NSF-DOE Thermoelectrics Partnership:

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

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R. Bosch LLC

ACE067

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Overview

Timeline

- Start – January 2011
- End – December 2013
- ~66% complete

Barriers (2.3.2)

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

Budget

- $1.22 Million (DOE+NSF)
- FY13 Funding = $423K
- Leveraging:
    - ONR (FY09-11)
    - Fellowships (3 NSF, 2 NDSEG, Sandia, Stanford DARE)

Partners

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

nanoheat.stanford.edu

Relevance: Addressing Key Challenges for Thermoelectrics in Combustion Systems

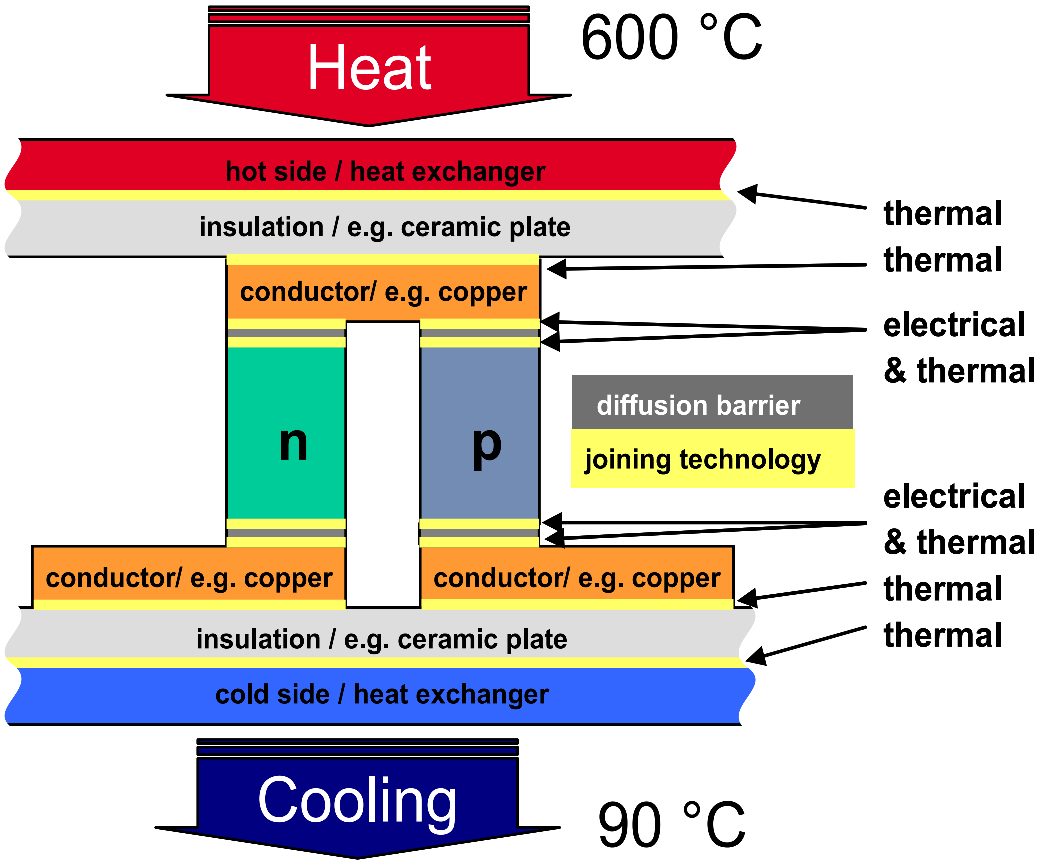
Improvements in the intrinsic ZT of TE materials are proving to be very difficult to translate into efficient, reliable power recovery systems.

Major needs include…

…Low resistance interfaces that are stable under thermal cycling.

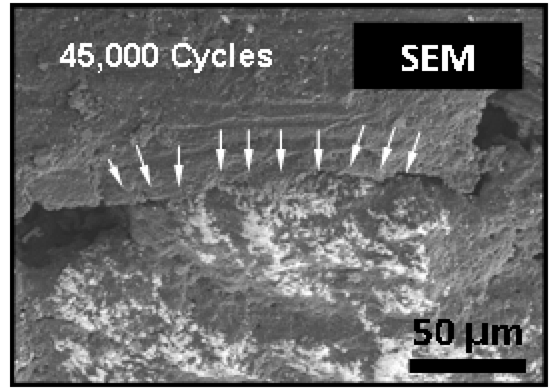
…High-temperature TE materials that are stable and promise low-cost scaleup.

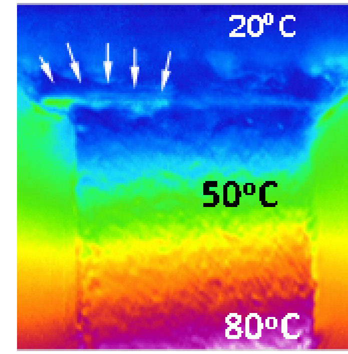
…Characterization methods that include interfaces and correlate better with system performance.



Relevance: Thermoelectric Interface Challenge

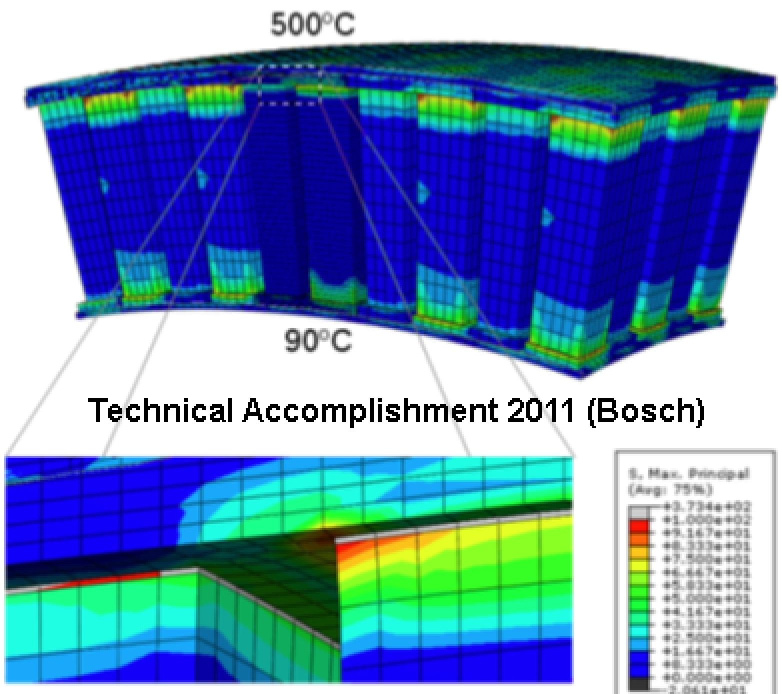
- Combustion TEG systems experience enormous interface stresses due to wide temperature spans.
- Thermal cycling degrades interface due to cracks, delamination, reflow, reducing efficiency.
- Our simulations show importance of thermodynamic stability (chemical reactivity, inter-solubility, etc.) and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

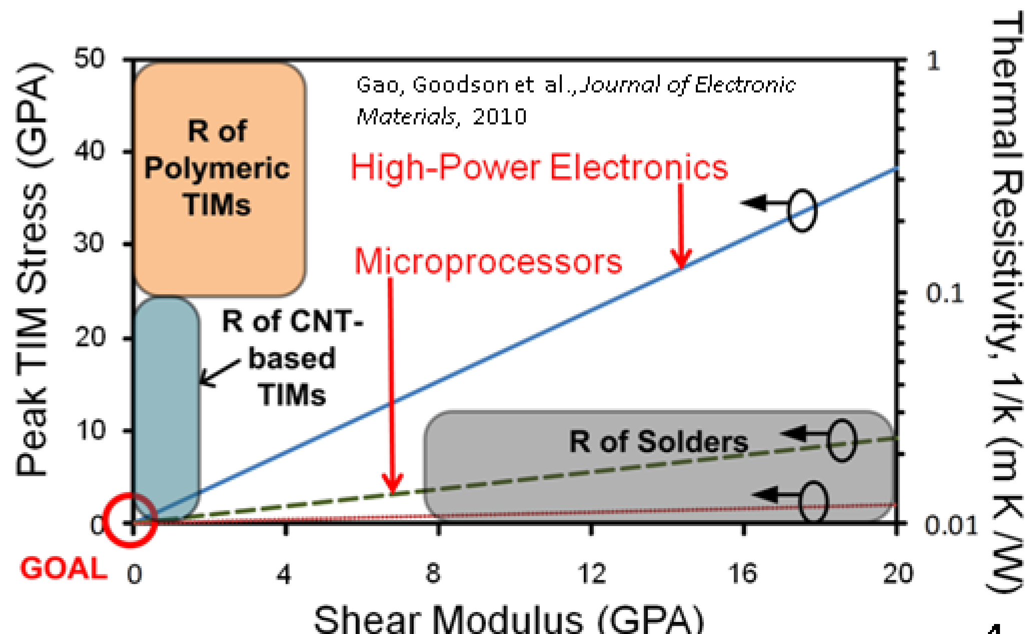




Infrared

Barako, Park, Marconnet, Asheghi, Goodson, J. Electronic Materials, Vol 43, Issue 3 (2013)





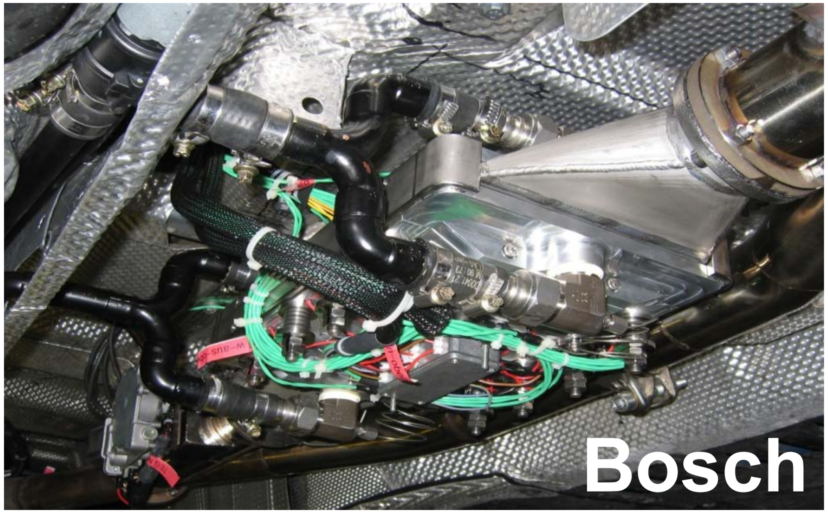
Research Objectives & Approach

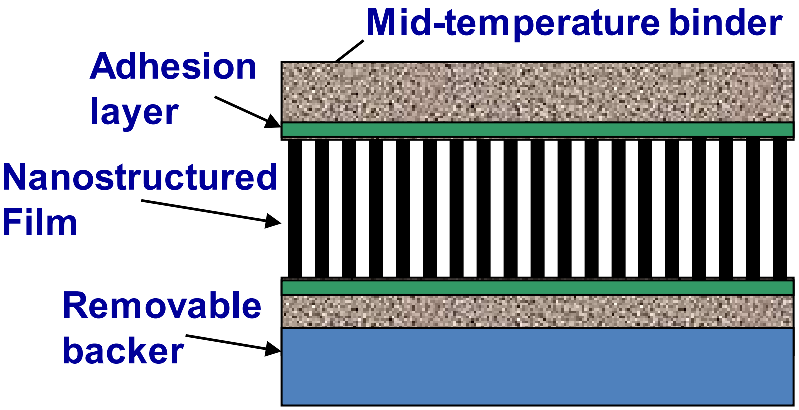
OBJECTIVES

Develop and assess the impact of novel interface and material solutions for TEG systems for automobile applications

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., US Patent (2007)
Hu, Goodson, Fisher, et al., *ASME JHT* (2006)
Won, Kenny, Fisher, et al., *CARBON* (2012)

APPROACH

Multiphysics simulations ranging from atomic to system scale

Advanced materials development including CNT and metal nanowire interface materials and high temperature thermoelectric materials

Development and application of novel thermoelectric metrology, including pico/nanosecond thermoreflectance, cross-sectional IR thermometry, and MEMS-based electrothermal and mechanical characterization

Research Approach

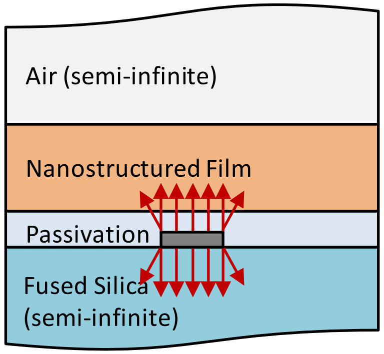
Additional Faculty & Staff beyond PIs
Prof. Mehdi Asheghi, Stanford Mechanical Engineering
Dr. Yoonjin Won, Stanford Mechanical Engineering
Dr. Winnie Wong-Ng, NIST Functional Properties Group
Dr. Yongkwan Dong, USF Department of Physics

Stanford Students:
Michael Barako (NDSEG fellow)
Marc Dunham (NDSEG fellow)
Yuan Gao* (NSF Fellow)
Lewis Hom* (NSF Fellow)
Saniya Leblanc* (Sandia Fellow)
Sri Lingamneni
Amy Marconnet* (NSF Fellow)
Woosung Park
* Graduated as of start of FY13

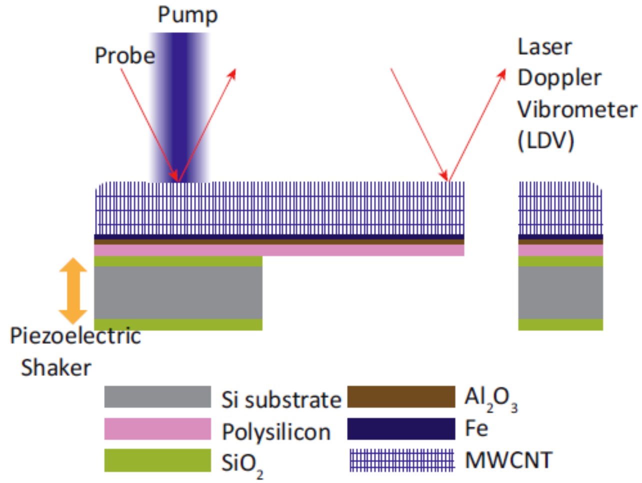
Interfaces 100%	Nanostructured films & composites, metallic bonding Ab initio simulations and optimization	Stanford Bosch
Metrology 100%	$(ZT)_{eff}$ including interfaces, thermal cycling High temperature ZT	Stanford USF/NIST
Materials 100%	Filled skutterudites and half Heusler intermetallics Ab initio 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 and Mechanical Properties

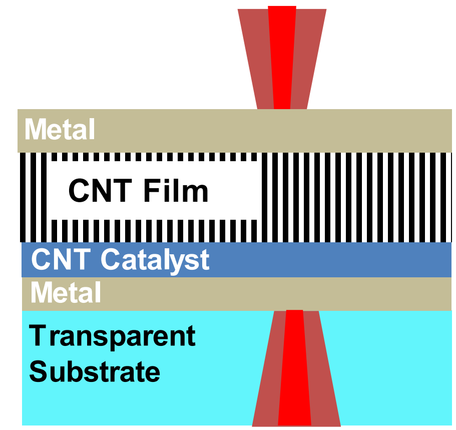
MEMS-based Thermal and Mechanical Characterization



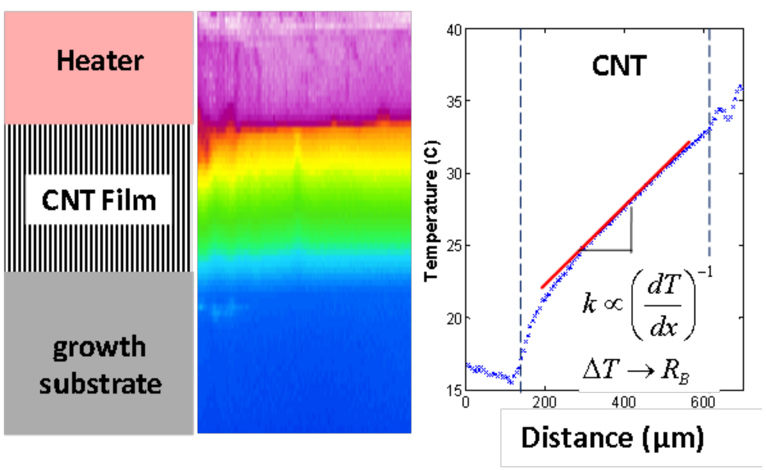
The 3ω Technique



Pico/Nanosecond Thermoreflectance



Cross-sectional IR Microscopy with in-situ Thermal Cycling



Associated Publications:

Gao, Marconnet, Goodson, et al.	*IEEE Trans. CPMT*	(2013)
Barako, Gao, Goodson et al.	*J. Electronic Materials*	(2013)
Gao, Won, Godson, et al.	*Carbon*	(2012)
Won, Gao, Panzer, Goodson, et al.	*Carbon*	(2012)
Marconnet, Panzer, Goodson, et al.	*ACS Nano*	(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*	(2006,07)
Pop, Dai, Goodson et al.	*Nano Letters*	(2006)
Pop, Dai, Goodson et al.	*Physical Review Lett.*	(2005)

