WSi_2 in $Si_{1-x}Ge_x$ composites: processing and thermoelectric properties

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Thermoelectricity

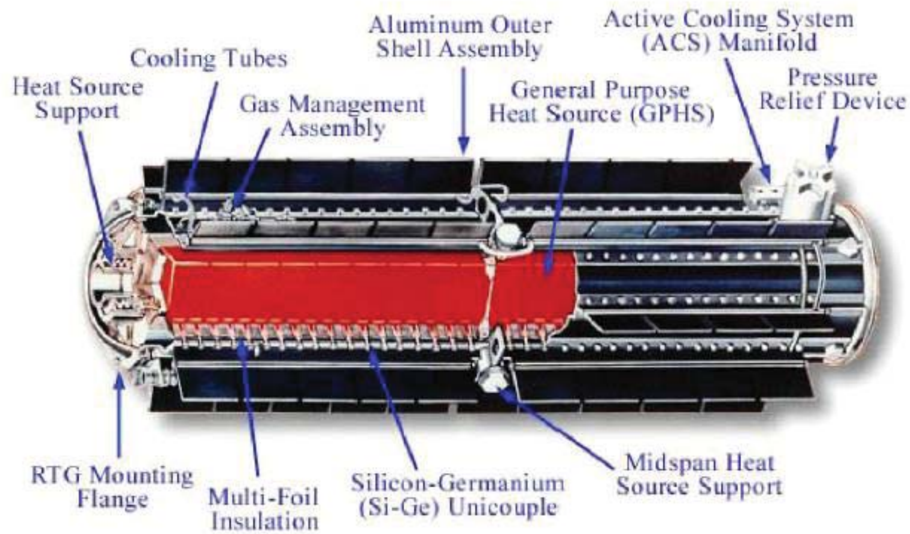
- Study of the coupled transport of electrical and thermal energy.
- Solid-state phenomenon requires no moving parts or working fluids, and generates no noise, torque, or vibrations.
    - As a result thermoelectric devices are extremely reliable.
- Power Generation
    - Spacecraft, automotive, aerospace, 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.
    - Voyager (1977), Ulysses (1990), Cassini (1997), New Horizons (2006), and Curiosity (2011).

Lange et al. Energy Conversion and Management **49** (2008) 391-401.

GPHS-RTG (Galileo/Ulysses)



Bennett et al. AIP Proceedings **969** (2008) 663-671.

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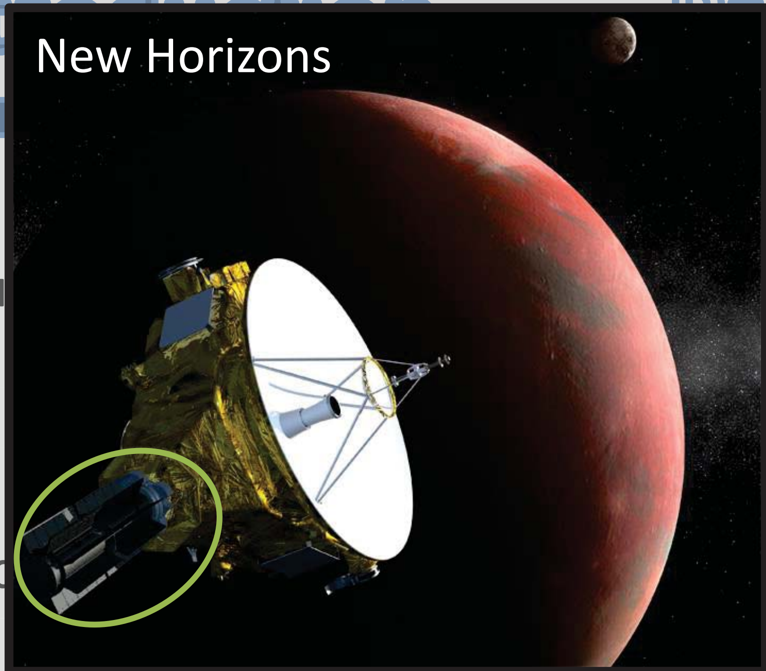

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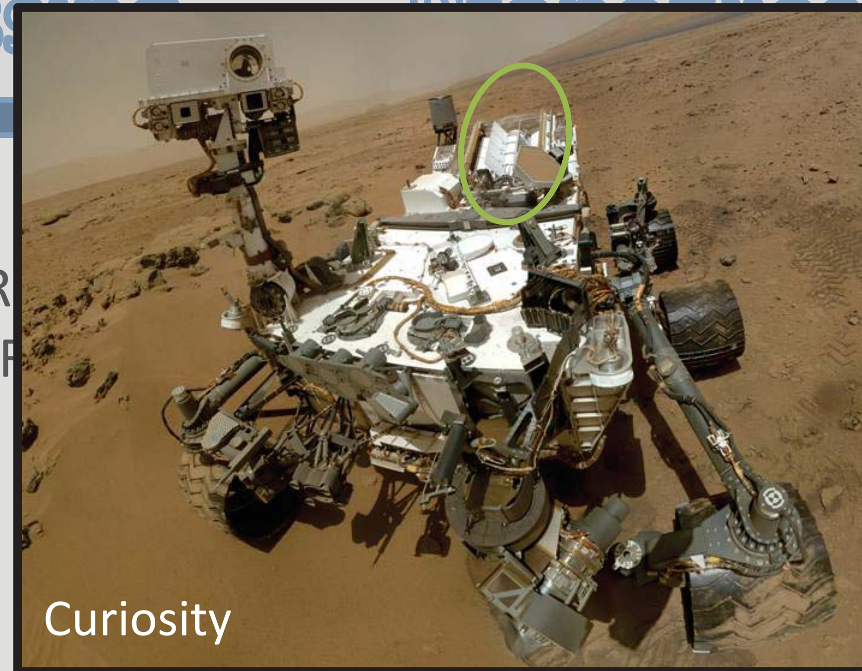

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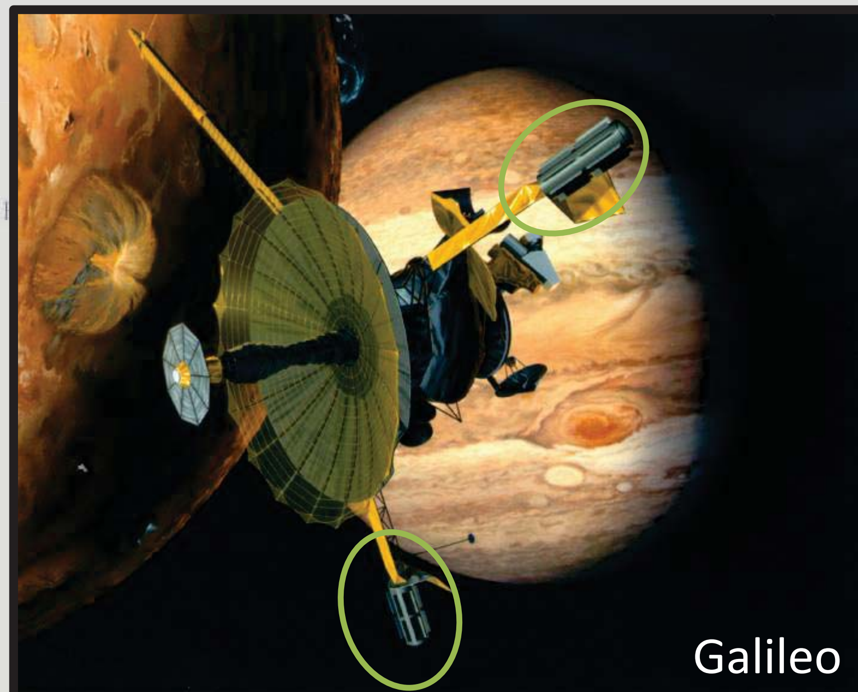

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Photos nasa.gov

Introduction

Processing

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• As a result thermoelectric

