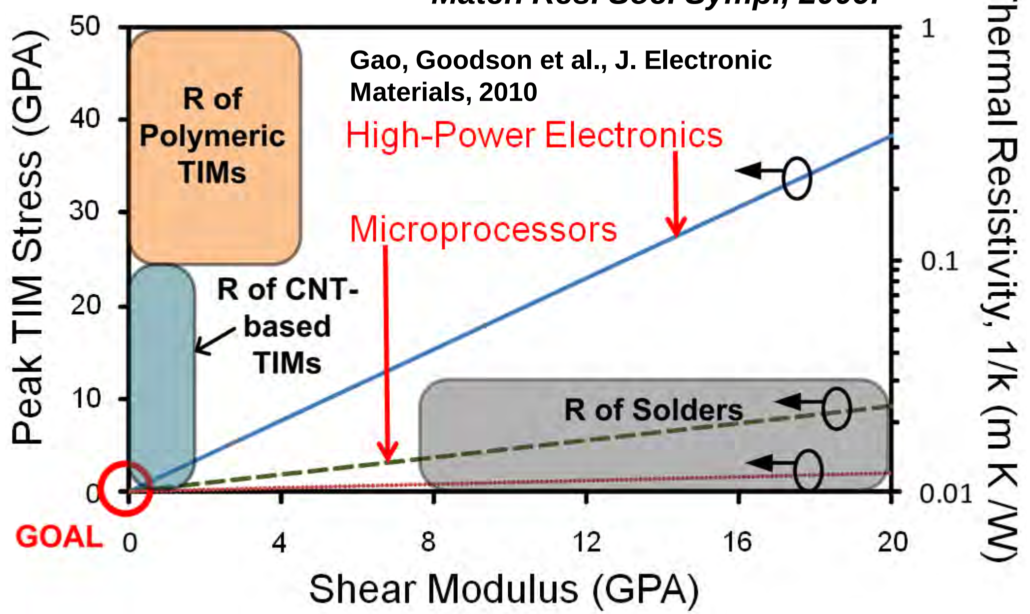
- Combustion TEG systems experience enormous interface stresses due to wide temperature spans.
- Thermal cycling degrades interface due to cracks, delamination, reflow, reducing efficiency.
- Our simulations show importance of thermodynamic stability (chemical reactivity, inter-solubility, etc.) and elastic modulus.



Hatzikraniotis et al., Proc. *Mater. Res. Soc. Symp., 2009.*



Technical Accomplishment Q1 2011 (Bosch)



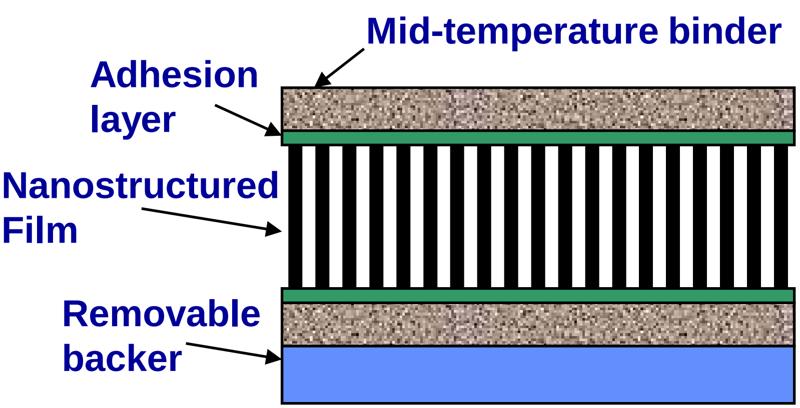
Research Objectives & Approach

OBJECTIVES

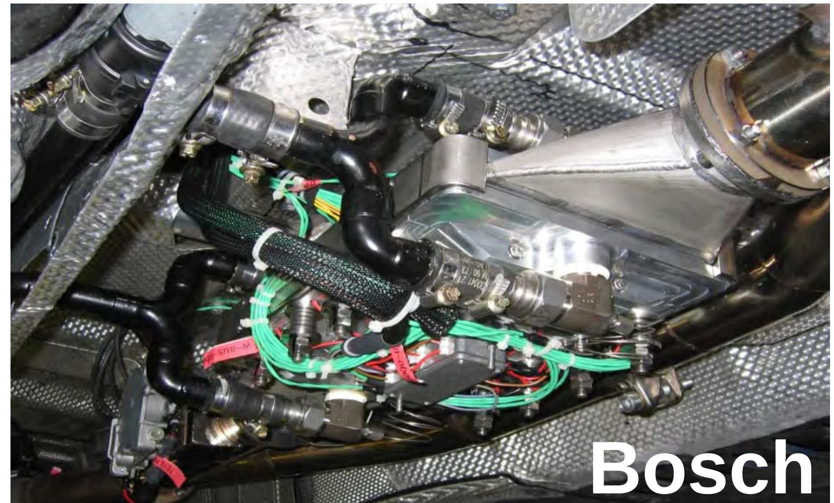
Develop, and assess the impact of, novel interface and material solutions for TEG systems of particular interest for Bosch.

Explore and integrate promising technologies including nanostructured interfaces, filled skutterudites, cold-side microfluidics.

Practical TE characterization including interface effects and thermal cycling.



Panzer, Goodson, et al., Patent Pending (2007)
Hu, Goodson, Fisher, et al., ASME JHT (2006)



Prototype TEG in exhaust system

APPROACH

Multiphysics simulations ranging from atomic to system scale.

Photothermal metrology including Pico/nanosecond, cross-sectional IR. MEMS-based mechanical characterization.

System design optimization by combining all thermal, fluidics, stress, electrical and thermoelectric components.

Research Approach

Additional Faculty & Staff beyond PIs
Prof. Mehdi Asheghi, Stanford Mechanical Engineering
Dr. Winnie Wong-Ng, NIST Functional Properties Group
Dr. Yongkwan Dong, USF Department of Physics

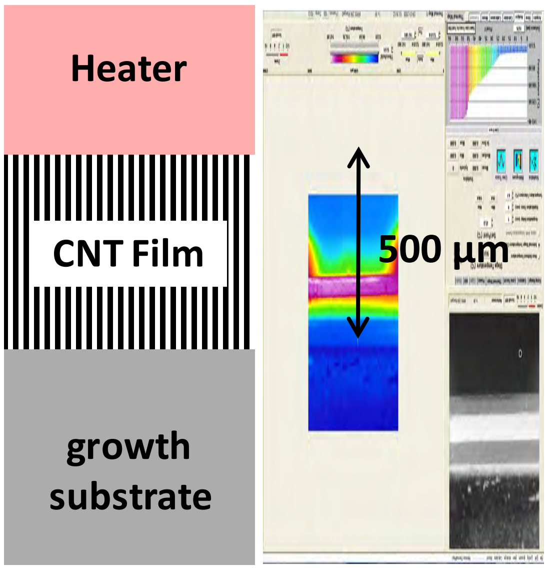
Stanford Students:
Yuan Gao, Lewis Hom, Saniya Leblanc, Amy Marconnet, Sri Lingamneni, Antoine Durieux

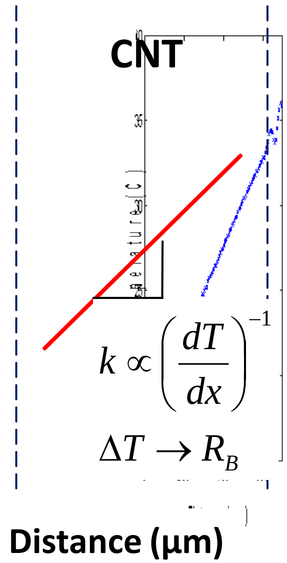
Interfaces **100%**	Nanostructured films & composites, metallic bonding Ab initio simulations and optimization	Stanford Bosch
Metrology **100%**	$(ZT)_{eff}$ including interfaces, thermal cycling High temperature ZT	Stanford USF/NIST
Materials **100%**	Filled skutterudites and half Heusler intermetallics Ab initio simulations for high-T optimization	USF Bosch
Durability **50%**	In-situ thermal cycling tests, properties Interface analysis through SEM, XRD, EDS	Stanford Bosch
Heat sink **50%**	Gas/liquid simulations using ANSYS-Fluent Novel cold HX using microfluidics, vapor venting	Bosch Stanford
System **50%**	System specification, multiphysics code Evaluation of research impacts	Bosch Stanford

Approach: Thermal & Mechanical Properties of CNT Interface Films

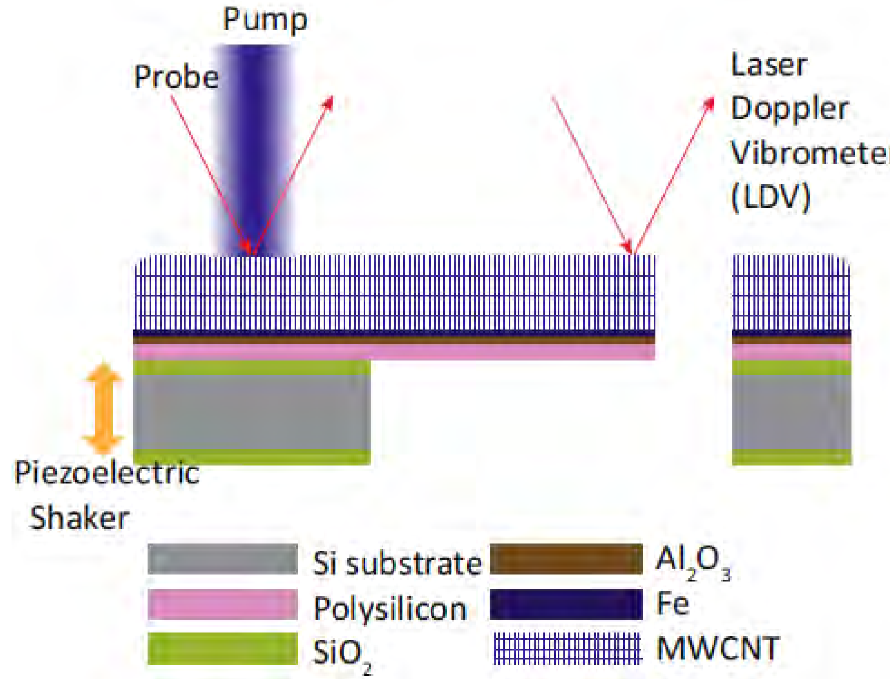
(Developed under ONR/Mark Spector)

