Multilayer Thin Film Thermoelectric Materials for Vehicle Applications

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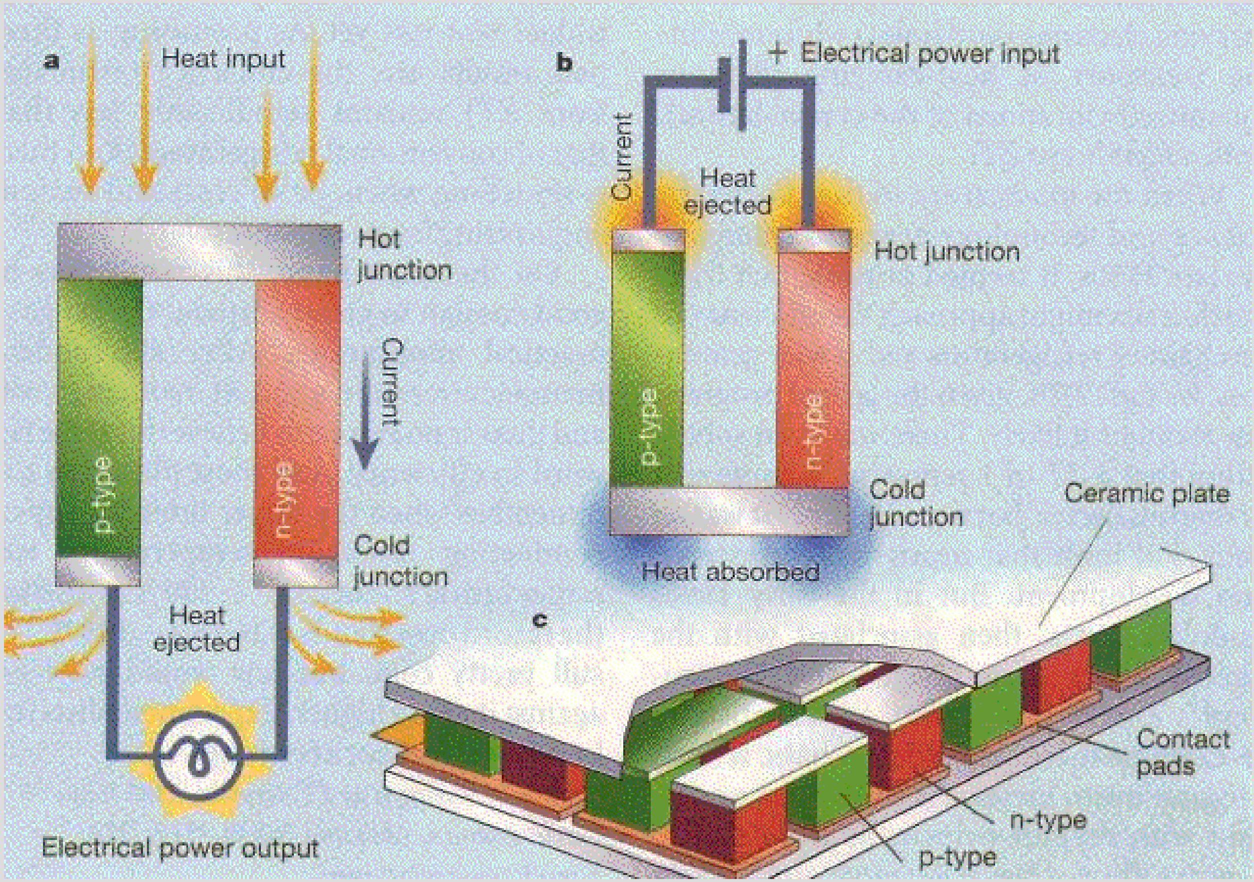
Thermoelectric Applications

- Power Generation
  - Radioisotopes
  - Nuclear reactor systems
  - Engine Exhaust
  - Process Industries
- Thermoelectric heating/cooling for temperature/ climate control
  - Equipment, components
  - Vehicular systems
- Thermoelectric conversion efficiency >>15% desired

TE Power Generation | TE Heating/Cooling



R&D Objectives at PNNL

- Develop economical fabrication processes for multilayer thin film thermoelectric materials with high conversion efficiency
- Establish measurement protocols for thin film thermoelectric materials
- Test and validate basic properties and conversion efficiency of promising thermoelectric materials
- Assist industry partners with testing and integration of thermoelectric materials in modules and vehicular systems

Thermoelectrics Projects

- Scale-up of Multilayer Quantum Well Thin Films for Vehicular Applications (DOE-EERE/FCVT)
- Thermoelectric materials for waste heat recovery from glass and aluminum production (DOE-EERE/ITP)

Why thin films?

