Nanostructured Multilayer Films for Advanced Detector and Thermoelectric Applications

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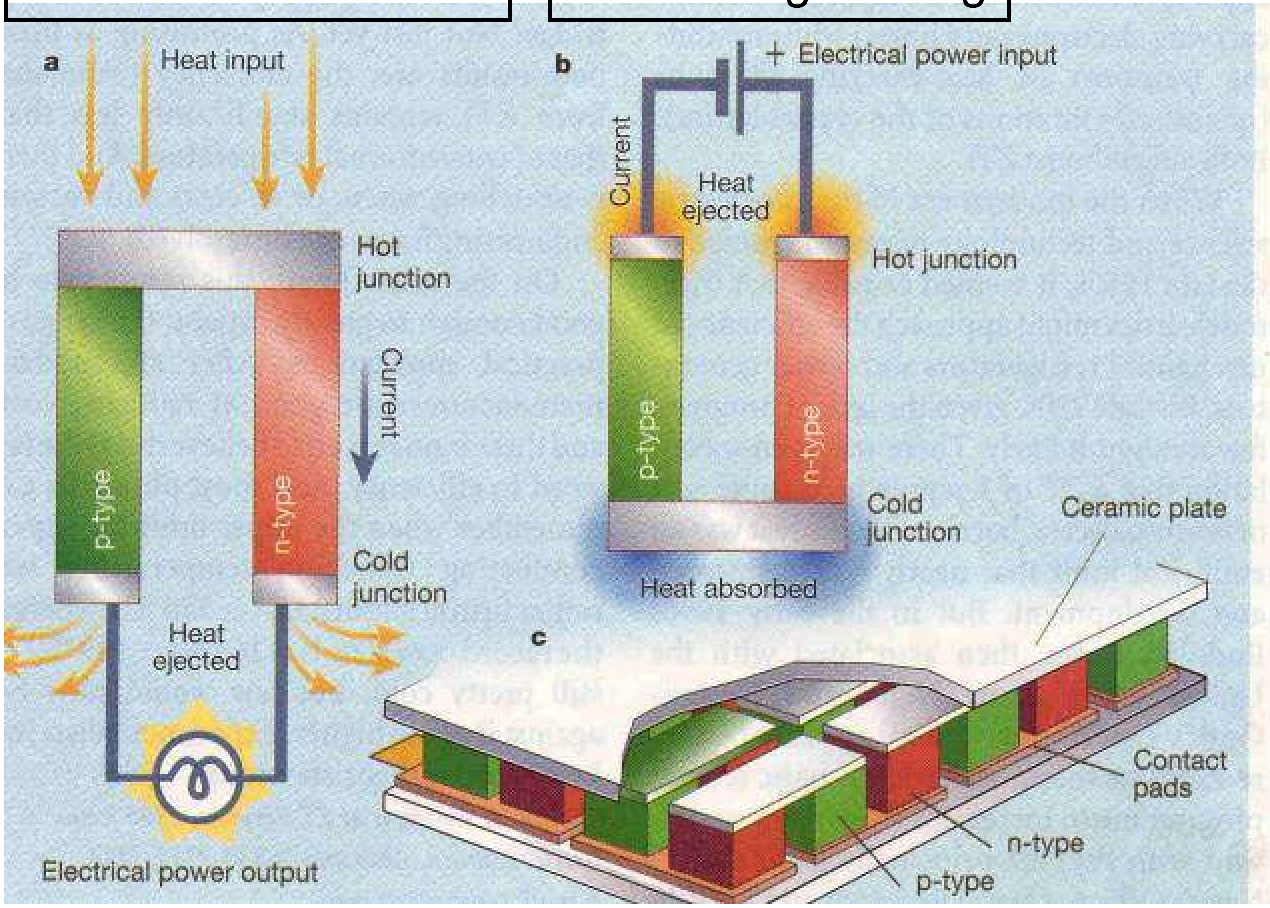
Thermoelectric Applications

- 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

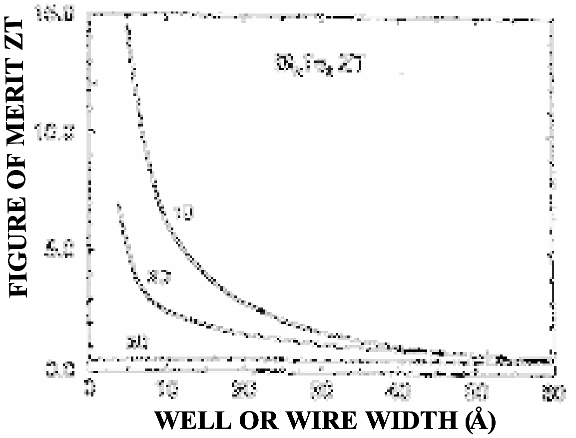
TE Heating/Cooling

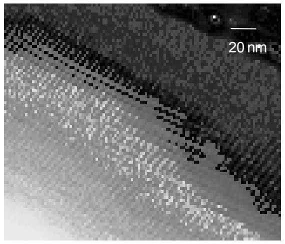


Detector Applications

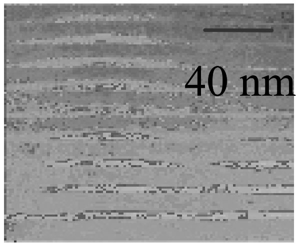
- Low voltage power source
- Stand alone wireless sensory devices
- Photonic
- Neutron

Tailored nanostructured materials could be key to high ZT and reliable performance