Cross-sectional IR Microscopy

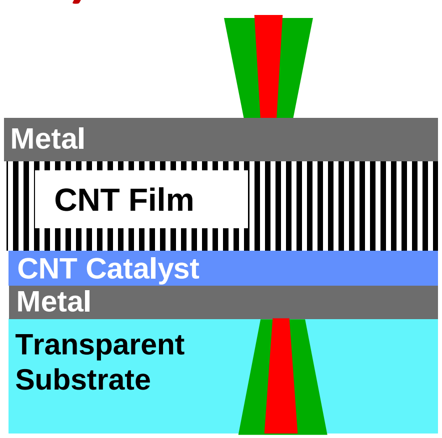




Mechanical Characterization



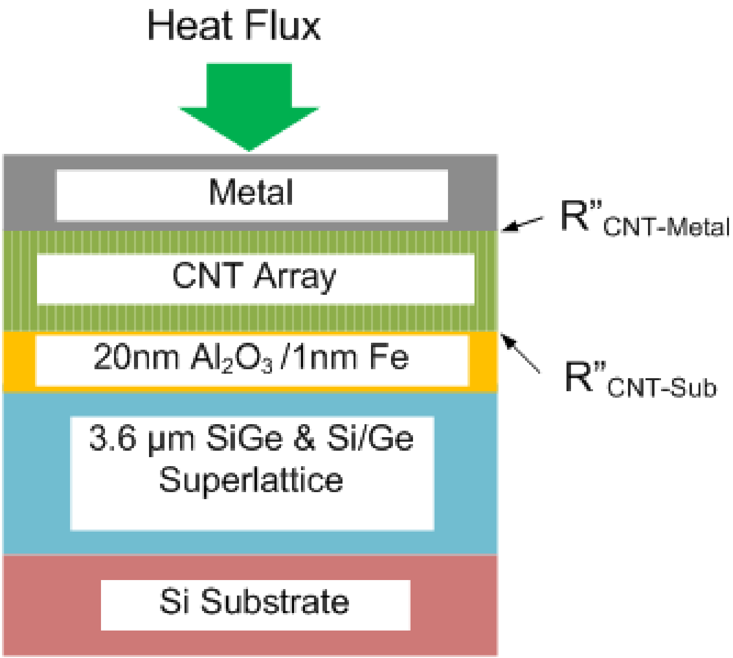
Pico/Nanosecond Thermoreflectance

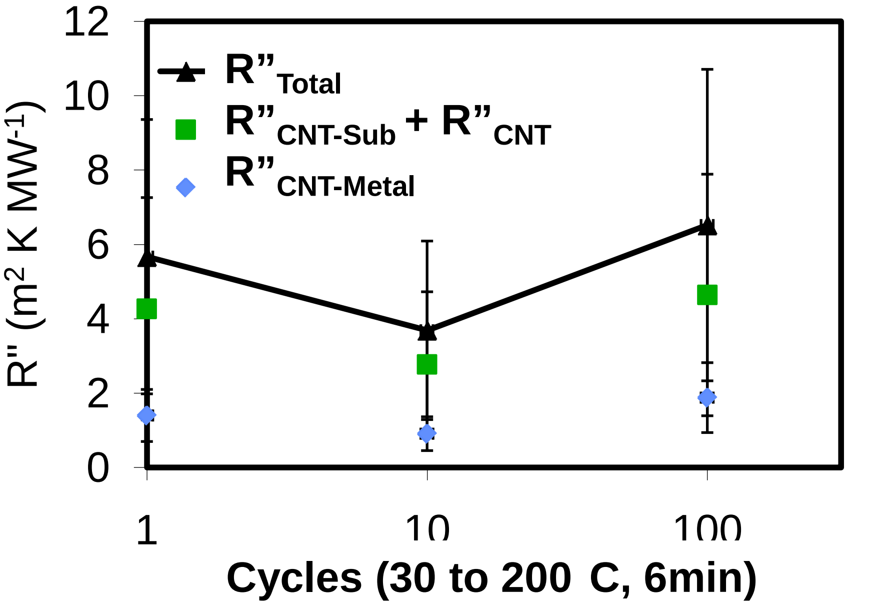


Won,Gao,Panzer,Goodson, et al.	Carbon	(sub. 2011)
Marconnet,Panzer,Goodson, et al.	ACS Nano	(sub. 2011)
Gao,Shakouri,Goodson et al.	J. Electronic Materials	(2010)
Panzer,Murayama,Goodson et al.	Nano Letters	(2010)
Panzer,Goodson	J. Applied Physics	(2008)
Panzer,Dai,Goodson et al.	J. Heat Transfer	(2008)
Hu,Fisher,Goodson et al.	J. Heat Transfer	(2006, 2007)
Pop,Dai,Goodson et al.	Nano Letters	(2006)
Pop,Dai,Goodson et al.	Physical Review Lett.	(2005)

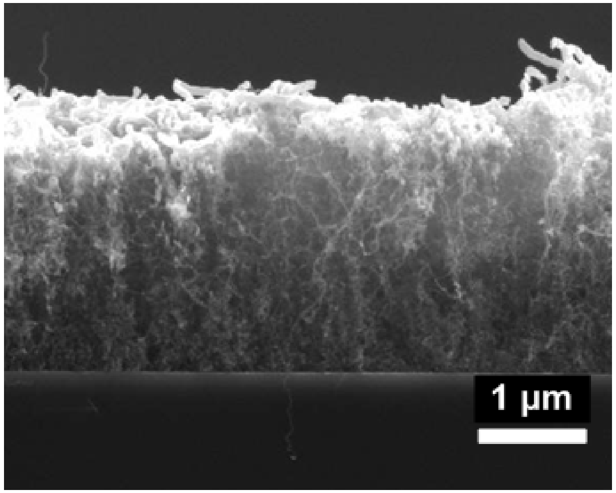
Approach: Interface Characterization on Thermoelectric with Thermal Cycling

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

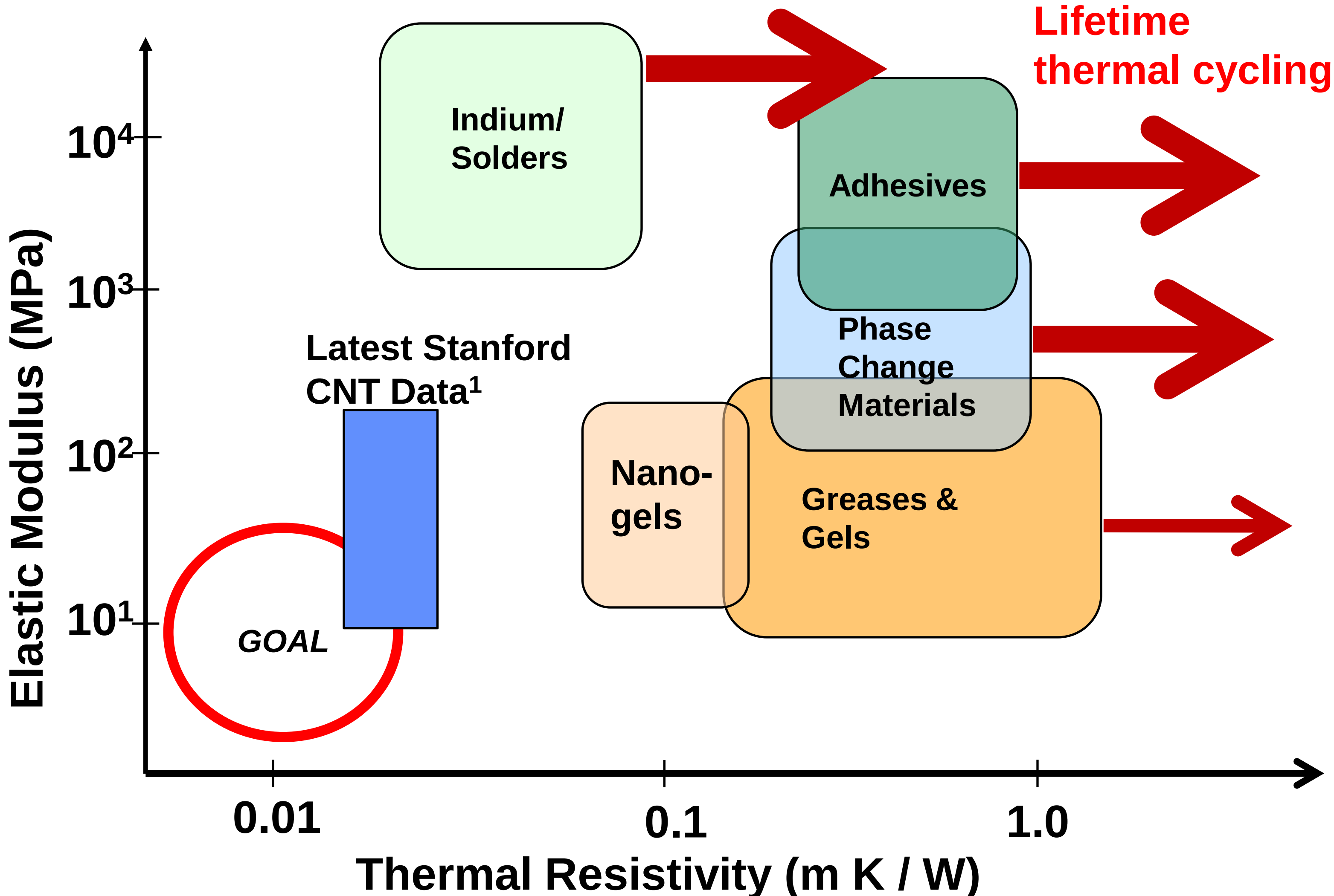




Resistances for 1.5, 2.5, and 40 micron thick CNT films varied between 0.035 and 0.055 cm^2 ^{o}C/W, with evidence of decreasing engagement with increasing film thickness.



Approach: Nanostructured Interfaces



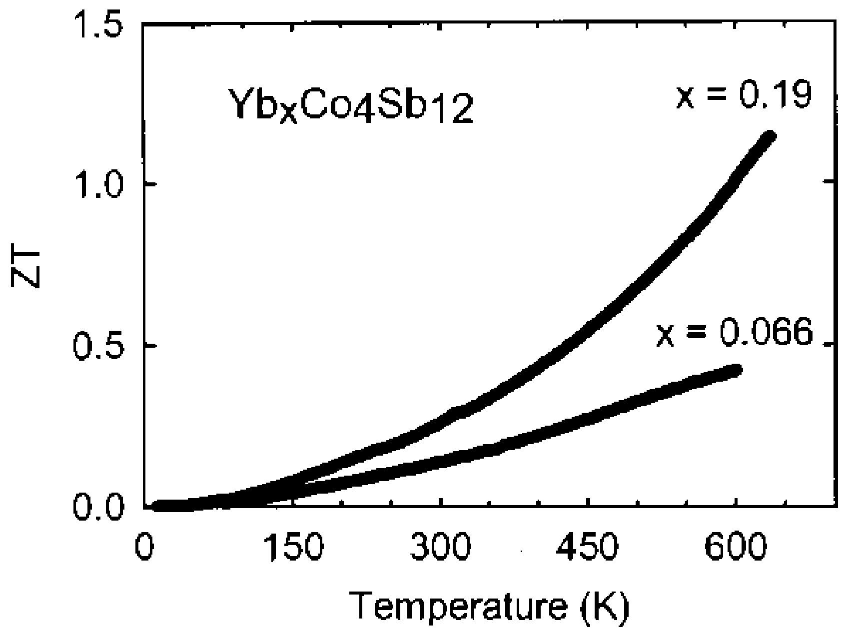
[1]Q1 2011 Accomplishment:
Gao, Goodson, et al., J. Electronic Materials (2010).
Won, Goodson, et al., Carbon, submitted (2011), also unpublished 2011

