Recent Device Developments with Advanced Bulk Thermoelectric Materials

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3rd DOE Thermoelectric Applications Workshop

Outline

- **Acknowledgements**
- **Thin-film Thermoelectrics**
  - Thin-film Superlattice Thermoelectrics Developed at RTI, relevance to nano-bulk
  - Technology transitioning to **Nextreme** and commercialization status
  - New Thin-film SL Materials Development and DoD applications continuing at RTI
- **Focus on Advanced Bulk Thermoelectric Technology for Energy Harvesting**
  - Nano-bulk Materials for low, mid, and high-temperatures
    - Collaboration partners and Bulk Materials Development
  - Device development
  - High-level DoD applications being developed at RTI
  - Transitioning to commercial applications

Acknowledgements

- RTI International
  - Peter Thomas, Dr. Bruce Cook, Mike Mantini, Dr. David Stokes, Nick Baldasaro, Dr. Gary Bulman, Dr. Phil Barletta, Gordon Krueger and other team members
- North Carolina State University
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- Ames Lab
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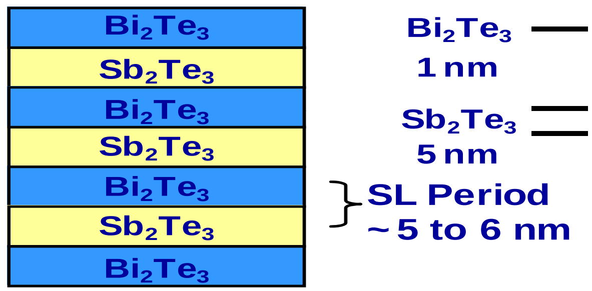
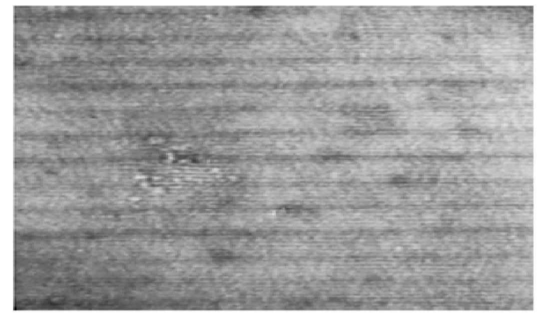
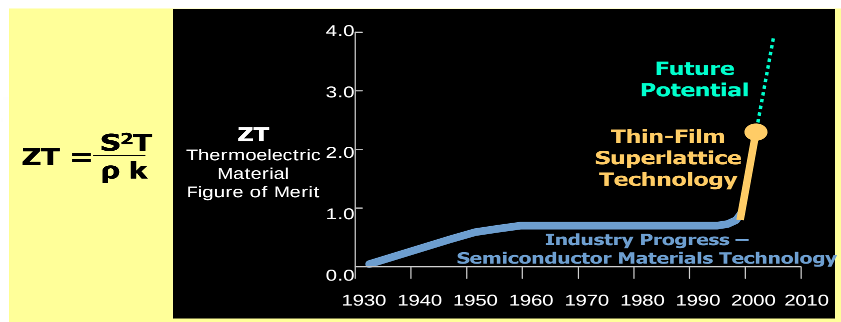
- University of Virginia
  - Prof. Joe Poon, Wu Di
- UC Berkeley
  - Prof. Chris Dames
- Clemson University
  - Prof. Terry Tritt
- Nextreme Thermal Solutions
  - Bob Collins and rest of the Nextreme team

First set of Nano-scale Material Demonstrations to show Increased ZT beyond ~1

- **Epitaxial P-type Bi_2Te_3/Sb_2Te_3 Superlattices (RTI International)**
  - ➢**ZT~2.4 at 300K (*Nature* 413, Oct. 2001)**
- **Epitaxial PbTe/PbTeSe Nano-dots (MIT Lincoln Labs.)**
  - ➢**ZT~ 1.6 at 300K (*Science* 297, Sep. 2002)**
- **Naturally-forming nano-structures in bulk Ag $Pb_{18}SbTe_{20}$ (Michigan State University)**
  - ➢**ZT ~ 2.2 at ~850K (*Science* 303, Feb. 2004)**



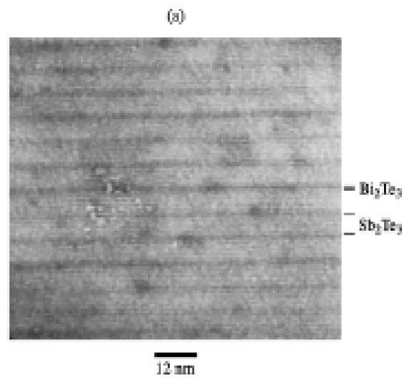


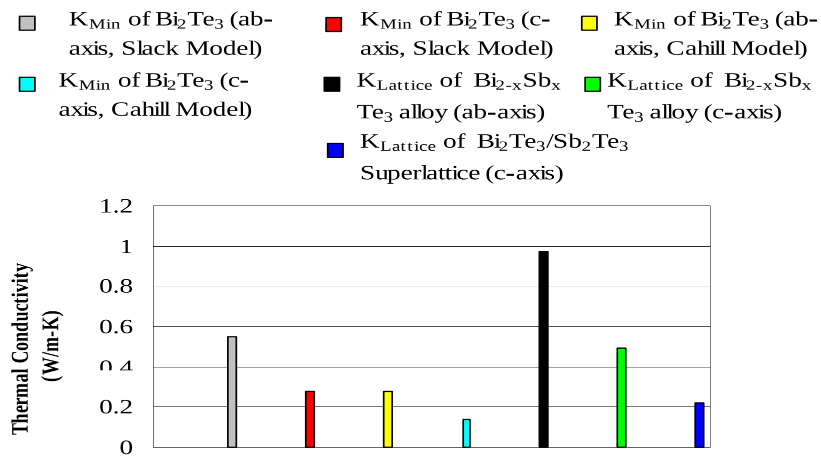


Nature, 413, 597-602 (2001)

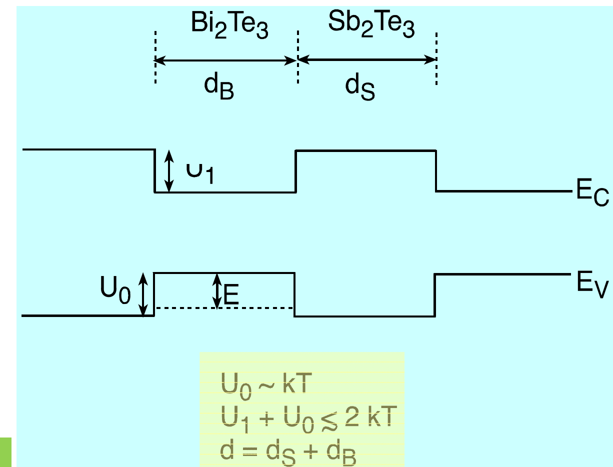
Phonon Blocking Electron Transmitting Structures