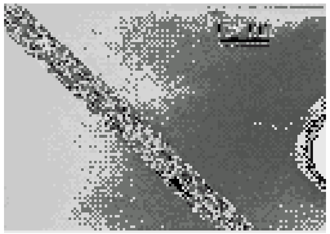




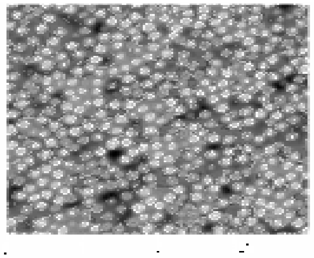
Bulk



Superlattice
2D



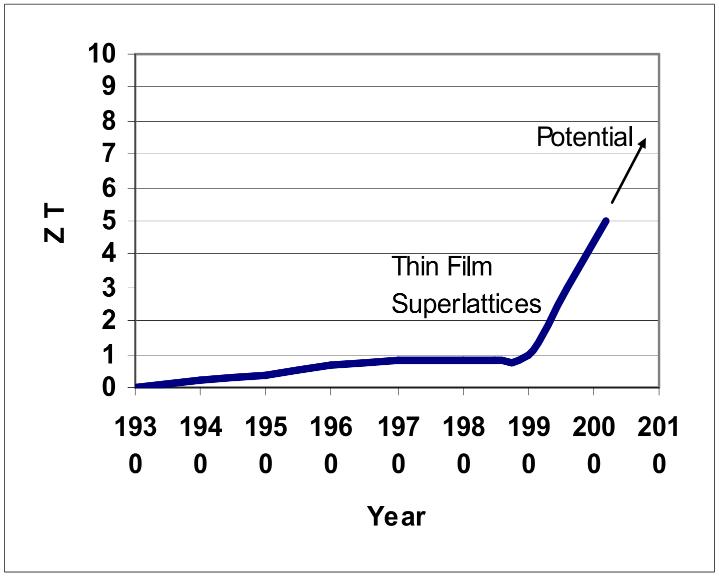
Nanowire
1D



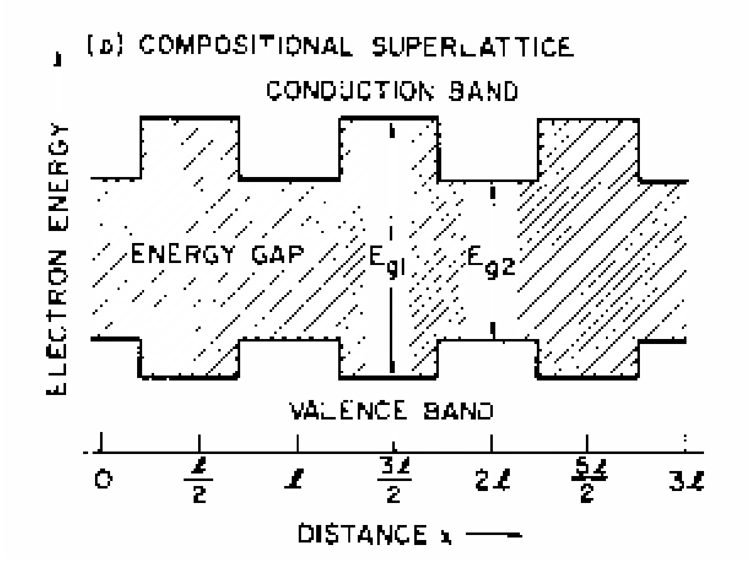
Quantum Dots
0D

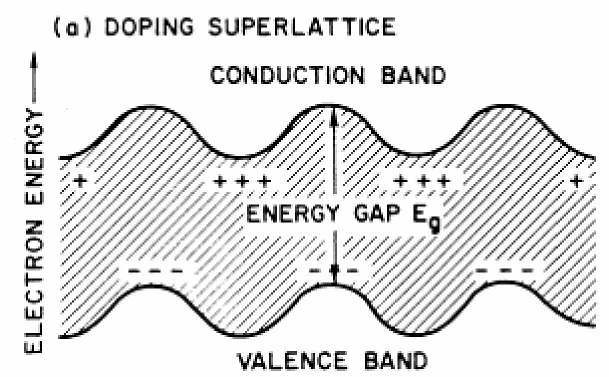
Promise of Quantum Confinement in Nanostructures

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



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.

