Scale Up of Si/ $Si_{0.8}Ge_{0.2}$ and B_4C/B_9C Superlattices for Harvesting of Waste Heat in Diesel Engines+

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

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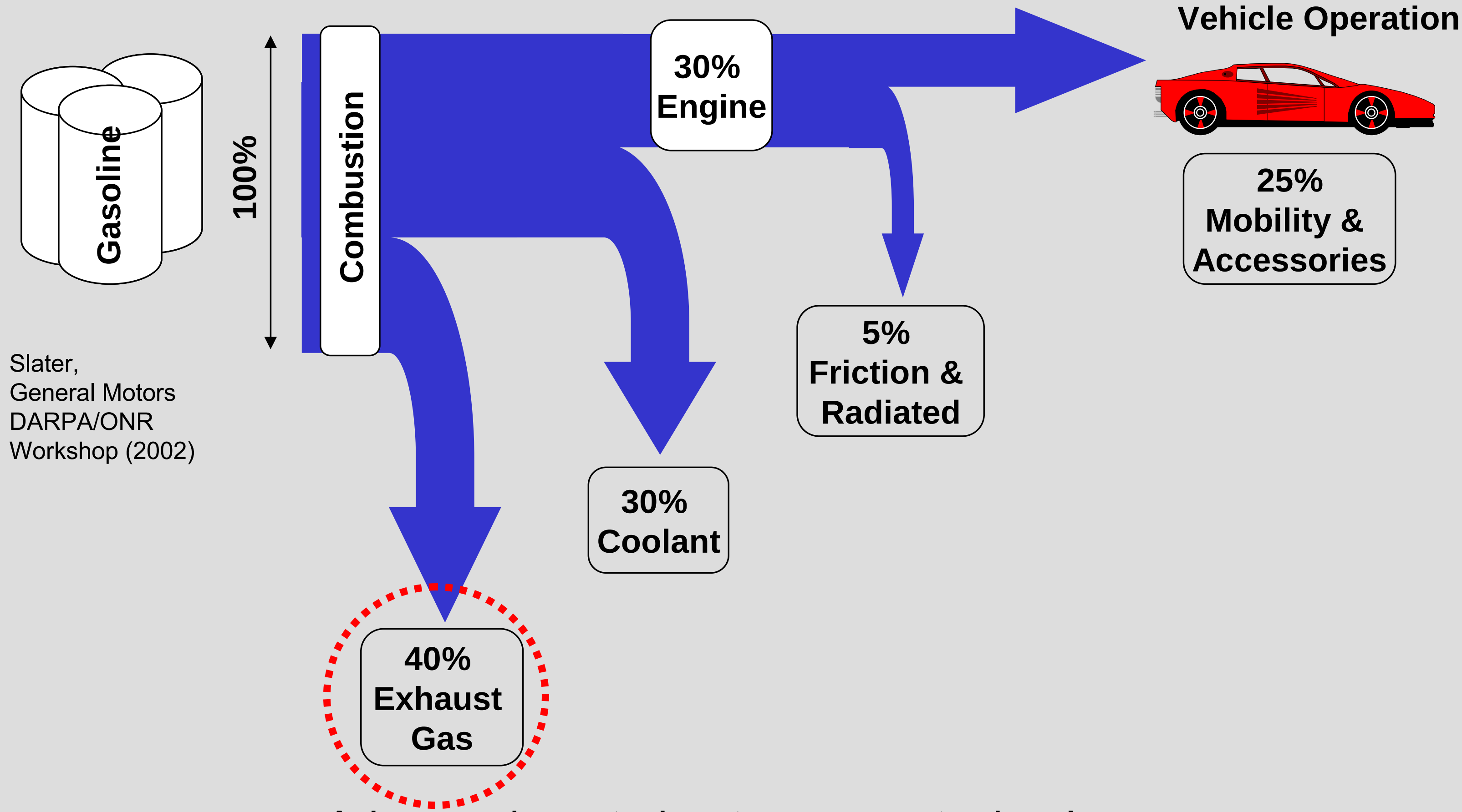
Program Objectives

- Scale up the deposition process for Si/SiGe and B_4C/B_9C thermoelectric quantum well structures for waste heat recovery from diesel engines
- Verify thermoelectric properties of Si/SiGe and B_4C/B_9C 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