Approach: Nanostructured TIMs

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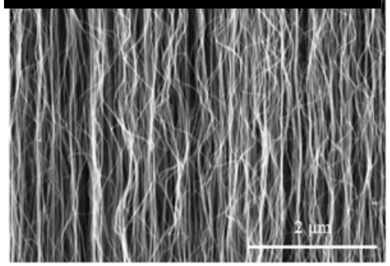
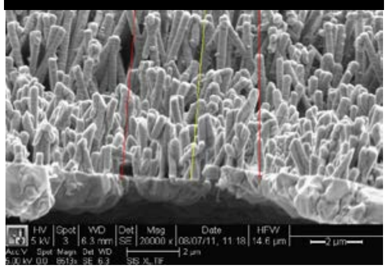
Nanostructured Interfaces

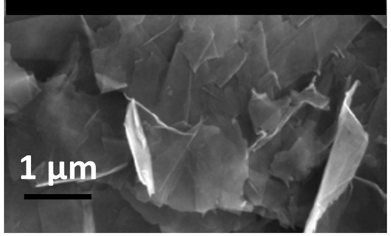
Carbon Nanotubes



Copper Nanowires

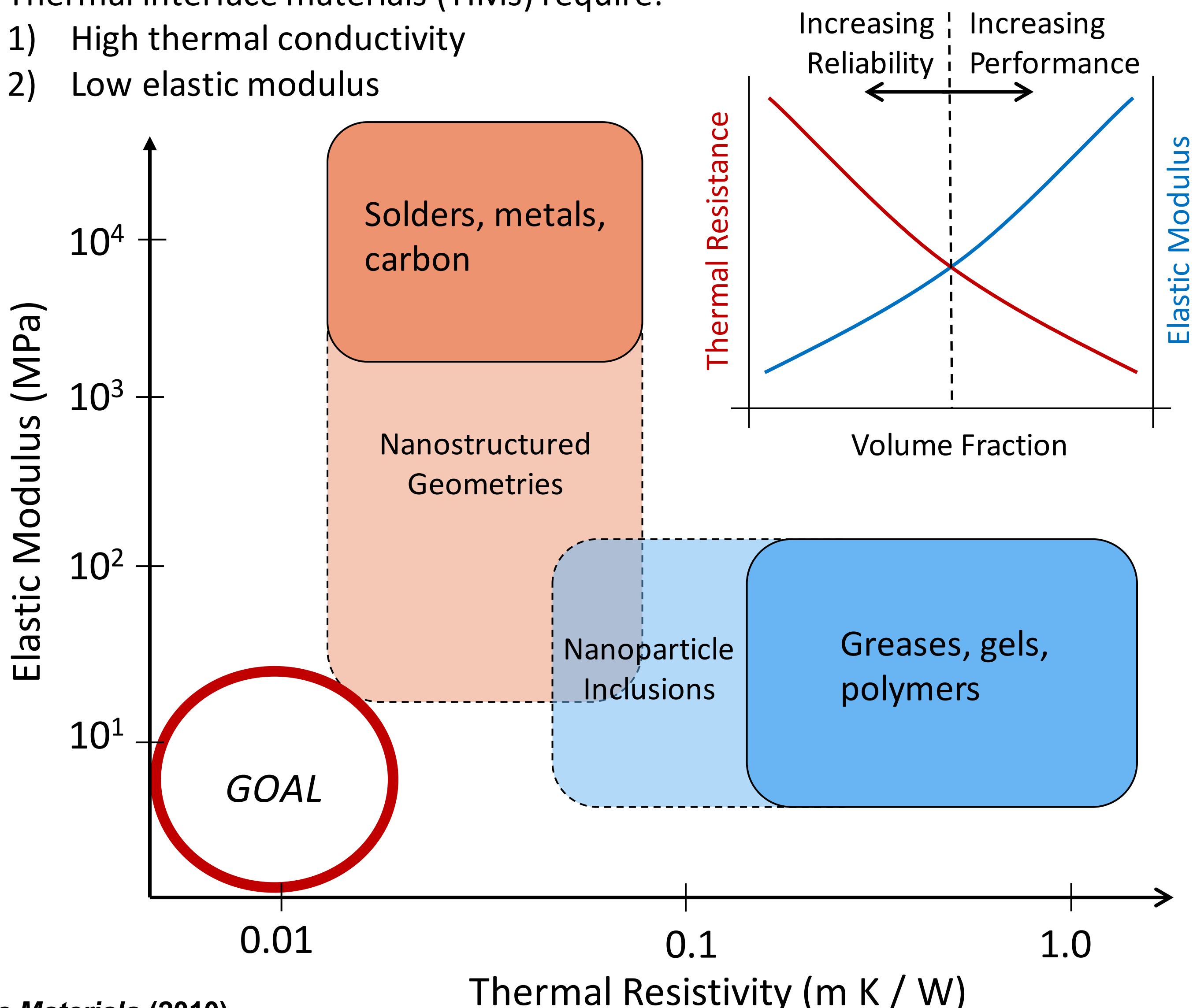


xGNP Composites



Thermal interface materials (TIMs) require:

1) High thermal conductivity
2) Low elastic modulus



Gao, Goodson, et al., J. Electronic Materials **(2010).**
Won, Goodson, et al., Carbon **(2012a, 2012b)**

Technical Accomplishments: Stanford Overview

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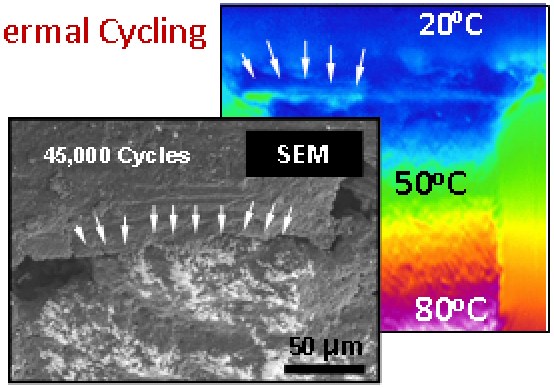
Thermal Cycling Failure Modes

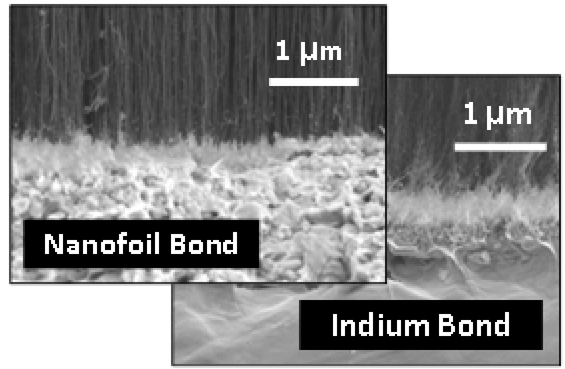
Thermal Cycling



Barako, Park, Marconnet, Asheghi, Goodson, J. Electronic Materials (2013)

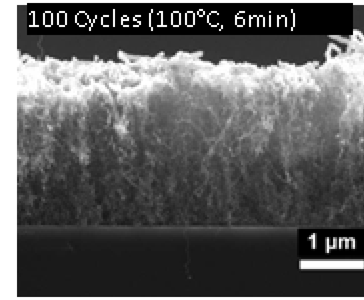
Nanostructured Interfaces

Solder-Bonded Nanotube Thermal Interface Materials



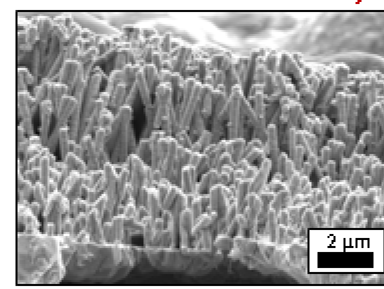
Barako, Gao, Marconnet, Asheghi, Goodson, Proc. of ITHERM (2012)

Thermal Cycling



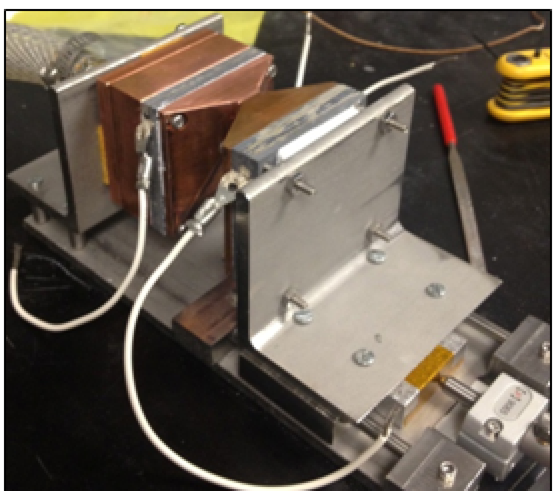
Gao, Panzer, Goodson et al., J. Electronic Materials, 2010

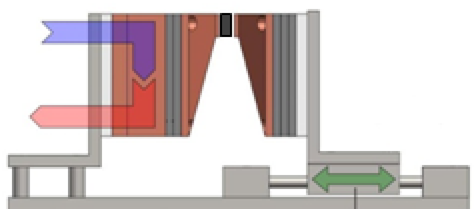
Metal Nanowire Arrays

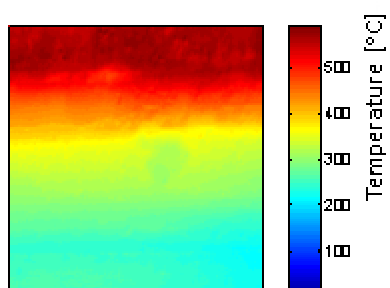


In-Situ Thermal Imaging during Cycling

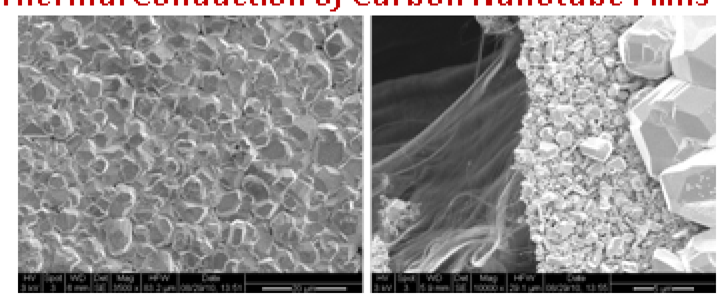
High Temperature Infrared Imaging & Characterization







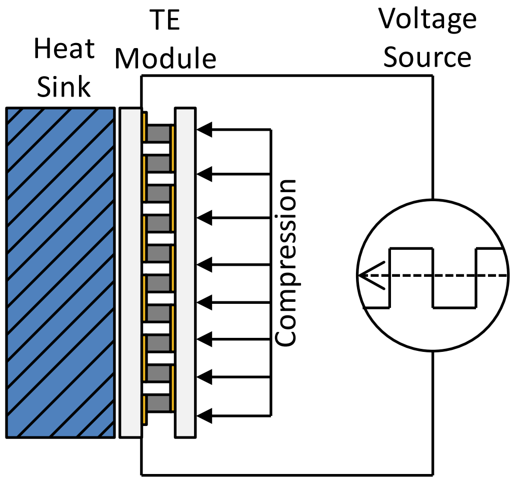
Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films

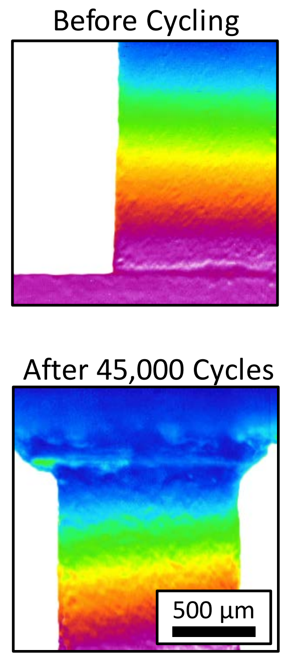


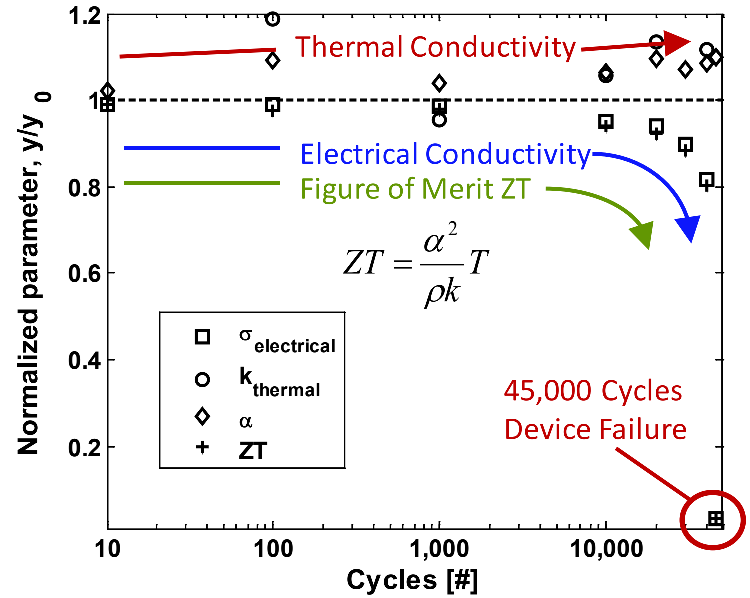
Marconnet *et al*, *Proc. of ITHERM* (2012)

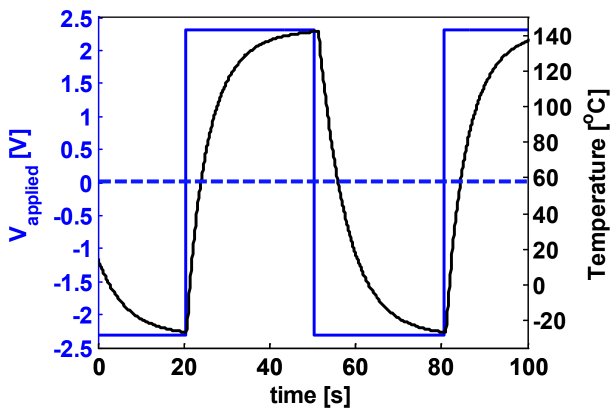
Technical Accomplishments:
TE Module Failure Modes with Thermal Cycling

Thermal cycling was performed on a commercial TE module. Temperature of the convective surface oscillates between +146°C and –20°C.

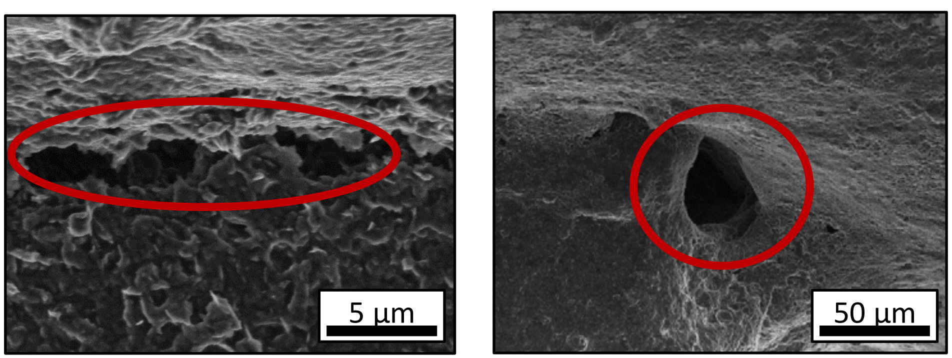








After 45,000 Cycles



Microcracks Voids

Barako, Park, Marconnet, Goodson, *et al.*, *J. Elec. Mat.* (2013)

Technical Accomplishments:
In-Situ Thermal Imaging and Reactive Metal Bonding

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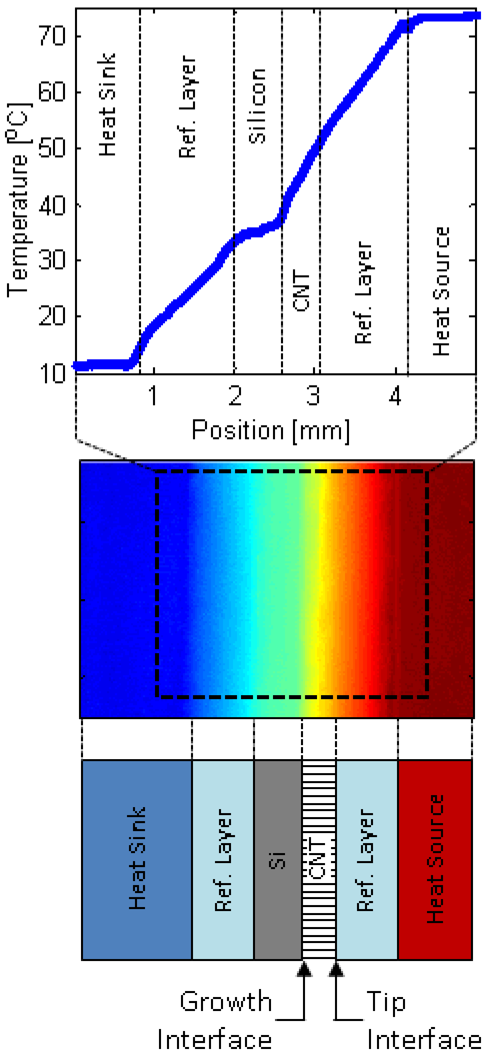
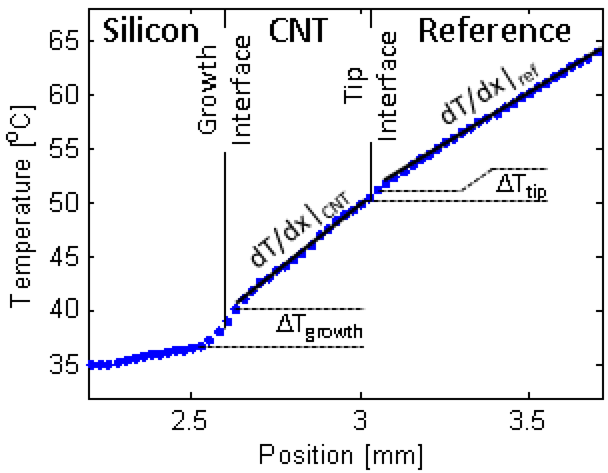
Comparative IR microscopy:





