# Superlattice Thermoelectric Technology

**Rama Venkatasubramanian**
Center for Thermoelectrics Research (CTR)
RTI International
Research Triangle Park, North Carolina

**February 18, 2004**
**2004 DOE/EPRI High Efficiency Thermoelectrics Workshop**

Acknowledgements: DARPA/DSO & ONR DTEC Program (Dr. Valerie Browning and Dr. Mihal Gross); DARPA/DSO & ARO Palm Power Program (Dr. Valerie Browning and Dr. Richard Paur); Staff of RTI's CTR

RTI INTERNATIONAL

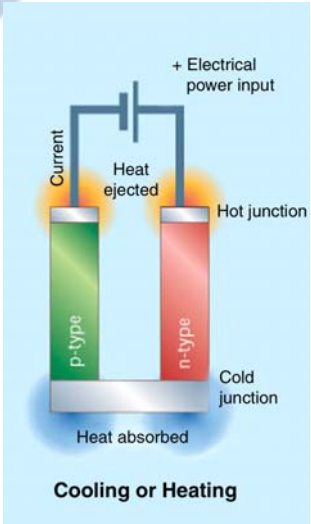
# Outline

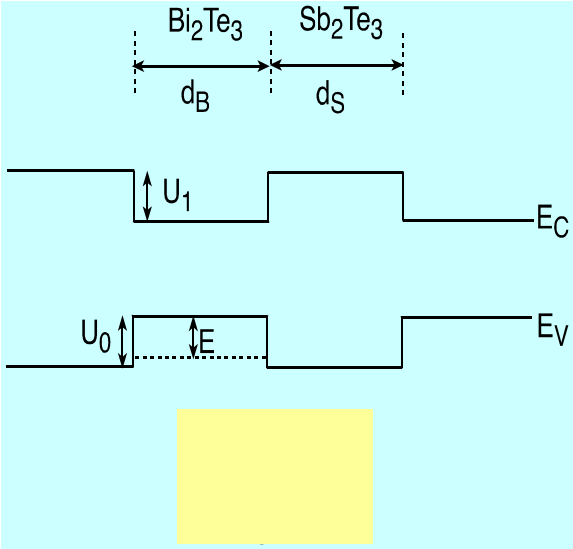
- Scientific Overview
  - Superlattice Materials with Enhanced Figure of Merit (ZT)
  - Physics of Materials and Relevance to Low Temperatures
  - Early Device Results
- Technology Transitions
  - Power Devices Beginning to Benefit from the Enhanced ZT, Enhanced Power Density, Ultra-High Specific Power
  - Cooling Results near 300K Corroborating the Enhanced ZT and Enhanced Power Density
  - Twice the Cooling using Superlattice Devices Compared with Bulk Devices at Low-Temperatures (~123K)
- Progress in Applications Toward High-flux Thermal Management in Electronics and Photonics
- Further Science with Phonon-Blocking, Electron-Transmitting Superlattice Structures

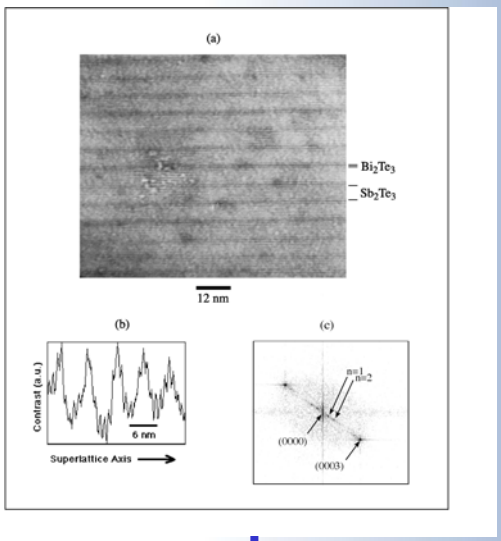
# Demonstrated Approaches to Enhanced 3-dimensional ZT-Progress with Bulk Materials and Nano-scale Materials

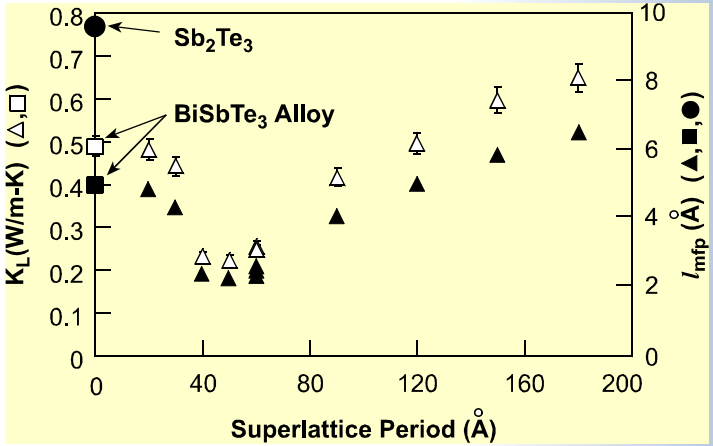
- **Cs $Bi_4Te_6$ and Ag $Pb_{18}SbTe_{20}$ (Michigan State University)**
  - **Bulk Materials with a ZT~ 0.8 at 225K but <1 at 300K (*Science* 287, 1024-1027, 2000)**
  - **Bulk Materials with a ZT ~ 2.2 at ~850K potentially from low-dimensional structures (*Science* 303, 818, 2004)**
- **Filled Skuterrudites (JPL)**
  - **Bulk materials with a ZT ~1.35 at 900K (Proc. Of 15th International Conf. On Thermoelectrics, 1996)**
- **PbTe/PbTeSe Quantum-wells and Quantum-dots (MIT, MIT Lincoln Labs.)**
  - **ZT~ 1.6 at 300K (*Science* 297, Sep. 2002)**
  - **Most of the improvement would come from thermal conductivity reduction rather than quantum-confinement effects? (Chen et al., ICT 2003, France)**
- **$Bi_2Te_3/Sb_2Te_3$ Phonon-Blocking Electron-Transmitting Superlattices (RTI)**
  - **ZT~2.4 at 300K in devices with all properties measured at the same place, same time, with current flowing (*Nature* 413, 597-602, Oct. 2001)**
    - ✓ **Thermal conductivity reduction, removing alloy scattering of electrons, removing electrical anisotropy without quantum-confinement effects**
  - **Focus on Devices to Take Advantage of Nanoscale Materials with Planar Microelectronics (Proc. of MRS Symposium, Boston, 2003)**

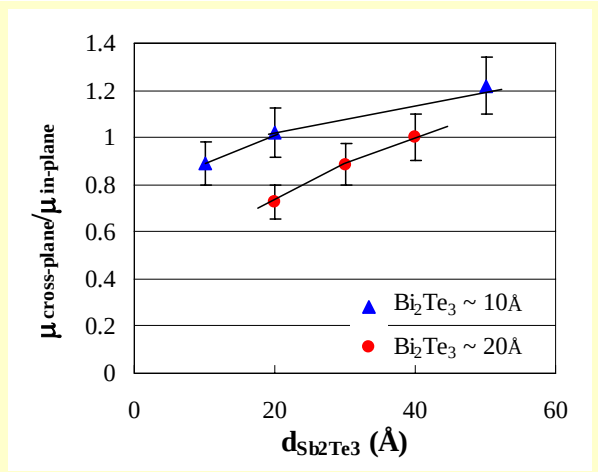
# Phonon-Blocking, Electron-Transmitting Superlattices with ZT ~ 2.4 at 300K



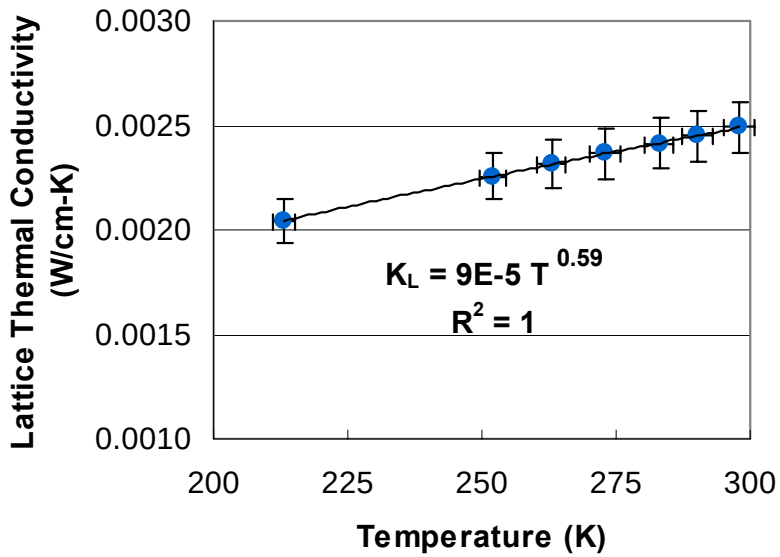



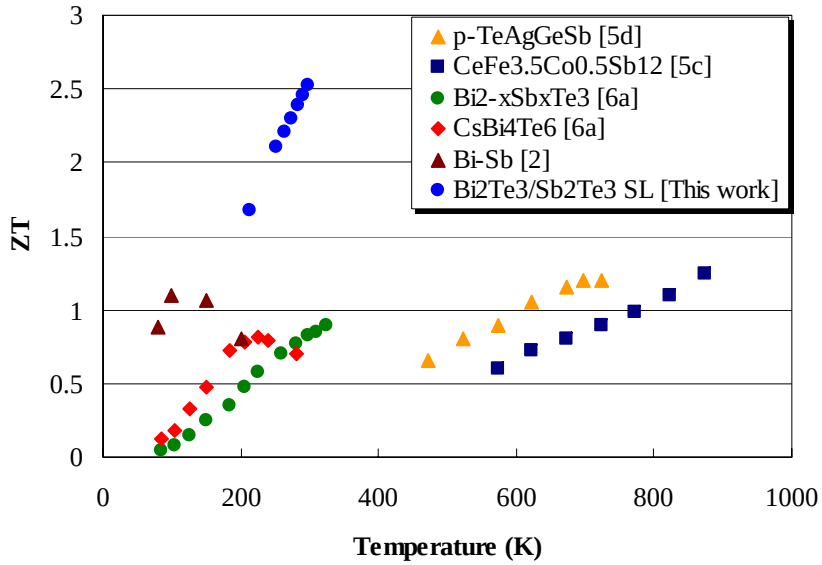




RTI INTERNATIONAL *Nature*, 413, 597-602 (2001)