Approach: Bulk TE Materials for Vehicles

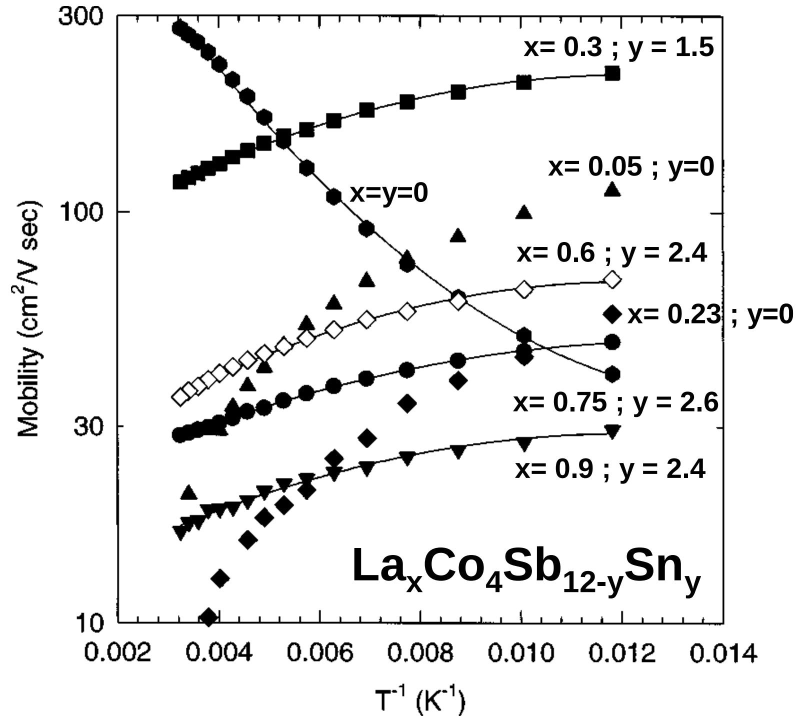
Nolas, Kaeser, Littleton, Tritt, APL 77, 1855 (2000), Nolas, JAP 79, 4002 (1996)
Lamberton, G.S. Nolas, et al APL 80, 598 (2001)

- *Skutterudites with partial filling using heavy, low valence "guest" atoms*

Heavy-ion Filling Yields Lower Thermal Conductivity. Low Valence Filling Facilitates Optimization of Power Factor.



Partial Filling – Optimization of Power Factor & Thermal Conductivity



- *Half-Heusler alloys: small grain-size provides for disordered state*

George S. Nolas
Department of Physics,
University of South Florida

Novel Materials Laboratory
University of South Florida

Approach: Materials Computation

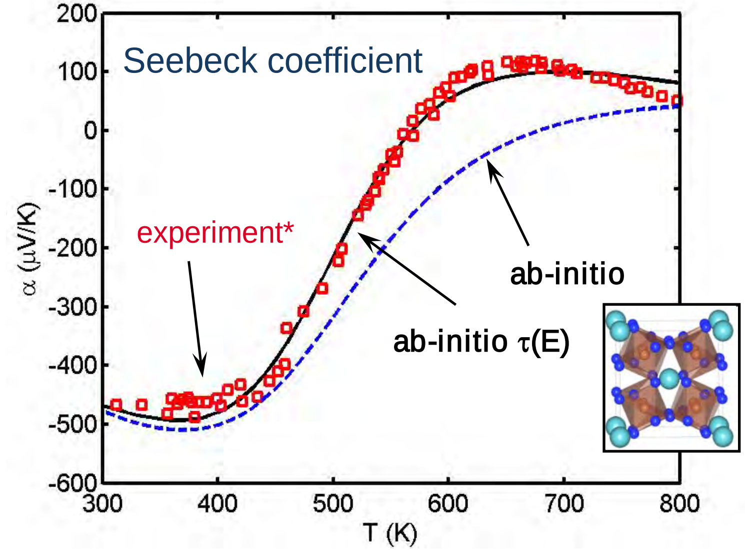
- ➔ Predictive computations of TE materials
  - Electronic conductivity
  - Seebeck coefficient
  - Thermal conductivity

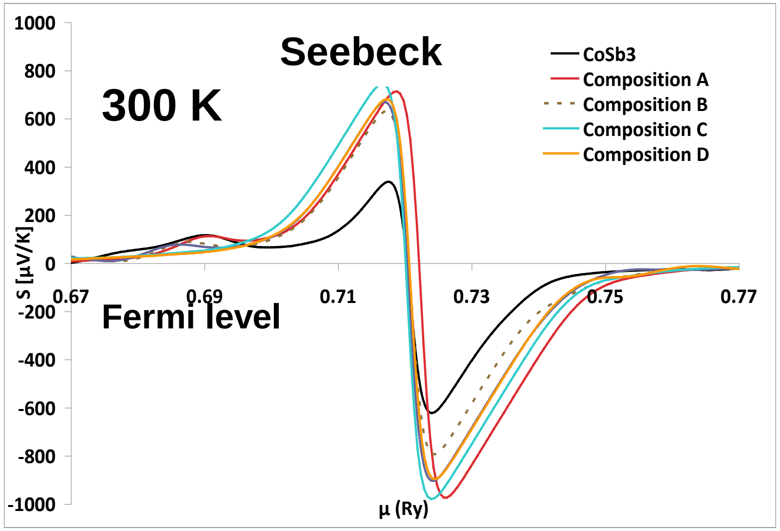
➔Understanding of transport mechanisms on atomic level and composition trends from ab-initio

- ➔ Composition screening in skutterudites
  - Several new compositions predicted with higher Seebeck than base-line $CoSb_3$

➔ Trade-offs with conductivity investigated

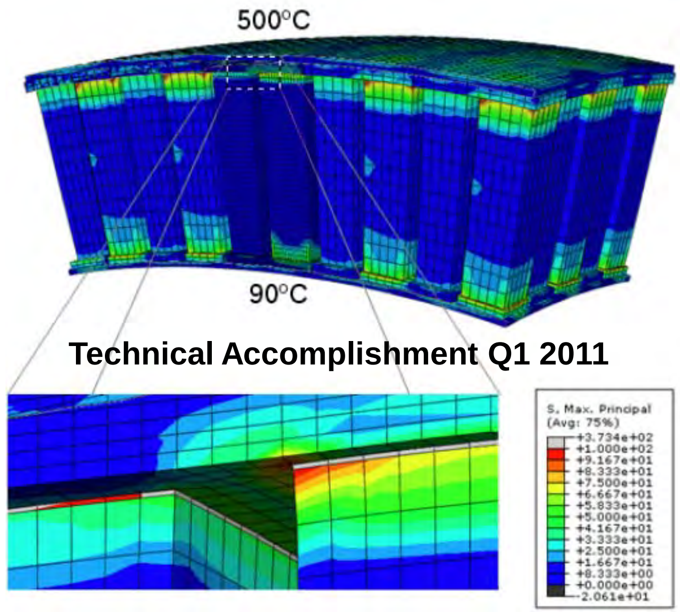
➔Collaborative work with Nolas group focuses on Yb and Eu-filled skutterudites

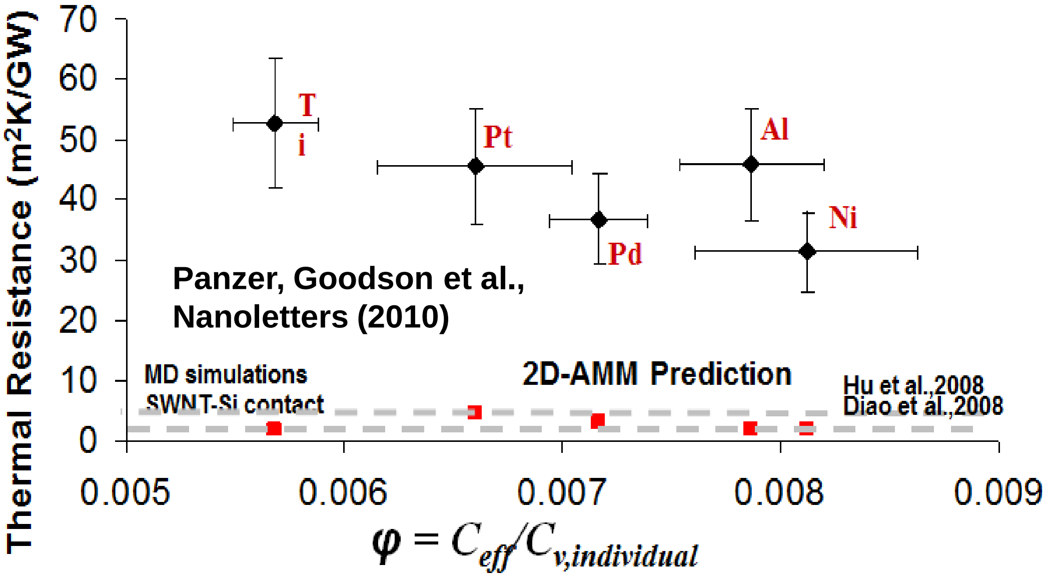


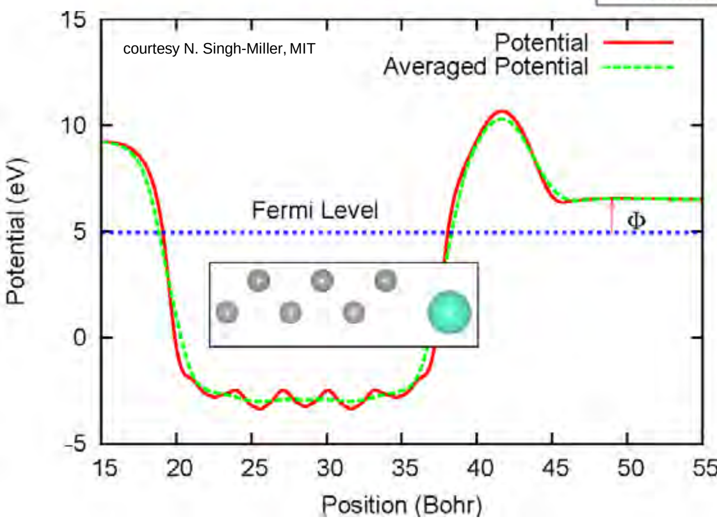


Approach: Interface Optimization

- **Thermal characterization** focuses on interface engagement, nanotube wetting, and stability
- **Mechanical modeling** of interfaces allows screening of compositions to improve thermo-mechanical stability
  - Chemical reactivity at interfaces considering phase stability
  - Ab-initio computations and measurements of modulus, CTE
  - Q1/2011: Analysis of mechanical stresses at interfaces – in-plane stress limitations using computed and measured CTE
  - Q1/2011: Cross-section of leg found to be related to the critical stress, strong implications for materials strength for cost reduction
- **Electronic transport across contacts**
- Work function and barrier calculations set up and calibrated
- Key numerical screening criteria identified: Fermi level and band offsets, Schottky barrier heights



