Integrated Design and Manufacturing of Thermoelectric Generator using Thermal Spray

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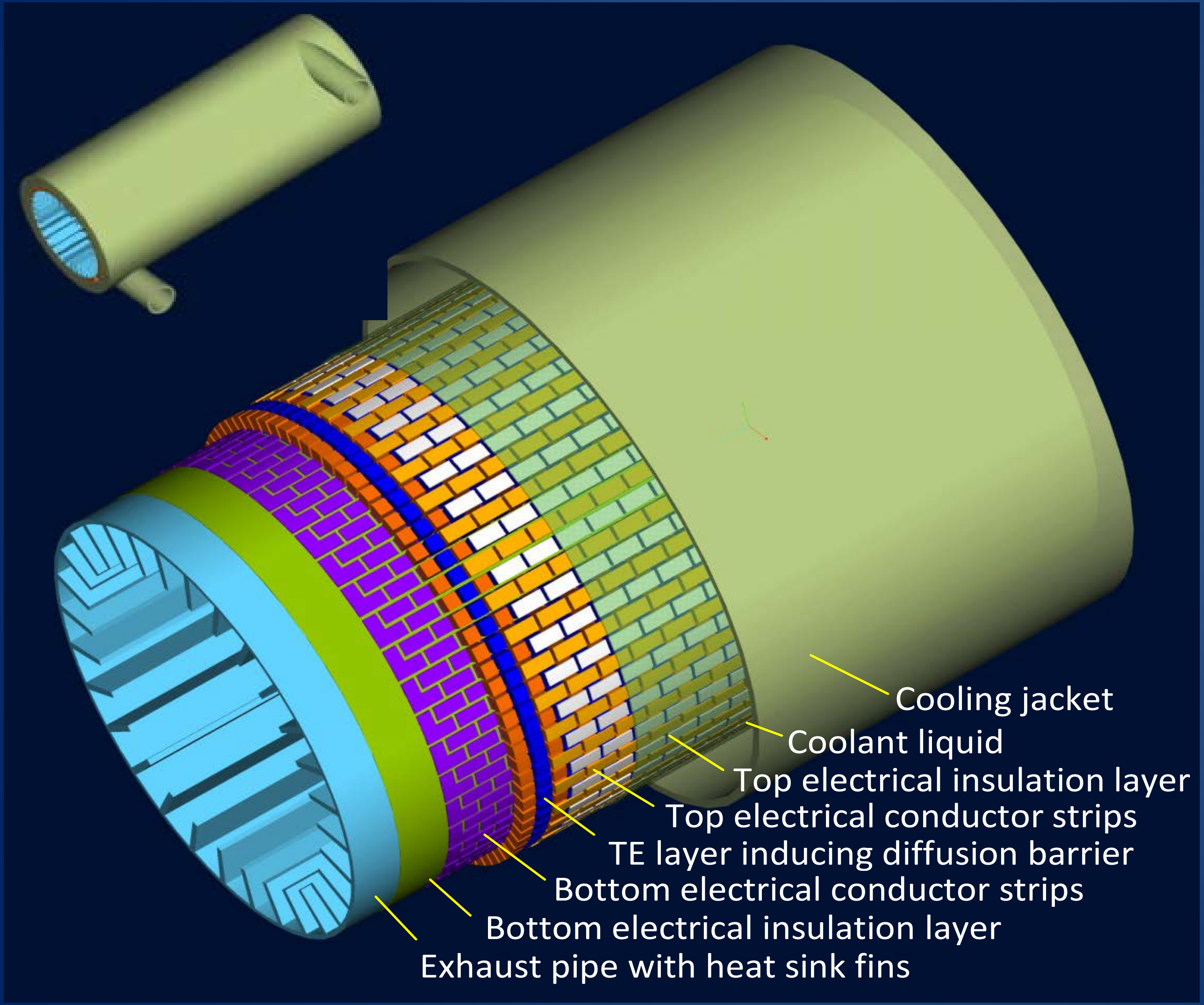
Presentation Outline

- Overall Concept
- Recent Progress
  - Thermal spray of Mg_2Si
  - Melt spinning of $MnSi_{1.75}$ (High Manganese Silicide)
  - 3D device fabrication
- Summary and Future Work

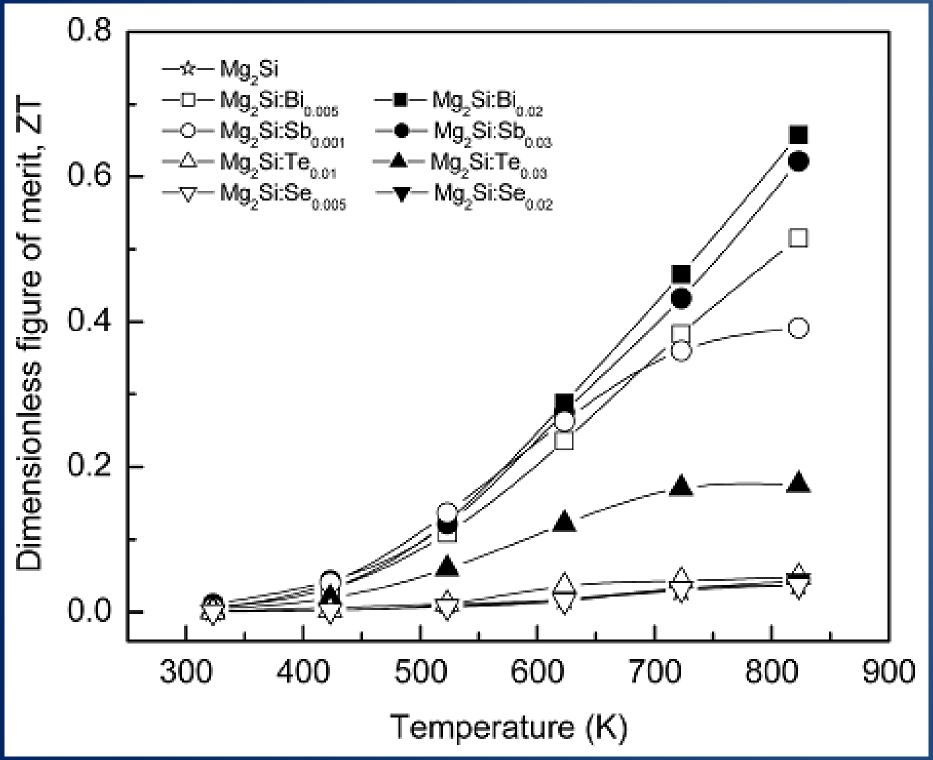
Integrated Design and Manufacturing



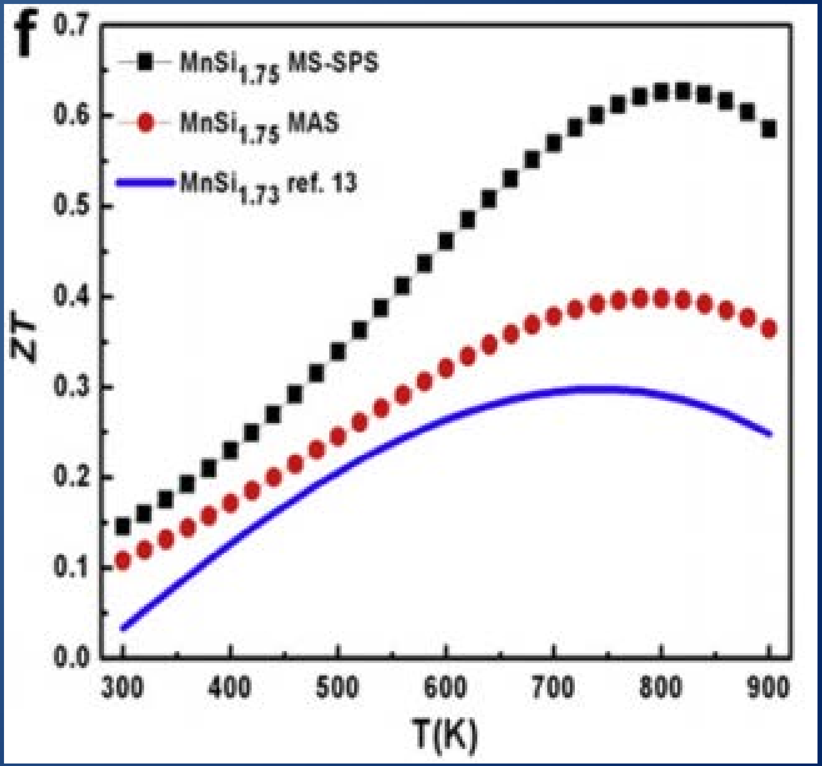
- Abundant low-cost feedstock
- Directly fabricate onto exhaust pipes
- Non-equilibrium synthesis for improved *ZT*
- Industrial process-based: thermal spray and laser micromachining
- Reliable interface and durability without soldering or clamping

Material Selection: Metal Silicides (Mg_2Si and $MnSi_{1.75}$)

- Metal Silicides: slightly lower *ZT*,
  but abundant, inexpensive, no toxicity issues.



