Recent Progress in the Development of High Efficiency Thermoelectrics

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Hi-Z Technology Inc.

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*Presenter

Current Program Sponsor

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Department of Energy

Washington, D.C.

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Outline

- Current Vehicle Programs
- Background in Thermoelectrics
- Discussion of Quantum Wells
  - Theory
  - Testing
- Applications
- Programs
- Introduction to Cooling

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Current Vehicle Generator Programs at Hi-Z

- 1 kW Generator for Heavy Duty Trucks (DOE)
  - Current generator with BiTe alloy modules
    - Undergoing over-the-road testing (400,000+ equivalent miles)
  - Design, fabricate and test prototype Quantum Well module
- 300 Watt Generator for Light truck (Clarkson)
  - Preliminary design complete
  - Final design recently released
  - Initial module loading BiTe module
- 200 Watt Generator for Hybrid Truck (Ohio State)
  - Generator Rebuilt with BiTe modules
  - Delivered to Ohio State
  - Developing interface to 300 V bus

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High Conversion Efficiency QW Thermoelectrics

- ZT values up to now have hovered at ~1 to 1.4
- ZT values of 3 to 4 have recently been obtained at Hi-Z
- Efficiency of 14% has been measured on a couple
- Efficiency values in the 20-30% range now appear feasible at a T_H 250°C and T_C of 70°C
- Newer materials and higher T_H should increase efficiency further

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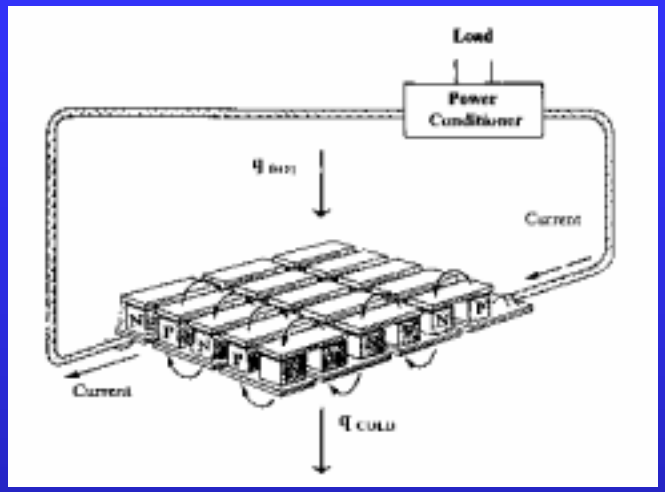
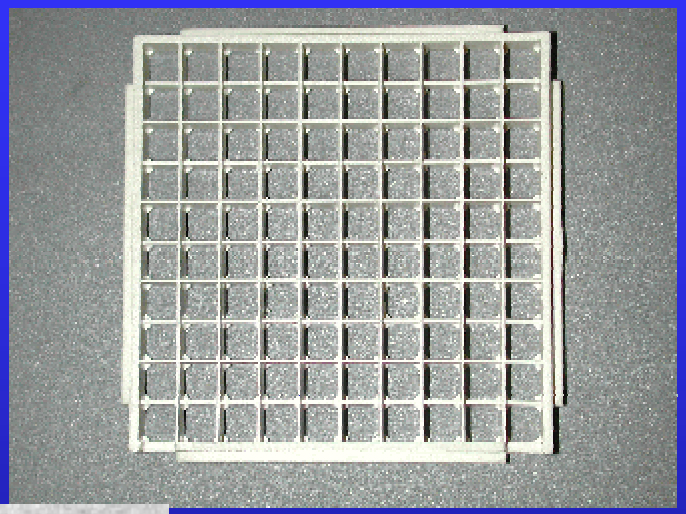
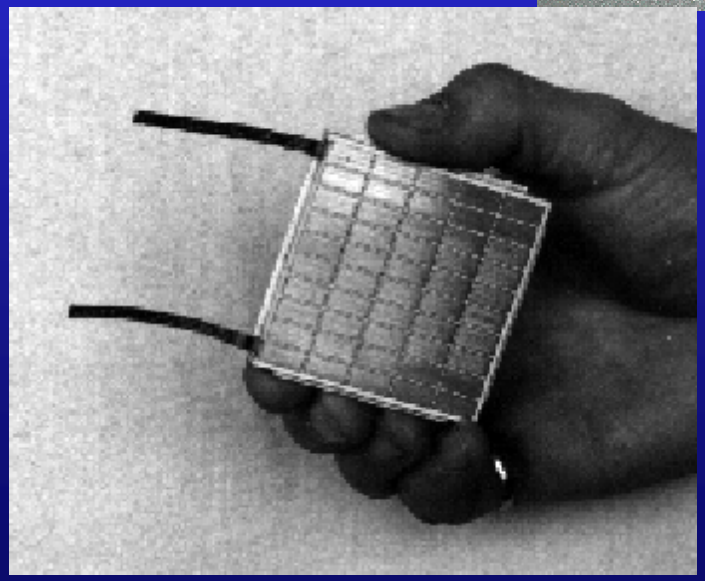
TE Module







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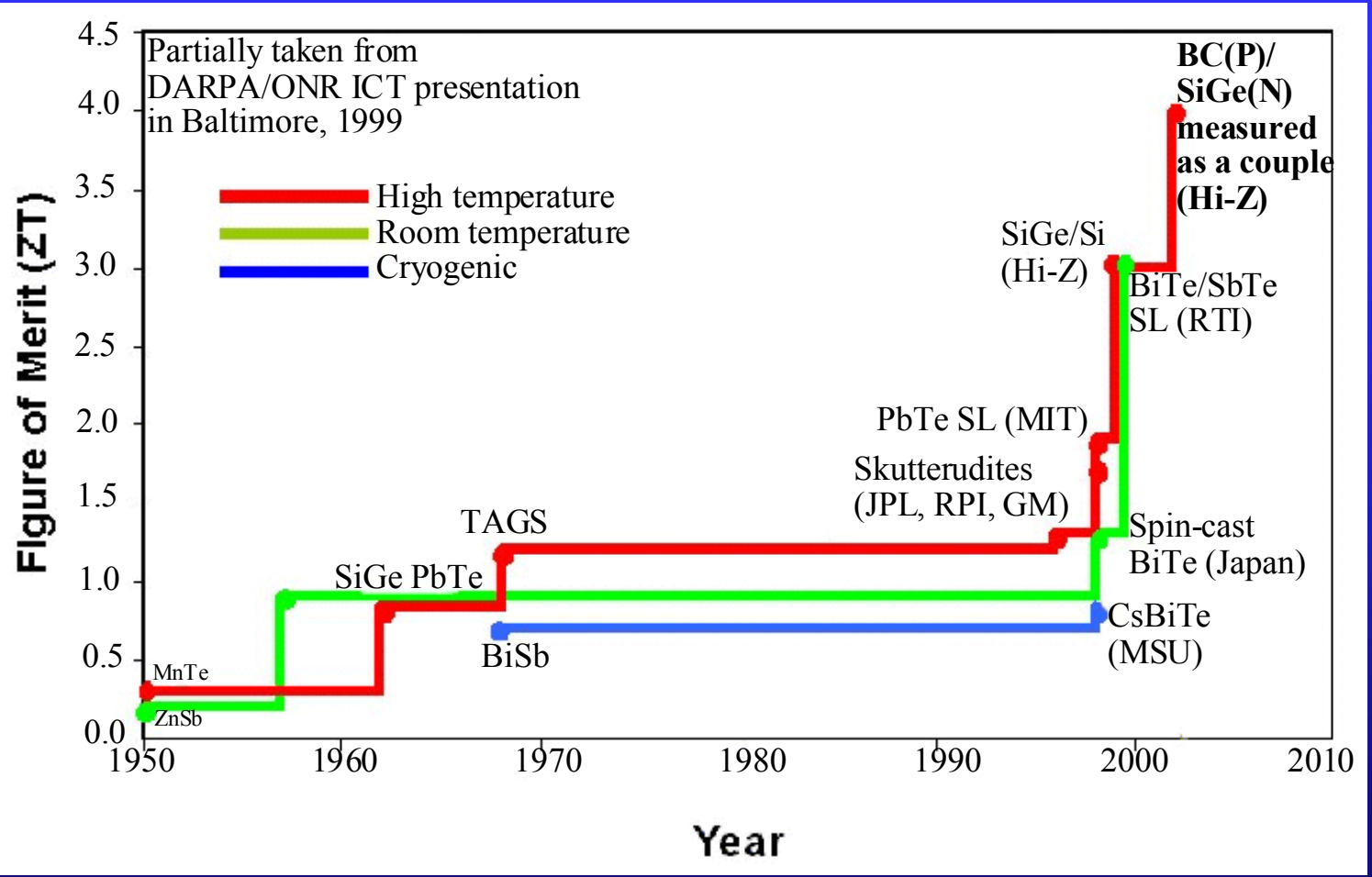
ZT Time Line