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

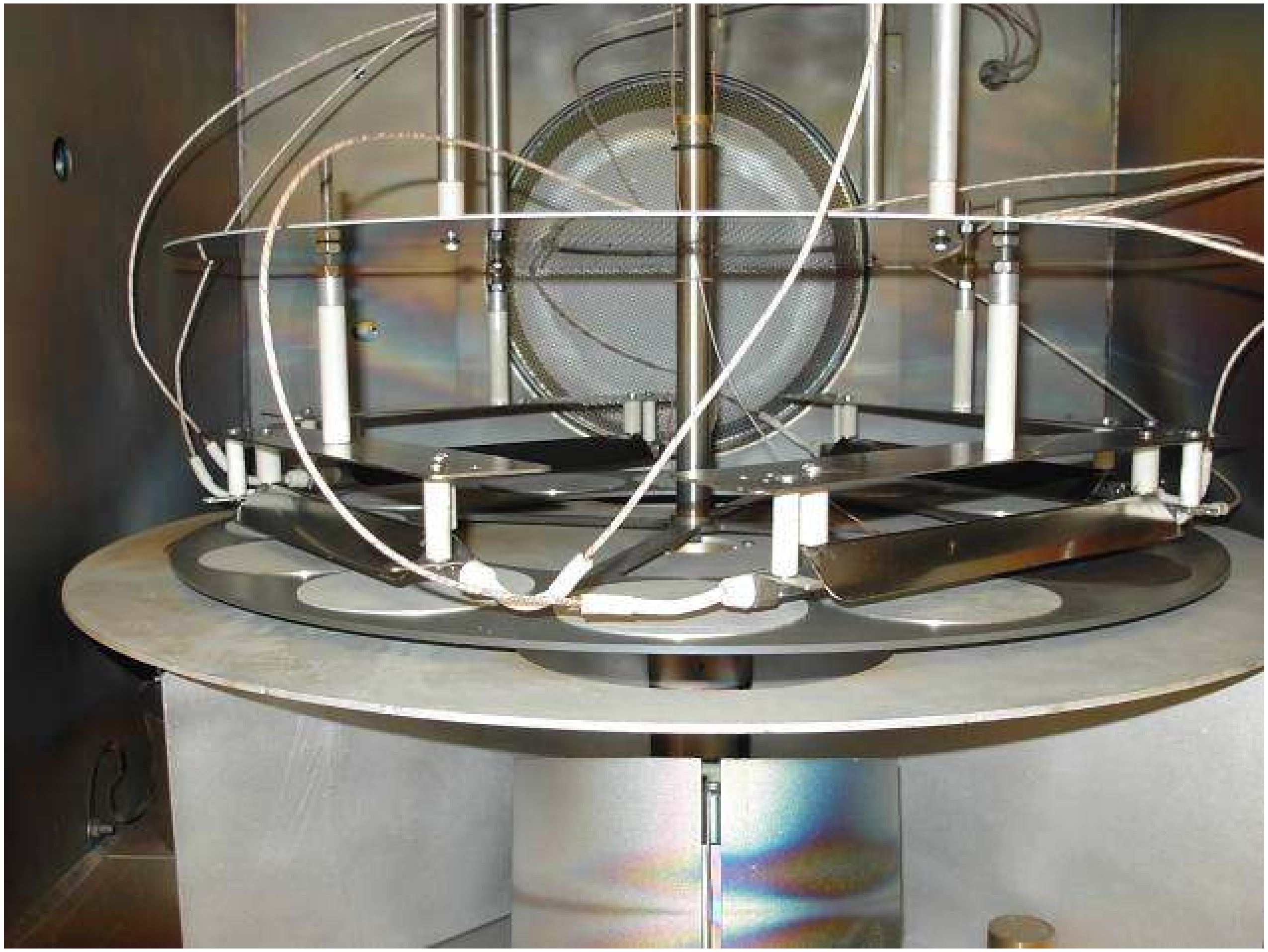
Important TE Properties

- Figure of merit $ZT = \sigma S^2 T/\kappa$
- TEG efficiency derived from ZT
- Power factor = $\sigma S^2 T$ (excludes κ)
- PF between 0.01 and 0.05 desirable
  - For $\kappa \sim 0.02$ W/cmK

TE Materials/Device Development at PNNL

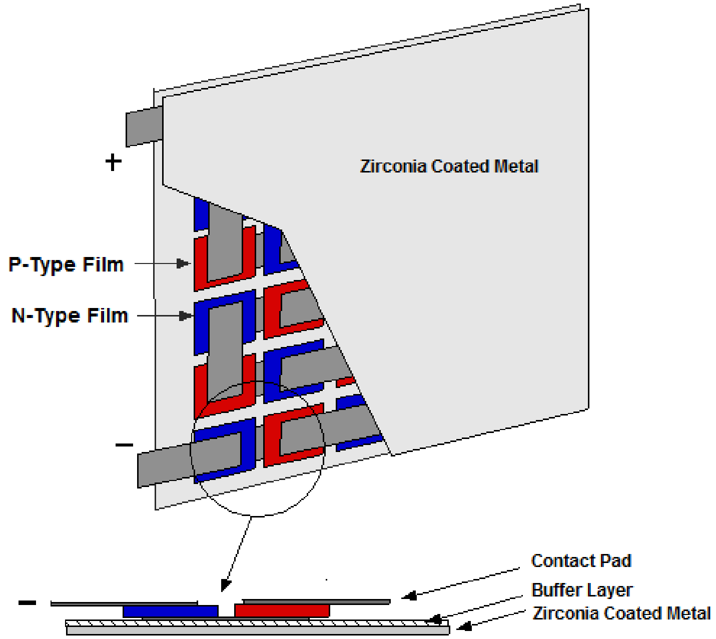
- Multilayer thin film TE materials developed on single crystal Si
  - Si/SiGe
  - BC (Ge)
  - Power factors of multilayer > single layer films
  - High Power factor -> ZT > 2 (300K)
- Process for multilayer thin film coatings scaled up to 0.5 m^2
- *Development of multilayer thin film TE materials on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

Scale up to 0.5 m^2 Substrate



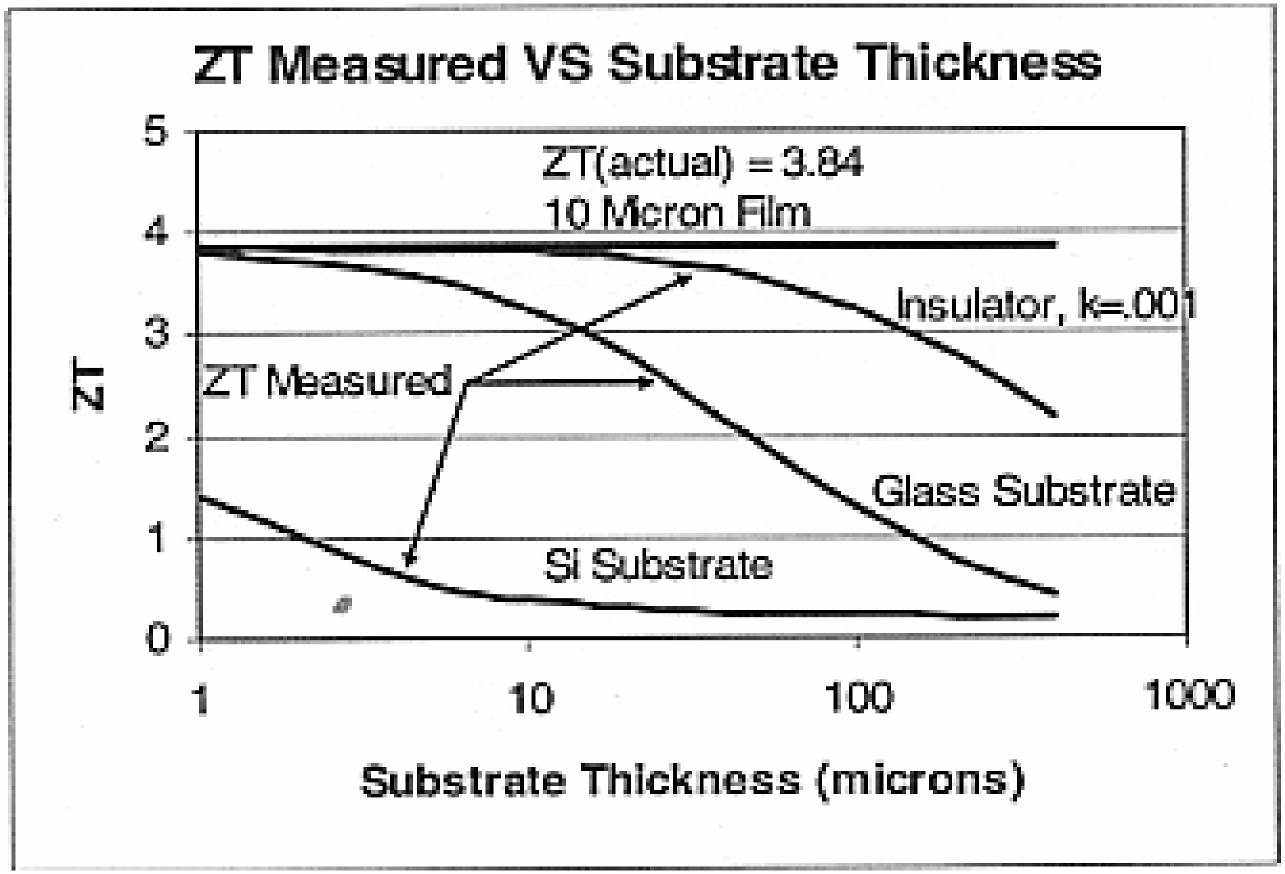
Improved thin-film materials, low-cost scale-up, device design and packaging, and thermal management required for applications