*Physical Review B, 61, 3091 (2000)*

# Lattice Thermal Conductivity Reduction with Superlattices at Low-Temperatures and Impact on ZT



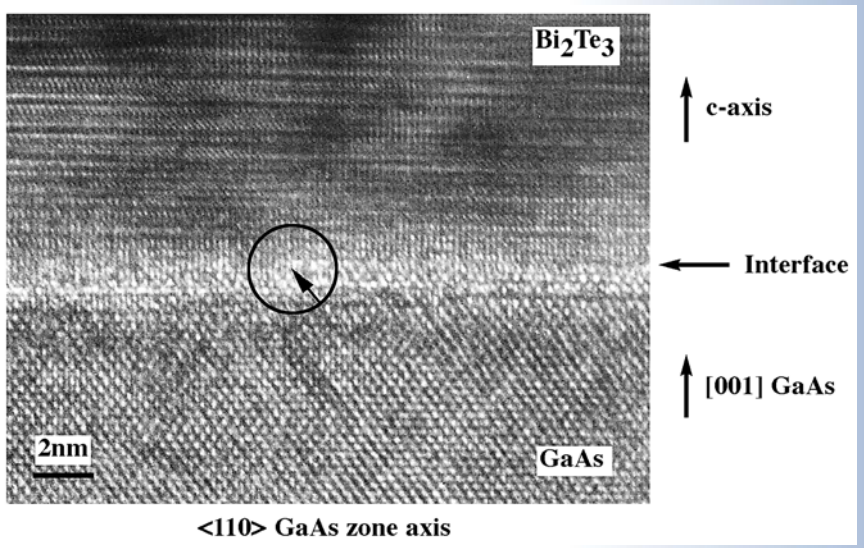

*Nature*, **413**, 597 (2001)

- **Note lattice thermal conductivity decreases at lower temperatures**

**- Similar observations in a study of Si/Ge Superlattices Lee, Cahill, Venkatasubramanian, Appl. Phys. Lett., 55, (1997).**

RTI INTERNATIONAL

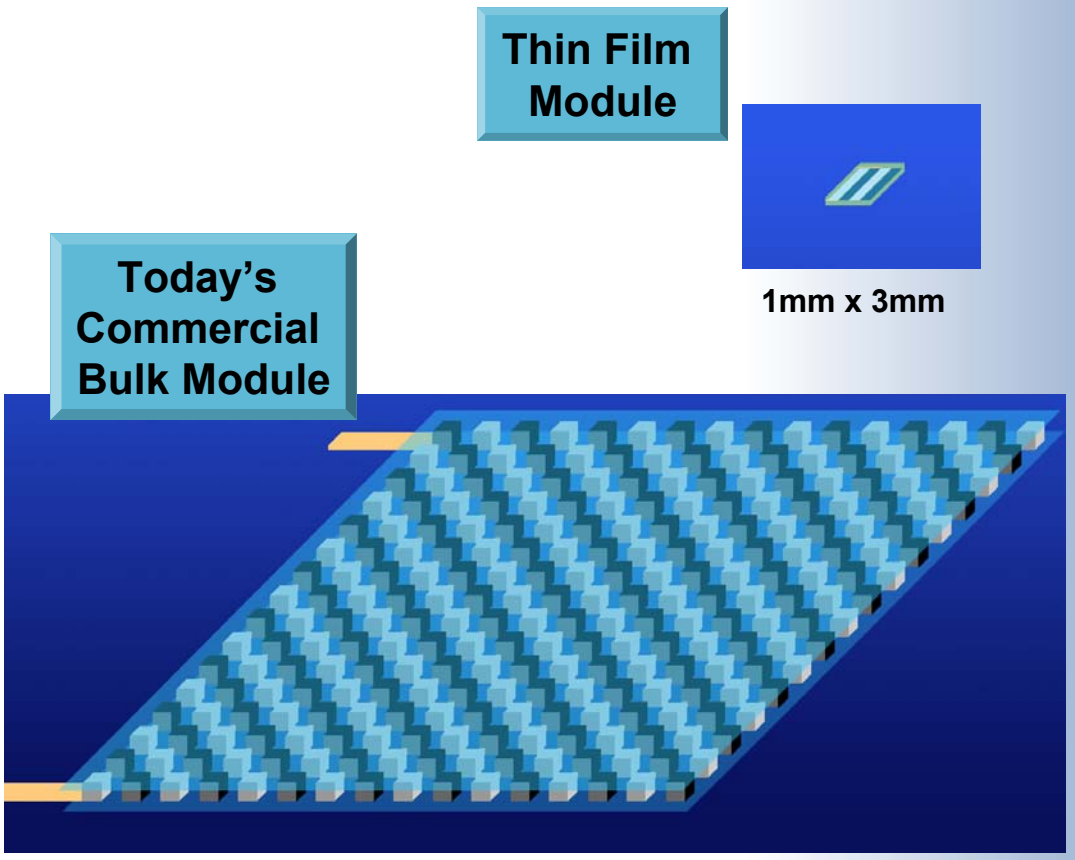
# Superlattices Grown by Metallorganic Chemical Vapor Deposition




- **Low-temperature growth needed to enable formation of low-energy van der Waals bond along the growth direction**
- **In-situ ellipsometry for nanometer-scale control of deposition**
- **MOCVD Scaleable to Multi-Wafer, Large-Areas for Low-cost Modules**
  - **Such growth processes are used today for large-scale space PV panels**

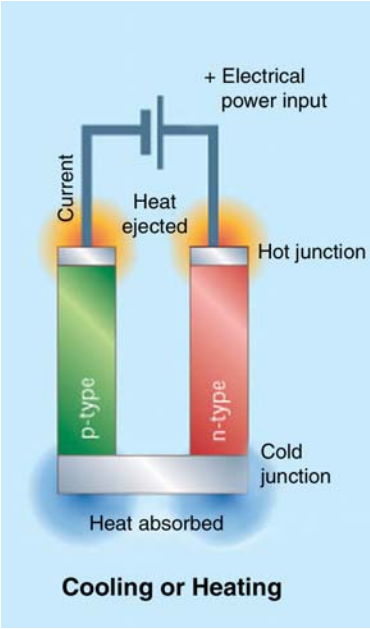
# Advantages of RTI's Superlattice Thermoelectric Technology

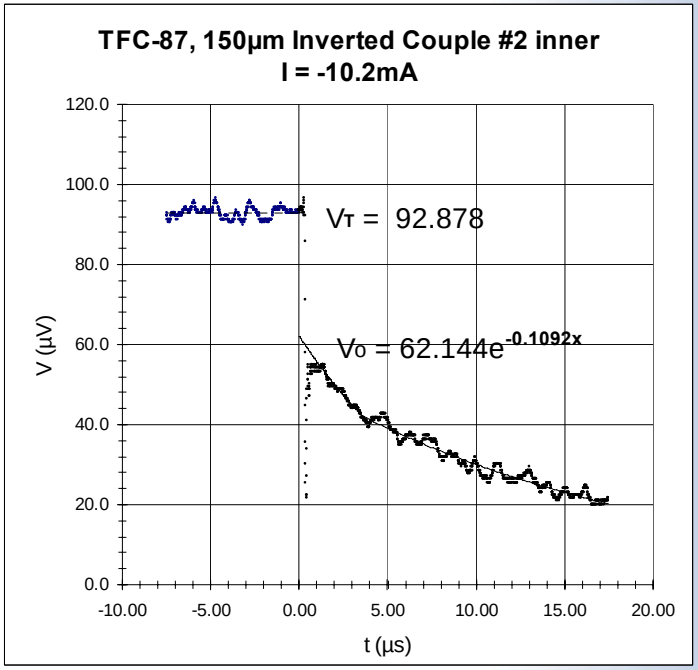
- Enhanced efficiency
- Super-fast cooling and heating
- Enhanced power density
- Localized cooling/ heating technology
- 1/40,000th the actual TE material requirement of bulk technology for same functionality
  - Not just thin-film but smaller-area as well
  - low recycle costs
  - Eco-friendly technology

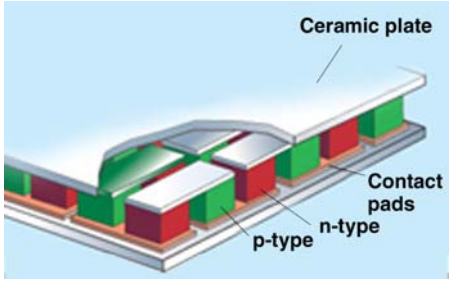


# Advancement to Device Performance

# Progress in Thin-film P-N Couples – the fundamental cooling or power conversion unit for transitioning to modules




- **Best** ZT of 2 at 300K in a p-n couple
  - Typical ZT in the range of 1.2 to 1.6, depending on the quality and consistency of the n-type superlattice component