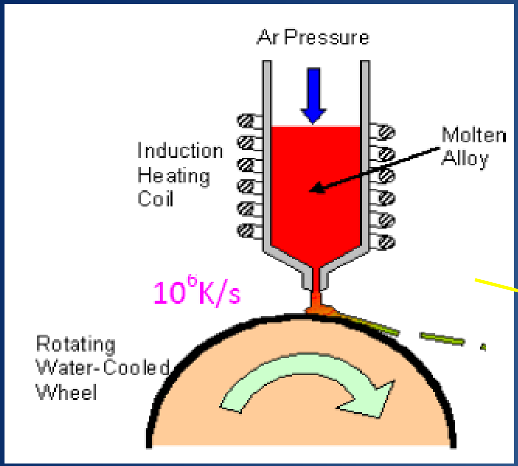
J-Y Jung and I-H Kim, Electronic Materials Letters, 2010



W. Luo, H. Li, Y. Yan, Z. Lin, X. Tang, Q. Zhang, and C. Uher, Intermetallics, 2011

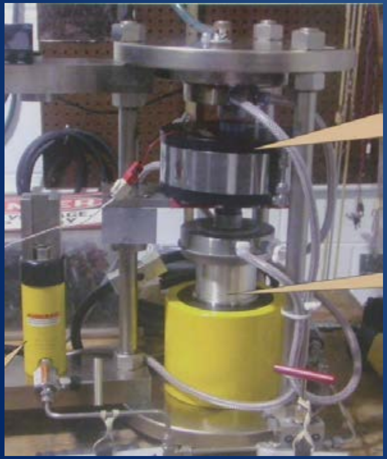
Non-Equilibrium Synthesis: Melt Spinning and Thermal Spray

Melt spinning



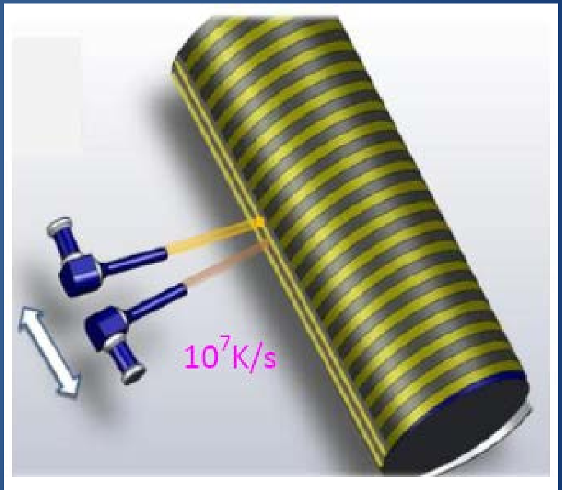
Rapid quench

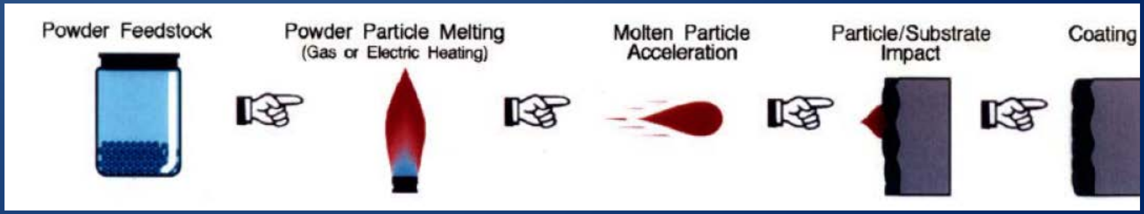
Hot press



High Pressure

Melting, rapid quenching and consolidation in a single process





Non-equilibrium Synthesis: Reduced processing time from days to minutes

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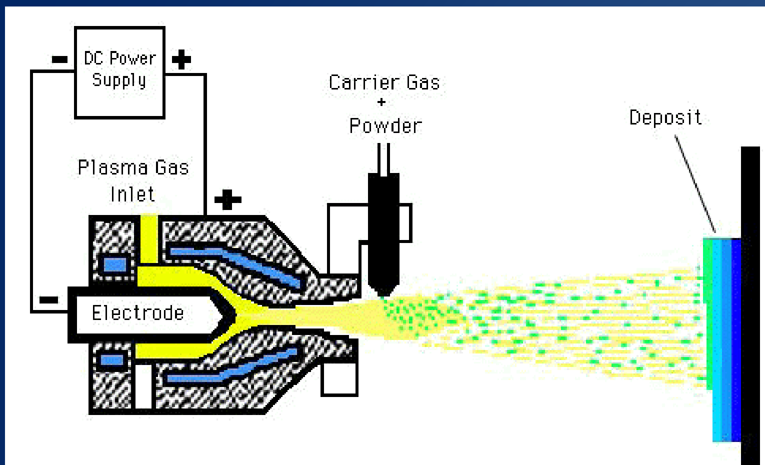
Types of Thermal Spray



High Velocity Oxygen Fuel (HVOF)

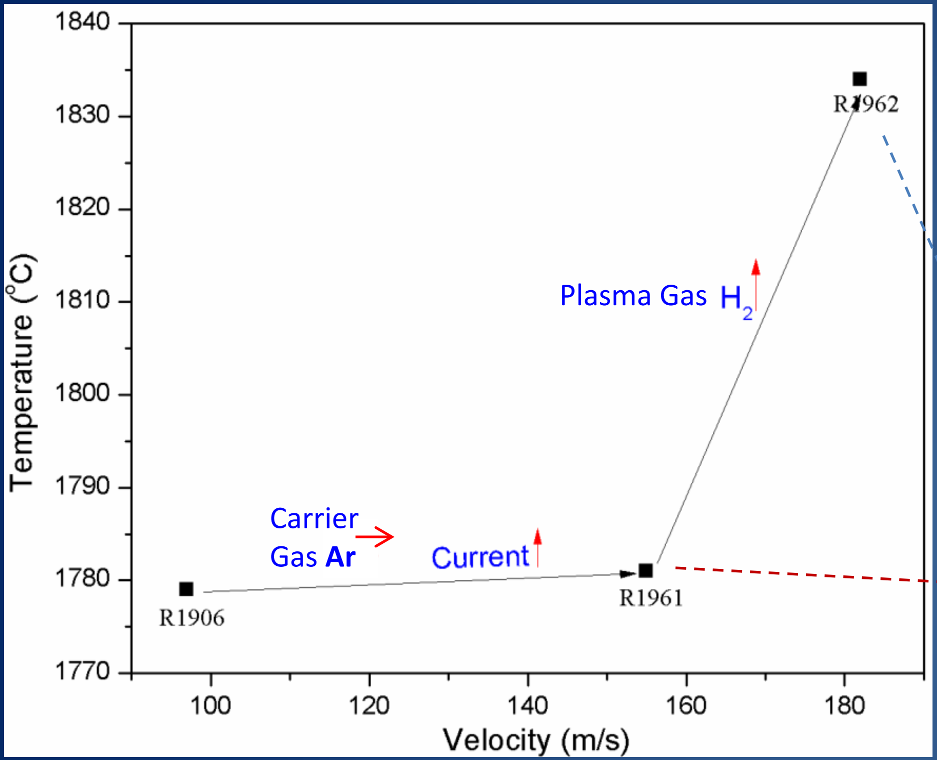
http://www.gordonengland.co.uk/hvof.htm

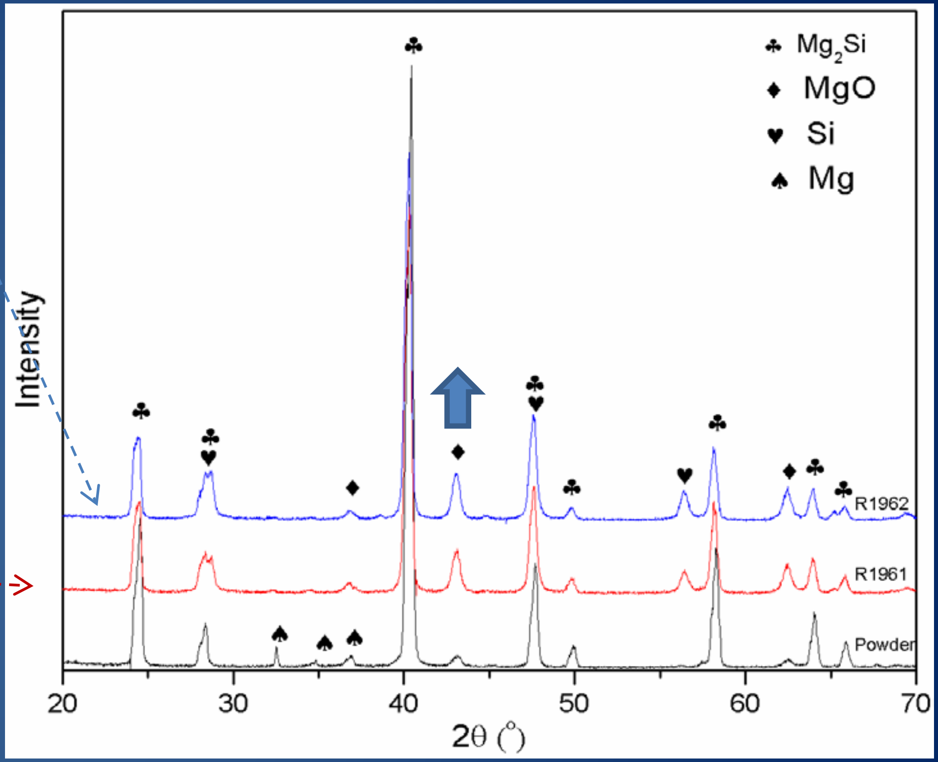
Atmosphere Plasma Spray (APS)