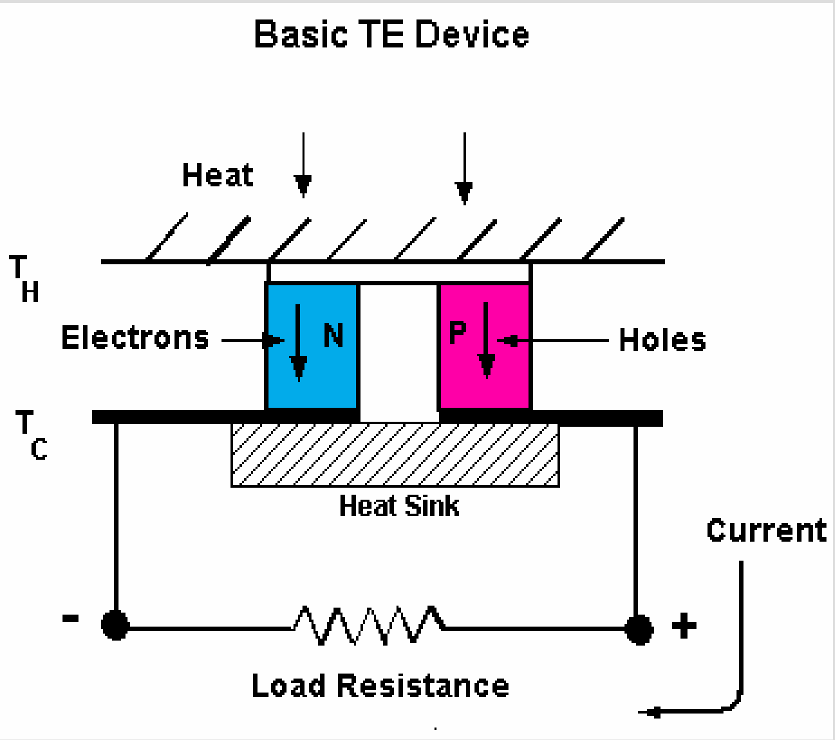
Less than 25% of fuel energy in gasoline goes to useful shaft work



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:

$Z = S^2\sigma/k$

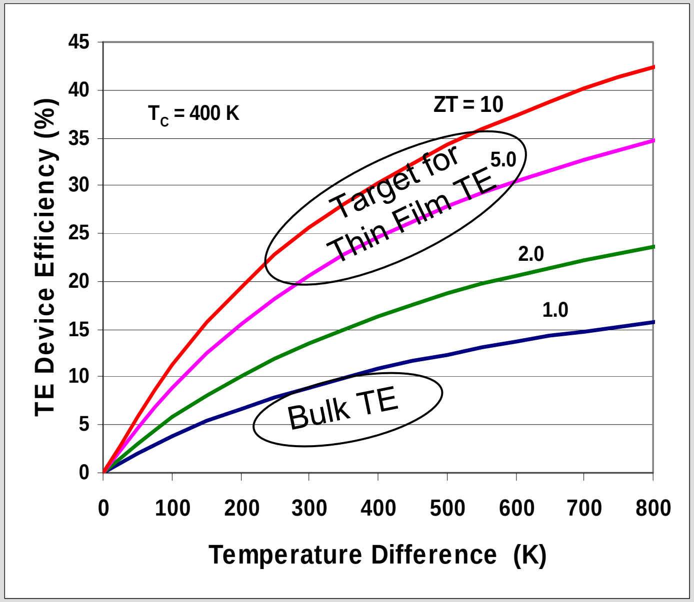
S = Seebeck Coeff = dV/dT

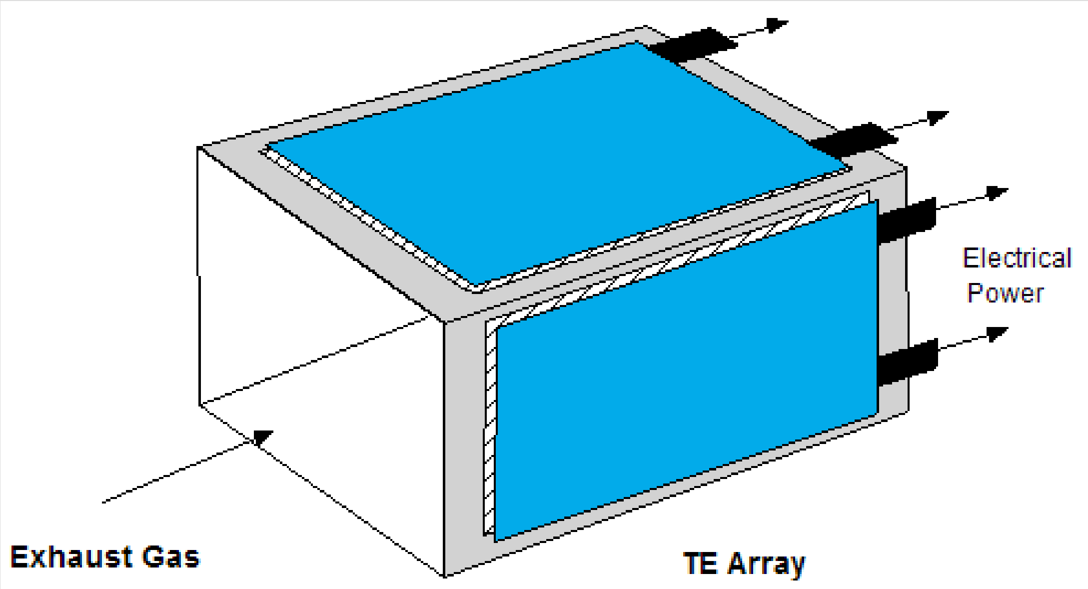
σ = Electrical Conductivity

k = Thermal Conductivity

Waste heat >> Electricity

Thermoelectrics generators for waste heat recovery



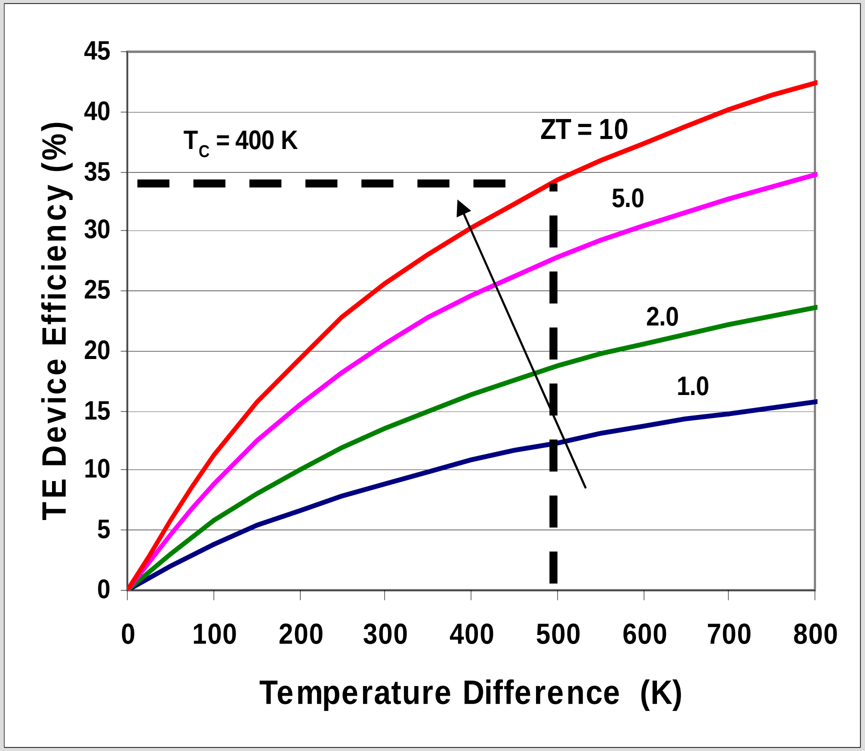


Target conversion efficiency with advanced thermoelectrics = 30%
(automotive/truck/stationary applications)

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

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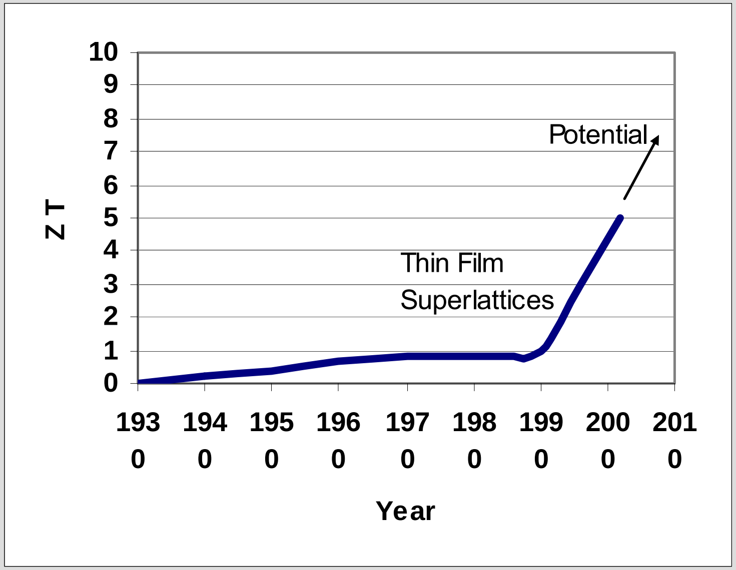
Thermoelectrics development needs

- 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

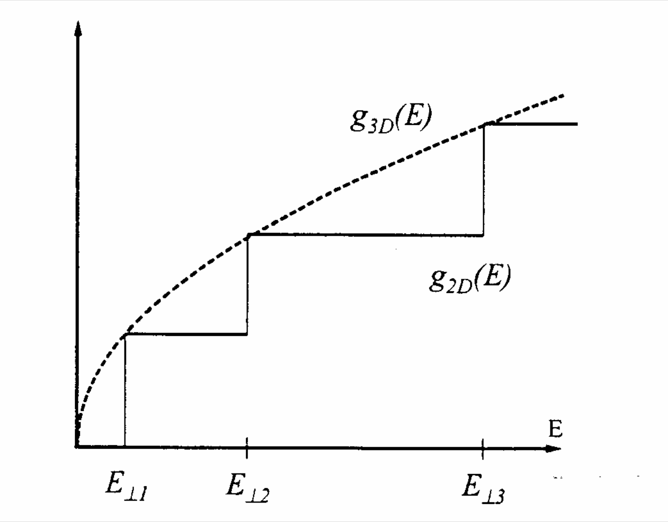
Promise of Quantum Confinement in Nanostructures