Epitaxy: Venkatasubramanian et al., *Nature* 413, 597-602 (2001)

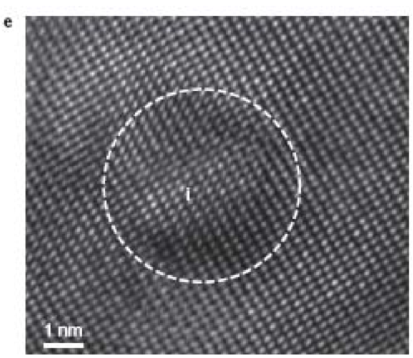


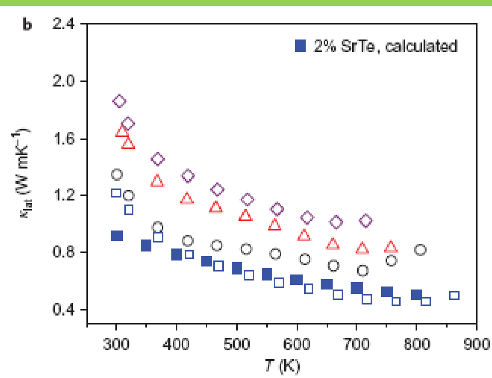


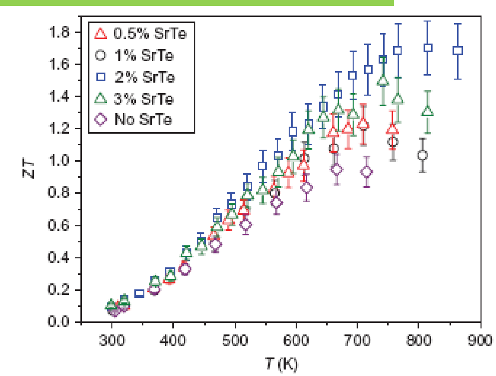
Efficient Cross-Plane Hole Mini-band Transport

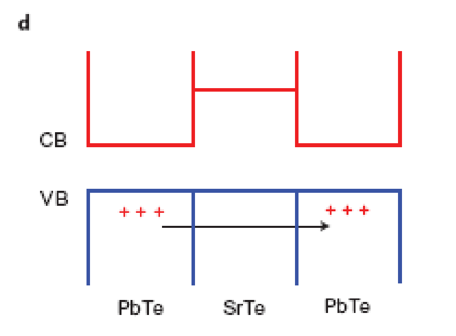


Endotaxy: Kanatzidis et al., *Nature Chem.* 3, 162-165 (2011)









Nanostructured TE: Vineis, Shakouri, Majumdar & Kanatzidis, Adv. Materials **22**, 3970-3980 (2010)