Vacuum Plasma Spray (VPS)

http://www.siemens.com/press/en/presspicture/?press=/en/presspicture/pictures-photonews/2008/pn200807/pn200807-01.htm

Mg_2Si by APS (First Trial)





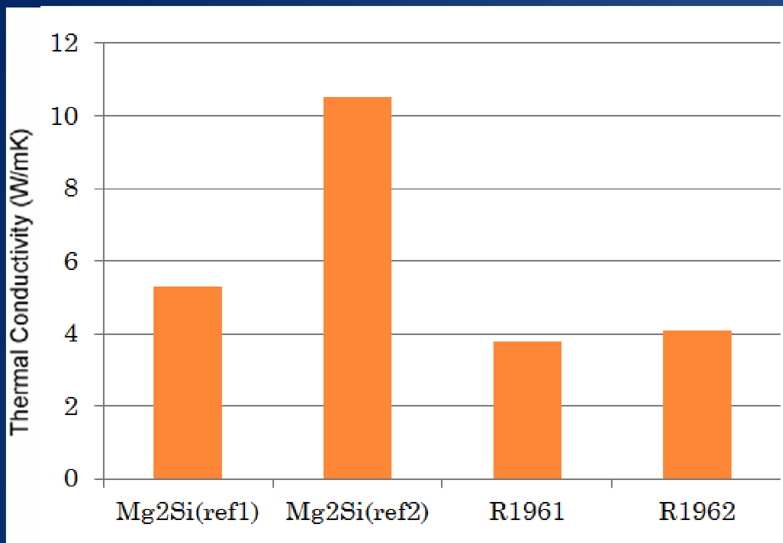
To test the thermal spray process, we used Mg_2Si with 98% purity;

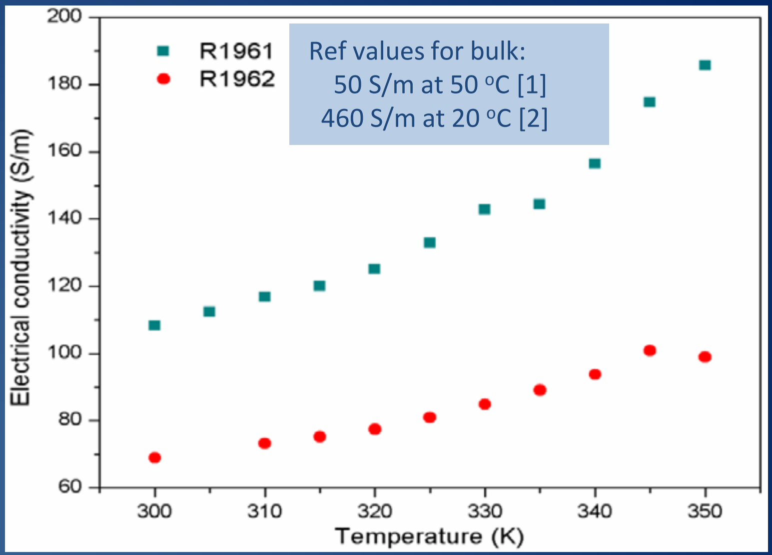
* Lower temperature and higher speed are better.

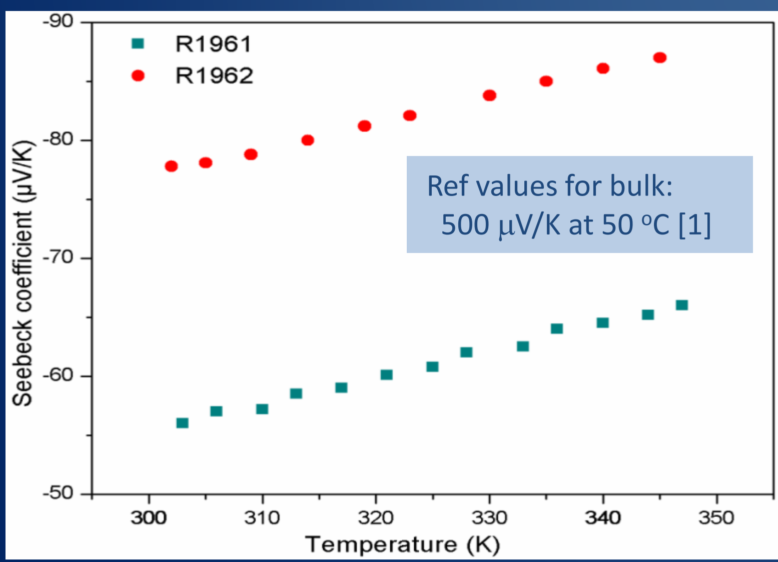
* After thermal spray: MgO and Si phases appear:

$$Mg_2Si + O_2 \xrightarrow{450\ ^oC} MgO + Si$$

Undoped Mg_2Si by APS (cont)







APS samples show:

- Reduced thermal conductivity
- Comparable electrical conductivity
- But:
  - Low Seebeck coefficient
  - High oxidation (10-16%)

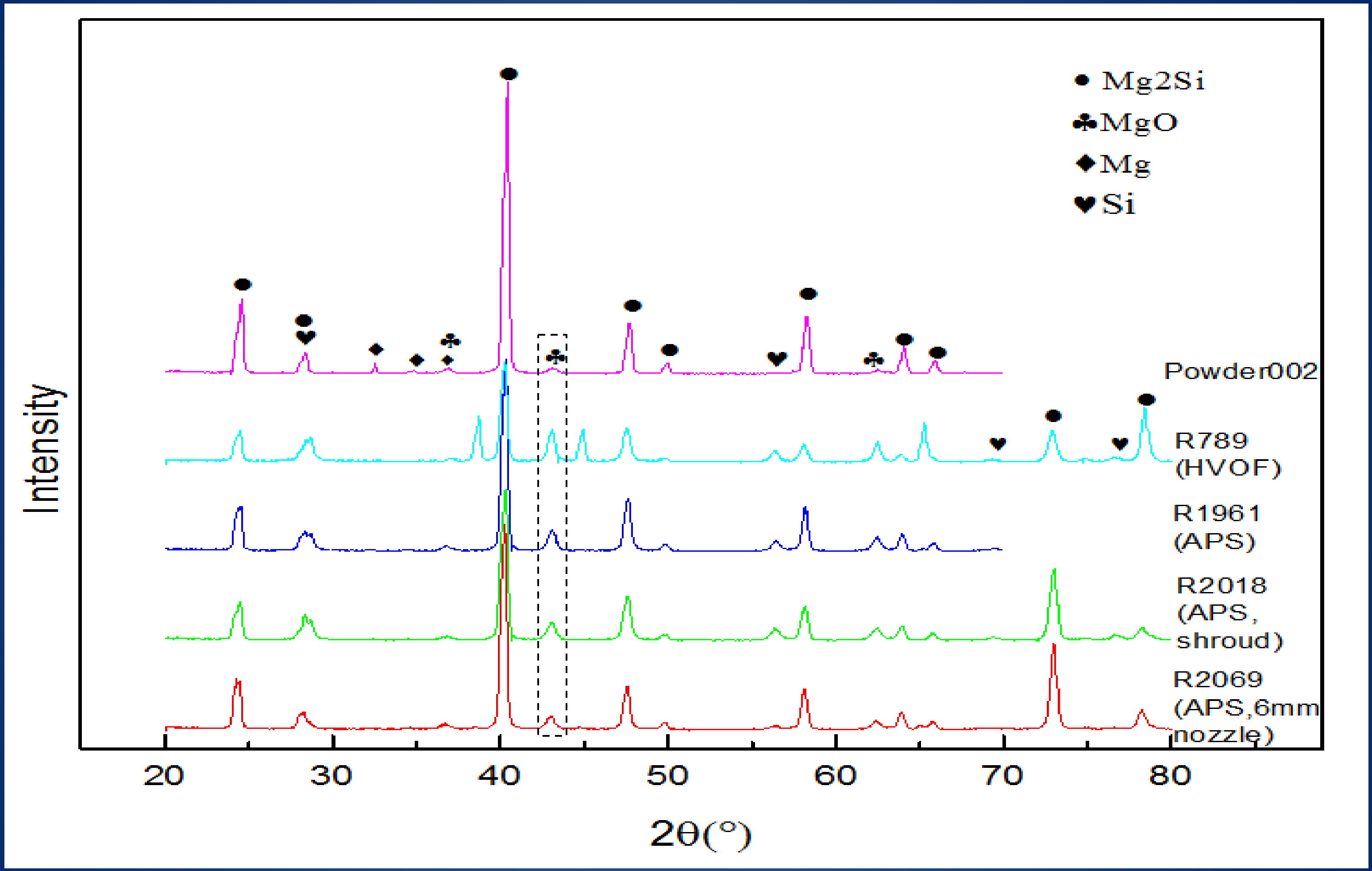
[1] J-Y Jung and I-H Kim, *Electronic Materials Letters*, 2010. (using solid state reaction/hot press method)