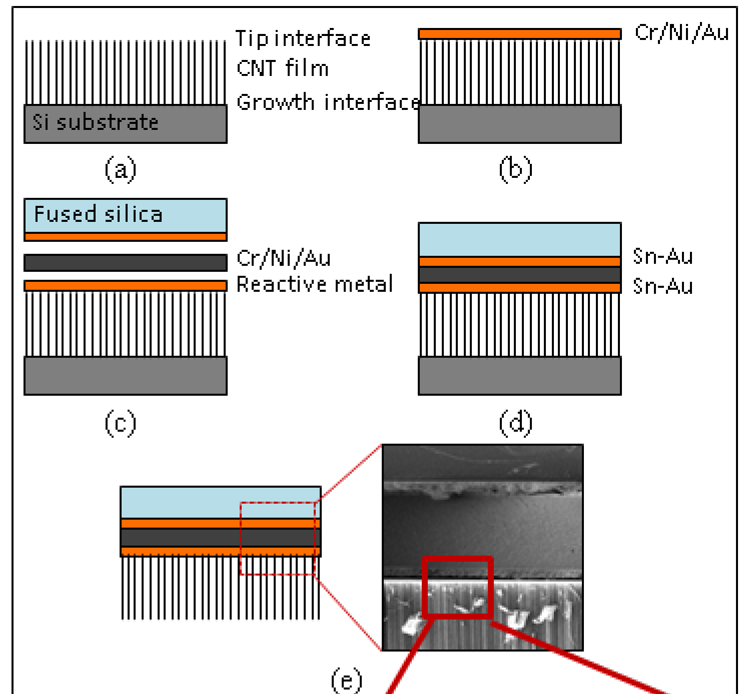
Thermal Boundary Resistance

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

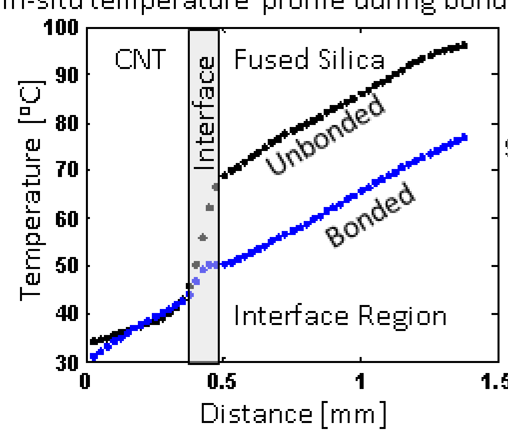
Thermal Conductivity

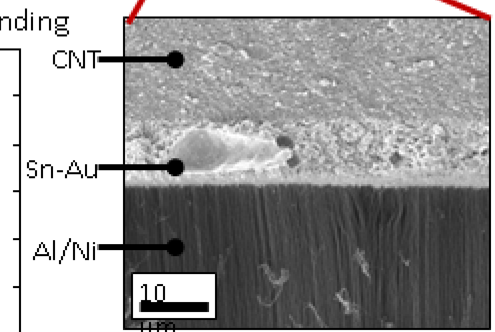
$$\frac{k_{sample}}{k_{ref}} = \frac{\left. \frac{dT}{dx} \right|_{ref}}{\left. \frac{dT}{dx} \right|_{sample}}$$

Reactive metal bonding procedure:



In-situ temperature profile during bonding



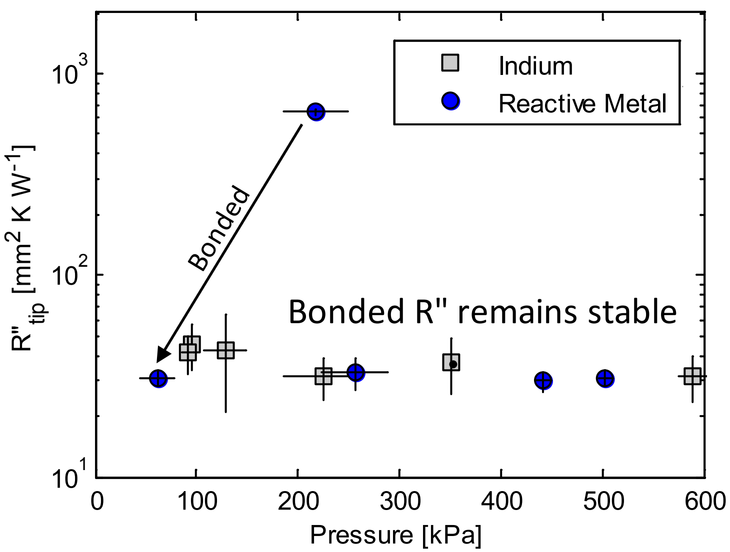


Marconnet, Yamamoto, Goodson, et al., ACS Nano (2011)
Barako, Gao, Marconnet *et al.*, Proc. of ITHERM (2012)

Technical Accomplishments: CNT Thermal Performance

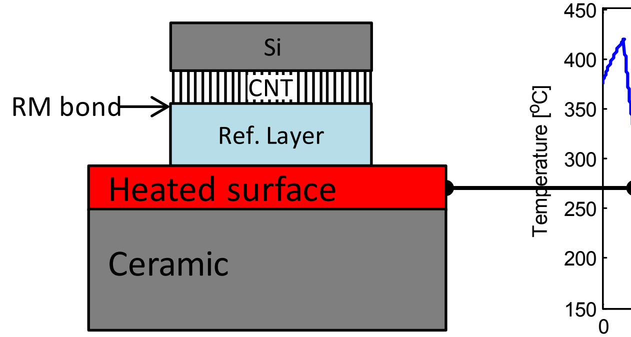
Reactive metal bonding has been used to demonstrate a reduction in thermal interface resistance of nearly two orders of magnitude over unbonded CNT films

R" of bonded CNT films

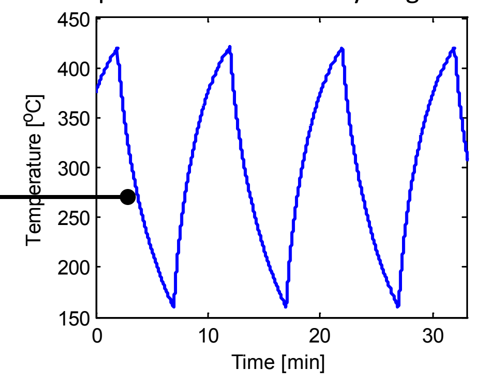


CNT Interface	R"$_{int}$ [mm^2-K/W]
Unbonded Contact	500-1500
Growth Interface	130-185
Indium Bonding	30-47
Reactive Metal Bonding	27-41

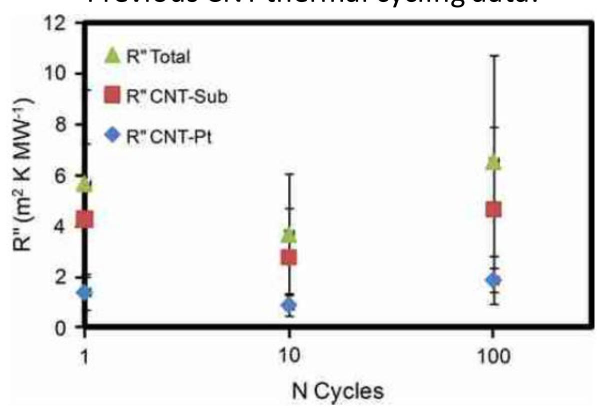
Reactive-metal bonded CNT films were subjected to thermal cycling to assess the evolution of thermal properties through use.



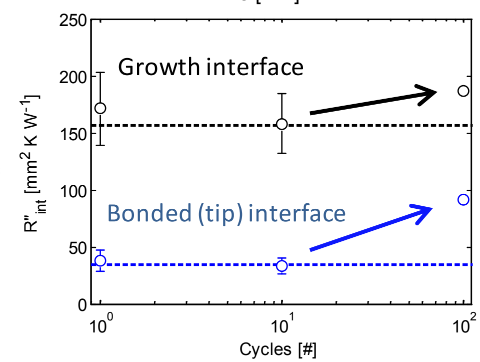
Temperature of thermal cycling surface

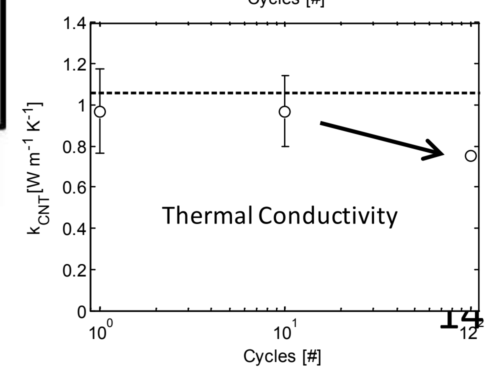


Previous CNT thermal cycling data:



Gao, Marconnet et al., JEM (2010)





Barako, Gao, Marconnet, Goodson, *et al.*, Proc. of ITHERM (2012)

Technical Accomplishments: Mechanical Resonator Technique for CNT Arrays

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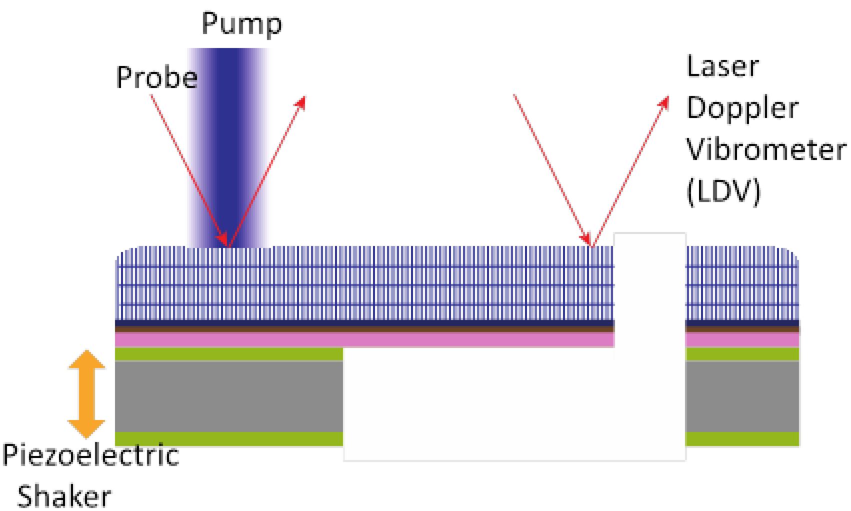
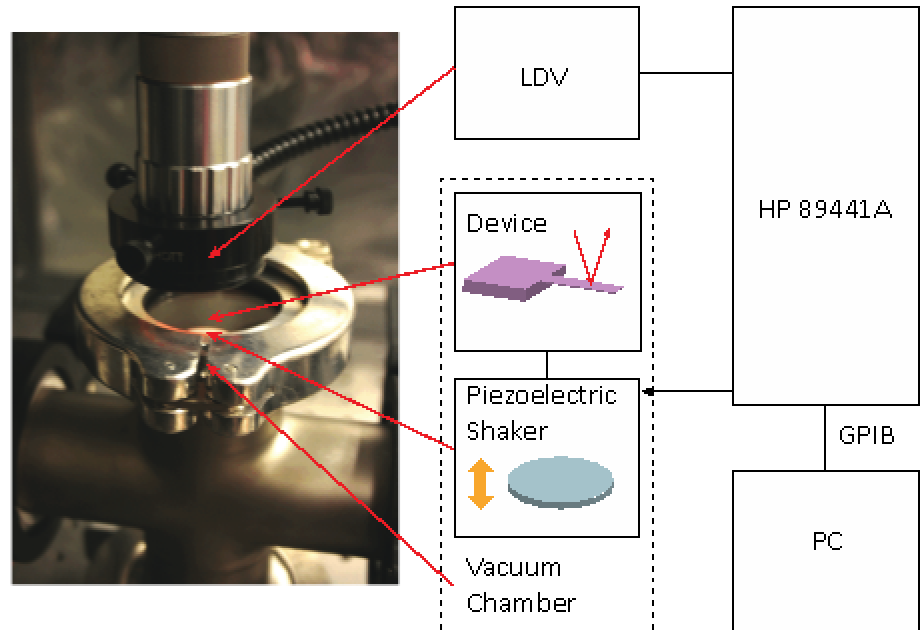
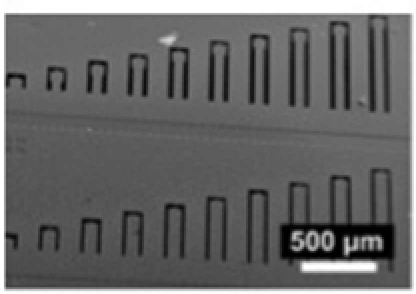
Thermal and Mechanical Characterization



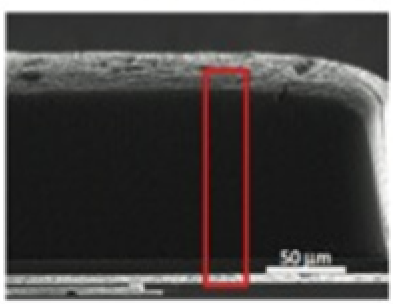
Experimental Setup



Resonator length and shape variation



CNT on a Cantilever

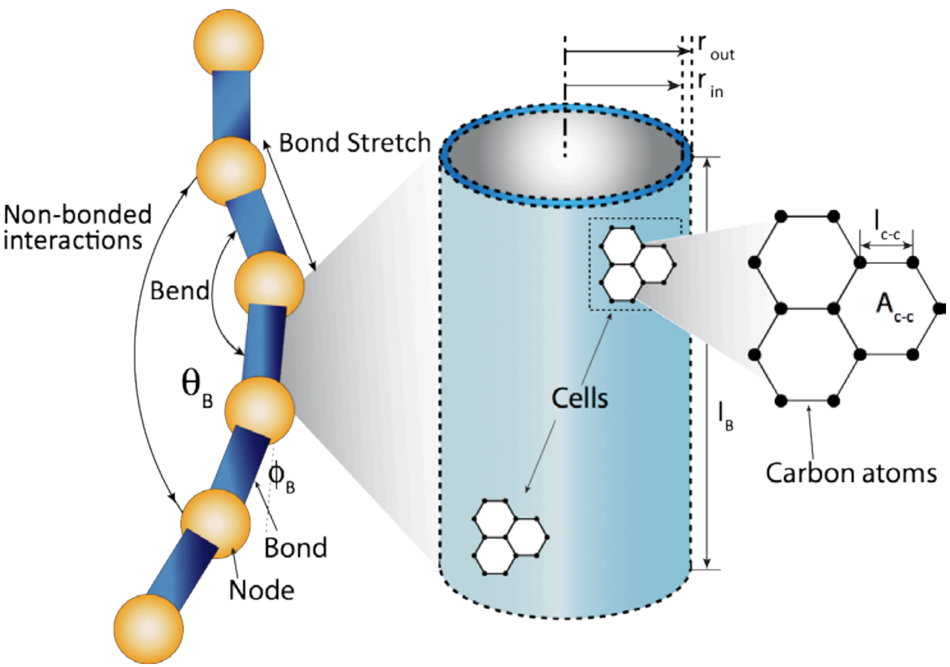


- LDV (laser Doppler velocimetry) experimental setup : resonant frequency of various thickness films.
- Resonant frequency shift : mechanical modulus
- Ring-down and fitting measurements : quality factors