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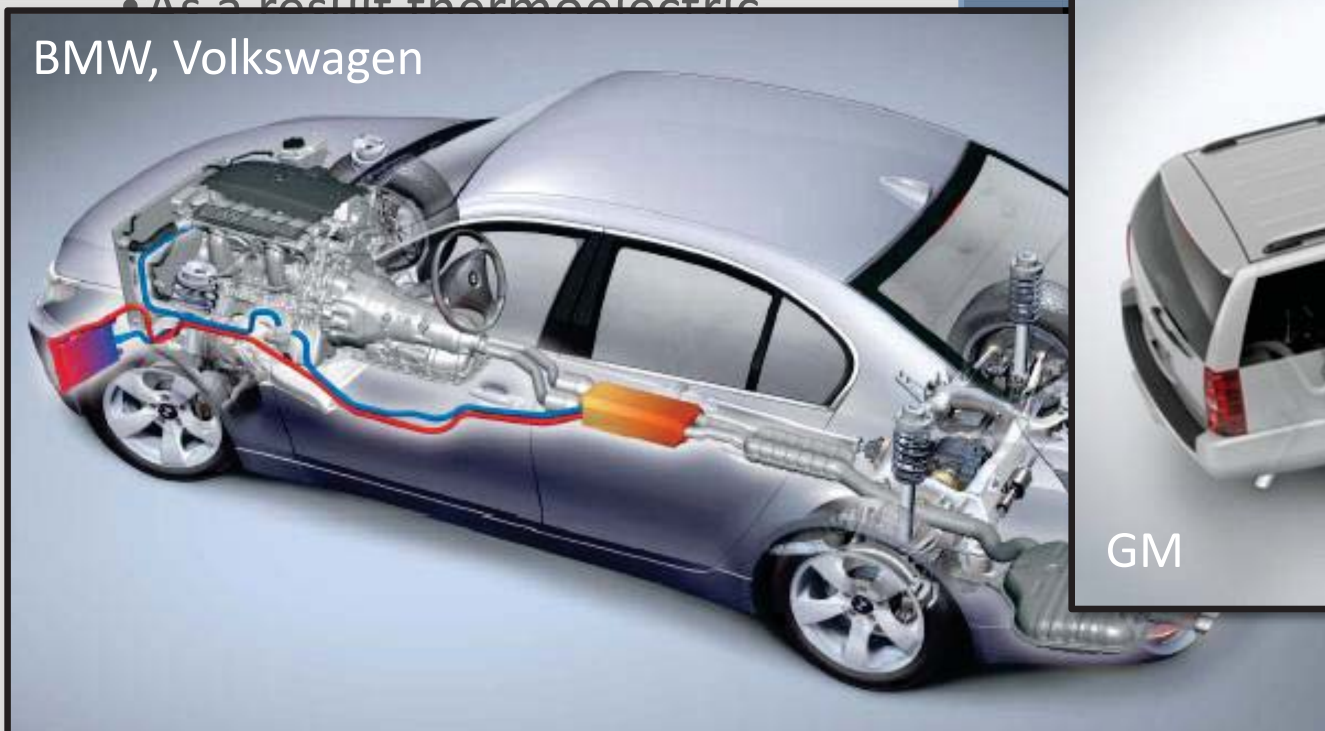

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Silicon Germanium Alloys

- 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).

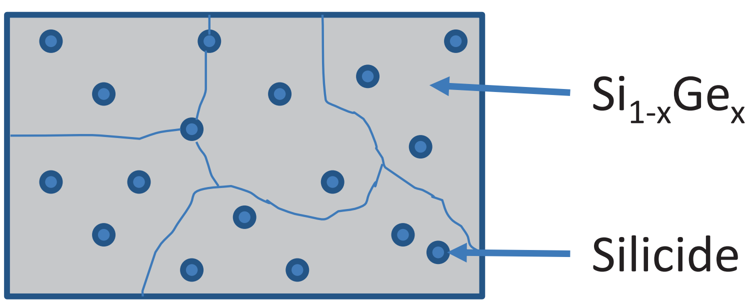
$$ZT_{Material} = \frac{S^2 \sigma T}{k}$$

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

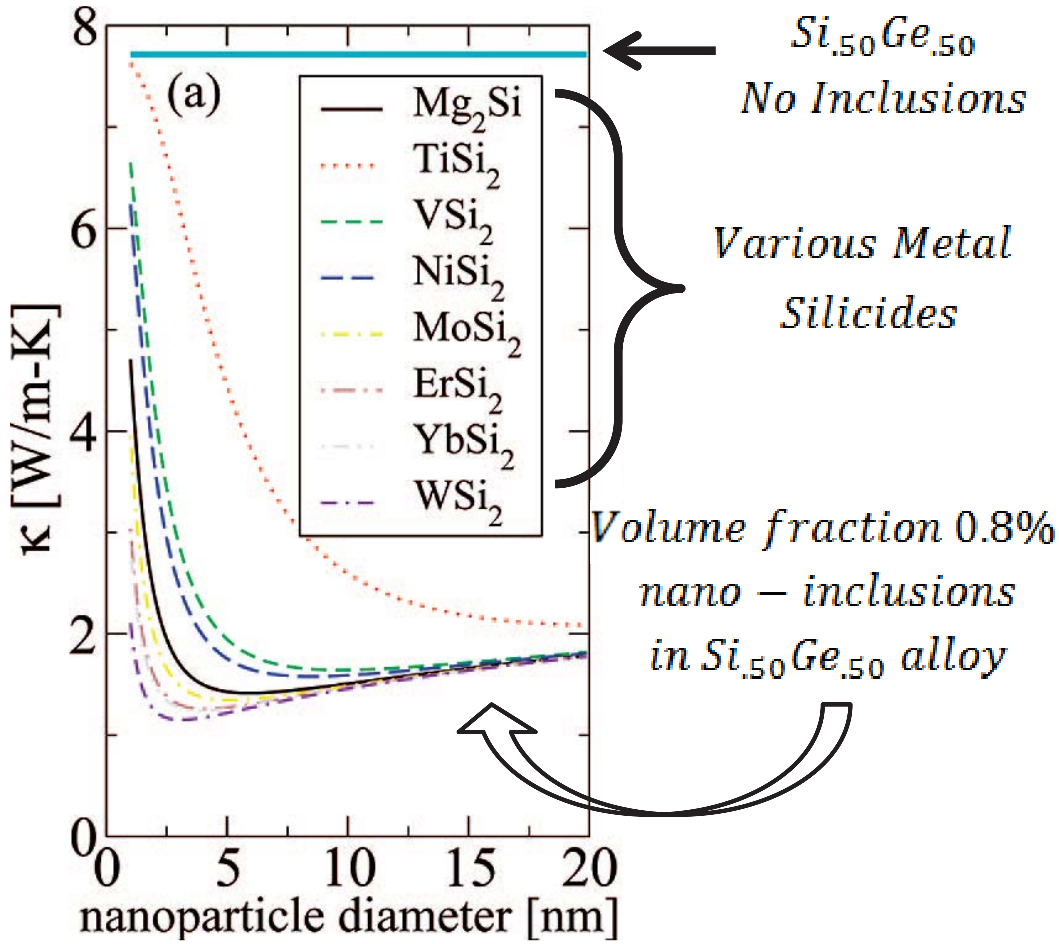
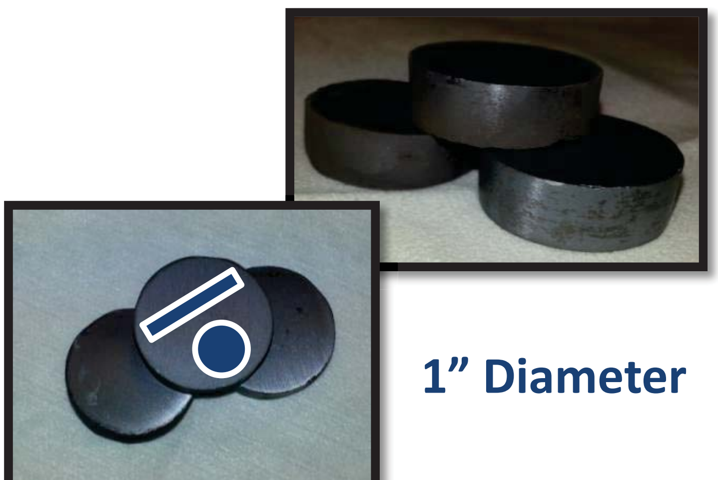


FIGURE: Mingo et al. Nano Letters **9** (2009) 711-715.