[2] J. Tani and H. Kido, Thermoeletric properties of Bi-doped Mg_2Si semiconductors, *Physica B*, 2005. (SPS method)

Key: Reducing Oxidation with Process Conditions

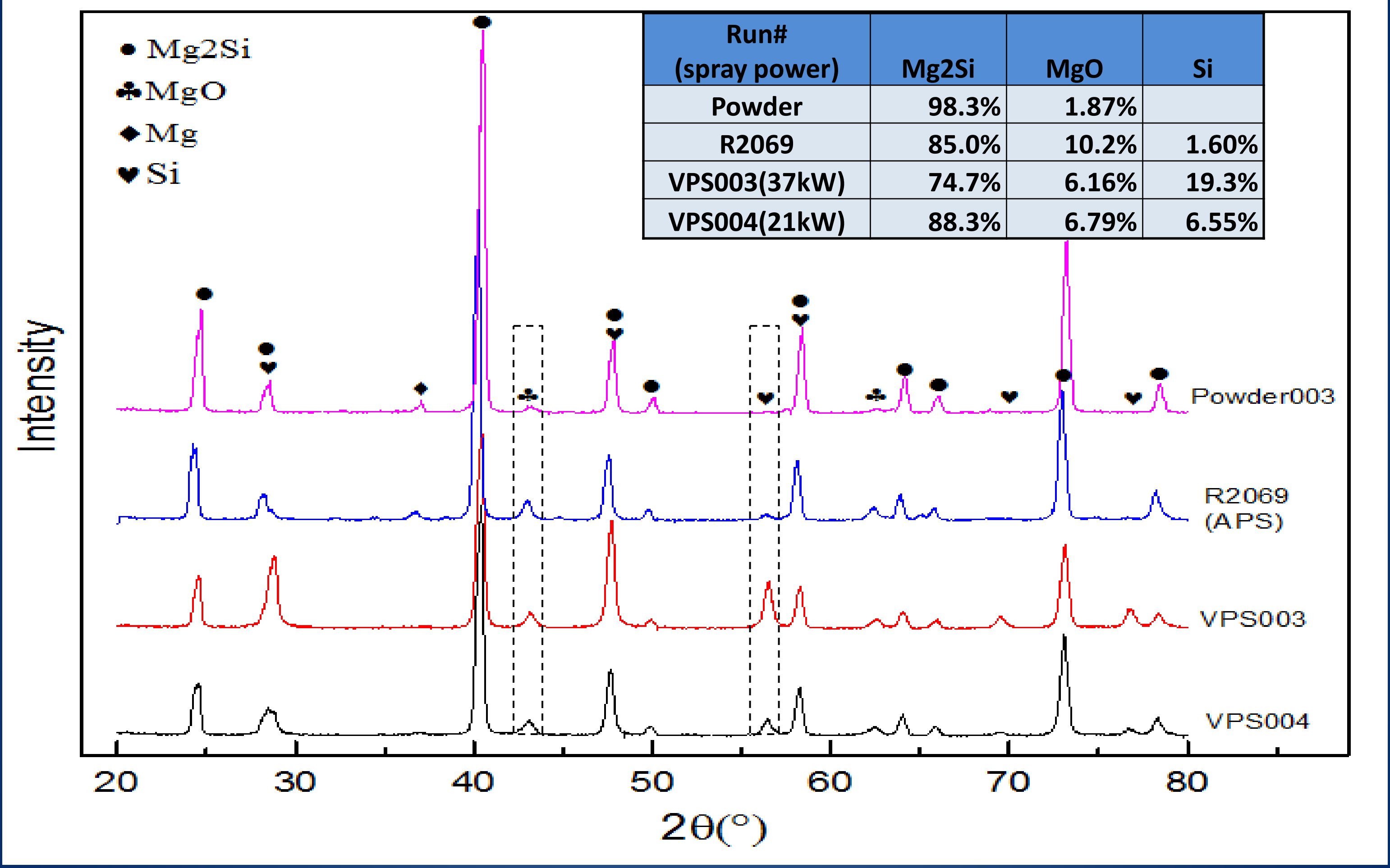
- Reducing oxidation through:
  - Spray type: APS, HVOF, VPS
  - Processing conditions (temperature, particle velocity, etc.)
  - Using a *shroud* (inert gas injected around thermal spray plume to minimize oxidation)
  - Spraying in an inert-gas environment (VPS)

Reducing Oxidation (cont)



- HVOF is worst
- Shroud doesn't help much
- Higher velocity (smaller nozzle helps, but improvement limited)

Mg_2Si by Vacuum Plasma Spray (VPS)



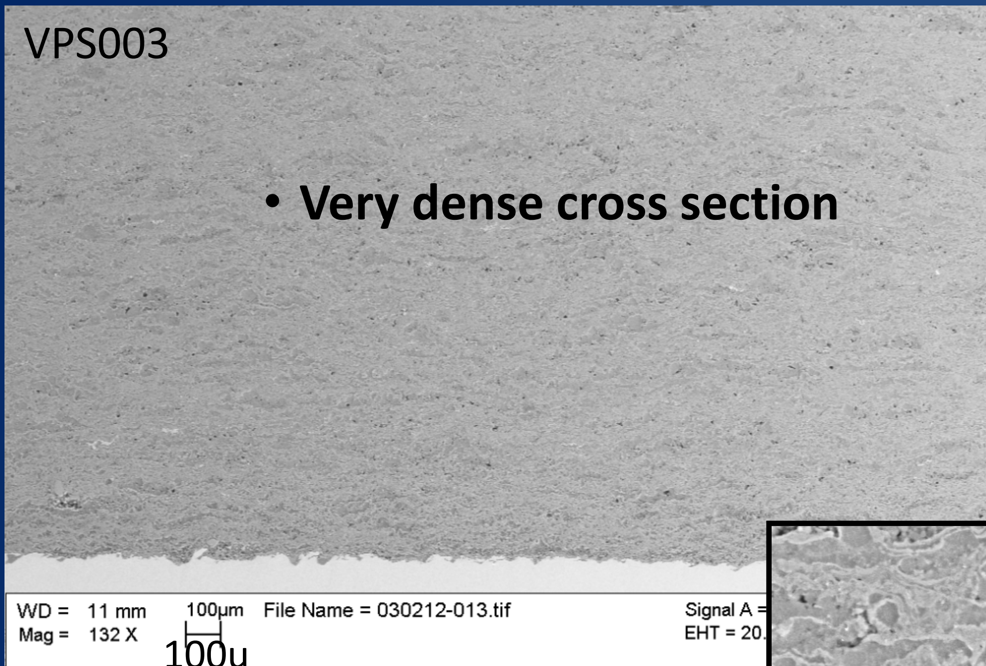
Run# (spray power)	Mg2Si	MgO	Si
Powder	98.3%	1.87%	
R2069	85.0%	10.2%	1.60%
VPS003(37kW)	74.7%	6.16%	19.3%
VPS004(21kW)	88.3%	6.79%	6.55%

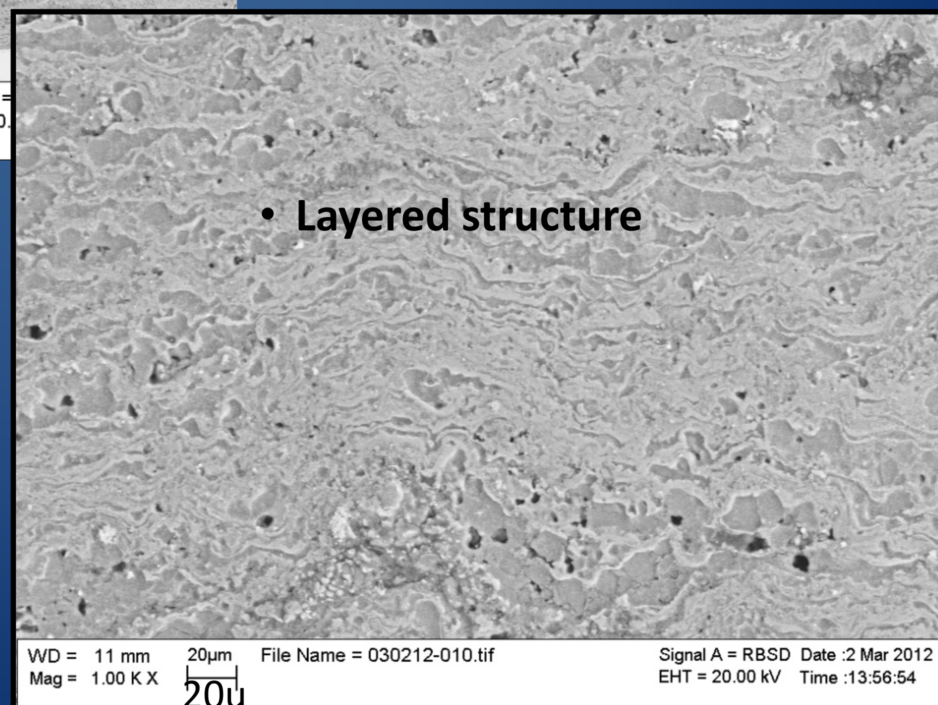
Oxidation significantly reduced: 10-16% (APS) → 6-7% (VPS)