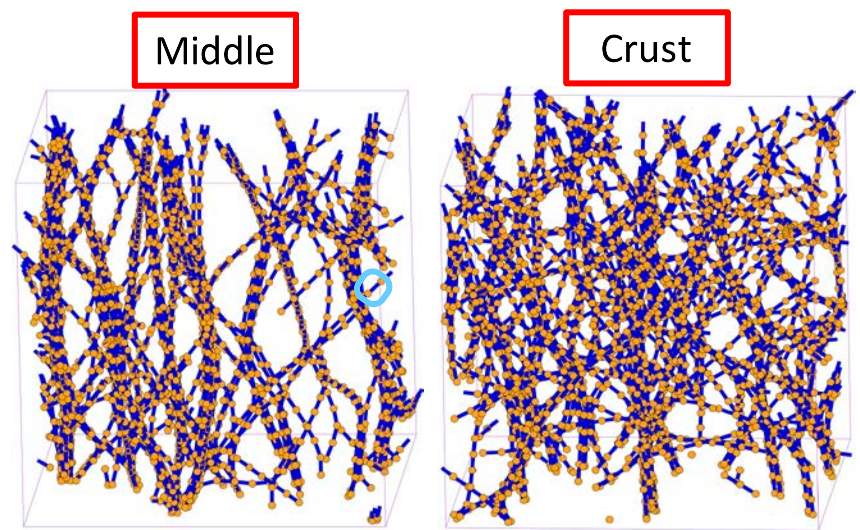
Thermal: Gao, Marconnet, Goodson et al., IEEE Trans. Comp. (2013)
Mechanical: Won, Gao, Goodson et al., Carbon (2012)

Technical Accomplishments: CNT Coarse-Grained Molecular Simulation

- Unit tubes act as elastic beams, showing stretching and bending behavior.
- Non-bonded nodes are interacting with van der Waals forces.
- Weak connections between nanotubes can be quantified.
- Different morphology using image analysis result can be demonstrated.
- Energy calculation: $E_{total} = E_S + E_B + E_{LJ} = \sum_{bond}\left(\frac{1}{2}k_S(l_B - l_{B,O})^2 + k_B(\cos\theta_B + 1) + \frac{C_{12}}{r_{CNT}^{12}} - \frac{C_6}{r_{CNT}^{6}}\right)$



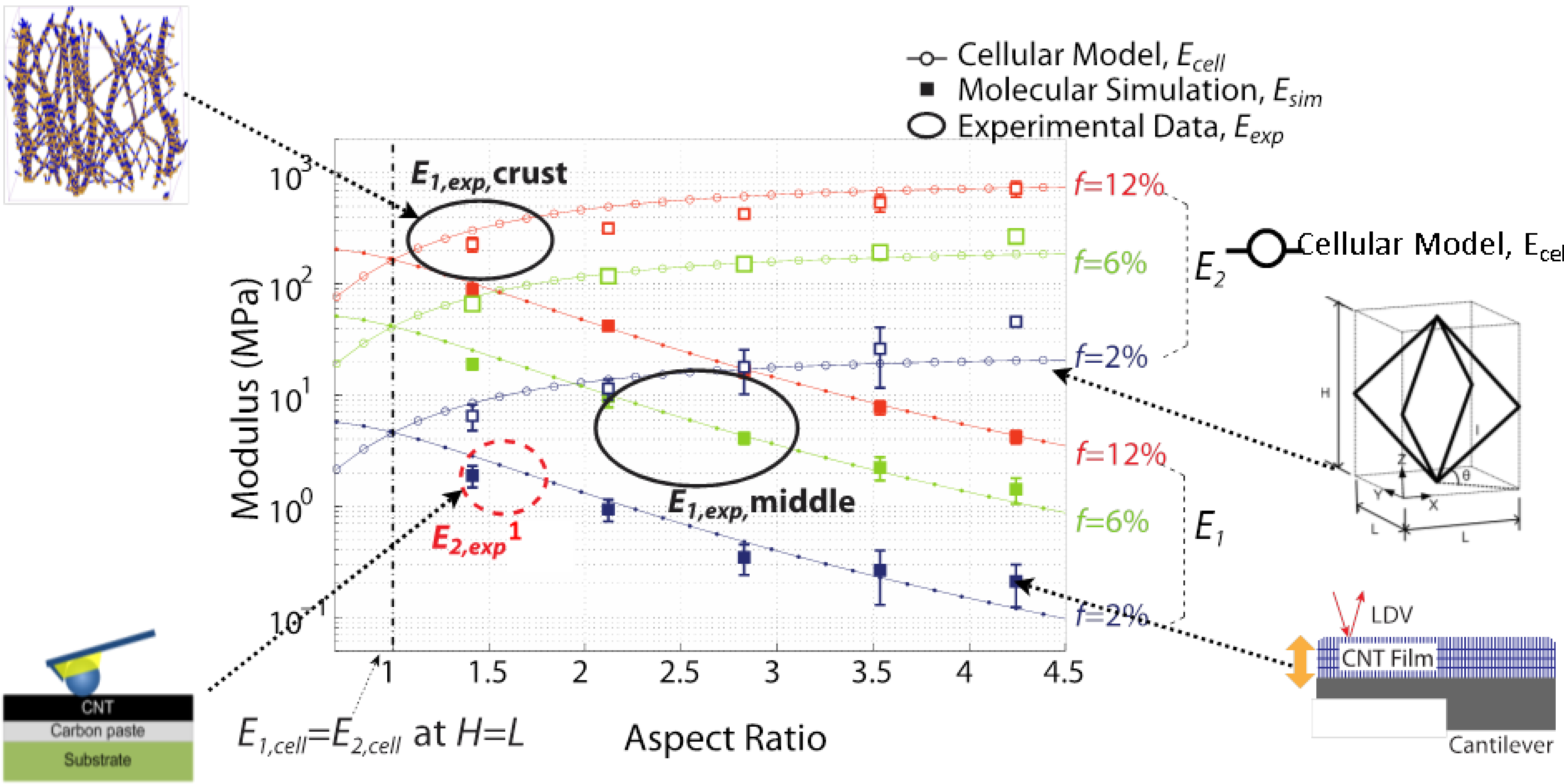
Simulation Box



Won, Gao, Goodson, *et al.*, submitted and under review (2012)
(with W. Cai Group, Stanford)

Technical Accomplishments:
CNT Mechanical Simulations and Experimental Data

Nanotube Simulation, E_{sim}



Nanoindentation Data, E_{exp}

Resonator Experimental Data, E_{exp}

Gao *et al.*, Carbon (2012)

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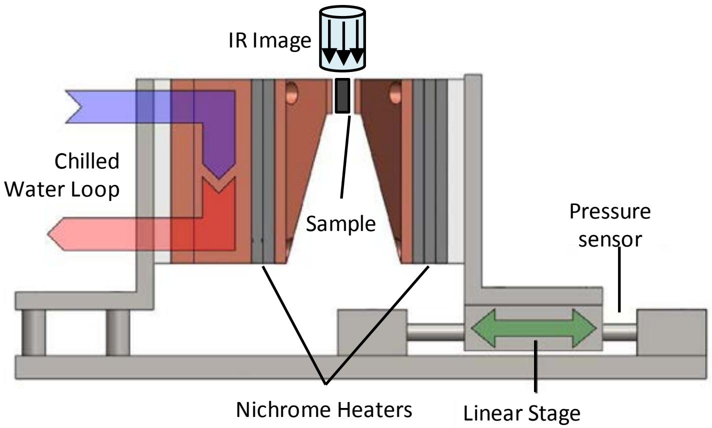
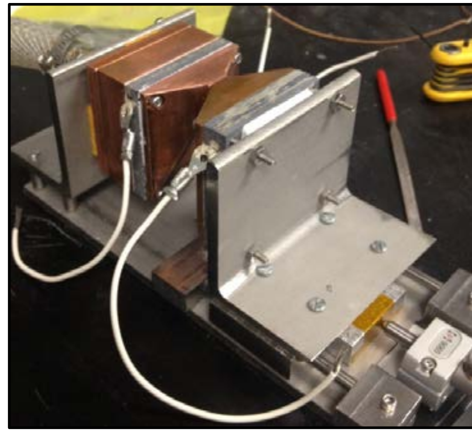
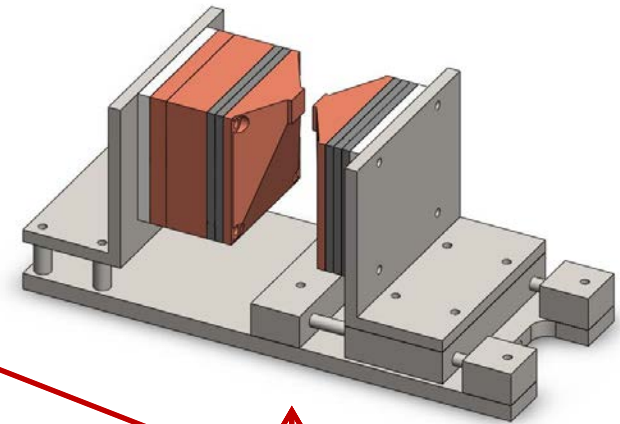
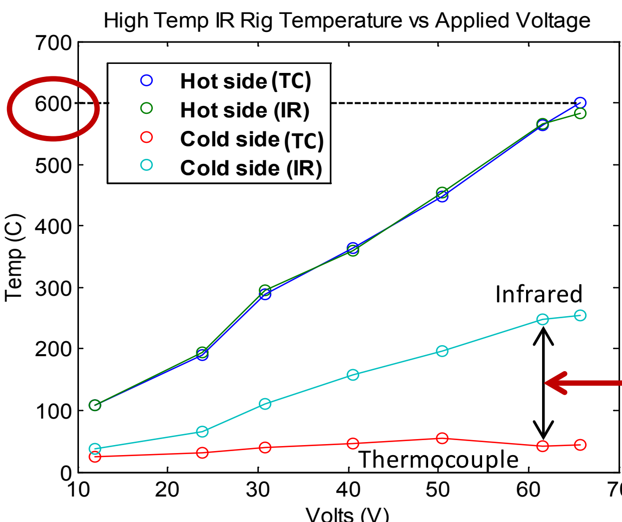
Technical Accomplishments: High-Temperature In-Situ Thermal Imaging

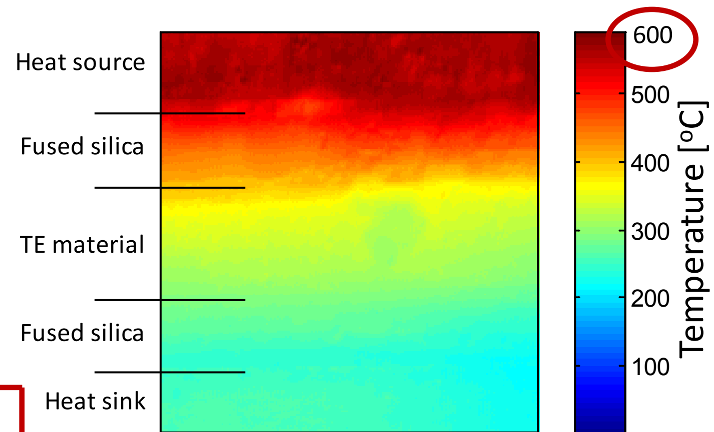






Outreach FY12: Designed and built by two summer undergraduate research assistants as part of the Stanford outreach activities





Technical Accomplishment FY12: Target maximum temperature achieved

FY13 goal

For large temperature gradients, the IR signal intensity spans several orders of magnitude. It is difficult to accurately measure the signal at each pixel simultaneously under these conditions.

$$I_{rad} \propto q''_{rad} = \varepsilon \sigma T^4$$

Two generations have been constructed by the end of FY12

	1st Generation: FY11	2nd Generation: FY12
Max T [°C]	400	>600
Time constant [min]	200	15
Mass [kg]	20	5

Technical Accomplishments:
Fabrication of Metal Nanowire Thermal Interfaces

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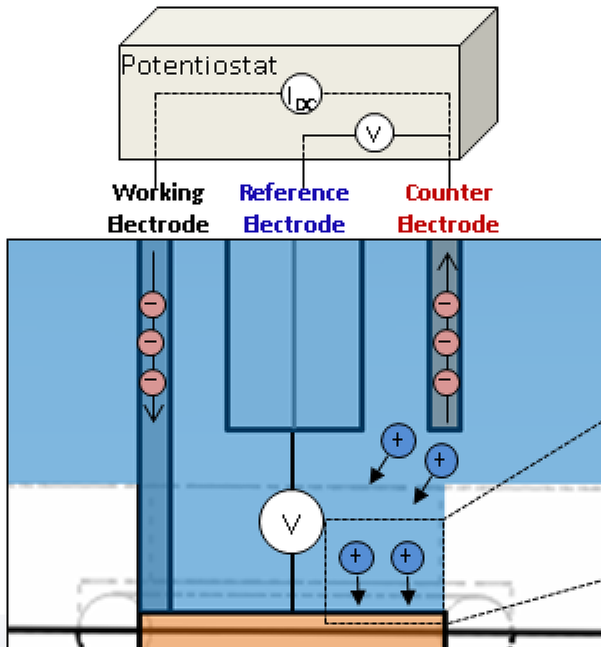
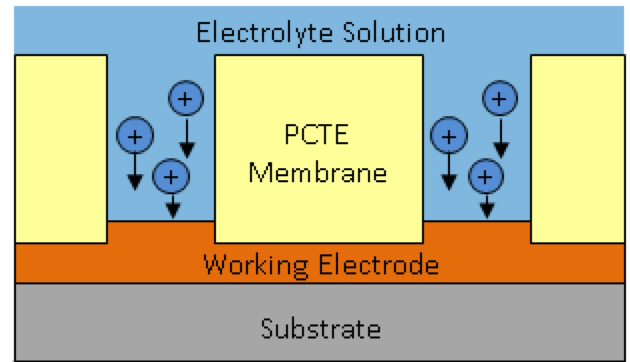
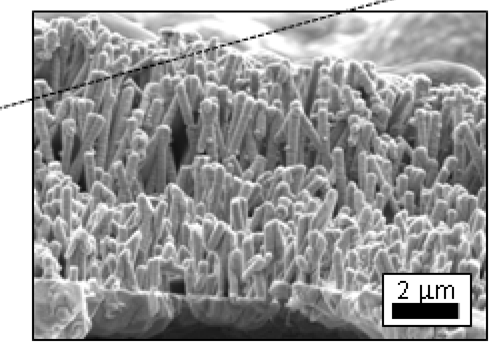
Half-reaction at WE (cathode):

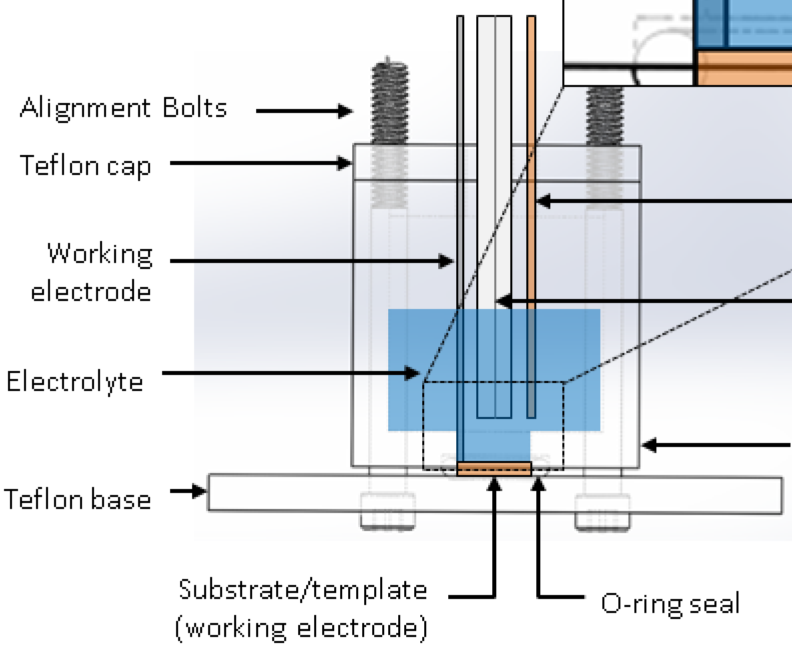
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

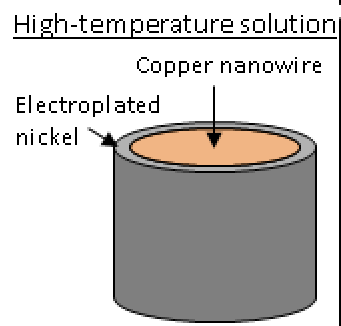
Reduction reaction at **WE** surface deposits copper onto surface

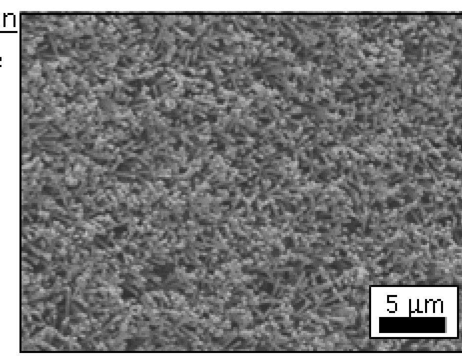












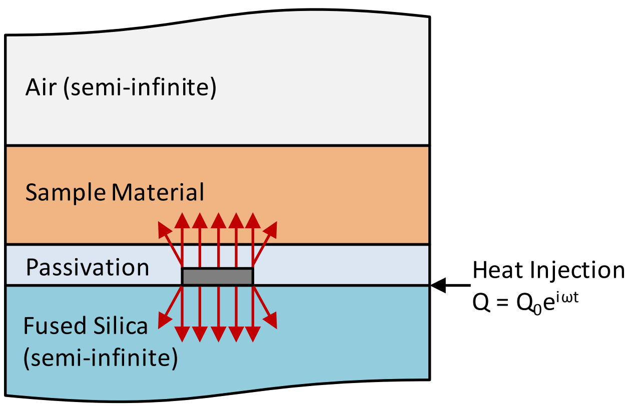
Metal nanowires are grown by depositing metal into a sacrificial porous template

