

***Scale Up of Si/ $\text{Si}_{0.8}\text{Ge}_{0.2}$ and $\text{B}_4\text{C}/\text{B}_9\text{C}$
Superlattices for Harvesting of Waste Heat in
Diesel Engines⁺***

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+ Work supported by the U. S. Department of Energy

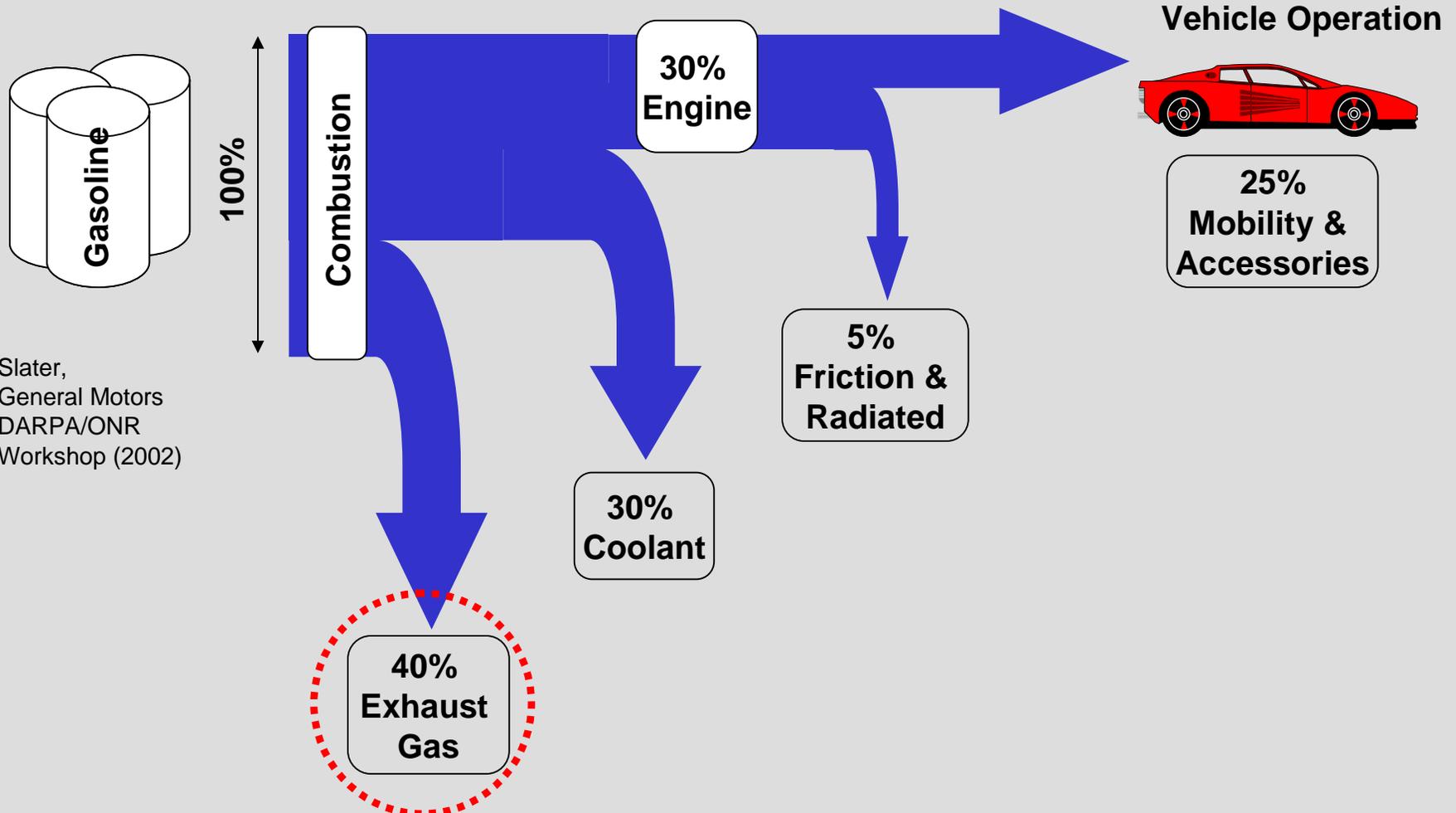
Program Objectives

- ▶ Scale up the deposition process for Si/SiGe and B₄C/B₉C thermoelectric quantum well structures for waste heat recovery from diesel engines
- ▶ Verify thermoelectric properties of Si/SiGe and B₄C/B₉C quantum well structures
- ▶ Develop economical process to fabricate thermoelectric quantum well structures
- ▶ Support Hi-Z for full scale device development

Thermoelectric Power Generation

- ▶ Harvest electrical energy from waste heat sources
 - Exhaust gases from diesel engines
 - Gas turbines
 - Industrial processes
 - Reactor systems
- ▶ Power generation from heat flow (Seebeck)
- ▶ Cooling from current flow (Peltier)
- ▶ Power conversion efficiencies for bulk devices currently < 10 %
- ▶ > 20% power conversion goal

