WSi₂ in Si₁₋ₓGeₓ composites: processing and thermoelectric properties

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Thermoelectricity

- Study of the coupled transport of electrical and thermal energy.
- Solid-state phenomenon requires no moving parts or working fluids, and generates no noise, torque, or vibrations.
  - As a result thermoelectric devices are extremely reliable.
- Power Generation
  - Spacecraft, automotive, aerospace, gas pipelines, well sites, and offshore platforms.
- Refrigeration
  - On chip cooling, electronics, and automotive.
- High reliability, low conversion efficiency.

Spacecraft Power

- Radioisotope thermoelectric generators (RTG) have powered 45 spacecraft.

GPHS-RTG (Galileo/Ulysses)


WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites
Thermoelectricity

- Study of the coupled transport of electrical and thermal energy.
- Radioisotope thermoelectric generators (RTGs) have powdered spacecraft.

As a result, thermoelectric devices are extremely reliable.

Photos nasa.gov

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites

Thermoelectricity

- Study of the coupled transport of electrical and thermal energy.
- Radioisotope thermoelectric generators (RTG) have powdered spacecraft.
- As a result, thermoelectric generators are extremely reliable.
- High reliability, low conversion efficiency.
- Globally, TE has applications in spacecraft, automotive, aerospace, gas pipelines, well sites, and offshore platforms.

As a result, thermoelectric devices are extremely reliable.

BMW, Volkswagen

WSi₂ in Si₁₋ₓGeₓ Composites


GPHS-RTG (Galileo/Ulysses)

**Silicon Germanium Alloys**

- Popular choice for RTG systems:
  - High temperature, mechanically robust, stable in air or vacuum, reasonable ZT, Stivers (1964).
  - N- and p-type doped with P and B, respectively.
  - Enhancement from Si/Ge alloy phonon scattering, Abeles et al. (1962), Abeles (1963).
- Traditional samples were solidified and homogenized with zone-leveling, Dismukes et al. (1964).

\[
ZT_{Material} = \frac{S^2 \sigma T}{k}
\]

**Enhancing Si/Ge**

- Powder processing provides some microstructure control.
- Grains of 2-5 μm show 10% ZT improvement over large grains, Rowe et al. (1993).
- Original nano-structuring theory developed by Hicks and Dresselhaus (1993).
  - Reduce lattice conductivity, enhance power factor.
- SOA, Nano sized grains show 30% ZT improvement, Joshi et al. (2008), Wang et al. (2008).
  - Thermally induced grain growth can hinder practical usefulness.
**Silicide in Si/Ge Approach**
- Thermally stable silicide nano-precipitates in Si/Ge.
- Precipitate size can preferentially scatter phonons over charge carriers.
- Experimentally verified for:
  - CrSi$_2$-Si$_{80}$Ge$_{20}$, Zamanipour & Vashaee (2012).
  - MoSi$_2$-Si$_{92}$Ge$_8$, Favier et al. (2014).

**Silicide in Si/Ge Theory**
- Figure: Mingo et al. Nano Letters 9 (2009) 711-715.
- Various metal silicides with different volume fractions.
- No inclusions in Si$_{50}$Ge$_{50}$ alloy.

**WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites**
- Graph showing thermal conductivity ($\kappa$) vs. nanoparticle diameter [nm].
**Powder Processing**

- Planetary milling:
  - 8 hours @ 300-580 rpm
  - Ball to powder ratio 3-5
- Spark plasma sintering:
  - 800-1100°C
  - 70-90 Mpa
  - 5-10 min hold
- Powders handled under Argon atmosphere.

**Test Matrix**

<table>
<thead>
<tr>
<th>Si/Ge at% Ratio</th>
<th>70/30</th>
<th>80/20</th>
<th>90/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Dopant</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>P-Type, B</td>
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<td></td>
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<tr>
<td>N-Type, P</td>
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**Tungsten Silicide Volume Fraction**

- 0%
- 1%
- 2%
- 5%

**WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites**
Microstructure

- Study on milling profile.
  - a) Milled powder profile 1
  - c) Milled powder profile 2
  - b) Sintered pellet of powder a)
  - d) Sintered pellet of powder c)

Aggressive milling alloys Si and Ge, but does not form the WSi$_2$ phase.
WSi$_2$ phase formed during sintering.
Silicide precipitate size ranged from <90 nm to micron range. Difficult to control with powder processing.

Sintering Study

- Analyzed ram travel data from SPS.
- W influences sintering kinetics by lowering the sintering strain rate and increasing required dwell time.
Si/Ge at% Ratio
70/30
80/20
90/10

Tungsten Silicide Volume Fraction
0% X
1% X
2% X
5% X

P-type, B
N-type, P
2% Doped

Start End Reset

Start End Reset

Never fully recovers

Dopant Segregated
Dopant Re-distributed

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites

End
Start
Cooling
Heating

Resistivity (Ohm-cm)

Temperature (Celsius)
Introduction

Processing

Properties

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites

Si/Ge at% Ratio

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<tr>
<td>X</td>
<td>O</td>
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2% Doped

P-type, B

N-type, P

Dopant Segregated

Dopant Re-distributed

Start

End

Reset

Electrical Properties

Thermal Properties

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites
Figure of Merit

Nano grain SOA n-type
Nano grain SOA p-type
RTG n-type
RTG p-type

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites
• Investigated influence of oxygen contamination on samples.
• Loaded SPS dies in both Argon and Air.
• Silica formation did not alter electrical properties significantly.


• Silica formation reduced lattice thermal conductivity.
• Lower thermal conductivity leads to 10-40% ZT improvement.
• N-type samples are not as sensitive to oxygen contamination.
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**Two Couple Device**

- Fabricated 2-couple proof of concept device.
- Operated in air for over 5 months.

**Device Characterization**

**Endurance Testing**

WSi$_2$ in Si$_{1-x}$Ge$_x$ Composites
Conclusion

- Silicide phase successfully reduces lattice thermal conductivity.
- Increased ZT for silicide composites as compared to baseline Si/Ge.
- Oxygen contamination further reduces lattice thermal conductivity.
- Tungsten silicide phase offers tuning of carrier concentration.
- Silicide phase does not hinder thermal stability.

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