Partially taken from
DARPA/ONR ICT presentation
in Baltimore, 1999
High temperature
Room temperature
Cryogenic
BC(P)/
SiGe(N)
measured
as a couple
(Hi-Z)
SiGe/Si
(Hi-Z)
BiTe/SbTe
SL (RTI)
PbTe SL (MIT)
Skutterudites
(JPL, RPI, GM)
TAGS
Spin-cast
BiTe (Japan)
SiGe PbTe
CsBiTe
(MSU)
BiSb
MnTe
ZnSb
Figure of Merit (ZT)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1950
1960
1970
1980
1990
2000
2010
Year

Quantum Well Thermoelectrics

Objective

- Exploit the features of quantum well structures
- Obtain high efficiencies via high figure of merit TE materials (Z):

$$Z=\alpha^2/(\rho.\kappa)$$

Where:

α=Seebeck Coefficient

ρ=Resistivity

κ=Thermal Conductivity

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Thermoelectric Efficiency

$$Efficiency = \frac{T_H - T_C}{T_H} \; x \; \frac{M-1}{M + \frac{T_C}{T_H}}$$

M is defined as

$$M = \sqrt{1 + \frac{1}{2}\bar{Z}\,(T_C + T_H)}$$

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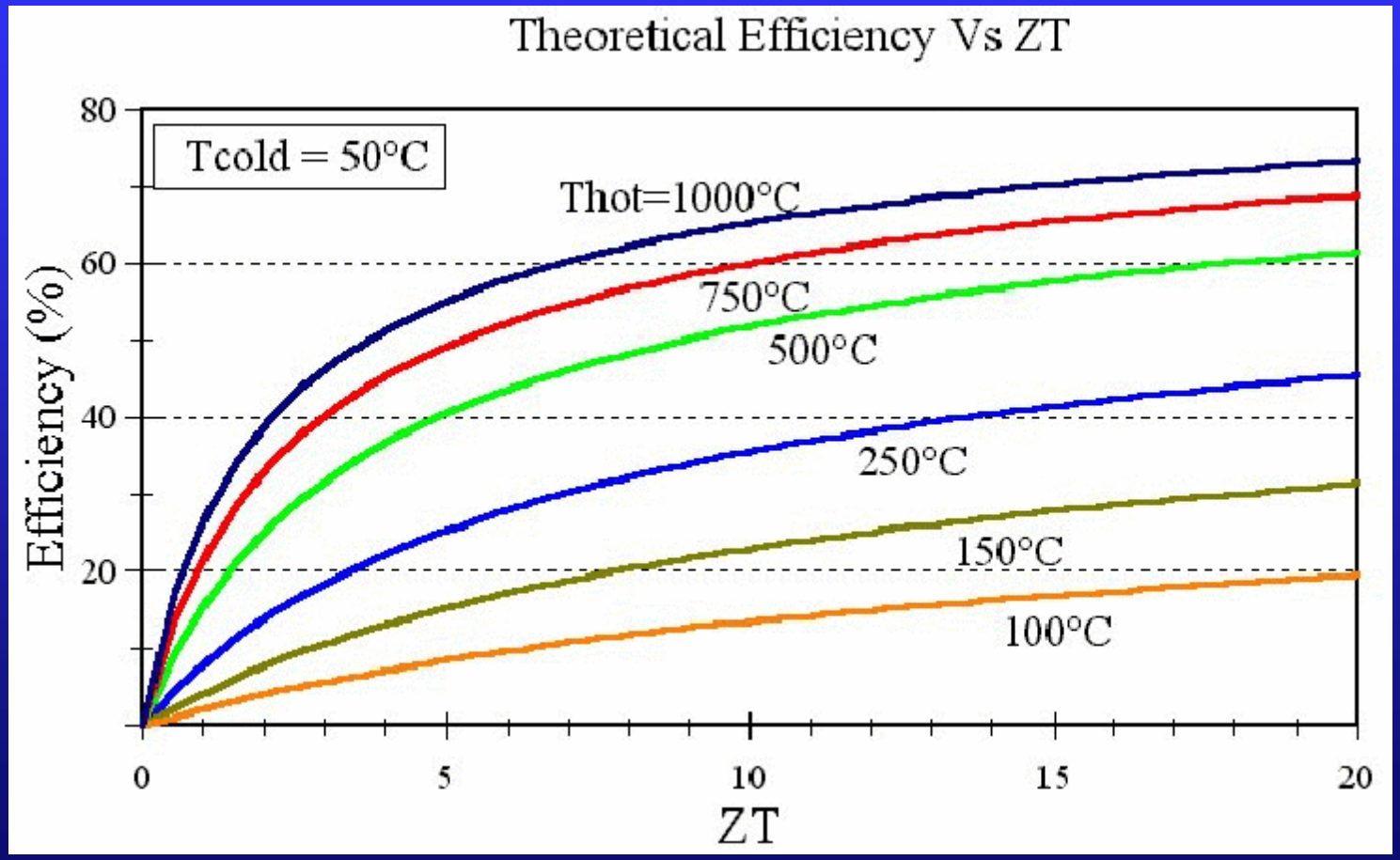
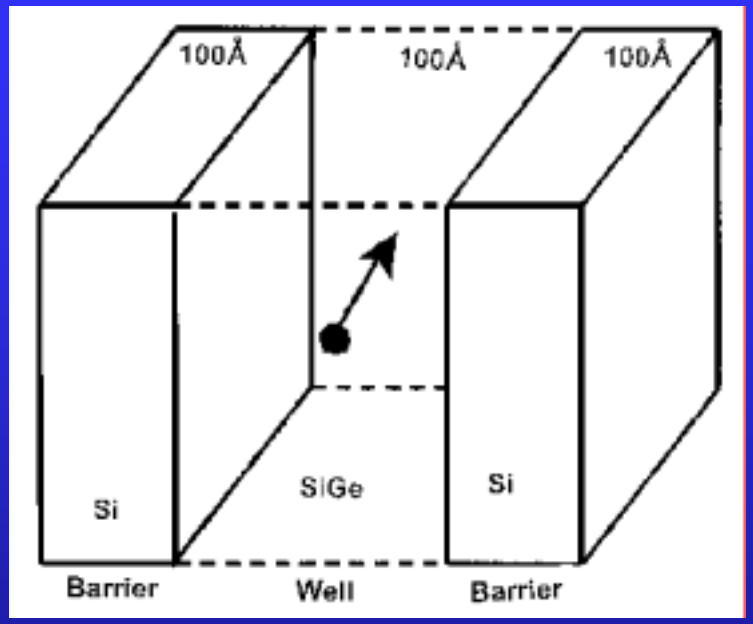
Why Large Z ?
Generation of Power