Less than 25% of fuel energy in gasoline goes to useful shaft work

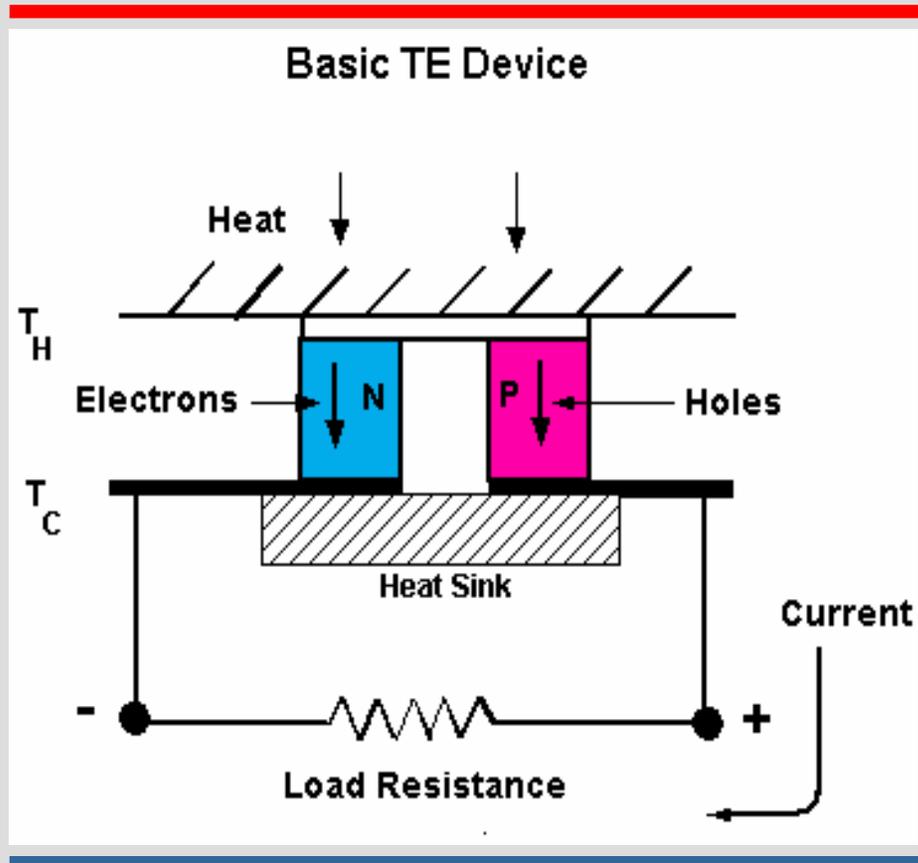


Slater,
General Motors
DARPA/ONR
Workshop (2002)

Advanced waste heat recovery technology
can improve overall efficiency and reduce fuel consumption

Thermoelectric(TE) energy conversion

Hot side (“Waste Heat”)



Cold side

Heat-to-electricity conversion efficiency depends on a figure of merit, Z , that is material-specific:

$$Z = S^2\sigma/k$$

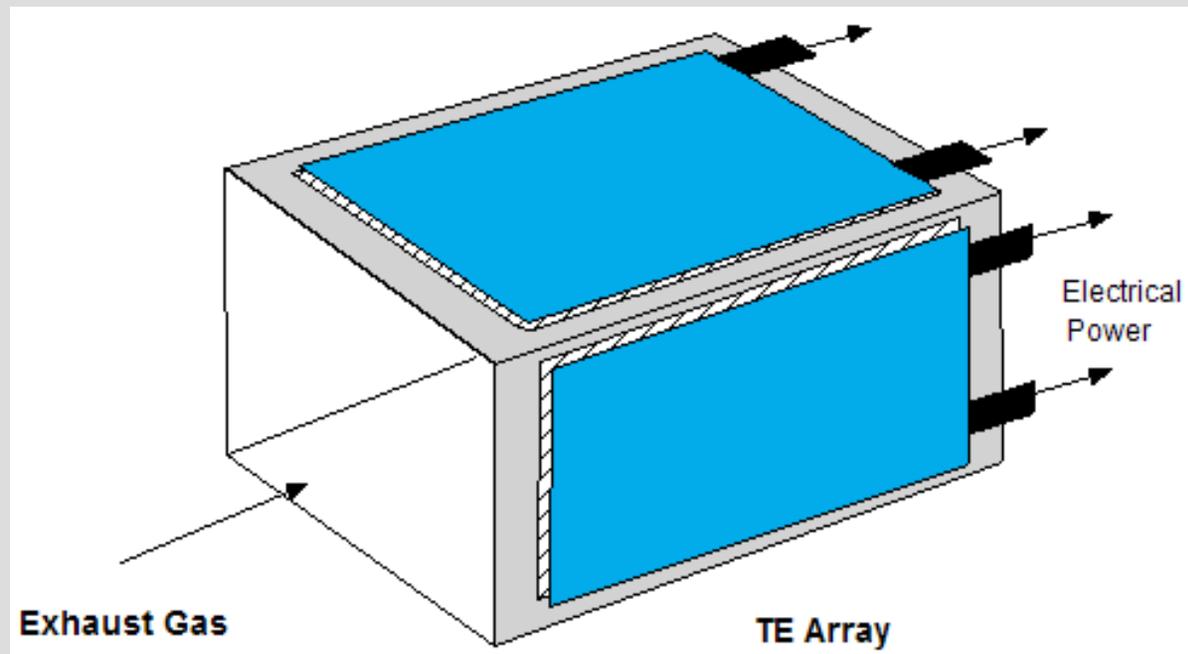
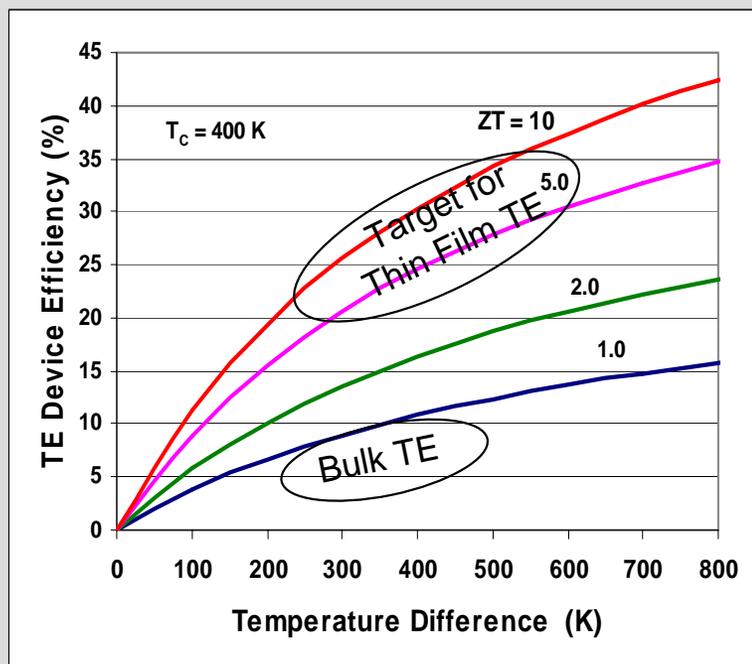
S = Seebeck Coeff = dV/dT

σ = Electrical Conductivity

k = Thermal Conductivity

Waste heat \gg Electricity

Thermoelectrics generators for waste heat recovery



Target conversion efficiency with advanced thermoelectrics = 30%
(automotive/truck/stationary applications)