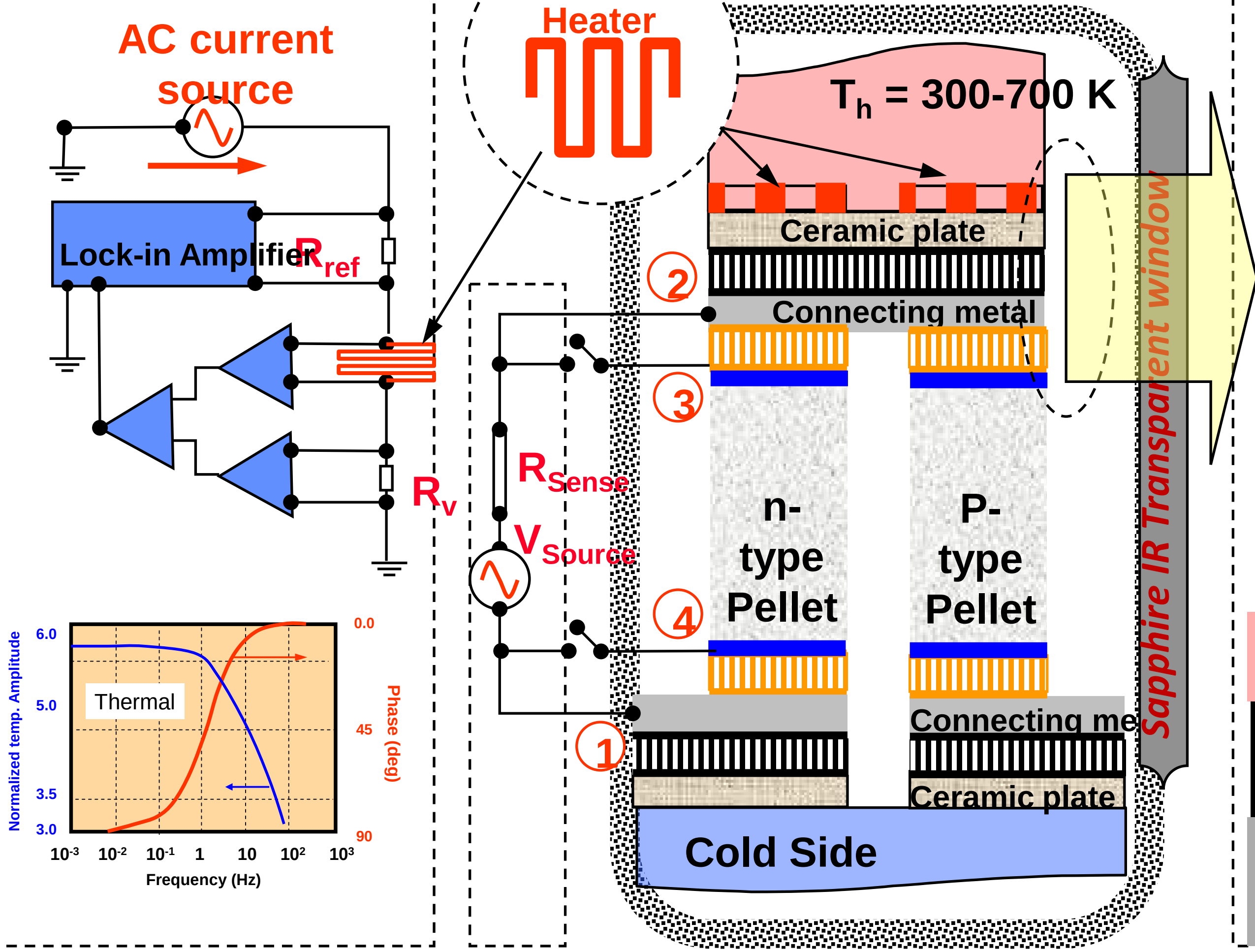




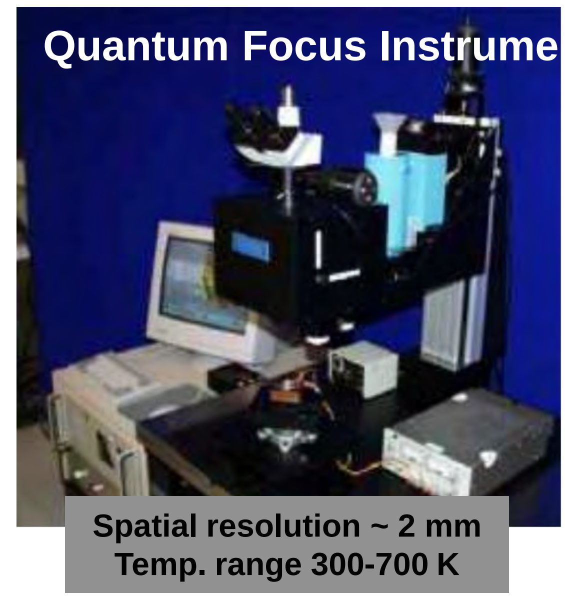
Computed electrostatic potential

Approach: $(ZT)_{eff}$ Through Electrical Heating & Cross-Sectional IR Thermometry

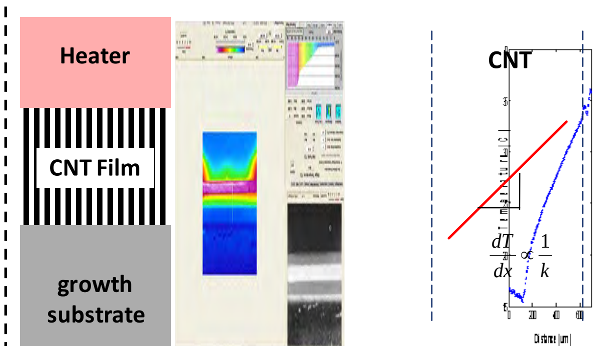
Heating/thermometry Setup



IR microscope system



Cross-sectional IR Microscopy

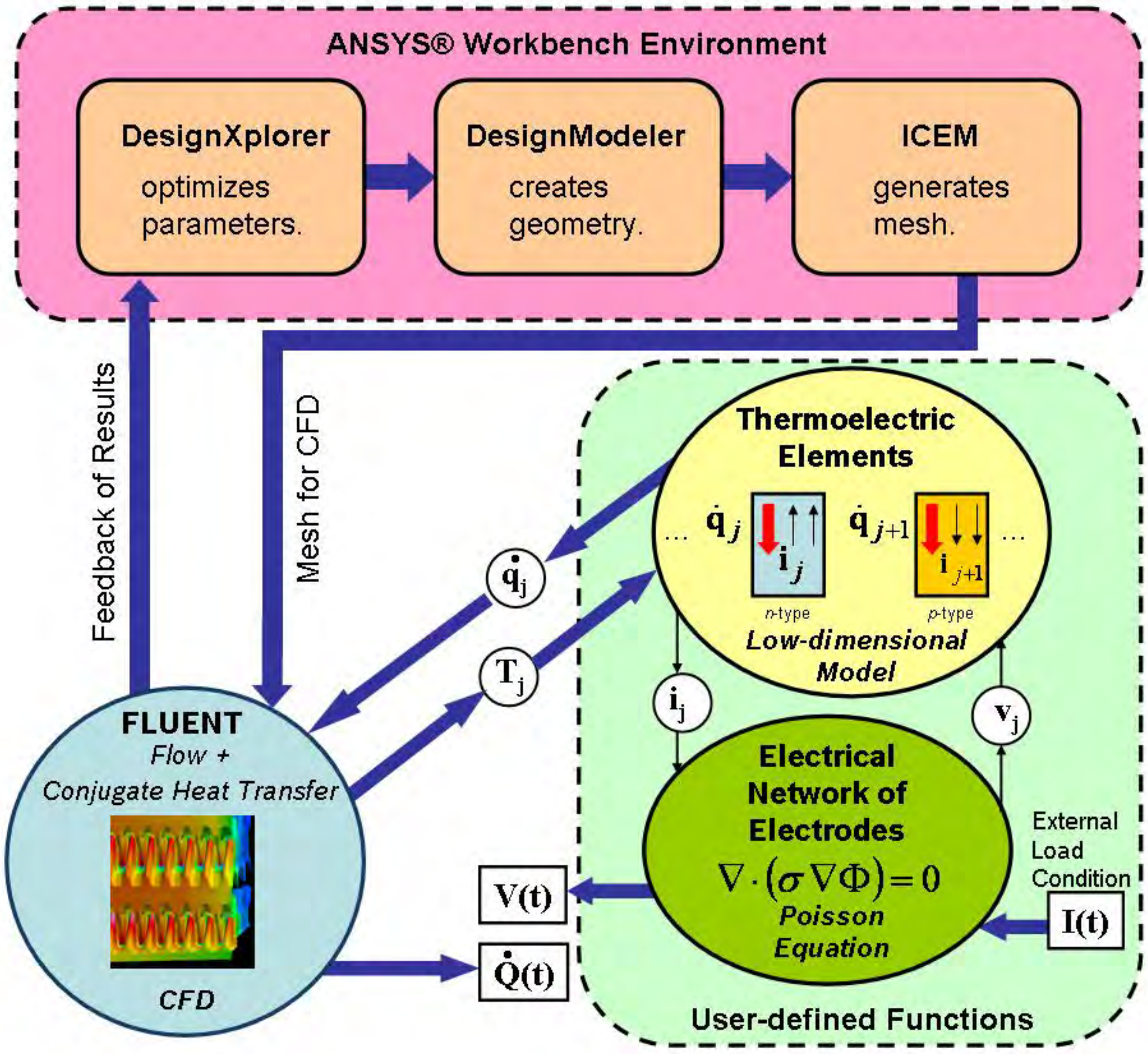


Approach: HX and System Simulations

- **Goal: system optimization**
  - **Parameter sensitivity**
  - **Locate bottlenecks**

- **Multiphysics modeling**
  - **material**
  - **device**
  - **system**

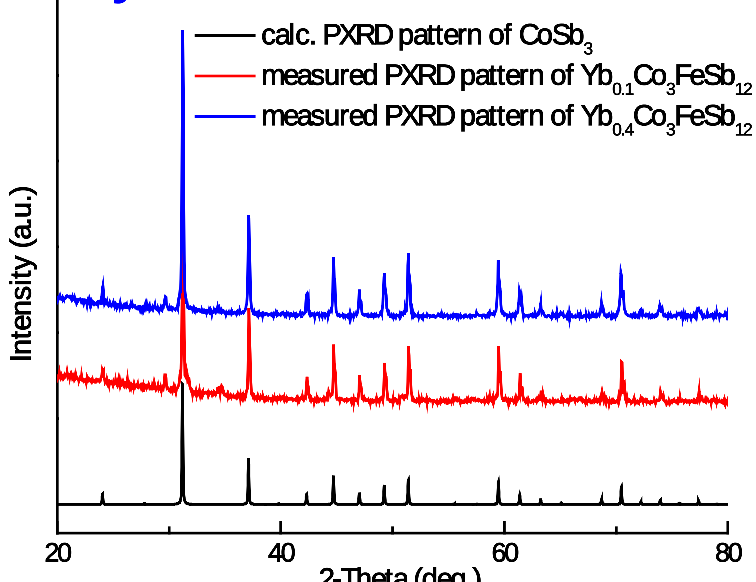
- **Coupled FEM/heat flow thermoelectrical model**