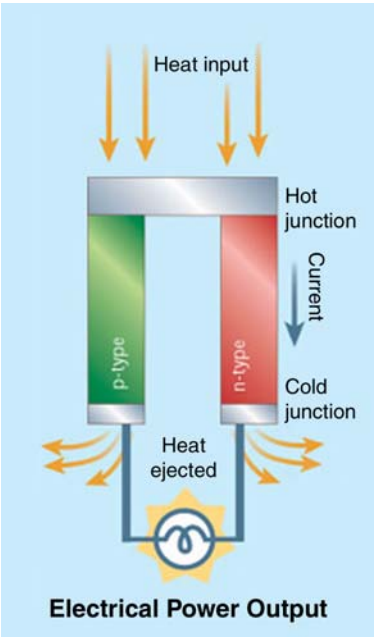
RTI INTERNATIONAL

# Power Device Benefiting from the Enhanced ZT and Power Density

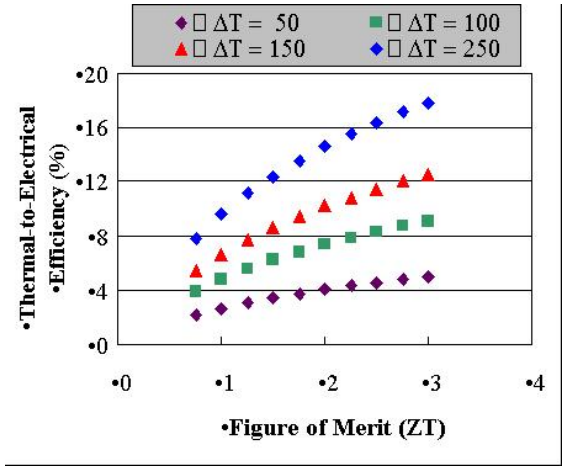
RTI INTERNATIONAL

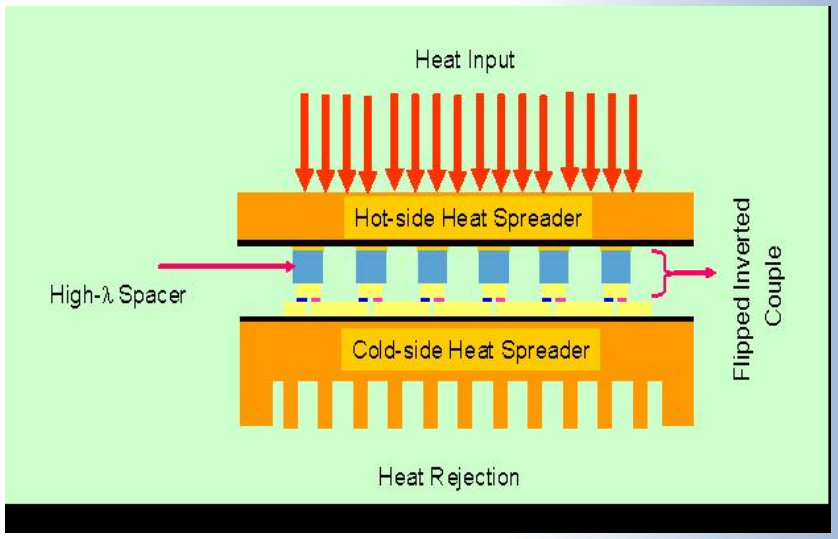
# Device Considerations

- P-N couple is the fundamental power conversion unit whose ZT and the $\Delta T$ across it determine the module-level efficiency
- Optimize ZT and Maximize $\Delta T$ across the device
- Developed the High Active Flux, Low Input-Output Flux (HAF-LIOF) Concept for Thin-film Devices by encapsulating TE elements between two high-$\lambda$ heat-spreaders
  - Low Packing Fraction so that ~2300 W/Cm$^2$ through TE elements for a large active $\Delta T$ but ~20 W/cm$^2$ to a few W/cm$^2$ at source and sink for easier thermal management



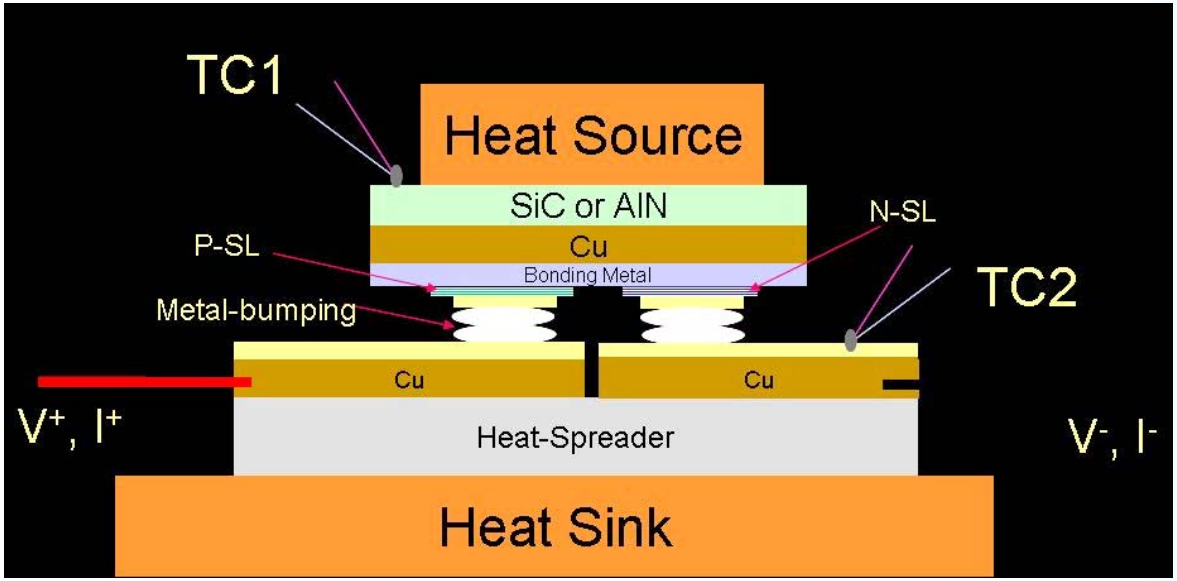

$$\psi = \frac{(T_h - T_c)}{T_h} \frac{\{(1+ZT)^{1/2} - 1\}}{\{(1+ZT)^{1/2} - 1\} + T_c/T_h}$$




• Work supported by DARPA/ARO Palm Power Program

# Device Power Conversion Efficiency Measurement




- **Heat flow through device from internal ΔT and measured thermal conductivities**
  - **Internal ΔT from $V_{oc}$ and measured Seebeck coefficients**
- **Efficiency from measured max. electrical power and heat flow**
- **Efficiency =[ $\Delta T_{int}/(2T_{mean}+(\Delta T_{int}/2)+4/Z_{ave})$] (Ref: Goldsmid)**
- **From $Z_{ave}$, ZT calculated at 300K**

# Early Studies - ZT Data from Power Conversion Efficiency

| $\Delta T_{int}$ (K) | Voc (mV) | Isc (mA) | Pmax (mW) | Efficiency(%) | ZT at 300K |
|---|---|---|---|---|---|
| 8.4 | 4.59 | 829 | 0.95 | 0.6 | 1.44 |
| 12.5 | 6.88 | 1301 | 2.24 | 0.9 | 1.6 |
| 17.5 | 9.63 | 1670 | 4.02 | 1.2 | 1.41 |

- **Only small $\Delta T$ investigated for this study to avoid over-influence of device parasitics**
- **Even so, from $Z_{ave}$, <u>ZT of the device</u> at 300K ~ 1.49 ± 0.1**
  - **Consistent with a ZT of ~ 1.3 at 300K by Harman Method in the same p-n couple**

# Recent Power Conversion Results ($\eta$, $P_d$) with Large DT across devices – by improving thermal interfaces

**Best Single p-n couple producing 52.7 mW with a $\Delta T$ across couple of ~111K with an active power density of 93.2 W/cm$^2$ and total mini-module power density of 14.6 W/cm$^2$ based on 600 $\mu$m x 600 $\mu$m area**

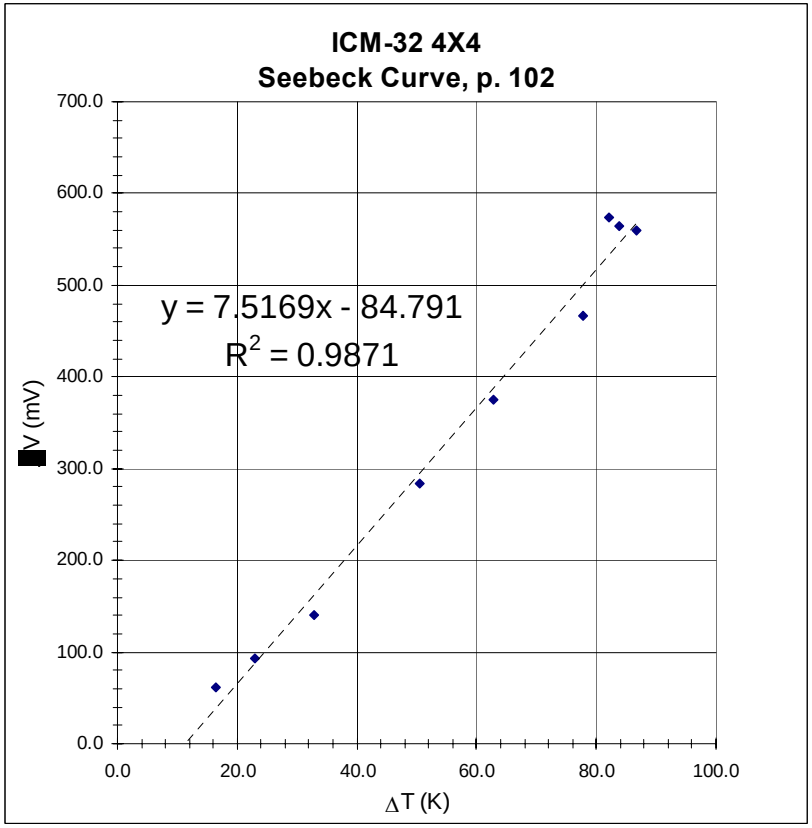
- **Efficiency, corrected for lead resistances, ~6.4% at $\Delta T_{int}$ ~111K ($T_{heat\text{-}source}$ ~152$^o$C, $T_{heat\text{-}sink}$ ~33$^o$C); $\Delta T_{ext}$ ~ 119K; $\Delta T_{int}$ ~111K ; 93% transfer**
  - **ZT~1.26 at 300K and ZT~1.68 at 400K at mini-module level!**
  - **Potentially can achieve an efficiency of ~9% with $\Delta T$~150K**