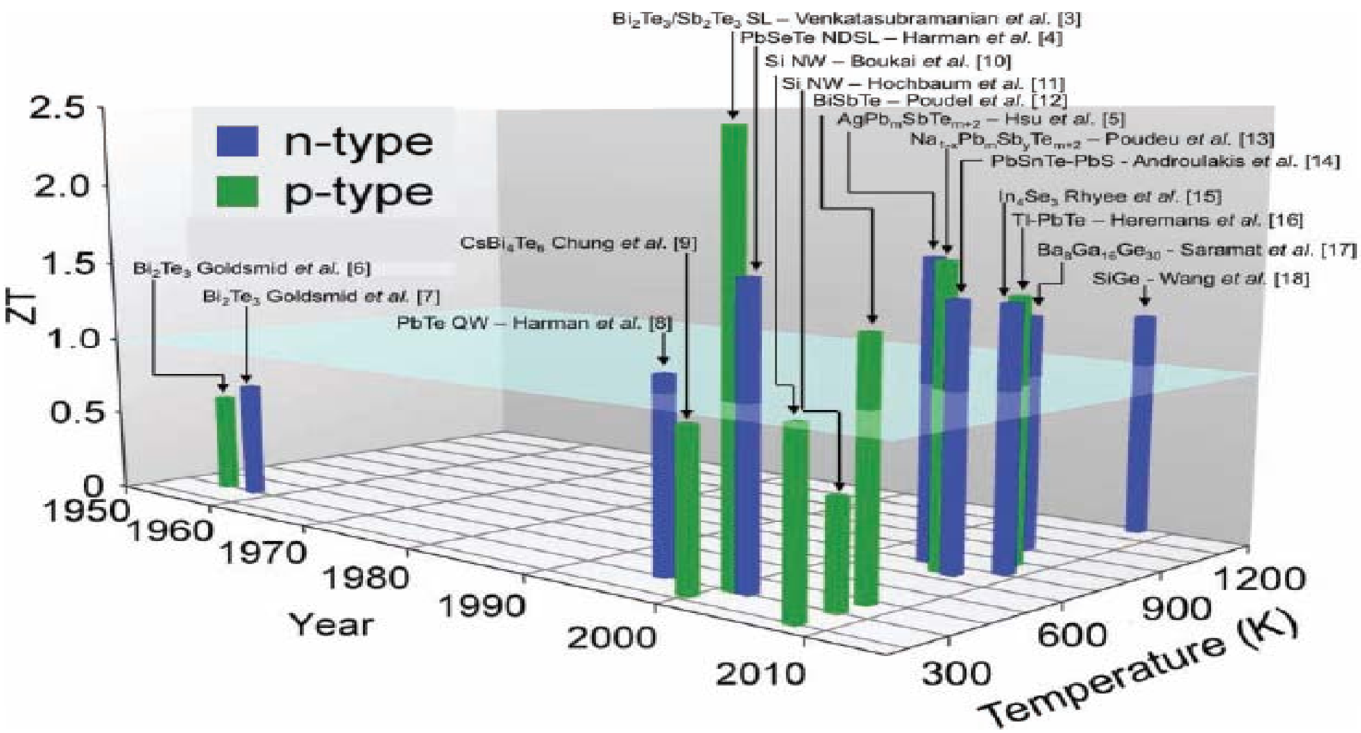
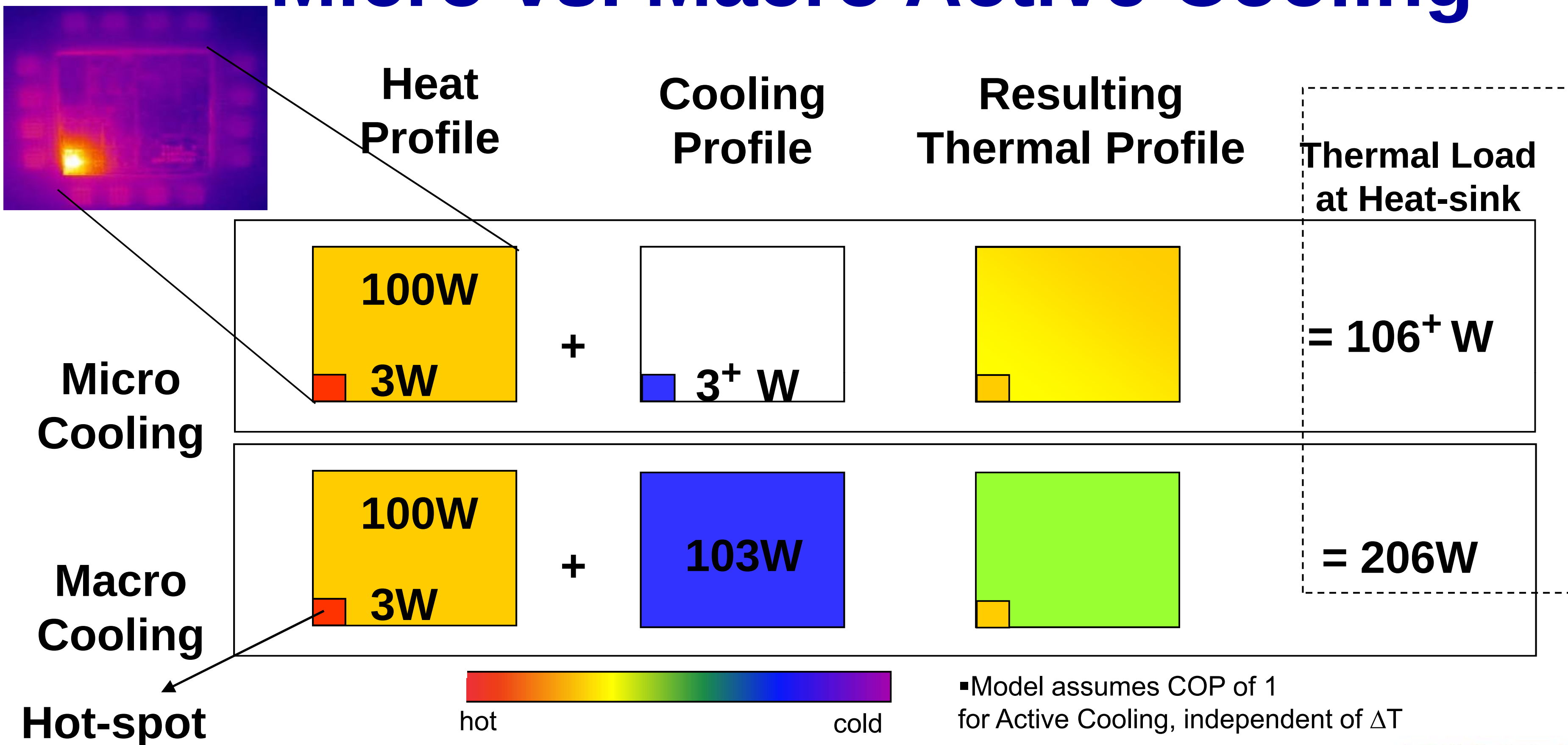


Figure 1. Thermoelectric figure-of-merit *ZT* as a function of temperature and year illustrating important milestones. Although there have been several demonstrations of $ZT > 1$ in the past decade, no material has yet achieved the target goal of $ZT \geq 3$. The material systems that have achieved $ZT > 1$ have all been based on some form of nanostructuring.

Micro vs. Macro Active Cooling



- Model assumes COP of 1 for Active Cooling, independent of ΔT
- Some pumping of background by the spot-cooler

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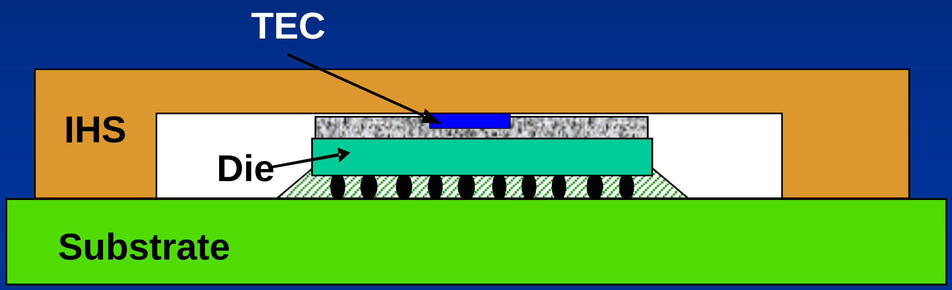
First fully functional nanostructured thermoelectric micro refrigerator in a state-of-the-art silicon chip package [Nature Nanotechnology 4, 235-238 (2009)]



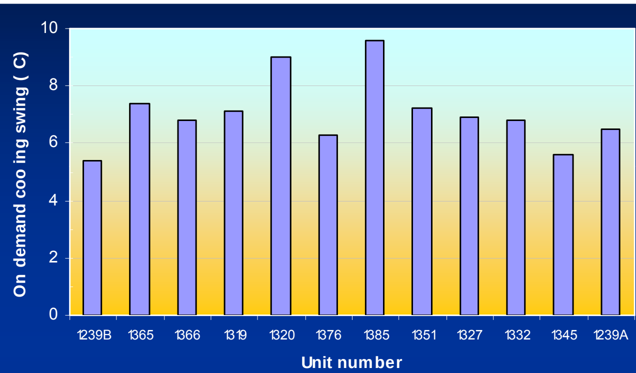
TEC mounted on the cavity side of the IHS