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

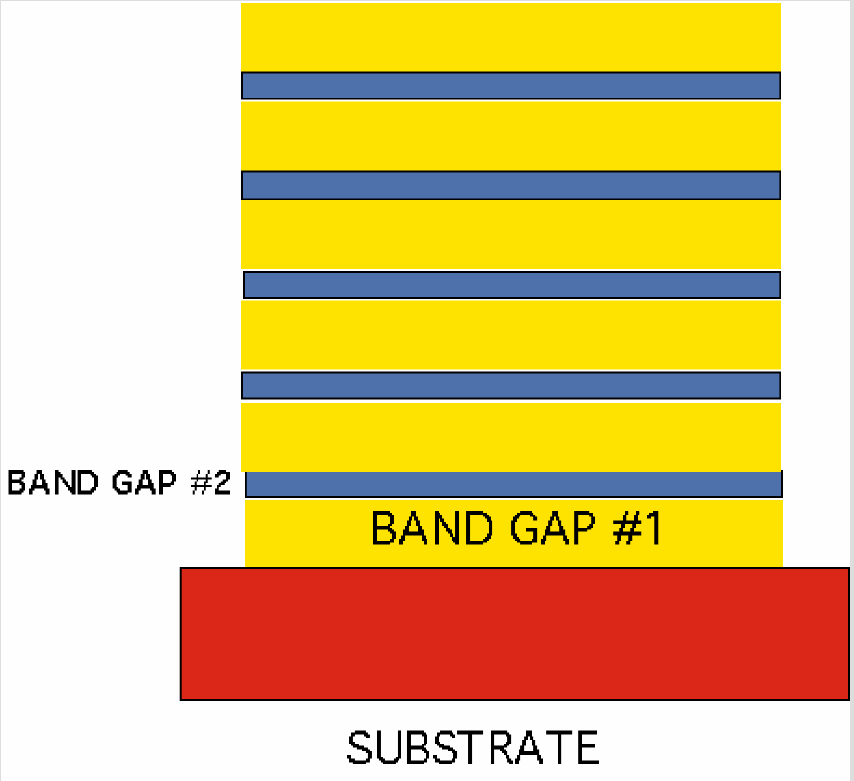


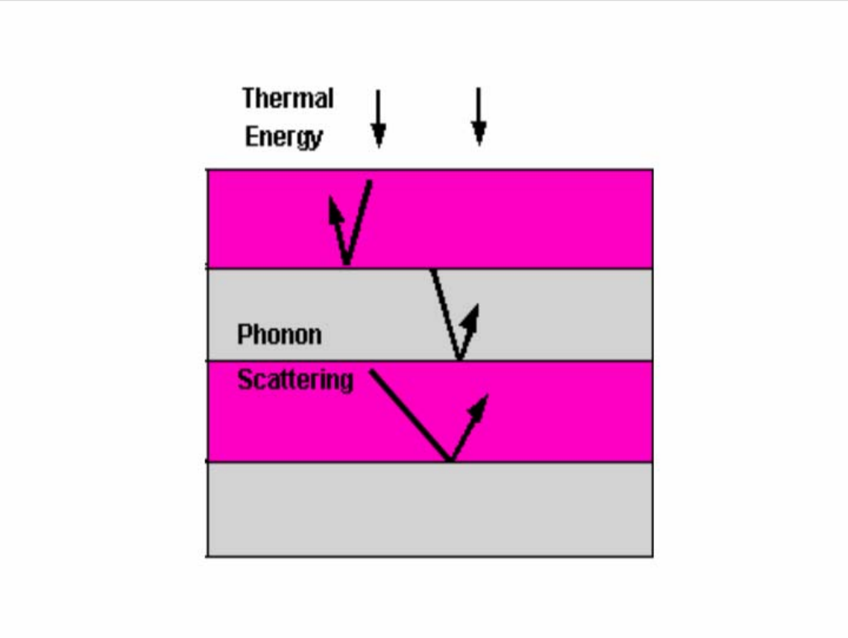
TE Semiconductor Superlattices

- 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

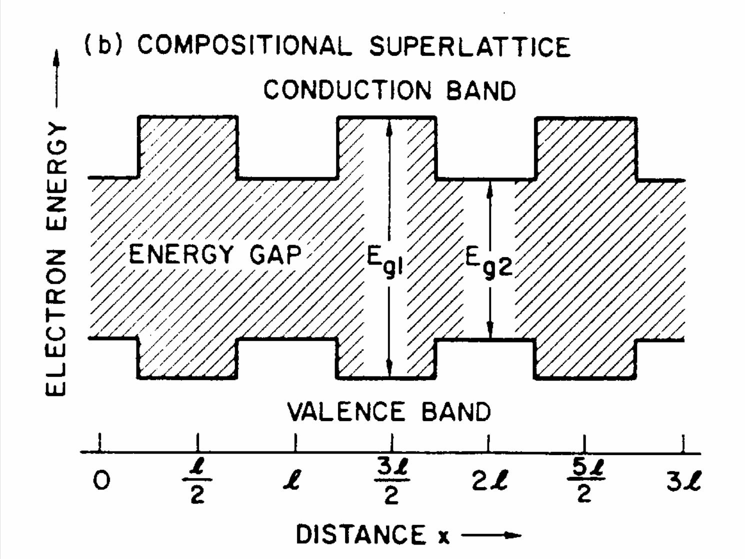


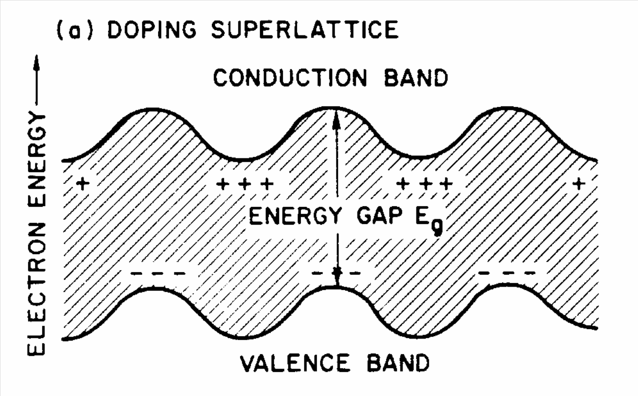
Superlattice Structure





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

- $Si/Si_{0.8}Ge_{0.2}$
  - 50 - 100 Å layers