VPS with reduced temperature decreases Si from 19% to 6% (still high)

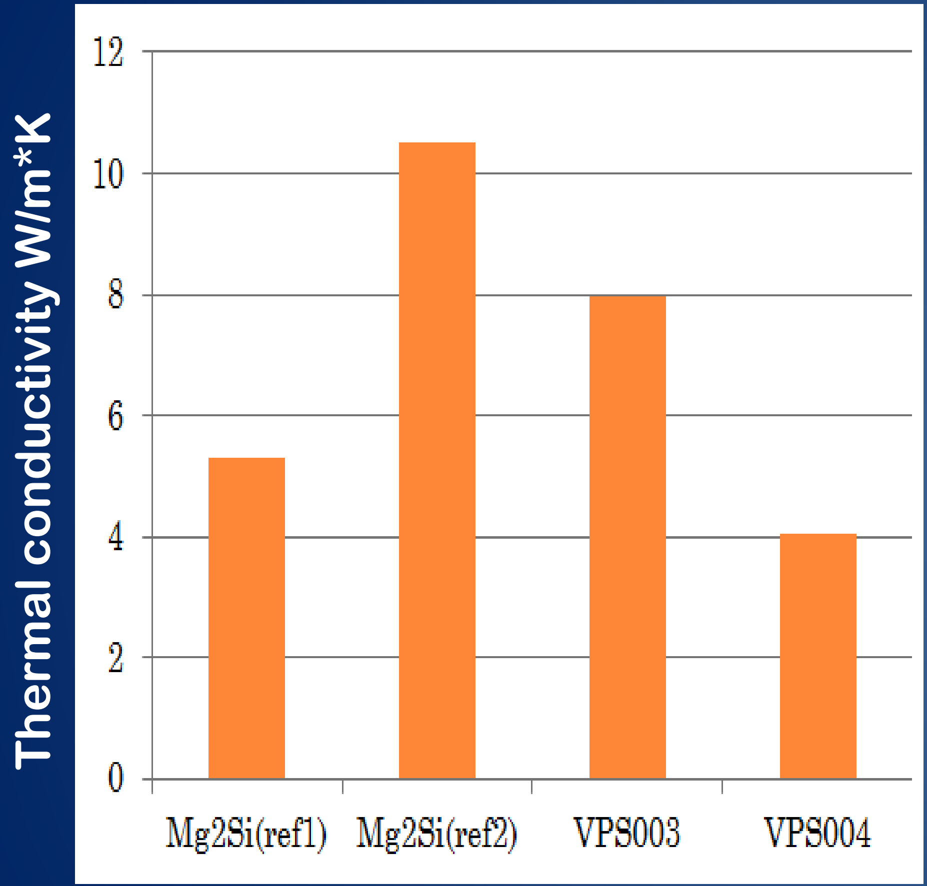
Need to optimize process temperature to minimize Si and MgO

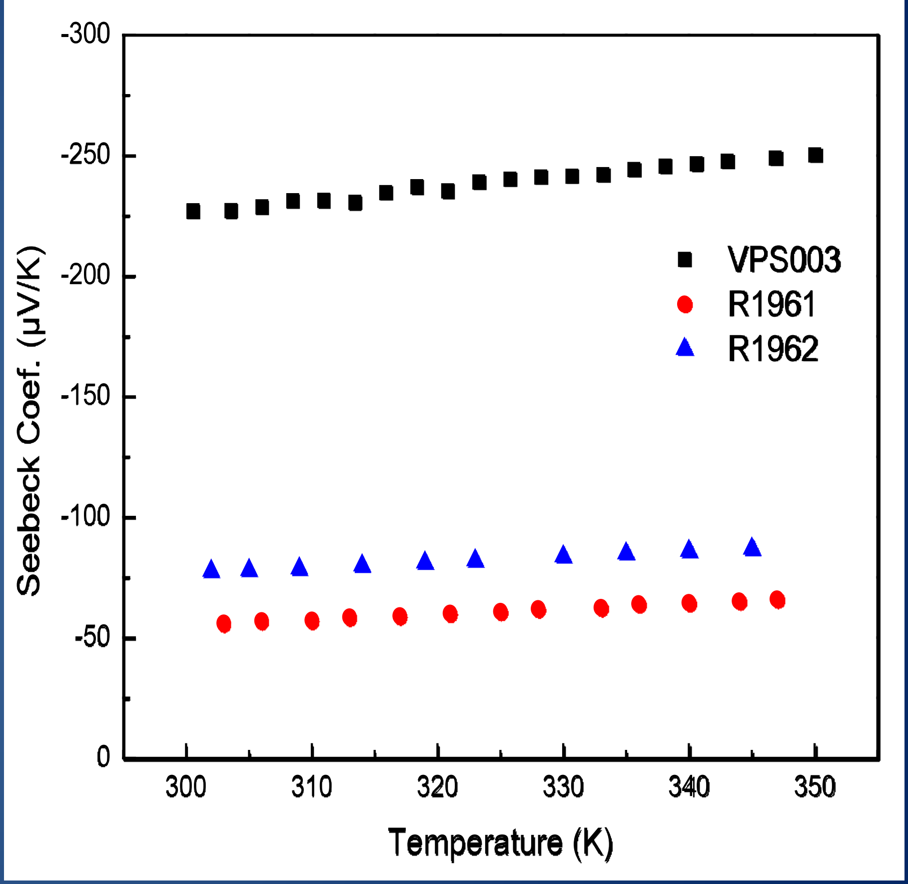
Mg_2Si by VPS


VPS003
• Very dense cross section
WD = 11 mm
Mag = 132 X
100µm
100u
File Name = 030212-013.tif
Signal A =
EHT = 20.


• Layered structure
WD = 11 mm
Mag = 1.00 K X
20µm
20u
File Name = 030212-010.tif
Signal A = RBSD
EHT = 20.00 kV
Date :2 Mar 2012
Time :13:56:54

Mg_2Si by VPS





Seebeck characterization of newest VPS sample (VPS004) is underway

→ VPS is a promising deposition technique

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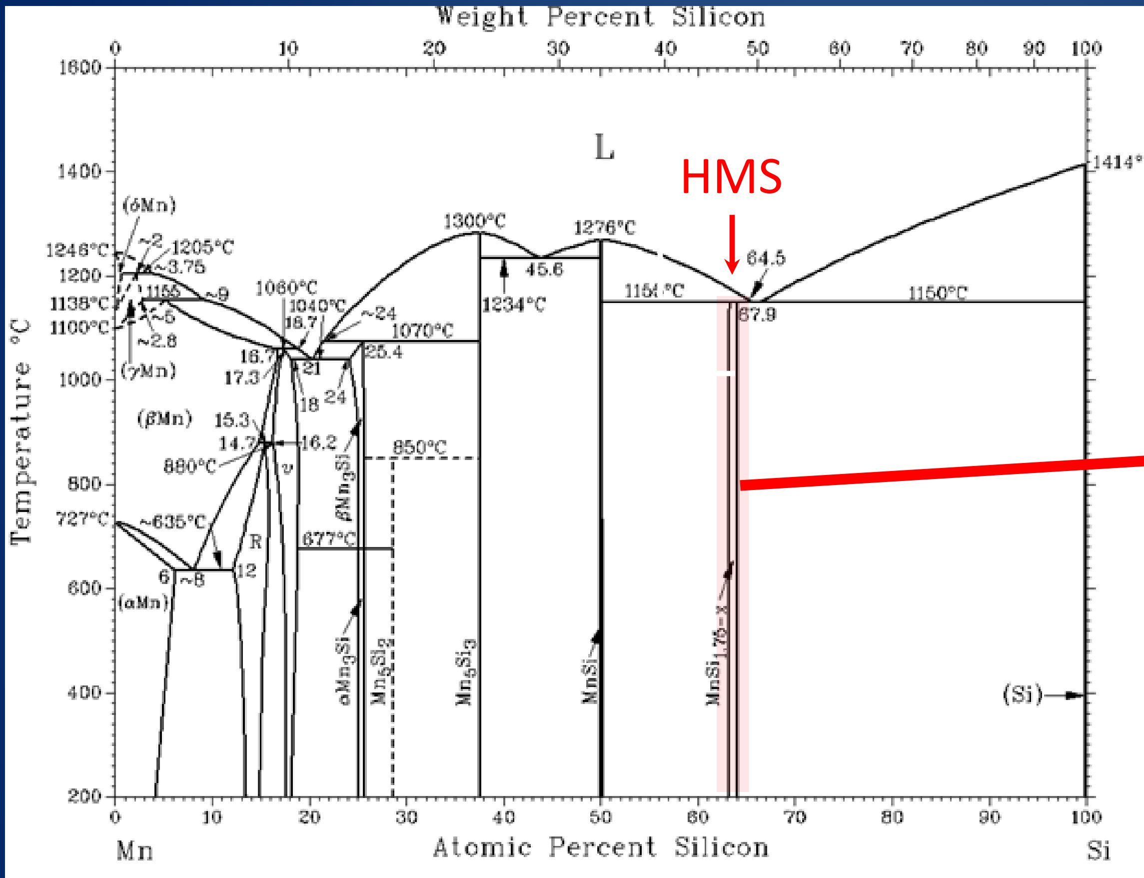
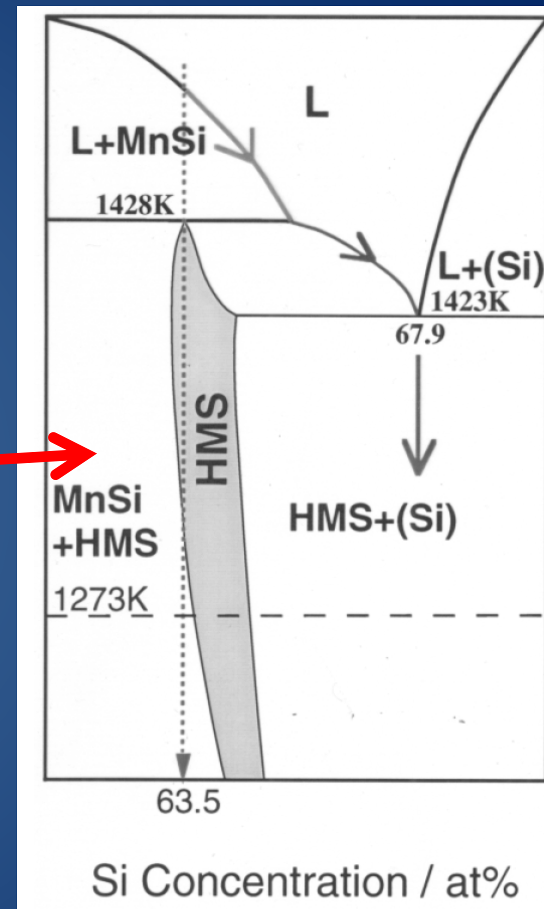
$MnSi_{1.75}$ by Melt Spinning