- Properties of bulk materials determined primarily by composition and microstructure
- Properties of thin films
  - Microstructure
  - Composition
    - New and more compositions possible
  - Quantum and quantum well effects
  - Nanostructures
  - Thickness
  - Band gap engineering
- Higher TE power per gram possible
- New TEG device configurations
- Higher TEG power output

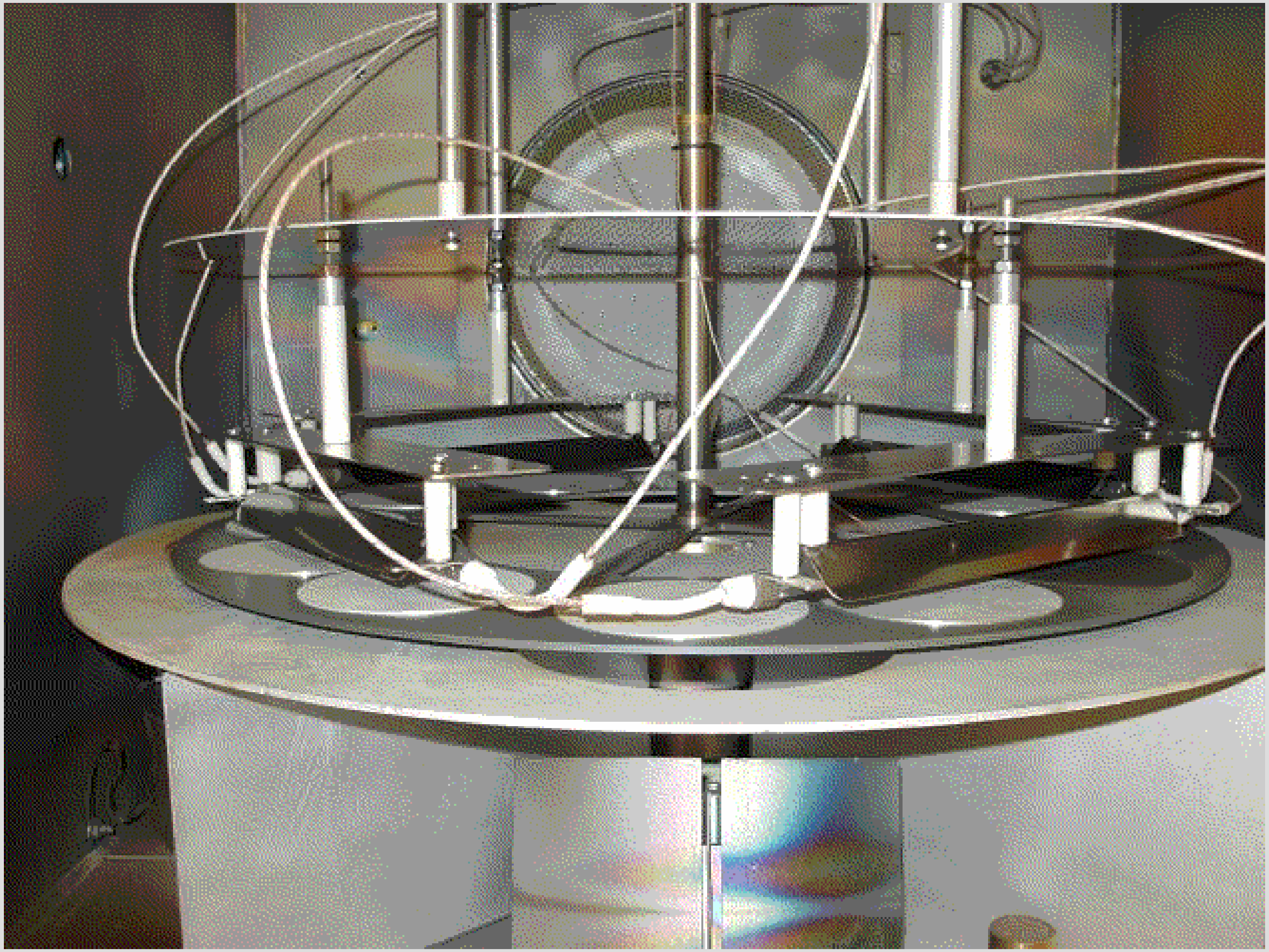
Important TE Properties

- Figure of merit ZT = sS2T/k
- TEG efficiency derived from ZT
- Power factor = sS2T (excludes k)
- PF between 0.01 and 0.05 desirable
  - For k ~ 0.02 W/cmK

TE Materials/Device Development at PNNL

- Multilayer thin film TE materials developed on single crystal Si
  - Si/SiGe
  - BC (Ge)
  - Power factors of multilayer > single layer films
  - High Power factor -> ZT > 2 (300K)
- Process for multilayer thin film coatings scaled up to 0.5 m2
- Development of multilayer thin film TE materials on non-Si substrates initiated
- Integration of thin film materials into TEG modules
- TEG efficiency measurements

