NASA’s integrated vehicle health management (IVHM) program offers the potential to improve aeronautical safety, reduce cost and improve performance by utilizing networks of wireless sensors. Development of sensor systems for engine hot sections will provide real-time data for prognostics and health management of turbo-engines. Sustainable power to embedded wireless sensors is a key challenge for prolong operation. Harvesting energy from the environment has emerged as a viable technique for power generation.

Thermoelectric generators provide a direct conversion of heat energy to electrical energy. Micro-power sources derived from thermoelectric films are desired for applications in harsh thermal environments. Silicon based alloys are being explored for applications in high temperature environments containing oxygen. Chromium based p-type Si/Ge alloys exhibit Seebeck coefficients on the order of 160 μV/K and low thermal conductance of 2.5 to 5 W/mK. Thermoelectric properties of bulk and thin film silicides will be discussed.
Self-Powered Wireless Sensors

Fred Dynys & Ali Sayir
NASA Glenn Research Center
Cleveland, OH
Integrated Vehicle Health Monitoring

Real Time Health Diagnostics From Remote Airplane

Examine Sensor Data for Early Detection of Component Failure

Wireless Sensor Network to Monitor Vehicle System

Repair

Proactive Maintenance

Future airplanes will have a wireless sensor network for monitoring vehicle system health, flight environment and structural integrity.
RF Wireless Sensor

Physical Event

Sensor → Processor → Actuator

Physical Response

MEMS Device

Memory

Radio → Controller → Sensor/Actuator

Power Supply

Energy Storage
Energy Harvesting

• Reduction in MEMS energy consumption is the key to enabling energy harvesting
• Looking for renewable energy sources in the application environment.
• Infinite power source.

MEMS Technology

300 cm³

10 cm³

Power

1 mW

500 mW

Power Supply

Battery

Energy Harvesting

Fuel Cells

Pressure

Air Flow

Vibration

Solar

Thermal

Biological

<table>
<thead>
<tr>
<th>Source</th>
<th>μW/cm³</th>
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<td>Solar</td>
<td>15 -15000</td>
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<tr>
<td>Air Flow</td>
<td>~380</td>
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<tr>
<td>Biological</td>
<td>~330</td>
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<tr>
<td>Vibration</td>
<td>100 - 400</td>
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<tr>
<td>Thermal</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Pressure</td>
<td>&lt;100</td>
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</table>
Wireless Sensors

Wireless technology allows sensors to be placed in remote locations

Self powered wireless sensors require technological advancement in energy harvesting

Sensors/power supply fabricated from materials that are operational in high temperature environments

GRC Sensors
Temperature
Heat Flux

J. Wrbanek & G. Fralick
Thermoelectric Converters

Seebeck Effect

ΔT

ΔV

Low Efficiency (<7%) – Niche Markets

Radioisotope Thermoelectric Generator

Proven Technology

• Long Life-Continuous Power- 20+ years
• Durable in Harsh Environments
• No Moving Parts
Thermoelectrics

Desired Properties of TE’s
- High Seebeck coefficient (S)
- High electrical conductivity (σ)
- Low thermal conductivity (κ)

Efficiency

\[ \eta_{\text{max}} = \frac{\Delta T}{T_{\text{hot}}} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT+T_{\text{cold}}}/T_{\text{hot}}} \]

Nanotechnology

Figure of Merit

\[ ZT = \frac{S^2 \sigma}{\kappa} \]

Conversion Efficiency (%)

Low ΔT - Low Efficiency

YEAR

Average ZT

ΔT=20 °C

ΔT=15 °C

ΔT=10 °C

ΔT=5 °C

ΔT=1 °C
Standard Thermoelectric Materials

Operational Conditions
• Temperatures 300 - 600 °C
• Environment – Varying $P_{O_2}$

Silicides
• Environmental/Chemical Stability
• Low Electrical Resistance
• Low Formation Temperature
## Electrical Transport