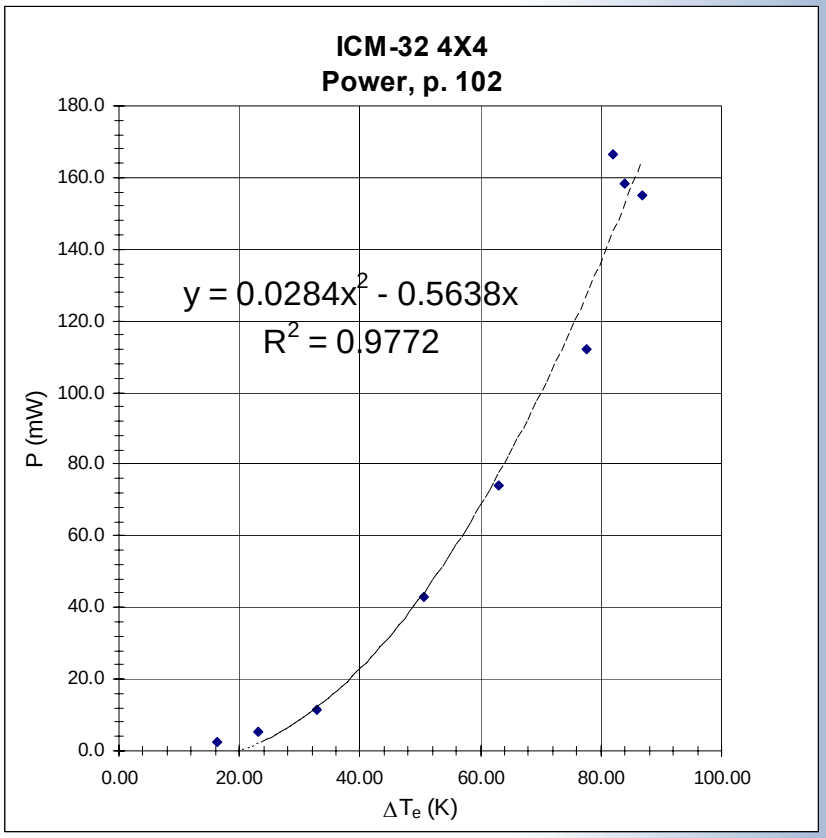
| $\Delta T_{ext}$ | $\Delta T_{int}$ | Isc (mA) | P (mW) | $P_{density}$ at die-level (mW/cm$^2$) |
|---|---|---|---|---|
| ~0 | ~0 | 12.7 | 0.001 | 0.19 |
| 8.8 | 6.3 | 232.6 | 0.185 | 51.4 |
| 54.4 | 49.6 | 1762 | 11 | 3056 |
| 92.7 | 87.9 | 2736 | 30.2 | 8397 |
| 119 | 111 | 3790 | 52.7 | 14639 |

• Work supported by DARPA/ARO Palm Power and the DARPA/ONR DTEC Programs

RTI INTERNATIONAL

# Initial Results on larger Modules - $V_{oc}$ >0.5Volts and Power Output of 166 mW for an area of 0.0625 $cm^2$ for a DT of ~80K



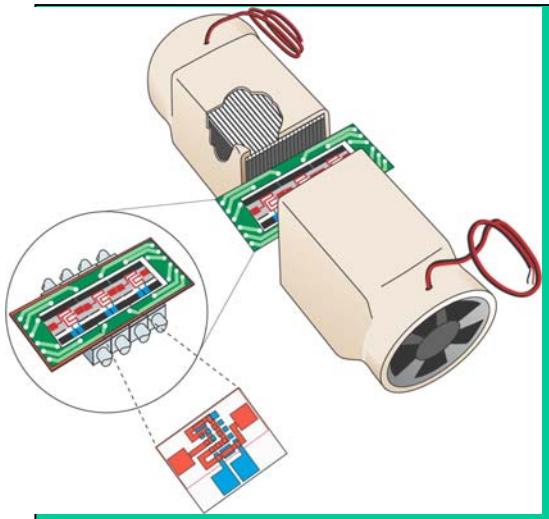



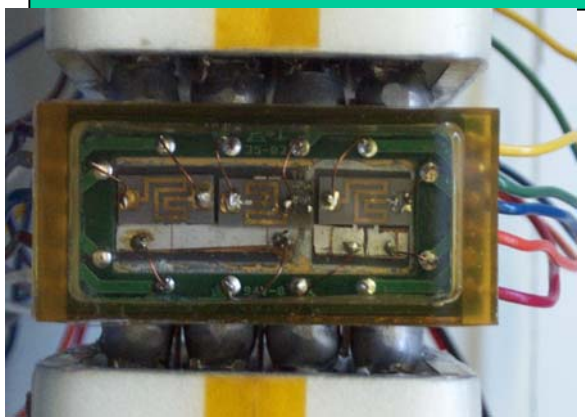

- **$P_d$ ~ 2.7 W/$cm^2$; larger ΔT will lead to higher $P_d$**

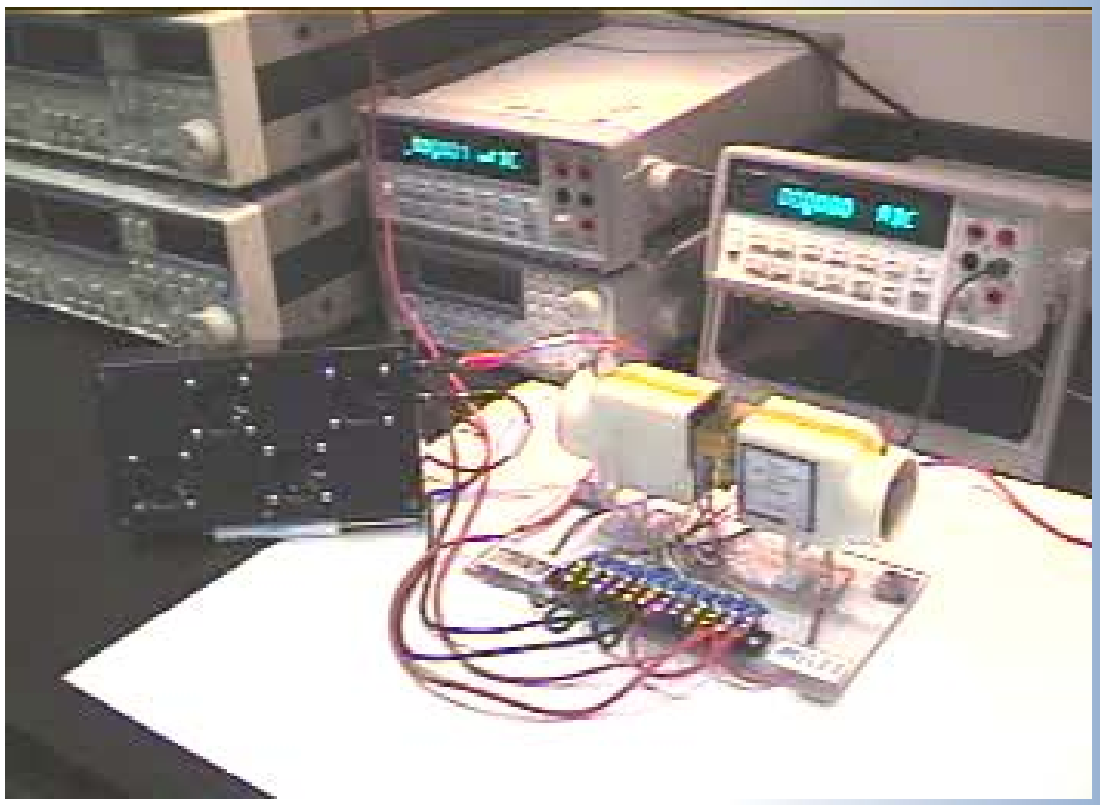
RTI INTERNATIONAL

# Power Conversion Under Steady State Current Flow – Integration with BSST Heat-Pipe Heat Exchangers to Manage Large Heat Fluxes at Heat-sink