Technical Accomplishments:
High-sensitivity Electrothermal Interface Characterization

STANFORD nanoHeat

Measurement Overview:

Current at frequency 1ω generates Joule heating at 2ω, and the oscillating temperature of the heater is measured indirectly by detecting a voltage at 3ω



Frequency-Modulated Properties:

1ω: Frequency of AC current source driving line heater

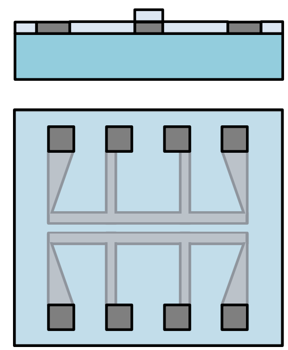
2ω: Joule heating at 2ω
Temperature fluctuation at 2ω
Heater resistance is perturbed at 2ω

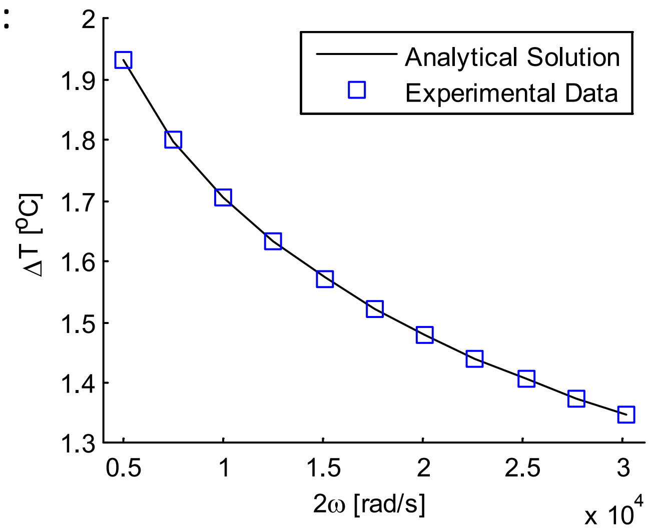
3ω: V = I x R leads to voltage at 3ω

Thermal Diffusion Length: $L \propto \sqrt{\frac{\alpha}{\omega}}$

Device calibration:

Device is calibrated prior to growth of Cu Nanowires

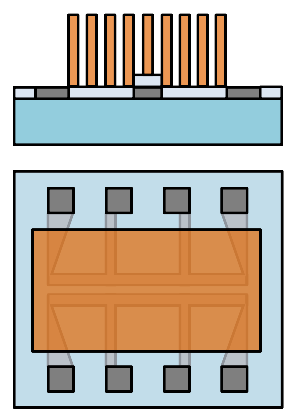


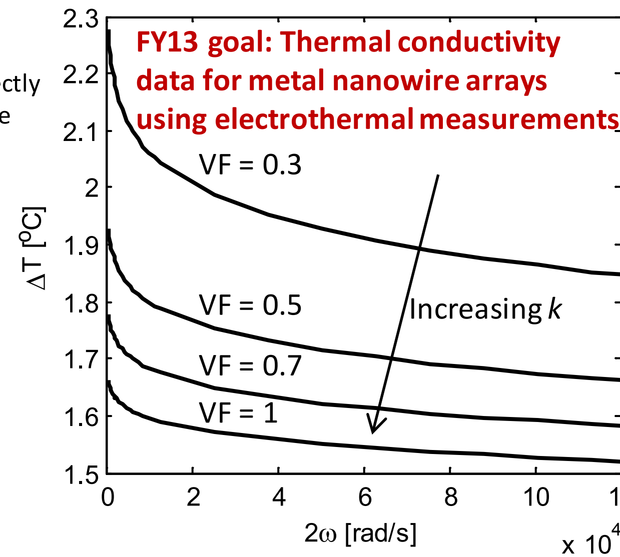


Courtesy: Shilpi Roy

Simulated data:

Cu nanowires are grown directly onto top surface of 3ω device





Technical Accomplishments: Stanford-USF Student Visit

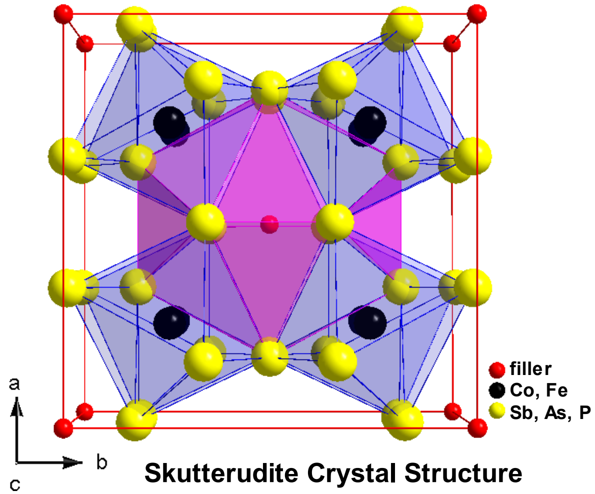
During January 28th – February 1st, Stanford graduate student Michael Barako was hosted by Prof. George Nolas and Dr. Yongkwan Dong at USF to learn about TE material synthesis and characterization techniques, including:

- Hot/cold pressing
- Spark plasma sintering (SPS)
- Arc melting
- X-ray diffraction
- Energy-dispersive spectroscopy (EDS)
- Simultaneous thermal, electrical, and Seebeck characterization

STANFORD nanoHeat

NOVEL MATERIALS LABORATORY
UNIVERSITY OF SOUTH FLORIDA

Approach: Bulk TE Materials for Automotive Applications



Skutterudite Crystal Structure

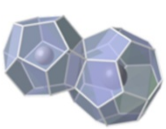
Glen Slack initiated the PGEC concept with skutterudites:

- ✓ Fillers should be loosely bond to the cage-forming atoms.
- ✓ Fillers 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.

- Yb partially-filled skutterudites
  - Partial filling optimizes lattice thermal conductivity reduction[1]
  - Yb possesses an intermediate valence in $CoSb_3$ thereby maximizing the filler concentration while minimizing the added carriers[2]
- P-type partially filled skutterudites (high-T measurements at NIST, Clemson U. & ORNL)
- Amorphous intermetallic alloys[3] (in collaboration with General Motors)
- Bi_2Te_3-alloys for High Resolution Infra-Red Thermometry (in collaboration with Marlow Ind.)
- 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)

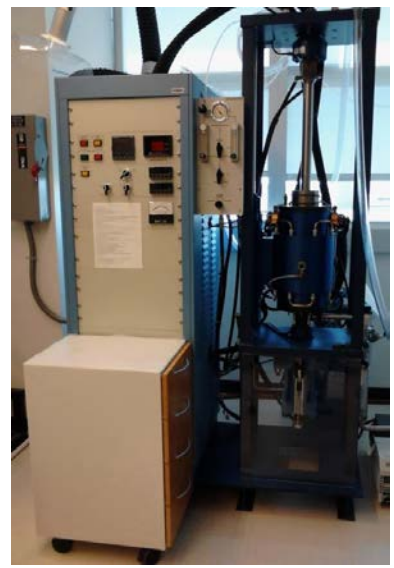
http://shell.cas.usf.edu/gnolas

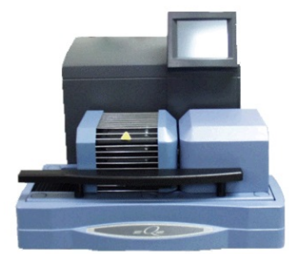


Novel Materials Laboratory
University of South Florida

Approach: Experimental Capabilities at USF

- **Synthesis**
  Furnaces: crystal growth, annealing, arc melting, induction, SPS
  Preparation: glove boxes, hoods, wire saw & diamond wheel
  Supplemental: glass blowing station, ultrasonic cleaning
- **Densification: hot press & spark plasma sintering with custom designed and built die tooling, separate sample preparation areas**
- **Transport: Low-T *S*, *ρ*, *κ* & Hall w/sample mounting stations, RT *S* & *ρ***
- **Characterization: DTA/TGA,** XRD, SEM w/EDS, optical spectroscopy



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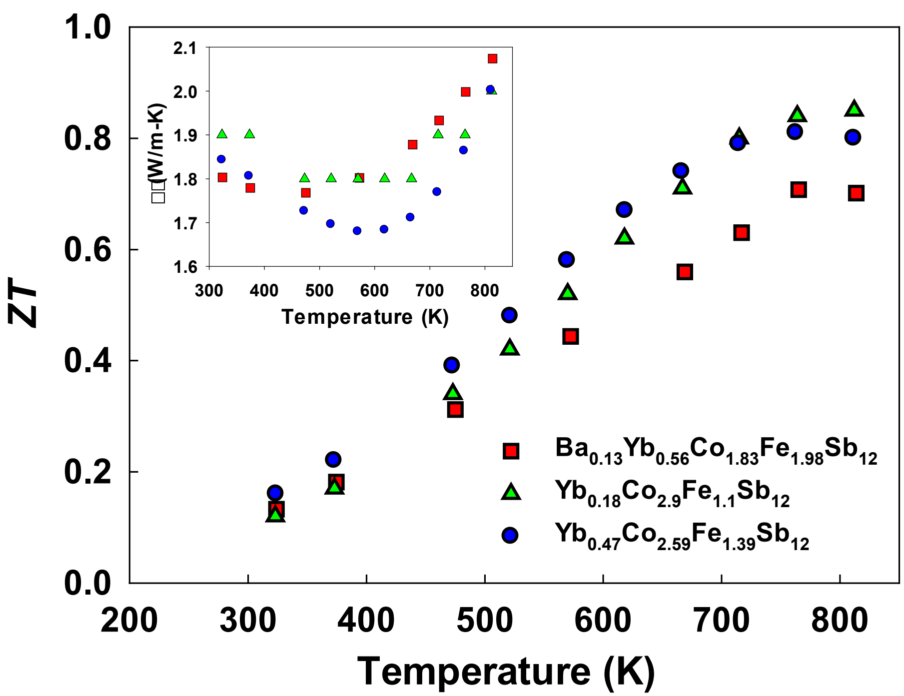
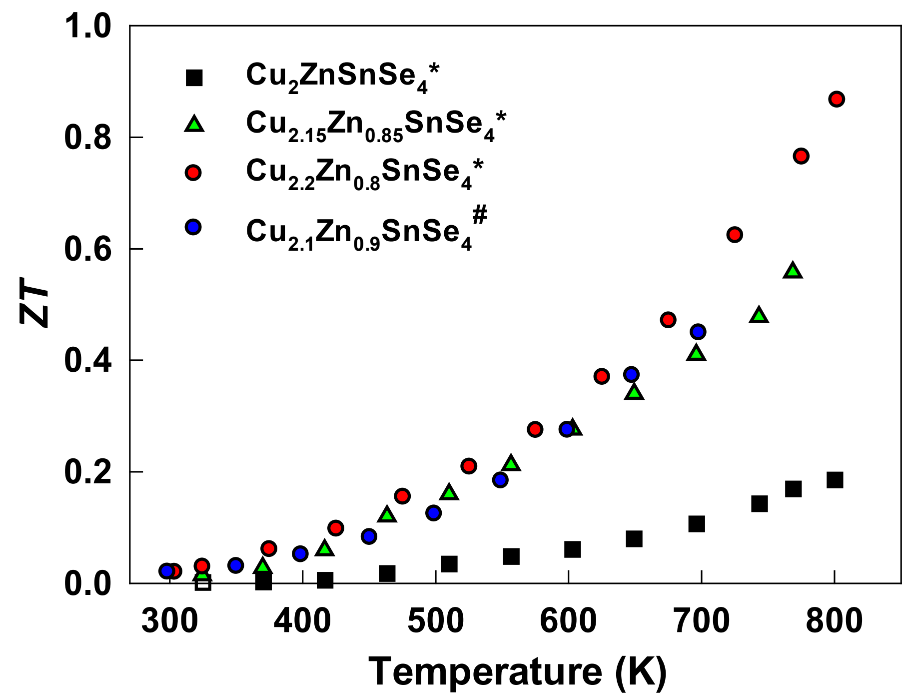
Technical Accomplishments: High *ZT* *p*-type Materials

Skutterudites



Chalcogenides



* Current work at USF

\# M.-L. Liu et al, Appl. Phys. Lett. 94, 202103 (2009)

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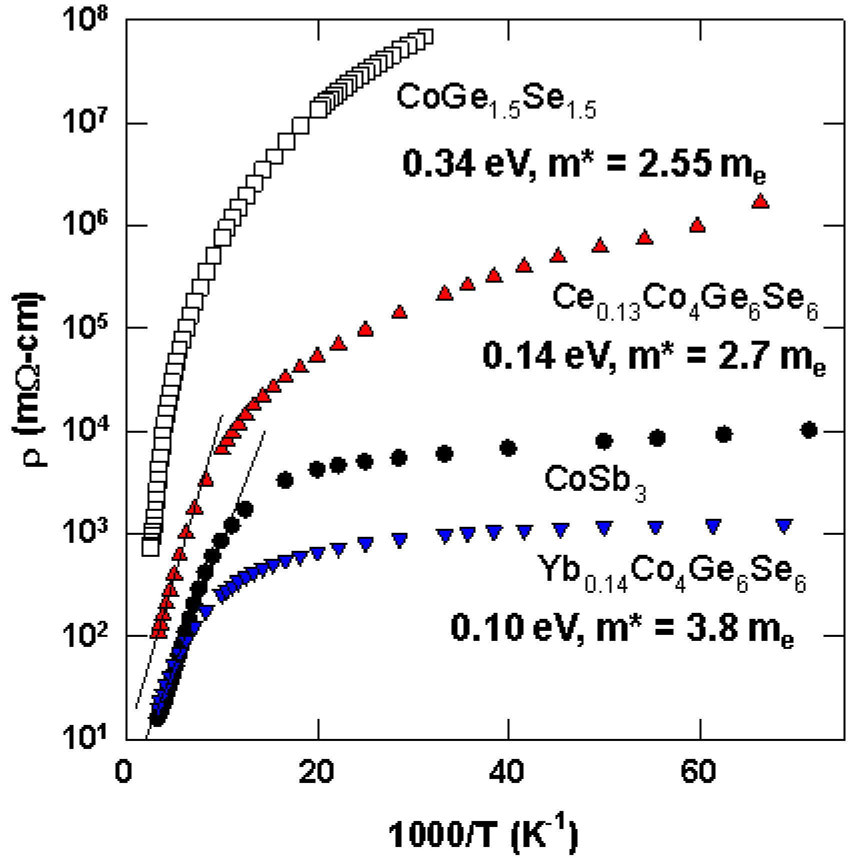
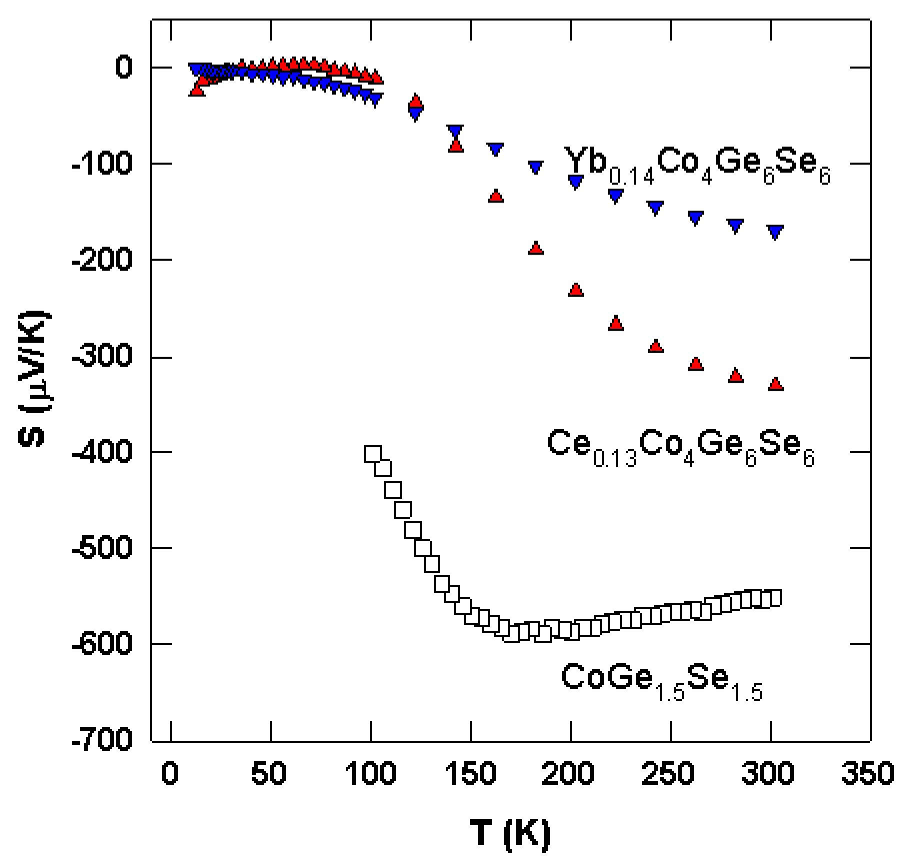
Technical Accomplishments: Transport Measurements & Analyses





