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

Project Leadership
Prof. Ken Goodson, Stanford Mechanical Engineering
Prof. George Nolas, USF Department of Physics
Dr. Boris Kozinsky, Energy Comp. & Modeling, Bosch
Prof. Mehdi Asheghi, Stanford Mechanical Engineering
Dr. Winnie Wong-Ng, NIST Functional Properties Group

Staff
Dr. Yongkwan Dong, USF Department of Physics
Dr. Matt Panzer, Stanford Mechanical Engineering

Students:
Yuan Gao, Lewis Hom, Saniya Leblanc, Amy Marconnet

Leveraged Support:
Northrop Grumman, AMD/SRC, ONR, AFOSR
Fellowships from NSF, Sandia National Labs, Stanford DARE

Program Managers:  John Fairbanks, Tom Avedisian (DOE).  Arvind Atreya (NSF)
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 TEG systems.*

**Major needs include...**

...Low-thermal-resistance interfaces with tailored electrical properties, which 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.
Thermoelectric Interface Challenge

“Nanostructured Interfaces for Thermoelectrics,”
Pettes, Hodes, Goodson, Trans. Advanced Packaging, 2009

- Combustion systems experience enormous stresses at interfaces due to large temperature differences.
- Interfaces must offer low thermal resistance, targeted electrical performance, mechanical compliance.

![Graph showing power vs TEM thickness](image1)

- No interface
- Thermal grease
- Solder
- CNT array

LeBlanc, Gao, Goodson, Proc. IMECE 2008

![Graph showing power vs TEM thickness](image2)


 Clin et al., J. Electronic Materials, 2009
Thermoelectric Interface Challenge

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• Combustion systems experience enormous stresses at interfaces due to large temperature differences.
• Interfaces must offer low thermal resistance, targeted electrical performance, mechanical compliance.

GOAL

![Graph showing comparison of materials](image)
Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

GOALS

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

METHODS

Multiphysics simulations ranging from ab-initio (band structure) to system scale.

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

System impact assessment considering the interplay of thermal, fluidic, mechanical, electrical, and thermoelectric phenomena.


## Research Overview

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<th>Area</th>
<th>Specifics</th>
<th>Source(s)</th>
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<tr>
<td>Interfaces</td>
<td>Nanostructured films &amp; composites, metallic bonding Ab initio simulations</td>
<td>Stanford Bosch</td>
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<tr>
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<td>and optimization</td>
<td></td>
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<td>Metrology</td>
<td>((ZT)_{\text{eff}}) with independent (k) and (c_p), thermal cycling</td>
<td>Stanford USF/NIST</td>
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<td>High temperature ZT</td>
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<td>Materials</td>
<td>Filled skutterudites and half Heusler intermetallics Ab initio simulations</td>
<td>USF Bosch</td>
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<td>for high-T optimization</td>
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<td>Durability</td>
<td>In-situ thermal cycling tests, properties Interface analysis through SEM,</td>
<td>Stanford Bosch</td>
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<td>50%</td>
<td>XRD, EDS</td>
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<td>Heat sink</td>
<td>Gas/liquid simulations using ANSYS-Fluent Novel cold HX using microfluidics</td>
<td>Bosch Stanford</td>
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<td>50%</td>
<td>vapor venting</td>
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<tr>
<td>System</td>
<td>System specification, multiphysics code Evaluation of research impacts</td>
<td>Bosch Stanford</td>
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<tr>
<td>50%</td>
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<tr>
<td>Outreach</td>
<td>TE for vehicles competition, UG Lab, K-12 outreach</td>
<td>Stan&amp;USF</td>
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Bulk TE Materials for Automotive Applications


• 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 and ZT.

George S. Nolas
Department of Physics, University of South Florida
Bulk TE Materials for Automotive Applications


• **Skutterudites with partial filling using heavy, low valence “guest” atoms**

Partial Filling – Optimization of mobility & thermal conductivity

![Graph showing mobility vs. temperature for different compositions of LaₓCo₄Sb₁₂₋ₙSnₙ.](image)

• **Half-Heusler alloys: from small grain size towards the disordered state**

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

- Ab-initio/BTE computations will assist the optimization of TE material stoichiometry.

- Past work at Bosch predicted the effect of Ba filling on CoSb$_3$ skutterudites using DFPT.

- Collaborative optimization with Nolas group will focus on filled skutterudites, mobility, seebeck, and interfaces with metallics.
Simulations examine thermodynamic stability of TE material phases and assess potential for interdiffusion.

Simulations examine interface electrical conduction and optimize resistance considering band structure.

Mechanical & thermal simulations will focus on the expansion coefficients and transport through low-dimensional contacts.