Two-Dimensional Quantum Well TE

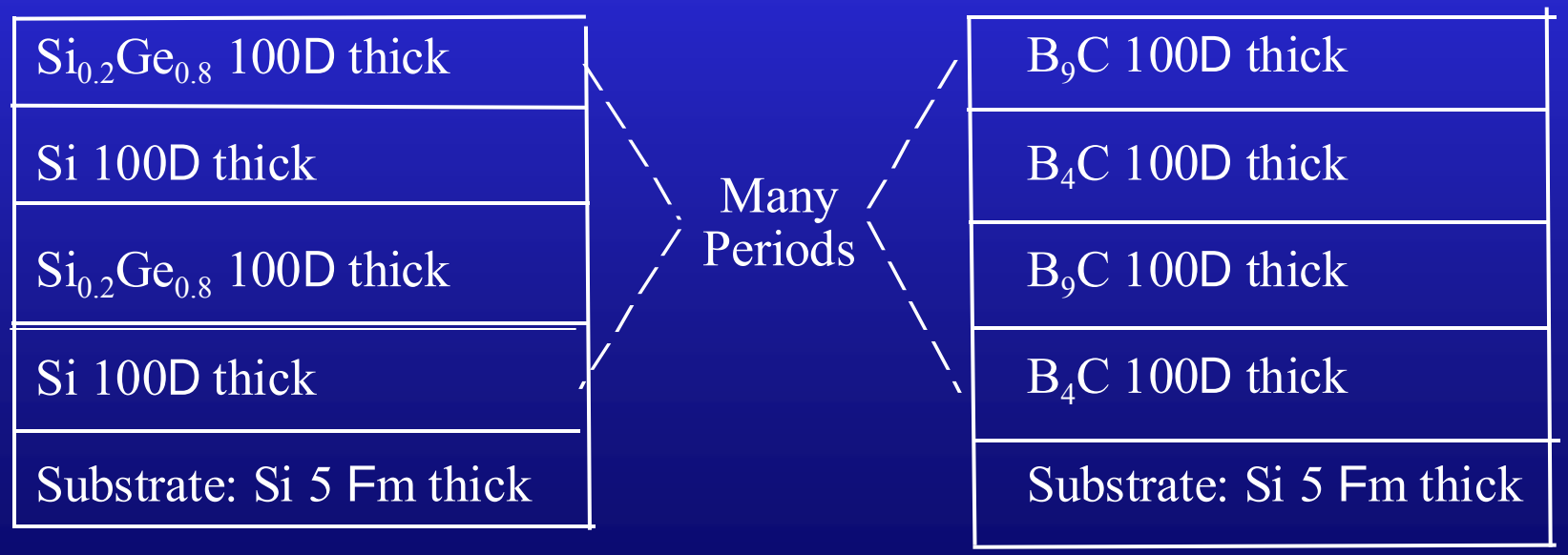
- Active layer sandwiched between materials with band offset to form a barrier for the charge carriers
- Increased Seebeck coefficient (α) due to an increase in the density of states
- Significant reduction on resistivity (ρ) due to quantum confinement of carriers
- Significant reduction on thermal conductivity (κ) due to strained lattice and other factors
- Quantum Well (QW) effects become significant at a layer thickness of <200Å



$$Z=\alpha^2/(\rho.\kappa)$$

Quantum Well (QW) Programs at Hi-Z

- Si/SiGe: Multilayer Quantum Well film thermoelectrics
- P-type B_4C/B_9C: High temperature thermally stable multilayer Quantum Well films
- Si/SiC Quantum Well development underway to replace Si/SiGe for power (higher temperature) applications



Si/SiGe Films

B_4C/B_9C Films

Fabrication Advantages of Si/SiGe and B_4C/B_9C as QW Materials

- Si and Ge form a solid solution
- Also B_4C and B_9C form a solid solution
- In both systems, thermoelectric properties are good over a range of composition
- Bi_2Te_3 and PbTe require exact compositions

Payoff: Fabrication parameters need not be stringent and costs will be lower

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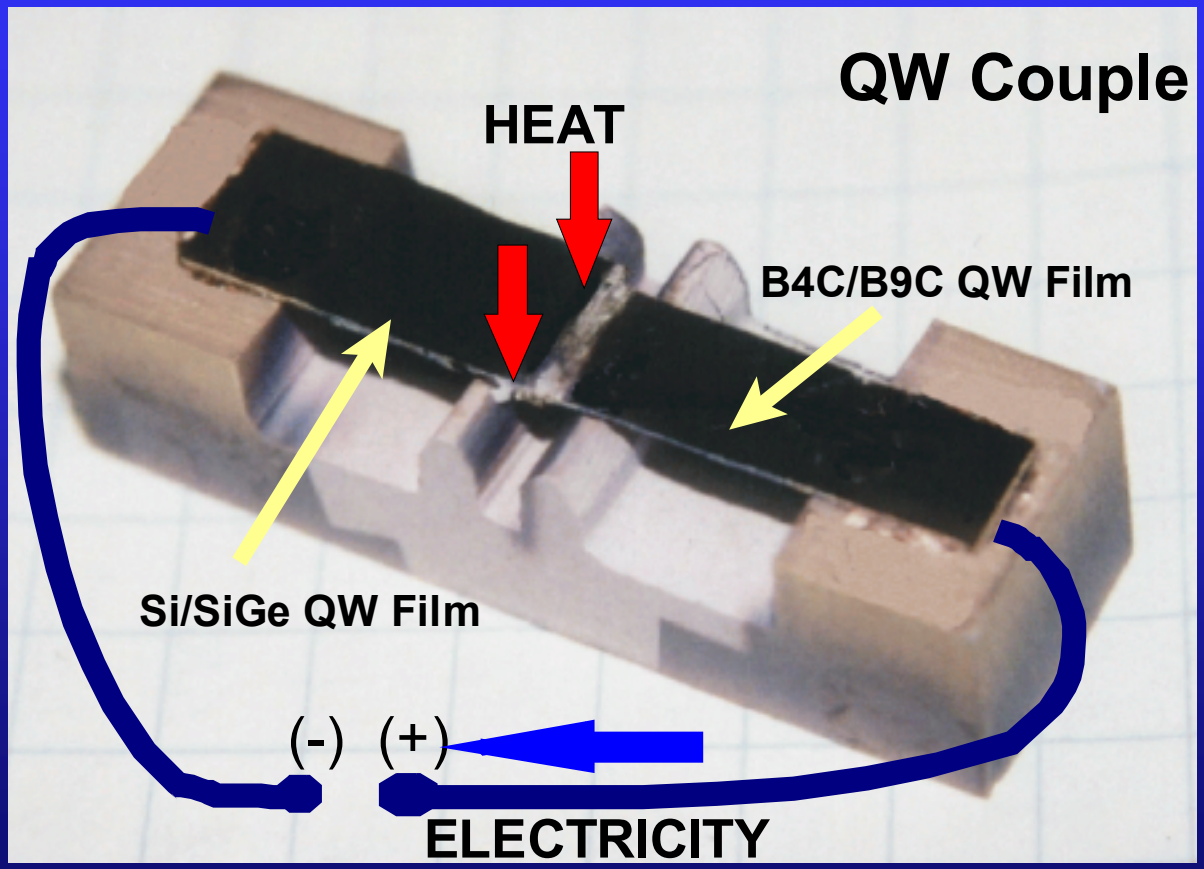
QW Experimental Couple



5 µm Si Substrate
11 µm B_4C/B_9-Si/SiGe

QW Device Raw Test Data

11 Fm thick B_4C/B_9C and Si/SiGe on 5 Fm Si

T_{cold} = 70EC T_{hot} = 250EC

Power Into Heater			Power Out From Couple			Efficiency
Voltage	Current	Power	Voltage	Current	Power	
0.1413V	47.1 mA	6.657 mW	0.365 V	2.608 mA	0.952 mW	14.30%
2.510	0.836 A	2.098 W	0.034 V	3.15 A	0.107 W	5.10%