- **Power Generation Using Superlattice Modules ($T_{hot}$ ~ 100°C)**

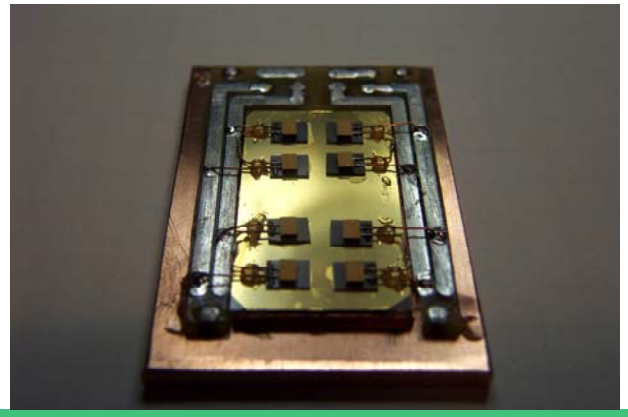






# What could this mean potentially for Renewable Energy?

## Superlattice Thin-film TE vs. Si PV Array



**Area = 1-cm$^2$ TE elements**

**0.0001 cm$^3$ active-volume TE**

**Natural $\Delta T$ = 10K**

**Electric Power attainable ~ 2 to 5 Watts**

**-- use the earth or ocean and atmosphere as two thermal terminals?**

**-- Heat can be channeled through spreaders using HAF-LIOF concept to set up the $\Delta T$, if necessary**

**-- $\Delta T$ available most of the time?**

**Area = 100 cm$^2$ array**

**~100-cm$^2$ active-area Si**

**10 cm$^3$ active-volume Si**

**1-sun (10% efficient)**

**Electric Power = 1 Watt**

**-- Basically, PV arrays Operate line of sight**

**-- Light Available ~10 hr/day**

To be Published

RTI INTERNATIONAL

# What could this mean potentially for Space Power?

**Lightweight, high-efficiency technology can potentially lead to very high specific power**

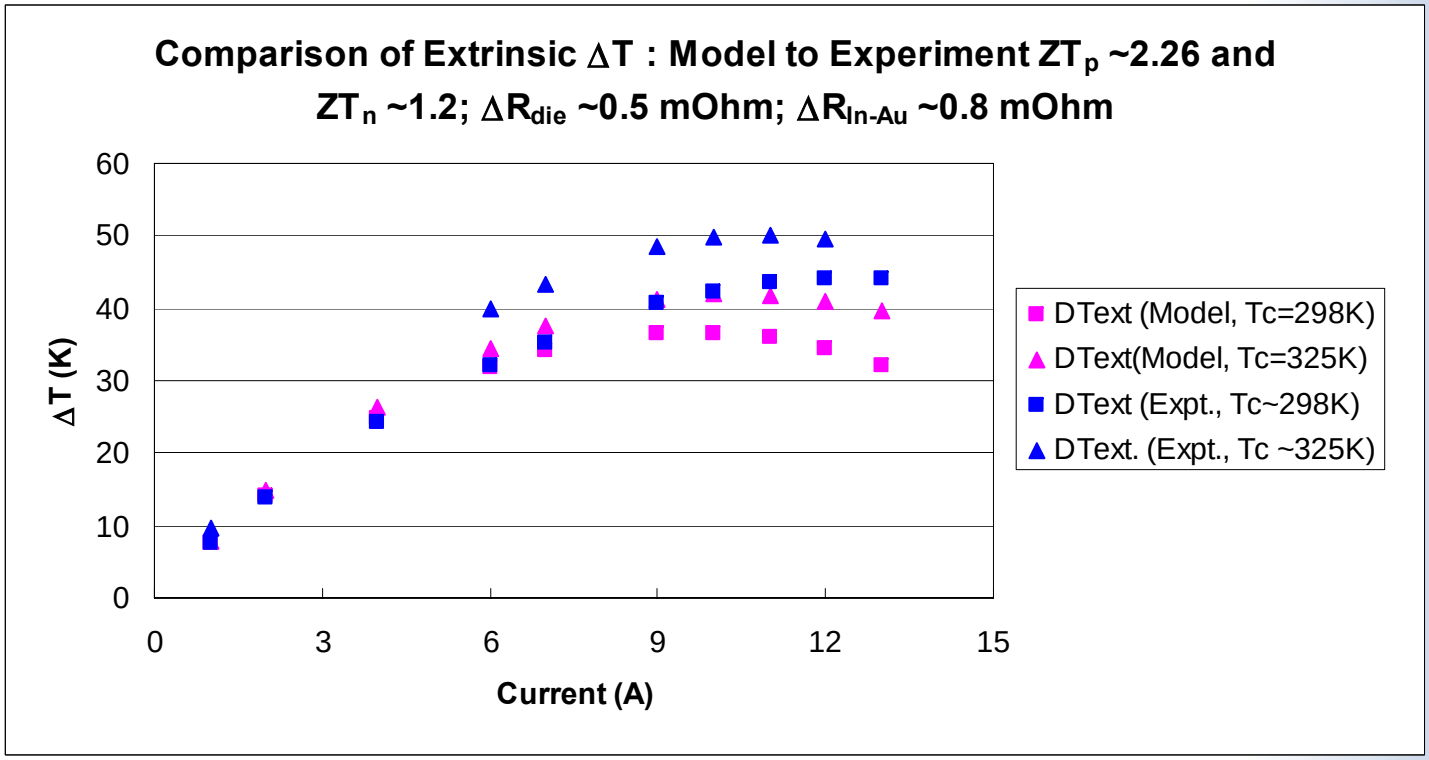
- **Best Space PV for satellites would offer ~0.3 W/gm compared to 20W/gm for superlattice thin-film TE using ΔT ~70K with current device efficiencies**
- **Use natural heat sources or other intentional heat-sources**
  - ✓ **ΔT between a surface facing sun and another surface not facing sun in a space environment can be ~100K**
  - ✓ **Combine thin-film thermoelectrics with novel concepts for radiant dissipation of heat can revolutionize space propulsion and exploration**
    - **Time to reach Jupiter and other outer planets can be cut by nearly half**

# Cooling Device Results Benefiting From the Enhanced ZT and Power Density

RTI INTERNATIONAL

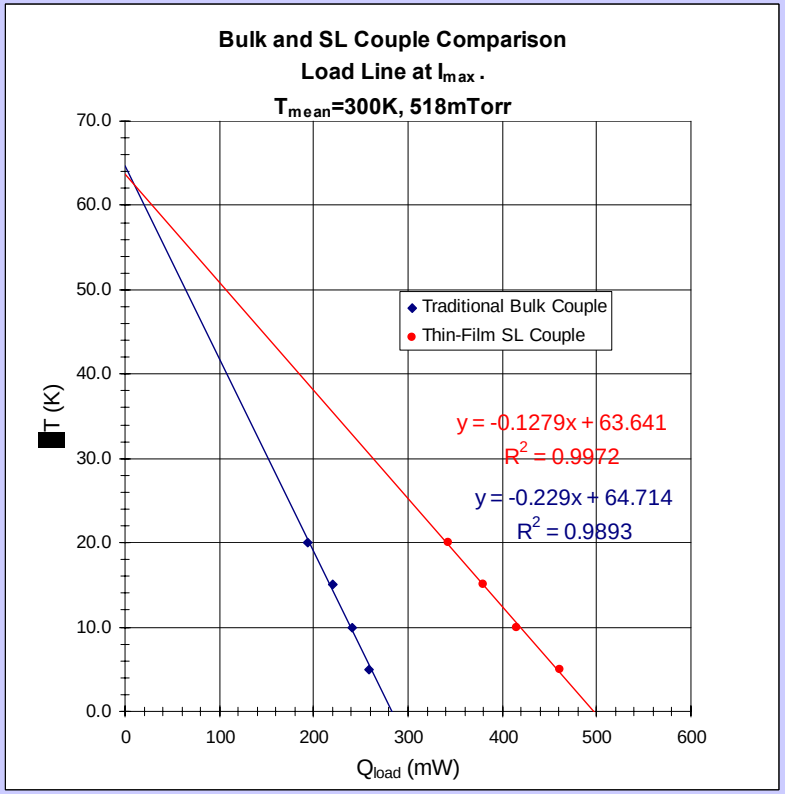
# Realizing the Cooling Associated with High ZT Materials in Cooling Modules is a Tough Thermal Optimization Problem

- **Exact Matching of p and n-legs' thermal conductance at $\Delta T_{max}$**
- **Exact matching of p and n-legs' electrical resistances at $Q_{max}$**
- **Thermal drop across many interfaces through which heat is pumped**
- **Even so, lower-current cooling data consistent with $ZT_p$ >2.2, $ZT_n$ ~ 1.2**

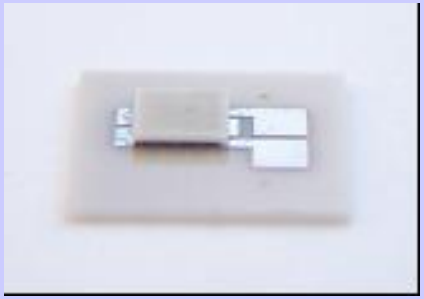


# Superlattice Couple at $Q_{max}$ – Producing Higher Heat Pumping than Typical Bulk Couple

- $Q_{max}$ of ~0.5 Watts seen in one couple, area ~0.0036 $cm^2$
- 1-year old data

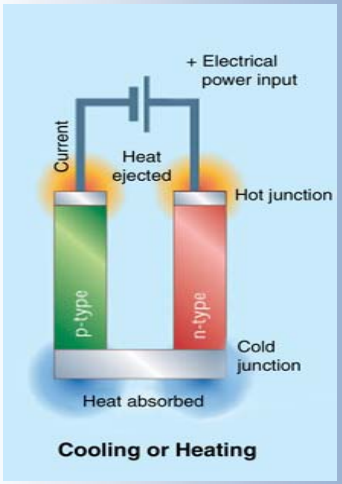



- $Q_{max}$ of >1 Watt seen in one couple, area ~0.0036 $cm^2$
- Recent data



- $Q_{max}$ of ~10 Watts seen in an array 4 x 4 couples, area ~0.063 $cm^2$
- **Module Cooling Power Density >150 W/$cm^2$**
- Potential Near-Term Impact for Hot-Spot Electronics Cooling
- Potential Long-Term Impact on Solid-state refrigeration

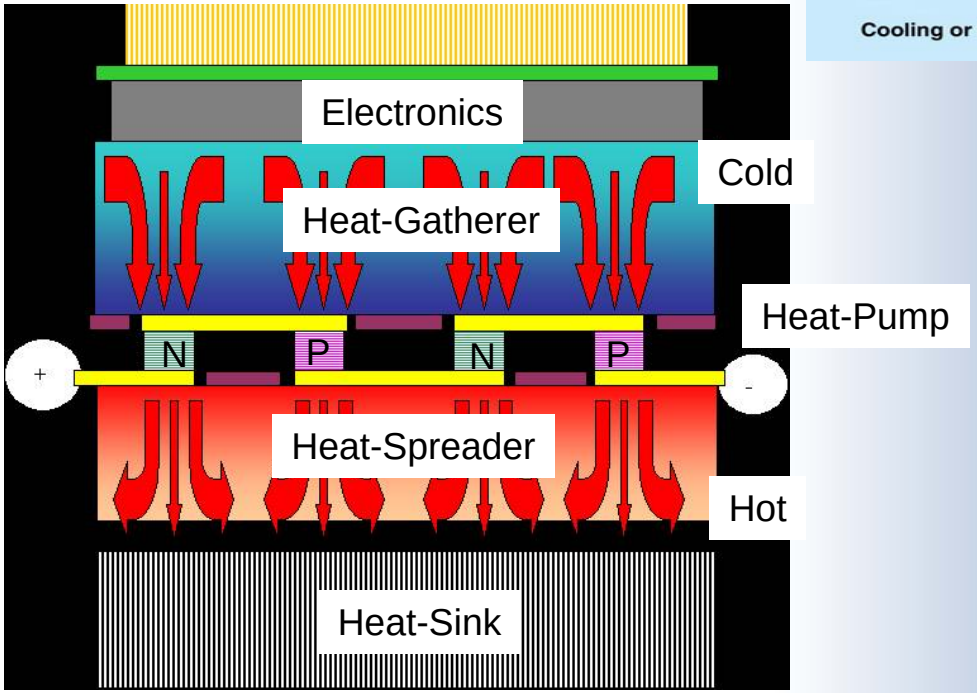
# One of the remaining major hurdles in transitioning the Thin-film P-N Couple Performance to External Performance at the Module Level