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.

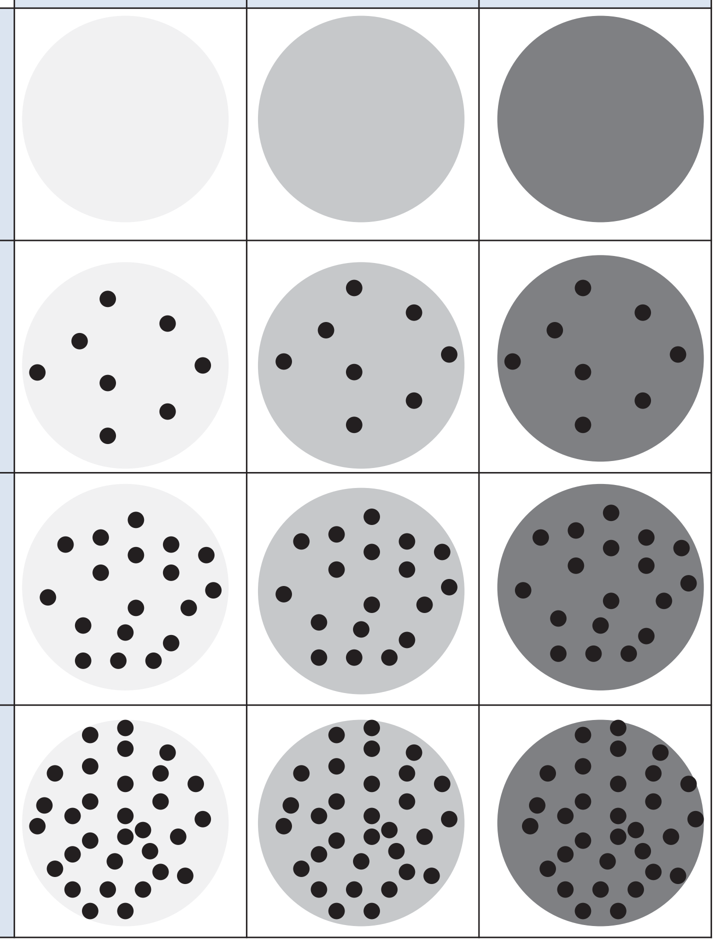


1” Diameter

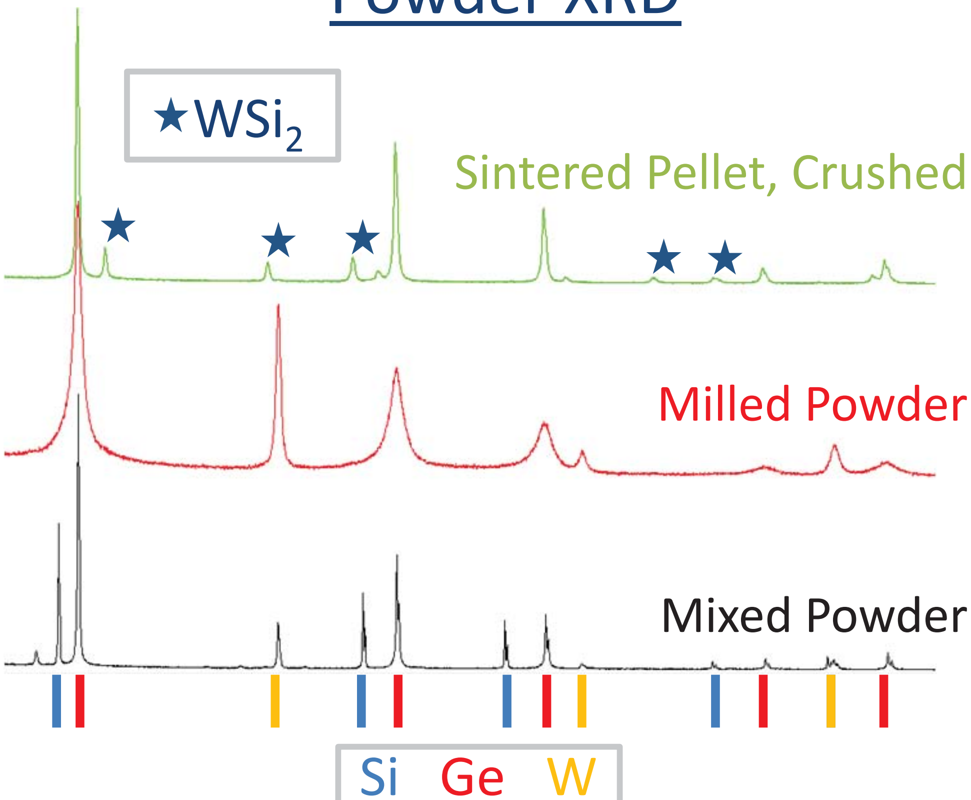
Test Matrix

2% Dopant
P-Type, B
N-Type, P

		Si/Ge at% Ratio		
		70/30	80/20	90/10
Tungsten Silicide Volume Fraction	0%			
	1%			
	2%			
	5%			

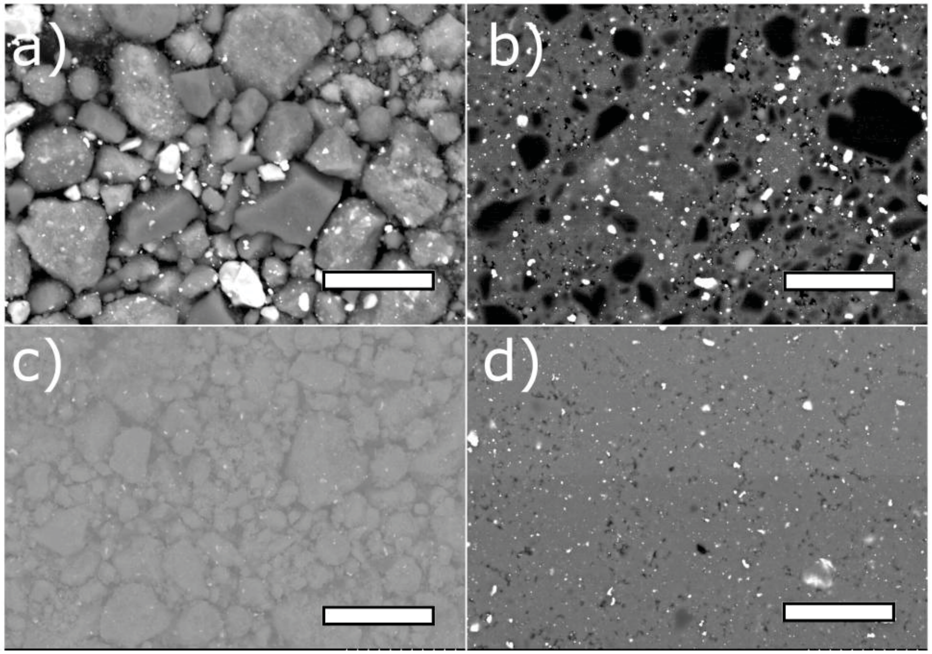


Powder XRD



- Aggressive milling alloys Si and Ge, but does not form the WSi_2 phase.
- WSi_2 phase formed during sintering.