  - N-type layer
  - Up to 3,000 layers needed for power generation
  - ZT ~ 1 on small scale
- B_4C/B_9C
  - 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

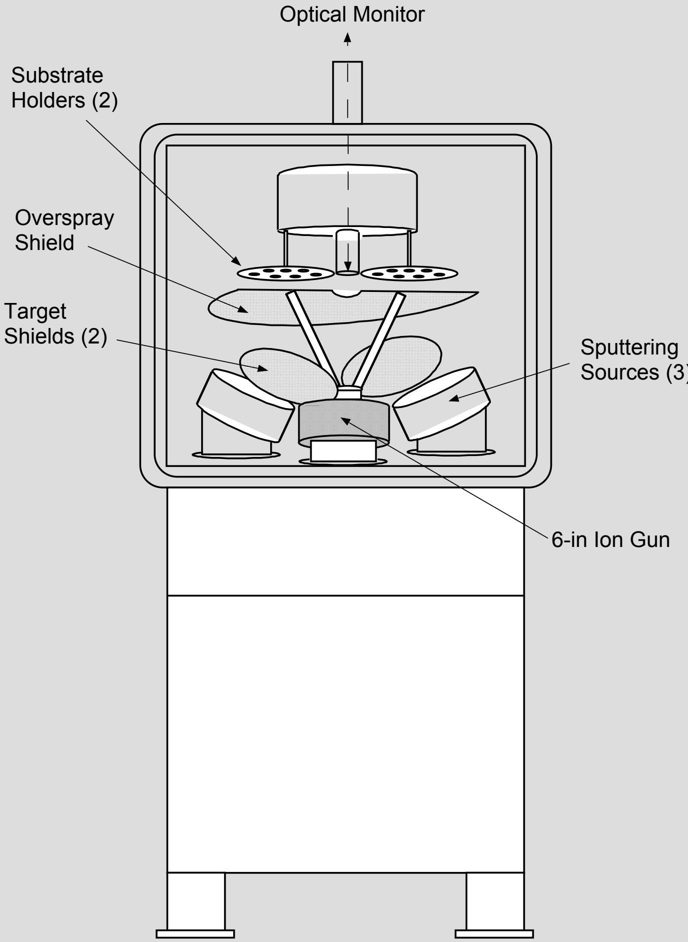
Approach To Sputtering Si/SiGe Films

General

- Si And $Si_{0.8}Ge_{0.2}$ Targets
- Target Diameter = 15.2 cm
- RF Power Of 1.0 To 3.3 W/cm^2
- High Purity Argon Gas
- Substrate Temperature: Amb to 600ºC
- Deposition Rates 1 To 6 Å/s

