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

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NIST

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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

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


Courtesy of Dr. Kozinsky, Bosch
Composite interface material combines nanotubes with low melting temperature binders.

Binders improve thermal contact to substrates and allow attachment during packaging/assembly.

Adhesion layer wets nanotubes and promotes adhesion of binder (Pd, Pt, or Ti).

Upon heating, the low melting binder conforms to CNT and substrate topography.

~100 nm is the typical variation in CNT height.

Nanostructured Interface Solutions

Patents issued (SRC sponsorship)
Thermal Interface Materials Requirements

**Thermal Resistivity (m K / W)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greases &amp; Gels</td>
<td>0.01</td>
</tr>
<tr>
<td>Phase Change Materials</td>
<td>0.1</td>
</tr>
<tr>
<td>Indium/Solders</td>
<td>1.0</td>
</tr>
<tr>
<td>Adhesives</td>
<td>10.0</td>
</tr>
<tr>
<td>Nano-gels</td>
<td>100</td>
</tr>
</tbody>
</table>

**Elastic Modulus (MPa)**

- **Carbon Nanotube**
- **Copper Nanowire**

**Goal**

104

103

102

101

*Our Latest CNT Data*

Gao et al., (2010)

See next page

**Nanostructured Interfaces**

A Brief Overview of the Research Activities at Stanford

**ThermoElectric Module/Pellet**

<table>
<thead>
<tr>
<th>Thermal Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>45,000 Cycles</td>
</tr>
<tr>
<td>50 μm</td>
</tr>
</tbody>
</table>

**Nanostructured Interfaces**

<table>
<thead>
<tr>
<th>Solder-Bonded Nanotube Thermal Interface Materials</th>
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<table>
<thead>
<tr>
<th>Thermal Cycling</th>
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</thead>
<tbody>
<tr>
<td>100 Cycles (100 °C, 6min)</td>
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</tbody>
</table>

**High Temperature IR Imaging & Characterization**


**Electrodeposited Metal Nanowire TIMs**

Michael Barako, Unpublished research

**Nanoscale Conformable Coatings for Enhanced Thermal Conduction of CNT Films**

Approach: Interface Characterization on Thermoelectric with Thermal Cycling


Resistances for 1.5, 2.5, and 40 micron thick CNT films varied between 0.035 and 0.055 cm² °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.

Thermal conductivity and Seebeck coefficient remain relatively stable.
A modified Harman technique was developed to measure the TE figure of merit $ZT$ and the electrical resistance $R$. 
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

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_{\text{melt}} = 156.6°C)

† Indium foil by Indium Corp.
Nanofoil Bonding

• 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

‡ 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:

\[
\frac{k_{\text{sample}}}{k_{\text{ref}}} = \frac{dT}{dx}_{\text{ref}} \frac{dT}{dx}_{\text{sample}}
\]

Thermal Boundary Resistance

Using the temperature drop at the interface and Fourier’s Law:

\[
R''_{\text{CNT-ref}} = \frac{\Delta T_{\text{int}}}{q''} = \frac{\Delta T_{\text{int}}}{k_{\text{ref}} \left( \frac{dT}{dx} \right)_{\text{ref}}}
\]

Compressive Measurement Apparatus

[Diagram of the apparatus with labels for Linear Actuator, Load Cell, 3-axis, 3-angle stage, Infrared Camera, Sample, Heat Sink, Chilled Water, TE Heater, Copper Adapters, TE Cooler]
Thermal Properties Before Bonding

1. CNT-CNT Boundary Resistance

2. CNT-metal Dry Contact

3. Variation in CNT Heights

Intrinsic Thermal Conductivity, $k_{\text{CNT}}$

Thermal Boundary Resistance, $R''_{\text{int}}$

Marconnet et al., ACS Nano, in press
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, $R''_{int}$

![Graph showing thermal properties and bond states](image-url)

- Dry Contact
- Unbonded (In)
- Bonded (In)
- Unbonded (NF)
- Bonded (NF)

**Graph Details:**
- $R''_{CNT-In-FS}$ vs. Axial Pressure [kPa]
- Log-log scale for $R''_{CNT-In-FS}$
- Data points for different bond states and pressure conditions

**Diagram Notes:**
- Nanoscale metal-CNT interface resistance (phonons)
- Partial nanotube engagement
- Heat Sink
- Growth interface resistance
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

- 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)
**Electrodeposited Metal Nanowire TIMs**

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

**a)** Polycarbonate membrane is etched to create cylindrical pores

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

**c)** Metal is electrodeposited into the pores

**d)** Membrane is etched away, leaving freestanding nanowires

**Thermal Conductivity vs. Volume Fraction**

- Upper limit copper (Cu)
- Upper limit Nickel (Ni)

**Notes:**
- Picosecond thermoreflectance technique.
- Uncertainty is due to current sample preparation techniques.

**SEM of copper NW film:**

- 2 μm
- 10 μm
Nanoscale Conformable Coatings for Enhanced Thermal Conduction of Carbon Nanotube Films

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.
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\(_2\)Te\(_3\)-alloys for High Resolution Infra-Red Thermometry (in collaboration with Marlow Ind.)