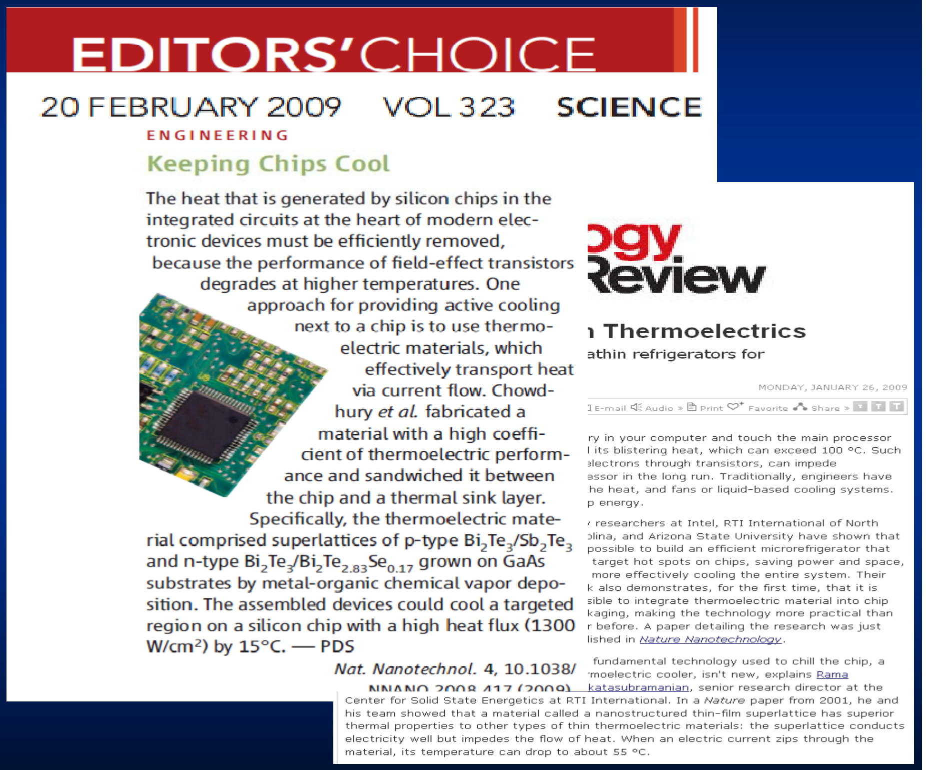
- **Repeatable demonstration of TEC performance**
- **Active plus passive hot-spot cooling >14°C has been achieved at a heat flux ~1250 W/cm^2**
- **Opens up on-demand, site-specific thermal management (SSTM)**

RTI INTERNATIONAL   intel Leap ahead   Nextreme THERMAL SOLUTIONS

First fully functional nanostructured thermoelectric micro refrigerator in a state-of-the-art silicon chip package

[*Nature Nanotechnology* **4**, 235-238 (2009)]





EDITORS' CHOICE

20 FEBRUARY 2009 VOL 323 SCIENCE

ENGINEERING

Keeping Chips Cool

The heat that is generated by silicon chips in the integrated circuits at the heart of modern electronic devices must be efficiently removed, because the performance of field-effect transistors degrades at higher temperatures. One approach for providing active cooling next to a chip is to use thermoelectric materials, which effectively transport heat via current flow. Chowdhury *et al.* fabricated a material with a high coefficient of thermoelectric performance and sandwiched it between the chip and a thermal sink layer. Specifically, the thermoelectric material comprised superlattices of p-type Bi_2Te_3/Sb_2Te_3 and n-type $Bi_2Te_3/Bi_2Te_{2.83}Se_{0.17}$ grown on GaAs substrates by metal-organic chemical vapor deposition. The assembled devices could cool a targeted region on a silicon chip with a high heat flux (1300 W/cm²) by 15°C. — PDS

Nat. Nanotechnol. 4, 10.1038/ NNANO.2008.417 (2009).

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Review

n Thermoelectrics

athin refrigerators for

MONDAY, JANUARY 26, 2009

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ry in your computer and touch the main processor l its blistering heat, which can exceed 100 °C. Such electrons through transistors, can impede essor in the long run. Traditionally, engineers have the heat, and fans or liquid-based cooling systems. p energy.

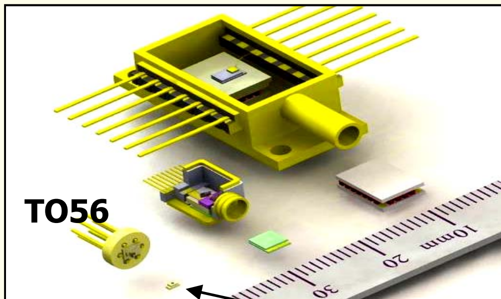
y researchers at Intel, RTI International of North olina, and Arizona State University have shown that possible to build an efficient microrefrigerator that target hot spots on chips, saving power and space, more effectively cooling the entire system. Their k also demonstrates, for the first time, that it is sible to integrate thermoelectric material into chip kaging, making the technology more practical than r before. A paper detailing the research was just lished in *Nature Nanotechnology*.

fundamental technology used to chill the chip, a rmoelectric cooler, isn't new, explains Rama katasubramanian, senior research director at the Center for Solid State Energetics at RTI International. In a *Nature* paper from 2001, he and his team showed that a material called a nanostructured thin-film superlattice has superior thermal properties to other types of thin thermoelectric materials: the superlattice conducts electricity well but impedes the flow of heat. When an electric current zips through the material, its temperature can drop to about 55 °C.

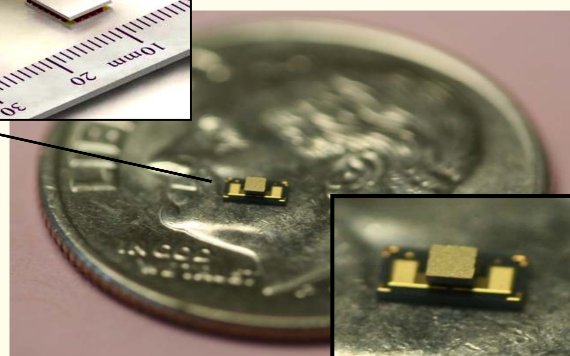
- **Repeatable demonstration of TEC performance**
- **Active plus passive hot-spot cooling >14°C has been achieved at a heat flux ~1250 W/cm²**
- **Practical application of nanostructured thermoelectrics to solve a real-world chip problem**