Technical Accomplishment Q1 2011: Bulk TE Materials

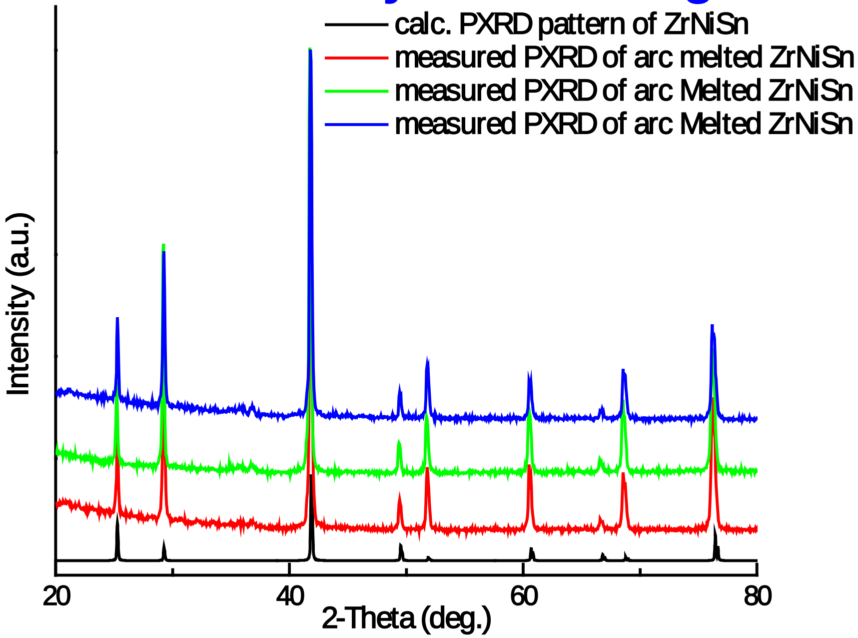
- p-type partially filled and Fe-substituted Skutterudites: $Yb_xCo_{4-y}Fe_ySb_{12}$
- Double filled and Fe-substituted Skutterudites: $Ba_xYb_yCo_{4-z}Fe_zSb_{12}$
- n- and p-type Half-Heusler alloys
- Bi_2Te_3-alloys for High Resolution IR Thermometry (in collaboration with Marlow Industries, Inc.)
- Survey of other material systems with potential for enhanced thermoelectric properties

Yb-filled Fe-substituted $CoSb_3$ by solid state reaction



Thermopower of hot pressed $Yb_{0.4}Co_3FeSb_{12}$ ~ 60μV/K at room temp.

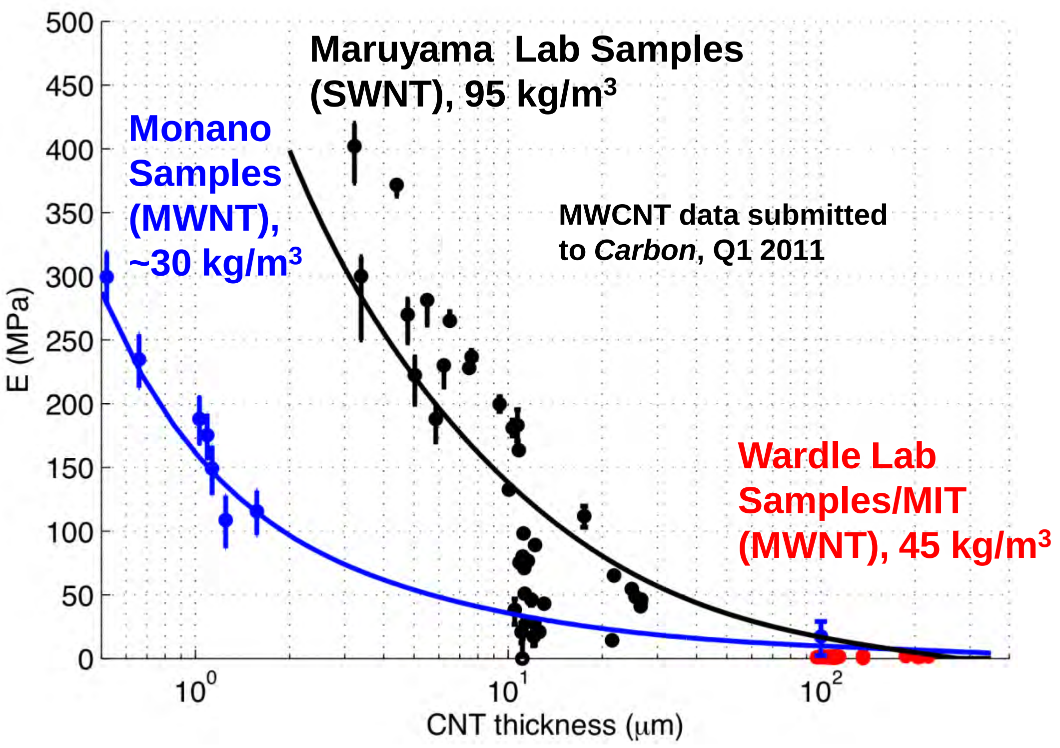
ZrNiSn by Arc Melting

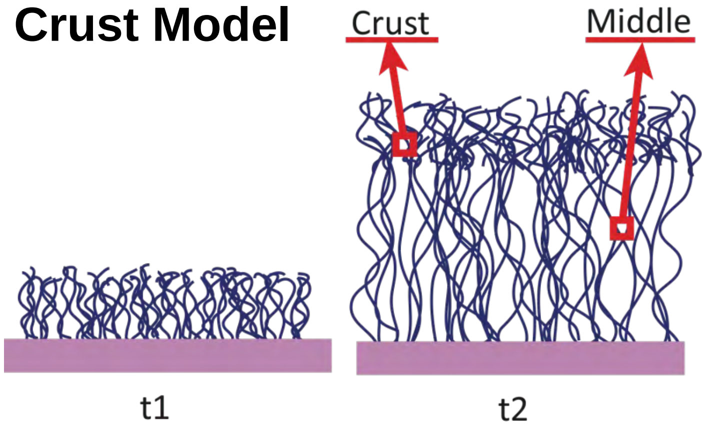


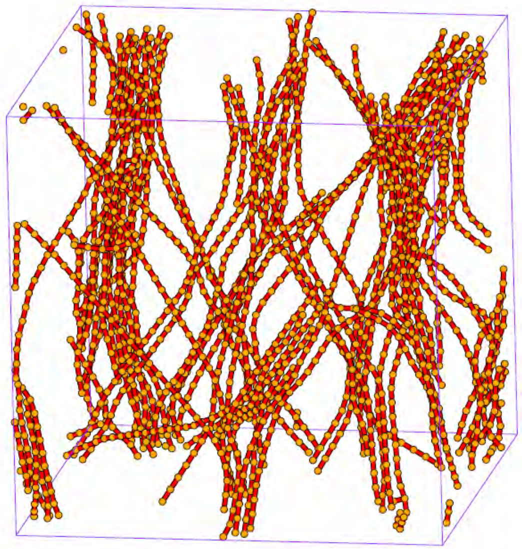
In collaboration with GM R&D for melt-spun processing in investigating amorphous and fine-grained Half-Heusler alloys.

Technical Accomplishment Q1 2011: Mechanical Behavior of CNT Films

	Thickness (µm)	Modulus (MPa)	Density (kg/m^3)
$SWCNT_{Top}$	1	600	110
$SWCNT_{Middle}$	0-25	0.5	95
$MWCNT_{Top}$	0.4	300	40
$MWCNT_{Middle}$	0-150	10	29
Polysilicon	5.8-8.7	155e3	2330







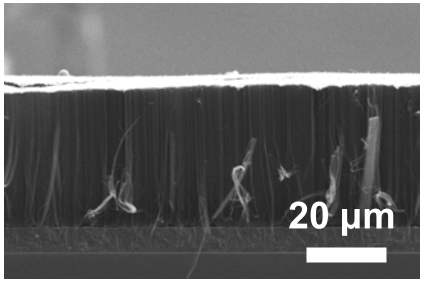
Zipping/Velcro Model

With W. Cai Group, Stanford

Technical Accomplishment Q1 2011: CNT Engagement/Thermal Props

(See Also Panzer, Murayama, Wardle, Goodson, et al., Nano Letters, 2010. Gao, Goodson, Shakouri et al., J. Electronic Materials, 2010)

- Eight samples with varying CNT film thicknesses from same growth process.
- Measured density near 7%
- Key Properties: $R_{CNT\text{-}metal}$, $R_{CNT\text{-}sub}$, k_{eff}, $C_{v,eff}$

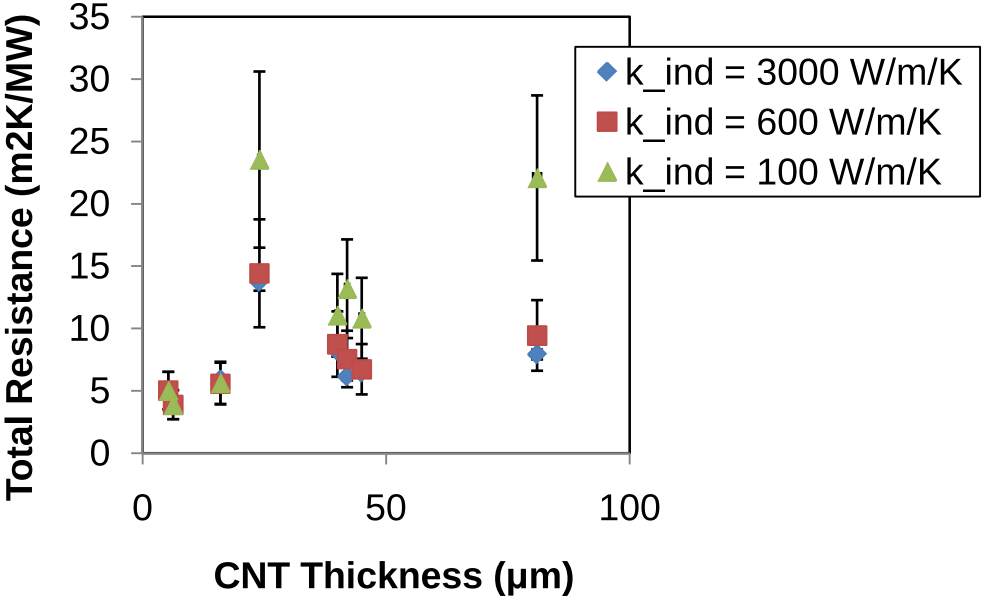


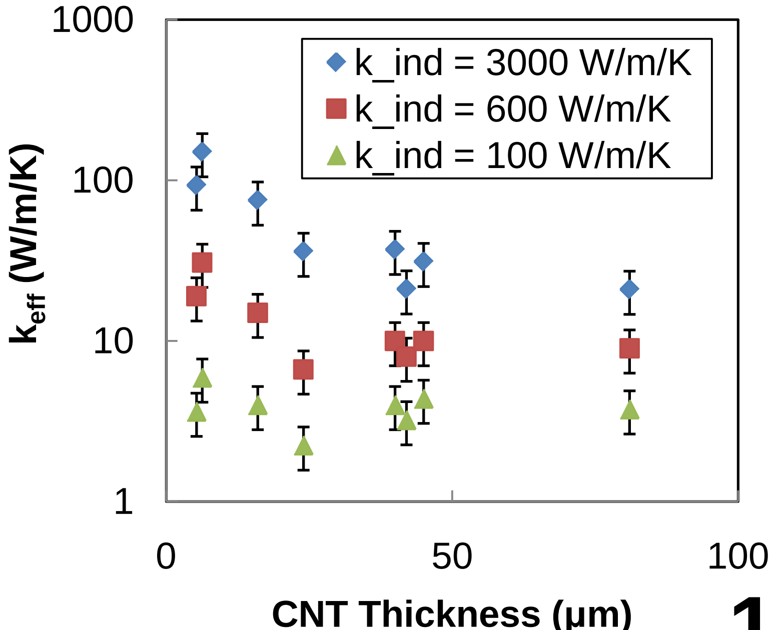
R”$_{CNT\text{-}metal}$ = 0.5 to 2 m^2K/MW