- ➢Hard to obtain single-phase HMS through conventional processing
- ➢Melting followed by water quenching is effective for reducing second phases

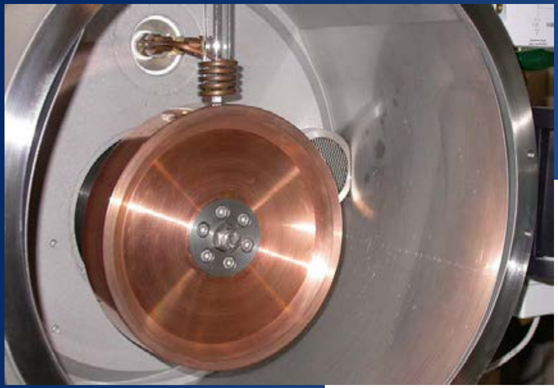
$MnSi_{1.75}$ by Melt Spinning

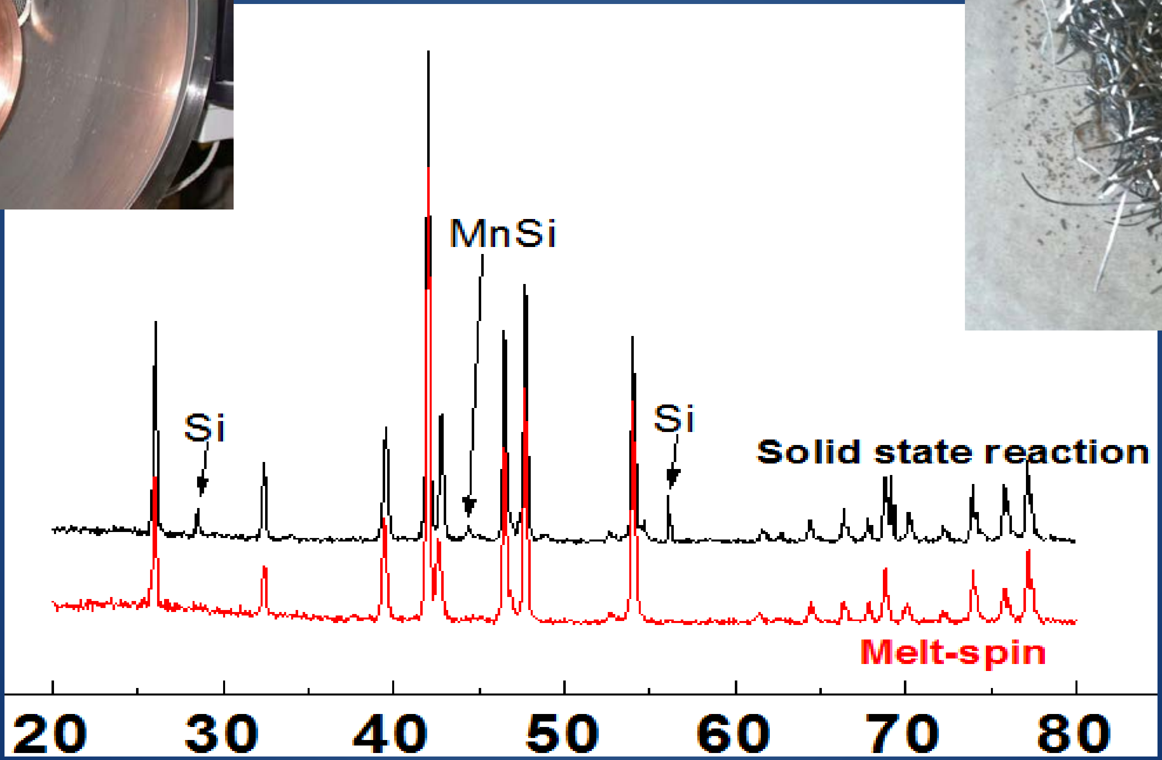
Melt-spinning (MS)	Solid state reaction (SSR)	Melt and quench (MQ)
Mn + Si Powder mixing (10 min)	Mn + Si Sealed and anneal @1373 K for 2 days	Mn + Si Sealed and melted @1473 K for 12 hrs Then water quench
↓	↓	↓
Melt-spinning (10 min)	Ground and cold pressed Sealed and anneal @1373 K for 2 days	Annealed @ 1273 K for 5 days

↓

SPS
@1123K for 10 min with 50 Mpa pressure

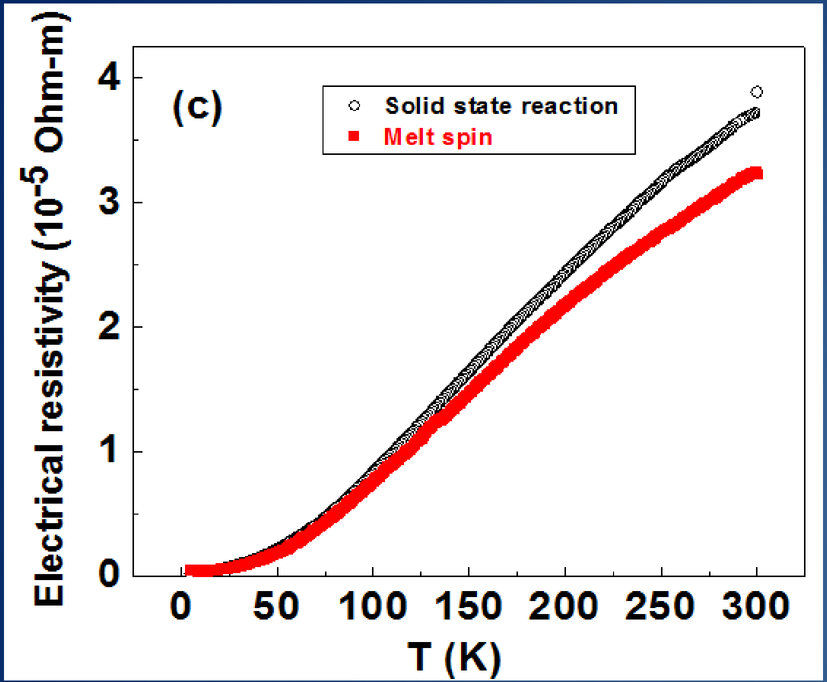
$MnSi_{1.75}$ by Melt Spinning

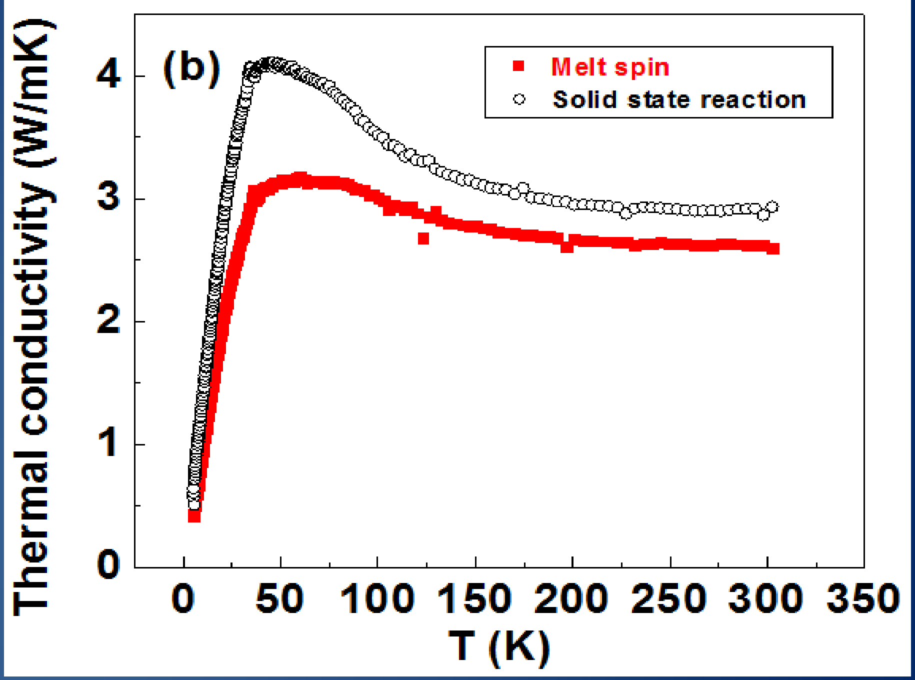




- Single-phase HMS can be obtained in < 30 mins
- Solid state reaction not suitable for HMS