Photonics
Telecom—Laser Diode

Meeting New Challenges

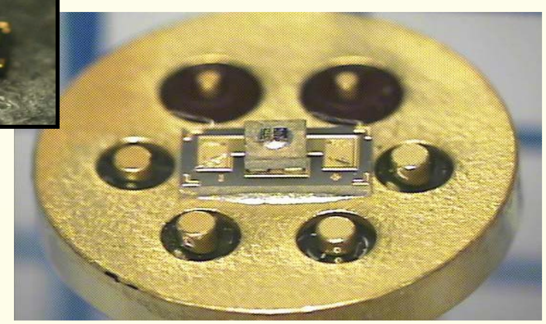


Smallest Size



– Nextreme has demonstrated necessary size & performance as well as 4x efficiency in laser diode cooling

Highest Pumping Power



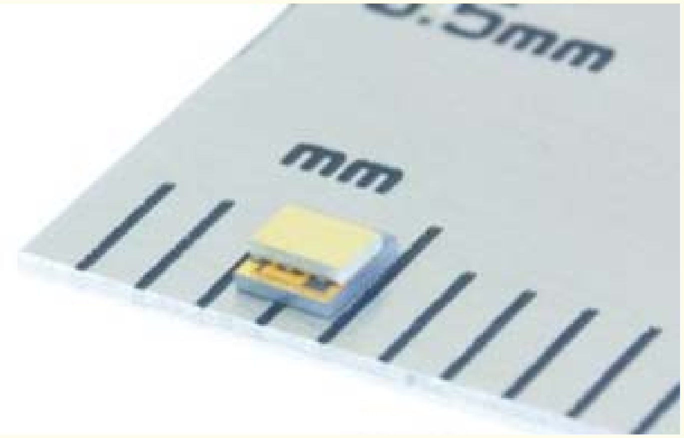
Nextreme THERMAL SOLUTIONS

Recent Developments – ΔT_{max} in Thin-film Modules Comparable to bulk TE, while offering >10 in power density, form factor and 1/1000th Tellurium usage

Nextreme Achieves New Milestone in Cooling Performance for Thin-Film Thermoelectrics

Microscale heat pump surpasses 60°C temperature differential at room temperatures

DURHAM, N.C. (February 6, 2012) — Nextreme Thermal Solutions, the leader in micro-scale thermal management and power generation solutions, today announced that its thin-film thermoelectric technology has achieved a 60.1°C temperature difference between its cold and hot sides at an ambient temperature of 24.7°C, bringing it on par with the performance of bulk thermoelectric technology. The 60°C temperature milestone, known as the ΔTmax, reflects the ability of the thermoelectric device to pump heat efficiently. This new level of performance translates to improved cooling efficiency, lower input power requirements, and greater opportunities for solving thermal issues in electronics, photonics, automotive, avionics, and high-speed PCR applications.



Nextreme will be introducing new products with this higher level of cooling performance in 2012.

Nextreme THERMAL SOLUTIONS

Recent Developments – Laird Technologies will begin selling and designing in Nextreme thin-film thermoelectric modules

Laird Technologies and Nextreme Thermal Solutions Announce World-Wide Strategic Distribution and Design Partnership

Nextreme's Products Expand Laird Technologies' Thermal Management Portfolio

St. Louis, Missouri and Durham, North Carolina, USA – February 29, 2012 – Laird Technologies, Inc., a global leader in the design and supply of customized performance-critical components and systems for advanced electronics and wireless products, and Nextreme Thermal Solutions, the leader in micro-scale thermal management and power generation solutions, today announce the formation of a world-wide strategic distribution and design partnership. With this alliance, Laird Technologies will be the exclusive global reseller for Nextreme thermal management and power generation products.

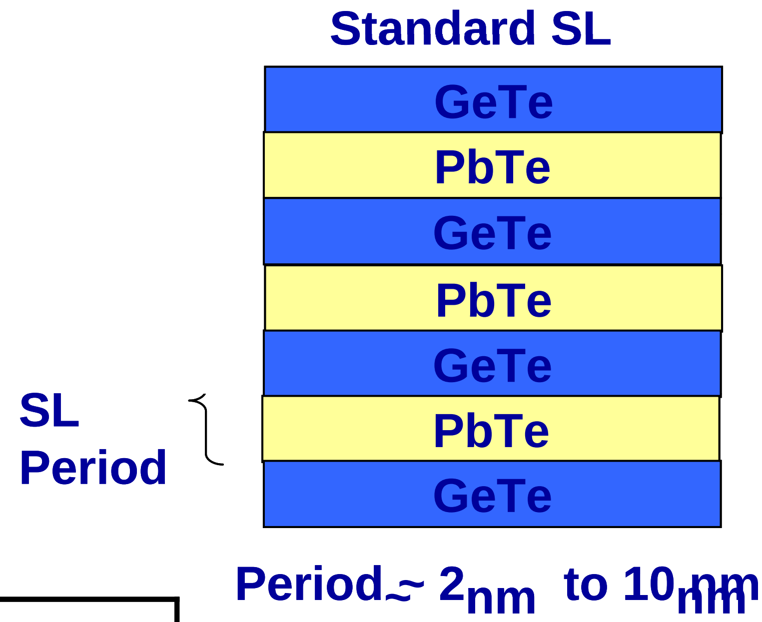
As a value-added reseller of Nextreme products, Laird Technologies will leverage its design centers in support of new applications using Nextreme's thin-film thermoelectric products. Laird Technologies and Nextreme will work together to build strategic relationships with companies that will support long-term business opportunities and growth.

Nextreme THERMAL SOLUTIONS

Some highlights of thin-film SL Materials

PbTe/GeTe Superlattices for Mid-temperature Applications

- Why this system?
  - Band gaps can be nearly identical.
  - Lattice mismatch is small enough to make epitaxial hetero-structures
  - Good cross-plane carrier transport with lattice thermal conductivity reduction achievable?
  - P-type system likely due to the presence of GeTe



Material	Band Gap (eV)	Lattice Constant (nm)
PbTe	0.32	0.645
GeTe	0.32 (crystalline) 0.8 (amorphous)	0.600 N/A