$\rho = \rho_0 exp(E_a / k_B T)$ and $E_g \sim 2E_a$

$CoSb_3$: D. Mandrus, et al, Phys. Rev. B52, 4926 (1995)
$CoGe_{1.5}Se_{1.5}$: G.S. Nolas et al, Phys. Rev. B68, 193206 (2003)
Y. Dong et al., Phys. Rev. B, submitted

Carrier concentration
No filler: 3.5 x 10^{18} /cm^3
Ce: 5.0 x 10^{19} /cm^3
Yb: 6.1 x 10^{20} / cm^3

Technical Accomplishments: Transport Measurements & Analyses

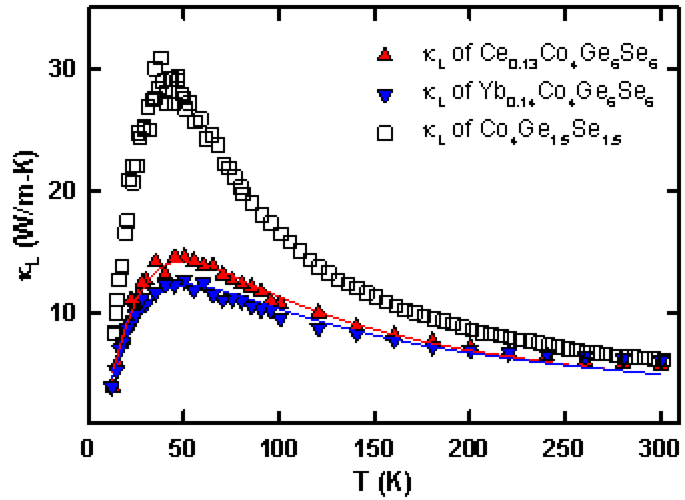
Fit of κ_L using the Debye approximation:

$$\kappa_L = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_C^{-1}(e^x - 1)^2}\,dx \qquad x = \frac{\hbar\omega}{k_B T}$$

Phonon scattering relaxation time:

$$\tau_C^{-1} = \frac{\upsilon}{L} + A\omega^4 + B\omega^4 T \exp\left(-\frac{\theta_D}{3T}\right) + \frac{C\omega^2}{\left(\omega_0^2 - \omega^2\right)^2}$$

	L (μm)	A (10^{-43} s^3)	B (10^{-18} s·K^{-1})	C (10^{-33} s^{-3})	ω_0 (10^{12} s^{-1})
$CoGe_{1.5}Se_{1.5}$	1.3	4.7	6.7	-	-
$Ce_{0.13}Co_4Ge_6Se_6$	1.1	21	5.8	4.5	15
$Yb_{0.14}Co_4Ge_6Se_6$	1.3	30	4.8	4.8	11

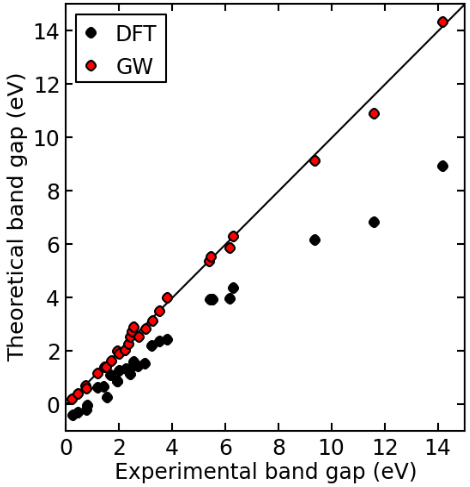


$CoGe_{1.5}Se_{1.5}$: G.S. Nolas et al, Phys. Rev. B 68, 193206 (2003)
Y. Dong et al, Phys. Rev. B, submitted

Approach: Boltzmann transport materials computation modeling

Electron and phonon transport coefficients are computed by solving Boltzmann transport equation. Requires the following as input data:

- Electronic band structure
  - We previously used DFT (density functional theory) which is known to underestimate band gaps.
  - We recently switched to GW method (many-body perturbation theory) which gives accurate band gaps.
- Electronic relaxation time
  - Constant electronic relaxation time fit to experiment
- Phonon band structure
  - From DFPT (density functional perturbation theory)
- Phonon relaxation time
  - From DFPT (density functional perturbation theory)



Data taken from: S. G. Louie in *Topics in Computational Materials Science*, edited by C. Y. Fong (World Scientific, Singapore, 1997)

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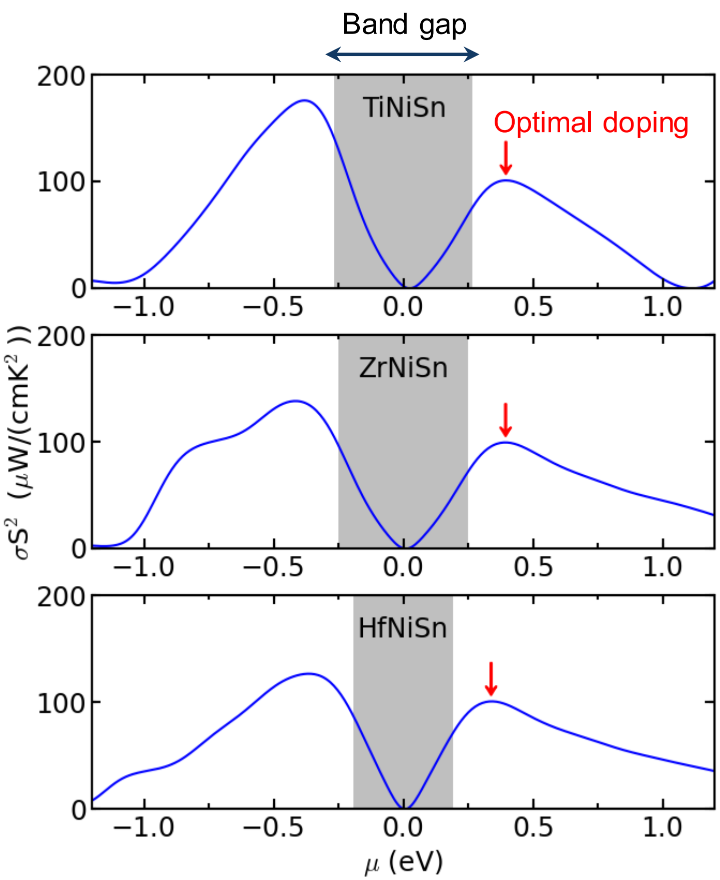
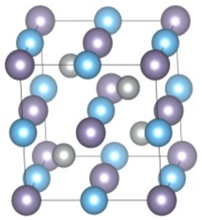
Optimization of power factor of n-type Half-Heuslers by varying the carrier concentration (doping) within the Boltzmann formalism





T = 400^0C

	E_g	σS^2	μ	x
TiNiSn	0.53	101	0.39	0.031
ZrNiSn	0.50	100	0.39	0.020
HfNiSn	0.38	101	0.34	0.019

E_g	Band gap (eV)
σS^2	Power factor (μW/(cm K^2))
μ	Chemical potential (eV)
x	Doping (electron/unit cell)

Optimal compositions: $(Ti|Zr|Hf)NiSn_{0.98}Sb_{0.02}$

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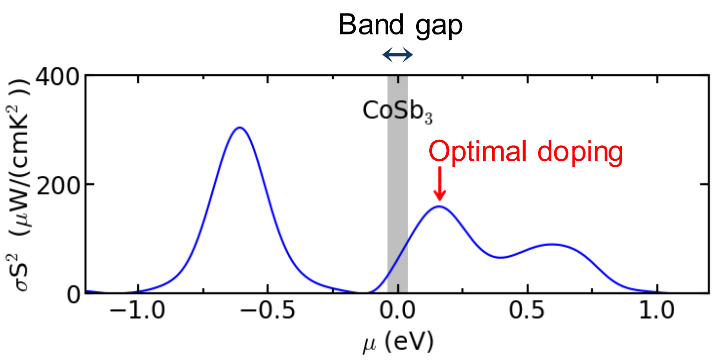
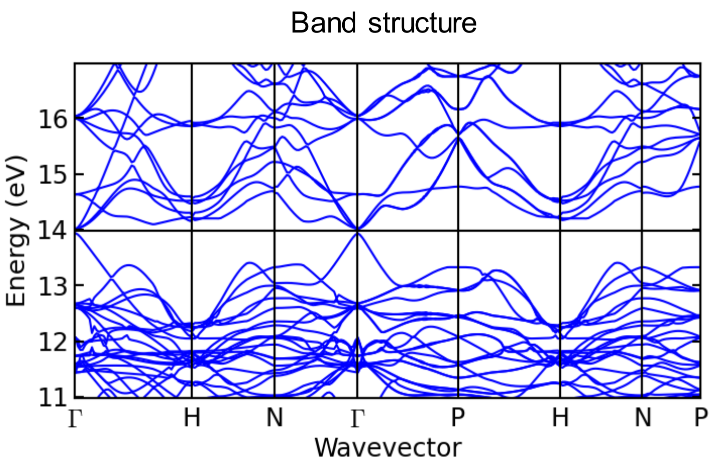
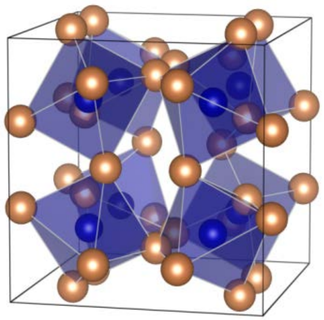
Technical Accomplishments: Electronic transport

Optimization of power factor of n-type Skutterudites by varying the carrier concentration (doping) within the Boltzmann formalism







T = 400^{0}C

	E_g	σS^2	μ	x
$CoSb_3$	0.08	160	0.16	0.205

E_g	Band gap (eV)
σS^2	Power factor (μW/(cm K^2))
μ	Chemical potential (eV)
x	Doping (electron/unit cell)

Optimal compositions: $(Ba_{0.10}|La_{0.07}|Yb_{0.07})Co_4Sb_{12}$

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Technical Accomplishments: Thermal transport modeling

Quasi-harmonic analysis of Skutterudites

- Capture first-order anharmonic effects (nonideal crystal) at elevated T
- Compute vibrational structure: phonon spectrum at different distortions
- Using a model equation of state predict realistic measurable properties

Free energy → $F(V,T)$; Ground state → $E(V)$; Volume-dependent phonon frequencies → $\omega_{\mathbf{q},\lambda}(V)$

$$F(V,T) = E(V) + \sum_{\mathbf{q},\lambda} \frac{\hbar\omega_{\mathbf{q},\lambda}(V)}{2} + k_B T \sum_{\mathbf{q},\lambda} \ln\left(1 - \exp\left[-\beta\hbar\omega_{\mathbf{q},\lambda}(V)\right]\right)$$

- Estimate formula[1] for *k* adapted to ab-initio

$$k_{l,T=\Theta_D} \approx \frac{B M \delta \Theta_D^2}{n^{2/3}\gamma^2}$$

- Good agreement for $CoSb_3$
- Need to test applicability limits →

$CoSb_3$ results (300K)	Computed	Expt
CTE α (10^{-6}/K)	**10**	10.5 [2]
Bulk modulus B (GPa)	**100.1**	112 [3]
Debye temp. Θ_D (K)	**304**	307 [4]
Gruneisen param. γ	**1.66**	
Th. cond. κ (W/mK)	**4.8**	5.0 [4]

[1] Slack & Tsoukala, J. Appl. Phys. 76, 1665 (1994)
[2] Zhao et al, Journal of Alloys and Compounds 477, 425 (2009)
[3] Slack & Tsoukala, J. Appl. Phys. 76, 1665 (1994)
[4] CRC Handbook of Chem and Phys, pp. 12-85 (2009)

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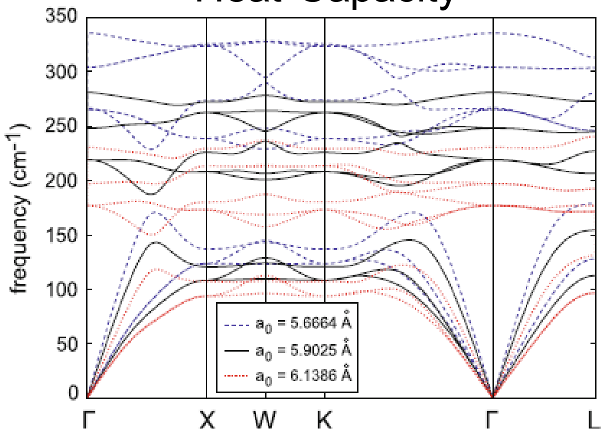
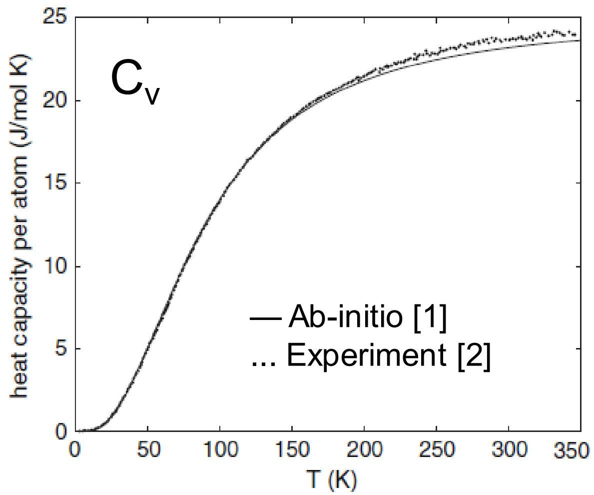
Technical Accomplishments: Heat Capacity and Thermal Conductivity

n-type Half-Heusler TiNiSn

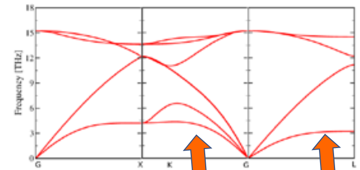
Heat Capacity

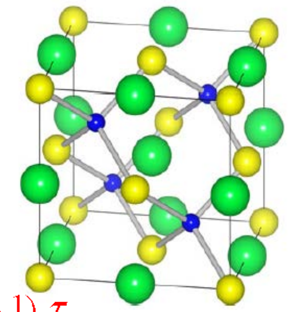




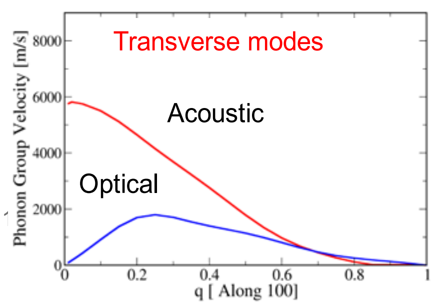
[1] Wee, Kozinsky, et al, JEM, 2012
[2] B. Zhong, M. thesis, Iowa State, 1997

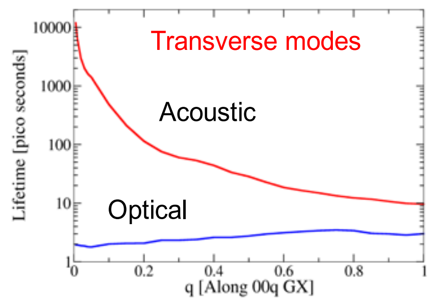
Thermal Conductivity





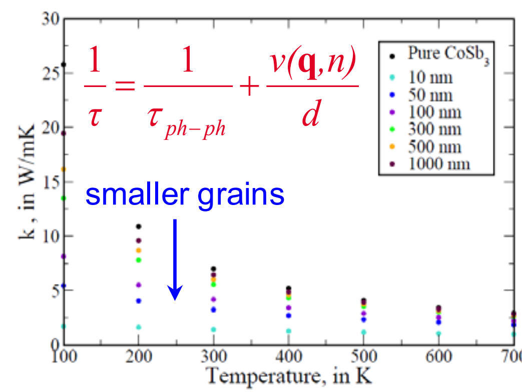
$$k = \frac{\hbar^2}{3N_0\,\Omega k_B T^2} \sum_{qs} c_s^2(q)\,\omega^2(qs)\,\bar{n}_{qs}\,(\bar{n}_{qs}+1)\,\tau_{qs}$$





Skutterudite $CoSb_3$

- Grain boundary term included in thermal conductivity
- Effect of scattering noticeable at 300K for 500nm grains
- Grain boundary scattering much less effective at high T



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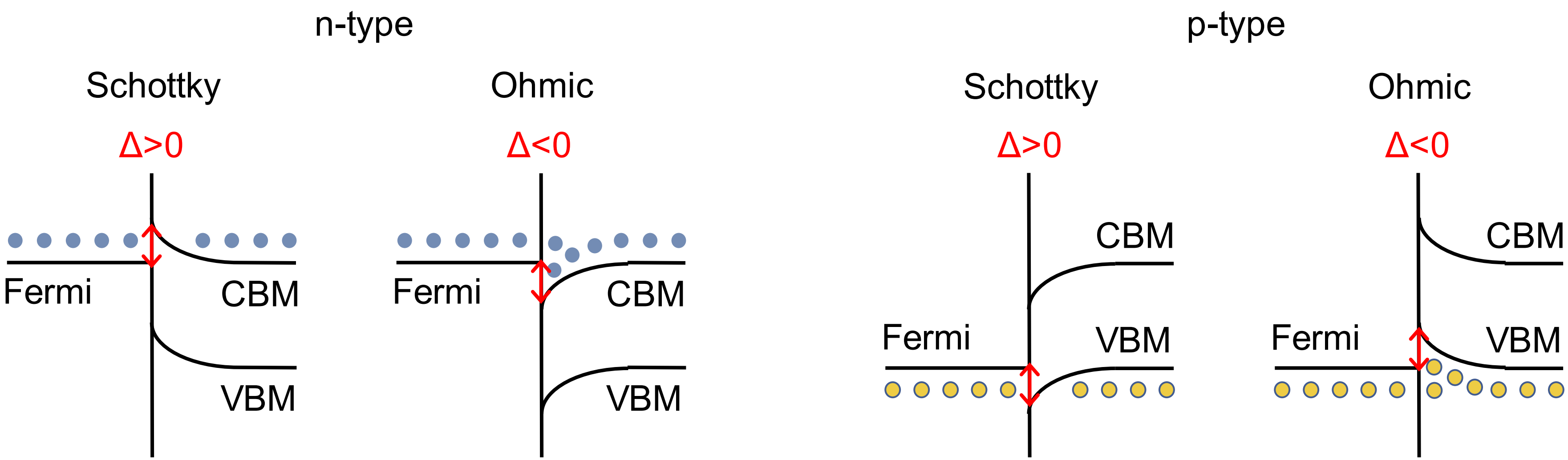

- Schottky barrier at the interface between metal and semiconductor.
- Schottky barrier height is given by the difference between the workfunction of metal and CBM of n-type (VBM of p-type) semiconductor (Schottky-Mott model).
- Our goal is to identify metals which form low-resistance Ohmic electrical contacts (Δ<0) to thermoelectric materials.
- We compute Schottky barrier heights and perform screening of different metals.