$MnSi_{1.75}$ by Melt Spinning





Room temperature thermoelectrical performances

sample	Electr. Resist. ρ (10^{-5} Ohm-m)	Seebeck (μVK^{-1})	**Power factor ($\mu Wcm^{-1}K^{-2}$)**	Carrier Density p_H (10^{21} cm^{-3})	Electron Mobility μ_H ($cm^2V^{-1}S^{-1}$)	Effective mass m^*/m_e
MS	1.95	119	**7.2**	1.24	2.5	7.4
MQ	2.14	112	**5.8**	0.88	3.1	5.5
SSR	2.30	110	**5.2**	1.04	2.6	6.0

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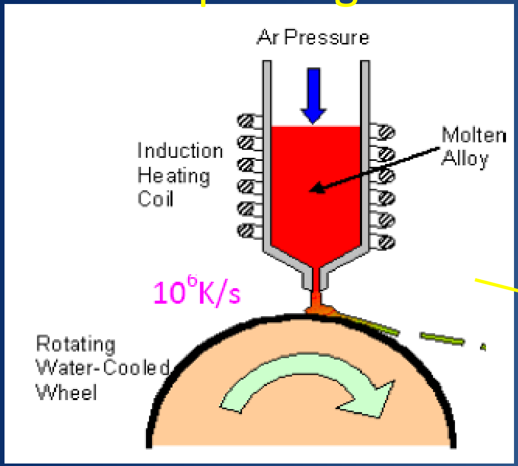
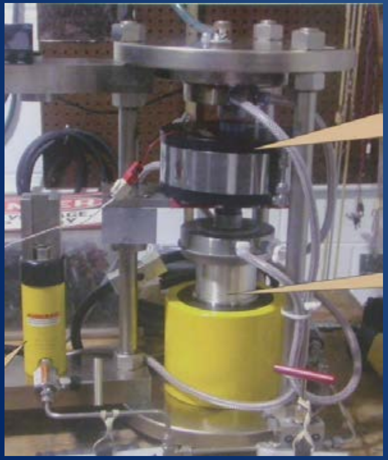
Goal: Transition Melt Spinning to Thermal Spray

Melt spinning



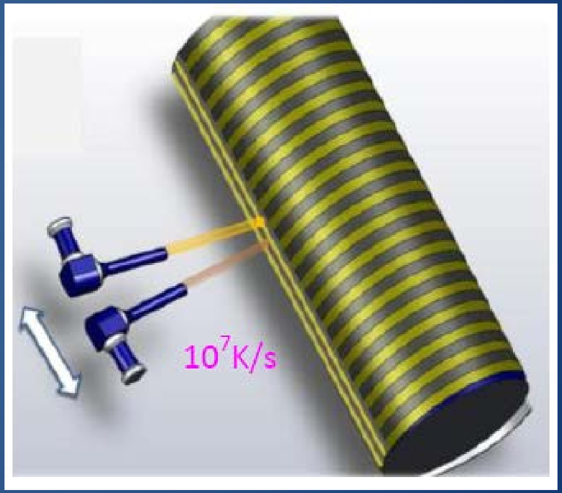
Hot press



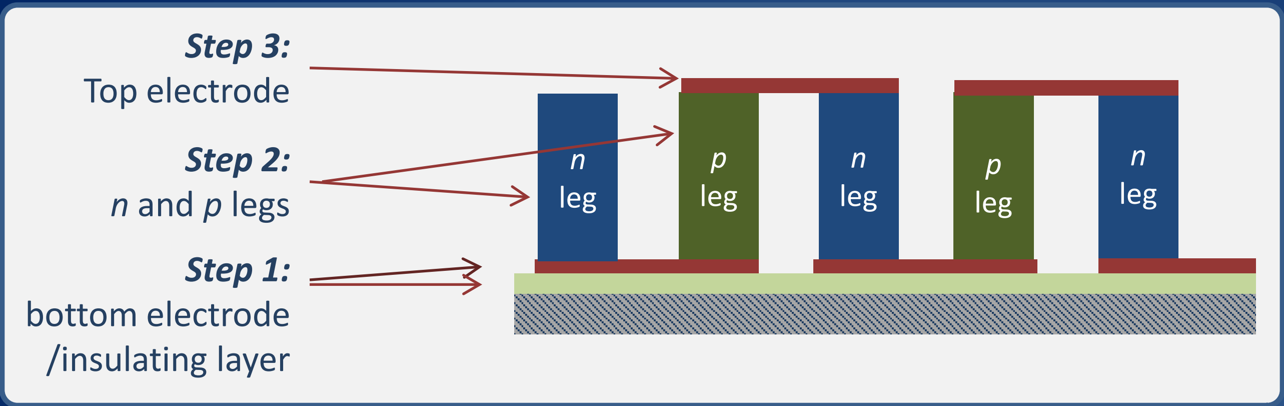
Rapid quench

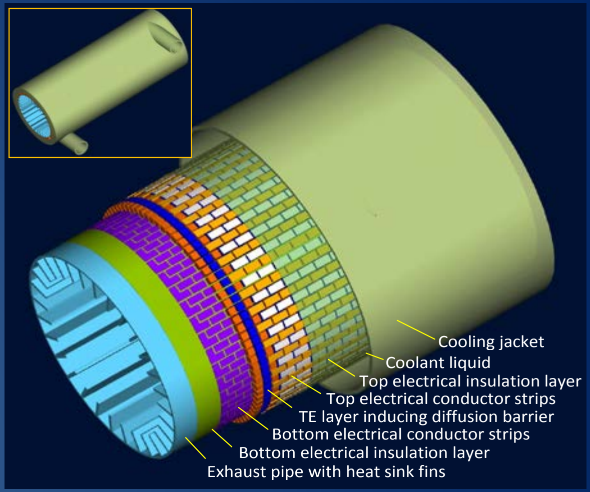
High Pressure

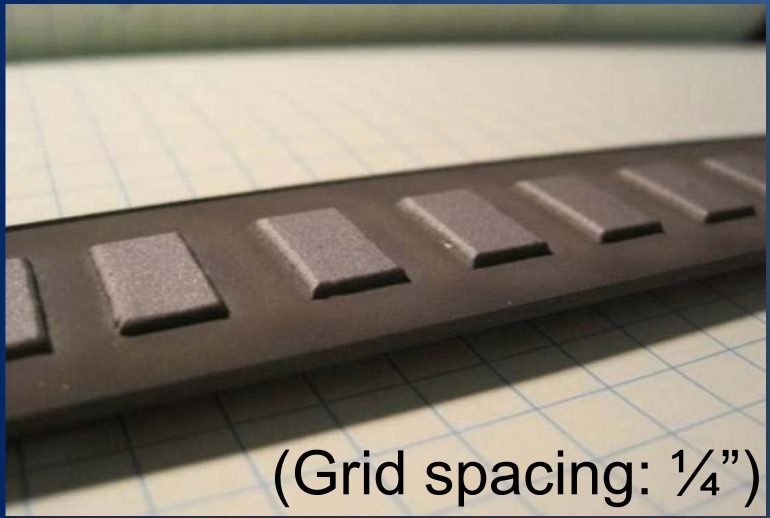
Thermal Spray



3D Device Fabrication with Thermal Spray







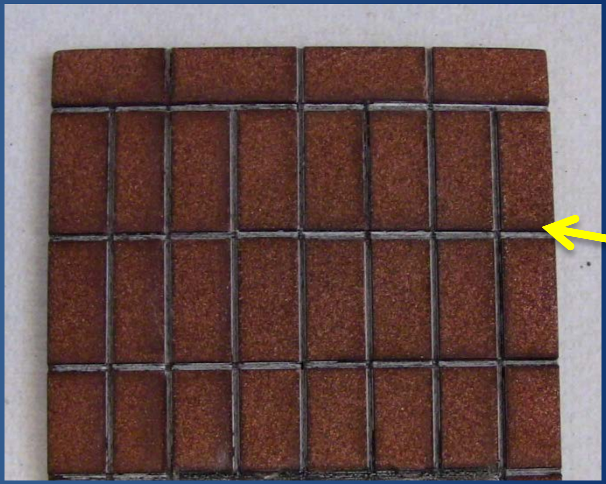
Thick deposits (3-4 mm) of FeSi for TE layer