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.

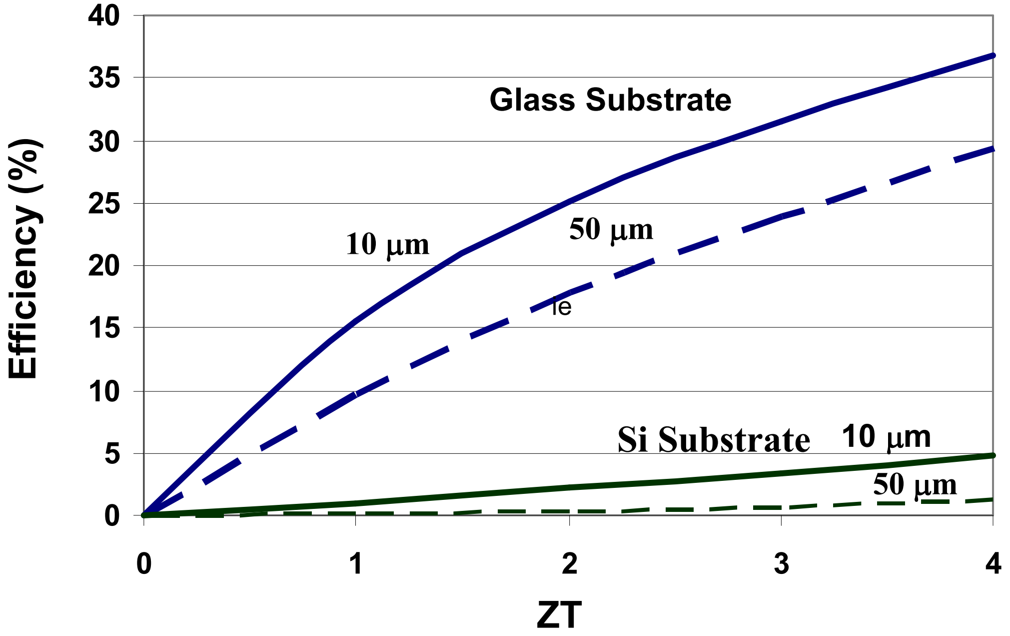
Reality check

- 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

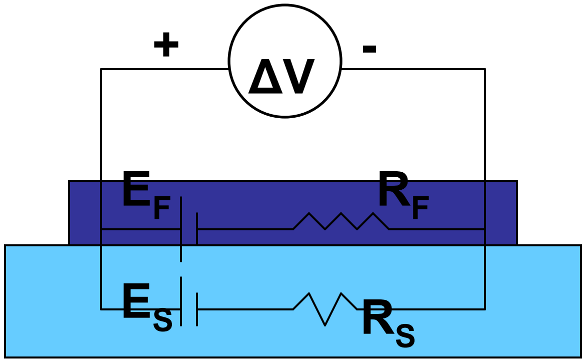
- Presently the power factor of TE films on NC substrates is an order of magnitude less than those on Si
- *Grow highly oriented crystalline thin film multilayer materials on low cost, non crystalline substrates*
  - *Large area*
  - *Low cost*
  - ***Web substrates might be important***
- *Easy assembly/connection 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



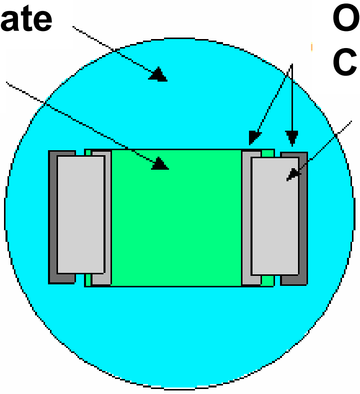
$E_F = S_F(\Delta T)$

$E_S = S_S(\Delta T)$

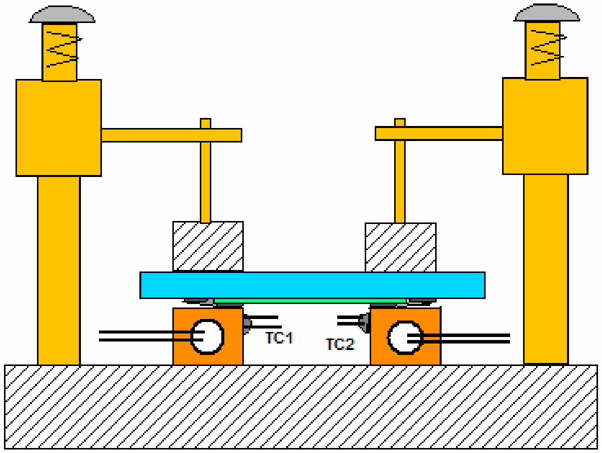
$$R_{MEAS} = \frac{R_F\,R_S}{(R_F + R_S)}$$