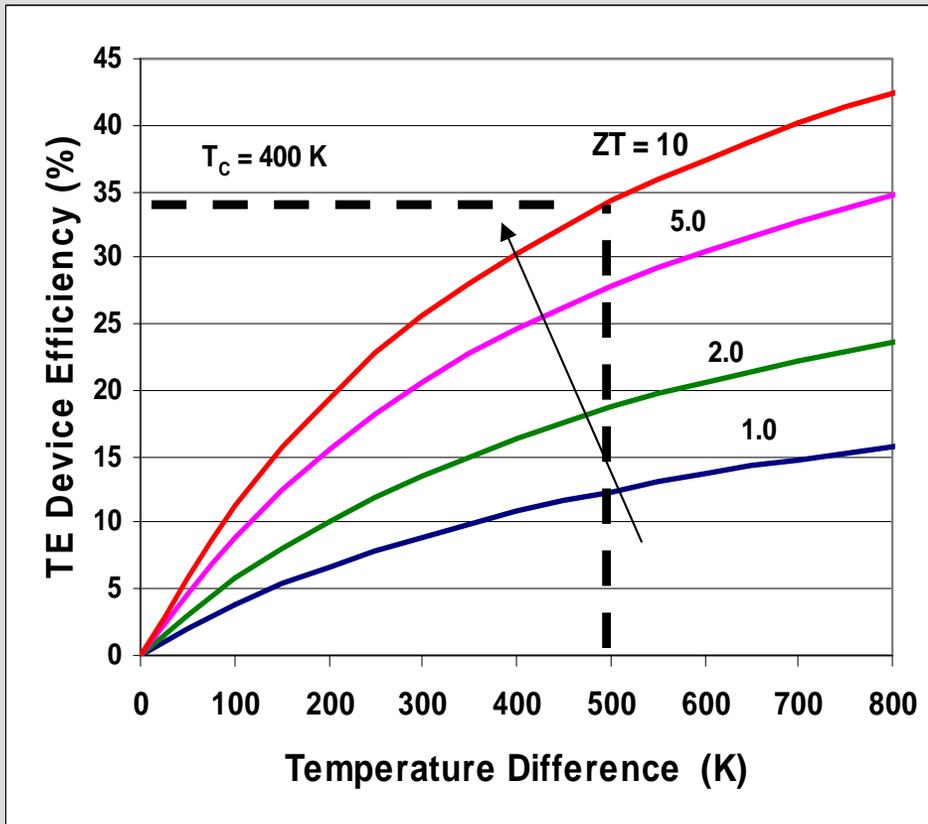
Figure of merit (ZT)

▶ Power conversion **Efficiency**

▶ $ZT = (S^2\sigma/\kappa)T$

- Seebeck coefficient ($\Delta V/\Delta T$)
- Maximize conductivity σ
- Minimize thermal conductivity κ
- Bulk materials pegged at ~ 1
- Defines power conversion efficiency of a TE device
 - $\text{eff} = \frac{(T_1 - T_2)}{T_1} \cdot \frac{(M - 1)}{(M + T_2/T_1)}$
 - $M = (1 + ZT)^{1/2}$

Thermoelectric (TE) Energy Conversion



For a given ΔT , higher the ZT, higher the heat-to-electric conversion efficiency

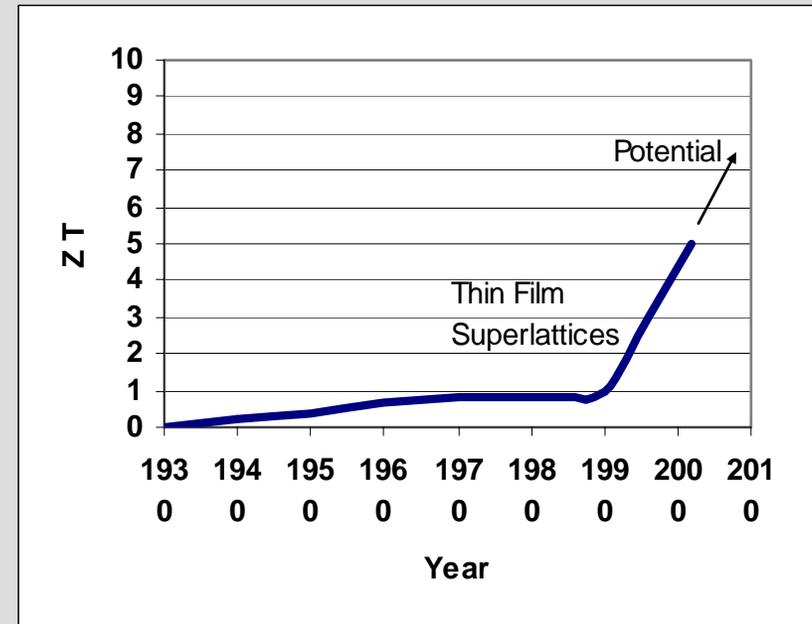
If ZT of 10 can be achieved, a theoretical conversion efficiency of ~35% is possible for ΔT of ~500C

Thermoelectrics development needs

- Measurement standardization
- Performance validation
- Tailored nanoscale materials
- Materials design for ZT enhancement
- Low resistance contacts and interconnects
- Process scale-up
- Prototype device design and engineering
- Thermal management and packaging
- Device and system modeling
- Manufacturing process optimization

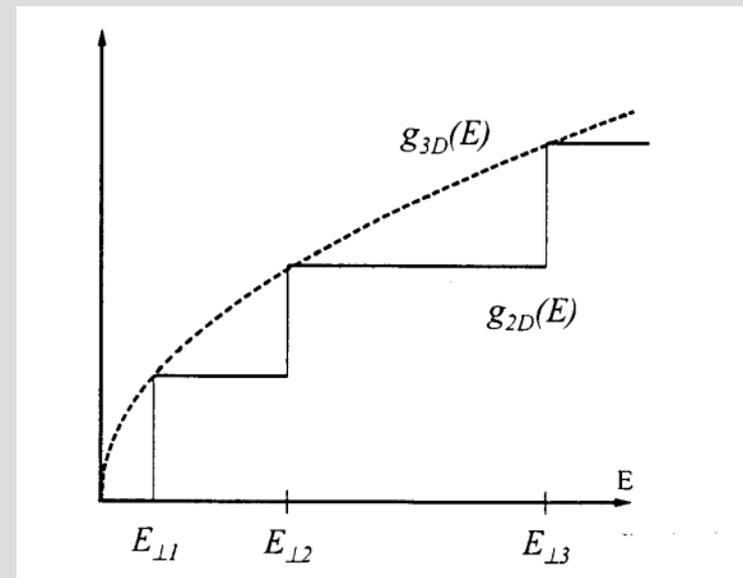
Promise of Quantum Confinement in Nanostructures