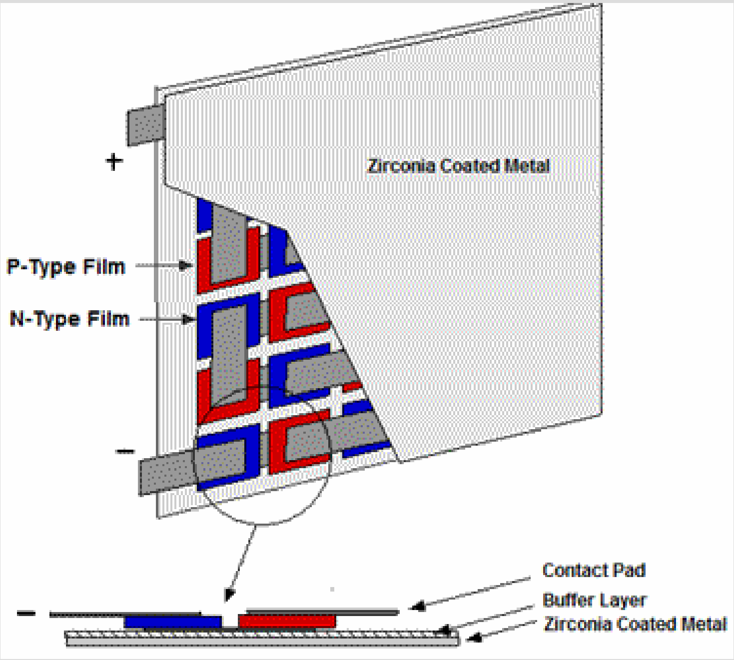
Scale up to 0.5 m2 Substrate



Battelle

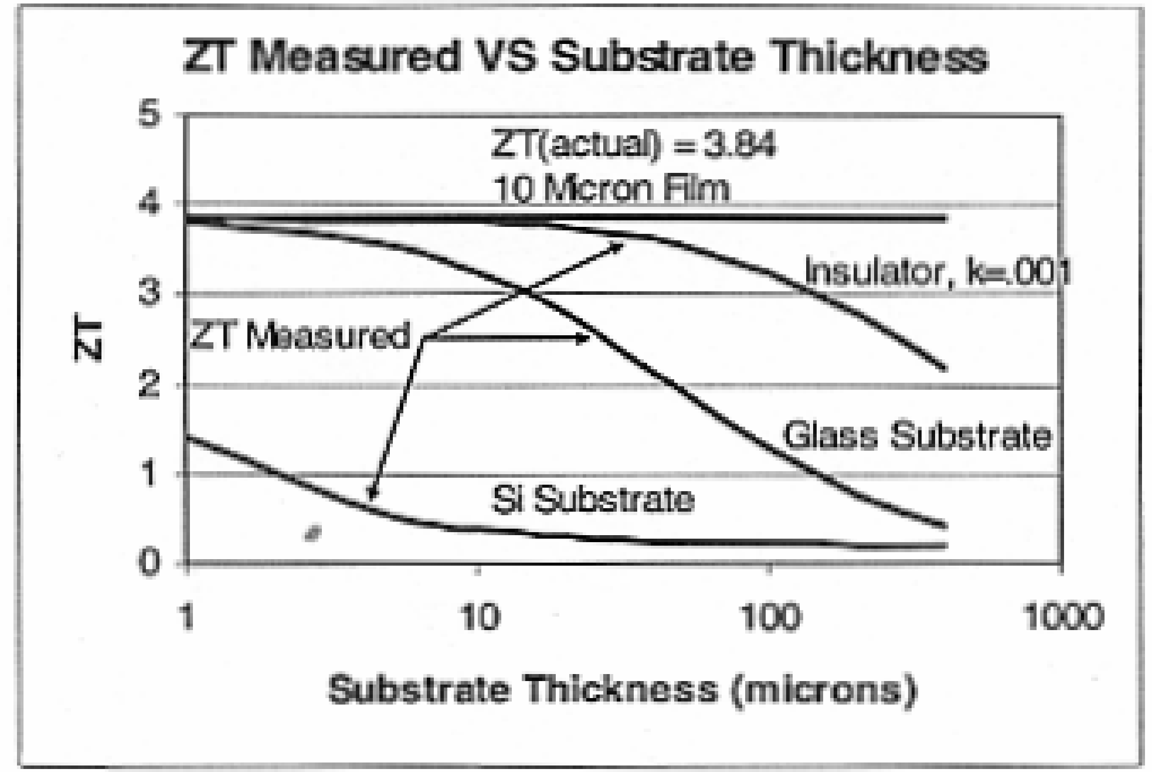
Improved thin-film materials, low-cost scale-up, device design and packaging, and thermal management required for applications

Large-Area Sputter Deposition



Device Design Schematic

Calculated Effective ZT



Bottom Line: High-efficiency TEG devices cannot be realized with high-ZT materials on Si substrates.