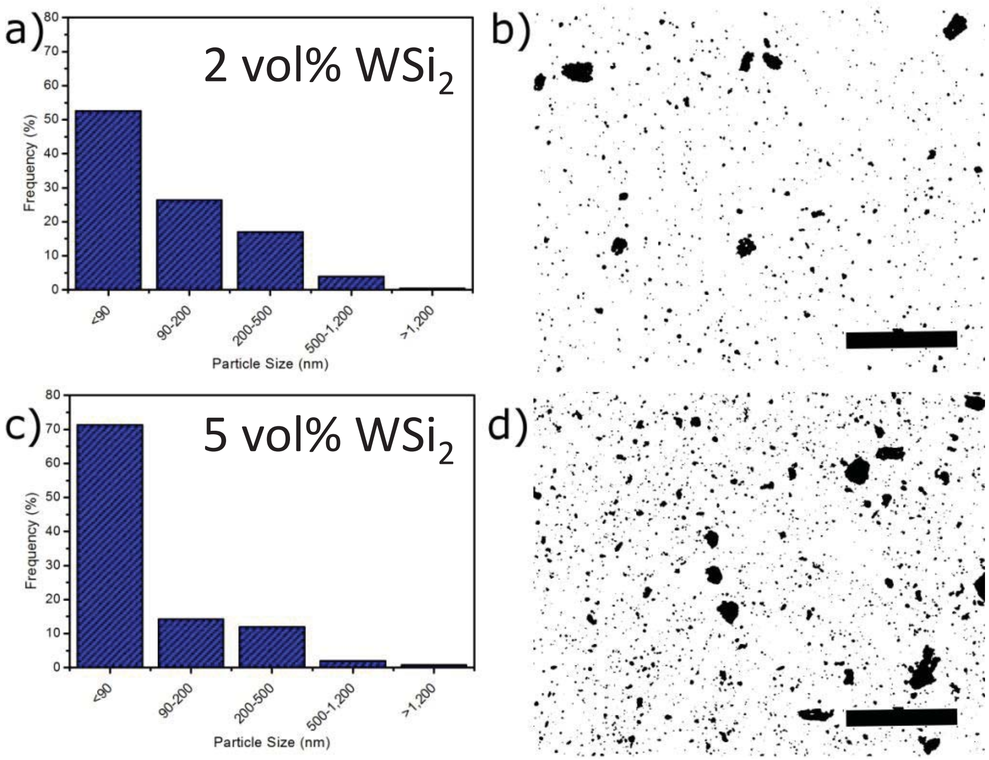
Microstructure



Scale Bar 15µm

- 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)

Silicide Precipitate Size



Scale Bar 15µm

- Silicide precipitate size ranged from <90 nm to micron range.
- Difficult to control with powder processing.

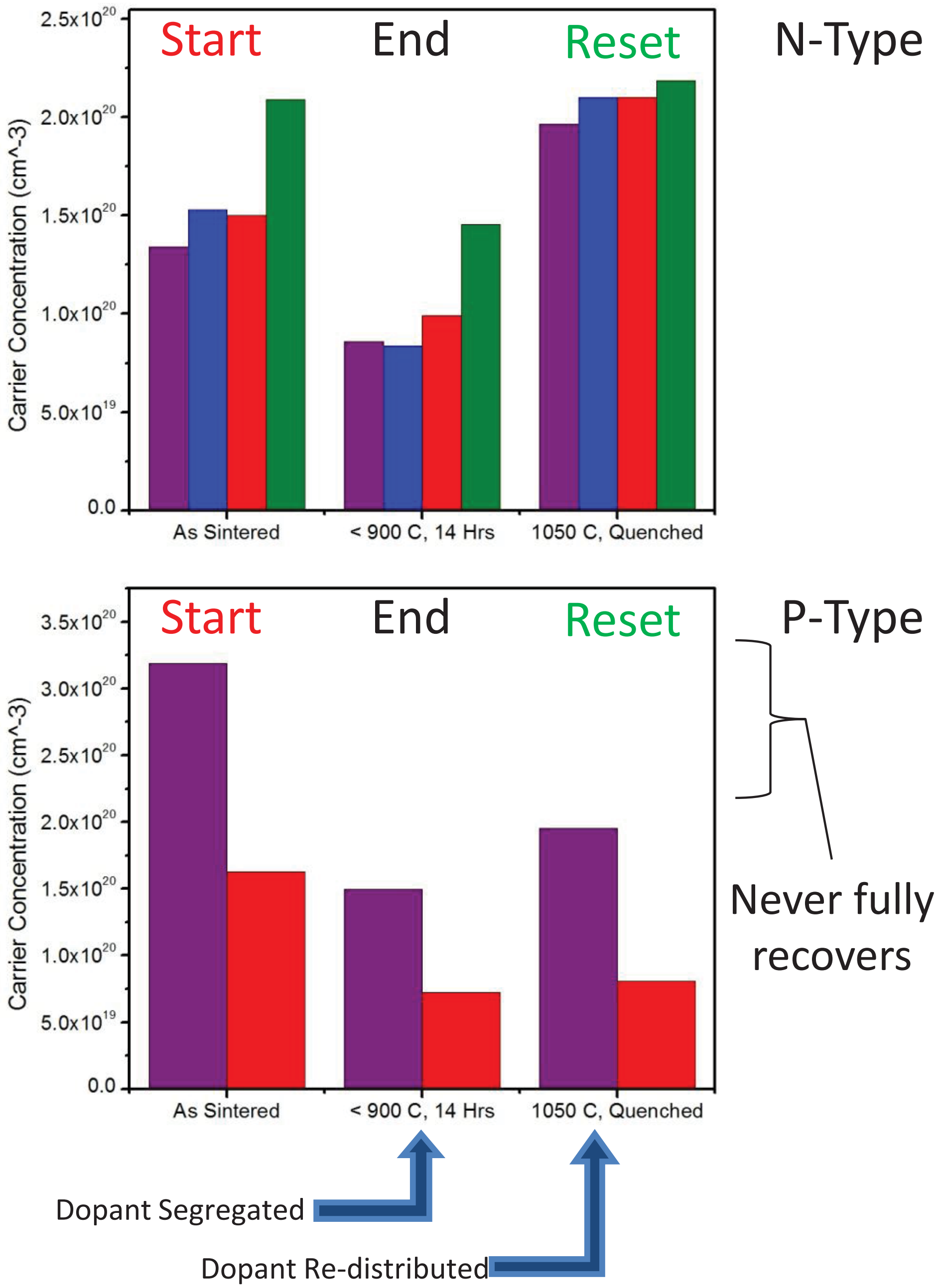
Sintering Study

W Source	Dopant	Strain Rate* (%/min)	Density (%)	95% Time** (min)
Micron Powder	P	2.9	97.0	3.1
Nano Powder	P	5.1	97.1	2.5
None	P	6.6	95.8	2.6
Micron Powder	B	5.9	95.8	2.3
Nano Powder	B	8.5	95.8	2.2
None	B	9.1	95.5	1.9

*Strain rate calculated at the beginning of the dwell step during the SPS run.

**Time to 95% of maximum ram travel

- Analyzed ram travel data from SPS.
- W influences sintering kinetics by lowering the sintering strain rate and increasing required dwell time.