Advanced Bulk Thermoelectric Materials and Devices

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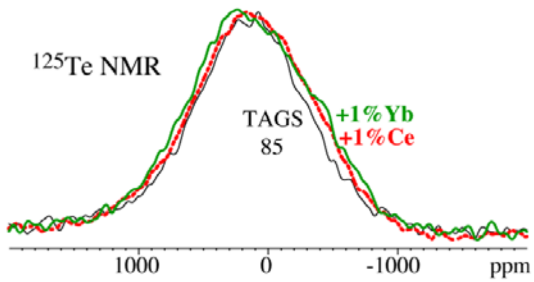
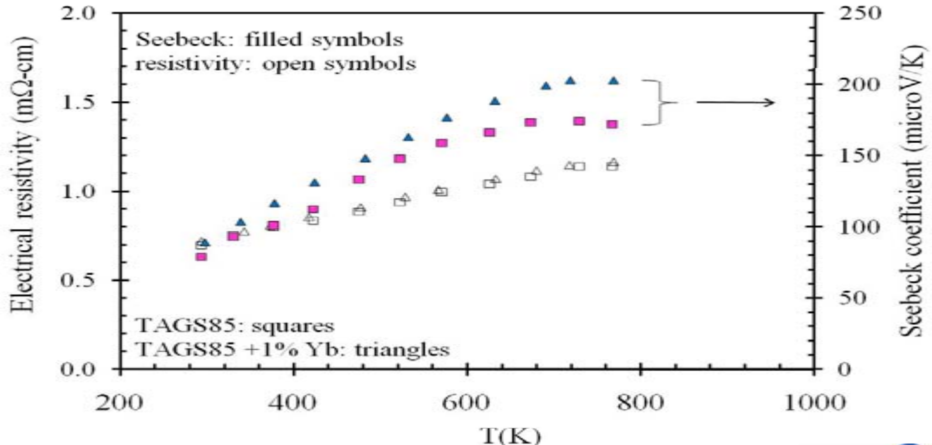
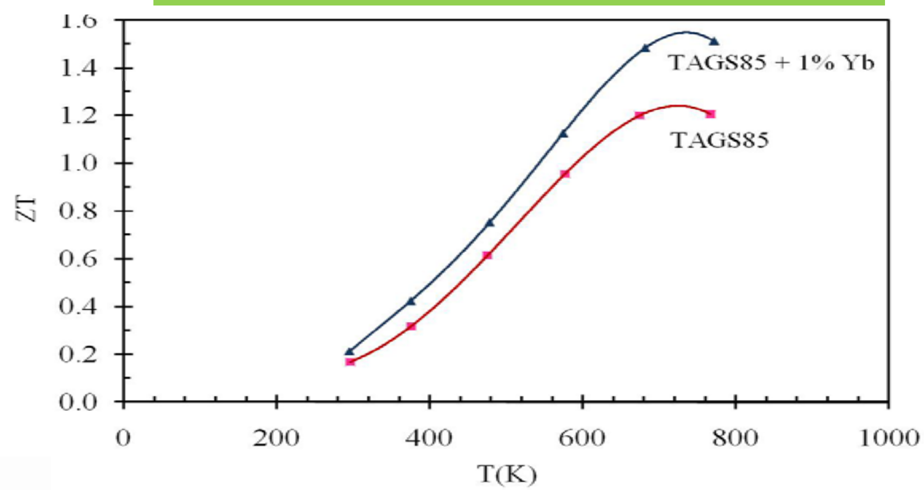
Bulk Materials with Rare Earth Addition
(Mid temperature)



Rare earth atoms can potentially increase magnetic scattering of carriers, leading to enhanced Seebeck coefficient

Advanced Functional Materials, 2010, DOI: 10.1002/adfm.201001307





Patent Pending

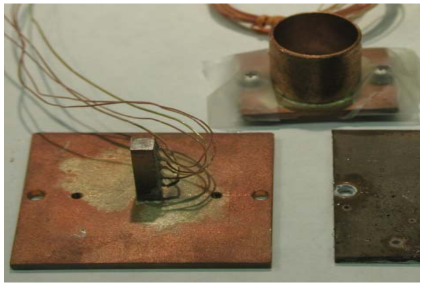
The Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

IOWA STATE UNIVERSITY

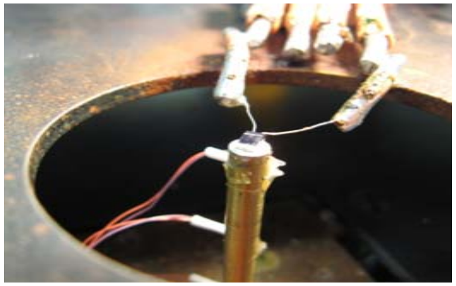
RTI INTERNATIONAL

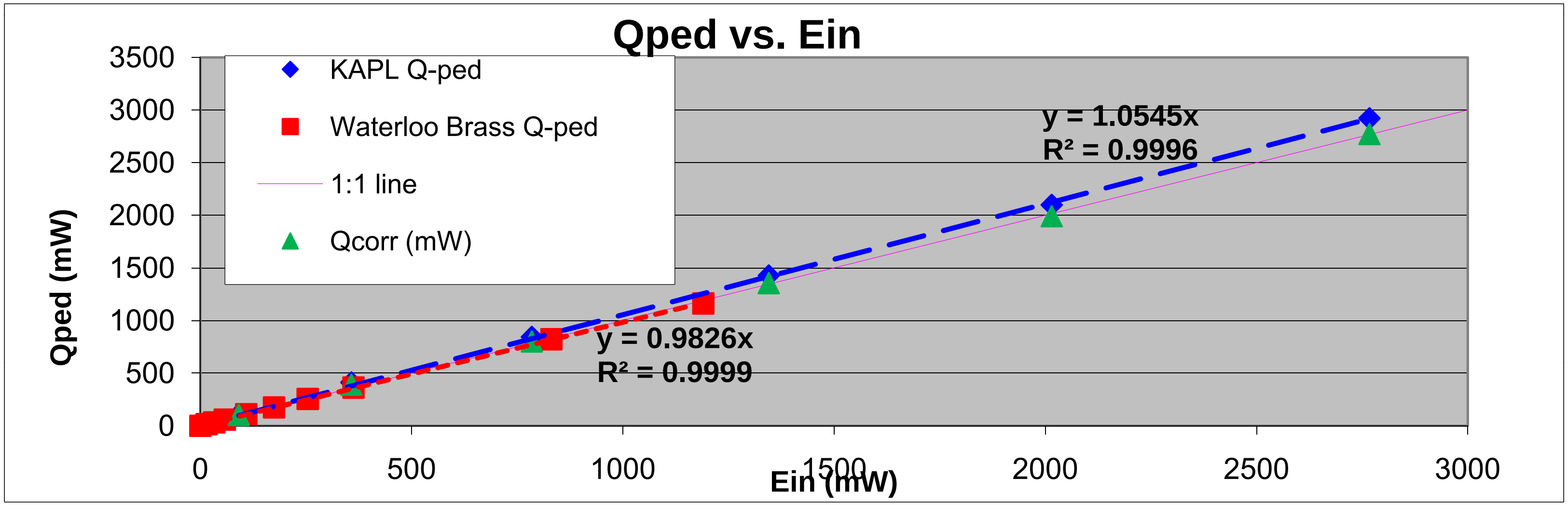
Calibration of Q pedestal with electric heat input