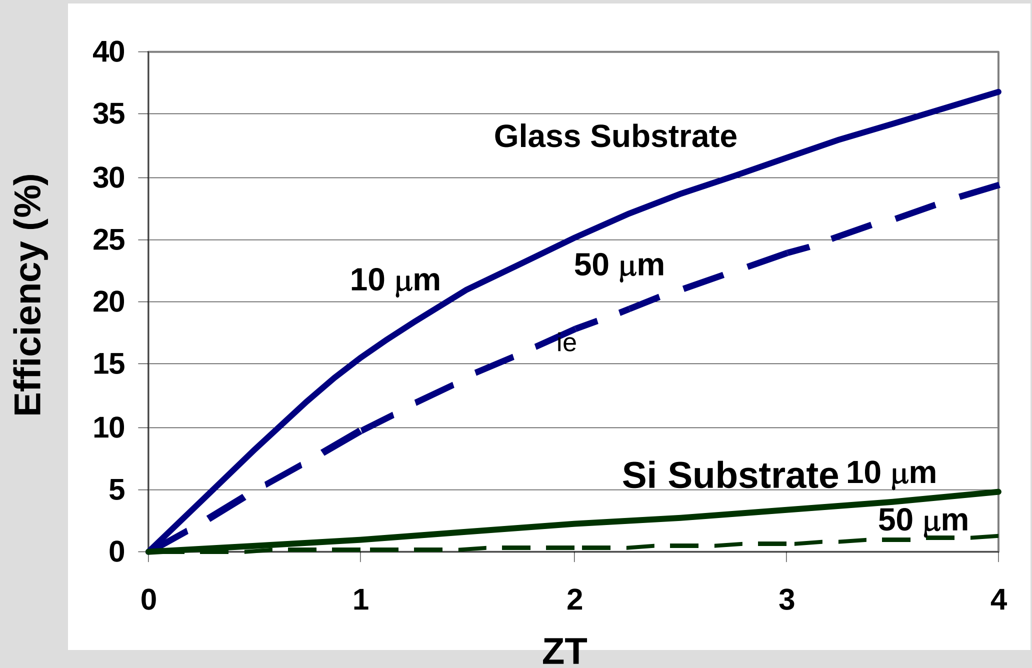
Reality check

- A lower ZT structure on a NC substrate will result in a higher TEG efficiency than a high ZT structure on a Si substrate

Effect Of Substrate For TE Thin Films

Assumptions

- 10 µm TE Film
- Z Constant from 300°K to 700 K
- ZT Calculated for T = 300°K
- Estimated Efficiency for ΔT = 400°K



The Challenge

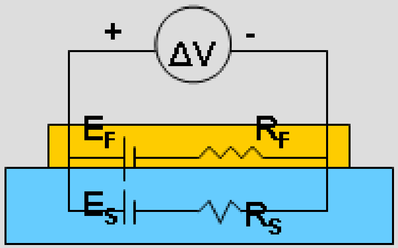
- Presently the power factor of TE films on NC substrates is an order of magnitude less than those on Si
- Grow highly oriented crystalline thin film multilayer materials on low cost, non crystalline substrates
  - Large area
  - Low cost
- Easy assembly/connection in a TE module
  - Not the same as bulk!

Measurement Approach

Key Features

- Ohmic Contacts Applied to Film and Substrate
- Soldered Thermocouples
- Gold Plated Heater Assemblies