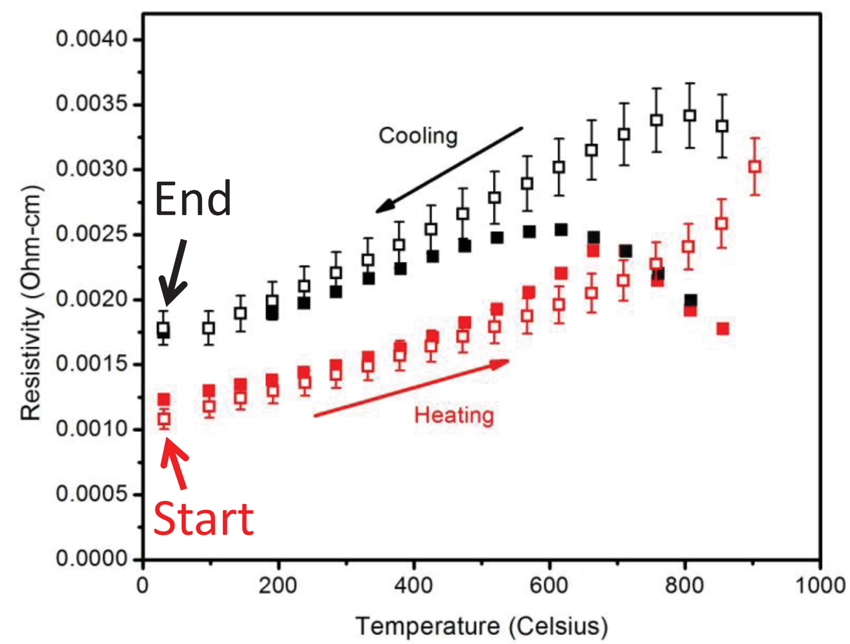


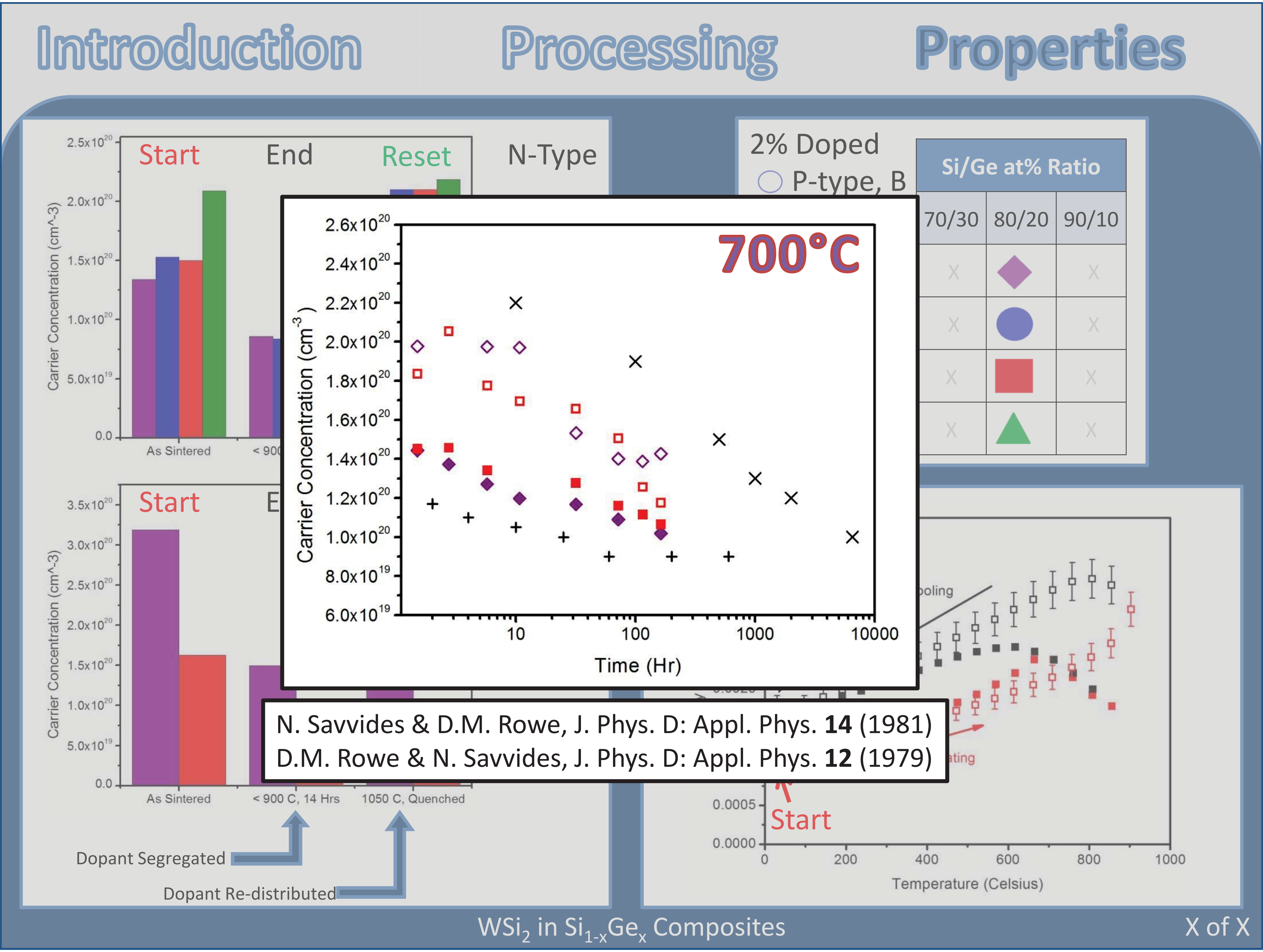
2% Doped

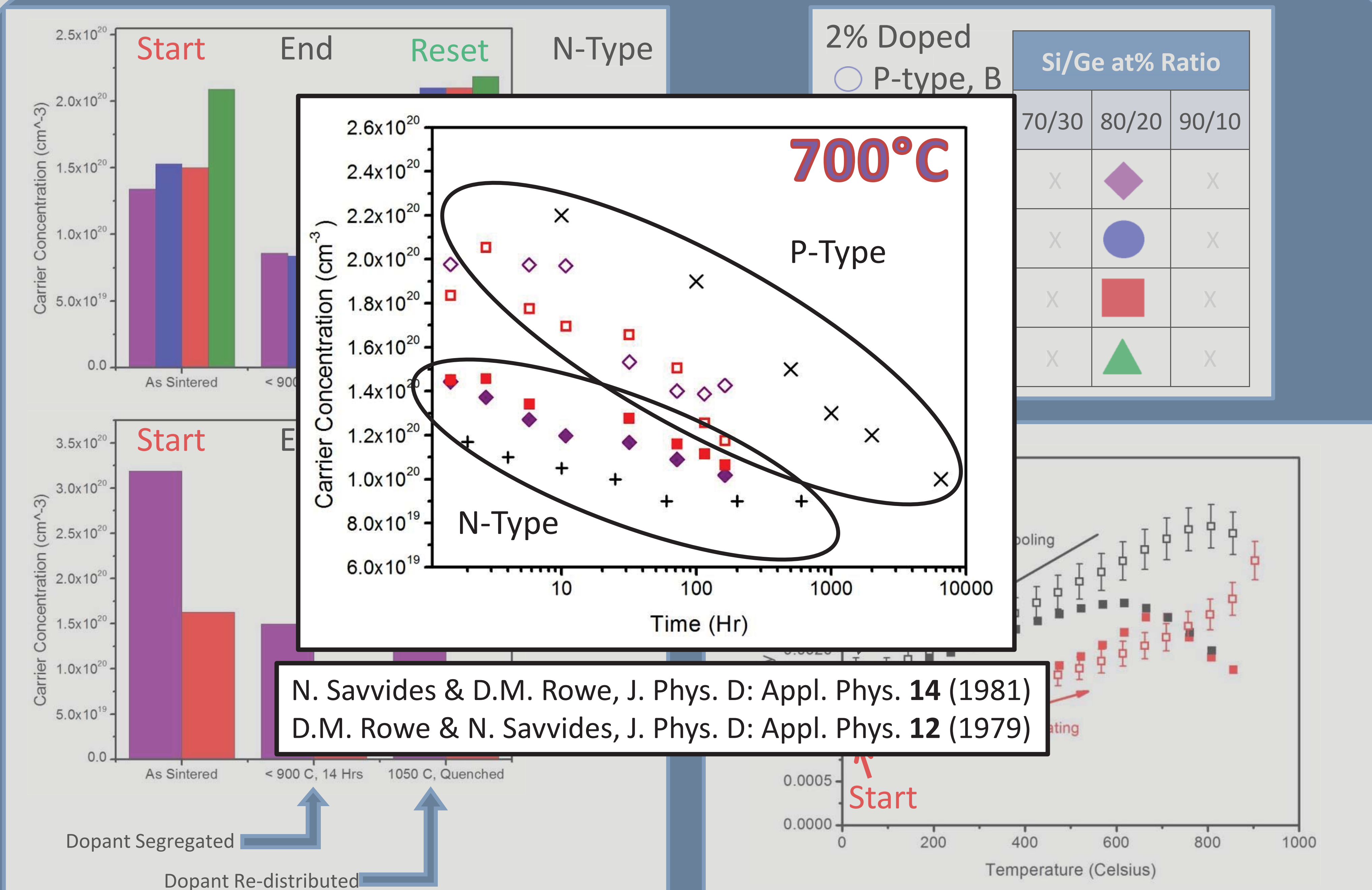
○ P-type, B

● N-type, P

Tungsten Silicide Volume Fraction	Si/Ge at% Ratio 70/30	80/20	90/10
0%	X	◆	X
1%	X	●	X
2%	X	■	X
5%	X	▲	X