CTE of TiNiSn Half-Heusler Alloys

(Bosch) exp

ab-initio

Co-Sb phase diagram

Unfilled CoSb₃ (stable)

Monoclinic CoSb₂ (Stable)
Conduction Physics in CNT Films

Nanoscale metal-CNT interface resistance (phonons)

Individual CNT conductance

Inter-tube contact

Partial nanotube engagement

Spatially varying alignment

Growth interface resistance

Thermal and Mechanical Characterization of Aligned CNT Films

**Nanosecond Thermoreflectance**
- Probe laser for thermometry
- Pulsed Laser Heating
- Sample Film
- Heat Sink (Si or metal substrate)

**Cross-sectional IR Microscopy**
- Heater
- CNT Film
- growth substrate
- 500 μm

**Picosecond Thermoreflectance**
- CNT Catalyst Metal Coating
- Transparent Substrate (e.g. quartz)

**Mechanical Characterization**
- Laser Doppler Velocimeter
- Vibrometer, ω

\[ k \propto \left( \frac{dT}{dx} \right) \]
\[ \Delta T \rightarrow R_B \]

Distance (μm)

- Si substrate
- Polysilicon
- Oxide
- CNT
Metallization and CNT Thermal Resistance using Nanosecond Thermoreflectance


\[
\phi = \frac{C_{\text{eff}}}{C_{v,\text{individual}}}
\]
# Mechanical Behavior of CNT Films

**Students:** Yoonjin Won, Yuan Gao, Matt Panzer. **Collaborators:** Prof. Wei Cai, Stanford ME

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

**Maruyama Lab Samples**
- (SWNT), 95 kg/m³

**Monano Samples**
- (MWNT), ~30 kg/m³

**Wardle Lab Samples/MIT**
- (MWNT), 45 kg/m³

**Crust Model**

**Zipping/Velcro Model**
Thermal & Mechanical Requirements at Interfaces

Thermal Resistivity (m K / W)

1.00.1

Elastic Modulus (MPa)

Greases & Gels

Organic Phase Change

Metallic Alloys

Adhesives

Nano-gels

Lifetime thermal cycling

Research Goal
Thermal & Mechanical Requirements at Interfaces

Thermal Resistivity (m K / W)

Elastic Modulus (MPa)

- Metallic Alloys
- Adhesives
- Organic Phase Change
- Greases & Gels

Nano-gels

Lifetime thermal cycling

Our Latest CNT Data
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.
(ZT)\textsubscript{eff} Characterization with Electrical Heating & Cross-Sectional IR Thermometry

**Heating/thermometry Setup**

- **AC current source**
- **Lock-in Amp.**
- **Resistive Heater**
- **Ceramic plate**
- **n-type Pellet**
- **p-type Pellet**
- **Connecting metal**
- **Cold Side**
- **Th = 300-700 K**

**IR microscope system**

- **Sapphire IR Transparent window**
- **Spatial resolution ~ 2 mm**
- **Temp. range 300-700 K**

**Cross-sectional IR Microscopy**

- **Heater**
- **CNT Film**
- **growth substrate**
**HX and System-Level Simulations**

**ANSYS® Workbench Environment**

- **DesignXplorerer** optimizes parameters.
- **DesignModeler** creates geometry.
- **ICEM** generates mesh.

→ **Bosch-lead system simulations** explore impact of improved parameters on system efficiency.

→ **Multiphysics simulations** of thermal/thermoelectric transport in TE material, and interface transport incorporating ab initio results.

→ **HX design and optimization** accounts for novel pressure drop designs including Stanford Vapor Escape technology.

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**Research and Technology Center North America**

Boris Kozinsky (CR/RTC2-NA) | 12/14/2010 | © Robert Bosch GmbH 2010. All rights reserved, also regarding any disposal, exploitation, reproduction, editing, distribution, as well as in the event of applications for industrial property rights.
Educational Engagement

Thermoelectrics for Vehicles Challenge: Multi-University Competition

*Long-term vision:* Teams of undergraduates work with commercial TE components and heat sinks to extract waste heat from demo vehicle exhaust.
- 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-conversion research in Stanford’s Microscale Heat Transfer Laboratory.*
Interactions and Flow of 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

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

**USF**
- Develops high-T, high efficiency TE materials
- Transport properties ($\rho$, $S$ and $\kappa$) and Hall measurements (10 - 300K)
- Structural, morphological and thermal (DTA/TGA) analyses

**NIST**
- Transport properties ($\rho$, $S$ and $\kappa$) and Hall measurements (1.8-390K)
- Specific heat, Power Factor measurement at 300 K.
- Custom-designed precision TE properties measurement system (300 – 1200 K)

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