Assumed Model

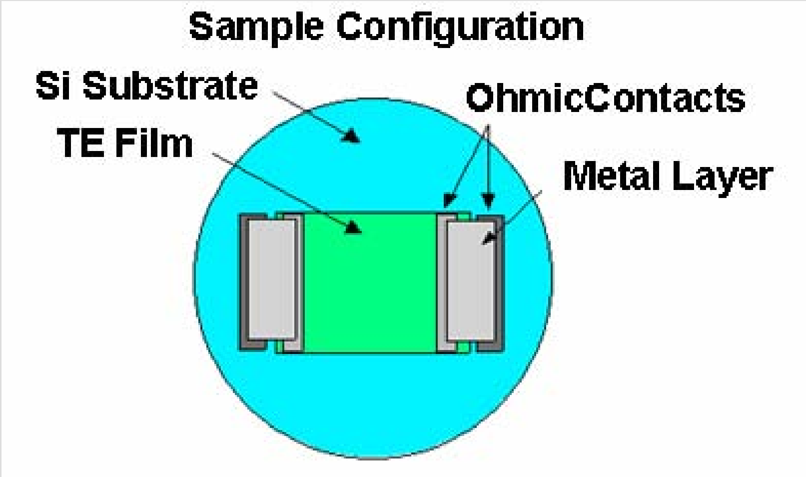


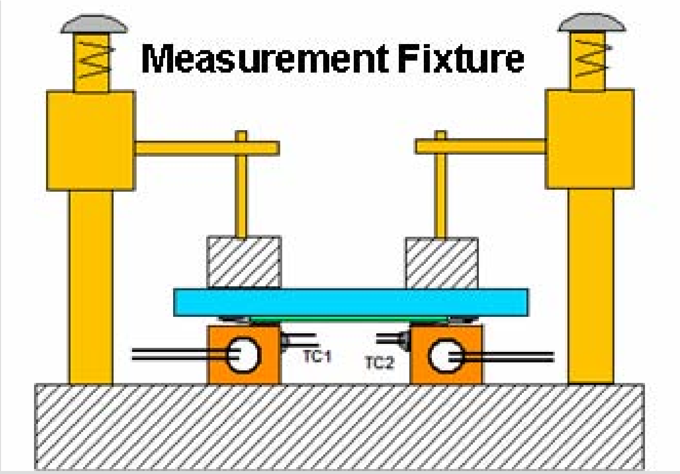
$$E_F = S_F(\Delta T)$$

$$R_{MEAS} = \frac{R_F R_S}{(R_F + R_S)}$$

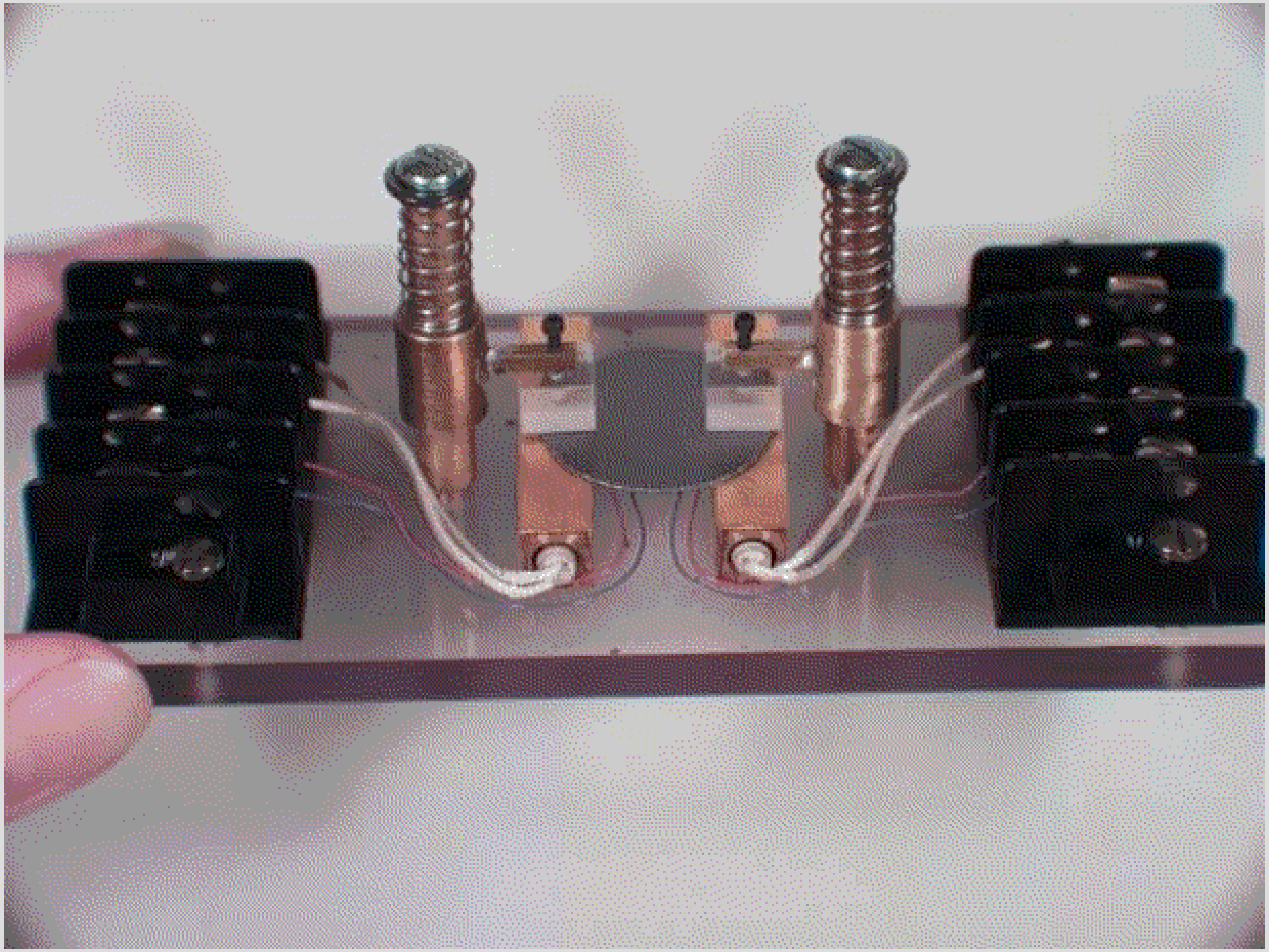
$$E_S = S_S(\Delta T)$$

$$S_{MEAS} = S_F + R_F\left(\frac{S_S - S_F}{R_S + R_F}\right)$$





Measurement Fixture



Thin film $Si/Si_{0.8}Ge_{0.2}$ on Si

Material	Electrical Conductivity ($ohm^{-1}cm^{-1}$)	Seebeck Coefficient (μV/ºC)	Power Factor
N-Silicon	60	600	0.0065
N-SiGe	35	800	0.0067
N-Si/SiGe ML	300	750	0.051

Thin film BC Results

Sample	Process	σ $(\Omega\text{–cm})^{-1}$	S (μV/ºC)	PF
B_9C-Ge	600 ºC	35	340	0.0012
B_9C-Ge	HT @ 1000ºC	1660	223	0.025
$(B_4C/B_9C\text{-}Ge)^{20}$	600 ºC HT@1000 ºC	2560	201	0.031
$(B_4C/B_9C\text{-}Ge)^{10}$	600 ºC	4160	233	0.068*
B_9C/ sapphire	600ºC HT @ 1000 ºC	118	170	0.001