Knolls Atomic Power Lab Cu Q-ped

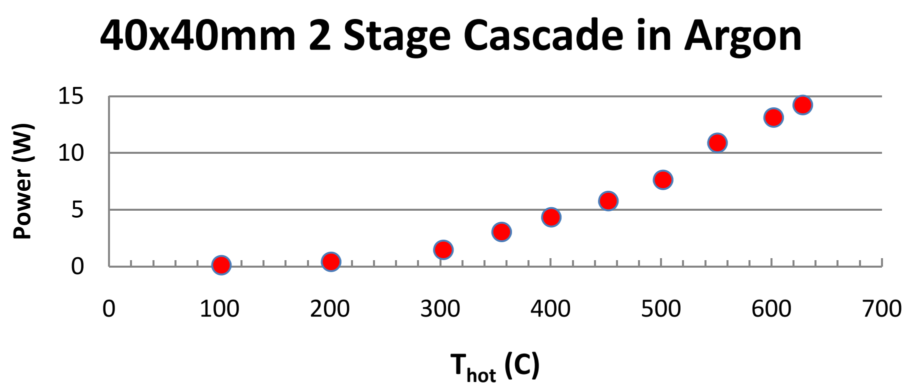


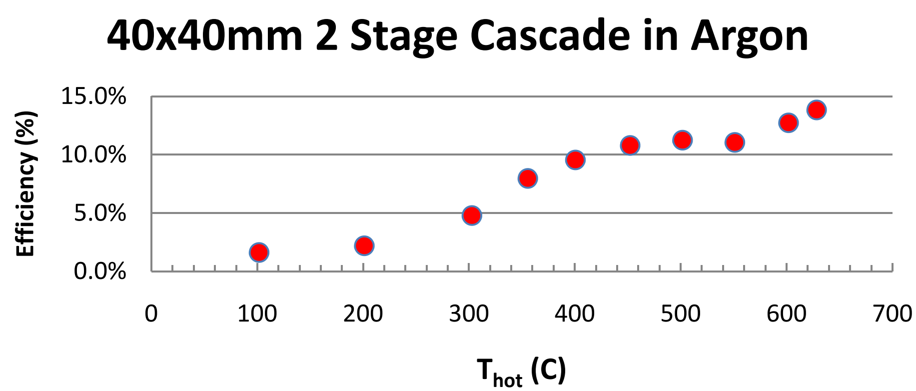
Univ. of Waterloo Brass Q-ped





40x40 mm Two-Stage Cascade Module Performance in an Argon ambient



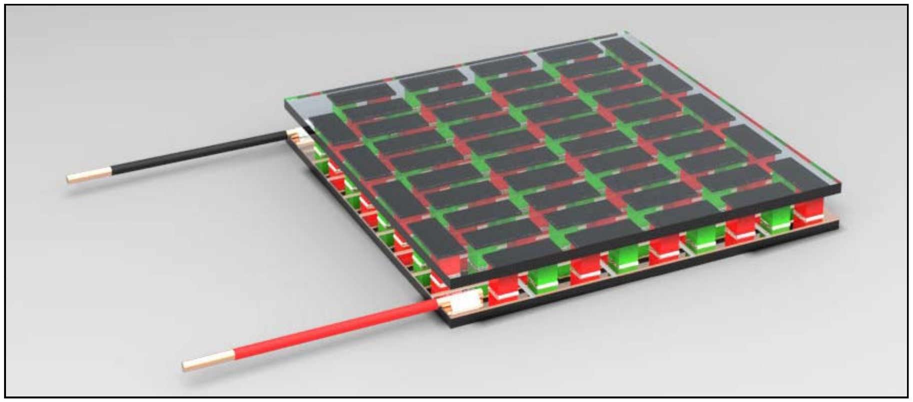


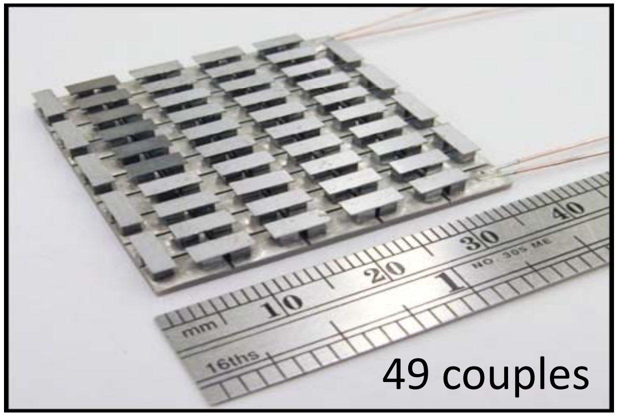
- T_{hot}~628°C, efficiency of ~13.8% at maximum power of 14.2 Watts at T_{cold}~ 44°C
- Peak Efficiency expected >14%
- Efficiency Measured with a Q-meter for heat flow (similar to previous slide but using a larger Q-meter); **2nd stage device using half-Heusler for T_{hot}~628°C**
- **Looking at scale up to power levels of 100 to 1000 Watts and achieve efficiency of ~13% or better**