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

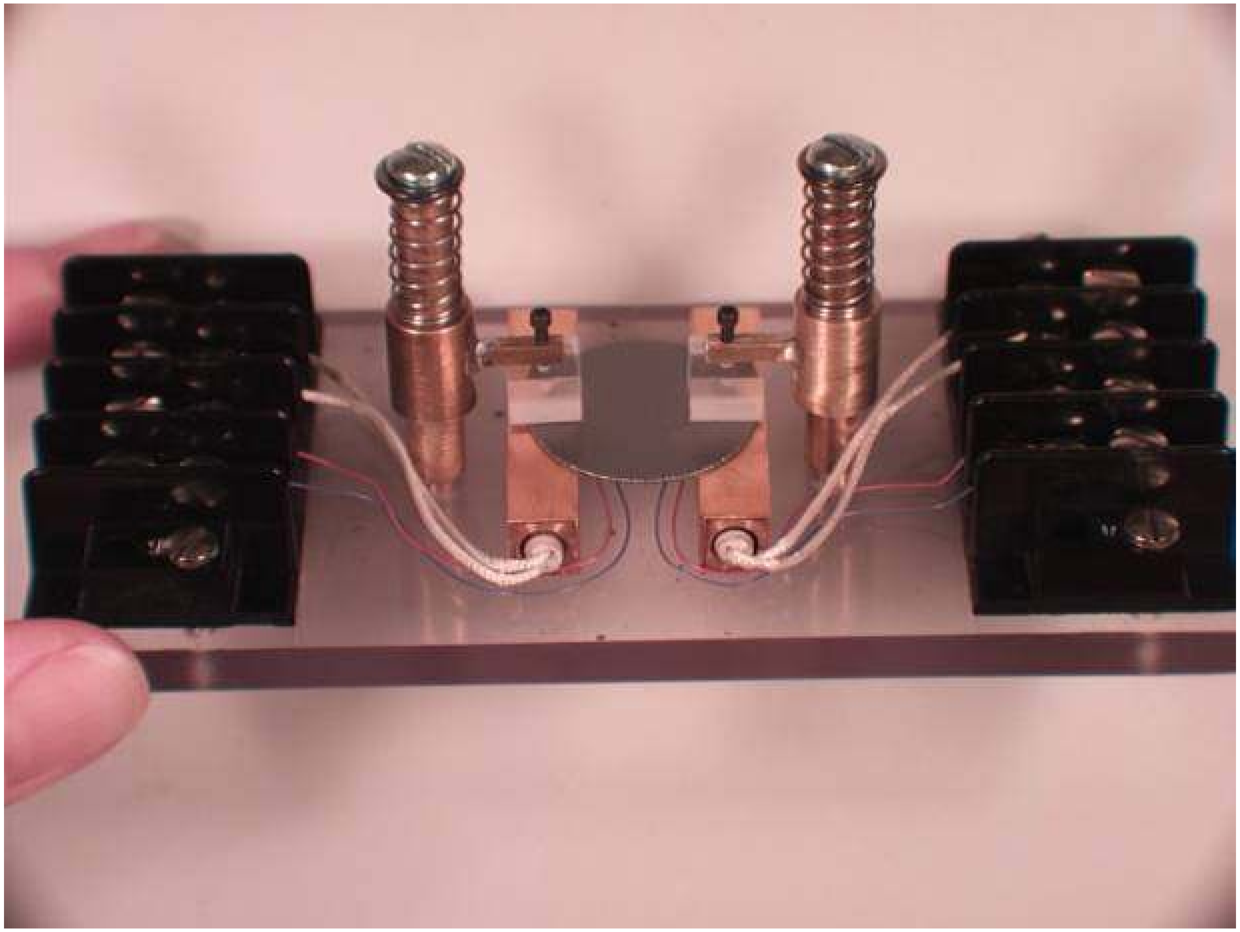
Sample Configuration



Measurement Fixture



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)	$\sigma(\Omega.\text{cm})^{-1}$	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

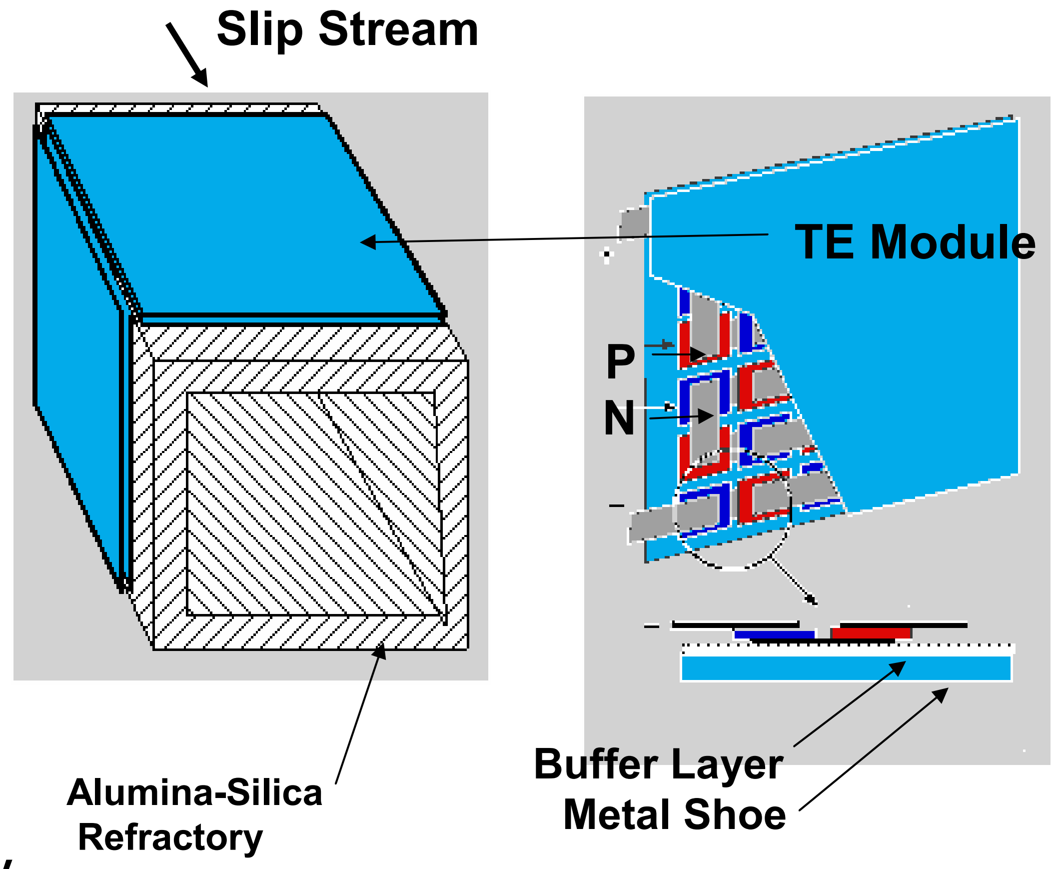
- Heat Exchanger Coupled to Waste Heat Source
- TEG Module
- Cold Side Heat Exchanger