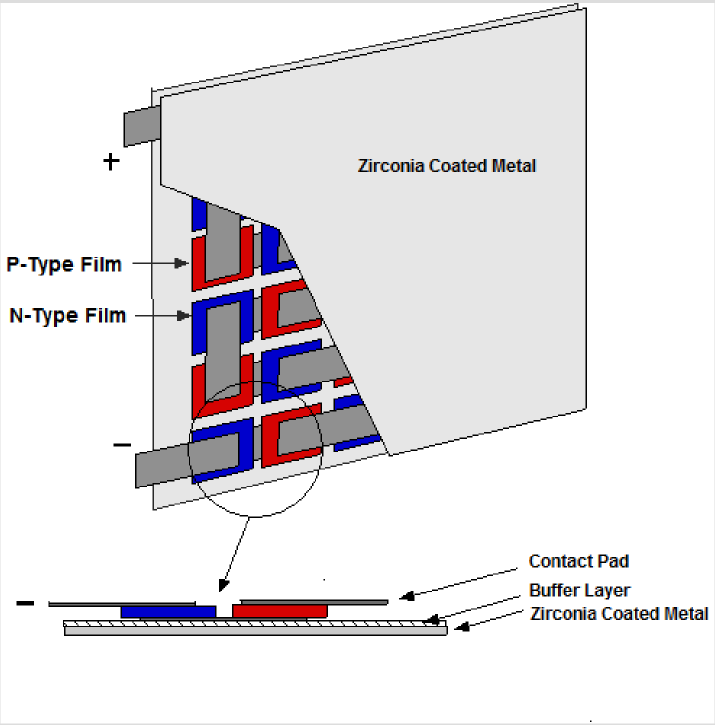
Growth Process

- 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

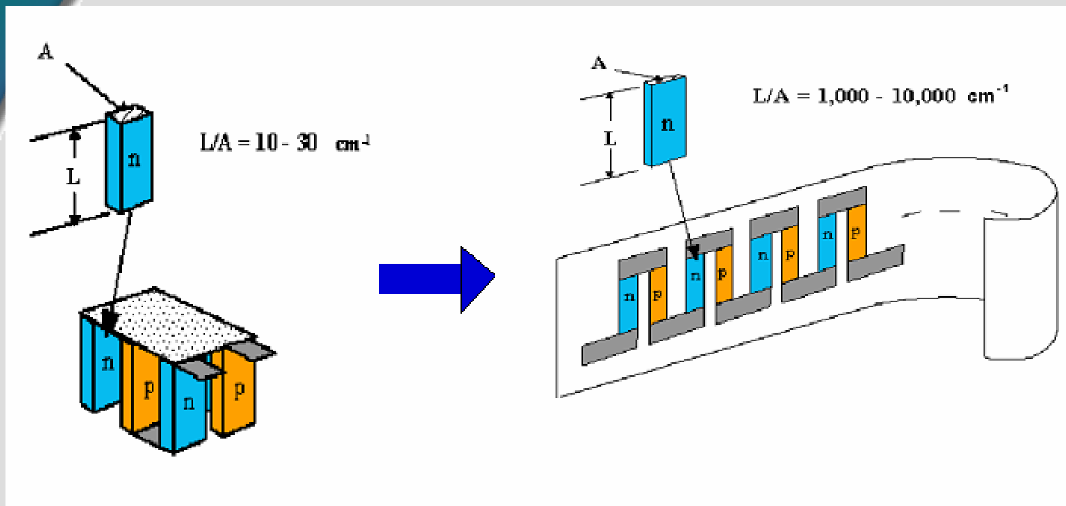


Improved thin-film materials, low-cost scale-up, device design and packaging, and thermal management required for applications

