National Aeronautics and Space Administration

Composite Silicide Thermoelectric Materials for Power Generation

F. Dynys[1], J. Mackey[3], A. Sehirlioglu[2] & A. Sayir[1]

[1]NASA Glenn Research Ctr., Cleveland, Ohio, USA

[2]Case Western Reserve University, Cleveland, Ohio, USA

[3]University of Akron, Akron, Ohio, USA

www.nasa.gov

National Aeronautics and Space Administration

Hypersonic Vehicle

Power Generation

- No rotating shaft for electric energy generation
- Electrical power generation by batteries and APU's add mass and volume

Vehicle Systems Safety Technologies

Wireless technology allows sensors to be placed in remote locations

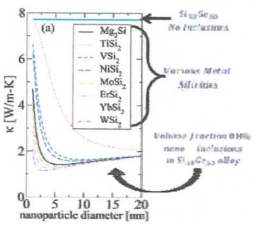
100 MHz Wireless Pressure Sensor -300°C

www.nasa.gov

National Aeronautics and Space Administration

TE Materials

TE - Si/Ge Alloys, Silicides, Ceramics
Temperature Range – 500 – 1000 °C
Environment – O_2, NO_x, CO, CO_2, H_2O



- Phonon Scattering
  - Nano inclusions
  - Alloyed Si/Ge matrix
- Mingo et al.
  - 2-10 nm - optimum size
  - ~~WSi_2 Best Silicide!~~

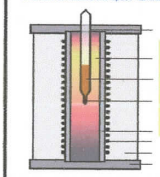
Mingo N, et al. "Nanoparticle-in-Alloy", *Nano Letters*, 9 (2009), 711–715

www.nasa.gov

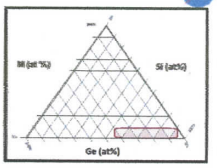
National Aeronautics and Space Administration

Directional Solidification Systems

YSi_2 VSi_2 $TaSi_2$
$ZrSi_2$ $MnSi_{2-x}$ Mg_2Si
$TiSi_2$ $CrSi_2$ $MoSi_2$
WSi_2 CoSi

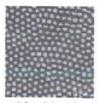


Melt ➡ Solidification



Advantages

- Stable High Temperature Interfaces
- Unique microstructures
- Coherent Interfaces

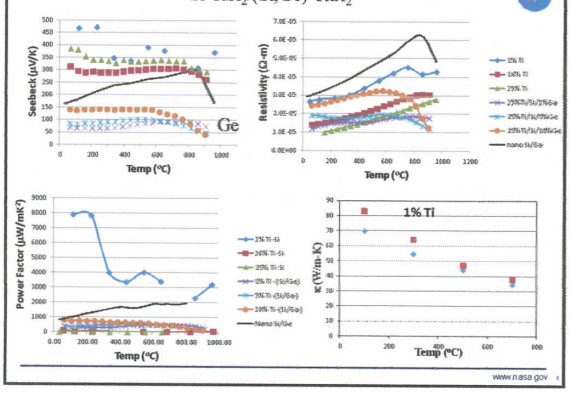


Parameter	
Temperature	1525 °C
Growth Rate	50 - 300 mm/min
Temp. Gradient	85 °C/cm
Heating Rate	10-20 °C/min
Time	5-20 Hours
Crucible	Boron Nitride Glassy Carbon SiO_2 + $CaCl_2$

www.nasa.gov

National Aeronautics and Space Administration

Si-$TiSi_2$/(Si,Ge)-$TiSi_2$



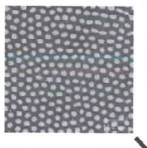
www.nasa.gov

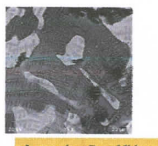
National Aeronautics and Space Administration

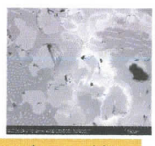
Si-$TiSi_2$/(Si,Ge)-$TiSi_2$

Solidification Microstructures

25%Ti/0-1% Ge ➡ 5% Ge ➡ 10% Ge

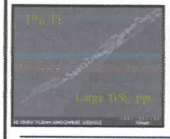


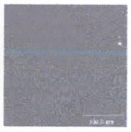


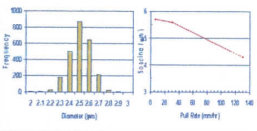


- Increasing Ge addition creates larger precipitates.
- Ge segregation observed.

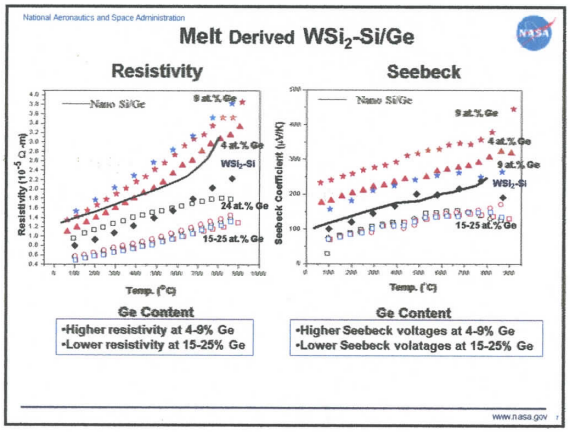
Lower Ti Conc.