Preliminary Concept for Waste Heat Conversion Test Bed

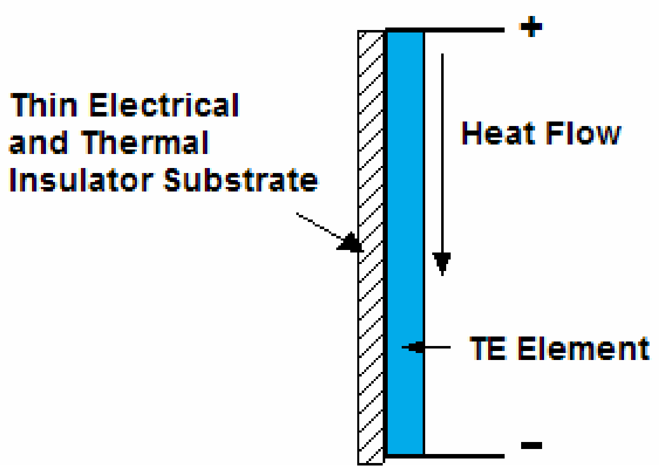
- **Assumptions:**
  - **Utilize Slip Stream from Oxy-Furnace-Gas at 2700°F**
  - **Temperature at Hot Shoe 1160ºF (900°K) with 1 cm Firebrick**
  - **Using Water Cooling Cold Shoe at 73°F (300°K)**

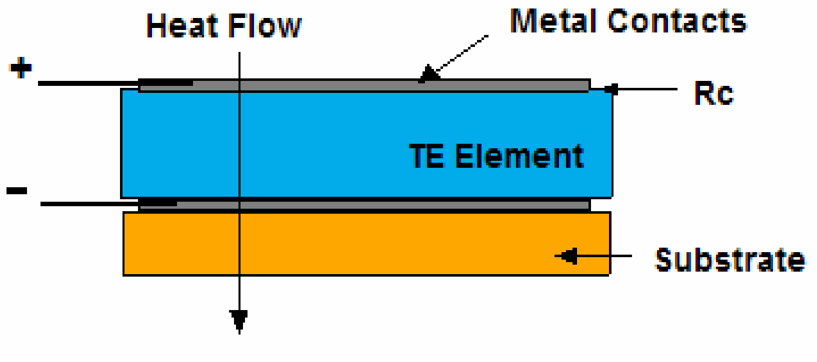
- **Heat Flow into TE Modules: 1.3 W/cm^2**

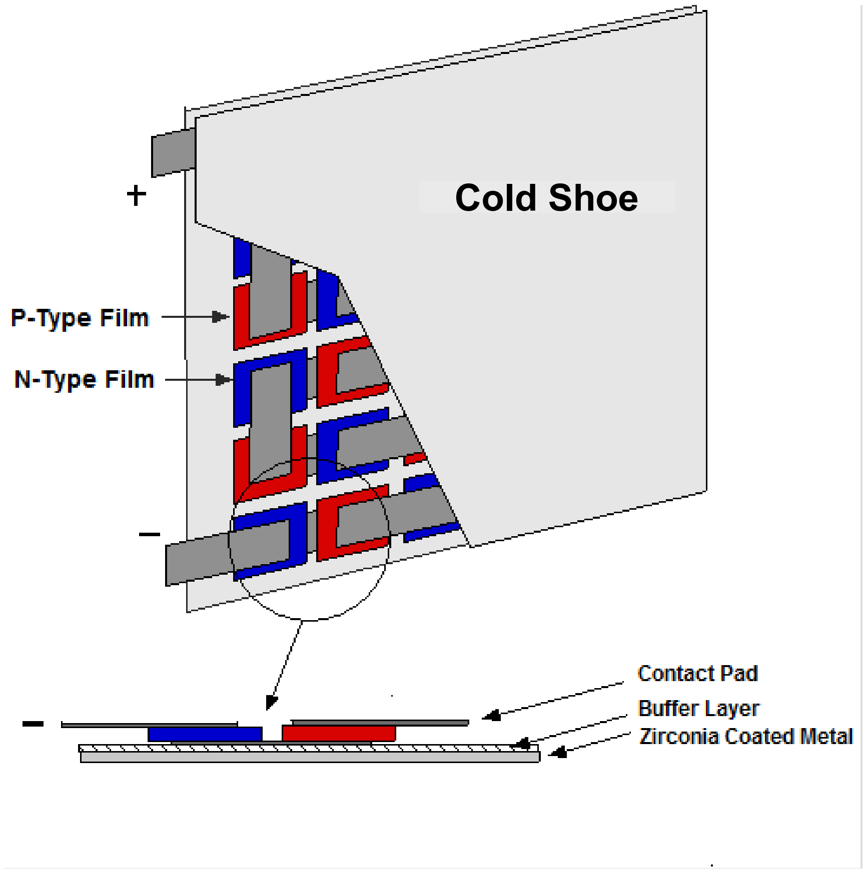
- **Four 1 meter x 10 cm TE Converters:**
  520 Watts @ 10% Efficiency
  1040 Watts @ 20% Efficiency