- Heat-Rejection at the Hot-side, after active electronic heat-pumping, by methods such as air-flow, liquid-flow, heat-pipes, liquid impingement etc. have to be improved

- Heat-flux at device-element level can approach ~2000 W/cm$^2$, which can be spread down to ~20 W/cm$^2$

  - **High Active Flux, Low Input-Output Flux (HAF-LIOF) Concept**

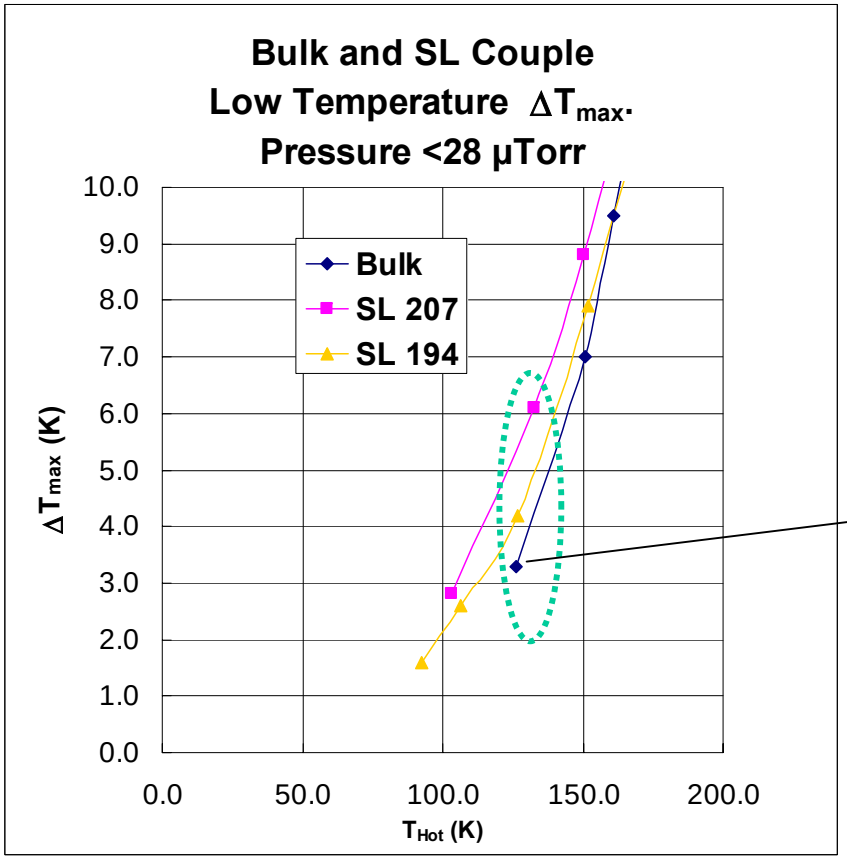


# Preliminary Device Cooling Comparison with Bulk Devices at Low-Temperatures

# Why Superlattices are More Attractive at Cryo Temperatures?

1. Superlattice Thermal Conductivity Reduction More Efficient at Lower Temperatures
2. Other aspects of superlattices such as Seebeck coefficient variation with temperature are advantageous at lower temperatures as well
3. Better performance, today, at cryogenic temperatures in spite of several parasitics unique to thin-film devices

# Impact of Higher ZT of Superlattices at Low-Temperatures in Device Performance




ZT ~0.9 at 300K

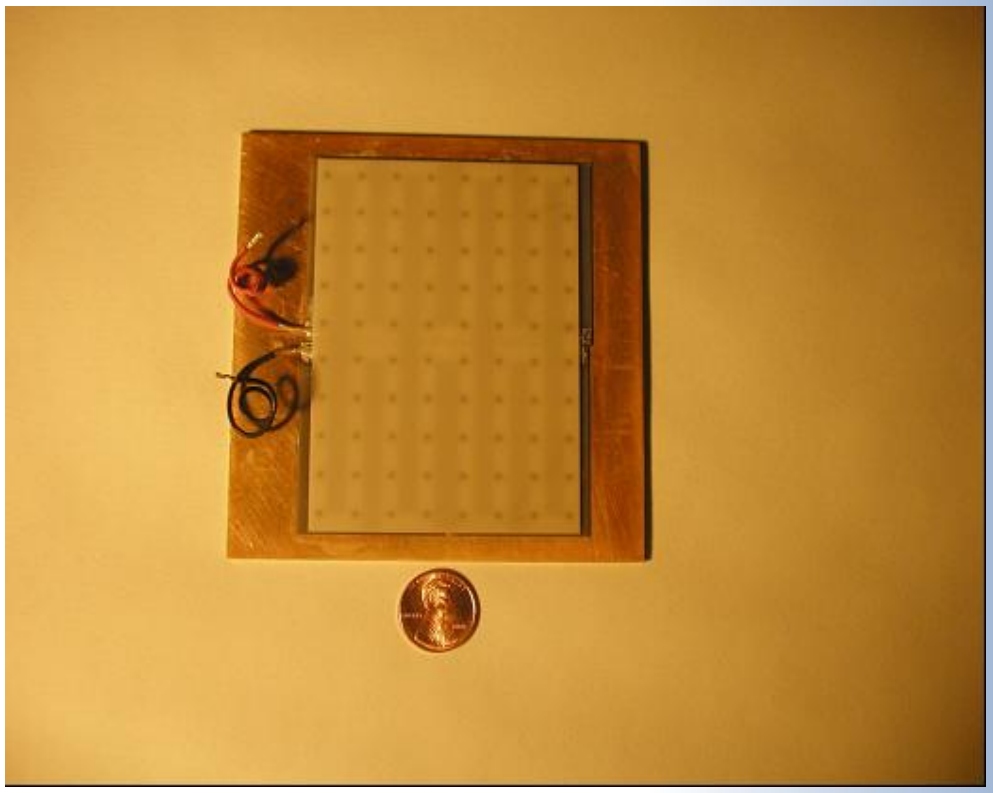
- **Nearly twice the cooling in SL couple compared to state-of-the-art bulk device in spite a lot of parasitics for the thin-film device**
- Expect a factor of 5 improvement, when fully optimized
- Makes TE attractive for a low-temperature cooling stage in the near-term

RTI INTERNATIONAL

# Superlattice Thermoelectrics for Advanced Electronics, Photonics & Power Electronics Thermal Management

RTI INTERNATIONAL

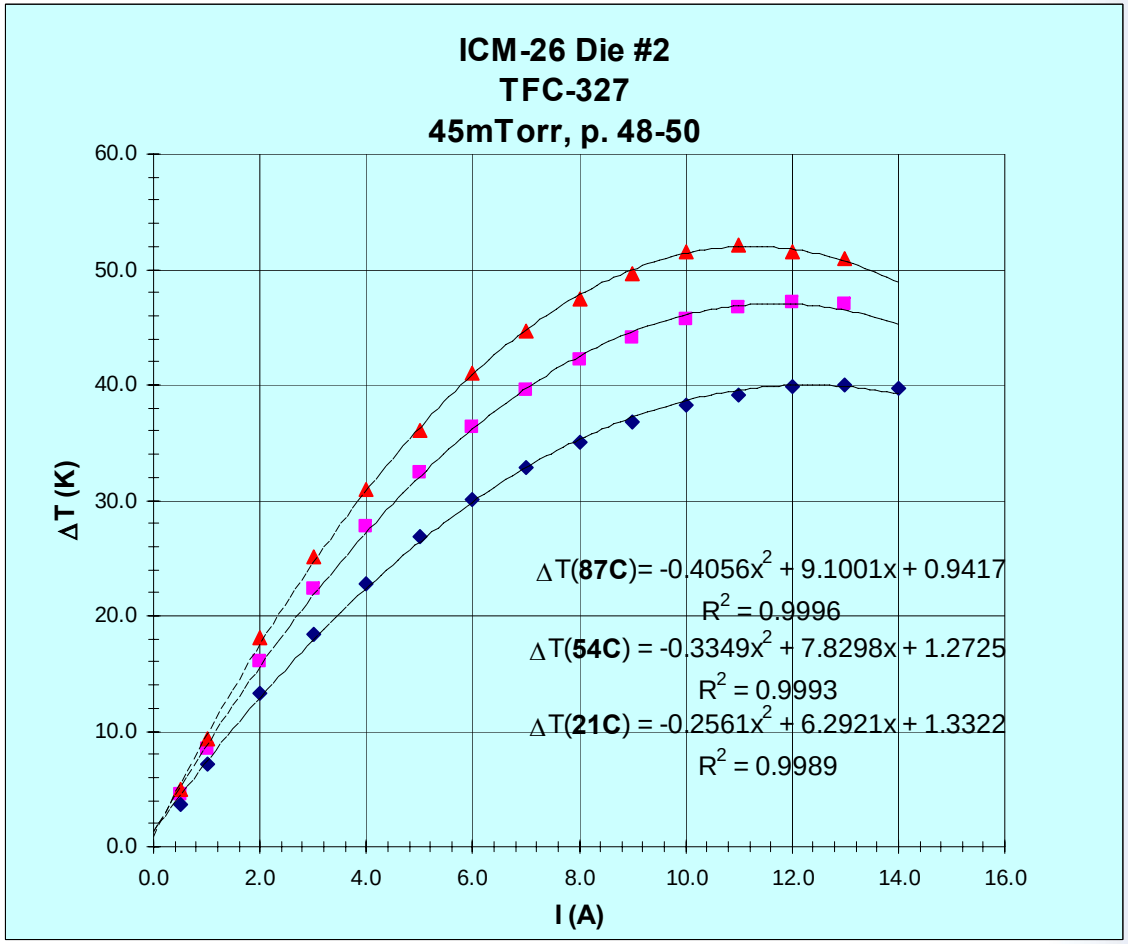
# Range of Modules Depending on Application