R”$_{CNT\text{-}sub}$ = 1 to 11 m^2K/MW

Engagement factor $\phi = C_{v,eff} / C_{v,ind}$

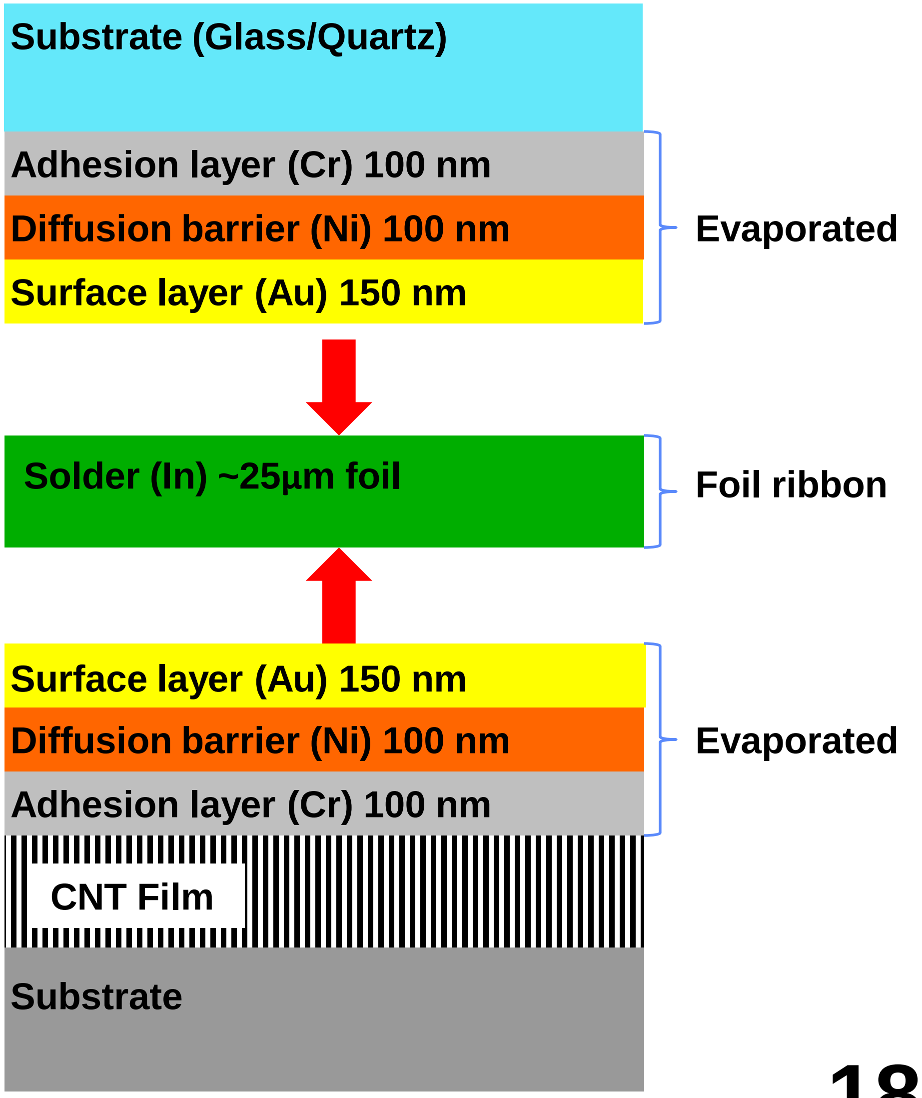
$$k_{eff} = \phi * k_{ind}$$





Technical Accomplishment Q1 2011: CNT Metallization & Bonding

- Bonding the CNT films to relevant substrates is a major challenge as not all materials are compatible with the CNT growth procedure.
- Recent progress utilizing a combination of metallizations allows CNT films grown on sacrificial silicon wafers to be successfully transferred to a range of substrates using thin indium foils as binding layers.
- This is a key step towards developing the free standing CNT tape for thermal interface applications.



Technical Accomplishment Q1 2011: CNT Bonding Procedure

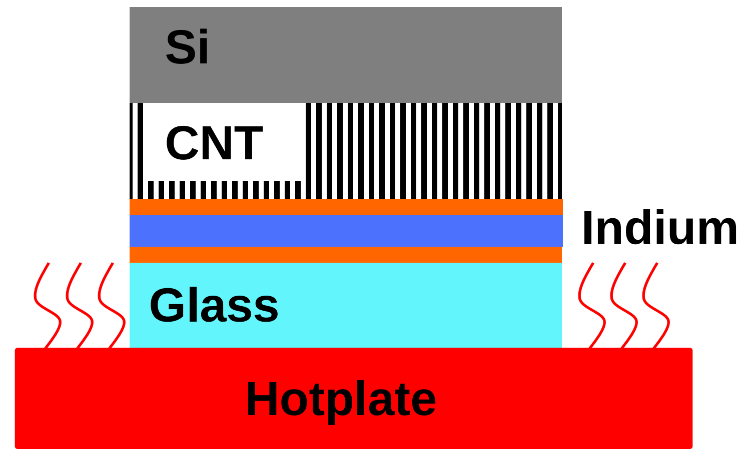
1) SAMPLE PREPARATION

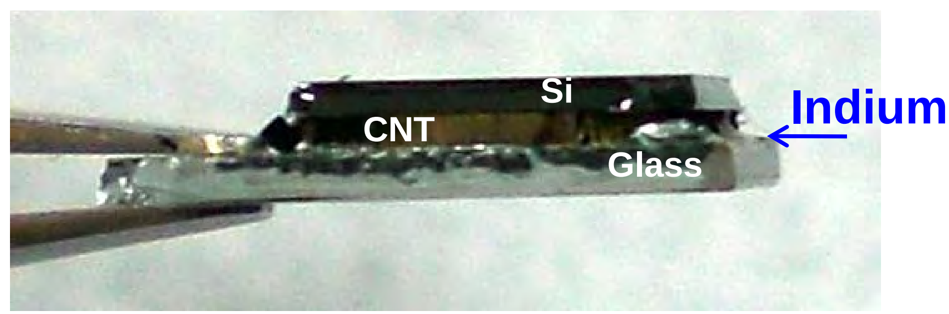
a) Evaporate Au/Ni/Cr on CNT and glass substrates

Au/Ni/Cr coated CNT film on Si

b) Clean indium foil or apply flux

2) THERMAL BONDING

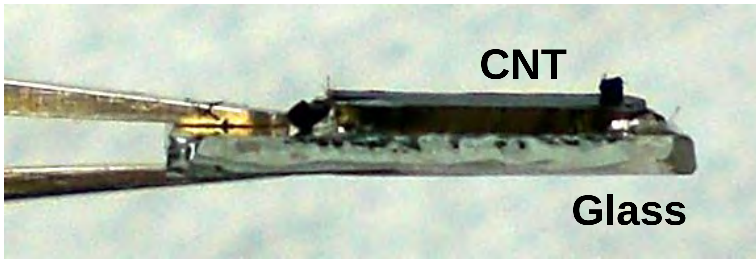


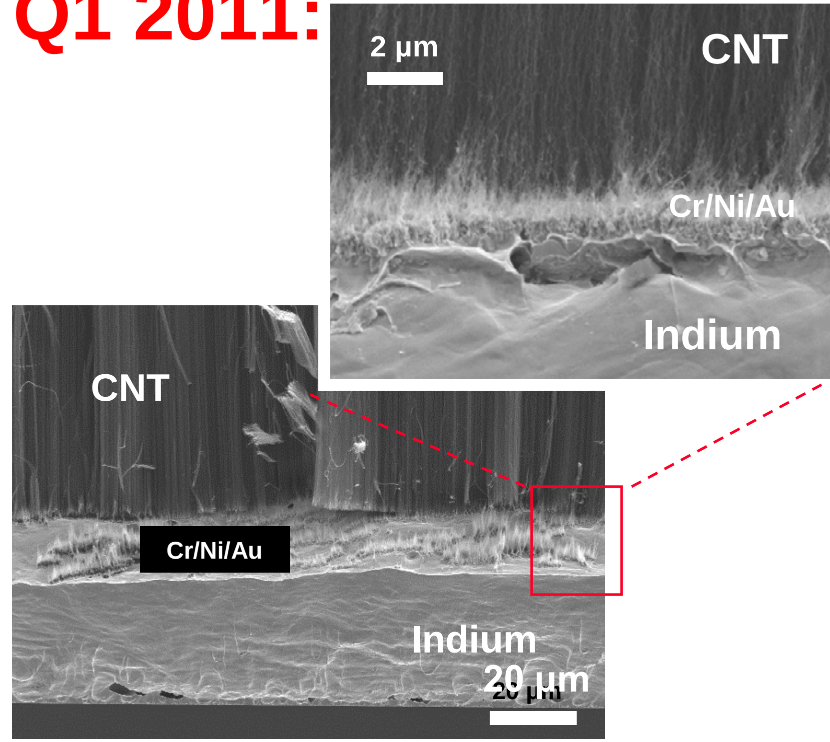


CNT film bonded to glass, before removal of Si substrate

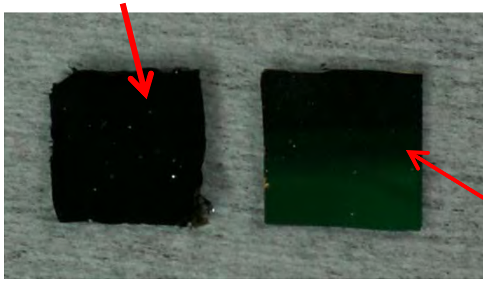
Technical Accomplishment Q1 2011: CNT Bonding Procedure