Back Calculated ZT = 4

$Z = 9.4 \times 10^{-3}$EC

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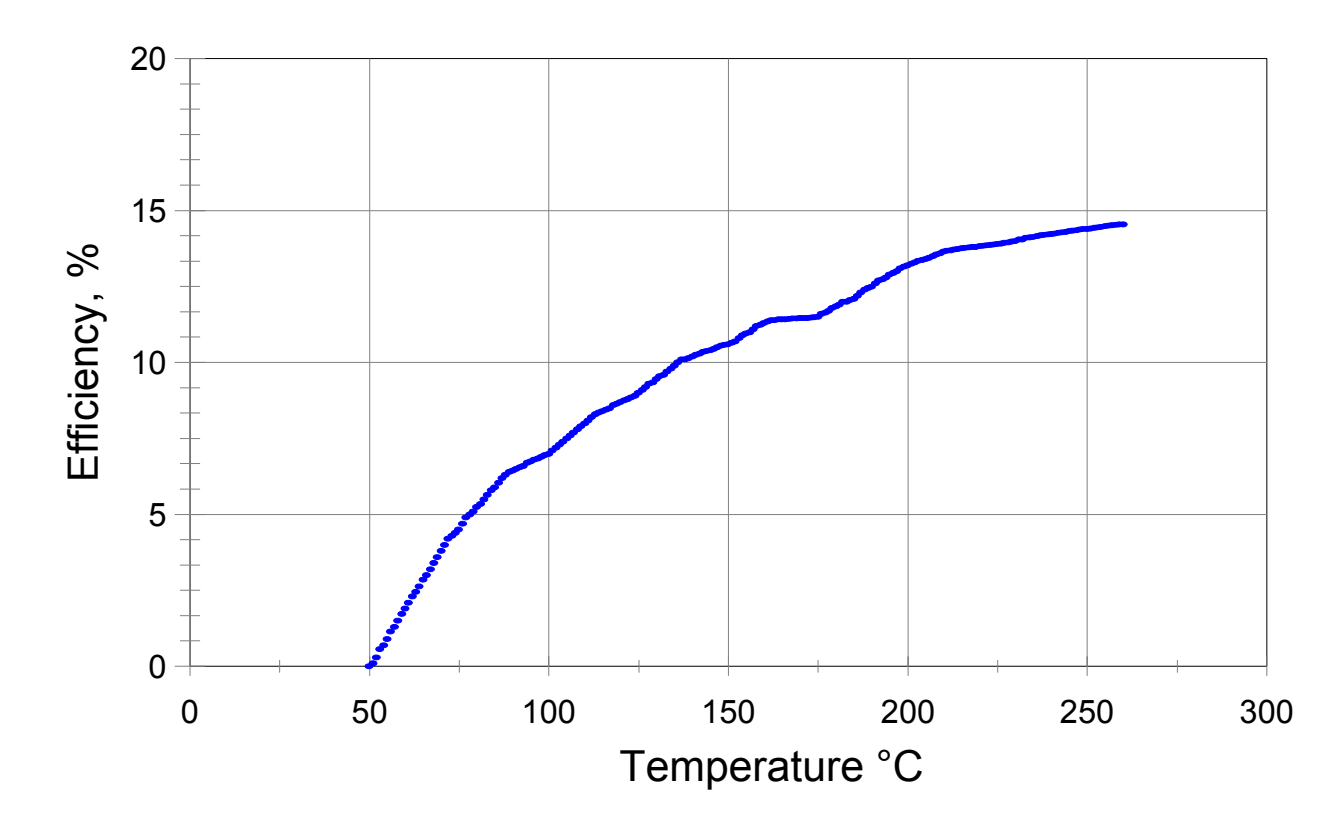
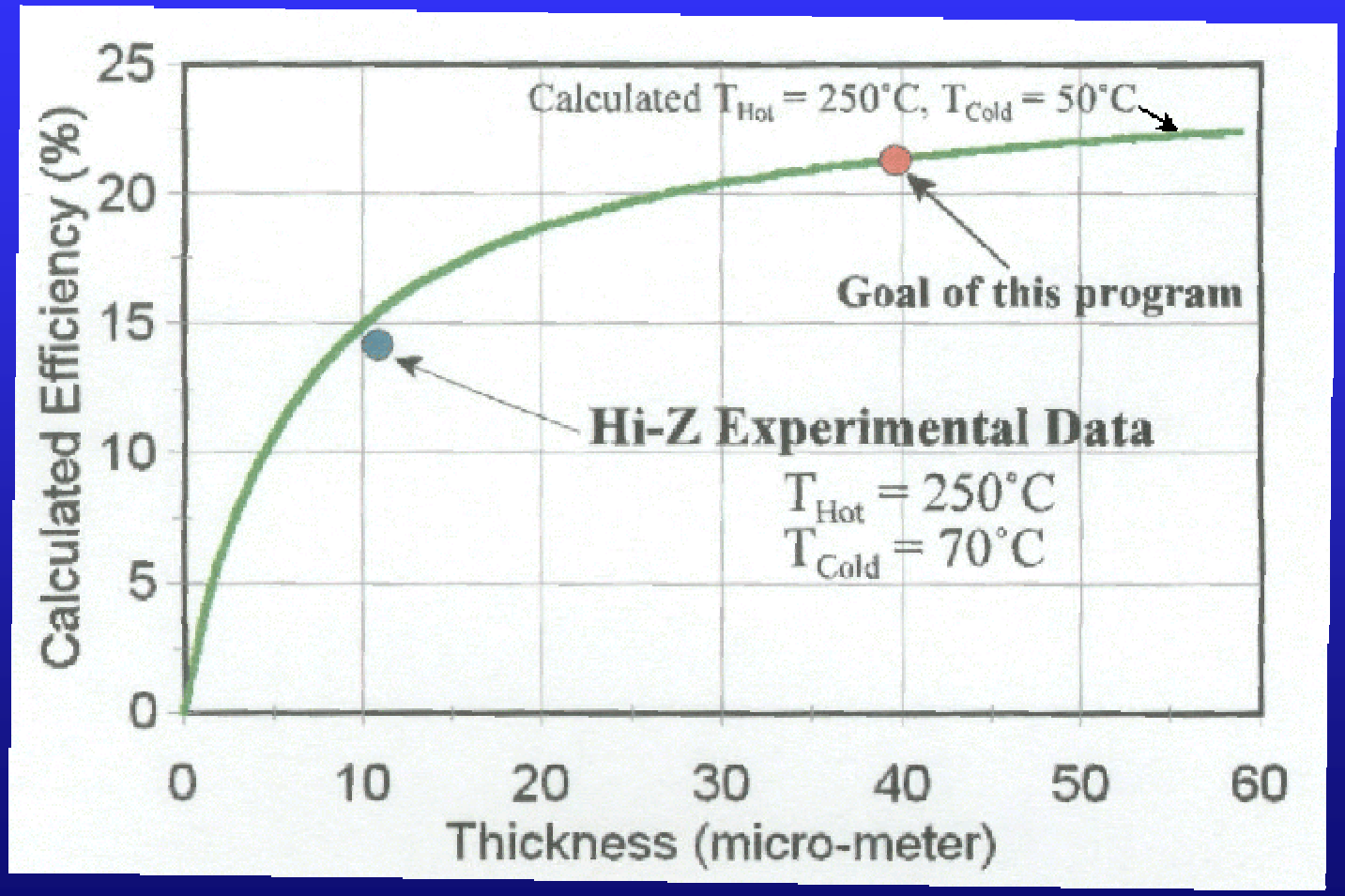
Measured QW Couple Efficiency Versus Temperature