Introduction
Processing
Properties
Start
End
Reset
N-Type
Carrier Concentration (cm^-3)
As Sintered
< 900 C, 14 Hrs
1050 C, Quenched
Dopant Segregated
Dopant Re-distributed
2% Doped
P-type, B
Si/Ge at% Ratio
70/30
80/20
90/10
700°C
Carrier Concentration (cm-3)
Time (Hr)
N. Savvides & D.M. Rowe, J. Phys. D: Appl. Phys. 14 (1981)
D.M. Rowe & N. Savvides, J. Phys. D: Appl. Phys. 12 (1979)
Temperature (Celsius)
WSi2 in Si1-xGex Composites
X of X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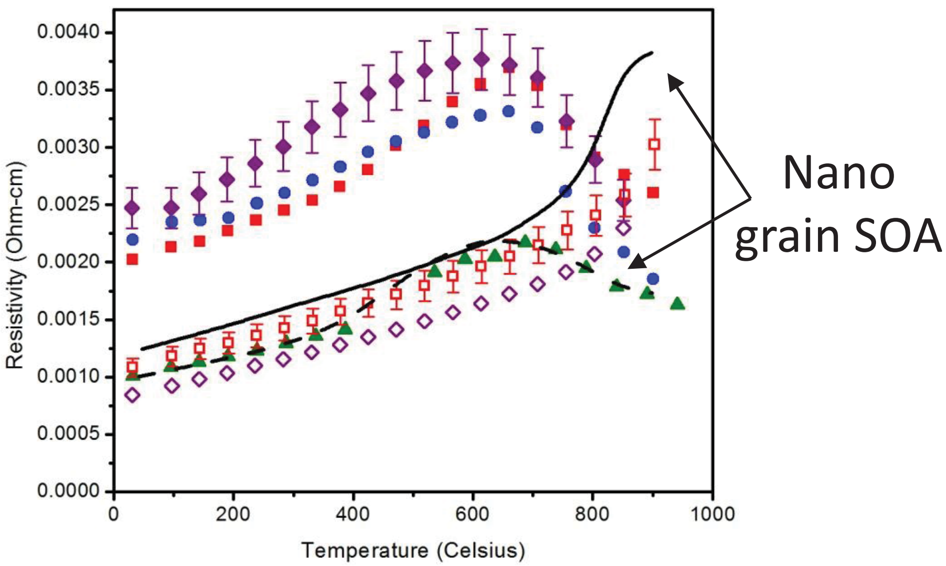
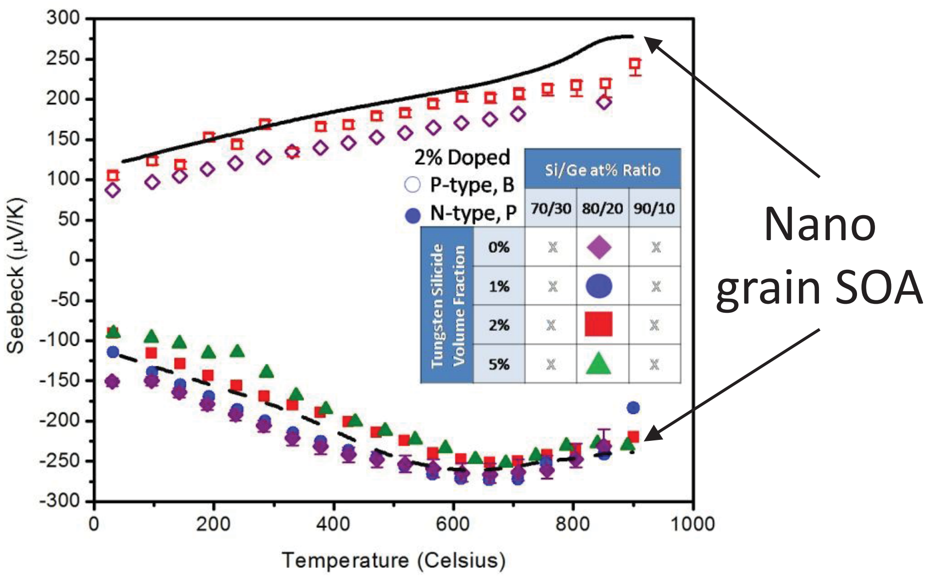
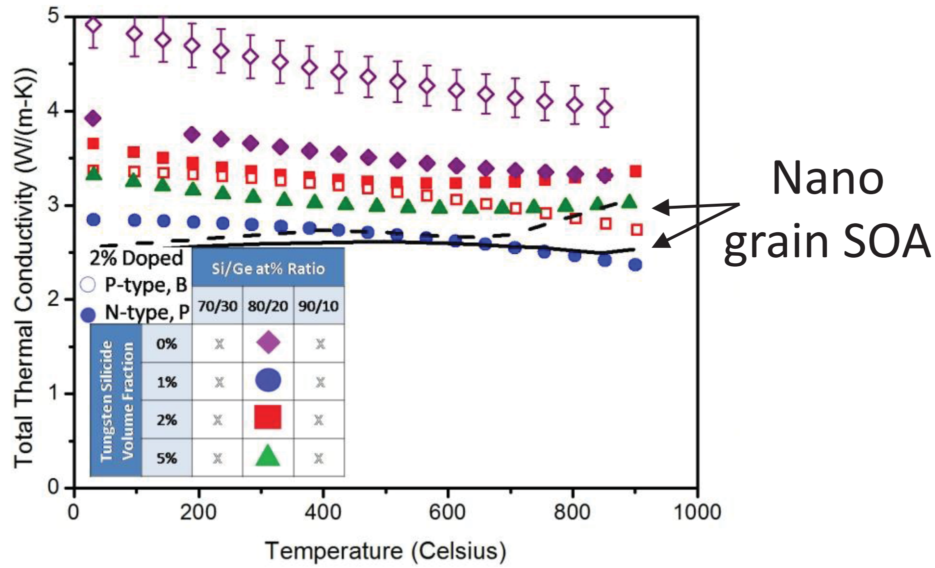
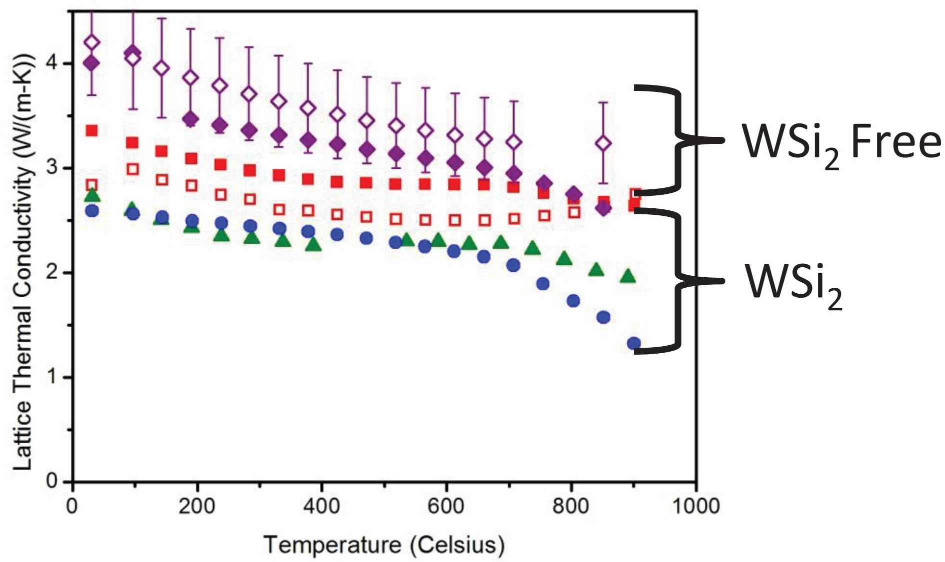
Electrical Properties