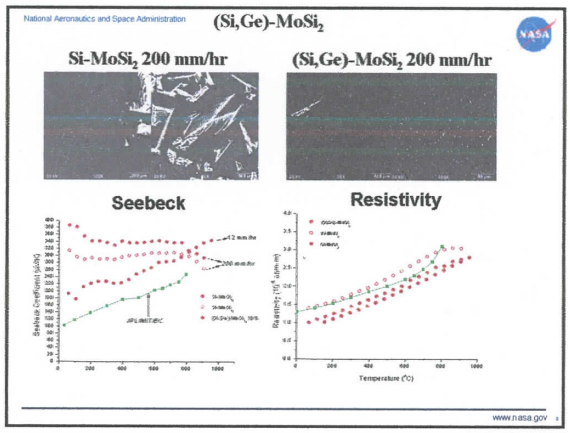


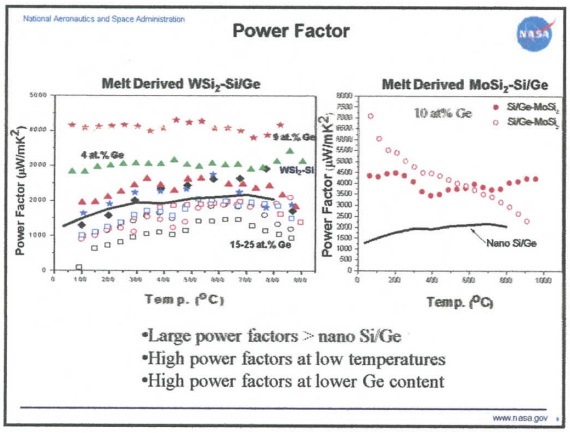


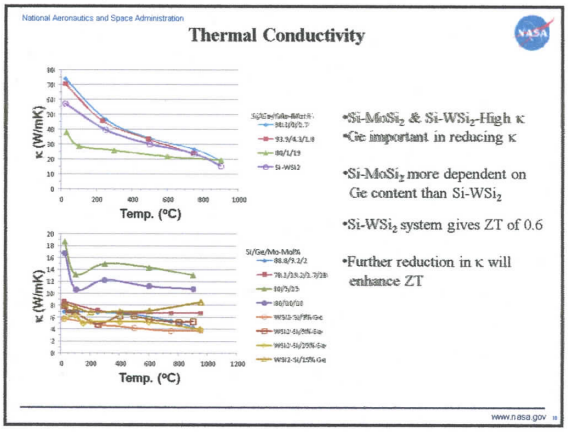


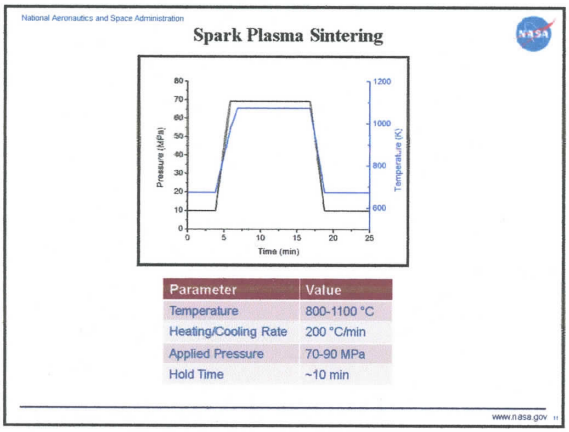
www.nasa.gov

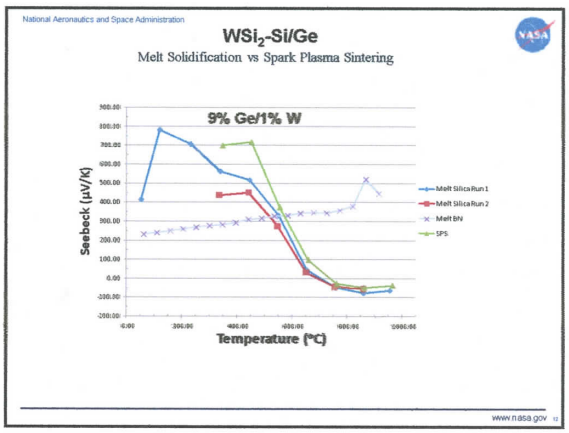

National Aeronautics and Space Administration
Melt Derived WSi_2-Si/Ge
Resistivity
Seebeck
Nano Si/Ge
9 at.% Ge
4 at.% Ge
WSi_2-Si
24 at.% Ge
15-25 at.% Ge
Resistivity (10^{-5} Ω-m)
Seebeck Coefficient (μV/K)
Temp. (°C)
Ge Content
•Higher resistivity at 4-9% Ge
•Lower resistivity at 15-25% Ge
Ge Content
•Higher Seebeck voltages at 4-9% Ge
•Lower Seebeck volatages at 15-25% Ge
www.nasa.gov


