Nanostructured Multilayer Films for Advanced Detector and Thermoelectric Applications

Peter M. Martin, L. C. Olsen
Pacific Northwest National Laboratory
Richland, WA
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**
  \[ \gg 15\% \text{ desired} \]
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.
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

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 $\kappa$)
• PF between 0.01 and 0.05 desirable
  – For $\kappa \sim 0.02 \text{ W/cmK}$
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
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
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

\[ E_F = S_F(\Delta T) \]
\[ E_S = S_S(\Delta T) \]
\[ R_{MEAS} = \frac{R_F R_S}{R_F + R_S} \]
\[ S_{MEAS} = S_F + R_F \left( \frac{S_S - S_F}{R_S + R_F} \right) \]
Measurement Fixture
Thin film Si/\text{Si}_{0.8}\text{Ge}_{0.2} \text{ on Si}

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Conductivity (ohm$^{-1}$cm$^{-1}$)</th>
<th>Seebeck Coefficient (µV/ºC)</th>
<th>Power Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Silicon</td>
<td>60</td>
<td>600</td>
<td>0.0065</td>
</tr>
<tr>
<td>N-SiGe</td>
<td>35</td>
<td>800</td>
<td>0.0067</td>
</tr>
<tr>
<td>N-Si/SiGe ML</td>
<td>300</td>
<td>750</td>
<td>0.051</td>
</tr>
</tbody>
</table>
# Thin film BC Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Process</th>
<th>$\sigma$  ((\Omega\cdot\text{cm})^{-1})</th>
<th>$S$  ((\mu\text{V/°C}))</th>
<th>PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_9C$-Ge</td>
<td>600 °C</td>
<td>35</td>
<td>340</td>
<td>0.0012</td>
</tr>
<tr>
<td>$B_9C$-Ge</td>
<td>HT @ 1000°C</td>
<td>1660</td>
<td>223</td>
<td>0.025</td>
</tr>
<tr>
<td>$(B_4C/B_9C$-Ge)$^{20}$</td>
<td>600 °C</td>
<td>2560</td>
<td>201</td>
<td>0.031</td>
</tr>
<tr>
<td>$(B_4C/B_9C$-Ge)$^{10}$</td>
<td>600 °C</td>
<td>4160</td>
<td>233</td>
<td>0.068*</td>
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<tr>
<td>$B_9C$-Ge/ sapphire</td>
<td>600°C</td>
<td>118</td>
<td>170</td>
<td>0.001</td>
</tr>
</tbody>
</table>
## New Materials: results to date

<table>
<thead>
<tr>
<th>Sample No.</th>
<th># Layers</th>
<th>$S(\mu V/K)$</th>
<th>$\sigma(\Omega\cdot cm)^{-1}$</th>
<th>Power factor</th>
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</thead>
<tbody>
<tr>
<td>1Q-S/FS</td>
<td>186</td>
<td>235</td>
<td>116</td>
<td>0.002</td>
</tr>
<tr>
<td>1S-S/FS</td>
<td>200</td>
<td>110</td>
<td>110</td>
<td>0.0011</td>
</tr>
<tr>
<td>1T-S/FS</td>
<td>300</td>
<td>127</td>
<td>127</td>
<td>0.0012</td>
</tr>
</tbody>
</table>
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 1160°F (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
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 $\text{Bi}_2\text{Te}_3$ 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 $\text{Bi}_2\text{Te}_3$: $\text{ZT} \sim 1$
  - Marlowe

- $\text{Bi}_2\text{Te}_3/\text{Sb}_2/\text{Te}_3$ quantum well: $\text{ZT} \sim 2$, maybe 2.5
  - MBE
  - RTI

- $\text{PbTe}/\text{PbSnTe}$ quantum dots: $\text{ZT} > 2$
  - MIT Lincoln Laboratory
  - MBE

- Nanoparticle Ag in oxide