11 m thick P type B_9C/B_4C and N type Si/SiGe on 5 m thick Si

Second couple fabricated and tested

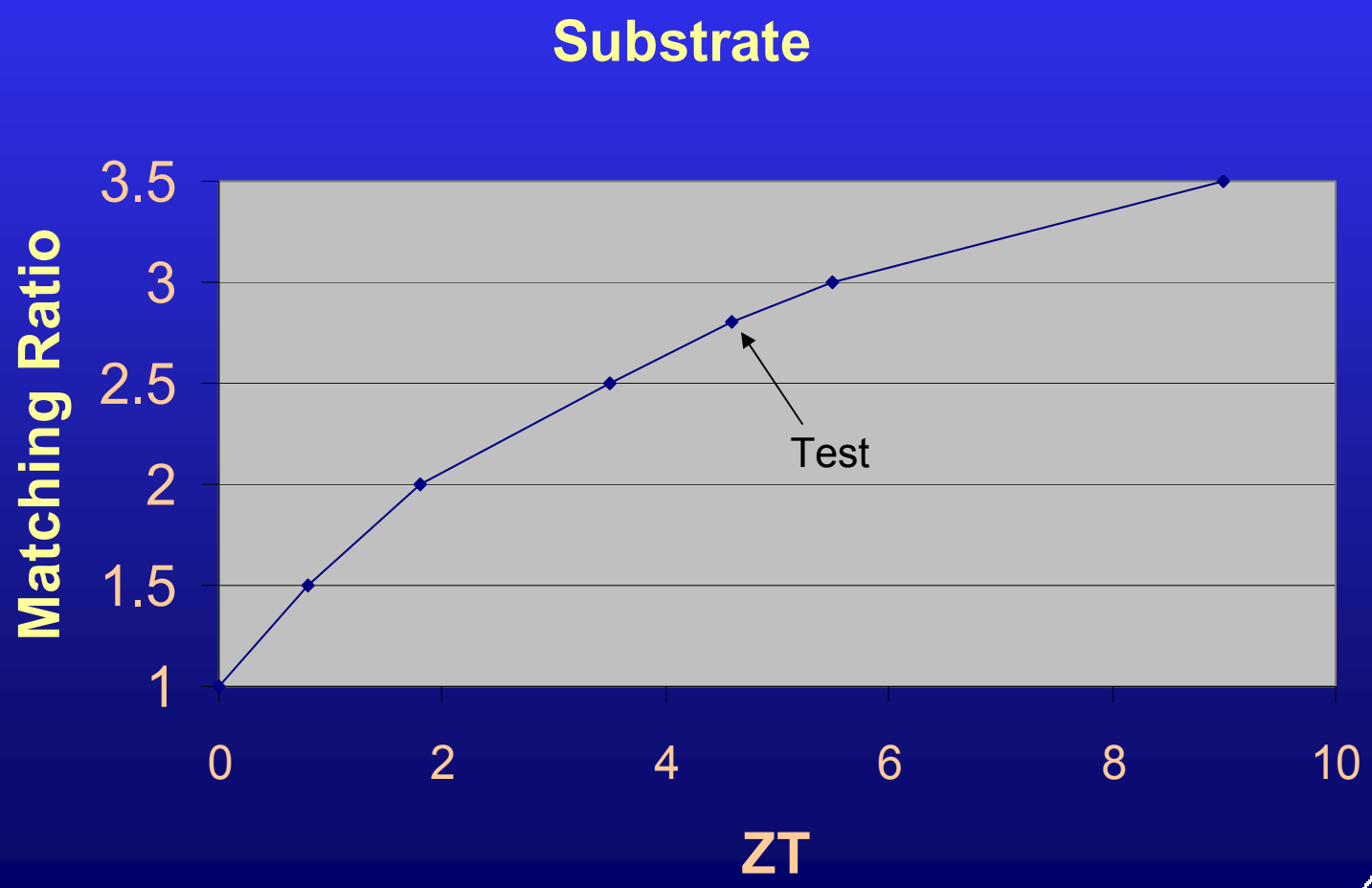


Recent Efficiency Measurement on QW Couple



11 m thick QW films on 5 m thick Si substrate

Resistance Matching Ratio Versus ZT for 11μm Thick QW Film on 5 μm Thick Si Substrate



Thermoelectric Properties of Newly Fabricated Multi-layered QW Si/SiC Sputtered Film

Samples at Room Temperature	Thickness (D)	D, Resistivity (mS-cm)	", Sebeck Coefficient (: V/EC)
03-01	400	2.15	-750
03-02	800	2.16	-755
03-03	1000	2.14	-745
03-04	1000	2.12	-753
03-05	1600	2.15	-754
03-06	1600	2.11	-758
03-07	1400	2.17	-760
03-08	1400	2.14	-750
03-09	1600	2.12	-752
03-10	1600	2.14	-755

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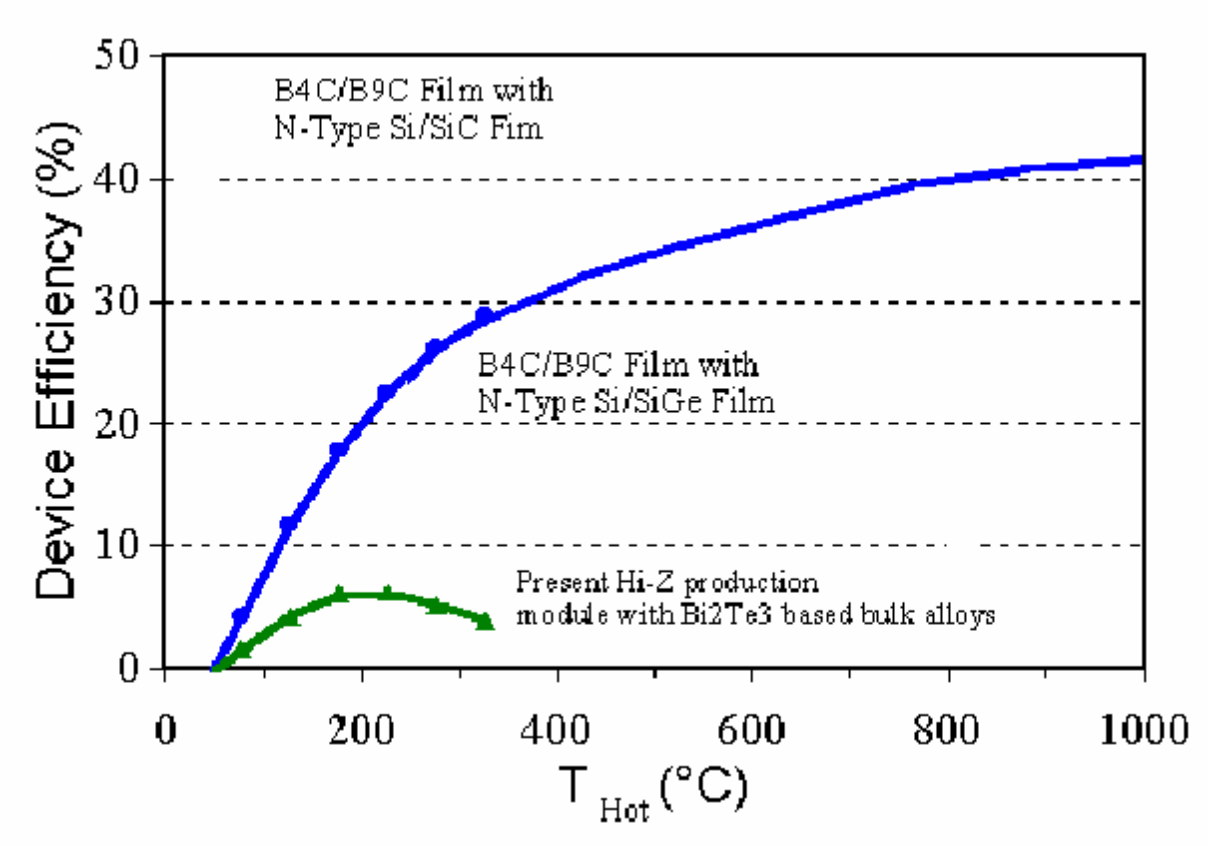
Calculated Couple Efficiency Versus Hot Side Temperature for B_4C/B_9C P- leg With a Si/SiGe or Si/SiC N-leg