- ▶ Quantum confinement increases density of states
- ▶ Increased conductivity
- ▶ Increased Seebeck coefficient
- ▶ Increased ZT
- ▶ ***Increased power conversion efficiency***

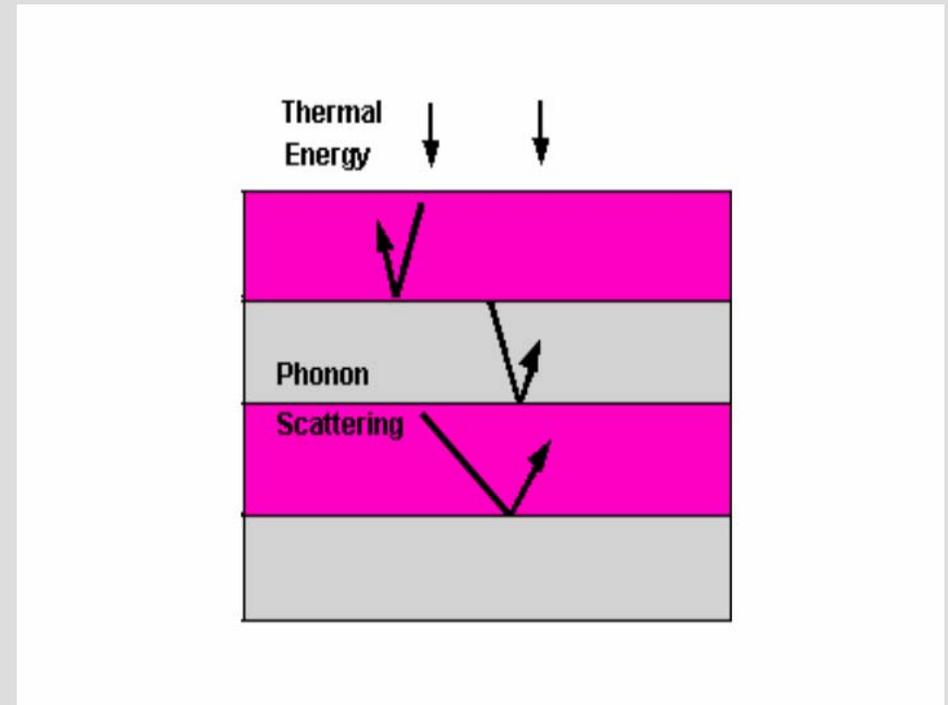
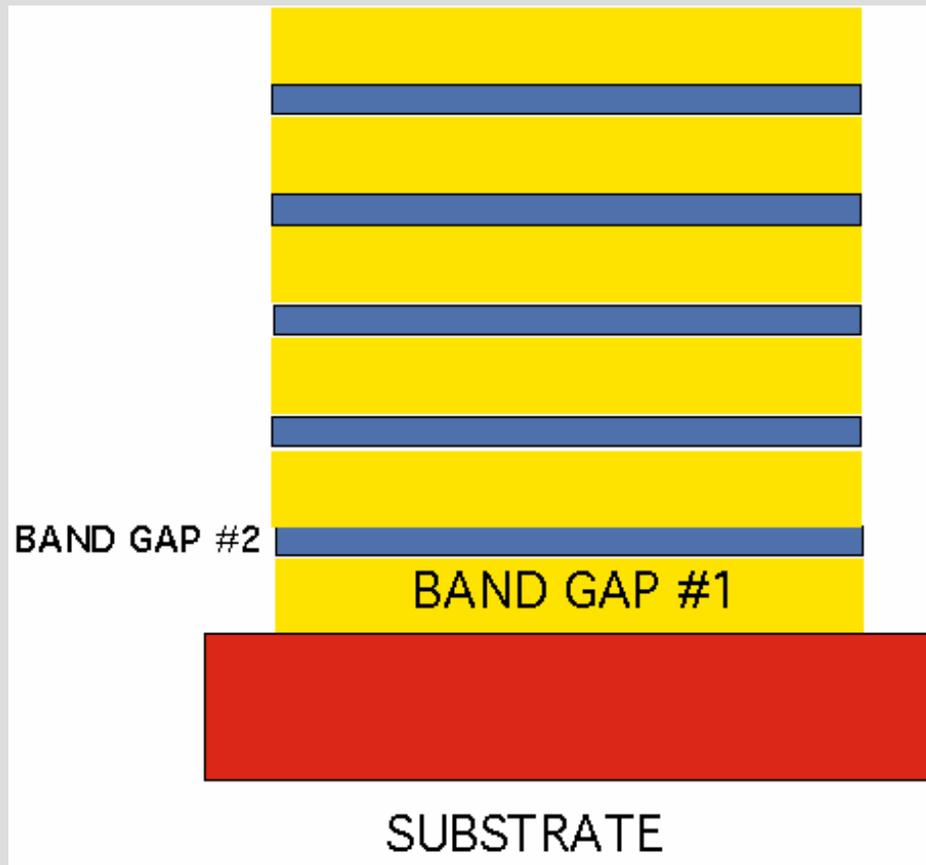