New Materials: results to date

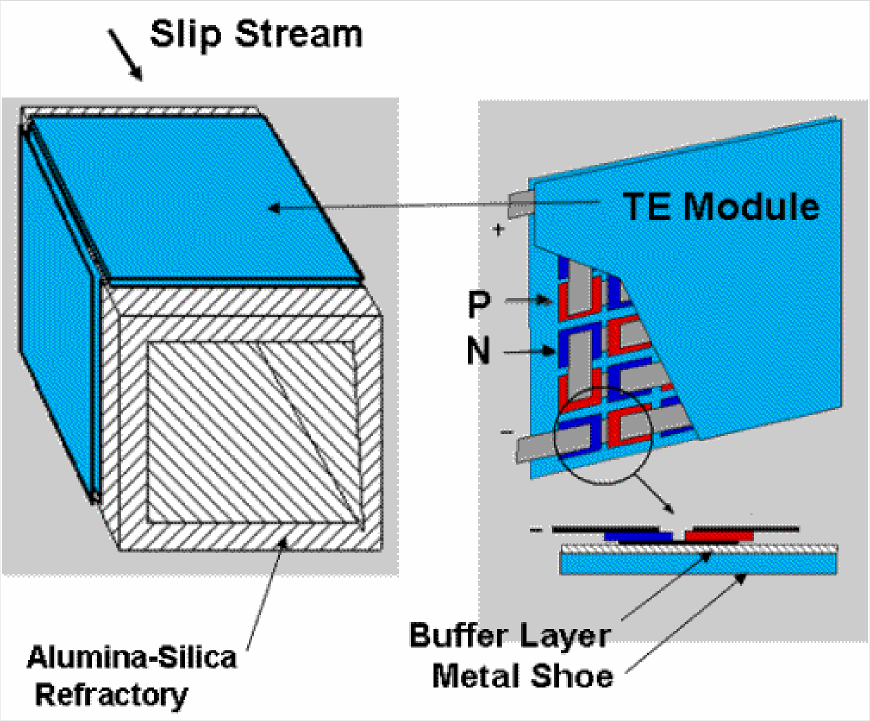
Sample No.	# Layers	S(μV/K)	$\sigma(\Omega.cm)^{-1}$	Power factor
1Q-S/FS	186	235	116	0.002
1S-S/FS	200	110	110	0.0011
1T-S/FS	300	127	127	0.0012

TEG System Components

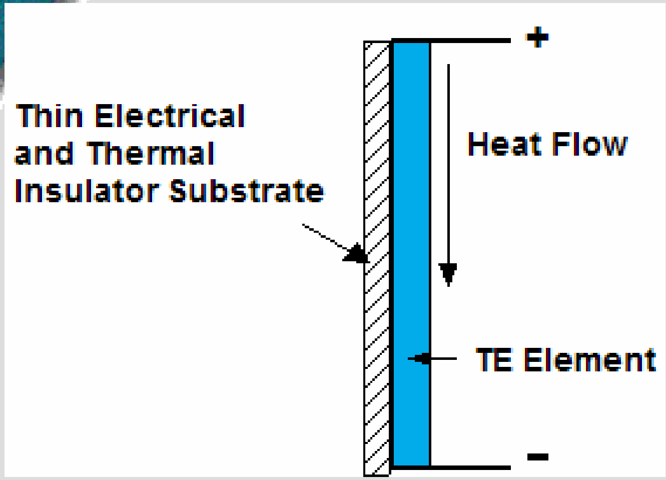
- Heat Exchanger Coupled to Waste Heat Source
- TEG Module
- Cold Side Heat Exchanger

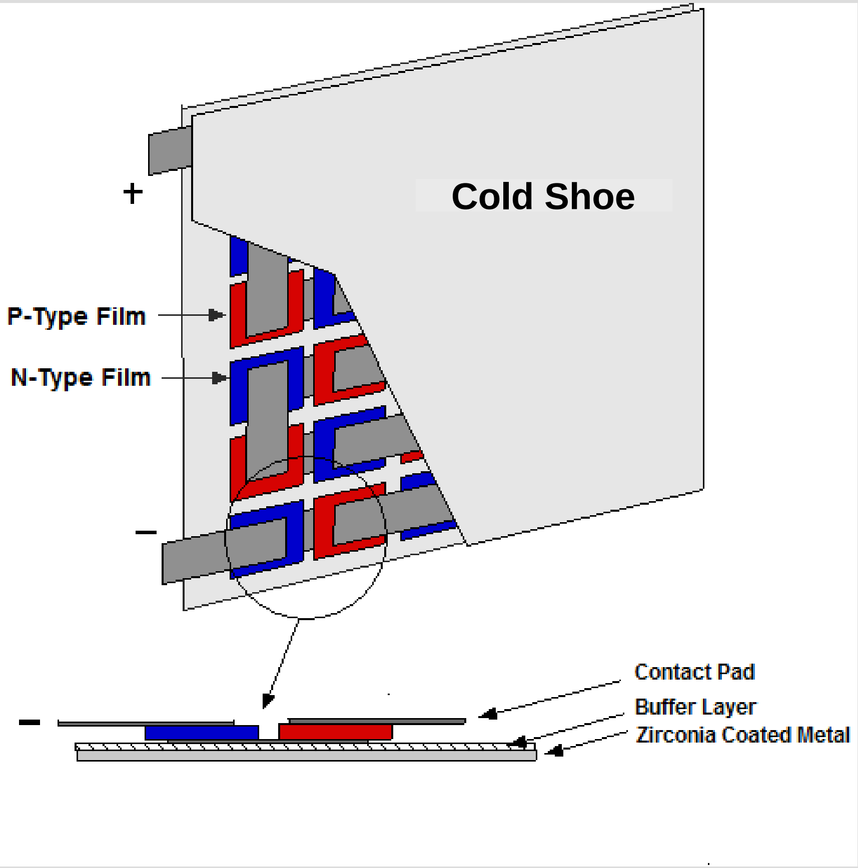
Preliminary Concept for Waste Heat Conversion Test Bed