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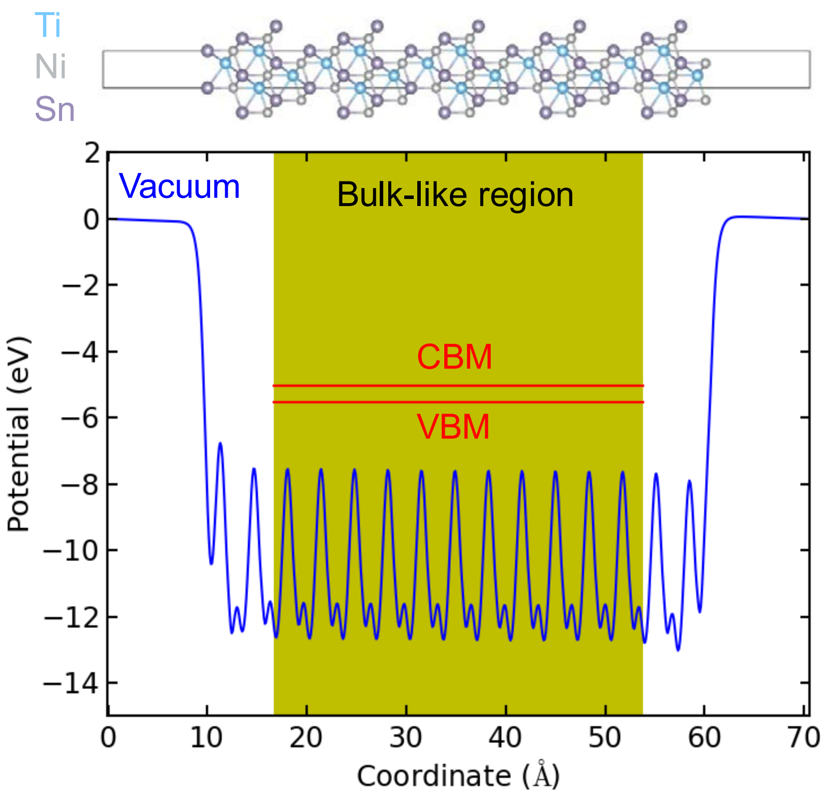
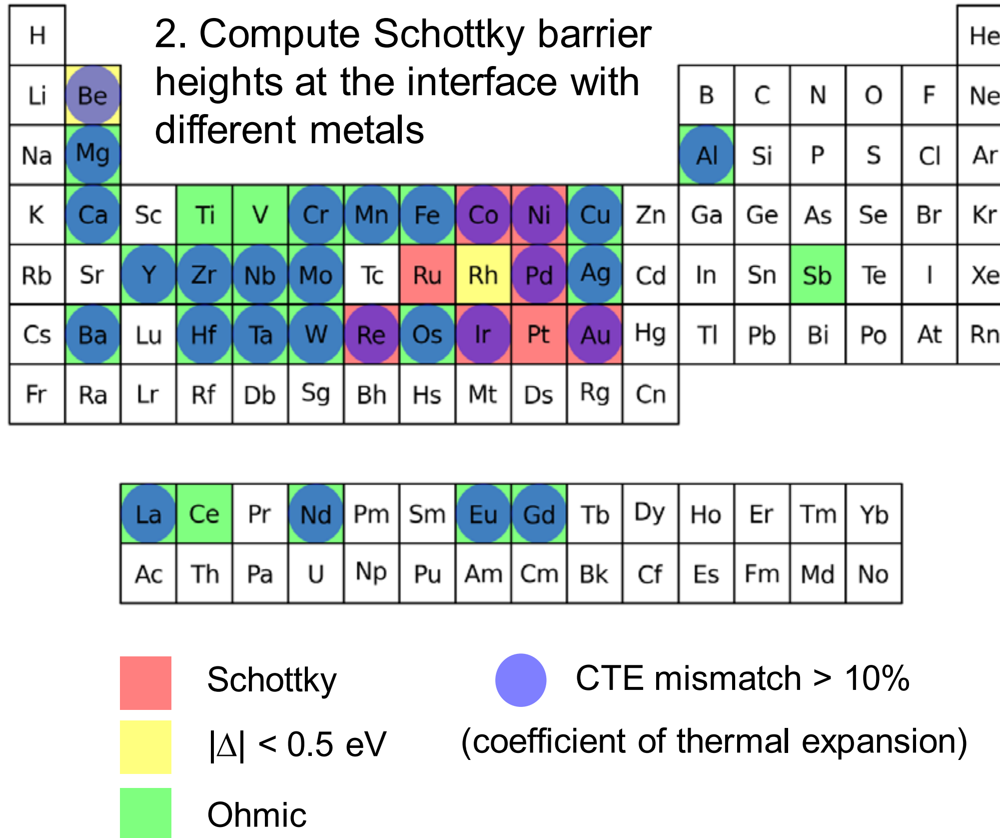
Technical Accomplishments: Schottky barriers

Screening of metals for electrical contacts to n-type half-Heusler TiNiSn by computing Schottky barrier heights at the interface between metal and thermoelectric material.

1. Compute VBM, CBM relative to vacuum:



2. Compute Schottky barrier heights at the interface with different metals



3. Candidates for low-resistance Ohmic electrical contacts to n-type half-Heusler TiNiSn: Ti, V, Sb, Ce

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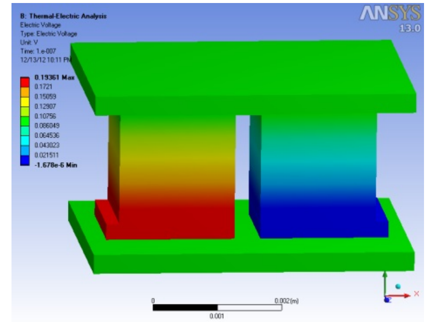
Technical Accomplishments: Transient Simulation of TEGs

1D Model Features:

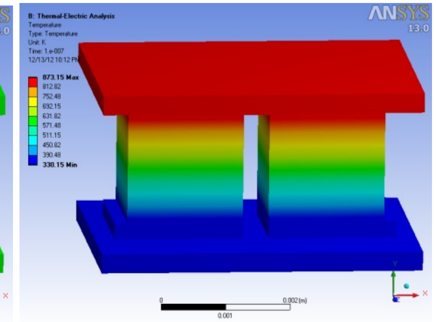
Electrical Network
- ➔ Series/Parallel connectivity can be prescribed
- ➔ Overall system power/current/voltage characteristics predicted

Multiple 1D elements
- ➔ Different 1D elements tracked along the gas channel
- ➔ Effect of varying length/width considered
- ➔ Different arrangement of devices also considered

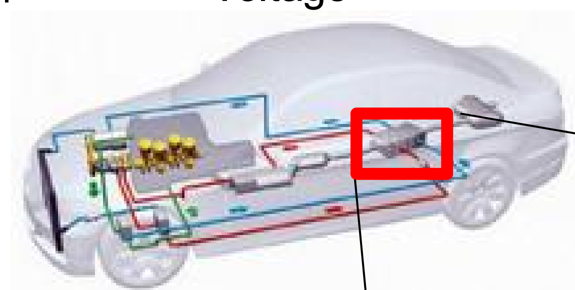
Transient Analysis
- ➔ Effect of heat capacity of different layers considered

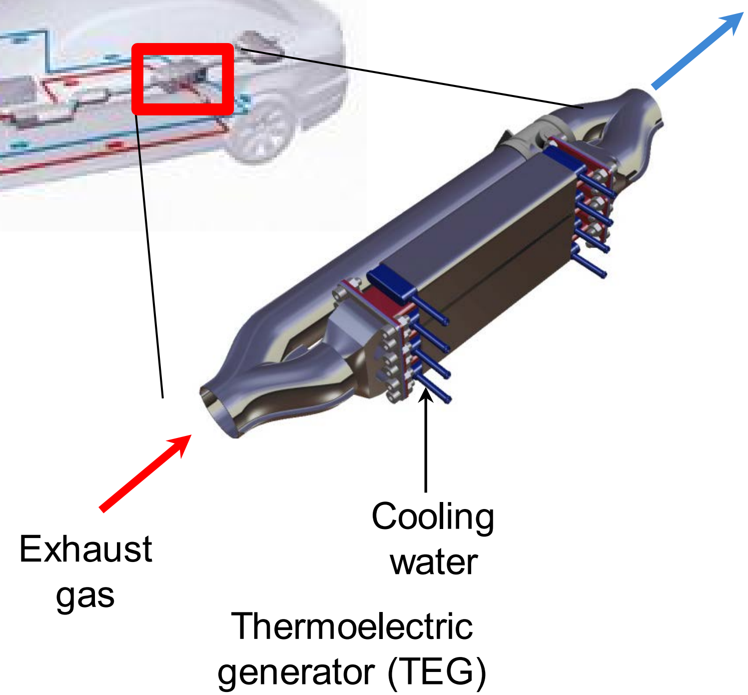


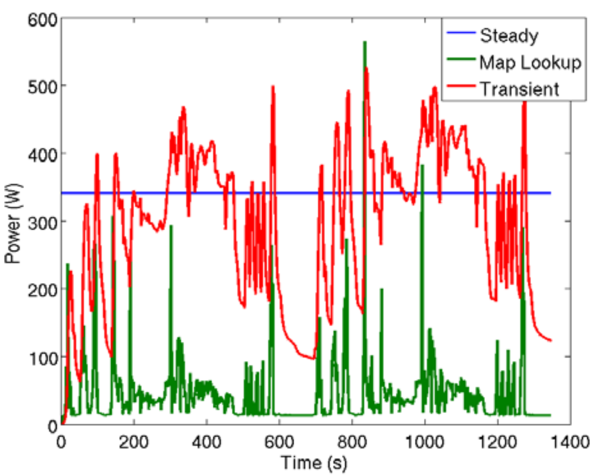
Voltage



Temperature







Approach	Mean Power (W)	Voltage (V)
Steady	341.6	29.5
Map Lookup	41.5	8.8
Transient	289.0	26.3

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Accomplishments: Outreach & Engagement

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Industry Initiatives in Science and Math Education (IISME) – Summer 2011

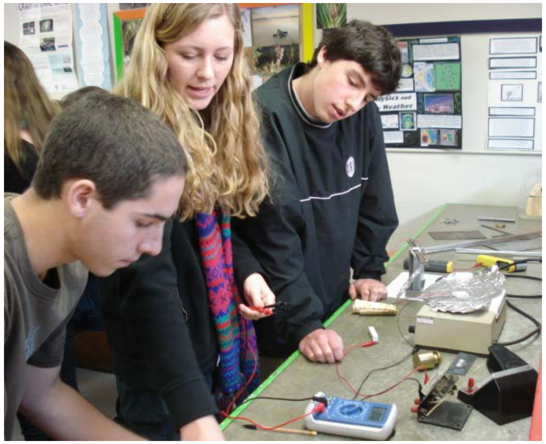
Mentorship of a public high school teacher for summer research experience and curriculum development using thermoelectrics

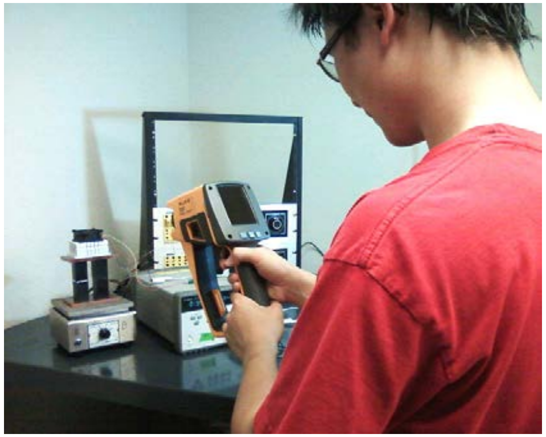
- Designed engineering course which is now taught at a public high school
- Experienced first-hand application of thermoelectric modules

K-12 Educational Outreach – Fall 2011-present

Students at Stanford are now partnered with a public high school to provide materials and mentors for a TE design lab

- Introduces high school students to thermoelectric modules and their applications each semester
- Hands-on design lab to engage students in engineering





Instructional YouTube Videos on Thermoelectric Metrology

Movies were produced to describe heat transfer metrology and were made publicly available via Stanford's YouTube channel

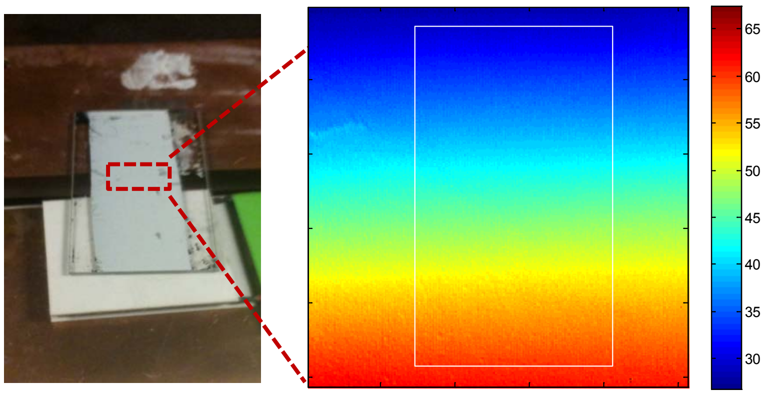
- Videos describe infrared thermometry, thermocouple thermometry, heat sink analysis, and thermal boundary resistance
- Produced through the mentorship of a novice engineering student under the guidance of a more experienced senior graduate student

Accomplishments: Outreach & Engagement

Undergraduate Research Mentorships – Jan 2012 - present

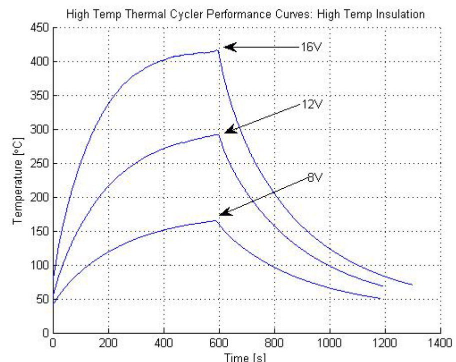
Mentorship of a four (4) undergraduate students for graduate level research experience