3) CNT FILM RELEASE

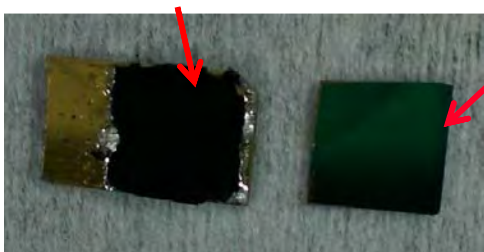




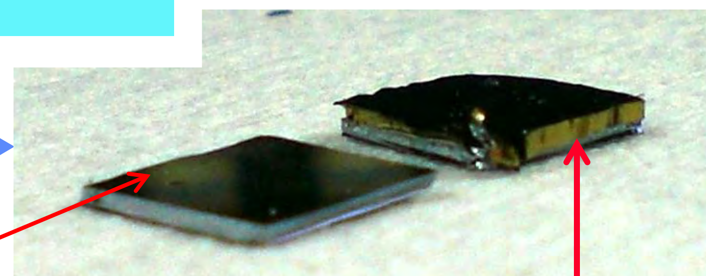
CNT bonded to Si



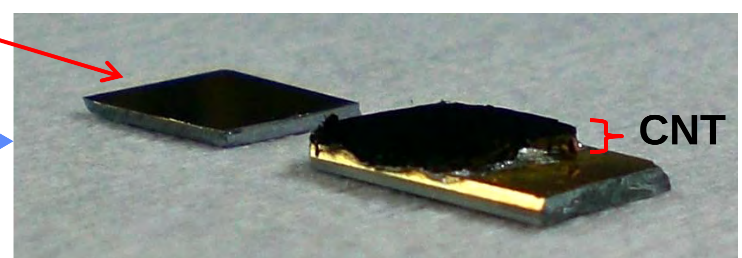
CNT bonded to glass



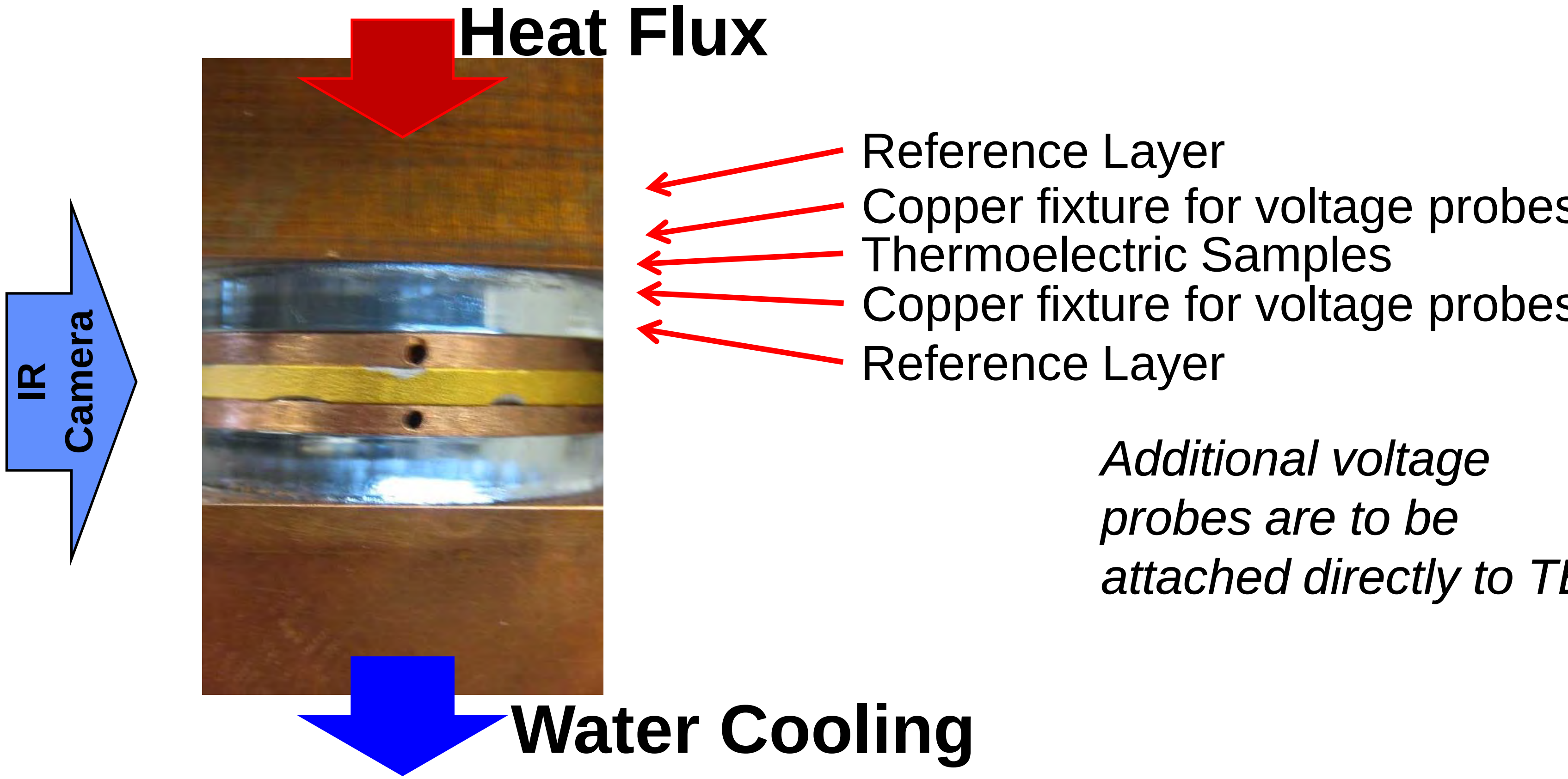
Original CNT substrate, with no CNT remaining



CNT (side is covered with Au from metallization)



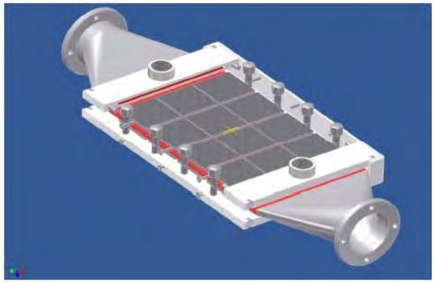
Technical Accomplishment Q1 2011: $(ZT)_{eff}$ Preliminary Measurement Setup



Additional voltage probes are to be attached directly to TE

- Reference layers allow determination of heat flux through sample for thermal conductivity measurements and can be removed or placed outside of copper voltage probe fixtures for measurements of electrical properties
- Thermal interface materials (i.e. CNT films) are grown or deposited on the thermoelectric material to examine effects of boundary resistances

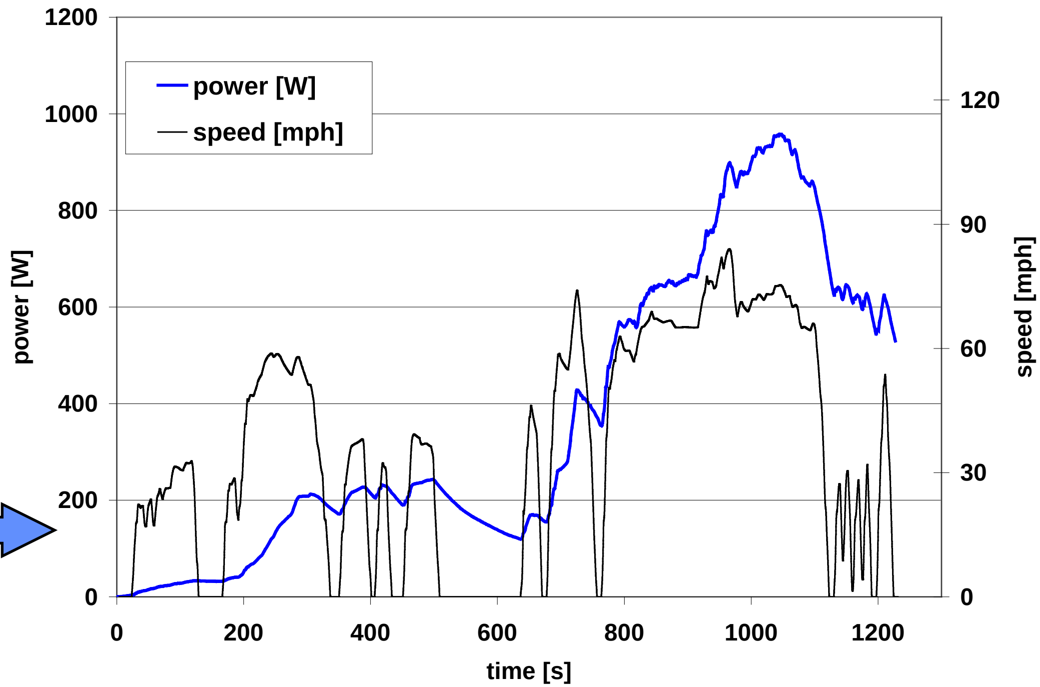
Technical Accomplishment Q1 2011: Thermoelectric System Optimization



- ➔ Input: exhaust gas temperature and mass flow over driving cycle (Vehicle measurement US06)
- ➔ Step 1: Heat exchanger geometry optimization

- ➔ Input: Active material parameters
- ➔ Step 2: Thermoelectric module geometry optimization (number and size of legs)

- ➔ Coupled system optimization solution
- ➔ Output: Predicted electrical power over a realistic driving cycle



Collaboration & Coordination

1- Interface
2- System-level
3- Durability
4- Materials
5- Heat sink
6- Metrology

Samples

Information

Stanford

- Prepares CNTs samples on TE materials
- Transport property measurements of CNT-TE pellet combination, thermomechanical reliability tests on interface (300-800 K)
- Process development for CNT TIM tape

1, 2, 3, 5

Bosch

- Ab-initio simulations of transport properties of TE materials and interfaces.
- System-level simulation and optimization

1, 3, 4, 6

1, 3, 4

USF

- Develops high-T, high efficiency TE materials
- Transport properties (ρ, S and κ) and Hall measurements (10 - 300K)
- Structural, morphological and thermal (DTA/TGA) analyses

4, 6

NIST

- Transport properties (ρ, S and κ) and Hall measure- ments (1.8-390K)
- Specific heat, Power Factor measurement at 300 K.
- Custom-designed precision TE properties measurement system (300 – 1200 K)

Proposed Future Work (FY 2011)

- *Bulk TE Materials*: Develop p-type partially/double filled Fe-substituted Skutterudites, n- and p-type half heusler alloys for melt-spun processing, thermal stability tests of materials and joints.

- *CNT Thermal Tape Development and Characterization*: Optimization of density and length, optimization of metallization, extension to 600^{o}C, thermal stability investigation, explore xGNP.

- *High-T $(ZT)_{eff}$ Characterization Facility Implementation*: Preliminary demonstration on conventional thermoelectrics, vacuum chamber development with IR transparent window.

- *Ab-Initio Simulations*: Band gap calibration for skutterudite and half-Heusler families, focussed computatios on phase stability, Seebeck coefficient, and transport properties.

- *System Simulations*: Assessment of impacts of interface properties including lifetime degradation.

Summary Slide

- With this award, DOE & NSF are enabling an academic-corporate team to focus on the key practical challenges facing TEG implementation in vehicles: interfaces, system-relevant metrology, and materials compatibility

- We are developing metrology for fundamental properties of nanostructured interfaces, as well as $(ZT)_{eff}$ metrology for half-Heusler and skutterudite thermoelectrics considering interfaces. Simulations include atomistic and ab initio results for TE materials and interfaces, and system & heat exchanger level optimization with the corporate partner.

- Key Q1 2011 results include: (a) process development of CNT tape (Stanford), (b) mechanical characterization of CNT films (Stanford), (c) development of a setup for thermal characterization of TE pellets and corresponding interfaces (Stanford), (d) interface modeling & optimization (Bosch) and (e) process development (arc melting, melt spun) for bulk TE materials (USF)

Technical Back-Up Slides

Educational Engagement

Thermoelectrics for Vehicles Challenge: Multi-University Competition

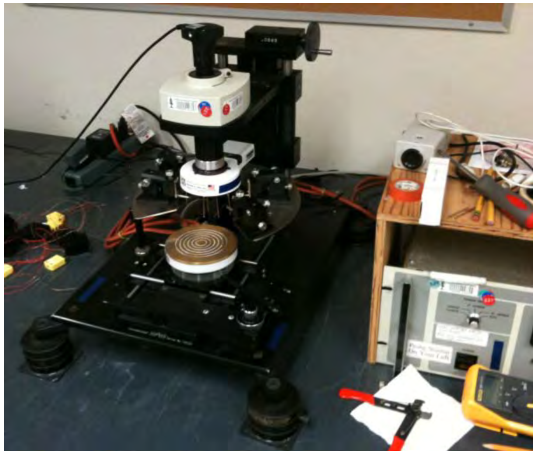
Teams of undergraduates create a vehicle waste heat recovery system utilizing thermoelectric technology.