National Aeronautics and Space Administration
(Si,Ge)-$MoSi_2$
Si-$MoSi_2$ 200 mm/hr
(Si,Ge)-$MoSi_2$ 200 mm/hr
Seebeck
Resistivity
Temperature (°C)
www.nasa.gov


National Aeronautics and Space Administration
Power Factor
Melt Derived WSi_2-Si/Ge
Melt Derived $MoSi_2$-Si/Ge
Power Factor (μW/mK^2)
9 at.% Ge
4 at.% Ge
WSi_2-Si
15-25 at.% Ge
10 at% Ge
Si/Ge-$MoSi_2$
Si/Ge-$MoSi_2$
Nano Si/Ge
Temp. (°C)
•Large power factors > nano Si/Ge
•High power factors at low temperatures
•High power factors at lower Ge content
www.nasa.gov


National Aeronautics and Space Administration
Thermal Conductivity
κ (W/mK)
Temp. (°C)
•Si-$MoSi_2$ & Si-WSi_2-High κ
•Ge important in reducing κ
•Si-$MoSi_2$ more dependent on Ge content than Si-WSi_2
•Si-WSi_2 system gives ZT of 0.6
•Further reduction in κ will enhance ZT
www.nasa.gov


National Aeronautics and Space Administration
Spark Plasma Sintering
Pressure (MPa)
Temperature (K)
Time (min)
Parameter | Value
Temperature | 800-1100 °C
Heating/Cooling Rate | 200 °C/min
Applied Pressure | 70-90 MPa
Hold Time | ~10 min
www.nasa.gov

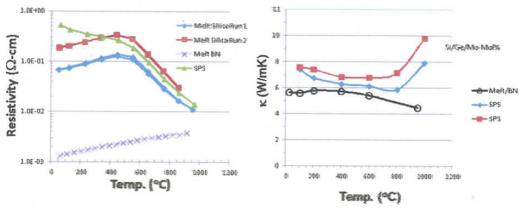

National Aeronautics and Space Administration
WSi_2-Si/Ge
Melt Solidification vs Spark Plasma Sintering
9% Ge/1% W
Seebeck (μV/K)
Temperature (°C)
Melt Silica Run 1
Melt Silica Run 2
Melt BN
SPS
www.nasa.gov

National Aeronautics and Space Administration

Si/Ge-WSi_2

Melt Solidification vs Spark Plasma Sintering

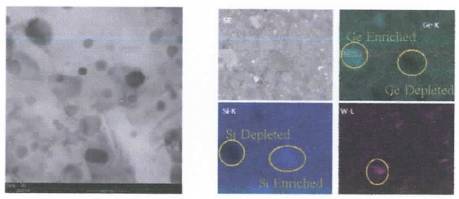
9% Ge/1% W



National Aeronautics and Space Administration

Spark Plasma Sintering P-Type

Si/Ge/W 1100 °C 10 min 35 KN



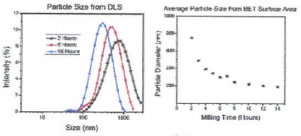
Nano-WSi_2

Inhomogeneity

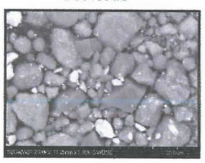
ICP – O_2 Content – 1-3 Wt.%

National Aeronautics and Space Administration

Planetary Milling



Previous

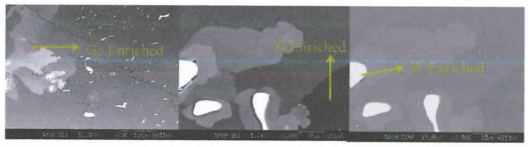


New

National Aeronautics and Space Administration

Melt Processed

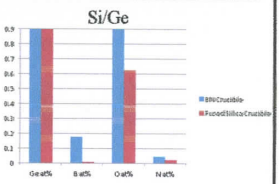
Si/9%Ge/1%W



ICP – Chemical Analysis

Sample	Melt	HP 1000	HP 1050	HP 1100	
Boron	0.069	0.072	0.072	0.086	wt%
Carbon	0.004	1.419	0.323	0.348	wt%
Carbon	0.004		0.269	0.364	wt%
Germanium	95.6	95.4	97.9	97.7	wt%
Oxygen	2.955	1.335	1.265	1.574	wt%
Oxygen	0.049	1.771	1.211		wt%
Silicon	Ballance	Ballance	Ballance	Ballance	
Tungsten	2.75	3.56	3.83	3.78	wt%

Si/Ge



National Aeronautics and Space Administration

Summary

- W ,Mo & Ti systems gave high power factors (more than twice the nano-Si/Ge).
- W,Mo & Ti - large power factors at low temperatures.
- ZT = 0.55 for WSi_2-Si/Ge eutectic is demonstrated.
- WSi_2-Si/Ge - Potential higher ZT - reducing thermal conductivity
- SPS – Have not achieve good TE properties