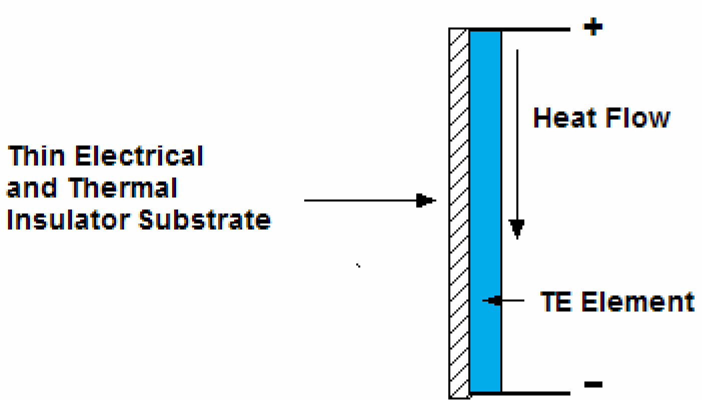
Configuration for Thin Films in Modules





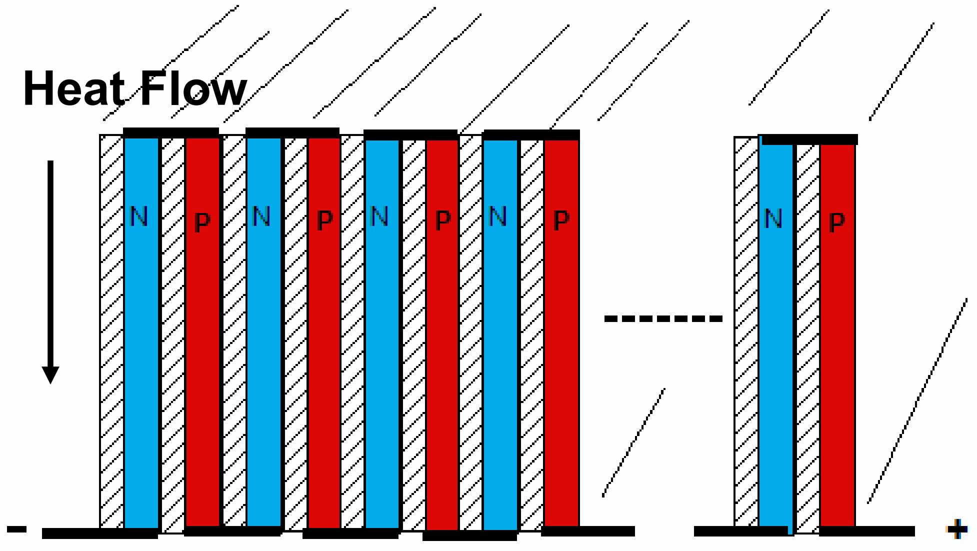


Thin Film Modules – Parallel Flow



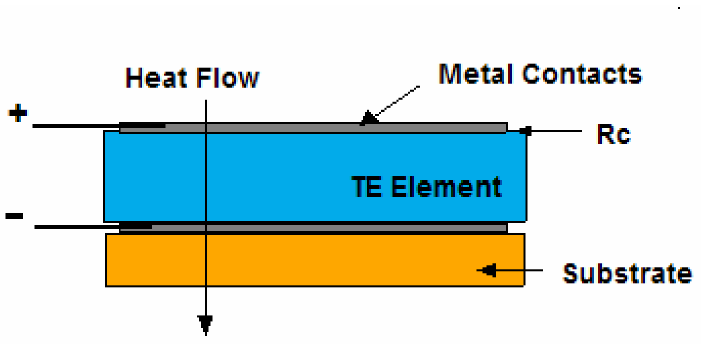
Key Issues

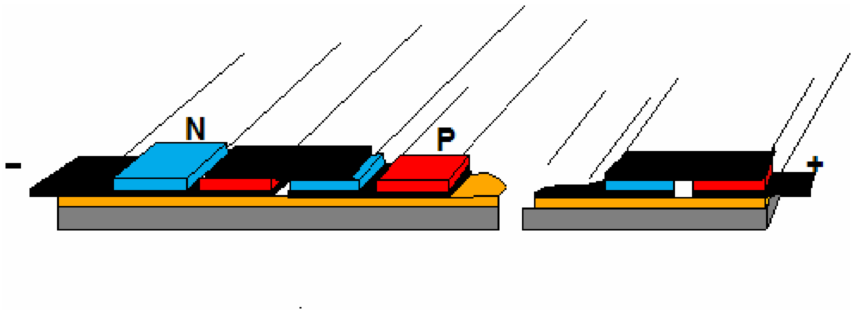
- ☐ **Thin Film Deposition on Thin Insulating Substrates**
  - Thickness (10s of microns)
  - Stress in Films
  - TE Properties of Films
- ☐ **Substrates**
  - Thickness < 1 mil
  - Low Thermal and Electrical Conductivity
- ☐ **Contact Technology**