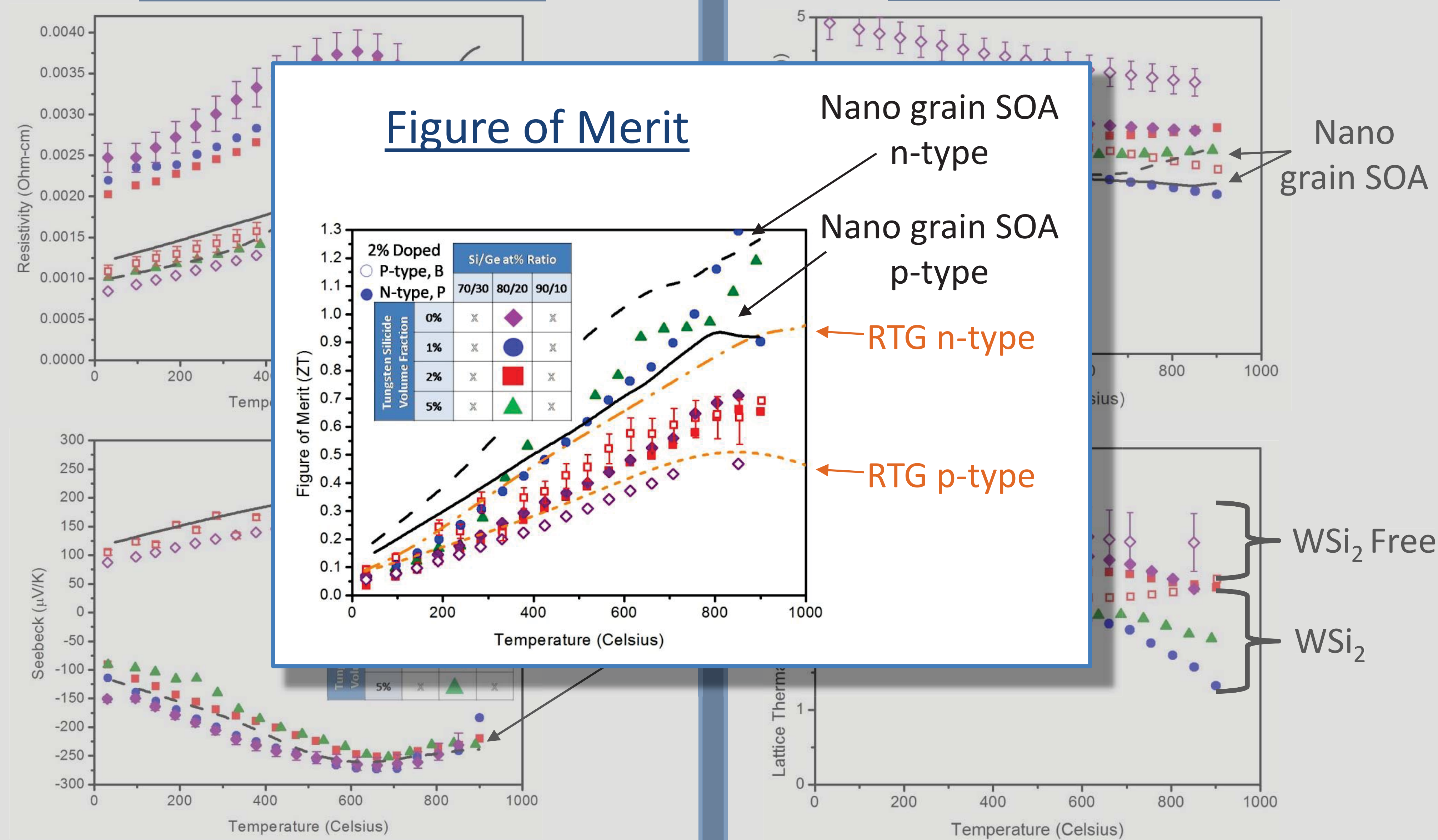
Thermal Properties



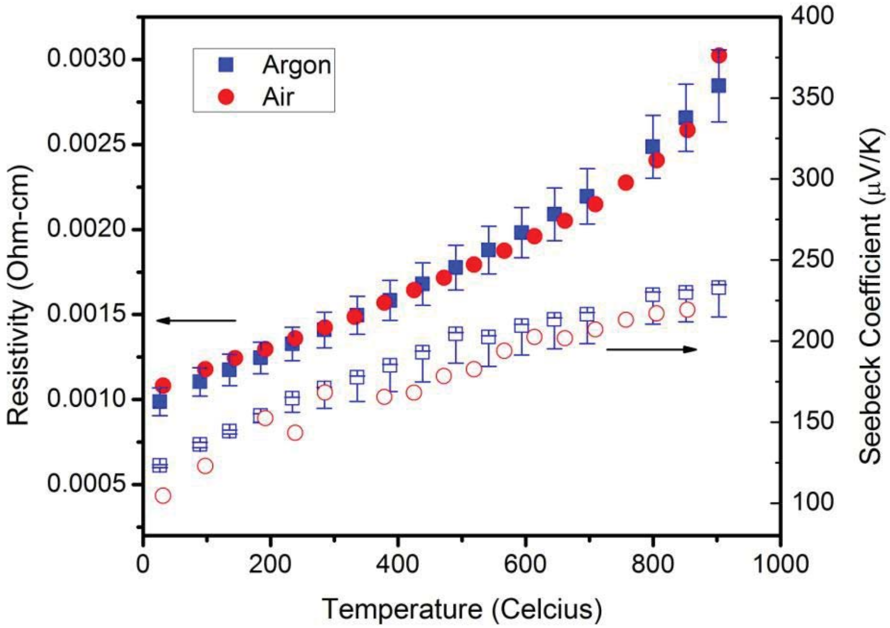


Electrical Properties

Thermal Properties



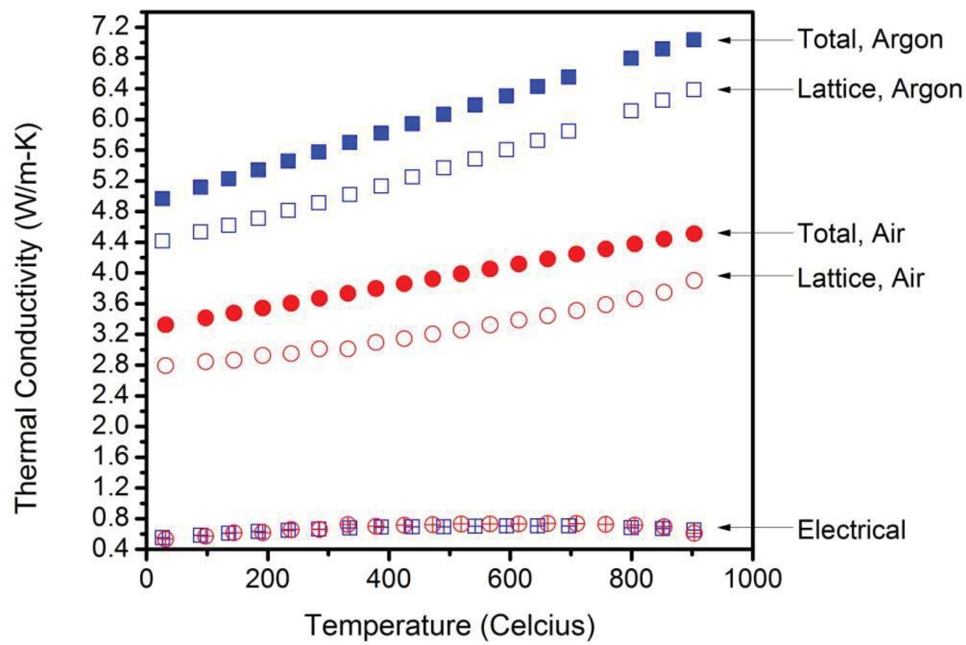
P-Type Oxygen Contamination



- Investigated influence of oxygen contamination on samples.
- Loaded SPS dies in both Argon and Air.
- Silica formation did not alter electrical properties significantly.

Bernard-Granger et al. Scripta Materialia **93** (2014) 40-43.