### Semiconductor/Metallic Behavior

<table>
<thead>
<tr>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>VIIIIA</th>
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<td>TiSi₂</td>
<td>V₃Si</td>
<td>V₃Si₂</td>
<td>Cr₃Si</td>
<td>MnSi₁.₇</td>
<td>α–FeSi₂</td>
<td>CrSi₂</td>
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<tr>
<td></td>
<td>V₅Si₃</td>
<td>V₅Si₃</td>
<td>Cr₅Si₃</td>
<td></td>
<td>β–FeSi₂</td>
<td>CrSi₂</td>
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<tr>
<td></td>
<td>VSi₂</td>
<td>V₅Si₃</td>
<td>CrSi₂</td>
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<td>Co₂Si</td>
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<td>Ni₂Si</td>
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<td>YSi₂</td>
<td>ZrSi₂</td>
<td>Nb₃Si</td>
<td>NbSi₂</td>
<td>Ru₂Si₃</td>
<td>RhSi₂</td>
<td>Pd₂Si</td>
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<tr>
<td>HfSi₂</td>
<td>TaSi₂</td>
<td>ReSi₁.₇</td>
<td>OsSi₂</td>
<td>IrSi</td>
<td>IrSi₃</td>
<td>PtSi</td>
</tr>
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</table>

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<tr>
<th></th>
<th>Band Gap</th>
<th>Type</th>
<th>Mobility Cm²/SV</th>
<th>K W/mK @300 K</th>
<th>S mV/K @500K</th>
<th>ρ 10⁻⁵ Ω–m @500K</th>
<th>TE 10⁻⁶/°C</th>
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<tr>
<td>CrSi₂</td>
<td>~0.35 ev</td>
<td>P</td>
<td>15</td>
<td>6.8</td>
<td>220</td>
<td>7.2</td>
<td>11-14</td>
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<tr>
<td>MnSi₁.₇</td>
<td>~0.7 ev</td>
<td>P</td>
<td>40</td>
<td>2.9</td>
<td>160</td>
<td>3.1</td>
<td>16</td>
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<td>CoSi</td>
<td>------</td>
<td>N</td>
<td>----</td>
<td>14.3</td>
<td>-50</td>
<td>0.2</td>
<td>11.1</td>
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</table>
Thermoelectric Module I

**TE Materials**
- Thickness $\sim$ 10’s $\mu$m
- Electrical conductivity $\geq 10^4 \, \Omega^{-1}\text{m}^{-1}$
- Larger $\Delta T$
- Thick film stresses

**Substrate**
- Thickness
- Low thermal conductivity
- Electrically insulating

**Interconnect Technology**
- Low contact resistance

Compact geometry permits parallel connection of modules for reduced series resistance.

Source: P.M. Martin et al., PNNL

![Graph of ZT vs Substrate Thickness](image)

Micro-Cooler
Thermoelectric Module II

**TE Materials**
- Thickness ~ 100’s μm
- Small ΔT – Limited TE Thickness
- Electrical Conductivity

**Substrate**
- Good thermal conductivity
- Electrically insulating

**Interconnect Technology**
- Low contact resistance

![Diagram of Thermoelectric Module II](image)

ΔT

252 Legs
Magnetron Sputtering

- Lower Deposition Pressure
- Reduces Contamination
- Increases Deposition Rate
- Complex Alloys

3 RF Guns
600 W

Sample Rotation
Heater
RT – 800 °C
Magnetron Sputtering

**Deposition Rate**
- Distance – \(1/(d)^{1/2}\)
- Material
- Pressure

**Targets**
- Commercial Sources
- Single Crystal – B-Si, Sb-Si

**Co-Sputtering**
Adjust Deposition Rate To Control Composition

![Graphs showing deposition rate vs. RF power and power vs. deposition rate for different materials and pressures.]