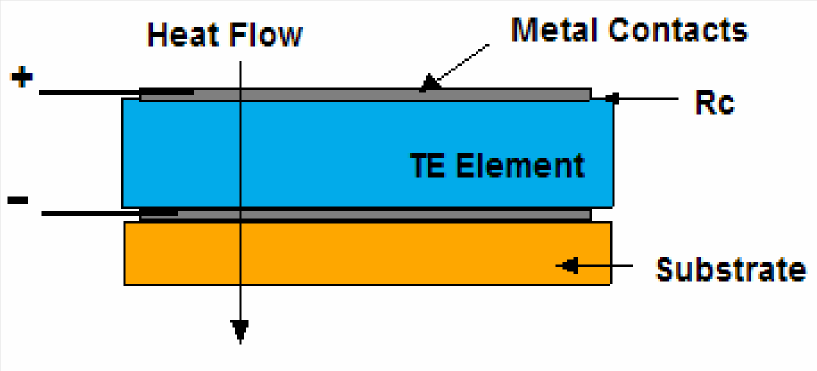
- Assumptions:
  - Utilize Slip Stream from Oxy-Furnace-Gas at 2700°F
  - Temperature at Hot Shoe 1160ºF (900°K) with 1 cm Firebrick
  - Using Water Cooling Cold Shoe at 73°F (300°K)
- Heat Flow into TE Modules:1.3 W/cm2
- Four 1 meter x 10 cm TE Converters:
  - 520 Watts @ 10% Efficiency
  - 1040 Watts @ 20% Efficiency