Design Goals/Approaches

- Achieve the Same Heat Flux Requirements as Used With Present Modules
  - Present Hi-Z Thermoelectric Modules are Designed for $\leq$ 10 Watts/cm^2 to Minimize ΔTs Across Module Interfaces
- Supply Users Voltage Requirements Without Using a DC to DC Converter
- Incorporate Redundant Circuitry When Feasible
- Deposit on a Substrate That Can be Retained in Use

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Design Goals/Approaches (Continued)

- Minimize Substrate Thickness to Reduce Thermal Losses
- Si is Available at 5 μm Thickness
- Kapton Substrate Has Little Effect on Performance
  - No Seebeck
  - Very High Resistivity
  - Low Thermal Conductivity

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Applications

Energy conversion with high efficiency for

- Waste Heat Recovery From Vehicles
- Self-Powered Auxiliary Power Units (APUs)
- Self Powered Engine Preheaters
- Space Power: Solar or Isotopic Heating
- Low Temperature Detector Cooling
- Air Conditioning and Refrigeration
- Energy Harvesting for Wireless Sensors

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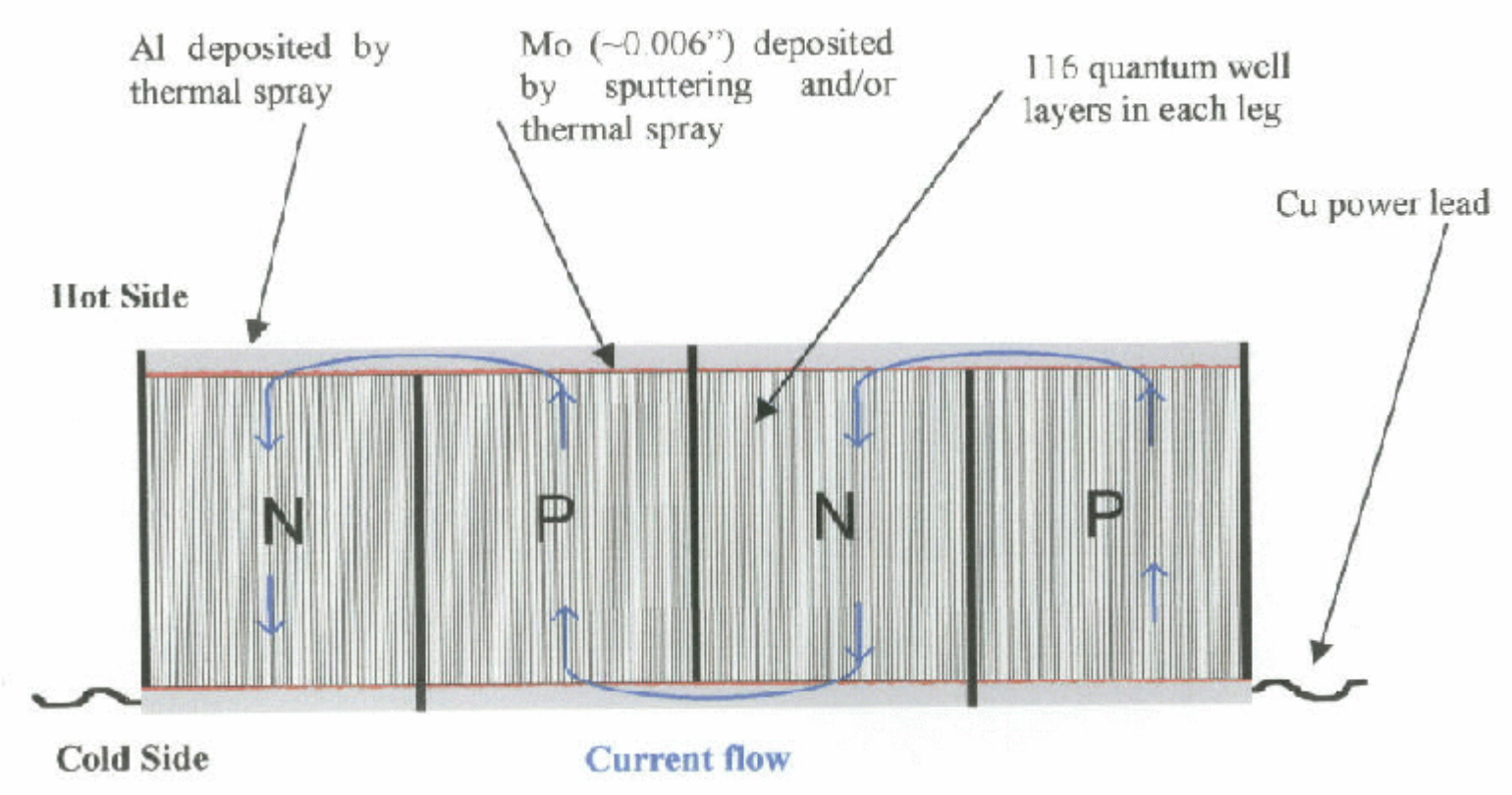
Hi-Z's Approach for Loading an Eggcrate With QW Films



Current Quantum Well T.E. Programs

- Generator for Heavy Duty Diesel Trucks – DOE
- Energy Harvesting for Wireless Sensors – Navy
  - Phase 1 SBIR
- New Film Production Methods – DOE
- QW Development for Space Applications – NASA
- Development of QW Films – DOE Morgantown*
- Measurement of QW Film Properties Made by Alternate Methods** - NYSERDA

*Recently notified of award
**Subcontract

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Current Direction

- Thicker Films
- Increased Film Production Rate
  - Larger Machines
  - Alternate Production Methods
- Fabricate Prototype Modules
  - Truck Applications
  - High Temperature Space Applications
  - Energy Harvesting for Wireless Sensors
  - Cooler Modules
- Continue to Improve I.P. Position

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QW Film ZT From Cooling Data