TE Semiconductor Superlattices

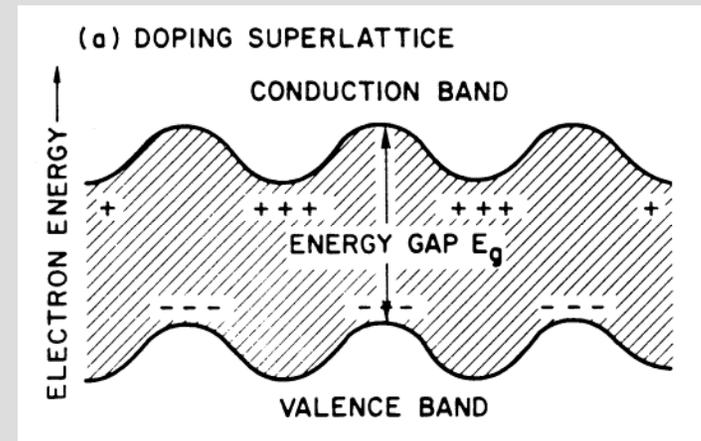
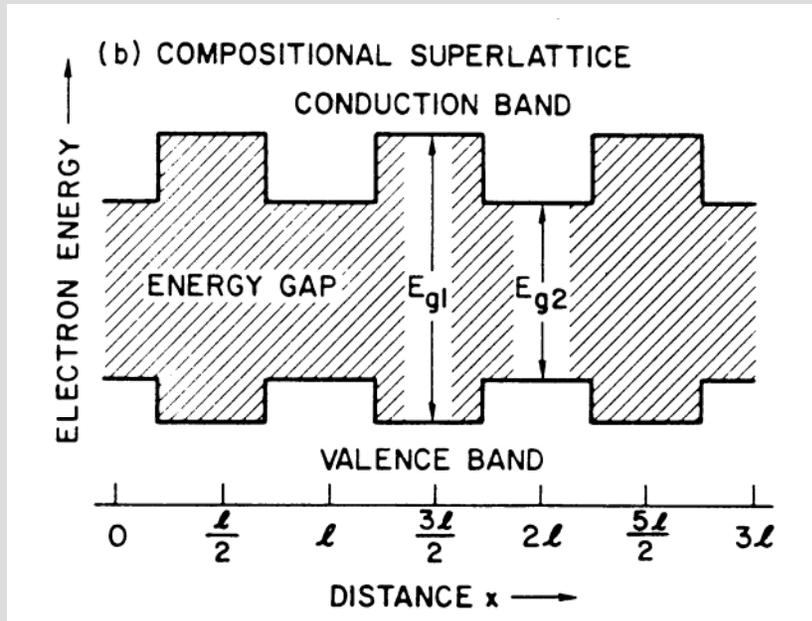
- ▶ Bulk materials show little promise for $ZT > 1$.
- ▶ 2-D quantum confinement of charge carriers, phonons shows promise to improve ZT
- ▶ Enhanced ZT
 - Increases density of states for charge carriers: optimize conductivity
 - Enhanced phonon scattering to minimize thermal conductivity



Superlattice Structure



TE Superlattice Concept



J. M. Chamberlain, L. Eaves, J. C. Portal, *Electronic Properties of Multilayers and Low-Dimensional Semiconductor Structures*, Plenum Press, New York, 1990.

Sputtered TE Superlattice

- ▶ $\text{Si}/\text{Si}_{0.8}\text{Ge}_{0.2}$
 - 50 - 100 Å layers
 - N-type layer
 - Up to 3,000 layers needed for power generation
 - ZT ~ 1 on small scale
- ▶ $\text{B}_4\text{C}/\text{B}_9\text{C}$
 - P-type layer
 - ZT ~ 4 on small scale (Hi-Z)

Scale Up Issues

- ZT increase looks promising for *small scale* TE devices
- Scale up for TE power generation from exhaust systems of heavy duty trucks will have to address:
 - Substrate size/surface
 - Economics: Low cost substrates/process
 - Coating thickness uniformity
 - Same or better performance than small scale systems
 - Correct thermoelectric property measurements on films and devices

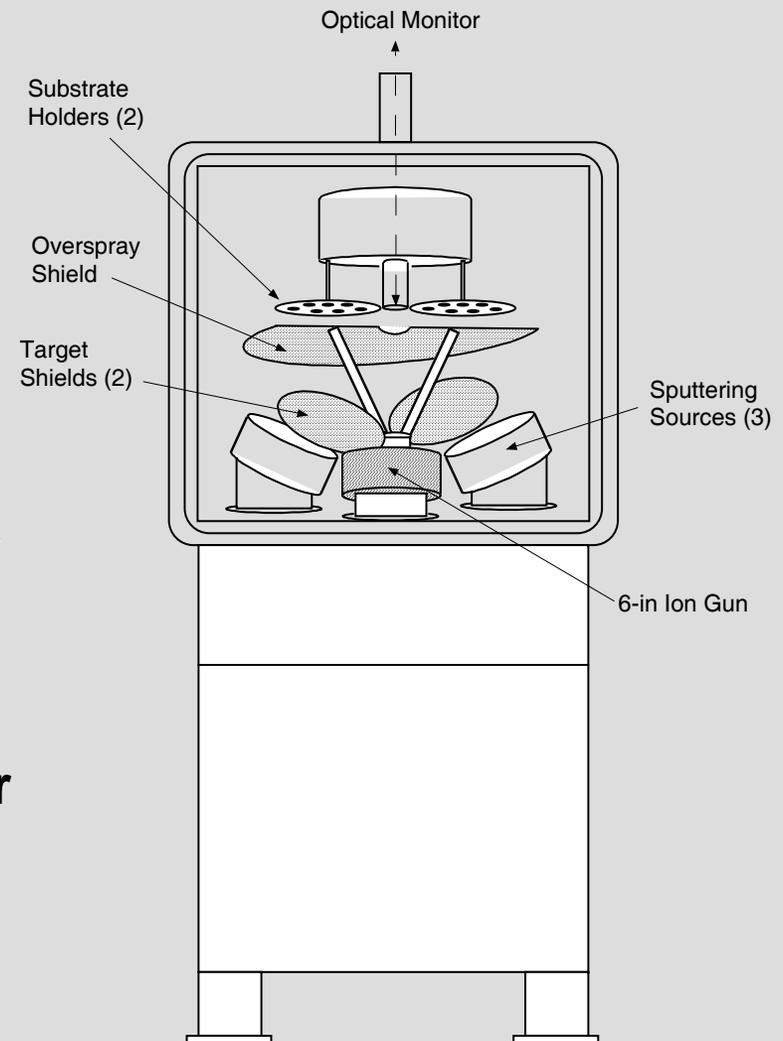
Approach To Sputtering Si/SiGe Films

General

- Si And Si_{0.8}Ge_{0.2} Targets
- Target Diameter = 15.2 cm
- RF Power Of 1.0 To 3.3 W/cm²
- High Purity Argon Gas
- Substrate Temperature: Amb to 600°C
- Deposition Rates 1 To 6 Å/s