**Small foot-print, High Heat-Flux Cooling**

**Large foot- print, Low Heat-Flux Cooling**

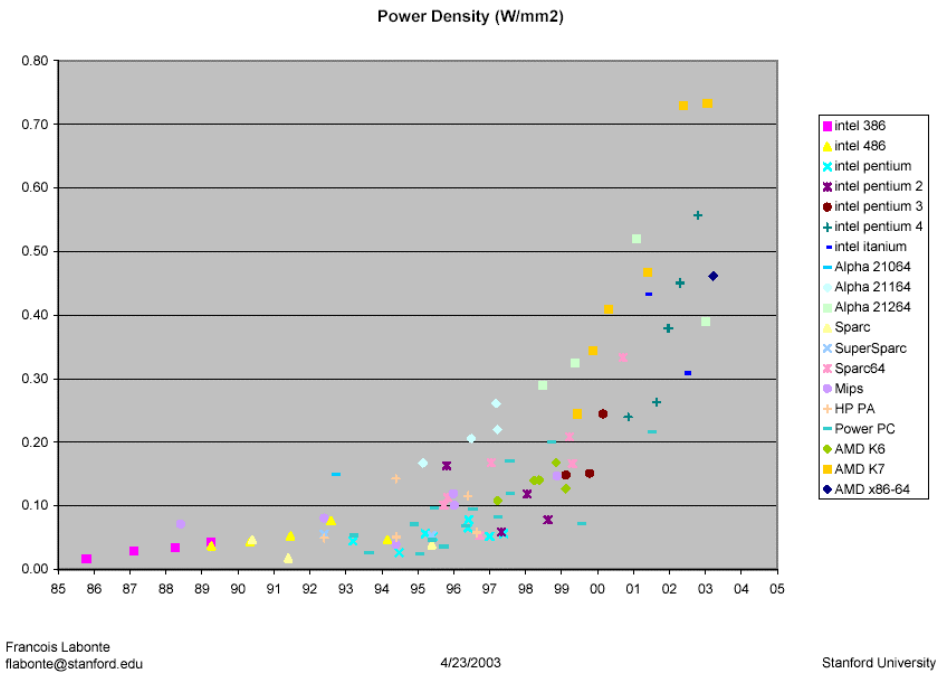
# Superlattice Module Performance for Thermal Management

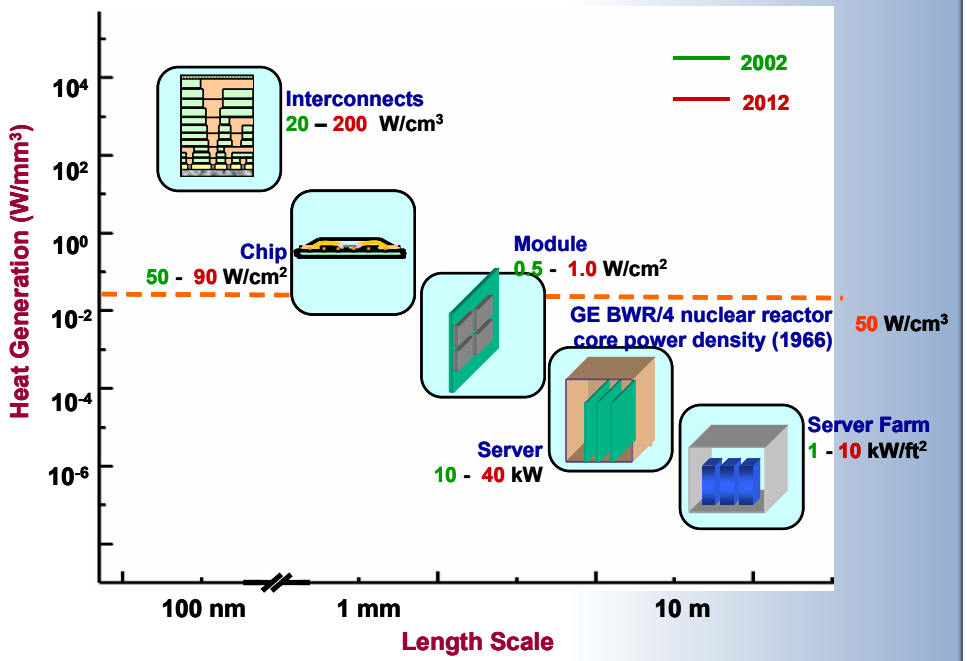



**600 micron x 600 micron Device Cooling ΔT of over 50C, providing heat-flux pumping capability of several hundred Watts/cm$^2$**

RTI INTERNATIONAL

# Power Density from the Device-Level to Chip-Level to System-Level

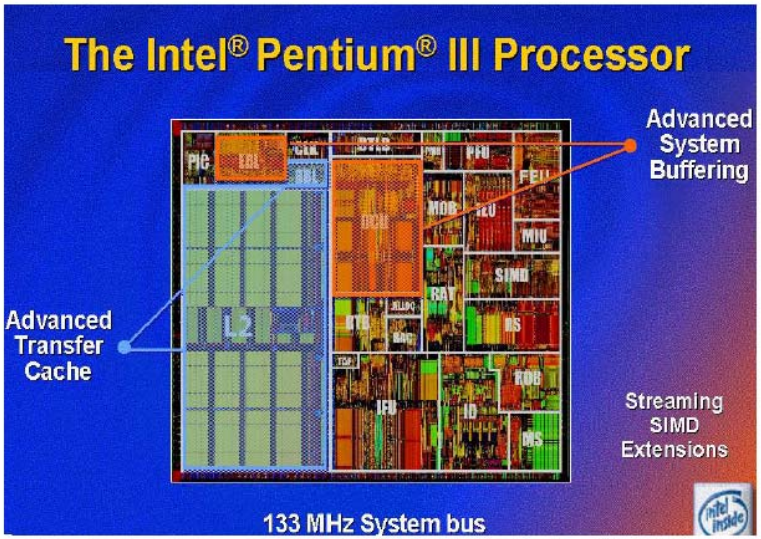


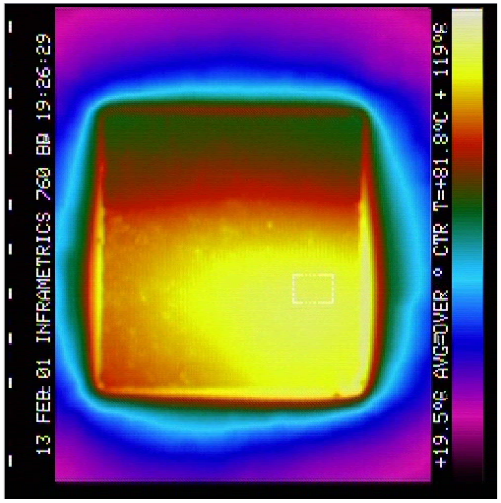




Ref: F. Labonte, Stanford University

Ref: P. Kohl, Illinois Institute of Technology, Chicago

# Hot Spots on typical Pentium 3 Architecture

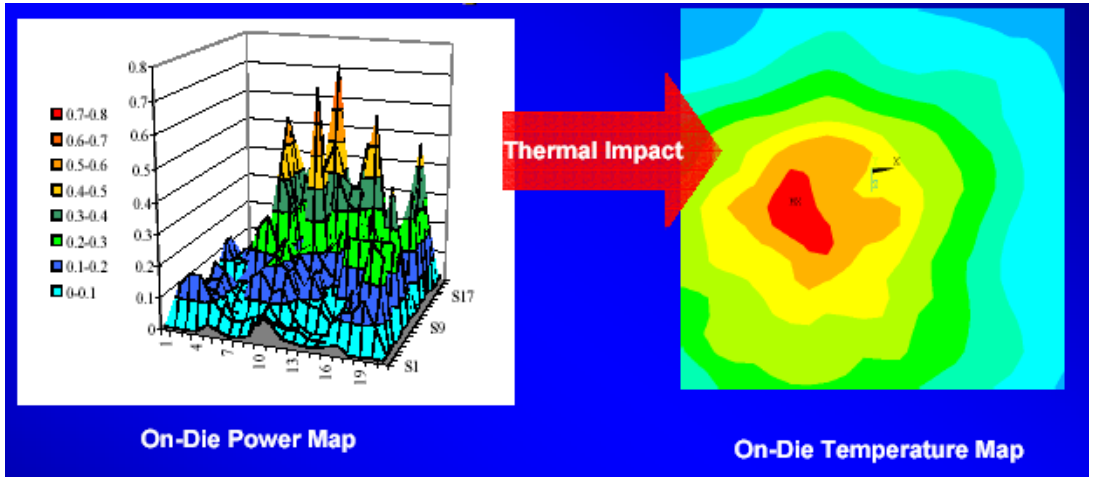


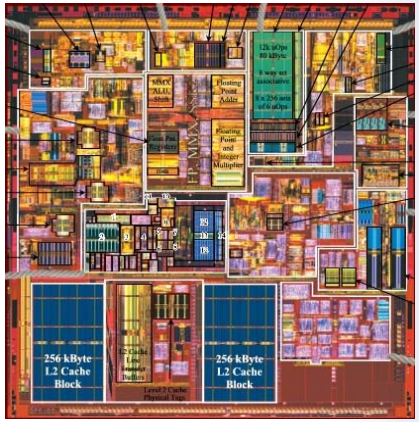

Was easily Manageable Without an Integrated Heat Spreader (IHS) but an OEM heat-sink