Survey of other material systems with potential for enhanced thermoelectric properties

Thermal Conductivity of Yb-filled Skutterudites

Partial filling optimizes lattice thermal conductivity reduction

Increasing Yb concentration

Increasing Ba concentration


p-type Ba + Yb filled Skutterudites

Ternary-substituted skutterudites may hold more potential for n-type
\[ XCo_4B_{12} \quad B = Sb \rightarrow (Ge,Sn)/(S,Se,Te) \]
- Higher Seebeck coeff than CoSb_3
- Filling of ternary skutterudites weakly affects the Seebeck maxima
- Changes the carrier concentration significantly

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

Smaller grains

\[
\frac{1}{\tau} = \frac{1}{\tau_{ph-ph}} + \frac{v(q,n)}{d}
\]

Band Gap (eV)

Filling Factor x

Computational Composition Engineering

Nanostructure Design for Thermal Transport

Seebeck coeff
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 2nd year of the DOE-NSF project.*

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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 scenarios.
- 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]

<table>
<thead>
<tr>
<th>Material</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-CNT-Quartz</td>
<td>Yang et al. (2002, 2004)</td>
</tr>
<tr>
<td>Si-CNT-Ag</td>
<td>Tong et al. (2006)</td>
</tr>
<tr>
<td>Si-CNT-Al</td>
<td>Tong et al. (2006)</td>
</tr>
<tr>
<td>Si-CNT-Pt</td>
<td>Tong et al. (2007)</td>
</tr>
<tr>
<td>SiGe-CNT-Pt</td>
<td>Pal et al. (2008)</td>
</tr>
<tr>
<td>Si-CNT-Ag</td>
<td>Son et al. (2008)</td>
</tr>
<tr>
<td>Si-CNT-Pt</td>
<td>Xu et al. (2006)</td>
</tr>
<tr>
<td>Si-CNT-Ag</td>
<td>Xu et al. (2006a)</td>
</tr>
<tr>
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<td>Si-CNT-Pt</td>
<td>Marconnet et al. (2012)</td>
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</table>
Modulus Variation with CNT Thickness

Crust Model for Monano Samples

<table>
<thead>
<tr>
<th></th>
<th>Thickness (μm)</th>
<th>Modulus (MPa)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT\text{Top}</td>
<td>0.4</td>
<td>140</td>
<td>&gt;29</td>
</tr>
<tr>
<td>CNT\text{Middle}</td>
<td>0-150</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>Si</td>
<td>8.7</td>
<td>155e3</td>
<td>2330</td>
</tr>
</tbody>
</table>

Maruyama Lab Samples (SWNT), 95 kg/m³

Monano Samples (MWNT), ~30 kg/m³

Wardle Lab Samples/MIT (MWNT), 45 kg/m³
Effect of Interface Resistances on Thermoelectric Device Properties

<table>
<thead>
<tr>
<th>Interface Material</th>
<th>$R''_\text{th}$ [W/m²/K]</th>
<th>$R''_e$ [Ω m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solders And Ideal CNT</td>
<td>~10^{-7}</td>
<td>~10^{-12}</td>
</tr>
<tr>
<td>High Quality CNT</td>
<td>~10^{-6}</td>
<td>~10^{-10}</td>
</tr>
<tr>
<td>Lower Quality CNT</td>
<td>~10^{-5}</td>
<td>~10^{-8}</td>
</tr>
<tr>
<td>Thermally &amp; Electrically Conductive Grease</td>
<td>~3x10^{-6}</td>
<td>~3x10^{-9}</td>
</tr>
<tr>
<td>Thermal Conductive Grease</td>
<td>~8x10^{-6}</td>
<td>~3x10^{-7}</td>
</tr>
<tr>
<td>Electrically Insulating Grease</td>
<td>~8x10^{-6}</td>
<td>&gt;10^{-5}</td>
</tr>
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