Conductor layer – good mechanical bonding; dense coating

Step 1: Bottom Conductor & Laser Patterning

<u>Design:</u> 0.5mm thick Alumina
+ 0.5mm Copper
on 2” x 2” Aluminum Substrate

<u>Laser Micromachining:</u>
- Nd:YLF laser: 20W, 532 nm, 150 ns, 1 kHz rep rate



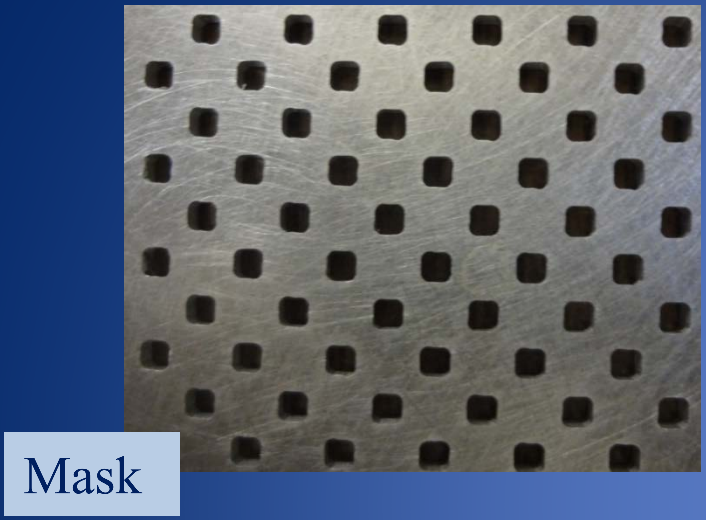
0.050” Gap

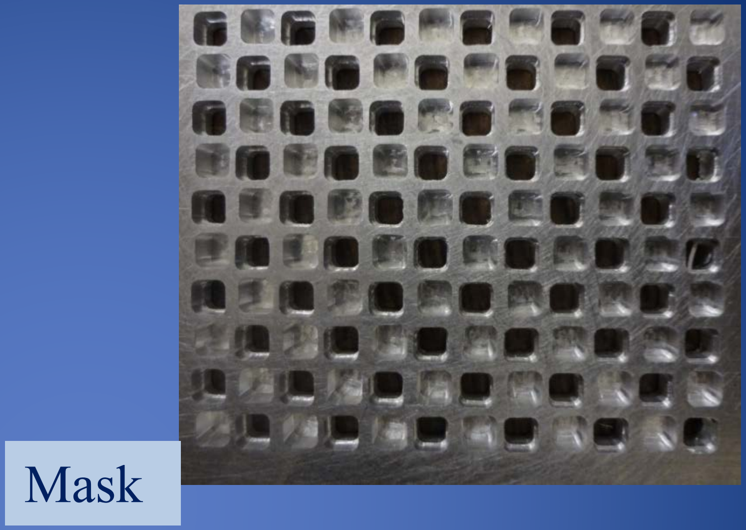
Side View

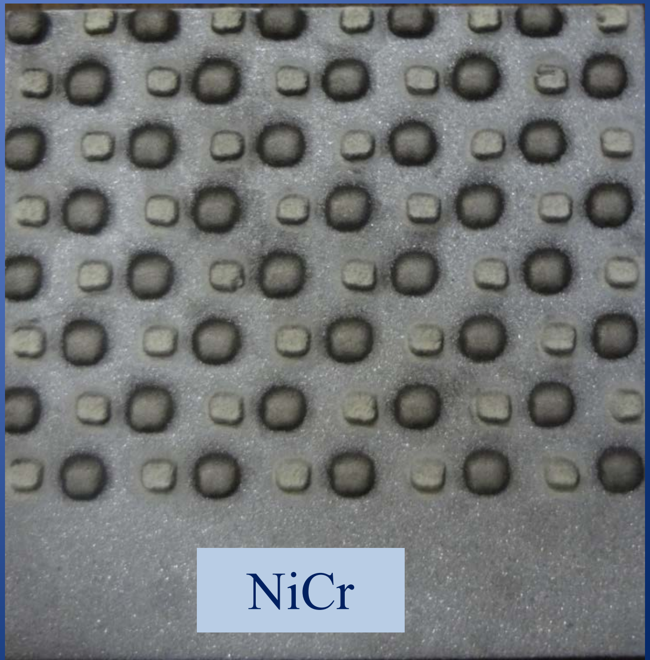
Cu layer

Insulating alumina layer

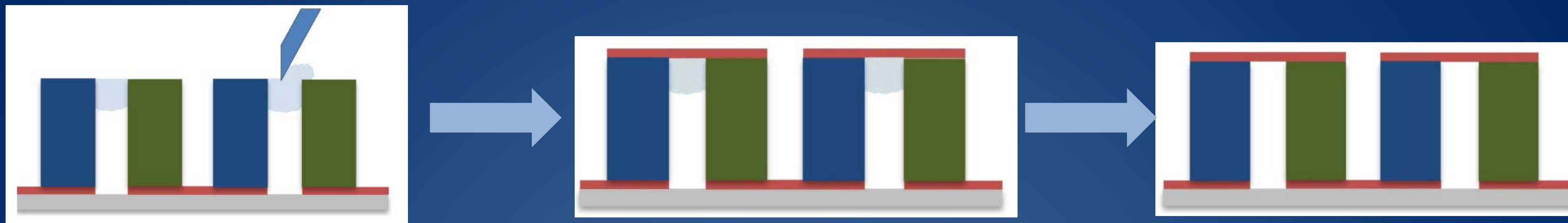
Step 2: *p* and *n*-type TE materials





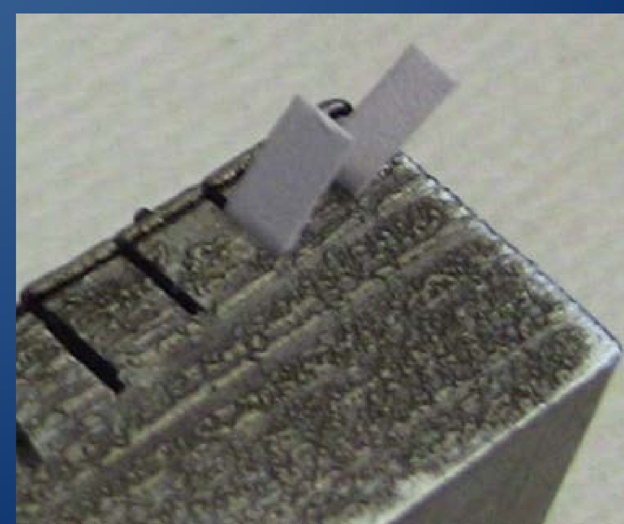


Step 3: Forming Top Electrode - Bridging

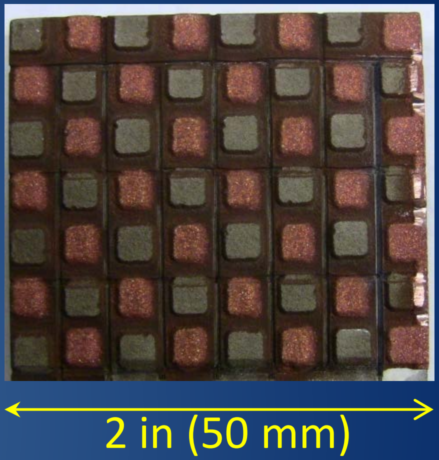


Apply filler material | Spray Top Electrode | Remove bridging matl

- Polyvinyl alcohol (PVA) + fine sand filler used.
- Apply, let dry, then spray. Bake at 400°C to remove
- Gaps in aluminum test substrate successfully bridged; top contacts formed



Putting it all together



- Cu and Alumina pillars on Cu laser-cut substrate
  - Steps 1 and 2 demonstrated on same sample (using non-TE mat’ls)
  - Step 3 in progress
- Next steps:
  - bridge gap with top electrode
  - Use TE mat’ls, e.g., thermocouple alloys

Facilities

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Atmospheric Plasma Spray System

Summary

- Thermal spray TE mat'ls: reduced thermal conductivity, reasonable electrical conductivity, but oxidation is an issue
  - APS shows high oxidation; degrades electrical properties
  - HVOF shows even more oxidation
  - VPS reduces oxidation; process temperature now being optimized
- Melt spinning achieves good result on $MnSi_{1.75}$
- Thermal Spray 3D TE structures
  - Good mechanical bonding of bottom conducting layer as sprayed
  - Thick checkerboard pattern sprayed for eventual TE materials
  - Bridging by thermal spray for top electrode fabrication demonstrated

Future Work

- Further property improvement using VPS
- Exploration of high-magnesium silicide (HMS) – transfer the success of melt spinning to thermal spray
- Fabricate functional TE prototype using thermal spray

Acknowledgements

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  - NSF and DoE through the *NSF/DoE Thermoelectrics Partnership: Integrated Design and Manufacturing of Cost-Effective and Industrial-Scalable TEG for Vehicle Applications* (CBET-1048744)
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