Growth Process

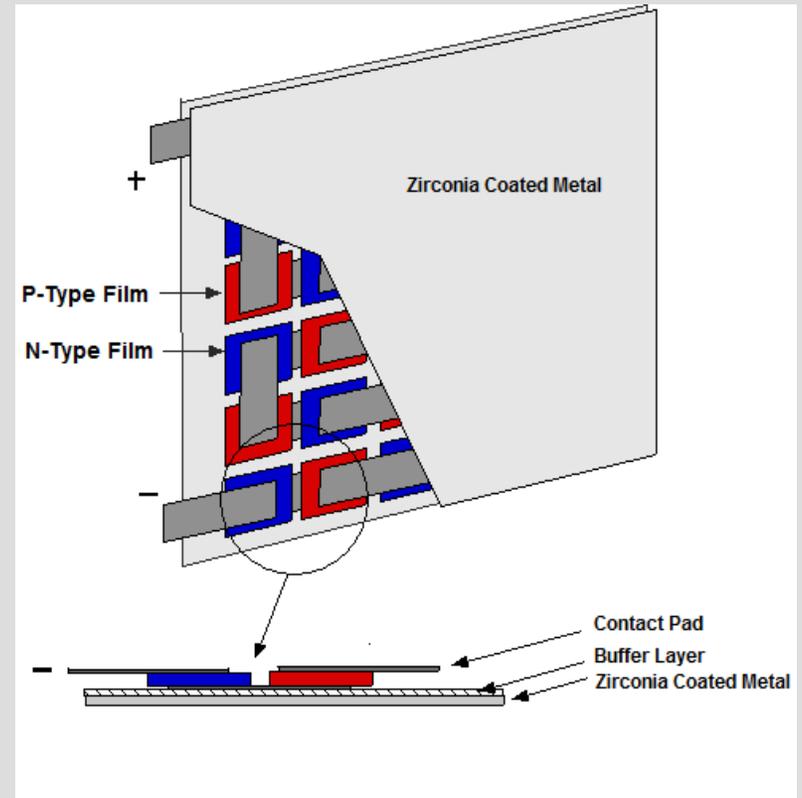
- Phase 1: Substrates Moved Sequentially From Over The Si Target To Over The SiGe Target -- 16 Hours For 1 μm Film
- Phase 2: Scale-Up Process Utilizes A Rotating Substrate Holder – 2 Hours For 1 μm Film



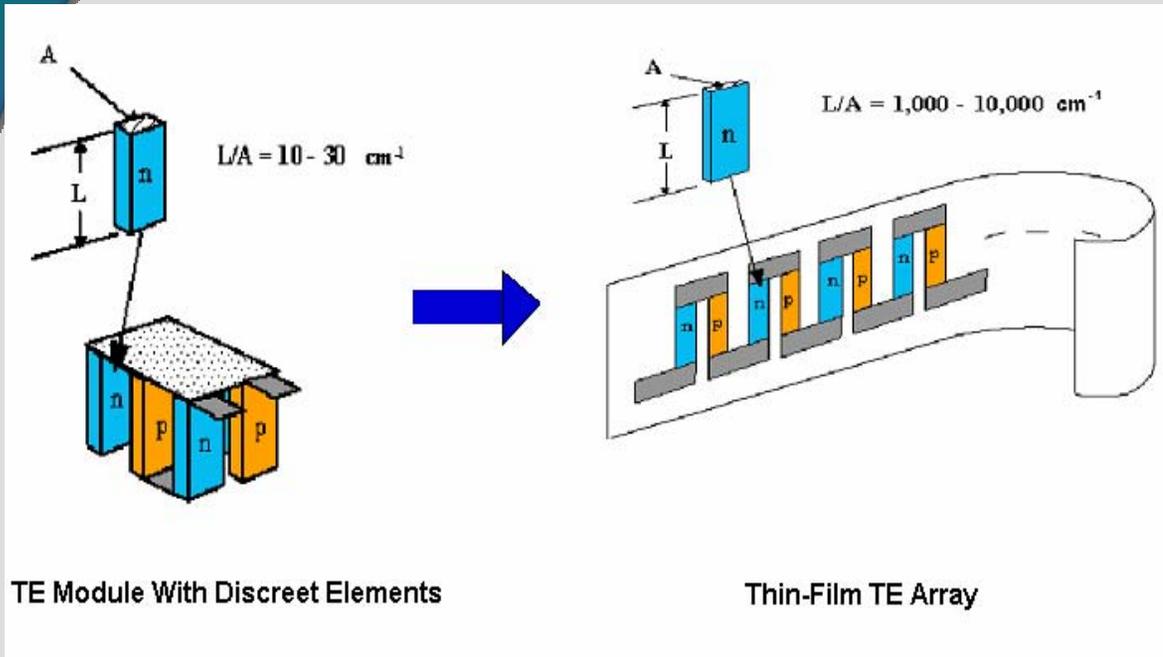
Improved thin-film materials, low-cost scale-up, device design and packaging, and thermal management required for applications