- **Deposition Rate** vs. **RF Power (Watts)**
  - Distance 13 cm
  - B doped Si
  - Sb doped Si
  - 5 mT, 10 mT, 20 mT, 40 mT

- **Deposition Rate** vs. **Power (watts)**
  - Distance 13 cm
  - Pressure 5 mT
  - Ge, Si, Cr, Mn, Co, CrSi₂
Y$_2$O$_3$ Stabilized ZrO$_2$ Substrate

Surface Roughness 500 nm

Deposit film retains the substrate surface roughness

\[
\text{YSZ} \sim 2.5 \text{ W/mK Thermal Conductivity}
\]
\[
11 \times 10^{-6}/\text{K Thermal Expansion}
\]

Total Film Stress = $\sigma_{\text{TE}} + \sigma_{\text{process}} + \sigma_{\text{external}}$

Film Failure is a Concern-Thickness > 1 $\mu$m
TE Property Measurements

Seebeck/Resistivity

ZEM-3

ΔT 0-50 °C/Furnace RT-1000 °C

6-25 mm

4-8 mm

Hall Measurement

Capability-RT-527 °C/Field-2 Telsa

 Carrier Mobility & Density

\[ ZT = \frac{S^2 \sigma}{\kappa} T \]

Power Factor

\[ S^2 \sigma \]

\[ \approx 10^{19} \]

Carrier concentration [cm\textsuperscript{-3}]
Silicon Films

Si, B-Si, Sb-Si & Si/Ge Films

- Amorphous Films
- Deposition Temperatures – up to 750 °C
- High Resistivity – $10^9 \, \Omega \cdot m$
- Anneal – 800 °C - Resistivity – $10^6 \, \Omega \cdot m$

Metal Induced Crystallization

Silicon Film

Substrate

Pre-layer Ni, Cr

Lower Crystallization Temperature

Knaepen et al., Thin Solid Films, 516, 4946, 2008
Mn-Si

Deposition Temperature – 450 °C
XRD – Crystalline Phases – Mn$_{15}$Si$_{26}$
Film Thickness – 2.4 μm & 2.6 μm

800 °C Anneal

No Adhesion Failures – Tape Test

*2 Hou et al., Appl. Phys. A, 80, 1807, 2005
Mn-Si

Hall Measurements

<table>
<thead>
<tr>
<th>Si/Mn 78/22 %</th>
<th>$\rho$ ($10^{-5}$ $\Omega$–m)</th>
<th>Carrier (1/cm$^3$)</th>
<th>Mobility (cm$^2$/VS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Deposit</td>
<td>14.1</td>
<td>$2 \times 10^{21}$</td>
<td>0.25</td>
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<td>600°C-4 hrs</td>
<td>31</td>
<td>$5 \times 10^{20}$</td>
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<td>800°C-2 hrs</td>
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<td>$2 \times 10^{20}$</td>
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</table>

<table>
<thead>
<tr>
<th>B-Si/Ge/Mn 61/37/2 %</th>
<th>$\rho$ ($10^{-5}$ $\Omega$–m)</th>
<th>Carrier (1/cm$^3$)</th>
<th>Mobility (cm$^2$/VS)</th>
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<td>As Deposit</td>
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<td>0.3</td>
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<td>600°C-4 hrs</td>
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<td>800°C-2 hrs</td>
<td>50</td>
<td>$2 \times 10^{19}$</td>
<td>7.3</td>
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</tbody>
</table>