P-Type Oxygen Contamination

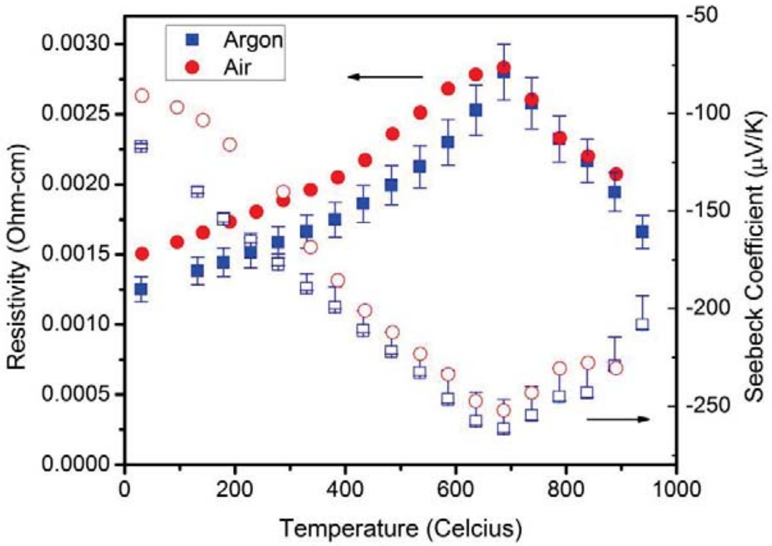


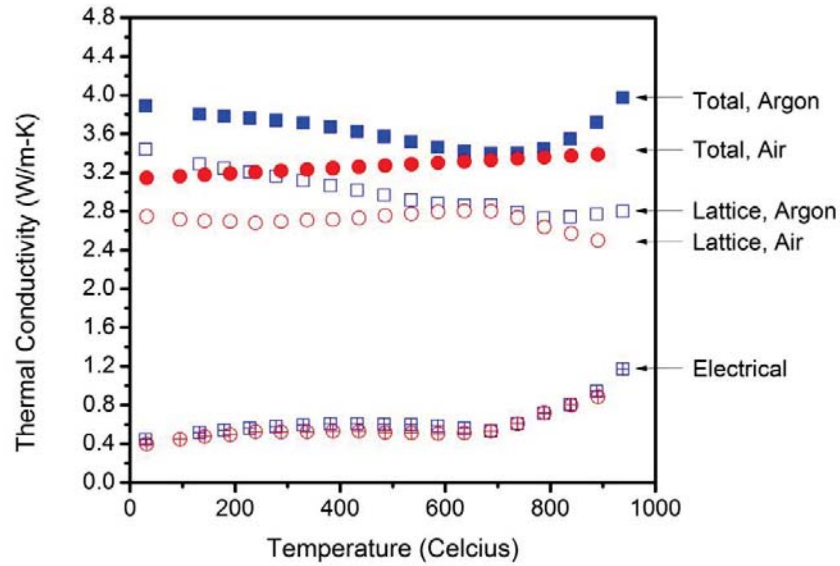
- Silica formation reduced lattice thermal conductivity.
- Lower thermal conductivity leads to 10-40% ZT improvement.
- N-type samples are not as sensitive to oxygen contamination.

P-Type Oxygen Contamination

P-Type Oxygen Contamination

N-Type Oxygen Contamination





- Inve
  cont
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Bernard-Granger et al. Scripta Materialia **93** (2014) 40-43.

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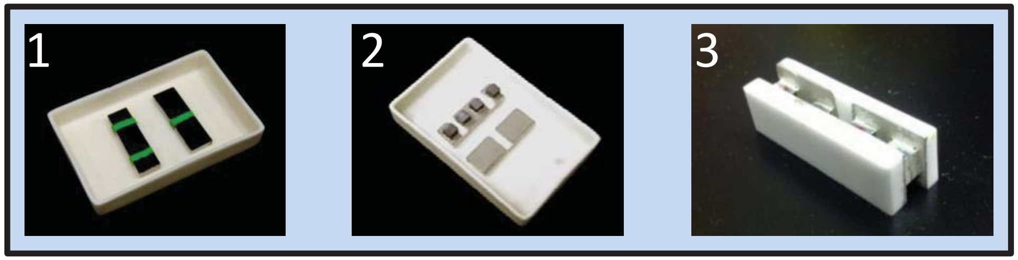
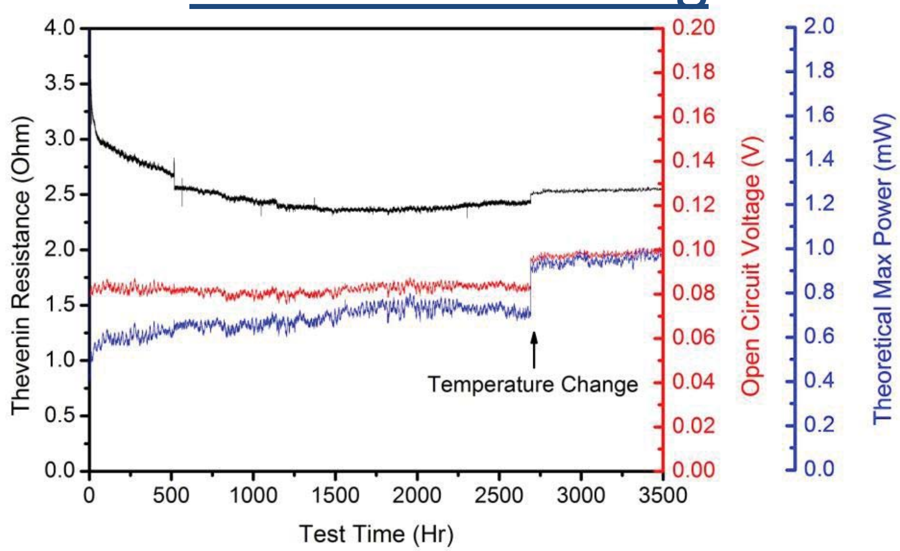
Two Couple Device

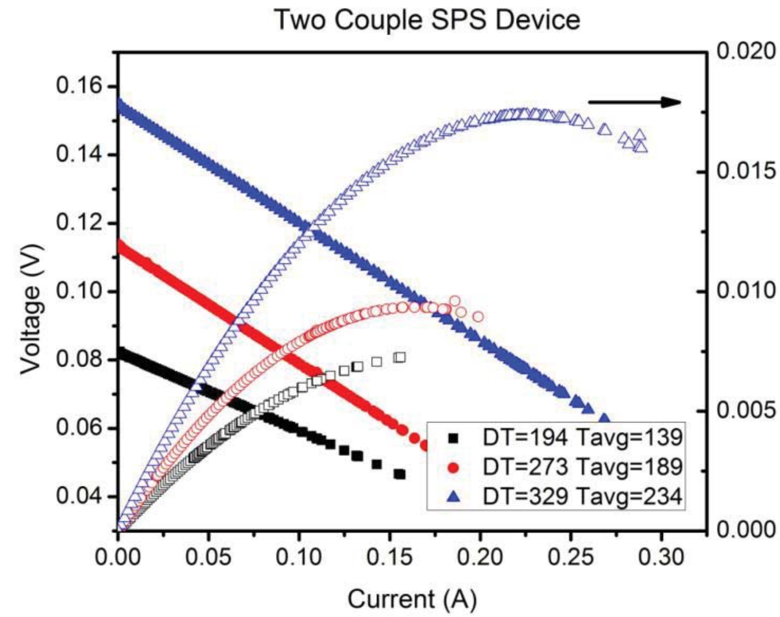
- Fabricated 2-couple proof of concept device.
- Operated in air for over 5 months.

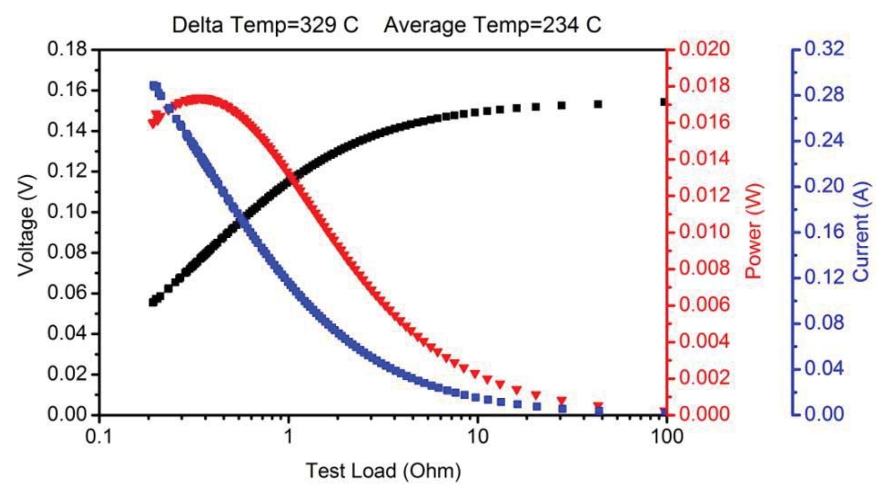


Endurance Testing



Device Characterization





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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