✓Connects classroom education and research & development.
✓Links students with industry, graduate & faculty advisors.

Undergraduate Thermoelectrics Lab

Stanford's heat transfer course (ME131A) will include a thermoelectrics laboratory experience.

✓Connects theory and practical applications.
✓Recruits undergraduates for research experiences in thermoelectrics with graduate student mentoring.



K-12 Educational Outreach

High school students and teachers will conduct energy research in Stanford's Microscale Heat Transfer Laboratory.

Recent Popular Press (January 2011)

EE Times News & Analysis

Home | News & Analysis | Business | EE Life | Embedded.com | Design | Products

News & Analysis
Latest News
Semiconductor News

EE Times Home > News and Analysis

News & Analysis

Nanotape could make solder pads obsolete

R. Colin Johnson
1/24/2011 12:01 AM EST

PORTLAND, Ore.—Solder pads could soon be made obsolete by a new nanotape material created by the Semiconductor Research Corporation (SRC) and Stanford University.

By sandwiching thermally conductive carbon nanotubes between thin metal foils, nanotape transfers heat away from chips better than solder but with a lightweight flexible material that is cheaper and and more compliant, according to researchers.

"Today, solder is made very thick to provide mechanical compliance,

Comment
2/11/2011 6:09 PM EST

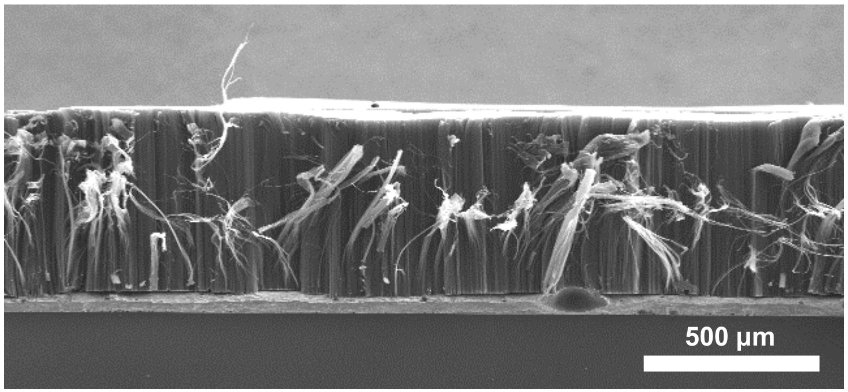
"…Stanford is also working with the National Science Foundation (NSF) on a project with the **Department of Energy Partnership on Thermoelectric Devices for Vehicle Applications**. Here, the nanotape will facilitate the recovery of electrical power from hot exhaust gases using thermoelectric…"

http://www.eetimes.com/electronics-news/4212401/Nanotape-could-make-solder-pads-obsolete

More Collaboration and Coordination

- CNT growth collaborations with Maruyama Group, U. Tokyo, Wardle group, MIT, Monano Corporation, Stanford (visits and/or extensive correspondence in Q1 2011)
- Thermoelectric characterization collaboration with Shakouri group, UC Santa Cruz (multiple visits Q1 2011)
- Interaction with Materials Modeling and TE groups, Sandia National Laboratories (multiple visits & seminars scheduled, Q2 2011)
- Collaboration with Northrop Grumman on CNT characterization (visits & seminar, Q2 2011)
- Metallization collaborations with AMD and Intel owing to expertise on thermal interfaces at these companies (visits and seminar, Q2 2011)

Technical Accomplishment Q1 2011: SEMs of CNT Film after Bonding & Release

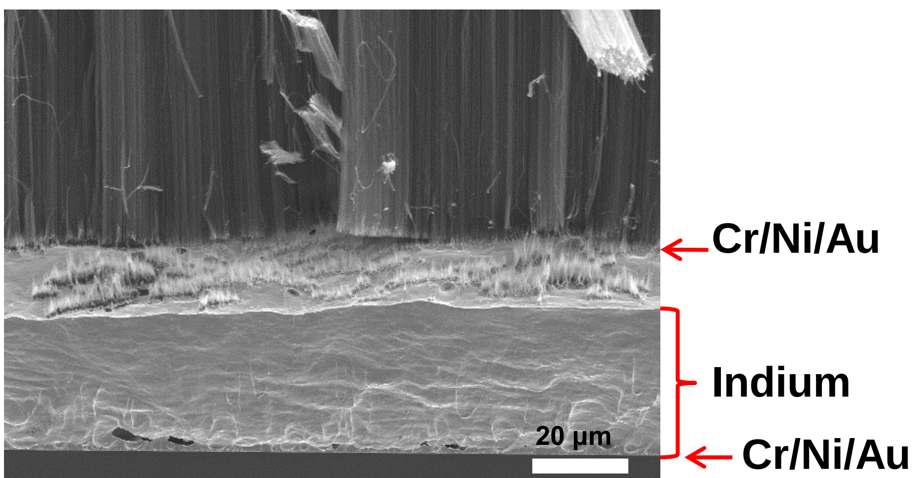


(a)

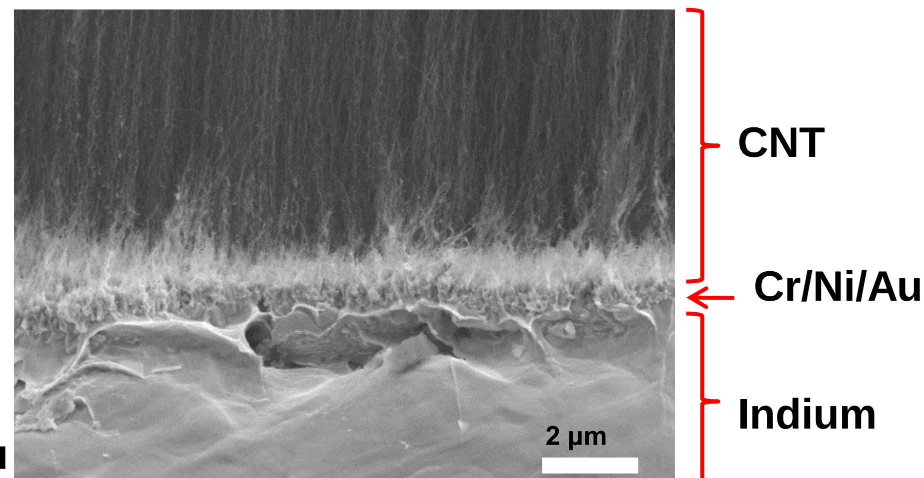
(a) SEM image of CNT film bonded to silicon substrate. Images are of a cleaved edge to show that no indium infusion into CNTs.

(b) The indium layer is ~30 µm thick. The tufts at the top may be CNTs ripped off during cleaving.

(c) Close up view of CNT – indium interface.

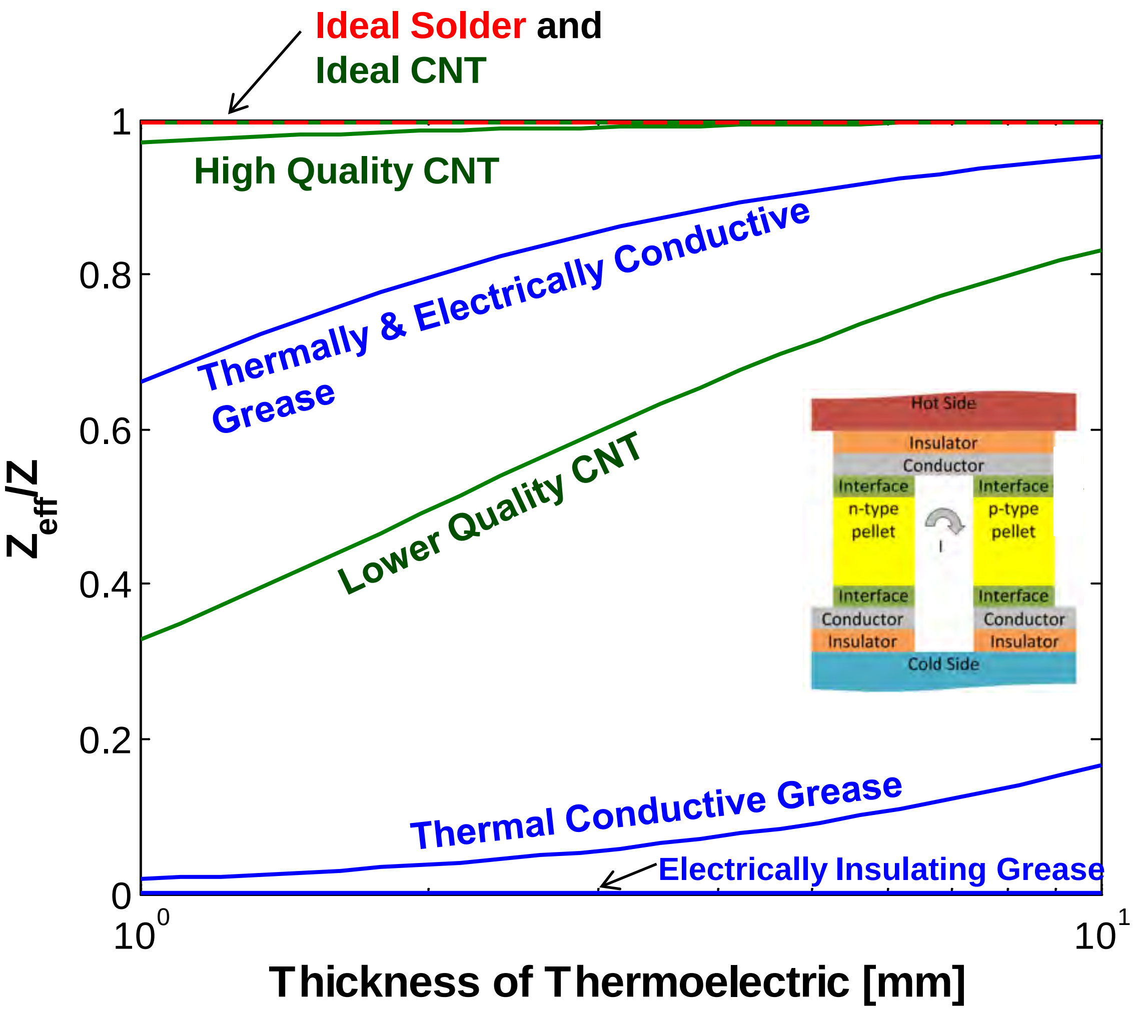


(b)



(c)

Relevance: Effect of Interface Resistances on Thermoelectric Device Properties



Interface Material	R''_{th} [W/m²/K]	R''_e [Ω m²]
Solders And Ideal CNT	$\sim 10^{-7}$	$\sim 10^{-12}$
High Quality CNT	$\sim 10^{-6}$	$\sim 10^{-10}$
Lower Quality CNT	$\sim 10^{-5}$	$\sim 10^{-8}$
Thermally & Electrically Conductive Grease	$\sim 3\times10^{-6}$	$\sim 3\times10^{-9}$
Thermal Conductive Grease	$\sim 8\times10^{-6}$	$\sim 3\times10^{-7}$
Electrically Insulating Grease	$\sim 8\times10^{-6}$	$>10^{-5}$

Using model of Xuan, *et al.* International Journal of Heat and Mass Transfer **45** (2002).