Thin Film Modules – Normal Flow

Key Issues

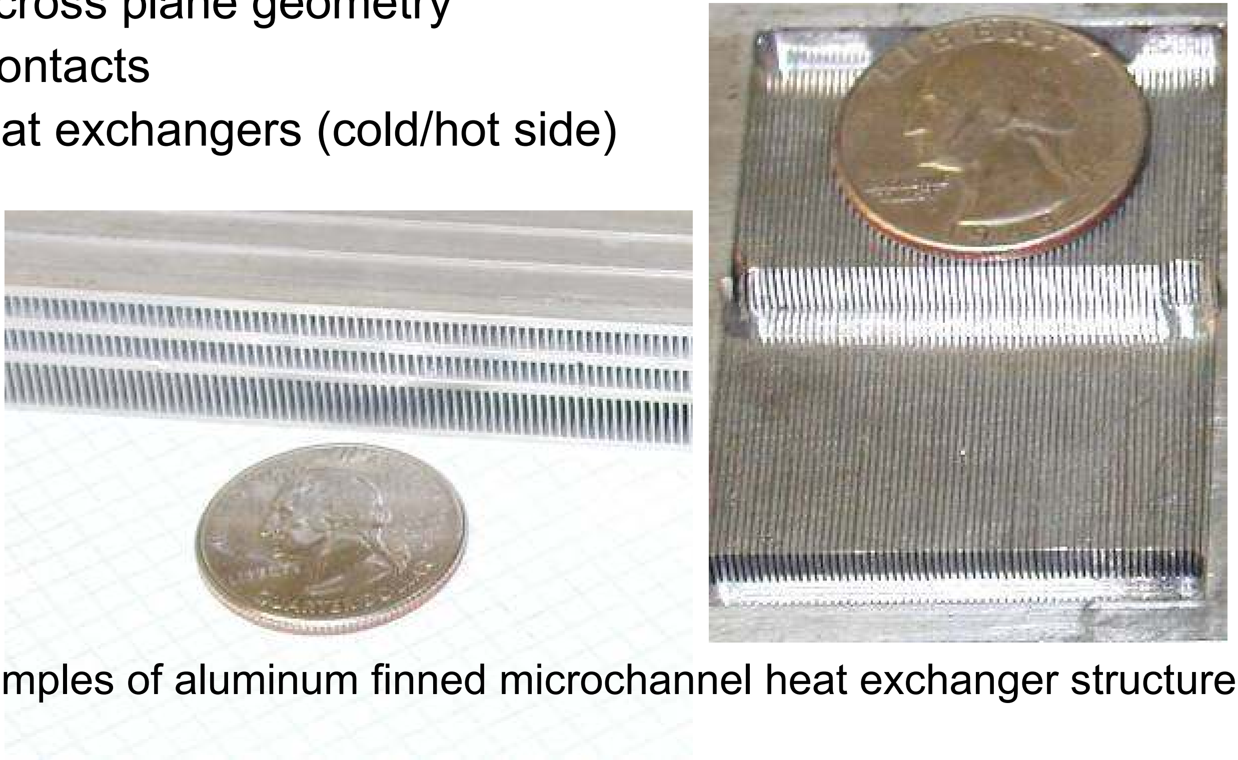




- ❑ **Thin Film Deposition**
  - Thickness (Need 100 microns)
  - Stress in Films
  - TE Properties of Films
- ❑ **Substrates**
  - Good Thermal Conductivity
  - Electrically Insulating
  - Can Be Coated Metal Sheet
- ❑ **Contact Technology**
  - Contact Resistance Must Be Very Low

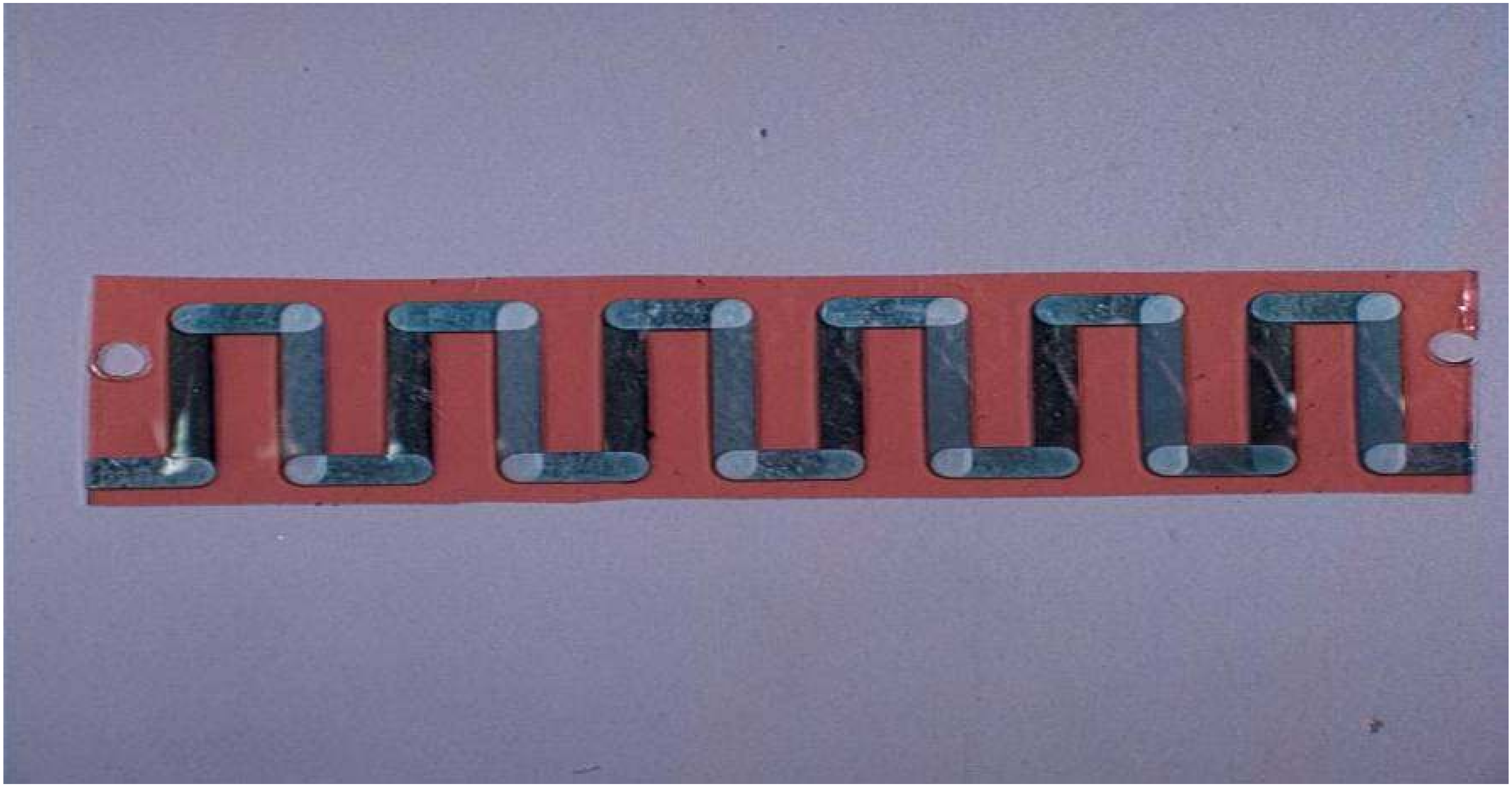
The Path Forward to Low Cost Thin Film TEG with High Conversion Efficiency

- 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

Thin film Bi_2Te_3 p-n TE module on polyimide web substrate



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

Other Nanostructured TE Materials Systems

- Bulk Bi_2Te_3: ZT ~ 1
  - Marlowe
- $Bi_2Te_3/Sb_2/Te_3$ quantum well: ZT ~ 2, maybe 2.5
  - MBE
  - RTI
- PbTe/PbSnTe quantum dots: ZT > 2
  - MIT Lincoln Laboratory
  - MBE
- Nanoparticle Ag in oxide

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