Configuration for Thin Films in Modules



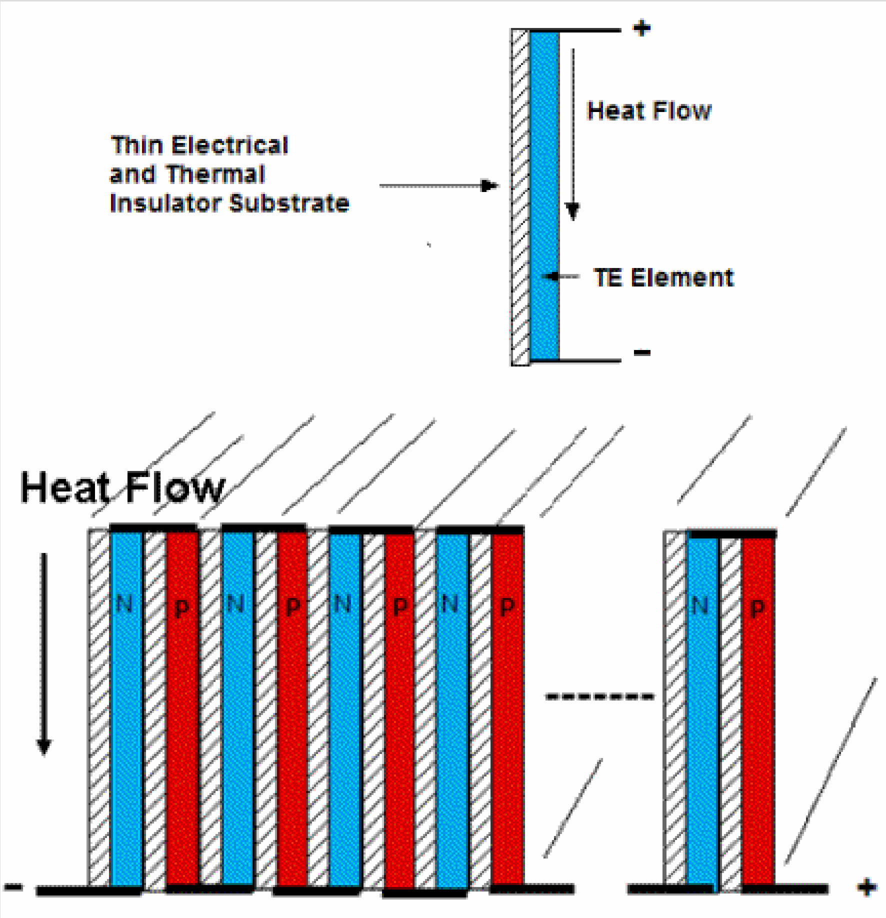




Thin Film Modules – Parallel Flow

Key Issues

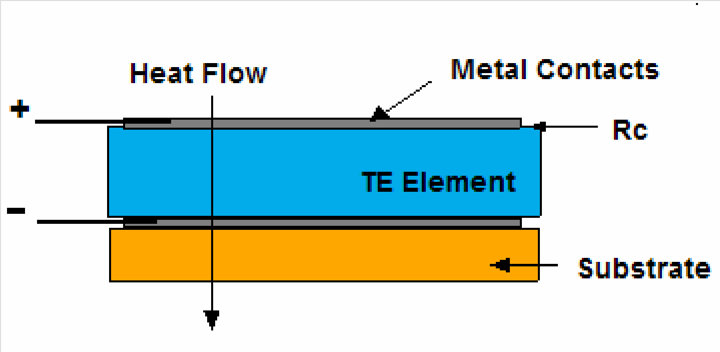
- Thin Film Deposition onThin Insulating Substrates
  - Thickness (10s of microns)
  - Stress in Films
  - TE Properties of Films
- Substrates
  - Thickness < 1 mil
  - Low Thermal and Electrical Conductivity
- Contact Technology



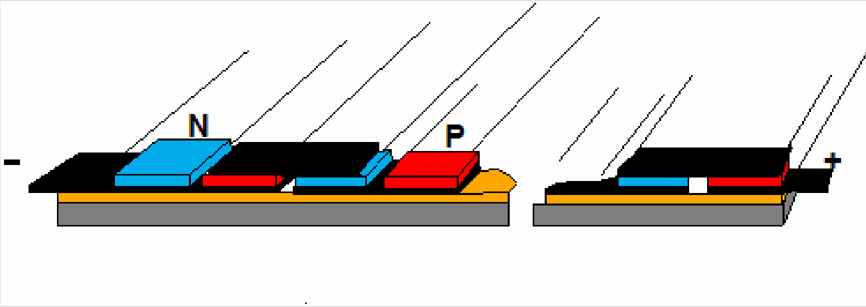
Thin Film Modules – Normal Flow

Key Issues

- Thin Film Deposition
  - Thickness (Need 100 microns)
  - Stress in Films
  - TE Properties of Films



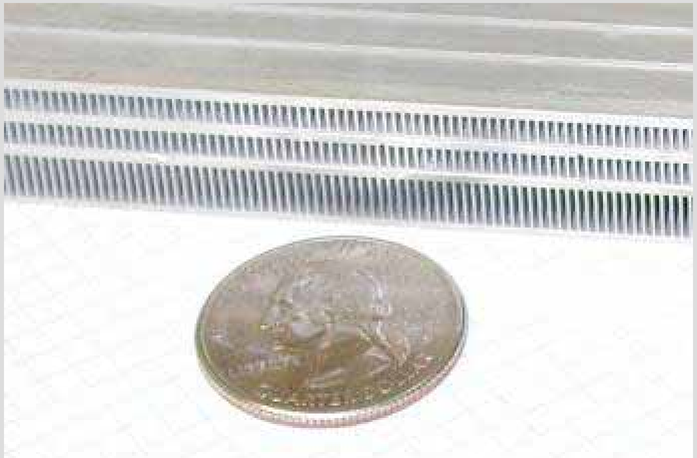
- Substrates
  - Good Thermal Conductivity
  - Electrically Insulating
  - Can Be Coated Metal Sheet



- Contact Technology
  - Contact Resistance Must Be Very Low

The Path Forward to Low Cost Thin Film TEG with High Conversion Efficiency

- Low cost deposition of multilayer TE thin film materials on non-Si substrates
- New TE materials – thin films and nanocomposites
- Integration into TEG module
  - Parallel or cross plane geometry
  - Electrical contacts
  - Efficient heat exchangers (cold/hot side)



Examples of aluminum finned microchannel heat exchanger structures

Status of TE Thin Films

- Multilayers perform much better than single layers
- Substrate thermal conductivity critical
  - Models show that high ZT and conversion efficiencies cannot be achieved using Si substrates (even for very high ZT ~ 4)
  - Disordered microstructure important for low thermal conductivity
- Low cost high efficiency thin film TE structures can be best realized on non-crystalline substrates
- All development work now focused on non-crystalline substrates
  - Presently BC system offer promise, but needs further work
  - New thin film materials being evaluated
  - Efficiencies > 15 % can be realized with ZT ~2

Accomplishments (all projects)

- Evaluated Si/SiGe and B4C/B9C multilayer coatings for TEG applications
- Critical measurements for thin film TE materials
- Initiated development of new thin film TE materials on low cost substrates
- Evaluated and proceeding with TEG module development
  - Materials and substrate requirements
  - Device components
  - Device geometries
  - Device assembly/contacts
  - Testing