Large-Area Sputter Deposition



Device Design Schematic



TE Module With Discreet Elements

Thin-Film TE Array

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VITEX SYSTEMS

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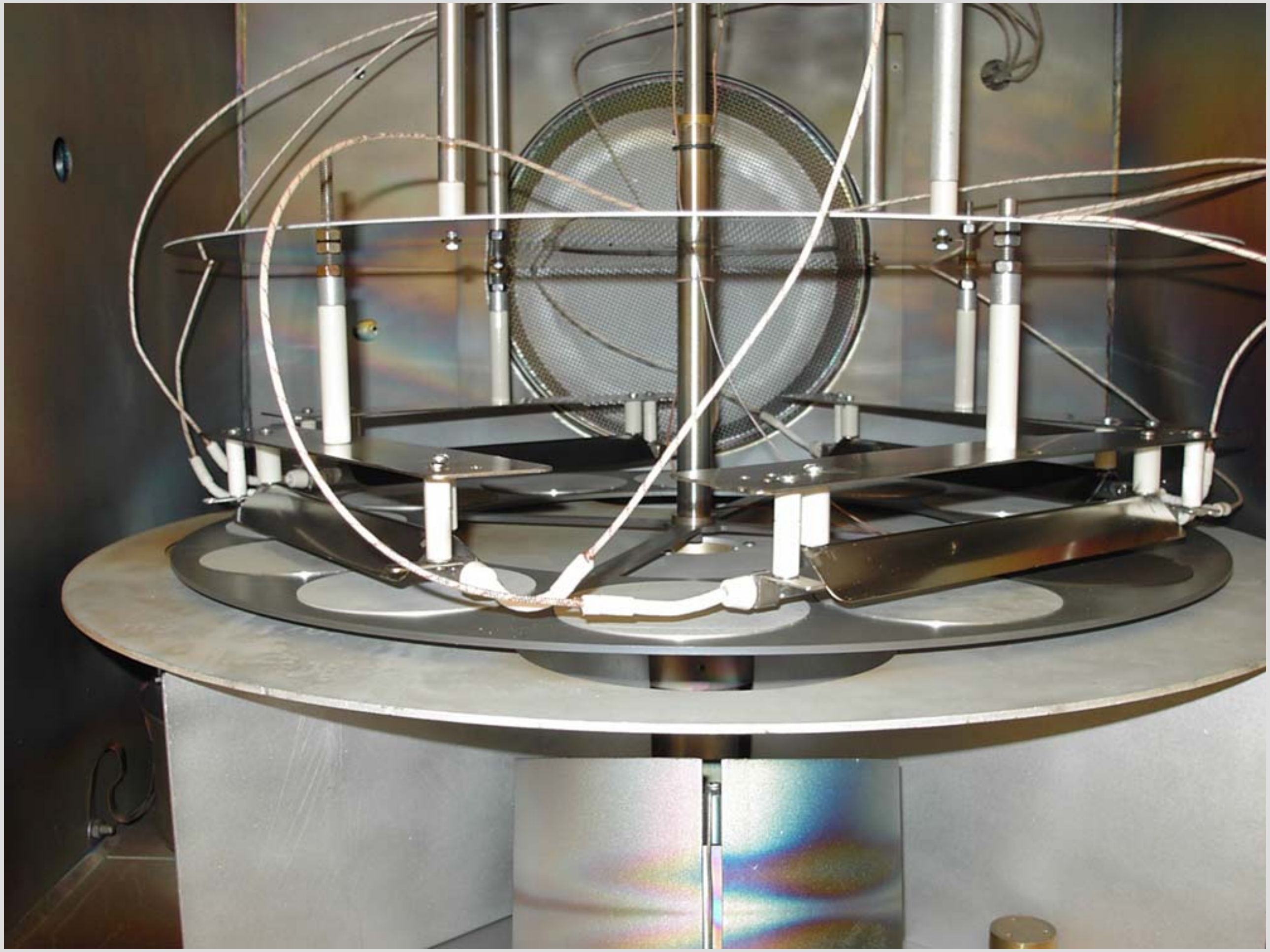
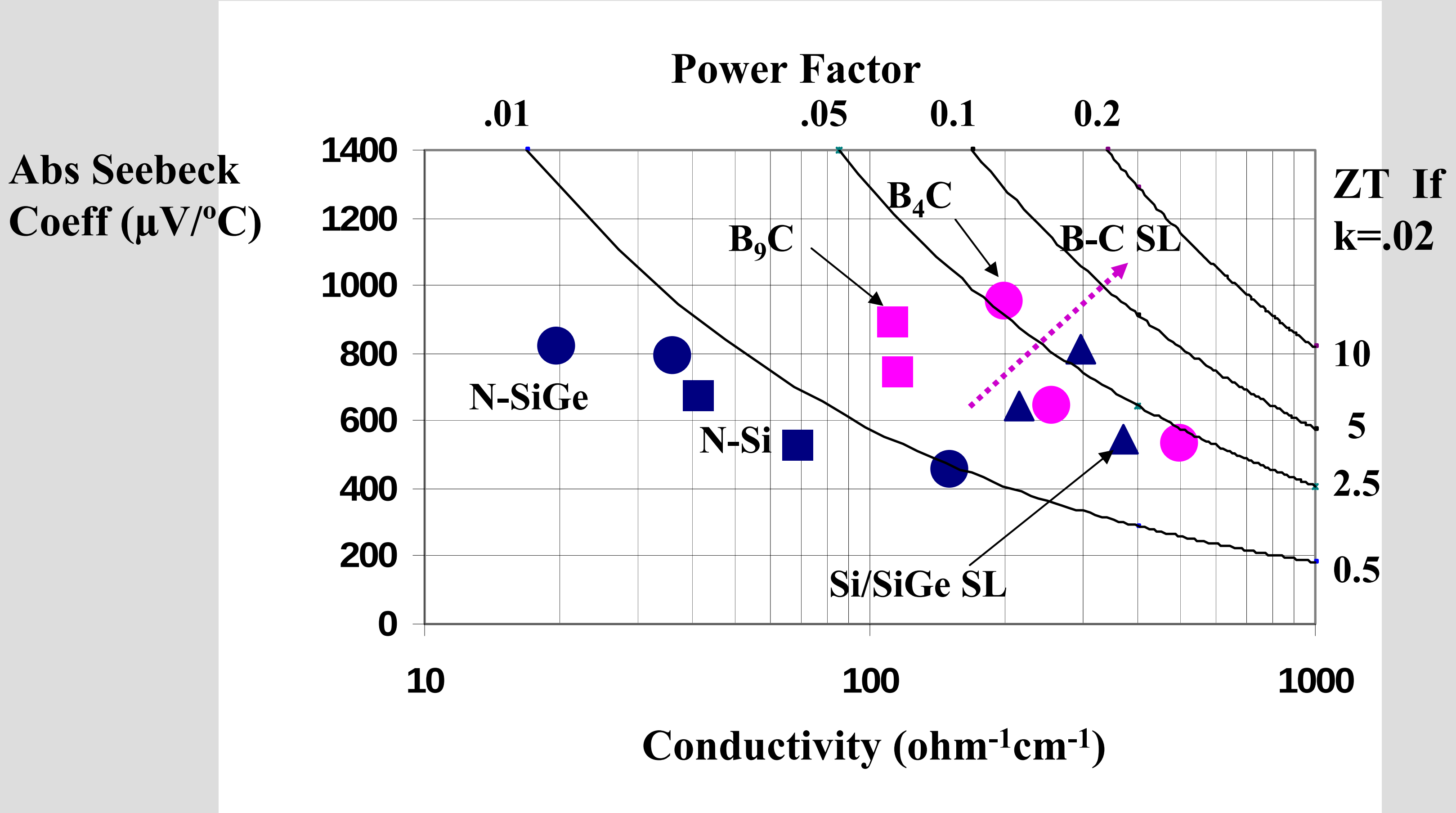
Deposition Geometry