Cancheevaram et al., RTI, Proc. of MRS, 2003

## Even with an IHS, we expect to deal with Multiple Hot Spots on Future Chips:



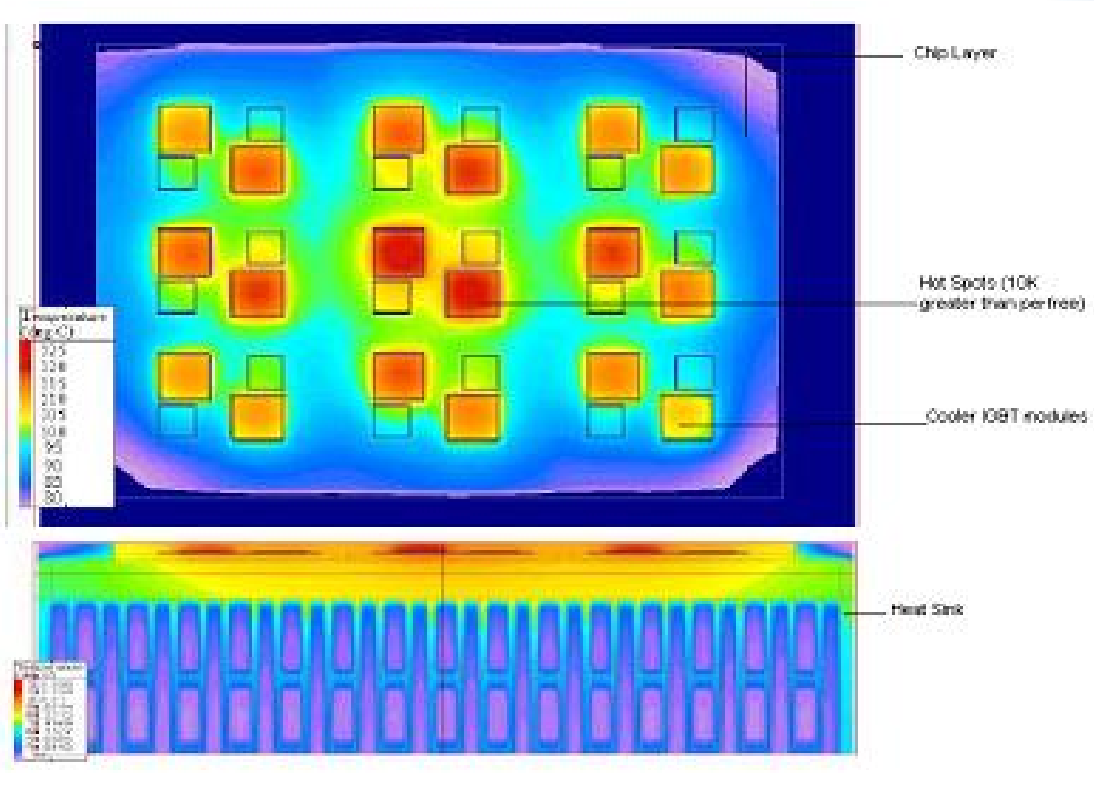

(Mahajan et al., INTEL)




(eg: Northwood Core, Ref: INTEL)

RTI INTERNATIONAL

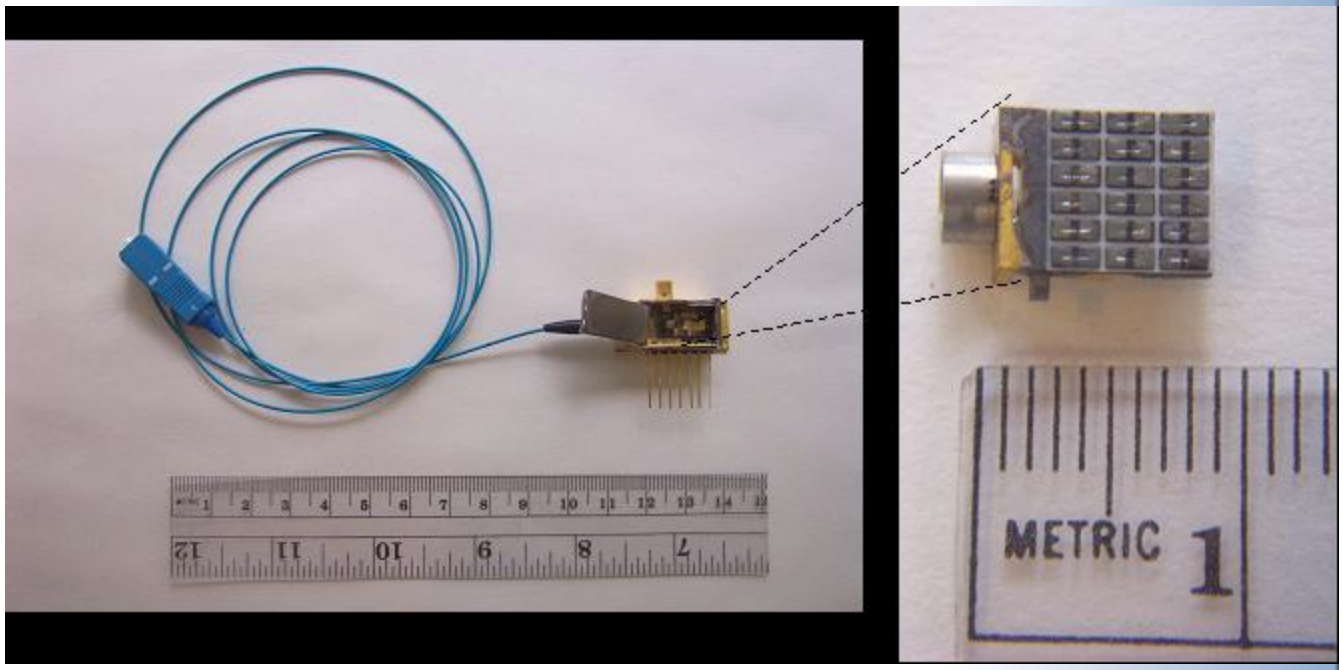
# Better System Efficiencies Possible in the Thermal Management of Power Electronics That Switch Large Powers



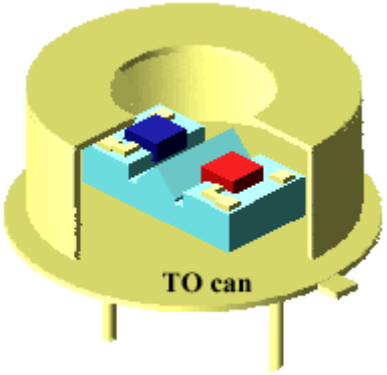

- Potential Application of High Cooling Power Density to IGBT Chip Cooling – Automotive Power Electronics
  - Most thermal management decided by hot-spots
- Cool the Hot-spots selectively so that system-level cooling needs are lower

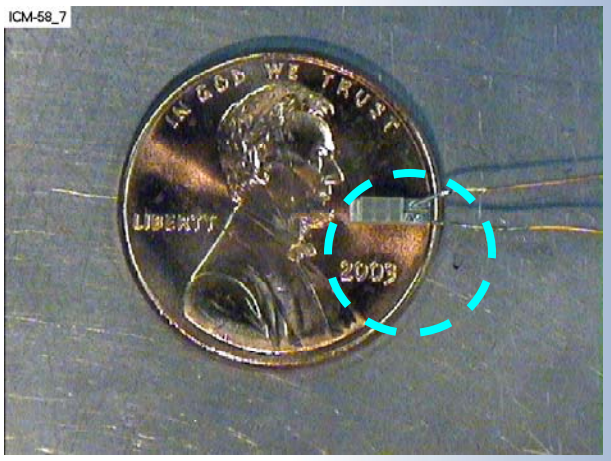
# Thermal Management of Lasers in Future Fiber-Optics

- **Bulk Thermoelectric Devices**
- **Large Volume Packages**
- **Inefficient**




- **Laser packages becoming smaller/complex**
- **Need efficient and high heat-flux removal from lasers**
- **High-performance superlattice coolers have been made**



# Further Science with Superlattice Thermoelectrics –

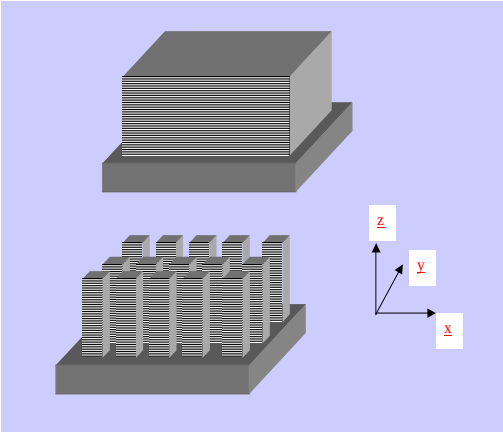
# Combine Phonon-Blocking Electron Transmission with Orthogonal Quantum Confinement

RTI INTERNATIONAL

# Transitioning from Two-dimensional Superlattices to One-dimensional Quantum-Wires and Quantum-Boxes

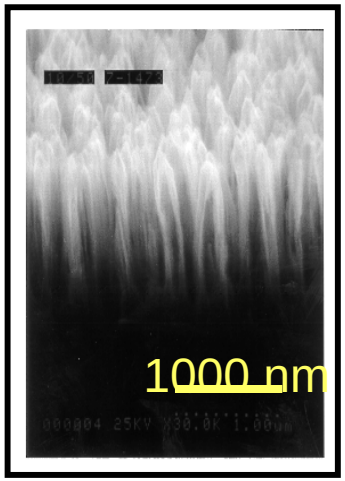
- Combine Phonon-Blocking, Electron-Transmitting Structures Along Heat Flow with Orthogonal Quantum-Confinement for ZT in the range of 4 to 5?

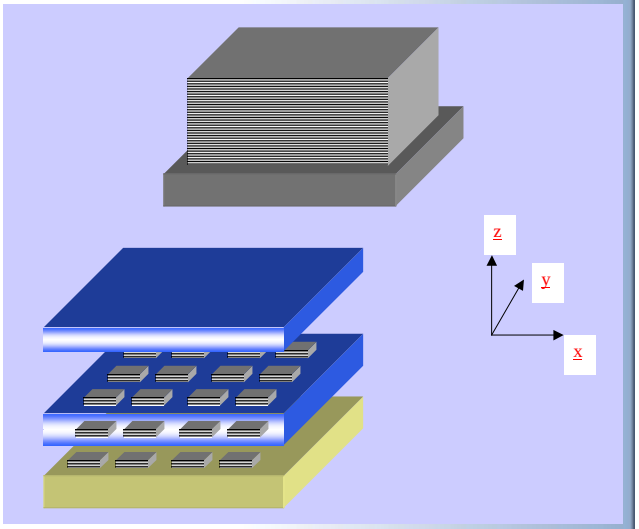
- Is the enhanced Seebeck coefficient, from larger density of states, isotropic?




**Layered SL Patterned to form 1-di Quantum-Wires – Orthogonal Quantum Confinement**

**Negligible Electronic Potential Barriers Along Current Flow as in today's SL**




**Layered SL Patterned to form Quantum-Boxes – Orthogonal Quantum Confinement**