Large-Area Sputter Deposition

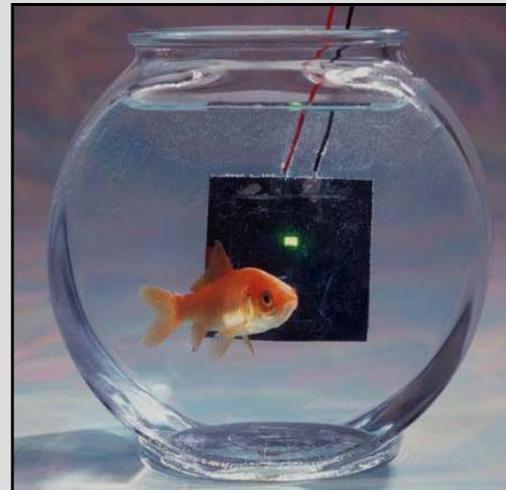


Device Design Schematic



TE Module With Discret Elements

Thin-Film TE Array



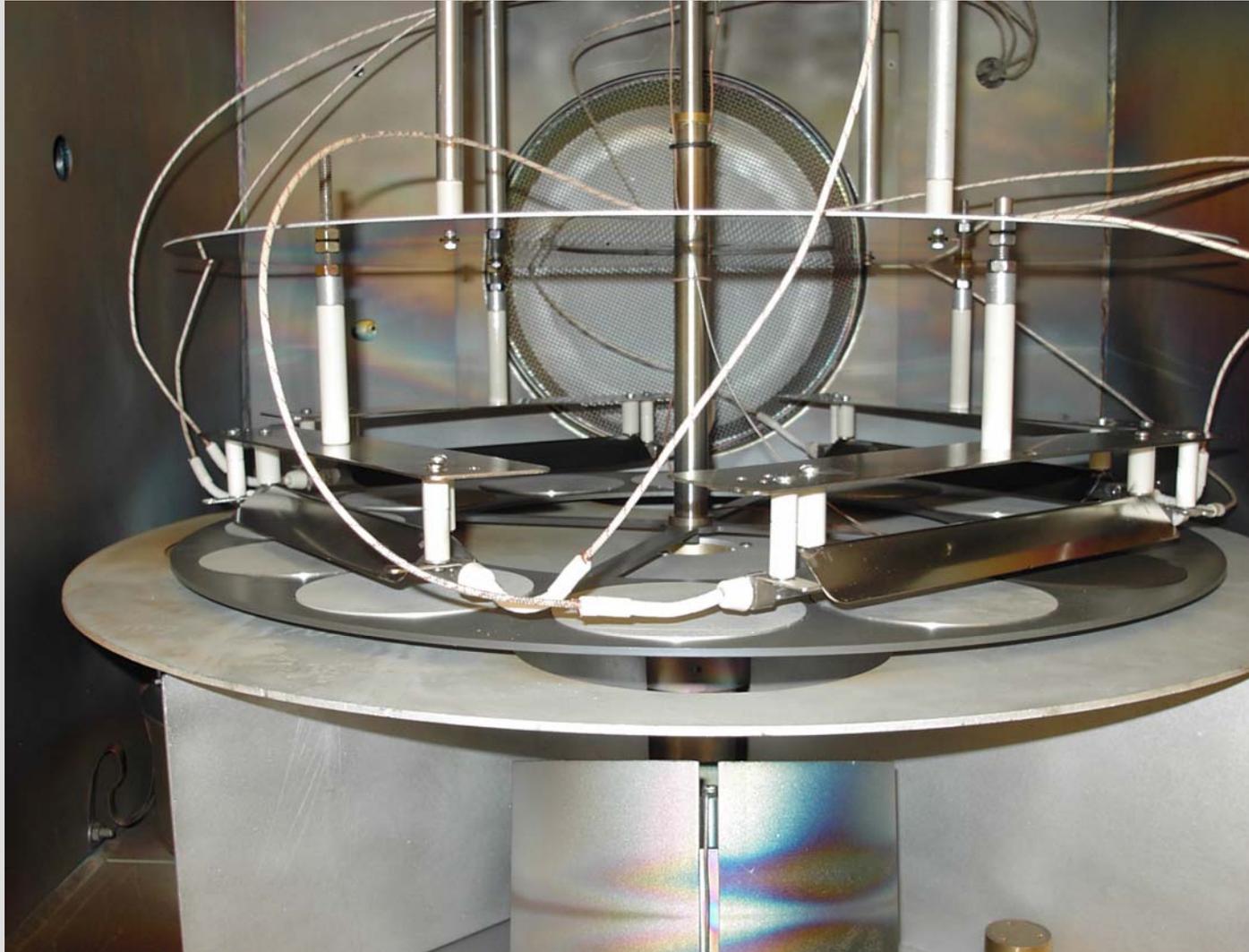
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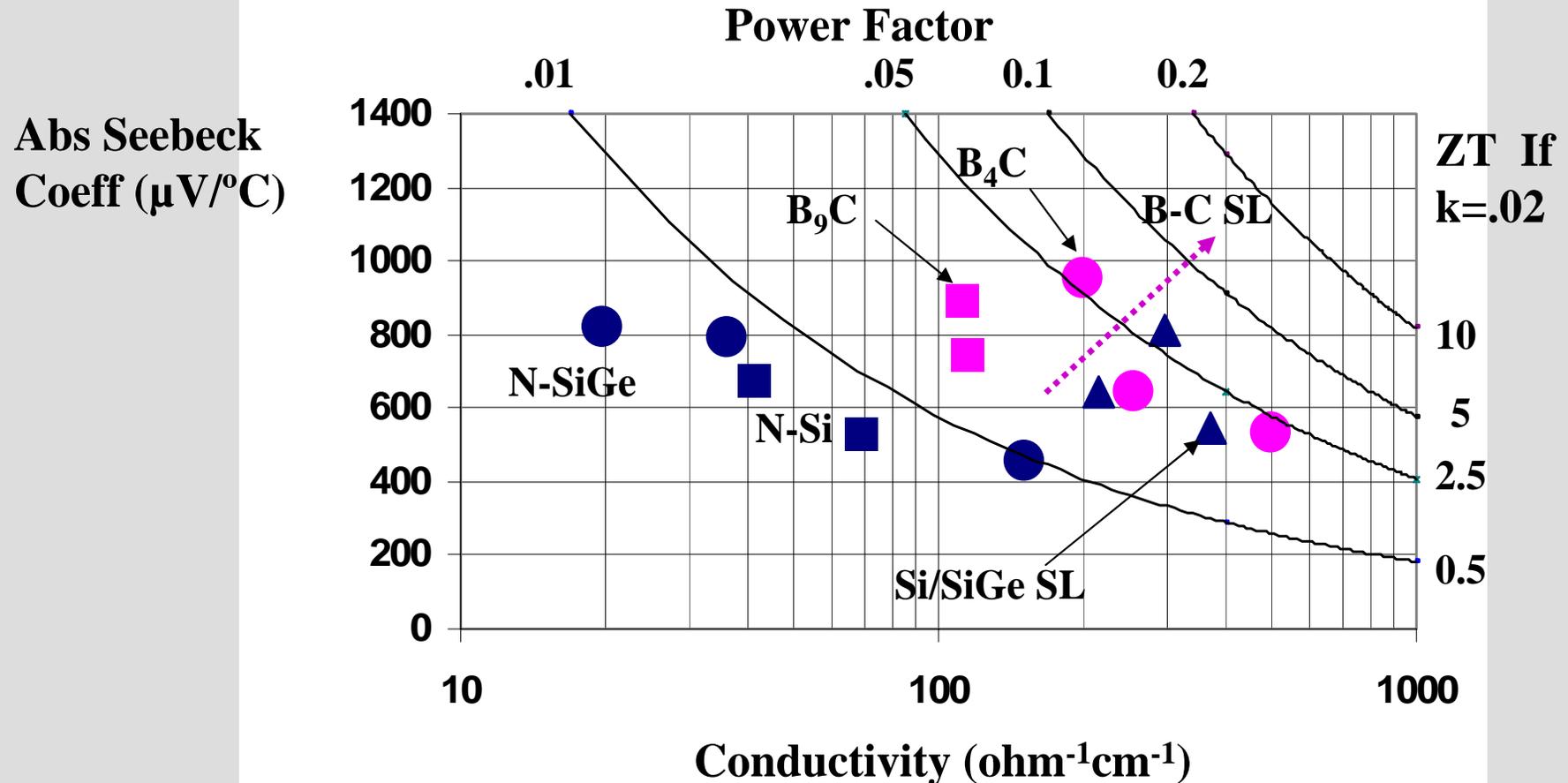
Battelle