Results For N-Type Materials



Representative Material Properties

Material	Electrical Conductivity ($ohm^{-1}cm^{-1}$)	Seebeck Coefficient ($\mu V/^{o}C$)	Power Factor
N-Silicon	60	600	.0065
N-SiGe	35	800	.0067
N-Si/SiGe SL	300	750	.051
N-B_4C	200	950	.054
N-B_9C	120	900	.029
P- B_4C	50	800	.010

Hall Effect Measurements

- Hall effect measurements on quantum well films indicate a carrier concentration ~ $10^{21}/cm^3$
- 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):

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

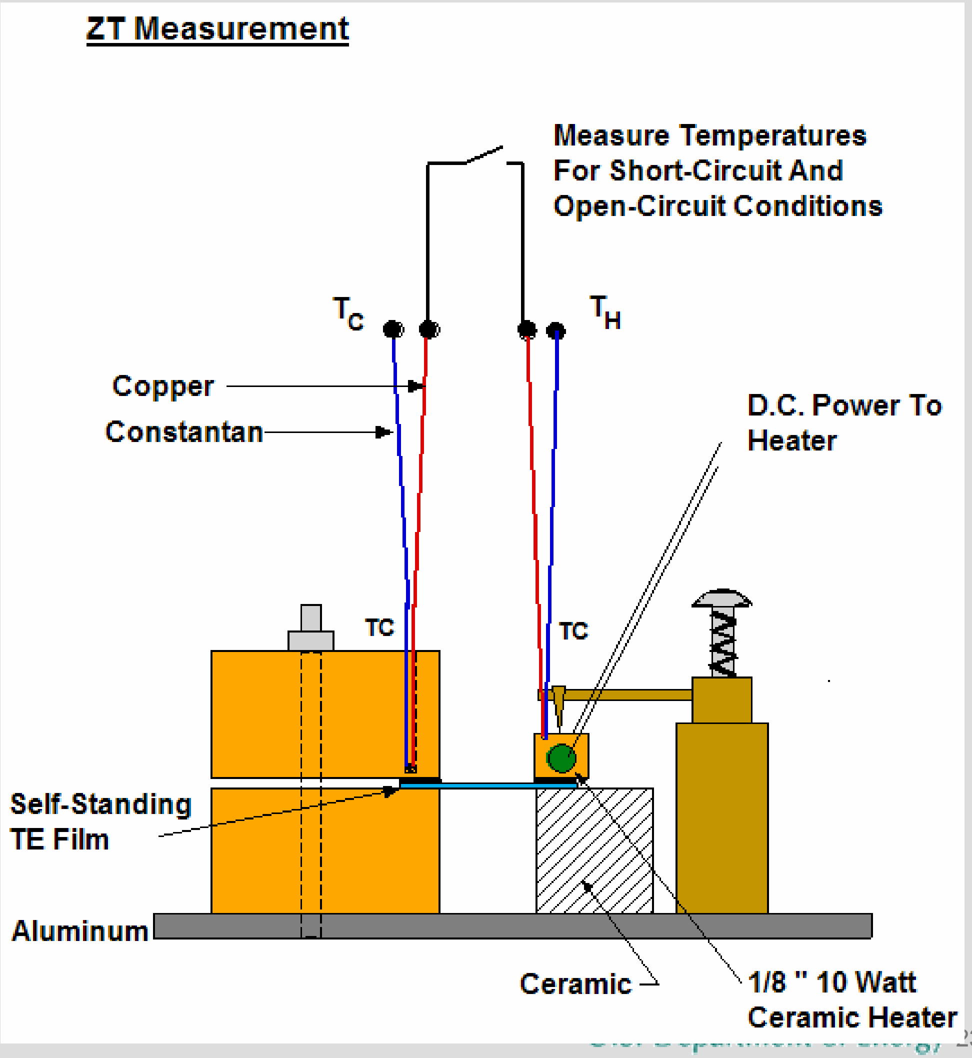
  $Q = ST_H I_s - (1/2)R(I_s)^2 + K \cdot \Delta T_s$

  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 m^2 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