ZnO Nanowire Film Thermoelectric Characterization

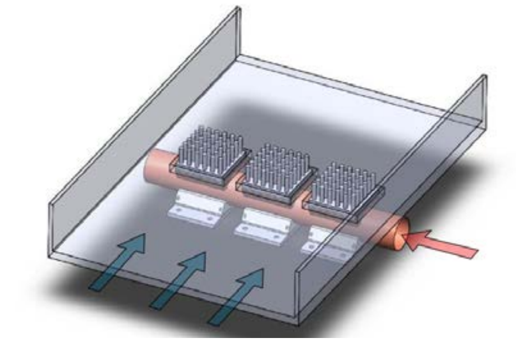


IR imaging to measure Seebeck coefficient
Courtesy: Jena Barnes

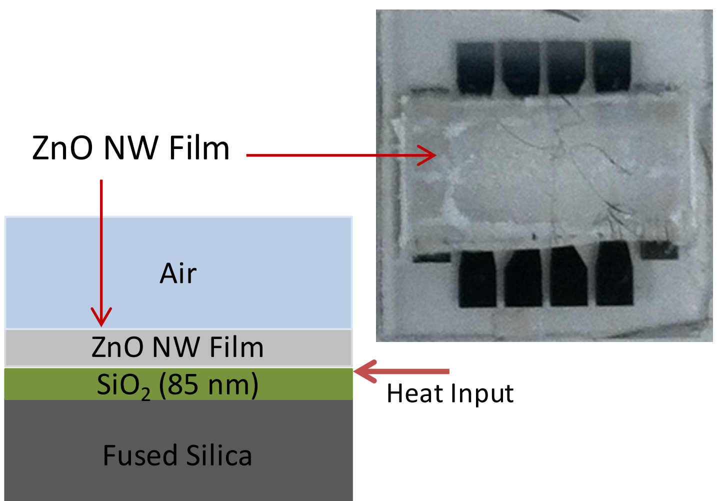
High-temperature Thermal Characterization Rigs



High-temperature thermal cycling apparatus



TEG for waste heat recovery testing apparatus



3ω measurement of cross-plane thermal conductivity
Courtesy: Maneeshika Madduri

High-temperature IR microscopy apparatus

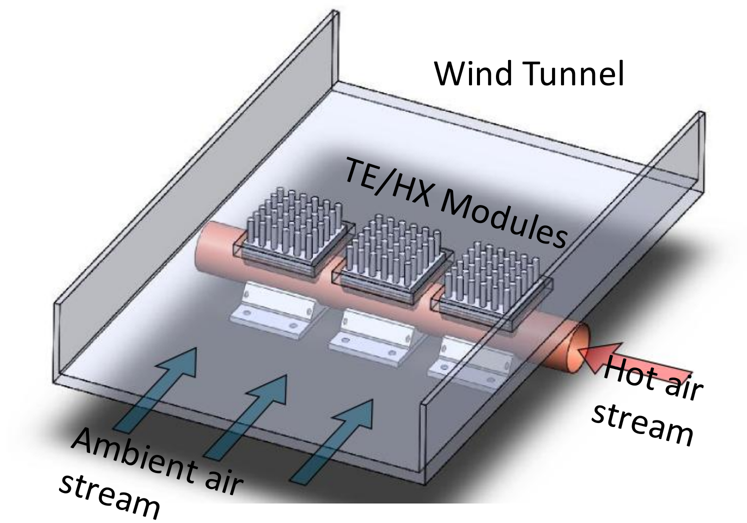
Courtesy: Kellen Asercion and Santiago Ibarra

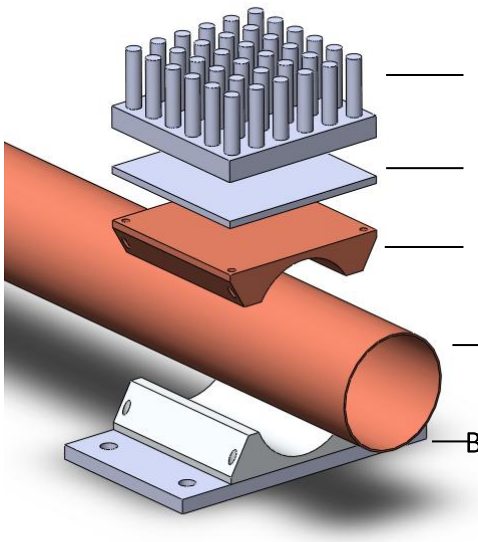
Accomplishments: Outreach & Engagement

<u>Undergraduate Thermoelectrics Lab</u> – On track for Fall 2013

TEG Waste Heat Recovery in Stanford Undergraduate Heat Transfer Laboratory

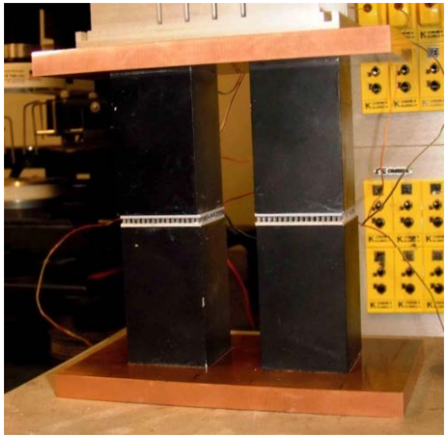
Heat sink design competition to maximize thermoelectric power generated using a hot air source and an ambient air sink. Designed by two undergraduate students through the Summer Undergraduate Research Institute (SURI) at Stanford under the mentorship of the Goodson group.





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

- Designed in conjunction with IISME teacher
- Lab exercise uses infrared microscopy with thermoelectric modules



Accomplishments: Outreach & Engagement

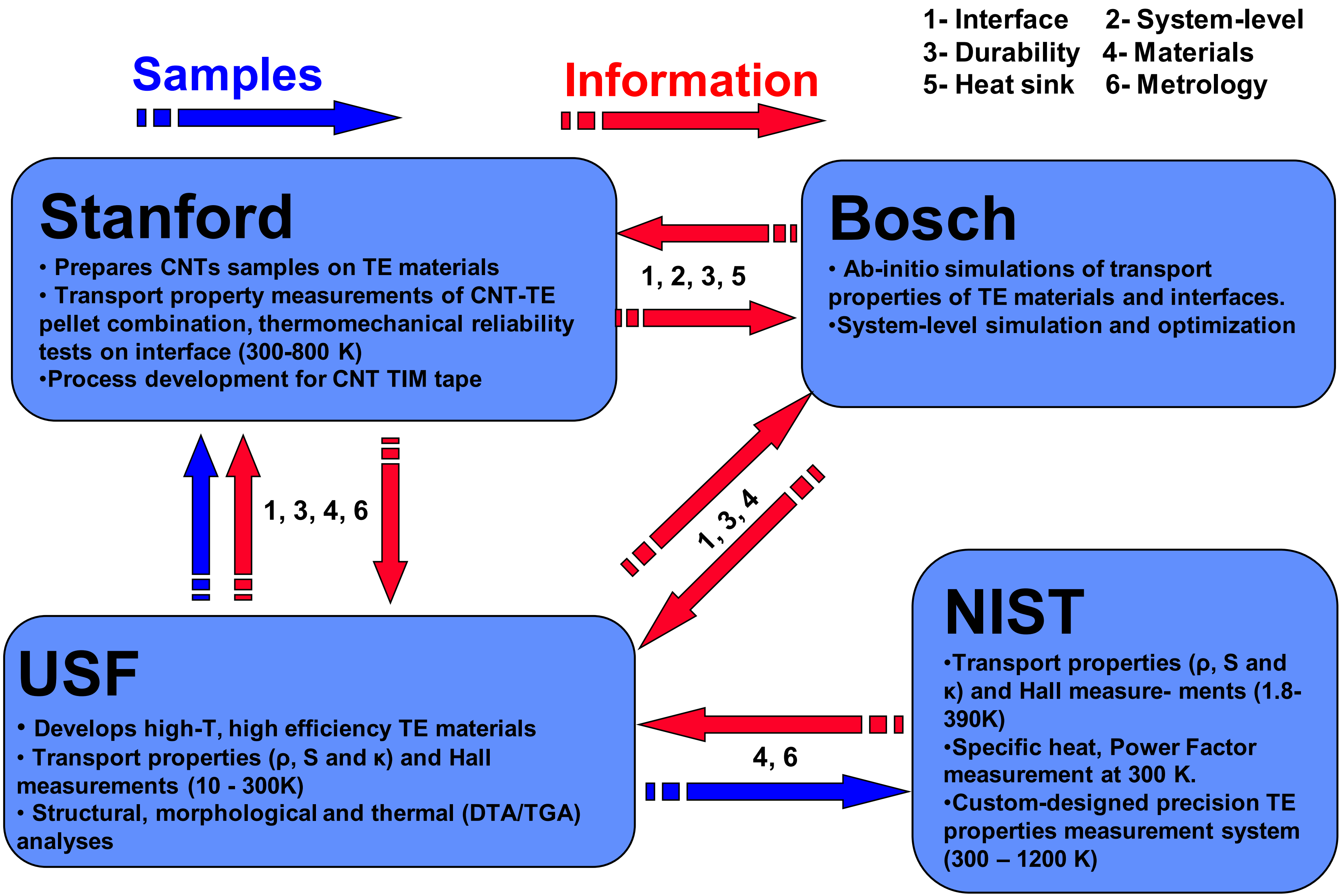
Outreach at the University of South Florida:

- Middle and high school science teachers from Hillsborough county (where USF is located) with an interest in applied researcher were given an overview of our recent research, including a lab tour, on June 20, 2012, with a question and answer period following the tour.

- Walter Hill, REU student from Jacksonville University, was involved in all aspects of our lab group's activities, including weekly lab meetings, lab presentations and studying scientific articles. He was encouraged to take charge of specific research tasks and obtained tangible results that he will be presenting at the upcoming American Physical Society March Meeting in Baltimore. He also presented his work by oral and poster presentation while at USF. As well as experimental skills, he interacted with mentor (Dr. Y. Dong), PI (Prof. G.S. Nolas) and the graduate students in the lab in discussing scientific aspects of the research project and obtained experience in a team oriented interdisciplinary research environment.

Novel Materials Laboratory
University of South Florida

Collaboration & Coordination



Proposed Future Work

- *Bulk TE Materials*: Develop modified skutterudites and related derivatives, half-Heusler alloys, and novel p-type chalcogenides

- *Integration of Nanostructured TIMs with Bulk TE Materials*: CNT arrays bonded to bulk TE materials and metal nanowire arrays grown directly on surface of bulk TE materials, and relevant thermoelectric properties measured of integrated thermoelectric-TIM system.

- *Nanostructured Metal Thermal Interface Materials*: Investigate thermal, mechanical, and electrical properties of metal nanowires, optimization of materials, geometries, and surface treatments for operation at 600^{o}C.

- *High-T $(ZT)_{eff}$ Characterization Facility Implementation*: Validation of experimental setup using Bi_2Te_3-alloys standards and novel skutterudites and Half-Heusler alloys produced by USF partners.

- *Ab-Initio Simulations*: Calculation of transport of metal-semiconductor interfaces including focus on phase stability, ab-initio calculation of electronic relaxation time, computational screening of skutterudite and half-Heusler compositions with the goal to maximize their power factors

Summary Slide

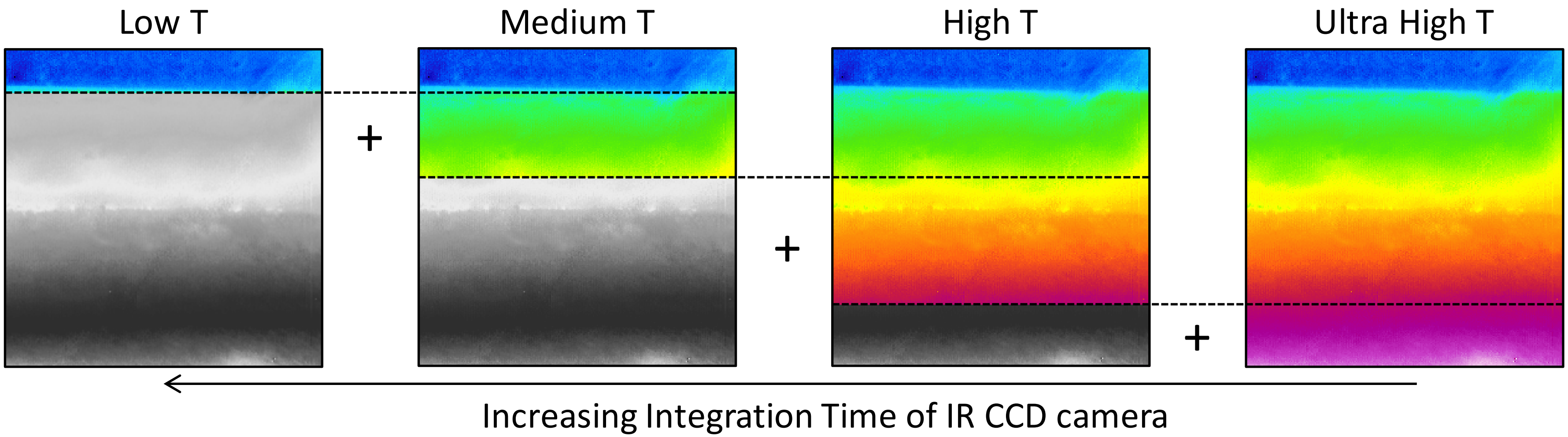
- With this award, DOE & NSF are enabling an academic-corporate team to focus on the key practical challenges facing TEG implementation in vehicles: interfaces, system-relevant metrology, and materials compatibility

- 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 FY2012 results include:
  - (a) process development of CNT tape and several bonding options (Stanford)
  - (b) detailed mechanical characterization of CNT films (Stanford)
  - (c) design and fabrication of electrodeposition system for metal nanowire fabrication and characterization (Stanford)
  - (d) demonstration of a high-temperature IR microscopy apparatus capable of reaching the target temperature of 600^{o}C (Stanford)
  - (e) development of ab-initio simulations for transport properties in TE materials
  - (f) process development (arc melting, melt spun) for bulk TE materials (USF)

Technical Backup Slides

Technical Accomplishments:
Improving Accuracy for High-Temperature IR Microscopy

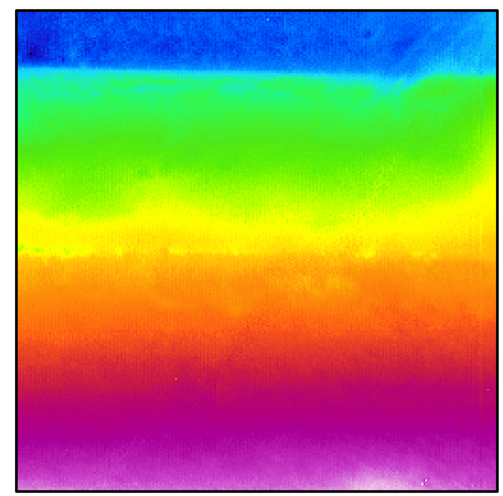


The high temperature challenge: $I_{rad} \propto q''_{rad} = \varepsilon\sigma T^4$

For large temperature gradients, the IR signal intensity spans several orders of magnitude. It is difficult to accurately measure the signal at each pixel simultaneously under these conditions.

FY13 goal:

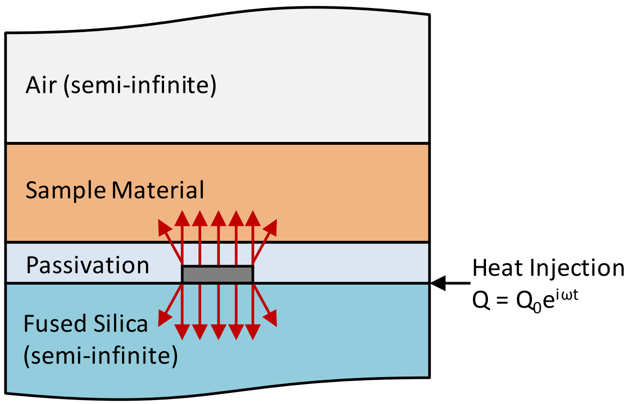
We propose to use a variable exposure sensitivity to record four images sequentially, each with different CCD integration times. A composite image is then produced from the independent images.



Approach: 3ω Experimental Analysis

Measurement Overview:

Current at frequency 1ω generates Joule heating at 2ω, and the oscillating temperature of the heater is measured indirectly by detecting a voltage at 3ω



Frequency-Modulated Properties:

1ω: Frequency of AC current source driving line heater

2ω: Joule heating at 2ω
Temperature fluctuation at 2ω
Heater resistance is perturbed at 2ω

3ω: V = I x R leads to voltage at 3ω

Thermal Diffusion Length: $L \propto \sqrt{\frac{\alpha}{\omega}}$

Feldman Solution to Heat Transfer in Multilayered Structure:

1D, steady heat equation modulated at frequency ω

$$\frac{d^2T}{dz^2} + i\frac{\omega}{\alpha}T = 0$$

General solution $T(z) = T_j^+ \exp(u_j z) + T_j^- \exp(-u_j z)$

where $u_j = -i\frac{\omega}{\alpha_j}$

Internal boundary conditions

$$T_i(\xi^-) = T_{i+1}(\xi^+)$$

$$k_i \left.\frac{dT_i}{dz}\right|_{z=\xi^-} = k_{i+1} \left.\frac{dT_{i+1}}{dz}\right|_{z=\xi^+}$$

External boundary conditions:
Semi-infinite media at T_{inf}

$$T_0 = T_0^+(0)$$

$$T_{N+1} = T_{N+1}^-(z_N)$$

Temperature rise at heater line as measured by $V_{3\omega}$

$$\Delta T = \frac{2V_{3\omega}\, dT/dR}{I_{RMS}}$$

Feldman, High Temperatures – High Pressures, 1999