Max. $\Delta T = 45°C$

$ZT \approx 3$ @ ~25°C

or

$ZT \approx 4$ @ ~150°C

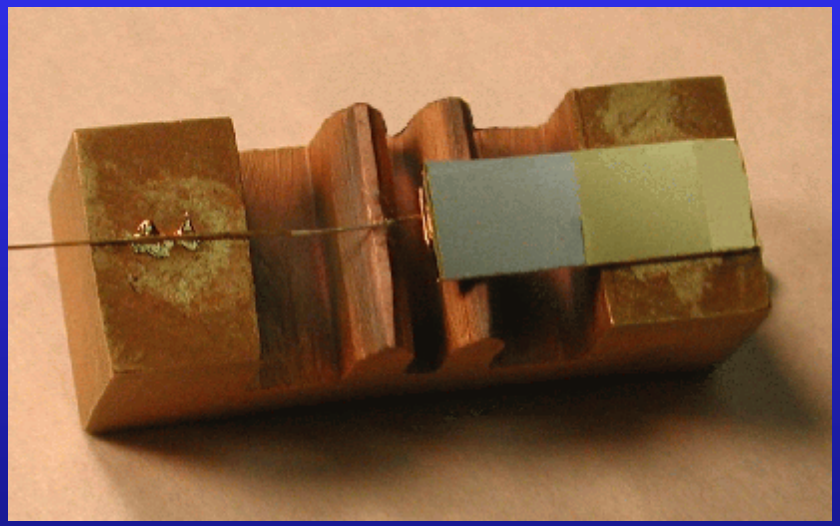
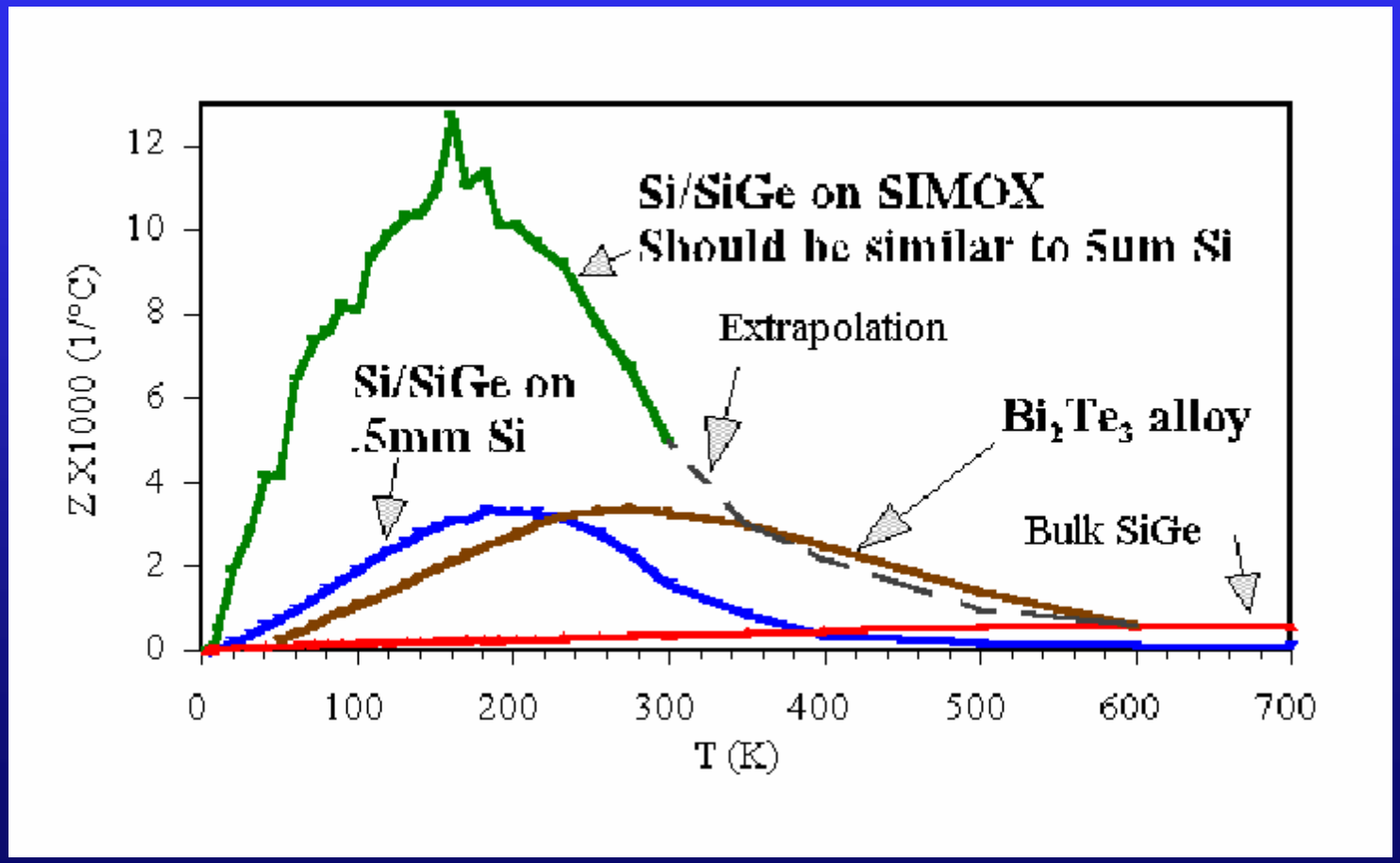


Figure of Merit (Z) of ML-QWF Deposited on Thick and Ultra-thin Si Substrate



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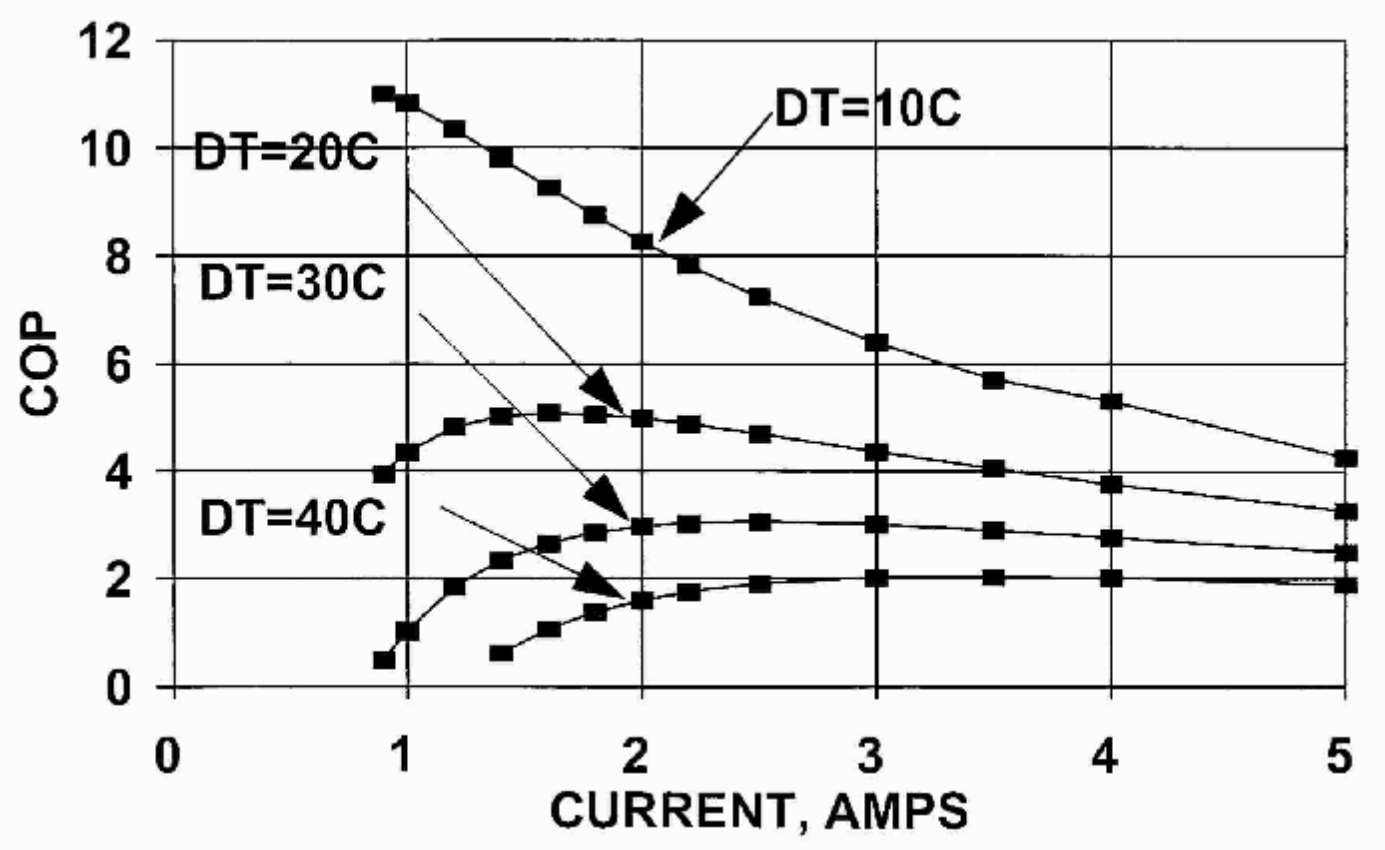
COP Vs Current

QW Cooler Design PT 25A, 30°C, 13.33V



QW Thermoelectric Device Cost Estimation

- High Volume Cost for Bulk TE: <$1/Watt
  High materials cost and low efficiency
- High Volume Cost for QW TE: Goal of 0.20 to 0.50/Watt