VITEX
SYSTEMS

Deposition Geometry



Results For N-Type Materials



Representative Material Properties

Material	Electrical Conductivity (ohm ⁻¹ cm ⁻¹)	Seebeck Coefficient (μV/°C)	Power Factor
N-Silicon	60	600	.0065
N-SiGe	35	800	.0067
N-Si/SiGe SL	300	750	.051
N-B ₄ C	200	950	.054
N-B ₉ C	120	900	.029
P- B ₄ C	50	800	.010

Hall Effect Measurements

- ▶ Hall effect measurements on quantum well films indicate a carrier concentration $\sim 10^{21}/\text{cm}^3$
- ▶ Confirms high electrical conductivity results

ZT Measurement

- ▶ Consider Two Conditions, Open Circuit And Short Circuit
- ▶ Key Requirement: Heat Flow Through Sample Is Same For Two Conditions

- ▶ Open Circuit: $Q = K \cdot \Delta T_o$, (1)
- ▶ Short Circuit (Closed Switch):

$$S \cdot \Delta T_s = R I_s \quad (2)$$

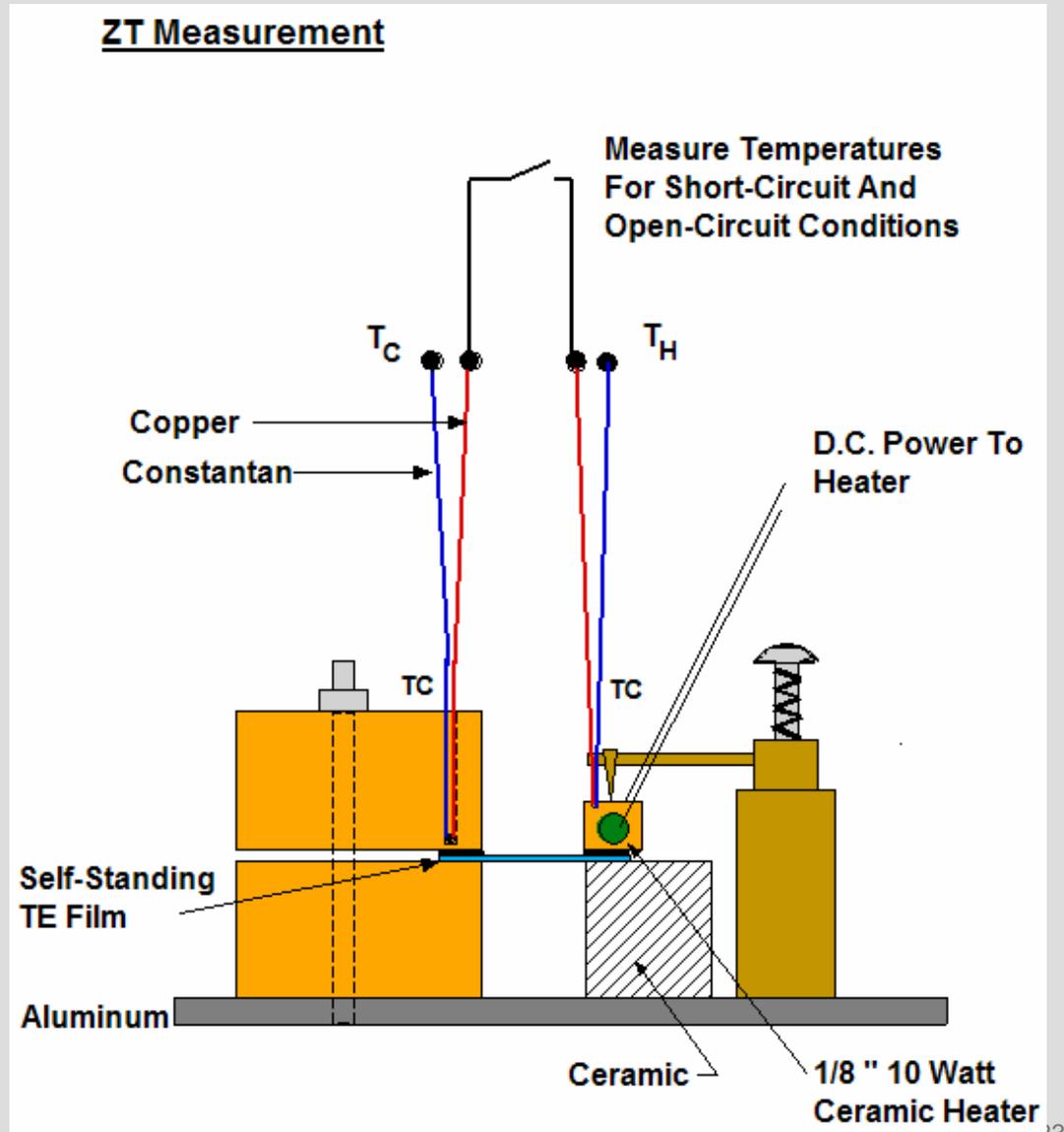
$$Q = S T_H I_s - (1/2) R (I_s)^2 + K \cdot \Delta T_s$$

Where $K = \kappa(A/L)$ $R = \rho(L/A)$

- Using (1) And (2) In Expression For Q, Find

$$ZT = 1 - (\Delta T_o / \Delta T_s)$$

- Also Obtain S and ρ



Results to Date

- ▶ Quantum well concept shows significant promise for economical waste heat recovery from diesel engines
- ▶ Initial performance results look promising
 - Results are *preliminary*, but consistent
 - Both n-type and p-type superlattices
 - TE and electrical properties look good
 - Conductivity of SL about 10 - 100 times that of single layer
 - Initial carrier concentration measurements encouraging
- ▶ Continued scale up process development needed to address cost and power targets

Next Steps

- ▶ Optimize thermoelectric performance of B_4C/B_9C superlattice
- ▶ Unambiguous ZT measurements
- ▶ Scale up to 1 m² substrates
- ▶ Determine where this technology needs to go based on performance results
- ▶ Work with High-Z and potential end users to validate quantum well concept and integrate quantum well films into functional prototype device