US Patent No. 7,638,705

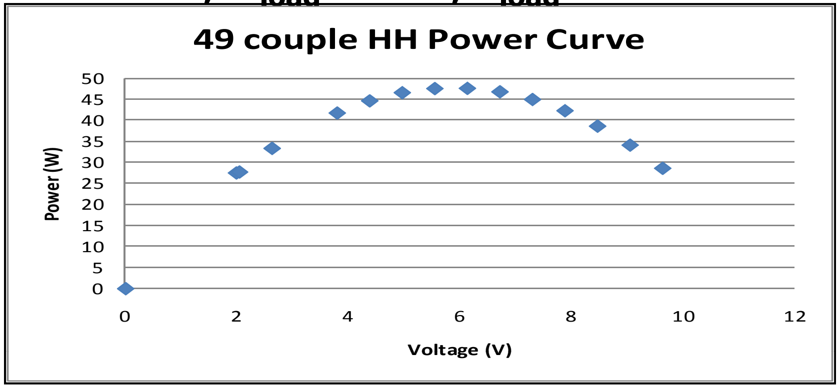
RTI INTERNATIONAL

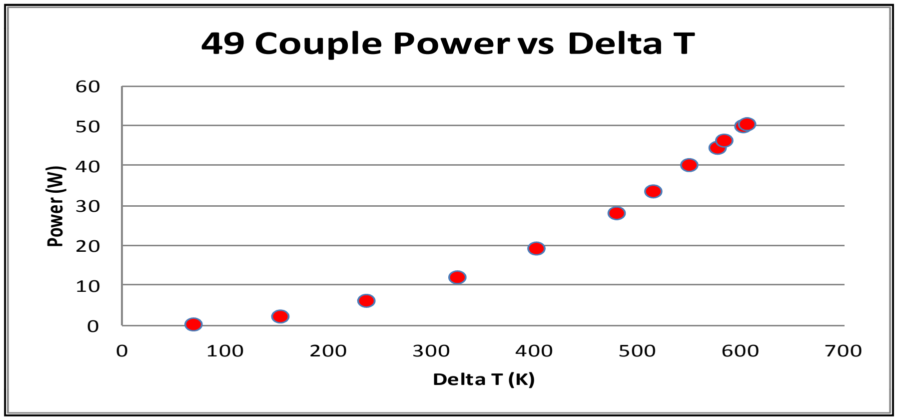
50-W, 4x4 cm, Power Generation Module using half-Heusler Materials





P=50W, V_{load}=5.9V, I_{load}=8.5A





Early results - S. Joseph Poon, Di Wu, Song Zhu, Wenjie Xie, and Terry M. Tritt, Peter Thomas and Rama Venkatasubramanian, ***Half-Heusler phases and nanocomposites as emerging high-ZT thermoelectric materials***, J. Mater. Res., *Invited Feature Papers*, Vol. 26, No. 22, Nov 28, 2011.

RTI INTERNATIONAL

Advanced Bulk Thermoelectric Applications

Less Dependence on Fossil Fuel for DoD Platforms & Systems

Ref: New York Times October 2010

- NATO supplies oil tankers after an attack
- >50% of total logistics cost is related to fuel logistics
- 1000 have died related to fuel transport and supply

Alternative Power

Energy Efficiency

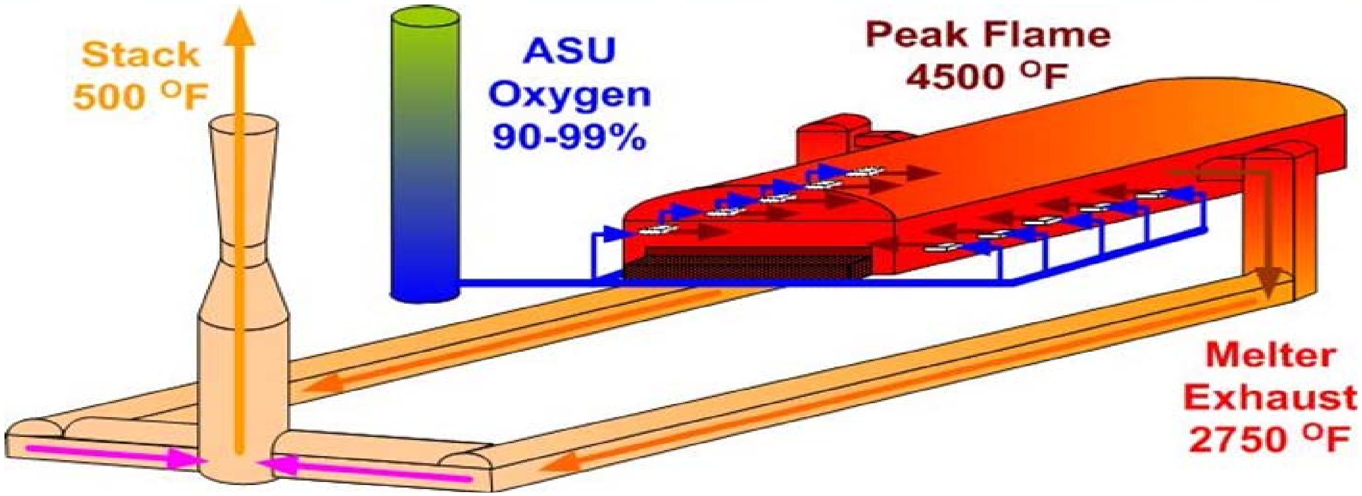
- Hybrid Systems
- Waste Heat Recovery

USS Makin Island – **Hybrid ship**

- Turbines at high speed
- Electric Drive for <10 knots

$250 M savings over lifetime of the ship

Industrial Waste Heat Recovery



- Oxyfuel glass melter used by PPG for industrial glass production was studied by DoE for waste heat recovery to lower production costs.

Solar Thermal Flat-Plate TE (potential) | **1-sun Flat-plate PV Array**

DoE/BES Workshop, 2005

- Thermoelectric Array Area = 200 cm^2
- Actual semiconductor Area = 2 cm^2
- 0.0002 cm^3 active-volume of semiconductors
- Natural ΔT across TE device = 50K to 100K
- Electric Power attainable ~ 1 Watt (with sun)
- ΔT available = 24 hr/day
- Energy Produced = 24W-hr/day
- Heat can be channeled through heat-spreaders and so not line-of-sight
- Expensive TE semiconductors needed <1% of total array area; <1% packing fraction
- Lower packing-fraction of TE also helps develop larger ΔT across TE and hence higher efficiency

- PV Array Area = 100 cm^2
- Semiconductor Area = 100 cm^2
- 10 cm^3 active-volume of Si
- Natural Lumens = 100 mW/cm^2
- Electric Power = 1 Watt (with sun)
- Light available = 10 hr/day
- Energy Produced = 10W-hr/day
- Basically, PV arrays operate line of sight
- Expensive PV semiconductors needed 100% of array area
- Additional electrochemical battery for energy storage to enable 24/7

Thermoelectric generators for solar conversion and related systems and methods (US Patent No. 7,638,705)

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TE Technology for Biomass Cookstoves

- **Higher efficiency/cleaner biomass stove**
  - Cleaner burning stove with improved efficiency
  - Biomass gasification (pyrolysis at T > 400°C)
  - H_2 gas mixes with air and burns
- **How it works?**
  1. Air enters through holes at the bottom.
  2. An electric fan blows air upward.
  3. A thermoelectric generator turns heat into electricity to power the fan and recharge its starter battery.
  4. By improving the ratio of air to fuel, the fan makes the fire burn hotter and more efficiently. That reduces fuel consumption and means less smoke and faster cooking
- **Significant reduction in emission of CO and particulate matter**

Power ~ 5V x 0.2 A = 1W