  Much lower materials cost and higher efficiency

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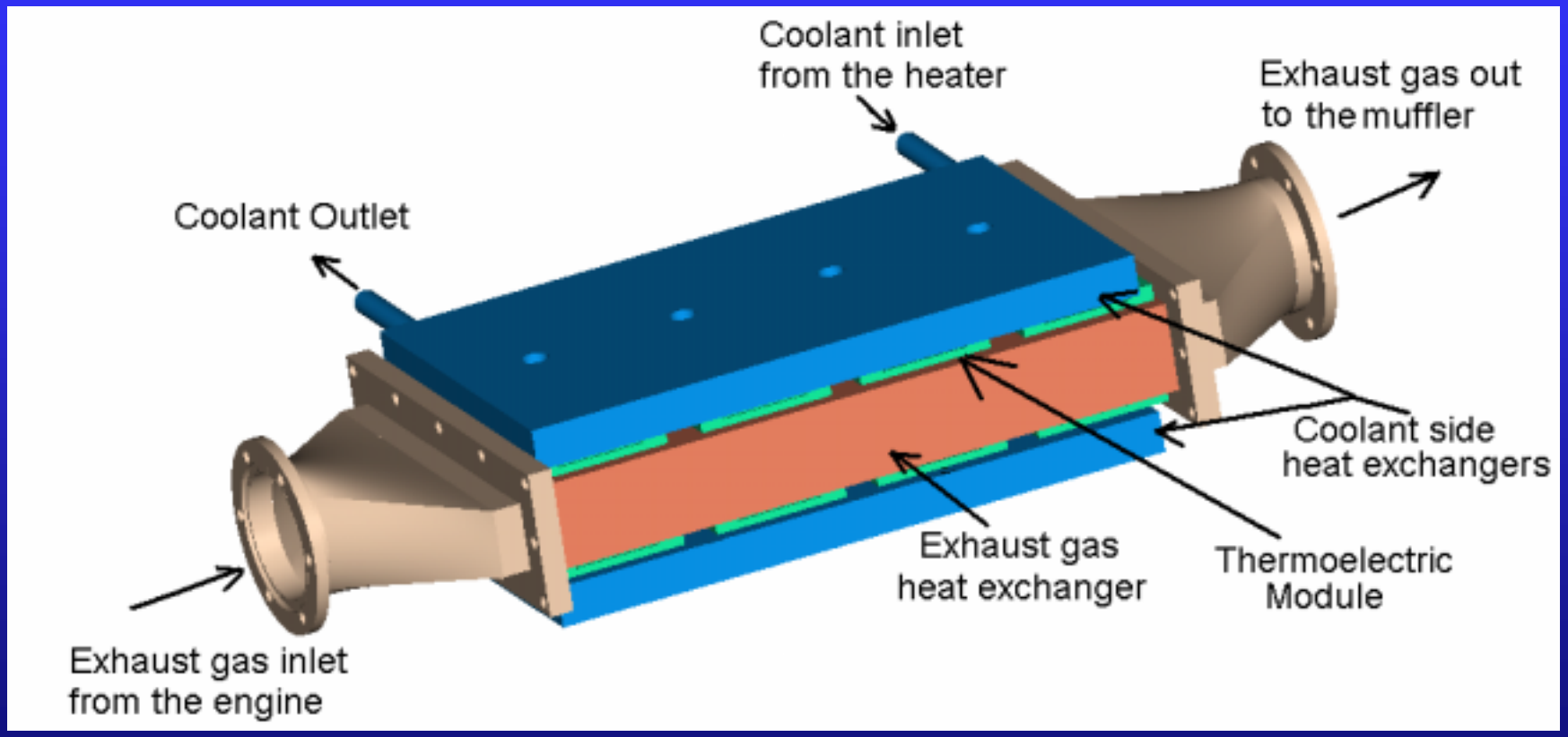
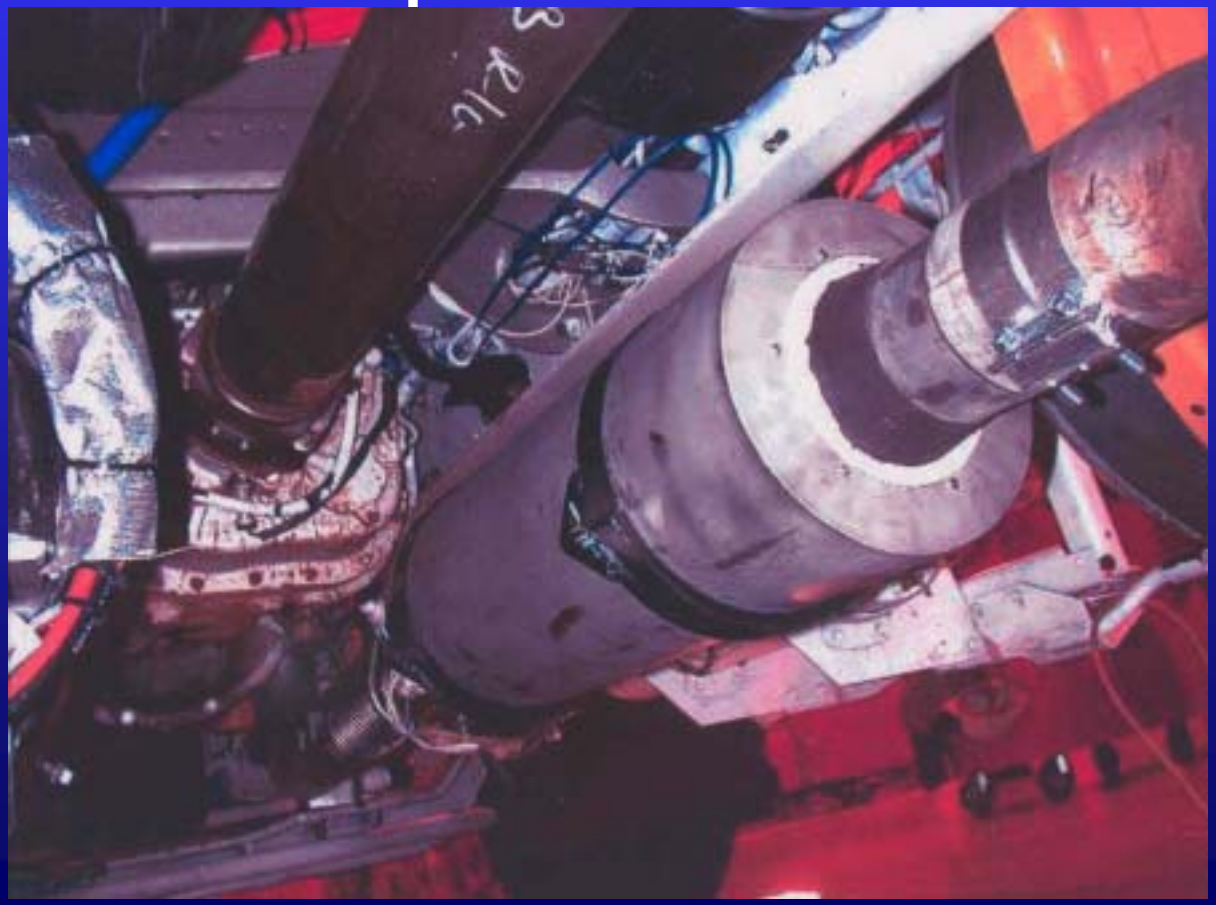
AETEG


Coolant inlet
from the heater
Exhaust gas out
to the muffler
Coolant Outlet
Coolant side
heat exchangers
Exhaust gas
heat exchanger
Thermoelectric
Module
Exhaust gas inlet
from the engine

Under View of the Thermoelectric Generator Mounted on the Truck Showing Rubber Bushing Shock Absorption Brackets



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