Microstructure

- Film Cracking
- No observable Grain Structure
- Defects due to Substrate
Co-Si

Deposition Temperature – 450 °C & 250 °C
Film Thickness – 1.5 μm & 1.8 μm

800 °C Anneal

No Adhesion Failures – Tape Test

*3 Ren et al., J. Alloys & Comp., 392, 50, 2005

Open Symbols 2nd Measurement
Co-Si

Hall Measurement

<table>
<thead>
<tr>
<th>Si/Co</th>
<th>$\rho$ (10⁻⁵ Ω·m)</th>
<th>Carrier (1/cm³)</th>
<th>Mobility (cm²/VS)</th>
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<tbody>
<tr>
<td>50/50 %</td>
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<tr>
<td>As Deposit</td>
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<td>5 x 10²⁰</td>
<td>11</td>
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<td>600°C-4 hrs</td>
<td>0.8</td>
<td>5 x 10²⁰</td>
<td>14</td>
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<td>800°C-2 hrs</td>
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<td>7 x 10²⁰</td>
<td>4</td>
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<tr>
<td>Sb-Si/Co</td>
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<tr>
<td>73/27 %</td>
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<tr>
<td>As Deposit</td>
<td>0.3</td>
<td>1 x 10²²</td>
<td>2.5</td>
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<td>600°C-4 hrs</td>
<td>0.1</td>
<td>1.5 x 10²²</td>
<td>5</td>
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<tr>
<td>800°C-2 hrs</td>
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<td>1 x 10²²</td>
<td>3</td>
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<tr>
<td>Sb-Si/Co</td>
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<tr>
<td>62/37 %</td>
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<tr>
<td>As Deposit</td>
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<td>800°C-2 hrs</td>
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<td>3 x 10²²</td>
<td>2</td>
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</table>

- Film Cracking
- No observable Grain Structure
- Defects due to Substrate
- Segregation?
Cr-Si

Deposition Temperature – 450 °C

XRD – Target CrSi\textsubscript{2} - Poorly Crystallized

Co-sputtered – Crystalline CrSi\textsubscript{2}

Film Thickness – 2.3 \(\mu\)m & 2.5 \(\mu\)m

800 °C Anneal

No Adhesion

Failures – Tape Test
Cr-Si

**CrSi$_2$ Target**

- Film Cracking
- No observable Grain Structure
- Defects due to Substrate

**Co-Sputtered**

**Hall Measurement**

<table>
<thead>
<tr>
<th>CrSi$_2$</th>
<th>$\rho$ (10$^{-5}$ Ω·m)</th>
<th>Carrier (1/cm³)</th>
<th>Mobility (cm²/VS)</th>
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<td>800°C-2 hrs</td>
<td>775.4</td>
<td>6 x 10$^{17}$</td>
<td>10</td>
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**B-Si/Ge/Cr 59/35/6 %**

<table>
<thead>
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<th>B-Si/Ge/Cr 59/35/6 %</th>
<th>$\rho$ (10$^{-5}$ Ω·m)</th>
<th>Carrier (1/cm³)</th>
<th>Mobility (cm²/VS)</th>
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<tbody>
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<td>269 x 10$^{5}$</td>
<td>2 x 10$^{17}$</td>
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<td>800°C-2 hrs</td>
<td>219</td>
<td>3.2 x 10$^{18}$</td>
<td>8.8</td>
</tr>
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</table>
Simple Module

Shadow Mask

Si\Mn\Ge
Large internal $\Omega$
Legs $\sim$ 40 M$\Omega$
650 $^{\circ}$C Anneal

N-leg Pt Si\Mn\Ge

Power $\leq 10^{-12}$ watts

\[\Delta T\]

Load=2.2 K$\Omega$

$\begin{array}{|c|c|c|}
\hline
\text{Voltage (10^{-6} V)} & \text{20} & \text{40} & \text{60} & \text{80} & \text{100} \\
\hline
\text{20} & \text{30} & \text{40} & \text{50} & \text{60} \\
\hline
\end{array}\]
Summary

• Low resistive Si & Si/Ge difficult to achieve by magnetron sputtering.
• Low resistive films achieved with silicides of Co, Mn and Cr.
• Good Seebeck coefficients achieved for Mn & Cr silicides with P-type behavior.
• Moderate Seebeck coefficients achieved for Co silicides with N-type behavior.
• Silicide films exhibit low carrier mobility.
• Extensive film cracking is a problem.